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CATALYSIS ON THE EVE OF THE XXI CENTURY. SCIENCE AND ENGINEERING

ABSTRACTS

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PART II

Open PART I

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"Catalysis on the Eve of the XXI Century. Science and Engineering"

ABSTRACTS

PART II

Novosibirsk - 1997

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POSTER SESSION I

Section1

Structural and Mechanistic Characterization of Heterogeneous and Homogeneous Catalysis on the Molecular Level. Methods of Quantum Chemistry and Molecular Dynamics.

^{13}C AND ^{1}H NMR SPECTROSCOPIC CHARACTERIZATION OF THE TITANIUM(IV) ALKYLPEROXO COMPLEXES $Ti(OOtBu)_n(OiPr)_{4-n}$, where n = 1, 2, 3, 4

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It is agreed that titanium(IV) alkylperoxo complexes are the key intermediates of the catalytic systems based on titanium compounds and organic hydroperoxides. However, the examples of the spectroscopic or X-ray crystallographic characterization of the titanium(IV) alkylperoxo complexes are very restricted[1-3].In this work we report first ^{13}C and ^{1}H NMR spectroscopic detection and characterization of the titanium(IV) alkylperoxo complexes $Ti(OOtBu)_n(OiPr)_{4-n}$, where n = 1, 2, 3, 4 in the reaction of $Ti(OiPr)_4$ with *t*BuOOH in CH_2Cl_2.

^{13}C and ^{1}H NMR monitoring of the interaction of $Ti(OiPr)_4$ with *t*BuOOH in CH_2Cl_2 ($CDCl_3$) at -70 – -30°C unambiguously showed that with the increasing of *t*BuOOH concentration (from 1:1 to 10:1 with respect to $Ti(OiPr)_4$) the alkoxo ligands of $Ti(OiPr)_4$ were successively replaced by alkylperoxo ones to form alkylperoxo complexes $Ti(OOtBu)_n(OiPr)_{4-n}$, where n = 1, 2, 3, 4 (Table 1, ^{13}C NMR spectra were recorded at -30°C in CH_2Cl_2, ^{1}H NMR spectra at -40°C in $CDCl_3$). The structure of the alkylperoxo complexes was determined based on the relative intensities of the ^{13}C resonances of the quaternary carbon atoms of the OO*t*Bu ligands and ternary carbon atoms of the OiPr ligands of $Ti(OOtBu)_n(OiPr)_{4-n}$, where n = 1, 2, 3, 4. The relative intensities of these resonances (NOE corrected) for $Ti(OOtBu)(OiPr)_3$, $Ti(OOtBu)_2(OiPr)_2$, $Ti(OOtBu)_3(OiPr)$ and $Ti(OOtBu)_4$ were 1:3, 2:2, 3:1 and 4:0, respectively. With the gradual increase of *t*BuOOH concentration, the intensities of the resonances of the OO*t*Bu and OiPr groups of the particular complex $Ti(OOtBu)_n(OiPr)_{4-n}$ successively reached their maximum and then decreased for n = 1, 2, 3. In the case of n = 4, the maximum intensity of the corresponding resonance of the OO*t*Bu groups was observed at the highest concentration of *t*BuOOH. Note that only one ^{13}C NMR resonance was observed for quaternary carbon atoms of the OO*t*Bu ligands and for ternary carbon atoms of the OiPr ligands of $Ti(OOtBu)_n(OiPr)_{4-n}$, for each value of n = 1, 2, 3, 4. This fact evidences in favor of the fast exchange (even at -70°C) between possible structural isomers of the particular titanium(IV) alkylperoxo complex. The difference in chemical shifts for quaternary carbon atom of the *t*Bu group in *t*BuOOH and in $Ti(OOtBu)_n(OiPr)_{4-n}$ is 6.9–7.5 ppm. The corresponding difference for primary carbon atom of the *t*Bu group is 0.25–0.75 ppm. The difference in ^{13}C chemical shifts for ternary carbon atom of the iPr group in iPrOH and in $Ti(OO\textit{t}Bu)_n(OiPr)_{4-n}$ is 14–15 ppm (Table 1). To define the mode of the coordination of OO*t*Bu groups to titanium we have compared the above differences with those for the specially prepared alkoxo complexes $Ti(O\textit{t}Bu)_n(OiPr)_{4-n}$, where n = 1, 2, 3, 4 (Table 2). It is seen that the corresponding differences for α-carbon atom of OiPr and O*t*Bu groups are 11.2–12.2 ppm, and those for β-carbon atom of O*t*Bu group are 1.04–1.09 ppm. Based on these data, it is natural to conclude that η_2 coordination of OO*t*Bu groups is preferable for all titanium(IV) alkylperoxo complexes found.

The presented results are the first example of the detection of the titanium alkylperoxo complexes with one, two, three and four alkylperoxo ligands.

Acknowledgment This study was supported by INTAS grant # 94-15-15.

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Table 1. ^{13}C and ^{1}H NMR chemical shifts for $Ti(OO\textit{t}Bu)_n(OiPr)_{4-n}$

n	$C^*(CH_3)_3$	$C^*H(CH_3)_2$	$C(C\underline{H}_3)_3$	$C\underline{H}(CH_3)_2$	$CH(C\underline{H}_3)_2$	$C(C^*H_3)_3$	$CH(C^*H_3)_2$
0	–	76.59	–	4.491	1.270	–	26.73
1	86.93	77.51	1.444	4.564	1.276	26.26	26.52
2	87.42	78.18	1.450	4.656	1.269	26.41	26.01
3	87.21	78.95	1.421	4.724	1.286	26.63	25.89
4	87.04	–	1.426	–	–	26.80	–

Table 2. ^{13}C and ^{1}H NMR chemical shifts for $Ti(O\textit{t}Bu)_n(OiPr)_{4-n}$

n	$C^*(CH_3)_3$	$C^*H(CH_3)_2$	$C\ (C\underline{H}_3)_3$	$C\underline{H}(CH_3)_2$	$CH(C\underline{H}_3)_2$	$C(C^*H_3)_3$	$CH(C^*H_3)_2$
0	–	76.59	–	4.491	1.253	–	26.73
1	81.28	76.36	1.316	4.488	1.248	32.35	26.71
2	80.98	76.14	1.313	4.484	1.248	32.35	26.71
3	80.68	75.85	1.308	4.476	1.243	32.35	26.71
4	80.33	–	1.298	–	–	32.35	–

XPS, TPD AND TPRS STUDY OF Cs-O OVERLAYERS ON SILVER

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Metallic silver is well-known to be the unique catalyst for ethylene epoxidation, with cesium being the most common promoter of such catalysts. To explain the promotional behavior of cesium, physical methods of surface analysis such as X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), low energy electron diffraction (LEED) etc. have been commonly applied. However, commercial catalysts which represent silver particles supported on α- alumina are "inconvenient" samples for the surface science investigations. For example, dielectric properties of Al_2O_3 cause charging problems for electron-based analysis. Therefore, most of the experimental data have been obtained using bulk silver: single crystals or foils. Discrepancy of the nature of bulk and dispersed metals known as the "material gap" problem hinders the application of these vast data to real catalysts. To solve the "material gap" problem we have used the following approach:

1. Comparison of XPS and TPD characteristics of Cs-O complexes on supported catalysts and Ag(111) single crystal with the aim to find those of them which are common for both types of the samples.
2. Design of a proper combination of Cs addition and oxygen adsorption in order to provide individual preparation of each of such Cs-O complexes.
3. Investigation of their structure and influence on adsorptive and catalytic properties of silver by physical methods.

Following this approach, we have revealed two different Cs-O complexes which are realized for both types of the silver samples: one of them is characterized by a $Cs3d_{5/2}$ core level spectrum with binding energy of 724.2 eV (I type), BE($Cs3d_{5/2}$) of the second one is equal to 725.0 eV (II type).

A detailed study of the I type Cs-O complexes has shown that:

PPI-1

1. According to the spectroscopic data (O1s and $Cs3d_{5/2}$ spectra) this complex can be determined as cesium oxide, Cs_xO_y.
2. The comparison of the $Cs3d_{5/2}$ and O1s intensities with taking into account the factor of XPS atomic sensitivity indicates that its stochiometry is close to Cs_2O_2.
3. The influence of the cesium oxide on silver catalytic properties consists in blocking the regular sites at the silver surface from the formation of ionically adsorbed oxygen which, as shown by us previously, is active only in total oxidation of ethylene.

Experimental techniques, XPS, ADXPS (angular dependent XPS), TPD, TPRS (temperature programmed reaction spectroscopy) results and their comparison with the literature data are discussed.

The data referred to the Cs-O complexes of the II type will be present later.

PPI-2

THE STRUCTURAL SENSITIVITY IN OXYGEN ADSORPTION AT SILVER SURFACES

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It is well-known that adsorption of O_2 molecule on metals proceeds via a number of transient species before chemisorbed oxygen atoms are formed:

$$O_2(g) \rightarrow O_2(s) \rightarrow O_2^{\delta-}(s) \rightarrow 2O^{\delta-}(s) \rightarrow 2O^{2-}(a).$$

The last stage of the scheme: the transformation of transient atomic oxygen, $O^{\delta-}(s)$, to the most stable oxide-like one, $O^{2-}(a)$, has usually been associated with the reconstruction of metal surfaces. The reconstruction facilitates highly endothermic process of electron transfer, $O^- + e \rightarrow O^{2-}$ (820 kJ) due to involving substantial Madelung interaction in a solid. Thus, the atomically chemisorbed oxygen species have different location with respect to uppermost layer of a metal. The transient oxygen has on-top location, while oxide-like species are incorporated into the uppermost metal layer. So, a number of researchers used other names for these atomic oxygen species, $O^{\delta-}(s)$ and $O^{2-}(a)$ - unreconstructed and reconstructed, respectively.

This scheme, which is commonly recognized for most of metals, has never been discussed for silver. The absence of direct experimental data is most likely to be explained by high mobility of silver atoms that provides easy reconstruction of clean silver surface to the structure of surface oxide with the formation of O^{2-}. Obviously, the attempts to find $O^{\delta-}$, and hence, to confirm the total scheme of adsorbed oxygen transformation should be concentrated on low temperature experiments.

The use of single crystals with different silver structures - Ag(111) and Ag(110), and various temperatures of adsorption from 300K to 470K allow us to prove the existence of unreconstructed atomic oxygen for oxygen adsorbed at silver. It has been shown that on closely packed Ag(111) plane at room temperature oxygen atoms adsorb in on-top position with its transformation into surface silver oxide at T > 420K. This conclusion is based both on the decrease in O1s core level binding energy by 1.6 eV and on the change in the depth concentration profile of oxygen with raising the temperature. In the case of the more opened Ag(110) plane, oxide-like oxygen is registered over the whole range of temperatures studied. These results are discussed in the context of various coordination of atomically chemisorbed oxygen by silver atoms.

REACTION ZONE WIDTH DURING PROPAGATION OF THE CO OXIDATION WAVE OVER Pt(100)

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Professor Ertl et al. have shown [1] that the oscillation mechanism for the rate of the CO oxidation over Pt(100) is determined by the phase transition (1x1)-(hex). The oscillations investigsted by the PEEM method (resolution ~1 μ) have shown the reaction waves propagation over the platinum monocrystals [2]. The detailed data on the distribution of the adsorbed particles in the reaction zone and on the zone width were obtained by Gorodetskii et al. [3] by the FEM method (resolution 20 A) over the platinum tip (100). As the wave moves, the reaction zone between the CO_{ads} and O_{ads} layers is shown to attain 50 A and the reaction rate is maximum near the boundary of the O_{ads} layer.

It was of special interest to elucidate which surface processes affect the reaction zone width. The present work concerns the study of the effect of the CO_{ads} diffusion on the reaction zone width in the wave propagation along the Pt(100) surface. The simulation was performed by the Monte-Carlo method according to the following reaction scheme:

1) CO adsorption: CO+hex→CO+1x1→CO-1x1.

2) O_2 adsorption: O_2 + 1x1→2O - 1x1.

3) COads desorption: CO - 1x1→1x1 + CO; CO - hex → hex + CO.

4) Reaction: O - 1x1 + CO - 1x1 → 2(1x1); O - 1x1 + CO - hex → 1x1 + hex.

5) Structural conversions: 1x1 → hex; CO - hex→CO - 1x1.

6) CO_{ads} diffusion: the diffusion is determined by the number of the recurrences of the inner diffusion cycle (Nd) during one of the Monte-Carlo steps. The calculated probabilities of stages (1-5) are close to the data in [4], Nd varied from 0 to 100.

In the initial conditions one part of the Pt(100) surface was covered with CO(1x1), and the other was covered with O(1x1), the boundary between them was a straight line.

parallel to the axis X. In the O_2 excess in the reaction mixture the «oxygen wave» is moved, as the reaction proceeds, to the CO_{ads} layer. The empty sites (1x1) formed during the reaction pass into (hex) with a 0.01 probability and were transformed back into CO(1x1) after the CO adsorption. The qualitative pattern of the «oxygen wave» propagation agrees with the data in [4] but in our case the wave is more «smeared» and its width is ~ 30-50 atomic rows. As the «wave CO_{ads}» moves during the reaction with the O_{ads} layer, in the CO excess in the reaction mixture a better defined boundary is observed. When the CO_{ads} adsorption is localized, i.e. Nd=0, the reaction zone width is only 2-3 atomic raws but the boundary is rough. On the "switch-on" of the CO_{ads} diffusion (Nd=10-100) the reaction zone width increases, while the reaction boundary, as the reaction wave propagates, remains the initial straight line (with slight fluctuations). This permitted us to obtain the distribution curves for the particle concentration and the reaction rate by summarizing the raw atoms along the reaction boundary. Figure 1 presents the concentration profiles for the high CO_{ads} diffusion (Nd=100). One can see that the reaction zone width is ~ 20 atomic raws (~ 50 A), which agrees with experimental date [3].

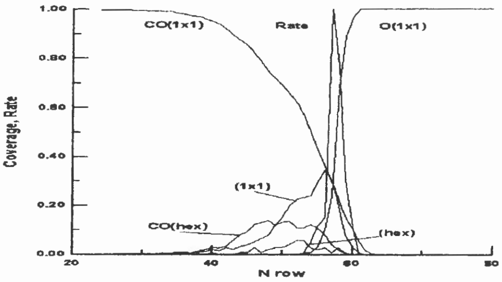

Fig 1.

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SURFACE EXPLOSION, ISLANDS, PHASE TRANSITIONS, ACTIVE CENTRES IN CO+NO/Pt(100) REACTION STUDIED BY HREELS AND TDS

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NO+CO reaction mechanism on Pt attracts considerable interest from both practical and theoretical points of view, especially in connection with new experimental data, allowing to throw the light onto a nature of sustained kinetic oscillations, surface waves. Under heating Pt(100) single crystal with the NO_{ads} and CO_{ads} layers up to T ~ 400 K reaction products, CO_2 and N_2, are known to evolve as extremely narrow desorption peaks (FWHM ~2-5 K) - so called "surface explosion". Availability of two stationary states, hysteresis, the rate oscillations observed in the NO+CO reaction on Pt(100) are associated with the reversible phase transition Pt(100)1x1 ⇔ hex. It was shown that the Pt(100) surface in the unreconstructed 1x1 phase exhibits a high catalytic activity in the NO+CO, $CO+O_2$, $NO+H_2$ reactions, since NO, O_2, H_2 molecules dissociate easily on this surface.

The surface of supported platinum crystallites with a size of 100-300 Å is mainly formed by the most dense (111), (100), (110) faces which differ dramatically in the adsorption properties, in particular, in the probability of NO dissociation being a rate determining step of the NO+CO reaction. Therefore, the search of methods of detection of surface structures active in the dissociative adsorption is necessary to build up the effective platinum catalyst. It is known that the developed adsorption methods (for example, the method based on the H_2+O_{ads} titration reaction) allow to determine only a total platinum surface in supported catalysts.

The purpose of this study consists in application of TPRS and HREELS methods for: (i) elucidation of the coordination of NO and CO molecules in mixed adsorption layers on the Pt(100)-1x1 and hex surfaces; (ii) finding out of the mechanism of the $NO_{ads}+CO_{ads}$ reaction; (iii) development of a new method for the measurement of concentration of the centres which are active in the NO_{ads} molecules dissociation.

We have studied a reaction ability of NO_{ads} and CO_{ads} molecules on the Pt(100)-hex and 1x1 surfaces by HREELS and TPRS methods. It has been found that at 300 K under consecutive filling of the Pt(100)-1x1 surface titration reactions $CO+NO_{ads}$ and $NO+CO_{ads}$

occur with evolution of the N_2 and CO_2 products as isothermal desorption peaks. On the reconstructed Pt(100)-hex surface at 300 K these reactions were not observed. Stable islands of 1x1 phase, covered with a mixture of the NO_{ads} and CO_{ads} molecules, form under consecutive filling of the hex surface. The reaction in the $NO_{1x1}+CO_{1x1}$/hex islands is initiated under heating up to 400 K and proceeds autocatalytically as a "surface explosion" that manifests itself in the extremely narrow desorption peaks of N_2, CO_2 and N_2O. *The chemical differences* observed in the properties of the hex and 1x1 surfaces allow to conclude that the NO_{ads} layer titration with carbon monoxide or vice versa at 300 K displays *a structural sensitivity*. The absence of reaction in the mixed adlayers of NO_{ads} and CO_{ads} on Pt(100)-hex is associated with impossibility of NO to dissociate in the islands of the 1x1 phase at 300 K.

It has been shown that the NO_{ads} dissociation on the 1x1 surface requires an adjacent vacant adsorption site. A clean-off reaction between CO_{ads} and O_{ads} results in the CO_{2gas} formation; then a recombination of two N_{ads} atoms leading to the N_2 evolution occurs accompanied by the release of the vacant adsites, necessary for the dissociation of further NO_{ads} molecules and for the CO adsorption. The reaction mechanism is described as follows:

$$CO + * \Leftrightarrow CO_{ads}$$

$$NO + * \Leftrightarrow NO_{ads}$$

$$NO_{ads} + * \rightarrow N_{ads} + O_{ads}$$

$$2\,N_{ads} \rightarrow N_2 + 2\,*$$

$$CO_{ads} + O_{ads} \rightarrow CO_2 + 2\,*$$

$$NO_{ads} + N_{ads} \rightarrow N_2O + 2\,*$$

Conclusion

The unreconstructed Pt(100)-1x1 surface shows a high activity in the $NO_{ads}+CO_{ads}$ reaction at 300 K accompanied by N_2 and CO_2 evolution. The reconstructed Pt(100)-hex surface appears to be inactive under the same conditions. The $CO+NO_{ads}$ and $NO+CO_{ads}$ titration reactions display *the structural sensitivity* and, apparently, can be used as *a test* for the presence of centres with 1x1 structure being active in the NO dissociation. The N_2 and CO_2 peak intensities measured during isothermal desorption experiment can be used for the determination of the active sites concentration.

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PPI-5

EFFECT OF ACOUSTIC EXCITATION ON CATALYTIC REACTION RATES OVER THIN FILM SINGLE CRYSTALS

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1. Introduction

A experimental system has been designed to study in detail the mechanisms by which very low frequency, low energy acoustic vibrations can influence microscopic processes at a crystal surface, involving the excitation of high frequency optical vibrational modes within the adsorbed layer. The experiments are carried out in a purpose built ultra high vacuum (uhv) chamber using thin film single crystals as catalyst. Surface Acoustic Waves (SAWs) (Rayleigh waves) are generated using a uhv compatible excitation system based on an InterDigital Transducer (IDT) device and can be studied accurately by means of an ultrahigh amplitude and frequency resolution acoustic spectrometer. A remarkable eight-fold increase of the rate of carbon monoxide oxidation has been observed when the IDT is used with a Pt{110} crystal. In addition, chemical oscillations in the CO_2 production rate are found to be initiated by acoustic excitation outside the normal existence range for these oscillations.

So far, there have been very few studies on the effects of acoustic waves on systems involving the gas-solid interface. The catalytic activities of palladium and copper thin films deposited onto the surface of lithium niobate piezoelectric InterDigital Transducers (IDTs) for ethanol oxidation have been reported by Inoue and co-workers to increase two or three fold when excited by acoustic waves during the catalytic reaction [1]. In another study, using an Edge Bonded Transducer (EBT) with a Pt{100} crystal, Brezhnev et al [2] demonstrated the influence of acoustic excitation on the rate of the $CO + O_2$ oscillatory reaction. Sharp peaks were found superimposed on the oscillating work function curve and were related to resonant features that simultaneously appeared in the response signal of the acoustic wave spectrum during the frequency scan. Moreover, these authors reported complex acoustic spectra which appeared to show surface sensitivity.

2. Experimental

The uhv chamber has a base pressure of 10^{-10} mbar and is equipped with the usual analytical facilities, i.e. an argon ion gun, a LEED optics system and a quadrupole mass spectrometer. A stainless steel reactor chamber has been especially constructed to carry out experiments under high pressure conditions. The reactor equipped with an ionisation gauge, has a base pressure of 5×10^{-8} Torr and is attached to the gas line of the uhv system pumped by a diffusion pump. It is connected to the main chamber via a leak valve, and analysis of the gases are made using the mass spectrometer.

A poled 128° Y-cut $LiNbO_3$ single crystal capable of generating Rayleigh waves is used as the substrate in the IDT excitation system. A pair of IDT electrodes consisting of a series of uniform metal electrodes in the form of two inter-spaced combs were fabricated on both ends of the crystal. The centre SAW frequency is around 19.5 MHz. A Pt{110} single crystal, 5000 Å thick, is bonded directly onto the piezoelectric surface, in the propagation path between the electrodes for SAW generation and detection. The estimated RF power introduced to the sample during the experiments with the IDT system is of the order of 1 Watt.

3. Current Work

2. Effect of acoustic excitation on the $CO+O_2$ rate

Using the IDT excitation system in the reactor, a phenomenal eight-fold increase in the rate of the catalytic carbon monoxide oxidation reaction over Pt{110} has been found, when the chemical system is excited with Rayleigh waves. This increase is certainly not attributable to artefacts, such as electromagnetic interference, since special measures to eliminate the latter have been taken and control experiments to measure it have been performed. The observed increase in reaction rate cannot be associated with a pure thermal effect arising from sample heating while applying the RF power. The acoustic excitation does not always result in an efficient increase in the reaction rate. A sample left in the reaction mixture at elevated temperatures for several hours responds more quickly to SAW excitation than a sample left in vacuum. Furthermore, we found that a temperature rise of more than 20 degrees produced only a two-fold increase in reaction rate. Finally, as will be described below, when the sample temperature is controlled to within ±0.2 K the acoustic wave induced enhancement in the rate is still observed.

3. Effect of acoustic excitation on the oscillatory regime of CO oxidation

Following repeated cycles of acoustic-wave-induced enhancement of the rate of CO_2 production, the CO_2 pressure began to oscillate, after the system had been left at constant temperature and O_2 and CO partial pressures, with no further acoustic excitation. The oscillations were quite periodic with 500 secs periods. Under steady state conditions with the temperature of the catalyst stable at 547 K. Here, a four-fold increase of the CO_2 pressure is observed when the SAW excitation is switched on, with continuous scans from 18.8 to 19.8 MHz and a scan duration of 75 secs. The temperature rose by 0.2 K but was quickly stabilised to the original value. The reaction rate continued at the same increased level for as long as the SAW was on. The system switched into the oscillatory regime after 40 minutes of acoustic excitation.

3. Further experiments in progress

As with our unique instrumentation we can provide clear evidence for the dramatic influence of acoustic excitation on catalytic reactions, we now proceed to a further investigation of the mechanism underlying this process. In addition to frequency and power dependence measurements we are performing IR and LEED studies in combination with narrowband acoustic excitation using Pt and Ni single crystals as catalysts. We intend to explore the use of acoustic excitation as a potentially efficient route to control the rate and the selectivity of heterogeneous catalytic processes.

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EFFECT OF THE VISUAL LIGHT ILLUMINATION ON PENTANE REACTIONS OVER SULFATED ZIRCONIA

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Sulfated zirconia has attracted considerable attention of researchers as a potential catalyst for skeletal isomerization of small alkanes. Electron acceptor (oxidizing) sites are among those claimed responsible for its unique activity [1].

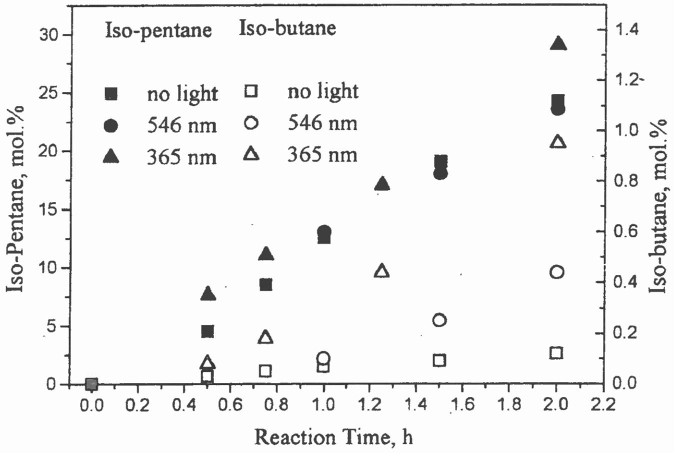
Sulfated zirconia has been reported to possess very strong acceptor sites capable of ionizing benzene (I_p=9.25 eV) to radical cations [2]. Irradiation with visual or near UV light proved to be an efficient way of their generation on strongly acidic catalysts [3]. In this paper we report the results of the first study on the effect of such irradiation on pentane isomerization and cracking over sulfated zirconia.

The catalyst was prepared by impregnation of hydrous zirconia with sulfuric acid followed by drying and calcination at 550°C. Pentane was purified from olefins and aromatic compounds. Reactions were conducted in sealed glass reactors at room temperature under argon or oxygen. The samples were irradiated with a monochromated mercury lamp light.

In the dark, n-pentane isomerized to iso-pentane with a 98-99% selectivity. Iso-butane and isomeric hexanes were also detected in almost equal molar ratios. Change of argon atmosphere to oxygen had no apparent effect on the activity or selectivity. Illumination in Ar also did not alter them.

Illumination in the oxygen atmosphere resulted in a substantial increase in the amount of iso-butane (Figure 1). We observed its two-fold increase after 2 hours under yellow light (579 nm). Iso-butane selectivity under 365 nm light was 6 times higher than in the dark. The induction effect observed suggests successive isomerization and cracking. The illumination had little effect on the isomerization activity in the whole spectral range.

The results obtained suggest that the process involves both acid and acceptor sites coexisting on the sulfated zirconia surface. The isomerization reaction, most likely, takes place on acid sites and follows an ionic mechanism. Contrary, cracking is likely to involve acceptor sites. Oxygen is known to strengthen the acceptor sites [4] and shift absorption of electron donor-acceptor complexes between the substrate and surface sites to longer wavelengths [5]. The visual light illumination results in the formation of unstable radical cations that initiate cracking.



The effect reported here is a unique example when a photoreaction of a small alkane could be initiated with visual light.

This work was supported in part by Russian Basic Research Foundation (Grant 94-03-08690).

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PPI-7

PHOTOCATALYTIC PROPERTIES OF FULLERENES ADSORBED ON γ-Al_2O_3 AND HY ZEOLITES

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Radical particles have been reported to form during fullerene adsorption on HY zeolites from different organic solvents [1]. In the present work we have studied photostimulated processes with fullerenes acting as spectral sensitizers. These reactions resulted in the formation of radical particles with ESR spectra typical for surface polycondensed structures. The reactions were observed in aromatic solvents (benzene, toluene, mesitylene) but not in CCl_4 or hexane and similar results were obtained on γ-$\mathbf{Al_2O_3}$ and **HY** zeolites.

In the dark fullerene (~85% $\mathbf{C_{60}}$ and 15% $\mathbf{C_{70}}$) adsorption from saturated solution in all the solvents studied resulted in weak ESR spectra with g_{av} =2.003 and ΔH=2.0 G (Spectrum **A**). Most likely, they belong to fullerene radical cations formed on surface acceptor sites [1]. In aromatic solvents, illumination with visual light (λ = 578 nm) led to a significant increase of their concentration and formation of new radical particles (Spectrum **B**). Their ESR parameters (g_{av} = 2.004 and ΔH ~11 G) are typical for polycondensed structures stabilized on oxide surfaces. After the illumination concentration of the radical cations decreased with time while that of the new particles slightly increased (Spectrum **C**).

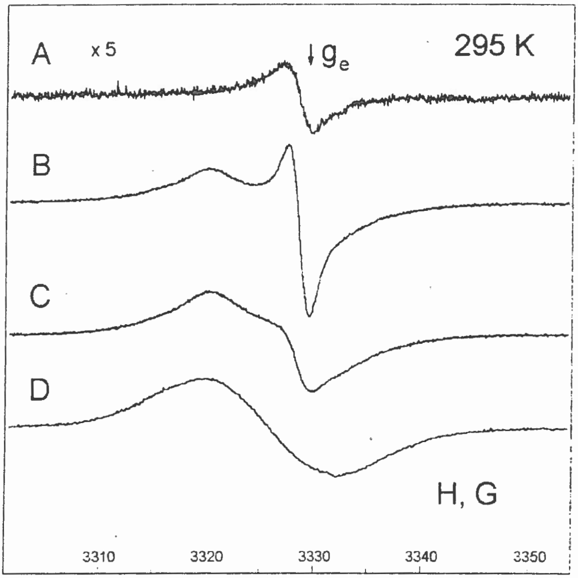
ESR spectrum of polycondensed structures observed after toluene adsorption on fluorinated alumina in the dark is presented for comparison (Spectrum **D**). Surface acceptor sites of this catalyst are much stronger and able to initiate toluene polymerization.

The following regularities were observed:

1. No polymerization radicals were observed in the dark even at 80÷90° C.

2. Such radicals were not registered in pure solvents (without fullerenes) in the dark or under illumination (λ ≥ 365 nm).

3. Photoinduced reactions were observed only in aromatic solvents. In CCl_4 and hexane only fullerene radical cations (Spectrum **A**) were registered.



The results obtained make it possible to conclude that stabilized surface radicals (g_{av} = 2.004 and ΔH ~11 G) (Spectra **B**, **C**) result from the polycondensation of aromatic molecules which takes place on surface sites involving fullerene molecules. Excited fullerene molecules are likely to initiate the polycondensation.

Acknowledgment

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PPI-8

MULTINUCLEAR NMR STUDIES OF THE GLASS-CRYSTAL TRANSITION IN V_2O_5-$Cs_2S_2O_7$ SYSTEM

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Today a thorough knowledge of the structure of the V_2O_5-$Cs_2S_2O_7$ system is necessary due to its importance as an active component of the modern environmental friendly industrial catalysts for SO_2 oxidation. In order to understand more completely the behavior of the real catalysts in catalytic processes the details of the dynamics of V_2O_5-$Cs_2S_2O_7$ system on the atomic scale are required. For the elucidation of the structure of molten state at elevated temperatures it is possible to study glasses, formed during quenching of the melts.

Solid-state and high-temperature NMR became a powerful tool for the characterization of glassy and crystalline materials as well as their melts [1, 2]. NMR is highly sensitive to the local environment of the nuclei and therefore is very well suited for the structural analysis of glasses and dynamic processes taking place during glass-crystal transition. The latter includes the alkali cations and anions diffusion, the restricted molecular reorientation, the cooperative motions of the networks, the exchange due to the bond breaking-formation processes.

Here we present detailed NMR studies of the glass-crystal transition in V_2O_5-$Cs_2S_2O_7$ melt-quenched glasses.

Melt-quenched glassy V_2O_5-$4Cs_2S_2O_7$ demonstrates an axial anisotropic and broadened ^{51}V NMR line attributed to V-atoms in distorted octahedral oxygen environment with one short V=O bond. The ^{133}Cs NMR spectrum of the same sample shows a broad line that does not narrow under magic angle spinning (MAS) conditions. These results suggest the continuous random network formation in the glassy sample which consists of the vanadium-sulfate (pyrosulfate) fragments with Cs-cations occupying some of positions between them.

Increasing of the temperature of the melt-quenched glass one can determine the temperature of the beginning of its relaxation to the equilibrium. We associate this temperature with a glass transition temperature T_g. At this temperature the viscosity of the glasses is rather low and they pass into meta-stable supercooled melt.

A progressive increase of the temperature up to 220°C is accompanied by the narrowing of the line both in ^{51}V and ^{133}Cs NMR spectra till the minimal value of the line width is achieved at 220°C. This temperature is the glass transition temperature, T_g, for Cs/V=4 composition. At first, both spectra are isotropic due to high mobility of Cs-cations as well as due to the rapid motion of the fragments of anion network. These processes result in the fast crystallization of the sample. During the crystallization at T_g the line width of ^{133}Cs NMR increases and in the crystalline sample spectrum comprises a superposition of two anisotropic lines as expected for equilibrium mixture of $Cs_2S_2O_7$ and $Cs_4(VO)_2(SO_4)_4$ [3]. The ^{51}V NMR spectra of this sample also indicate the formation of the regular $Cs_4(VO)_2(SO_4)_4$ phase.

The further increase of the temperature leads to the narrowing of the ^{133}Cs NMR line. At 500°C (which is above the melting point of the sample [3]) a narrow isotropic ^{133}Cs NMR line typical for liquids with low viscosity is detected. The ^{51}V NMR spectrum at this temperature is also isotropic indicating high mobility of anion framework of the melt.

Acknowledgments. The authors wish to thank INTAS (93-3244-Ext) and Russian Foundation for Basic Research (95-03-08365a) for support of this work.

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MONTE CARLO MODEL OF SELF-OSCILLATIONS IN $CO+O_2/Pt(100)$ REACTION CAUSED BY NONLINEAR LAW OF SURFACE RECONSTRUCTION

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Since the first discovery of a correlation between reconstruction and kinetic oscillations in CO oxidation over $Pt(100)$ by Ertl e.a. [1], this surface has become one of the most extensively studied oscillatory systems in heterogeneous catalysis. The mechanism giving rise to oscillatory behaviour in the $CO+O_2$ reaction on a $Pt(100)$ is attributed to a *hex* → (1×1) phase transition induced by adsorbed CO. Critical CO coverage $\Theta_{CO} \approx 0.08$ with local concentration of $CO_{ads} \approx 0.5$ ML within islands transforms the *hex* structure into the 1×1 surface. The lifting of the *hex* reconstruction is accompanied by an increase in the oxygen sticking coefficient from $\approx 10^{-3}$ (*hex*) to $\approx 10^{-1}$ (1×1), thus inducing a transition from a catalytically inactive state into an active state with high sticking coefficient for oxygen. The growth of (1×1)-CO islands on an extended $Pt(100)$ plane was recently studied by Hopkinson e.a. [2]. It was found that the rate of the *hex* →(1×1) transition followed strongly nonlinear power law $\Theta_{1\times1} \sim (\Theta_{CO})^n$, with $n \approx 4$. Later the mathematical description of oscillatory behaviour of CO oxidation on $Pt(100)$ had been proposed [3] using this new experimental findings. This nonlinearity is of key importance for the reported Monte Carlo model of oscillating $CO+O_2/Pt(100)$ reaction as well.

The catalyst surface was represented by a square N×N lattice with periodic boundary conditions. Each lattice cell corresponds to the platinum active site *, both $*_{hex}$ and $*_{1x1}$, which can mutually transform under appropriate conditions. In particular, when a square of four neighbour cells is fully covered by CO_{ads}, all these cells can be (with corresponding probability) transformed into the (1×1) state (fourth order process). The reverse phase transition (1×1) → *hex* obeys the linear law: $*_{1x1} \rightarrow *_{hex}$. These processes are included in the total list of elementary stages used for the simulation of the spatio-temporal behaviour of the system under study (when $*_{1x1}$ as well as $*_{hex}$ can participate in the given stage, the indices are omitted):

1) $CO + * \rightarrow CO_{ads}$, (*CO* adsorption on both $*_{1x1}$, and $*_{hex}$ sites)
2) $CO_{ads} \rightarrow CO + *$, (*CO* desorption conserving the type of the site)
3) $4CO_{ads} \rightarrow 4CO_{ads}^{1x1}$, (phase transition *hex* → 1×1)

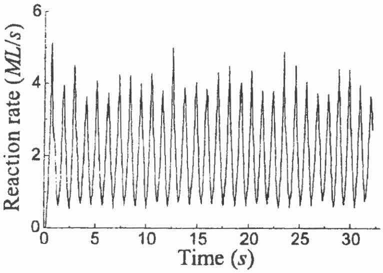
4) $CO_{ads}+*\rightarrow*+CO_{ads}$, ($CO_{ads}$ diffusion over all the sites of the lattice)

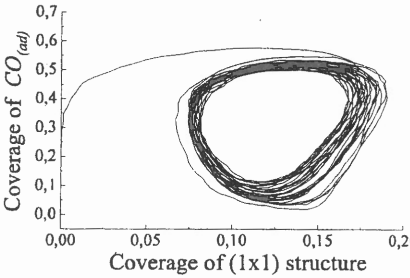
5) $O_2+2*_{1\times1}\rightarrow2O_{ads}^{1\times1}$, (oxygen adsorption on $*_{1x1}$ sites)

6) $O_{ads}^{1\times1}+CO_{ads}\rightarrow CO_2+*_{1\times1}+*$, (surface reaction conserving the type of the sites)

7) $*_{1\times1}\rightarrow*_{hex}$, (reverse phase transition $(1\times1)\rightarrow hex$)

Using these assumptions the model evolution was simulated with the standard Monte Carlo algorithm, that had been explored in our previous modeling of oscillatory behaviour of catalytic reactions due to the influence of the «subsurface» oxygen [4]. The distinctive feature of the present model is the availability of the strong nonlinear stage 3 ($hex\rightarrow(1\times1)$ phase transition of surface reconstruction). The parameters of the elementary processes 1)-7) were partly taken from the available literature. The model reproduces the self-oscillations of the reaction rate under the conditions very close to the experimental observations. The oscillations are accompanied with the autowave behaviour of surface phases and adsorbate coverages. The dependencies of oscillation features *versus* reaction parameters had been studied. The figures below show an example of reaction dynamics simulation: the left one displays the temporal behavior of the reaction rate, the right one - the simulated limit cycle projection on the plane ($\Theta_{CO}\times\Theta_{1\times1}$).





Acknowledgement. The financial support by INTAS Grant # 93-0964 and by RFBR Grants ## 96-03-33211 and 96-03-34403 is highly appreciated.

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PPI-10

Characteristic features of Raman band shifts of V_2O_5 and β-$VOPO_4$ catalysts exchanged with the $^{18}0$ tracer and active sites for reoxidation

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Introduction: It has been generally established that the redox mechanism takes place in the oxidation reactions on V oxide catalysts. What oxygen species of V oxide such as V-O-V and V=O are responsible for catalytic oxidation has been discussed(1). In this work, the oxide ions of V_2O_5 and β-$VOPO_4$ catalysts were exchanged with ^{18}O tracer via n-butane or but-1-ene oxidations. The Raman spectra of partly exchanged V oxides were measured and preferential shifts of the bands were compared. The correlation between the Raman bands and the stretching modes reported previously on these oxides(2-4) was applied to the estimation of oxygen species and anion vacancies.

Methods: Using a closed circulation system, the oxide ions of V_2O_5 and β-$VOPO_4$ catalysts were partly exchanged with ^{18}O by reoxidation with $^{18}O_2$(98%) after reduction with n-butane or but-1-ene and by a catalytic oxidation with n-butane or but-1-ene and $^{18}O_2$ at around 723-793K. The product selectivities to butenes or butadiene were ca.60% and to $CO+CO_2$ ca.40% for both catalysts. The Raman spectra data were stored on a computer and used for band-shape analysis.

Results and discussion: V_2O_5;The oxygen ions of V_2O_5 were exchanged sufficiently using $^{18}O_2$ at 873K in order to get final shift position of the bands of V_2O_5. The bands at 998, 703, and 530 cm^{-1} are shifted to 964, 685, 523 cm^{-1}, respectively. According to Abello et al.(3) and Beattie et al.,(2), the band at 998 cm^{-1} corresponds to V-O_A(1. 58A) bond, i.e., terminal oxygen. The band at 703 cm^{-1} corresponds to V-O_C(1.88A) bond, i.e., edge sharing oxygen ions between two octahedra. The 530 cm^{-1} band corresponds to V-O_B(1.78A) by Abello et al., which is corner sharing oxygen, but it is not used here for band-shape analysis since its shift was very small.

Fig.1 shows the spectra of exchanged V_2O_5 catalyst which were reduced by n-butane 710-790K and reoxidized by $^{18}O_2$. The band at 703 cm^{-1} shifts to low frequencies and shows line broadening. A new band appears at 964 cm^{-1} shifted from 998 cm^{-1}. With the band at around 700 cm^{-1}, the band-shape analysis was carried out using 703 and 685 cm^{-1}. The intensity ratio of 998 and 964 cm^{-1} was also determined by the analysis. The fractions of 685 cm^{-1} band ranges from 27 to 56% as the average ^{18}O exchange% ranges from 4 to 17%, which obtained from ^{18}O content in products. While the fractions at 964cm^{-1} ranges from 9 to 29%. The fractions at 685 cm^{-1} are 2-3 times larger than those at 964 cm^{-1}, suggesting that oxygen insertion take place at the V-O_C(1.88A) position rather than the V-O_A(1.58A) position. In the exchange by the catalytic oxidation, similar results were obtained.

β-$VOPO_4$; The model of β-$VOPO_4$ structure is shown in Fig.2. According to the previous reports,(5) the VO_6 octahedra are linked by corner sharing oxygen of V=O. Two kinds of P-O_b-V

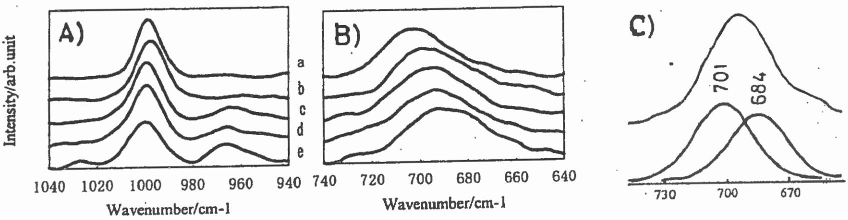

Fig.1 Raman band shifts of 998 and 703 cm^{-1} as a function of average exchange % with ^{18}O. A) and B), a) zero%, b)4%, c)6%, d)10%, and e)17%. C)an example of band-shape analysis for d).

are linked within the VO_6 chains while P-O_a-V are bonded across the two VO_6 chains as shown in Fig.2. Lashier et al.,(4) have proposed that the bands at 1076 cm^{-1} corresponds to P-O_a-V vibration, 1002 to V=O, and 992 and 900 to two P-O_b-Vs.

Fig.3 shows the spectra of β-$VOPO_4$ catalystswhich were exchanged with ^{18}O via reduction by but-1-ene and reoxidation by $^{18}O_2$. According to the band-shape analysis, the results show that the band intensity at 992 cm^{-1} decreases with the increase in a new shifted band intensity at 965 cm^{-1}. The same tendency is found between the 900 cm^{-1} band and the shifted 880 cm^{-1} one.The V=O band at 1002 cm^{-1} exhibits less exchange. The band at 1076 cm^{-1} also exhibitsno exchange at initial stages.These results indicate that the oxygen insertion takes place at the sites corresponding to the P-O_b-V position selectively. The oxygen ions whose V-O bond is not strong seem to be active for oxidation reactions.

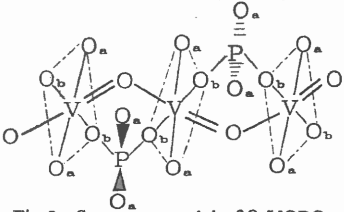

Fig.2 Structure model of β-$VOPO_4$

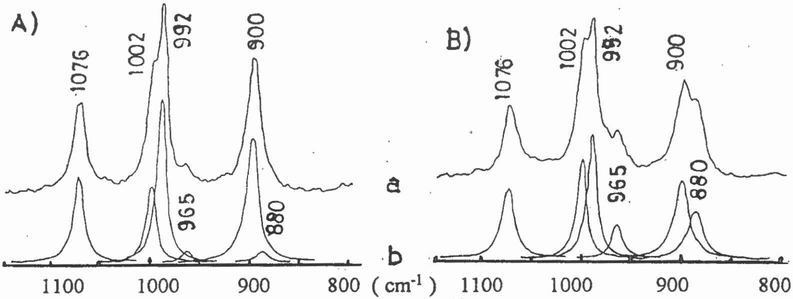

Fig.3 Raman spectra of β-$VOPO_4$ exchanged with ^{18}O. A) 5% oxygen exchanged, B)14%.
a: observed spectra, b: separated peaks.

References:1)e.g., K. Tarama et al., Proc. 3rd Congr.Catal., Amsterdam, 1964, p.287; J.G. Eon et al., J. Catal., 145, 318(1994).2)I.R.Beattie et al., J. Chem. Soc. A, 2322(1969). 3) L.Abello et al., Spectrochim. Acta, 39A, 641(1983). 4) M.E.Lashier et al.,J. Catal., 128, 113(1991). 5) E.Bordes et al., Ann. Chim. 8,105(1973).

PPI-11

ADSORPTION AND REACTION ON THE «LIVING» SURFACES: A MONTE CARLO APPROACH

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It is reliably stated now that most of all catalytic reactions cannot be correctly described in the frames of Langmuir kinetics. Despite of plentiful experimental evidences of flexibility of the catalytic surfaces to the variation of adlayer composition and external conditions, there are almost no theoretical studies of adsorption and catalytic processes on 'real' rough surfaces with dynamically changing morphology. In our study we consider the monomolecular and dissociative adsorption of gaseous species with subsequent reaction on such 'living' surfaces by means of imitating modeling (statistical lattice model using the Monte Carlo technique).

To model the surface we used a solid-on-solid (SOS) model. The model crystal of the catalyst is formed by cubic unit cells interacting with their neighbors through lateral faces with attraction energy J_{mm}. The morphology of the surface at every instant can be specified by the set of integers $\{h_{ij}\}$ - the heights of columns (i,j) above the square lattice $N \times N$ with periodic boundary conditions. The surface morphology is changed by the topmost atom transfer (diffusion) from any column onto the neighbour one in accordance with the standard Metropolis algorithm. As a result of this procedure the surface becomes rough due to the thermal excitation.

To simulate the adsorption and reaction processes the surface was preliminary roughened up to the achievement of the equilibrium state at each temperature value. Adsorption of a gas species A (or B_2) proceeds on one (or two) free topmost surface sites lying on the same level. After the successful adsorption attempt the adsorbed molecule B_2 dissociates immediately and B_{ads}, as well as A_{ads}, can diffuse on the surface; the desorption can happen only for two neighbouring B_{ads} lying on the same level. After each adsorption/desorption attempt several acts of diffusion of the substrate and adsorbate atoms were made in order to achieve the equilibrium state. The probabilities of the adsorption attempts are determined by the adsorption rate coefficients and by the ratio of adsorbing gas pressures. The probabilities of desorption are temperature dependent. An adsorbed molecule interacts (with energy J_{ma}, in general case different for A_{ads} and B_{ads}) with the nearest neighbour substrate atoms. Therefore, probabilities of adsorption, desorption and diffusion are determined by the nearest environment of adsorbed particle. We did not consider the transfer of the substrate atom on the adsorbed particle, thus the formation of a subsurface layer of adsorbate is forbidden. The surface reaction between A_{ads} and B_{ads} proceeds immediately when these species appear in the nearest neighbourhood due to adsorption or diffusion.

A series of isotherms for adsorption processes was simulated at different temperatures and values of lateral interactions between adsorbate and substrate. The theoretical estimations show that the isotherms for dissociative adsorption will be the same as for monomolecular adsorption to within the substitution: $p \to \sqrt{p}$. The most interesting peculiarity of these isotherms is that they converge to the Langmuir isotherm not solely at high temperatures, when the dimensionless energies of interaction adsorbate-substrate are low, but at low temperatures as well, when these energies are high enough (here the dimensionless energies are (E / kT)). The largest deviation from the Langmuir isotherm is observed at intermediate temperature values (excluding the case of high adsorbate-substrate attractive interactions at low temperatures). The reason for the low temperature isotherm convergence to the Langmuir isotherm follows from the fact that the surface of the SOS-model at low temperatures is flat, i.e., adsorbate-substrate interactions are negligible. However when the adsorbate-substrate bond is strong and even stronger than the substrate-substrate one ($J_{ma} > J_{mm}$), one should expect the adsorbate-induced reconstruction of the substrate surface even at low temperatures. In particular, in the case of dissociative adsorption the metastable state is formed, consisting of diagonally ordered point defects on the surface. As stated by simulations, the relaxation of this state to the equilibrium one at low temperatures, unlike high temperatures, is enormously slow.

The reaction $A + B_2$ proceeding *via* Langmuir-Hinshelwood mechanism was simulated under various conditions: different temperatures and reagent concentrations, with and without diffusion, different surface roughness degrees and diverse ratios between J_{mm} and J_{ma} for each reagent. In most cases the kinetic characteristics of the reaction on the rough surfaces differs markedly from the ones on the smooth surfaces and most of all from the predictions of the ideal surface layer hypothesis (Langmuir kinetics). In particular, due to the restricted mobility of adsorbates the reaction rate on the rough surface is considerably lower in comparison with the reaction on the smooth surface.

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PPI-12

PHOTOINDUCED FORMATION OF O_2^- RADICAL ANIONS ON ZrO_2 SURFACE IN THE PRESENCE OF ORGANIC SOLVENTS.

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Molecular O_2^- radical anions are well known to form on oxide surfaces as a result of electron transfer from preadsorbed organic molecules [1]. In our group photostimulated electron transfer reactions on oxide surfaces were shown to proceed in several cases parallel to thermal ones [2]. Often such reaction can be initiated by absorption of visual light by surface complexes.

In the present work photoinduced formation of O_2^- anion-radicals on ZrO_2 surface in the presence of organic solvents was studied. Three different zirconium dioxide samples were used. The first one was tetragonal and had 180 m^2/g surface area. The second one was monoclinic with the surface area only 2 m^2/g. The third sample contained a mixture of the two crystal phases with the surface area 60 m^2/g.

The samples were preactivated at 573 ÷ 973 K in air and filled with an organic solvent at room temperature. Kinetics of the O_2^- accumulation with or without illumination and its dependence on the solvent and preactivation conditions was studied.

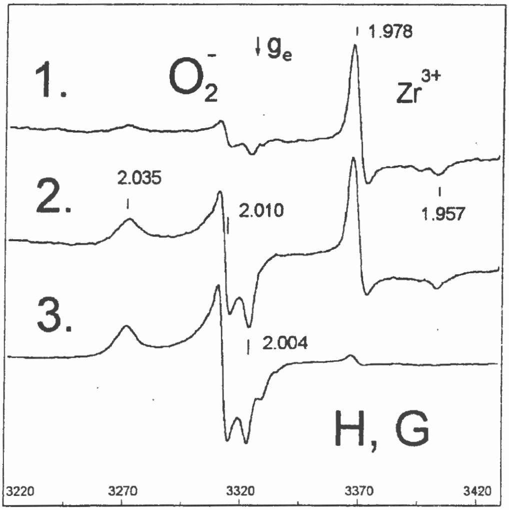
Typical ESR spectra observed during toluene adsorption on ZrO_2 are shown in Figure. Spectrum 1 was recorded in 24 h after the adsorption without any illumination, Spectrum 2 after additional 1 hour irradiation with monochromatic light ($\lambda = 436$ nm), Spectrum 3 after additional 10 minute irradiation with unfiltered mercury lamp light.

The following regularities were found:

1. In all the cases both thermal and photoinduced reactions were observed. Increase of the activation temperature resulted in a decrease in the activation energy of thermal reactions and red shift of the photoreaction red edge.

2. Total radical concentrations depended only on the properties of the catalyst and were independent of the radical generation procedure. On samples activated at 973 K, the maximum radical concentration was achieved in several minutes after the adsorption. If the activation temperature was 673 K, thermal processes were very slow.

Illumination increased the concentration of the radicals up to the value close to that observed at higher activation temperatures.



On the basis of the above results, the following reaction mechanism can be proposed. Thermal or photoexcitation of electron donor acceptor complexes between surface active sites and adsorbed molecules results in the charge separation and stabilization of O_2^- radical anions. The activation energy of thermal reactions and the photoreaction red edge are determined by the strength of the surface active sites. The latter increases with the activation temperature as a result of the formation of coordinately unsaturated sites due to the surface dehydroxylation. It is important that **all the reactions discussed here can proceed under irradiation with visual light.**

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ISLAND FORMATION MODEL IN GAS CHEMISORPTION ON METALS

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The present study of the kinetics of gas adsorption on the surfaces of solids is based on the classic Langmuir works where the concept of the model of ideal adsorbed layer (biography and energy homogeneity) was formulated. However, the developing modern physical methods of surface study permitted obtaining a great number of data reflecting how surface defects, lateral interactions in adsorbed layer and phase conversions in adsorbed layer (clusters, domains, structures, islands) affect the kinetics of gas chemisorption. The effect of island processes on the above kinetics and heterogeneous catalytic reactions is most poorly studied. To investigate these processes, topochemical models designed for the "gas - solid" reactions are usually used. However, this allows only a formal process description, since there is no possibility to reveal the causes of the adsorption island formation and adsorption structure growth with time. Another approach is based on using the modern data on the dynamics of the gas - solid surface interaction for simulation of surface processes. These data show that chemisorption on metals may proceed by two main mechanisms. The "direct" mechanism consists in a gas molecule impact against a free adsorption site, resulting in the formation of activated complex. Then the molecule overcomes the activation barrier and is chemisorbed at this site. The "indirect" mechanism is realized when the molecule strikes against the surface and passes into a weakly bound precursor state, in which it may migrate over the surface and be chemisorbed. Using these assumptions, Becker [1,2] proposed the model of gas chemisorption as a combination of "direct" and "indirect" chemisorption, which permitted explaining the island behavior of chemisorption. The adsorption islands are initiated through "direct" chemisorption, and the "indirect" one is responsible for the islands growth.

To study the dynamics of the occurrence, growth and overlapping of island adsorption structures, chemisorption was simulated by the model including "direct" and "indirect" adsorption, using the Monte-Carlo method. "Direct" adsorption led to the occurrence of the adsorption island centres. In the case of "indirect" adsorption the molecules were captured into the external precursor and migrated over the adsorbed molecules to the average distance $X=(2Dt)^{1/2}$, where D is the coefficient of surface diffusion, and t is the average life time of the particles in precursor. If before desorption the molecules reached free adsorption sites, they were chemisorbed. This led to the growth of adsorption islands. The calculations were performed for a square 200x200 lattice, using the Monte-Carlo method.

For the probabilities of "direct" (S_{dir}) and "indirect" (S_{indir}) chemisorption, equal to 10^{-5} and 10^{-2}, respectively, at the initial adsorption stage (Θ <0.01) "direct" chemisorption dominates. In this case the individual particles are chemisorbed on the surface, thus initiating the adsorption islands. As these islands appear, the more rapid "indirect" adsorption begins to dominate, which leads to the rapid growth of adsorption islands and adsorption acceleration. At a definite degree of surface coverage with adsorbate, the islands merge into a continuous film, the portion of free surface decreases, and adsorption is retarded. The coverage - time curve has a topochemical behavior: first the adsorption rate is low (island initiation), then adsorption is accelerated (island growth) and finally retarded, which is caused by the islands overlapping. The dependence of the efficient coefficient of sticking has a maximum, which is typical for the island processes. Variation in the ratio of "direct" and "indirect" chemisorption mechanisms (S_{dir}/S_{indir}) leads to essential changes in the behavior of the growth of surface adsorption structures. At a very low possibility of "direct" adsorption ($S_{dir}=10^{-6}$) and $S_{indir}=10^{-2}$ the adsorption islands are very slowly initiated, their concentration is low, so they grow to a large size. When the contribution of "direct" adsorption increases ($S_{dir}=10^{-5}$, 10^{-4}, 10^{-3}, 10^{-2}, $S_{indir}=10^{-2}$), the rate of the island initiation grows, their concentration rises, and before sticking the islands grow to a smaller size. The coverage - time dependence is gradually transformed from a S-shaped curve to a monotonic one. Using this model for the analysis of the experimental kinetic dependencies on gas adsorption on metals allows one to ascertain the nature of adsorption mechanism, elucidate the contribution of main adsorption routes, determine the parameters of elementary stages and the dynamics of surface structures growth.

Acknowledgement. This work was supported by the Russian Foundation for Basic Research, grant No. 96-03-32961.

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PPI-14

EFFECT OF THE DIFFUSION OF ADSORBED PARTICLES BETWEEN THE SURFACE DOMAINS OF MULTICOMPONENT CATALYSTS ON REACTION RATE

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In heterogeneous catalysis the energy of the bond between reacting molecules and catalyst plays an important role. Therefore the dependence of reaction rate on it has a volcano–shaped behavior [1, 2]. The general expression describing such a dependence was deduced by Boreskov [2]. For the reactions: I.A→ Aads; II.Aads+B(gas)→ P; the reaction rates are– $R_1=k_1\exp(\alpha_1 q/RT)P_A$; $R_2=k_2\exp[-(1-\alpha_2)q/RT]\Theta_A P_B$, where q is the adsorption heat, the activation energies corresponding to these q are determined by the Brensted–Polany equation (α_1, α_2). In the steady state $q_{opt}=RT/(1+\alpha_1-\alpha_2)\ln(\alpha_1)/(1-\alpha_2)$ and $\Theta_A= \alpha_1/(1+\alpha_1-\alpha_2)$ at q_{opt}. The rate variation R/R_{max} is determined as:

$$\Delta R/R_{max}=(1+(1-\alpha_2))/\alpha_1/\{\exp[\pm(1-\alpha_2)\Delta q/RT]+(1-\alpha_2)/\alpha_1\exp[\pm\alpha_1\Delta q/RT]\} \quad (1)$$

The surface of real multicomponent catalysts consists of domains of different nature. Let us suppose that the superadditive activity is caused by the diffusion (spillover) of adsorbed particles between various surface domains.

Let a catalyst surface consist of 2–type domains s_1 and s_2 with adsorption heats $q_1=q_{opt}-\Delta q$ and $q_2= q_{opt}+\Delta q$. Since the rate–determining reaction stages at isolated domains s_1 and s_2 are different, the steady state concentrations of adparticles (Θ_1 and Θ_2) are mutually not equilibrated. Starting from Boreskov equations (1), we can obtain the following equations for the steady state condition:

$a = c\Theta_1 + b\Theta_2$, , where

$$a = \alpha_1(s \exp[\alpha_1\Delta q/RT]+ (1-s)\exp[-\alpha_1\Delta q/RT];$$
$$b = s [\alpha_1\exp[\alpha_1\Delta q/RT] + (1-\alpha_2)\exp[-(1-\alpha_2) \Delta q/RT]; \quad (2)$$
$$c = (1-s)[(1-\alpha_2) \exp[(1-\alpha_2)/RT] + \alpha_1\exp[-\alpha_1\Delta q/RT];$$

Let us assume that E_{dif} are low and/or reaction temperature is high, and the equilibrium distribution of A_{ads} between the domains is established. Then $\Theta_1=k_d\Theta_2/(1 -\Theta_2+k_d\Theta_2)$, where $k_d=\exp(-2\Delta q/RT)$ (3)

Solution of equations (2) and (3) gives:

$$\Theta_2=[k_d(a-c)-(a-b)-[\ k_d(a-c)-(ab)]^2-4ab(1-k_d)^{1/2}]/2b(1-k_d) \quad (4)$$

$$\Theta_1=a/c-[b(a-c)-b(a+b)+[\ k_d(a-c)-(a+b)]-4ab(1-k_d)]/2bc(1-k_d)$$

$$R_{dif}/R_{max}=(1+\alpha_1-\alpha_2)/\alpha_1\{s\Theta_2\exp[-(1-\alpha_2)\Delta q/RT]+(1-s)\Theta_1\exp[(1-\alpha_2)\Delta q/RT]\} \quad (5)$$

In [3] the calculations for simple case $\alpha_1+\alpha_2=1$ and $s_1=s_2=0.5$ are given. Here the general rate variation depending on $[\pm\Delta q/RT]$ is considered for the isolated domains (R_{isol}/R_{max}, eq. (1)) and the domains between which diffusion occurs (R_{dif}/R_{max}, eqs. 4, 5) for any α_1, α_2 and domain fractions s1 and s2 ($s_1+s_2=1$). A series of calculations for R_{isol}/R_{max}, R_{dif}/R_{max} and α_1, α_2 depending on $[\pm\Delta q/RT]$ are performed for various α_1, α_2 and $s_1=s_2=0.5$. For $\alpha_1>\alpha_2$ the reaction rate is shown to grow if the diffusion is taken account, i.e. $R_{dif}/R_{max} > R_{isol}/R_{max}$. This is explained by the diffusion of adsorbed particles from the domains with a higher bond energy (s_2) to those with a lower energy (s_1) where the adparticles are more reactive. For $\alpha_2>\alpha_1$ the reverse "flowing" of particles occurs, and the R_{dif}/R_{max} is somewhat lower than R_{isol}/R_{max}.

The calculations of R_{dif}/R_{max} and R_{isol}/R_{max} depending on the s_2 portion at $\alpha_1>\alpha_2$ show that the $R_{dif}/R_{max}=f(s_2)$ dependence has a dome-shaped behavior, i.e. the introduction of s_2 domains onto the surface of s_1 domains (and vice versa) leads to the reaction rate increase.

Thus, the kinetic reaction conjugation at s_1 and s_2 domains via ad-particles diffusion results in the significant rate growth when $\alpha_1>\alpha_2$. This well agrees with the "remote control" mechanism proposed by Delmon et al. [4].

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PPI-15

HREELS-detection of NO + H_2 reaction intermediates on Pt (111) and Pt (100) surfaces

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According to concepts advanced by G.K. Boreskov in his fundamental works the elucidation of a nature of intermediate chemical interaction of reactant molecules with a surface of the catalyst, the detection of catalytic reaction intermediates is the main problem of the theoretical heterogeneous catalysis [1]. A rate-determining step of NO reduction by hydrogen on platinum is a dissociation of nitric oxide molecule resulting in a layer of active N_{ads} and O_{ads} atoms. The rate of NO dissociation is determined by platinum surface structure: (i) on Pt(111) surface NO does not dissociate; (ii) on unreconstructed Pt(100)-1x1 surface the dissociation proceeds rather easily even at 300 K; (iii) reconstructed Pt(100)-hex surface is not active in the NO dissociation, but molecular adsorption of nitric oxide is accompanied by a back reconstruction of the surface into an active 1x1 structural phase. A chemical nature of surface intermediates of the low-temperature NO+H_2 reaction was studied on three different platinum surfaces: Pt(111), Pt(100)-1x1 and Pt(100)-hex. The experiments were carried out by high resolution electron energy loss spectroscopy (HREELS, a resolution of 50-80 cm^{-1}) and temperature programmed reaction spectroscopy (TPRS).

Pt(111). NO adsorption on (111) surface occurs in bridge and on-top molecular states. The reaction of the bridge NO_{ads} with hydrogen at T ~ 300-350 K was shown to result in formation of HNO_{ads} particles bonded to the surface through nitrogen and oxygen atoms. It was established that HNO_{ads} serves as an *intermediate* of the reaction: its interaction with hydrogen produces N_{ads} which further attaches subsequently three hydrogen atoms resulting in NH_{3ads}.

Pt(100)-1x1. At the initial stage, NO adsorption proceeds on the (100) surface at 300 K with dissociation. Then NO occupies molecular NO_{1x1} state. NO_{ads} layer in the reaction with hydrogen at 300 K produces N_2 and H_2O. We succeeded in finding out NH_{2ads} particle in the reaction of an H_{ads} layer with nitric oxide. Analysis of loss intensities in the corresponding HREEL spectrum allowed to conclude that the NH_{2ads} particle is bonded to two platinum atoms through nitrogen atom, and the molecule plane is close to normal with respect to the surface plane. NH_{2ads} particle appeared to be *a reaction intermediate* which gives rise to ammonia: the evolution of NH_3 into the gas phase with simultaneous NH_{2ads} disappearance occurs under heating of NH_{2ads} and H_{ads} coadsorption layer up to 350 K.

Pt(100)-hex. The NO adsorption on the Pt (100)-hex surface at 300 K, similar to the Pt(111) surface, proceeds without dissociation. The adsorption is accompanied by the back surface reconstruction, hex → 1x1, leading to the formation of the islands of unreconstructed phase saturated with molecular NO. Two molecular states of NO_{ads} were determined by HREELS technique: the NO_{1x1} state located in the islands of the 1x1 phase, and NO_{def} state associated with the population of structural defects caused by the hex → 1x1 reconstruction. Kinetic peculiarities of the NO_{ads} layer titration with hydrogen were considered in detail in Refs. [2,3]. The reaction was shown to be characterized by an induction period during which only the NO_{def} state is consumed. The formation and disappearance of NH_{ads} particles, presumably adsorbed on the structural defects, are observed during the induction period. The analysis of loss intensities in the corresponding HREEL spectrum proves that the axis of NH_{ads} molecule is inclined to the surface plane.

Conclusion. For the low-temperature $NO+H_2$ reaction on platinum there are the effects of the structure of the catalyst surface on:

(i) N-O bond breaking {a direct NO_{ads} dissociation on the Pt(100)-1x1 surface and via the HNO_{ads} intermediate formation on the Pt(111) surface};

(ii) chemical nature of stable reaction intermediates {HNO_{ads}, N_{ads} on the Pt(111) surface, NH_{2ads} on the Pt(100)-1x1 surface and NH_{ads} on the Pt(100)-hex surface}.

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PPI-16

QUANTUM-CHEMICAL ANALYSIS OF NITROXIDES COORDINATION BY LEWIS ACID SITES OF THE ALUMINA SURFACE

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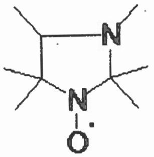
The method of paramagnetic complexes of probe molecules is successfully applied for investigation of acidic properties of oxide catalysts, for example Al_2O_3 [1]. Stable nitroxides are very informative probes. Under their adsorption on oxide surfaces donor-acceptor complexes with Lewis acid sites (LASs) may be produced. These complexes can be investigated by means of EPR. The theoretical analysis of such complexes is useful for the understanding of their structure [2].

In accordance with experimentally found similarities between magnetic resonance parameters of donor-acceptor complexes of nitroxides with $AlCl_3$ in unpolar solvents, and with surface LASs of alumina the latter were modeled by covalent cluster $Al(OH)_3$. This method has been widely approbated in non-empirical and semi-empirical quantum-chemical calculations of chemisorbed molecular forms.

All quantum-chemical calculations were made in accordance with unrestricted method of Hartree-Fock (UHF): non-empirical ones were done by means of STO-3G, STO-6G, 3-21G and 6-31G while semi-empirical calculations were made by means of the valence approximations MNDO, AM1 and PM3. To select the method of analysis the $H_2NO \cdots Al(OH)_3$ complex has been studied. Three types of calculations have been carried out. The first type corresponded to the full optimization of both radical and cluster. The geometry of the cluster was fixed in the another type of calculation. The third type differedfrom the second one by mobile Al atom in the simulated surface complex.

Our analysis has revealed that the MNDO method is better than non-empirical methods in the calculation of the bond distance N-O, energy of complexing, spin densities and the constant a^{N}_{iso}. The best results have been obtained using the second type of calculations.

To pass on real investigated objects some imidazoline and imidazolidine nitroxides (I-IV) have been calculated.



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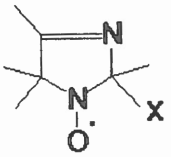

II: $X = CH_3$ III: $X = C_6H_5$
IV: $X = n\text{-}C_8H_{17}$

These radicals have two possible ways of coordination with LASs on the alumina surface. The energy of complexing can be used as the measure of the advantage of the formation of the complex type. Our calculations have revealed that the radical I formed the complex through the oxygen but the radical II formed the complex through the nitrogen, what is in accordance with the experiment. The experimentally observed superposition of the spectra in the case of the radicals III and IV can be explained by similar calculated energies of complexing by two concurrent ways.

Thus, with the help of the quantum-chemical analysis we have confirmed experimental data on the structure of the adsorption centers and the orientation of the complex-bonded molecules.

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QUANTUM CHEMICAL CALCULATIONS OF THE ROLE OF ELECTRONIC STATE OF Ni ATOMS IN THE ACTIVE COMPONENT OF HYDRODESULFURIZATION CATALYSTS

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Nickel- or cobalt- molybdenum sulfide catalysts are extensively used in the hydrodesulfurization (HDS) process. Especially the role and the chemical (electronic) state of the cobalt and nickel atoms in the sulfide catalysts is a subject of numerous experimental and theoretical investigations. The most of the investigators claim that the increasing of catalytic HDS activity is purely a promotion effect, while by our opinion [1], the promoter atoms are themselves the catalysts. That is the reason of our attention to calculation of the detail electronic structure of Ni in the Ni/MoS_2 catalysts.

We have performed ab initio calculations of the $Ni(S_2C_2H_2)_2$ {Ni(BDT)} as a molecular model of active centers (AC) in HDS catalysts. It was shown that in the square-plane coordination Ni has d^8 electron configuration corresponding to the formal oxidation state Ni(II) [2]. In this state Ni is not active for adsorption of donor molecule as H_2S [3]. Accounting for the tendency of Ni(BDT) complex to form stable dimer structures with a Ni atom transferred from a plane of the complex, one can assume that there are the structures for which the unusual oxidation state of Ni(IV) with the electron configuration d^6 can occur. Our calculations of the H_2S:Ni(BDT) molecular adduct confirm such an assumption [3]. The possibility of Ni(IV) existence in the Ni/MoS_2 system may be proposed basing on the XPS data [1] giving the excess of positive charge on Ni in Ni/MoS_2 compared to NiS.

We have performed the ab initio calculations for the $NiMo_2S_{10}H_{10}$ cluster with d^8 electron configuration of Ni(II) and with d^6 electron configuration of Ni(IV). Also, we have carried out calculations of electronic properties for adsorbed H_2S complex on $NiMo_2S_{10}H_{10}$. All calculations were carried out with use of the LANL1 effective core potential for inner shells of Ni, Mo and S atoms and basis set single- ζ (MB) or double- ζ (DZ) for valence shells provided with the Gaussian 92 package . The electronic correlation was taken into account using the Moller-Plesset perturbation theory at the second order (MP2). Geometry-optimized calculations for H_2S molecule and its adsorption complex were carried out at the MP2 level with the split-valence 3-21G basis set for H atoms and LANL1DZ for S atom:

(i) According to the total MP2 energy values, the d^8-state of Ni in the cluster represents the most stable adsorbed complex of H_2S molecule. The corresponding MP2 energy value for the isolated $NiMo_2S_{10}H_{10}$ cluster with the same d^8- state of Ni and MP2 energy for the free molecule H_2S give minor bonding interaction (E_{ads} = 36 kJ/mol).

(ii) Computed MP2 total energies for cluster and adsorption complex with Ni(IV),

(iii) d^6 electron configuration are lower than for divalent Ni(II) (ΔE= 6.4 eV). Adsorption energy of H_2S molecule for Ni(IV), d^6 - state (E_{ads}=82.6 kJ/mol) is greater than for Ni(II), d^8 - state (E_{ads}=36.0 kJ/mol). Calculated equilibrium bond distances Ni - SH_2 are 2.60 A and 2.77 A for Ni(IV) and Ni(II) - respectively. By this means, adsorption energy appears to increase with increases in the formal oxidation state of Ni in the cluster.

A possible explanation in increase of the Ni oxidation state in the sulfide catalysts seems to be as follows. We believe that under the catalyst preparation and sulfurization under hydrogen atmosphere conditions the reaction of the oxidative addition of the hydrogen molecule occurs. This reaction of oxidative addition of H_2 to the square-planar complex was discovered over 30 years ago. It is well known that the square-planar complexes with d^8 electron configuration have a strong tendency to the oxidative hydrogen addition resulted in the transition metal atom with d^6 electron configuration. Based on these investigations we conclude that the high oxidation state of Ni into the active centers of the HDS catalysts resulted from the oxidative addition of H_2 under conditions of catalyst preparations [4].

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PPI-18

CATALYTIC CONVERSION 0F n-HEXANE. QUANTUM-CHEMICAL STUDY OF REACTION MECHANISM

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Dehydrocyclization of alkanes is one of the principal stages of reforming and the biggest source for production of benzene, toluene and xylenes. N-hexane was used as a model for investigation of alkane dehydrocyclization.

We have synthesized two types of Pt-Re/Al_2O_3 catalysts with different content of metals: based on monodisperse colloidal Pt sol (d=10 Å) and H_2PtCl_6 with $HReO_4$ addition.

Quantum-chemical calculations were carried out by EHM/AP method (extended Huckel method with Anderson's potential). Standard parametrization was used for atomic valence orbitals.

The electron microscopy analysis of samples was made on EM-125 microscope by replica method with extraction. Mainly fine-dispersed particles with d=10-12Å are present on the surface of catalysts based on Pt sol, whereas d=20-35Å particles occur seldom. The particles do not yield a microdiffraction pattern. Catalysts prepared from H_2PtCl_6 and $HReO_4$ consist of uniform and compact particles of 20-25Å size almost uniformly distributed on the support surface.

The dehydrocyclization of n-hexane was carried out in a flow reactor with a stationary catalyst at normal pressure. The optimal conditions of the process and the maximum yield of arenes were found out by variation of the volume rate from 2,4 to 12 h^{-1} and the reaction temperature from 773 to 923K.

In the presence of 0,35%Pt-0,35%Re/Al_2O_3 catalyst prepared on the base of Pt sol the hexane conversion varied within 34-100%.The yield of benzene changed from 18 to 82%mas. at 3,6 h^{-1} rate of raw material feed and variation of temperature from 823 to 923K. A maximum conversion of n-hexane was observed at 923K.

A decrease in Pt content from 0,35 to 0,15% led to n-hexane conversion of 96-93% (T=923K) and the benzene yield dropped from 82 to 66%. The reaction of n-hexane conversion on 0,35%Pt -O,35%Re/Al_2O_3 prepared from H_2PtCl_6 and $HReO_4$ proceeded with decrease in benzene yield (70-65%) at 873-923K.

A significant amount of polycyclic hydrocarbons (naphthalene, antracene etc.) was found in liquid products of the reaction by IR-spectroscopy and chromatomass-spectoscopy.

The dehydrocycliszation reaction is a complex process the basic stage of which are the oriented adsorption and dehydrogenation of alkane molecule, cyclization and desoprtion of formed. arenes and hydrogen from the catalyst. Each of the stages was studied individually by quantum-chemical method. To understand the catalyst surface structure the energy of metal-metal bonds in two septa-atomic Pt-Re clusters was estimated. For diatomic clusters the energy of metal-metal bonds increases in the row: Pt-Pt < Pt-Re < Re-Re. In mixed bimetallic clusters the Pt-Pt bond gets weaker whereas the Re-Re bond in low-spin complexes becomes stronger.

Hence it follows that on joint precipitation of metals from acids the surface of Pt-Re clusters will be enriched with platinum. The formation of rhenium structures on platinum cluster can be expected in the case of synthesis of the catalyst from Pt sol. Since the Re-Re bond is more stable than the Pt-Re bond rhenium would form small islands on Pt surface. The analysis of molecular orbitals of the adsorbed complexes shows rhenium centres to possess high affinity to hydrogen atoms. The migration of hydrogen on the rhenium cluster surface is hindered and requires significant activation energy. The state of atomic hydrogen on the platinum centre depends strongly on the surface structure, however in each case hydrogen keeps high mobility on platinum.

Quantum-chemical calculations make it possible to conclude that during the reaction rhenium centres are completely filled with hydrogen adsorbed. That is why the elementary act of interaction with an organic molecule involves only one rhenium atom from which hydrogen migrates onto platinum. On the contrary platinum centres of bimetallic catalysts easily desorb hydrogen and are actually accessible for interaction with hydrocarbon molecule. The result of this process can be the alkane dehydrogenation on Pt and appearance of highly active organic radicals able to form C-C bond with the chain growth or cycle closure.

PPI-19

CLUSTER QUANTUM-CHEMICAL MINDO/3 STUDY OF FORMIC ACID AND CARBON MONOXIDE INTERACTIONS WITH ZINC OXIDE

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Introduction

Chemical activity of metal oxides in the catalytic processes could be described by the existence of low-coordinated acid-base pair of centersin various structural defects of an oxide surface, i.e. steps, edges, corners, kinks, etc. This is also the case of ZnO, which is an n-type semiconductor of wurtzite type structure and hasa catalytic activity in olefin hydrogenation, CO oxidation, synthesis-gas conversion to methanol and higher branched or linear alcohols, decomposition of methanol, formaldehyde and formic acid, etc. In the present study results are reported on cluster quantum-chemical calculations by a modified MINDO/3 method for the interaction of formic acid with a nonpolar (1010) and carbon monoxide with a polar (0001) surface of zinc oxide. Based on these calculational results two channels of HCOOH dissociative adsorption, the nature of molecular adsorption of formic acids and carbon monoxide were discussed.

Method of calculation and surface model

luster quantum-chemical calculations were performed within the framework of the modified MINDO/3 method [1]. Zinc oxide modelled by a four-layer molecular cluster of $Zn_{16}O_{16}$, which allows us to analyse the participation of low-coordinated acid-base centers (Zn^{2+}_{LC} and O^{2-}_{LC} ions) in the adsorptive interaction. The influence of the cluster size on the energetics of dissociative adsorption of HCOOH was examined via using similar four-layer molecular clusters of Zn_nO_n at the experimental bulk structure geometry, where n = 4, 9, 16, 25, 36, 49.

Results and Discussions

On a nonpolar (1010) surface of zinc oxide molecular adsorption of cis- and trans-HCOOH proceeds with forming unidentate complex on a coordinatively unsaturated $Zn^{2+}{}_{2C}$ site and a six-member structure on a next-neighbour pair of $Zn^{2+}{}_{2C}$-$O^{2-}{}_{2C}$ acid-base centers, respectively. Regular (1010) surface of ZnO containing a three-coordinated pair of acid-base centers is inactive for a molecular adsorption. Dissociative adsorption of HCOOH via forming formate anion and proton leads to a substantial gain in energy. In this case, proton is connected to a basic site while a bridge or a bidentate structure is energetically more profitable for a formate anion compared to unidentate structure.

Carbon monoxide adsorbs on top position with C-end down on the polar (0001) surface of zinc oxide. Heats of its adsorption amounts 12.1 kcal/mol.Upon adsorption process CO stretching vibrational mode increases by 35 cm^{-1} compared to that of the free gas phase CO as calculated within the harmonic oscillator approach. A slightly charge transfer from an adsorbed CO to the surface take place. These findings are in good agreement with available experimental data.

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POSTER SESSION I

Section 2

Molecular Approaches to Design of New Homogeneous and Heterogeneous Catalysts and Processes

INVESTIGATION OF THE REACTION OF DIRECT OXIDATION OF HYDROGEN SULFIDE BY OPTICAL AND KINETIC METHODS

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INTRODUCTION

The problem of hydrogen sulfide utilization and processing is one of the most urgent tasks in the creation of environmentally safe processes in gas and oil mining and processing.

In Boreskov Institute of Catalysis a process of the purification of hydrogen sulfide containing gases has been developed, based on the reaction of direct selective oxidation of H_2S on the surface of solid oxide catalysts. Depending on the process condition, H_2S catalytic oxidation is carried out either in a fluidized bed of spherical catalyst granules or in fixed bed of honeycomb monolithic catalysts [1,2].

The objective of this work is the investigation of the mechanism of the reaction of direct H_2S oxidation to sulfur on a number of oxide catalysts by optical and kinetic methods.

EXPERIMENTAL

The following catalysts were used in experiments: $Fe_2O_3/\gamma\text{-}Al_2O_3$, $MgCr_2O_4/\gamma\text{-}Al_2O_3$, $TiO_2\text{-}SiO_2\text{-}Al_2O_3$.

The kinetics of the reaction of H_2S direct oxidation was studied on a flow setup. The temperature was varied in the range of 150-350°C. The initial mixture was 20% H_2S in nitrogen. The reaction was carried out at stoichiometric H_2S/O_2 ratio.

Infrared spectra were recorded on a spectrometer BOMEM MB-102 (Canada). CO adsorption was studied at -196°C, the adsorption and interaction with surface of H_2S and SO_2 were studied in the temperature range 25-350°C.

ESDR spectra were registered at room temperature using SPECORD M40 (Germany) spectrophotometer.

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RESULTS AND DISCUSSIONS

The study of the reaction kinetics showed that at residence time less than 0.3 s. 100% selectivity of the reaction to elemental sulfur is achieved on all catalysts studied. This is explained by low conversion of formed sulfur to sulfur dioxide upon consecutive oxidation. At longer residence time the decrease of the selectivity was observed when the temperature was raised to 250-300°C. The highest activity and selectivity in H_2S direct oxidation is achieved on the catalyst $MgCr_2O_4/\gamma\text{-}Al_2O_3$.

By the IR spectra of adsorbed CO it was shown that all the catalysts have both Lewis and Broensted acidic sites on the surface. However the nature, strength and number of sites are all particular for each type of catalyst. This leads to difference in adsorption and interaction with the surface reactions of H_2S and SO_2 on different catalysts.

Basing on IR spectroscopic study dissociative adsorption of H_2S on the catalyst surface was shown. As temperature is raised H_2S oxidation occurs, this process being most intensive on $MgCr_2O_4/\gamma\text{-}Al_2O_3$ in accordance with the kinetic data.

ESDR study showed that during the reaction various types of elemental sulfur: S_4-S_8 are formed on the catalyst surface (Fig. 1).

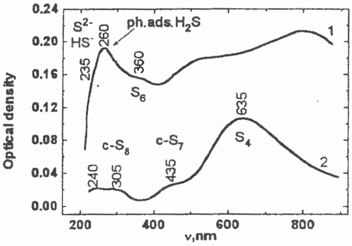

Fig. 1. ESDR spectra of H_2S adsorbed on TiO_2-SiO_2-Al_2O_3 (1) and Fe_2O_3/Al_2O_3 (2) catalysts.

The investigation performed allows drawing tentative conclusions about reaction routes: the reaction can proceed both by sulfur formation upon direct H_2S oxidation and by formation of SO_2 with its subsequent interaction with H_2S to form sulfur. The role of catalyst nature on the predominance of these two routes is discussed.

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FRACTALS: NEW INSIGHT IN HETEROGENEOUS KINETICS

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Scientific activity of G.K.Boreskov run, to a great extent, in parallel and in touch with the development of reaction kinetics in porous solids with a complex texture [1]. Recently new models of porous media and rough surfaces have been offered by fractal geometry [2,3]. The models are based on the idea of scaling symmetry and consider porous medium as a self-similar structure in which any small part resembles in general features the whole system.

Application of the fractal models appears to allow good progress in describing the kinetics of physical and chemical processes on catalysts and adsorbents. At the Boreskov Institute of Catalysis we have studied two groups of such processes. The former ones are the processes which depend on the mutual space distribution of interacting particles on a rough surface (electron tunneling and magnetic relaxation). The latter ones are controlled by diffusion to surface throughout a complex pore system (dissolution and gasification).

We derived analytical equations describing dipole-dipole magnetic relaxation between magnetic moments uniformly distributed on a fractal surface [4]. It was done for the mechanisms of spectral and instantaneous diffusion and for low and high frequency of spin-flips. Experimental kinetics of electron spin echo of F^+-centers on MgO surface strongly follows the theoretical equations and allows a determination of MgO surface fractal dimension [5].

Direct electron tunneling from donors to acceptors distributed on a fractal surface gives another exiting example of surface kinetics driven by surface structure. Our analytical analysis shows a great influence of surface geometry on the kinetic peculiarities of electron transfer [6]. Moreover, the fractal approach appears to be the most fruitful and sometimes the only way for analytical description of such systems.

Dissolution and gasification of porous solids with hierarchical (fractal) pore system examplify the processes controlled by diffusion to surface. As a main tool for theoretical study of these processes was taken a Monte Carlo simulation based on deterministic and random fractal models of the disperse solid which undergoes annihilation. It was found that the simple assumptions of surface chemical homogeneity and hierarchical pore system of the solid make it possible to describe the main kinetic peculiarities and the changes in the sample texture during its combustion. This approach has given a new insight in describing our experimental kinetics of Sibunit carbon gasification by oxygen [7].

Similar features have been revealed for dissolution of base-catalyzed SiO_2-aerogels in NaOH aqueous solutions. The aerogel structure appears to be determined by the synthesis conditions and shows a self-similar behaviour over 3-130 nm range [8]. New effect of the sharp increase of dissolution rate due to threshold disintegration of the aerogel fractal structure has been found and is being under study.

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THE ROLE OF THE 3d-METAL IN LOW TEMPERATURE METHANE DECOMPOSITION CATALYSTS

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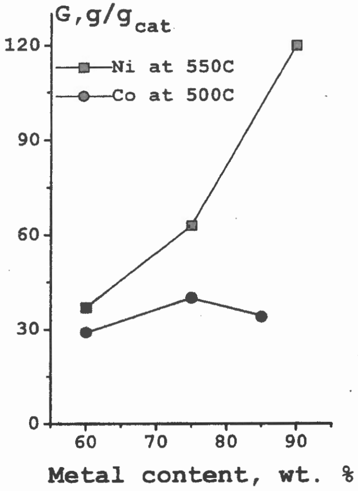
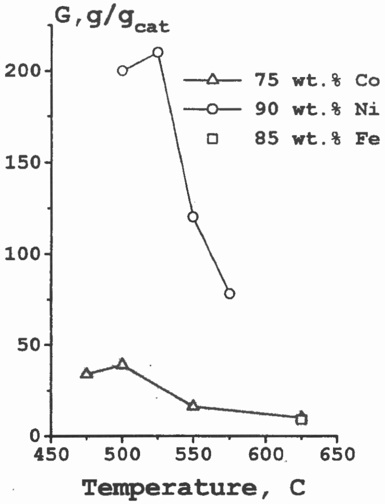
Catalytic decomposition of methane as a main component of the natural gas is one of the promising way of methane conversion to hydrogen. Since this process could be of commercial interest given by long-living catalysts, we aimed at development of catalysts of the low temperature methane decomposition following the scheme $CH_4 \Leftrightarrow C + 2H_2$, with both hydrogen and carbon as chemical products.

Today, it is well established that this reaction at low temperature is accompanied by formation of the filamentous carbon. This kind of carbon deposition could be called as self-regenerated process since the metal operates as continuous sink of the surface carbon atoms produced by decomposition. To characterize a stability of the catalysts, we have suggested to use a carbon capacity, G, i.e., grams of carbon deposited until complete deactivation per gram of the catalyst. Using catalysts prepared by different synthesis, we have found that, in general, the higher metal loading, the higher carbon capacity. Therefore, in order to produce the high loaded metal catalysts, coprecipitated techniques were developed.

Generally accepted model of the filament growth points out that the surface carbon atoms, produced by methane decomposition on the metal surface, diffuse through the metal particle and precipitate on the "back-side" of the metal particle. Our detailed study of the structure and evolution of the Ni-based catalysts showed that this process involved super-saturated carbon-in-metal state which promoted the formation of large (~50 nm) particles really performing the filamentous carbon deposition [1]. It appears that this evolution is generally also valid for other 3d-metals (Fe, Co).

We have found that a stability of the catalysts towards deactivation depends on temperature but mainly on the nature of the metal and its content (Fig.1). Data shows that carbon capacity measured for similar prepared catalysts follows the row Ni >> Co >> Fe. This is opposite to their location in Periodic system. We believe that the activity of the catalysts is likely connected with the affinity of carbon to 3d-metal. Indeed, the enthalpy of the surface carbide formation is found to be -117 kJ/mol, -50 kJ/mol and 4 kJ/mol for Fe, Co and Ni, respectively [2]. In addition, it is known that bulk nickel carbide, Ni_3C, decomposes at $T > 400°C$, while Co_3C can exist at $T \sim 500\text{-}800°C$, and Fe_3C phase is stable up to $T \sim 1050°C$, however, at $T < 500°C$, various non-stoichiometric iron carbide phases could be present. Comparing this with our catalytic data, we have suggested that for long-living catalysts of methane decomposition, a reaction temperature should be out of the existence of the bulk carbide phase, otherwise highly stable carbide phases could be produced at first moment





which are subsequently inert in methane activation.

TEM and EXAFS studies of the post-reacted 3d-metal catalysts have revealed that their deactivation could be attributed, first, to a fragmentation of the particles and encapsulation into the filament body ("channel"), second, to encapsulation of the most active metal faces responsible for methane activation and, third, to atomic erosion, observed in Ni-Cu alloy catalysts [1]. It appears that for Co and Fe catalysts, the particle fragmentation is dominant process of deactivation, meanwhile for Ni catalysts, the morphology and texture of growing carbon should be also taken into account when porous structure of carbon reaches highly dense state.

In summary, the most active and long-living catalysts of methane decomposition should be found among Ni catalysts. It appears that Ni-based bimetallic catalysts could be promising for development of the new generation catalysts of methane decomposition able to produce a huge amount of carbon as a catalyst support, adsorbent, etc.

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MULTINUCLEAR NMR SPECTROSCOPIC CHARACTERIZATION of Co(III) SPECIES - KEY INTERMEDIATES of COBALT ACETATE CATALYZED AUTOXIDATION

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Simple alkanes or alkylbenzenes can be selectively oxidized by molecular oxygen in AcOH with $Co(OAc)_2 \cdot 4H_2O$ as a starting material for the catalyst. It is generally agreed that active species of these oxidations are Co(III) complexes formed *in situ*, so-called "cobaltic acetate" [1,2]. However, despite numerous attempts, the structure of Co(III) acetate in solid or solution has been unknown [3-7]. Multinuclear NMR spectroscopy has opened up new avenues for the detailed characterization of Co(III) acetate in solutions. We have used the ^{59}Co, ^{13}C and ^{1}H NMR spectroscopies to characterize the structure and reactivity of Co(III) complexes existing in "cobaltic acetate" solutions in AcOH, CH_2Cl_2 and MeOH.

It was shown that, the samples of Co(III) acetate prepared by peracetic acid oxidation of Co(II) in acetic acid are the mixtures of the oxo-centred trinuclear cations $[Co_3O(OAc)_6(AcOH)_3]^+$ (**I**) and $[Co_3O(OAc)_5(OH)(AcOH)_3]^+$ (**II**) in 1:3 - 1:2 ratio. Immediately after dissolving in MeOH, **I** converts into cation $[Co_3O(OAc)_5(OMe)(MeOH)_3]^+$ (**A**) and **II** into cation $[Co_3O(OAc)_5(OH)(MeOH)_3]^+$ (**B**). The role of a counter ion can be played by OAc^-. Complex **B** slowly converts into complex **A** in MeOH ($\tau_{1/2}$ = 15 min at 293 K). The substitution of μ-OH group by μ-OR in ROH was reported for $[Co_3O(OAc)_5(OH)(Py)_3]^+$ [8-10]. Cations **I** and **II** are the major species in the freshly prepared solutions of Co(III) acetate in CH_2Cl_2 and AcOH. Upon heating the solutions of Co(III) acetate in AcOH complexes **I** and **II** convert into Co(II) species and another Co(III) complex **III**. The structure of complex **III** is still unclear. With the increase of water concentration in acetic acid the concentration of complex **I** decreases and that of complex **II** increases. The transformation of complex **I** to complex **II** occurred through the formation of intermediate complexes with separate resonances in the ^{59}Co NMR spectrum. Most probably, this effect is caused by the replacement of axial AcOH ligands by H_2O ligands in the complex **I**. Complex **II** in AcOH / H_2O is assumed to exist as the mixture of the type **II** complexes with various sets of axial H_2O or AcOH ligands.

Reactivity of **I**, **II** and **III** towards p-xylene was determined. Complexes **I** and **II** are rather stable in CH_2Cl_2. The addition of p-xylene to the sample containing **I** and **II** under anaerobic conditions in CH_2Cl_2 (1:3 p-xylene/ CH_2Cl_2 by volume, 293K) gave rise to gradual decrease of their concentration. The half-life was 2 hr for cation **II** and 1.3 hr for cation **I**. The observed small difference in the half-lives of complexes I and II can be explained by the conversion of complex I into complex II with the increase of water concentration in the course of the p-xylene oxidation. Complex III did not interact with p-xylene at noticeable rate at 293 K in AcOH. To determine the reactivity of complex III towards p-xylene, the samples in pure acetic acid and in a 1:1 AcOH/p-xylene mixture were compared at 373 K. The characteristic time of the reaction was 2 hours at 373 K. Note, complex III prevails among the other diamagnetic Co(III) species at high temperatures (373 K) in AcOH , these are conditions close to those for real oxidation. However, in the ^{59}Co NMR spectrum of the sample of Co(III) acetate in AcOH, prepared in the course of methylethylketone (MEK) autoxidaton in acetic acid at 335 K complexes I and II were detected, but no signals of complex III were observed. This means that complexes I and II are recovered rapidly by peroxyradicals in the course of MEK autoxidation at 335 K. Remember, that complex III is less reactive then complexes I and II. Thus, complexes I and II mainly drive the catalytic cycle of MEK oxidation under these conditions.

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PPI-23a

VISCOUS-ELASTIC PROPERTIES OF CONCENTRATED CARBON DISPERSIONS

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The assortment of formed goods made of carbon is very limited, their durability not exceeding 60 kg/cm^2. Therefore, new technology is required to prepare a wider assortment of goods with high durability (> 100 kg/cm^2). Extrusion of a plastic carbon paste is the main method for attaining this goal. Two fundamental rheologic characteristics of a material - viscosity and elasticity - are known to have decisive effect on the forming of dispersed systems. Thus, investigation of rheologic properties of concentrated carbon dispersions as a scientific basis of the forming process was the topic of the present study.

Viscosities and modules of resiliency and elasticity of plastic carbon compositions were calculated from experimental measurements performed on a shifting plastometer.

Carbon black (CB) P-514 was used as a dispersed phase, water and aqueous solutions of polyacrylamide (PAAm), polyetheleneoxide (PEO) and polyacrylic acid (PAA) were used as dispersion media. The polymers were chosen judging form their solubility in water and vitrification temperatures (T_v).

