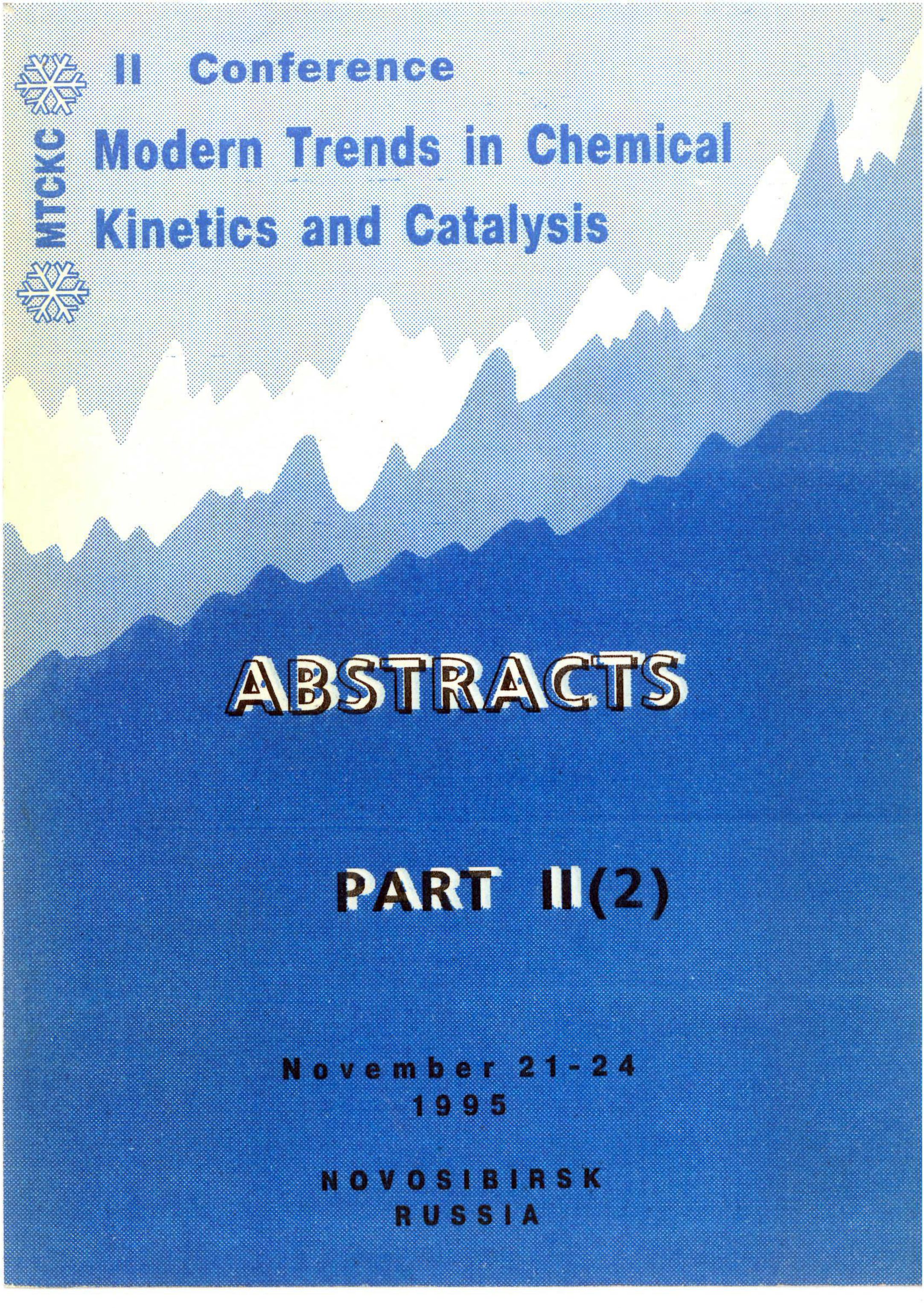

MTCKC

II Conference
Modern Trends in Chemical Kinetics and Catalysis

ABSTRACTS

PART II(2)

November 21-24
1995

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BORESKOV INSTITUTE OF CATALYSIS

INSTITUTE OF CHEMICAL KINETICS AND COMBUSTION

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"Modern trends in chemical kinetics and catalysis"

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CATALYSIS

POSTERS

PPC-95 – PPC-166

PPC-95

MONOOXYGENASE BIOMIMIC - PERFLUORINATED TETRAPHENYL PORPHYRIN Fe(III) IMMOBILIZED BY ALUMINIUM OXIDE AND RESISTANT TO OXIDANT AND TEMPERATURE

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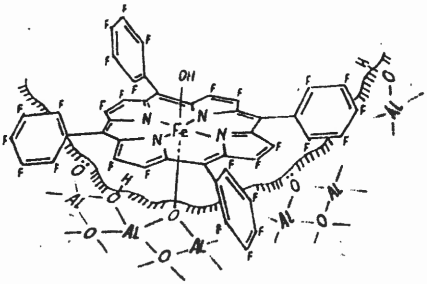
The creation and developing of the biomimics occupying the intermediate position between the fermentative and chemical catalysts is very actual problem.
In this aspect the two monooxygenase reactions - epoxidation and hydroxylation, carried out by enzyme cytocrome P-450 it represents of prime importance interest of organic catalysis.

We have synthesized the biomimetical catalyst



(perfluorinatedTPhPFe(III)OH/Al_2O_3) which has shown the remarkable epoxy activity in the reaction of propylene oxidation by hydrogen peroxide. On the optimum conditions of the process (180^{0}C,C_3H_6:H_2O_2 ratio of 1:1,2(molar) with the contact time of 1. sec) the highest yield of epoxide is 30% wt and the selectivity on the monooxyganase products is about 100% wt. In contract to the well-known mimics, our synthesized mimic has functioned in the gas-phase and shown the unique stability concerning to the temperature and destructive action of the oxidant and its intermediate products.

The detail study of the biomimetical C_3H_6-H_2O_2-H_2O-perfluorinatedTPhPFe(III)OH/Al_2O_3 system is allowed to establish the kinetic regularity of epoxidation of propylene in the wide range of the parametters of the reaction. It is shown the boundary conditions of passing of the monooxyganase reactions and chemical conjugation between the catalaze and monooxygenaze reactions.Quality and quantity is characterized the acid-basic active sites on the surface of the carrier by the thermal desorption method and