Composition of dispersion medium			Dispersion viscosity, 10^{10} Ps
Polymer	T_v, °C	Polymer content	
-	-	-	4.2
PAAm	-190	6	5.2
PAAm	-190	9	3.1
PAAm	-190	15	1.3
PEO	-67	0.5	5.7
PEO	-67	2.0	3.4
PAA	80	0.1	4.9
PAA	80	0.5	4.2
PAA	80	1.0	2.5

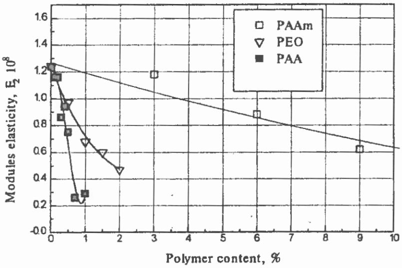
Viscosity of carbon dispersions in the solution containing polymers increases by 20-30 % after introduction of 6 % PAAm, 0.5 % PEO or 0.1 % PAA in comparison with that of the CB-water composition. This effect is connected with the increase of the adsorption interaction on the phase boundary. Further increase of the polymer contents results in a 1.5-2 fold decrease of the viscosity compared with the CB-water system. This may be explained by an increase in the number of large macromolecles sorbed on dispersed particles, and, hence, in the distance between CB particles resulting in a weakening of the interaction between them.

PPI-23 a

The observed dilatansion effect (viscosity increase with a shift tension increase) is not typical for dispersed systems and can result from an interaction strengthening of soot-polymer aggregates under shift.

Calculation of resiliency (E_1) and elasticity (E_2) modules for soot pastes of different composition has shown that resiliency modules E_1 are about 0.3-0.35 x 10^8 din/cm^2 in the whole concentration range. Modules E_2 monotonously decrease at introduction of polymers into the dispersion medium (see Figure).

The E_2 decrease is much more intensive for polymers with higher hardness (PEO, PAA) than for compositions containing a flexible chain polymer (PAAm). This decrease evidences increasing elasticity of the system as a whole. This fact is connected with the formation of the polymer layers on the surface of CB particles. As a result, the structure of the CB-water dispersion with prevailing point contacts is changed to a different structure consisting of interpenetrating nets of polymer and carbon-polymer gel. It is this transition what causes the appearance of large reversible deformations resulting in the decrease of the elasticity module.



Dependence of the elasticity module of soot dispersions on the polymer content in the dispersion medium.

We checked how technologic are soot dispersions of different composition in extrusion into elements of different form (rings, petals, microblocks). It was shown that carbon elements of satisfactory quality can be obtained by extrusion of soot compositions with a resiliency module of 0.3-0.35 x 10^8 din/cm^2, minimal viscosity and elasticity module at a constant amount of the dispersion medium in the plastic composition.

CREATION, INVESTIGATION, INDUSTRIAL EXPERIENCE OF NEW CATALYTIC SYSTEMS ON METAL DOPED SILICA FIBER GLASS WOVEN BASE FOR PROCESSES OF CATALYTIC HEAT GENERATION AND SULFUR DIOXIDE CONVERSION

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In the report an information is presented about the result of the next stage in the wide investigations program concerning a new class of the wide-purpose catalytic systems formed on the base of silica fiberglass amorphous matrices doped by the various metals and having a form of the articles with different types of the woven structure, namely the SFGC-catalysts protected by the patent [1]. The main features of the SFGC-systems (connected with their matrix structure and phase state, the fabrication and activation method, the products technology and exploitation conditions) giving grounds to define these catalysts as a separate class may be systematized as follows (for more detailes see [2-4]) :

1. SFGC are formed on the fiberglass silica matrixes amorphous in composition. Such base having characteristic phase metastability is non-traditional for the classical catalysis on the silica carriers (silicagels) which deals with the crystalline (polycrysalline) materials or with the materials having non-reglamented phase state. The non-equilibrium character of the SFGC-systems carrier state presents their principal feature since namely this factor defines in a large degree the possible appearance of the SFWC extreme catalytic properties.

2. The catalytic activation of the SFGC-systems is effected by the methods of the metal ions implantation into the amorphous silica matrix. As a result of this operation the glass-like matrix is taking the unusual catalytic properties and an element introduced into its structure (i.e. metal in the reduced or oxidized state) is firmly confined there and does not subjected to any migration transport, agglomeration or separation from the carrier. This method of a silica matrix activation based on its "doping" by the metals is nontraditional for the classical catalysis where the phases containing the catalytically active metal are simply applied on the carrier surface and the chemical, phase and mechanical unity of the "carrier-active layer" system as a whole can not be provided in full measure.

3. The SFGC-elements are characterized by the high catalytic activity at very low content of the metallic component in the matrix. This property of the SFGC-systems is available in the catalytic activation process of the whole inert silica matrix as a response to its doping by the metal ions and it is especially important for the creation of a new wide class of the catalysts having an active phase with some noble metals.

4. The SFGC-elements are characterized by a very developed catalytic surface. Their macroporosity is defined and regulated by the matching of a specific multifilament matrix structure which is formed by a twisting of the separate elementary filaments (3-9 microns in diameter) to working filament and by the special type of the woving interwave. The SFGC microporisity can be easily comtrolled by the special operations of the carrier fiberglass matrix pretreatment and the inner surface can be varied from ones to tens and hundreds m^2/g with the realized pores spectrum having dimensions from tens to hundreds microns.

5. The SFGC-elements are characterized by the high chemical and thermal resistance, mechanical strength, dusting and attrition fastness. These properties coupled with the stability of the metallic component introduced to the matrix provide the SFGC-systems good characteristics during a prolonged exploitation run (a working resource).

6. The SFGC-materials production process is characterized by a continuous

technologycal scheme easily turnable for a new article production and economical efficiency. The catalytic fabrics creation for the SFGC-materials production requires low investments due to the fact that such productions can be developed by introducing some supplementary stages in the already operating productions of the fiberglass materials (for the traditional thermo-, electroprotective and construction purposes).

In 1996 the authors concentrated their efforts on the search of the effective SFGC-systems for the catalytic heat generation and sulf ur dioxide oxidation processes. The annotation of this investigation stage results is given below.

CATALYTIC HEAT GENERATION

The SFGC-elements doped by platinum (up to the content 0.01-0.1 % mass) or chromium exhibit a high catalytic activity in the reactions of the hydrocarbons deep oxidation. An analysis of their usage efficiency for the catalytic heat generators of industrial and household exploitation shows their essential advantages over the traditional ceramic catalytic burners: the low cost; the technological simplicity of the catalytic element assembly, installation and renewal; the stability to the vibrational and impact loads. By now the first pilot lots of the catalytic heaters with the SFGC-elements have been produced. The information accumulated over the laboratory, experimental and industrial tests of the SFGC-elements in the flameless combustion of the gas-phase and liquid-phase hydrocarbon fuels is sufficient to allow conclusion that these catalytic systems are perspective for handling of the extremely important problem of modern energetics and engine production namely the gas-turbine units transfer from the torch mode of the working body generation to the low-temperature flameless mode of the fuel catalytic combustion which is characterized by lower heat losses and can prevent an appearance of nitrogen oxides in the working body exhausts.

CONTACT STAGE OF SULFURIC ACID PRODUCTION

The activity of SFGC-elements doped by platinum to the content about 0,05 % mass has sufficient superiority over the vanadium catalytic systems traditionally used for this process. The transfer of the sulfuric acid productions to the SFGC-elements allows one to lower the contact temperature by 40-60^0 C which in its turn will lead to the conversion rise of sulf ur dioxide and to its content reduction in the gaseous exhausts, i.e. allows to solve one of the most important ecological problem of the sulf uric acid production. The endurance tests (so called resource tests) of the silica woven catalysts were conducted using the SFGC samples loaded directly into a layer of the granulated vanadium catalyst of an operating industrial reactor. It was shown that the samples are not mechanically destroyed after a one year exploitation and their catalytic activity is preserved.

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MODELLING THE WATER GAS SHIFT MEMBRANE REACTOR

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The Water Gas Shift (WGS) reaction is among the oldest catalytic reactions applied in many industrial processes to produce hydrogen or ammonia synthesis gas [1]. It is a well known exothermic reaction, with equilibrium constant increasing in reverse order with temperature:

$$CO + H_2O = CO_2 + H_2 \qquad (\Delta H = -41.1 \text{ kJ/mol})$$

A lot of attention has recently been paid to the WGS reaction carried out using a membrane reactor. The growing interest in this reaction is shown by e.g. the amount of both experimental and modelling work appearing in specialised literature [2-14].

The concept is quite simple: a preferentially H_2-permeable membrane, combined with the WGS reaction, allows one to obtain higher conversion values compared to the equilibrium one. It has possible applications in relation to the recovery of tritium from the blanket of a fusion reactor, to vehicular emission control, to coal gasification plants, to removal of CO from combustion gases and conversion of water gas.

In our work, presented elsewhere [14], the WGS reaction has been carried out using a composite palladium membrane obtained by coating an ultrathin double-layer palladium film on the inner surface of the support of a commercial tubular ceramic membrane by a so-called co-condensation technique. For this system, the best operating conditions were determined at various H_2O/CO molar ratios, temperature, P_{lumen}, gas feed flow, with and without nitrogen sweep gas, for pure gas feed and for a mixture gas feed. Experimental conditions for obtaining complete conversion were determined.

In a previous work [9], a mathematical model was developed to analyse the behavior of a composite H_2 -permeable membrane by considering the WGS reaction for pure feed gas.

In this work, the experimental results are considered to simulate a WGS reaction membrane reactor both for pure gas feed and for a mixture gas feed. As far as the modelling work is concerned, two approaches have been considered:

1. The model assumes typical Langmuir-Hinselwood kinetics.
2. The model assumes that the reaction is not limited by chemical kinetics.

Both models assume isothermal reactor conditions, negligible effect of competitive reactions, plug flow fluid dynamic regime in each stage, ideal gas behaviour and negligible effect of the catalyst pebble on the evaluation of the resistance of the interface film between the composite palladium membrane and the gas. Due to the fact that during experiments we did not observe side-reactions, both simulations do not consider the formation of carbon.

The reactor is depicted as a series of tubular membrane reactors. In particular, two mass transfer resistances in series are considered:

1.The resistance through the film at the interface between the inside membrane wall and the gas mixture.

2. The total resistance through the composite palladium membrane.

For each model, differential mass balances for both co-current and counter-current flow mode are considered.

The difference between experimental results and simulation curves for both models is discussed in detail, trying to identify their respective range of validity.

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EFFECT OF La ON STRUCTURAL AND CATALYTIC PROPERTIES OF Pd/Al_2O_3

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Palladium-only three-way catalysts are attractive for application in catalytic converters [1], due to low cost of palladium and their high temperature durability. Palladium-on-alumina/lanthana catalysts show enhanced NOx reduction as compared to palladium on alumina [2]. Usually three-component Pd-lanthana-alumina catalysts are prepared by impregnation of Pd/Al_2O_3-La_2O_3 catalysts, prepared by sol-gel method.

Surface area measurements were carried out by low temperature N_2 adsorption in a Gemini 2600 from Micromeritics. Temperature programmed desorption (TPD) and reduction (TPR) spectra of hydrogen were measured using thermodesorption apparatus AMI-M, Altamira Instruments. Reduction of NO by hydrogen in the range 323-973 K was studied under atmospheric pressure in a continuous flow microreactor Multipulse RIG 100, In Situ Research Instrument. X-ray diffractograms were recorded with a Philips X'pert diffractometer. Transmission Electron Microscopy characterization of catalysts was carried out using a JEOL 2010 transmission electron microscope. Sample morphology was observed in a Jeol 5300 scanning electron microscope.

Lanthana-alumina (5.8 wt % of Al_2O_3) supports with surface areas around 320 m^2g^{-1} were prepared by sol-gel method. The surface area of alumina, prepared under the identical conditions was the same.

During TPR experiments a large excess of hydrogen was consumed due to the partial reduction of lanthana. The large excess of H_2 with respect to that necessary for the reduction of PdO (120 %) is attributed to a good intimate contact of Pd with La provided by the preparation method. Utilization of other preparation techniques according to literature data results in reduction of lower portions of lanthana.

Essential enhanced hydrogen adsorption (H/Pd = 8 to 15) detected by TPD are suggested to be a consequence of the large amount of reduced lanthana, promoted by very good dispersion of Pd on the surface. The ability to adsorb large amount of H_2 was found to depend on the type of catalyst treatment. Oxidation increases desorption while inert or hydrogen treatment reduces it. This phenomenon is attributed to spillover.

Lanthana-promoted palladium catalysts supported on alumina have a higher catalytic activity than non-promoted catalysts. They do not show any activity drop as a function of the temperature as typical palladium on alumina catalysts do. It is, suggested that for the latter catalysts at intermediate temperature of reaction, palladium is transformed by reaction media to palladium oxide causing the drop of activity. The further reduction of the oxide to the metallic state increases the activity again and results in N_2 selectivity rise. At elevated temperatures NH_3 selectivity is much higher on lanthana-promoted catalysts than on alumina catalysts.

Al_2O_3, prepared by sol-gel method, consists of small ($\leq$5 μm and less) particles, forming aggregates. Analogously prepared Al_2O_3-La_2O_3 along with these kind of grains contains larger ones (several hundreds μm). Lanthanum-containing phase forms shapeless conglomerates with high contrast (as seen by TEM), consisting in crystalline domains.

Alumina, prepared by sol-gel method, contains crystallites of η-Al_2O_3 with size about 5 nm. X-ray diffractograms of Al_2O_3-La_2O_3 along with η-Al_2O_3 contains additional peaks corresponding to conglomerates with high contrast. Attempts to assign this crystalline phase to any of the cards in the ICDD-PDF database were unsuccessful. The calcination in air for 3 h results in disappearance of this phase and formation of large crystals of metastable $LaAl_2O_3$ phase.

New alumina-lanthana phase, observed by HRTEM and X-ray diffraction, is suggested to be responsible for the change of catalytic properties of Pd/Al_2O_3-La_2O_3 as compared with Pd/Al_2O_3. High hydrogen desorption is supposed to be due to these phase also.

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Parametric analysis of nonlinear kinetic models

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As a rule, the dynamic models of catalyst surface are nonlinear. They have parameters which determine physical and chemical conditions of process. Parametric analysis includes the following steps: analysis of steady state number, construction the dependencies of steady states on the parameters, stability analysis, construction of parametric and phase portraits, numerical analysis of process dynamics. The proposed procedure of parametric analysis is demonstrated by a serie of basic nonlinear models of catalytic kinetics which can have the steady state multiplicity and self-oscillations.

For a kinetic model corresponding to reactions on catalyst surface

$$1)Z \rightleftarrows X, \quad 2)X+2Z \to 3Z, \quad 3)Z \rightleftarrows Y$$

the bifurcation curves of multiplicity and neutrality are obtained explicitly, the phase portraits are constructed. An influence of the form of the buffer step 3) on the parametric portraits is analyzed. The models corresponding to the steps of the form 3) are considered:

$$3')X \rightleftarrows Y, \quad 3'')2Z \rightleftarrows Y, \quad 3^*)Z+X \rightleftarrows Y, \quad 3^{**})2Z \rightleftarrows 2Y.$$

Two series of models corresponding to the schemes without autocatalytic steps: mechanism I:

$$1)Z \rightleftarrows X, \quad 2)X \rightleftarrows Y, \quad 3)2X+Y \to 3Z, \quad 4)Z \rightleftarrows S$$

and mechanism II:

$$1)2Z \rightleftarrows 2X, \quad 2)Z \rightleftarrows Y, \quad 3)X+Y \to 2Z, \quad 4)X \rightleftarrows S$$

are considered. The parametric analysis is carried out in accordance with the procedure mentioned above. Various buffer steps 4) are analyzed:

$$4')X \rightleftarrows S, \quad 4'')Y \rightleftarrows S, \quad 4''')Z \rightleftarrows S.$$

Thermo-catalytic oscillator

$$\begin{aligned}\dot{\Theta} &= \beta f(\Theta)(1-z)+s(1-\Theta),\\ \dot{z} &= f(\Theta)(1-z)-z,\end{aligned}$$

where Θ is the dimensionless temperature of catalyst surface, z is a part of free surface, is analyzed. In parameter plane the regions with self-oscillations and steady state multiplicity are discovered.

PPI-28

The existence conditions of oscillations on catalytic surface with account of buffer steps and diffusion exchange

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The existence conditions of self-oscillations for kinetic models of reactions on a catalyst surface are obtained. Two types of additional physical and chemical processes - diffusion exchange and buffer step - are considered.

The diffusion exchange is consedered as an exchange step between two types of active centers X_0, Z_0:

$$X_1 + Z_0 \rightleftarrows X_0 + Z_1, \qquad (1)$$

where X_1, Z_1 are intermediate substances of diffusion step. The step (1) completes the main reaction mechanism on surface:

$$\sum_{i=0}^{n} \alpha_{is} X_i \to \sum_{i=0}^{n} \beta_{is} X_i, \qquad s = 1, \ldots, m, \qquad (2)$$

where X_i are substances, α_{is}, β_{is} are stoicheometric coefficients, [1,2]. The buffer step completes the scheme (2):

$$\sum_{i=0}^{n} \alpha_{io} X_i \rightleftarrows X, \qquad (3)$$

where the substance X does not take part in scheme (2). For kinetic models (1)+(2) and (2)+(3) the existence conditions for self-oscillations in the terms of additional steps are obtained. The examples of two and three step catalytic reactions (with autocatalysis and without it) which make possible self-oscillations in accordance with processes (1) or (3) are given.

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THE INFLUENCE OF OXIDE-OXIDE INTERACTION ON THE CATALYTIC PROPERTIES OF Fe, Co AND Ni/Al_2O_3 IN CO HYDROGENATION REACTIONS

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On the example of Fe/Al_2O_3, Co/Al_2O_3 and Ni/Al_2O_3 catalysts the influence of oxide-oxide interaction on the catalytic properties of metals in CO hydrogenation reactions was investigated.

The oxide-oxide interaction was prevented by means of Al_2O_3 surface modification with magnesium oxide. The formation of $MgAl_2O_4$ in the surface layer of Al_2O_3 allowed to increase not only the rate but also the completeness of oxides reduction significantly.

In was shown that oxide-oxide interaction does not influence the catalytic activity of Fe, Co and Ni directly but determines the quantity of carbon residue on the surface. The decrease of oxide-oxide interaction permits to reduce the rates of carbon precipitation and, therefore, to decrease the catalyst deactivation.

PPI-30

Platinum-Catalysed Cyclopropanation of Olefins with Ethyl Diazoacetate

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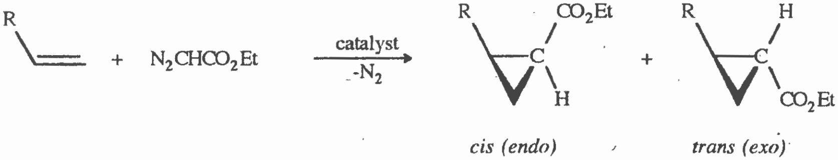
Transition-metal catalysed decomposition of diazo compounds in the presence of olefins is a general process for the construction of three-membered carbocycles. In this context, a number of excellent copper and rhodium(II) carboxylate and amide catalysts have been developed. These last years have seen the emergence of new catalysts based on iron, ruthenium, and osmium.



Very few is known on the use of catalysts based on platinum. For instance, ethyl vinyl ether was cyclopropanated by diazofluorene in the presence in a catalytic amount of $PtCl_2(CH_2{=}CH_2)(py)$ (86 % yield),[1] whereas $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ has been shown to be moderately active in the cyclopropanation of styrene with N_2CHCO_2Et. The conversion of ethyl diazoacetate to cyclopropanes was 20 %, and the *cis/trans* ratio was about 1:2.[2] On the other hand, it is well-established that diazo compounds, N_2CHR, react with platinum complexes of the type L_nPtX_2 to give mono- $[L_nPt(CHXR)X]$ and bis- $[L_nPt(CHXR)_2]$ insertion products.[3]

This poster reports on the use of various platinum complexes as catalysts for the cyclopropanation of olefins with ethyl diazoacetate.

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PPI-31

TEMPERATURE PROGRAMMED DESORPTION OF HYDROGEN CHEMISORBED ON Pt/Al_2O_3: NEW RESULTS

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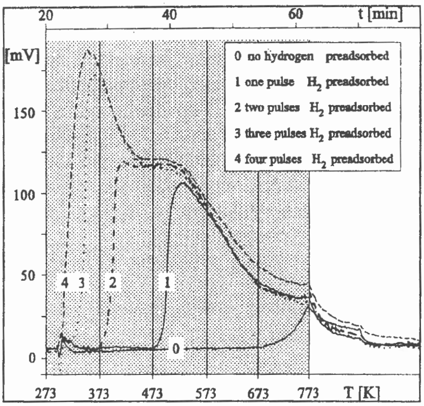
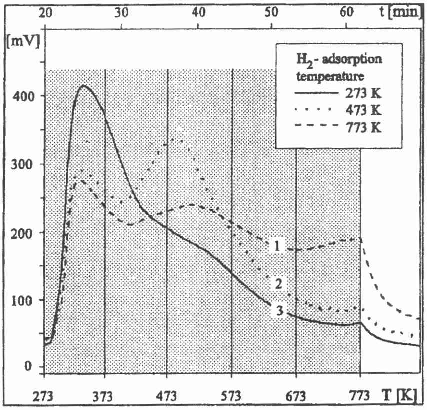
Using Temperature Programmed Desorption **TPD** and Pulse Adsorption **PA** we studied on Pt/Al_2O_3 (0,50 wt% Pt) the influence of the hydrogen surface concentration, of the adsorption temperature and of the surface water concentration on the hydrogen chemisorption characteristics.

Results

a.) Influence of hydrogen coverage on TPD
TPD profiles of hydrogen qualitatively characterize the desorption energy distribution, generally. The figure on the right shows the TPD curves after the adsorption of different numbers of hydrogen pulses (0 to 4 pulses, 1,65 μmol H_2 each). The desorption curves clearly prove the stepwise filling of a strongly inhomogeneous adsorption area. In the case of two defined species of adsorbed H we would observe a stepwise growing up of the low temperature peak after the high temperature peak being filled.





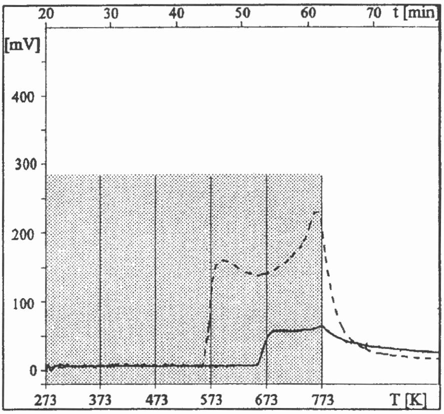
b.) Influence of adsorption temperature
Results of measurements at different adsorption temperatures are given on the left. The shapes of the curves strongly depend on the adsorption temperatures. After high adsorption temperatures **H**igh Temperature **D**esorption (HTD) of hydrogen takes place. At the same time temperature programmed reduction after oxygen treatment shows at this temperature range some excess hydrogen consumption (59 μmol/g catalyst, with the reduction of Pt^{IV} requiring only 51 μmol/g).

c.) Effect of water

The HTD of hydrogen occurs near the maximum temperatures, which the catalyst was exposed to. At these conditions the Al_2O_3 surface -OH groups become movable and could interact with reduced species on the carrier surface.

Thus, TPD was performed after reduction without previous hydrogen adsorption but adding water (10^{-4} mol or 3 - 4% of a monolayer) to the catalyst.

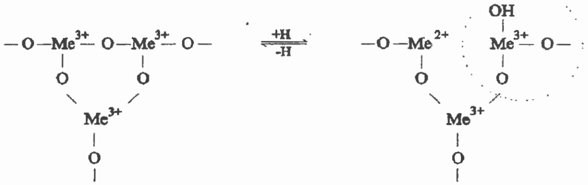
The figure on the right shows, that this exposition to water causes a remarkable amount of HTD hydrogen (dotted line).



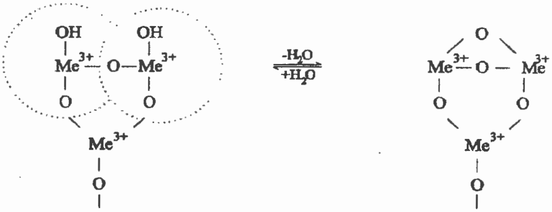
Discussion

As shown by the pulse experiments, the desorption energy of hydrogen strongly depends on the degree of surface coverage. The adsorption temperature influences not only the amount of chemisorbed hydrogen. The distribution of desorption energy strongly depends on it, too. With rising adsorption temperature the desorption energy distribution shifts to higher values.

The most exciting question is the origin of the hydrogen desorbed at high temperatures. Under high temperature reduction conditions the alumina surface (impurities on it) are reduced by spillover hydrogen, forming -OH groups, as shown by the right scheme:



Thus, this hydrogen accumulation on the catalysts surface proceeds via a reversible redox reaction. The decrease of high temperature H_2 desorption after high temperature argon pretreatment can be interpreted as a result of surface dehydration. The -OH groups formed by surface reduction are transformed to -O- bridges.



The high temperature H_2 desorption, usually interpreted as desorption of spilled over hydrogen, is the result of the reoxidation of reduced surface sites by water or OH-groups delivering H_2.

SIMILARITIES BETWEEN REACTIONS OF METHANOL WITH $Mo_XO_Y^+$ IN THE GAS PHASE AND OVER REAL CATALYSTS

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Studies with ion-cyclotron resonance (ICR) technique have been shown to provide valuable information about interactions in the gas phase at low pressure of various molecules with ions of metals that are present in real catalysts.

In this work the ion-molecular reactions of $Mo_xO_y^+$ ions with CH_3OH and CD_3OH were studied. The effusion chamber (Knudsen cell) was used for generating of $Mo_xO_y^+$ ions in ICR cell. $Mo_xO_y^+$ ions were formed by electron impact (70eV) of the vapor of the sample of $^{98}MoO_3$. Four groups of ions $Mo_xO_y^+$ (x = 1-4, y = 1-12) were observed.

Oxygenated molybdenum ions participate in four types of reactions with methanol molecule, namely:

(i) - Oxidative dehydrogenation to form formaldehyde from CH_3OH reagent and $Mo_xO_{y-1}(H_2O)^+$ ions from MoO_y^+ reagents.

(ii) - Abstraction of OH radical to form $Mo_xO_yCH_3^+$ ions.

(iii) - Dehydration to form $Mo_xO_yCH_2^+$ ions, i.e. carbene species CH_2O coordinated to the $Mo_xO_{y-1}^+$ ions.

(iv) - Abstraction of O atom to form $Mo_xO_yCH_4^+$ ions, i.e. methane coordination (perhaps, dissociatively) to $Mo_xO_y^+$ ions.

The most interesting fact is that $Mo_3O_9^+$ ions react with more than one CH_3OH molecules to yield $Mo_3O_9(C_2H_7)^+$, $Mo_3O_9(C_2H_5)^+$, $Mo_3O_9(C_3H_7)^+$ and $Mo_3O_9(C_3H_9)^+$ ions. Reactions represent coupling of two or three hydrocarbon fragments of CH_3OH to form longer hydrocarbon chains. Such coupling is well known for CH_3OH in acidic molybdenum oxide based homogeneous and heterogeneous catalysis.

The formation of acidic protons of $Mo_xO_yH^+$ (x=1-4, y=2-12) was found in interactions with $CH_3OH_2^+$ and its solvates $CH_3OH_2^{+}\cdot(CH_3OH)_n$ with n = 1, 2. Thus, via such processes methanol can prepare in the gas phase from $Mo_xO_y^+$ ions the acidic forms of multinuclear oxide ions. In solutions and on solid surfaces acidic protons are indeed known to be able to provide coupling of hydrocarbon fragments of alcohol molecules to produce finally alkenes and alkanes.

Thus interactions of $Mo_xO_y^+$ ions show rather profound similarities between reactions of methanol with these ions in the gas phase under ICR conditions and the reactions of methanol over heterogeneous and homogeneous catalysts containing molybdenum-oxygen sites. This fact suggests that ICR studies can be a useful tool to characterize in the gas phase, i.e. under most "pure" conditions, elementary reactions that are important for real catalysis.

SCR of NO with AMMONIA over ALUMINA and TITANIA SUPPORTED V_2O_5 ACCORDING to ^{15}N NMR DATA. CATALYST CHARACTERIZATION and REACTIVITY STUDY

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The removal of nitrogen oxides in exhaust gases is an important environmental problem. The most common method to diminish NO_x emissions is the selective catalytic reduction (SCR) of nitrogen oxides with ammonia. The principal advantage of NH_3 as a selective reductant is its ability to reduce NO in the presence of oxygen. The most common catalysts for this process are based on vanadia supported on alumina or titania. Zeolites were shown to be also active in the reaction [1].

Kinetic and infrared studies were used for elucidation of the SCR mechanism [1]. Recently, we have shown that the ^{15}N nuclear magnetic resonance (NMR) technique of ^{15}N enriched reagents (^{15}NO and $^{15}NH_3$) can also be effective for studying this process [2,3]. High sensitivity of the ^{15}N NMR parameters to the electronic state of N atoms allows one to obtain useful information about diamagnetic surface species, reaction intermediates and main features of the reaction.

In the present study the adsorption of nitric oxide (NO) with ammonia (together and without oxygen) over a series of alumina and titania supported V_2O_5 catalysts has been investigated using solid-state ^{15}N NMR. The results are compared with those for zeolites of ZSM-5 type.

The catalytic activity data have been correlated with the acid properties of the catalysts. Brönsted acid sites were characterized using ^1H NMR MAS data. The Lewis acidity has been tested using adsorption of nitrous oxide (N_2O) as a probe molecule [4]. Strong Lewis acid sites associated with surface coordinately unsaturated Ti^{4+} and V^{5+} centers have been detected on these supported oxide catalysts. The concentrations of Lewis sites formed on deposition of V_2O_5 on the Al_2O_3 or TiO_2 surface did not exceed *ca.* 10 % of the total amounts of supported metal ions.

An initial step in the NO+NH_3 reaction mechanism over supported V_2O_5 catalysts seems to be disproportionation of NO to N_2O and NO_2, as has been also shown for ZSM-5 catalysts. No N_2O has been revealed for oxygen-containing reaction mixtures, unlike zeolites showing formation of nitrous oxide as a parallel reduction product. The experiments with preadsorbed and subsequently pumped off NO have shown that NO molecules react with ammonia not in the gaseous state, but as adsorbed, strongly bonded species formed *via* disproportionation and partial oxidation of NO. Such species can not be registered by ^{15}N NMR technique because of their small concentration, low mobility and/or short lifetime (on the NMR time scale).

In some cases two distinct forms of adsorbed ammonia differing in their mobilities have been detected. The low field ^{15}N resonance line corresponds most probably to more strongly bonded form of ammonia, probably active form reacting with adsorbed species of NO.

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PPI-34

USE OF SELECTIVE POISONING OF THE ACTIVE SURFACE OF COPPER-CONTAINING CATALYSTS BY CHLORINE FOR DETERMINATION OF THE DETAILED REACTION MECHANISM WITH CARBON MONOXIDE.

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The basic scientific problem in catalysis is the explanation of activity on the surface of complex catalysts and predicting this on the basis of their efficiency in one or another process. There is a variety of approaches to the solution of this complex problem. One of them is the study of detailed mechanism of heterogeneous catalytic reactions. The knowledge of detailed activation mechanism of carbon monoxide conversion is important. There are two schemes according to which methanol synthesis goes either from carbon dioxide only, or in two directions from carbon mono- and dioxide depending on surface oxidation and other factors. In the first of these cases carbon monoxide participates in synthesis by first converting into carbon dioxide according to carbon steam conversion.

A simple treatment of experimental findings for one or another scheme is difficult because of the fact that all copper-containing catalysts for methanol synthesis act at the same time as catalysts of carbon monoxide conversion and vice versa. To overcome this problem in the present research, a new approach is used consisting in study of the poisoning effect of catalyst surface (by chlorine) on the activity in these two reactions. The results of study of catalysts CHM-1 and HTK-11 showed principally different behavior of these systems at the selective poisoning by chlorine. The catalyst CHM-1 which is inactive in carbon oxide steam conversion does not show the activity in methanol synthesis. In contrast, the catalyst HTK-11 continues methanol synthesis, in spite of carbon oxide conversion (chlorine poisoning) it did not show activity. All the studies were carried out in the same reactor without transfer of catalysts. It will be noted that by carrying out the experiment in this way we do not change directly the surface hydroxylation. This is because we strive for the elimination of carbon monoxide conversion by catalyst poisoning but not through purification from moisture traces. An experiment shows that on varying catalytic systems, different mechanism of methanol synthesis is realized. On the catalyst CHM-1, synthesis can be obtained only from carbon dioxide. On the catalyst HTK-11, methanol is formed from carbon mono- and dioxide which from our point of view is related to different surface hydroxylation, which in turn is related to different ratio of catalytically active sites containing zero- and univalent copper. This is confirmed by X-ray experiments with high-temperature chamber. Complex physico-chemical studies are carried out (kinetic, thermodesorption and spectral of absorption of carbon oxides, water, methanol). This allows an increase in the present knowledge of the mechanisms of catalytic effect of copper-containing catalysts and elementary actions on the surface reactions with carbon dioxides, hydrogen, water and oxygen-containing organic compositions.

In particular it is determined that in the temperature range of 120-300^o C and pressures of 1-10 atm, the dissociative water adsorption occurs. The specific effect of hydrogen as a reducing agent is for creating equilibrion, the hydrogen exchange between dissociatively absorbed water and reducing medium takes place. Under these conditions the partial oxidation of surface of copper-containing catalysts by OH-group condensation due to dissociation of carbon dioxide can occur. The process is promoted by the presence of hydrogen and at the preliminary treatment of the surface by methanol.

CHARGED MEMBRANE BIOREACTOR FOR COENZYME DEPENDENT DEHYDROGENATION REACTIONS

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Oxido-reductases NAD(P)H dependent catalyze reactions which have importance in enantio-specific synthesis. The industrial use of these enzymes is limited by the high cost and instability of the coenzyme. Retainment of NAD(H) has been achieved by using polymer-bound NAD(H) [1] and by using composite charged membrane reactor [2,3].

In the present work the possibility to retain expensive cofactors in a continuous stirred tank reactor (CSTR) using UF-charged membranes has been studied.

Different kind of membranes for NADP(H) rejection have been investigated.

Flat-sheet polyetheretherketone (PEEK-WC) membranes were prepared in our laboratories by phase inversion method [4, 5]. Bovin Serum Albumin (BSA) in alkaline solutions were ultrafiltered through the membranes, in order to create a gel layer negatively charged. The amount of BSA gelified on the membrane and the NADP(H) retained in the reaction vessel were measured by spectrophotometric methods, at 260 and 340 nm, respectively.

Membranes were characterized by measuring the water permeate flux and cofactor rejection before and after BSA gelification.

NADP(H) rejection was measured as a function of pH. A linear phenomenological relationship between NADP(H) rejection and pH of solution was observed.

Flat-sheet polypropylene (PP) membranes were also functionalized with BSA in alkaline solution. The water permeate flux was measured using the membranes as provided and after treatment with BSA. The cofactor rejection was measured at pH 7.00.

NTR-7410 and NTR-7450 membranes made of sulfonated polyether sulfone coated on neutral polysulfone, were supplied by Nitto, Japan. These membranes were used as provided. The permeate flux was measured before and after NADP(H) rejection tests, in order to see if any change occurred at the membrane performance. The cofactor rejection was measured at pH 7.

In most of studied cases, the charged membranes well retained the NADP(H) cofactor. NTR-7450 membranes showed the highest rejection coefficient (0.95). In the case of PEEK-WC + BSA membranes, rejection increased with the pH, since both cofactor and membrane carried a net negative charge.

Acknowledgments

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TAP-STUDIES: AN INTERROGATIVE KINETICS APPROACH

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On the basis of TAP (Temporal Analysis of Product)-system [1,2] the "interrogative kinetics (IK) approach" which is an alternative to the traditional kinetic approach in heterogeneous catalysis is developed. The IK approach involves a combination of two types of kinetic experiments, firstly, "state defining" (friendly) experiment that does not significant perturb the kinetic state of the catalyst. The second type is a "state altering" (typical) experiment, that perturbs the catalyst and changes significantly its composition. The "state defining" (friendly) TAP response experiments involve a very small number of molecules in comparison to conventional transient response experiments. TAP experiments are performed at Knudsen flow regime conditions, and the diffusivities of the individual components are independent on the gas composition. In difference with the traditional kinetic approach and surface science approach, TAP experiments do not eliminate gas transport, and the transport kinetics data are determined simultaneously. The "state defining kinetic parameter", or "kinetic parameter of catalyst" (K.P.C.) is defined as a characteristic of the kinetic state of the catalyst. K.P.C. is compared with the well-known kinetic characteristic , "turnover number".

The theory of TAP pulse response experiments is developed. Different deterministic models based on partial differential equationbs are analyzed, especially models of diffusion, irreversible adsorption/reaction, and reversible adsorption.

The standard diffusion curve (S.D.C.) which can be used for distinguishing the Knudsen regime was found. On the S.D.C. basis the simple Ht-criterium of Knudsen regime is proposed. The S.D.C. and Ht-criterium are shown to be useful for distinguishing the Knudsen flow regime in TAP experiments. The concept of relative flow, which is applied for irreversible adsorption/reaction case is proposed.

Different fingerprints of TAP data for adsorption/reaction and desorption cases are found. Using these fingerprints,different cases can be distinguished, especially is its adsorption reversible or irreversible, and the relative magnitude of adsorption/desorption parameters.

Application of the TAP-2 system and interrogative kinetics methodology for the selective oxidation of n-butane were found. The kinetics of irreversible reaction of n-butane over VPO catalyst in the absence of gas phase oxygen and on oxygen-treated VPO were studied. The "kinetic parameter of the catalyst" (K.P.C.) and energy of activation are found. Sharp changes of the K.P.C., especially increasing of activation energy on the oxidized catalysts, are correspondent to the changing the catalyst structure.

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PPI-37

SYNTHESIS AND *IR* INVESTIGATION OF CATALYTIC SYSTEMS ON THE BASE OF METAL COMPLEX COMPOUNDS OF NITROGEN CONTAINING CHARCOAL DEPOSITED ON THE SILICAGEL SURFACE

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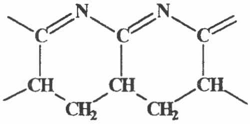
The catalysts of molecular oxygen activation on the base of metal complex compounds of nitrogen containing charcoal (MCCNCC) were worked out earlier [1]. For improvement of physical-mechanical characteristics of the given catalysts and for creation of new multifunctional catalytic systems, the method of synthesis of MCCNCC, deposited on the surface of SiO_2 and other matrixes, has been proposed.

The suggested method allows to vary widely the active phase and matrix composition, structure and mutual relation. The synthesis was based on the initial polymerisation of akrylonitril (AN) on the matrix surface by using of complex formers (chlorides of transition metals) and the following carbonization by programmed thermal processing. Silicagels with specific surfaces S=300, 200, 150, 70 m^2/g, aerosil (175) and γ-Al_2O_3 (150) has been used as the substrates. Chlorides of Co (II), Ni (II), Cu (II), Zn (II) have been used as the complex formers.

The initial composition of MCCNCC-SiO_2 system was chosen taking into account the proportion of metal (M) and nitrogen as $\nu_M:\nu_N = 1 : (4\text{-}36)$ and the content of metal within 5-10 wt.%.

The process of structure formation of MCCNCC-SiO_2 system was investigated by means of *IR* spectroscopy. In the *IR* spectrum, the absorption for bands of SiO_2 saturated with the chloride of metals and AN, appeared at 2280 cm^{-1} ($\nu_{C\equiv N}$), 1600-1610 cm^{-1} ($\nu_{C=C}$) that characterises valent vibration of absorbed AN. After the polymerisation at 60-80°C in the alcohol the intensity of absorption band of C=C bond decreased up to the their disappearance and the new absorption band corresponding to saturated C-H bonds valent vibration (2980-3070 cm^{-1}) appeared. At the same time, besides absorption band at 2280 cm^{-1} the new absorption bands appeared in the 2230-2250 cm^{-1} range. The increase of temperature up to 100°C leads to a changing of intensities of proportions of mentioned absorption bands and their disappearance at 120°C. At the temperature 150-200°C absorption bands of the complex appeared in the 1550-1580 cm $^{-1}$ region, the intensity of which rises and the form of spectrum is changed with the temperature increasing. According to literature data the mentioned absorption bands refer to the cyclic structure of type:



In the given structure, obviously, metallic forms are co-ordinated by means of atoms of nitrogen. The following thermoannealing up to 250-300°C leads to the decrease of the intensity of absorption bands in the region 1550-1580 cm $^{-1}$ and 2980-3070 cm $^{-1}$, which affirms the destruction and carbonisation of the mentioned structure, in the result of which MCCNCC-SiO_2 system is formed. MCCNCC-SiO_2 systems perform catalytic activity in the reactions of liquid phase oxidation of alkylbenzenes in the presence of dioxygen.

The work was conducted with assistance of International Fund **INTAS**

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PPI-38

A NOVEL METHOD OF $CO_2(CO)_8$ AND $CO(CO)_4^-$ SYNTHESIS BY MEANS OF CARBONYLATION OF $CoCl_2/CH_3OH$ IN THE PRESENCE OF THE RANEY-Ni UNDER AMBIENT CONDITION

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The cobalt carbonyls, Co_2 $(CO)_8$ or $Co(CO)^-_4$, which are important catalysts in many homogeneous reactions, have been synthesied by means of carbonylation of $CoCl_2$ in the presence of Raney-Ni at ambient condition.

Many synthetic methods have been proposed to prepare cobalt carbonyl, but there are some disadvantages for each method in a long term of studying the synthesis of cobalt carbonlys. We develop a novel method to prepare the carbonyl, effectively and simply.

Raney-Ni was prepared by a standard procedure. Ni- Al alloy powder was immersed at 60 ^{0}C by 20 % NaOH for 2 h, then washed by absolute alcohol. Raney-Ni was added during 5 minutes into a magnetically stirred suspension of $CoCl_2$ in CH_3OH at 35 ^{0}C while bubbling CO generated by dropwise addition of formic acid into concentrated sulphuric acid at 70 ^{0}C. The contents were further stirred for 2-3 h at 35 ^{0}C. The conversion of $CoCl_2$ was calculated by the amounts of CO absorption, and it is about 95% in 2.5 h. Comparing with this novel approach, the conversion is less than 5 % when the reactions are carried out with only Raney-Ni, or without $CoCl_2$ at the same reaction conditions (Fig. 1).

The IR spectrum shows that the liquid product of the carbonylation has a sharp band at 2025 cm^{-1}, which belongs to the vibration of CO in $Co_2(CO)_8$ (Fig 2). There is no band at 2131 cm $^{-1}$ or 2058 cm^{-1}, which belongs to the $Ni(CO)_4$, although it is very easy for the reaction of Ni and CO at room temperature.

The treatment of the carbonylation product with 16% NaOH shift the band at 2025cm^{-1} to 1895cm^{-1} which belongs to the vibration of CO in $Co(CO)^-_4$ (fig. 3). The band 1895cm^{-1} obtained in this way is very similar to the one obtained by the method in the literature.

In conclusion, we would like to point out that the present method of generation of $Co(CO)^-_4$ reagent using simple reagent under atmospheric pressure of CO for carbonylation of organic halides is a simple alternative method to the procedures available in literature.

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Fig.1. Carbonylation of $CoCl_2$ to $Co_2(CO)_8$ at ambient condition

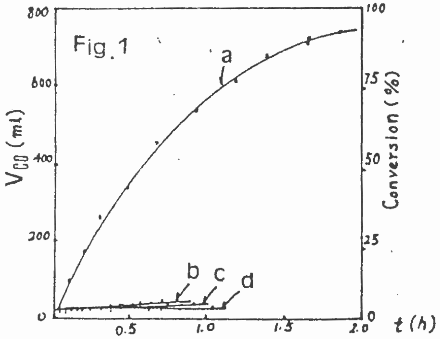
T: 35°C,P: 0.1 MPa, Sol:CH_3OH, CO% > 99,8%

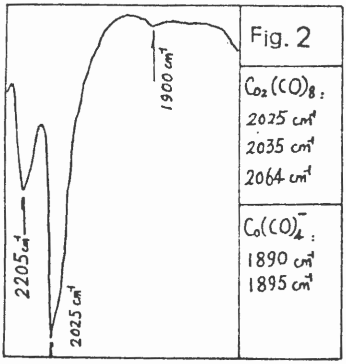
A: $CoCl_2$/R – Ni/CO/CH_3OH B: $CoCl_2$/CO/CH_3OH

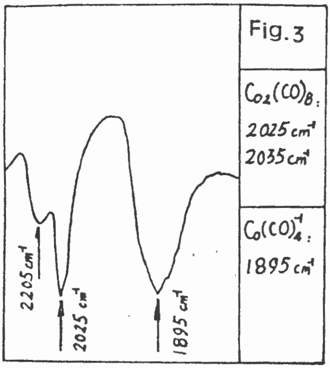
C: R – Ni/CO/CH_3OH D: CO/$CHCH_3OH$

Fig.2. IR spectrum of the product in the reaction A in Fig.1. IR-435 (Shimadzu Japan)

Fig.3. IR spectrum of the liquid obtained by NaOH treatment of the product in the reaction A in Fig.1.







PPI-39

On the Phosphorus Promotion of the HDS Activity of Coprecipitated Iron/Alumina Catalysts

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Introduction: Phosphorus is well known to promote the activity of CoMo and NiMo hydrotreating catalysts [1-10]. Phosphorus promotion has been attributed to several effects: e.g. increase of dispersion of the active compound on the carrier, surface phosphate formation which in turn reduces spinel formation [11]. Coprecipitated iron/alumina catalysts are of interest as first stage catalysts for heavy oil upgrading. In this context we have investigated the effect of phosphorus promotion on the hydrotreating activity of these catalysts. It has been shown by Eijsbouts et al. [12] that the HDS activity of iron catalysts supported on activated carbon is poisoned by phosphorus. However, Eijsbouts *et. al.* [12] used a pre-reactor bed to volatilise and transport the phosphorus to their catalyst, which suggests the continuous release of phosphorus during the HDS of thiophene. In our case two ways of introducing phosphorus into the iron/alumina system prior to reaction have been investigated, namely coprecipitation with ammonium phosphate which leads to phosphate incorporation and *in situ* pre-treatment with PH_3/H_2 [13].

Experimental: Iron/alumina catalysts were prepared by coprecipitation from the respective nitrate salt solutions using ammonia [14]. The Fe/Al molar ratio of the obtained mixed oxide was chosen to be three. 'Free' alumina as well as aluminium substituted hematite was present in the oxidic catalyst. A series of phosphate promoted iron/alumina catalysts (Fe/Al = 3) was prepared, the phosphate being introduced during the precipitation process in the form of ammonium-phosphate. All catalysts were sulfided at 673 K for two hours (10 Vol.-% H_2S/H_2). The phosphate free iron/alumina was subsequently treated with 5 Vol.-% PH_3/H_2 for another two hours at 673 K. The HDS of thiophene in the presence of 1 Vol.-% H_2S was investigated over the catalysts at 623 K, 20 bar, a wide range of space times and as a function of time on stream.

Results & Discussion: Phosphate incorporation increased the BET surface area of the sulfided iron/alumina catalyst significantly (110 m^2/g for 5 mol-% phosphorus compared to 67 m^2/g for the unpromoted Fe/Al). XRD revealed the same crystalline structure, namely pyrrhotite, for the sulfided iron/alumina catalysts with and without phosphate. However, much stronger particle growth appears to have occurred during sulfidation of the phosphate incorporated catalyst. The graphs of the time on stream experiments of the unpromoted and the 5 mol-% phosphate promoted iron/alumina catalyst are given in Figure 1. A similar deactivation profile was observed for the unpromoted as well as for the phosphate promoted iron/alumina. A comparison of the apparent reaction rate constants suggests a lower HDS activity of the phosphate incorporated catalyst compared to the unpromoted material.

Plots of time on stream for both the PH_3/H_2 treated and the untreated iron/aluminas are given in Figure 2. PH_3/H_2 treatment initially decreased the HDS activity of the iron/alumina catalyst, but with increasing time on stream an increased activity was observed. There seems to be an activity maximum after approximately 30 hours, whereafter the activity gradually declines. A similar, but less pronounced behaviour was observed for the iron/alumina catalyst which had been on stream for

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40 hours and had been subsequently treated with PH_3/H_2. It is interesting to note that the maxima of both time on stream plots of the phosphided catalysts occur around 30 hours. This may suggest that the catalysts lose sulfur during the phosphiding process and slowly adjust their composition according to the altered condition after the treatment. The phosphiding process probably causes an increased dispersion of the iron sulfide present. The apparent first order reaction rate constants of the PH_3 treated iron/alumina were considerably higher than for the unpromoted catalyst, even after 40 hours on stream. ICP as well as XPS measurements of the used catalysts indicate that the phosphided catalysts contain small amounts of phosphorus after 50 hours on stream.

In conclusion it is evident from our results that phosphate incorporation has no significant effect on the HDS activity of sulfided iron/alumina. PH_3/H_2 pre-treatment on the other hand increases the HDS activity of the sulfided catalyst considerably. The promotional effect is only observed after prolonged exposure to the reaction feed.

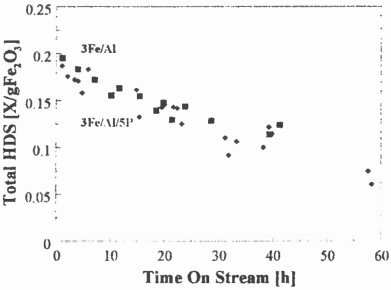

Figure 1: HDS of thiophene over unpromoted and phosphate incorporated iron/alumina as a function of time on stream

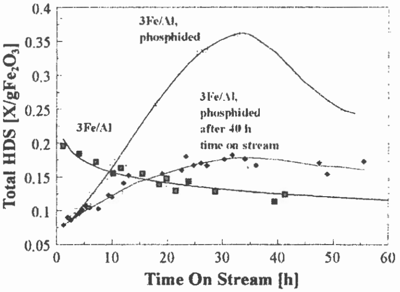

Figure 2: HDS of thiophene over unpromoted and PH_3 treated iron/alumina as a function of time on stream

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PPI-40

SURFACE COMPOSITION OF ATMOSPHERIC AEROSOLS

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At present, the problem "earth as a global photocatalytic reactor" is becoming very important. Many reactions could be catalysed by the action of solar light on atmospheric aerosols. Recently, this problem has been analysed by Zamaraev and et al. [1, 2].

Chemical composition of aerosols surface layers plays a main role in their catalytic activity. In the present paper, we have investigated aerosols collected in settlement Kluchi near Novosibirsk Akademgorodok.

The aerosols samples were collected by a large-volume collector onto Whatman-41 and AFA-HA filters in periods 8 days in August 1992 and 12 days in March 1993. The collection time of one sample was 24 h. Different fractions of aerosols with particle sizes of 1-3, 3-6, 6-9, 9-19 and above 19 μm were obtained.

SIMS measurements were carried on a MC-7201 spectrometer with a monopole mass analyser. The apparatus used for the experiments has been described elsewhere [3].

Elemental analysis of aerosols with the sizes of particles from 0,1 up to 19 μm has shown that the particles with $d > 9$ μm have increased contents of Fe, Ti and Al and are formed by industrial sources, whereas the particles with $d < 3$ μm are formed by soils erosion. The elemental composition of the Kluchi aerosols differs from the soil composition by increased contents of Na, K, Ca, as well as Co, Cu, V, Mn, Cr.

The main role in catalysis can be played by aerosols with the particle sizes less than 1 μm, as such particles have essentially higher (10-30 times) adsorption ability for hydrocarbons and water. Moreover, the atmospheric concentration of such particles is also higher than that of other particles.

Active component of the catalysts for the photocatalytic reactions can be alumosilicates, perovskites of $CaTiO_3$ type and TiO_2.

Common analysis of a composition of surface and adsorbed layers and a set of possible photocatalytic reactions [1, 2] shows that the investigated aerosols can catalyze the following reactions:

1. Reactions with participation of main components of atmosphere:

   Formations of ammonia and hydrazine from nitrogen and water:

   $N_2 + 3H_2O \longrightarrow 2NH_3 + 3/2O_2$; $N_2 + 3H_2O \longrightarrow N_2H_4 + O_2$

   Formation of organic compounds from CO_2 and H_2O:

   $$CO_2 + H_2O \longrightarrow HCOOH, CH_2O, CH_3OH$$

2. Reactions with participation of traced components of atmosphere:

   Oxidation of SO_2: $SO_2 + O_2 + H_2O \longrightarrow H_2SO_4$

   Decomposition of nitrogen oxides: $NO_x \longrightarrow 1/2N_2 + x/2O_2$

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PPI-41

THE MECHANISM FEATURES OF ETHYLENE OXIDATION ON SILVER

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The mechanism of the catalytic reaction of ethylene oxidation on silver is still under discussion.In this paper we formulate theses reflecting the essential features of the reaction mechanism. The mechanism interpretation is based on the investigations of our group and the literature, reviewed in article [1]. Also results, obtained recently on the silver films are taken into account.

The catalytic oxidation of ethylene on silver occurs by a stepwise redox mechanism and involves two main stages:

1. Dissociative adsorption of O_2, forming the atomically adsorbed oxygen layer with the same charac-ter of a chemisorption bond similar to the chemical bond in solid Ag_2O.
2. Interaction of ethylene with the uniform ato-mically adsorbed oxygen layer on silver, which causes ethylene oxide formation in parallel with complete ethylene oxidation.

The adsorbed oxygen layer is uniform, concerning the character of the chemisorption bond, but because of interaction of adsorbed atoms the differential adsorption heat decreases with increasing coverage.
This dependence causes variation of the activation energy values of surface reactions, which involve oxy gen transfer to silver or the reverse process. The activation energy follows the Bronsted - Polyani correlation. The decrease of energy bond of adsorbed oxygen with increasing coverage explains the

phenomenon that ethylene epoxidation is observed at the surface coverages by oxygen higher than a certain threshold value.

Dissociative adsoption of oxygen forms multiplet complexes, which consist of silver oxide species (Ag(I) and O_{ads}) and active multiplets Ag^*_m. Partial and complete ethylene oxidation occur by interaction between ethylene and multiplet complexes and involve intermediate activation of ethylene on the multiplets.

The surface intermediates (ethylene conversion products) have a modifying action on the silver catalyst surface, resulting in suppression of complete ethylene oxidation in the absence of a considerable effect on the rate of partial ethylene oxidation. As a result, the selectivity of ethylene oxide formation icreases significantly.

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PPI-42

EVOLUTION OF THE STRUCTURE OF Co-Mg OXIDE CATALYSTS UNDER HYDROGEN OR CARBON MONOXIDE ATMOSPHERE. THE EFFECT OF THE ACTIVE COMPONENT PARTICLES SIZE ON THE CATALYST SELECTIVITY IN THE REACTION OF CO DISPROPORTIONATION

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Solid solutions of Co- and Mg- oxides are found to exhibit dramatic transformations during their treating in the hydrogen atmosphere and in the carbon monoxide atmosphere when raising the temperature up to 750°C. We have analyzed the influence of the initial sample composition, method of preparation as well as conditions of the catalyst treatment on the crystal structure, morphology, and microtexture of the samples.

It was found that Co^{2+} ions, when being initially a component of a solid solution, are reduced in the H_2 flow at 360-600°C to form the cubic (β-) Co^0 phase. It was observed also that the Co^0 phase obtained from the CoMgO solid solutions is significantly more disperse than that obtained from individual oxide CoO.

When treating the reduced samples by the CO flow, the reaction of CO disproportionation to CO_2 and carbon was observed starting from the temperatures of 290°C. The reaction provides formation of two types of the solid carbon phase with graphite-type structure: "shells" (100 A width) which cover "large" Co^0 particles (of diameter > 200 A), and thin nanotubes (with the outer diameter ca. 100 A and the inner diameter ca.

30 A) which are connected with the "small" Co^O particles (of diameter ca. 100 A).

The structure of the "large" Co particles after the CO treatment appears to be highly defective, while the structure of the “small” Co particles seems to be ideal cubic.

It was found that formation of the carbon "shells" occurs at lower temperatures (with the maximum reaction rate at ca. 420°C) than that of the nanotubes (with the maximum reaction rate at 550-580°C) resulting in a fast deactivation of Co^O particles due to shielding the Co^O particles by the “shells” of carbon. At the same time the “small” particles are active up to 750°C and do not lose their activity during long time.

A quantitative analysis of thermodynamic equilibria on the "amorphous carbon"-"solution C in Co" and "graphite carbon"-"solution C in Co" phase boundaries together with an analysis of the experimental data evidence a possibility of fluidization of the “small” Co^O particles during the CO disproportionation due to the formation of oversaturated solutions of carbon in Co^O. Thus, the liquid state of the carbon solution in Co is probably responsible for nanotubes formation.

PPI-43

Alkene Oxidations by Various Oxygen Donors Catalyzed by Transition Metal Substituted Heteropolyanions

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Transition metal substituted heteropolyanions (HPAs) attract much attention as oxidation catalysts due to inorganic nature of their coordination sphere which makes them stable towards oxidative degradation. We have investigated alkene oxidation by various oxygen donors (H_2O_2, t-BuOOH, PhIO, $NaIO_4$, $KHSO_5$, N_2O, N-methylmorpholine N-oxide (MNO), m-chloroperoxybenzoic acid (m-CPBA) and O_2/isobutyraldehyde (IBA)) in the presence of tetra-n-alkylammonium salts of mono- and trisubstituted Keggin-type heteropolytungstates, $XW_{11}MO_{39}^{n-}$ ($XW_{11}M$; X=P, Si; M=Co^{II}, Mn^{II}, Ni^{II}, Cu^{II}, Pd^{II}, Fe^{III}, Cr^{III}, Ti^{IV}, Zr^{IV}, Ru^{IV}, Ce^{IV}, Nb^{V} and V^{V}) and $SiW_9M_3O_{37}^{m-}$ (M=Co^{II}, Mn^{II}, Cu^{II} and Fe^{III}), respectively. Cis- and trans-stilbene, cis- and trans-heptene-2 as well as cyclohexene were used as model substrates. Oxidations with all oxidants studied, except $NaIO_4$ and $KHSO_5$, were carried out in MeCN medium, while the reactions with latter two oxidants were performed in two-phase system (dichloroethane-H_2O). Alkene oxidation was found to be readily provided when using 30% H_2O_2 ($PW_{11}M$ with M=Zr^{IV}, Cr^{III}, Fe^{III} and Nb^{V}), t-BuOOH (M=Mn^{II}, Cu^{II}, Co^{II}, Ru^{IV}, Ti^{IV}, V^{V} and Nb^{V}) [1], PhIO (M=Ru^{IV}, Mn^{II} and Co^{II}) [2], $KHSO_5$ (M=Mn^{II}, Co^{II}) and O_2/IBA (M=Co^{II}, Cu^{II}, Pd^{II}, Ti^{IV}, Zr^{IV}, Ru^{IV}, V^{V}) [2,3]. The composition of oxidation products depends on the olefin structure, the oxygen donor and the catalyst used. Oxidation by H_2O_2 and t-BuOOH requires elevated temperatures (50-60°C), while oxidation by PhIO and O_2/IBA easily proceeds at room temperature. Only slight differences were observed for catalytic properties of $XW_{11}M$ with Si and P central atoms. The size of the tetra-n-alkylammonium cation (C_4-C_8) has practically no influence on HPAs catalytic activity. $NaIO_4$ produces alkene double bond oxidative cleavage when $PW_{11}Ru^{IV}$ is used as the catalyst and is inactive with other HPAs. The reactions of alkenes with MNO and N_2O in the presence of $PW_{11}M$ gave no detectable products within 6-8 h at 60°C. Most HPAs studied display negligible catalytic effect on alkene epoxidation with m-CPBA, however, $PW_{11}Ru^{IV}$ was found to mediate double bond oxidative cleavage. Dioxygen in the presence of IBA was found to be the most efficient oxidative system for catalytic alkene epoxidation. Thus, the selectivity of trans-stilbene epoxide formation in the presence of $PW_{11}M$ (M=Co^{II}, Cu^{II}, Pd^{II} and Ti^{IV}) is as high as 82-93% at complete alkene conversion [2,3].

Trisubstituted HPAs turned out to be less active and selective catalysts than monosubstituted ones when t-BuOOH and PhIO were used as the oxidants, however, when oxidation with O_2/IBA system was performed, trisubstituted HPAs exhibit better catalytic properties as compared to their monosubstituted analogs.

Orders of catalytic activity of $PW_{11}M$ in trans-stilbene epoxidation differ remarkably for the oxidants studied. In contrast to oxidation with PhIO, the reactions with t-BuOOH and O_2/IBA show induction periods and are inhibited by small additives of radical scavengers such as 2,6-di-tert-butyl-phenol and hydroquinone. These facts indicate that alkene epoxidation with t-BuOOH and O_2/IBA proceeds via chain radical mechanism, alkylperoxy and acylperoxy radicals, respectively, being most probably the active epoxidizing species. As a consequence, these reactions are extremely sensitive to microimpurities of catalysts and inhibitors. Catalyst-inhibitor inversion is observed with increasing HPA concentration, moreover "critical" phenomena are observed in some cases that can be explained by participation of a catalyst in chain termination. We have found that activation of H_2O_2 also proceeds via a homolytic route. On the contrary, oxidation with PhIO has the heterolytic nature and most likely involves the formation of active metal-oxo species. Epoxidations of cis-alkenes catalyzed by HPAs proceed in a non-stereospecific manner. This fact allows to exclude any known concerted mechanism for oxygen transfer from the activated oxidant to alkene and supports the formation of free-rotating intermediates. The mechanisms of alkene oxidation catalyzed by $PW_{11}M$ strongly depend on the nature of the oxygen donor used and resemble those established for metalloporphyrins in the absence of organic bases [4].

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PPI-44

MICROWAVE EFFECT ON REACTION RATE IN ETHYLENE EPOXIDATION OVER SILVER CATALYSTS

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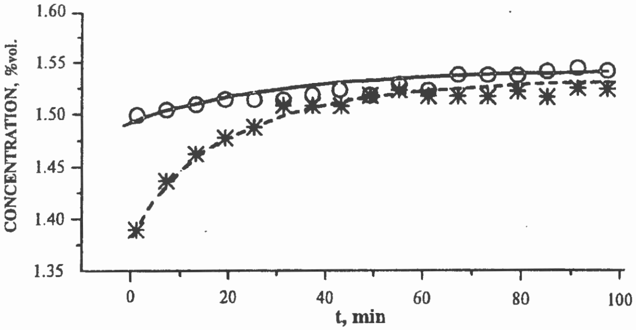
Most researchers consider microwave radiation as a specific source of heat energy for performing catalytic processes as well as an efficient method for water removal from a catalyst during a reaction or in the stage of the catalyst preparation. At the same time only a few papers concern the specific, rather than heat, microwave radiation effect on the rate of catalytic reaction. Thus, in [1] a sharp selectivity increase in the isomerization of 2-methyl pentane over alumina-supported platinum catalyst was observed. The high selectivity is kept for a long time after the microwave radiation cut-off. This effect is explained by the modification of the structural and electron properties of the Pt particles under the microwave action.

The present work concerns the study of the nonheat action of microwave radiation on the activity of the silver catalysts for ethylene epoxidation. For this purpose a special flow reactor was designed, which permits one to perform the reaction at given temperature in the presence and absence of microwave radiation (Microwave oven MICRO-TIME FM 2938 E). The reaction mixture composition was chromatographically determined with time. As a catalyst, $Ag/\alpha\text{-}Al_2O_3$ powder with silver particles predominantly of size 2000-5000 A was used.

It has been experimentally found that the microwave supply to the catalyst prereduced in H_2 flow causes the ethylene conversion increase which disappears as the system approaches a steady state (Fig.1). The catalyst activity increases both towards ethylene epoxidation and deep oxidation, so the reaction selectivity remains constant. At the same time under transient or steady-state reaction conditions microwave radiation has no significant effect on the ethylene conversion over the sample preoxidized in oxygen flow. It is significant that under steady-state conditions the activity and selectivity both of the oxidized and reduced samples coincide within the experimental error (3%). The TEM studies have shown that the redox treatments do not lead to the change in the Ag particle size. These results indicate that the catalyst is not heated under the action of microwave radiation, since this effect otherwise would be reflected by increase in the reaction rate. The estimated heating of the catalyst bed due to microwaves does not exceed 0.5-1 K.

Fig.1. The time dependence of C_2H_4 concentration upon admission of reaction mixture (2.3% C_2H_4 + 5.6% O_2 + 92.1% He) on the Ag/α-Al_2O_3 catalyst prereduced in H_2 flow. T=215°C.

O - without microwave radiation, ✱ - under microwave radiation



The activity increase in the initial period of reaction and its subsequent decrease is explained by the silver surface defects forming under the action of the reaction medium [2, 3]. The reduced silver is more regular, while the oxidized, or steady-state, one has more defects and is characterized by a lower electron density. Since the microwave radiation results in the reaction rate increase in the initial period namely, one can assume that such radiation somehow slows down the process of the defects formation or roughening. This may be caused by the increase in the electron density on the Ag surface, for example, due to the transfer of some electrons from the metal bulk by the microwave field. However, as the defects on the Ag surface are generated at the expense of the reaction energy and stabilized by the oxygen penetrating into the subsurface layers, the electron exchange between the volume and surface of the silver particles may be hindered. Since the energy of the microwave radiation quanta is low (10^{-5} eV), the microwave radiation action should decay as the steady state is approached, which is really observed in the experiments.

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PPI-45

THE SIMPLEST THREE-STAGE TRIGGERS IN HETEROGENEOUS CATALYSIS

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The establishment of the simplest schemes (mechanisms) for describing a complex behaviour of concrete catalytic reactions is one of the directions of research in kinetics of heterogeneous catalysis. In particular, the search of scheme-"triggers" describing multiplicity of stationary states (MSS) in isothermal conditions of a gradientless differential reactor is of some interest. In paper [1] the detailed analysis of consecutive and parallel three-stage triggers describing MSS in the S- form dependences (Hysteresis) is given when the values of reaction rate ($r>0$) on a plane "rate-parameter" are positive. These kinetic dependences characterize the conformities of reaction kinetic behaviour when their rate in direct direction prevail over the rate in inverse one. However, such dependences cannot be full when all the possibilities of reaction kinetic behaviour are described. It is connected with the fact that in the region of negative values of reaction rate one can find complex kinetic S-curves. By analogy with the existence of MSS at $r>0$ when additional information on a reaction mechanism is obtained, the existence or absence of MSS at $r<0$ permits to check the correctness of the choice of a reaction mechanism.

In paper [2] the principal possibility of describing MSS both at $r>0$ and at $r<0$ with the help of the simplest stage schemes is given. Below the results of the analysis of three-stage schemes in order to establish all possible triggers are given. They describe MSS both at positive and at negative values of reaction rate. For the establishment of such schemes a packet of computer programs of MSS investigation [3] was used. The generation of all possible three-stage schemes was held also automatically on the base of the program "Gener". This program constructed unrepeated matrixes of stoichiometric coefficients of stage schemes which are correct according to the theory of stationary reactions and the molecularity of constituted stages (not more than three).

The above-mentioned analysis permits to form a lot of schemes of three-sta triggers having MSS both in the region of positive and negative values of reaction rat The few of obtained schemes are given in the Table.

Stoichiometric stage coefficients

N	1	2	3	N	1	2	3
1	300=201	210=300	001=010	5	300=012	021=210	001=01
2	300=012	210=300	001=100	6	300=012	012=201	001=10
3	300=012	111=300	001=100	7	210=102	120=201	001=01
4	300=012	012=210	001=100	8	210=021	120=012	001=10

Here the groups of three numbers to the left and to the right of the equality sign me stoichiometric coefficients of the intermediate substances on the surface of th catalyst which corresponds to each stage.

Thus, we have carried out the systematization of all possible three-stage schem of heterogeneous catalytic reactions describing MSS both at positive and also negative rate values. When the kinetics of reversible heterogeneous-catalytic reactions studied experimentally, it is necessary to investigate the conformities of the proceeding both in direct and inverse directions. This permits to construct full kinet dependencies for an investigated reaction. Their comparison with rated kinet dependences for alternative stage schemes permits to establish a reaction mechanism details.

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PPI-46

MECHANISM OF CARBON DIOXIDE ACTIVATION ON METAL AND OXIDE CATALYSTS

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Interaction of CO with hydrocarbons over most catalysts proceeds via two steps: 1) dehydrogenation of hydrocarbons and 2) CO_2 reduction by hydrogen. Regularities of CO_2 reduction by H_2 have been studied on model catalysts. On Fe And Re this reaction proceeds via the intermediate formation of formiates. On MnO_x this reaction proceeds by the simple redox mechanism.

We have studied the interaction of CO_2 with hydrocarbons and alcohols on metal and oxide catalysts [1-3]. The reaction of CO_2 with methane and higher alkanes has been studied in many details by different scientists on Ni an platinum metal catalysts. This reaction in most cases leads to synthesis gas formation. The proposed mechanisms include dissociation of CO_2 into CO and O_{ads}, dissociation of hydrocarbons into C_{ads} and H_{ads}, and formation of an equilibrium mixture of CO, CO_2, H_2 and H_2O corresponding to the water gas shift reaction. Nickel catalysts are most often employed to obtain synthesis gas, but they are poisoned by coke. Iridium and ruthenium catalysts are active and are not strongly poisoned by carbon, but they are expensive.

In our works we have shown that catalysts based on MnO_x and rare earths are not poisoned, but they operate at high temperatures (700 - 950°C). Their productivity is not very high, but they can be promoted by additions of alkaline oxides (Li, Na, K) and by transition metal oxides (Cr_2O_3). Such catalytic properties of MnO_x and rare earths can be explained, firstly, by the fact that these oxides give rise to moderately strong carbonates, which may decompose during the reaction. Secondly, these oxides can be readily oxidized and reduced under the reaction conditions. The process of carbonate decomposition can coincide with the redox process

$$MnCO_3 + H_2 = MnO + CO + H_2O \qquad (1)$$

When alkaline oxides are used the stability of these carbonates increases, while the addition of acid oxides (Mo, V) diminishes the stability. Alkaline oxides shift the process towards oxidative dehydrogenation, while acid ones shift it towards oxidative cracking.

The predominant route of the CO_2 reaction with hydrocarbons is dehydrogenation of the hydrocarbon with subsequent oxidation of hydrogen by CO_2 (reverse water gas shift reaction)

$$C_mH_{n+2} = C_mH_n + H_2 \qquad CO_2 + H_2 = CO + H_2O$$

The latter reaction has been studies by many investigators mainly on metal catalysts. Interesting and still not explained peculiarities were observed: 1) the rate of CO_2 hydrogenation very often exceeded that of CO hydrogenation; 2) both methane and higher hydrocarbons were formed during CO hydrogenation, but only CH_4 was formed during CO_2 hydrogenation.

We have studied the CO_2 reduction on the catalysts Fe/Al_2O_3 , Re/Al_2O_3 and $Cr-Mn-O/Al_2O_3$ by means of temperature programmed reduction. A sharp increase of the rate of oxidation of Fe/Al_2O_3 and Re/Al_2O_3 and that of interaction of CO_2 with the surface carbon were observed after introduction of 1-2 % H_2 into the CO_2 flow. At high concentrations of hydrogen in the $CO_2 + H_2$ mixture the CO_2 transformation leads to CO CH_4 formation. This phenomenon has been explained by schemes (2) and (3):

$$\begin{gathered} Fe + 0.5\,H_2 = Fe\,(H) \qquad Fe\,(H) + CO_2 = FeHCOO \\ FeHCOO + Fe = FeO + Fe\,(H) + CO \end{gathered} \tag{2}$$

and

$$\begin{gathered} Re + 0.5\,H_2 = ReH \qquad ReH + CO_2 = ReHCOO \\ ReHCOO + 4H_2 = ReH + CH_4 + 2H_2O \end{gathered} \tag{3}$$

These schemes are very similar to chain reaction schemes. Thus, methane can be formed via intermediate formate formation, but not via CO_2 dissociation and CO hydrogenation. This hypothesis was proved by experiments with addition of formic acid to the mixture $CO_2 + H_2$, HCOOH increased the rate of the reaction.

The $CO_2 + H_2$ reaction on the $Cr-Mn-O/Al_2O_3$ catalyst did not change after addition of HCOOH and only CO was formed. The mechanism of CO_2 reduction in this case includes reaction (1), that is H_2 reaction with carbonate fragments, which are formed after CO_2 reaction with MnO_x. From the practical point of view this is convenient because only syngas is formed without losses on CH_4 formation.

Rhenium is situated in the same group of the periodic system as manganese. It can be even more active than Mn in some reactions of hydrocarbons with CO_2. We have studied the $CO_2 + H_2$ reaction on Re/Al_2O_3 and $Mo-Re-O/Al_2O_3$ catalysts. It was shown that CH_4 formation prevailed on the Re catalyst, but CO was formed on $Mo-Re-O/Al_2O_3$. It was proposed that the modification of Re/Al_2O_3 by molybdenum decreased the basicity of the surface. This leads to changes in the ratio of adsorption to reduction of CO_2. Thus, the correct choice of modificators can regulate the catalytic properties of catalysts of the CO_2 reduction.

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PPI-47

MECHANISM OF POISONING WITH OXIGEN OF AMMONIA SYNTHESIS CATALYST

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Study of poisoning of the catalyst of ammonia synthesis

$$N_2 + 3H_2 = 2NH_3 \qquad (1)$$

allows to develop the theory of catalysis and chemisorption of gas mixtures on nonuniform surfaces. The purpose of this work was investigation of alteration of kinetics of reaction (1) under the influence of surface oxygen. The source of that oxygen may be, in particular, the water vapor in hydrogen-nitrogen mixture.

Kinetic models of reaction (1) in presence of water vapor were developed. The derivation of the equations was based on concepts of Temkin's theory of ammonia synthesis and on proposal that the poisoning is a result of occupation of adsorption sites on nonuniform surface by oxygen atoms. The reaction rate was determined not only by the the rate of adsorption of nitrogen, but also by the rate of hydrogenation of adsorbed nitrogen.

Two different cases were considered: when the bonding energy of oxygen atom is the same for each adsorption site and when this energy decreases with decreasing of bonding energy of adsorbed nitrogen. For these cases dependencies of the order of the reaction retardation with ammonia were obtained.

For testing of obtained equations the experiments on determination of the orders of the retardation with ammonia before and after poisoning were performed. The experiments were carried out on industrial iron catalyst in circulation flow system with stoichiometric hydrogen-nitrogen mixture at 350°C and near to atmospheric pressure. Poisoning with oxygen was performed by treating of the catalyst with reaction mixture containing small amounts of water vapor. Different partial pressures of ammonia at the same total pressure were obtained by variation of the gas mixture flow rate. During experiments the activity of catalyst slowly increased because of setting free of surface from oxygen. Corrections were made to obtain the reaction rate under the same surface coverages of oxygen and different partial pressures of ammonia.

On the poisoned sample the partial pressures of ammonia were less then 7 Pa, when accordingly to above considered theoretical kinetic models the order of retardation with ammonia must be around zero. But on the poisoned catalysts the order of retardation by ammonia was near to unity. So we can conclude that poisoning of catalyst with oxygen does not result in blocking of adsorption sites: the surface oxygen influences upon properties of unoccupied part of the surface. That proposal coincides with conclusion of [1], that under the poisoning of the catalyst with oxygen heat of adsorption of nitrogen does not change, but activation energy of nitrogen adsorption increases. From data of our work it follows that on the poisoned sample the rate of adsorption of nitrogen decreases less than the rate of its hydrogenation. As a result the retardation of the reaction with ammonia proceeds at smaller partial pressure than on unpoisoned catalyst.

The results of the present study, as those of the paper[1], we may explain in the following way. The activated complex of the nitrogen chemisorption is charged negatively. The value of that charge exceeds the charge of chemisorbed nitrogen and the charge of activated complex of the stage of hydrogenation of adsorbed nitrogen. The adsorbed oxygen is acceptor of electrons, so it increases the activation energy of chemisorption of nitrogen and has little influence on the heat of nitrogen adsorption and on the rate of the stage of hydrogenation of adsorbed nitrogen.

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PPI-48

ON THE ROLE OF SLOW AND FAST ELEMENTARY STEPS IN THE DYNAMICS OF CATALYTIC REACTIONS $AZ + BZ \xrightarrow{\infty} AB + 2Z$

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It is not rare case when mechanism of a catalytic reaction has elementary steps which reaction constants are of different order of magnitude. This situation has strong impact both on the observed kinetic behavior and on the methods of its analysis. If successful such an analysis results in fast formulation of the reaction mechanism, isolation of the areas of parameters with certain type of kinetic behavior, simplification of procedures of kinetic parameter estimation. The theory of integral manifolds proved to be very powerful tool for such studies. Combined with variable elimination methods it allows to obtain explicit results for important models. Several patterns of steady state, quasi-steady state and dynamic kinetic dependencies will be discussed:

- A. Slow reaction: slow relaxation in the case of Rate Limiting Step
- B. Fast reaction: the fingerprints of fast surface reaction of two different adsorbates
- C. Slow exchange and Fast reaction: Five steady states in Catalytic CSTR
- D. Slow and Fast: Relaxation self oscillations in the system with buffer step
- E. Fast desorption and even faster surface reaction: the dynamics of Hydrogen oxidation
- F. Fast surface reaction and even faster surface reconstruction: self oscillations

A. The situation of rate limiting step is classical: if the reactions are reversible the fast reactions will be in thermodynamic equilibrium and the steady state reaction rate will be defined by the rate of rate limiting step. The dynamic behavior of the system will be defined by faster processes: the system typically reaches the steady state in the time scale of fast reactions. In the case of non linear reaction mechanism , however this picture is a little more complicated: there may be additional points where fast reactions are close to equilibrium: the boundary steady states. They are located outside the positive concentration ortant but very close to its boundary. If initial conditions are selected near such a boundary the system may show slow relaxation. The detailed analysis of Langmuir-Hinshelwood reaction mechanism shows that there may be a situation when the boundary steady state is multiple. In this case there may be relatively significant region of initial conditions that give rise to slow relaxation.

B. As was proved by author [1] the fast surface reaction of two different adsorbates is the reason of breaks on monoparametric kinetic dependencies. At present it is clear that explanations that involve the addition impact reaction (Temkin and Kuchaev) were not necessary: it is possible to describe the observed kinetic behavior on the base of 3step adsorption mechanism. Thus the major pattern ("fingerprint") of the fast reaction shown in the title of this paper are breaks (discontinuous derivatives) on the kinetic curves. Actually this break is point of self intersection of corresponding curve. However the condition of it is of asymptotic nature: that makes this point typical. If we turn to real life example - CO oxidation on noble metals we could expect the breaks in high vacuum conditions that provide the smallness of adsorption parameters (Oxygen desorption usually is negligible). Thus the really necessary condition of this effect would be relatively small in comparison with the reaction constant of CO desorption. The analysis of the dynamics shows that in the case of fast surface reaction there are two distinct regions: fast relaxation in the fast reaction time scale and slow one governed by adsorption processes of reactants. As surface concentration of either of reactants is small the phase portrait shows the "skin effect": the system trajectory most time belongs to the boundary of reaction space.

C. The assumption about the fast surface reaction combined with usual assumption about the slower than reaction mass exchange process allows to understand many intriguing facts on the open catalytic system: CSTR. We found explicit conditions of such exotic situations as 5 steady states (3 of which may be stable, 2 stable steady state and stable oscillations) as well as isola like and loop like steady state dependence.

D. Addition of slow buffer step allows for generation of relaxation self oscillations in the Langmuir-Hinshelwood model of catalytic reaction. The characteristic feature of these oscillations in the case of fast surface reaction is the fact that during the high conversion portion of period the system shows the constant reaction rate. More detailed analysis shows the second order effect: the faster is fast reaction the slower (in the log scale) the oscillations. It also shows some way of experimental estimation of "fast" reaction parameters: if one adds the slow process it becomes possible to have slow dynamics that is affected by fast constant.

E. We analyzed the situation of fast desorption of hydrogen and even faster surface reaction to understand the dynamics of pulse experiments on oxidation on the Pd-MOS system. The analysis of the system with two small parameters resulted in explicit formulas for surface dynamics. One very simple corollary was the fact that maximum of reaction rate during the transient period does not depend on initial conditions.

F. Authors [2] studied by Monte Carlo method the oscillatory kinetics of S catalytic reaction with surface reconstruction simulated by variations in the catalytic properties of the surface. This work deals with deterministic version of this model that is based on the following mechanism

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$A + Z \xrightarrow{k_1} AZ$ adsorption of component A

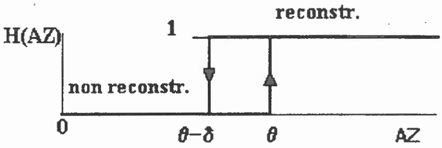
$B_2 + 2Z \xrightarrow{k_2} B_2Z_2$ non dissociative adsorption of component B

(1)

$B_2Z_2 \xrightarrow{k_3 H(AZ)} 2BZ$ surface reconstruction induced by adsorption of A

$AZ + BZ \xrightarrow{k_4} AB + 2Z$ surface reaction

The H(AZ) function has the form



To reproduce the assumptions [2] (immediate surface reaction of adjacent A and B particles as well as immediate dissociation of adsorbed B_2 particles into B particles if A-coverage reaches θ) the parameters of model (1) should satisfy the conditions

$$k_1P_A\,,\ k_2P_{B_2} \ll k_4 \ll k_3\,,$$

Comparison with Monte-Carlo simulations [2] shows the similarity in the case of regular mode oscillations. At the same time it was proved that deterministic model can not provide the existence of chaotic patterns. The patterns that were observed in [2] could be interpreted as a result of integration of different modes of deterministic oscillations over the catalyst surface.

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EFFECTS OF MICROSTRUCTURE ON THE ELECTROCATALYTIC PROPERTIES OF GRAPHITE SUPPORTED PLATINUM

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Electrocatalysis is of considerable interest in such areas as energy conversion and storage, electrosynthesis, water purification etc. Progress in electrochemical science and the emergence of new important applications, such as fuel cells, has raised the question of specific electrochemical properties of supported finely dispersed metals.

The micrograined structure of real electrocatalysts is often neglected when studying the size effects in electrocatalysis. Meanwhile it has been recently shown that the presence of grain boundaries in microstructured materials may drastically alter their physico-chemical and catalytic properties [1, 2].

The present work is aimed at the evaluation of the effects of microstructure on the electrocatalytic properties of graphite supported platinum. Anodic oxidation of ethylene glycol is studied as a model structure-sensitive electrochemical reaction.

Graphite supported platinum electrodes (Pt/C) have been prepared with the help of the electrochemical deposition from H_2PtCl_6 solutions. The detailed analysis of the electrodes structure and morphology using high resolution TEM and X-ray diffraction proved that Pt particles formed on the graphite surface were composed from randomly oriented micrograins with the average size ca. 12 nm.

Pt/C electrodes in neutral aqueous Na_2SO_4 solution demonstrate well defined peaks of hydrogen and oxygen electrochemisorption in the potential range from -1.0 to 1.0 V vs. Ag/AgCl/KCl(sat.) electrode (Fig.1A).

Electrooxidation of ethylene glycol on Pt/C electrodes includes parallel adsorption- and diffusion-controlled reactions which are manifested by three anodic peaks (Fig.1B).

PPI-49

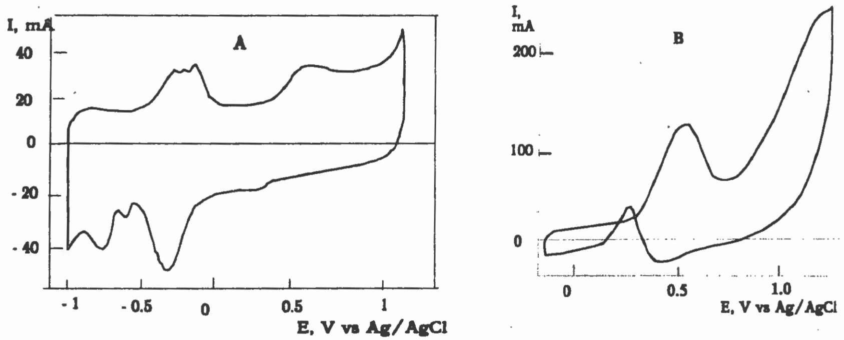

Fig.1 Cyclic voltammograms of Pt/C electrode with the real surface area 127 cm^2 in Na_2SO_4 1 M in the absence (A) and presence (B) of ethyleneglycol 0.1 M at the sweep rate 0.1 V/s.

Comparison of the supported and polycrystalline platinum electrodes in Na_2SO_4 solutions in the presence and absence of ethylene glycol reveals marked differences between the electrochemical properties of these materials resulting apparently from the differences in the electrode microstructures [3].

An influence of the surface structure and morphology on the poisoning of the electrode with the adsorbed organic residues is also discussed.

Acknowledgement: Financial support from INTAS (Grant N 95-0255) is gratefully acknowledged.

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NMR Studies of Reduced Dodecamolybdophosphoric Heteropoly Acid

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One of the most characteristic properties of heteropoly acids (HPA) of the Keggin type, $H_mXM_{12}O_{40}$ ($M=Mo,W^{6+}$), is their ability to yield upon reduction intensively coloured blue products ("blues") retaining the parent heteropoly anion (HPAn) structure. Reduced HPAn contains up to four extra electrons or formally four M^{5+} atoms. But actually the added electrons are evenly distributed over the whole $M_{12}O_{36}$ cage by means of very fast hopping between the structurally equivalent M^{6+} cations. Paramagnetic one-electron (1-e) blues were traditionally studied by ESR spectroscopy. Diamagnetic 2- and 4-e blues can be studied by NMR . As a rule, paramagnetic species cannot be studied by NMR. It was found however [1] that 1-e $H_3PW_{12}O_{40}$ in solution gives a narrow ^{31}P NMR peak shifted only a little downfield relative to that of non-reduced HPAn.

HPA $H_3PMo_{12}O_{40}$ and its reduced forms are widely used in practice including catalysis. In [2] there were studied concentrated (~0.5M) reduced solutions of the HPA using ^{31}P NMR and there were detected 2-e (a- and b-isomers) and 4-e blues by the peaks broadened due to electron exchange. 1-e blue was not observed. In this work we have studied more dilute solutions with the HPA concentration in the range 0.1-0.001 mol/l and the reduction degree of 0.25 to 4e. We have managed to detect 1e blue by rather a narrow (~5Hz) peak at +0.2 ppm. 2-e blues (both isomers) and 4-e blue were detected at -6, -6.6 and -13 ppm, respectively (fig.). The dependence of chemical shift values and the peak widths on the degree of reduction show that the intermolecular electron exchange occurs in the reduced solutions, with the rate decreasing with dilution. The electron exchange between 1-e blue and non-reduced HPAn occurs most rapidly and its rate is in the intermediate/fast exchange region of the NMR time scale depending on the HPA concentration. For 1e-2e and 2e-4e forms the rate of exchange is in slow region at 0.1 mol/l and it is not practically detected at concentrations <0.01 mol/l.

The 0.1M 4-e reduced solution containing 4e blue as single species was also studied by ^{95}Mo and ^{17}O NMR. At 330K the blue gives in ^{95}Mo spectrum a line at 307ppm (relative to 1M Na_2MoO_4) about 3kHz in width. In ^{17}O NMR spectrum a large downfield shift for the bridging O atoms of the HPAn was observed showing that the "blue" electrons are delocalized through the system of Mo-O-Mo bridging bonds.

The reduction of the HPA solutions was made with hydrazine. For obtaining the reduction degrees >2e the prolonged heating at 60-70° C was needed. The degree of reduction was determined from the ^{31}P NMR peak intensity ratios. The NMR spectra were run on Bruker MSL-400 spectrometer at 161.67, 26.08 and 54.24 MHz for ^{31}P, ^{95}Mo and ^{17}O, respectively.

The data obtained show that NMR spectroscopy is more appropriate technique for studying reduced solutions of $H_3PMo_{12}O_{40}$ than ESR spectroscopy [3] where due to the fast intra- and intermolecular electron transfer and electron coupling there is no quantitative correlation between sygnal intensities and the degree of reduction.

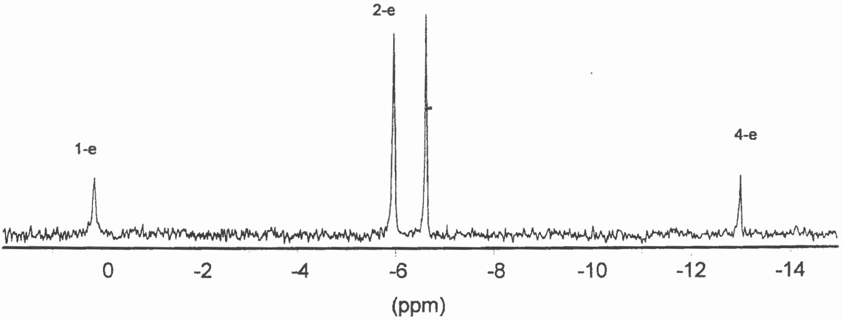

Fig. ^{31}P NMR spectrum of 0.01M solution of $H_3PMo_{12}O_{40}$ reduced on 2e

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Titanium oxides modified and activated under the effect of chain reactions as catalysts for hydrocarbon selective oxidation

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The modification and activation of solid phase catalysts by various chemical and physico-chemical actions obviously is one of the possible ways for the production of efficient catalysts for heterophase processes

It is well-known that titanium oxides, in particular titanium dioxide (TiO_2) possesses a definite catalytic activity for the oxidation processes.

The structural changes, particularly the change of different phases (anathase, rutil, bruckit) ratio, the partial reduction (partial extraction of oxygen) by the formation of non-stoichiometric oxides, the extraction of other metals slight impurities, *etc.* may result in the change of titanium oxides catalytic activity. With this purpose a new approach was applied in presented investigation. It is based on the possibility of realization of solid phase inorganic compounds conversion processes under the effect of gas phase chain reactions.

Both chemically pure titanium dioxide, as well as technical titanium dioxide, containing impurities of other metals, have undergone modification and activation. The experiments were carried out at flow conditions. The flow of gases, reacting with each other by chain mechanism, contacted with titanium dioxide which was placed into the reactor. The experiments were carried out at temperatures of 800-1200 K, at various contact times (τ = 1-40s) depending on the temperature in reactor and the ratio of initial mixture of reacting components. Chemically pure titanium dioxide partial reduction and structural modification process was carried out under the effect of hydrocarbon (propane-butane mixture) and also hydrogen oxidation chain reactions. Technical titanium dioxide was purified from iron and other metal oxides at conditions of chlorination chain reaction of the same propane-butane. The impurities were extracted in the form of trichlorides, sublimating into the gas phase, and flown away from the reactor by gas flow. At the same time the purified dioxide has underwent structural changes and was modified. The process was stopped when titanium dioxide itself began to undergo chlorination after the complete extraction of impurities.

In all the cases the changes of solid phase were indicated by X - ray -phase analysis.

The modified and processed samples were tested for catalytic activity. Iso-butane oxidation has been studied as a test reaction. The process was carried out at comparatively low temperature (T=380^{0}C) in an U-shaped flow reactor at gas flow constant contact time. The initial gas mixture of constant composition (iso-C_4H_{10}:O_2= 2:1) entered the reactor. The process was carried out at atmospheric pressure. Iso-butane oxidation has been studied without any catalyst and in the presence of the catalyst. For the comparison non-modified initial titanium dioxide was tested as well. The catalytic activity and the catalytic effect were judged by the change of definite reaction products yields. In particular we followed the yield of such significant products as formaldehyde, methanol, also deep oxidation products - CO and CO_2.

The results obtained show that the samples modified and activated by chain reactions exert more powerfull and selective effect on the process than the non-treated titanium dioxide. The processed samples exert more powerfull effect on the suppression of deep oxidation products yield and also on the formation of such undesirable products as methane and C_3-hydrocarbons, the yield of methanol is changed insignificantly. At the same time, in definite cases, it is observed that the concentration of the desirable product - aldehyde is increased by several fold (more than fourfold).

Thus the modified catalyst proved to be more active and may provide more selective oxidation process.

The results obtained allow us also to come to the conclusion that the effect of chain reactions on solid phase compounds can be a perspective method for the activation and creation of heterogeneous catalysts.

The results included in this report were obtained in work supported by INTAS (ref. No 94-0771).

PPI-52

FORMATION OF MULTILAYERED TIN ORGANOMETALLIC SPECIES OVER SUPPORTED METALS. A NEW WAY TO OBTAIN SELECTIVE HYDROGENATION CATALYSTS.

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ABSTRACT

The use of tin and lead tetraalkyl compounds to prepare modified skeletal and supported metal catalysts have been used in different laboratories [1-4]. The application of the above organometallic compounds is based on surface reaction between hydrogen adsorbed on different supported metals and tin (or lead) tetraalkyls. In case of supported platinum and tin tetraalkyls the following surface reactions take place:

$$PtH_a + SnR_4 \longrightarrow \underset{PSC\ I}{Pt\text{-}SnR_{(4-x)}} + x \cdot RH \tag{1}$$

$$Pt\text{-}SnR(4\text{-}x) + (4\text{-}x)/2\ H2 \longrightarrow Pt\text{-}Sn + (4\text{-}x)\ RH \tag{2}$$

Under properly chosen conditions reactions (1) and (2) are very selective, i.e. only saturated hydrocarbons were formed. The drawback of this approach is that it is difficult to obtain catalysts with high Sn/Pt or Sn/M ratio (M = Ni, Pd, Ru, Rh). This is due to the fact that the amount of tin anchored in the form of Primary Surface Complex (PSC I) is strongly controlled both by the size (methyl, ethyl, etc.) and the number of alkyl groups left in PSC I. As emerges from experimental data over supported Pt (with dispersion=0.5-0.8) the formation of -SnR_3 and -SnR_2 surface species was evidenced. Both experimental data and results obtained by computer modeling indicates that in case of tin tetraethyl the surface coverage of -SnR_3 is in the range of 0.3 - 0.4. This value can be increased to 0.5 - 0.6 if tin tetramethyl is used.

We have observed that in the presence of adsorbed oxygen or CS_2, in addition to the formation of PSC I (with x=1 or 2) anchored SnR_4 species are also formed. In this case the adsorbed oxygen or carbon disulfide is involved in the tin anchoring process resulting in a second layer of anchored organometallic species in the form of SnR_4. The proposed forms of anchored tin organic species are shown in Figure 1.

It has also been demonstrated that other metals, such as Ni, Pd, Ru and Rh have similar behaviour as Pt. Upon using oxygen and CS_2 during the tin anchoring process (surface reaction (1)) catalysts with high Sn/M ratio (M = Ni, Pd, Ru, Rh) were obtained.

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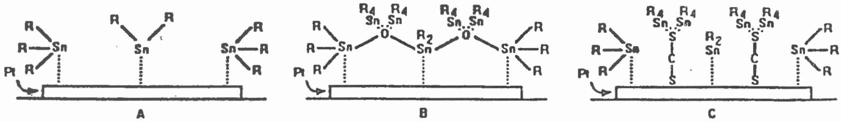

Figure 1. Different surface organometallic species anchored onto supported platinum. a) in the absence of coadsorbants; b) in the presence of adsorbed oxygen; c) in the presence of CS_2.

The Sn-Pt bimetallic catalysts were used in different selective hydrogenation reactions. For instance, Sn-Pt/SiO_2 catalysts were tested in the hydrogenation of crotyl aldehyde into crotyl alcohol. These results are shown in Table.1. Upon introduction of tin into platinum the selectivity to the formation of crotyl aldehyde increased, however high selectivity values were only obtained in the presence of catalysts with high Sn/Pt ratio.

Table 1. Hydrogenation of crotyl aldehyde over different Sn-Pt catalysts

Catalyst	Sn/Pt_{surf} (at/at)	reaction rate * mol/(g x s) 10^{-5}	Selectivity, % **		
			Butyl-aldehyde	Butyl-alcohol	Crotyl-alcohol
Pt/SiO_2	-	7.50	88	12	0
Pt-Sn/SiO_2	0.56	24.50	53	11	36
Pt-Sn/SiO_2	1.60	16.50	35	9	56
Pt-Sn/SiO_2	2.93	6.20	22	2	76

Preactivation temperature: 583 K, Reaction temperature: 353 K, $P_{substrate}$ = 10 torr.
* initial rate at zero conversion, ** obtained at 15 % conversion

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SURFACE ROUGHNESS DRIVEN BY STRONG ADSORPTION: FRACTAL APPROACH

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Academician G.K.Boreskov was one of the first scientists who clearly formulated that a catalyst is not "a dead substance" but may change its structure and composition during catalytic reaction due to action of reagents and products. Recently the geometrical roughening of a surface driven by strong mono- and bimolecular adsorption was studied by Monte Carlo modeling [1,2]. Here we use a fractal and autocorrelation function approaches to answer a question, whether the generated surface is self-similar or not, or, in the other words, is it possible to use the advantages of the fractal approach for quantitative description of the rough surface.

According to [1,2] the mutual action of adsorption and surface rearrangement processes may lead to a significant growth of surface roughness induced by adsorption. Commonly, the proper measure of surface irregularity is an autocorrelation function

$$G(r) = \langle h(x) - h(x+r) \rangle^2,$$

where h(x) is a height of an atom at x position over a zero plane, and the corner brackets imply the averaging over the whole surface. Both theoretical and computer modeling of a *thermally disordered* surface have shown that the generated surface is not self-similar and predicted the appropriate autocorrelation function in the form

$$G(r) = A \cdot \ln(r) + B, \qquad (1)$$

where A and B are constants [3]. Starting from this finding we, first, checked if this function also describes the surface roughness caused by strong adsorption as simulated in [1,2], and, then, performed similar analysis with the autocorrelation function

$$G(r) = A \cdot \left({r^\alpha}\Big/{t^\beta} \right). \qquad (2)$$

The function was suggested for a fractally rough surface which is grown far from its equilibrium state [4]. Here t is the time coming from the beginning of the growing process, A, α, β are constants which may be connected with the surface fractal dimension.

The Monte-Carlo computer simulation of the surface evolution in the presence of adsorbate molecules was based on the Metropolis algorithm and was carried out making use of solid on solid (SOS) surface model on a square lattice of 64*64 size. The equivalent metal-metal interaction energy was considered to be 800 K (in temperature units), whereas the energy of the metal-adsorbate interaction was varied from 0 to 800 K. The calculations were carried out at temperature 800 K and different adsorbate coverage (0, 24, 50%). All additional simulation details may be found elsewhere [2].

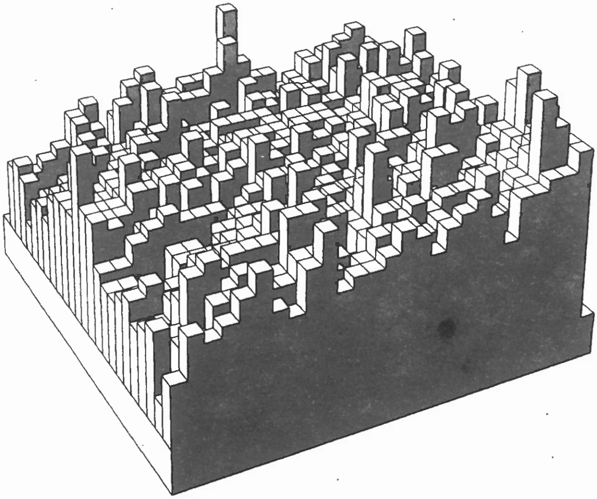

Figure 1

The 24*24 fragment of the equilibrium surface at 50% adsorbate coverage (fig.1) shows a significant surface roughening. The surface autocorrelation function was found to follow well both relations (1) and (2). The first formula describes better a short-range correlation (the low r region), although at $r \geq 2$ both equations give nearly the same accuracy. This trend keeps up for the adsorbate covered surfaces as well as for clear one. As modern experimental methods of surface roughness study make use of the long-correlation tail of the autocorrelation function, a conclusion may be drawn that within the experimental errors it looks impossible to distinguish whether the surface roughness generated by the adsorbate-substrate interaction has a structure predicted by eq.(1) or a fractal one. It is likely to mean that for formal description of such a rough surface the mathematical tools of the fractal geometry may be used.

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PPI-54

Surface Complexes of Acetone with Brönsted and Lewis Sites

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Introduction: Numerous studies[1-3] have been devoted to the adsorption-transformation of acetone (AC) by acid zeolites at ambient temperature. Since the transformation of AC by strong acids in the liquid phase was well documented,[4] the role of Brönsted acid sites has been particularly emphasized.[1] However, the role of Lewis sites deserves some attention, since it is difficult to prepare an acid zeolite without having some dealumination. Lewis sites are present on non-framework alumina within the zeolite microcrystals.[5,6] Thus, the conjugated effect of the two kinds of acid sites can not be neglected. In order to gain information on this possibility, the adsorption of AC on a transition alumina and on NH_4-ZSM5, deammoniated at the lowest possible temperature, has been followed by FTIR. The transformation on the surface was also followed by IR and the nature of the product established by mass analysis of the gas phase in equilibrium with the adsorbed phase.

Experimental: The preparation of a nanosized alumina very rich in coordination defects has been described earlier.[7] Before use, it was calcined in vacuum for 10 h and in the presence of O_2 for 1 h at 600°C in the infrared cell. Two types of Lewis sites with aluminum in distorted tetrahedral and pentahedral coordination exist on this alumina.[8] The total number of Lewis sites was about 0.4 meq/g, the surface area was about 300 m^2/g. HZSM-5 (Si/framework Al=18) was calcined at 500°C in a residual pressure of $\sim 10^5$ torr for 5 h and cleaned from organic

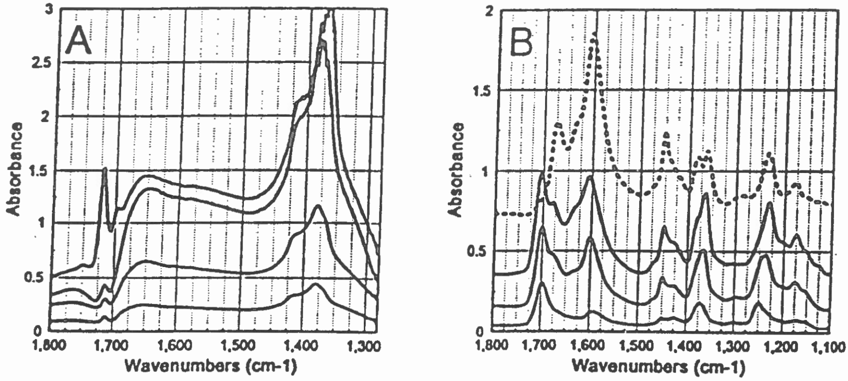

Figure 1: A. Infrared spectra of AC adsorbed of HZMS-5 containing ~0.8 meq Brönsted sites[6] per gram and no Lewis sites. From bottom to top, increasing doses of AC: 0.19; 0.56; 1.82 and 2.61 mmol/g. B) Infrared spectra observed after the following additions of acetone to an alumina containing ~0.4 meq Lewis sites[6] per gram. From bottom to top, 0.4; 1.9; 3.9 mmol/g. Top spectrum: mesityl oxide on the same alumina: 1 mmol/g.

residue by calcination in 50 torr O_2 for 1 h. It contains ~0.83 meq Brönsted sites per g and no Lewis sites.

AC, 99.9% +; mesityl oxide (MO), 99%; and diacetone alcohol (DA), 99%, were dried over 4 A molecular sieves and purified by repeated freezing and thawing.

Results and Discussion: The results to be described are summarized in Figure 1A showing the IR spectra recorded in a wafer of HZSM-5 exposed at room temperature (RT) to increasing doses of acetone. In Figure 1B the solid was the nanosized alumina.[7] On the HZSM-5, the main spectroscopic feature when the AC coverage is less than 1 molecule per Brönsted site is a broad band centered at 1649 cm^{-1} which can be assigned, in agreement with Kubelkova *et al.*, to hydrogen-bonded AC.

Haw *et al.*[2] have shown by ^{13}C NMR that an adsorption complex 1 mole AC/1 mole Brönsted is formed at RT on HZSM-5. The shift is in agreement with the IR data[1,3] and with Figure 1A. At higher loading a band of "free" CO is observed at ~1720 cm^{-1} (physically adsorbed AC). At this loading a slow evolution is observed with the formation of mesityl oxide (band of 1452 cm^{-1}) which probably gets protonated (band at 1554 cm^{-1}) and water (broad band at 1618 cm^{-1}). These bands are observable after 2 h and well pronounced after 12 h.

On alumina, AC interacts with Lewis sites but it transforms immediately into mesityl oxide (see Figure 1B) and water, irrespective of the coverage.

The activation of the carbonyl group and the reactivity towards a second acetone molecule is, therefore, very different on Brönsted and Lewis sites. The origin of this difference is discussed.

As expected from the above observation, the adsorption of AC on dealuminated mordenite combines the features attributable to Bönsted and Lewis sites, a fact which seems to have been overlooked. Hence, the transformation of acetone, at RT, is more rapid on zeolites with nonframework aluminum.

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INFLUENCE OF PLATINUM CLUSTER STRUCTURE ON HYDROGEN ACTIVATION IN BENZENE HYDROGENATION

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The increase of platinum catalysts efficiency becomes more and more actual problem in the petroleum refining industry. Fast development of the organometallic compound chemistry makes it possible to improve the methods of synthesis of the effective catalysts by attaching them to the oxide support surface and producing of high dispersed heterogenized systems. The benzene hydrogenation is usually used as a model reaction allowing to define the influence of electronic state, structure and dispersity of active metal on the reforming process.

The catalysts supported on γ-Al_2O_3 from allyl platinum complexes solutions in benzene or methylene chloride as well as from aqueous solutions of H_2PtCl_6 with additions of organic ligands were investigated in the gas phase benzene hydrogenation in a stationary flow reactor at atmospheric pressure.

It was shown that the use of organometallic complexes for synthesis of the catalysts followed by their reductive treatment made it possible to increase the extent of benzene conversion by 2-3 times compared to traditional 0,3% Pt/Al_2O_3. In the products of the reaction only cyclohexane was found. On increasing the experiment temperature above 473K the activity of the catalysts dropped due to sintering of the platinum particles. The catalysts from the organometallic complexes showed low ability for reactivation because of surface carbonization with destroyed residues of the organic ligands.

More thermostable and no less active catalysts were produced as a result of addition of the polar organic ligands to impregnating aqueous solutions of H_2PtCl_6. The properties of these catalysts didn't change after calcination at 673K.

By the electron microscopy method it was established that the active phase of the catalysts prepared from the solutions of H_2PtCl_6 with the additions of the polar organic ligands consisted of high dispersed particles (15-20Å) with largely uniform size distribution (>60%).

The comparison of our X-ray diffraction results with the known data shows that these particles on the support surface have no metal structure and represent the clusters consisting of repeatedly coupled tetrahedrons. Owing to acid nature of the support they carry a positive charge. It may be assumed that their surface structure is largely defective and has high free energy.

Quantum chemical investigation of hydrogen activation on the clusters containing 1-4 Pt atoms was carried out by EH method modified by taking into account the core-core interaction in Anderson's approximation. The atomic hydrogen is weakly bonded to Pt surface and is highly mobile with a minimum migration activation energy 1,6 kJ/mol. The H_2 adsorption with coordination over Pt atom (atop), over Pt-Pt bond (bridge) and perpendicular to this bond (μ-bridge) leads to dissociation of the adsorbate molecule with activation energies of 50.6, 120.7 and 44.6 kJ/mol respectively. The last form is the most stable. Depending on the surface structure these values change and on Pt (III) surface the minimum activation energy corresponds to μ-bridge structure. We haven't found any effect of the surface positive charge on the state and activation of hydrogen. Probably, due to a bend on the small clusters the change of the surface structure facilitates the dissociative chemisorption of hydrogen by means of the formation of the adsorbed molecular complex. The defects of surface can show the same influence.

Thus, an increase in the activity of high dispersed platinum catalysts observed in the reaction of the gas phase benzene hydrogenation may be related to the specific effect of the cluster surface defects. The benzene molecule activation will be considered by the quantum chemical method for more complete determination of the process mechanism.

The obtained experimental results point to perspective use of impregnation solutions with the organic ligand addition for synthesis of reforming process catalysts which would possess the properties of increased activity and thermostability.

TRANSIENT KINETIC STUDIES OF NO REDUCTION BY CH_4

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Abstract

In heterogeneous catalysis, the knowledge of the kinetics of chemical reactions, i.e., of the way in which the rates of reactions depend upon process conditions, forms the basis for the design and optimisation of both catalysts and chemical reactors. Within the frame of a study confined to the steady-state kinetics, only lumped kinetic parameters can be estimated from a regression of steady-state kinetic data.

By generating transients input signals, such as step functions in the gas concentration, one observes signals out of the steady-state (transient decrease of the product yield, thermodesorption), the relaxation of which may be related to the time scale on which the corresponding global reaction occurs at the steady-state. One unique way to get these time constants pertaining to steady-state conditions is to generate isotopic step functions, which let the overall surface occupancy unperturbed and therefore give access to true time constants of the reactive intermediates and to their concentration. This technique is referred to a steady-state isotopic transient kinetic analysis (SSITKA). It can be coupled to an *in situ* spectroscopic investigation such as DRIFT spectroscopy.

Another way to generate transient kinetics was recently developed by means of the temporal analysis of product (TAP) reactor which consists in pulsing small and known amounts of reactants through a catalyst bed maintained under vacuum and analysing the pulse expansion and relaxation at the reactor exit with a time resolution below the millisecond.

This paper presents isotopic and non isotopic transient kinetic data obtained for the reaction of NO reduction by CH_4 over Co/ZSM-5 catalyst, carried out either in the presence or in the absence of oxygen. The main catalytic steps and the coverage of the most significant reacting intermediates are investigated, in view of a better understanding of the overall reaction mechanism.

PPI-56

TPD-STUDY OF NH_3 ADSORPTION/DESORPTION PROCESS ON THE SURFACE OF COMMERCIAL V/Ti, V/Al, Pd/V/Al CATALYSTS

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Introduction

An effective option for control of NO emission from stationary sources is the use of selective catalytic reduction of NO_x by ammonia on V/Ti, V/Al based catalyst. A large number of studies focus on various aspects of these reactions, but there is still no agreement of opinion on the nature of active sites and the mechanism of SCR over this catalyst. It is generally believed that the catalytic reaction involves the adsorption of ammonia on Lewis and Brønsted acid sites. In the present study NH_3 adsorption/desorption process on the surface of commercial V/Ti, V/Al, Pd/V/Al based catalyst samples has been investigated by using temperature-programmed desorption (TPD).

Results

The main characteristics of the commercial catalyst samples investigated are following:

Table

Catalyst	S.S.A.(m^2/g)	Nominal content(wt, %)				
		V_2O_5	WO_3	Pd	Ti	Al
$10V/Al_2O_3$	86.5	10	-	-	-	
$Pd/V/Al_2O_3$	66.6	7	-	0.1	-	
$6V/W/TiO_2$	33	6.4	9.2	-	39.6	
$2V/W/TiO_2$	35	2.2	8.4	-	23.1	0.224

Ammonia is adsorbed on 1 g of samples for 1 h at 25, 100, 300, 350, 400 ^{0}C from 1%vol. NH_3/air gas mixture at a flow 40 ml/min. TPD spectrum from all catalysts indicate the presence of sites which adsorb ammonia with different strength. The deconvolution of the curves suggests that they are constituted by overlap of three peaks. The low-temperature peak (90-270 ^{0}C) characterizes the desorption states with activation energies of 8-10 kcal/mol, medium - temperature peak (325-520 ^{0}C) can be described with activation energies of 17 -24 kcal/mol, high - temperature (540-720^{0}C) one corresponds with the states with activation energies of 26 -29 kcal/mol. Ammonia is held most strongly on the 2V/W/TiO_2, followed by 6V/W/TiO_2, and it is bonded most weakly on the 10V/Al_2O_3 and Pd/V/Al_2O_3 catalysts. A drop in the activation energies is observed as ammonia coverage increases, but they are practically unaffected by the adsorption temperatures. Fractional amounts of ammonia adsorption sites depend on temperature of ammonia adsorption T_{ad}. For all samples at T_{ad} = 25-100 ^{0}C low-temperature sites concentration is rather small as compared to medium and high-temperature states and growing with temperature, correlating with the NO reduction activity. With T_{ad} increased up to 200-400 ^{0}C fractional surface coverage of medium and high-temperature sites reduces from 40-75% and 20-40% respectively to 10-20% (for 10V/Al_2O_3 and Pd/V/Al_2O_3) and 3-20 % (2V/W/TiO_2 and 6V/W/TiO_2).

At ammonia desorption from strongly bonded sites corresponding to second and third peaks is accompanied by partially NH_3 decomposition to nitrogen and nitrous gases. Nitrogen formation depends on T_{ad} and increase significantly at T_{ad}=300-400 ^{0}C, declining in a row 2V/W/TiO_2, 6V/W/TiO_2, Pd/V/Al_2O_3, 10V/Al_2O_3 . Obviously, the medium and high-temperature states are responsible for ammonia decomposition. The most strongly adsorbed states of ammonia (with activation energies for desorption of 22-29 kcal/mol) undergo the dehydration to atomic nitrogen, which may recombine to molecular nitrogen or interact with vanadium, titanium and aluminum, producing surface nitrides. These nitrides may be destroyed with formation of N_2 by keeping of the samples at 800^{0}C. Time of NH_3 desorption in third peak for 10V/Al_2O_3 and Pd/V/Al_2O_3 is higher than that for 2V/W/TiO_2 and 6V/W/TiO_2 samples.

A general conclusion of this work will be that all adsorbed states of ammonia on V-containing catalytic systems coexist in dynamic equilibrium and may transform from one to another.

PPI-57

EXAFS study of $TiCl_4$ complexes on $MgCl_2$ surface

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EXAFS has been used to study supported catalyst $TiCl_4/MgCl_2$ for ethylene polymerization containing 1.8 wt.% of Ti, which was obtained by supporting of $TiCl_4$ on highly dispersed $MgCl_2$ [1] in heptane at 98° C. Titanium environment was studied by EXAFS at the Ti K-edge. To analyze experimental data, we used the curve fitting procedure with software EXCURVE-92.

The experimental EXAFS spectrum was found to have four maxima. To find the elements distribution in the coordination spheres of Ti we considered several monomer and dimer complexes of $TiCl_4$ on (100) and (110) $MgCl_2$ faces [2]. The elements distribution in the coordination spheres of Ti has mainly the following order: Cl, Cl, Mg, Cl. The correction of EXAFS distances regarding the above order of elements distribution produces the following set of experimental distances: 2.1, 3.0, 3.5, 4.0 Å.

This set of distances correspond to that for the $TiCl_4$ monomer complex on (100) face of $MgCl_2$. However, the $TiCl_4$ monomer complex disagrees with a high experimental intensity of peak for the fourth coordination sphere at a distance of ~4Å. In contrast to monomer complexes, the $TiCl_4$ dimer complex on (100) $MgCl_2$ face contains distance Ti-Ti, which can increase the peaks intensities within distances 3.5-4.0 Å. In this case correlation was much better.

So, the analysis of experimental EXAFS spectrum shows that in studied catalyst $TiCl_4$ predominantly exists on the $MgCl_2$ (100) face as dimer complexes. Chlorine atoms of the first coordination sphere are replaced from Ti at a distance of 2.1 Å. Distance Ti-Ti is 3.95 Å. The distances between Ti and chlorine atoms of $MgCl_2$ lattice equal 3.0 and 3.9 Å. The $TiCl_4$ dimer complex is a "bridge" structure with two non-equivalent "bridging" chlorine atoms. Most likely, in dimer $TiCl_4$ complex an asymmetric bridge occurs: Cl is bonded to one Ti (Ti-Cl=2.1Å) and, at the same time, form a weak coordination bond with the second Ti (Ti-Cl ≥2.8Å).

Being reduced by co-catalysts, dimer complexes produce stereospecific active centers [2]. At the same time, catalyst $TiCl_4/MgCl_2$ (without internal and external electron donors) has a low stereospecificity in propylene polymerization. Perhaps, a part of $TiCl_4$ can be adsorbed on the $MgCl_2$ (110) face (forming the precursors of non-stereospecific active centers) and does not appear in the EXAFS spectrum due to the relatively low accuracy of the method (up to 20% regarding the identified element). This value far exceeds the content of active centers in the Ti-Mg catalyst (several percent of Ti content in the catalyst [3]).

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PPI-58

Interactive „antisense“-oligonucleotides with multiple substrate turnover

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Therapeutic „antisense oligonucleotides“ should be designed in such a way, that they exhibit high efficiency at low dose. An approach to this goal is the preparation of oligonucleotide conjugates, which (a) interact irreversibly with their nucleic acid target, e.g. through intrachain cleavage; (b) perform this cleavage with multiple turnover of their substrate. Conjugate groups that have been explored as „mRNA cleaver“-substituents include hydrophilic porphines[1], bleomycin[2], or a recently discovered peptide sequence with RNase-like activity.

Studies on oligonucleotide conjugates with hydrophilic porphyrines have demonstrated that the „photodynamic“ cytotoxic effect exhibited by e.g. tetracarboxy-porphine, can be achieved at 20fold lower concentration, if the oligonucleotide sequence, covalently linked to the porphyrine group, directs the conjugate to its target.

It was shown that bleomycin-oligonucleotide conjugates can form duplexes and ternary complexes and site-specifically cleave ss and ds DNA targets respectively. It was demonstrated that the bleomycin covalently bound to the oligonucleotide preserves its ability to degrade the ss DNA target in catalytic manner. Catalytic and site-specific activity of oligonucleotide bleomycin conjugate was realized both in repeated cleavage of single DNA target molecule and several DNA target molecules by one molecule of the reagent from duplexes. Catalytic activity of bleomycin-oligonucleotide conjugates has been shown to be the highest in the temperature range close to the melting temperature of the reagent-target complex, i.e., under conditions where the oligonucleotide reagent can form complementary complexes and easily dissociate to contact with next molecule of the target. For the first time it was registered that the catalytic and site specific cleavage of DNA target may be carried out by bleomycin derivatives of short (tetramer) oligonucleotides in the presence of effectors (diphenazinium derivatives of oligonucleotides), which are capable to stabilize duplex formed by short oligonucleotide and target.

In this work we synthesized and studied a number of conjugates of oligodeoxyribonucleotides and peptides with alternating hydrophobic (Leu) and base (Arg) aminoacid residues. The synthesis of peptidyloligonucleotides was performed by the reaction between oligonucleotides and peptides in the presence of triphenylphosphine, 2,2-dipyridyldisulfide and nucleophilic catalyst 1-methylimidazole. The hybridisation properties of peptidyloligonucleotides obtained were investigated to estimate melting points of their duplexes with complementary oligodeoxyribonucleotide. The slight increase (1-5°C) in T_m of complementary complexes was found to depend on the length of peptide residues.

The comparative study of peptidyloligonucleotide ability to cleave oligoribonucleotides was performed. It was shown that the interaction of the RNA-target and conjugates yields site specific cleavages of phosphodiester bonds of ribooligonucleotide and reaches to 80% for n=4 (48 h, 20°C, pH 7.5).

Thus, it was demonstrated that peptidyloligonucleotides bearing alternating hydrophobic (Leu) and base (Arg) aminoacid residues are promising to catalyse the hydrolysis of phosphodiester bonds of RNA and to act as a specific artificial ribonuclease.

THE KINETICS OF METAL PHASE SINTERING IN HETEROGENEOUS CATALYSTS

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Every time researcher developing the new catalytic systems is forced to decide the threefold task: creation of active, selective and, at last, stable catalyst.

In this work we will discuss the process of sintering of the metal containing catalysts. When we say "sintering" we mean the change of active surface of catalysts observing at high temperature.

The detailed analysis of the kinetic models appropriate to various mechanisms of sintering of metal on support developed in [1]. These authors have offered the common kinetics equation for many different mechanisms of sintering of metal catalysts:

$$S(t)^{-n} = S(0)^{-n} + k't \qquad (1)$$

where S(t) and S(0) - specific surface of metal at time (t) and at the initial moment accordingly; n - parameter that can vary from 2 to 7 for various mechanisms of process; k' - constant of the sintering rate.

The equation (1) is inconvenient for the practical use due to the necessity to know three constants (S(0), n and k') for description of metal phase sintering. This equation could be simplified. At first we can pass from specific surface of metal to its dispersity. After simple transformation we get:

$$\ln(D(t)) = \ln(D(0)) - kt \qquad (2)$$

or in exponential form:

$$D(t) = D(0)\exp(-kt) \qquad (3)$$

where D(t) and D(0) are values of dispersity of metal at time (t) and at the initial moment accordingly; k - is the magnitude proportional to (k') and depends on the constant (n) of equation (1):

$$k = [k'(Z\,D(0))^{n}]/n$$

So, the experimental values of the constant k can be determined simply. Some of the results for the metals sintering in hydrogen atmosphere are presented in table 1.

Table 1.

The constants of metal containing for catalysts sintering.

Catalyst	T(K)	k (1/h)	Ref
Ni/Al_2O_3	923	0.001	[2]
Ni/Al_2O_3	973	0.002	[2]
Ni/Al_2O_3	1023	0.005	[2]
Ni/SiO_2	923	0.006	[2]
Ni/SiO_2	973	0.010	[2]
Ni/SiO_2	1023	0.017	[2]
Pd/TiO_2	623	0.019	[3]
Pd/TiO_2	773	0.032	[4]
Pt/C	673	0.016	[5]
Pt/C	673	0.005	[5]
Pt/C	673	0.002	[5]
Pt/C	773	0.030	[5]
Pt/C	773	0.040	[5]
Pt/C	773	0.061	[5]
Pt/C	773	0.007	[6]
Rh/SiO_2	773	0.088	[7]

Value k expresses the relative change of dispersity per unit of time. As shown in the Table 1, k rarely exceeds 0.06. Thus, in hydrogen atmosphere, degree of metal dispersion changes on 1-6 % per hour.

The most useful consequence of this investigation is the possibility to describe a sintering process qualitatively. And then it is possible to interpolate experimental data in any time interval.

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HIGH-EFFECTIVE CATALYSTS ON THE BASIS OF TRANSITION-METALS PHTHALOCYANINE COMPLEXES AND CALCIUM ALUMINATES

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The transition-metals phthalocyanine complexes are one of the most interesting and perspective types of the catalysts, because the structure of these compounds is similar to the structure of the natural ferments.

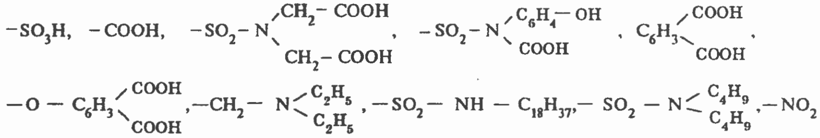
These complexes are widely used in the process of refining of petroleum distillates from mercaptans. This process is typically designed to effect the oxidation of offensive mercaptans with the formation of innocuous disulfides. In the traditional types of this process the transformation of mercaptans is carried out in the presence of aqueous caustic solution, which converts RSH into reactive anionic form. Howerever, the utilization of aqueous caustic solution complicates the technology of processes, it leads to the formation of toxic sulpherous-alkaline flows. One of the perspective directions, which allows to perfect this process, is found at the use of bifunctional catalysts. These catalysts have the active centres, which turn RSH into RS^-.

In this study the facts of creation and investigation of new bifunctional catalysts have been adduced. These catalysts are compositions, which comprise the transition-metal phthalocyanine complex and calcium aluminate. These catalysts have get the adsorption of the phthalocyanine complexes from aqueous caustic solution or organic solvents on the surface of calcium aluminates.

The catalysts were tested on the model mixtures of n- and tret- dodecylmercaptans in octane.

In this study a large number of cobalt and iron phthalocyanine complexes with various electronic-attracting and electronic-releasing groups in macrocycling ligand, such as

PPI-60



$$-SO_3H,\ -COOH,\ -SO_2-N\begin{array}{l}\diagup CH_2-COOH\\ \diagdown CH_2-COOH\end{array},\ -SO_2-N\begin{array}{l}\diagup C_6H_4-OH\\ \diagdown COOH\end{array},\ C_6H_3\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array},$$

$$-O-C_6H_3\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array},-CH_2-N\begin{array}{l}\diagup C_2H_5\\ \diagdown C_2H_5\end{array},-SO_2-NH-C_{18}H_{37},-SO_2-N\begin{array}{l}\diagup C_4H_9\\ \diagdown C_4H_9\end{array},-NO_2$$

and calcium aluminates with the different specific surface (from 4,4 to 228 m^2/g) were used.

We studied the influence of the phthalocyanine complex structure and physicochemical properties of carrier on the catalytic activity.

The investigation of dependence of the catalytic activity on the nature of central metal ion of complex showed, that not only electronic effect influences at the activity, but the factor connected with the degree of association of complex on the carrier surface. The investigation of dependence of the catalytic activity on the nature of groups in macrocycling ligand show, that three factor influence upon the activity: electronic and steric effects, and factor, connected with the degree of association of complex at the carrier surface.

On the most active catalysts we studied the structure of adsorptive layer of phthalocyanine complex at the calcium aluminate surface in detail. It was determined, that the adsorptive layer of complex contains the monomeric and assocuated forms It was showed, that the formation of associates goes according to the mechanism of unlimited two-contact association, which is accompanied by the weakening of intermolecular contacts with the increasing of associates. It was determined that the amount of monomeric form in the adsorptive layer structure of phthalocyanine complex grows with the increasing spesific surface of the calcium aluminate.

TRANSIENT ISOTOPIC KINETICS TO STUDY OF HETEROGENEOUS CATALYSIS

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The isotope methods can provide comprehensive information about the pathways of reagents transformation to reaction products [1, 2]. Transient isotope kinetics studies seem to be the most informative with regard to reaction mechanism. These methods allow to estimate the kinetic parameters of stages and life-times of key intermediates [3]. The main idea is that in reaction steady state the isotope composition of one of the input reagents changes step-wise. If there are no kinetic isotope effects, the concentration composition in the gas phase and on the surface remains unchanged. Meanwhile the rate of isotope exchange in the reaction products, and thus the character of response curves, is determined by the isotope label transfer and steady state reaction rates.

In the present paper we consider how to use the above techniques to elucidate the reaction mechanism. Proposed unified approach to model the isotope and chemical kinetics allows to use the obtained results in going from one study to another. We also consider a possibility of mechanism discrimination and reliability of parameters determined accounting for experimental errors in catalytic reactors used in practice.

It was shown using the simplest scheme of catalytic reaction that independently of expressions for the stage rates, the shape of isotope curves remains the same. After isotope lable introduction into the feed gas the isotope composition of the surface species and reaction products changes monotonously. The dynamics of labelled species Θ_i^* is determined by the rate of chemical stages $r_i^* = k_i \Theta_i^* f(\overline{C}, \overline{\Theta})$. In steady state $f(\overline{C}, \overline{\Theta})$=const, and the rate of isotope substitution is expressed as $r_i^* = K_i \Theta_i^*$. The isotope-dynamic model is the analog of linearized kinetic equations. General solution can be represented as:

$$C_i^*(t) = \sum_{k=1}^{N} A_k e^{\lambda_k t} + C_i^o,$$

where C_i^* is the concentration of labelled component in the gas phase; λ_k are the eigenvalues of the corresponding Jacobian matrix of the isotope-dynamic equations set, λ_k depend on K_i only; A_k are some constants depending on K_i, $\overline{C}$, $\overline{\Theta}$. The solution for $C_i(t)$, expressed as a sum of exponents, simplifies substantially the further data processing.

By analyzing (qualitalively) the character of transient isotopic curves the preliminary mechanism of label transfer can be proposed. Numerical modeling allows to estimate a number and concentration of surface species involved in the isotope exchange, as well as K_i. The set of K_i at different C_i, θ_i is implicit function $k_i f(\overline{C},\overline{\Theta})$. Then, we may try to decode these functions to find their explicit form and estimate the constant of reaction stages.

To perform the isotope data processing we should take into account the experimental features of used reactors. It has been shown that the shape of transient isotope curves in CSTR reactors is changed drastically depending on reaction conditions. To obtain correct results definite requirements to transient isotope kinetics studies are elaborated. In this regard the plug-flow reactor is preferential. However, in this case we face with difficulties related to solving of hyperbolic differential equations. Approximate solutions of such equations are proposed, the accuracy of used mathematical methods being estimated.

This approach was applied to ethylene epoxidation over silver catalyst [4]. Basing on the transient isotope data oxygen pathways towards ethylene epoxidation and its deep oxidation were found out. Unexpectedly, the concentration of oxygen species involved in both reactions was extremely low (around 1% of monolayer). Meanwhile, the catalyst contains a very high amount of inactive oxygen (more than a monolayer). Moreover, it has been proved that the both reactions proceed extremely fast. According to our estimation the characteristic time of epoxidation acts does not exceed 10^{-6} sec.

Acknowledgement

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PPI-62

SYNTHESIS OF HIGHLY-EFFICIENT MEDICINE "SULPYRID": DESIGN OF CATALYTIC STEPS

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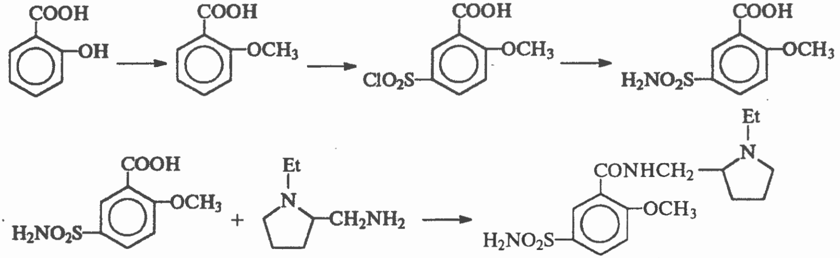
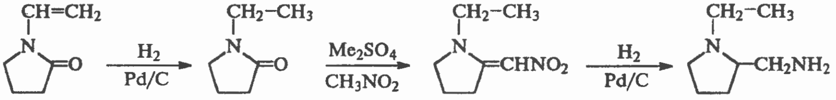
Modern medicines, as usual, are complex organic molecules that can be produced via multi-steps synthesis. The scheme of such process may be significantly simplified by using the combination of synthetic and the catalytic steps. In the present work this approach has been taken for preparation of medicine "Sulpyride", which is applied in the treatment of nervous disorders caused by drugs and alcohol as well as of stomachial diseases [1].

We have proposed the "Sulpyride" synthesis scheme where EAMP is the key product:



(EAMP) (Sulpyride)

EAMP preparation scheme includes two catalytic steps: 1)VP hydrogenation to form EP; 2)ENMP hydrogenation to form EAMP.



(VP) (EP) (ENMP) (EAMP)

The aim of the present work is to study the catalytic steps of the "Sulpyride" preparation process.

EP synthesis. The carbon-carbon double bond is very easily reduced over all the platinum metals. However, under hydrogenation reaction conditions a side polymerization process favored by polarization of C=C group in VP molecule occurs. This side process results in decrease EP yield as well as the catalyst deactivation due to polyvinylpyrrolidinon adsorption on the catalyst surface.

The special features of VP polymerization under hydrogenation reaction conditions were studied. VP oligomers formation was observed even at room temperature and the polymerization rate increased sharply above 70°C.

The effect of temperature, hydrogen pressure, catalyst concentration, process duration and VP purification method on hydrogenation rate, EP formation selectivity and the shape of hydrogen uptake curve were studied. It has been found that hydrogenation rate is of the zero order in respect to VP concentration and the first order in respect to hydrogen pressure as well as to catalyst concentration. It has been shown that freshly distilled VP hydrogenation over the Pd/C catalyst at 15-70°C and hydrogen pressure 1-10 atm gives EP with the yield more than 80%.

EAMP synthesis. Aliphatic nitro compounds can be hydrogenated over the platinum metals. However, ENMP hydrogenation is complicated by a side reaction occurring due to the high lability of ENMP molecule.

It was shown by NMR ^1H, ^{13}C; IR and GLC methods, that the ENMP hydrogenation products consist of EAMP, 1-ethylpyrrolidinon and methylamine. The scheme of two routes of ENMP conversion has been proposed: a) ENMP hydrolysis with the formation of 1-ethylpyrrolidinon and nitromethane, which can be catalytically reduced to methylamine, b) ENMP hydrogenation with EAMP and H_2O formation.

The kinetic peculiarities of ENMP hydrolysis were studied. It has been found that the hydrolysis of ENMP is an acid-base process, where the strong base EAMP (product of ENMP hydrogenation) can act as a catalyst. The observed reaction rate of ENMP hydrolysis is of the first order with respect to [ENMP] and of second order with respect to $[OH^-]$. The mechanism and the equation of ENMP hydrolysis have been proposed.

The peculiarities of ENMP hydrogenation were studied. The influence of used solvent on the hydrogenation rate and selectivity of EAMP formation has been studied. It has been found that the high selectivity and low hydrogenation rate are observed when the process is carried out in non aqueous and aprotonic solvents. The maximum hydrogenation rate, and yet minimum selectivity are achieved in an aqueous solution. The effect of hydrogen pressure, catalyst concentration and reaction temperature on the selectivity and rate of EAMP formation has been studied. The kinetic equation of ENMP hydrogenation has been proposed.

The comparative analysis of the kinetic principles relating to the conversion of ENMP by hydrogenation and hydrolysis routes has been performed, and the parameters determining the selectivity of ENMP hydrogenation have been established. It has been found that the decrease of $[OH^-]$ and [ENMP] and the increase of catalyst content and hydrogen pressure result in the growth of ENMP hydrogenation selectivity. Method of ENMP hydrogenation in CO_2 presence was proposed. Role of CO_2 in selective ENMP hydrogenation was studied by NMR, IR and pH methods. It was shown that CO_2 interacts with EAMP producing intra molecule carbamic acid salt and, thus, during the conversion of ENMP to EAMP a nearly neutral pH is created. The process of this salt formation is reversible and EAMP can be recovered by CO_2 pumping away.

CONCLUSIONS

The kinetic peculiarities of VP conversion by the main route (hydrogenation on catalyst Pd/C) as well as by the side route (polymerization) have been studied. The method of high-purity EP (98%) preparation has been worked out.

The complex process of ENMP conversion including the routes of hydrogenation over Pd/C catalyst and hydrolysis (acid-base catalysis) has been studied. The new method of selective ENMP hydrogenation has been developed to prepare the high-purity EAMP (98.5-99.0%) for medicines synthesis.

According to design scheme the synthesis of "Sulpyride" sample suiting to the pharmaceutical standard requirements has been performed.

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Sulfur resistance of supported Pt-Pd bimetallic catalysts: An XPS and H_2-TPD study

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INTRODUCTION

Metal alloy catalysts are of great importance in chemical technologies due to their performances with respect to monometallic systems. Despite supported Pt-Pd systems have been studied for rather long time [1,2], no data on sulfur resistance of this bimetallic were found by now. The objective of this work is to characterize sulfided Pt-Pd catalysts supported on two carriers: HY zeolite and γ-Al_2O_3 using XPS and H_2-TPD techniques.

EXPERIMENTAL

The catalysts with total metal load of ca. 2 wt.% with different Pt/Pd ratio were supplied by Haldor Topsoe A/S. All samples were reduced at 573 K in flowing H_2 followed by sulfidation with 1000 ppm H_2S/H_2 mixture for 2 h at the same temperature. Selected catalysts were subjected to treatment with 1000 ppm NH_3/H_2 for 1 h before sulfidation.

XPS spectra were recorded with a Kratos XSAM 800 spectrometer using Mg Kα radiation as X-ray source. Si 2p line (B.E.= 103.1 eV) from the support was used as a reference for charging correction. TPD experiments were performed in the adsorption static unit with MS analysis of the gas composition.

RESULTS AND DISCUSSION

Main results are shown in Table. XPS allows us to elucidate the Pt-Pd electronic state before and after sulfidation as well as surface atomic ratios while H_2-TPD provides the information on metal dispersion.

Sulfidation leads to significant binding energy growth for both metals. For Pt this effect, however, is less straightforward due to strong overlapping of Pt 4f and Al 2p peaks. In general, additional B.E. shift caused by sulfidation is higher for Pd than Pt. This shift in both metals spectra along with sulfide ions gives *direct evidence* of sulfide species formation presumably of bulk character.

Sulfidation degree tends to increase with Pt load; the proportionality between sulfur coverage and Pt concentration is clear for Al_2O_3-supported samples. The zeolite-supported catalysts at any Pt/Pd ratios demonstrate higher stability to sulfur poisoning than Al_2O_3-supported ones. In contrast, metallic area loss caused by sulfidation is higher for the former. The effect of sulfur on surface segregation in bimetallic system has been discussed.

The sulfidation degree of the NH_3-treated samples is 1.2-1.5 times higher as compared with directly reduced catalysts. This tendency is evident especially in the case of zeolite-supported specimens. The above observation is discussed in terms of metal electronic state modification caused by neutralization of zeolite acidity.

Table.

Support	Pd/Pd+Pt, %	Degree of sulfidation[a]	Dispersion, %[b]
HY	0	75	90/33
	50	70	65/27
	65	50	51/18
	80	50	42/14
	100	40	25/11
γ-Al_2O_3	0	200	85/30
	52	190	79/39
	65	140	75/30
	80	120	77/27
	100	95	74/33

[a] S/S_{Me}, %.

[b] Before/after sulfidation (apparent value in the latter case).

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INFLUENCE OF CUPRIC CATION COORDINATION IN CuH-ZSM-5 ON ELECTRON-ACCEPTOR PROPERTIES OF Cu^{2+} CATALYTIC SITES

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CuH-ZSM-5 system is widely investigated last years due to its unique ability to catalyze NO decomposition, SCR of NO_x, and total alkane oxidation. Characterization of CuH-ZSM-5 by different physical methods often yields contradictory results about the changes in the coordinative and valence states of copper in Cu-ZSM-5 treated under different conditions. The mechanism of CuH-ZSM-5 deactivation upon high-temperature treatment of the catalysts is also not fully understood. Previously, it was assumed that unusually high intrinsic activity of CuH-ZSM-5 in oxidation reactions is caused by ability of the zeolitic matrix to stabilize isolated Cu^{2+} ions in very reactive square-planar coordination [1 - 3].

Earlier we demonstrated that systematic ESR study of interaction between zeolites and unsaturated test-molecules (differing in both geometric size and ionization potential (IP)) gives an important complex information about redox site number, strength, and distribution [4, 5]. The aim of present work is to evaluate the change in the state and oxidative activity of isolated copper ions in CuH-ZSM-5 upon interaction of parent and deactivated samples with benzene, anthracene (***An***) and phenanthrene (***Ph***) test-molecules.

EXPERIMENTAL

CuH-ZSM-5 samples (1.3% wt. of Cu) were prepared by either conventional ion-exchange of H-ZSM-5 (Si/Al = 25) with Cu acetate solution or by impregnation of the same zeolite with $Cu(NO_3)_2$ solution. After oxidative treatment in an air flow (500°C, 6 h) the samples are identical in copper distribution and properties.

Weighted sample was placed into quartz ESR ampoule, precalcined at given temperature, cooled to 20°C, and immediately impregnated with benzene and ***An*** or ***Ph*** solutions. Then ESR spectra were periodically registered during 16-48 h. The ESR spectra, at 20°C, were taken in the X-band on the reflecting-type spectrometer. Origin 3.5 program was used for computer treatment (normalization, double integration, baseline correction) of the recorded spectra.

RESULTS AND DISCUSSION

Small difference in effective sizes between ***An*** and ***Ph*** molecules is, however, of crucial importance in H-ZSM-5 case: anthracene is able to penetrate inside zeolitic channels, and phenanthrene interacts with sites located on the outer surface of zeolitic crystals only (comparative evaluation of the number of moderately strong redox sites). Testing with benzene (IP = 9.25 eV) permits to discriminate strong sites of one-electron transfer in zeolitic samples.

Pure H-ZSM-5 is characterized by rather low absolute concentration of both strong and moderate sites of one-electron transfer (<0.3% from the number of the lattice Al ions). Stabilization of copper ions in zeolitic structure results in drastic rise in the redox site number, i.e., the majority of the radical-forming sites in CuH-ZSM-5 is formed by isolated Cu^{2+} ions introduced into parent H-ZSM-5.

The main part of Cu^{2+} cations introduced in H-ZSM-5 by either ion-exchange or solid-state reaction is not able to interact with ***Ph*** molecules wich have too big to enter inside zeolitic channels. For the sample prepared by impregnation it confirms once more an effective migration of cupric ions in cationic positions upon the sample calcination.

Interaction of benzene and ***An***, at 20°C, with the most reactive square-planar Cu^{2+} cations (CuH-ZSM-5 calcined at 500-550°C) results in reduction of the cupric ions and formation of the aromatic cation-radicals. Calcination of CuH-ZSM-5 at 800-850°C results in rearrangement of the local structure of Cu^{2+} sites without either aggregation or encapsulation of isolated cupric ions [3]. However, a change in the local site structure only (transfer from square-planar coordination to higher local symmetries) leads to a drastic decrease in the electron-acceptor properties of the altered Cu^{2+} sites. Strong radical-forming Cu^{2+} sites capable to ionize benzene molecule disappear completely as a result of CuH-ZSM-5 calcination, and the number of ***An*** cation-radicals forming sites reduces drastically.

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PPI-65

Quantitative studies of the reactivity of the low-spin ferric hydroperoxo complexes. The elucidation of their role in Gif-type catalytic oxidation

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Hydroperoxo iron(III) complexes are supposed to be reactive intermediates in non-Fenton catalytic oxidations of alkanes [1,2]. However, until now there were no quantitative data on their reactivity. The impact of these species to the total oxidation was hard to estimate. Recently, we have found by EPR new low-spin ferric hydroperoxo complexes with supposed structures $[Fe(bpy)_2(OOH)Py]^{2+}$ (**2a**) and $[Fe(phen)_2(OOH)Py]^{2+}$ (**2b**) (bpy - 2,2'-bipyridine, phen - 1,10-phenantroline) in the reaction of HOOH with $[Fe_2O(bpy)_4 \cdot 2H_2O](NO_3)_4$ (**1a**) and $[Fe_2O(phen)_4 \cdot 2H_2O](NO_3)_4$ (**1b**) [3] in Py / AcOH mixture as a solvent, so called "Gif" catalytic systems [4]. The main goal of this study was to determine the rate constants for the reactions of **2a** and **2b** with cyclohexane and based on these data to elucidate their role in "Gif" oxidations.

We have measured the concentrations dependencies on time for complexes **2a** and **2b** in 2:1 Py/AcOH mixture with and without cyclohexane. Based on a treatment of these data it was found that the pseudo-first-order rate constants of **2a** and **2b** reaction with C_6H_{12} (1 M) have the following values: $k_a = 0.05\ min^{-1}$ (at 288 K), $k_b = 0.2\ min^{-1}$ (at 273 K) respectively. In the presence of C_6H_{12} ($[C_6H_{12}] = 1$ M), concentrations of **2a** and **2b** were practically steady-state ($[\mathbf{2a}] = 5 \cdot 10^{-5}$ M at 288 K, $[\mathbf{2b}] = 6 \cdot 10^{-4}$ M at 273 K). Thus, the expected rates for accumulation of cyclohexane oxidation products *via* reactions with **2a** and **2b** can be determined by the following equations:

$R_a = [\mathbf{2a}] \cdot k_a = 2.5 \cdot 10^{-6}\ M \cdot min^{-1}$ (at 288 K); $R_b = [\mathbf{2b}] \cdot k_b = 1.2 \cdot 10^{-4}\ M \cdot min^{-1}$ (at 273 K)

The experimental rates of accumulation of the oxidation products (cyclohexanone and cyclohexanole) determined by GC were the following: $R_a = 2 \cdot 10^{-5}\ M \cdot min^{-1}$ (at 288 K), $R_b = 2 \cdot 10^{-4}\ M \cdot min^{-1}$ (at 273 K).

Thus, for the catalytic system $[Fe_2O(bpy)_4 \cdot 2H_2O](NO_3)_4$/ HOOH only minor part (c. a. 10%) of cyclohexane oxidation products can be formed *via* reaction of **2a** with C_6H_{12}. For the catalytic system $[Fe_2O(phen)_4 \cdot 2H_2O](NO_3)_4$/ HOOH the reaction of **2b** with C_6H_{12} can be a major pathway. Further studies are needed to elucidate whether hydroperoxo complexes **2a** and **2b** directly react with C_6H_{12} or *via* reversible formation of iron-oxo intermediates.

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PPI-66

THE PECULIARITIES OF THE CO CHEMISORPTION MECHANISM ON THE MULTIMETALLIC CATALYSTS OVER THE WIDE RANGE OF PRESSURES AND TEMPERATURES

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The understanding of the catalytic reactions mechanism at the molecular level depends upon the careful investigation of surface state and the character of the lateral interactions between the adsorbed molecules in the model systems. However we have less information about the effect of intermolecular interactions.

Here we report the results of the study of CO chemisorption on bi- and multimetallic model catalysts based on Co, Rh, Ir, over the wide range of pressures(10^{-4} -10 Torr) and temperatures (25-500°C) using infrared spectroscopy. These catalysts have the wide application in the catalytic reactions including the carbon monoxide which is initial and important stage in the catalysis.

The sensitivity of CO spectral parameters (vibrational frequency, intensity, half-width of the band) to the nature of the active sites and lateral interactions allows us to study the CO chemisorption mechanism from the low to saturation coverage. The formation and state of bi- and multimetallic surface are discussed.

Among the questions to answer is one of the most important problems: the effect of the lateral interactions on the structure and stability of the chemisorbed layer at various pressures.

The analysis of CO spectral parameters at various coverages (θ) has shown that in the range $\theta \approx 0,2-0,7$ the "islands" from the linear MCO species are formed. From $\theta \approx 0,7$ up to the saturation of the surface the "islands" become more dense. However the disordering of the adlayer is not observed. The thermal desorption results in the destruction of "islands", starting from 25-50°C. This can be seen from "ν_{CO}-T desorption" dependence.

It was established that the interactions between adsorbed molecules cannot be ignored even at low coverages. With increasing coverage such interactions can become significant. These interactions can alter the spatial distributions of adsorbates on the metallic surface.

The character of lateral interactions depends upon the nature of the system considered.

For the model catalysts investigated in this work the effect of the lateral interactions can be manifested as the tendency to ordering of adlayers and the formation of "islands" from CO molecules.

The surface composition influences lateral interactions. For example, in the case of the coexistence of several surface sites (the linear and bridge sites or various types or metal atoms) occurs a considerable mixing of the vibrations of molecules adsorbed on these sites. It results in the predominance of the high-frequency band in the IR-spectrum. This should be taken into account in the determining of the quantity and the proportion of different kinds of surface species from intensities of IR-bands.

One area for future development is the research of the effect of lateral interactions not only on the chemisorption mechanism but also on the catalytic reactions.

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THE MECHANISM OF BENZENE HYDROGENATION BY SULFIDE CATALYSTS

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The saturation of aromatic compounds in diesel fuels has received substantial attention in recent years because of the health hazards associated with undesired emissions in exhaust gases. Therefore environmental regulations are being tightened all over the world leading to limitations on aromatics. Processes of dearomatization of distillate feedstocks are carried out largely over typical hydrotreatment catalysts composed of Ni(Co) with Mo(W) in sulfide form. This paper deals with the study of the mechanism of benzene hydrogenation over well-characterized sulfide Ni-Mo(W) catalysts prepared via metal complex precursors [1,2].

Despite of the great practical importance of dearomatization the amount of works devoted to study of the active component structure of the sulfide hydrogenation catalysts and of the mechanism of its catalytic action is very scarce in the scientific literature [3,4]. We have studied general regularities of benzene conversion under 2 MPa of hydrogen pressure. We have found that the rate constant of benzene conversion increases 30-70 times under unsteady-state regimes of catalyst performance. It was shown the active sites of benzene conversion are formed from the active sites responsible for the C-S-bond hydrogenolysis reaction after removal from the last mentioned sites sulfur atoms as H_2S. The amount of sulfur removed corresponds to S:Ni=0.7-1.0 depending on catalyst composition.

The mechanism of benzene hydrogenation is considered to proceed via adsorption of benzene molecules on Ni atoms entering into the composition of sulfide bimetallic species (SBMS), while hydrogen activation occurs on the terminal sulfur atoms enframed of SBMS. The catalytic cycle occurs in the coordination sphere of SBMS without participation of anion vacancies which can be formed after removal of the structure-forming sulfur atoms. The mechanism proposed relates to concerted mechanisms of heterogeneous catalysis.

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HETEROGENEOUS-CATALYTIC ACTIVATION OF AMMONIA-AIR FURNACE ATMOSPHERE IS A NEW WAY IN SURFACE NITRIDING OF METALS AND ALLOYS TECHNOLOGY

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The report is oriented to a development of notions connected with mechanisms and kinetics of the reactions proceeding when the ammonia-containing gaseous media interact with the surface of different metals and alloys. Such reactions which constitute the base of the widely used in the machine-building technology processes namely the low-temperature thermochemical processing of the metallic articles by the surface azotization method. In spite of the fact that this problem apparently is related to physical metallurgy and is not directly connected with catalysis, the authors were fortuned on the base of new notions about the azotizing action mechanisms of the ammonia-air media on the metal surface to establish theoretically and to prove in actual practice the possibilities of the essential widening of the azotizing process applications field and the new properties confering to the acticles by introduction into the muffle furnace a catalytic element being able to regulate the transformations of the azotizing ammonia-air furnace atmosphere at the "in situ" regime.

The initial principle which served as a starting point of the study was a concept non- traditional for the existing theory of the azotizing. The concept is based on an assumption, whereby the authors advocate that during the metal azotizing the active components of the gaseous medium are not stable, equilibrium products of the furnace atmosphere interaction (in the most typical case these are the products of ammonia oxidation by air oxygen) but intermediate, labile and chemically high-active formations (radicals containing nitrogen, hydrogen or oxygen, ions and ion-radicals). Namely such non-equilibrium but sufficiently long-lived " fragments" (having the high activity, small size and ability to penetrate into the solid metal matrix and to react with it) make a decisive contribution to the real effect of the surface azotizing of the metal or alloy particles.

The natural next logic step was an idea that it is worthwhile to use during the process a catalytic factor subjecting of the ammonia-air medium transformations in the act of its interaction with the metallic surfaces ("in situ" regime). The catalyst use allows to control in purposeful and selective fashion the parallel routes of the ammonia oxidation reaction, i.e. the whole spectrum of the intermediate and final reaction products formed during the process.

Even the first experiments realizing practically this idea verified the correctness of the initial premises and the azotizing process have changed its character very strongly both in the regime parameters and the quality of the particles treated. As an example when the reactor equiped with the silica fiberglass woven catalyst having Pt content up to 0,1 % mass (design and production JSC "Chemphyst") was installed on the ammonia-air mixture manifold the catalytic activity of the gaseous medium during the steel surface azotizing had the following new peculiarities: the alpha-solid solution range was very widened (the supersaturated alpha-solid solution was realized containing up to 1.4 % nitrogen content with an abnormally great lattice parameter); the control of the final nitrogen content in steel was realized in the range from 0.1 to 8.5 % which is inaccessible under the traditional azotizing; the corrosion resistance of structural steel was increased; the hardness of the treated article was increased to the depth more than 1 mm; the decarburizing process during the azotizing was strongly depressed; the azotizing process was sufficiently accelerated simultaneously with the multiple decrease of the ammonia consumption rate; the catalytic activity of the furnace atmosphere gave rise to the azotizing operations usage for the previously non-azotizing systems (the powder metallurgy articles, the high-speed steels, the cuprous and aluminium alloys).

The authors have performed the investigations cycle of the azotizing process regularities under the catalytic activation of different types of catalysts. The new catalytic systems designed by the authors on the silica woven materials base, doped with Pt, Pd and Cr, offer the greatest promise. The first report of the given development was published in [1].

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PPI-69

THE PHENOMENON OF LOW TEMPERATURE PERIODIC ACTIVATION OF CATALYST IN THE REACTIONS OF ALKYL BENZENE LIQUID PHASE OXIDATION

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The phenomenon of periodic regeneration of activity and selectivity of catalyst (t_1, t_2, t_3 in Fig. 1) in the reactions of alkyl benzene liquid phase oxidation has been observed during the periodic cooling of reaction mixture from 80-120°C to 15-20°C at some definite time interval (10-20 min.).

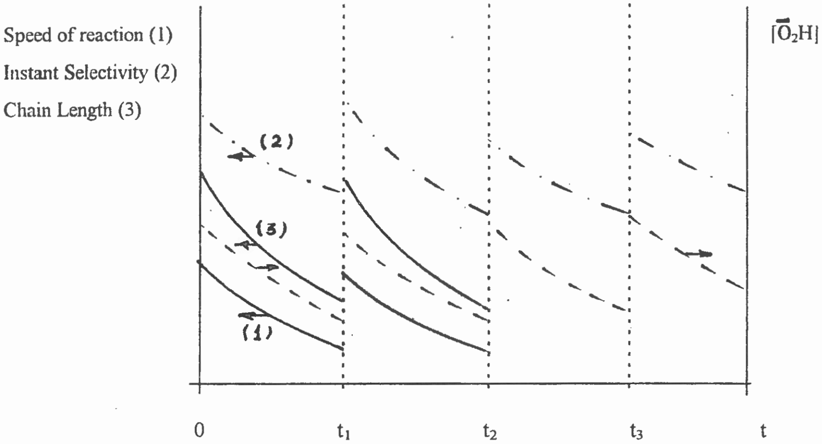

Figure 1. Oxidation of ethyl benzene, catalyst MCCNCC-Ni, T=90°C

The catalysts that were synthesised on the base of metal complex compounds of nitrogen containing coal (MCCNCC) by the principle of chemical bionics have been used as the heterogenous catalysts with the chemical composition $MC_{25-36}H_{8-15}N_{5-8}$. The electronodonor influence of the MCCNCC substrate on the active metallic complex, established by method RPES, promotes the formation of surface active forms of oxygen (ion-radical of oxygen $\overset{\bullet}{\bar{O}}_2$, hydroperoxide group $\bar{O}_2H$)

The big chain length of the chain process and, correspondingly, high speed and selectivity of the reaction of alkyl hydroperoxide formation are conditioned by the transmission of the chain into the surface. The latter is implemented by means of $\bar{O}_2H$ groups (Fig. 1)

$$R\dot{O}_2 + S - \bar{O}_2H \rightarrow RO_2H + S \ldots \overset{\bullet}{\bar{O}}_2 \qquad (1)$$

(transmission of the chain into the surface)

$$S \ldots \overset{\bullet}{\bar{O}}_2 + RH \rightarrow S \ldots \bar{O}_2H + \dot{R} \qquad (2)$$

$$\dot{R} + O_2 \rightarrow R\dot{O}_2, \qquad (3)$$

where

$\dot{R}$ - $Ph\dot{C}HCH_3$ or $Ph(CH_3)_3\dot{C}$,

S - surface.

Reduction of activity and selectivity of the catalyst during the reaction is connected with the annihilation of surface hydroperoxide groups by means of alkyl radicals

$$S \ldots \bar{O}_2H + \dot{R} \rightarrow S \ldots \overset{\bullet}{\bar{O}} + ROH \qquad (4)$$

(destruction surface active form)

$$S \ldots \overset{\bullet}{\bar{O}} + RH \rightarrow S \ldots \bar{O}H + \dot{R} \qquad (5)$$

During the decrease of the temperature the speed of destruction stage (4) decreases significantly. At the same time, under these conditions the catalytically active surface hydroperoxide groups are regenerated at the presence of hydroperoxide

$$S \ldots \bar{O}H + RO_2H \rightarrow S \ldots \bar{O}_2H + ROH \qquad (6)$$

(regeneration of surface active form)

The work was conducted with assistance of International Fund INTAS

Synthesis of chiral organophosphorous ligands based on methyl 3,4-O-isopropylidene-L-threonate

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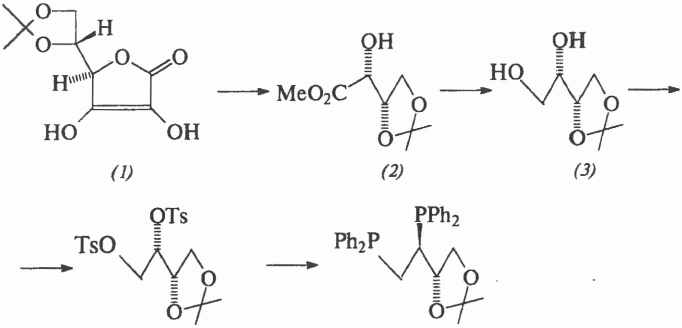
The success in applying transition metal complexes as catalysts for enantioselective processes is to a great extent dependent on the nature of chiral ligands surrounding the metal center. A great number of papers were devoted to synthesis of chiral ligands, mainly phosphorous-containing one. The approaches based on carbohydrates /1/, ethers of L- and D-tartaric acids /2/, derivatives of the binaphthyl row /3/ are of the most practical interest.

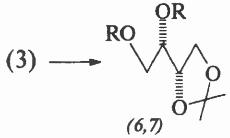
When furthering our own studies in the field, we synthesized optically active *bis*-phosphine (5) and *bis*-phosphinites (6, 7), which are structurally related to the bidentate ligand DIOP /2/. The starting chiral compound was methyl 3,4-O-isopropylidene-L-threonate (2), the product of oxidative splitting of 5,6-O-isopropylidene-L-ascorbic acid (1). The compound (2) was reduced by $LiAlH_4$ to produce diol (3) (62%, $[\alpha]_D^{20}$ +3.5° (c, 4.0, $CHCl_3$)) which was transformed to the target *bis*-phosphine (42%, $[\alpha]_D^{20}$ +20.3° (c, 0.7, $CHCl_3$)) *via* a corresponding ditosylate (4) ($[\alpha]_D^{20}$ +12.1° (c, 0.8, $CHCl_3$)).

The reaction of diol (3) with PPh_2Cl and $(C_6F_5)_2PCl$ in the presence of pyridine was used to synthesize chiral *bis*-phosphinites (6) (78%, $[\alpha]_D^{20}$ +2.8° (c, 1.8, $CHCl_3$)) and (7) (80%, $[\alpha]_D^{20}$ +0.43° (c, 4.0, $CHCl_3$)).

Chiral complexes (8) to (10) were produced by chelating ligands (5) to (7) with $[Rh(1,5\text{-}COD)Cl]_2$ in the presence of $NaClO_4$. Their catalytic activity and stereoselectivity were tentatively estimated with the reaction of hydrogenation of itaconic acid (11) and its ether (12) (1 atm of H_2, Et_3N, THF) as an example.



(1) *(2)* *(3)* *(4)* *(5)*

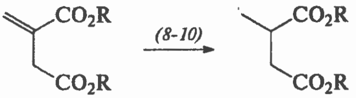


(6,7)

R=Ph$_2$P (*6*); R=(C_6F_5)P (*7*)

$$[Rh(1,5\text{-}COD)Cl]_2 \xrightarrow{(5,6,7)} Rh(1,5\text{-}COD)(5)\text{or}(6)\text{or}(7)]^+ClO_4^-$$

(8-10)



R=H(11); R=Me(12)

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THE EFFECT OF SURFACE DEFECTS ON CO ADSORPTION ON POLYCRYSTALLINE Ni.

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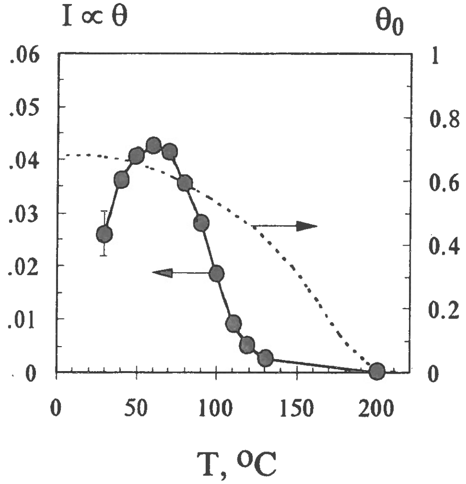
It has recently been shown that the defects on Ni surface result in the occurrence of weakly-bound state of CO with the desorption temperature 30 - 130 °C [1] and with the cross-section of ion-stimulated desorption $\sigma = 18 \cdot 10^{-19}$ м^2 [2]. Moreover, CO is known to adsorb at first on the defects [3].

In this work, the results of the temperature dependence (30 - 200 °C) of ion-stimulated adsorption of CO on polycrystalline nickel are presented. Under the ion-stimulated adsorption should be understood the process of surface bombardment and simultaneous CO adsorption.

The experimental instrument and methods are described elsewhere [2]. It should be noted that the instrument has been modified so that the sample can be heated up to 800 °C with accuracy of ± 3 °C.



The figure shows the temperature dependence of the NiCO$^+$ and Ni$^+$ intensity ratio, $I = I_{NiCO^+}/I_{Ni^+}$. The ambient CO pressure during the experiment was $2 \cdot 10^{-5}$ Pa and the density of ion beam was 0.02 A/m^2. At first-order approximation the NiCO$^+$ and Ni$^+$ ratio is proportional to the CO coverage - $\theta(T)$ [4]. As it is seen from the figure, the temperature dependence of

CO coverage has two peculiarities: the growth of CO coverage at 30 - 60 °C and sharp decrease at T = 80 - 120 °C.

The dashed curve of the figure represents the dependence of saturated CO coverage - θ_0 on temperature for CO/Ni(100) at the same ambient CO pressure but without ion bombardment [5]. It should be stressed that the calculations for kinetics of CO adsorption via precursor state [6] at our experimental conditions show that the term describing the ion-stimulated adsorption can not be responsible for the decrease in coverage at T = 80 - 120 °C.

The observed effect of coverage decrease at T = 80 - 120 °C may be accounted for by the fact that the weakly-bound state of CO on defected surfaces is an intermediate state in the process of CO adsorption at tightly-bound state. Indeed, the weakly-bound state at T = 130 °C is practically absent, therefore, the rate of CO adsorption at tightly-bound state can be expected to decrease drastically.

The coverage increase at T = 30 - 60 °C can be accounted for by the scheme proposed as well if the transition from weakly-bound state to tightly-bound state is activated. The latter is quite possible since the defects hinder the diffusion of adsorbed molecules.

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On the Nature of Oscillations in Methane Oxidation in Combined Catalytic Bed

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The analysis of critical phenomena, such as hysteresis and self-oscillations, gives a very valuable information about the intrinsic mechanism of catalytic reactions. Recently we have observed the critical phenomena during methane oxidation in the combined catalytic bed containing oxide and metal components [1]. Whereas the oxide component (10% Nd/MgO) itself is very efficient as the catalyst for oxidative coupling of methane (OCM) to higher hydrocarbons, in the presence of inactive low-surface area metal filament (Ni-based alloy) the selectivity shift towards CO and H_2 takes place and oscillatory behavior arises. In the present work the following aspects of these phenomena have been analyzed: (i) the effect of the state of the surface on the kinetic behavior; (ii) the location of the oscillatory process.

The metal filament placed co-axially into the reactor filled with oxide catalyst simultaneously played the role of thermocouple making us possible to detect temperature oscillations in addition to oscillations of concentrations of the components of reaction mixture measured by combined GC/MS analysis.

The effect of the state of the surface on the kinetic behavior was studied using the feeding of the reactor with methane-oxygen mixture alternating with treatment in inert (He), oxidizing (O_2), and reducing (H_2) gases. After treatment in the inert gas the process starts from the high activity and then proceeds in the regular oscillatory regime.

The oxidative treatment leads to the disordering of oscillations. After some period of time the regular oscillations restore.

If the catalyst bed was treated by hydrogen, following catalytic oxidation of methane proceeds in a steady-state regime. The oscillatory behavior can be restored only by the oxidative treatment of the catalyst(s).

The reaction parameters obtained in oscillatory regime are presented in Table. The data in columns A and B are attributed to the low- and high-activity states of the same oscillations. Column C corresponds to the low-activity state of another oscillations observed at higher reactor temperature. Although the measured temperature in columns B and C is the same, the reaction parameters differ dramatically.

The analysis of the heat balance in the reactor shows that the additional heat production which is due to the additional conversion of the reactants in the high-activity state is not enough to heat both oxide and metal components in the catalyst bed. The comparison of the reaction parameters obtained in oscillatory regime (see

Table) with the results of analysis of heat balance indicates that the oscillatory process is likely localized on the metal filament surface.

Table. Reaction parameters of methane oxidation in oscillatory regime (total pressure 40 kPa, $CH_4 : O_2 = 6.7$)

	A	B	C
t, °C	630	690	690
O_2 Conversion, %	32.3	44.7	64.0
CO Selectivity, %	40.5	41.3	38.8
CO_2 Selectivity, %	54.2	52.4	41.7
C_2's Selectivity, %	5.3	6.3	19.5
H_2 Selectivity, %	49.9	44.1	41.6

The results obtained in this study indicate that the oxide component is a source of the active intermediates (likely CH_3 radicals). In the absence of the second component they further undergo the recombination in the gas phase with C_2-hydrocarbons formation. The surface of the second component (metal filament) is not active enough to be able to activate methane molecule. However, if the active intermediates formed on the oxide component reach the metal surface, they undergo there the further transformation into CO_x and H_2.

Oscillations are likely to be caused by the variations of the state of the metal filament surface accompanied by the changes of their properties. According to [2], the reaction rate oscillations may be due to the existence of different oxygen forms. In the case of our experiments, the high-activity state corresponds to the filament surface free of weakly bound adsorbed oxygen species. One may assume that this state of the surface is preferable for chemisorption and/or dissociation of CH_3-radicals.

The total disappearance of the oscillatory behavior after treatment in H_2 may indicate that the metal component in high-activity state contains some kind of strongly-bound oxygen which takes part in the formation of the final products.

We acknowledge the financial support of the International Science Foundation (ISF Grant # MN2000/MN2300) and the Russian Foundation of Basic Research (Grants No. 93-03-18479 and 96-03-42522).

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DIRECT CONVERSION OF SYNGAS TO HIGHER ALCOHOLS OVER Cu/Zn OXIDE PROMOTED BY ALKALI METALS. *IN SITU* X-RAY STUDY OF REDUCTION CATALYST STATE

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The activity and selectivity of the Cu/Zn catalyst for methanol synthesis varies upon introduction of an alkali promoter in its composition. Along with methanol, higher alcohols are formed over such a catalyst. This work was the study of various methods for introduction of the alkali promoter into a Cu-Zn oxide catalyst, the optimum method was chosen to maintain a certain phase composition of the oxide species of the catalyst – the solid solution of copper ions in the zinc oxide from which the active catalyst species are formed under the reaction conditions.

Catalytic properties of the alkali promoted copper-containing catalyst were studied at pressure of 75 atm, temperature 250–290°C and the gas mixture $CO/H_2 = 2/1$. The formation of higher alcohols in amount of up to 30% of a total of all alcohols was shown to occur under these conditions. If there was no CO_2 in the syngas, no more than 0.2% of water was found in the reaction products.

In situ XRD technique was used to observe changes in the promoted catalyst resulted from its reduction by hydrogen at various temperatures followed by the treatment with $\leq$ 0,04 vol.% O_2 in inert gas. The reduced species of the promoted catalyst and unpromoted one of the same composition were compared. It was shown that the promoted sample is characterized with two reduced states of metallic Cu – one of them disappeared after exposure to helium with $\leq$ 0,04 vol.% O_2 and appeared again under repeated reduction in hydrogen – the so called reversible state of copper. Another state of metal copper is stable. At the same time only first type of Cu metal species was observed in the case of the unpromoted sample. Based on these results active sites for methanol and higher alcohols formation are proposed.

PPI-74

THE CO/H_2 REACTION CATALYZED BY Cu/Co-CONTAINING OXIDES. *IN SITU* XRD AND TEM STUDIES OF THE GENESIS OF ACTIVE CATALYST STATE

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Synthesis of alcohols from non-petroleum feedstocks (coal, natural gas, etc.) via gasification is among the processes of greatest potentialities to produce transportation fuels. Cu-Co-Al, Cu-Co-Zn and Cu-Co-Mg oxide catalysts (with no alkali promoter) were studied in CO/H_2 reaction at 50 atm and 200-400°C. Preferable formation of hydrocarbons was shown to occur at 200-290°C; higher alcohols, along with hydrocarbons, are produced within the range 290-370°C; at above 380°C no alcohols, but only hydrocarbons are observed in the reaction products.

The influence of hydrogen and syn-gas on state of model Cu- Co oxide were studied using *in situ* high temperature X-ray and *ex situ* transmission electron microscopic techniques. The study was carried out at the characteristic temperatures - 250, 350 and 400°C - at which essentially different pathways of CO/H_2 reaction were observed.

Upon activation with hydrogen at 230°C model Cu-Co oxide becomes completely converted to Cu-Co alloy. Interaction of CO/H_2 with reduced sample at 250°C brings about no change in the phase composition, there is only the Cu-Co alloy phase. Upon an elevation of temperature up to 350°C the alloy is partially destroyed to produce cobalt carbide and copper metal. And just the heating up to 400°C results in the destruction of Co_2C and Cu-Co alloy to form isolated phases of copper and cobalt metals and carbon.

Thus, it was shown that in the case of high yields of alcohols (310-350°C) the influence of the reaction medium results in formation of a cobalt carbide along with metal Cu and Cu-Co alloy. Decomposition of Co_2C and Cu-Co alloy is in time with catalyst deactivation with respect to oxygenated compounds. Metallic states - the Cu-Co alloy or individual Co and Cu metal exist at the temperatures of hydrocarbons synthesis.

IN SEARCH OF GENERAL KINETIC LAW OF COMPLEX CHEMICAL REACTIONS

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The idea of the general law of chemical transformations is one of the primary ideas in chemistry. In 1862-67 Gul'dberg and Waage suggested the quilibrium formulation of the mass-action-law and later in 1879 proposed the dynamic formulation of this law. It is evident that Gul'dberg and Waage proceeded from the mechanical foundation of chemical laws. (According to Gul'dberg and Waage "In chemistry, like in mechanics the most natural method will be to determine forces in their equilibrium state") In 1884 Van't Hoff suggested the main types of normal chemical transformations. ("Etudes de Dynamique Chimique") He put forward the principle "The process of chemical transformation is characterized solely by the number of molecules whose interaction provides this transformation". The well known Van't Hoff's rate equations are in agreement with this principle (first-, second- and third-order rate equations).

Van't Hoff thought he found the general law of chemical kinetics. Also it should be mentioned that Van't Hoff was very sceptical about the mass-action-law concept ("As a theoretical foundation I have accepted not the concept of mass-action-law. I had to leave this concept in the course of my experiments").

But the real kinetic data do not obey Van't Hoff's "normal classification". The history of chemical kinetics in the XX century was the set of attempts to save and improve Van't Hoff's paradigm.

Now it is time to make the declaration that in chemical kinetics there was no general law of complex chemical reactions. A complex mechanism is represented by a sum of elementary (simple) steps. Each step consists of two elementary reactions. Kinetic model which is correspondent to this complex mechanism is not law but rather traditional construction [1]. Also it seems that the various attempts to generate general kinetic rate expressions on the basis of some variational principles were as a rule unsuccessful (Bachareva, Gyarmati, Heymann and Yablonskii).

New approachs for the solution of this difficult problem are based on a combination of classical pseudo-steady-state hypothesis with modern algebraic theory. The application of the theory of resultants and the theory of logarithmic residue has proven that system of steady-state (or pseudo-steady-state) equations can be transformed to the so called kinetic\ polynomial related to the variable R, the steady-state (or pseudo-state) reaction rate. The free term of this kinetic polynomial corresponds to the overall reaction, and its coefficients have the well-known Langmuir form of concentration polynomials.

The foundations of kinetic polynomial theory were developed by Yablonskii and Lazman in 1980-1990s. [2-4]. The most important properties of the kinetic polynomial (K.P.) are the following:

A) K.P. can be defined as an equation of the state of an open chemical system relating the reaction rate to parameter of the process: temperature and composition of the reaction mixture.

B) K.P. is not an empirical regression. It is obtained from the system of equations corresponding to the reaction mechanism.

C) K.P. is thermodynamically correct. The condition of thermodynamic equilibrium is equivalent to zeroth value of free term which is correspondent to the overall reaction equilibrium.

D) In the general case, K.P. is a non-linear equation. ts physically meaningful solutions are correspondent to the different stable and unstable regimes. The K.P. technique can be applied to specify regions of parameters with special kinetic behavior, in particular the regions of multiplicity of steady-state, kinetic self-oscillations, and so on.

E) At significant high values of parameters of some non-linear steps K.P. can be represented as a product of some polynomials of the same type but low dimension. The results of this simplifications are interesting:

1) the reation rate at some bifurcation points can be determined just by one reaction parameter (adsorption, desorption parameter),
2) there are simple algebraic correlations between reaction rates at critical points,
3). Sometimes these correlations are equivalent to thermodynamic (or pseudo-thermodynamic) correlations.

F) The particular cases of K.P. are Langmuir-type and Hougen-Watson-type kinetic equations and kinetic equations which are obtained for inear mechanisms of heterogeneous catalytic (Yablonskii, Bykov, Yevstigneev) and enzyme (Vol'kenstein, Gol'dstein) reactions.

G) By the help of the K.P. technique it is possible to solve the classical Boreskov-Horiuti problem regarding the correlations between forward and backward rate expressions.

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PPI-76

COMPENSATION EFFECT AND COMPENSATION OFF ENERGY IN THE LOW TEMPERATURE H_2-D_2 EXCHANGE ON FILMS OF TRANSITION, RARE EARTH METALS AND Ln-Cu ALLOYS

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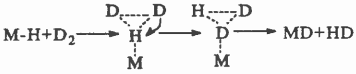
Kinetics of reaction of isotope exchange in molecular hydrogen has been studied on films of all lanthanoides, REM-Cu alloys and also on Sc, Y, La, Hf, Zr, Ru, Mo, Ni, Rh, Pd and Pt under the same conditions by static method at 66.6 Pa pressure of gas mixture in the temperature range 77-273 K. An abrupt break on Arrhenius plots was found for exchange on most metals and alloys [1]. Results discussed here were found in a more narrow interval: from 77 K till T of the break. On the base of experimental data of Ks (molec/cm^2 s), activation energy E and pre-exponential factor B were calculated in this temperature interval. Compensation effect (CE) was found for exchange on REM and separately on transition d-metals (fig.1, lines 1 and 2). Occurrence of CE can be explained by the hypothesis that both E and B depend on one common parameter - the heat of chemisorption of atomic H bonded weakly but irreversibly, which takes part in exchange by Eley mechanism. Existence of CE makes not effective comparison of Ks at 77 K in the series of REM [1] because the point of crossing of Arrhenius lines occurs at 85 K. That's why the comparison will be made for E and lgB. A straight line dependence was found for lgB and ΔHs - heat of sublimation of all metals studied (fig. 2a). Comparison of E and ΔHs shows a more complicated situation (fig.2b):

9 REM form straight line 1	E = 0.01 ΔHs - 0.4 (kJ/mol)
Pd, Gd, Y, Pt, Mo form straight line 2	E = 0.01 ΔHs - 2.1 (kJ/mol)
Ce, Ni, Rh, Zr, Hf, Ru form straight line	E = 0.01 ΔHs - 3.4 (kJ/mol)

So, values E contain 2 terms, the first for all metals being 0.01 ΔHs, but the second is characteristic for each group of metals and means the energy compensating the first term (Ec). This phenomenon may be explained if we consider mechanism of Eley:



$$\mathrm{M\text{-}H+D_2} \longrightarrow \overset{\mathrm{D\cdots D}}{\underset{\mathrm{M}}{\mathrm{H}}} \longrightarrow \overset{\mathrm{H\cdots D}}{\underset{\mathrm{M}}{\mathrm{D}}} \longrightarrow \mathrm{MD+HD}$$

We suppose that exchange proceeds due to "turning" of active complex. the energy required to break the bond M-H being compensated partly by creation of new bond M-H. This is just explanation of the fact that E contains 2 terms and that E has so low values at low temperatures. The ratio of the second term (Ec) to the first one is the "degree of compensation" æ in accordance with how G.K. Boreskov has formulated this conception [2].

Alloying of REM with Cu leads to the extreme increasing of Ks [1] which approaches to that of Hf at 77 K. This proceeds due to decreasing of E, as well as due to increasing of B. In fig.1 it is seen that points for alloys are moved to line 2. These points are indicated by marks of REM, but really they mean intermetallic compound (IMC) $LnCu_2$. Fig. 2a and 2b can be used for explanation of results found on allows. So, if we know experimental value of B, we can find the energy of bonding ΔHs in IMS formed on the surface of the film. Then transferring this value to fig. 2b and having the experimental value of E, we find the place for point of $LaCu_n$ on this fig. 2b. Here we demonstrate only some examples: points for $GdCu_n$, Ycu_n, $HfCu_n$ are placed at the beginning of line 3, points for $SmCu_n$, $TbCu_n$, $TmCu_n$ are on the line 2, points for $PrCu_n$, $DyCu_n$, $ScCu_n$, $YbCu_n$ are placed between lines 2 and 3. So a conclusion can be made that in these cases alloying leads to the strengthening of metal bonds due to formation of IMS (and probably strengthening of the bonds M-H), and increasing of degree of energy compensation for the reaction of isotope exchange. The nature of the latter have to be explained from the position of the electron interaction.

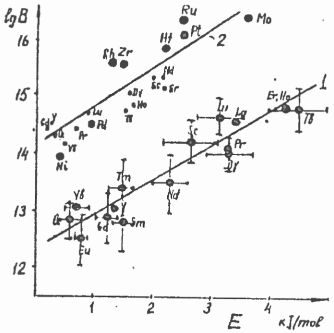


Fig.1 Correlation between E and lgB for isotope exchange in molecular hydrogen at low temperatures on films of REM (1), transition d-metals (2) and also on $LnCu_n$ ( ).

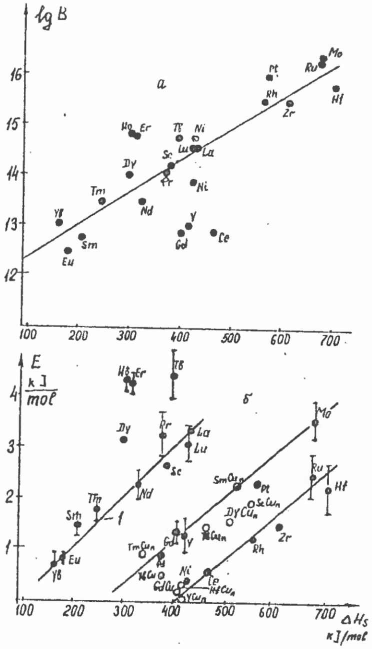


Fig.2 a) Correlation between lgB and ΔHs of metals. b) Correlation between E and ΔHs of metals and alloys.

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Isotopic Kinetics of Dihydrogen Exchange: the Application to Study the Mechanism of Catalytic Activation of Dihydrogen by Palladium Phosphine Complexes in Acid Solutions

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A rigorous kinetic theory of isotopic exchange of two-atom molecules, developed earlier by Muzykantov, Popovskii and Boreskov [1] and widely used in the investigations of heterogeneous catalytic activation of O_2 [2], has been for the first time applied to study the mechanism of homogeneous catalytic activation of H_2 by metal complexes in solutions. The classification of types of dihydrogen exchange according to a character of atom rearrangements is given: **I**) ZH + ZH, **II**) ZH + (H) and **III**) (H) + (H). It is based on that after fragmentation of H_2 molecule by activation the hydrogen atoms (ions) formed can incorporate into another component (H) and/or into intermediates ZH (proportion of the latter being low). The formal tools of isotopic kinetics for the case of simultaneous realization of all three types of the exchange by multistage mechanisms and the absence of kinetic isotope effects are outlined. The procedure of assessment of kinetic parameters of the $^{*}H_2/H^+$ -exchange (general rate ρ and contributions of the exchange types κ_i, $i = 1, 2, 3$) using the experimental data on redistribution of isotopic dihydrogen molecules is described in details for different isotopic variants of the initial dihydrogen $^{*}H_2$: A) D_2, B) $H_2 + D_2$ and C) HD (D - deuterium). The mode of interpretation of the computer-calculated values of kinetic parameters of the exchange is discussed in terms of a nature of intermediates, the character and rates of possible stages of the complex mechanism.

It was found for the investigated systems "$Pd(OAc)_2$ - phosphine ligand - CF_3COOH/ H_2O - H_2" that dihydrogen homoexchange (type **I**) did not occur (i.e. $\kappa_1 = 0$), while dihydrogen heteroexchange (types **II** and **III**) was realized with contributions κ_2 and κ_3 widely varied (essentially from 0 to 1) depending on the system composition [3]. Taking into account a spectroscopic (NMR ^1H and ^{31}P) information on the equilibrium composition of palladium complexes in the systems [3, 4], the observed regularities of the exchange were interpreted in terms of the mechanism involving the consecutive equilibrium stages of heterolysis of H_2 and rearrangements of palladium hydride complexes (P = phosphine ligand, $X^- = CF_3COO^-$):

$$[P_2PdX]^+ + H_2 \longrightarrow P_2Pd(H)X + H^+ \qquad (1)$$

$$P_2Pd(H)X + P \longrightarrow [P_3PdH]^+ + X^- \qquad (2)$$

$$[P_3PdH]^+ \longrightarrow P_3Pd^{\circ} + H^+ \qquad (3)$$

The rates of these stages were shown to be unequivocally connected with kinetic parameters of the exchange by the following relations: $W_1 = \rho$, $W_{23} = \rho\kappa_2/\kappa_3$, where $W_{23} = W_2W_3/(W_2 + W_3)$.

The kinetic theory of dihydrogen isotopic heteroexchange for the case of occurence of kinetic isotope effects (KIE) was advanced and the procedure of a computation of the KIE values from experimental data was developed. The application of this procedure to data treatment made it possible to infer the absence of KIE in the course of dihydrogen heteroexchange in the investigated systems over a wide range of the reaction conditions. Furthermore, direct experimental measurements of the rates of $*H_2/H^+$ -exchange in the "$Pd(OAc)_2$ - PPh_3 - CF_3COOH/H_2O - $*H_2$" system in the experiments with one ($*H_2 = D_2$ vs HD) and two ($*H_2 = D_2$ vs HT ; T - tritium) isotopic labels also allowed a definite conclusion on the absence of KIE (with an accuracy of 20 ÷ 30 %). Nevertheless, previously [5] in the course of $HT/*H^+$ -exchange ($*H^+ = CF_3COOH/H_2O$ vs CF_3COOD/D_2O) appreciable isotope effects were discovered, the values of which (k_{H+}/k_{D+}) being widely varied depending on the acid concentration: 1 for 100% CF_3COO*H and 5 for 80% $CF_3COO*H/*H_2O$. A special NMR ^{31}P spectroscopic investigation showed that the observed solvent isotope effect was of thermodynamic nature and was due to different equilibrium composition of palladium phosphine complexes in the CF_3COOH/H_2O and CF_3COOD/D_2O solutions of the same concentration.

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POSTER SESSION I

Section 3

Mechanisms of Selective Oxidation in Heterogeneous and Homogeneous Systems

ACTIVITY OF SUPPORTED LIQUID-PHASE CATALYSTS IN THE FRAMEWORK OF LATTICE MONTE-CARLO APPROACH

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Supported liquid-phase catalysts (SLPC) are catalysts whose active components are dispersed on a porous support and are either totally or at least partially liquid under reaction conditions. They provide promising possibilities for heterogenization of homogeneous catalysis.

The reaction behaviour of SLPC is affected by a number of factors including the structure of solid phase support, the character of liquid distribution, the physical and chemical properties of the components, and so on. The problem of special importance is to find an optimal liquid loading, so that to achieve the greatest possible activity of the catalyst. The complexity of such systems makes the adequate theoretical analysis rather difficult. In the years, a considerable progress is made in understanding the mechanism, which determine the behaviour of SLPC [1-3]. However the general solution of the problem is yet unknown, and so the development of new approach and models is welcome.

In the present report we introduce a new model aimed at the analysis of the activity of SLP catalysts. The model is based on Monte-Carlo simulation in the framework of lattice "bond problem". The bonds of three-dimensional dense-packing lattice refer to (microscopic) volumes of the physical space, which may be occupied by the solid or liquid state phases or by air. All the phases are treated on an equal footing, so that the proportion between their volume fractions is realized as the proportion between the corresponding numbers of bonds.

The efficiency of a model catalyst is estimated from the total rate of a catalytic reaction. The reagent may reach the catalytic centers either by a direct diffusion in liquid or by a diffusion in gas and a subsequent diffusion through the gas-liquid interface. To describe each of these processes we have to solve the relevant diffusion equations in the lattice representation:

$$\sum_{j_{\mathrm{Gas}}} D_{ij}(C_i^G - C_j^G) + d_i(C_i^G - C_j^L) = 0 \tag{1}$$

$$\sum_{j_{\mathrm{Liq}}} D_{ij}(C_i^L - C_j^L) + d_i(C_i^L - C_j^G) = -\,r_i C_i^L \tag{2}$$

Here D_{ij} are the effective diffusivities, d_i are the effective diffusivities through the gas-liquid interface, C_i^G and C_i^L stand for the concentrations of the reactant in the gas and in the liquid, respectively. r_i characterize the reaction activity. The numerical solution of the above equations is found by the means of standard relaxation technique.

The model can be easily generalized for the case of several reacting components. Also, the reaction must not be necessarily of the first order. The effective diffusivities may depend on the concentrations of the reactants and the products. If desired, one can introduce variations in the pore sizes thus treating the effective diffusivities in the pores D_{ij} as random numbers distributed according to a definite law.

Our models differ from the analytical approach [2] in several points, apart from the technical method of calculations. We do not make any assumptions on the behaviour of the tortuosity factor. Instead, it may be well predicted within the same model.. We do not assume that the concentrations of the reactant in the gaseous and liquid phases are always in equilibrium. The degree of equilibrium depends rather on the effective interface diffusivity. Neither we assume the additivity principle for the fluxes through the gas and the liquid subsystems. The presence of the gas-liquid interface is the peculiar property of our model. Such details as the randomly varying pore sizes or the inhomogeneities of liquid loading are not necessary but may be also taken into account.

To test our model we have considered many examples of the dependence of the activity on the liquid loading. The method shows enough flexibility to be adjusted to very different situations, and so experimental dependencies of various kinds may be successfully described within the same model. This approach allows a clear comparison between different SLP systems. It may serve as suitable ground for understanding their properties.

The work is supported by the Russian Foundation for Basic Research (grant no. 95-03-08606).

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PPI-79

Formation mechanism of $Pd(Acac)_2PPh_3 + NaH_2PO_2$ catalytic system and features of hydrogenation in its presence

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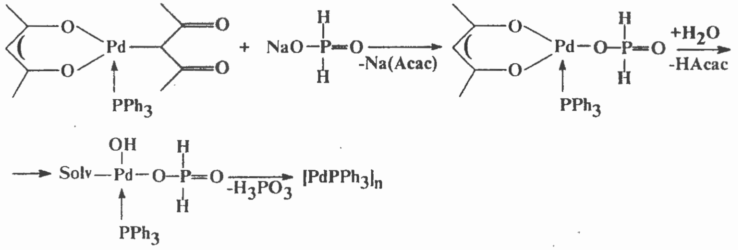
Formation mechanism and catalytic properties of metal complex hydrogenation catalyst based on bis-acetylacetonato(triphenylphosphine)palladium and sodium hypophosphite have been studied. By use of ^1H, ^{31}P NMR spectroscopy and GLC it has been shown that the interaction process between the initial components of the catalytic system occurs through a series of steps including the substitution of carbon - bonded acetylacetonato ligand for hypophosphite anion, further hydrolysis of formed mixed - ligand $Pd(Acac)P(O)OH_2 \cdot PPh_3$ composition complex and the reductive elimination according to following scheme:



$$H_3PO_3 + Na(Acac) \longrightarrow NaH_2PO_3 + HAcac$$

Reduction of initial complex is followed by side - process of catalytic oxidation of sodium hypophosphite leading to formation of sodium phosphite and molecular hydrogen:

$$NaH_2PO_2 + H_2O \xrightarrow{Pd} NaH_2PO_3 + H_2$$

Appearance of hydrogen in reaction system in turn causes the dephenylation of triphenylphosphine ligand and formation of polynuclear palladium complexes with various compositions and structures, in particular, of trinuclear $[Pd_3(PPh_2)_3(PPh_3)_3]^+Acac^-$ and

$[Pd_3(PPh_2)_2(Acac)(PPh_3)_3]^+Acac^-$ type palladium complexes. The content of trinuclear clusters in reaction system does not exceed 3-5%. Phosphide and phosphine ligand polynuclear palladium complexes with brutto formula $[Pd(PPh_2)Pd(PPh_3)]_n$ according to elemental analysis data have been suggested as main products of the reduction of initial palladium complex.

A high activity (150 - 180 mol Sb per mol Pd for min) of considering system in the hydrogenation of hydrocarbons with terminal double and internal triple bonds has been established. A high stereoselectivity of palladium complex catalyst is observed. An activation effect of catalyst in the hydrogenation of α-acetylene derivatives has been observed. This effect is connected with an abrupt rise of activity and selectivity of the catalytic system under addition of a new portion of substrate.

Various factors influencing on the formation of catalytically active species have been considered. More deep dephenylation of organophosphorus ligands of palladium complex catalyst during the hydrogenation of unsaturated hydrocarbons has been shown to be the main reason for the activation of the system based on $Pd(Acac)_2 \cdot PPh_3$ and sodium hypophosphite. It has been shown that in the case of α-acetylene derivatives dephenylation occurs only after complete hydrogenation of the substrate to alkene whereas under the hydrogenation of α-olefins and disubstituted acetylene derivatives dephenylation is observed at initial moment of time. Obtained differences are produced by a different thermodynamic stability of palladium α-olefin, disubstituted and α-acetylene derivative π-complexes. The microheterogeneouns character of the catalyst has been established. It has been shown that the role of unsaturated hydrocarbons in the activation of palladium complex catalyst is in the stabilization of catalytically active palladium complexes formed as a result of dephenylation. It has been also shown that the fraction of catalytically active species does not exceed 15% even in the case of the most active system. The general action scheme of catalyst in the hydrogenation of α-acetylene derivatives has been suggested.

This work is supported by Russian Foundation for Basic Researches (grant № 96-03-33667a).

PPI-79a

ENANTIOSELECTIVE OXIDATIONS CATALYZED BY Ti(IV) AND Zr(IV) PEROXOCOMPLEXES

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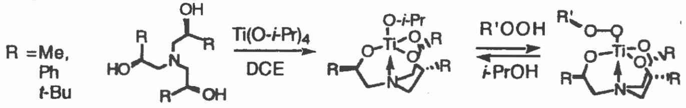
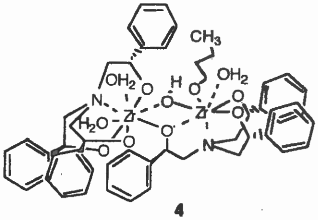
Enantioselective oxidations catalyzed by chiral transition metal complexes are among the most appealing transformations in asymmetric synthesis.[1] We recently reported a new class of titanium(IV) peroxocomplexes **3** bearing enantiopure, homochiral C_3 symmetric trialkanolamines **1** as chiral ligands,[2] which oxidize alkylarylsulfides to the corresponding sulfoxides.[3] In these processes a significant overoxidation to sulfones (20-70%) has been observed, proceeding with cooperative enantioselectivity with respect to the sulfoxidation reaction. Sulfoxides with e.e. up to 84% have been obtained. Differently from the previously reported enantioselective titanium-based oxidation systems, the tetracoordinate nature of **1** allows the use of as little as 2% of catalyst **2** to form the highly robust, monomeric peroxocomplex **3**.



1 **2** **3**

The extension of the protocol to zirconium (IV) has given also interesting results. As compared to the titanium derivatives, the zirconium species show a greater tendency to give aggregates in the presence of small amounts of water. A dimeric catalyst, **4**, whose structure has been deduced on the basis of elemental analysis, molecular weight determinations and NMR experiments, has been obtained and its oxidative ability is under study. With respect to the titanium-based system, catalyst **4** oxidize alkylarylsulfides with a higher enantioselectivity (e.e. up to 91%), affording sulfoxides with opposite absolute configuration, thus providing a remarkably efficient and complementary oxidation protocol.



4

It is worth of comment that, in the zirconium mediated reactions, the oxidation of sulfoxides to sulfones is faster than the oxidation of sulfides. In particular the selectivity ratio for the oxidation of *p*-tolylmethyl sulfide, catalyzed by **4**, has been determined to be $k_S/k_{SO}=0.32$. Such an aspect is unprecedented for formally electrophilic oxidants like d^0 transition metal peroxides. The same mechanistic feature, even if to a lower extent, is also found in the titanium catalyst rectivity behavior.

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PPI-80

INFLUENCE OF CHEMICAL NATURE OF DOPANTS ON THE CATALYTIC PROPERTIES OF V-Ti-O CATALYSTS IN METHYLPYRAZINE AMMOXIDATION

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V-Ti-O catalysts are highly active and selective in oxidation and ammoxidation of different organic compounds. Activity of these catalysts have been associated with the presence of various surface vanadium species.

In the present study we report the effect of chemical nature, in particular acid-base characteristics, of additives on the catalytic properties of V-Ti-O catalysts in methylpyrazine (MP) ammoxidation.

We have studied samples of the composition 20 V_2O_5 - (80-n) TiO_2 - n AxOy, where n=1, 3, 5, 10, 15 % mas. Additives of acidic (Mo, W, Sb, P) and basic (Na, K) nature were used.

The samples were prepared by mixing aqueous solutions of vanadium and promoters salts with titanium dioxide followed by drying at 100°C and calcination at 500°C.

Catalytic activity was determined in a flow setup with a chromatographic analysis of the reagents. Experiments were carried out in wide temperature interval (220-400°C) in the reaction mixture of the composition (% vol.): 1-1.5 MP - 7-8 O_2 - 15-17 NH_3 - 15-17 H_2O, the rest being N_2.

Selective products obtained were amidopyrazine (AP) - the main one, and cyanopyrazine (CP) to a small extent. Pyrazine (P) and carbon oxides were by-products.

Rather weak organic base - methylpyrazine converts also to weak bases - AP and CP during ammoxidation reaction. The change of the surface acid-base properties modifying catalysts by various dopants of different electronegativity enables one to vary the composition and stability of intermediates and therefore to affect the catalytic activity and selectivity.

Actually, the introduction of alkaline dopants (Na, K) is accompanied by a decrease of activity, which is the greater, the higher the additive content. Selectivity to AP changes in a similar manner. It is believed that incorporation of such dopants results in poisoning of acidic centres and decreasing of the amount of active centres.

Modification of V-Ti-O catalyst by acidic dopants (Mo, W, Sb, P) leads to increase both of activity and of selectivty to AP and CP and hence to its yield grows. Notice that the dependence of the catalytic properties (the 1st order constant of the total MP conversion and yield to AP+CP) has extremum when W and Sb are introduced. The optimum contents of these dopants are 3% for Sb_2O_5 and 5% for WO_3. The constants and yields for V-Ti-P and V-Ti-Mo catalysts gradually rise when content of the dopants is increased. In this case positive effect of acidic promotors on the activity and yield to AP+CP increases in a following rows W < P < Sb < Mo and Sb ~ P < W < Mo, respectivly.

Table presents the data for the samples with optimum (acidic dopants) or minimum (alkaline ones) content of the promoters. We use $\gamma_{r^{n+}} = I_n / r^{n+}$ [1], where I_n - ionization potential, r^{n+} - orbital radius of the corresponding cation, as energy characteristic of acid-base properties.

A_xO_y content, % mas.	A / V, atomic ratio	$K^1\ 10^6$ mol/m^2 s (T = 300°C)	Yield, %		$\gamma_{r^{n+}}$	
			AP	AP+CP		
	0	1.7	47.8	59.4	V^{5+}	- 153.8
					V^{4+}	- 112.0
1 K_2O	0.09	1.3	34.7	56.7	K^+	- 7.3
1 Na_2O	0.14	1.6	33.9	54.5	Na^+	- 18.5
5 WO_3	0.10	1.8	52.2	67.4	W^{6+}	- 107.0
5 MoO_3	0.16	2.6	53.1	71.9	Mo^{6+}	- 123.6
3 Sb_2O_5	0.14	2.4	49.4	64.5	Sb^{5+}	- 145.7
5 P_2O_5	0.19	2.2	50.8	64.0	P^{5+}	- 361.2

It seems likely that unmonotonic character of the dependences of the catalytic properties on acid-base ones (see $\gamma_{r^{n+}}$ in table) and on dopants content is due to the requirement of the optimum acidic strength of the active centres.

Thus, data obtained reflect the influence of acid-base properties on the behaviour of V-Ti catalysts in MP ammoxidation.

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CATALYTIC OXIDATION OF METHANOL FOR FORMALDEHYDE

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Partial pressure of methanol is the main commercial way of formaldegyde production. The method is accomplished on silver catalysts. We carried out various investigations directed to the elaboration of catalysts with low silver content. The difficulty of solving the problem consisted in stabilization of the initial structure with a fine dispersion of silver on support surface during a long catalyst on-stream time. Small silver crystals form big agglomerates at temperatures 873-973 K and bare the surface.

To prevent the agglomeration we carried on the catalyst modification with system of oxides of III and IV groups p-elements. Catalysts were prepared by means of the soak of catalyst grains with the mixture of chemical compounds. This mixture is able to form the particles of metal silver and the particles of thermal resistance oxides. Thermal resistant oxides play a role of mechanical barriers, which prevent silver"slipping down" and improve silver catalytic properties because of the effect of strong metal-oxide interaction. Silver quantity in the catalyst was 10-15%.

Kinetic investigations on silver catalysts in a wide range of technological parameters were fulfilled. Some of the obtained results are shown in the table.

Temperature in the catalyst layer, K	O_2 conversion efficiency	CH_3OH conversion efficiency	selectivity as for CH_2O	CH_2O yield	composition of exit gases			
					H_2	CO_2	O_2	CO
753	91,5	62,4	91,2	56,9	16,7	3,8	2,1	0
773	92,2	65,0	91,9	59,7	17,2	3,6	1,8	0
803	92,4	67,6	92,2	62,3	17,4	3,5	1,6	0
833	93,3	69,5	92,5	64,3	17,7	3,4	1,4	0,1
863	93,4	71,4	92,7	66,2	17,8	3,3	1,3	0,2

The analysis of the data obtained showed high activity and selectivity of the designed catalyst.

As for the process mechanism, the investigations showed that formaldehyde formation proceeds in two directions: oxidation and dehydrogenation of methanol. Formaldehyde portion, which is formed by dehydrogenation reaction, is nearly 70%. This allows to increase the mole ration of oxygen to methanol without increasing the process temperature because the reaction of dehydrogenation is endothermal and doesn't require the heat expenditures. The processes of heat and mass transfer are the limiting stages of the reaction. External diffusion brake action improves the process selectivity as for formaldehyde. However, if the exchange coefficients between gas flow components and catalyst surface are insignificant, the following phenomena happen: the accumulation of formaldehyde on the surface through slow rate of its desorption: the interaction with adsorbed oxygen resulting in formation of carbon dioxide or its decomposition down to carbon monoxide.

The following basis of stichiometrical routes was chosen for the process description.

$$CH_3OH + 0{,}5O_2 \xrightarrow{K1} CH_2O + H_2O$$
$$CH_3OH \xrightarrow{K2} CH_2O + H_2$$
$$H_2 + 0{,}5O_2 \xrightarrow{K3} H_2O$$
$$CH_2 \xrightarrow{K4} CO + H_2$$
$$CH_2O + O_2 \xrightarrow{K5} CO_2 + H_2O$$

The kinetic model obtained has the following view:

$$W_{CH_3OH} = -K_1 C^{0,5}_{CH_3OH} C_{O_2} - K_2 C_{CH_3OH} \qquad (1)$$

$$W_{CH_2O} = K_1 C^{0,5}_{CH_3OH} C_{O_2} + K_2 C_{CH_3OH} - K_4 C_{CH_2O} - K_5 C_{CH_2O} \qquad (2)$$

The solution of afore-cited system of equations allowed to find the rate constants K_1-K_5 according with the above mentioned routes; to determine the process rates; to calculate the conditions of commercial trials.

The designed catalyst underwent industrial trials during one year and indicated high activity, selectivity and thermal stability. One of the main advantages of the designed catalyst consists in increase in the productivity by 5-10% due to higher dehydrogenative ability as compared with the productivity of the catalysts already in use in the chemical industry.

PPI-82

THE MECHANISM OF LOW TEMPERATURE CO OXIDATION ON Pt(100) SURFACE.

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In his work dedicated to the chain catalysis theory prof. G.K.Boreskov has repeatedly considered the possibility of accumulation of the reaction free energy on exited intermediate species or local sites on the catalyst surface. It was concluded that these phenomena can be observed only for highly exothermal reactions as side-effects, not being a basic mechanism of catalysis by solids [1]. Nevertheless, such a phenomenon has been found for CO oxidation on platinum. The oxygen adsorption on Pt is known to proceed through the sequence of different adsorbed states: $O_2 \rightarrow O_2^- \rightarrow O_2^{2-} \rightarrow O^- \rightarrow O^{2-}$. It has appeared that molecular oxygen dissociation on a platinum surface results in formation of exited "hot"oxygen adatoms, highly active in oxidation of adsorbed CO molecules [2].

The object of the present work is to study the reactivity of "hot" oxygen adatoms in low temperature CO oxidation on Pt(100) surface by methods of high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS).

According to HREELS data, at 90K O_2 adsorption on reconstructed Pt(100)-hex surface results in formation of molecular peroxide O_{2ads}^{2-} state with bond axis parallel to the surface and characterized by ν(OO) band at 900cm^{-1}, Fig.1a. Molecular oxygen is stable below 120K and is entirely desorbed at 140K. The molecular CO adsorption on Pt(100)-hex occurs in an on-top state and is characterized by ν(Pt-CO) bands at 450 см$^{-1}$ and ν(CO) at 2120 см$^{-1}$, Fig.1a. CO is known to coordinate via carbon atom with its axis parallel to the surface normal. Opposite to Pt(100)-hex, the heating of the molecular oxygen layer on Pt(100)-1x1 surface from 90K up to 200K is accompanied by dissociation of O_{2ads}^{2-} state with formation of oxygen adatoms O_{ads}, characterized by ν(Pt-O) band at 500 cm^{-1}. According to TDS data, simultaneously with dissocation a partial O_2 desorption occurs at 160 K.

We have found that interaction of atomic oxygen layer O_{ads} with CO_{ads} on the Pt(100)-1x1 surface is accompanied by formation of two high-temperature CO_2 peaks: at 280K and at 360K. The interaction of CO_{ads} with molecular peroxide O_{2ads}^{2} state on the Pt(100)-1x1 as well as the Pt(100)-hex surfaces additionally produces low temperature CO_2 desorption peaks at 140K and 190K, Fig.1b. The low-temperature (<200 K) CO_2 evolution is suggested to follow the reaction between CO_{ads} molecule and "hot" oxygen adatom generated during O_{2ads}^{2-} dissociation.

Different properties of Pt(100)-hex and 1x1 surfaces in O_2 molecules dissociation accompanied by the "hot" O adatoms generation may lead to a new understanding of mechanism of self- consistent oscillations in CO + O_2 reaction on this surface.

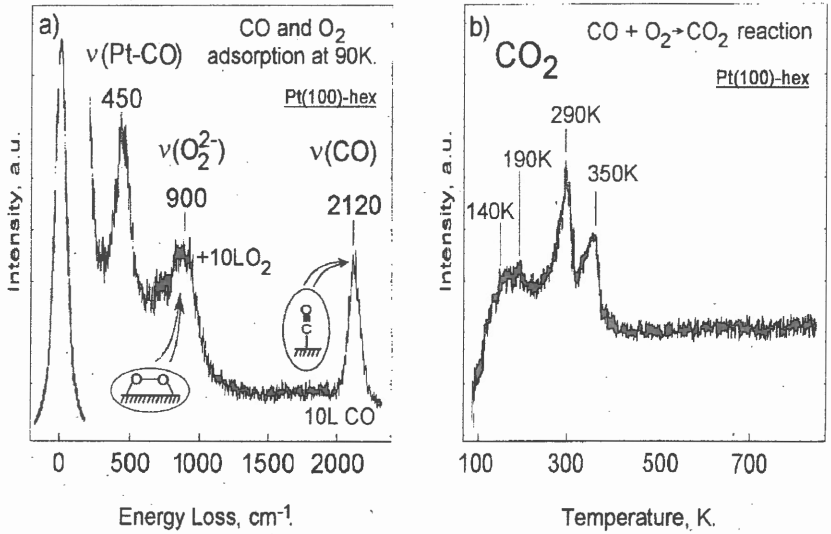

Fig. 1 Low temperature CO and O_2 adsorption (a) and reactive CO_2 desorption in the course of CO_{ads} + O_{2ads} reaction (b) on a Pt (100) -hex surface.

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Acknowledgements

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PPI-83

The Effect of Reaction Medium on the Catalysts of the Ethylene Oxidative Chlorination

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It was found that, when the catalyst support chemically interacts with the salt system, the formation of copper chloride catalysts of the ethylene oxidative chlorination during the catalyst preparation defines the chemical composition, the aggregation state of salt phases, and the distribution of the salt component on the surface.

The formation of the catalytic system is completed under conditions of the real process, while one of the critical factors is the composition of the reaction medium.

These facts forced us to study the changes of the catalytic systems of oxidative chlorination in the reaction medium and basic technological parameters of the process under conditions of small and great values of HCl/C_2H_4 ratio.

The samples of catalysts CatI, CatII, and CatIII were similar in their texture, fractional composition and copper content, but differed in the phase composition of the catalyst support (SupI is γ-Al_2O_3 and θ-Al_2O_3, SupII is mostly θ-Al_2O_3, SupIII is mostly γ-Al_2O_3). These catalysts were studied by the adsorption methods, differential thermal analysis and X-ray phase analysis at the initial state and after the action of the reaction medium. The study of technological parameters was performed on a laboratory-scale fluidized bed reactor. The catalyst activity and selectivity were measured.

Initial catalysts were different in the composition of salt phases and their distribution. The CatI sample included several copper-containing phases: $CuCl_2$, copper aluminates, CuO. The major portion of the salt component was copper hydroxychlorides $Cu_2(OH)_3Cl$ and $Cu_{3,0-3,2}Cl_4(OH)_{2,0-2,2} \cdot 2H_2O$, which were excessive in the sense of interaction with the surface of phases. Copper chloride $CuCl_2$ is considered as impurity against the background of these hydroxychlorides.

In the CatII sample, the salt component is highly dispersed. The distribution of copper-containing phases, which was characterized by the distribution of surface areas according to the heats of HCl adsorption, is distinctive in the considerable portion of the surface on which copper (in the aluminate form) is incorporated in the lattice of the catalyst support. The portion of the surface that is free from salt phases therewith noticeably increases. A portion of the salt component exists as irregular several-layer weakly-crystallized phases joined with the surface.

The CatIII sample does not contain the CuO phase. Besides the hydroxychloride $Cu_2(OH)_3Cl$, the following phases are formed: $Cu(OH,Cl)_2 \cdot 2H_2O$ and $AlCl_3 \cdot 4Al(OH)_3 \cdot 4H_2O$ and $Al_{11}(OH)_{30}Cl$ (the products of the support chlorination, aluminum hydroxychlorides, the formation of which agrees well with the noticeable amorphic nature of SupIII).

The difference in the catalyst structures defines the difference in their behavior in the ethylene oxychlorination reaction. When the process is conducted so as the HCl/C_2H_2 ratio is high (ethylene is in 2–3% excess), the conversion of reagents over CatII is greater than those over CatI and CatIII. In the case of CatI and CatIII catalysts, the agglomeration of particles is observed, which leads to the disrupture of fluidized bed hydrodynamics, the decrease of the catalyst activity; and the intensification of the process of sweeping the catalyst away from the reactor. In the presence of CatII, the similar effect is not observed within the entire range of HCl/C_2H_2 variations, including the case when HCl is in excess.

The reaction medium causes reorganization of the catalysts, which in turn causes the changes in the salt component and acid-base sites of the support. The "amorphization" of the salt component is observed. When the HCl/C_2H_2 ratio is high, the salt components of samples have spatial microstructures with long-range defects and chlorine-copper anionic sublattice, which is similar to those in the phase systems of $KCuCl_3$ and K_2CuCl_4. Whereas copper of CatII is stabilized in the bivalent state, samples of CatI and CatIII contain excess Cu^+ that forms the nonstoichiometric complexes with a reaction water, $HCuCl_2 \cdot 0.5H_2O$. The melting point of this complex is low, and this favors the agglomeration of particles and the disrupture of fluidized bed hydrodynamics.

Under the conditions of excess ethylene and low HCl/C_2H_2 ratio, part of Cu^{2+} is reduced to Cu^+. The salt component changes to the $CuCl–CuCl_2$ system, which is characteristic of all samples.

Our studies showed that the decrease of the HCl/C_2H_2 ratio results in the increasing yield of the deep oxidation byproducts (CO and CO_2). In the case of CatII, this effect is less pronounced because the copper-containing center Cu^+ reduced by ethylene can be an active site of dichloroethane oxidation in the presence of adsorbed oxygen. The concurrent chemisorption of HCl and dichloroethane on aprotic centers of the support surface also favors the reaction.

PPI-84

MECHANISM OF NEW CATALYTIC PROCESSES WITH PARTICIPATION OF CO_2 AND NORBORNA-2,5-DIENE

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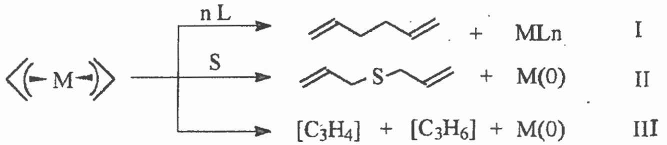
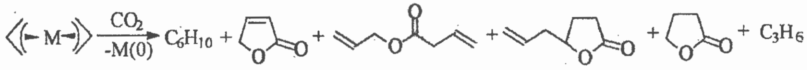
Numerous reactions of homoligand η^3-allyl transition metal complexes may be considered to proceed by one of the three possible directions: recombination of allyl ligands (I), ligand coupling combined with substrate insertion(II), and allyl ligand disproportionation(III). The mechanism of reaction III is relatively little-studied.



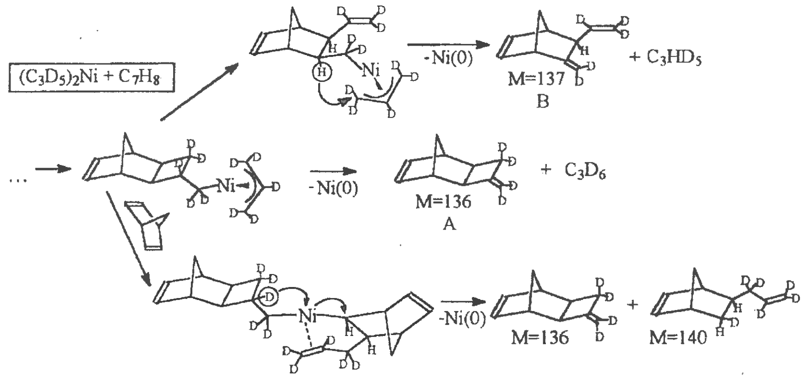
The reaction of these complexes with CO_2 was found to proceed via all above-mentioned directions giving rise to the mixture of products:



In the case of nickel complexes the ratio in which products are formed depends on the charge of the metal center. X-ray photoelectron spectroscopic data and results of theoretical calculations for the complexes studied are summarised in the table.

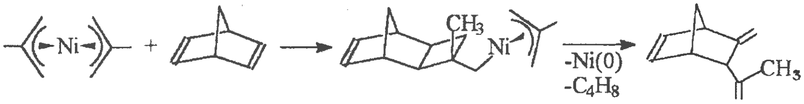
COMPLEX	Yield, %			$Ni2p_{3/2}$, eV	q Ni	q Ni_{calc}
	I	II	III			
$Ni(1\text{-}CH_3C_3H_4)_2$	92	-	8	854.1	0.32	-
$Ni(C_3H_5)_2$	58	-	42	854.4	0.49	0.66
$Ni(2\text{-}CH_3C_3H_4)_2$	2	88	10	855.2	0.92	1.07

Disproportionation of allyl ligands becomes the only direction in the reaction of η^3-allyl complexes with 2,5-norbornadiene [1,2]. It is observed for many metal centers (Fe, Co, Ni, Rh, Pd, Pt) and allyl ligands of various structure [3]. Kinetic and spectroscopic studies as well as modeling of separate stages in this reaction enabled us to propose the mechanism which involves η^3-η^1-isomerization of the allyl ligand, substrate insertion into η^1-All-M-bond, cyclization, C-C-bond cleavage, and β-hydride shift. The latter stage is the key and evidently rate-limiting process and was investigated more carefully using deuterium-substituted reagents $(C_3D_5)_2Ni$ + C_7H_8 (scheme) and $(C_3H_5)_2Ni$ + C_7D_8.



In various substrates hydride transfer can occur either from allyl ligand (with the formation of product A) or from the NBD molecule (forming product B).

Formation of the only product in the case of $(2\text{-}CH_3\text{-}C_3H_4)_2Ni$ also supports this mechanism:



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Acknowledgements

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PPI-85

HETEROGENEOUS CATALYTIC REDUCTION OF ALIPHATIC CHLORIDES BY CHLOROALANES ETHEREATES

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It was previously shown that liquid chloroalane ethereates in the presence of crystallic aluminium chloride reduced to a great extent aliphatic chlorides at temperatures of 20-60°C [1,2]. General equation of catalytic reduction process of alkylchlorides is as follows.

$$AlH_nCl_{3-n}O(C_2H_5)_2 + RCl \longrightarrow AlH_nCl_{4-n}O(C_2H_5)_2 + RH.$$

To clear up a mechanism of reactions the special investigations were carried out in which aliphatic chloride-chloroalane ratio was varied, composition of chloroalane was changed, rates of isotope exchange of chlorine labelled by chlorine-36 isotope in the system were determined.

Obtained experimental data demonstrate that autocatalytic character of kinetic curves of reduction reaction and chlorine exchange in $AlH_nCl_{3-n}O(C_2H_5)_2 - AlCl_{3(cr.)} - RCl$ is determined by catalyst activity increase. Process kinetics is complicated by different factors: catalyst dissolving; change in hydrogen-chlorine ratio on its surface as reaction proceeds; change of concentrations of chloroalane, sorbing onto catalyst. Comparison of reduction rates of aliphatic chlorides allows to arrange them in the following series of chlorine mobility at reduction and depending on the structure:

$$C_2H_5Cl > CCl_4 > 1,2\text{-}C_2H_4Cl_2, CHCl_3.$$

Dichloroethane is reduced more quickly than chloroform at temperature over 40°C and more slowly at temperature below above temperature. Since ethyl chloride is reduced faster than dichloroethane it becomes evident that dichloroethane reduction product is ethane but not ethyl chloride. Chlorine of such a strong coordinately saturated compound as aluminium chloride ethereate does not enter into homogeneous exchange with chlorine of aliphatic chlorides. However such a chlorine exchange proceeds rather rapidly in the presence of crystallic aluminium chloride. Kinetics of

isotope exchange in $AlCl_3 \cdot O(C_2H_5)_2 - AlCl_{3(cr.)} - RCl$ system has been studied over temperature range $0-80^0$C. In regard to structure of aliphatic chloride a rate constant is within $0.7-86.10^{-4}$, sec^{-1} range, and activation energy within 83-107 kJ/mol. A row series of chlorine mobility for exchange reaction is as follows:
$C_2H_5Cl > CCl_4 > CHCl_3 > 1,2C_2H_4Cl_2 > C_2HCl_5 > 1,1,2,2\ C_2H_2Cl_4$.
The identity of chlorine mobility row in reactions of chlorine exchange and its reduction suggests that mechanism of limiting stage of reduction - is a ionization replacement.
A scheme of exchange may be presented in the following manner. At the first stage dynamic equilibrium is reached upon hydrogen between solution volume and catalyst surface:
$Al_nCl_{3-n}O(C_2H_5)_2 + AlCl_{3(sur)} = Al_{n-1}Cl_{4-1}O(C_2H_5)_2 + AlHCl_{2(sur)}$
Equilibrium constant of the first stage is likely more than one. i.e. hydrogen is predominantly concentrated onto the surface of crystallic aluminium chloride. Chlorine replacement by hydrogen on catalyst surface as well as a possible chloroalane ethereates sorption decreases the catalytic activity in comparison with crystallic aluminium chloride. However the catalyst proved to be sufficiently active for disruption or strong polarization of chlorine-carbon bond in aliphatic chloride at the second limiting stage $RCl \dashrightarrow R^+Cl^-$. Further carbocation or polarized transient complex interacts with hydride-ion but chlorine-ion is bonded with aluminium.

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PPI-86

Catalytic synthesis of aliphatic nitriles

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Investigations aimed at development of new syntheses based on C_1-chemistry are notably promising. The homologisation reactions of alcohols, benzene, pyridine and methylamine with the syngas are known. We showed that aliphatic nitriles (acetonitrile, propionitrile) reacted with the syngas with formation a homologue containing one more C-atom than the initial nitrile:

$$CH_3CN + CO + H_2 \longrightarrow C_2H_5CN$$
$$C_2H_5CN + CO + H_2 \longrightarrow C_3H_7CN$$

We used M/γ-Al_2O_3 catalysts where M=Zn, Mn, Fe, Ag, Cu, Co, Cr, Mo, W. In their presence propionitrile was obtained at 350-400°C, 1 atm, space velocity of 100 h^{-1} from the mixture containing CO - 71.0 vol.%, H_2 - 30.5, CH_3CN - 8.5. Conversion of CO (K_{CO}) was 5-14%. Formation of CH_4 and CO_2 along with the main product was observed. No propionitrile formed on Cr/γ-Al_2O_3 catalyst with the use of the gas mixture containing 8.5% of CH_3CN in argon or hydrogen. A decrease in acetonitrile conversion with increasing synthesis temperature was observed for all the catalysts used. K_{CO} amounted to the highest values at a temperature of 425-475°C. The largest yield of propionitrile was achieved in the same temperature range.

Methanol reacts with nitriles in a similar manner to the CO/H_2 mixture. We performed the synthesis of propionitrile and acrylonitrile from acetonitrile and methanol in the presence of zeolite catalysts with supported salt Cs_2CO_3/NaY (400-450°C, 1 atm):

$$CH_3CN + CH_3OH \longrightarrow C_2H_5CN + C_2H_3CN$$

The detailed investigation of catalytic properties of NaY-type zeolites promoted with additives of alkali metals showed that both nature of salt of alkali metal and its content in the contact affected activity and selectivity of the catalysts (see the Table). Selectivity of the process does not change essentially: propionitrile whose yield in the optimal conditions (450°C, space velocity of 1 h^{-1}, CH_3CN:CH_3OH=1:2 mol.) amounted to 20% (against initial acetonitrile) is dominant product of the synthesis.

Table

Influence of catalyst nature on nitrile yield (450°C, CH_3CN:CH_3OH=1:2 (mol.), space velocity of 1 h^{-1})

Catalyst	Cs:Na (atom.)	Yield against CH_3CN, %	
		C_2H_5CN	C_2H_3CN
Cs_2CO_3/NaY	0.3	7.7	—
Cs_2CO_3/NaY	0.6	17.6	2.8
Cs_2CO_3/NaY	1.0	20.7	—
Cs_3PO_4/NaY	0.6	3.6	0.9
K_2CO_3/NaY	1.0	9.0	3.3
Na_2CO_3/NaY	1.0	9.3	—

Activity of CsY zeolites prepared by ion exchange method in ethylbenzene and styrene synthesis from toluene and methanol was shown. The comparison of our results with the data obtained by ion-exchanged Cs forms of Y zeolites testifies comparable activity of the catalysts in the similar conditions of performing both processes (space velocity, temperature). Taking into account the similarity of the reactions and the catalysts, one can conclude that these processes have similar mechanisms. It was assumed that the synthesis of ethylbenzene and styrene from toluene and methanol proceeded through an intermediate stage of forming formaldehyde which reacted with toluene with formation of styrene. It can be assumed that an oxygen-containing intermediate which takes part in the propionitrile and acrylonitrile synthesis is formed in our case also.

PPI-87

Influence of gas additives on the hydrocarbon synthesis from CO and H_2

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The hydrocarbon synthesis from CO and H_2 is a promising industrially important process to produce motor fuel components and valuable chemical compounds from non-oil feed (coal, natural gas, organic wastes, *etc.*). The syngas obtained from these sources contains usually gas admixtures (CO_2, N_2, CH_4). Their percentage affected by a feed used and technique of its treatment may amount to 50% in some cases. The influence of these components in the syngas on the hydrocarbon synthesis from CO and H_2 has been investigated.

Tests were carried out in a flow catalytic unit provided with a fixed-bed reactor with Co-catalyst. The synthesis conditions were: 0.1 MPa, 160-230°C, $H_2/CO=2$, 100 h^{-1}. The concentration of gas additives was 0-50 mol.%.

The following transformations can occur during the hydrocarbon synthesis from CO and H_2:

$CO + H_2 \leftrightarrow [-CH_2-] + H_2O$
$CO + H_2 \leftrightarrow [-CH_2-] + CO_2$
$CO_2 + H_2 \leftrightarrow [-CH_2-] + H_2O$
$CO + H_2O \leftrightarrow CO_2 + H_2$ (WGS reaction)
$2CO \leftrightarrow C + CO_2$ (Boudouard-Bell reaction)

CO and CO_2 can take part in these reactions as either reactants or products. Thus, conversion of CO or CO_2 evaluated in conventional manner does not reflect its true value. For example, the total conversion of CO_2 may be zero or even negative if carbon dioxide participates in the three reactions from the above ones.

We found that on Co-catalysts only methane is formed from CO and H_2 at 0.1 MPa and a small amount of light hydrocarbons is synthesized under elevated pressure.

It was demonstrated that over the temperature range of a Fischer-Tropsch synthesis (150-250°C) the water gas equilibrium shifts to the right and the WGS reaction affects significantly the hydrocarbon synthesis from CO and H_2.

It was found that an increase in concentration of CH_4, N_2 or CO_2 in the stoichiometric feed mixture $CO+H_2$ leads to a decrease in specific activity of Co-catalysts. Yields of all hydrocarbon products fall with content of CO and H_2 in the feed because of the dilution. More detailed consideration of the data obtained, however, allows to reveal some distinctions between the effects of these gases on the hydrocarbon synthesis.

Thus, liquid hydrocarbon yield under addition of CO_2 and CH_4 to the syngas falls with increasing concentration of these gases to a greater extent than this would result from the decrease in the part of "pure" syngas. This testifies to catalyst inhibition by these gases. When CO_2 concentration is above 50%, however, an increase in hydrocarbon yield is observed. This fact can not be explained by direct participation of CO_2 in the formation of these products and is caused, probably, by CO_2 incorporation in side reactions.

A high percentage of nitrogen (up to 50%) in the feed gas does not affect specific activity of the catalyst. When using this gas, a decrease in liquid hydrocarbon yield occurs to a noticeably lesser extent than that caused by the dilution. Thus, liquid hydrocarbon yield converted from "pure" syngas increases with N_2 content in the feed. The influence of N_2 was suggested to be due to blocking of a part of the catalytic surface.

Therefore, the presence of a significant amount of carbon dioxide, nitrogen or methane in the feed syngas affects the hydrocarbon synthesis from CO and H_2. The presence of carbon dioxide lowers the probability of side reactions of CO. Nitrogen favors polymerization processes. The presence of methane deactivates the catalyst.

PPI-88

HYDROGEN TRANSFER FROM ALIPHATIC ALCOHOLS AS A SOURCE OF HYDROGEN FOR CATALYTIC HYDRODECHLORINATION OF ORGANIC CHLORIDES

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Chemical remediation of chlorinated hydrocarbons waste, both at the source and in the environment, is an ongoing and pressing problem. Hydrodechlorination (HDC) of organic chlorides is now the object of great scientific interest due to the possibility to solve this environmental problem[1].

In this study HDC of chlorobenzene, 1,2-dichlorobenzene, 1,3,5-trichlorbenzene, pentachlorphenol, polychlorinated biphenyles (PCBs) proceed in the presence of Ni or Pd containing impregnated catalysts and aliphatic alcohols as a hydrogen source under 300-350°C. HDC can proceed completely (chlorobenzene, o-dichlorobenzene, 1,3,5-trichlorbenzene) or partially (pentachlorphenol, polychlorinated biphenyles). The alcohols used were methanol, ethanol, propanol-2 or tret-butanol. All of them were appropriate for this reaction, but for tret-butanol the better temperature range was 350-380°C. The mechanism of the reaction can include the catalytic decomposition of alcohols and then the participation of decomposition products (H_2, CO) in HDC, as well as the direct substitution of Cl in organic chloride by the hydrogen from alcohol. The data obtained don't permit to exclude any of these two possibilities.

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PPI-89

CATALYTIC CONVERSION OF LOW ALKANETHIOLS INTO DIALKYL SULFIDES

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Hydrocarbon feedstock of some gas-condensate oil-field contains substantial amounts of low alkanethiols that are toxic and corroding substances. Today they find no practical use, when isolated from gases by various methods.

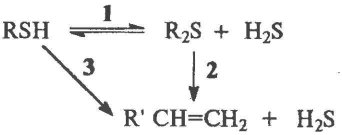
In the present work we studied the regularities of catalytic conversions of alkanethiols RSH (R = C_1-C_3) both in the presence of alkylating agents and in the inert medium. A new process based on these reactions allows simultaneous purification of thiole-containing gases and production of dialkyl sulfides. Runs were performed in a flow setup, charged with acidic catalysts, under atmospheric pressure, and at temperatures ranging from 200 to 500°C.

At T > 200°C, alkanethiols appear to disproportionate into dialkyl sulfides and hydrogen sulfide on the catalysts of various composition:

$$2\ CH_3SH \rightleftharpoons (CH_3)_2S + H_2S$$

When the catalysts contain proton sites (SiO_2, H_3PO_4/SiO_2, AlSi, HNaY, silicotungstic acid supported on SiO_2), disproportionation goes at a low rate and selectivity. On catalysts with paired acidic-basic sites, namely Al_2O_3 modified with acidic additions, reaction rate is two orders of magnitude higher.

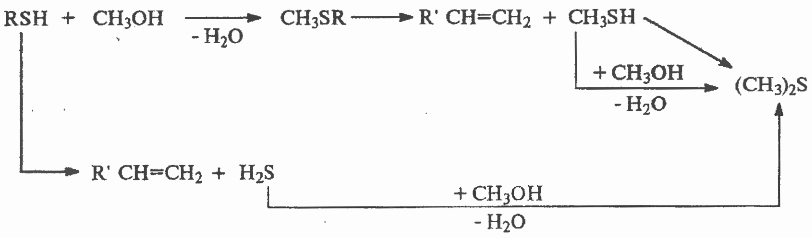
For alumina catalysts, methanethiol converts quantitatively into dimethyl sulfide, while the proportionation of its homologue is less selective, especially at a high alkanethiol conversion. Our kinetic studies show, that the reaction with methanethiol homologues proceeds via the parallel-consecutive route:



where R = C_2H_5 or iso-C_3H_7; R' = H or CH_3. The decomposition of alkanethiol and dialkyl sulfide via routes 2 and 3 is considerably higher for propanethiol than for ethanethiol.

The reactivity of alkanethiols decreases in a row: iso-C_3H_7SH > C_2H_5SH > CH_3SH, while the selectivity towards dialkyl sulfide formation changes reversely.

In the presence of alkylating agents, such as methanol, the isolated hydrogen sulfide is completely bound owing to the following reactions:



Taking into account the properties of reactants and catalysts, kinetic and adsorption data, we have postulated the mechanism of the alkanethiols conversion into dialkyl sulfides. The dissociative chemisorption of alkanethiol and methanol governs the formation of alkoxide groups, which reacting with alkanethiol and hydrogen sulfide, activated on the basic sites, produce dialkyl sulfide. Alkanethiol and dialkyl sulfide are dissociatively chemisorbed producing alkylthio-groups, bound through a sulfur atom with the acidic site and through a β hydrogen atom with the basic site. This yields decomposition accompanied by the alkene elimination.

For the conversion of alkanethiols mixture, the rate of total conversion of alkanethiols decreases slightly owing to their competitive adsorption on the catalyst surface, while the selectivity towards dialkyl sulfides does not change. Hydrocarbons do not affect reaction indexes. This allows the processing of thiol containing gases. Under particular conditions, alkanethiols and hydrogen sulfide are completely converted into dialkyl sulfides on the catalyst designed. Sulfide mixtures, isolated from hydrocarbons, can serve as odorant, extracting agent, flotation reagent and as the feedstock for preparing various biologically active materials.

PHENOL CATALYTIC OXIDATION DURING ACTIVATED CARBON REGENERATION

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Adsorption of dilute pollutants on activated carbon (AC) followed by catalytic decomposition over impregnated catalyst [1, 2] is emerging technology, alternative to thermal regeneration of spent AC. The advantages of this new method are: (a) The process will be accelerated by the high concentrations of pollutants eluted from the adsorbate; (b) A large number of adsorption-regeneration cycles are expected to proceed without loss in capacity; (c) The low temperature regeneration will be conducted in-situ, even in small units [1]. This process is intended to replace the common method of AC thermal regeneration, that is economically feasible only for large systems that use more than 200,000 kg AC per year [3].

The aim of our work was to study the oxidation of adsorbed phenol, as prominent toxic pollutant, during processes, in which spent AC undergo thermal and catalytic regeneration. The catalytic regeneration tests of spent AC have been performed on both the chaste and impregnated granular AC Filtrasorb-400 with mixture of copper (II), iron (III) oxides and additivities of chromium (III) oxide or inert silica. A primary reason of catalytic activity of iron (III) oxides is high dispersity of impregnated catalyst crystallites. The mechanisms of oxidation of phenol, oxidative activation of carbon surface and development of impregnated catalysts during AC regeneration are dealt. The possible conjugation of these processes is suggested.

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PPI-91

ADVANCES IN CATALYTIC SYNTHESIS OF K AND E GROUP VITAMINS

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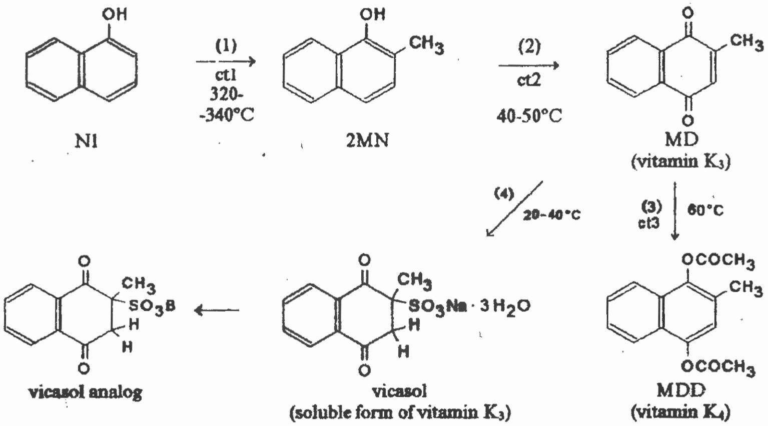
The manufacture of K-and E vitamins is a significant branch of fine organic synthesis. The conventional technologies of their synthesis based on non-catalytic reactions are harmful to environment and not feasible.

As a base of new VIKASIB technology for K-vitamins production we proposed a series of novel catalysts and catalytic reactions from 1-naphthol (N1) as available raw material:

Scheme 1. "VIKASIB" TECHNOLOGY REACTIONS :



For methylation of N1 to 2MN by CH_3OH in reaction (1) we used the heterogeneous catalyst (ct1) that is a mixture of Fe_2O_3, V_2O_4 and some other oxides [1]. Selectivity of reaction (1) is more than 85%. By-product is 2,4-dimethyl-1-naphthol (24DMN) that also can be oxidated to MD in the reaction (2).

For oxidation of 2MN and 24DMN to MD in reaction (2) we developed new homogeneous catalysts (ct2) [2,3] that are aqueous solutions of Mo-V-phosphoric heteropoly acids $H_{3+n}PV_nMo_{12-n}O_{40}$ (HPA) or their acidic salts. The reaction (2) is carried out in a system of two immiscible phases. The aqueous phase contains the ct2; the organic phase contains 2MN and reaction products. Selectivity of the reaction (2) is 75-80%. Reoxidation of reduced forms of HPA by dioxygen is to be carried out in a separate reactor. A homogeneous modification of the reaction (2) involves one phase consisting from 2MN, catalyst ct2', and reaction products. It is carried in dioxygen atmosphere, and reduced forms of ct2' are regenerated by dioxygen in course of the reaction (2).

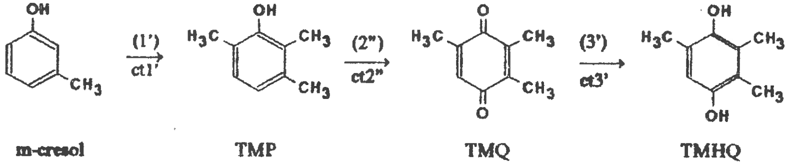
We developed new polyfunctional catalysts (ct3) for hydroacetylation of MD to MDD by dihydrogen and acetic anhydride in reaction (3) [4]. The catalyst for the reaction (3) is Pd supported on active carriers (TiO_2, ZrO_2 or Zr phosphate) that are stable to mixture of acetic anhydride and acetic acid. The yield of MDD is more than 90%.

Non-catalytic interaction of MDN with $NaHSO_3$ (4) leads to vicasol. [5]

The technology VIKASIB is friendly to environment. It was successfully tested in its separate parts on pilot plants. The prepared vicasol was successfully tested in poultry farms of Novosibisk and Altai regions.

The catalysts for the reactions (1) and (2) are suitable for preparation of methylated quinones of benzene series which are raw materias for E-vitamins synthesis. The catalyst ct1' can be used for methylation of m-cresol to 2,3,6-trimethylphenol (TMP). The heteropoly acid catalysts ct2" can be used also for TMP oxidation to 2,3,5-trimethyl-1,4-benzoquinone (TMQ). The last compound can be reduced to appropriate hydroquinone. The catalysts ct1' and ct2" and the appropriate reactions can be a background of new technology for E-vitamin synthesis [6].

Scheme 2. SOME REACTIONS OF VITAMIN E TECHNOLOGY:



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PPI-92

Photostimulated processes on alkaline-earth metal fluorides

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Last years in connection with the development of new technological branches the role of alkaline-earth metals fluorides has significantly increased.

However, MeF_2 surface properties were investigated to less extent than the properties of such typical adsorbents and catalysts as metals, semiconductors and dielectrics with small width of forbidden zone. Thus, the data about acid-base parameters of CaF_2, SrF_2, BaF_2 surfaces are practically absent. The number of works devoted to the consideration of simple gases molecules adsorption on fluorides is very small and the information about the proceeding of such processes under influence of radiation, which doesn′t cause irreverse change of substance, is completely absent.

Meanwhile the probability of irradiation stimulated processes is rather great, because the tendency to the increase of photosorption and photocatalytic activity of materials with the rise of forbidden zone width is known.

In present work metal fluorides industrial samples of different types were used: CaF_2 (KO-3) and “pure”, SrF_2 (“particularly pure”), BaF_2 (“pure”), MgF_2 (“pure, for hot pressing” and “pure, for optical ceramics”). Complex of investigation methods and analysis was applied.

As the result of realized investigations the photosorption of gases (O_2, H_2, CH_4, CO, CO_2) was found. Adsorption centres, which were created or stimulated by exposure of the samples to total light of mercury lamp, have both electron-acceptor and electrondonor properties, however, the acceptor molecules photosorption (O_2, CO_2) proceeds more actively. The identity of O_2 and CO_2 photosorption centres was shown.

Some peculiarities of photostimulated processes were found: the irreversibility and the saturation, kinetic dependencies, the existence of photostimulated post-adsorption on MgF_2 and BaF_2. The previous history of the sample has an influence on photosorption properties of fluorides, however, the main peculiarities of processes proceeding don't depend on the type of MeF_2.

On the basis of alkaline-earth metals and Mg fluorides properties investigation three spectral areas were selected, corresponding to the fundamental absorption, improper absorption and the absorption of pointed color centres.

Depending on the area of excitation the differencies in activity of radiation stimulated processes proceeding, in kinetics and thermodesorption spectra of adsorbed oxygen are observed.

The reactions of dark H_2 oxidation, H_2, CO photooxidation and CO_2 photolysis were discovered. On the basis of realized kinetics investigation the probable mechanism of H_2 photooxidation reaction was suggested. Oxygen photosorption is the essential stage of the process. In the limiting stage of the reaction the electron-exited states of photosorbed oxygen interact with molecular H_2 in gaseous phase, and they are deactivated by oxygen of gaseous phase.

PPI-93

HETEROGENEOUS MODIFICATION OF CATALYSTS FOR ALCOHOL SYNTHESIS - SELECTIVITY CONTROL

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Selectivity of industrial copper catalysts for methanol synthesis is high enough, however the yield of by-products increases appreciably due to some changes in composition of the feed or in the load. Components of catalysts involved perform several functions consisting in structure forming and speeding up certain stages of the catalytic reaction. Optimum conditions for the realisation of these elements are not the same in the given catalyst technology. It is possible to prepare separate parts of catalyst which influence favourably some of the reaction steps and then to mix them either in the form of powder or in granules of the size suitable for charging into the reactor.

This trend was approved for use of copper-zinc-aluminium and zinc-chrome catalysts for methanol and higher alcohol synthesis. In methanol synthesis carried out under laboratory conditions at normal pressure the selectivity of the process is monitored by the yield of methane. The latter sharply increases on CuO. ZnO.Al_2O_3 catalysts at temperatures above 300 ^{0}C, less methane is formed on copper-zinc catalysts where fine-dispersed zinc oxide acts as an active phase. Simultaneous charging of the catalysts involved makes it possible to upgrade the quality of the process, i.e. to reduce the yield of methane and to extend the temperature range of its stable operation, productivity of the system being kept in the level of copper catalysts. The effect observed is explained from the point of view of spillover of hydrogen being activated on zinc oxide.

High-dispersed zinc oxide may be obtained in the supported system $ZnO/CuO/Al_2O_3$ at low component concentration and calcination temperature, which results in some instability of alumina lattice and is accompanied by formation of surface aluminate. With the components properly selected, mechanical mixture of thus obtained supported and main catalysts improves the quality of the product, namely: under laboratory conditions the yield of methane decreases, reaction carried out under industrial pressure gives paraffin hydrocarbons in a low yield.

To synthesise the mixture of aliphatic alcohols the base composition of methanol catalysts both zinc-chrome and copper-containing ones is promoted by alkali metal compounds, potassium as a rule. One can improve low selectivity and stability of these systems by introducing potassium in the form of silicates

Table

Usage of heterogeneous modifying additives with
the base composition of industrial catalysts

N	Process	Mixture of Catalysts		Catalysts Modification Efficiency Modified / Base compos.	
		Base compos.	Modifying additive		
1	Methanol synthesis (P=5 MPa)	$CuO.ZnO.Al_2O_3$	$ZnO/CuO/Al_2O_3$	Methanol yield, h^{-1} 1.50/1.51	Paraffins C_{17+}, mas.% 0.005/0.025
2	Carbon oxides hydrogenation (P=0.1 MPa)	$CuO.ZnO.Al_2O_3$	$ZnO.CrO_3$	Methanol yield, h^{-1} 0.034/0.030	Methane yield, $10^3\ h^{-1}$ 0.18/0.53
3	Alcohols synthesis (P=20 MPa)	$ZnO.CrO_3$	$K_2O.SiO_2/Al_2O_3$	Alcohols C_{2+} yield, h^{-1} 0.11/0.04	Selectivity $C_4/\Sigma C_i$ 0.075/0.025

dispersed on separate carrier such as alumina. The mixture of the base composition of high-temperature zinc-chrome catalyst for methanol synthesis with modifying additive $K_2O.SiO_2/Al_2O_3$ causes the yield of higher alcohols to increase, especially that of isobutanol (Table).

Promoter efficiency depends on fractional composition of mixed components. Fine grinding of base catalyst mass and the modifier as well as liquid-phase mixing do not produce the desirable effect and results in lowering of system production, which is likely to account for overlapping of modifying additive active surface. In particular, the best results in inhibiting the reaction of paraffin hydrocarbons formation in the synthesis of methanol are achieved by using of a mixture of grains of industrial size.

When reducing mixed oxide systems,account is to be taken of changes both of the chemical reaction kinetic parameters and a granular layer thermophysical properties. This necessitates further studying of kinetics and modelling of process taking place in the industrial reactor.

Thus the mode of catalysts usage being under development makes it possible to solve a number of problems concerning the improvement of carbon oxides hydrogenation process selectivity.

PPI-94

Hydrogenation of phenylacethylene on the catalytic system $(NR)_2PdCl_4$ $+PPh_3+$ $Co(Acac)_3$

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We have obtained that the system $(NR_4)_2$ $PdCl_4$ + PPh_3 + $Co(Acac)_3$ (I) formed in the mixture of solvents $CHCl_3$ -H_2O or C_6H_6-H_2O exhibits a catalytic activity in the hydrogenation of phenylacetylene and styrene without reductant and activation with O_2.

The most typical results obtained under studies of catalytical activity of the system in the hydrogenation of styrene and phenylacetylene are presented in table.

Table

Homogeneous hydrogenation of phenylacetylene and styrene on the catalytic system I (solvent $CHCl_3$- H_2O [A] or C_6H_6- H_2O [B] , T= 25 C°,P_{H2} = 0,1 MPa)

nn	$C_{Pd+}\cdot 10^3$, mol/l	P/Pd	Co/Pd	τ_{ind},min	V_{specif}, mol H_2/mol Pd ·min	Solvent	Selectivity,%
1	30	1	3	40	0,15	A	94,6
2	30	0,5	3	0	1,0	A	90,0
3	30	1	6(Fe)	0	0,21	A	94,2
4	5	1	3	200	0,80	A	95,5
5	5	0,5	3	0	1,05	A	92,0
6	5	1	3	15	2,5	B	96,7
7	5	3(PBu_3)	10	28	6,7	A	styrene
8	10	1	3	0	1,02	A	94,3

As it is obvious from the results in table , the homogeneous hydrogenation of phenylacetylene occurs with selectivity 90-97% (at substrate conversion 90-99%) and the absorption rate of hydrogen during the induction period is 10-15 times lower than that during the constant action period.

By using IR- and UV-spectroscopy it has been shown that the transformation of initial palladium compounds to complexes activating molecular hydrogen proceeds according to following sequence :

$(NR_4)_2PdCl_4 + 2\,PPh_3 = (PPh_3)_2PdCl_2 + 2\,NR_4Cl$
$NR_4Cl = NR_3 + RCl$

$(NR_4)_2PdCl_4 + (PPh_3)_2PdCl_2 = [PPh_3PdCl_2]_2 + 2\,NR_4Cl$

$[PPh_3PdCl_2]_2 + 2\,NR_3 = 2\,PPh_3PdCl_2NR_3$

The complex $PPh_3PdCl_2NR_3$ is able to activate hydrogen by a heterolytic route . The presence of organopalladium Cl-Pd-$(PhC{=}CH)_n$Cl type polymers in the system along with palladium phosphine complexes is indicated by the appearance besides of absorption band at 1635 cm^{-1} characterising double bond of styrene, of bands at 1672 cm^{-1} (vibrations of -(RC=CH)-trans type bonds) and 1608 cm^{-1} (conjugated -$(RC{=}CH)_n$,where n >>2) in IR-spectrum as well as by the increasing of absorption intensity of the system in UV-spectrum and its shift to the low frequency field.

If has been proposed that the liberation of "Pd_{MET}" which has to be formed in the system under the condition of phosphine shortage is hindered by quarternary ionic salt ($Bu_3Bz\,N^+Cl^-$ or $BzPh_3P^+Cl^-$) which plays the role of stabilizing ligand.

Under the hydrogenation process, the reduction of Co(3+) to Co(2+) (which migrates to water layer) has to occur but the role of cobalt in catalyst formation still remains unclear.

This work is supported by Russian Foundation for Basic Researches (grant No. 96-03-33667a).

PPI-95

SELECTIVE OXIDATION OF METHANOL TO FORMALDEHYDE ON MIXED IRON-CHROMIUM, IRON-ALUMINIUM AND IRON-INDIUM MOLYBDATES

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Introduction: Multicomponent oxide systems based on Fe-Me-Mo-O (Me = Cr, Bi, Te, Co, etc) are active catalysts for partial oxidation of alcohols and hydrocarbons. Our studies and investigations of other authors have shown that addition of other components to the Fe(III) molybdate allows modification of some principal volume and surface properties of this compound, which affect directly its specific activity and selectivity in oxidation reactions.

The effect of a second metal ion ($Me^{3+} = Cr^{3+}, Al^{3+}, In^{3+}$) in the stoichiometric system $(FeMe^{3+})_2(MoO_4)_3$ on the specific activity and selectivity of the catalysts was investigated. In the same time studies on the reducibility of mixed molybdates by methanol vapours were performed in order to establish the stability and the oxygen reactivity of these compounds.

Experimental: Mixed $(FeMe^{3+})_2(MoO_4)_3$ were prepared by addition of required amounts of aqueous $Fe(NO_3)_3.9H_2O$ and $Me^{3+}(NO_3)_3.9H_2O$ to vigorously stirred aqueous $(NH_4)_6Mo_7O_{24}.4H_2O$ at room temperature, followed by evaporation, drying at 120°C and calcination at 700°C for 8 hours. The phase composition of the catalysts obtained was established by X-ray diffraction and the unit cell parameters were determined. The samples were characterized and by IR and Mössbauer spectroscopy. The catalytic activity was measured in a gradientless flow-circulation apparatus. The reduction process was investigated in a mixture of 4,0 vol.% CH_30H/Ar at a flow rate of 120 ml/min. Mössbauer measurements were carried out on the catalysts in order to study the bulk reduction at 400°C as a function of time.

Results and Discussion

Catalyst structures: The physicochemical characteristics of the mixed molybdates give the following information:

i. All investigated catalysts are of monophase composition.

ii. The mixed $(FeMe^{3+})_2(MoO_4)_3$ catalysts are isostructural (type P_1a, monoclinic structure).

Catalytic properties:

The following order of the catalytic activities of the mixed molybdates has been found:

$$(FeCr)_2(MoO_4)_3 > (FeIn)_2(MoO_4)_3 > (FeAl)_2(MoO_4)_3$$

Under extreme reaction conditions (400°C and 100 hours reaction time) $(FeAl)_2(MoO_4)_3$ shows stable activity, whereas the activity of $(FeCr)_2(MoO_4)_3$ decreases by about 15%. According to the experimental data the catalytic stabilities of the samples change in the sequence:

$$(FeAl)_2(MoO_4)_3 > (FeIn)_2(MoO_4)_3 > (FeCr)_2(MoO_4)_3$$

Reduction of the catalysts

In Fig. 1 the Mössbauer spectra of fresh and reduced $Fe_2(MoO_4)_3$ and $(FeMe^{3+})_2(MoO_4)_3$ are presented.

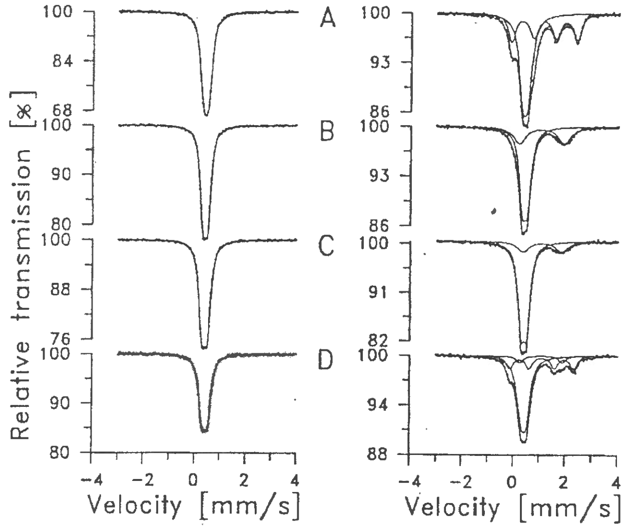

Fig. 1. Mössbauer spectra of the initial and reduced (t = 400°C, 35 min) catalysts: **A** -$(Fe)_2(MoO_4)_3$; **B**-$(FeCr)_2(MoO_4)_3$; **C**-$(FeAl)_2(MoO_4)_3$; **D**-$(FeIn)_2(MoO_4)_3$.

The principal conclusions on the influence of modifying trivalent metal ions on the catalyst composition could be proposed:

i. The pure $Fe_2(MoO_4)_3$ is reduced mainly to ß-$FeMoO_4$, while after reduction of some mixed molybdates (Me^{3+}=Cr and Al) an α- form of Fe(II) molybdates is observed. The $(FeIn)_2(MoO_4)_3$ catalyst has a long induction period under reduction conditions when a polymorphic transition from α - to ß-form of Fe(II) molybdate occurs.

ii. The presence of Cr^{3+}, In^{3+} and Al^{3+} ions influences the oxygen mobility in the $(FeMe^{3+})_2(MoO_4)_3$ solid solutions and hinders the reduction by methanol in the sequence:

$$Fe_2(MoO_4)_3 > (FeCr)_2(MoO_4)_3 > (FeIn)_2(MoO_4)_3 > (FeAl)_2(MoO_4)_3.$$

PPI-96

INFLUENCE OF THE COMPOSITION OF Cr_2O_3-MoO_3/γ-Al_2O_3 CATALYSTS ON THEIR ACTIVITIES IN CYCLOHEXANE DEHYDROGENATION

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γ-Alumina-supported mixed chromium and molybdenum oxides are of great importance because they can catalyze dehydrogenation of hydrocarbons in the presence of water steam (as well as molybdena systems) but, besides that, exhibit more enhanced activities as compared to those of molybdenum oxide catalysts. It is of special interest to elucidate how supported metal oxides and the order of their deposition onto γ-alumina influence the dehydrogenation activity of Cr_2O_3-MoO_3/γ-Al_2O_3 systems, and what is the optimal composition of these catalysts in the reaction discussed.

Chromium, molybdenum and mixed chromium-molybdenum oxides supported on γ-Al_2O_3 (hereinafter denoted as Cr-Al, Mo-Al and Cr-Mo-Al, respectively) were prepared by pore volume impregnation of the γ-alumina support ($S=200$ m^2/g) with solutions of $(NH_4)_2Cr_2O_7$ and ammonium paramolybdate, followed by drying (393 K, 4 h) and calcining (873 K, 6 h) after each component deposition. Activities of the catalysts obtained have been investigated in dehydrogenation of cyclohexane as a model reaction of unsaturated hydrocarbon formation. The results of catalytic experiments are presented in Fig. 1. Efficiency of the catalysts tested in the reaction of cyclohexane dehydrogenation decreased in the order of :

Cr-Al>Cr-Mo-Al(MoO_3=const)>Mo-Cr-Al(Cr_2O_3=const)>Mo-Al .

XPS, ESR and DRS studies revealed that with chromia increasing up to ~10 wt%, highly dispersed superficial chromate *species* comprising Cr^{6+}

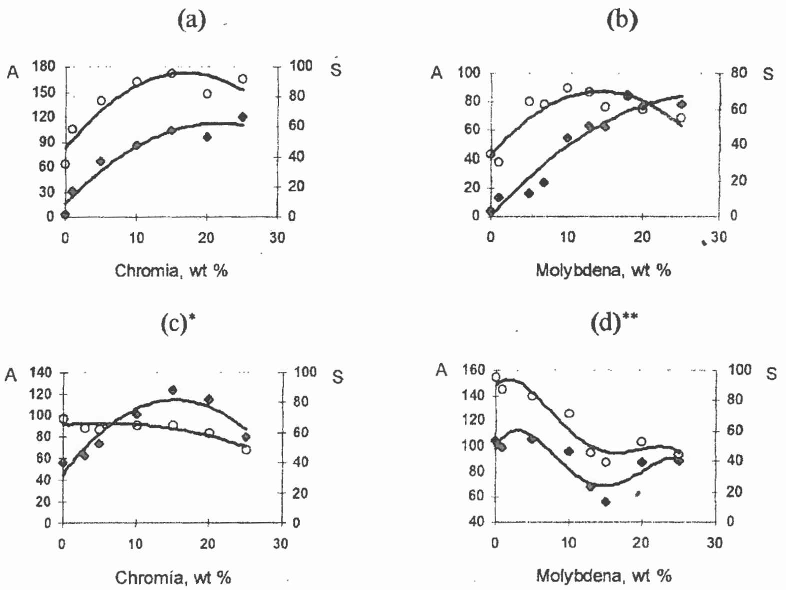

Fig. 1. Catalytic properties of $Cr_2O_3/\gamma\text{-}Al_2O_3$ (a), $MoO_3/\gamma\text{-}Al_2O_3$ (b) and $Cr_2O_3\text{-}MoO_3/\gamma\text{-}Al_2O_3$ (c,d) catalysts in cyclohexane dehydrogenation *versus* supported metal oxide loadings: A (♦) - specific dehydrogenation activity, $mmol/m^2 \cdot s \times 10^6$; S (o) - selectivity, %. Reaction conditions: pulse technique, T=873 K, τ_c=1 s, V_p~2μl.

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[*] At constant MoO_3 concentration ~ 13 wt %; the order of impregnation: 1) Mo; 2) Cr.

[**] At constant Cr_2O_3 concentration ~ 15 wt %; the order of impregnation: 1) Cr; 2) Mo.

and Cr^{5+} ions as well as $\gamma\text{-}(Cr_xAl_{1-x})_2O_3$ solid solutions and Cr_2O_3 microcrystallites comprising octahedral Cr^{3+} ions were preferentially formed in Cr-Al and Cr-Mo-Al (MoO_3=const) catalysts. The formation of these highly active structures provided considerably enhanced dehydrogenation activity for Cr-Mo-Al systems as compared to that exhibited by Mo-Cr-Al ones. In the latter case, the intensive formation of superficial chromium centers was suppressed at the expense of interaction between molybdenum and chromium ions. Thus, deposition of chromia onto Mo-Al catalysts resulted in more effective catalytic systems for dehydrogenation of cyclohexane .

PPI-97

THE PECULIARITIES OF CATALYTIC ACTION OF 12-MOLYBDO-PHOSPHORIC ACID AND ITS K_3 SALT IN THE DECOMPOSITION OF FORMIC ACID

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Many studies have been done for clarifying the mechanism of decomposition of formic acid on metals and the metal oxides. The formate anion stabilized on the Lewis acidic sites has been suggested to be a surface intermediate in the reaction of decomposition of formic acid.

In the present paper we studied the catalytic activities, structure of the adsorbed species and mechanism of surface reaction of decomposition of formic acid on the hydrated forms of $H_3PMo_{12}O_{40}$, $H_3PMo_{12}O_{40}/SiO_2$, $K_3PMo_{12}O_{40}$, that have no surface Lewis sites.

EXPERIMENTAL.

SiO_2 ($S=175\ m^2/g$) was impregnated with reactive $H_3PMo_{12}O_{40}$ (HPA) (50% wt.). $K_3PMo_{12}O_{40}$ was precipitated from the HPA water solution by potassium chloride. The samples were dried at 110^oC.

The catalytic properties were determined in a flow-circulating setup with a chromatographic analysis of reaction products.

IR spectra were recorded on the Specord M-80 spectrometer. The catalyst was pressed into pellets with density 12-13 mg/cm^2. The samples were heated in air at 150^oC before studies.

RESULTS and DISCUSSION

The hydrated forms of $H_3PMo_{12}O_{40}$, $H_3PMo_{12}O_{40}/SiO_2$, $K_3PMo_{12}O_{40}$ (HPC) are active catalysts for the HCOOH decomposition (Table).Formic acid is decomposed exclusively by dehydration to CO and H_2O on acidic oxide catalysts, as well as on V-Ti-O (Table).

IR spectroscopic analysis of adsorbed species of formic acid on $K_3PMo_{12}O_{40}$ at 25^oC show only presence of moleculary adsorbed acid with bands of $\nu_{O\text{-}H}=3260$ (3570), $\nu_{C\text{-}H}=2945$ (2943), $\nu_{C=O}=1735$ (1770), $\delta_{C\text{-}H}=1380$ (1387), $\delta_{COH}=1315$ (1229), $\nu_{C\text{-}O}=1160$ (1105) cm^{-1}. (The frequencies of gas phase HCOOH are shown in brackets). Increase of the interaction temperature up to 150^oC resulted in an intensity decrease of the bands of molecular adsorption of acid and appearance of a new band at 1620 cm^{-1}. This band belongs to water resulting from the HCOOH decomposition.

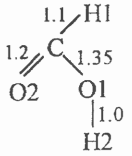
Table. Catalytic Activity of HPC for the HCOOH decomposition at 120°C and the contact time 4s.

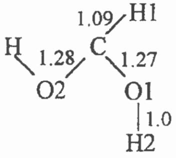
Catalyst	X,%	Selectivity, %		$Wx10^4$ mol/g h
		CO	CO_2	
$H_3PMo12O_{40}$ /SiO_2	39.0	99.5	0.5	11.6
$H_3PMo_{12}O_{40}$	21.1	99.4	0.6	5.4
$K_3PMo_{12}O_{40}$	10.0	99.3	0.7	1.1
20%V_2O5-80%TiO_2	7.0	95.6	3.4	0.9

Similar results were obtained for $H_3PMo_{12}O_{40}/SiO_2$.

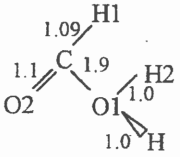
The hydrated forms of HPC are essentially Brønsted acids, as indicated by adsorbtion of pyridine.

Ab initio SCF MO LCAO method was used to calculate the interactions between the formic acid and the proton H^+. Two structures were considered (S1 and S2).





(S1)



(S2)

In these structure the O atoms of HCOOH of C-O-H (O1) or C=O (O2) groups interact with the surface H^+. When H^+ interacts with O(2) the stable protonative adsorbed complex (S1) is formed. The interaction of H^+ with O(1), which is more nucleophylic than O(2), produces the protonative intermediate (S2). The distinctive property of structure (S2) is localization of positive charge on the fragment O=C-H and a bond C-O1 lenghtened up to 1.9A. The interaction of protonative species (S2) with a nucleophylic particle, as in surface O^{2-} , leads to decomposition of intermediate (S2) to form carbon monoxide and water.

Thus, the decomposition of formic acid on the hydrated forms of HPC proceeds by the addition of surface proton to HCOOH via protonative complex (S2).

This work was supported by Russion Basic Resurch Foundation (Grand 96-03-33016).

PPI-98

STRUCTURE AND PROPERTIES OF $\mathbf{Ru\text{-}Al_2O_3/Al_2O_3}$, $\mathbf{Ru\text{-}TiO_2/Al_2O_3}$ AND $\mathbf{Ru/Al_2O_3}$ CATALYSTS

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The dispersity, structural features of the Ru particles and the Ru electronic state in $Ru\text{-}Al_2O_3/Al_2O_3$, $Ru\text{-}TiO_2/Al_2O_3$ and Ru/Al_2O_3 catalysts (0,3-0,5 % Ru), have been considered by means of EM, EXAFS and XPS. $Ru\text{-}Al_2O_3/Al_2O_3$ and $Ru\text{-}TiO_2/Al_2O_3$ catalysts as $Ru\text{-}Al_2O_3$ and $Ru\text{-}TiO_2$ microheterogeneous films on porous support (spherical $\gamma\text{-}Al_2O_3$) were obtained by the thermal decomposition of ruthenium chloride added with aluminium resinate ($Ru\text{-}Al_2O_3/Al_2O_3$ catalyst), titanium resinate ($Ru\text{-}TiO_2(R)/Al_2O_3$) and titanium alkoxide ($Ru\text{-}TiO_2(A)/Al_2O_3$), in air (500°C, 2 h) and then in H_2. As a comparison, Ru/Al_2O_3 catalyst was prepared by impregnation of Al_2O_3-support with $RuCl_3$ solution and annealing in air and H_2. The significant advantage of $Ru\text{-}Al_2O_3$ and $Ru\text{-}TiO_2$ microheterogeneous systems are thermal stability of high dispersed Ru particles. Strong electronic interaction between components of the film structures (stronger in the case of $Ru\text{-}TiO_2$) promotes the formation of higher dispersed Ru particles in $Ru\text{-}TiO_2/Al_2O_3$ than that in $Ru\text{-}Al_2O_3/Al_2O_3$. According to EM data the predominant Ru particle sizes are: 80-100 Å in Ru/Al_2O_3, 50-60 Å in $Ru\text{-}Al_2O_3/Al_2O_3$, 30-40 Å in $Ru\text{-}TiO_2(A)/Al_2O_3$, 20 Å and below in $Ru\text{-}TiO_2(R)/Al_2O_3$. The results of the EXAFS study of the Ru-catalysts show that the Ru-Ru interatomic distance in the high dispersed Ru particles is 0,06-0,10 Å shorter than in the bulk metal. HCP structure of these particles is distorted. Correlation between Ru particle size and Ru-Ru interatomic distance is established. The higher dispersed particles possess shorter interatomic distance. According to EXAFS and SIMS, the presence of partially reduced RuO_x species, leading to destruction of Ru cell, is probable.

By means of XPS, Ru oxidised states on the Ru particles' surface were detected. Thus, intermediate ruthenium valence state Ru^{2+} (RuO) simultaneously with more stable states – Ru^0 and Ru^{4+} (RuO_2), is observed in Ru/Al_2O_3 and $Ru\text{-}Al_2O_3/Al_2O_3$.

In the Ru $3p_{3/2}$ XPS spectra of Ru-TiO_2/Al_2O_3 we can identify the lines with binding energies, corresponding to various Ru valence states, from Ru^0 to Ru^{8+}. Moreover, oxidised Ru states (Ru^{2+} - Ru^{8+}) quantitatively predominate above Ru^0 on the surface of Ru-TiO_2 films reduced in H_2.

The interaction of Ru with high-defective TiO_x structure probably may lead to the stabilisation of usually unstable oxidised states of ruthenium. The formation of TiO_2-RuO_2 solid solution structure in an unreduced Ru-TiO_2/Al_2O_3 catalyst during the pyrolysis of initial Ru and Ti compounds could promote the easier interaction between Ru and TiO_x. In this case an effect of Ru and Ti upon the electronic states of each other is observed. The reduction of Ti^{4+} in the RuO_2-TiO_2 systems occurs more readily, while reduction of Ru^{4+} is hampered.

Owing to the strong mutual influence of the components in the RuO_2-TiO_2 systems, ruthenium in oxidation states from Ru^{2+} to Ru^{8+} and partially reduced Ti states Ti^{2+} and Ti^{3+} are stabilised.

The difference in activity and selectivity of investigated catalysts in the CO hydrogenation as well as CO and other reducing gases oxidation has been found. CO hydrogenation on Ru/Al_2O_3, Ru-Al_2O_3/Al_2O_3 and Ru-TiO_2(A)/Al_2O_3 yields mainly CH_4, whereas on Ru-TiO_2(R)/Al_2O_3 and Al_2O_3 support – methanol. Highest conversion of reactants is observed on Ru-Al_2O_3/Al_2O_3 and Ru-TiO_2(A)/Al_2O_3. These catalysts possess similar selectivities. It should be noted, that the samples with similar catalytic properties possess similar Ru particles' size distribution. It is determined that catalysts containing 30-60 Å Ru particles allow to obtain maximal yield of high-molecular hydrocarbons. Ru-TiO_2(R)/Al_2O_3 catalyst with 20 Å Ru particles is more active in the methanol formation.

Thermocatalytic sensors with RuO_2/Al_2O_3, RuO_2-Al_2O_3/Al_2O_3 and RuO_2-TiO_2/Al_2O_3 catalysts are sensitive to CO at 300-350°C. No response to hydrocarbons (methane, propane, petrol vapour) in this temperature range is observed. Sensors are sensitive to C_mH_n at 480°C and above. The significant difference in optimal detection temperatures allows to detect CO and C_mH_n selectively by means of sensor temperature mode control.

PPI-99

FORMATION OF THE SURFACE OF THE OXIDE CATALYST UNDER THE INFLUENCE OF THE REACTION MIXTURE OF AMMONIA OXIDATION

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The peculiarities of reactants adsorption and the proceeding of high temperature reaction of ammonia oxidation were studied by means of programmed thermal desorption, secondary ion mass spectrometry, X-ray diffraction, epitaxial decoration, electron diffraction and laser spectrometry. The catalyst is a solid solution of ammonia with corundum structure in iron oxide.

The analysis of thermal desorption spectra showed the desorption of NH_3, NH_2, NH, N complexes at T=600K. Desorbed nitrogen portion is increased and ammonia portion is decreased with growing temperature. Hence, ammonia adsorption isn't the limiting stage of ammonia oxidation process. At low temperatures oxygen is adsorbed on catalyst surface as molecules with low bonding energy E=1.45 eV/molecule. Adhesion coefficient for oxygen S=0,3 and maximum covering $n=4{,}5\cdot10^{14}$ molecules/cm^2 were calculated using the areas under desorption curves. The treatment of desorption curves front indicates order of desorption and gives the value of frequency factor $V=1\cdot10^{13}$. Such oxygen has low reactivity for the reaction of ammonia oxidation to nitrogen oxide (II). The surface oxygen of oxide catalyst also doesn't react at temperatures lower then 600K. At temperature growth bonding energy between adsorbed oxygen and catalyst increased and reached 2.1 eV. This value is near to the bonding energy of oxygen with platinum surface.

The catalytic reactor with two-channel feed of reaction mixture was installed into secondary ion mass spectrometer for control of the surface state during the reaction.

The experiments showed that at the reagents feed at T=300K the surface was covered with OH-groups which disappear at the temperatures more than 500K. Besides the reduction of the surface (in the form of circles with growing size) started under the influence of the reaction mixture.

The dependencies of the rate of the reduction under ammonia effect and reoxidation of the catalyst surface under oxygen effect at T=800K were investigated. It should be noted that the reduction till 60% of monolayer surface has reverse character and reverse direction of the curve (area occupied with oxygen ion S=0.784 nm; maximum monolayer covering $n=64\cdot10^{14}$ molecules/cm^2)

The rate of oxidation-reduction processes of oxide catalyst was compared with the rate of products formation to investigate the reaction mechanism and the role of the reduction of the surface.

The obtained results, dealing with the reactants adsorption (ammonia and oxygen) and reaction on oxide catalyst in the case of high temperature catalysis, have a great significance.

At the temperatures higher than 600K the reduction of the surface takes place under the influence of ammonia of the reaction mixture. In this case the reducing rate dependency upon the surface reduction degree has extreme character unlike this process at low temperatures. Such dependency corresponds to the deoxidation of larger surface sections which become greater.

In the case of incomplete deoxidation of oxide catalyst surface, reoxidation occurs according to the same curve in the reverse direction. Such character of the dependency of oxidation and reoxidation upon the surface reduction degree indicates the possibility of modeling the reduced areas of the surface with circles, which become bigger or smaller. The deviation of oxidation curve from deoxidation graph in the case of reaching the monolayer deoxidation indicates the oxidation due to the growth of the surface sections of oxide phase.

It was ascertained that the rate of ammonia oxidation reaction was essentially greater than the rate of the surface oxidation and deoxidation.

It should be stressed that the reaction selectivity as for nitrogen oxide (II) depends on surface reduction deoxidation degree and reaches the maximum value at deoxidation degree 0,35 from monolayer covering. The surface deoxidation was calculated in the portions of monolayer covering. The area of reduced sections coincides with the epitaxial decoration data. Simultaneously, SIMS data show that the ion deoxidation with the reaction mixture doesn't take place. Hence, in the reaction process oxygen is adsorbed at 800K on partly reduced areas with activation desorption energy E=2,1 eV, it coincides with the value for platinum catalyst.

The obtained results show that in the case of high temperature ammonia oxidation on the solid solution of alumina in the iron oxide associative mechanism is realized. The mechanism is based on the following statements:

- the partly reduced surface areas are formed under the influence of reaction mixture;
- oxygen is adsorbed on these areas with the bonding energy (E=2,1 eV) which provides maximum formation of nitrogen oxide (II);
- smaller value of bonding energy of oxygen directs the reaction of ammonia oxidation to nitrogen formation;
- greater value of oxygen bonding energy on the reduced areas put on the brakes the process with reaction products.

Thus, the process of choosing composition and preparation technique surves to the definite aim. The aim is that adsorbed oxygen must have the bonding energy as oxygen on the most active platinum catalyst has. Under these energy conditions oxide catalyst has maximum selectivity.

PPI-100

ARTIFICIAL METALLOENZYMES AND CATALYSTS OF HYDROLYSIS OF PHOSPHOROUS ACIDS ESTERS

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Reactions of nucleophilic substitution of esters of phosphorus acids are of major synthetic importance in view of environment (hydrolysis of toxic pesticides) as well s due to phosphoryl transfer process in living cells. One of directions of efficient catalysts search for these reactions is the design of synthetic metalloenzyme mimics. They simulate enzyme active sites action in organized systems such as cell membranes. Examples of these artificial metalloenzymes combining the advantages of the micellar and metal complex catalysis are micromicelles (complexes of a transition metal with functional surfactants) and complexes with bifunctional ligands in micellar solutions of surfactants. Such catalysts exhibit high hydrolytic activity in mild conditions.

We have obtained functional surfactants (I) - N,N-dimethyl-N'-tetradecylethylenediamine, N,N-dimethyl-N'-tetradecylpropylenediamine, their complexes with Cu (II) (compounds II) abd bifunctional ligand 2-dimethylaminomethylphenol (HL). The effect of non-ionic surfactant Triton-X-100 (T-X-100) on the complex formation of HL with Cu (II) has been investigated spectrophotometrically, pH-metrically and by the computer simulation of equilibria in solutions. It was shown that the composition and stability constants of the complexes depend on the concentrations of T-X-100 and pH of solutions - [T-X-100] = 0.05 M: $[CuHL]^{2+}$, $[Cu_2(HL)_2L]^{3+}$; [T-X-100] = 0.01 M: $[Cu(H_2L)_2HL]^{4+}$, $[CuH_2L(HL)_2]^{3+}$.

The hydrolysis kinetics of p-nitrophenyldiphenylphosphate (1) and p-nitrophenyl-bis(chloromethyl)phosphinate (2) in the presence of ligands I, HL and their copper complexes in water and micellar solutions of T-X-100 has been studied by spectrophotometry. Dependence of the observed rate constants (k_{obs}) of 1 hydrolysis on concentrations of I and II, an 2 hydrolysis in the presence of copper complexes of HL on T-X-100 concentrations has been determined. The form of $k_{obs} = f(C_{I,\ II,\ T\text{-}X\text{-}100})$ function (reaching a plateau) allows to interpret the results in terms of pseudophase model of micellar catalysis and to calculate substrate binding constants (K_b), rate constants in the micellar phase (k_m) and critical concentration of micelles formation. The effect of pH on the c_{obs} values is also considered. Analysis of "k_{obs} - $C_{I,\ II,\ T\text{-}X\text{-}100}$" and "$k_{obs}$ - pH" dependencies permit to conclude that sorption and catalytic activity contribute to the high hydrolytic efficiency of metallomicelles II at neutral pH. For example, K_b of substrate 1 for II is equal to 3500 - 1000 M^{-1}. In addition, micellar environment and coordination with copper (II) decrease pK_a of water molecules for II or nucleophilic hydroxyl groups of ligand HL. Accelerations of 1 hydrolysis in the presence of II (k_m/k_{H_2O}) at pH 8.0 and 2 hydrolysis at pH 7.0 in the presence of th most efficient complexes $[CuHL]^{2+}$ or $[Cu(H_2L)_2(HL)]^{4+}$ are equal to ca. 10^5-fold and 10^3-fold, respectively.

PPI-101

PROBLEMS ON STRUCTURE AND CATALYTIC ACTIVITY OF CATIONIC Ni(I) COMPLEXES

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For 25 years since the first report on Ni(I) complexes in Ziegler type catalytic systems a great number of different in composition and structure Ni(I) complexes formed during the formation of metal complex catalysts has been identified *in situ* by of ESR spectroscopy [1]. The most stable structures have been isolated and characterized by physical and physic-chemical methods.

In this work we present results of investigations on the structure of Ni(I) cationic type complexes which constitute the basis of highly active catalysts for transformations of unsaturated hydrocarbons and on the clearing the role of Ni(I) ions in these catalytic processes.

I. Geometric and electronic structures of Ni(I) cationic complexes.

A wide use of transition metals in catalysis is caused, mainly, by their ability to form σ- and π-bonds with other molecules and ligands. This ability is determined by the availability in transition elements of different in geometry and, chiefly, close in energy valent orbitals, which is the reason of the appearance of Jahn-Teller effect in coordination compounds. Cationic Ni(I) complexes with $3d^9$ electronic configuration are of substantial interest as a subject of application and development of vibronic theory which, first, are available for comprehensive investigation by use of most informative ESR method and, second, exhibit high activity in transformations of unsaturated hydrocarbons.

Systematic investigation of Ni(I) complexes caused the necessity of performing theoretical studies of the influence of metal-ligand bond nature on vibronic interactions in heteroligand structures. The difference of this problem from already “classical” description of Jahn-Teller effect is that suggested approach the nonequivalence of ligands has been taken into account by addition of substitution operator to the hamiltonian of electron-vibrational interaction of the homoligand complex, which provides dissemination of vibronic interaction concepts onto low symmetric structures [2].

On the base of theoretical development the analysis of geometric and electronic structures of a great number of cationic Ni(I) complexes obtained by original procedure of oxidation of Ni(0) phosphine complexes with boron trifluoride and further substitution of phosphine ligands for phosphite, carbon monoxide and butadiene have been performed.

According to vibronic model the planar complex $[Ni(DPE)_2]^+$, where DPE is diphenylphosphinoethane, has tetragonal structure differing from similar composition low-spin Co(II) and Fe(I) complexes, which have rhombic distortion.

Tetrahedral cationic complexes $[Ni(PBu_3)_4]^+$ have tetragonal geometry which indicates the preferential interaction of electron with double degenerated *e*-vibrations of tetrahedron. In cationic π-complexes $\{Ni(\eta^4\text{-}C_4H_6)_2\}^+$ the static Jahn-Teller effect is pronounced weakly. Cationic tetrahedral Ni(I) complexes with mixed compositions $\{Ni(PPh_3)_{4-n}[P(OR)_3]_n\}^+$ (R=Et, Bu, n=1, 2), $\{Ni(PBu_3)_{4-n}[P(OBu)_3]_n\}^+$ (n=1-3), $\{Ni(PBu_3)_3(CO)\}^+$, $\{Ni(PPh_3)_2(\eta^4\text{-}C_4H_6)\}^+$, $\{Ni(PPh_3)[P(OEt)_3](\eta^4\text{-}C_4H_6)\}^+$ independently of the number of homoligands exist in form of trigonal structures, in which the molecular orbital occupied by nonpaired electron is oriented along the Ni-P bond.

For three-coordinated cationic Ni(I) complexes with composition $\{Ni(PR_3)_3\}^+$ Jahn-Teller stabilization energy constitutes averagely 60% of the value of splitting of d-orbits in the ligand field and increases in the row of phosphine ligands: PPh_3<P(*i*-Pr)$_3$<PCy_3. The ground state for two former complexes is $|x^2-y^2>$, for the latter is $|xy>$.

Presented data on the structure of heteroligand cationic Ni(I) complexes convincingly indicate of how much importance vibronic effects are for realization of one or another geometric configuration and, consequently, related electronic state even in the cases of the absence of degeneration. Moreover, as a result of redistribution of Jahn-Teller stabilization energy between minimums at the potential surface, vibronic effects become more substantial for heteroligand structures than for homoligand ones.

II. Vibronic aspects of coordination catalysis.

The foundation of modern views on chemical reaction paths is the second order Jahn-Teller effect proposed by Bader and evolved in detail applying to the reactivity of coordination compounds by Pearson. According to these views the stability of systems relative to nuclei remove along coordinates on which the determined symmetry conditions are imposed is as low as small is the difference between energies of ground and excited states, which, in turn, determines the pathway of chemical (catalytic) reactions. Unfortunately these ideas have not found a wide development because of intricate of numerical calculations of electron, especiacy pseudodegenerated, states. Theoretical developments have not been beyond the scope of the problem of activation of substrate molecule which, in addition, may be solved in adiabatic approximation by more simple tools. In connection with it the further development of productive concepts of vibronic interaction is of necessity to elaborate the simplest rules available for wide practical uses of them in coordination catalysis.

We have suggested and theoretically justified the fundamental tenets in accordance with which a wide range of catalytic reactions proceeding with low symmetric active complexes may be described in context of the dynamic Jahn-Teller effect representing an active complex as a result of ligand substitution in high symmetric structures [3]. The fundamental tenets of suggested concept are the following:

- labile (potentially active) are the structures, normal electron state of which correlates with E- and T-terms of initial octahedron.
- catalysis is a form of manifestation of the dynamic Jahn-Teller effect (the transformation of a substrate in coordination sphere is a transition of an active complex from one equilibrium state to other).

In context of suggested concept reasons have been explained for:

- high stability of octahedral polyhydride compounds of Co(3+) and Fe(2+).
- two-peak pattern of the dependence of activity of transition metal oxides in hydrogen exchange reactions on number of electrons on the d-orbit of central atom.
- high activity of Ni(I) cationic complexes in olefin dimerization.

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PPI-102

REDOX PROCESS BETWEEN Ni(I) AND Ni(III) DURING BUTADIENE TRANSFORMATION

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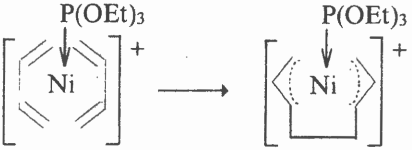
Since the finding of Ni(I) intermediate compounds in Ziegler type catalytic systems repeatedly have been made attempts to clear the role of Ni(I) complex compounds for catalysis. Obtaining no simbatic dependence between the concentration of Ni(I) intermediate compounds and the activity of catalytic systems for oligomerization process of olefins, investigators came to conclusion that Ni(I) complexes because of low kinetic stability of their alkyl (hydride) derivatives exhibit no activity for transformation of unsaturated hydrocarbons, but play an important role for regeneration of catalytically active Ni(II) hydrides [1]. In recent years more and more data are being amassed on various stoichiometric and catalytic processes proceeding with participation of ionic Ni(I) compounds. For instance, Ni(I) ions supported on oxides are reported to be active species in selective transformations of ethene and propene to α-olefins [2,3], cyclotrimerization of acetylene and oligomerization of ethene [4]. Data indicating high activity of cationic Ni(I) complexes for propene dimerization have been obtained by us in work [5]. The basis for all these works is the correlation dependence of the activity of system on the initial concentration of Ni(I) ions measured before the beginning of catalytic process itself. However these indirect evidences leave place for doubts of the possibility of Ni(I) transformation to Ni(II) or Ni(0) at initial moment and during further catalytic reaction on nickel ions in usual oxidation states by hydride mechanism or mechanism of oxidative conjugation respectively. For the purpose to clear the possibility to realize reversible oxidation of Ni(I) to Ni(III) under oxidative conjugation of substrate on cationic Ni(I) complexes we have investigated model reaction of butadiene transformation on coordinately unsaturated cationic complex $\{Ni(PPh_3)_3\}^+$ at low temperature. Interaction of substrate with $\{Ni(PPh_3)_3\}^+$ reveals the subsequent substitution of phosphine ligands for butadiene molecules forming in final step tetrahedral π-complex with composition $\{Ni(\eta^4\text{-}C_4H_6)_2\}^+$ without change of transition metal oxidation state. Addition of less bulky and more acceptor in comparison with PPh_3, $P(OEt)_3$ ligand into the system is followed by insertion of phosphite into coordination sphere of π-complex and oxidation of Ni(I) to Ni(III) as a result of conjugation of butadiene ligands by probably scheme:



Ni(III) π-allyl complexes dissociating quantitatively transform into tetrahedral Ni(I) complexes with compositions $\{Ni(PPh_3)[P(OEt)_3](\eta^4\text{-}C_4H_6)\}^+$ and $\{Ni(PPh_3)_3[P(OEt)_3]\}^+$ which are more inert toward substitution reaction of phosphine ligands for butadiene as compared with coordinately unsaturated complex $\{Ni(PPh_3)_3\}^+$ and by this reason the concentration of Ni(III) at stationary conditions constitutes less than 10% of Ni(I).

By this means for the first time has been shown principal possibility to transform Ni(I) into Ni(III) during oxidative conjugation of butadiene on cationic Ni(I) complexes.

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PPI-103

ON THE MECHANISM OF ALKENE INSERTION INTO Pd-Ar BOND HECK REACTION

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Catalysts based on palladium compounds still remain one of the most promising for catalytic organic synthesis. It refers to catalytic transformations of unsaturated hydrocarbons for which the insertion of alkene into Pd-C bond is one of most often postulated elementary steps. For the purpose to investigate in details electronic mechanism of this step in real conditions of catalysis the regioselective regularities of Heck arylation reaction [1] for 16 various alkenes have been studied.

Three types of effects determining reaction regiochemistry may be set apart- charge-, frontier- and steric-controlling effects. Quantitative influence of electronic effects on the regioselectivity may be described by the equation (1) which connects both the "hard and soft acid and base" and perturbation theory principles [2]:

where E is the total perturbation energy; q_r and q_s are the total charges respectively on interacting atoms r and s; Γ is Coulomb repulsion term between atoms r and s; ε is the local dielectric constant of the medium; c_r^m are the coefficients of the r-atomic orbitals on all unoccupied molecular orbitals of the reagent considered as a nucleophile, c_s^n are the coefficients of the s-atomic orbitals on all unoccupied molecular orbitals of the reagent considered as nucleophile as an electrophile; E_m^r and E_n^s are energies respectively of nucleophile occupied MO and unoccupied electrophile MO; β is the value of the resonanse integral; Δ_{sol} is the correction to perturbation energy produced by solvation of molecule when the reaction occurs in solution.

Making a number of assumptions, the main of which is the linearity between activation and perturbation energies characterizing the facility of reaction occurring and taking into account kinetic studies data according to which regioselectivity of main catalytic process is determined by the ratio of insertion step rates leading to the formation of different regioisomers on the base (1) the following equation has been taken:

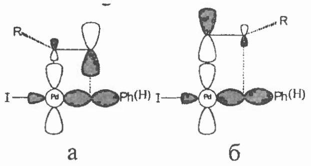
$$\ln\frac{\beta}{\alpha} = a_0 + a_z(q_\beta - q_\alpha) - \frac{a_{LUMO}\left(\left(c_\beta^{LUMO}\right)^2 - \left(c_\alpha^{LUMO}\right)^2\right)}{\left|E_{LUMO}^{ALKEN} - E_{HOMO}^{Pd}\right|} - \frac{a_{HOMO}\left(\left(c_\beta^{HOMO}\right)^2 - \left(c_\alpha^{HOMO}\right)^2\right)}{\left|E_{HOMO}^{ALKEN} - E_{LUMO}^{Pd}\right|} \quad (2)$$

where $\frac{\beta}{\alpha}$ is the ratio between β- and α-products of the reaction; a_o, a_z, a_{LUMO}, a_{HOMO} are constant coefficients; $(q_\beta - q_\alpha)$ - is the difference between total charges respectively on β and α carbon atoms of vinyl group (estimated from NMR ^{13}C spectra) c_a^{HOMO}, c_β^{HOMO}, c_a^{LUMO}, c_β^{LUMO} are contributions of Pz-AO respectively of α- and β-carbon atoms of vinyl group into HOMO and LUMO of alkene (calculated by semiempirical quantum chemistry methods such as PM3, MNDO and AM1); E_{HOMO}^{Pd}, E_{LUMO}^{Pd} are the energies of HOMO and LUMO respectively.

Having experimental data on the distribution of regioisomers ($\frac{\beta}{\alpha}$) for the series of alkenes and using the multiple regression method one may calculate the constant coefficients in (2), which characterize the influence degree of various effects on the regioselectivity of the reaction, as well as the values of E_{HOMO}^{Pd} and E_{LUMO}^{Pd}.

Calculations have shown that the determing role in distributions of regioisomers belongs to the location type of LUMO on the vinyl group of alkene but not to the form of HOMO and charge distribution as ssuggested in [3]. It allows to make a conclusion that the key stage of olefin insertion into Pd-Ar bond which determines the energy of transition state is the electron density transfer from HOMO of metal complex to LUMO of olefin. We have suggested the mechanism of frontier-controlled regioselectivity which is in agreement with experimental data:

PPI-103



and according to which the most favorable coordination of palladium from views of both steric hindrance and orbital overlapping is achieved in the case when relatively great in size palladium atom adjusts to carbon atom, the contribution of atomic orbitals of which into olefin LUMO is the smallest (Structure "a").

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PLATINUM CARBONYL CLUSTERS OF VARIOUS NUCLEARITY AS PRECURSORS FOR HIGH DISPERSITY AND THERMOSTABLE PLATINUM SUPPORTED CATALYSTS FOR HYDROCARBONS CONVERSION

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Formation stages of supported catalysts Pt/Al_2O_3 and Pt/C, prepared from platinum carbonyls of different nuclearity Pt_6-and Pt_{15} - clusters, their properties: dispersity, structure of the surface forms, thermostability and catalytic activity in deep oxidation and dehydrogenation of saturated hydrocarbons were investigated in this work.

High-nuclear platinum carbonyl $[Pt_3(CO)_6]_{10}H_2$ was used as an origin compound. IR and NMR - spectroscopy methods were used to reveal than. $[Pt_3(CO)_6]_{10}H_2$ - cluster in CO atmosphere is subsequently converted into less nuclear particles: $[Pt_3(CO)_6]_{10}^{2-} \rightarrow [Pt_3(CO)_6]_5^{2-} \rightarrow [Pt_3(CO)_6]_3^{2-} \rightarrow [Pt_3(CO)_6]_2^{2-}$ under the influence of bases with different strength.

Adsorption isotherms of Pt_{15} - cluster from water-acetone solutions show that its interaction with alumina is rapid and practically irreversible till loading of 5% Pt. Maximum sorption capacity corresponds to 10% Pt which is 2 times higher than for H_2PtCl_6. Adsorption on γ-Al_2O_3 (Henry coefficient $2*10^3$ ml/g) is four fold stronger than on coal ($5*10^2$ ml/g). It is related to the presence of strong acceptor centres on alumina surface forming strong bond with the carbonyl cluster - electron donor by its nature.

Dispersity of platinum, supported from carbonyl, (H_2-O_2 titration method) for both Pt/γ-Al_2O_3 and Pt/C-catalysts are higher than for catalysts prepared from H_2PtCl_6.

D~1 for platinum-alumina catalyst and this means a practically monoatomic platinum distribution on the support surface. Herewith, the difference is revealed not only in the particle size, but also in their macrostructure. Platinum, supported from carbonyl, forms bidimensional layers, whereas, in the samples obtained from H_2PtCl_6 crystallites are observed. It was shown by means of method of drawing radial distribution functions that there is no platinum phase with f.c.c. structure on the catalyst's surface prepared from Pt_{15}-cluster. A stable surface platinum compound with γ-Al_2O_3 is formed. In the catalyst prepared by supporting of Pt_6-cluster both metallic platinum and surface platinum-alumina compound is observed. This corresponds to its weaker interaction with the support surface than in case of Pt_{15}-cluster.

The peculiarity of Pt/γ-Al_2O_3 catalysts prepared from carbonyl clusters is the high thermostability of supported platinum in high dispersity state. Namely, the dispersity did not change at temperature raise from 300° C to 500° C. This property is connected with fast, " multipoint" interaction of cluster with alumina.

Catalytic properties of the catalysts prepared from clusters are investigated and compared with the properties of platinum catalysts prepared from H_2PtCl_6 in the hydrocarbons conversion reactions proceeding under moderate and rigid conditions.

Methane oxidation (400-500° C). Activity of the samples prepared from Pt_{15} - clusters is 3-6 times higher than that of the traditional catalyst. This may be conditioned by lower "oxidability" of platinum atoms and absense of chlorine-ions stabilizing Pt in oxidative state.

Cyclohexane dehydrogenation (300° C). Activity decreased 4 times while transition from the traditional catalyst to the one prepared from Pt_{15}- cluster in the case of Pt/γ-Al_2O_3, and it increased 3 times for Pt/C - catalysts. It is known that cyclohexane dehydrogenation takes place on platinum metal crystallites. It was shown by means of method of drawing radial distribution functions that there is no Pt-metal phase in the catalysts prepared from cluster precursor and supported platinum is present in the form of thermostable surface compound. This is the main reason why activity decreases when Pt_{15}-cluster is used as a precursor of active component.

Interaction of the cluster with the carbon support is not so strong and it is observed at adsorption stage already. This factor favours formation of metallic platinum from the cluster and, as it was shown, with higher dispersity than from H_2PtCl_6. That is why the catalyst Pt/C prepared from the cluster is more active than the usual one.

PPI-105

HYDRODECHLORINATION OF POLYCHLORINATED BENZENES CATALYZED BY PHASE TRANSFER CATALYST AND Me^o/C.

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Analysis of the various methods of detoxication of organic chlorides leads to the conclusion that hydrodechlorination reactions are more ecologically favorable that oxidative ones and they allow polychlorinated aromatics to be reduced without the production of waste [1]. Previous results [2] showed that in the dehalogenation of polychlorinated aromatic compounds catalyzed by Pd/C or Ni-Raney with hydrogen at atmospheric pressure in a two-phase system (aqueous KOH and organic solvent) the presence of Aliquat 336 (methyltricaprilammonium chloride) as Phase-Transfer (PT) catalyst lead to considerable increasing the reaction rate. Such reactions are very prospective for organic syntheses.

The aim of this paper is to study the wide range PT and metallic catalysts available for effective and selective halide hydrogenolysis of organic compounds under mild conditions. Liquid phase dechlorination of 1,2,4,5-tetrachlorobenzene, hexachlorobenzene, polychlorinated biphenyls have been studied at 50°. The catalysts of choice are the transition metals supported on a carbon support (where Me^0 - Pd, Ni, Cu and bimetallic Pd-Ni, Ni-Cu). The carbon is necessary because of the corrosive nature of the reaction medium. "Sibunit" and CFC - catalytic filamentous carbon as carbon material were used. Methyltricaprilammonium chloride, tetramethylammonium chloride, tetraethylammonium chloride, tetraethylammonium hydroxide were used as Phase-Transfer catalyst. Sodium borohydride, sodium hypophosphite and hydrogen were used as hydrogen sourse.

According to the studies catalysts Pd/C or Ni-Pd/C - mixed hydride showed the highest activity and allowed to carry out effective dechlorination of polychlorinated benzenes at 50°C. Kinetic studies showed the hydrodechlorination of these compounds to be concecutive reaction and under the conditions described may produce less-chlorinated compounds. Thus, the method allows selectivity remove halogen from the aromatic ring and providing the new methods for organic synthesis.

Obtained results for hydrodechlorination of hexachlorobenzene. with Pd-Ni supported on Sibunit, carried out on variety PT catalysts , showed that the reaction is faster in the presence methyltricaprilammonium chloride.

It was found that varying the metallic catalyst considerably induces the selectivity of the hydrodechlorination of polychlorinated aromatics.

In the hydrodechlorination of hexachlorobenzene catalyzed by Pd-Ni/C with hydrogen at atmospheric pressure has been observed that dehalogenation proceeds though a rapid and progressive displacement of the chlorine atom from polychlorinated benzenes to benzene (fig. 1).

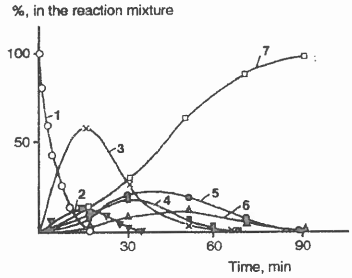

Fig. 1. Hydrodechlorination of hexachlorobenzene with $Ni_{95}Pd_5/C$ and $(CH_3)_3N^+CH_3Cl^-$ (PT catalyst).

1 - hexachlorobenzene;
2 - pentachlorobenzene;
3 - tetrachlorobenzenes isomers;
4 - trichlorobenzenes isomers;
5 - dichlorobenzenes isomers;
6 - chlorobenzene;
7 - benzene.

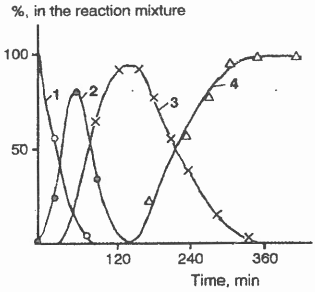

Fig. 2. Hydrodechlorination of hexachlorobenzene with $Ni_{92}Cu_8/C$ and $(CH_3)_3N^+CH_3Cl^-$ (PT catalyst).

1 - hexachlorobenzene;
2 - pentachlorobenzene;
3 - 1,2,4,5-tetrachlorobenzene;
4 - trichlorobenzenes isomers.

But the data in Fig. 2 show, that in the presence Ni-Cu/C catalyst with hydrogen at atmospheric pressure has been observed that the dehalogenation proceeds only to trichlorobenzene isomers.

This hydrodechlorination method has been successfully applied to commercial mixture of polychlorinated biphenyl (Sovtol-10).

Sovtol-10 is a common biphenyl pollutant mixture that contain a fraction of environmentally persistent tetra-, penta- and hexachlorinated congeners and therefore is an especially significant mixture for the reductive dechlorination.

The results show that the Pd_5Ni_{95} are effective catalysts for dechlorination of Sovtol-l0. High conversion (99%) of polychlorinated biphenyl to biphenyl was achieved.

Basing on kinetic studies we suggest a scheme of dechlorination mechanism. According to this scheme, the HCl produced in reaction adsorbed on the surface of catalyst is quickly removed by strong alkaline media. It is possible, as result Phase-Transfer agent transfers OH anion (alkali) from aqueous phase to surface of catalyst, so allowing a faster regeneration of the catalyst surface.

According to these results it could be possible to set up conditions on selective dehalogenation useful for synthetic purposes and detoxication methods of enviromentally problematic compounds. This reaction allows polychlorinated aromatic to reduced to the parent hydrocarbons without production of waste.

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PPI-105a

THE ACCELERATION OF LIQUID-PHASE OXIDATION REACTION BY SOME PETROLEUM SYSTEMS

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As a rule, high-molecular fractions extracted from oil have the properties of inhibiting of radical reactions. Although the content of inhibiting molecules is not high in such objects (for example, it is maximum in asphaltenes and is equal to 0.6-0.7 mole/kg), their activity is sufficiently high in the reactions of inhibitor-peroxiradical and the constant has some the value $n*10^4$ as for the industrial antioxidants. Various petroleum systems extracted by different methods have been studied by the microcalorimetric method [1] as inhibitors of radical reactions. In general, their behavior was not beyond the established limits, nevertheless, it was found that some objects among the studied ones speed-up radical processes. In Table 1 there are data on the acceleration of the oxidation speed in the model reaction of cumene oxidation when petroleum fraction residues extracted on the laboratory installation are added into the system [2].

Table 1. Relationship between the speed of the model reaction of cumene oxidation and the concentration of petroleum system in the reaction cell.

Residue-91		Residue-92		Residue-94	
C, g/l	$w_{OX}\,10^{-6}$, mole/l sec	C, g/l	$w_{OX}\,10^{-6}$, mole/l sec	C, g/l	$w_{OX}\,10^{-6}$, mole/l sec
0	7.88	-	-	-	-
1.3	8.67	1.3	9.16	1.4	6.71
3.9	10.65	2.6	9.41	3.8	4.84
5.6	13.63	3.9	5.66	5.0	9.21
9.2	14.53	5.0	4.85	7.6	9.21

For the purpose of explanation of this accelerating effect of petroleum systems on the radical reactions, oil from the Strezhevoy oil field (well №11) has been separated into the following fractions: hydrocarbons, polycycloaromatics, neutral resins, acidic resins, asphaltenes. As to the fractions studied the fraction «acidic resins» has the accelerating effect, thus, it is reasonable to suppose acid catalysis of bimolecular decomposition RO-O-H into radicals and further speed-up of the oxidation.

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ABOUT THE ROLE OF SURFACE OXYGEN OF COPPER-CONTAINING OXIDE CATALYSTS FOR METHANOL SYNTESIS

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Methanol synthesis proceeds on copper-containing catalysts and it is described by equations [1]:

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad (1)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (2)$$

Reactions (1) and (2) are oxidation-reduction ones. The catalyst surface consists of metal and oxygen ions. According to the modern notions the active site in methanol synthesis is the solid solution of copper ions in the zinc oxide lattice, where copper plays a role of an adsorbent of reacting substances. However it was found that the adsorption of CO, CO_2, H_2, H_2O proceeds better on oxygen ions [2].

Studying the kinetics of methanol synthesis on SNM-1, ICI-51-2 catalysts and carbon oxide conversion with water vapour allowed to determine the activation energy of these reactions. It appeared that the energy for both reactions is the same one and it is equal to 60 kJ/mol. The value of activation energy of the limiting stage of catalytic reaction is determined by changing the energy of one of bonds, breaking or forming at the creation or the transformation of the surface compound. For methanol synthesis and carbon oxide conversion with water vapour on copper-containining catalysts the most probable bond is the following: surface oxygen-catalyst. The comparison of the energies of the reactions (1) and (2) with the bounding energy of oxygen in the surface oxides CuO, ZnO, Cr_2O_3 (71,223,109 kJ/mol, respectively) [3] showed that the bond energy of oxygen-catalyst coincides with the bond energy of oxygen in surface CuO. We suggested that surface oxygen should take part in catalytic conversion. The energy of its bond with the catalyst and hence its reactivity depend on the encirclement with cations. In this case the propeties of SNM-1, ICI-51-2 catalysts depend on the properties of copper ions bonding with oxygen.

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All mentioned above correlates with the earlier suggested mechanisms of synthesis [4] and CO conversion with water vapour:

$$CO(g) + 2[Cu^{2+}] + 2[O^{2-}] = [CO_3^{2-}] + 2[Cu^{+}] + [\ ] \tag{3}$$

$$[CO_3^{2-}] = CO_{(2)} + [O^{2-}] \tag{4}$$

$$H_2O(g) + [O^{2-}] + [\ ] = 2[OH^{-}] \tag{5}$$

$$2[OH^{-}] + 2[Cu^{+}] = H_2(g) + 2[O^{2-}] \tag{6}$$

$$CO_2(g) + [O^{2-}] + [Cu^{2+}] = [CO_3^{2-}] + [Cu^{2+}] \tag{7}$$

$$[CO_3^{2-}] + 2[Cu^{2+}] + H_2(g) = [H_2CO_3] + 2[Cu^{2+}] \tag{8}$$

$$[H_2\ CO_3] + 2[Cu^{2+}] = H_2O(g) + [CO_2] + 2[Cu^{+}] \tag{9}$$

$$[CO_2] + 2[Cu^{+}] + 2H_2(g) = CH_3OH[O^{2-}] + 2[Cu^{2+}] \tag{10}$$

$$CH_3OH[O^{2-}] = CH_3OH(g) + [O^{2-}] \tag{11}$$

were $[Cu^{2+}]$, $[Cu^{2+}]$, $[O^{2-}]$, $[CO_3^{2-}]$ - cation and anion centres of the lattice of ZnO with corresponding ions; $[H_2CO_3]$ - anion centre of the lattice of ZnO with H_2CO_3 molecule.

Methanol molecule formation occurs stage by stage. Carbon oxide takes away oxygen from the catalyst, but water returns oxygen to the catalyst. Stages (3-5) with the participation of 2 copper ions take place simultameously. It relieves the transfer of the electrons through the catalyst and leads to reducing the energy barrier. So, the move of electrons, oxygen ions end even copper ions take place [5].

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PPI-107

CATALYSIS AND AUTOCATALYSIS IN THE REACTIONS OF METAL ION REDUCTION IN AQUEOUS MEDIUM

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Catalytic phenomena are of essential importance in chemical reactions of reduction of noble and many non-noble metals (copper, nickel, cobalt, etc.) by reducers (formaldehyde, borohydride, hypophosphite, etc.) in aqueous medium or solution. General peculiarities of the reactions stimulated by metals of different dispersity. their mechanisms and problems aimed at extension of their practical application are considered in the report.

1. The reactions considered are related to the two types: (a) reactions of solid metal compound reduction; (b) reactions of ion metal reduction which are present in solution in the form of different complexes. Products of reactions proceeding in bulk of solution are highly dispersed metals and alloys (Ni-P, Ni-B, Ni-Co, Ni-Cu, etc.), films of regulated thickness formed on a solid surface (discontinuous or as patterns of defined topology). The selectivity of autocatalytic and catalytic metal deposition from solution(electroless deposition) on solid surfaces is attained by the extent of local formation of catalytic active centres on this surface using different photochemical processes.

2. The principal difference in the mechanism of catalysis of metal ion-reduction from solution by metal particles of different size is revealed. It consists in the realisation of spatial separation of anodic and cathodic steps of the redox-reactions. Possibilities of appearance of the catalytic activity by metal clusters which are instable thermodynamically in the reaction medium are discussed.

3. Directions of possible usage of the reactions of chemical reduction of metal ions (electroless deposition) are considered for a wide range of scientific and applied tasks: (i) determination of reducing centres on solid surfaces with catalytic activity (in the combination with electron microscopy); (ii) production of catalysts (in the form of ultrafine powders and films); (iii) intensification of photographic images with small optical densities; (iv) formation of the polychromic (multicolor) photographic images without dyes; (v) in the processes of metalization of dielectics; (vi) production of "amorphous" metals with controlled electroconductivity, etc.

PPII-108

THE REVERSED MICELLES OF NONIONIC SURFACTANTS ARE THE CATALYSTS OF NUCLEOPHILIC SUBSTITUTION REACTIONS

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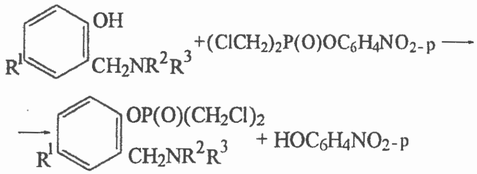
The reversed micelles (RM), one of the most simple colloidal systems formed by associates of surfactants in nonaqueous low-polar media, are interesting as catalysts of various chemical processes. The use of RM for syntheses of various compounds, for example surfactants, simple esters, photosemiconductive colloids is known. In addition, micellar systems are especially interesting because they are predecessor of more highly organized systems (such as liquid crystals), playing important role in the function of biological membranes. We have researched the influence of RM of nonionic surfactants (oxyethylic derivatives of fatty acids and alkyl phenols) on nucleophilic substitution reactions of phosphorus acids esters in toluene. The reactions of phenolysis



1: $R^1 = i\text{-}C_9H_{19}$, H, Cl; $R^2 = R^3 = CH_3$;
2: $R^1 = R^2 = H$; $R^3 = C_nH_{2n+1}$, n= 5, 8, 12, 16;
3: $R^1 = R^2 = H$; $R^3 = CH_2CH_2N^+Me_2C_{14}H_{29}$;

and aminolysis

$$R^4NH_2 + (ClCH_2)(PhO)P(O)OC_6H_4NO_{2}\text{-}p \longrightarrow$$
$$\longrightarrow (ClCH_2)(PhO)P(O)NHR^4 + HOC_6H_4NO_{2}\text{-}p,$$
$R^4 = C_nH_{2n+1}$, n=1,4,16,

were chosen as objects.

The character and the degree of the influence of polyethylene glycol-600-monolaurate (PM) micellar aggregates on phenolysis reaction depend on the structure of ortho-aminomethylphenols (AMP) and the concentration of surfactant and nucleophile in solution. The AMP (1) reactions are catalyzed by RM. Both catalytic and inhibition micellar effect take place for AMP (2) depending on the ratio of surfactant and nucleophile concentration. Inhibition of the reaction is observed in the presence of high PM concentration and low AMP (2) concentrations. There is an inhibition (more than one order of magnitude) by micellar aggregates in the case of AMP (3) with ionic structure. Different effect of nonionic micelles on phosphinate phenolysis may be caused by the dependence of nucleophile binding constants on AMP structure and differences in nucleophile localization, resulting in change of separation degree of reagents solubilized by RM.

The presence of PM, diethylene glycol monolaurate and Triton-X-100 micelles results in essential (more than four orders of magnitude) increase of observed rate constants of phosphonate aminolysis. The catalytic efficiency of micelles increases with decrease of the concentration and the alkyl radical length in amine and increase in the extent of surfactant oxyethylation.

Increase of the apparent values of the activation energy and decrease of the absolute values of the activation entropy of phenolysis and aminolysis at high surfactant concentration point out that catalytic effect of nonionic micelles in toluene is due to more favourable entropy factor.

The results obtained show that the RM of oxyethylic surfactants exert an essential influence on the nucleophilic substitution of esters of phosphorus acids and allow to change observed rate constants of the process in wide limits (the catalysis and the inhibition) depending on the surfactant and reagents structure and their concentration.

PPI-109

THE NOVEL FORMATION METHODS FOR CATIONIC Ni AND Pd COMPLEXES AS CATALYSTS FOR TRANSFORMATIONS OF UNSATURATED HYDROCARBONS

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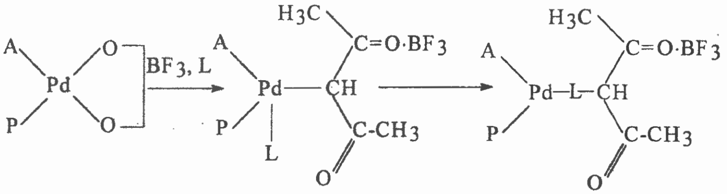
Cationic complexes of transition metals are effective catalysts for transformations of unsaturated hydrocarbons. In this work, we present new untraditional methods for purposeful designing *in situ* of coordinately unsaturated Ni and Pd cationic complexes in systems based on β-diketonates of named metals, for instance, $Ni(Acac)_2$-PR_3-$AlEt_3$-BF_3OEt_2, $Pd(Acac)_2$-BF_3OEt_2 and $Pd(Acac)_2$-PR_3-BF_3OEt_2. Two key reactions were used for the formation of Ni cationic complexes in various oxidation states: one-electron oxidation of Ni(0) phosphine complexes to Ni(I) with boron fluorides and two-electron oxidation of reduced forms of Ni with Broensted acids containing complex anions of type $H^+BF_3X^-$, where HX is HF, H_2SO_4, H_2O and ROH [1,2], according to following scheme:

$$\begin{tikzcd}
NiP_4 \arrow[r, "BF_3, L"] \arrow[d, "HX, BF_3"] & {[P_2NiL]BF_4} \arrow[r, "BF_3, L"] \arrow[d, "HX, BF_3"] & {[PNiL_2]BF_4} \\
{[P_2NiH]^+A^-} & {[P_2NiH]^{2+}2A^-} &
\end{tikzcd}$$

where P is PR_3; BF_3 is BF_3OEt_2; A^- is BF_3X^-; L is unsaturated hydrocarbon.

In this case the formation of Ni(0) phosphine complexes in the first step occurs through the interaction between the components of $Ni(Acac)_2$-PR_3-$AlEt_3$ systems and both the nature of PR_3 and the ratio P:Ni may be varied in a wide range. A high activity of $[(PR_3)NiL_2]BF_4$ complexes for positional isomerization of α-olefins, low molecular oligimerization of ethene and dimerization of propene has been established. In particular, the activity of these complexes for propene dimerization runs up to $2.7*10^5$ mol C_3H_6 /mol Ni*h. Cationic Ni(I) complexes containing two or more phosphine ligands exhibit no activity in propene dimerization. However, a treatment of such complexes with $H^+BF_3X^-$ results in the formation of most probable Ni(III) active for propene dimerization hydrides, similarly to the formation of Ni(II) hydrides from Ni(0) [1]. The activity of Ni(III) hydrides runs up to $2*10^5$ mol C_3H_6/mol Ni*h.

The interaction between the components of palladium catalysts leads to the formation of $(PR_3)_nPd(H)L_{2-n}BF_4$ complexes. In this case the formation of Pd-H bond occurs without traditional participation of alkylating or hydrogenating reagents. The first step of the synthesis of named palladium hydrides includes a substitution of one acetylacetonato ligand at Pd for F of BF_3 and further formation of complex BF_4^- anion. Depending on the number of organophosphorus ligands and substrate nature the complex anion may be bonded to Pd in the form of charge transferring complex or anion transferring complex. The second step is the formation of Pd-H bond with direct participation of unsaturated hydrocarbon. In this case the second acetylacetonato ligand at Pd transforms by following equation:



Decomposition of a new formed Pd-C bond by β-elimination mechanism is the last step of the formation of Pd-H bond. Catalytic systems based on $Pd(Acac)_2$ and BF_3OEt_2 are exhibiting relatively high activity and selectivity for dimerization of propene and styrene, low molecular oligomerization of ethene and telomerization of butene with diethylamine [3,4]. In particular, for dimerization of styrene to 1,3-diphenylbut-1-ene (up to 100%) conversion of styrene to products runs up to $7.5*10^5$ mol C_8H_8/mol Pd for 7 h at 343K; for telomerization of butene with diethylamine to N-octa-2,7-dienyldiethylamine (up to 100%) conversion of butene to products runs up to $1.84*10^4$ mol C_4H_6/mol Pd for 3 h at 353K.

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PPI-110

Gas Phase Catalytic Oxychlorination of Chlorinated Hydrocarbons by Hydrochloric Acid.

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The utilization of off-gas hydrogen chloride has been one of the main problems in the industrial chlororganic synthesis both for the compete utilization of chlorine raw materials and from the enviromental point of view. In the production of chlororganic products by the conventional methods of chlorination and dehydrochlorination hydrogen chloride is necessarily formed and the principal method of processing was until recently the conversion of it into hydrochloric acid with the following utilization. However, " off-gas" hydrochloric acid contaminated with chlororganic compounds is not always marketable, and the methods of its purification to the demanded quality are rather laborious. Due to the fact the problem of qualificated utilization of off-gas hydrogen chloride seems to be mostly important and pressing. It is solved at present by hydrogen chloride returning to obtain chlororganic products with the result that the whole production becomes chlorine-balanced, i.e. the whole chlorine fed is consumed only for the end products.

The principal methods of off-gas hydrogen chloride processing are hydrochlorination and oxychlorination processes. Great progress is made in the development of chemistry and technology of such processes.

One of the ways of off-gas hydrochloric acid utilization is its processing during oxychlorination process, particularly during high temperature processes for chlororganic solvent production from the different kinds of hydrocarbon raw materials and in the first place from the chlororganic production wastes. Besides, hydrochloric acid is formed during the very high temperature oxychlorination processes [illegible]. By putting its recycle into the reactor one can attain practically 100 % hydrogen chloride conversion and obtain chlorine - and hydrocarbon-balanced as well as enviromental processes for solvent production.

The greatest interest presents the use of acid in oxychlorination processes carried off in the reactors with a fixed-layer catalyst but their realisation is complicated by high heat effects and catalyst area overheats. There was conducted the study of the possibility of hydrochloric acid utilization in the chlororganic solvent production process by polychlorides C_2-C_3 high-temperature oxychlorination method.

The study included laboratory works (with the choice of effective catalytic system, optimal conditions for process conducting, solution of a number of other questions) as well as process pilot plant operation. Hydrocarbon raw materials were vinyl chloride and epichlorohydrin production wastes and chlorinating agent was hydrochloric acid of different concentration and air (oxygen). Laboratory and pilot plant operation studies of oxychlorination process were carried off in the reactors with fixed-layer catalysts.

Hydrochloric acid utilization in polychlorides C_2-C_3 oxychlorination process did not demand the development fundamentally new catalytic systems. The process was successfully conducted on catalysts developed for process with hydrogen chloride utilization. Catalytic systems $CuCI_2$ -KCI/ carrier with limited surface proved to be the most appropriate. The content of catalytically active components as well as carrier were varied depending on the kind of processed hydrocarbon raw material though there was exhibited the possibiliy of processing raw materials of various composition on the same catalysts.

PPI-111

PHASE-TRANSFER MICELLAR METAL COMPLEX CATALYSIS IN THE REACTION OXIDATION OF ALKYLBENZENES BY MOLECULAR OXYGEN

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The developing of various methods of phase-transfer and micellar catalysis is an important stage in the elaboration of catalysts for organic synthesis processes. The perspective direction appears to be the combination of these two variants that is simultaneous utilization in organic synthesis of advantages of phase-transfer catalysis connected with interface existence and micellar catalysis effects which are caused by the accumulation of various reagents in micelles. It allows to carry out synthetic processes with high rate and selectivity without usage of expensive solvents and explosive agents.

For reactions of alkylaromatic hydrocarbons oxidation the most interesting variant is phase-transfer micellar catalysis based on phase-transfer catalysis of "insulting" type. It means insertion of organic substrate from organic phase into aqueous phase, containing water soluble catalyst, in combination with reagents concentration in normal type micelles of surfactant by means of substrate solubilization and catalyst ions adsorption on micellar surface.

This work is aimed to investigate alkylaromatic hydrocarbons (i-propylbenzene, p-metyl-i-propylbenzene, m- and p-di-i-propylbenzenes) oxidation reactions under conditions of phase-transfer micellar metal complex catalysis. The system "metal (II) dodecylsulphate - $(C_{12}H_{25}OSO_3)_2Me\ 4\ H_2O$; Me = Cu; Co; Ni; Mn" was chosen as micellar metal complex catalyst.

The kinetic model of this process allowed taking into account separate stages of radical-chain reaction in different phases in good agreement with experimental data is suggested.

THEORETICAL INVESTIGATION OF METHANE, ETHANE AND PROPANE OXIDATIVE ADDITION TO DIHALOGENOBIS(PHOSPHINE)PALLADIUM(II) COMPLEXES, $PdX_2(PH_3)_2$ (X=F,Cl, Br, I). COMPARISON OF ALTERNATIVE REACTION PATHWAYS

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Hydrocarbon activation *via* oxidative addition of substrate CH bond to transition metal complexes is in focus of many theoretical works now. [1] Nevertheless they deal solely with thermodynamically favourable oxidative addition products and do not consider any results showing positive values of free energy of oxidative addition. Recently we have first obtained experimental results which demonstrate existence of a new group of hydrocarbon activation reactions which are thermodynamically unfavourable. [2,3] Due to both low stability of organometallic hydrocarbon activation products and its high reactivity they are very attractive, in particular, in design and elaboration of new hydrocarbon functionalization reactions.

In the presented work we consider three possible reaction pathways (1)-(3) for methane and dihalogenobis(phosphine)palladium(II) complexes, $PdX_2(PH_3)_2$ (X = F, Cl, Br, I), which served us as a model of more complex previously studied systems. These pathways are electrophilic alkane hydrogen substitution, oxidative alkane halogenation (bond metathesis) and alkane CH bond oxidative addition to palladium:

$$PdX_2L_2 + CH_3H \longrightarrow CH_3PdXL_2 + HX \quad (1)$$

$$PdX_2L_2 + CH_3H \longrightarrow HPdXL_2 + CH_3X \quad (2)$$

$$PdX_2L_2 + CH_3H \longrightarrow CH_3Pd(H)X_2L_2 \quad (3)$$

Using *ab initio* calculation with geometry optimisation on MP2 level theory we have carried out a theoretical investigation of reaction system alkane - the palladium complex. In a gas phase all mentioned reactions are thermodynamically unfavourable and are characterised with almost the same energy. Oxidative addition pathway has been studied more comprehensively. Geometry and relative stability of six diastereoisomeric oxidative addition products, hydridomethylpalladium(IV) complexes, $CH_3Pd(H)X_2(PH_3)_2$, were calculated. Both main features of their structure and order of their relative thermodynamic stability depend on position of only two most trans-influencing ligands, methyl and hydride. The most stable diastereoisomer is characterised with cis-position of two halogens, trans-position of two phosphines and cis-position of methyl to hydride ligands. Considering row of halogen complexes one can mark increasing endothermicy of oxidative addition leading to formation of the most stable organopalladium(IV) products of similar structure due to increasing repulsion of two halogen ligands in the most stable diastereoisomer.

Calculation on oxidative addition energy of methane, ethane and both primary and secondary CH bond of propane showed the following row of thermodynamic substrate and regioselectivity, i-Pr-H > n-Pr-H > Et-H > Me-H, which is consistent with available experimental data. Formation of weak η^2-alkane complexes was detected for both PdX_2L_2 and 14 electron complex $PdCl_2L$ ($L = PH_3$).

Kinetic barriers for methane oxidative addition and reductive elimination were calculated. Using method of internal reaction co-ordinate trajectory of methane oxidative addition was investigated. According to the results obtained the oxidative addition is concerted reaction with late transition state. Structural features of transition state for different halogen ligands are marked and discussed.

Results of the presented theoretic investigation are in good qualitative agreement with available experimental data on hydrocarbon activation with palladium(II) complexes.

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PPI-113

CONCERNING MECHANISM OF CATALYTIC CHLORINATION OF ALKANES AND ARENES WITH TETRACHLOROMETHANE IN THE PRESENCE OF PLATINUM(II) COMPLEXES, $PtX_2(PPh_3)_2$ (X = Cl, Me, Ph)

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Recently we have found that palladium(II),[1,2] platinum(II)[3] and rhodium(I)[4] complexes possess distinct catalytic activity in metathesis of alkane/arene CH bonds and polyhalogenomethane carbon-halogen bonds, C-X (X = Cl, Br, I) in the temperature range of 60-140°C:

$$R\text{-}H + CH_nX_{4-n} \longrightarrow R\text{-}X + CH_{n+1}X_{3-n} \qquad (1)$$

[M] = $Pd(Cl, Br, I)_2(PPh_3)_2$, $Pt(Cl, Me, Ph)_2(PPh_3)_2$, $RhCl(PPh_3)_3$
where X = Cl, n=4; X=Br or I, n=3
RH = PhH, PhMe, n-C_6H_{14}, cyclo-C_6H_{12}

In several cases preparatively high results in the reaction (1) were achieved.[2] In our previous works we considered two schemes of the reaction (1) catalytic cycle,[1-4] which include either C-H or C-X bond activation with metal complex. In the presented work we report results of detailed mechanistic study of the catalysis with platinum complexes. Platinum(II) complexes served us as model compounds which possess modest catalytic activity in the reaction (1) but allow easily to characterise catalytic effect quantitatively and usually allow to observe some reactive intermediate due to their relative kinetic inertness.

Our kinetic investigation on cyclohexane, n-hexane, benzene and toluene chlorination with tetrachloromethane resulted in determination of reaction (1) orders on each reagent involved and platinum complex. It turned out that reaction follows first order on n-hexane, cyclohexane, tetrachloromethane and platinum complex but is zero order on toluene. Surprisingly from the point of view of radical chain mechanism cyclohexane CH bond is nearly as reactive as benzylic toluene CH bond at the same concentration of bonds to be activated. Activity of the platinum complexes studied decreases in the row: $PtMe_2(PPh_3)_2 > PtCl_2(PPh_3)_2 \approx PtPh_2(PPh_3)_2 > Pt(CH_3CN)_2Cl_2$, as the electron density on platinum atom decreases. Stability of the catalysts under the reaction condition were determined using NMR ^1H and ^{31}P spectroscopy. All the compounds give in the course of the reaction similar mixture of platinum phosphin complexes. The catalytic systems studied are partly inhibited with additives of both benzoquinone and hydroquinone and completely inhibited by additive of iodine. The mentioned features of the reaction investigated are not clear neither from the point of view of chain radical nor non-radical mechanism.

In order to get additional information about intimate features of the catalytic reaction (1) we studied and compared substrate and regioselectivity of both catalytic and non-catalytic reaction. (The last reaction was at least one order of magnitude slower than the former.) The results obtained show that both regioselectivity of n-hexane chlorination and substrate selectivity in concurrent chlorination of cyclohexane and toluene (1) with tetrachloromethane are very close both for catalytic and non-catalytic processes. These facts may indicate that in both cases CH bonds react with the same active species such as trichloromethyl free radical. It appears by thermolysis of hydrocarbon - tetrachloromethane mixtures or as a result of C-Cl bond activation with platinum(II) complex in the case of catalytic reaction. At the same time formation of $CCl_3\bullet$ and its consecutive reaction with hydrocarbon CH bond may occur in one solvent cage, so that no kinetically free radicals are observed.

Formation of organoplatinum(IV) compounds in the reaction mixtures is discussed.

Acknowledgements. Authors are grateful to Russian Foundation for Basic Research for financial support, Grant No 94-03-08412a.

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MILD OXIDATIVE ALKOXYLATION OF CYCLOHEXANE AND TOLUENE WITH DIBROMOPALLADIUM(II) COMPLEX - SODIUM ALKOXIDE SYSTEM

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Palladium(II) complexes are well known as reagents and catalysts for alkane functionalization reactions. [1-2] Usually they are used in *strongly electrophilic* media such as sulfuric or trifluoroacetic acid which enhance ability of palladium(II) containing cationic species to activate electrophilically hydrocarbon C-H bonds. Recently we have found several new alkane functionalization reactions both catalytic and stoichiometric on palladium(II) complexes, [2a] which proceed in pure hydrocarbon media in the *absence of acid additives* and seem to include alkane activation of different kind, oxidative addition of alkane CH bond to palladium. [2b] Now we suggest new alkane functionalization reaction, synthesis of alkyl ethers directly from hydrocarbon and alcohol, which proceeds in *basic* media containing sodium alkoxide and dibromopalladium(II) complex. Formally, in the course of the reaction hydrocarbon oxidation with palladium(II) compound takes place and one of hydrogen atoms of substrate is substituted with alkoxo group:

$$RH + [PdBr_2] + 2\,NaOR' \xrightarrow[\text{1-2 hours}]{30^o - 60^oC} R\text{-}OR' + 2\,NaBr + [Pd^o] \qquad (1)$$

where $[PdBr_2]$ and $[Pd^0]$ are certain palladium complexes
R-H = cyclo-C_6H_{11}-H, $PhCH_2$-H; R' = Me, Et, i-Pr

A range of alcohols and hydrocarbon substrates have been studied. Yields of ether reach 50-80% on palladium compound depending on reaction condition and alcohol used. Tertiary butanol is not reactive. Benzene is inert under the reaction conditions, toluene gives both benzylic and tolyl ethers. All possible ethers are formed if reaction mixture contains more than one alcohol taken in equal amounts. In this case main product resulted from the most nucleophilic alkoxide.

Mechanism of the reaction (1) was studied experimentally. Effect of alcohol, sodium alkoxide, hydrocarbon substrate, palladium(II) complex concentrations and effect of phosphine additives on the reaction rate was determined. The reaction scheme was proposed. It includes active palladium(0) complex which is formed in the course of redox reaction between palladium(II) compound and sodium alkoxide. Then oxidative addition of hydrocarbon C-H bond to palladium(0) active species takes place to produce organopalladium(II) compound. Its following transformations into ether may occur either *via* direct nucleophilic substitution of palladium at palladium bound carbon atom or *via* intermediate organopalladium(II) alkoxide complex which then undergoes reductive elimination of alkyl and alkoxo ligands. The mechanistic scheme was used to explain reaction selectivity.

Theoretical investigation of the two alternative reaction mechanisms has been performed. It is based on *ab initio* calculations of thermodynamic properties of suggested reaction intermediates and kinetics of their reactions in gas phase.

Perspectives of synthetic application of the described reaction and some other similar processes of oxidative coupling of alkanes with nucleophiles are discussed.

Acknowledgements. Authors are grateful to Russian Foundation for Basic Research for financial support, Grant No 94-03-08412a.

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OXIDATION OF ETHYLENE GLYCOL ON Cu - Ag CATALYST

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Glyoxal is widely used as a monomer in the production of polycondensation materials, synthetic resins, medicine, heterocyclic compounds, as well as in textile and leather industries. Taking into account the great need for glyoxal and the increasing ecological requirements to the processes of organic synthesis, the development of an ecologically safe process of catalytic oxidation of ethylene glycol to glyoxal becomes actual.

In the present work the process of ethylene glycol oxidation on two layed Cu - Ag catalyst has been studied in the wide variation of the process conditions: temperature 673 - 923 K, ratio of oxygen / alcohol 0.6 - 1.3, ratio of nitrogen / alcohol 4 - 8.5, concentration of ethylene glycol in water 30 - 70%. The best parameters of the process were discovered to be : temperature 863 - 873 K and ratio of oxygen/alcohol 1 - 1.1. Water vapour decreases the dehydration of ethylene glycol leading to acetaldehyde formation and polycondensation, which results in the coking on the catalysts surface. The addition of nitrogen in the reaction mixture exerts favourable influence on the process. Both the increase of ethylene glycol conversion and glyoxal output take place.

The interaction of ethylene glycol and oxygen (T_{ads} = 293 - 673 K) on the silver surface was investigated by means of the method of temperature - programmed desorption (TPD) and by the temperature - programmed reaction (TPR) to specificate the mechanism of the process. Three forms of the oxygen desorption from the silver surface were found by the TPD method : a desorption peak at 403 K and desorption peaks at 538 K and 703 K , which are characterized by different strength of oxygen - Ag bond. A high - temperature subsurface form (a desorption peak at 780 K) has been detected as well.

PPI-115

Ethylene glycol is reversibly adsorbed on the clean Ag surface with the formation of multilayer state. The desorption activation energy for this state was estimated to be 59.6 kJ/mol. Treatment of catalyst surface by oxygen sharply changes the desorption spectrum. The character of ethylene glycol surface interaction depends on the strength of O - Ag bond and on the adsorption form of alcohol.

The reversible form of ethylene glycol adsorption at 473 K on the oxydized surface of Ag ($T_{ads} O_2$ = 473 K) is responsible for glyoxal formation by means of dehydrogenation according to scheme :

$HOCH_2CH_2OH\ (g) \rightarrow HOCH_2CH_2OH\ (a)$ (1),

$HOCH_2CH_2OH\ (a) + O\ (a) \rightarrow HOCH_2CH_2O\ (a) + OH\ (a)$ (2),

$HOCH_2CH_2O\ (a) + OH\ (a) \rightarrow OCH_2CH_2O\ (a) + H_2O\ (a)$ (3),

$H_2O\ (a) \rightarrow H_2O\ (g)$ (4),

$HOCH_2CH_2OH\ (a) \rightarrow HOCH_2CH_2OH\ (g)$ (5),

$OCH_2CH_2O\ (a) \rightarrow O{=}CHCH_2O\ (a) + H\ (a)$ (6),

$O{=}CHCH_2O\ (a) \rightarrow O{=}CHCH{=}O\ (g) + H\ (a)$ (7),

$H\ (a) + H\ (a) \rightarrow H_2\ (g)$ (8).

While increasing the temperature of oxygen adsorption above 573 K the glyoxal formation takes place according to the oxidation way as it was evidenced by the absence of hydrogen in the desorption products. Simultaneously, a part of ethylene glycol is adsorbed on the oxydized surface of Ag with the decomposition leading to the formation of secondary products : formaldehyde and CO_2 (desorption peaks at 603 and 703 K).

PPI-116

OLEFIN HYDROSILYLATION, OLYGOMERIZATION, AND POLYMERIZATION CATALYZED BY GROUP III AND IV TRANSITION METAL COMPLEXES

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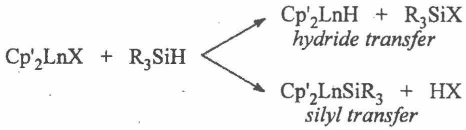
Scope and mechanism (including kinetics) of olefin hydrosilylation and hydrostannylation as well as side reactions, such as selective olefin dimerization, olefin hydrogenation - silane coupling, H/D exchange, dehydrogenative coupling of silanes and tin hydrides catalyzed by organolanthanide and -yttrium complexes are discussed in details.

The present report involves the consideration of two problems. The first one concerns the structure of organometallic intermediates of catalytic reactions. We have shown that *monomeric* lanthanide hydrides are the most efficient catalysts of olefin hydrosilylation. This is caused by the specific ability of the intermediates to add olefin very fast. However, the association of lanthanide catalyst in solution seems to be a conventional phenomenon because of extraordinary stability of the most lanthanide compounds with various bridgings $Cp'_2Ln(\mu\text{-}X)(\mu\text{-}Y)LnCp'_2$ (X, Y= H, Alkyl, Cl, OAlkyl, etc.). In the course of the catalytic reactions *the organometallic associates turned out not to dissociate completely*. This can result in unexpected selectivity of olefin hydrosilylation, dimerization, etc.

Another important problem is the study of unusual dual reactivity of lanthanide compounds including Ln-H, Ln-C, and Ln-Si bonds toward silanes, i.e.



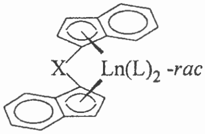
$$Cp'_2LnX + R_3SiH \rightarrow Cp'_2LnH + R_3SiX \quad \text{(hydride transfer)}$$

$$Cp'_2LnX + R_3SiH \rightarrow Cp'_2LnSiR_3 + HX \quad \text{(silyl transfer)}$$

Here we describe first example of the concerned silyl transfer involving lanthanide hydrocarbyl formed during the catalytic *cyclo*-olefin hydrosilylation. The study of both stoihiometric and catalytic reactions of considerable theoretical and probably industrial interest as well as ZINDO/1 calculation of geometry and orbitals of the corresponding organoyttrium adducts and transition states for concerned hydride and silyl transfers give valuable information on the reaction pathways and reveal some important factors, which can result in the change of reaction mechanism of above-mentioned catalytic reactions.

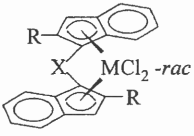
PPI-116

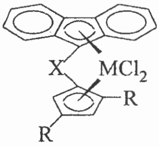
The present report also includes description of the synthesis and structure of new promising polymerization catalysts based on chiral *ansa*-metallocenes of divalent europium, samarium, and ytterbium, i.e. (X= CMe_2, CH_2, $SiMe_2$, L= THF, Et_2O):



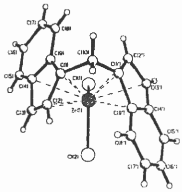
The compounds were found to be effective catalysts for stereospecific polymerization of styrene, methylmetacrylate as well as some other substrates.

Here we describe also new straightforward synthetic methods, structure in solution and in the solid state, reactivity and catalytic activity for a number of new and some known *ansa*-metallocenes of zirconium, hafnium, and particularly titanium. It means both chiral and sterically strained *ansa*-metallocenes, such as (M= Ti, Zr, Hf; X= CMe_2, CH_2, $SiMe_2$, etc.; R= H, Me, etc.):

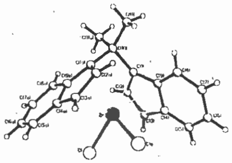




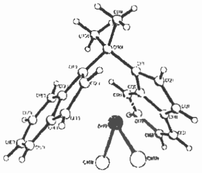
A number of the compounds were characterized by X-ray crystal analysis, e.g.



rac-$H_2CInd_2ZrCl_2$



rac-$Me_2CInd_2ZrCl_2$



meso-$Me_2CInd_2ZrCl_2$

Producing inter-conversion of *meso* complexes into the corresponding *racemates*, convenient synthesis of a number of starting ligands as well as catalytic activity of the compounds, i.e. their dialkyl and cationic derivatives, in stereospecific olefin polymerization and dehydrogenative coupling of primary silanes are considered.

SUPPORT INFLUENCE ON ACTIVITY OF Pd-CONTAINING CATALYSTS OF CO OXIDATION

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Catalytic activity of supported metallic catalysts is sufficiently affected by chemical nature of support. In this work the effect of support nature on the activity of palladium in carbon monoxide oxidation was investigated. Titanium compounds with different part of metallic component in the chemical bond ($TiC_{0.85}$; $TiN_{0.65}$; TiO_2) and Al_2O_3 were taken as supports.

Catalytic activity of the above substances in CO oxidation was investigated. The catalytic activity was found to decrease in the following row :

$$TiC_{0.85} = TiN_{0.65} > TiO_2 >> Al_2O_3$$

Al_2O_3 is inert in the CO oxidation. It can be noticed that decrease of metallic component part in chemical bond takes place in this row. So, catalytic activity of these substances rises with increase of their metallicity.

Supported palladium catalysts were prepared by impregnation with palladium nitrate solution followed by reduction with hydrazine hydrate. Pd content in the catalysts was 0.5% mas. The supported catalysts showed the following row of activity:

$$Pd/Al_2O_3 > Pd/TiO_2 > Pd/TiN_{0.65} = Pd/TiC_{0.85}$$

(temperature range is 400 - 480 K). It is clear that this row of activity is opposite to that of pure supports.

Presumably, support effect on palladium is determined by Pd-support interaction including electron transfer from palladium onto support. This transfer is more effective for metal-like compounds than for oxides, especially for alumina. According to XPS data bonding energy of 3d-electrons of palladium (335.0 eV) supported on oxides corresponds to that of metallic Pd while in case of $Pd/TiN_{0.65}$ bonding energy is 335.5 eV, that is 0.5 eV shift is observed. It shows electron density transfer from palladium to the support.

We suppose that the decline of electron density on supported palladium causes stronger chemisorption of CO. Therefore the weakest chemisorbed CO species exist on Pd/Al_2O_3 and it is a reason of the highest catalytic activity of this supported system.

The reaction kinetics is studied on all above palladium catalysts. Temperature and concentration peculiarities are characterized by unstationary phenomena - hysteresis on temperature and concentrations. These phenomena are also observed for bulk palladium catalysts.

PPI-118

SURFACE POTENTIAL IS A PREDOMINANT FACTOR OF MICELLAR CATALYSIS

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The major factor determining the catalysis of ion-molecular reactions by normal ionic micelles is the surface potential. Nucleophilic substitution reactions may be catalyzed (by cationic micelles) or inhibited (by anioinic micelles) depending on the charge sign of the head groups.

The kinetic study of ion-molecular reactions in the ionic micelles as connected with the high ions concentration. Correct treatment of the salt effect is a weak point of the micellar catalysis models and require further efforts. Counter-ion was identified as a principle subject of the salt effect no matter what its origin. It allows to use the same criterion for interpretation of all the results and recognize the surface potential as a predominant factor of micellar catalysis.

The object of our kinetic study was the reaction of basic hydrolysis of p-nitrophenol acetate (I), bis(p-nitrophenyl)methylphosponate (II), O-ethyl-S-propyl O(2,4-dichlorophenyl)thiophosphate (III) and p-nitoranilide of bis(chloromethyl)phosphinic acid (IV).

Cationic micelles of cetyltrimethylammmonium bromide (CTAB) accelerate basic hydrolysis of I 3-fold and that of II more than 100-fold. Anionic micelles of sodium dodecyl sulfate (SDS) retard ca.200-fold basic hydrolysis of III.

Decrease of the inhibition effect of SDS micelles and catalytic effect of CTAB micelles with increasing concentration of counter-ion constituting buffer (up to 10-fold), or nucleophile (ca. 4-fold), or inert salt (more than 100-fold) has been shown.

Increase of counter-ion concentration produces sphere to rod transition in the micellar structure. Investigation of basic hydrolysis catalysis of I and II and equilibrium shift of IV by CTAB micelles in the presence of KCl, KBr, KAc, KNO_3, has qualitatively shown the reactivity change with micellar structure modification. Analysis of the apparent rate and equilibrium constants dependence on the logarithm of salt concentration has revealed the critical points on the plots, the same for each sort of counter-ion in all of the processes (Fig. 1). In accordance with literature data these critical concentrations were identified as sphere to rod transition concentrations.

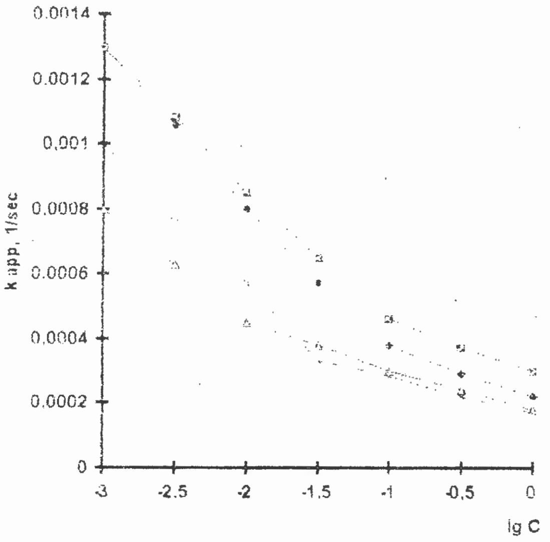

Fig. 1. Dependence of apparent rate constants of basic hydrolysis of p-nitrophenyl acetate on the logarithm of concentration of Kbr (-◆-), KNO_3 (-☐-), KAc (-△-), KCl (-x-).

PPI-119

INVESTIGATION OF THE HYDROGENATION MECHANISM OF CARBON DIOXIDE ON NICKEL-IRON CATALYSTS

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The problem of carbon dioxide utilization, i.e. using it as a source of carbon in organic synthesis, is urgent, since this gas is erupted by engines, plants, power stations into the atmosphere in large amounts. Systems for carbon dioxide hydrogenation are proposed in a number of papers.

In spite of a considerable number of papers devoted to the hydrogenation mechanism of CO_2, there is no common opinion on the role of CO in CO_2 methanation. Here we present our results of studying the hydrogenation mechanism of CO_2 on nickel-containing catalysts.

CO_2 hydrogenation was studied in running conditions within 300-450°C at P=0.1 MPa and a CO_2:H_2 ratio of 1:4. The catalyst was prepared by means of impregnation of aluminium oxide (γ-Al_2O_3) with a specific surface of 190 m^2/g with nickel nitrate solution. The nickel content in the catalysts was 1, 3, 5, and 10 wt % on a metallic nickel basis.

Under these conditions, CO_2 is hydrogenated to methane and CO with the rate of the process depending on temperature, contact time, and nickel content in the catalyst. The maximal rate of methane formation was achieved on the catalyst containing 5 wt % of nickel within 350-400°C.

Several schemes for CO_2 hydrogenation are proposed in the literature. According to one of them [1], hydrogenation begins with hydrogen activation and then goes by interaction of CO_2 molecules with adsorbed hydrogen. Another scheme [2] regards only two forms of adsorbed CO_2 as capable of reacting with hydrogen.

CO_2 and H_2 adsorption on the nickel catalyst was studied. Both of them have been shown to adsorb on the catalyst surface in forms able to interactions.

Besides methane, CO_2 is present in the products of CO_2 hydrogenation. No CO was found in the interaction products of both adsorbed H_2 and adsorbed CO_2 with the second component from the gaseous phase.

In order to clear up the role of carbon monoxide in CO_2 hydrogenation, conversion of CO_2 on a mixed catalyst (composed of the nickel-containing catalyst under study and the iron-aluminium one which promotes CO_2 hydrogenation to CO only) was studied. The methane output and the rate of its formation were found to fall in comparison with those for the nickel catalyst. A bright example appeared when the mixed catalyst was loaded one layer at a time. This evidences that CO is not an intermediate product in CO_2 hydrogenation to methane; on the contrary, it poisons the catalyst.

Hence, the above data enable us to propose the following scheme of CO_2 methanation on the nickel catalyst:

1) $H_2+2Z=2HZ$
2) $CO_2+Z=CO_2Z$
3) $CO_2Z+HZ=COOHZ+Z$
4) $COOHZ+HZ=COHZ+ZOH$
5) $COHZ+HZ=CHZ+OHZ$
6) $CHZ+HZ=CH_2Z+Z$
7) $CH_2Z+HZ=CH_3Z+Z$
8) $CH_3Z+HZ=CH_4+2Z$
9) $OHZ+HZ=H_2O+2Z$

CO formation from CO_2 may proceed according to the scheme:

1) $CO_2+2Z=COZ+OZ$
2) $COZ+OZ+H_2=CO+2Z+H_2O$

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PPI-120

CO_2 HYDROGENATION IN THE PRESENCE OF NICKEL-CONTAINING CATALYSTS

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Consumption of natural fossil fuels increases every year, and emission of carbon dioxide into the atmosphere constantly grows. In this connection, serious attention is paid to development of catalytic systems of CO_2 hydrogenation.

The present paper reports the results of our studies of how the nickel content in catalysts and the nature of support influence the main parameters of interaction between carbon dioxide and hydrogen.

CO_2 hydrogenation was studied in running conditions within 350-500°C at $P=0.1$ MPa and a CO_2:H_2 ratio of 1:4. The catalysts were prepared by means of impregnation of aluminium oxide (γ-Al_2O_3) and sibunite with nickel nitrate solution. The nickel content in the catalysts was 1, 3, 5, and 10 wt % on a metallic nickel basis. The rate of reaction product formation was used to characterize the catalytic activity.

The maximal rate of methane formation has been shown to depend on the nickel content and to be achieved with the catalyst containing 5 wt % if Ni (in the temperature range 350- 400°C).

CO_2 hydrogenation proceeds with the formation of CH_4 and CO. The catalyst with 1 wt % of Ni showed a higher selectivity to monoxide than that to methane at all temperatures. As the nickel content increases up to 5 wt %, the selectivity to methane grows sharply while that to carbon monoxide decreases. During further increasing the nickel content up to 10 wt %, the selectivity to methane remains practically constant within 450-500°C.

The Ni/Al_2O_3 catalyst has been shown to differ from the Ni/sibunite one by a higher degree of CO_2 and H_2 conversion and by a higher methane content in product gases.

The optimal temperature of methane synthesis has been found to be determined by the nature of support and to be slightly higher for Al_2O_3 than for sibunite.

The influence of contact time on hydrogenation rate was studied. Contact time has a strong effect on the rate of methane formation.

This rate is also influenced by the feed rate of the source gas mixture. It is maximal at the volume rate of 100 h^{-1}.

POSTER SESSION II

Section 4

Molecular Sieve Effects in Catalysis

FORMATION OF AN ACTIVE STRUCTURE FOR ZEOLITE CONTAINING Al-Ni-Mo CATALYSTS FOR HYDROUPGRADING OF OIL CUTS

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Deepening of oil refining requires new, more effective catalysts for hydroupgrading of oil products. One of the trends in the development of catalysts with a view to improve activity and selectivity is their modification with various oxide additives. This work involved a study of an effect of Y-zeolite on a formation of a support structure and catalytically active phases of the aluminonickelmolybdenum catalysts (Al-Ni-Mo).

The introduction of zeolite into alumina support results in the formation of new 100-300 Å pores therein. A strong chemical interaction between zeolite and Al_2O_3 does not take place. Zeolite crystallites in the support are covered with Al_2O_3 particles.

The study of zeolite additive effect on the formation of oxide Ni-Mo phases has shown that the introduction of Y-zeolite results in the quantitative increase of Ni and Mo interaction on the support surface and inhibits penetration of Ni and Mo ions into the support with the formation of catalytically inactive bulk structures of spinel type. Analysis of the surface chemistry has shown an increase of Ni/Al and Mo/Al ratios at the introduction of zeolite into Al-Ni-Mo catalysts. Ferromagnetic resonance signals of these catalysts have much higher intensity and arise at lowers temperatures compared to zeoliteless samples. These date indicate higher dispersity of hydrogenation metals on the surface of the zeolite Al-Ni-Mo catalyst. The study of Al-Ni-Mo catalysts acidity has shown that the introduction of 5-10% of Y-zeolite into Al-Ni-Mo catalyst results in the increase of adsorption sites weakly binding ammonia (50-200° C); the increase of stronger acid sites has not been found.

Thus, the addition of Y-zeolite increases the amount and dispersity of active surface Ni-Mo phase in the Al-Ni-Mo catalyst, which become apparent in the increase of the catalyst hydrodesulfurizing activity. Besides, the zeolite addition permits to control porous structure and improves regeneration properties of the Al-Ni-Mo catalyst, enabling more complete removal of coke from the catalyst at lower temperatures.

The data obtained were used to develop a number of commercial hydroprocessing catalyst. Now base catalysts used for hydrotreatment of various fractions are represented by zeolite catalysts - GKD. The GKD-202 catalysts are used for hydrotreatment of kerosene ($P = 3,5$ MPa, $V = 6\ h^{-1}$) and diesel fractions ($P = 4$ MPa, $V = 4\ h^{-1}$). The GKD-202 catalyst is more effective in the same processes, especially in hydrotreatment of high-sulfur (1-1,5 mass. % S) diesel fuel cuts. At 4 MPa and 330-350°C this catalysts ensure desulfurisation level exceeding >90 %. The life-time of this catalyst before regeneration is 24 months minimum, the total life-time is 6-7 years. GKD-202 catalysts are used for vacuum gas oil hydrotreatment. This catalyst is successfully used during 4 years in a hydrotreatment section of catalytic cracker at 4MPa and 350-370°C, providing the production of high quality feedstock for catalytic cracking.

CATALYTIC CRACKING WITH REDUCED HAZARDOUS ATMOSPHERIC EMISSIONS

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The FCC process plays an important role in oil refining In the process of used catalyst regeneration. From one FCC unit up to 10 tpd SO_x, 120 tpd carbon monoxide, up to 2 tpd catalyst particles are emitted to the atmosphere. Due to the fact that the environmental protection regulations are becoming more stringent the problem of hazardous emissions reduction is rather acute.

One of the most reasonable and promising trend in improving the cracking catalyst regeneration process consists in the technology of CO controlled oxidation and SO_x fixation in the reactor volume using special promoters. For the oxidation of CO to CO_2 we have developed KO-9M and KO-10 promoters such as alumina support coated with platinum through impregnation.

The use of the KO-10 oxidation promoter provides residual coke reduction from 0,25 to 0,1%, an increase in gasoline yield by 1,0%, elimination of CO emissions to the atmosphere, temperature stabilization and energy conservation.

To reduce SO_x emission the PS-17 additive was used. An alumina support with a surface area in the range of 100 to 150 m^2/g and pore volume of 0,3-0,4 cm^3/g proved to be optimum. After the introduction of PS-17 the content of SO_x in the regenerator gases was reduced by 60-67% (rel.). It has been revealed that the removal of SO_x causes a beneficial effect on the KO-10 oxidation promoter stable activity. It has to be noted that in the presence of the oxidation, the depth of SO_x removal is raised by 10-12% (rel.).

The results of commercial testing on 1A/1M and GK-3 FCC units at Angarsk Refinery have shown that the yield of the main FCC products remained on the previous level. The use of PS-17 permits to recover additional 500 t sulfur or 1,5 t of sulfuric acid on FCC unit per year. The use of CO oxidation promoters and sulfur fixation additives permits to improve substantially the environmental situation due to the reduction of hazardous emissions to the atmosphere, at the same time enhancing the technico-economic indices of the FCC unit operation.

PPII-3

Modifying of Super-Siliceous Zeolites ZSM with the Electrochemical Treatment

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High-siliceous zeolites are efficient catalysts for a number of oil chemistry and oil refinery processes. A catalytically active H-form of zeolite can be obtained by the treatment of Na-ZSM with the solution of a mineral acid (I) or ammonia salt (II). When the latter is the case, the annealing of NH_4-form results in ammonia elimination and H-ZSM formation.

In our papers it has been shown that H-ZSM can also be produced when treating the aqueous zeolite suspension in the anode chamber of the diaphragm electrolyzer. The decationation method involves the treatment of the aqueous zeolite suspension in the electrolyzer anode chamber. The anode water electrolysis generates ions H_3O^+ or OH^- which through the interaction with the zeolite bring about its decationation as well as the changes of the acid-base properties. The electrodialysis diffuses the Na^+ ions into the cathode chamber of the electrolyzer and concentrates forming Na hydroxide. The treatment of zeolite in the anode chamber causes its decationation to the residual content of Na_2O less than 0.1%, and the crystallinity of the zeolite increases.

The present paper aims at optimizing the decationation according to the following parameters: the nature and the concentration of the electrolyte, hydromodle, the duration of treatment, the interchamber partition material.

The main efficiency criterion was the residual content of Na^+ in the zeolite.

The effect of the method of decationation of zeolite on its catalytic properties is presented in Tabl. 1. The aromatization of ethylene - target product and the fraction - has been taken as a model reaction. The experiments were carried out in a microreactor V=2 cm^3 of the flowing type, W=1.5 h^{-1}.

Table 1

№ sam.	The method, conditions of decationation	The catalyst composition, 4 h, % wt			Σ arom., % wt.			Na_2O % wt.	The time of operation after regeneration, h
		B	T	X	4 h	7 h	10 h		
1	I; 0,1N HCl	28	49	21	53/24**	49/0	30/0	0,07	6
2	II; NH_4Cl	24	55	20	71/61	56/52	46/34	0,06	>9
3	III; Anode chamber, 0,2% KCl	21	53	23	74/60	61/37	23/8	0,06	9
4	III; Anode chamber, without electrolite	29	47	18	66/60	65/63	66/52	0,05	>15

** numerator- before regeneration, denomination- after regeneration

Table 1 shows that the most efficient catalyst for the ethylene aromatization is the sample № 4- it has the longest interregeneration period and is steadily active. The Table 2 shows the data of the research of the acid-base properties of decationated zeolites with the IR-spectroscopy. The decationation method I causes considerable dealumination of the zeolite frame (the sum content of B- and L-centers is proportional to the total aluminium concentration in the zeolite). The low catalytic activity of the sample № 1 is likely to be due to the low content of the B-centers.

Table 2.

№ sum	The concentration of Lewis acid centers, µmole/g				The concentration of Broendsted acid centers, µmole/g			ΣL_i+B_i µmole/g
	L_1^*	L_2	L_3	ΣL_i	B_1^{**}	B_2	ΣB_i	
1	78	36	15	129	165	34	200	329
2	135	52	25	212	250	75	325	537
3	121	40	14	175	235	64	299	474
4	100	33	18	151	220	34	254	405

* L_1 - the weakest L-centers, Q_{co}=34-30 kG/mole,
L_2 - the centers of medium strength, Q_{co}=41-48 kG/mole,
L_3 - the strongest L-centers, Q_{co}=49-51 kG/mole,
**B_1 - the bridge hydroxyle groups of the inner surface of the zeolite ν_{oh}=3605-3610 sm^{-1}, the proton tear-off energy from the acid residue 1180 kG/mole;
B_2 - the bridge hydroxyle groups of the outer zeolite surface ν_{oh}=3720-3725 sm^{-1}, the proton tear-off energy from the acid residue 1180 kG/mole.

The most active sample is № 2. The sample № 3 is characterized by a high content of B-centers, its value (299 µmole/g) is intermediate between the sampls № 4 and № 2. However, with close amounts of B-centers 299 and 254 µmole/g the latter has the smallest concentration of the L-centers (151 µmole/g) and hence the longest interregeneration periode. Similar regularities can be observed when aromatizing directly distilled oil fractions.

The data obtained show that the decationation of high-siliceous zeolite in the electrolyzer chamber allows to change the acid-base zeolite properties. This can be used in producing active and steadily operating catalysts.

PPII-4

Carbonylation of Small Alkanes on Acidic Zeolites at Moderate Temperatures: NMR Observation of Carboxylic Acid Formation from Alkane, CO and Water in H-ZSM-5 at 373-473 K.

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Alkanes are inert hydrocarbons toward their interaction with usual reagents to produce chemically useful products. For this reason catalytic reforming and vaporcracking, which necessitate the use of noble metals and high temperature, are the main operations used to convert alkanes into primary chemical blocks such as olefins, dienes, aromatics. However, from economical point of view it is of importance to fulfill a conversion of alkanes to the useful chemicals at low temperature and with the aid of catalysts, which contain no noble metals.

Recently, it has been established that small alkanes undergo H/D exchange with acidic OH groups of zeolites at comparatively low temperature (373 - 473 K), while other transformations such as cracking reaction were not observed [1-3]. It was concluded that both intermediate olefins and carbenium ions, which are in equilibrium to each other provides the observed H/D exchange on acidic zeolite [2,3]. Taking into account the known property of carbon monoxide to react with olefins inside acidic zeolites to give carboxylic acids via trapping carbenium ions generated from olefins [4,5], one could expect small alkanes would interact with CO at temperature of the observed H/D exchange, while alkane cracking reaction does not occur.

In this paper, by using ^{13}C CP/MAS and ^{1}H MAS NMR we have presented evidences that small alkanes (e.g., propane, isobutane) can be carbonylated with carbon monoxide at 373-473 K in H-ZSM-5 zeolite and alkane converted in the presence of water into useful chemical products - a carboxylic acid. The reaction occurs without excess of carbon monoxide, just upon coadsorption of equal amounts of alkane, CO and water on H-ZSM-5, no side reactions such as cracking have been observed.

Isobutane has been found to transform selectively into trimethylacetic acid via tertiary C-H bond activation and abstraction of molecular hydrogen (Scheme 1), the percentage of alkane conversion being *ca* 1 % at 373 K and 2 % at 423 K.

$$(CH_3)_3CH + CO + H_2O \xrightarrow[373\text{-}423\ K]{H\text{-}ZSM\text{-}5} (CH_3)_3C\text{-}COOH + H_2$$

Scheme 1.

In case of propane, C-C bond cleavage occurs and isobutyric acid is selectively formed with the conversion of *ca* 0.5 % at 373 K and 1 % at 473 K, methane and ethane being formed as the other reaction product (Scheme 2).

$$C_3H_8 \xrightarrow[373\text{-}473\ K]{H\text{-}ZSM\text{-}5} CH_3\text{-}CH_2^+ + CH_4$$

$$CH_3\text{-}CH_2^+ + C_3H_8 \longrightarrow C_2H_6 + CH_3\text{-}CH^+\text{-}CH_3$$

$$CH_3\text{-}CH^+\text{-}CH_3 + CO + H_2O \longrightarrow (CH_3)_2CH\text{-}COOH$$

Scheme 2.

It should be noted that the reactions observed on H-ZSM-5 proceed in a complete accordance with the order of reactivity of single bonds in alkanes in superacidic solutions [6], the most reactive being tertiary C-H bond of isobutane. In the case of propane the reaction via C-C bond cleavage is more preferential than via secondary C-H bond.

Thus, we have obtained the first evidences for the alkanes to be transformed into valuable chemical products - carboxylic acids - on acidic zeolite catalyst at moderate temperature, when alkane is not still involved into cracking reaction.

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PPII-5

ZEOLITE ENCAPSULATED Cu(SALOPH-CL$_2$): PREPARATION AND CHARACTERIZATION

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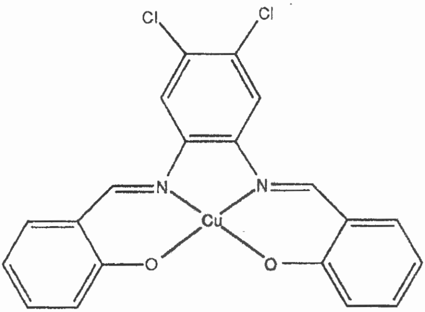
The application of zeolite encapsulated metal complexes in redox catalysis is a promising area of research (1-3) since it is anticipated that the occluded complexes will retain much of the original homogeneous catalytic properties, but the shape selectivity, electrostatics and acid-base properties of the zeolites are expected to synergistically enhance the reactivity of the complexes towards the redox reactions. Several routes can be followed to heterogenise transition metal complexes; one of the methods is the reaction of ion exchanged zeolites with the ligands in two different approaches: (i) *in-situ* ligand condensation around the intrazeolite metal ion, *template synthesis*, yielding complexes with dimensions that prevent their exit from the supercages; (ii) diffusion of pure ligands into the zeolite through the pores, where upon coordination with the intrazeolite metal ion form complexes too large to exit. In this work we report the encapsulation of the complex [Cu(saloph-Cl$_2$)], *bis*(salicylaldehyde)-(3,4-dichloro-*o*-phenylene-diiminate)-copper(II) (Scheme 1) in the supercage of zeolite Y, by using the method (ii), ligand adsorption from solution on Cu(II) exchanged zeolite.

The ligand *saloph-Cl$_2$* (4) and the Cu^{2+} exchanged NaY were prepared as described in literature. (5) A Cu^{2+} exchanged NaY was suspended in ethanolic ligand solution and refluxed for 24 hours. The complex-containing zeolite was carefully extracted with ethanol and N,N´-dimethylformamide to remove surface species, and then stirred with NaNO$_3$ to reexchange uncomplexed copper(II).

The resulting bright green material, [Cu(saloph-Cl_2)NaY], was characterized by chemical analysis, spectroscopic methods (FTIR, UV/vis) and electron paramagnetic ressonance (EPR): the results provide evidence for the encapsulation of Cu(II) complexes inside Y zeolite supercages.



Scheme 1: [Cu(saloph-Cl_2)]

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PPII-6

STRUCTURAL, ENERGETIC AND MECHANISTIC ASPECTS OF THE SPECIFICITY OF CATALYTIC ACTION OF COPPER AND COBALT OXIDIC CLUSTERS LOCATED WITHIN ZSM-5 ZEOLITE CHANNELS IN THE REACTION OF THE NOx SELECTIVE REDUCTION BY LIGHT HYDROCARBONS IN THE EXCESS OF OXYGEN.

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Selective catalytic reduction of nitrogen oxides by hydrocarbons (HC-SCR) is now among the most intensively studied catalytic reactions in the world. Earlier, using a spectrokinetic approach, we have proved participation of strongly bound nitrite-nitrate complexes in the rate-limiting stage of the propane SCR catalyzed by copper- and cobalt-exchanged zeolites. However, a question remains why cobalt cations are capable to catalyze CH_4-SCR, when Cu-ZSM-5 only burns methane without NO_x reduction. In general, such difference can be assigned to a different structure and bonding strength of nitrite-nitrates stabilized on these cations, specific routes of hydrocarbons activation, selective/nonselective interaction of various forms of ad-NOx species with propane or methane, transformation of nitrates into molecular nitrogen via different intermediates. All these hypothesis were checked, and main results are given here.

EXPERIMENTAL

Two types of powdered zeolites H/ZSM-5 with Si/Al ratio equal to 25 and 15 were used to prepare copper -(2. 60 wt. %) and cobalt -(2.25 wt. %) exchanged samples, respectively.

EXAFS spectra of the K-edge of Co and Cu X-ray absorption were obtained at the EXAFS Station of the Siberian Center of Synchrotron Radiation, Novosibirsk using vacuum-tight cells. EXCURVE-92 procedure was used to determine interatomic distances and coordination numbers from the EXAFS spectra.

Steady-state activities of the catalysts estimated from the values of NO_x conversion into N_2 were tested in a quartz flow reactor. A reaction mixture contained propane or methane (1300 ppm), nitric oxide (1000 ppm) and oxygen (1%) in helium. Similar reactor was used for the TPD and pulse titration experiments. Surface nitrite-nitrates were titrated by pulses of hydrocarbons (1300 ppm) in He both with oxygen (1%) and without it.

Kinetics of the surface adspecies transformation was studied in situ using a static infrared cell-reactor. Spectra were recorded on IFS-113 v Bruker spectrometer.

Heats of oxygen desorption and NO adsorption with formation of various types of nitrite-nitrates were calculated by semiempirical Interacting Bonds Method.

RESULTS AND DISCUSSION

Structure of copper and cobalt clusters and its relaxation. For oxidized Cu-ZSM-5, EXAFS data were best fitted by the model of a square planar type of copper coordination by oxygen with two common bridging oxygen per each pair of copper atoms. For Co-ZSM-5, the most probable structure is described by a string of corner-sharing tetrahedra. Both NO adsorption and weak reduction in He are accompanied by the increase of the Cu-Cu coordination number, while such changes were considerably less pronounced for cobalt clusters. In implies that formation of nitrite - nitrates is accompanied by creation of coordinately unsaturated Cu^+ centers while cobalt cations remain coordinately saturated. This hypothesis was confirmed by using IR spectroscopy of adsorbed CO. Heats of NO adsorption with formation of nitrates calculated with a proper attention to such difference in the coordination relaxation (Cu-O bonds are broken and Cu-Cu bonds are formed, while Co-Co bonds do not appear) are close to the experimental values (ca 26-36 kcal/mole for nitrates), being somewhat higher for species located on the cobalt oxidic clusters. Hence, from a microscopic point of view, in the presence of NOx copper and cobalt systems differ by a nature of centers capable to activate hydrocarbons. For Cu-ZSM-5, these are coordinatively unsaturated centers -cuprous cations known for their ability to activate C-H bond. Here CH_3 radicals thus formed can further react either with the extralattice oxygen (ELO) in a route of complete oxidation, or with nitrate adspecies forming organic nitrates (a route of NOx-SCR), the latter being less probable. For Co-ZSM-5, hydrocarbons can be activated only by interaction with ad-NO_x species yielding organic nitrates as a primary product. In this case, high selectivity in HC consumption for NOx reduction is expected that is indeed observed. This conclusion agrees well with the fact that for Co-containing zeolite, a rate of HC oxidation is increased when adding NO to a He+O_2 + HC mixture, while it decreases for Cu-ZSM-5. For both systems, activation energies of HC oxidation were found to be identical (ca 25 kcal/mole) and not changing after NO addition thus evidencing the same rate-limiting stage- C-H bond breaking. All this means that the first reason for a different behavior of these two systems in CH_4-SCR is the different type of cations coordination in oxidic clusters as well as its different rearrangement in the course of nitrates formation.

2. Structure and reactivity of NOx adspecies. As was inferred from the IR experiments with isotope substitution of the nitrogen and oxygen atoms, at reasonable operating temperatures (> 200-300 C) the most abundant species are bridging nitrates, whose structure is more or less similar. Their energy of formation as well as kinetic parameters of their interaction with gas - phase HC yielding organic nitrates as intermediates are also comparable. For both systems, the rate of this surface reaction is quite insensitive to the presence of oxygen in the gas phase. Hence, this stage, though being rate-determining in HC-SCR in the presence of gas-phase oxygen for both systems, is clearly not responsible for their different behavior in CH_4-SCR.

3. Nature and reactivity of C,N-containing intermediates. A scheme of organic nitrates transformation leading to a final product - molecular nitrogen was found to be quite different for copper-and cobalt -exchanged zeolites. For the former, with propane as a reducing agent, organic nitrates are rapidly transformed into carbon dioxide, water and nitrogen under the action of gaseous NO and/or via interaction with ad-NOx accompanied by formation of a very reactive kethene-type intermediate. With methane as a reducing agent, kethene-like species were not detected. For Co-ZSM-5, organic nitrates are mainly converted into nitryles and isocyanates, whose rate of transformation into the final products including molecular nitrogen is greatly enhanced in the presence of the gas phase oxygen. The same types of adspecies were detected when using methane as reductant at higher operating temperatures. Probably, higher thermal stability of nitryles and isocyanates bound with cobalt cations is one of the reasons of ability of cobalt -exchanged zeolites to ensure NOx selective reduction by methane. Indeed, at lower operating temperatures and using propene as reductant, such intermediates as isocyanates and nitryles were also observed for some Cu-containing systems. Moreover, we have found that by using alkaline-earth promoters capable to stabilize isocyanates and nitryles, even Cu-ZSM can be made a selective CH_4-SCR catalyst. From the structural and energetic point of view, such situation is expected: nitryles should be more strongly bound with tetrahedrally coordinated cations as compared with a rather weak axial bond with copper (2+) cations while all equatorial positions are blocked by oxygen atoms.

Conclusions. Atomic-scale reasons for specificity of the catalytic properties of Co and Cu-cations in the HC-SCR appear to be different types of cations coordination, various routes of hydrocarbons activation as well as stability of C, N-containing intermediates.

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PPII-7

QUANTUM SIZE EFFECTS FOR II-VI AND III-V SEMICONDUCTOR CLUSTERS ENCAPSULATED IN ZEOLITE MATRICES

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The properties of nano-size clusters of various inorganic and organic materials (metal, metal oxides, salts, dyes, etc.) encapsulated in microporous matrices attract nowadays attention, because the nanotechnologies provide a means to design and synthesize new catalysts, optical devices and other objects with intriguing characteristics. One of the most fascinating examples of such systems is the class of zeolites with encapsulated inorganic semiconductors of the II-VI (for instance, CdS, CdSe, ZnS, etc.) or III-V (Ga-As, Ga-P) types. It is dreamed that the use of zeolites with various architecture (channels or cavities of different sizes and geometry) and with various acid-base properties (cationic or H-forms or neutral lattices) will make it possible to govern the synthesis of semiconducting materials in a controlled manner. The most important features of such nano-size clusters would be the uniform (regular) and well-shaped structure of the cluster superlattices of different dimentionality and the unusual quantum size effects because of the very small size of the zeolite voids (channels and cavities) of the order of 3 - 10 A.

However, by now the synthesis of encapsulated semiconductor clusters was performed only by ion-exchange or MOCVD method. It appears to be attractive to use simple and waste-free technique of incipient wetness impregnation for preparation of these materials. Another objective of this work was to study the effect of different zeolite structures on the properties of the materials thus synthesized. This work is focused on the synthesis and comparative spectroscopic characterization of CdS and other semiconductor clusters encapsulated in the Na- forms of faujasites and mordenites and KL-type zeolites.

The samples were prepared (1) by ion exchange or (2) by impregnation from aqueous solutions of appropriate salts followed by calcination and sulfidation step or (3) by gas-phase reactions of organometallic compounds. Diffuse-reflectance UV-VIS and FT-IR spectra were measured using an M-40 Carl Zeiss or IMPACT-410 Nicolet spectrometers. Treatments and adsorption were carried out in a vacuum setup.

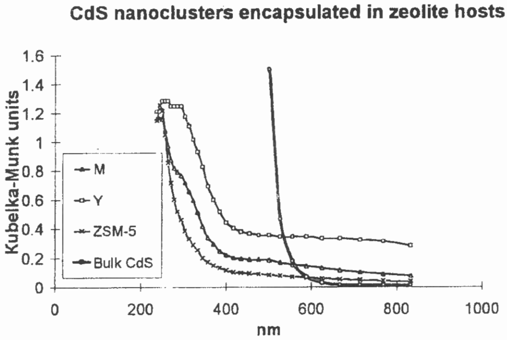

Fig. 1. UV spectra of CdS clusters encapsulated in MOR (1), Y (2), and ZSM-5 (3) zeolites. The Cd loading was 3 wt. %. Spectrum 4 corresponds to the bulk CdS sample.

The data obtained show that in the case of the CdS/NaFAU zeolites prepared by both ion exchange and impregnation, nano-size CdS clusters are formed, which is evidenced by the shift of the charge-transfer band in the UV spectra from 500 nm for the bulk CdS to 250 - 400 nm for the encapsulated clusters (Fig. 1).

The formation of the CdS clusters in the samples prepared by impregnation occurs under milder conditions compared to the ion-exchanged samples. However, CdS in impregnated samples show tendency to migrate outside zeolite host and form bulk CdS on the outer surface after high-temperature treatment.

On the other hand CdS clusters in ion-exchanged zeolites are less stable upon thermal treatment and lose sulfur as H_2S. Upon thermal treatment CdS clusters “dissolve” in zeolite matrix and Cd^{2+} ions return to cationic sites which is indicated by disappearance of Broensted acid sites (the OH stretching frequency of 3650 cm^{-1}).

It is also shown that the thermal stability of semiconductor clusters in the zeolites with a channel structure is higher than in the zeolites with cavities. The important finding is also the larger size of the clusters in mordenites, L and ZSM-5 zeolites, as compared with the faujasites.

PPII-8

REGIOSELECTIVE IODINATION OF TOLUENE OVER ZEOLITES Y

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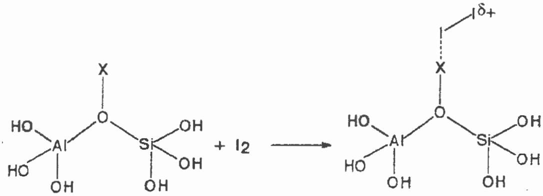
Iodoarenes are useful reagents in fine organic synthesis. Conventional methods for aromatic iodination imply the use of highly toxic heavy metal compounds (Hg, Tl etc.) or mineral acids [1] which is undesirable from the ecological point of view. Moreover, these methods do not always allow to control regioselectivity of the reaction. Zeolites are reputed to increase regioselectivity of electrophilic aromatic substitution reactions including halogenation [2]. It has been reported on the use of zeolites in iodination of aromatics [3-5]. However, there is a need in better understanding of the mechanism of iodination in the presence of zeolites.

We have studied a liquid phase iodination reaction of toluene in the presence of several cation exchanged forms of zeolite Y (Table). High *para*-selectivity observed is obviously due to effect of shape selectivity. Electrophilic species formation was simulated by the model reaction (1) with the use of the MNDO method (MNDO-92 program [6]). Calculated heats of the reaction are given in the Table.



(1)

X = H, Li, Na, K, Cs

Table. Iodination of toluene in the presence of zeolites Y (20 °C, hexane, 24 hours) and calculated heats of reaction (1)

Zeolite	Conversion of toluene, %	Calculated heat of reaction (1), kcal/mol
HY	0	- 0.1
LiY	0	- 1.5
NaY	0	-11
KY	28 [a)]	-29
CsY	64 [a)]	-40

a) *para*-Iodotoluene is the only product observed

These results seem to be in agreement with the Raman spectra of iodine adsorbed on zeolites Y (Figure).

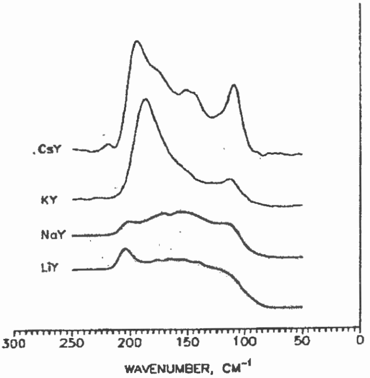


Figure. Raman spectra of iodine adsorbed on zeolites Y

The bands at 195-205 cm^{-1} may correspond to "physically adsorbed" iodine molecules (*cf.* a band at 210 cm^{-1} for the solution of iodine in hexane). When passing from LiY to CsY one can observe intensity increasing of the band at 110-120 cm^{-1} which probably corresponds to iodine molecules polarised by alkali metal cations inside zeolite lattice because "soft" iodine molecules are more effectively polarised by "softer" Cs and K cations than by "harder" Na and especially Li cations.

Based on the reactivity and regioselectivity observed as well as on the quantum chemical simulations and Raman spectra of iodine adsorbed on zeolites we can presume that iodination reaction of toluene occurs inside zeolite cavities, electrophilic species being iodine molecules polarised by alkali metal cations.

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POSTER SESSION II

Section 5

Catalysis by New Materials and Non-Traditional Application Areas of Catalysis

PPII-9

Using of Nickel Complexes with Non-Phosphine Ligands as Catalysts of Aryl Halides Reducing Coupling

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Reducing coupling of halogen aromatic compounds catalyzed by nickel phosphine complexes in the presence of zinc proceeds under mild conditions and gives biaryls in high yields[1-8]. However, with using such systems, the reducing coupling demands the use of large quantities of phosphine ligands, which imposes essential difficulties on the target products isolation and purification. This work offers a way of overcoming these difficulties by replacing phosphines by other ligands.

Transformations of substituted halogen benzenes and some 1-halogen naphthalenes occur under the action of zinc in the presence of catalytic amounts of nickel compounds generated in situ from nickel chloride and such ligands as 2,2'-bipyridine, 1,10-phenanthroline, 1-amino-, 1-hydroxyanthraquinones, acenaphthenequinone were studied (***Scheme***):

$$\mathrm{ArHal} \xrightarrow[\mathrm{Zn,\ DMF,\ 60\text{-}80^{0}C}]{\mathrm{NiCl_2,\ ligand}} \mathrm{ArAr}$$

Scheme

ArHal: 4-bromoanisole (65%), 4-bromotoluene (80%), chlorobenzene (81)%, bromobenzene (78%), 4-bromo-1-fluorobenzene (78%), 4-bromo-1,2-xylene (75%), 4-bromo-1,3-xylene (79%), 3-bromo-1,4-xylene (76%), pentamethylbromobenzene (65%), 4-bromo-tert-butylbenzene (76%), 4-chloroacetophenone(75%), 1-chloronaphthalene(65%), 1-bromonaphthalene (70%), 5-bromoacenaphthene (80%).

Ligand: 2,2'-bipyridine, 1,10-phenanthroline, 1-amino-, 1-hydroxyanthraquinones, acenaphthenequinone.

The aryl halides shown above except for 4-chloroacetophenone and 4-bromobenzaldehyde give dimers in DMF under mild conditions (60-80°C) in high yields.

A different situation arises with 4-chloracenaphtophenone and 4-brombenzaldehyde. When conducting the reaction in DMF, 4-chloroacetophenone shows low reactivity. Thus, the conversion extent does not exceed 10% within 4 hours. 4-Brombenzaldehyde gives rise to a mixture of products, which is likely to be attributable to aldehyde group reduction under the conditions similar to ours[9]. In going from DMF to DMA an essential change in reactivity is found. Reducing coupling of 4-chloroacetophenone and 4-brombenzaldehyde takes 4 hours to give the corresponding dimers with the yields of 75 and 80%.

Complex compounds of nickel with 2,2'-bipyridine and 1,10-phenanthroline turned to be more efficient then those with 1-amino-, 1-hydroxyanthraquinones and acenaphthenequinone. Thus in the case of the first mentioned two compounds the reaction was performed at 60-70°C, while in the case of quinones - at 90-120°C. However, mixed nickel complexes generated from nickel chloride, quinones and 2,2'-bipyridine (or 1,10-phenanthroline) with a quinone and 2,2'-bipyridine ratio varying from 9:1 to 4:1 were found to be nearly as efficient as nickel bipyridine and phenanthroline complexes.

Financial support by the State Scientific Centre Russian Federation "NIOPIK" (grant No. 566c) is gratefully acknowledged.

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THE STABILITY OF DEHYDROGENATION CENTERS IN SUPPORTED PLATINUM CATALYSTS

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The dehydrogenation function of Pt/Al_2O_3 catalysts was studied in cyclohexane dehydrogenation as a model reaction. Fresh and coked catalysts were tested in two ranges of reaction conditions:

- model (laboratory) conditions (T=280-340 °C, P=1 atm);
- conditions similar to those of naphtha reforming process (T=420-460 °C, P=15 atm).

The identity of intrinsic properties of the dehydrogenation active centers were found throughout conditions (see Fig. 1).

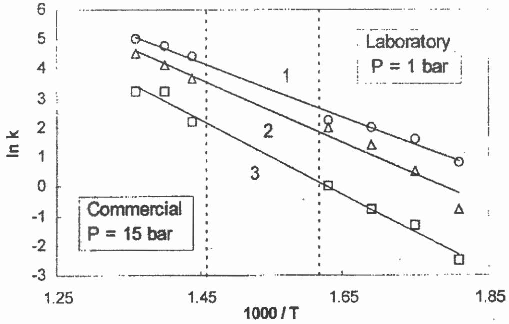

Fig. 1. Dependence of the rate constant k (s^{-1}) on temperature for the fresh (1) and coked (2, 3) catalysts Pt/Al_2O_3 at model and commercial condition.

The principal result is that the experimental points lie on the same line for both model and commercial conditions. It means that the values of apparent activation energy (E) and of pre-exponential coefficient (k_o) are invariable throughout both ranges of conditions. Apparently, such variation of reaction condition does not change the specific properties of dehydrogenation active centers.

As it clearly seen from Fig.1, this result is true not only for the fresh but also for the coked catalysts, despite of deactivation. So, the coke deposits only block the part of active centers without its qualitative modification.

This result permits to test the dehydrogenation function of reforming catalysts (for their comparison) in "model" conditions, using model reaction of cyclohexane dehydrogenation and laboratory equipment at atmospheric pressure.

PPII-10

THE ORIGIN OF NON-FARADAIC ELECTROCHEMICAL MODIFICATION OF CATALYTIC ACTIVITY: THE CASE OF CARBON MONOXIDE OXIDATION

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Recently much attention has been paid [1, 2] to the study of oxidative conversion of gases (CO, CH_4, C_2H_4, CH_3OH) over metal electrode-catalysts in a solid oxygen conducting electrolyte cell:

$$\text{gas} + O_2\text{, metal catalyst} \mid ZrO_2\ (8\text{-}10\ \text{mol}\ \%\ Y_2O_3) \mid \text{metal, air}$$

The current passing through the cell (a flow of O^{2-} ions through the electrolyte) was found to change remarkably and reversibly the activity of the metal catalyst. The induced change in the catalytic rate exceeded by several orders of magnitude the rate of oxygen flow through the electrolyte. This effect has been termed non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA effect).

The NEMCA effect has been already studied for more than 30 catalytic systems and it is a general phenomenon [1,2]. This effect was demonstrated for carbon monoxide oxidation on Pt [2,3], Pd [2], Ag [2], Au [4] and Ag-25 at% Pd alloy electrodes.

The nature of NEMCA effect was discussed by Vayenas et al. in a number of publications [1,2]. According to Refs. [1,2] the essence of the NEMCA effect is that the electrode work function changes at polarization of metal electrode, i.e. when current is passing through the cell. This leads to changes in the strength of the chemisorptive bond of adsorbed oxygen and, hence, in catalytic properties of the electrode for oxidation reactions. We have considered this concept as questionable [4,5] and formulated a chain reaction mechanism involving electrochemically generated oxygen species to explain NEMCA phenomenon [6].

Here we would like to discuss the experimental data on NEMCA effect in the case of CO oxidation on Pt, Au, Ag-Pd alloy electrodes in terms of the chain reaction mechanisms. The chain reaction mechanism might be as follows:

(at cathodic polarization)		(at anodic polarization)
$2Z_o + O_2 \rightleftarrows 2Z_oO$ $Z_oO + CO \longrightarrow CO_2 + Z_o$	ordinary catalytic reaction	$2Z_o + O_2 \rightleftarrows 2Z_oO$ $Z_oO + CO \longrightarrow CO_2 + Z_o$
$2Z + O_2 + 2e \longrightarrow 2ZO^-$ $Z_o + O_2 + e \longrightarrow Z_oO_2^-$ $ZO^- + Z_oO \longrightarrow Z_oO_2^- + Z$	initiation	$Z + O_V^{2-} \longrightarrow ZO^- + e$ $ZO^- + Z_oO \longrightarrow Z_oO_2^- + Z$
$Z_oO_2^- + CO \longrightarrow CO_2 + Z_oO^-$ $Z_oO^- + Z_oO \longrightarrow Z_oO_2^- + Z_o$	propagation	$Z_oO_2^- + CO \longrightarrow CO_2 + Z_oO^-$ $Z_oO^- + Z_oO \longrightarrow Z_oO_2^- + Z_o$
$ZO^- + e \longrightarrow Z + O_V^{2-}$	termination	$2ZO^- \longrightarrow 2Z + O_2 + 2e$ $Z_oO_2^- \longrightarrow Z_o + O_2 + e$

were Z_0 is a catalytically active site on the gas-exposed surface of the metal electrode; Z_0O is atomic oxygen species on the catalytically active site; Z_0O^- and $Z_0O_2^-$ are charged oxygen species on the catalytically active site; Z is an electrochemically active site on the three-phase boundary gas–metal–YSZ; ZO^- and ZO_2^- are charged oxygen species on the electrochemically active site; O_V^{2-} is the oxygen anion in the bulk of YSZ.

As example Figs. 1 and 2 show the experimental data on CO oxidation over Pt and Ag-25 at% Pd alloy electrode-catalysts under NEMCA conditions and results of the calculation at realistic rate constants of steps for above chain reaction mechanism. The experimental data are seen to fit satisfactorily the theory.

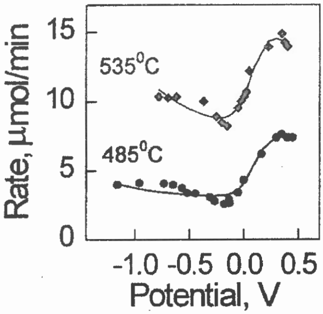

Fig. 1. Effect of potential on the rate of CO_2 formation over Pt electrode. $[CO]_o = 0.25$ vol%; $[O_2]_o = 11.3$ vol%. Points - experiment [2]; lines - theory.

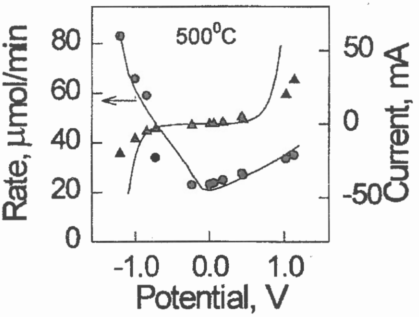

Fig. 2. Effect of potential on current and on the rate of CO_2 formation over Ag-Pd alloy electrode. $[CO]_o = 5$ vol%; $[O_2]_o = 25$ vol%. Points - experiment; lines - theory

So, in the case of carbon monoxide oxidation over metal electrodes in the cell with YSZ electrolyte, the chain process involving electrochemically generated oxygen species is, most probably, the key factor for appearance of NEMCA effect.

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PPП-11

MECHANISM OF HETEROCYCLIZATION OF BUTADIENE OXIDE INTO 2,5-DIHYDROFURAN IN THE PRESENCE OF APROTIC SOLVENT AND BIMETALLIC COMPLEX, INCLUDING IODIDE OF ALKALI METAL AND TRANSITION METAL HALIDE

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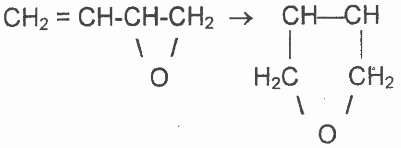
Intramolecular cyclization of unsaturated oxides of olefines proceeds under the influence of iodocontaining compounds, in particular, iodides of alkali metals. Their activity considerably rises in the presence of transition metal halides.



During the study of heterocyclization of butadiene oxide in the presence of aprotic solvent and bimetallic complex, including iodide of alkali metal and transition metal halide, the catalytic activity dependence of the complex on the nature of alkali metal, transition metal and anion bonded with it, and also from the nature of complexating solvent was determined. The activity of alkali metal iodides in the complex with zinc chloride and N-methylpyrrolidone changes in the following way:

$$\mathrm{LiI} > \mathrm{NaI} > \mathrm{KI}$$

The dependence obtained satisfactorily correlates with the values of the metal electronegativity, which is a combined estimation of their donor-acceptor properties. The higher electronegativity of alkali metal in the bimetallic complex, the higher is the reaction rate. "Acid" properties of cations weaken from Li^+ to K^+. This leads to reduction of alkali metal iodide interreaction both with the basic solvent, and with the transition metal halide. As a result, the activity of bimetallic complex iodine anion, which functionates due to its high nucleophilic reactivity as a bridge during the transfer of electron from bimetallic complex to double bond of butadiene oxide molecule, reduces.

The study of influence of transition metal nature in the presence of lithium iodide and N-methylpyrrolidone shows that the catalytic activity of metal chlorides decreases in the following way:

Zn > Co > Ni > Cu

The metal with low electronegativity displays the greatest activity. Forming unstable complex with aprotic solvent, the metal unites with alkali metal iodide into complex salt. The stability of this complex salt grows with increase of alkali metal electronegativity.

Acquiring mobility, the complex salt anions attack the butadiene oxide molecule: iodine anion - double bond, transition metal anion - C^2-atom of oxirane ring carbon, which because of polarization of the butadiene oxide molecule assumes partial negative charge, that results in weakening of its bond with oxygen atom. The halogen atom with low basicity will be most effective for this attack. The breaking of double bond and oxirane ring leads to formation of 2,5-dihydrofuran.

PPII-12

POLYCONDENSATION OF PHENOL WITH FORMALDEHYDE IN THE PRESENCE OF SULPHOCATIONITES BASED ON SILICA

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The phenolic alcohols, being the primary products of polycondensation of phenol with formaldehyde, are widely used in production of thermoisolation materials and for some other purposes. In industry the phenolic alcohols are obtained in presence of sodium or barium hydroxide.

We have elaborated a method of phenol condensation with formaldehyde using as catalysts sulphocationites based on wide-porous silica.

The average molecular mass of condensation products determined by the decrease of melting point of camphora is 240 m.w. when the ratio phenol : formaldehyde is 1 : 1.5.

The reaction proceeds with practically quantitative yield and very high rate in temperature interval 70-95^{0}C.

There is a sieve effect that limits maximum dimension of molecules which are formed in polycondensation reaction.

The results of experiments permit to generalize that the pore diameter of carrier, of catalyst used for preparation, and certain compound of reacting substances, directly is defined by linear sizes (m.w.) of formed phenolic alcohols. Thus a reasonably narrow fraction of connections with the same polymerization degree, that presents doubtless interest from the practical point of view.

Generated reaction products can be easily filtered from catalyst. The catalyst is regenerated by washig with acetone and can be used repeatedly. The obtained product is notable for its low content of polymeric compounds and initial monomers.

SURFACE PROPERTIES OF CARBON-SILICA ADSORBENTS PREPARED BY PYROLYSIS OF DICHLOROMETHANE. TOPOGRAPHY AND MORPHOLOGY OF CARBON DEPOSITS

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The complex carbon-mineral adsorbents (CMA) have become recently very attractive materials for many analytical and technological processes as well as in many research works [1-5]. The present interest in CMA results from the need for utilization of wastes, partially or completely carbonized adsorbents and catalysts, application of (properly prepared) CMA as carbon adsorbents substitutes or using them for preparation of carbon materials of special properties [6]. Great research and application possibilities appear using CMA of programmed porous structure, programmed morphology and topography of adsorption centers [7].

This new type of adsorbents proves to be very useful in adsorption processes on a technical scale e.g. in water and sewage purification as well as in petroleum derivative products removal from polluted waters [3].

The specific properties of CMA: hydrophilic of the mineral adsorbent and hydrophobic of the imposed carbon deposit are used in the adsorption process. Depending on CMA preparation conditions it is possible to prepare adsorbents partially or completely covered with a carbon deposit or the materials possessing a mosaic topography of the surface [7,8].

Because of great possibilities of CMA application, determination of carbon deposit morphology and topography is one of the most important tasks. Very few of such studies have been carried out so far and their analysis suggests the need for more intensive investigations in this field.

The paper presents the studies of texture and structure of a series of carbon-mineral adsorbents (carbosils) differing in carbon deposit contents 0.8–35.0 % w/w) based on the data of gas and liquid adsorption, electron microscopy, small angle X-ray scattering, e.t.c. A theoretical approaches presented by Fenelonov et al. [9,10] and by Kamegawa and Yoshida [11,12] are used in description of texture models of the complex carbon-mineral adsorbents. The results of these studies made it possible to determine the shave of carbon deposit in the total porous structure of the complex adsorbents. To determine a crystallographic structure of the above adsorbents the small angle X-ray scattering (SAXS) studies were carried out. The applicability of the SAXS method for the investigation of the specific surface and the pore size distribution function for the studied samples has been demonstrated. For the silica gels with small amounts of the deposited carbon the diffuse profile of electron density in the boundary has been estimated.

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ORGANIC SUBSTANCES OXIDATION IN ELECTROLYSIS OF MELTED CATALYST

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Ethanol and alkylbenzenes oxidation on melted catalysts - the mixture of KVO_3-V_2O_5, 1, 3 and 5 mass % solutions of $K_3V_5O_{14}$ and NaOH in eutectic of KCl-LiCl - in electrolysis of melted salts during the potential change on platinum electrodes from +1 to −1 V has been studied.

The experiment was designed so that organic substances should not be exposed to oxidation on the electrodes, this being judged about from the invariance of the form of volt-amperegram of the melted catalysts studied including the conditions of carrying out the process as well.

The dependence of ethanol oxidation products composition change on the value and potential sign of the working electrode indicates that in the conditions studied organic substances oxidation goes in the scope of the melted catalyst whereas regeneration (reoxidation) of the catalyst occurs as a result of electrochemical reactions on electrodes as well as in case of oxygen presence in gas phase ($P_{O_2} > 0{,}0125$ MPa) at the expense of interaction of oxygen with the catalyst.

It has been shown that changing the electrochemical, oxidation and reduction potentials of melted catalyst one may influence its catalytic activity. Ethanol conversion and the amount of acetaldehyde formed from the latter increase at the potential changes from 0 to 0.45 V. In the area of potentials exceeding 0.45 V in absolute value a sharp increase of ethanol conversion and the amount of CO_2 yield is observed, in addition, acetaldehyde and ethylene yield decreases.

The dependence of the working electrode potential value on partial oxygen pressure in atmosphere containing ethanol fumes is not direct. The potential reaches 0.7 V in absolute value at partial oxygen pressure of 0.0125 MPa, this corresponding to the smallest content of oxygen ions in melted catalyst into which the working electrode is immersed.

Variation of the working electrode potential, especially in the anode area, almost does not influence the conversion of ethanol when the reaction goes in the melted catalyst KCl-LiCl. On the contrary, the selectivity of acetaldehyde formation depends on the working electrode potential and is the greater the higher vanadate and NaOH concentration is. In fact, ethylene is not formed on melted catalysts containing NaOH, however, CO and methane yield is less in melted catalysts having vanadates in their composition.

As it follows from experimental data, in case of electrocatalysis melted catalyst composition influences only the conditions (potential, partial pressure, oxygen, etc), of performing the process of organic substances oxidation, as all inorganic salts and oxides in the presence of oxygen and at definite electrode potential are capable of generating oxygen ions which ultimately define the intensity and direction of oxidation reaction.

The composition of products of alkylbenzenes oxidation depends on the catalyst character CO_2, H_2O, benzene, benzoic acid, the ratio of which depends on temperature and partial oxygen pressure in gaseous phase are found on KVO_3-V_2O_5 catalyst in the products of toluene oxidation. The transformation of toluene on the catalyst containing NaOH proceeds with the formation of CO_2, H_2O, 1,2-diphenylethene and 1,2-diphenylethylene.

INFLUENCE OF MECHANO-CHEMICAL TREATMENT ON PHYSICAL-CHEMICAL PROPERTIES OF ZrNi-H, HfNi-H AND Pr-Co-Cu-H SYSTEMS

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In the recent years investigations of mechano-chemical activation of various types of reactions are carried out. In our research work we have obtained some data on influence of mechano-chemical treatment on creating active surface of catalysts based on intermetalic compounds and their hydrides in reactions of carbon monoxide conversion.

The catalytic activity was investigated on ZrNi and HfNi systems and their hydrides along with $PrCo_xCu_{5-x}$ (x = 0;3;5) and corresponding hydrides.

The catalysts based on hydrides have higher activity than corresponding intermetalic compounds, however intermetalic compounds have similar activity and phase composition to corresponding hydrides after activation process in hydrogen atmosphere. Formation of hydride phases $ZrNiH_x$ and $HfNiH_x$ was shown for ZrNi and HfNi, respectively, and formation of Co, Cu and PrH_2 phases was shown for systems $PrCo_xCu_{5-x}$ (x = 0;3;5).

It was found out that methane and CO_2 are the products of CO conversion on catalysts based on ZrNi and HfNi systems, but methane is the only product of CO conversion on Pr-Co-Cu-H systems, their activity is proportional to quantity of copper in initial system in the range of investigation.

Some data on heterophase exchange between gas and hydride during mechano-chemical activation were obtained.

PPII-16

DESIGN AND TESTING OF CATALYSTS Ru/SIBUNIT FOR AMMONIA SYNTHESIS UNDER MILD CONDITIONS

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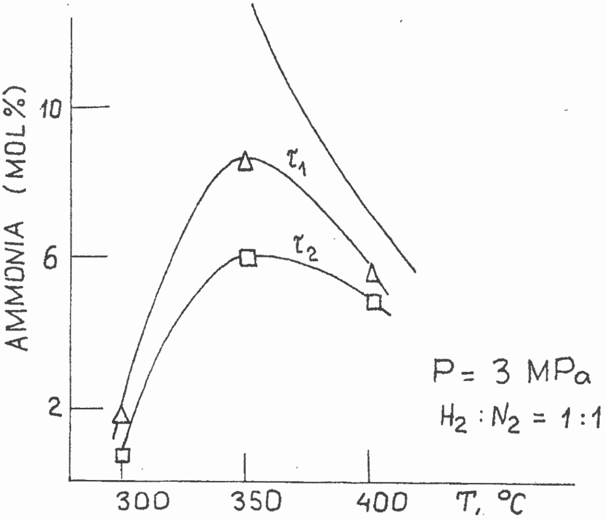
Nowadays methods of ammonia synthesis involve nitrogen interaction with hydrogen in the presence of various modifications of melt iron catalyst promoted by potassium oxide and alumina. Industrial processes are performed at 280 - 320 atm and T > 400°C due to thermodynamic and kinetic restrictions. According to [1-3] it is possible to design highly efficient catalyst for ammonia synthesis at moderate pressures (5-50 atm) and lower temperatures (250-350°C) using systems containing Ru and alkaline or alkaline-earth metals supported on activated carbons. A newly designed graphite like carbon material "Sibunit" opens new ways in this field. The Sibunit has unique properties and meets a wide application as adsorbent and catalyst in many catalytic processes. This study presents the results characterizing new ruthenium-on-Sibunit catalysts for the mild conditions ammonia synthesis.

Catalysts were prepared using various precursors: nitrates $Ru(NO)(NO_3)_3$, chlorides $RuCl_3 * 3H_2O$ and hydrochlorides $RuOHCl_3$. Promoters (K and its compounds) were introduced either after Ru deposition and reduction to metal state or simultaneously using the single stage impregnation with water solutions of K compounds. Catalyst activity was studied in a flow two-reactor setup at 200-400°C, pressure 5-50 atm, volume flow rate (2-30) x 10^3 h^{-1} using mixtures (H_2 + N_2) in a ratio of 1 : 1 or 3 : 1. Chromatography was used to analyze the starting mixtures and ammonia. Oxygen admixture content, controlled by "Istok" analyzer, was less than 1 ppm. For comparison commercial ammonia synthesis catalyst SA-S was tested. Equilibrium ammonia concentrations were calculated using program "Astral". The figure shows the temperature dependencies of ammonia yield over ruthenium catalyst C-4-4. Experiments were performed within 300-400°C, temperature being risen to the maximum one and then lowered back. Both stoichiometric and non-stoichiometric mixtures were used. Apparently, equilibrium occurs at low temperatures, ammonia yield being maximum at 350°C.



Therefore, experiments show that:

1. Designed catalysts allow efficient ammonia synthesis at the studied temperatures and pressures.

2. The activity of Ru/Sibunit catalysts significantly depends on (1) the choice of (a) precursor (main active component is metal ruthenium), (b) promoters; on (2) thermal treatment conditions; on (3) method of chemical activation of catalyst; on (4) support activation conditions.

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PPII-17

Structure and Texture of Filamentous Carbon Produced by Decomposition of CH_4 over Ni and Ni-Cu Catalyst

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Catalytic filamentous carbons (CFC) produced by decomposition of methane on Ni/Al_2O_3 and $Ni-Cu/Al_2O_3$ catalysts were investigated by adsorption techniques and mercury porosimetry.

Comparison of the different CFC samples shows that the pore size distribution and its evolution depend on the original catalyst (Ni or Ni-Cu). However, generally three ranges of mesopores were detected (Fig. 1). The pore size distributions have two maxima centered at d_1=3 - 4 nm (region *I*) and d_2=20 - 30 nm (region *II*) as well as a small wide peak at the range of $d_3>10^2$ nm (region *III*). In accordance with scanning electron and tunneling microscopy data we proposed that the region *I* corresponds mainly to the pores between hemisphere-like surface species of ca. 5 nm in diameter on the filament surface. The regions *II* and *III* were attributed to the pores between filaments with relatively dense and loosely packed structure, respectively. The growth of the filaments leads to the continuos filling of the large pores (region *III*) which gradually transform to the pores of type *II* (see Fig. 1). During CFC growth the porosity measured was found to approach the upper limit value. Appropriate "partial" porosity values of the different type pores were also calculated.

Comparative approach showed that the CFC samples have a small volume of micropores. Moreover, it was found that ratio of the micropore volume and surface area of mesopores was near constant during the CFC growth. Therefore, it implies that the micropores distribution is uniform on the filament surface. To evaluate the characteristic size of the micropores we have compared the chromatographic and adsorption data measured with different test-molecules. Following this way we found that the micropore size is about 0.35 nm, i.e., very close to interlayer distance in graphite d_{002}=0.345 nm. Furthermore, calculations showed that the micropores extend to the filament bulk by ca. 1-2 nm.

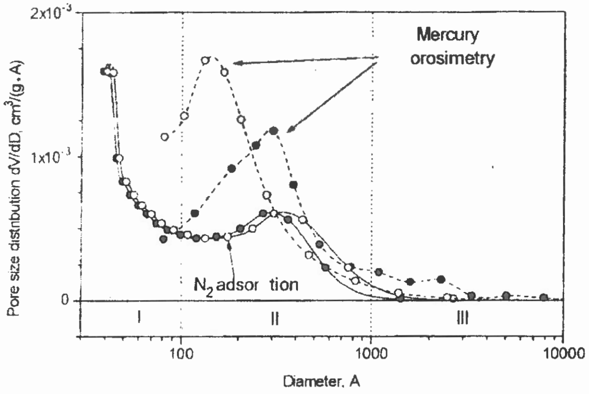

Fig.1. Pore size distribution of CFC after 5 h (solid) and 38 h (opened) growth.

In addition, XRD data pointed the turbostratic structure of the carbons studied. The treatment of CFC samples with various hydrocarbons vapors have affected the XRD patterns that means a strong interaction of the hydrocarbons with CFC. An increase of the ***d_{002}*** values after treatment indicates some kind of intercalation process while adsorption.

Therefore, we have suggested that in addition to closed layer structures recently proposed there are also opened edge planes of graphite on the filament surface. This surface was estimated to be ca. 3-6 % of a total carbon surface. However, these are most active sites in CFC oxidation, adsorption at the micro-concentration level and anchoring of active species while preparation of catalysts.

In summary, the structure of the filament surface was shown to be reconstructed to a depth of 1-2 nm. Such a surface reconstruction leads to decreasing of the surface energy and made most of the surface (90-98%) to be covered by deformed fragments of basal planes of graphite, while the rest of the surface is formed by the edge graphite planes. Slit-like pores of size close to the interlayer distance in graphite were likely formed due to the different lengths of these edge planes. Therefore, the hierarchy in the levels of porous structure of the carbon filaments could be classified as follows: 1)micropores in the filaments; 2) mesopores produced by rough filament surface 3) two types of mesopores of various size in dense and loosely packed parts of the carbon granules.

PPII-18

HIGH TEMPERATURE GAS CHROMATOGRAPHY MOLECULAR PROBES METHOD

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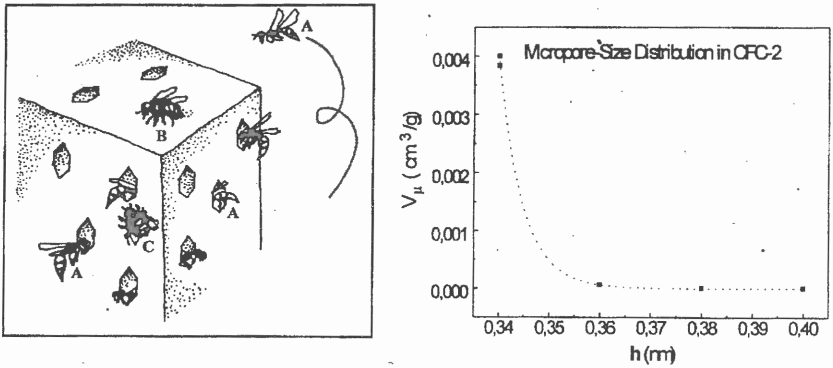
In the present work a new technique of micropore-size distribution (MSD) research in Carbon Molecular Sieves and other Microporous Carbons is offered (range MSD 0.3 ÷ 2.0 nm). The technique is based on *retention volume R* measurements for molecules-probes of the different size and form by high-temperature gas-chromatographic method at "infinite dilution". In this case values of ***R*** allow to determine *Henry's adsorption isotherms factors* (Γ). One can make a comparison of obtained Γ values with the results of measurements on nonporous samples. This comparison allows to determine *micropore volumes* $\mathbf{V}_\mu$ (i), accessible for different molecular-probes, if $\mathbf{V}_\mu$ and *mesopore surface* **S** for one member of the used series is known. This technique has an advantage comparing with any known techniques of MSD-measurements by molecular-probes, since it solves problems of a) *independent adsorption inside and outside of micropores*; б) *activated diffusion*, especially sharp in conditions of low-temperature adsorption, frequently used in usual methods. The second problem is solved by providing the expe-riment in conditions of high-temperature gas chromatography with reliable Arrenius interpolation. We have carried out MSD measurements on a sample of catalytic fibrous carbon CFC-2, obtained by CH_4 decomposition on Ni-Cu catalyst at 600° C. The series of halogene-containing benzene derivatives (**C_6H_5X, where X=H, F, Cl, Br, I**) was used in the experiments. Critical Van-Der-Vaals sizes **h** are various for different molecules. Designed MSD is shown on Fig. 1.



a) b)

Fig. 1 a) Micropores of calibrated size are available for molecules of type **A**, not available for molecules of type **B**, **C**; but molecules of all types can be adsorbed on the surface of mesopores; b) MSD calculated for CFC-2;

Development of Pressure Swing Adsorption (PSA) technology for gas separation

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The research and development methodology for Carbon Molecular Sieves (CMS) and processes of gas mixtures separation by a PSA method is reported. This methodology is based on **hierarchical system of models**, including experimental research and computer modelling at following levels:

a) Micro-texture element defined as a single void (possibly with "windows") or a site of a surface;

b) Domain of micro-texture elements;

c) Lattice of domains with expansions and narrowings - windows, simulating a 3-D pores labyrinth;

d) Adsorbent particle;

e) Layer of particles (adsorber).

f) Multiadsorber plant flowsheeting.

Modeling the processes at levels a), b) and c) allows to predict adsorption and kinetic parameters that are important for controlled synthesis of adsorbents with an optimum structure, and for adequate models construction at levels d) and etc..

Given methodology is a basis for the development of adsorbents and PSA processes to separate hydrocarbon and other gas mixtures for the following fields:

a) ***Micro-PSA*** (with a capacity of 0.01-1 l/min.; gas generators and purificators for laboratory equipment and so on);

b) ***Meso-PSA*** (with a capacity of 1-10 m^3/hour; like some kinds of O_2 generators for medicine, N_2 or CO_2 - for protection atmospheres and so on);

c) ***Macro-PSA*** (with a capacity over 100 m^3/hour; industrial technology);

In this direction the following work was carried out:

1. Experimental infrastructure is organized. Methods and equipment for studying adsorption kinetics, dynamics and statics at low (1-2.5 atm.) and high (up to 16 atm.) pressure are used. New variant of a molecular probes method for the Micropore-Size Distribution (MSD) analysis is offered.

2. CMS texture design for light hydrocarbons separation by a PSA method is offered. The first CMS samples with the calibrated size micropores were obtained by adjustable phyrocarbon depositing on Microporous Carbon Adsorbents (MCA). (experiments have shown their effectiveness for hydrocarbons separation by PSA).

3. Research of industrial and experimental samples of CMS and MCA was carried out.

Separation characteristics for a number of adsorbents were determined by pulse-chromatography method. Adsorption equilibrium constants and effective diffusivities were determined for CO, methane, ethane and so on.

4. The software for PSA processes modelling was developed. It includes algorithms and programs for numerical study of particle and layer dynamics proceeding at typical stages of a PSA-cycle. Modelling of a methane-ethane separation on CMS and MCA was performed particularly.

5. A separation of a number of model mixtures by PSA-cycle using CMS and MCA were studied on the pilot setup. The experimental results will be compared with numerical experiments.

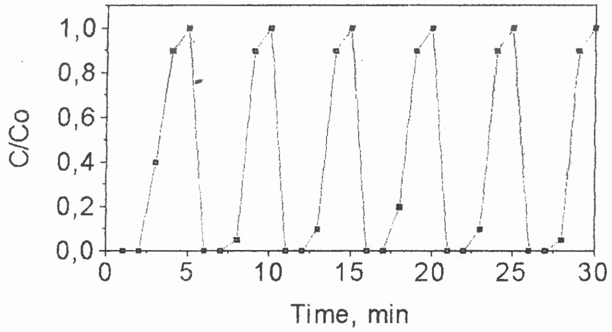

Figure 1. Typical PSA cyclogram obtained on a pilot setup.

OXIDATION OF METHANE TO SYNGAS OVER Ni-BASED ELECTRODE IN A SOLID OXIDE ELECTROLYTE CELL

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Introduction: Recently, much attention have been paid to investigation of catalytic selective oxidation of methane to synthesis gas. It was shown that this reaction proceeds on supported metal catalysts, including nickel-containing system at high temperature. Here we report the results on electrochemical oxidation of methane to synthesis gas over a Ni-based electrode-catalyst in a cell with a solid oxygen conducting electrolyte, viz. yttria stabilized zirconia (YSZ). Schematically, such a cell is similar to the solid oxide fuel cell (SOFC):

$$CH_4 + N_2, Ni \mid YSZ \mid Pt, air.$$

The electrochemical oxidation of CH_4 in SOFC is a new way for syngas production from methane. Only few reports are known in this field [1-3]. At oxidation of methane in the SOFC the methane flow did not contain oxygen. It was fed directly into the reaction zone by passing anodic current through the cell. In this case O^{-2} ions are formed at the air electrode. Then, these ions transfer to the electrode-catalyst through the YSZ electrolyte, where they can either discharge to produce O_2 or oxidize methane.

Experimental: Electrochemical cell was a YSZ electrolyte tube, in which two porous metallic electrodes were supported on the inner and outer surfaces. A working Ni-based electrode-catalyst was inside the YSZ tube and the counter Pt electrode outside it. The geometrical area of the electrodes was 3 cm^2 .

The experiments were carried out at atmospheric pressure within the temperature range of 750 - 850°C. The methane-nitrogen mixture flow, containing 3 - 10 vol % of methane, was varied between 0.4 and 1.5 cm^3/s. The anodic current flowing through the cell was varied in the range of 90 - 400 mA.

Results and discussion: The effects of temperature, residence time, methane concentration and current (or electrode potential) on the methane conversion, product distribution, carbon monoxide selectivity and the yield were studied. The typical experimental results are presented in Fig. 1.

In Fig. 1a the conversion of methane and yield of carbon monoxide are plotted against temperature. Practically 100 % conversion of electrochemical oxygen pumping to the reaction zone was observed and only H_2, CO, CO_2 and

H_2O were detected as the products. The outlet concentration ratio $[H_2]/[CO]$ was ca. 2. An increase in temperature results in higher CH_4 conversion and CO yield. Their values are closed to the thermodynamic equilibrium ones at 800 - 850^{0}C.

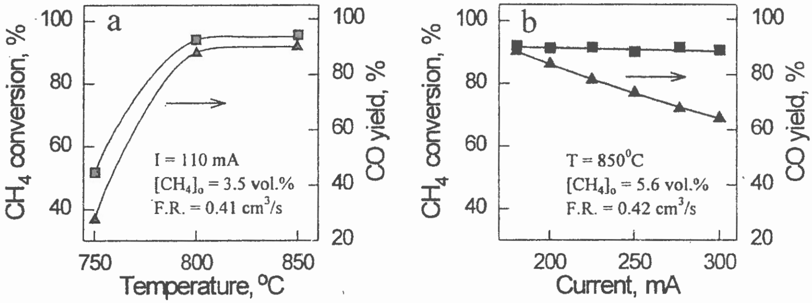

Fig. 1. Effects of temperature (a) and anodic current (b) on CH_4 conversion and CO yield at electrochemical oxidation of methane.

Fig. 1b shows CH_4 conversion and CO yield versus anodic current. The conversion of methane is 92 % and does not change with increasing current, while CO yield decreases from 88 to 64 %.

These results allowed the conclusion that the Ni-based electrode is an active electrode-catalyst for electrochemical conversion of methane to synthesis gas in the SOFC system.

On the basis of the data obtained we will discuss the reaction mechanism and prospects of syngas production from methane in the SOFC system with Ni-based electrode-catalyst.

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FORMATION OF XEROGEL POROUS STRUCTURE OF THE 4TH GROUP OXIDES PREPARED BY PRECIPITATION

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Oxides of the 4th group of Periodic system (TiO_2, ZrO_2, SnO_2) represent an important class of dispersion materials finding wide application in heterogeneous catalysis, adsorption and ion exchange, electronic engineering and chemistry of sensors. The peculiarities of these objects are connected with an opportunity to vary purposefully their chemical and phase structure, and texture-mechanical properties. A method of precipitation allows to carry out consistently and in controllable conditions separate stages of formation of primary particles of an oxide phase and their subsequent aggregation and crystallization.

Hydrolysis of initial salt is the first stage of formation of any oxide phase precursors. The oxide phase is formed as a result of heterogeneous nucleation at saturation of formed polyhydroxo complexes. A morphology and dispersion of particles are defined both by individual and general fundamental properties of the oxide phases.

Our results allow to assert that the ratio of rates of start salt hydrolysis and hydroxide phase nucleation renders essential influence on formation of xerogel porous structure. The initial components of a nuclear with large probability overcome a power barrier of nucleation, thus providing favorable conditions for formation of primary particles and their growth when the rate of nucleation exceeds rate of low molecular forms of polyhydroxo complexes (LMF) formation. The fundamental property of oxide systems is that the minimum size of these globules for the majority oxides is 3-5 nm. Thus, even the dense random packing of such globules forms a meso-porous structure.

At alternate variant when the hydrolysis rate prevails, there is the excess of LMF at simultaneous reduction of number of nuclear primary oxide globules in intermicelliar media. Xerogels obtained from such gels should contain appreciable porous volume, the size of which is commensurable with the size of fragments LMF, i.e. micropores. Thus, it is possible to synthesize purposefully meso- or microporous structures by changing the ratio of rates of oxide phase nucleation and hydrolysis.

As follows from the heterogeneous nucleation theory the rate of nuclear formation (J) is supervised by value of free energy of stable nuclear (ΔG_k): $J= A \exp. (-\Delta G_k/kT)$, where A is a coefficient defined by properties of steady nuclear and poorly dependent on temperature. The value of ΔG_k parameter is a specific property of particular system determining a direction of process of the xerogel texture formation.

Thus, pH of precipitation, determining depth and rate of hydrolysis and also a surface charge of dispersion, and temperature of precipitation, determining rate of a phase hydroxide nucleation, are the major factors that regulate porous structure of the 4th group oxides. We have considered the regularities of porous structure of tin dioxide [1], zirconia [2] and titania [3-5] formation.

Experimental data allow to assert that the formation of microporous structure is especially characteristic for SnO_2, and at $pH > 5$ extremely micro- and supermicroporous structure is formed, which is, however, rather not thermostable. ZrO_2 displays similar properties, though significant volume of mesopore is formed simultaneously with micropores. At the same time, the micropores formation is not characteristic for TiO_2 obtained from hydrochloric acid $TiCl_4$ solution and it is possible to obtain insignificant volume of micropores only in special conditions of synthesis [4]. On the other hand, absence of significant amounts LMF in TiO_2 structure allows to adjust mesopores distribution by changing a surface charge of a dispersion [3]. The regulation of surface charge is reached by changing ions sorption on a surface of dispersion. It is possible to change purposefully both pore volume and pore size distribution in xerogels at drying of hydrogels. For example, we have shown [5] that the change of surface charge value allows to vary the porous structure from uniform up to bimodal.

Distinctive peculiarity of researched systems is their rather slow crystallization that influences on the porous structure formation. The study of TiO_2 porous structure genesis [6] demonstrates a role of aggregation-disaggregation processes of crystal phase of anatase on final porous structure formation.

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INVESTIGATION INTO THE POSSIBILITY OF FORMING THE NICKEL-CALCIUM-CONTAINING CATALYSTS WITH DIFFERENT AGENTS AND POSSIBLE USAGE FOR PURIFICATION OF EXHAUST GASES.

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The rigid operating conditions of catalysts for purification of exhaust gases specify that a number of requirements are met. They are as follows: high activity in the wide temperature range, thermostability up to 100° C, high strength, low resistance to gas flow, resistance to poisoning, availability of raw materials and simple preparation. At present it will be noted that there is a lack of designs meeting the requirements in full. The contacts are being searched, combining the desired properties.

The preparation of catalyst by a simple waste-free process has been of particular importance. The main way of reducing raw material costs is partial or complete replacement of Pt, Pd, Rh, Ru-containing components with more available compounds of other transition metals of alternating valence. The problem of low-waste technology can be solved to a great extent by mixing in water or other media if there are no noxious gases and industrial water wastes.

The Novomoskovsk Institute of Nitrogen Industry is experienced in developing such catalytic systems based on cements (calcium aluminates) for diverse processes. The use of cements and waste-free mixing process in water or water-ammonia medium allows to prepare contacts of high strength and thermostability. Available investigations of nickel-alumino-calcium catalysts with different agents for gas purification from carbon oxides, hydrocarbons and nitrogen oxides allow to make catalysts with the desired properties for purification of exhaust gases.

The complex physico-chemical study of formation mechanisms of nickel-alumino-calcium catalysts with different agents and tests in the process of purification of exhaust gases from diesel engines have been carried out. The principal possibility of making catalysts with satisfactory physico-chemical properties and low cost in comparison with catalysts based on Pt, Pd, Rh, Ru is shown. Selected catalytic composition and production process allow a substantial reduction in carbon deposits. For bench tests at the Engine Institute (and one of the motor works) the catalysts were used in the form of tablets, extrudates and balls. Pilot catalysts batches were prepared at the plant of the catalyst department of NIAP. To reduce resistance in the neutralizer, catalysts in the form of rings are used.

The best results were obtained with Ni-Cu-compositions. Conversion of exhaust gases (e.g. Ni-Cu-catalysts) developed with some agents CO became 40%, NO_X at 20%. This is close to foreign results published by scientific centre of Ricardo and Hokkaido universities.

The relationship of some mechanisms of forming catalysts studied with regard to their properties in purification process is discussed. The possibility of simultaneous using Pd-free catalysts and those containing some Pd has been studied. The new effect of Pd-addition on the function of catalytic neutralizer in general is detected and explained as neither additive nor synergetic action of components. The character of this effect is also discussed. The results show the perspective of continued study in respect of improvement of catalyst performances.

PPII-23

DETERMINATION OF CATALYSTS AND CATALYST SUPPORTS TEXTURE CHARACTERISTICS

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In 1953 at the All-Union conference on the heterogeneous catalysis problems G.K.Boreskov at the first time brought publicly forward the thesis about the approximate permanence of specific catalytic activity of the catalysts with identical chemical structure, where specific activity is the activity related to the catalyst surface area. This is the basic idea in modern heterogeneous catalysis, where it is very important to know the specific activity, its changes in various conditions and factors, causing deviations from permanence of specific activity. But in all of these cases it is necessary to determine not only the activity but also the specific surface area.

Besides, the majority of industrial heterogeneous catalysts work in conditions, where the speed of process is limited by reagents or reaction products diffusion. In these cases it is obligatory to measure the porosity and pore size distribution. More detailed measurements of the texture characteristics (surface area, porosity, pore structure, pore volume and etc.) are necessary when developing of the new catalysts or optimisation the known ones. The success of work in this area is mostly depends on accuracy and reproducibility of the texture characteristic determination. The old reliable partner of the Institute of Catalysis in the field of texture characteristics precise measurements is the firm Micromeritics. The only lack of this firm's devices is the frequently upgrade of their models. In a while after of purchase of the last model of this firm's device - the new essentially improved models appear. This fast modernisation with the use of the last scientific achievements in adsorption, programming, automation of experiment and etc. is the feature of firm Micromeritics that is in continuous dynamic development from its foundation in 1962.

It is natural, as one of the founders of this firm was Dr. Clyde Orr - the famous specialist in the field of porous and dispersion materials investigation. In 1959 he and J.M.DallaValle wrote the monograph "Fine Particle Measurement" (McMillan,N.Y.) where they summarised the methods of investigation in this field. In this monograph they proposed some new interesting methods (for example improved method of pore size distribution calculation, based on analysis of isotherm desorption branch). In that time physical chemists were forced to build their own apparatus for surface area measurements and to improve the analysis techniques themselves. The analyses were very time-consuming and results were inconsistent from one hand-built device to the next. But the scientific experiment and its instrumental support very often - are the different things. Dr. Clyde Orr found his own solution of these problems - he decided to create the firm for manufacturing of modern devices. Probably, it would be very interesting to combine G.K.Boreskov and Dr. Clyde Orr together - that would be remarkable team. And now the leading scientific centre in the field of catalysis - Institute of Catalysis uses the Micromeritics' equipment for precise investigations.

As illustration for mentioned above - some information about latest models of the devices from this firm:

ASAP 2010 System - fully automated surface area and porosity analyser (pore diameter from 30 to 4000 angstroms); WINDOWS-driven multitasking software; wide variety of data reduction techniques including: DFT, BET & Langmuir, BJH, Harkins Jura; easily upgraded to Multigas (analysis of low surface area materials by krypton gas), Micropore (measures micropores from 3.5 to 30 angstroms) and Chemisorption options (determines metal surface area and % dispersion).

ASAP 2405 - high throughput, 6 port surface area and porosimetry analyser; 12 independently controlled degas ports; powerful multitasking operating software

Gemini - fast surface area analyser using adaptive rate static volumetric technique (five-point BET analysis for 10 min), no mixed gases required.

AutoPore III Porosimeter - determines pore size distributions, total pore volume and surface area and bulk density; 60,000 psia yelds 360 to 0.003 um pore diameter data, WINDOWS-driven multitasking software.

TPD/TPR 2900 - desorption, adsorption, reduction, oxidation; temperature rampable up to 1100 deg.C at 50 deg/min; physisorption mode available.

SediGraph 5100 - automatic particle size measurement by sedimentation technique, measurement range from 300 to 0.1 microns.

AccuPyc 1330 - fast, automatic determination of true density of solids and powders, highest accuracy to ±0.001 g/cc or better.

GeoPyc 1360 - determines bulk(envelope) density of irregular shaped objects, uses patented displacement technique.

In Institute of Catalysis are used ASAP 2400, porosimeters - AutoPore and PoreSizer and other devices and they have recommended themselves well.

PPII-24

METHANOL SYNTHESIS OVER Cu/ZnO CATALYSTS PREPARED BY BALL MILLING

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Introduction:

Copper containing catalysts are widely used in industry. The main applications include methanol production from synthesis gas, oxo-alcohol manufacture from hydroformylation processes and fatty alcohol synthesis by ester hydrogenolysis. Due to their economic importance considerable research efforts continue to be directed towards these catalysts. Another aspect contributing to the interest in copper catalysis is the fact that still controversy exists on the active site for methanol synthesis [1,2]. What has been established is that a good intimate mixture of Cu and ZnO (or Cu-Zn-Al/Cr) must be obtained during catalyst preparation in order to achieve high methanol activity [1,3]. For the commercial type Cu-Zn catalyst this is achieved by coprecipitation of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ solutions with subsequent ageing and calcination [3]. In this poster high intensity mechanical mixing of copper powder and zinc oxide without high temperature treatment is studied as a novel approach to obtain such well-mixed sytems.

Obviously, ball milling has long been known as a technique for refining particles of a large variety of solid materials. Formation of amorphous alloys by mixing on an atomic scale of elemental metallic powders and uniform dispersions of oxide particles in metal alloys (mechanical alloying) or amorphisation of pre-alloyed intermetallic compounds (mechanical milling) and formation of solid solutions by high intensity mechanical mixing have also been reported (for a review, see [4]). Recently, mechanical milling has been applied in the preparation of various catalysts such as ion-exchanged montmorillonite clays [5]; mixed VPO/Bi_2O_3 and $VPO/BiPO_4$ oxidation catalysts [6] and binary solid solutions of CeO_2 with Zr, Hf or Tb [7].

In this poster the influence of the gas phase and milling time on the activity of mechanically mixed Cu-ZnO catalysts in the methanol synthesis reaction from a $H_2/CO/CO_2$ feed mixture is investigated. The high intensity ball milling process is analysed by x-ray diffraction (XRD), nitrogen physisorption, N_2O chemisorption and temperature programmed reduction (TPR).

Results:

The Cu/ZnO catalysts were prepared by high intensity mechanical mixing of copper and zinc oxide powder in air and under vacuum at a Cu/Zn atomic ratio of 30/70. During milling in vacuum gradual amorphisation of the constituents occurs, as evidenced by broadening of the Cu^o and ZnO diffraction peaks in XRD, but the two original phases remain. The result of such treatment is a catalyst with low BET area and low Cu metal surface area. Consequently, the activity of the vacuum milled samples in batch methanol production from synthesis gas ($CO/CO_2/H_2$ = 20/5/75) at 50 bar and 250°C is low. Milling in air leads to oxidation of the copper metal phase and much higher BET surface area and, after reduction, also high Cu metal area. Some evidence for formation of a solid solution of Cu^{2+} in ZnO is derived from TPR and XRD. The activity in methanol synthesis for the air milled samples is comparable to a conventional Cu/ZnO catalyst prepared by coprecipitation. It is concluded that high intensity ball milling at ambient conditions is a promising method to prepare mixed oxide catalysts or catalyst precursors.

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PPII-25

The investigation of catalytic processes in the flame doped by dimethyl methylphosphonate

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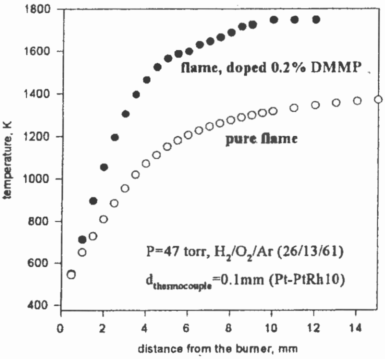
There are results of investigations on the structure of a premixed flat $H_2/O_2/Ar$ flame doped with dimethyl methylphosphonate (DMMP) at low pressure involving molecular beam mass spectrometry (with soft ionization), temperature profile measurements by thermocouples and comparison of experimental data with modeling of $H_2/O_2/Ar$ flame with 0.2% of DMMP carried out using both literature rate constants (Twarowski) and pre-estimated ones. One can see on the fig.1 that in the presence of OPC additives the maximum flame temperature increases by several hundred degrees, and also temperature gradient near the burner increases. This additive results in flame promotion. The effect on the flame temperature of the heat release from additional fuel (0.2% DMMP) is not sufficient to account for an increase of the gaseous mixture temperature of several hundred degrees. This is confirmed by thermodynamic calculations carried out using the CHEMKIN code. The OPC additive accelerates the chemistry and makes the flame approach equilibrium conditions more quickly. Ionization efficiency curves for the main mass peaks of final products of OPC destruction in the flame were obtained. Identified phosphorous oxides and acids: PO (47amu), PO_2 (63amu); HPO_2 (64amu), HPO_3 (80amu), H_3PO_4 (98amu) are the main final phosphorus containing products of OPC destruction [1]. The possible explanation of promotion is the following. The phosphorus oxides as well as intermediate products of DMMP destruction can catalyze H and OH recombination according to possible paths suggested by Twarowski [2]:

$H+PO_2+M \rightarrow HOPO+M$, $OH+H_2 \rightarrow H_2O+H$,

$H+HOPO \rightarrow H_2+PO_2$, $H+HOPO_2 \rightarrow PO_2+H_2O$

$PO_2+OH+M \rightarrow HOPO_2+M$.

The catalytic recombination of H and OH is an exothermic process, which increases the heat release rate and thus the temperature, in



turn increasing the reaction rate and the completeness of combustion. A mechanism for DMMP decomposition in flame was suggested basing on experimental data. Basing on the mechanism cited in [3], OPC experimental profiles and using a mechanism cited by Twarowski as well, rate constants of unknown stages can be matched and flame with an additive can be modeled. The DMMP additive has different effects in different flame zones. It inhibits the consumption of oxygen in a low-temperature flame zone (near the burner surface). As the additive concentration increases from 0.2 to 0.4% the inhibition effect increases. DMMP is known as a fire retardant to polymers. The inhibition effect of DMMP is possibly connected with its influence on a branch termination as a result of DMMP reaction with H and (or) OH atoms (the first stage of above mechanism) diffusing from a hot flame zone. **Conclusions: 1.** The additive of OPC accelerates the chemistry and makes the flame approach equilibrium conditions more quickly. **2.** Phosphorous oxides and acids are the main final products of OPC destruction in the flame. **3.** Possible explanation of promotion is the following. The phosphorus oxides as well as intermediate products of OPC destruction can catalyze H and OH recombination. **4.** Modeling demonstrated the main regularities observed in experiments: 1) similar concentrations profiles of DMMP, H_2, O_2, H_2O, H, OH, intermediate and final products of OPC destruction; 2) decrease of H concentration in the presence of additive; 3) promoting effect of additive and inhibiting effect at the increasing its initial concentration.

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PPII-26

A NEW ROUTE TO THE PREPARATION OF NANOPHASE COMPOSITES CONTAINING FINE TRANSITION METAL PARTICLES

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Nanophase composites containing fine transition metal particles are of interest as catalysts. A promising route to the preparation of nanophase composites with fine particles of transition metals via layered intercalation compounds of aluminium hydroxide with lithium salts has been shown. Their structure consists of positively charged layers, $[LiAl_2(OH)_6]^+$, separated by intercalated, charge balancing anions X and water molecules [1]. In the case of the thermal decomposition of intercalates, where X is a complexonate-anion involving a transition-metal cation and some carboxylate groups, we presuppose the metal cations to be reduced to metal state. Considering that the nearest cations in the initial compound can be far apart from each other (0.8 - 1 nm) , we expected that the process of formation of metal particles from atoms is hindered by diffusion. To explore the possibility to realize this approach, we used intercalation compounds containing $[CuEdta]^{2-}$, $[CoEdta]^{2-}$, $[NiEdta]^{2-}$. Edta is an anion of ethylenediaminetetraacetic acid forming stable complexes with transition metals.

In order to synthesize the intercalates by ion exchange procedure, an intercalation compound with chloride (LADH-C1) was used. This compound was obtained by treating of crystal gibbsite, $Al(OH)_3$, with a concentrated LiCl solution. Chemical composition of the resulting compound was close to $[LiAl_2(OH)_6]Cl \cdot 1.5H_2O$. LADH-C1 was treated with the aqueous solutions of sodium salt containing the $[MEdta]^{2-}$ anions. The solid phase was separated from the liquid after the treatment, washed with a small amount of water to remove the sodium or lithium salt, and dried on the air. Li, Al, Na, Cl and, in some cases, C and N contents of the air-dried samples have been determined. Lithium was determined using flame photometry, aluminum with the help of complexometry and mercurimetric technique was used to determine Cl^-. To measure carbon and hydrogen contents the samples were burned in the flow of oxygen in a CHN-3 analyzer. The data obtained (chemical analysis, IR- and optical spectroscopy; XRD) enable to give the following formulae for the synthesized compounds: $[LiAl_2(OH)_6]_2[CuEdta] \cdot 4H_2O$, $LiAl_2(OH)_6]_2[CoEdta] \cdot 4H_2O$ and $[LiAl_2(OH)_6]_2[NiEdta] \cdot 4H_2O$. Thermal decomposition of such materials in vacuum or an inert gas has the following stages.

At a temperature up to 200^{0}C, removal of molecular water from a crystal prevails. The process of dehydration of interstitially located water molecules proceeds in two stages approximately at $60\text{-}90^{0}$C and $140\text{-}180^{0}$C for all MEdta-intercalates. Subsequent heating (above 200^{0}C) results in destruction of the hydroxide matrix. The process occurs before the decomposition of organic anion excepting LADH-[CuEdta], where both processes start to go near-concurrently. On a further increase of temperature, the process of thermolysis proceeds differently. For the nickel-containing intercalate at a temperature up to 300^{0}C, the decomposition process goes with the predominant release of water molecules into the gas phase, which is caused by the destruction of hydroxide layers. In the case of the copper and cobalt containing intercalates, water removal is accompanied by the simultaneous formation of gaseous products with 28 and 44 m/e, which were referred to CO and CO_2. At temperatures above 300^{0}C, for all compounds, one can observe not only the release of CO, CO_2 and H_2O (18 m/e) , but also the appearance of NH_3 (16 m/e) and H_2 (2 m/e), which indicates the deep destruction of Edta. The considerable content of carbon is determined in the products of vacuum decomposition, which points to the carbonization of the samples in the course of thermolysis. The C/M and N/M ratios show that approximately one half of the carbon and nitrogen content is removed from the initial intercalates upon thermolysis. Decomposition in vacuum or in an inert gas results in the appearance of nanoscale metal particles (2-50 nm). The data of high resolution transmission electron microscopy (HREM) confirm the formation of round nickel particles with a narrow size distribution spread uniformly in the matrix upon the thermolysis (400^{0}C) of LADH-[NiEdta]. On the nickel particles well regulated lattice lines are seen that testifies that the particles are well-crystallized and do not possess inner defects. In the case of the [CuEdta]-containing intercalate (400°C), along with the formation of small particles (2-5 nm), much larger ones (up to 50 nm) comprising disoriented fragments form. They placed disorderly in the amorphous matrix.

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PPII-27

WASTE-FREE SYNTHESIS OF LITHIUM ALUMINATES

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Lithium aluminates of various composition, both pure compounds ($LiAl_5O_8$, α- and γ-$LiAlO_2$,α- and β-Li_5AlO_4) and doped with different elements (Fe, Cr, etc.) are used as catalysts, solid electrolytes with lithium conductivity, initial materials to obtain tritium. A traditional method of obtaining aluminates is based on ceramic technology which incorporates thermal treatment of the mixture of lithium carbonate and aluminium oxide [1]. This method of synthesis seems to be easily realized. However, in order to obtain the final product with high phase purity, prolonged calcination of the mixture at sufficiently high temperature and the intermediate cake homogenization are needed. For the purpose of decreasing the synthesis temperature and obtaining the products with more homogeneous phase composition, the method of precursors is used. Precursors contain the major components of the compound to be synthesized, i.e., aluminium and lithium. The most widely used approach to the synthesis of precursors is based on their recovery from the solution (sol-gel methods, coprecipitation). This method is seen to involve large amounts of solvents, often non-aqueous ones. For example, additional amounts of reagents are needed to obtain 1 t of lithium monoaluminate: nitric acid – 3.2 t, (hydrochloric acid – 1.9 t), sodium hydroxide – 2 t. The process is accompanied by the formation of 2.9 t of sodium chloride (4.3 t of sodium nitrate). This means that the synthesis is accompanied by the formation of large amounts of liquid wastes. The formed compounds are gel-like, as a rule. They can hardly be filtered and washed off the reaction products. Therefore, the search for new precursors and methods of their synthesis free from large amounts of wastes and allowing low-temperature synthesis of lithium aluminates is of interest for practice.

The essence of the proposed approach is that the precursors are intercalation compounds of aluminium hydroxide with lithium salts $Li_nX \cdot mAl(OH)_3 \cdot pH_2O$ (LADH-X), where X is the anion of either organic or inorganic acid. These compounds can be easily obtained in the interaction of crystalline aluminium hydroxide (gibbsite, bayerite) with aqueous solutions of lithium salts[2] by the reaction:

$$mAl(OH)_{3(SOLID)} + Li_nX + aq = Li_nX \cdot mAl(OH)_3 \cdot pH_2O_{(SOLID)}$$

Since aluminium and lithium cations are "mixed" at the molecular level in these compounds, the formation of lithium aluminates can take place under more soft conditions of thermal treatment of the mixture containing these compounds than those of the traditional ceramic synthesis method.

The use of the intercalation compound with various Li/Al atomic ratio and different anions X allows reducing the time of the high-temperature treatment of mixture several times, decrease in the temperature of treatment by 100-150°C, increased purity of the product thus obtained in comparison with the traditional ceramic method of synthesis of lithium aluminate from aluminium oxide and lithium carbonate. Unlike the sol-gel or coprecipitation technique, this approach allows either excluding salt wastes at the stage of precursor synthesis (the first variant of the synthesis) or decreasing their amount by a factor of 7 (the second variant of the synthesis). The volume of required solvents is thus decreased by a factor of 2–3, and the use of an acid or an alkali is excluded (see the Scheme). Thus obtained solid phases are well crystallized which allows to separate them easily from the solutions.

Scheme of lithium aluminate synthesis by intercalation technique

1.Stage of precursor synthesis:

variant 1

$mAl(OH)_{3(SOLID)} + Li_nX + aq = Li_nX{\cdot}mAl(OH)_3{\cdot}pH_2O_{(SOLID)}$

variant 2

$2Al(OH)_{3(SOLID)} + LiCl + aq = LiCl{\cdot}2Al(OH)_3{\cdot}1.5H_2O_{(SOLID)}$

$nLiCl{\cdot}2Al(OH)_3{\cdot}1.5H_2O_{(SOLID)} + Na_nX + aq = Li_nX{\cdot}mAl(OH)_3{\cdot}pH_2O_{(SOLID)} + nNaCl$

2.Stage of aluminate synthesis:

$Li_nX{\cdot}mAl(OH)_3{\cdot}pH_2O_{(SOLID)} + Li_2CO_3$ ----> heating---->

---> Aluminate $+ H_2O + CO_2$ (X- organic anions)

---> α-$LiAlO_2 + H_2O + CO_2 + Li_nX$ (X- Cl^-, SO_4) for the synthesis of intercalate used at the stage 1

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PPII-28

FINE ALUMINIUM HYDROXIDE WITH LOW ALKALINE CONTENT. NEW APPROACH FOR WAST-FREE PREPARATION

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Fine aluminum hydroxide with low alkali content is extensively used for the production of carriers, catalysts and sorbents. Traditional method of synthesis of this hydroxide is based on precipitation from the solutions. Precipitation includes dissolving technnical-grade gibbsite in an acid (alkali) and subsequent deposition with an alkali (acid). A shortcoming of this method is irrevocable use of large amounts of acids and alkalis. So, in order to produce 1 ton of precipitated hydroxide, it is necessary to use 2.4 t of HNO_3 (or 2 t of H_2SO_4) and 1.5 t of NaOH. In this case, 3.3 t of $NaNO_3$ (or 2.7 t of Na_2SO_4) is formed which must be utilized. All this necessitates the search of new methods for the production of fine aluminium hydroxide without the formation of wastes. The solution of the problem is the use of the process of intercalation - deintercalation of lithium salts into gibbsite. It has been shown that gibbsite can react with the concentrated solutions of lithium salts with the formation of the compounds in the reaction:

$$Li_nX + mAl(OH)_3 + pH_2O = Li_nX \cdot mAl(OH)_3 \cdot pH_2O \text{ (LADH-X) [1].}$$

The interaction process involves the intercalation of lithium ions, water molecules and anions between aluminium-hydroxide layers of gibbsite [2,3]. The intercalation leads to an abrupt increase in the distance between the aluminium-hydroxide layers. The conservation of aluminium hydroxide layers at increasing the distance between them causes the appearance of elastic stress in the zone of contact between the initial aluminium hydroxide and the reaction product. Relaxation of this elastic stress causes dispersion of the initial aluminium hydroxide, along the cleavage planes and displacement of the aluminium-hydroxide layers relative to each other in the plane (001). Intercalation is a reversible process. The treatment of LADH-Cl with water causes deintercalation of lithium chloride and the formation of aluminium hydroxide [4]. The broadening of the diffraction peaks and the bands of valence oscillations of OH groups connected by hydrogen bonds indicates the presence of package defects in the hydroxide produced. In order to use this approach for the development of fine hydroxide production technology, it is necessary to have information on the influence of the most important factors on the processes of intercalation-deintercalation of lithium salts and to know the possible application areas of the aluminium hydroxide produced.

Influence of lithium salts concentration, dispersity of aluminium hydroxide, and the process temperature on the intercalation-deintercalation rate were investigated. An unusual dependence of the transformation degree on the particle size of aluminium hydroxide is observed for every lithium salt. A normal dependence of the transformation degree on the particle size must be characterized by the monotonous decrease of the transformation degree caused by the increase of the particle size. But lithium chloride, bromide, sulphate and nitrate exhibit a reverse dependence for the whole size interval studied (1-20 μm). We considered the influence of lithium salt concentration on the degree of transformation during the intercalation of LiBr, $LiNO_3$, Li_2SO_4, and LiCl. At small concentrations, the transformation degree is insignificant. It abruptly increases with the increase of concentration then and flattens out. We investigated the influence of temperature and lithium chloride concentration on the deintercalation process from LADH-Cl .

As a result of the cycle of intercalation-deintercalation, initial gibbsite is transformed into fine aluminium trihydroxide with the specific "layered" morphology and surface area from 6 to 8 m^2/g. The mean diameter of fine "layered" hydroxide particles is about 10-15 μm. The mean layer thickness is about 0.1-0.2 μm. Sodium content of such samples is less than 0.02%. Lithium content may also be rather low, 0.01 - 0.02 %. This method of synthesis is essentially clean, since it allows the use of the aqueous solutions of lithium salts after deintercalation at the beginning of the process. It is found that the calcination of the hydroxide produced leads to practically complete conversion of it (>98%) into corundum already at 1190- 1200^0 C. The specific surface area of the corundum produced depends on the temperature and is about 10 m^2/g at 1200^0C. Sodium content of such samples is less than 0.02%.

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PPII-29

EFFECT OF THE POINT AND EXTENDED DEFECTS ON THE CATALYTIC ACTIVITY OF $La_{1-x}Sr_xMnO_3$ PEROVSKITES

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In heterogeneous catalysis, one of the most complex problems concerns the effect of the chemical composition and parameters of synthesis of various classes of catalysts on their performance. Among various aspects of this problem, an impact of the real (defect) structure of the surface and bulk of solids on their catalytic properties has recently attracted much attention. For oxide catalysts, this problem was considered both for simple as well as complex oxides including those with a perovskite structure [1-3]. In perovskites, point defects generated by a partial substitution of lanthanum by alkaline-earth cations or due to oxygen nonstoichiometry are usually thought to be the most essential for catalysis. However, for manganites [3-5] as well as cobaltites [5,6], extended defects seem to be even more important. In particular, strontium substitution for lanthanum is capable also to generate a phase transition from a hexagonal to a cubic perovskite structure, so that a maximum of activity versus strontium content observed for some systems could be assigned to such structural transition. Further, reaction mixture can effect a state of the surface or bulk of the samples thus making a problem even more complicated. In the work presented, all these problems were considered for $La_{1-x}Sr_xMnO_3$ perovskite system as related to reactions of butane and CO oxidation.

EXPERIMENTAL

Samples for study were prepared by ceramic, mechanochemical and plasmochemical methods. Catalytic activity in the reaction of CO oxidation was estimated using a pulse/flow microcatalytic installation and a reactor with a vibrofluidized bed of catalyst. Before experiments, samples were pretreated in the flow of dry oxygen, and both initial (in the first pulse of a reaction mixture 1% CO+ 1% O_2 in He) and steady state activities in the temperature range of 100-227 °C were then determined. Rates of butane oxidation at 400 °C were found in the batch-flow installation at a stationary concentration of butane in air equal to 0.2 vol. %. Real structure of samples was studied by electron microscopy (JEM - 100CX microscope), X-ray structural analysis (URD-6 diffractometer, Cu Kα radiation, range of angles 2θ = 22-100°), X-ray Small-Angle Scattering and Mössbauer spectroscopy of the ^{57}Fe tracer. Surface layer composition was studied by SIMS, and specific surface area was found by Ar thermal desorption.

RESULTS AND DISCUSSION

Effect of the point defects generated by a partial substitution of Sr for La was studied on the $La_{1-x}Sr_xMnO_3$ samples prepared by a ceramic technique and annealed at a high (1100 °C) temperature which allows to exclude any possible impact of the genetic nonequilibrium defects. For the initial low-temperature activity in the reaction of CO oxidation, a moderate maximum was observed at x=0.2. In this case, activity of the most active sample is ca 3 times higher than that of the pure lanthanum manganite. Here a maximum of activity was observed within the same type of structure, and it clearly does not correspond to any phase transition. Moreover, this maximum is not mirrored in the surface concentration of Mn, which changes monotonously. Hence, for initial low-temperature activities, point defects really seem to be of importance. The most probable explanation is based upon the model of a charge compensation due to a Sr substitution for La. In this case, at a low degree of substitution, cation vacancies in the A sublattice appear to be accompanied by a simultaneous increase of a charge of some Mn cations from 3+ to 4+ . Due to a lower bonding energy of oxygen with Mn^{4+}, some increase of activity is observed. At a higher degree of substitution, another mechanism of charge compensation via generation of the anion vacancies operates [4]. As a result, a number of Mn^{4+} cations decreases leading to a fall of activity as x increases. Hence, this explanation of a maximum of the initial low-temperature activity is based upon a decisive role of a manganese charge. In the case of a high-temperature activity, where a strong effect of the reaction media is expected, such maximum should disappear. Indeed, for this series of samples, no maximum was observed for the steady-state activities in both reactions of catalytic oxidation.

To obtain samples of perovskites with a high density of extended defects, nonequilibrium methods of preparation such as plasmochemical and mechanochemical were used. The most detailed studies were carried out for samples of lanthanum manganite synthesized by these methods. A sample prepared via plasmochemical route was found to have the most disordered structure due to a high density of both point (cation vacancies in the lanthanum sublattice) and extended (small-angle boundaries and twins) defects. According to data of Mössbauer spectroscopy, extended defects could be considered as thin slabs enriched with manganese, whose local structure is of a braunite (β-Mn_2O_3) type. In our experiments, the density of point as well as extended defects was changed by a ball milling and/or a thermal annealing. Only at operating temperatures around 100 °C, an initial catalytic activity in CO oxidation seems to be determined by point defects, that correlates well with the behavior of Sr-substituted samples. On the contrary, steady-state activity in the reaction of CO oxidation was found to correlate with the density of extended defects. Enhanced activity of centers associated with extended defects seems to be due to a decreased bonding strength of oxygen located on such clusters of manganese cations as compared with that bound with an isolated manganese cation in a regular position on the most developed faces of the (100) and (110) type. Hence, at middle operating temperatures, bulk extended defects are more stable in the reaction media than point defects.
Only high temperatures of calcination (up to 1000-1100 °C) were found to anneal all genetic defects making specific catalytic activities of lanthanum manganite samples of a different origin practically identical.

Hence, in both pure and partially substituted samples of lanthanum manganite, point defects play some role in the initial low-temperature activity, and this effect is rapidly annealed in reaction media. A steady-state catalytic activity in the reactions of CO and hydrocarbon oxidation depends upon the density of extended defects associated with a microheterogeneity of the particles.

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PPII-29a

THE CHARACTERISATION OF ACTIVATED CARBONS USING ADSORPTION AND EXCHANGE PROCESSES.

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Introduction

High surface area carbons are used to remove ppm levels of impurities in solvents in several fields. This work investigates the adsorption properties of three types of carbon for low levels of two substituted aromatics (phenyl acetylene and benzonitrile) in dodecane. The adsorption profiles were measured using UV-vis spectroscopy. We also report on the acid/base properties of the carbons using a novel ^{3}H radiotracer technique.

Adsorption Results

Three types of adsorption experiments were carried out, injecting small aliquots of the test adsorbates into solutions of dodecane containing carbon, i.e.

(i) Single adsorptions of each of the test adsorbates
(ii) Co-adsorption, injecting both adsorbates simultaneously, and
(iii) Pre-adsorption experiments, where the test adsorbate was injected into a solution which already contained the other adsorbate.

In each of the phenyl acetylene experiments 0.182 mmoles of phenyl acetylene was injected per gram of carbon. For the benzonitrile experiments 0.196 mmoles was injected in total per gram of carbon. The results from the adsorption experiments are shown in Table 1 below.

Table 1 : Adsorption Capacities for Phenyl Acetylene and Benzonitrile

	Phenyl acetylene adsorption mmoles/g carbon			Benzonitrile adsorption mmoles/g carbon		
	Single adsorption	Co-adsorption with benzonitrile	Pre-adsorption with benzonitrile	Single adsorption	Co-adsorption with phenyl acetylene	Pre-adsorption with phenyl acetylene
Sutcliffe DCL 230	0.049	0.049	0.052	0.116	0.087	0.024
Sibunit D010	0.093	0.078	0.04	0.032	0.102	0.089
Norit RX3	0.044	0.068	0.062	0.083	0.086	0.089

Physical Characterisation

The three carbons used were characterised by nitrogen adsorption, mercury porosimetry, and XPS. The results from these characterisations are summarised in Table 2 below.

Table 2 : Characterisation of the Carbons

	BET surface area (m^2g^{-1})	**External area (m^2g^{-1})**	**Micropore volume (cm^3g^{-1})**	**Total Intrusion volume (cm^3g^{-1})**	**Surface atomic %O by XPS**
Sutcliffe DCL 230	1513	78	0.12	2.731	11
Sibunit D010	350	39	0.05	1.186	3.55
Norit RX3	1336	11	0.27	0.704	6.8

Acid/Base Properties

The acid/base properties were investigated using two techniques. The first method involved measuring the pH by a water extract method.

The second method investigated the number of replaceable hydrogens present in the samples using a novel technique of hydrogen/tritium exchange developed at the University of Surrey. The loss of radioactivity is a measure of the number of replaceable hydrogens present on the carbon samples.

Table 3 : Acid /Base Properties of the Carbons

	% decrease in radioactivity	**pH**
Sutcliffe DCL 230	20%	3.45
Sibunit D010	8%	9.67
Norit RX3	15%	6.56

Discussion

The three carbons investigated has very different acid/base properties as shown by two different techniques, pH and hydrogen/tritium exchange. The acid/base character has a major effect on the adsorption properties of the three carbons.

PPII-29a

The acidic Sutcliffe carbon showed a high adsorption of benzonitrile in the single adsorption experiment, which fell steeply with the coadsorption of phenyl acetylene and again with the preadsorption of phenyl acetylene.

The basic Sibunit carbon showed the opposite behaviour to the Sutcliffe carbon, with a high single adsorption of phenyl acetylene falling steeply on the coadsorption of benzonitrile and again with the preadsorption of benzonitrile.

These adsorption behaviours can be explained by polar interactions between the adsorbates and the carbon surfaces. The slightly basic N atom of the benzonitrile is attracted to the acidic Sutcliffe carbon, whereas the phenyl acetylene, with its acidic hydrogen is attracted to the basic Sibunit carbon. Both of these polar interactions, however, appear to be weaker than the physisorption of the other adsorbate, as shown by the coadsorption and preadsorption experiments. Physisorption is more likely to be an interaction between the π electrons of the aromatic ring and the π electrons of the carbon rather than an interaction between the substituent of the aromatic ring and the surface.

The Norit carbon, which is virtually neutral, demonstrates no gross changes between single, coadsorption and preadsorption experiments.

CATALYSTS FOR THE INTENSIVE OXYDATION OF HEAVY PETROLEUM RESIDUES

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Application of catalytic additives (chlorides and oxides of Fe, Cr, Mn, Ni, Co etc.) in the heavy hydrocarbon raw materials oxidation proccess to bitumens is known [1-3].

This served as a prerequisite to study the possibility of costly individual compounds replacement by the metallurgy wastes.

An approach to synthesis of polymetallic chloride-oxide additives based on the salt chlorinator fusion cake (waste of titano-magnesium production) and such not reclamed or poorly reclamed wastes as open - hearth and aluminium production slags, scale, salt melts of metallic aluminium is worked out.

By the mechanochemical activation of above mentioned waste mixtures the additives are obtained, which effectively carry out the oxidation of heavy hydrocarbon raw materials (fuel oils, fluxes, bitumens and petroleum products wash-off from store ponds and so on) to bitumens of different marks.

The possibility of bitumens formation rate control in a wide range by the variation of the catalyst content of total mass is shown.

The additives composition substantially influences the rheological properties (for example, softening point, penetration) of bitumens obtained.

Thus, with increasing of iron compounds content in an additive the rate of softening point growth also increases. Additives with a higher aluminium compounds content allow to decrease the drop of penetration rate, substantially influencing the bitumens quality.

The kinetics of carboxylic acids and esters accumulation in oxidates was studied.

It was shown, that the accumulation rates of the saponifiable compounds in bitumens are symbatic with softening point and penetration changes.

Additives, which accelarate bitumens softening point growth, carry out the more deep oxidation of the initial hydrocarbon mixture to carboxylic acids and esters.

PPII-30

In contrast to 3d metal carboxylates (C_{21} and more) the accumulation of saponifiable compounds in the presence of the studied additives passes monotonously without maxima on kinetic curves.

The possible causes of relationship between the saponifiable compounds content in bitumens and their reological properties are discussed in report.

It is found that the rate of the growth of the carbonic acids concentration in the oxydate may be described satisfactory by the polylinear equation. Contents of Fe(III), Al, Cl, and ratio of the last summer contents of Fe and Al in the additives are the varied parameters of this equation.

The rate of the oxydated tars acidic number increasing may be used as one of the quantitative characteristics of the oil bitumen obtaining processes.

It's revealed that the system of the two polylinear equations have described satisfactorily the rate of the oil bitumen forming process. Variable parameters in this case are the additives content factors and rate of the carbonic acids accumulation in the additives presence.

The worked out oxidation process of heavy petroleum remainders can be easily realised on standart equipment.

Obtained results create prerequisites for complex solving of a number of environment protection, resource-saving and power-saving problems during the heavy petroleum remainders and different metallurgic wastes processing.

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PPII-31

INVESTIGATION OF MECHANISM AND CONDITIONS OF H_2O_2 ELECTROSYNTHESIS BY REDUCTION OF DIOXYGEN ON THE GAS-DIFFUSION ELECTRODES ON THE BASE OF METAL COMPLEX COMPOUNDS OF NITROGEN CONTAINING COAL

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In the present time the creation of electrochemical reactors for industrial synthesis of hydrogen peroxide by cathode reduction of dioxygen is restricted by absence of effective gas-diffusion electrodes with high working resources. In this respect metalporphirines (particularly pyrolized) and their analogs are perspective compounds.

The study of H_2O_2 decomposition on the surface of series of heterogeneous metal complex compounds of nitrogen containing coals (MCCNCC) synthesised in our laboratory [1] has shown that most active to H_2O_2 decay are those containing Co and Mn, and least active are compounds doped with Ni, Fe, and some other metals. Thus, depending on MCCNCC composition (nature of metal) they can serve as effective electrocatalysts for oxygen electrodes in fuel and metal-air cells as well as for electrosynthesis of hydrogen peroxide (in "peroxiders").

It is accepted that electroreduction of dioxygen in alkaline solutions proceeds by two electron mechanism that can be presented as consecutive reactions:

$$O_2 + e \rightleftharpoons O_2^- \qquad (1)$$

$$O_2^- + H_2O \rightleftharpoons H\dot{O}_2 + OH^- \qquad (2)$$

$$H\dot{O}_2 + e \rightleftharpoons HO_2^- \qquad (3)$$

$$HO_2^- + H_2O \rightleftharpoons H_2O_2 + OH^- \qquad (4)$$

Besides the process limiting is the reaction (1) of electron joining to adsorbed dioxygen molecule. The choice of MCCNCC as material for cathode has been conditioned by the following reasons:

a) electrondonor influence of the nitrogen containing substrate on the metal complex that promotes the formation of oxygen ion radical;

b) passivity of MCCNCC containing some metals to reactions of catalytic decomposition of H_2O_2;

c) their small specific surface that also promotes the stability of generated H_2O_2 in reaction zone.

The gas-diffusion electrodes obtained by us according to known procedure (hydrophobization, pressing, thermal annealing) were used in electrochemical cells having original design. The effect of various conditions of electrosynthesis (rate and pressure of dioxygen and electrolyte flow, their concentration, distance and electrical potential between electrodes, current density, temperature, type of membrane , method of electrode preparation) on the current effectivity and concentration of H_2O_2 in catholyte was studied. The H_2O_2 concentration has reached about 3% in optimal regimes. The solutions with this content of H_2O_2 can be used, for example, for cleaning of water from organic contaminations or as bleaching agent.

In the work it is presented also the design of H_2O_2 electrosynthesis process on the base of electrodyalizer-peroxider complex.

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The work was conducted with assistance of International Fund INTAS.

The Influence of oxidizing and reducing pre-treatment on Acidic and Basic Properties of Zirconium Dioxide Catalysts, Modified by Y^{3+} Cations

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Zirconium dioxide finds a great practical application as a base for supported catalysts and as a catalyst in hydrogenation, dehydrogenation reactions and selective reduction of nitrogen oxides with hydrocarbons. However, pure ZrO_2 is low mechanical strength material. It is possible to give new properties of a surface ZrO_2 and simultaneously to improve its mechanical characteristics by way of its modifying by oxides of rare earth elements, witch have basic character, for example Y_2O_3.

We have been carried out the systematic investigation of the pre-treatment influence on Lewis acidic and basic properties of zirconium dioxide surface, modified by Y^{3+} cations. The samples were obtained by the respective nitrate solutions impregnation of the monoclinic ZrO_2 or by co-precipitation method from nitrate solution with using NH_4OH. Doped oxide containment was varied from 0.1 to 4 % weight for samples, which were obtained with impregnation method, and 1 - 10 % mol. for co-precipitated oxides. The characterization of this samples was carried out by BET, XRD, ESR and IR diffuse reflectance spectroscopy. Acidic properties of modified ZrO_2 surface (after vacuum treatment at 400 - 600°C) were investigated by infrared spectroscopy with carbon monoxide as a probe and ESR spectroscopy with TEMPO as a probe.

According to IR data of adsorbed CO and ESR data of adsorbed TEMPO, there are two types Lewis electron acceptor centers on the surface of modified ZrO_2, which are observed and on pure zirconium dioxide also. New types Lewis centers, corresponded to Y^{3+} cations on the surface, are not observed. The electron acceptor force and concentration of Lewis centers decrease with growth of concentration Y^{3+} cations on the surface.

At concentration above $4 \cdot 10^{18}$ Y^{3+}/m^2 new absorption bands of adsorbed carbon monoxide occur with frequencies equal 2096, 2110 and 2122 cm^{-1}. The intensity of these absorption bands grows with an increase of modifying oxide concentration . It indicates, that in a structure of adsorption centers, which interacts with CO, yttrium cations are included. We assume, that the given adsorption centers are basic centers, consisting from bridged oxygen atom and cus cation Y^{3+} with different structure.

According to of IR-spectra of CO, the intensity of absorption bands 2096-2122 cm^{-1} is essentially reduced after reducing pre-treatment of a surface (in atmosphere of a hydrogen 50 Torr, t=500°C). Thus occur other absorption bands, appropriate to interaction CO with partially reduced Zr^{3+} and Y^{2+} cations.

Pre-treatment in oxidizing conditions does not cause appreciable change intensity of the absorption bands 2096-2122 cm^{-1} in a spectrum of adsorbed CO.

The Lewis acidic centers concentration decreases after reducing pre-treatment, and after oxidizing pre-treatment as well.

It can be concluded, that doped component concentration and pre-treatment technique major affect ZrO_2 surface acid and basic sites formation.

This data may be used for creation catalysts on the ZrO_2 base with new properties.

PPII-32a

Selective C- and O-methylation of catechol by methanol over modified γ–aluminas

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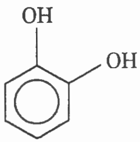
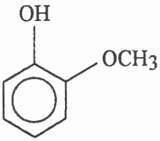
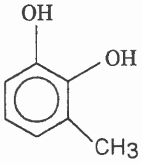
Alkylation of catechol is an important industrial reaction. Monomethylated derivatives of catechol are useful organic intermediates in the pharmaceutical and agrochemical industries:



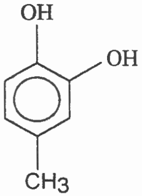
catechol
(1,2-benzenediol)



guaiacol



3-methyl catechol



4-methyl catechol

Previous studies in our laboratory [1-3] revealed that vapour phase catechol alkylation by methanol over γ-alumina takes place in the temperature range 260-350°C. This is a promising approach to produce selectively guaiacol and 3-methyl catechol. A competition was observed between O- and C-methylation depending on the reaction parameters: temperature, reactant concentrations, conversion and acid-base properties of the catalyst used.

This work intends to correlate the catalytic activity and selectivity of catechol methylation with the catalyst acid-base properties, aiming at the increase in selectivity towards O- or C-alkylated products formation. The catalyst acid/base properties were varied modifying γ-Al_2O_3 with Li^+, La^{2+}, Mg^{2+}, B^{3+}, P^{5+}. The catalysts were prepared by impregnation of commercial γ-Al_2O_3 (purity 99.9%) by nitrate salts or acids, and subsequent calcination in air. Incorporation of Li^+ and Mg^{2+} into the γ-alumina lattice results in spinel formation (as seen by X-ray data) and decreases surface acidity (TPA-TPD data).

Catalytic activity and selectivity towards monomethylated products formation were measured at low conversion (X<5%). Under these conditions the monomethylated products were formed in parallel pathways and no other products were observed. This allowed to evaluate the influence of catalyst acid/base properties and not the influence of reaction conditions on the activity and selectivity.

PPII-32a

Selectivity towards guaiacol formation (O-alkylation) increased with surface acidity and reached 89% over phosphated alumina (270°C). A 20-fold change in the O/C-methylation ratio was achieved by varying only the catalyst acid/base properties (see Fig.1).

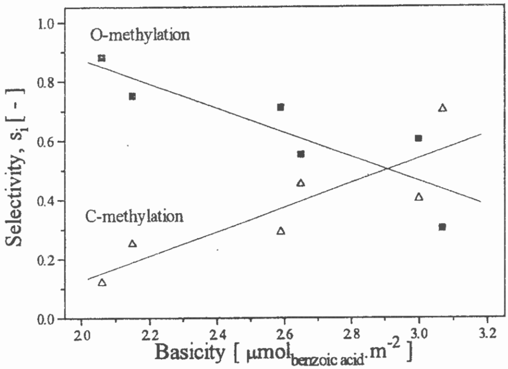


Fig.1. Selectivity towards O- and C-methylated products as a function of surface basicity

The C-methylation of catechol was observed to be preferentially in *ortho*-position irrespective of the catalyst used. Catalytic activity, characterised by the differential reaction rate was found to decrease with decrease in surface acidity at the same temperature. According to TPD of methanol data this effect may be due to the increase of energy for methanol activation.

Further improvement in the selectivity was found by variation of the reaction temperature and the level of conversion. The selectivity towards 3-methyl catechol formation over Li^+/Mg^{2+}-modified alumina (320°C) went up to 90% from 26% for pure γ-Al_2O_3 (270°C).

Surface acid/base properties and catalysts structure characterisation via BET, X-ray, XPS, TPD, FTIR measurements of probe molecules (CO_2, methanol) was carried out and will be reported in detail.

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NANOPARTICLE FORMATION IN A MICROEMULSION MATRIX FOR CATALYST APPLICATIONS

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There is ample evidence that properties of catalysts depend very much on the size and uniformity of the particles of the active component which often is a transition metal. The preparation of small catalytic particles homogeneous in size is an important task in heterogeneous catalysis. By varying the size of the metal particle, changes in the catalytic properties of the catalyst can be observed. Usually the activity increases when the particle size decreases and a different selectivity may be brought as well. Catalysts have to be designed to provide a desired activity and selectivity in a given reaction. Thus, many attempts were made to improve the modes of preparation of the catalysts.

A novel method (1), based on the properties of microemulsion solutions, for obtaining catalysts with very narrow particle size distribution, was developped at the Institute for Surface Chemistry in Stockholm in the early 80´s .

A microemulsion generally consists of a mixture of surfactant, water and solvent. The surfactant forms uniform aggregates which can dissolve either solvent or water. By varying the amount of the component dissolved in the aggregates, their size is modified. Consequently, a microemulsion offers a suitable matrix for the preparation of homogeneous dispersions of metal particles. The cores of the aggregates in which the precursor is dissolved, serve as nuclei of the particles.

The preparation of catalytically active metal particles is usually carried out by reduction with various reducing agents of a metal salt that has been dissolved in the water pool of an oil continuous microemulsion.

Metal particles obtained from microemulsions were characterized by different techniques in order to get information about :

- the average size and size distribution of the particles (T.E.M.).
- evidence that a mixture of the two metals in the bimetallic particles is homogeneous (E.X.A.F.S.) (3).
- the oxidation state of the metals in the particle (X.P.S.).
- their catalytic properties, using various hydrogenation and isomerization test reactions.

In order to use these particles in catalytic reactions (2) which take place at a temperature higher than 250°C, as in the case of hexane isomerization, for example, these particles were deposited on various carriers (Al_2O_3, TiO_2, CeO_2). The characterization of the supported catalysts was carried out by the same techniques as mentioned above.

The studies showed that the catalysts prepared from microemulsion displayed different properties than those prepared by an impregnation method. For example, the Pt/TiO_2 catalysts prepared from microemulsion did not exhibit strong metal-support interaction (SMSI) effects while the catalysts prepared by impregnation exhibited these particular properties (4).

This method could be successfully applied to preparing metal oxide particles.

In addition, using the microemulsion technique, it was possible to develop a novel method of the preparation of a mixed metal- metal oxide catalyst. This method involved two steps in the preparation: the first one was the microemulsion technique to prepare a suspension of metal particles, in the second one, the oxide material is prepared by the sol-gel process.

-The combination of the sol- gel process and the microemulsion technique could render possible the formation of Pt particle surrounded by a fine layer of titanium oxide that results in an increase of the interphase metal -support.

- A Pt-TiO_2 catalyst prepared by this novel method (5) has been tested on the laboratory scale in the reaction of selective hydrogenation of crotonaldehyde in order to elucidate the influence of the mode of preparation on the selectivity of the reaction.

The characterization of the interface platina-titania in the catalyst was done by X-ray Photoelectron Spectroscopy (XPS) and TEM-EDAX.

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PPII-34

CATALYTIC HYDROSTABILIZATION OF OIL SHALE TAR FRACTIONS

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Oil shale is one of the most convenient sources for oil substitutes production namely motor fuels and a great number of chemical products. Chemical composition of tar obtained by thermal processing of oil shale is extremely unique, because the correlation between hydrogen and carbon in the tar is approximately equal to middle correlation for oils - 8.5÷8.9 (for example, the tar of Estonia's oil shale). The chemical structure of oil shale tar on the whole is paraffin-naphthene hydrocarbons, and such tars may be used for liquid motor fuels and lubricants production. Besides the oil shale tars contain a great number of heteroorganic compounds (about 60%), including significant for agriculture compounds (for example, alkylrezorzines) and a great part of undesirable compounds. The presence of such compounds in tars requires to carry out the secondary processing of liquid fractions.

In this work we suggest a new technology of obtaining benzine and chemical products by thermocatalytical processing of vapour-gas mixture (VGM) of oil shale semicoking products.

At present generatory method is the main industrial method for oil shale processing, which allows to produce gas and oil shale tar. The tar yield in generatory process is about 18÷20 % on the feed (i.e. 120÷190 kg/t). At the same time in this process another products such as liquid boiler fuel - 90÷50 kg/t, gaseous benzine 7.9÷10 kg/t, gas - 400÷450 cub.m/kg, gas-turbineous fuel - 40÷20 kg/t may be produced.

One of the most significant components of oil shale tars is phenols. Their yield is about 30 % on the feed. The quantity of water-soluable alkylrezorzines in oil shale tars is about 6 %. At present only 50 % of water-soluable phenol from the total amount may be extracted from tar. But the cost of production of such phenols is much higher than profit from realization of other products. Therefore it is necessary to increase the quantity of phenols in producing tar and also to investigate all ways for increasing the grade of extraction from tar. All these allows to bring a good economic effect.

Traditionally, in all industrial methods for semicoking of oil shale obtained tars are processed after condensation. We suggest to process a vapour-gas mixture of semicoking products in the presence of catalyst. The suggested technology makes it possible to produce benzine - 30÷40 kg/t, i.e. near 40000 tonn/year, to increase in 2.5 times the yield of alkylrezorzines, to simplify the technology of tars processing.

Besides in our work we studied the process of hydrostabilization for light oil shale tar fraction. This process allows to decrease the quantity of heteroorganic compounds and to produce good benzine.

Similar technologies do not exist, but in some countries (Israel, Great Britain, USA) the same investigations are carried out.

Our technological scheme allows to solve the important ecological problem - removal of sulphurous compounds. In the above mentioned technology we suggest to catch and process these compounds for producing good products.

Thus, involving the block of catalytic treatment of vapour-gas mixture into ordinary scheme allows to increase the yield of benzine-kerosine fraction and to regulate the chemical products composition.

SELECTIVE CATALYSTS IN HYDROCRACKING PROCESS OF HEAVY ORGANIC RAW MATERIALS

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In accordance with modern opinions on heterogeneous catalysis most of catalysts for hydrocracking process may be refered to hard acidic catalysts. Fundamental investigations in the field of heterogeneous catalysis allow to set a new task - to change the catalyst selectivity by alternating of acidic centres strength and number.

G.K. Boreskov in his fundamental works predicted a great future for catalytic contacts on the base of o-phosphorous acid, and besides he said about possibility to form various hard high-molecular compounds in such contacts.

Nowadays we have worked out various methods of synthesis of Fe-containing inorganic polymeric catalysts with different degree of polymerization, with different strength and number of acidic centres, with different contents of Fe as an active component in catalysts composition.

A number of polymetalic catalysts was synthesied, their acidic properties and chemical composition were investigated by chemical methods and methods of emissional and atomic-absorbtional spectroscopy. Correlational dependence between composition of matrix, composition of Me-catalysts and their activity in the hydrocracking processes of heavy oil raw materials (petroleum asphalt; pyrolysis tars; sour petroleum asphalts, containing free sulfuric acid; products of oil shale thermodestruction) and also in process of hydroliquefication of coal was established.

Changing concentration (0.2-0.9 mmol/g) and strength of matrix acidic centers (0,5-6) leads to alteration of catalyst selectivity rather than activity. Due to a developed amorphous heleous structure our catalysts may be used in high pressure processes, as they don't have abrasive properties and have good exploitational quality.

It is known that incresing of yield of liquid products in oil processing may be reached by incresing a depth of oil processing. At present some technological processes that allows to produce from 1 ton of petroleum asphalt about 70 % of liquid fuel are known. But in these processes special catalysts, containing precious and rare-earthen metals (Pt, Pd, Ru, Mo, Ni) are used. Such catalysts require to carry out a frequent regeneration with loss of active components. Deep processing of petroleum asphalts with using such catalysts in industry is not used because of their high price.

Using of our bifunctional catalyst in hydrogenation process of petroleum asphalts ($\tau > 20$ h, $v = 1$ h^{-1}) allows to produce: 5% (wt.) - hydrocarbon-gas, 20% - benzine, 50% - liquid fuels, 15% - lubricants, 10% - hard carbogeneous remain on catalyst. It is established that such results are associated with high concentration of acidic centres of low and middle force. Creation of bifunctional matrix for cracking and hydrogenation allows to obtaine good technological parameters of process, to increase the selectivity of removal of polar heteroorganic compounds and decrease the gas-formating effect and quantity of coking deposits. The degree of sulphur removal in hydrocracing process of petroleum asphalts under the condition of 4 MPa and 425 ^{O}C is about 60-80% ; free sulphuric acid is not detected by chemical analyses.

A number of experiments for hydroliquefication of brown coal (Irsha-Borodinsk coalfield) was carried out. Obtained products and catalyst were investigated by means of group chemical analysis, UR- and NMR- spectroscopy. Obtained results shows that using in process 3% wt/ of catalyst with acidic centres of low and middle strength allows to increase the selectivity on lubricants above 60% and besides the conversion don't decrease more than 5%.

On the base of phisico-chemical spectral investigations we can judge about individual stages of mechanism of selective hydrocracking of complex heteroorganic raw materials on weak-acidic centres of matrix of hard-acidic polymeric Fe-containing catalysts.

PPII-36

THE INFLUENCE OF PREPARATION CONDITIONS ON THE PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF TITANIUM OXIDE SYSTEMS

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The effective catalysts of olefins isomerization, Claus process and morpholine synthesis were produced on the base of intermetallic compounds of Ti-Ni-H system.

The influence of preparation conditions upon physico chemical properties of Ni-containing titanium oxide systems was investigated. It was shown that using as initial substance $Ti_2NiH_{2,1}$ hydride permits to obtain the samples with developed surface (300 m^2/g). It was established that the increase of calcination temperature leads to the increase of the nickel titanate film on the samples surface. According to the X-ray diffraction data, the surface of samples calcinated at 773 K consists of nickel titanate solely.

The investigation of obtained samples by thermoprogrammed H_2-desorption and IR-spectroscopy methods showed that calcination temperature essentially influenced the Ni valence state at the reduction. Increasing of the calcination temperature up to 773 K led to the Ni^+ appearance during reduction at 723 K. The increase of the reduction temperature of samples up to 873 K contributed to reduction of surface Ni compounds to the Ni (0).

Obtained samples had been tested in the reaction of hexene-1 isomerization. It was shown that migration of binary bond takes place on metal nickel containing centres, whereas skeleton isomerization passes on centres, including nickel compounds in the intermediate oxidation degree.

PPII-37

CARBIDOCARBONYL FERH CLUSTERS ON OXIDE SUPPORTS: CHEMISTRY AND CATALYSIS OF ALCOHOL SYNTHESIS FROM CO AND H_2

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INTRODUCTION

Advances in the synthesis of mixed metal carbonyl clusters allowed to use them for the preparation of supported catalysts. It is often the case that these catalysts exhibit strikingly higher activity and selectivity in syn-gas reactions compared to the conventional systems. It is known that silica supported FeRh cluster derived catalysts, with Rh atoms dominating in initial clusters framework, show high activity and selectivity for oxygenates in CO hydrogenation [1]. We have prepared a set of silica supported catalysts containing FeRh carbidocarbonyl clusters with Fe atoms prevailing in cluster framework, characterized them and studied their catalytic properties in CO hydrogenation.

EXPERIMENTAL

The supported catalysts were prepared by impregnation of silica, alumina and magnesia with $Rh_4(CO)_{12}$, $[TEA][Rh_5Fe(CO)_{16}]$, $Rh_2Fe_4C(CO)_{16}$, $[TEA][Rh_3Fe_3C(CO)_{15}]$, $[TEA][RhFe_4C(CO)_{14}]$, $[TEA][RhFe_5C(CO)_{16}]$, $[TEA]_2[Fe_6C(CO)_{16}]$ (TEA = $(C_2H_5)_4N$) carbonyl clusters dissolved in dry and degassed acetone (for ionic compounds) or hexane.

The catalysts were characterized with transmission electron microscopy (TEM), ESR, XPS, Mössbauer (NGR) spectroscopy, FTIR spectroscopy, TPD of pre-adsorbed CO and H_2.

The catalytic experiments were performed in a differential fixed-bed reactor. CO con- version was maintained within 0.01-0.1%.

RESULTS AND DISCUSSION

The most part of the supported clusters does not change with time in inert medium, but partial conversion of $[RhFe_5C(CO)_{16}]^-$ on the surface of support to $[RhFe_4C(CO)_{14}]^-$ was observed following impregnation. Conversion of $[RhFe_5C(CO)_{16}]^-$ to $[RhFe_4C(CO)_{14}]^-$ is completed at 50°C, with $[RhFe_4C(CO)_{14}]^-$ cluster yielding $Rh_2Fe_4C(CO)_{16}$ and $[Rh_3Fe_3C(CO)_{15}]^-$ mixture at 100-150°C on silica and alumina and yielding $[Rh_2Fe_4C(CO)_{15}]^-$ on magnesia. At the same time Fe^{2+}, Fe^{3+} surface ions were registered by Mössbauer spectroscopy, XPS and ESR. The surface sites of FeRh/SiO_2 samples reduced by H_2 consist of Rh^0, Fe^0, Fe^{2+}, and Fe^{3+} species (NGR, XPS, ESR data) of 5-10 E in size (TEM data).

A few results for the CO hydrogenation over silica supported cluster derived FeRh catalysts have been provided in the table. All the catalysts had initially higher rates for hydrocarbons and lower rates for oxygenates, but changed gradually to oxygenates-producing catalysts. In each case, the catalytic activity slightly increased for first 2-5 h on stream, then reached steady state and remained constant for subsequent several tens hours.

Rh_4/SiO_2 catalysts prepared from $Rh_4(CO)_{12}$ produced hydrocarbons C_1-C_5 in 87% selectivity. The selectivity toward oxygenates in products was 13%; methanol mainly was obtained and some ethanol and propanol were produced. Fe_6C/SiO_2 prepared from an anion cluster $[Fe_6C(CO)_{16}][TEA]_2$ demonstrated surprisingly high selectivity toward ethanol which reached 13% with 20% toward oxygenates in general.

Table. CO Hydrogenation on SiO_2-Supported RhFe Carbonyl Cluster-Derived Catalysts[a]

Precursor/SiO_2	Total specific activity[b]	Selectivity (wt. %)[c]					
		CH_4	C_2-C_3	C_{3+}	CH_3OH	C_2H_5OH	$C_{3+}OH$
$Rh_4(CO)_{12}$	235	21	22	44	8	2	3
$[Rh_5Fe(CO)_{16}][TEA]$	57	78	9	1	8	2	1
$[Rh_3Fe_3C(CO)_{15}][TEA]$	8[d]	40	8	1	28	16	6
$Rh_2Fe_4C(CO)_{16}$	11[d]	55	7	1	15	5	17
$[RhFe_4C(CO)_{14}][TEA]$	267[d]	24	2	<1	33	38	2
$[RhFe_5C(CO)_{16}][TEA]$	37	76	7	3	12	1	<1
$[Fe_6C(CO)_{16}][TEA]_2$	17	21	33	26	5	13	2

[a] Reaction conditions: catalyst 0.3 g, total metal loading 2 wt.%, reaction temperature 300°C ± 2°C, $CO/H_2 = 1$, total pressure 5.0 x 10^6 Pa, space velocity 1000 h^{-1}, prior to catalytic run all the catalysts were reduced by H_2 at 325°C for 1 h. [b] $mmol_{CO} \cdot (mol_{Rh+Fe})^{-1} \cdot h^{-1}$ in 2 h on stream. [c] Selectivities were calculated as follows: $100 \times C_i/\Sigma C_i$, i - carbon number of the product molecule, C_i - weight concentration of the product molecule. [d] In 5 h on stream.

Among hydrocarbon products C_3-C_4 olefins prevailed. On all FeRh bimetallic catalysts with the exception of Fe_5RhC/SiO_2 prepared from $[Fe_5RhC(CO)_{16}][TEA]$ selectivities for oxygenates were substantially increased. Notably, the selectivity toward ethanol was strikingly increased on Fe_4RhC/SiO_2 and reached 38%. Over-all selectivity toward oxygenates on this catalyst was more than 70%. Increased selectivity toward methanol was observed for Fe_3Rh_3C/SiO_2 and Fe_2Rh_4C/SiO_2 catalysts. The feature of the last catalyst is the marked formation of propanol. The FeRh catalysts promote methane formation as well, but relative enhancement of rates for oxygenates was much higher than for methane. Accordingly, the selectivities toward hydrocarbons C_{2+} decreased from 66% for Rh_4/SiO_2 and 59% for Fe_6C/SiO_2 to less than 3% for Fe_4RhC/SiO_2. The last catalyst had the highest catalytic activity, which exceeded that of Rh_4/SiO_2. The activities of other FeRh catalysts were close to or even less than that of Fe_6C/SiO_2 sample.

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ECOLOGICALY SAFE TECHNOLOGY OF PRODUCING CARRIERS AND CATALYSTS BY THE PRECIPITATION METHOD

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Transition metal oxides are most commonly used as carriers and catalysts in petrochemical and petroleum-refining processes. They are produced according to the followng scheme:

1. $Me_1A + Me_2(OH)_n \rightarrow Me_2(OH)_n\downarrow + Me_1A$
2. $Me_2MeO_n + HA \rightarrow Me_2(OH)_n\downarrow + Me_1A$

where A is an anion,
Me_2 is an alkali metal or ammonia,
Me_1 is a transition metal.

Complex catalytic systems synthesized by the precipitation method may be produced practically in the similar wea. In this case: $Me_1A = \Sigma M_i$.

As a rule, the morphology and physicochemical properties of carriers and catalysts are formed at the precipitation stage. When hydroxide is precipitated, one of the precipitaiting reagent ions is generally in functional use. A counterion becomes most often an "impurity" ion, and its content in a catalyst considerably lowers catalytic activity. Minimization of foreign ion proportion is determined by the volume of chemically purified water used at the stage of rinsing the obtained sediment. Since wash waters are 3-5 % solutions they are not to be recuperated, they present the main factor of this technology ecological hazard.

Mixing the solutions with different pH (a precipitant and a precipitating agent) results in local jumps of temperature and pH in the mixing zone. The latter process influences the qualitative characteristics of the sediment and the technology reproducibility.

A reprecipitation technology with the elements of applied chemistry has been suggested by the authors. The essence of the technology is that the precipitating ion (H_3^+O, OH^-) is generated at the reactor - electrolyzer electrode when the electrolysis of the metal salt water solution is conducted. In the process the following basic reactions will take place at the electrodes:

$H_2O + e \rightarrow \frac{1}{2} H_2 + OH^-$ at the cathode,

$H_2O - e \rightarrow 2H^+ + \frac{1}{2} O_2$ at the anode.

In the case when the cathode and anode space of the electrolyzer is divided by a partition (diaphragm, membrane), the generated ions react with a metal salt solution, e.g. $H_3^+O + AlO_2^- \rightarrow Al(OH)_3\downarrow$ an anode chamber,

$3\,OH^- + Al^{3+} \rightarrow Al(OH)_3\downarrow$ an cathode chamber.

Under the influence of an electric field, counterions in this situation diffuse into the opposite chamber forming an alkali or an acid respectively which are used to prepare starting solutions.

$Na^+ + OH^- \rightarrow NaOH$ a cathode chamber,

$SO_4^{2-} + H_3O^+ \rightarrow H_2SO_4$ an anode chamber.

The suggested approach has been realized in order to produce an active aluminium oxide according to the aluminate and the sulphate precipitation technologies. An active aluminium oxide has the following characteristics. A pilot plant (the aluminate version):

the basic substance content - 99.8 %
the content of impurities :
Na_2O - no more than 0.06-0.015 %,
Fe_2O - no more than 0.02 %
S_{sp} - 150-300 m^2/g
phase composition of hydroxide (pseudoboehmite) more than 97%
the total volume of pores - 0.4-0.7 cm^3/g
maximum particle size - 14-34 Å.

The analysis of the economic efficiency of the technology demonstrates the active aluminium oxide cost reduction by 20-25 %.

The approach mentioned has been implemented for the synthesis of an extremely pure zink oxide, silica gel.

The key advantages are (an active aluminium oxide, aluminate version) :

1. The reduction of reagent consumption (alkali recycle), the abandonment of the precipitating acid application.
2. The elimination of long-run and energy - consuming washing operations.
3. The lack of waste waters.
4. The possibility of synthesizing aluminium oxide with preset properties.

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SUPPORTED NICKEL CATALYSTS IN THE REACTION OF HYDRAZINE DECOMPOSITION

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The reaction of catalytic hydrazine decomposition is practically important because hydrazine and its derivatives are used as rocket fuel due to high heat of oxidation and the formation of gaseous products during their decomposition.

The method of preparation of new metallic catalyst for reaction mentioned before was worked out in this paper. Catalyst was prepared by the reduction of silica-supported nickel chloride with help of hydrazine in alcoholic alkaline solution. Methanol, ethanol, i-propanol, butanol were used as solvents. It was found that the reduction of catalyst under 40-80° C is preceded by the period of induction, the duration of which is defined by the concentration of the alkali and hydrazine in solution and also by temperature but only less depends from the origin of an alcohol. The small admixtures of copper chloride to supported nickel chloride promotes the reaction of reduction.

The catalytic properties of our samples in the reaction of hydrazine decomposition in liquid phase under the temperature of 60-80°C and pressure of 0,1 MPa were investigated. It was concluded that the decomposition rate is defined by the hydrazine content and the temperature of this process. The gaseous products of decomposition were also determined, moreover it was found that the nature of alcohol used as a solvent have a strong influence on $N_2 : H_2 : NH_3$ ratio in gaseous products. In comparison with Reney's nickel and impregnation analogues our catalysts have higher specific activity, high stability to the influence of water and oxygen.

On the base of results obtained possible mechanism of the reaction of hydrazine decomposition in presence of high dispersed nickel contacts is being discussed.

The catalysts made by us can be active in liquid phase hydrogenation of alkenes and alkines after the removing of hydrazine excess.

SELECTIVE HYDROPEROXIDE OXIDATION OF LOW REACTIVITY OLEFINS IN PRESENCE OF MODIFIED MOLYBDENUM CATALYSTS

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Cumene hydroperoxide (CHP) epoxidation of low reactivity olefins (e.g. propylene) catalyzed by usual molybdenum complexes ($MoO_2(diol)_2$, $Mo(CO)_6$ e.a.) is characterized by low selectivity on hydroperoxide. Molybdenum catalysts modification by Ph_3X ligands (where X - P, As, Sb) or diphosphine oxides significantly increase the yield of epoxide (Table).

There is no influence of the initial structure of molybdenum complexes on the ligand modifying effect and, consequently, the catalytic center nature is equal in both cases (runs 1-4). It was established that Rh_3XO is an active ligand form (runs 4,5). It was observed that the relation between initial rates of epoxide formation (W_e) and CHP consumption (W_s) depends on the ligand nature. In the presence of Ph_3XO the CHP catalytic decomposition is inhibited and the propylene epoxidation is activated. Consequently, selectivity increases. This feature can be explained by the fact that different catalytic complexes are active species in epoxidation and decomposition reaction. Epoxidation active intermediate has Rh_3XO ligand in molybdenum coordination sphere.

The effect of Rh_3XO correlates with ligand (runs 4,6,7) basicity which increases in order $Ph_3SbO > Ph_3AsO > Ph_3PO$.

The correlation of the basicity and ligand effect of diphosphine oxides (runs 8-10) was shown by $NMP^{31}P$.

The decrease of effective epoxidation constants (k_e) in runs 9,11,12 is determined by chelate cycle stability.

The lowest value k_e is observed in run 13. This indicates conformation hidrance influence on active species formation. The effect of Rh_3X (Rh_3XO) and diphosphine complexonates on $Cp(CO)_2MoPh_3XHlg$ activity (Hlg - Cl, I, Br; runs 15-17) do not confirm the traditional epoxidation mechanism.

We suggest that cytochrom P-450 model may be more preferable for description of our experimental data.

Table

CHP epoxidation of propylene catalyzed by modified molybdenum systems

T=120°C, solvent - cumene, $[CHP]_o$ = 0.9 mol/l, $[C_3H_6]_o$= 4.5 mol/l, $[Mo]_o$ = 5.4×10^{-4} mol/l, D:Mo=1:1 (mol), reaction time 60 min

N	Catalyst	Ligand (D)	Conversion CHP,%	Selectivity %	$W\times10^4$ mol/l×s ($k\times10^2$, min^{-1})	$W_э\times10^4$ mol/l×s ($k_э\times10^2$, min^{-1})	δ^{31P}
1	$MoO_2(diol)_2$	-------	83	32	-----	-----	-----
2	$MoO_2(diol)_2$	Rh_3P	90	71	-----	-----	-----
3	$Mo(CO)_6$	-------	82	38	6,7	2,7	-----
4	$Mo(CO)_6$	Rh_3P	91	71	13,3	13,0	-----
5	$Mo(CO)_6$	Rh_3PO	99	70	12,3	12,0	-----
6	$Mo(CO)_6$	Rh_3As	93	87	16,8	16,7	-----
7	$Mo(CO)_6$	Rh_30Sb	92	91	173	17,2	-----
8	$Mo(CO)_6$	$(Ph_2PO)_2CH_2$	84	83	(4,9)	(3,8)	24,6
9	$Mo(CO)_6$	$(Ph_2PO)_2C_2H_4$	97	83	(9,7)	(8,3)	32,5
10	$Mo(CO)_6$	ΛΛP(O)Ph_2 |( )| VVP(O)Ph_2	96	82	(9,2)	(9,2)	31,2
11	$Mo(CO)_6$	$(Ph_2PO)_2C_3H_6($ $Ph_2PO)_2C_3H_6$	91	76	(6,4)	(5,8)	32,5
12	$Mo(CO)_6$		87	75	(5,9)	(5,2)	32,5
13	$Mo(CO)_6$	ΛΛP(O)Ph_2 |( )| V | \P(O)Ph_2	85	75	(3,0)	(2,5)	30,4
14	$Mo(CO)_6$	транс- $(Ph_2PO)_2CH=CH_2$ ---------- ---------- ----------	86	67	(4,4)	(3,3)	21,7
15	$Cp(CO)_2MoPh_3PCl$		85	71	7,8	7,0	-----
16	$Cp(CO)_2MoPh_3AsCl$		96	75	15,4	13,1	-----
17-	$Cp(CO)_2MoPh_3SbCl$		99	72	31,6	25,0	-----

NEW CONCEPTION FOR EXTRUSION FORMING OF CATALYST MASSES.

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One-screw extruders are used for moulding of pellets with certain form and dimension in the catalyst industry. In the screw-press the catalyst dough-like mass flows through dies driven by screw pivoting inside cylindrical corps. Flowing through dies mass acquire the necessary mould and the suitable dimension (the method of flow-passage moulding).

One-screw extruders were used in the sulfoacidic vanadium catalyst production (ИК-1-6, СВС, СВД).

The process of moulding the dough-like catalyst masses can be represented by stages which are realised in the following zones of screw-press : charging, concentration, dosage (moulding), die casting. All of this stages are closely interrelated with each other but the whole process is determined by the last two stages.

The processing of dough-like catalyst masses in the screw-press is characterized by sharp increase of pressure in the die zone within certain narrow limits of mass velocity of moulding (output rate) changes. It is also characterized by practically permanent pressure when the velocity is increased further. If the critical level of velocity is exeeded, frustration of mass from reef can occur, followed by sharp decrease of the velocity to zero, i.e. complete processing loss.

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The frustration of mass from reef occurs due to the character of development of the shearing deformation process in the dough-like catalyst masses. It can result in cohesion discontinuity.

The stability condition of the moulding process is the following :

$$\gamma' < \gamma_{cr}$$

The actual shearing strenght index is calculated on the basis of the shearing deformation in the most critical axial-flow section of the pressing zone :

$$\gamma = {}_0\int^{t_k} \gamma_{max}\, dt\ .$$

Hence, for the calculation of the actual shearing strength index it is necessary to determine precisely the field of the shearing velocity, field of stress, field of the linear velocity in the screw channel in the gap between the flange and reef and in the root of the channelling plug. In the proposed model the flowing of the mass in the indicated fields is described by separate systems of the equations. The solutions of separate systems are consistent for the fields limits.

Such approach in mathematical simulation make it possible to get the most accurate description which takes into account the construction features of the screw-press and it's construction opportunities. For the description of the velocity and stresses fields in the gap and the root of the reef a rectangular system of co-ordinates is used, for the screw channel- a cylindrical system of co-ordinates.

According to the above-mentioned mathematical model for the flowing dough-like catalyst masses developed by us is based on the shearing strength criteria accurate description of physical-mechanical characteristics of the dough-like catalyst masses and screw-press construction.

NEW METHODS OF SYNTHESIS OF HETEROPOLYACIDS AND HETEROPOLYACID BASED CATALYSTS

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There are known about 100 different heteropolyacids (HPA), which are used in acid and oxidizing catalysis [1]. The methods of their manufacturing, developed more than 35 years ago, do not correspond to the modern requirements. In Institute of Catalysis a number of new methods of preparing the HPA and HPA based catalysts have been developed, including the methods of an electrodialysis and mechanochemical activation (MCA).

The method of electrodialysis consists in electrochemical desalting of a solution of the initial components of HPA, in a two-cell electrodialyzer of a flowing type supplied with the cation-exchange membrane. The synthesis occurs in the anodic chamber, for example:

$$Na_2WO_4 + H_3PO_4 \xrightarrow{-Na^+} H_3PW_{12}O_{40}$$

Changing conditions of electrodialysis, one can obtain from the same components different HPA such as: $H_3PW_{12}O_{40}$, $H_6P_2W_{18}O_{62}$, $H_6P_2W_{21}O_{71}$. Technique of synthesis a HPA has been developed also for HPA: $H_4PW_{11}MO_{40}$ (M=V,Nb), $H_5PW_{10}V_2O_{40}$, $H_5PW_{11}MO_{40}$ (M=Ce,Ti,Zr), $H_6PW_{11}BiO_{40}$, $H_{10}(PW_{11}O_{39})_2Ce$, $H_6P_2Mo_{18}O_{62}$ and others. The mixtures of the HPA are more easily obtainable and they can be used directly as catalysts. The HPA yield is 100% with respect to W or Mo and 15-30% to current. The method has passed the pilot-scale test on the example of synthesis of HPA $H_3PW_{12}O_{40}$.

MCA is a method of the direct synthesis of HPA from the ingredients subjected to MCA. The MCA is known to increase the chemical activity of oxides [2]. MoO_3 subjected to MCA is quickly dissolved in solution of H_3PO_4 with forming HPA. Changing the conditions of dissolving it is possible to obtain HPA $H_3PMo_{12}O_{40}$, $H_6P_2Mo_{18}O_{62}$ or mixtures of different P-Mo HPA which can be used as acid catalysts without separation into the components. The HPA of composition $H_{3+n}PMo_{12-n}V_nO_{40}$ (n=1-6) are also easily prepared, and some of them can be prepared directly in solid phase without dissolving. Similarly, the HPA can be prepared as salts. At synthesis of P-Mo and P-Mo-V HPA the yield on Mo and V is 100%. At synthesis of $H_4SiMo_{12}O_{40}$ the yield on Mo achieved 80%. At synthesis of tungsten HPA the yield on W is 10-12%. Other important application of the method is in regeneration of the spent catalysts after their calcination, for example, from phases of composition $P_2O_5 \cdot nMoO_3$.

The developed methods of synthesis of HPA are characterized by high efficiency, absence of the wastes and the lowered energy consumption.

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PHASE ANALYSIS OF HETEROGENEOUS CATALYSTS BY THE DIFFERENTIAL DISSOLUTION TECHNIQUE: MODERN STATE AND PERSPECTIVES

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The first information on a reference-free method of phase analysis, differential dissolution method (DD) has been published in 1986 year [1]. And in the last 10 years intensive studies followed four main directions: theory, methodology, apparatus, matters for analysis [2].

The DD-method is based on the regularities of a dynamic regime when the concentration and/or temperature of a solvent increase during dissolving a solid. In the differential dissolution procedure initial data for stoichiographic calculations are a set of kinetic curves of the elements dissolution. They transform in a set of stoichiograms. The stoichiographic calculations allow to determine:i) the simplest empirical or fragmental formulas of phases, ii) quantities of individual phases of the multiphase sample. The equation in terms of a model of a contracting sphere is given for a two-phase mixture. It describes a degree of co-dissolution of the phases. Calculations and experiment show that an effective separation of the phases can be achieved changing dynamic regime dissolution conditions.

The following series is a typical set of solvents including water:

$$NaOH \leftarrow NH_4OH \leftarrow H_2O \rightarrow HCl \text{ (or } HNO_3, \text{ or } H_2SO_4) \rightarrow$$

$$\rightarrow HCl{+}HNO_3 \rightarrow HCl{+}HF \rightarrow HF \rightarrow H_2SO_4{+}HF \rightarrow H_2SO_4{+}H_3PO_4{+}HClO_4$$

The solvent temperature can alter in the range from 0 to 300 °C. Below the main concepts working out the DD-technique are presented: (1) dissolution must be performed without an occurrence of precipitates and gaseous products; (2) metrological characteristics of adequate method determining the elemental composition of the solution formed should not be impaired during change of dissolving conditions; (3) variation of temperature and concentration of a solvent may be carried out by a given program (for example, linearly) or by stoichiographical titration. The stoichiographic titration is a new analytical procedure. This specific high-effective procedure allows to optimize differential dissolving of the phases for which no composition, no amount, no dissolving rate are known *a priori*.

An apparatus, stoichiograph, was designed for the phase analysis of differential dissolution. There is no possibility to transform the classic "wet" method to an instrumental method of the phase analysis. "Wet" procedures are performed manually, they take much attention of a technician and are too unwieldy. The design of an adequate analytical complex for differential dissolution is necessary and possible. Such complex named stoichiograph has been created in Boreskov Institute of Catalysis. The procedure of phase analysis performed by this stoichiograph is very close to that made by the chromato-mass-spectrometer.

Block-scheme of the stoichiograph is discussed. It consists of containing solvent components; peristaltic pumps; electronic device regulating the solvent composition and temperature by means of the given program; mixer of the solvent components; flow reactor thermostatted; sampling and sample pretreatment blocks; detector-analyzer for elemental analysis; block of memory and data-processing. The blocks join together through capillaries. The work of the whole complex as well as recording and processing experimental data and stoichiographical calculations are performed by computer. If an AES ICP is used as a detector-analyzer, up to 38 elements can be simultaneously determined in the solution formed. The sensitivity is maintained at the level of $\sim 10^{-3}$ μg/ml, the error is 1 - 5%, and the periodicity of measurements is ≥ 1 s. The initial information is recorded as kinetic curves of elements dissolution in a differential form. The final information is given as kinetic curves of dissolution of individual phases or in the tabulated form.

DD-method has been used to analyze heterogeneous catalysts, high-temperature superconductors, segnetoelectric and magnetic materials, inorganic pigments, native minerals, atmospheric aerosols and others. Analyzing the kinetic dependencies an information can be obtained on chemical and structural inhomogeneity of mono- and multiphase samples and spatial distribution of the phases in the sample. Above 60 elements composed the materials covered by this analysis. The main results are presented in the 50 publications of different chemical journals. Therefore, there is a good chance to characterize the DD-method as a new reference-free, high-performance, chemical tool of the phase analysis of solids.

The prime importance problem in study of properties of heterogeneous catalysts is determining their phase composition. Usually the phase analysis is performed by the physical methods, mainly by the x-ray diffraction. Contribution of chemical methods of selective dissolution to this problem is infinitesimally small. A new reference-free chemical DD-method was used to study the phase composition of several hundreds different catalysts of initial, intermediate and final stages of the preparation. The samples had crystalline or amorphous structure, and phase compositions of different complexity. Both massive catalysts and supported ones with high and low content of active components were in this group of catalysts. The variety of the techniques are presented and results of the phase analysis by DD-method of multicomponent catalysts consisting from metals, oxides, sulphides of different elements of periodic system are shown. Solutions of HCl, HNO_3, H_2SO_4, HF and their mixtures were choosen as solvents for the differential dissolution techniques.

Using multicomponent oxide catalyst Bi-Fe-Co-Ni-K-P-Si-Mo of propylene selective oxidation detail study has been made to optimize the dynamic regime conditions, to analyze the solution formed during dissolving, to prepare the sample analyzed. The order in which stoichiographic calculations of qualitative and quantitative phase composition of this catalyst must be performed is shown. The phase composition of the catalyst was at a time investigated by the x-ray diffraction to compare the information with the DD-method results. New data was obtained on the elemental composition, stoichiometry and quantities of the complex molibdate phases of this catalyst using DD-method. Amorphous and varying composition phases were also detected in catalysts. Composition and amounts of products resulting from an interaction between the catalyst carriers (SiO_2, Al_2O_3) and the active components of these catalysts were determined. Factors limiting and leading to problems of the phase analysis of heterogeneous catalysts by DD-method are discussed.

Interpretation of the differential dissolution results is valued in the case of complete separation of the phases. The main factors which lead to an incomplete separation of phases from a multiphase sample were determined. They were: close values of their chemical potentials, non-simultaneous contact of the phases with the solvent, a broad spectrum of the particles which differ in real structure.

The long-term purposes developing the DD-method are achieving a level similar to that in modern chromatography, chromato-mass-spectrometry and voltammetry. It is clear that it may be realized only at the scaled extending of this method. To do this we focus our efforts on developing all directions mentioned above.

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THE NEW IRIDIUM CONTAINING CATALYTIC SYSTEMS ON METALLIC CARRIERS

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It is known that iridium shows low activity in the majority of catalytic reactions. However, its use in combination with other platinum metals allows to obtain more efficient catalysts for some processes, for instance, reforming. Besides, partial replacement of high-priced platinum and palladium by cheaper iridium contributes to reducing catalyst cost. The aforesaid affords ground to suppose, that using iridium in new catalytic systems on metallic carriers we have developed will allow to get perspective catalysts for a number of industrial processes.

Mono- or polymetallic Ir-containing catalyst samples (Ir, Ir-Pt, Ir-Pd, Ir-Pt-Rh, Ir-Pd-Rh) on metallic carriers (nickel and chrome steel, stainless steel, aluminum) are obtained by joint reduction of platinum metals ammines by intersphere ammonia in autoclave conditions. Total content of platinum metals in samples is 0.05-0.2 wt.%.

For samples on nickel and chrome steel and stainless steels data are received by their initial activity in model reactions of full oxidation n-hexane in mixtures with the air. It is found that. temperature of beginning of reactions over Ir-containing catalysts is 250 °C, that is 100 °C higher, than for similar platinum or palladium samples. In the interval of temperatures 250-350 °C the conversion of n-hexane is near 40-90%. At 400 °C and above, degree of oxidation of n-hexane, for the majority of explored samples, reaches 99.9%. Following dependencies have been determined: using a carrier nickel and chrome steels as a carrier is more preferable than stainless steels; Ir-Pt, Ir-Pd bimetallic catalysts are more active samples, than those containing only iridium, moreover composition Ir-Pd is more efficient than iridiuin combination with platinum; the addition of a third componenRh practically does not change activities of catalyst.

Samples, containing Ir, Ir-Pt, Ir-Pt-Rh on the aluminum carrier are explored in reactions of hydrogehation of model hydrocarbon (toluene). Reaction was realized in the pressure of hydrogen 0.25 MPa, for the flow speed of hydrogen 10 000 h^{-1}, concentrations of toluene 4-5 g/m^3, temperature 30-150 °C. Conversion of toluene in methylcyclohexane (selectivity of reaction is 100 %) over the catalyst Ir/Al is 86 % at 150 °C. Similar platinum sample at the same temperature shows smaller activity (degree of conversion of toluene is 71.3 %). Ir-Pt/Al or Ir-Pt-Rh/Al samples at the given temperature transform toluene in methylcyclohexane completely. Polymetallic samples show high hydrogenation activity even at 30-50 °C. The yield of methylcyclohexane at 50 °C over Ir-Pt/Al catalyst is 98 %, Ir-Pt-Rh/Al it is 70 %.

The results obtained can be used for making efficient and cheap catalysts of leave gases peeling from organics and hydrogenation of hydrocarbons.

THE PROMOTION EFFECT OF INACTIVE COMPONENT IN BIMETALLIC Rh-CATALYSTS

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The addition of inactive second metal to transition metal catalyst can alter activity, selectivity, resistance towards poisoning due to formation of bimetallic clusters (Sinfelt model) with electronic interaction between two metals. Rh-catalysts doped by metals nonmixed with Rh such as Cu and Ag and also rare earth metals (REM) are the interesting systems because Rh is a good catalytic converter in CO oxidation and hydrogenation.

The goal of our study was the investigation of the adsorption and catalytic properties of supported and film-like Rh-catalysts modified by Cu, Ag, lanthanides (Gd, Ce, La) and Y.

The experimental part included the study of adsorption of carbon monoxide and hydrogen (isotherms, kinetic data of adsorption and desorption and IR spectrum have been obtained) in vacuum conditions and catalytic experiments in flow condition with chromatographic analysis. Some quantum clusters calculations (EHT-Hoffmann method) were carried out.

A different effect of Cu and Ag in CO methanation on film catalysts was found. The apparent activation energy of methane formation is decreased in case of Rh-Cu system and increased in Rh-Ag, as well as Rh-Gd catalyst (see table 1).

Table 1.

Processe	E_a , kJ/mol						
	initial state				after oxidative treatment		
	Rh	RhAg	RhCu	RhGd	Rh	RhAg	RhGd
$CO+H_2$	46	21	60	78 (44)	37	5	80 (38)
CH_x+H_2	50	58	100	50 (78)	116	-	78 (80)
desorption	initial state				after reaction $CO+H_2$		
CO	33/250	-	228(207)	-/100	Abs.	-	17/190
H_2	70	-	36/250	9/60	Abs.	-	6/128

( ) - values for Rh in case RhGd or RhCu catalysts ; / - two forms

In case of Gd modifier the great increase of CH_4, C_2H_4 and C_2H_6 formation was obtained that became more intense after oxidative treatment ΠworkedP catalysts. On the contrary, Cu and Ag decreased the activity without formation C_2-products. The promotional effect of Gd is connected with activation of surface carbon (Chx particles titration by H_2) -

its bond energy decreases in Gd presence. Cu and Ag with oxophylic properties also didn't show such effect.

Energy bond of reactants (activation energy of desorption) also is changed: Gd addition (10% from Rh surface) decreases $E_{a,des}$ H_2 and CO and reactivates the adsorptive ability. New information has been obtained by work function measurements: on Rh $CO^{+\sigma}$, $H^{+\sigma}$ (forms of adsorption dominate in catalytic conditions, but on RhGd - $CO^{-\sigma}$ and $H^{-\sigma}$ forms.

FTIR spectrum of CO demonstrates the increase in the ratio of bridge forms of CO to linear forms and appearance of carbonate-carboxylate forms.

In CO+O_2 reaction the promotional effect of REM (Ce, La, Gd) results in shift of the temperature area to low temperature region for both Rh/SiO_2 and Rh films (Gd on Rh films inhibits the catalyst deactivation).

The same promotional effect has been found for yttrium, but its degree depended on ratio CO/O_2. Experimental bond energy CO_{ads} increases on 24 kJ/mol (50 for Rh and 74 for RhY), that is in good agreement with quantum calculations made for Rh_{13}/100/, Rh_{13}/111/ clusters (Rh-CO, Rh-O, Rh-CO-O), where adsorbates and Y atom were placed in different positions with varying the adsorbate-metal distance. In all cases Y is in form Y^{+3}. In Y presence the bond energy CO-Rh in Rh/100/-O-CO system increases, but bond energy O-Rh decreases greatly. For Rh/111/ bond energy of CO and O decreases.

The data obtained for RhCu supported and film catalysts of CO oxidation reaction agree with D.W.Goodman et al. results [J.Cat.1994, v.145] obtained for Cu/Rh(100): activation energy of reaction did't change up to 1 ML of Cu. In flow condition Cu doesn't influence the area of reaction, but alter essentially CO_2 formation on Rh/SiO_2 catalyst at low temperatures (see data for T=373 K in table 2).

Table 2.

Catalysts	Rh	RhCu(30% at.)	RhCu(50%)	RhCu(75%)	Cu
Relative activity	1	7,1	7,8	11.2	0.3

Adsorption data show that Cu induces the growth of CO_{ads} quantity with temperature increase and stimulates CO_{ads} to dissociate resulting in CO_2 formation.

The explanation of modification effect for inactive metal added to active base metal has been proposed: thermodynamic analysis of surface two-dimensional electron gas state shows the rise/lowering of the metal electron density near neutral or charged adatom (modofier), that leads to the change of adsorptive potential and its turn the change of the catalytic properties.

CATALYTIC POLYMERIZATION ON SOLID SURFACES: A METHOD FOR INTRODUCTION OF FILLERS INTO POLYMERS

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In recent years, new direction in polymer chemistry employing the immobilization of metallocomplex catalysts on a solid support appeared, namely the polymerization filling of polyolefins. In this case the support not only plays the role of site where the catalyst is fixed but is also simultaneously incorporated as a filler in the polymer formed on its surface and , finally, in the polymer composite produced. To date, a number of new materials having specific properties was developed on the base of polymerization-filled polyolefins.

The fillers used for polyolefins (various oxides, salts, metals, carbon black and polymeric materials) are substantially different in nature, chemistry of surface and structure. All of these factors are important in the selection of a method of formation and type of supported metallocomplexes to be employed for formation on the surface of a filler-support of centres active in olefin polymerization. Attempts have been made to use in the synthesis of filled polyolefin composites virtually all supported catalysts known.

In this paper, we consider the efficiency of various methods of immobilization of catalysts based on transition metals on the surface of various filler-supports. We also consider the relation between the nature of filler-support, the type and composition of immobilized active species, the peculiarities of their catalytic properties (kinetics of olefin polymerization on activated surfaces), the structure and characteristics of polymer formed.

One of the essential factors that governs the catalytic properties of such systems is the nature of the interaction of the transition metal compound with the surface of support. The catalysts containing isolated complexes in which transition metal is covalently bonded to a support display lower activity in polymerization of olefins than supported catalysts involving nM tCl_3 associates [1, 2] or donor-acceptor complexes of transition metal with surface alkylaluminoxane obtained by reaction of alkylaluminum and surface water of support [3]. The influence of surface structure of catalyst is most pronounced in propylene polymerization (both activity and stereospecifity) [4] and relative reactivity of ethylene and propylene in copolymerization [5].

The characteristics of the active centres formed when the catalyst is immobilized on the surface might be affected not only by the neighboring molecules of the transition metal compound but also by the surface atoms of the support (filler). It was shown that the general problem of heterogeneous catalysis - the effect of the nature of support on the catalytic activity of immobilized catalysts is especially important for the task of polymerization filling of polyolefins.

The nature and composition of supported catalysts influences the structure of a macromolecule, one may control the structure and properties of the polymer matrix of the composite produced directly in the course of synthesis. A striking example of such control is the synthesis of filled isotactic and frost-resistant polypropylene with supported titanium [4] and vanadium [6] catalysts respectively .

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PPII-47

ACTIVE CARBONS AS CATALYST CARRIERS IN LARGE-SCALE PRODUCTION OF POLYMERIC MATERIALS

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Active carbons (ACs) find wide and successful use as catalystcarriers for the organic synthesis such as the gas-phase synthesis of vinyl chloride and vapor-phase synthesis of vinyl acetate. The most high performances (catalytic activity and working time of synthesis plants) are shown by AC impregnated with zinc acetate or with combination of zinc, cadmium or vismuth acetate in the synthesis of vinyl acetate and by active carbon with mercuric chloride (sublimate) applied on it in the synthesis of vinyl chloride.

The synthesis of vinyl chloride is carried out in static catalyst bed tubular reactors at a temperature of 120-220^0 C. Sublemate catalyst (the mean content of sublemate is 10% by weight) is distinguished by high activity and selectivity: the conversion of acetylene is > 99% and the selectivity for vinyl chloride is > 98-99%. The production rate of the reactor is 2-10 ths. tons in year. As catalyst carriers granular ACs (АГН-1) are used.

According to the character of carrying out the synthesis of vinyl acetate from acetylene and acetic acid either coarse granular ACs in static catalyst bed plants or crushed ones in fluidized bed plants are used.

In this case AC as a carrier, the character of its porous structure, physical-chemical properties and uniformity of its surface play an important part in the two catalytic systems.

The properties of the catalyst can be improved by acting on the chemical surface of carbons-carriers. In preparing АГН-2 carbon-carrier ethylenediamine is added to the charge. In order to increase stability of the sublimate catalyst, at the stage of preparing a carbon-resin composition and in place of ethylenediamine we used chemical modifier-carbamide, which interacting with carbon on heating decomposes into carbon dioxide and ammonia to increase chemical uniformity of the surface of the carbon-carrier. In contrast to ethylenediamine used for production of АГН-2 carbamide also is non-toxic, less costly and produced in large sales.

Porous structure and sorption properties of the carbon-carrier are determined largely by the choice of starting carboncontaining material and its preparation. The advantages of the carboncarrier based on raw charcoal are evident, however its drawback is the non-optimized porous structure due to the texture of starting wood. The macropore volume is excessive and amounts to 70-80% of the total pore volume that decrease bulk density and strength of AC, very important characteristics. At the same time the ~~coal-~~base ACs exhibits good strength and small macropore volume, but activity of the catalysts on their base is lower. Advantage of the useful properties of different types of carboncontaining starting material has been taken in the development of АГН-3 AC-carrier. In preparing carbon-resin compositions the mixture of ground coal and raw charcoal in an amount of 5-30% by weight was used. To improve the surface uniformity chemical modifier, carbamide, was added in amount from 3% to 10% by weight. Characteristics of the carboncarriers are shown in the table below.

Porous structure of active carbons as catalysts carriers

Characteristics	Grade of AC		
	АГН-1	АГН-2	АГН-3
Bulk density, g/l	559	504	498
Mechanical strength, %	78.0	75.0	71.0
Total porosity, cm^3 /g	0.60	0.65	0.80
Pore volumes, cm^3/g			
V - micro	0.30	0.33	0.40
V - meso	0.03	0.05	0.07
V - macro	0.27	0. 27	0. 33
Characteristic adsorption energy in micropores, Eo, kj/mole	17. 5	17. 1	14. 4

The prepared АГН-3 active carbon-carrier combines good strength and small macropore volume inherent in the coal-base Acs and good catalitic activity characteristic of the wood-base Acs. Chemical modification improves the surface uniformity of the active carbon-catalyst carriers for the synthesis of vinyl chloride and vinyl acetate.

MODEL CATALYSTS INVESTIGATION. TESTING OF ACTIVITY

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The program of model catalysts investigation in BIC includes preparation of supported platinum catalysts InCatPt-1, InCatPt-2, InCatPt-3 [1], their characterization by different physical methods, and activity testing in the reactions of benzene hydrogenation, cyclohexane dehydrogenation, pentane isomerization and heptane reforming. The catalysts differ by support, Pt loading and "metallic" (Pt^o) and "ionic" (Pt^σ) platinum contents:

Catalyst	Support	% Pt	% Pt_{SURF}	% Pt^σ
InCatPt-1	SiO_2	3.1	50	0
InCatPt-2	γ-Al_2O_3	2.6	84	60
InCatPt-3	γ-Al_2O_3	0.3	71	65

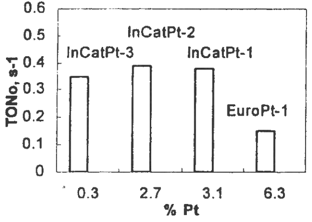
The specific activity is reported as turnover number (TON, molecules / at $Pt_{SURF} \cdot$ sec). Two types of TON were determined: TON_t - referred to the total surface platinum Pt_S^t; and TON_o - referred to the "metallic" surface platinum Pt_S^o.

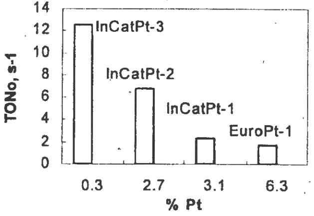
The principal results have been formulated as:

1. In benzene hydrogenation only "metallic" exposed platinum atoms take part in the reaction. TON_0 values and activation energies are close, excluding EuroPt-1 (fig. 1). The presence of "ionic" platinum increases the catalyst stability in poisoning by sulfur.

2. In cyclohexane dehydrogenation a strong dependence of TON_0 vs. platinum surface concentration is observed (fig. 2). The influence of this parameter is much more important than the "ionic" platinum content. The "ionic" platinum promotes catalyst stability in coking rather than in poisoning.

3. In pentane conversion the selectivity of terminal hydrogenolysis is attributed to the "ionic" platinum, that leads to the lower isomerization selectivity. After the poisoning of catalyst by sulfur the isomerization selectivity is increased sharply on the samples with Pt^σ but practically remains constant on Pt^o.





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PEROVSKITES AS CATALYSTS OF HIGH-TEMPERATURE METHANE OXIDATION IN THE STOICHIOMETRIC MIXTURES

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Mixed oxides with perovskite structure of ABO_3 type have attracted much attention as promising catalysts for complete oxidation of hydrocarbons (in particular, methane) and CO [1]. For mixtures with the excess of oxygen, rather thorough studies of the effect of the nature of transition metal cation, its charge, partial substitution in the A or B sublattice and nonstoichiometry have been carried out. On the contrary, for stoichiometric mixtures and/or mixtures with an excess of hydrocarbons, such data are scarce though being of great importance for such application as fuels combustion. The present work aims at filling this gap by comparing catalytic properties of cobaltites, manganites and cuprates of lanthanum in the reactions of complete oxidation in mixtures with excess of oxygen and stoichiometric ones.

EXPERIMENTAL

Perovskite samples were prepared by arc plasma thermolysis of the mixed nitrate solutions with a subsequent calcination at 900° C in air. Phase composition of the samples before and after high temperature experiments in stoichiometric methane + oxygen mixtures was studied by X-ray diffraction (XPA) and infrared spectroscopy of the lattice modes (IR). Catalytic activities were determined using a batch-flow reactor for CO and butane oxidation in the oxygen excess (operating temperatures not higher than 400° C), while an integral plug-flow reactor was used to study methane oxidation. In the latter case, experiments were carried out in the temperature range 700-850° C (not reached in any of the previous works) and at contact times in the range of 0.144-0.02 sec with mixtures containing 7-12% of methane, 3.5-6% of oxygen in He, keeping as a rule a degree of methane conversion not higher than 30%. Before experiments, samples were calcined in a He flow for 2 h at 850°C. Any possible impact of a homogeneous reaction was minimized by using quartz chips to fill a free volume of the reactor.

RESULTS AND DISCUSSION

According to XPA and IR, in all samples before experiments a perovskite phase predominates. For lanthanum cuprate La_2CuO_4, IR data correspond to a orthorhombic phase, while XPA indicates also admixtures of $LaCuO_3$, and, probably, CuO. A structure of lanthanum manganite $LaMnO_3$ was found to be of a distorted orthorhombic type. Lanthanum cobaltite $LaCoO_3$ has a rhombohedral structure, and some admixtures of Co_3O_4 were revealed by both methods.

For CO and butane oxidation in mixtures with the excess of oxygen, a following order of activity was found for both reactions: $La_2CuO_4 < LaMnO_3 < LaCoO_3$. While activities of manganites and cobaltites are comparable, a lanthanum cuprate activity is more than an order of magnitude lower. In general, activities of perovskites in the reactions of complete oxidation appear to be mainly determined by a nature of a transition metal cation, being comparable to activities of corresponding simple oxides [2]. In most cases, activities of copper and cobalt oxides in the reactions of complete oxidation are closely allied [3]. Hence, some drastic changes of the copper reactivity are observed when inserting it into the perovskite structure. Usually, catalytic activity of oxides in the reactions of complete oxidation is determined by the bond energy of the most reactive surface oxygen. The results obtained here might indicate some drastic modification of this parameter for copper in a perovskite structure as compared to that in pure CuO (tenorite). At the molecular level, this phenomenon can be explained by a change of the copper coordination, its charge state or atomic structure of the most developed surface faces.

For the reaction of the high-temperature methane oxidation in stoichiometric mixtures, the same trend of activity of various perovskites as that found for the low or middle-temperature oxidation reactions under oxygen excess was obtained (vide supra). Moreover, the same activity scale (cuprate is ca. an order of magnitude less active than cobaltite and manganite) was maintained. It is not so trivial taken into account high operating temperatures in the case of methane combustion as well as some changes in the perovskites phase composition due to a weakly reducing reaction media effect. Namely, a segregation of transition metal oxides accompanied by a rearrangement of the parent perovskite structure was observed. Hence, even at high operating temperatures, catalytic properties of perovskites studied here seem to be mainly determined by their properties before reaction despite of the clearly visible effect of reaction mixture on the phase composition.

The most interesting kinetic feature observed for perovskites in the methane oxidation is a sharp dependence of the selectivity of various products formation upon contact time. For all samples, at a small contact time methane is converted exclusively into carbon dioxide and water. As contact time increases, CO, hydrogen and C_2 appear, at last becoming predominant products. It means that for these systems, primary selectivities are determined by the reaction of methane oxidation into water and carbon dioxide. At a higher contact time, a secondary and more slow endothermic reaction of methane reforming (by steam as well as carbon dioxide) takes place generating carbon monoxide and hydrogen. Probably, some inhomogeneities in the temperature pattern along the catalyst layer due to a highly exothermic nature of the methane oxidation reaction could favor a local reduction of the transition metal to lower oxides (or even to a metallic state), which act as active sites for methane reforming. From this point of view, perovskite structure ensures high-temperature stability of such reduced patches by keeping them in a highly dispersed state and suppressing a carbon formation.

CONCLUSION

Catalytic properties of perovskites in the high-temperature reaction of methane combustion in stoichiometric mixtures appear to be determined by the chemical nature of transition metal cations along with the effect of perovskite matrix on their charge and coordination. Primary reaction is methane oxidation into carbon dioxide + water followed by more slow endothermic reactions of methane reforming. High temperature stability of perovskites in weakly reducing reaction mixtures is demonstrated.

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PPII-49

STRUCTURE AND SURFACE COMPOSITION OF NEW HIGH POROUS CELL-TYPE CARBON SUPPORT FOR CATALYSTS

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Porous carbons (Sibunit) produced by hydrocarbons pyrolysis on carbon black surface [1] as well the filamentous carbons (CFC) prepared by CH_4 decomposition over Ni (CFC-1) and Ni-Cu (CFC-2) catalysts [2] are of considerable interest as a supports for the catalyst preparation. Recently, the new carbon with unusual cell-type structure was discovered [3]. In present communication the results of the structure investigation of cell-type carbon in the comparison with a regular carbon supports Sibunit, CFC-1 and CFC-2 are presented.

Samples of cell-type carbons (CTC) were grown up on the walls of outlet line of the flow reactor charged with carbon black during propane - butane mixture pyrolysis at the temperatures 700-1250 K. Prepared samples have the cylindrical shape with diameter 40 mm and 30-50 mm length.

The chemical analysis of the CTC gives the molar ratio $H/C = 1/4$. This ratio can be achieved in the planar regular polygonal fragment of graphite net consisting of 37-44 benzene rings. In view of C-C distance in graphite 0.142 nm, the dimension of such fragment was estimated to be 1.56-1.70 nm.

The density of CTC determined by helium displacement is equal to density of pyrolitic carbon deposed on carbon black (1.82 g/cm^3) and much less then the density of Sibunit (2.08 g/cm^3), CFC-1 (2.05 g/cm^3) and CFC-2 (2.06 g/cm^3). The pore volume of CTC (66 cm3/g) calculated from the helium density and bulk density (0.015 g/cm^3) is about 100 times higher then that of regular carbons. According to the low temperature N_2 adsorption data CTC has a smooth surface with specific area 4.2 m^2/g.

The results of X-ray diffraction analysis show that CTC has a graphite-like structure with the biggest interplanar spacing ($d_{002} = 0.356$ nm) and smallest crystallite size ($La < 1.0$ nm, $Lc = 2.0$ nm) to compare with Sibunit, CFC-1 and CFC-2. The crystallite represents a packet of 5-6 graphite nets.

The texture of CTC was investigated by scanning electron microscopy, high resolution transmission electron microscopy, electron microdiffraction methods. It was shown, that CTC matrix is formed by carbon layers with thickness 30-150 nm. Carbon layers are connected in knots making up the threedimensional net. Carbon layers consist of graphite-like microcrystallites oriented by basal plane to each other. The edges of basal planes of this microcrystals are exposed to the surface. The basal plane of carbon microcrystals are predominantly oriented along the longitudinal direction of the carbon layer.

Thus, CTC combines the defects of small microcrystallites with the regularity of their arrangement in carbon matrix.

The ESCA data show the great difference of CTC surface composition to compare with Sibunit, CFC-1 and CFC-2. In C1s spectra of CTC were observed four components (BE = 283.5 eV, 284.4 eV, 286.0 eV and 289.0 eV), attributed to C atoms of graphite structure, electron-donor and electron-deficient carbon atoms. The number of the surface oxygen species and their concentration depends on the sample microstructure. The O1s peak (BE = 532.5 eV) was observed in spectra both CFC-1 and CFC-2. Two O1s peaks (532.5 eV and 531.1 eV) were presented in Sibunit spectra. The O1s peak intensity for CTC is much higher then that for Sibunit, CFC-1 and CFC-2. This is in a good agreement with results on CTC structure study. The edges of small packets of graphite nets, decorated with fragments of hydrocarbon molecule can easily react with oxygen giving the high concentration of surface oxygen groups.

CONCLUSION

The new cell-type carbon material possess the unique porous matrix morphology, microcrystal structure and surface chemical composition in contrast to Sibunit and CFC carbons. The cell-type carbon can be a promising support for studying the problems of catalysts preparation.

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PPII-50

Application of plasma spraying in preparation of metal supported catalysts

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Metal supported catalysts are very promising to use in high temperature catalytic processes where high heat transfer is required or in car converters [1]. Preparation of catalysts on metal substrates usually includes the preliminary washcoating of the metal surface by chemical methods [2]. The catalysts developed are widely used today, but the room for the further improvement of catalyst chatacteristics still remains.

Plasma spraying, or plasma powder coating techniques, gives unique possibility to synthesize the washcoating layer on the metal surface with rather strong adhesive and high thermal stability properties. But, notwithstanding the fact that alumina coatings deposited by different plasma spray technologies on metallic substrate are rather common, the problems of sufficient stability of such coatings still exist. This is connected with problems of adhesion and cohesion strength, inherent to this methods, and with the dependence of permanent stability of coatings on its crystalline structure.

The crystallinity defines the functional properties of the coating in high temperature and aggressive media and stability under conditions of cyclic loadings. So the examination of different methods of plasma spraying of alumina coatings and study of their fine structure are useful both for the further development of possibilities of such method and for the reason of raising the competition with other gas-thermal methods.

There is general disadvantage of the conventional DC plasma spray torches to the effect that deposition of the coating is performed in the condition of turbulent plasma jet outflow which meets the significant difficulties for production of the homogeneous structure and phase composition coatings with required porosity.

The subject of this paper is the use of DC plasma torch [3] with interelectrode insert and "diffusive" (distributed) attachment of arc on an anode surface for the deposition of the alumina coatings under different regimes of a jet outflow (laminar, transient and turbulent) on the metal substrates of different geometry (plates, foams) for consequent synthesis of perovskite catalysts.

These modes were provided by the variation of the plasma-forming gas (air) flow rate over a wide range (from 0.5 up to 2 g/s) that has made it possible to change the particles velocity and their aggregate state, and hence, the coating micro- and macro-structure over the wide range.

The alumina coatings deposited on a metal surface under laminar, transient and turbulent regimes of a jet flow were characterized by a complex of physical chemical methods: XRD, BET, SEM and TEM. The BET data showed that specific surface area of coatings did not depend on the regime of a jet flow used. The coatings consisting of α-alumina had BET surface of 0.2 m^2/g magnitude. On the contrary, SEM and TEM revealed that the morphology of sprayed alumina layer strongly depended on the regime of a jet flow used.

The $LaCoO_3$ catalysts were synthesized on metal surface covered by sprayed alumina layer by the use of two different methods: direct impregnation of sprayed alumina layer by La and Co nitrates with subsequent calcination, or impregnation of sprayed alumina by La and Co nitrates with preliminary modifying of sprayed layer by La-containing γ-alumina with subsequent calcination. $LaCoO_3$ phase was detected by XRD analysis in the samples synthesized by both techniques. The distribution of active component in the sprayed alumina coatings was studied by SEM.

The data obtained show that the application of plasma spray technique is perspective in the development of metal supported catalysts to be used in high temperature combustion.

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OXIDE CATALYSTS VIA ALKOXYACETATE RESINS AS PRECURSORS.

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For decreasing a chemical interaction between a support and a catalytic multicomponent oxide coating produced by chemical wet process it is necessary to lower the temperature of heat treatment required for the formation of crystalline phase, for example, perovskite or spinel. This is reached by decreasing the particle sizes of initial simple oxides or their precursors. Using the precursors with EOE^I- and $EOROE^I$-linkages (E, E^I - chemical elements, R - organic biradical) is more preferable way. The well-known Pechini method based on this way is very complicated, expensive and inconvenient for the production of coatings.

We have studied the process of producing catalysts via the alkoxyacetate resins (AR). The synthesis of AR is simple. It consists in heating the mixtures of different acetates and high-boiling alcohols having more than one OH-group (for example, ethylene glycol, glycerin, di- and triethanolamine, *etc*). During the synthesis acetic acid and water are distilled. The following reaction of the process is the main one:

$$M(OAc)_n + M^I(OAc)_m + HOROH \rightarrow (AcO)_{n-1}MOROM^I(OAc)_{m-1} + 2AcOH,$$

where Ac - $C(=O)CH_3$; R - CH_2CH_2, $CH_2CH(OH)CH_2$, $C_2H_4N(C_2H_4OH)C_2H_4$, *etc*; M, M^I - metals, for example, Co, Cu, Cr, La, Sr, Ce, *etc*.

The substitution of the AcO-group by the ORO-linkage continued until the formation of AR which contained polymeric chains, rings, sheets and three-dimensional network.

AR have some advantages:

(1) the higher solubility in water and alcohols (the solubility of many acetates is less than 10%);

(2) capability to form amorphous films after an evaporation of solvents (the separate crystallisation takes place in the mixtures of the acetates);

(3) binding property that can be used at producing catalysts (many acetates have no binding property).

The process of the transformation of AR in the oxides $LaCoO_3$, $La_{0.9}Ce_{0.1}CoO_3$, $CuCr_2O_4$, *etc* and producing the catalytic oxide coatings have been studied. Using of AR and using of the mixtures of the acetates have been compared. It was found that the self-ignition of AR began at approximately 300 ^{0}C and the temperature rose up to 800 ^{0}C and above for a short time (a few seconds). This effect is very important because interaction between generated coating and support decreases.

Catalytic activity of the prepared powders and coatings has been studied in the process of CO oxidation to CO_2. It was found that catalysts based on AR were more active than those from the mixtures of acetates. For example, the CO conversion on the $LaCoO_3$ powders prepared from AR and from the mixture of acetates achieved 100% at 185 and 255 ^{0}C respectively.

Our approach permits to produce multicomponent oxides of different chemical elements in any proportion at lower temperatures. For the preparation of AR not only acetates but different inorganic salts may be used ((i) precipitation of hydroxides, carbonates or hydroxycarbonates, (ii) dissolving precipitates in acetic acids, (iii) heating with high-boiling alcohols). It is important from practical point of view.

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SYNTHESIS OF ALUMINIUM HYDROXIDE IN ALUMINIUM-TRIETHANOLAMINE-WATER SYSTEM.

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Alumina used as catalytic supports or catalysts is often prepared by Bayer process (the synthesis of sodium aluminate from sodium hydroxide and some alumina containing minerals followed by it decomposition) or by the alkoxide sol-gel process (the hydrolysis of aluminium alkoxides produced from aluminium and alcohols).

We have been carried out the synthesis of aluminium hydroxide using some elements of these processes. The synthesis was carried out by heating mixtures with different quantity of the components of the aluminium-triethanolamine-water system at 100 °C. A liquid part (thin slurry) of the reaction mixture was periodically separated from aluminium and diluted with water. The precipitated aluminium hydroxide was filtrated, washed with water, dried at 20 - 100 °C. The filtrate was concentrated by the evaporation and added to aluminium. Thus, the synthesis of aluminium hydroxide may be carried out uninterruptedly with the addition of aluminium (foils, granules) from time to time. The synthesized aluminium hydroxide was hydrated boehmite containing about 70-75% alumina. The surface areas of alumina generated from these aluminium hydroxides were about 250 and 85-150 m^2/g after a thermal treatment for 2 h at 500 and 900 °C respectively.

Some experimental facts indicate that the reaction of dissolving of aluminium includes a generation of aluminate as in Bayer process. The formation and subsequent hydrolysis of aluminium alkoxides, as in the alkoxide sol-gel process, are less-probable.

Some correlations between reaction and heat treatment conditions, on the one hand, and catalytic properties and texture of alumina produced, on the other hand, have been studied.

The following advantages of this process are:

1) the higher safety in distinguish with the alkoxide sol-gel process;

2) an absence of any sodium impurity in aluminium hydroxide in contrast to Bayer process;

3) nontoxicity and sufficient cheapness of triethanolamine having high boiling point.

PPII-53

HIGH-ORDER POLYNUCLEAR COPPER COMPLEXES WITH ORGANIC DONORS AS CATALYSTS FOR CONVERSIONS OF HALOGENATED HYDROCARBONS

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Polynuclear mixed-valence copper complexes with organic donors open up new possibilities in creation of effective catalysts for chemical reactions. The presence of metal ions of different oxidation states can favour the process of electron transfer wich is the limitation stage of many catalytic reactions. The energy of electron transfer appears to be minimum if it proceeds between the centers of one complex without significant change of its geometry. The mechanism of catalytic action of polynuclear copper complexes with organic N-, S-, P-donors may be close to that one of natural Cu-containing enzymes. Some low-weight copper complexes with organic donors could be considered as analogues of related biological systems. Therefore studies of structures and catalytic properties of these complexes are of great importance.

The formation of mixed-valence copper complexes with dialkyl sulfides or triphenylphosphine in catalytic isomerisation of dichlorobutenes was investigated by kinetic and spectroscopic (UV-Vis, IR, ESR, NMR) methods. Complexes containing 3 or 4 copper ions in different oxidation states, substrate and donor molecules were found to play a key rôle in catalysis. Chloroolefins with allylic chlorine atom may stabilize mixed-valence complexes as bridging ligands between Cu(I) and Cu(II). The effect of self-organization was observed in these systems. The nuclearity or oxidation state of Cu in precursors is not significant: in the reaction media in presence of O_2 for Cu(I) and in presence of some excess of phosphines and sulfides for Cu(II) the same active polynuclear mixed-valence complex is formed. The activity of this complex is one or two orders higher than activity of mononuclear analogues.

The immobilization of these complexes on surface of inorganic supports gives additional possibilities both in theoretical studies and in technological use. The main structure of polynuclear center and a part of ligands remain in supported complex. At the same time coordination with active centers of surface allows not only to fix active forms but to control catalytic activity.

Supported catalyst formed on SiO_2 from solution of $(CuCl_2)_2.(dmf)_4$ as precursor is an active catalyst for new reaction of halogen exchange between alkanes and halogenalkanes. In the case of supported polynuclear bridged catalyst we also observed the maintaining of the optimal ratio metal-ligand: in reaction conditions a part of dmf was lost and simultaneously reaction speed increased. Further slow loss of ligand resulted in decreasing of catalytic activity. The removal of dmf by vacuuming or heating the catalyst or forming the supported catalyst from precursors not containing dmf are followed by forming considerably less active form. Therefore, all factors are responsible for high catalytic activity: polynuclear center, organic donor and surface.

The reaction velocity is decreased significantly by adding phenols or O_2. The products of recombination of radicals are found in reaction mixture. So the radical-chain mechanism of the process is suggested.

The use of solvated or supported polynuclear copper complexes as catalysts in halogenated hydrocarbons is very perspective for development of new catalytic technologies.

APPLICATION OF HYDROPHOBIC PLATINUM CATALYST FOR A NUMBER OF PROBLEMS IN THE HYDROGEN ISOTOPES SEPARATION TECHNOLOGY

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Progress in nuclear industry has made very important the problem of environmental protection from hydrogen radioactive isotope - tritium. Another today's important problem of hydrogen isotope separation is utilization of deuterium containing wastes of conversion and disarmament programs of Russia.

Theoretical analysis shows that both problems can be effectively solved by using the method of chemical isotopic exchange for hydrogen isotopes separation in the system "hydrogen-water". This process requires a catalyst which must have high catalytic activity and stability. The hydrophobic platinum catalyst is suitable for this system.

The height of transfer unit (HTU, hoy) is the important characteristic of the process effectiveness. The HTU value depends on both the catalytic activity and the conditions of reagent transport and the rate of phase isotopic exchange between vaporous and liquid water. The investigations show the HTU doesn't depend on the catalyst activity if the latter one is more than 5 s^{-1}. In this case the process of isotopes separation is limited by phase isotopic exchange.

During the investigations it was shown that hydrophobic platinum catalyst on copolymer of styrene with divinilbenzene as a support has to obtain the hoy values in the range of 8-15 cm under the catalyst temperature 313-363K and hydrogen pressure 0.05-0.15 MPa. The catalyst activity was stable during several thousand hours run. The special series of experiments with tritium containing water has shown that catalytic activity doesn't changed after irradiation with integral dose more than 1 MGy.

The usage of this catalyst give us the possibility to develop several installations for economic reprocessing of heavy water wastes. One of these installations is presented in this report, it has no analogy in the world and gives the possibility to produce about 2000 kg conditional heavy water with deuterium concentration 99.98 mol.% and tritium content less than 3 mCi/l. The catalyst in this installation contains about 15 g of platinum.

The effectiveness comparison of distillation and chemical isotopic exchange methods for solving the same problems is made in the final part of report. The conclusion about the preference of the last method has been done.

PPII-55

CATALYTIC OXIDATIVE CONVERSION OF METHANE FROM NATURAL GAS TO C_2- HYDROCARBONS ON CATALYSTS FROM Mo AND W HETEROPOLY COMPOUNDS OF 12 SERIES

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Light alkanes (C_1-C_4) form a part of natural and accompanying oil gases and do not find wide application in practice. They are used as fuel, in industrial processes, for producing synthesis-gas and carbon, for noncatalytic pyrolysis and other, but are mainly burned as a part of exhaust gases in "torches".

Catalysts for removal of hydrocarbons from industrial and automobile exhaust gases by deep oxidation are developed. An alternative method of utilization of alkanes by catalytic partial oxidative conversion to commercially useful products is of interest.

The catalytic action of supported catalysts, prepared by using Mo and W heteropoly acids (HPA) of 12 series as an active component with Si central atom and their salts of 1,2 groups elements of Periodic system was investigated in reactions of partial oxidation and oxidative dimerization of CH_4 to oxygen - containing compounds and C_2 - hydrocarbons. Tests were made in reaction mixtures containing CH_4, O_2, inert gas (N_2, Ar) with or without water vapour. CH_3OH, CH_2O, C_2H_6, C_2H_4, H_2, CO_2 were found to have formed. The sequence and discreteness of formation of these products as the temperature increased, were shown. The products form the following series according to optimal temperatures of formation: CH_3OH (300-350^{0}C), CH_2O (600-650^{0}C), C_2H_6 (650-750^{0}C), C_2H_4 (750-800^{0}C), H_2 and CO_2 (above 700 and 800^{0}C).

Influence of HPA content over the support on the yield and selectivity of C_2H_4 (800^{0}C) and CH_2O (600^{0}C) formation from CH_4 was established for 0,5 - 20% HPA / aluminosilicate (HPA: $H_4SiMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$). Curves for yield (C_2H_4, CH_2O) and selectivity have polyextremal character for low - percentage (<5% mass. HPA) catalysts. The yield and selectivity changed little on a further increase in the HPA content. It was shown by IR - spectroscopy and TPR methods that the polyextremal change of the catalytic properties is due to formation of compounds in the HPA - support system. The latter caused change of the binding strength, reactivity of structural oxygen in the catalyst and its acid - base properties. Correlation between the yield and selectivity of CH_2O formation in the process of partial oxidation of methane and the content of Broensted acid centers of certain strength (ESR, ionization potential 7.55 - 8.12 eV) was established. Positive effect of water vapour on this process was noted.

Influence of the nature of an acid - forming cation (Mo, W) and substituent of proton on the activity and selectivity of their action in the reaction of partial oxidation of methane to formaldehyde (POMF) or oxidative dimerization to ethylene (ODM) were studied for $[SiW_{12}]$ - and $[SiMo_{12}]$/ aluminosilicate catalysts. The catalysts based on HPA of 12 series of Mo had maximum activity and selectivity in the process of partial oxidation of methane. The yield and selectivity of CH_2O formation somewhat increased on passing from HPA to its salts in the following sequence of elements: Mg > Ba > Li > H > Sr.

The supported catalysts based on HPA of W had maximum activity and selectivity in the process of ODM. The yield of C_2H_4 on the catalyst from $[SiW_{12}]$ - HPA salts depended on the nature of the cation in the salts and decreased essentially in the series of salts of the following elements: Mg > Ca > Na > Fe , H.

Catalysts based on Mo and W HPC supported on aluminosilicate showed thermal stability on POMF (Mo - containing) and ODM (W - containing) processes at 650^0C and 800^0C, respectively, at long operation in the presence of water vapour.

Study of the genesis of supported catalysts by X-ray spectroscopy, IR - spectroscopy, electron spectroscopy diffuse reflection methods showed that under optimal conditions, at 2-30 % mass HPC concentration a part of heteropoly compound gets linked with the support, and stabilization of its structural fragments before 700^0C ($SiMo_{12}$) and 800^0C (SiW_{12}) occurs. The reactive form of oxygen is easily regenerated at the moment of reaction in those structural fragments by the effect of reactive components (O_2, CH_4, water vapour).

PPII-56

A NEW CATALYST FOR PURIFICATION OF WASTE GASES

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Systems composed of metal plate supports with a composite covering are proposed as catalysts for purification of industrial and exhaust waste gases.

A porous material (the Russian name FNS-5) containing iron, chromium and nickel, on which aluminium, copper, and extra nickel were applied, was used as a support. Aluminium was applied by means of diffuse fusion to obtain coverings connected with the metal backing most closely while copper and nickel were deposited by means of impregnation of aqueous solutions of the corresponding salts [1].

To apply an aluminium layer on the support, our experience of aluminizing steel things by the contact method in solid-granular burying with an addition of ammonium chloride was used.

The burying had the following composition: aluminium powder - 10%, aluminium oxide - 88%, ammonium chloride - 2%. The inert addition of aluminium oxide was necessary to prevent sintering of aluminium powder at high temperatures. Ammonium chloride was added to pickle the surface of aluminium powder and the covered surface in order to eliminate the effect of the oxide layer [2, 3].

The catalytic activity of the obtained systems was examined on a running-type set under atmospheric pressure within 200-600 °C with the volume velocity of gas within 800-5000 h^{-1}. The model gas mixture was proportioned from the average actual contents of carbon monoxide, nitrogen oxides, and hydrocarbons in exhaust gases of automobile Diesel engines.

Under these conditions, the elaborated catalysts provide the degree of carbon monoxide conversion from 40 to 100% within 350 -600°C and the range of its content in the gas mixture from 1.5 to 2.5 vol %. In the specified temperature range, the degree of nitrogen oxide conversion was 50-100% at the NO_x content of 1.3 -1.5 vol %.

A study was made on pure-metallic plate catalysts modified by transition metal compounds. It has been shown that their high-temperature annealing (600°C) in air flow raises their activity sharply, up to the activity of the deposited alumo-platinum catalysts. At 450-550°C the annealed catalysts are even more active with respect to reduction of nitrogen oxides.

This increase in activity is associated with formation of spinel-structure compounds ($NiAlO_x$, $CuAlO_x$, $FeAlO_x$) on the catalyst surface.

The results obtained show the developed catalysts on a plate metal support to be promising for purification of waste gases. Moreover, such properties as high heat conductivity, the ability to be used as a convenient construction material and to form different composite structures on the surface, let these systems simultaneously perform a double function, namely, as a catalyst and as a construction material for exhaust gas neutralization for internal-combustion engines.

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PPII-57

DEVELOPMENT OF METHODS OF TOP LAYER FORMATION ON DIFFERENT ALUMINAMEMBRANE SUPPORTS

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It is known that the properties of membrane supports: the pore structure, defectness, gas permeability, etc. determine the properties of membrane.

In the last 10-20 years alumina ceramic materials and articles are applied as membrane supports for membrane technologies.

As shown previously [1,2], the porous structure of alumina ceramics can be controlled without using the burning out additives, but on the basis of variation of the properties of initial aluminum containing components and their correlation in extrusion mass.

The properties of alumina ceramics as membrane support in the tube shape were discussed in [3].

Single tubes on the base of alumina ceramics were used for the preparation and study of membranes.

Sol of aluminum hydroxide with pseudoboehmite structure was used for the preparation of γ-alumina top layer on the α-Al_2O_3 tubes. This sol formed during reaction between hydroxide and nitric acid serves both as binder and source of γ-Al_2O_3 after calcination. The results of experiments allow to choose the optimal preparation conditions for the formation of γ-alumina top layers on the alumina ceramics tubes. These parameters include: concentration of anhydrous alumina in the sol; amount of HNO_3; dipping time; number of dipping; drying and calcination heating rate.

Structural characteristics of membranes were studied by SEM and TEM .

The properties of prepared optimal membranes with γ-Al_2O_3 top layer are given in the Table. It is seen that the variation of synthesis procedure leads to the variation of thickness of top layer and to the change of pore structure of membranes. Properties of used ceramic tube support and γ-alumina substrate as well as properties of membranes with other top layers studied are also given in the Table.

Properties of membrane tubes. Table.

Size, mm	Phase composition	S_{BET}, m^2/g	Pore structure			Thickness of membr. layer, mkm
			V_{tot}, cm^3/g	D_{ef}, mkm	Porosity, %	
$D_{out}=10$ $D_{inn}=5$	SiC/α-Al_2O_3	1.3	0,15	D_1~15 D_2~0,3	35	5-15
$D_{out}=10$ $D_{inn}=5$	SiC+ZrO_2/α-Al_2O_3	3.2	0,25	D_1~15 D_2~0,01	50	15-20
$D_{out}=5$ $D_{inn}=2,5$	α-Al_2O_3 (support)	3,2	0,17	0,16	40	-
-	non-supported γ-Al_2O_3	210	0,35	0,011	58	-
$D_{out}=5$ $D_{inn}=2,5$	γ-Al_2O_3 /α-Al_2O_3	5.7	0,23	~0,15	48	5-15
$D_{out}=5$ $D_{inn}=2,5$	C /α-Al_2O_3	8.1	0,28	D_1~0,15 D_2~0,003	55	5-15

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PPII-57a

CATALYTIC INFLUENCE OF COPPER TO THE IRON PHTHALOCYANINE SYNTHESIS

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Metalphthalocyanines are well known owing to the semiconductor properties, high dying ability, catalytic activity in different reactions. The effectiveness of phthalocyanine application depends on the type of crystallographic modification, dispersity that, in its turn, is determined by the conditions of their production. Iron phthalocyanine (PcFe) can be synthesized at 300^0 C from phthalonitrile and ferrocene.

The purpose of this study in the development of the method for the production of PcFe from 1-amino-3-iminoisoindolenine (Is) and ultrafine Fe powders produced by electroexplosion of wire (EEW). At the production of powders there have been used iron and copper plated iron wires with the diameter 0.5 mm. The iron content was 99.9999-99.0000 %, the value of the introduced specific energy was 0.8-1.0. In accordance with the RFA data the composite powders represent solid solutions of Cu in Fe and of Fe in Cu, intermetallides have not been found.

The direct contact of the electroexplosion Fe powder with Is in the DMFA medium at the boiling temperature of the solvent does not lead to the PcFe formation. At the same time, in analogous conditions PcFe is formed at the quantity yield. The reaction takes place through the formation of the soluble complex (λ =690 nm). At the complection of the interaction the metal copper is deposited on the reactor walls.

The attempt to produce PcFe using the mechanic mixtures of electroexplosion Cu and Fe powders in the proportion 1:100 did not give the positive result. Probably, the conditions of the electroexplosion provide more intense dispersion and more close contact between copper and iron, therefore, the electrochemical mechanism of the phthalocyanine formation involving the galvanic couple Fe-Cu becomes possible /1/.

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CATALYSIS ON THE DUST GRAINS: SYNTHESIS OF METHANOL AND FORMALDEHYDE IN PROTOPLANETARY ACCRETION DISKS

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Nowadays there are no data on biological and chemical evolution as well as physical conditions proceeding on the Earth surface for the first 700-800 million years of its existence because of destruction of the primary crust under the geological processes and cosmic bombardment. At the same time ancient geological rocks dated as 3.5-3.8 billion years old manifest rather earlier spring of Life. The main difficulties of extraterrestrial synthesis of prebiotic molecules are the absence of the biotic organic forms discovered anywhere save the Earth as well as rapid destruction of complex organic molecules in Space. The property of homochirality as well as the thermodynamic problem 'from being to becoming' appear to be the most common ones for all the approaches to the sources of prebiotic molecules.

These difficulties made us to suggest a new approach to the problem of sources and the origin of Life from the point of view of search and study of a global chemical reactor, where synthesis of prebiotic molecules took place. Our basic idea is that the whole dust-gas cloud, where and from which the planets of the Solar system were formed for 60 million years, was namely such a reactor.

The Sol was born in a cloud for approximately 1 million years under the gravitational collapse. Therefore the energy and possibly the substance from the solar thermonuclear reactor came to the planetary nebula reactor. Abundance of chemical elements was supposed as a primary composition of the dust-gas cloud with H_2, He and CO chief components. The dust seems to be composed mainly of particular metal compounds of the 'iron peak' which appear to be the classic catalysts of synthesis of complex organic molecules from the most abundant reagents mentioned above. Taking into account the loss of H_2 and He, we have found that more than 10^{28}g of organic substance with regard to CO was incorporated into the mentioned global organic synthesis. The appearance of more than 10^{18}g of dry biotic substance on the Earth surface represents only a "fluctuation" at the space - Earth interface as compared to the above giant flows of organic compounds. Due to considerable predominance of H_2 over other substances, the reactions with formation of CH_3OH, CH_2O, NH_3, HCN, hydrocarbons and other prebiotic molecules should prevail. Intensive mixing and separation of molecules at the rotation of accretion disk round the Sol, electric charges of the dust, availability of large scale electromagnetic fields, intensive solar irradiation, central and distributed gravitational fields, etc. provided the required conditions to make the state of the global chemical reactor far remoted from the equilibrium as well as generation of the "advantage factor" [1] for appearance of the molecular homochirality. These prebiotic organic and other chemical molecules appeared in a lot of ion-molecular, gas-phase, heterogeneous catalytic and other reactions. Computer simulation, lab-scale experiments and a verification made on the basis of some astrophysical and astrochemical data are the subsequent steps in the study on the sources of prebiotic molecules.

The goal of our study on the first stage is to find the distribution of H_2, CO, dust concentrations and substance accretion in the solar nebula, where Solar is presented as a singularity. Thus we intend to reproduce by a computer simulation the energy- and mass exchange in the heterogeneous chemical reactor of the solar nebula and to define the temporal changes of the chief macroscopic and thermodynamic parameters in the parasolar space at the initial stages of the solar system evolution. These parameters are found by a set of equations that manifest the main conservation laws for a two-phase medium with regard to the solar gravitational field.

The results of the computer simulation of the dust precipitation toward the equatorial plane and formation of the protoplanetary disk at the dust-gas dynamics with a rotation are presented. The flow in the protoplanet disk is followed by development of a collective instability with respect to the medium fragmentation to separate macroscopic bunches. Such dust-gas bunches, being the future primary protoplanetary condensates, heat up under the solar irradiation and dissipation of mechanical energy. The above condensates become the centers of the catalytic synthesis of methanol and formaldehyde on the dust grains.

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HOMOGENEOUS CATALYST FOR EPOXIDATION OF OLEFINS WITH ORGANIC HYDROPEROXIDE

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Transition metal compounds of V and VI groups of Mendeleev's table are used as catalysts of hydroperoxide epoxidation. Today generally accepted oppinion is that molybdenum-containing catalysts are the most active for this process. But "active" catalyst is not always selective. So, catalytic properties of molybdenum catalyst depend on ligands in coordination sphere of central atom. Therefore, a catalyst active and selective during the whole epoxidation process can be synthesized by purposeful exchange of ligand nature.

Molybdenum catalyst modified by boron-containing substance is offered for olefins epoxidation with tertiary butyl hydroperoxide (TBHP) and cumene hydroperoxide (CHP). It is shown that this catalytic system acts best of all in epoxidation of easy polymerized olefins, for instance styrene. Thus, epoxidation of these olefins in presence of common molybdenum catalyst (temperature 100°C, reaction time 60 min) is characterized by hydroperoxides conversion less than 80%, yield of styrene oxide 70%, the polymere yield based on styrene 20%. In the presence of boron-containing substance, CHP conversion achieves 85%, TBHP - 90%, yield of styrene oxide equal 80 and 85% accordingly. The yield of polymers decrease to 5...8% (CHP) and 3...5% (TBHP).

The investigation of boron-containing substance influence the activity of molybdenum catalytic systems in styrene epoxidation (by CHP), on catalytic CHP decomposition and on styrene polymerization have been made. Phenol and acetone formation is the main way of CHP decomposition catalyzed by molybdenum complexes. The reaction has heterolytic nature. Curves of CHP decomposition have autocatalytic feature. Introduction of boron-containing substances decreases the initial rate of CHP decomposition and increases the finished hydroperoxide conversion. The main products of CHP decomposition are phenol and acetone.

The influence of boron-containing substance on styrene polymerization (without CHP) in similar condition have been studied. It was defined that in presence of these substances styrene polymerization decreases from 40% to 7%.

The kinetic study of model olefin octene-1 (unlike styrene this olefin is not polymerized) with CHP using molybdenum-boron-containing catalysts has been made. It was shown that octene-1 is not oxidized by CHP in presence of boron substance only (without molybdenum catalyst). And therefore boron compounds play role of modifier, but not of catalyst. Dissociation complex constants K^{S}_{CHP}, K^{M}_{CHP}, K^{S}_{OL}, K^{M}_{OL} and epoxidation rate constant in presence of molybdenum catalyst and molybdenum-boron catalytic system have been calculated.

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Constant	Catalytic system	
	molybdenum	molybdenum-boron
K^{S}_{CHP}, mol/l	0.37	0.57
K^{M}_{CHP}, mol/l	0.62	1.11
K^{S}_{OL}, mol/l	8.70	14.30
K^{M}_{OL}, mol/l	14.69	27.82
k_{o}, s^{-1}	126.33	320.00

Thus, boron-containing substance increase acid properties of molybdenum catalyst at olefins epoxidation by organic hydroperoxides.

THE ACID-BASE CATALYSIS IN THE BIOLOGICALLY ACTIVE COMPOUNDS SYNTHESIS

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Acidic catalytic reactions are quite widely used in the organic synthesis. The study of such reactions is of great theoretical and practical interest because the determination of their mechanism is a difficult problem and the reactions themselves are the stages of many processes. Two reactions lying in the base of important technological syntheses and catalyzed by acids are considered in the report - the allyll transformation of 3-methylpenten-1-in-4-ol-3 to 3-methylpenten-2-in-4-ol-1 and hydrogenation of 9-(2,3,4-trimetoxy-6-methylbenzoyl)nonane acid ethyl ether carbonyl group to methylene one.

Cys-isomer of 3-methylpenten-2-in-4-ol-1 is a semiproduct in vitamin A synthesis. It's obtained by isomerization of 3-methylpenten-1-in-4-ol-3.

Nowadays the industrial isomerization of 3-methylpenten-1-in-4-ol-3 to cys-isomer is carried out in toluene medium with the addition of diluted sulphuric acid. The yield of primary acetylene carbinol is about 70%. It is known from the literature about the study of 3-methylpenten-1-in-4-ol-3 to 3-methylpenten-2-in-4-ol-1 allyl regrouping using petroley ether as an organic solvent in the presence of nitrogen and temperature influence (60-65 °C) during 1 hour.

Catalyzed by solid acid method for 3-methylpenten-2-in-4-ol-1 cys-isomer obtaining by allyl regrouping has been offered. Water has been the solvent and the yield of cys-isomer has reached 78%. The isomerization has been carried out in the presence of homogeneous and heterogeneous catalysts. The kinetics of isomerization has been studied.

Liquid-phase catalytic hydrogenation of 9-(2,3,4-trimetoxy-6-methylbenzoyl)nonane acid ethyl ether (A_1) carbonyl group to methylene one with obtaining of 10-(2,3,4-trimetoxy-6-methylphenyl)decane acid ethyl ether (A_2) is one of the stages of new technology for obtaining of 2,3-dimetoxy-5-methyl-6(oxydecil)1,4-benzochinone (idebenon) - the biologically-active compound, the field of medical application of which is connected with cerebrum functions disorders treatment.

In the course of the experiments carried out the activative acid action at the process of A_1 hydrogenation (the reaction doesn't take place without acids) and the influence of carbon support nature on the activity of Pd-catalysts used have been determined. The most active and hydrogenation selective in conversion of carbonyl group A_1 to methylene was - 4% Pd on the carbon material "Sibunit" support.

The solvent nature was determined to influence considerably on the reaction investigated: isopropanol has been found to be the best of the solvents studied. The process has been studied in the wide temperature, concentrations and hydrogen pressure intervals.

The kinetics and physico-chemical investigations of catalytic systems and substrates have been conducted have permitted to suppose that both reactions are carried out by carbonium-ionic mechanism.

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KINETICS AND MECHANISM OF SELECTIVE C-C-BOND CLEAVAGE IN THE CATALYTIC OXIDATION OF LIGNINS BY OXYGEN

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Lignin is one of the main wood components. Its oxidation by oxygen is used in the processes of vanillin production and cellulose bleaching. In both cases catalysts are applied to increase selectivity of the processes. Several hypotheses on the mechanism of lignin oxidation were suggested: the cleavage of carbon-carbon bonds by alkali-promoted retrograde aldol reaction; pathway beginning from the oxidation of benzylic group of lignin structure; oxidation *via* dioxetane formation. The origin and mechanism of catalyst influence on the selectivity of oxidation was not discussed practically.

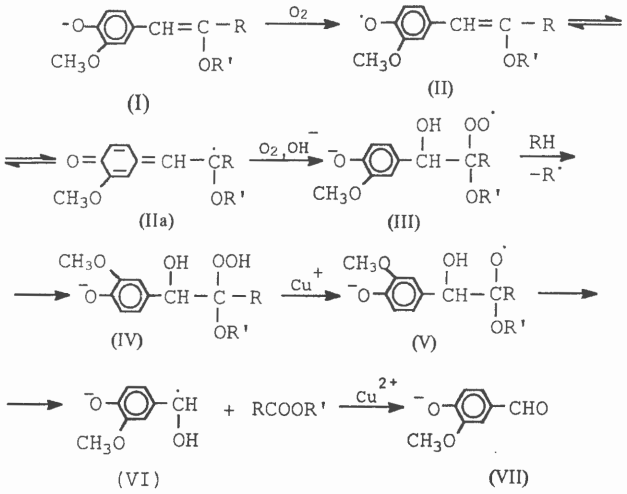
In the present paper the influence of catalyst, pH and temperature on the vanillin yield and the rate of oxygen consumption has been studied and a new mechanism of vanillin formation in the alkaline catalytic oxidation of lignins has been suggested.

The experiments were carried out in a 0.1-liter stainless-steel shaken reactor at 110 - 160°C and partial pressure of O_2 0.2 Mpa. Commercial Syas paper-mill (Leningrad region, Russia) fermented sodium-base spent sulfite liquor produced from softwood were used as substratum. 60 ml of mixture consisting of 180 g/l solids of spent liquor, 120 g/l NaOH, and $CuSO_4$ solution were charged into reactor. Samples of reaction mass for the analysis of vanillin concentration were taken out through a special valve during the experiments.

Some experimental data are summarized in Table 1. They indicate that the conditions affect the rate of oxygen consumption and the vanillin yield in the process by principally different pathways. Hence catalysts do not accelerate oxidation of substratum, but change the pathways of some intermediate conversion. To explain the results obtained we have combined the well known mechanism of catalytic conversion of hydroperoxides and oxyradicals in autooxidation processes and the data on quinone methoxide chemistry (see the scheme). According to scheme the reaction begins with dehydration of the lignin origin structural unit to styrene (I). Its oxidation with oxygen gives consequently the methomeric radical (II) and hydroperoxide (IV). The latter is reduced by Cu(I) to the oxyradical (V) with a subsequent fragmentation to the methomeric radical anion (VI) followed by oxidation into vanillate ion (VII). The mechanism suggested includes formation of radical anion (VI), which, according to the literature data on similar

Table.1. The influence of catalysts and temperature on the initial rate of O_2 consumption and parameters corresponding to the maximum of vanillin concentration.

No	Catalyst, g/l	T°C	Initial rate, g/min. O_2	Parameters for the maximum of vanillin yields		
				[V], g/l	Time, min.	Final pH
1	- -	160	0.094	6.5	60	9.7
2	$Cu(OH)_2$ 3.24	160	0.110	8.7	60	10.4
3	$Cu(OH)_2$, 6.51	160	0.136	11.3	40	9.8
4	$Cu(OH)_2$ 9.75	160	0.080	13.9	40	9.9
5	$Cu(OH)_2$ 16.3	160	0.103	14.7	40	10.9
6	$Cu(OH)_2$ 26.0	160	0.137	11.4	20	10.6
7	- -	110	0.018	5.4	70	-
8	$Cu(OH)_2$ 9.75	110	0.050	7.7	70	9.9
9	AgOH, 12.5	110	0.042	5.7	70	9.5
10	$Cu(OH)_2$ 9.8 + AgOH, 12.5	110	0.092	7.0	90	10.0



semiquinone species, could be rather stable. Radical intermediate with life time approximately 5 min. has been registered in the process by ESR method. The value of the radical g-factor (g = 2.0040) corresponds to the proposed structure of intermediate (VI). The structure of copper catalyst in solution is discussed.

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FORMATION OF COPPER-, NICKEL-, COBALT-, AND ZINC-ALUMINA CATALYSTS PREPARED BY INTERACTION OF ACTIVATED ALUMINUM ALLOYS WITH WATER

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The catalysts distinguished by absence of non-controlled impurities, in particular of catalytic poisons, can be prepared by interaction of activated aluminum alloys with water. As source compounds there are used the aluminum alloys and the activators such as gallium and indium. We investigated the formation of new generation of Cu-, Ni-, Co-, and Zn-alumina catalysts, prepared by the interaction of activated aluminum alloys with water, using the methods of thermal analysis (DTA-DTG), XRD analysis, adsorption, thermoprogrammed reduction, IR spectroscopy, and XPS. At the hydroxide stage there are formed the pseudoboehmite (PB) and bayerite (B). The ratio between PB and B depends on the temperature of interaction of alloys with water and on the concentration and nature of active components. Besides it, after the interaction of alloys with water we detected the phases of intermetallides (aluminides) of Cu, Ni or Co (but no Zn), metallic In, Al, Zn, and Cu, copper oxide, and zinc hydroxoaluminate. With an increasing concentration of active component (Cu or Co), the relative content of bayerite increases while that of pseudoboehmite decreases. The PB phase predominates when the concentration of active component is low or moderate.

After thermolysis PB and B transform into various low-temperature modifications of Al_2O_3, zinc hydroxoaluminate converts to solid solution ZnO-Al_2O_3 with liberating of ZnO excess. In oxidative conditions the metallic In, Zn, and Co forms below 550°C In_2O_3, ZnO, and CuO, respectively. At the higher temperatures (~1000°C) in oxidative conditions the high-temperature modifications of Al_2O_3 and aluminum spinels (of Cu, Zn, Ni) are formed. In reductive conditions below 650°C In_2O_3 transforms to In, while Co_3O_4 and Co-containing compounds do to β-Co; CuO and Ni-containing compounds change to Cu and Ni, respectively.

On the example of Cu-containing catalysts it was shown that the concentration of In at the surface is lower than in the bulk. Unlike indium, gallium is distributed more or less uniformly between the surface and the bulk and cannot be revealed as a separate phase by XRD.

Lewis acidity (revealed by pyridine adsorption) of activated Cu-containing catalysts is a function of the surface concentration not only of Cu, but In and Ga too. The catalysts with Cu, Ni, Co or Zn exhibit at hydroxide and oxide stages developed surface areas(100-300 m^2/g) and diverse porous structures. The surface of these catalysts is rather thermostable and its specific area hardly changes within the wide temperature interval (120-600°C). With increasing of the content of various metals under consideration, the specific surface area of catalysts decreases similarly.

The investigation was carried out under partial supporting of the Russian Foundation for Fundamental Researches (grant 94-03-08611).

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PHOTOADSORPTION AND PHOTOCATALYTIC REACTIONS ON THE ALKALINE EARTH METAL OXIDES MIMICKING COMPONENTS OF TROPOSPHERIC AEROSOLS UNDER EARTH ATMOSPHERE CONDITIONS

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Tropospheric conditions are favourable to photoadsorption and photocatalytic reactions for several reasons [1]. Indeed, in the Earth troposphere, the intensity of solar radiation with wave lengths more than 300 nm is rather high, while concentration of solid aerosols, composed predominantly of insulator oxides SiO_2, Al_2O_3, MgO, CaO and semiconductor oxides Fe_2O_3, TiO_2, ZnO, SnO_2, etc., exceeds 10^{-5} g/m^3. The specific surface area of solid aerosols is more than 10 m^2/g. Note also that high tropospheric concentration of oxygen and the presence of water vapours are favourable to photoadsorption and photocatalytic oxidation reactions.

On the other hand, photoadsorption and photocatalytic oxidation have a negligible or even negative activation energy; it is known also that photocatalytic reaction can occur at very small concentration of an oxidizing component. For these reasons, photoadsorption and photocatalytic reactions can result in efficient decomposition or chemical transformation of most types of various compounds polluting the Earth atmosphere.

Traditionally before performing experiments or using in various chemical processes, the surfaces of adsorbents and catalysts (including photoadsorbents and photocatalysts) are exposed to a rigid pretreatment of various kinds. It can be a pretreatment in vacuum, in an appropriate gas environment, at a certain pressure and temperature, etc. with the purpose to obtain either reproducible results of other researchers or the maximum of adsorption or catalytic (accordingly, photoadsorption or photocatalytic) activity. It is essential that the rigid pretreatment of a surface may result in some sufficient changes of chemical composition of the adsorption layer, stoichiometry of the surface and near-surface layers.

On the contrary, the aerosol particles in the natural atmospheric conditions are not exposed to any rigid pretreatment of the above mentioned types. So the state of their surface corresponds approximately to the state of a surface oxide obtained in rather soft conditions after long-duration contact with air.

In this work we studied an influence of illumination on the chemical interaction of some freons of the methane set ($CFCl_3$ - freon 11, CF_2Cl_2 - freon 12, CHF_2Cl - freon 22, CHF_3 - freon 23) and the ethane set ($C_2F_3Cl_3$ - freon 113, CH_2FCF_3 - freon 134^a), and also $CHCl_3$ and CH_2ClCH_2Cl with the surface of MgO contacted with air for a long time. Note that magnesia is one of the basic solid aerosol components of the troposphere.

The atmosphere exposed magnesia was found to adsorb light in the near-UV spectrum region (shorter than 400 nm) with a distinct band adsorption at 360 nm [2]; a magnesium hydroxylcarbonate diffusive reflection being the reference standard. After a long-time oxygen-vacuum treatment of MgO we observed neither photoadsorption of freons nor a band absorption at 360 nm. For pure MgO the red boundary absorption lies at 178 nm.

The revealed absorption at 360 nm is retained after a long-time evacuation of MgO at 620 K, resulting in the removal of "natively" adsorbed nitrogen oxide from a surface oxide. Therewith experiment shows the desorption of ca. 1% monolayer of $2NO + N_2$, 10% monolayer of CO_2 and one monolayer of H_2O.

It is established that under illumination an efficient nonreversible destructive photoadsorption of many mentioned freons takes place, the spectral dependencies of the quantum yield of the photoadsorption of the freons coinciding with the long-wave band absorption of magnesia.

The performed studies suggest that the atmosphere exposed magnesia possessed a pronounced photoadsorption activity towards hydrocarbonaceous compounds containing simultaneously fluorine and hydrogen atoms. Most likely, the photoadsorbed freons cover the MgO surface replacing the lattice oxygen of magnesia by fluorine anions.

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POSTER SESSION II

Section 6

Innovations in Catalysis for Environmental Protection

PHYSICO-CHEMICAL PARAMETERS OF ORETO RIVER WATER AND PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS DISSOLVED IN ITS WATER

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Oreto river is one of the source from which the city of Palermo derives its water supply. The river has been subjected in last years to a dramatic pollution due to uncontrolled civil and agricultural activities. The present paper reports a systematic analytical investigation carried out on four sites and in different seasons. The main physico-chemical parameters that were determined are: temperature, pH, dissolved oxygen (DO), specific conductance, COD, BOD_5, concentration of nitrogen containing species (NH_4^+, NO_2^-, NO_3^-), phosphorous, anionic surfactants.

In particular, the temperature of the river ranged between ca. 8 and 23°C, the pH between 7.5 and 8.5, the dissolved oxygen between 8 and 126 (saturation percentage), the specific conductance (determined at 20°C) between 418 and 1248 $\mu S \cdot cm^{-1}$, the COD between 2 and 640 $mg \cdot l^{-1}$, the BOD_5 between negligible values and 130 $mg \cdot l^{-1}$, NH_4^+, NO_2^- concentrations between negligible values and 38.1 and 8.5 $mg \cdot l^{-1}$, respectively, NO_3^- between 0.4 and 26.3 $mg \cdot l^{-1}$, phosphorous (as P_2O_5) between negligible values and 14.0 $mg \cdot l^{-1}$, the anionic surfactants between negligible values and 12.4 $mg \cdot l^{-1}$.

The significant oscillations observed were mainly due to the different flow rate of the river, depending on the season. It has been noticed that the highest values of the parameters above reported, i.e. the highest pollution level, was found in the vicinity of the mouth and of small villages and fields.

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In order to prove the effectiveness of the photocatalytic method to degrade organic pollutants dissolved in actual aqueous effluents, some selected experiments were carried out in a commercial Pyrex batch reactor (1.5 L) by using two different photocatalysts: a polycrystalline TiO_2 sample Degussa P25 (mainly in the anatase phase) and a home prepared polycrystalline TiO_2 sample. A medium pressure Hg lamp (500 W, $\phi_i = 19.3$ mW·cm^{-2}) immersed within the photoreactor was used and oxygen was continuously bubbled during the runs. The solid was suspended in the water samples withdrawn from the river and the total organic carbon concentration (TOC) was monitored at different time of irradiation of the suspensions.

The photocatalytic method has been successfully used for the degradation of many organic molecules in heterogeneous aqueous systems in which polycrystalline semiconductors have been suspended and the potentiality of the method has been highlighted by several authors [1-2]. Synthetic aqueous solutions of a large number of single pollutants or mixtures of them have been successfully treated but to-date only few studies dealing with actual aqueous effluents or reporting the scale-up of photoreactors for the remediation of polluted sites do exist [3-5].

The results obtained in this work showed that TOC (1.3-2.7 mg·l^{-1}) became virtually zero after ca. 7 hours of illumination and no significant differences were observed for the home prepared and commercial TiO_2 specimens.

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CATALYTIC SYSTEM BASED ON HPCM FOR CLEANING ENGINE EMISSIONS

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From 1977 in RETC PM catalysts based on high porosity cellular materials (HPCM) are developed, in particular unique catalysts for convertion of fuel for supersonic flying apparatus and stabilization of gas environment in super-power laser were developed. Since 1990 were developed and passed through industrial tests catalytic systems for clearing gas exhausts from metallurgical and chemical manufactures, transport, power objects. In 1994 RETC PM carried out export de- livery of catalysts to Austrian firm "Chemi-Linz" and for the first time in Russia and NIS received the certificate of conformity on catalytic convertor of engine emission.

In 1995 an experimental party of 40 convertors of engine emission to automobiles ZIL-130 for municipal transport in Moscow was supplied and resource test in 150 thousand km of covered distance was completed by convertor of engine emission to the diesel engine of the automobile KAMAZ-5511 in Perm.

In 1996 RETC PM carried out 2 contracts on delivery of pilot-scale samples of convertor of engine emission to carburettor engines for Japanese firm "Honda" and within the framework of joint work supplied filters-afterburner of soot and hydrocarbons in exhaust gases from diesel engines for Indian National Institute of Researches in the field of guards of an environment and Kharkov NPO named in honour of Malishev - the main producer of diesel engines in Ukraine.

In 1996 at Kirov NPO (Perm) catalytic set up developed in RETC PM with heating blocks from current-conductor HPCM for afterburning of engine emission from reactors, working in conditions of dynamic vacuum (1-10 millmeter of Hg) started to operate, that expanded opportunities of application catalytic afterburning of exhaust gases at low temperature and concentration of toxic organic compounds, and allowed to refuse from complex system for absorbtion of flying organic compounds, which put out of action working bodies of pumps and poisoning an atmoshere at industrial apartments. This catalytic system can find application at cleaning of exhaust gas from chemical reactors, biochemical installations, in varnished manufactures, in fuel tanks, in furnaces for reburning wastes, installations for casting accordint to burning models, engines of internal combustion at cold start-up.

At present at Perm enterprises the following systems for cleaning of gas emission in atmosphere based on HPCM are established:

1. Joint-stock company "Kamkabel" - four-year operation of catalytic systems for reburning ejections from porcelain wires, replacement of import catalytic blocks and their regeneration. A degree of reburn is 90 %. Cleaning of exhaust gases on chromate bay (clearing up to PDV of chromium anhydride) cleaning of exhaust gas in foundry site.

2. Kirov NPO - cleaning up to extreme permissible exhaust emissions from manufacture "Akril" on filters-absorber, catching dioctylphthalate from manufacture of penoplen and oil-cloth on filters of exhaust gases, degree of cleaning is 60 %, reburning and catching of acrolein in emissions from vacuum pumps of chemical reactors in manufacture of pitches.

3. Joint-stock company "Kamtex" - HPCM in systems of fire barrier and catching filters of acids and alkalis aerosols.

4. Joint-stock company "Velta" - pilot-scale catching filter of chromium anhydride from electrolytic manufacture.

Experience of operation of systems for cleaning gas exhausts based on HPCM shows that quality of cleaning gases and the resource of work corresponds to the best world samples at smaller material capacity.

NO CONVERSION UNDER INFLUENCE OF OXYGEN FROM $YBa_2Cu_3O_{6+x}$

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The superconducting ceramic $YBa_2Cu_3O_{6+x}$ catalyzes NO reduction in the presence of oxygen excess [1]. The molecular oxygen in gas mixture allows even to rise NO conversion for another catalysts [2].

In the present work the catalytic NO decomposition (1% NO, 99% O_2) on the ceramic $YBa_2Cu_3O_{6+x}$ (x=6,91 for A-sample and x=6,68 for B-sample) is studied to reveal the role of its nonstoichiometric oxygen. It is found that there are two areas of oxygen thermodesorption for A-sample (with peaks at 500 and 630^{0}C) and only one for B-sample (the peak at 630^{0}C). We believe that it is connected with different forms of weakly bonded oxygen. The NO conversion curve like the oxygen thermodesorption curves. The reaction goes according to $2NO \rightarrow N_2+O_2$ stoichiometry. The start and finish of oxygen thermodesorption coincide with start and finish of NO conversion. It is obvious, that the nonstoichiometric oxygen escaping (O_2-lattice->O-ads.->O_2) is a part of conversion process and provides the NO reduction and, probably, appearing of active centers due to the formation of new anion vacancies in ceramic studied.

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Peculiarities of the Selective Reduction of NO with Alkanes in Presence of CO over Multicomponent Oxide Catalysts

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Selective catalytic reduction (SCR) as a method of reducing NO_x content in exhaust emissions from both mobile and stationary sourses attracts intent attention nowadays in connection of using hydrocarbons as possible alternative reducing agents instead of toxic ammonia and its derivatives. Basic achievements in this field of ecological catalysis are connected with working out new zeolite catalysts containing ions of different metals [1-3].

However, from our point of view, the investigations don't cover a wide field of commercial catalysts that don't relate to SCR process.We fill in this gap in our research where we investigated commercial oxide catalysts that don't contain neither zeolites nor noble metals.

Peculiarities of redox reactions in the process of NO reduction with alkanes (CH_4 or C_3H_8) in presence or absence of CO were investigated over multicomponent metal oxide (Cu, Fe, Cr, Ni, Zn) catalyst (MC) in laboratory flow reactor with fixed-bed catalysts in a flow of N_2. The catalyst was prepared from only commercial materials. Activity tests were carried out in a on-line temperature range 200-500°C at GHSV range 10'000 - 17'000 h^{-1} with gas chromatograph (Chrom - 5) and gas analyser (TestTerm). The model gas mixtures contained :

(1) 400 ppm NO; 0.38 % vol. C_3H_8; 3.8 % vol. O_2; balance N_2;
(2) 300 ppm NO; 0.32 % vol. C_3H_8; 0.34 % vol. CO; 3.2 % vol. O_2; balance N_2;
(3) 400 ppm NO; 0.35 % vol. C_3H_8; 1.0 % vol. CO; 6.0 % vol. O_2; balance N_2;

(4) 440 ppm NO; 0.047 % vol. CH_4; 0.08 % vol. CO; 3.0 % vol. O_2; balance N_2;
(5) 290 ppm NO; 0.12 % vol. CH_4; 0.05 % vol. CO; 3.8 % vol. O_2; balance N_2;

Our results show that propane is more effective at nitric oxide conversion than methane over MC catalyst. In mixtures (2,3) containing propane the maximum conversion value is higher ($X_{NO} \approx 73$ %) than the same for the model mixtures (4, 5) containing methane($X_{NO} \approx 32$ %).

Oxidation of hydrocarbons and CO to CO_2 over MC catalyst run quantitatively at temperature ranges 350-500°C and 250-500°C accordingly.

Adding CO into the mixture, containing C_3H_8 as a reducing agent, increases conversion of NO from 40 % (for mixture 1) up to 73% (for mixtures 2,3) and this effect doesn't depend on concentration of CO in 0.34-1.0 % vol. range.

Functions of conversion from temperature for NO, CO, CH, O_2 are shown in Fig. 1 in comparison with the data received over Cu-ZSM-5-59 catalyst [3]. The upper results show that the multicomponent oxide catalyst has high activity and selectivity that translates to its high three-way performance.

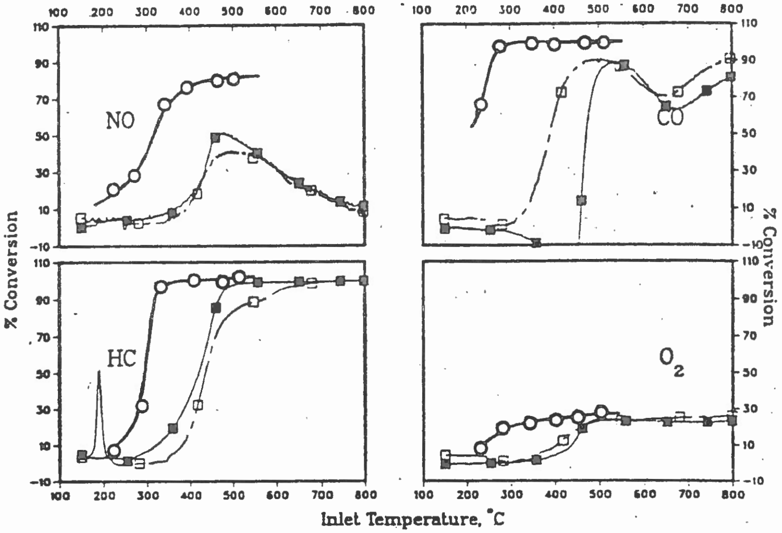

Fig.1 Conversion of NO, CO , HC, O_2, as function of temperature over Cu-ZSM-5-59 with propene (■) or propane (□) [3] and over MC catalyst with propane (O).

The multicomponent catalyst was examined for lean-burn NOx reduction in real exhaust gases of a gasoline engine with carburator without addition of supplementary reduction agents. Efficiency of decreases in content of toxic components in real exhaust gases consists NOx - 55 %, CH - 67 %, CO - 75 %.

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Density Function Investigation on the Decomposition of Nitrogen Oxide on Cu Sites

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Nitrogen oxides, in addition to SO_2, are among the most common gaseous emissions which pollute the air and environment. Their source is essentially the thermal combustion of fossil fuels, various mechanisms are involved in their formation. The reverse reaction $NO \rightarrow \frac{1}{2} N_2 + \frac{1}{2} O_2$, which is thermodynamically preferred, is however, nearly completely inhibited by the high activation energy. The modest yield can be increased if it is possible to lower the activation energy through the use of catalysts.

Since the 1970s, increasing international effort has been directed toward the establishing of selective catalytic decomposition (SCD) on an industrial scale, as this mechanism is in principle superior to other nitrogen oxide control measures [1]. Currently the main objective is to produce catalysts with sufficiently high SCD activity which at the same time offer acceptable service lives on a laboratory scale. At the present, the fact that the associated mechanisms are largely unexplained is a major obstacle to developing catalysts for SCD on a fixed time schedule.

Recently copper ion exchanged zeolites have been under investigation as catalysts for NO decomposition [2]. Following recent studies the catalytic copper species should be Cu(I) [3], as fact which also was topic of our research.

Although much work was done on kinetic studies, there is little known about the molecular properties of the catalytic process. Our aim was to investigate the molecular level of NO decomposition in order to evaluate the catalytic mechanism.

The work was done with the Gaussian 94 program, using mainly its DFT feature to determine structures and energies of intermediates such as Cu^+-NO, ON-Cu^+-NO, Cu^+-ON and NO-Cu^+-ON at a high level of theory.

As reported in several publications[4] the Si/Al-ratio in ZSM-5 is of great influence to the catalytic activity. We also evaluated the effects of the zeolite environment on the stability of Cu(I). This work was done with semiempirical methods, because of the large number of calculated atoms.

The results confirm the nature of the catalytic mechanism and the oxidation state of the involved catalytic sites.

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FLUID-SOLID SYSTEMS IN A NEW ENERGY-SAVING ENVIRONMENT PROTECTION TECHNOLOGIES: RESEARCH STUDIES AND INDUSTRIAL APPLICATIONS

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The novel conceptions in application of dense fixed, moving and fluidized beds of granular catalysts-adsorbents for adsorptive-catalytic and thermocatalytic decontamination of volatile organic compounds (VOC) from industrial exhaust gases are suggested.

Some findings of theoretical and experimental research studies of mechanical, structural, and physico-chemical properties, micro-and macrokinetic adsorptive, catalytic and regenerative characteristics of heterogeneous low-percentage catalysts applied for decontamination of such typical industrial VOCs as alcohols, ethers, phenols, aldehydes, ketones, aromatic hydrocarbons and their mixtures in different concentrations and contents are reported. Basic results on fluid and solid dynamics, heat and mass transfer in fixed, gravity-moving, and fluidized catalyst beds functioning in a new gas cleaning equipment are presented. Correlations for calculation of the parameters under investigation are proposed. Fundamental results obtained in research were used as guidelines in the development of advanced industrial systems and equipment for VOC decontamination.

The schematics are shown and operating principles of novel energy-saving (1) adsorptive-catalytic with gravity-moving, fluidized beds and pneumatic conveying system, (2) thermocatalytic with a quasistationary fluidized bed, and (3) thermocatalytic with a fixed catalyst bed and deep intercyclic heat-recovery technologies of industrial toxic VOC decontamination are described.

It is shown that at the optimal calculated design and operation parameters of the suggested VOC decontamination systems, their dimensions may be essentially decreased, high value of gas cleaning efficiency (up to 98-100%) and thermal energy (heat) recuperation (up to 96%) are attained.

NEW COMMERCIAL CATALYST FOR PHTHALIC ANHYDRIDE PRODUCTION

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Catalyst is a factor certifyng the level of technology for a phthalic anhydride production plant. It is obvious that the process equipment and auxiliary facilities should be able to use fully the catalyst employed. Protection of catalysts from thermal destruction or slow deactivation is a common problem for reactor designers and catalyst producers. Despite design limitations, especially referring to efficient heat exchange, increasing expectations from phthalic anhydride producers resulted in the solution of the problem.

1. Reaction gases containing over 60 g/Nm^3 of hydrocarbons cause no risk of catalyst's thermal destruction. Modelling a catalyst bed contributed to solving this problem[1]. Using of two catalyst beds of different activity specifications slows the reaction down in the reaction gases feed zone. Hence, the temperature of hot spot is lowered. The temperature profile along the catalyst bed reveals the second peak which is located in the catalyst's bottom layer. More uniformly distributed reaction rate did not reduce the overall yield of phthalic anhydride.

2. For economic reasons, the prevailing process solutions are those which assume complete conversion of o-xylene. Hence, the phthalic anhydride product is accompanied in the reaction outlet gases only by the products resulting from over -oxidation: maleic anhydride, benzoic acid, citraconic anhydride and carbon oxides. In this case, even the yield of phthalic anhydride is 75-80 % mol., about 50 % of reaction heat is formed during oxidation of o-xylene to maleic anhydride and carbon oxides. Attempts to define the reaction network[2] pointed to the new direct preparation of the catalyst with results:

- increased selectivity to phthalic and maleic anhydrides;
- decreasd selectivity to carbon oxides.

Lower exothermic effect allows one to use very high concentrated reaction mixture and to increase production capacity of phthalic anhydride.

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THE EFFICIENCY OF CLAUS CATALYST IN TECHNOLOGY OF SULFIDE GASES UTILIZATION

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Instability of technological gas performance and fluctuations of its components contents are the main features of metallurgical off-gases that can lead to decreasing of their utilization efficiency. As applied to elemental sulfur recovery from sulfide roaster gases, the actual efficiency of Claus catalyst unit at Norilsk Copper smelter plant was investigated. The data set of a large-scale (35000 m^3/h of feed gas) pilot catalytic converter survey that was performed during routine manufacturing of elemental sulfur in operation periods of 1993-1994 was used.

The obtained results of measurements and their analysis show that the activity of the traditional alumina based Claus catalyst with grain size above 5 mm towards the recovery of elemental sulfur is low. Indeed, the experimental data show that elemental sulfur yield (about 75 rel. %) is maximum at 250 - 280°C, whereas in line with equilibrium model, the highest yield is supposed to achieve almost 100 % at lower temperatures. The characteristic difference between the equilibrium model forecast and experimental data at temperatures below 280°C allows to identify the principal route and limitation mechanism of the process.

The main reason for impairing of the activity towards the recovery of elemental sulfur from both hydrogen sulfide and sulfur dioxide is the catalyst aging by sulfation that occurs mainly because of stoppages. Using data sets on catalyst converter survey, we have found the catalyst activity increases from 0 to 90 % of maximum activity during 10 hours of continuos operating on line. Thus fact can be interpreted as an evidence of the catalyst regeneration in the reduced sulfide gas environment.

The available statistical data on malfunctions make ti possible to estimate the elemental sulfur yield losses because of catalyst sulfation. It was found that in practice the mean yield of elemental sulfur in real metallurgical off-gas utilization processes is one-third or one-forth less than in non-stopped one.

Another significant result of our investigations is that when real catalysts are employed, the effect of the reducing agents to oxidants ratio in feed gas on conversion coefficients of H_2S, CO, COS, H_2, SO_2 is negligible in comparison with the agreed-upon opinion. This fact, form our point of view, is a result of kinetic limiting conditions due to the low activity of the real catalyst.

By using varying intervals between sampling (the method of varying sampling frequency) the spectral power density of fluctuations of concentrations for the main components of technological gas in the frequency range 10^{-5} - 10^{-2} c/s was measured. Basing on the spectral density measurements and our empirical model for conversion coefficients as functions of technological gas composition, we arrived to a conclusion that there is no need in designing and using a special monitor and adjustment system to control the feed gas (metallurgical off-gas) composition.

Generally the results of large-scale pilot catalytic converter survey show that the catalytic activity diminishes greatly under unsteady operating conditions, for example, in the studied case of metallurgical off-gases utilization technology.

Model Systems of SO_2 Oxidation Catalysts: Thermal, Spectroscopic and Electrochemical Characterization

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Introduction

The industrial catalyst for oxidation of SO_2 is in the oxidized state well described by the model system $K_2S_2O_7$-V_2O_5. It has therefore been of great interest to investigate this system in order to establish the phase diagram and identify the compounds formed in the melt. At rather low vanadium concentrations the phase diagram was established by using electrical conductivity and DSC. However, at higher concentrations this was very difficult due to the dark colour and high viscosity combined with ability to form glasses in stead of crystalline compound in the V_2O_5 rich side of the phase diagram. Only recently it was possible to measure the liquidus temperatures in this concentration interval by recording ^{39}K high temperature NMR spectra at several temperatures for each composition. By plotting the line width versus the temperature two almost linear region were found and the intercept taken as the liquidus temperature.

During operation the catalyst is partially reduced to V(IV) by SO_2 which at temperatures below around 430 °C precipitates into crystals like $K_4(VO)_3(SO_4)_5$. However very little is known about the V(IV) complexes in the liquid state. In order to investigate the V(IV) complex formation a potentiometric cell has been constructed to measure the sulphate coordination to V(IV) in the liquid state.

Results

The phase diagram of $K_2S_2O_7$-V_2O_5 is presented in figure 1. Two compounds are formed at $X(V_2O_5) = 0.25$ and 0.33. Additional crystallographic work has shown a compound is formed at $X(V_2O_5) = 0.5$. The melting points are 352 °C, 398 °C and 425 °C respectively. The compounds may be formulated as $K_3VO(SO_4)_3$, $K_4(VO)_2O(SO_4)_4$ and KVO_2SO_4. Three eutectics are found at $X(V_2O_5) = 0.17$ (melting point 314 °C), $X(V_2O_5) = 0.27$ (melting point 348 °C) and $X(V_2O_5) = 0.39$ (melting point 366 °C). This phase diagram deviates significantly from diagrams published by others[1,2] where only one eutectic has been found and with peritectics and no maxima. These diagrams are however made by thermal methods which are not reliable due to the glass formation.

A potentiometric cell consisting of two chambers separated by an electrical conducting sintered glass filter disk was constructed. The measuring chamber contained $K_2S_2O_7$ almost saturated with K_2SO_4, the reference chamber contained $K_2S_2O_7$ completely saturated with K_2SO_4. Small crystals of V_2O_5 was added to the measuring chamber in an atmosphere of 1 bar of SO_2. The potential was measured with a 6½ digit multimeter (internal resistance > 10 MΩ). The coordination number defined as number of sulphate ions coordinated per vanadium atom is plotted versus $p([SO_4^{2-}])$. The curve approaches a coordination number of 1.5 for increasing sulphate concentration. This result is consistent with the following reaction:

$$V_2O_5 + S_2O_7^{2-} + SO_2 + SO_4^{2-} = 2VO(SO_4)_2^{2-}$$
$$VO(SO_4)_2^{2-} + SO_4^{2-} = VO(SO_4)_3^{4-}$$

An EPR spectrum recorded on the sample at highest V concentration (0.075 M) at 450 °C confirmed that V(IV) indeed is a monomer complex.

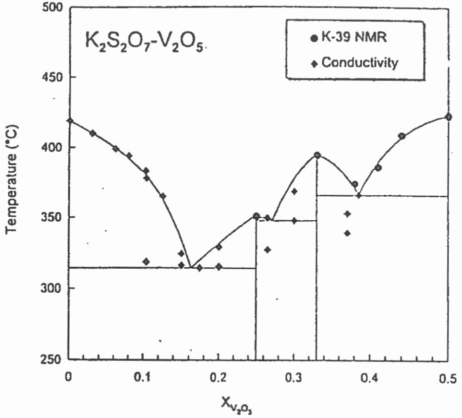

Figure 1. Phase diagram of the $K_2S_2O_7$-V_2O_5 system.

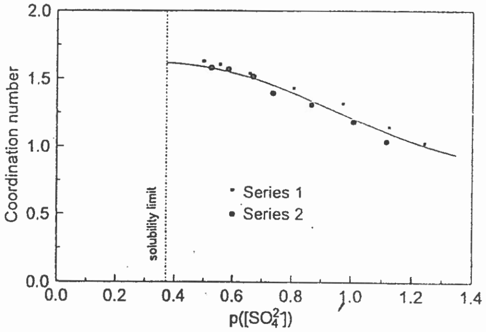

Figure 2. Coordination number of SO_4^{2-} to V(IV) at 450 °C, C(V) < 0.075 M

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NON-TRADITONAL APPLICATION OF CATALYSIS - DESTRUCTION OF MIXED RADIOACTIVE ORGANIC WASTES

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At nuclear material processing plants in Russia and the USA there are large quantities of accumulated mixed organic wastes of complex composition containing industrial and vacuum pump oils, used extractants and their solvents and various hazardous organic compounds contaminated with uranium, plutonium and their fission products. These wastes represent a threat to the environment upon their storage and treatment because of the combination of inflammability, explosiveness, toxicity and radioactivity. Development of environmentally clean technology for destruction of these wastes is an urgent problem. The method of high-temperature flame incineration is hazardous for the environment because it leads to secondary waste streams and generation of sub-micron radioactive particles emitted into the atmosphere.

At Boreskov Institute of Catalysis (BIC) a method of environmentally clean fuel burning and destruction of hazardous wastes using flameless catalytic fluidized bed combustion has been developed [1, 2]. A unique feature of this method is the possibility of total oxidation of organic compounds in stoichiometric mixtures with air at low temperatures (600-750°C) to prevent thermal NOx formation. This technology was tested in pilot and prototype plants for combustion of various fuels and organic wastes, including spent scintillation fluids. The tests revealed the following main advantages of the proposed waste incineration technology: high efficiency of waste destruction; suppression of the formation of pollutants (NO_x, CO, HC); elimination of secondary waste streams.

We have initiated the project "The development of technology of catalytic fluidized bed destruction of mixed organic waste containing radionuclides" in cooperation with a number of nuclear processing enterprises of Russian Ministry of Atomic Energy (Minatom) [2-5]. The purpose of the project is to develop a new, environmentally safe process of destruction of mixed wastes and create a prototype demonstration plant with a capacity of 50 t per year at the Plant of Chemical Concentrates in Novosibirsk. The other institutions participating in the project are nuclear material processing plants in Tomsk-7, Krasnoyarsk-26, Krasnoyarsk-45 and Angarsk, and foreign collaborators from USA, UK and France.

Initially the experiments on catalytic destruction of model mixtures representing mixed wastes from nuclear material processing plants were carried out. For this purpose the experimental setup was built at NGPII VNIPIET for the study of simulated waste catalytic oxidation and purification of exhaust gas from acid gases and dust particles. It includes catalytic reactor, cyclone, jet scrubber, two absorber-condensers and aerosol filter. At the BIC efficient catalysts were developed, and catalyst batches were manufactured for the joint studies of waste catalytic destruction in this installation. The experiments on fluidized bed destruction of various oils (AI-50, VM-4 etc.) and tributylphosphate solution in hydrocarbon solvents, supplied from nuclear material processing plants were carried out. The experiments showed high efficiency of waste destruction. Environmentally clean flameless catalytic oxidation combined with efficient gas cleaning system provided low concentrations of pollutants in the exhaust gas. The process optimization allowed to bring down the concentrations of NO_x to 5-30 ppm, CO to 1-20 ppm and SO_2 to 1-10 ppm. The tests carried out on the experimental setup at the Plant of Chemical Concentrates confirmed high efficiency of the method of catalytic fluidized bed combustion for destruction of real radioactive wastes of the Plant.

Basing on the results of these experiments technological scheme and design documentation of the demonstration plant for mixed waste destruction were developed. Currently the construction of the plant is in progress.

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INFLUENCE OF ANION MODIFYING OF TiO_2 ON PROPERTIES OF COPPER-TITANIA OXIDE CATALYST

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Copper-titania oxide catalysts are active in reactions of deep oxidation and selective catalytic reduction (SCR) of NO by ammonia. It was shown that the activity of the catalytic system depends on the nature of impurity in parent titania. There are two main industrial ways to prepare TiO_2: sulfuric acid treatment and chlorination of titania-containing raw materials. As a result of these ways of preparation TiO_2 contains either SO_4^{2-} or Cl^- anions. According to literature data impurities of those in TiO_2 influence distribution of acid-base sides of anatase surface.

The aim of the work was to study the influence of titania modifying by Cl^- and SO_4^{2-} ions on properties of Cu-Ti-O catalysts. It includes study of acid-base and adsorption properties of modified carriers and catalysts, states of copper ions in catalysts and catalytic activity at SCR of nitric oxide by ammonia.

Impregnation of anatase by copper nitrate, chloride or sulfate solutions and adsorption from copper-amino complex were used to prepare the catalysts. The carriers were pure titania or one specially modified by chloride or sulfate ions as well as industrial samples prepared via sulfate or chloride technologies.

Adsorptive and acid-base properties of carriers and catalysts surface were studied by IR-spectroscopy and TPD of CO, NO, NH_3 used as test molecules. Interaction of Cl^- ions and TiO_2 was shown to block strong Lewis centers completely. According to NH_3 adsorption data Bronsted acid sites were found out at introduction more then 1 wt. % of Cl^- ions in the carriers. The coordination of sulfate adspecies with anatase depends on a concentration of sulfate ions on surface. Finally as the SO_4^{2-} concentration increases the formation of a phase of titanyl sulfate occurs. It was accompanied by growth of Lewis and Bronsted acid sites. The introduction of Cl^- and SO_4^{2-} ions influences spectra TPD of NO variously. In the case of chloride ions the bond strength of NO with titania surface was decreased. At the presence of sulfate ions on titania surface new high-temperature peaks were observed in TPD spectra.

States of copper ions in catalysts were studied by diffuse-reflectance UV-VIS spectroscopy, TPR by H_2, X-ray analysis, ESR. The described changes of surface TiO_2 properties at introduction of the anion additives was shown to be reflected in a specific interaction of the modified carrier with copper salt used and in catalytic properties of catalysts synthesized. Various states of copper ions on titania surface were described and its contents were appreciated.

The introduction of chloride anions at synthesis of catalysts reduces a catalytic activity at SCR of NO by ammonia within the temperature interval (150-400°C). Modifying of the initial carrier by SO_4^{2-} ions decreases the activity of the catalysts in the low-temperature region (150-200°C) but increases it in the high-temperature one (250-400°C). The catalysts synthesized by above mentioned technique are stable to poisoning sulfur oxides.

Thus various influence of sulfate and chloride impurities on acid adsorptive property as well as on catalytic activity of Cu-Ti-O catalysts has been shown. Multiformity of copper ions states and their relative content was shown to depend on contents and nature of anion additives as well as concentration of copper salts and method of catalysts preparation. So the knowledge received enable to synthesize new catalysts with required properties.

REGULARITIES OF DEEP AND SELECTIVE OXIDATION OF HYDROGEN SULFIDE

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Several kinds of fuel and tail gases contain H_2S that must be separated to satisfy the sanitary and technological demands. Selective oxidation by O_2 to sulfur is the most desired way to purify of gases from H_2S. But in some cases especially for detoxication of waste gases containing toxic organic and sulfur organic substances complete oxidation to CO_2 and SO_2 is suitable method for gas cleaning.

In both cases of deep and selective oxidation, the sulfation of the surface of catalysts is the main reason of reduction of the activity, surface area and mechanical strength. The formation of metal sulfates is detected by XRA, XPS and chemical analysis of samples of catalyst treated in the atmosphere containing oxygen and sulfur compounds. Mixed oxide catalysts were found more stable against sulfation. Copper chromite in the form of spinel demonstrates good stability in both cases and don't loose greatly its potential during long time experiments.

By selective oxidation of H_2S to sulfur in the temperature range 120-200°C the fall of the activity of catalysts takes place due to the adsorption of sulfur on the surface of catalysts. The catalyst may be regenerated to initial activity by evacuation of sulfur in different ways. By use commercial chromite catalysts (IKT-12-8 K-16U) it is possible to oxidize H_2S without visible oxidation of hydrocarbons, that is important for purification of natural gas.

The choice of catalyst of high selectivity to produce sulfur shows that typical catalysts of deep oxidation demonstrate high activity in H_2S oxidation, but low selectivity. According to the Boreskov's conception oxide catalysts contain surface active oxygen bound with ions of transition metal in high oxidation state. This oxygen is responsible for oxidation catalyst activity. In the case of H_2S, the interaction with such oxygen gives SO_2 and SO_3 molecules. As it was noticed by operations with V_2O_5-catalyst partial removal of active oxygen increases the selectivity of sulfur production. Possibility of 2 regimes of reaction yielding sulfur or SO_2 was shown. Periodic changes of parameters may be registred in the course of time. The mechanism of oscillations may be connected with the competitive processes of sulfur and oxygen adsorption on the surface of catalysts. On the base of laboratory and pilot scale experiments of H_2S oxidation some recommendations are given for technological applications of the processes.

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SYNTHESIS AND STUDY OF PALLADIUM CATALYSTS PREPARED FROM PALLADIUM ACETATE FOR OXIDATIVE CLEANING OF GAS EXHAUSTS

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It is known that industrial catalysts of oxidative cleaning of exhaust gases of benzene and diesel engines contain palladium. Due to increased requirements to the cleaning of gases from hydrocarbons, improvement of SPAK-0,5 (0,5% Pd) palladium catalyst supported on granulated alumina has been carried out using teta-Al_2O_3 as a support, palladium acetate as a starting compound, impregnation in a flow-circulation apparatus from toluene solutions with addition of acetic acid and its salts. Optimal conditions of synthesis of catalysts with a decreased content of palladium (0,1-0,2%) have been determined: the palladium concentration in the impregnation = 0,19-4,37 g/l; the mole ratio of palladium acetate to acetic acid = 1:(0,25-3,3); the circulation rate of the impregnating solution = 25-100 h^{-1} with the subsequent drying in nitrogen and reduction in a nitrogen - hydrogen mixture or heating in air at 300-400° C. Compared with SPAK-0,5 the above catalysts provide better cleaning of exhaust gases from CO (89-97%) and hydrocarbons (62-86%) at ratio of air: fuel $\geq 0{,}96$ under thermal cyclization conditions on a panel within 80h [1,2].

With the new method of preparation, Pd and Pd with Co (in the mixed catalyst) are uniformly distributed to 0,1-0,25 mm (in Pd/Al_2O_3) and 0,4-0,5 mm ($Pd\text{-}Co/Al_2O_3$) depth which does not change on high-temperature heating (900° C, 25 h in air).

The pilot technology of Pd catalysts has been implemented on the equipment of the Katalyzator Company.

The electronic state, dispersity, and morphology of palladium particles and palladium structure as well as resistance to sulfuric anhydride has been studied by EXAFS, XPS, TPR, IR, electronic microscopy and X-ray low-angle scattering methods. It is shown that with the new method of preparation on the support surface there from cluster particles of Pd(O) uniform in size (40-60 Å for Pd/Al_2O_3 and < 20 Å for $Pd\text{-}Co/Al_2O_3$), different from SPAK-0,5 (impregnation by Na_2PdCl_4 solution + ethanol, 40 to 120 Å Pd particles). Those particles do not aggregate due to their surface oxidation with formation of associated polyhedra of PdO_4 with a reduced

(2,70-2,74 Å) Pd-Pd distance and, perhaps, mixed palladium and cobalt oxides. This creates active sites on the support surface for simultaneous activation of oxygen (PdO or mixture of Pd and Co oxides), carbon monoxide (Pd(O)) and a double propylene bond (Pd-Pd).

Introduction of cobalt into the catalyst hinders the formation of sulfates of active elements and aluminium causing poisoning of catalysts [3,4].

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PPII-75

Coal desulfurisation - some models for organic sulfur removal

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Catalysts for the hydrodesulfurisation of oils are well established but relatively little is known of the mechanism by which they operate. The organic desulfurisation of coal presents an even greater chemical and practical challenge.

It is believed that the bulk of organic sulfur in coal is present within "benzothiophenic" and "dibenzothiophenic" environments. It is known that there exist metal complexes which can actually desulfurise thiophene under mild conditions, but the reactions of these materials with benzo- and with dibenzothiophene do not proceed to the desulfurisation stage.

Investigations with compounds containing other group 6 elements (Se, Te) suggest that the difficulty presented by the more condensed thiophenes is thermodynamic rather than mechanistic in origin.

INNOVATIVE LOW TEMPERATURE OZONE-CATALYTIC TECHNOLOGY FOR VOC REMOVAL

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Catalytic methods of removal of low concentrations of VOC have a serious drawback - a considerable energy consumption for heating a gas mixture to maintain a required temperature in a reaction zone. Ozone-catalytic process is most economical on a large-scale purification of low-concentration gas exhausts. The reason is that the ozone amount which should be supplied to a reaction zone is proportional to the VOC content in the gas phase, while in conventional catalytic oxidation (at slight adiabatic heating) energy consumption for gas heating is proportional to the total gas volume. Therefore a development of the method of deep ozone-catalytic oxidation of VOC, permitting a sharp decrease in operation temperature, is of great practical importance. The process holds much promise, since owing to the extraordinarily high chemical activity of ozone the temperature threshold of catalytic oxidation of organic compounds significantly decreases.

We have studied the process of deep catalytic oxidation of hydrocarbon vapors by ozone over a mechanically activated copper (II) oxide catalyst ICT-12-9 promoted by 3-5% mass. Al_2O_3 (specific surface is 30±5 m^2/g), not containing noble metals. Studies have shown that at the initial aromatic-hydrocarbons concentration up to 150 mg/m^3, process temperature 40-60°C and GHSV of 10000 h^{-1} the oxidation degree is no less than 94%. The catalyst is highly active in dry and moderately moist gases.

Using a chromatographic mass spectrometer it has been established that under above conditions a deep hydrocarbons oxidation by ozone over ICT-12-9 yields no intermediate products.

The ozone-catalytic oxidation of toluene vapors shows that the rate of the process performed at 60°C is equal to the rate of the conventional catalytic reaction carried out at 225°C. Thus, using ozone permits one to decrease the process temperature for about 200°C under the same reaction conditions, which is of great importance for practical application of the process.

The direct proportional dependence of conversion on the residence time indicates a zero order of the reaction. This is explained by the strong toluene vapors adsorption on the catalyst surface at low temperatures. Using a zero-order equation for a reaction, the rate constants for the ozone-catalytic oxidation of toluene were calculated from the experimental data: the activation energy $E=14050\pm1070$ J/mol, pre-exponential factor $k_0=62.87$.

Most industrial off-gases are multicomponent, which is caused by using complex solvents and mixing of gas exhausts from various technological processes in the same ventilation system.

To reveal the regularities of oxidation of hydrocarbons of various types oxidation of both individual components and their mixtures have been studied. Oxidation of the acetone-toluene vapors mixture was performed at $T=60^{o}C$, gas humidity of 9 g/m^3, GHSV =10000 h^{-1} and ozone concentration of 1000 mg/m^3.

The positive results of the laboratory studies of the ozone-catalytic oxidation of organic-compound vapors over a copper oxide catalyst ICT-12-9 were used in the design of a pilot installation OKA-3000 of 3000 m^3/h capacity for the "Sever" Production Incorporation (Novosibirsk).

For efficient performance of ozone-catalytic VOC oxidation, the developed catalytic reactor with separate ozone introduction into each catalyst layer was used.

Placement of various catalysts in the adjacent sections permits detoxication of a variety VOC. Moreover, the catalyst in the last section may be used for ozone decomposition. A distinctive feature of the OKA-3000 installation is the presence of a passive element - adsorption dampher which is a layer of sorbent functioning under isothermal sorption-desorption regime. This approach leads to a sharp diminishing of fluctuations in VOC concentrations of the inlet to the ozone - catalytic reactor and, consequently, to reduction of ozone waste. The setup advantages include relatively low process temperature, low energy consumption, possible oxidation of gas mixtures or selective oxidation of individual component, efficient operation with variable initial concentrations, possible purification of moist gases, and no emission of unreacted ozone.

THE LIQUID CATALYTIC METHOD "SLP" FOR PURIFICATION OF INDUSTRIAL GASES GONTAINING TOXIC COMPOUNDS

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The nature-destroying character of industrial development has made scientists unite and work out the conception of so-called sustainable development. One of the requirements of this conception is environmental protection. So, the survival of mankind cannot be based on the existing technologies.

A number-of-years study of our researchers culminated in the method-SLP (Simultaneous liquid purification), which provides a basis for the technologies meant for the purification of industrial gases from SO_x, H_2, HCN, As_2O_3 and NOx.

The method was originally designed for cleaning "tail" gases of the Claus plants.

Unlike conventional absorption-reduction methods, the SLP process provides the Claus reaction in the liquid phase in the presence of a homogeneous catalyst.

Usually an up-lifting gas bubbler is used for chemisorbing SO_2. and H_2S from gases using the solution of ammonium phosphates and thiosulfates at T=20-60°C, pH = 6.5-4.5. $H_2S : SO_2$ ratio in the gasses supplied should range from 1.5 to 4.0.

Later, three versions of the SLP technology were suggested for processing the metallurgy gases [1]:

SLP-2: sulfur recovery from "low-concentration" sulfur containing gases (<3.5 vol.%);

SLP-3: complex processing of "low-concentration" and "high-concentration" sulfur containing gases to produce sulfur;

SLP-As: complex cleaning of gases containing sulfur and As_2O_3 to produce sulfur and arsenium sulfide (III).

To process acidic gases (H_2S + CO_2) produced by the coke-chemical and petrochemical manufactures, we suggest the SLP-COKE technology [2]. For the processing of acidic gases containing HCN, the method allows one to convert HCN absorbed into ammonium rhodanide under particular conditions of Claus reaction in the liquid phase. The application of this method is limited by the capacity of sulfur producing plant. Unlike conventional gas-phase Claus processes the technology becomes profitable if the plant capacity is below 15 thousand ton of sulfur per year.

The latest version of the technology is SLP-HPP (Heat power plant) which allows a complex cleaning of flue gases from SOx and NOx [3].

For all versions, the commercial products obtained allow one to return current operation expenses, while for plants processing the acidic gases (H_2S + CO_2), the production of sulfur will return the capital expenses in 2-3 years.

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Metallurgical slags based catalysts for gas-phase oxidation processes

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The certain metallurgical slags have a high content of transition metal oxide compounds (Mn, Fe, Cr, V, Ti). Slags are characterised by a high thermostability, mechanical strength and low cost. These reasons allow to consider the metallurgical slags as raw materials for gas-phase oxidation processes catalysts preparation.

Catalytic activity of slag depends on its chemical and phase compositions and process for application selected. Because of low specific surface area of the slags and including of the transition metal ions in the thermodynamically stable silicates the original samples have poor catalytic activity.

With the aim to increase the catalytic activity slags were treated by aqueous solutions of mineral and organic acids. The interactions between different phases of slags and solvent used take place with a different rates. The specific surface area, chemical and phase compositions of the slags changed as a result of "differential solving" and catalytic activity increased sharply.

After pretreatment by acid solution metallurgical slags were promoted with cobalt, copper and chromium by impregnation of the samples in aqueous solutions of appropriate salts. During thermal treatment of the samples the interaction between promoters and active components of the slags can take place.

Original (I), acid treated (II) and promoted (III) slags were tested as catalysts for different processes of deep oxidation. I and II - for high temperature fuel combustion and for the process of fuel gases purification from soot. II - for gas-phase naphthalene purification by catalytic oxidation of the more active admixtures (in the process of "precontact" production of the phtalic anhydride) ; for high temperature exhaust gases purification from CO and organic compounds. III - for purification of exhaust gases from polycyclic aromatic compounds in the processes of cable and phtalic anhydride production and coal tar and coal pitchcoke plants.

The data on catalytic activity of different slag catalysts are present in the Table.

Table.

The temperature (°C) of the 100 % -conversion on the various types of slag catalysts. (fixed bed reactor, 1 % vol. in air, SV 10000 h^{-1})

Catalyst	2-methylnapthalene	o-xylene	CO
I	850	500	700
II	520		450 - 500
III	400 - 420	400 - 420	220 - 280

The slag catalysts posses a very good thermostability and mechanical strength, they are less expensive in comparison with the ordinary catalysts of deep oxidation processes.

Production of slag catalysts is organised on AO "ZAPSIB".

PHOTOCATALYTIC TREATMENT OF PAPER PULP BLEACH EFFLUENTS

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Heterogeneous photocatalysis, one of the so called Advanced Oxidation Processes (AOP's), has been tested as a method for treatment of paper pulp bleach effluents. The manufacturing of paper pulp generates heavily polluted waste waters containing high levels of TOC (total organic carbon), AOX (adsorbable organic halides) and color. The destruction of such contaminants by conventional biological methods is not well developed.

On the other hand, the AOP's are based on the generation of hydroxyl radicals (HO), very powerful oxidizing species which are able to promote complete degradation of any organic to CO_2. Photocatalysis uses powdered semiconductors (TiO_2, ZnO, Fe_2O_3, CdS,...) and near-UV to generate highly reactive hole-electron pairs which are the responsible for HO production.

Remarkable decreases in TOC, AOX, and color levels have been obtained when irradiating synthetic and real samples of paper pulp bleach effluents in presence of TiO_2, a safe (non-toxic), stable and non-expensive material. The kinetics of the photocatalytic process follows a zero order rate equation as expected for and heterogeneous catalytic reaction governed by the Langmuir-Hinshelwood mechanism in presence of a large concentration of reactants. Other parameters like temperature, initial TOC levels, pH or mass of catalyst employed have shown little influence in the course of the reaction. The data has been collected in batch bench-scale and continuous flow pilot-scale reactors, and in both cases the results have been compared with the performance of others AOP's like oxidation with Fenton reagent (H_2O_2 + Fe(II)) and ozonization. The yields of pollutant removal indicate that photocatalysis could be successfully applied for the treatment of large volumes of effluents.

Nevertheless, the combination of at least two AOP's (e.g. photocatalys plus ozonization) renders the best results in terms of largely reducing the reaction time.

PPII-80

SURFACE ADSPECIES ON THE Cu-ZSM-5 CATALYST AT THE SELECTIVE REDUCTION OF NO WITH PROPANE

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Cu-ZSM-5 catalyst is used as a model system to study the reaction of selective reduction of NO with propane. By now a reaction kineticshas been studied on this catalyst, states of copper have been investigated, various schemes of reaction have been proposed. At the same time each of offered schemes has limitations that does not permit to select the ultimate mechanism.

To understand the conversion of surface intermediates in reactions of decomposition/reduction of NO it is useful to investigate a joint adsorption of reagents.

In the present work the interactions of NO, NO_2, N_2O, O_2 and C_3H_8 with surface of the Cu-ZSM-5 catalyst have been studied by TPD.

Cu-ZSM-5 (1.3% Cu, Cu/Al=0.28) was prepared from H-ZSM-5 (Si/Al=19.5) by the traditional ion-exchange procedure between zeolite and aqueous solution of copper-amino complex (0.07M).

Several types of surface species have been observed at adsorption of NO on initial zeolite H-ZSM-5 and on catalyst. As the temperature increases decomposition of some of them occurs yielding N_2O. The ratio of adspecies depends on initial pretreatment of a sample and presence of reductants or oxidants at adsorption (Table 1). The adspecies observed in TPD spectra of N_2O after NO adsorption are varied from those in TPD spectrum of adsorbed N_2O.

The interaction of NO and O_2 at their joint adsorption changes spectra TPD of NO and oxygen. A desorption at high-temperature peak has been increased in spectrum of NO. A low-temperature desorption peak disappeared but high-temperature one related with decomposition of nitrite also increased in spectrum of oxygen (Table 2).

Table 1. Amount of N_2O desorbed from H-ZSM-5 and Cu-ZSM-5

adsorption	Amount of N_2O (μmol/g) desorbed at				
	135-160°C	215-220°C	270-275°C	320-365°C	total
		H-ZSM-5			
N_2O^{**}	1.3	–	–	–	1.3
$NO^{*}+C_3H_8$ (0.2 vol.%)	–	5.5	0.4	1.5	7.5
NO^{*}		5.0	4.8	1.6	11.4
$NO^{*}+O_2$ (2.2 vol.%)	–	–	–	1.3	1.3
		Cu-ZSM-5			
N_2O^{**}	9.0	–	–	–	9.0
$NO^{*}+C_3H_8$(0.2 vol.%)	8.6	12.0	1.2	3.8	25.6
NO^{*}	–	3.2	1.0	3.7	7.9
$NO^{*}+O_2$(2.2 vol.%)	–	2.7	1.0	3.3	7.0
$NO_2^{**}+O_2$(2.2 vol.%)	–	1.2	0.9	3.5	5.6

* NO content was equal to 0.04 vol.% in all experiments

** 500 μl of pure N_2O or NO_2 were passed through sample bed at adsorption

There has been a new desorption peak with maximum at temperature about 260°C in spectra TPD of NO and C_3H_8 after their joint adsorption. A desorption activation energy of the peak equals 36.0 kcal/mol and pre-exponent factor does $1{\cdot}10^{13}$ s^{-1}. This peak was not observed in spectra after separate adsorption of reagents. NO and hydrocarbon appears to be involved in this surface complex. The ratio of carbon and NO in the complex is close to 3. The formation this complex has been accompanied by simultaneous decrease of amount of surface nitrite.

Table 2. Amount of NO desorbed from nitrosyl and nitrite species after joint adsorption of NO and oxygen at 50°C

Content in feed gas at adsorption (vol.%)		Amount of NO (μmol/g) desorbed		
O_2	NO	from nitrosyl	from nitrite	total
2.5	0.019	7.0	30.4	38.1
5.9	0.019	3.6	36.8	40.4
11.0	0.019	0.2	43.4	43.6
11.0	0.047	0.0	49.2	49.2
11.0	0.087	0.0	49.3	49.3

Thus the interaction of reagents with catalyst depends on initial state of a surface and oxidative action of reagent adsorbed. The quantitative analysis of interrelation of concentration of surface intermediates and reaction rate of selective reduction of NO with propane has been carried out.

PPII-81

SILICAPHOSPHATE GLASSES AS SUPPORT FOR COPPER CATALYST OF CYCLOHEXANOL DEGIDROHENATION

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Copper-magnezium systems are well-known and widespread industrial catalysts for cyclohexanol degydrogenation, one of the important stages of caprolactam production. In those systems copper is considered to be the active and hence indispenable component while a search for new support, other than magnesia, is still of interest.

The present study deals with cyclohexanol conversion over copper-containing catalysts where silicaphosphate glasses are a second component.

Silicaphosphate glasses in different forms were obtained from the wastes of electrothermoproduction of phosphorus - phosphorus slags. Three types of silicaphosphates were studed: original slag (calcium-magnesium silicaphosphates), slags treated with strong mineral acid (silicaphosphate samples with low calcium and magnesium content) and slags subjected to ion exchange for sodium (sodium silicaphosphate).

Varied techniques of catalysts preparation were used: silicaphosphates impregnation with copper salts solutions, mechanical activation of copper oxide - silicaphosphates mixtures, ion exchange of sodium for copper. All the catalysts were reduced in hydrogen flow at 300^0C.

Cyclohexanol conversion was carried out in a flow fixed-bed reactor operating at atmospheric pressure. The catalysts were tested at 280^0C, WHSV=2,4-3,6 h^{-1}.

The reaction products were analyzed by gas chromatography.

All the samples were found to have an essential catalytic activity.

Among them the activity of copper oxide - silicaphosphates mixtures was the Lowest one (up to 55% conversion of cyclohexanol). Mecanical activation of the mixtures was shown to increase the activity of and especially the stability of the catalysts. Only the products of cyclohexanol dehydrogenation were detected.

The samples obtained from original slag by an impregnation with copper salts were demonstrated to have both high activity (65-75% conversion) and high selectivity in cyclohexanol dehydrogenation.

The highest conversion over the saples containing slags treated with acids was associated with the moderate selectivity towards cyclohexanone. The majior by-product was cyclohexene. Acidic treatment appears to decrease basic properties of slags due to the elimination of 80-95% of the initial calcium and magnesium content.

Thus the silicaphosphate glasses obtained from electrothermophosphorus slags were proved to be the effective component of the catalysts of cyclohexanol dehydrogenation.

The request for a patent of Kazakhstan was done and the positive decision has been already obtained.

99,9 % SULPHUR RECOVERY WITH A TOTALLY CATALYTIC ROUTE

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Oil and Natural Gas contain harmfull sulphur components which must be separated before use. These so-called *sweetening* treatments produce streams of *acid gas* containing hydrogen sulphide, which is recovered as elemental sulphur. Constant development work in the field of acid gas treatment make it now possible to industrially reach an overall sulphur recovery from 95 - 99 up to - but not exceeding - 99.7 %. That means than non neglictible parts of huge amounts of sulphur are still released to the atmosphere, leading to atmospheric pollution in form of acid rains. A more definitive answer is still needed to get rid of this pollution : 99.9 % or more overall sulphur recovery.

The 99.9 % performance is presently achieved by wet processes through an overall catalytic conversion into H_2S of the sulphur compounds remaining in the tail gas, followed by solvent absorption. Although efficient, these wet processes are expensive, namely for high flowrates of tail gases, and generate liquid wastes to be treated.

`Hence Elf Aquitaine Production and Rhone-Poulenc decided to pursue their successful cooperation in the field of Sulphur Recovery in joining their knowledge and efforts to develop a new catalytic process able to allow an overall recovery of 99.9 % in a more economical way.

This new tail gas catalytic process is based on the Direct Oxidation Reaction of H_2S to Sulphur using a new catalytic formula. Typical Laboratory studies will be disclosed to show the feasibility of this new process : the *Advanced DOXOSULFREEN*.

PPII-83

EFFECT OF THE PHASE COMPOSITION OF ALUMINA SUPPORTS ON THE PROPERTIES OF THE Mn-Al-O-CATALYSTS FOR HIGH-TEMPERATURE OXIDATION

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The MnO_x/Al_2O_3 system is known as a highly efficient catalyst for deep oxidation, whose basis property is drastic activity growth after calcination at 900-1000°C (a thermal activation effect), as compared with the samples calcined at 500-600°C [1]. The previous results of our study of the Mn-Al-O-catalysts supported on modified γ-alumina were presented in [2,3]. It was shown that the effect of the modifying dope on the catalytic activity determined as the butane oxidation rate at 400°C depends on the sample calcination temperature. For the catalysts with the same chemical composition the absolute values of activity depend on the method of the raw alumina production.

The present work aims at synthesis and study of the properties of the modified MnO_x/Al_2O_3 catalysts, depending on the phase composition of the alumina (γ-Al_2O_3, γ-Al_2O_3 with the various χ-phase content, both pure and modified ones, and α- Al_2O_3), provided by its production conditions.

At all calcination temperatures (500, 900 and 1300°C) the nonmodified Mn-Al-O-catalysts prepared on α-Al_2O_3 basis were revealed to show the maximum activity.

Independently of the γ-alumina production method (reprecipitation or thermal decomposition) affecting the χ- phase content in this support, the Mn-Al-O-catalysts on γ-Al_2O_3 modified with MgO, La_2O_3, CeO_2, SiO_2 or TiO_2 follow the same regularity: among the samples calcined at 500, 900, or 1300°C the maximum activity is revealed for the La-containing, nonmodified, and Mg- and/or Ce-containing catalysts, respectively. The absolute values of activity are maximum for the catalysts containing 15% χ-phase in the support. However, after calcination at 1300 °C the maximum activity is observed for the Mg-Ce-containing catalyst based on γ-Al_2O_3 with 35% χ-phase. It this case absolute value of activity is close to that for the nonmodified α-Al_2O_3-based sample calcined at the same temperature.

Some regularities of the effect of the double and triple modifying dopes on the activity of the Mn-Al-O-catalysts with the different γ-alumina phase composition have been shown.

The correlation between the data of X-ray phase analysis and X-ray photoelectron spectroscopy, and the catalytic activity have been considered.

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PPII-84

Catalysts for Diesel engines with high emission of soot particles

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Summary

It is well known that solid particles emitted by Diesel engines are among the most dangerous constituents of exhaust gases produced by motor-cars. It has been found that the solids contain over 10000 chemicals compound . The most hazardous of them are the mutagenic and cancerogenic cyclic aromatic hydrocarbons. That is why in the closest future many countries will increase their legal requirements in respect to emission of solid particles, so called "Diesel soot". One of many activities, aimed at reduction of emission of the Diesel soot, is purification of exhaust gases. The most effective seem to be the solutions based on "catching" and further combustion of soot in regenerable catalytic filters. However, up-to date effective and economic filter/catalysts are not produced. Facing at the need for reduction of emission, to meet the future legal requirements, many renowned manufacturers begun implementation of simple flow-through oxidation catalysts in the form of typical open monoliths with a washcoat and an oxidation catalyst. The catalysts, operating at temperatures over 100°C, provide combustion of the hydrocarbons, which otherwise (below 50°C) would participate in emission of Diesel soot. The possibility for application of such catalysts for older heavy duty engines of city buses in Wroclaw Communal Enterprise has been examined by the Laboratory of Surface Engineering of Wroclaw Technical University. Exhaust gas compositions of the buses with and without catalysts were compared for various loads of the engines. There were examined new, used and regenerated catalysts. It has been noted however, that in case of the catalysts characterised by reduced activity (used, regenerated) further locking of active centers by soot resulted in emission of hydrocarbons. Particularly, emission of aldehydes and aromatic hydrocarbons considerably increased.

Simultaneously, there were also tested filter/catalysts designed by the Laboratory of Surface Engineering of Wroclaw Technical University. The filter/catalysts, developed for the older engines still used for communal transport purposes, consist of a catalytic filter for catching of soot particles, an electric heating system for boosting of regeneration of the filter during

operation of the bus and catalysts providing oxidation of carbon oxide and hydrocarbons. The filter consists of a pack of compressed heat-resisting steel wool covered by V/Cu catalytic layer, which reduces ignition temperature of soot below 400°C. The filter/catalysts were characterised by small flow resistance and by approx. 80% effectiveness of combustion of soot particles . Currently, mechanical design of the filter/catalysts is somewhat modified, to prevent collecting of soot in dead voids what may result in too exothermic combustion of the Diesel soot.

POSTER SESSION II

Section 7

Innovations in Catalytic Technologies and Design of Catalytic Reactors

PPII-85

SYNTHESIS OF POLYAROMATIC AMINOPHENOXYPHTHALIC ACIDS: THE REGULARITIES OF THE LIQUID PHASE CATALYTIC HYDROGENATION OF CORRESPONDING NITROCOMPOUNDS AND A MATHEMATICAL DESCRIPTION OF THIS PROCESS

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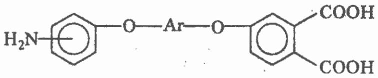
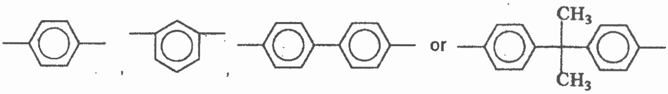
Recently, there has been a development in the use of aminophenoxyphthalic acids (APPA) as homopolycondensation monomers for polyimides (PI) and polyamidoimides (PAI). The improvement of the conversion of PI and PAI has been achieved by extending molecules of APPA, i.e. at the expense of increased distanse between aniline and phthalic acid groups. Applications of this type of homopolycondensation monomers have several advantages, most importantly, it is not necessary to regulate equimolar correlation as in traditional pairs diamine-dianhydride. We obtained several APPA with a general formula



where Ar =



and NH_2 - in meta- or para- position in regard to oxygen. APPA were obtained by the liquid phase catalytic hydrogenation of corresponding nitrophenoxyphthalic acids (NPPA). Another technological advantage of APPA is the possibility of obtaining it from NPPA, not in organic solvents, but in aqueous solvents with pH>7,5. We have established the basic regularities of catalytic hydrogenations of NPPA in aqueous solutions and propose a universal equation for the prognostication of the work of the periodical mixed reactor in sythesis APPA:

$$\tau = \frac{(1+A_2 P_{H_2}) \ln\frac{1}{1-X} + A_1 x\, C_N^O}{K\, P_{H_2}}$$

This equation determines the time of the reactions (τ), necessary for the achievement of some conversion of NPPA (x), in accordance with hydrogen pressure (PH_2), initial concentration of NPPA ($C_N{}^0$) and coefficients A_1, A_2 and K, which were determined for different conditions on the basis of absorption and kinetic data. We discuss the influence of the main parametres of the reaction (the type of catalyst, temperature, hydrogen pressure, initial concentration of NPPA and influence of a type of alkaline agent, pH and nuances of isolation upon the reaction rate, selectivity and yield of APPA and its use in the synthesis of PI and PAI.

This work is supported by Ministry of general and professional education (grant № 95-0-94-39).

PPII-85a

INFLUENCE OF TEMPERATURE INCREASING ON SCR REACTION DYNAMICS ON A CATALYST PARTICLE

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For the reverse-process of NO_x selective catalytic reduction (SCR) with NH_3 on a vanadium oxide catalyst, the transient behaviour of a single catalyst particle is very informative because of influence of catalyst adsorption capacity on the system dynamics [1,2].

Let us take a catalyst particle the active surface of which is covered with adsorbed ammonia. Then we put it into the air-NO_x mixture, heat the system from 60 to 360^{0}C with a constant rate *V* and keep the temperature of 360^{0}C after that. Ammonia previously adsorbed acts in two reactions: (a) interaction with NO_x from the gas phase and (b) oxidation with oxygen from the air. In the paper the influence of the rate of the temperature change on the system dynamics is studied for a particle of different size and shape (a sphere or a plate with radius R_0). The ratio φ of ammonia amounts (which was previously adsorbed inside the catalyst), which has reacted with oxygen in reaction (b) and with NO_x in reaction (a), is found out as well.

In the mathematical model the processes of gaseous NH_3 and NO_x diffusion within the particle, the reversible desorption of ammonia and both reactions (a) and (b) are taken into account. We assume that there is no diffusive limitation of oxygen and the particle is always isothermal. In developed numerical algorithm the collocation method is used for simulation of the transient behaviour.

In all cases the desorption of NH_3 is found out to be negligible. The dynamic properties are rather different for a big catalyst particle and a small one.

The transient behaviour of the process on a big particle demonstrates following properties:

- there are two specific zones inside the particle, namely one is near the outer surface where the reaction (a) takes place and the other is in the central part of the particle where mostly the ammonia oxidation is carried on (the former reaction starts at the temperature about 280^{0}C);
- the rate of reaction (a) goes through a maximum at a time t_a that is different from the similar time t_b of the second reaction (b); it is due to the difference in activation energies; Fig. 1 shows the reaction rates dynamics on the spherical catalyst particle while Fig. 2 corresponds to the plate, curves 1 for the reaction (a) and curves 2 for the reaction (b); $R_0=5$ *mm*, $V=5$ *K/sec*;

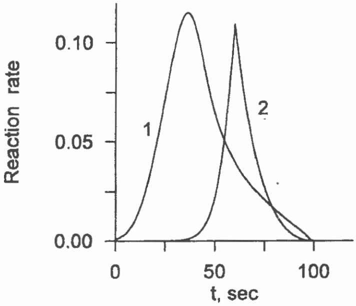

Fig. 1. Reaction on the spherical catalyst particle.

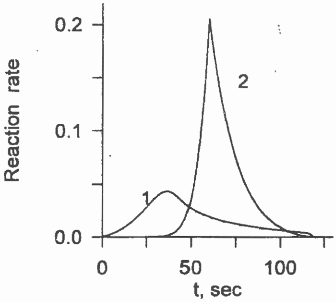

Fig. 2. Reaction on the catalyst plate.

- rate of temperature increasing affects significantly the maximal values of both reaction rates and the time difference $\Delta t = t_a - t_b$ (the higher *V* corresponds the higher maximum reaction rates and smaller Δt);

- the ratio φ depends strongly on the shape of the catalyst particle: at any temperature increasing rate *V* the value φ for the plate is higher then for the spherical catalyst of the same size and φ increases with faster temperature change (see Fig. 3, curve 1 for the sphere and curve 2 for the plate, $R_0 = 5\ mm$).

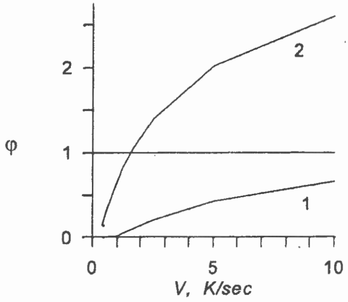

Fig. 3.

On a small particle on the contrary, it is impossible to find a specific zone for only one of the reactions; at fast temperature increase, the maximum rate of each reaction is achieved at the temperature of 360^{0}C; Δt is small as a rule; for rather slow change of the temperature, the value Δt may be as high as 30-60 seconds.

Conclusion. By means of mathematical modelling, it is shown that the forced change of the catalyst particle temperature effects significantly the ratio of amounts of previously adsorbed ammonia which reacts in different SCR reaction routes.

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PPII-85b

DETERMINISTIC APPROACH TO KINETIC CHAOS MODELLING IN HYDROGEN CATALYTIC OXIDATION

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Investigation of periodic and chaotic oscillations in different catalytic systems has developed very rapidly in recent years [1]. This paper will discuss a new scenario of kinetic turbulence (chaos) appearence. We mean the phenomena of chaotic behaviour of the heterogeneous reaction rate which concernes the nature of catalytic system, the mechanism of chemical interactions. One of the most important properties of the deterministic chaos is "sensitive dependence on initial conditions".

Let us consider the mechanism of the heterogeneous reaction of hydrogen oxidation on metallic catalysts [1, 2]:

$$\begin{array}{c} H_2 + 2\,[Me] \leftrightarrow 2\,[H\,Me] \\ O_2 + 2\,[Me] \leftrightarrow 2\,[O\,Me] \\ 2\,[H\,Me] + [O\,Me] \rightarrow 3\,[Me] + H_2O \\ H_2 + [O\,Me] \rightarrow [Me] + H_2O \\ [Me\text{-}v] + [H\text{-}Me] \leftrightarrow [Me\text{-}v\,H] + [Me] \\ [Me\text{-}v] + [O\,Me] \leftrightarrow [Me\text{-}v\,O] + [Me] \end{array} \qquad (1)$$

Here [Me] and [Me-v] are a vacant active site on the catalyst surface and an atom in the subsurface layer, respectively, [H Me], [O Me] and [Me-v H], [Me-v O] are hydrogen and oxygen atoms adsorbed on the surface and dissolved into the subsurface layer of the catalyst. We shall study the case when the activation energies of the third and fourth reaction steps may depend linearly upon the concentration of the reactants in the subsurface layer and upon the concentration of oxygen adsorbed.

The dynamic behaviour of the CSTR system is described by a set of 6 ordinary differential equations, presenting the concentrations of hydrogen and oxygen adsorbed on the metal surface (x_1 and x_2), dissolved into subsurface layer (x_3 and x_4) and in the gas phase (x_5 and x_6). Moreover, the rate constants of the 3rd and 4th steps are as follows

$$k_3(\mathbf{x})=k_{30} \exp (\mu_{32} x_2 + \mu_{33} x_3 + \mu_{34} x_4), \qquad k_4(\mathbf{x})=k_{40} \exp (\mu_{42} x_2 + \mu_{43} x_3 + \mu_{44} x_4),$$

where the parameters k_{30}, k_{40} are positive and μ_{ij} are real numbers. Note that the gradients of dissolved reagents are suggested to be small.

After some simplifications we can obtain several simpler models keeping the physical and chemical sense of the catalytic system dynamics and peculiarities which are of high importance to dynamic systems of complex irregular behaviour. In that sense, a general kinetic model of more simple kind looks as follows:

$$\delta \dot{x} = f(x,y,z), \qquad \dot{y} = g(x,y,z), \qquad \dot{z} = \varepsilon h(x,y,z), \tag{2}$$

where δ and ε are small parameters, x, y, z are identified as fast, intermediate and slow variables, respectively.

In the paper a new route from periodic behaviour to chaos is suggested, some reasons of chaotic behaviour appearence in the system of type (2) are given as well. We would like to point out:

(i) an attractor of a special structure is presented in the phase space of the system;
(ii) a subregion on the attractor exists with a high sensitivity to the initial conditions;
(iii) infinite times the trajectory comes back into this subregion.

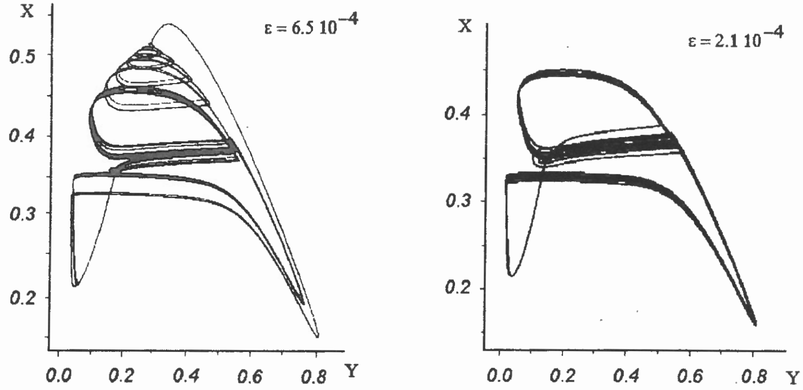

Figure. Examples of weakly stable dynamics.

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PPII-86

THEORY OF FAST AND SLOW HEAT WAVES CREEPING IN A CATALYST FIXED-BED

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Theoretical development and industrial applications of some new catalytic processes under periodical gas flow reversals stimulated the interest in studying the heat waves propagation phenomenon in a heterogeneous medium such as a catalyst fixed-bed blown with a chemically active gas mixture. A heat wave is a spatio-temporal structure that can form and exist in the catalyst fixed-bed as a result of self-organization. We analyze the basic regularities of the heat waves in the case of a single catalytic reversible first order reaction. The simplest pseudo-homogeneous mathematical model was used like in [1,2]. Besides the well known so-called slow heat waves (SHW), fast heat waves (FHW) are found to propagate in a sufficiently extensive bed.

In the coordinate system moving with the heat front the model is a system of two nonlinear ordinary differential equations. According to the theory of dynamic systems on the plane [3] a bounded solution of the problem under consideration (if it exists) converges in infinity to a singular point of the system. That may be either a thermodynamic equilibrium point or a point with the temperature equal to zero because only there the reaction rate is equal to zero.

The only FHW phenomenon is observed if the inlet conditions correspond to a thermodynamic equilibrium state, but the initial temperature T_n of the catalyst is different from inlet one [1,2].

FHW moves only in one direction with the gas stream. If the inlet conditions correspond to the inflection point I of the thermodynamic equilibrium curve, FHW are shown to exist at any T_n. Otherwise, there is an interval of temperatures T_n containing I, for which FHW does not exist. The FHW velocity is calculated directly from the integral laws of mass and energy conservation and does not depend on heat and mass exchange processes in the catalyst bed and on the chemical reaction kinetics. FHW is an automodel solution of the first type according to classification used in [4].

If the inlet temperature is low enough for chemical reaction rate to be negligible (though chemical reaction affinity is non zero) the SHW forms and its creep velocity is less than the heat mark transfer velocity in a fixed bed of an inert material.

Usually to study this phenomenon either the reaction has to be stopped at the temperature lower a special value ("a cutting temperature") or one should consider a semi-infinity reactor with a "cold plug" [4]. We have shown that if the inlet temperature is equal to zero the mathematical model has a one-parametric set of solutions. There is only single function physically reasonable which is SHW image. In SHW the reaction mixture comes to a thermodynamic equilibrium state with high temperature. Structure, maximum temperature and creep velocity of SHW are dependent on the heat and mass transfer processes in the catalyst bed and on the chemical reaction kinetics. SHW can be considered as an automodel solution of the second type [4].

We have obtained equation for entropy production in the heat front using methods of non-equilibrium thermodynamics. The surface of local entropy production has been studied in the FHW and SHW.

We have shown the local entropy production to be equal to zero at plus and minus infinity and to be a positive function in the heat front.

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PPII-87

CONTROL OF UNSTEADY STATE OF CATALYST IN PARTIAL OXIDATION REACTIONS

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The problem of control of an unsteady state of the catalyst is connected with technological and chemical aspects of catalysis and follows G.K. Boreskov's conception of influence of reaction conditions on a catalyst state. According to this concept the catalyst composition or, in the more general sense, its state under the effect of reaction mixture does not remain unchangeable [1]. This state depends on the surrounding reagents and the temperature.

The rate of reaction is determined by both catalytic steps, including the formation of active complexes, and various secondary processes such as diffusion processes in catalyst volume, phase transformation and so on. The secondary processes affect the state of the catalyst. Each of these processes is characterised by definite duration, i. e. relaxation time. For this reason changes in composition or temperature of the reaction mixture may have different effects on catalyst state and, consequently, on reaction rate, thus causing complex dynamic behaviour of the catalytic system.

The efficiency of the process can be increased considerably if the reaction is performed with the catalyst in unsteady state [2—3]. State of the catalyst can be controlled in two ways: (i) by the time-dependent regulation (or periodic operation) when the reagents concentrations, gas flow rates and/or temperature are changed periodically in fixed bed catalytic reactor input [4—5]; (ii) by spatial regulation when the input and output characteristics of reactor do not change with time, and the catalyst moves in a field of variable reagent concentrations and temperature either in fluidized bed [6] or a dual-reactor system [7].

In this paper we present the results of mathematical modelling of partial oxidation reactions in a dual-reactor system on the base of a simple kinetic model.

The peculiarity of this model is that partial oxidation and deep oxidation occur on the sites differing by their physical-chemical origin. These sites are able to transform into each other depending on reaction conditions. Reaction selectivity is determined by the ratio of sites. If we create such reaction conditions that the number of sites of the partial oxidation will be higher than in steady state, then the process selectivity shall increase. We have chosen such a model because using the simplest kinetic laws at a minimum number of steps we can demonstrate essential selectivity growth under unsteady state conditions. This scheme is a model of many reactions of partial oxidation.

The dual-reactor system consists of two reactors. Reaction mixture flow goes consequently through both reactors. Catalyst circulates between the reactors, so that the catalyst particles from the first reactor go to the second reactor, while the particles from the second reactor go to the first reactor. Each reactor contains a heat exchanger for temperature regulation.

Under circulation the catalyst particles move from one reaction conditions to other and permanently change their catalytic properties. Thus the catalyst can be in unsteady state with respect to reagents depending on the ratio between the time of catalyst stay in the reactor and the chemical relaxation time. In this case the concentration of active sites will differ from that at the steady state. Therefore, for mathematical modelling it is necessary to consider how the concentrations of intermediates change.

Using a simple kinetic model involving two types of active sites, we have analysed two ways how to increase the selectivity of partial oxidation reactions over unsteady state catalyst. The first way is periodic operation of temperature in reactor. The second one is using the dual-reactor system with catalyst circulation between the reactors. We can essentially increase the selectivity and desired product yield. As the contact time in the second reactor increases, the concentration of active sites for partial oxidation grows in the first reactor thus increasing the selectivity and desired product yield.

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PPII-88

o-XYLENE OXIDATION TO PHTHALIC ANHYDRIDE OVER UNSTEADY STATE OF THE CATALYST

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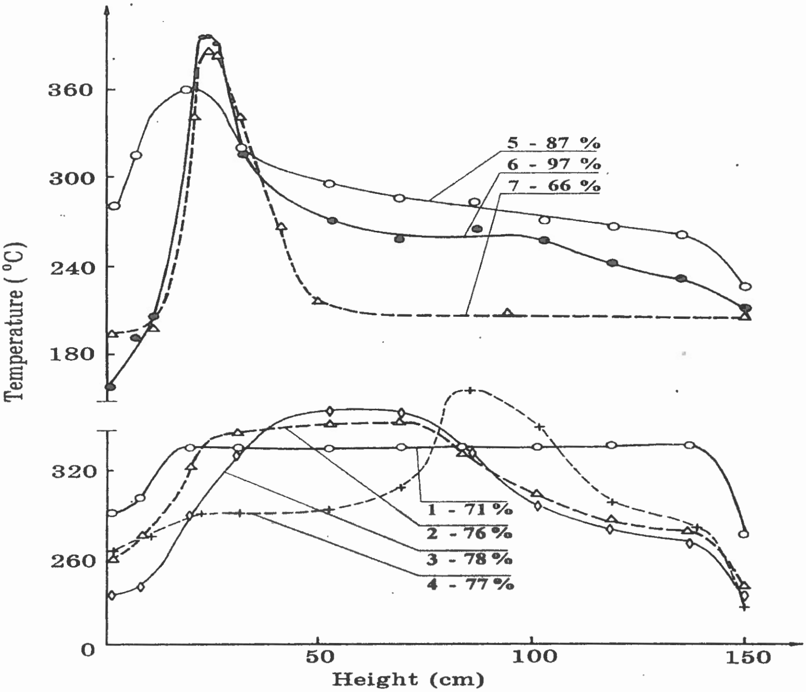
Nowadays V_2O_5/TiO_2 catalysts with promoters are usually used for o-xylene oxidation to phthalic anhydride (PA). Using of the best catalysts in industry for last 15 years allows to achieve phthalic anhydride yield of 80-82%. Presently improvement of the catalyst quality seems to be impossible. Reaction performed at the unsteady state of the catalyst opens new ways for the increasing of the process selectivity [1].

The unsteady state of the catalyst may be regulated in the non-isothermal fluidized bed [2], where the catalyst particles move in the field of reagent concentrations and temperature. If the characteristic time of particles movement is less than that of the catalyst chemical relaxation, the catalyst transfers into the unsteady state. Setting definite concentration and temperature profiles along the reactor height, one can affect the catalyst state and optimize the output reactor parameters.

In the present report we present the results of o-xylene oxidation over unsteady state of the catalyst in the non-isothermal fluidized bed [3]. The experiments were carried out in the glass reactor with 32 mm diameter and 1500 mm reaction zone height. The catalyst used in study was composed of $V_2O_5+K_3PO_4/TiO_2/SiO_2$, $S_{BET}=13$ m^2/g. Figure presents the temperature profiles along reactor height and the corresponding PA yields. In all experiments conversion for the maximum yields was about 99%.

Except experiment 4, the presence of the "hot" zone in the bed leads to a significant increase of the PA yield, as compared with the isothermal bed (experiment 1).

The results obtained in the non-isothermal bed cannot be explained by the temperature alteration only, since the selectivity of partial oxidation, according to the kinetic data, does not depend on the temperature. The PA yield increases, because in the fluidized bed the catalyst particles move chaotically along the reaction zone height in the temperature field and transfer into a high-selectivity unsteady state. The latter forms at the reduced temperature, while the main reaction proceeds in the "hot" zone. The unsteady state of the catalyst forms due to the slow side processes, whose characteristic time is comparable to the time of the catalyst particles movement in the fluidized bed and is about several dozens of minutes.



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PPII-88a

MONTE CARLO MODELING OF SPATIO-TEMPORAL PATTERNS IN BIMOLECULAR CATALYTIC REACTIONS

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The spontaneous appearance of instabilities in heterogeneous catalysis has been modeled by Monte Carlo simulations of the elementary reaction steps. Temporal reaction oscillations and spatial wave propagation on the catalyst surface have been investigated for the CO oxidation and the NO-CO reactions on metal surfaces of the Pt group. The known elementary reaction steps were implemented on a two-dimensional lattice model and have been studied over an extended range of the basic parameters, the partial pressure and the desorption rate of CO. Surface reconstruction proves to be a necessary ingredient for observing unstable reactions for the CO oxidation reaction. Similarly, the vacant site requirement for NO dissociation is crucial for instabilities of the NO-CO reaction. Global temporal oscillations and wave propagation on the catalyst surface only appear in a narrow range of the phase diagram. Surface diffusion, interaction between adsorbed molecules and pick-up processes are easily included in the simulations; they don't lead to any qualitative changes. It is straightforward to implement defects on the catalyst surface, to trigger the spatial patterns as in the experiments.

PPII-89

MATHEMATICAL MODELING OF SO_2 OXIDATION METHOD TAKING INTO ACCOUNT UNSTEADY STATE OF THE CATALYST

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The allowable SO_2 concentration in waste gases is defined now in most of the countries as 100 ppm. To achieve such concentration new effective methods of SO_2 catalytic oxidation are needed.

A method of sulphur dioxide oxidation in sulphuric acid production is offered in Boreskov Institute of Catalysis [1]. This method allows to lower the SO_2 concentration in waste gases to 50 ppm. That is possible due to the use of the unsteady state of the catalyst. The main difference of this method from conventional methods of "double contact - double absorption" is the organization of the second state. It consists of two catalyst beds (fig.1). The feed to each bed is cycled between air used for catalyst activation and gas mixture after intermediate absorption. The directions of air and gas mixture filtration are different. The air after catalyst bed is fed to sulphur burner.

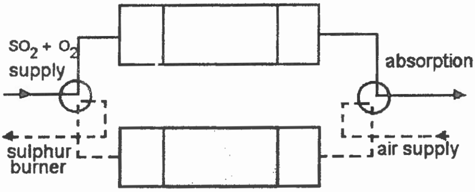

Fig.1. Schematic diagram of the second state of "double contact - double absorption" method [1].

This report is devoted to mathematical modeling of this scheme taking into account unsteady state of the catalyst. The unsteady state kinetic model of SO_2 oxidation over vanadium catalyst [2] is used to describe the dynamics of the catalyst state. One dimensional heterogeneous mathematical model [3] is used to describe the processes in the catalyst bed. This model assumes plug flow in the reactor and takes into account the inertia of the liquid phase concentration of SO_3 and of the reaction intermediates, the inertia of the solid phase temperature. Equilibrium states of fast processes of reactants dissolution in the melt and those of active component formation are present in the model.

Figure 2 shows the dependence of the SO_2 conversion on the input temperature of gas mixture and air when gas mixture is blown through the catalyst bed. Line 1 represents the results of mathematical modeling of the offered scheme (the air blow direction is opposite to the gas mixture one). Line 3 corresponds to the case when the air blow direction and the gas mixture one are the same. There are two cases without air blow as well: conventional steady state process (line 4) and reverse-flow process (line 2).

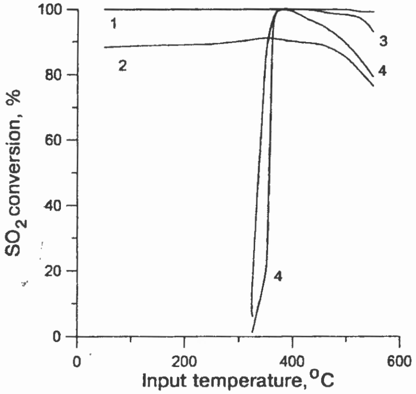

Fig.2. The dependencies of the SO_2 conversion on the input temperature for different processes. Space time = 4 c.; Cycle duration = 600 c.; C_{SO_2} = 1 %vol., C_{O_2} = 9 %vol. (when gas mixture supply); C_{O_2} = 21 %vol. (when air supply);

The dependencies represented above clearly indicate that the SO_2 conversion is higher and input temperature can be chosen lower in offered method than in conventional ones. We can explain the reasons of these observations in the following way. Large quantities of SO_2 are sorbed onto the active component of vanadium catalyst when it is exposed to gas mixture after it has been contacted with air. Sorption of SO_2 results in a reduction of catalyst activity. It may be explained by the formation of inactive vanadium complexes. When after that air is fed into the catalyst bed the SO_2 desorbtion starts and the catalyst activity increases (compare lines 1,3 for processes with air blow and lines 2,4 for processes without air blow). If the air blow direction is opposite to gas mixture one the high temperature zone does not leave the catalyst bed, so the process can be effectively carried out even under low input temperature (compare lines 1 and 3 respectively).

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НАРОДНЫЙ ЗЕМЕЛЬНО-ПРОМЫШЛЕННЫЙ БАНК

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Коммерческий банк “Народный земельно-промышленный банк” является акционерный обществом открытого типа. Лицензия ЦБ РФ на совершение банковских операций № 2873 получена 9 июня 1994 года.

Учредителями банка выступили крупнейшие в регионе предприятия военно-промышленного комплекса, химического и тяжелого машиностроения, в их числе: НПО “Алтай”, АО НПК “Алтай”, Бийский олеумный завод, ПМП “Металлургмонтаж”, “Бийскэнергомаш” и другие предприятия Бийска.

За истекший период банк провёл три эмиссии своих акций. В результате оплаченный уставной капитал вырос более чем в 100 раз и сегодня является одним из крупнейших в крае.

АКБ НЗПБ - первый банк Алтайского края, который открыл филиал в г. Новосибирске. Банк имеет два отделения в г. Бийске. Подтверждением признания результатов деятельности банка является выданная ЦБ РФ 24 мая 1996 г. расширенная валютная лицензия № 2873.

Банк имеет высококвалифицированный кадровый состав: 56 сотрудников имеют высшее образование, в их числе пять кандидатов наук. Средний возраст сотрудников составляет 36 лет.

Позиция банка на финансовом рынке:

⇒ ориентация на интересы клиентов, обеспеченные деловыми, партнёрскими отношениями;

⇒ утверждение образа банка, как солидного финансового учреждения - регионального лидера в банковской сфере;

⇒ поддержка рентабельных, инвестиционных проектов, социально ориентированных, образовательных и культурных программ своего региона.

Головной банк: 659322, Россия, Алтайский край,
г. Бийск, ул. Социалистическая,1
тел: (3854) 24-85-31; факс (3854) 31-36-55

Отделение №1: г. Бийск, ул. Вагонная, 63,
тел: (3854) 24-88-22

Отделение №2: г. Бийск, ул. Сенная, 104
тел: (3854) 22-13-27

Филиал банка: 630104, Россия, г. Новосибирск,
ул. 1905 года, 83, а/я 303
тел: (3832) 20-84-35; факс: (3832) 20-83-37

Некондиционные ракетные топлива **Нефтяные отходы** **Металлургические отходы**

НПО ЭКОГЕОХИМ

Высокоэффективные присадки для повышения октанового числа автомобильных бензинов и приготовления экологически чистых бензинов

Катализаторы процессов получения дорожных и кровельных битумов из гудронов, в том числе низкокачественных, и нефтеотходов прудов-отстойников

Карбамидофурановые смолы (КФ-90, КФ-40 и др.) Для изготовления отливок из серого и ковкого чугуна, стали и алюминия в литейном производстве машиностроительных предприятий в составе песчано-смоляных смесей

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SAMSUNG CHEMICAL GROUP

Reaching Out to the World's Customers in the Coming 21 st century

With the 21 st century just before us, the world is faced with unrestricted competition through changes in the international business environment. ◆ Accordingly, the *Samsung Chemicals Group* is expanding its business scope, based upon cutting-edge technology, and strengthening international competitiveness in order to grow into a major world player. ◆ We are also unfolding a future oriented business which can enhance the quality of life by giving top priority to the customer. ◆ The *Samsung Chemicals Group* will achieve an economy of scale and advance into new promising business areas. In order to grow into one of the word's top 10 general chemicals enterprises in the 21 st century, *Samsung* will construct production facilities in promising overseas regions, as well as expand high-added-value areas such as specialty chemicals and new materials. ◆ The *Samsung Chemicals Group* will also actively contribute to society. ◆ *Samsung* promises customer satisfaction by providing best products and services.

Chemical Affiliates

Company Name	Major Business
Samsung General Chemicals	Ethylene, Propylene, Benzene, HDPE, LLDPE, PP, SM, EO/EG, Para-Xylene, PTA
Samsung Petrochemicals	PTA (Purified Terephthalic Acid)
Cheil Industries	ABS, PS, EPS
Samsung Fine Chemicals	Urea, Melamine, Chlorine, Caustic Soda, Specialty Chemicals
Samsung BP Chemicals	Acetic Acid, VAM
Samsung Corporation (Chemical Division)	Export & Import of Chemical Products Developing Oversease Markets

Cheil Synthetics (PET Resin, Fiber, Filament) was divested as of June 1995.
Samsung SM Co. was established as of June 1995.

MOSCOW OFFICE

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Katalizator Company

KATALIZATOR (Catalyst) **Company** was founded in 1970 and for more than 25 years has been pushing forward the frontiers of technology in catalysts and supports.

KATALIZATOR Co. concentrates upon development of the catalysts' technology and manufacturing of industrial size, semi-industrial and laboratory size lots of catalysts and related materials. Also, we are developing catalytic technological processes for chemical synthesis and environment protection, and providing wide services.

Our customers' staff is continuously growing up and now includes industrial companies from Russia, C.I.S., United States, Germany, the Netherlands, Italy and Korea. Total annual output of products is about 1,500 tons.

In a close cooperation with Boreskov Institute of Catalysis (Russian Academy of Sciences, Siberian Branch) **KATALIZATOR Co.** pioneered some of the most basic advances in chemical industry, such as catalysts for olefins polymerization, environmental catalysts and process technologies, a family of alumina supports, and many others.

Main offerings include commercial catalysts, supports, related products and technologies.

- **Environmental catalysts for:**
  - VOC & CO abatement - Z-2, ICT-12-8, ICT-12-6, AOK-78-22;
  - CH_4 catalytic combustion - ICT-12-40;
  - NO_x high-temperature reduction - AOK-78-21;
  - Ozone decomposition - ICT-12-9.
- **Catalyst** for purification of nitrous gases from oxygen in HAS production - IC-3-12.
- **Catalyst** for selective hydrogenation of acetylene and diene fractions - ICT-3-30.
- **Catalysts** for synthesis of methyl mercaptan (ICT-31-1) and for conversion of dimethyl sulfide to methyl mercaptan (ICT-32-1).
- **Catalyst** for oxidation of methanol to formaldehyde - ICT-6-2-6.
- Corundum **support** for Ag-containing catalyst in ethylene oxide production - KN-8.
- Micro-spherical alumina **support** for ethylene oxychlorination catalyst - ICT-02-6.
- Micro-spherical silica gel **support** for gas-phase ethylene polymerization - ICT-04-6.
- Alumina trihydrate - binder, **universal raw material** for various products - AOK-63-91.
- **Technology** of noble metals recovery from the spent catalysts.
- **Technology** of Hg-containing waste water treatment.

POSSIBLE WAYS OF COOPERATION COULD BE AS FOLLOWS:

- Delivery of products to a customer.
- Granting licenses and know-how.
- Technical assistance in usage of supplied goods and technologies.
- R & D studies in the fields of mutual interests.
- Joint project works, establishing of Joint Ventures.

For more detailed information regarding **KATALIZATOR Co.** products and technologies, please contact us.

KATALIZATOR Company
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Акционерное общество "ХИМПЛАСТ" начинает свою историю с декабря 1941 г., когда на Новосибирском химическом заводе была получена первая продукция. В настоящее время мы можем предложить потребителям более 40 наименований химической продукции.

Акционерное общество "ХИМПЛАСТ" является одним из крупных химических предприятий Сибири и Дальнего Востока по производству продукции из пластифицированного поливинилхлорида.

АКЦИОНЕРНОЕ ОБЩЕСТВО "ХИМПЛАСТ"

Производим и реализуем:

- **КАБЕЛЬНЫЕ ПВХ ПЛАСТИКАТЫ** - марки И40-13А, О-40, ИО45-12, О-50, ведутся работы по внедрению негорючих марок пластикатов.
- **ЛЕНТЫ ЛИПКИЕ ПВХ** - для промышленности, для быта, для защиты труб от коррозии.
- **ЛИСТОВЫЕ ПВХ ПЛАСТИКАТЫ** - марки ППВ, ПХ-2, рец. 57-40
- **ПЛЕНОЧНЫЕ ПВХ ПЛАСТИКАТЫ** - пленка для парников и теплиц, клеенка медицинская компрессная, пленка сельскохозяйственного назначения.
- **ОБУВНЫЕ ПЛАСТИКАТЫ** - марки ПЛ-2, ПЛП-2.

Освоено производство ГИБКИХ ТРУБОК ИЗ ПВХ для защиты токоведущих частей различных электротехнических устройств, внутренний диаметр трубок от 6 до 30 мм.

Готовы выпускать гранулы ПВХ для производства полимерной тары (бутылок) для пищевых и непищевых продуктов.

Кроме того, АО "ХИМПЛАСТ" ПРОИЗВОДИТ:

- **пентаэритрит** - для лакокрасочной промышленности, в производстве полиграфических красок, пентапласта, смазочных масел.
- **формиат кальция** - для кожевенной промышленности в качестве агента для нейтрализации или предварительного дубления, в целлюлозно-бумажной промышленности как коагулянт при отбеливании бумаги, в строительстве для повышения морозостойкости бетона, в сельском хозяйстве в качестве консерванта кормов.
- **пластификаторы** - марки ДБФ, ДОФ, ДАФ-6, ДОС - для пластификации виниловых смол и других полимеров в производстве кабельных пластикатов, искусственных кож, резинотехнических изделий, полимерных строительных материалов, линолеумов, упаковочных пленок.
- **аминопласт** (марка КФА-2) - для изготовления изделий технического, электротехнического, бытового назначения, а также изделий, соприкасающихся с пищевыми продуктами.
- **пленки, ленты, изделия из фторопласта-4**

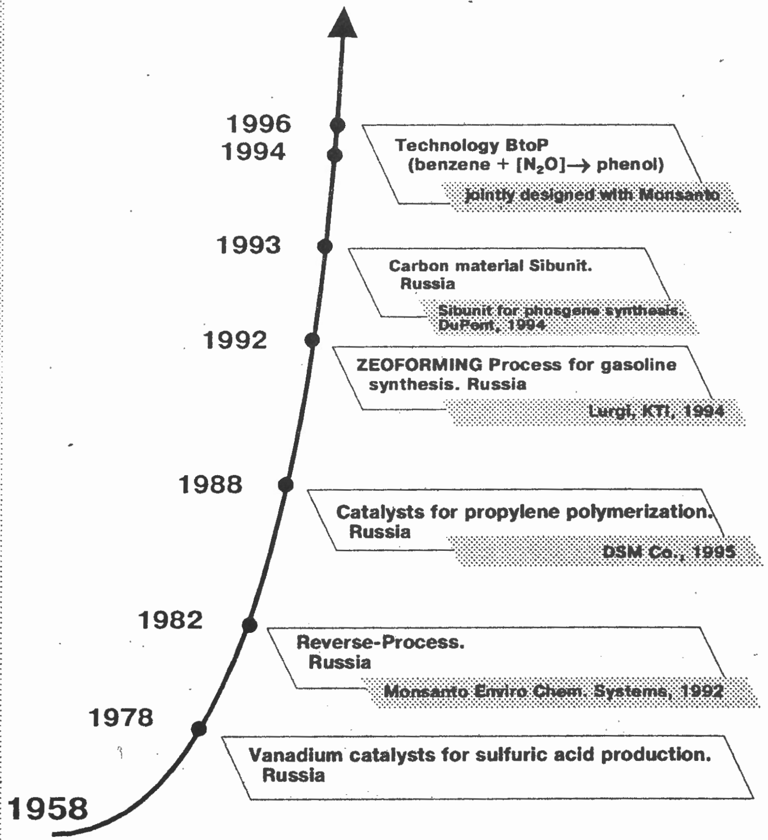
Имея более, чем 50-летний производственный опыт, передовые технологии, мощный производственный потенциал, конкурентноспособную продукцию, мы хотели бы на правах взаимовыгодного сотрудничества создать совместные производства, освоить новые технологии, расширить сферы сбыта нашей продукции.

ПРИГЛАШАЕМ К СОТРУДНИЧЕСТВУ!

630090, Россия, Новосибирск-007, ул.Фабричная, 10
Телефакс: (3832)10-23-32 Тел. (3832)23-33-27 (отдел сбыта) факс: (3832)23-99-42

BORESKOV INSTITUTE OF CATALYSIS

Catalytic Processes from molecular level to Industrial Plants



1996

1994

Technology BtoP
(benzene + $[N_2O] \rightarrow$ phenol)

jointly designed with Monsanto

1993

Carbon material Sibunit.
Russia

Sibunit for phosgene synthesis.
DuPont, 1994

1992

ZEOFORMING Process for gasoline synthesis. Russia

Lurgi, KTI, 1994

1988

Catalysts for propylene polymerization.
Russia

DSM Co., 1995

1982

Reverse-Process.
Russia

Monsanto Enviro Chem. Systems, 1992

1978

Vanadium catalysts for sulfuric acid production.
Russia

1958

KEY DESIGNS OF BORESKOV INSTITUTE OF CATALYSIS

Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences
Prospekt Akademika Lavrentieva, 5, Novosibirsk 630090, Russia

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The Second International Memorial G.K. Boreskov Conference "Catalysis on the Eve of the XXI Century. Science and Engineering"

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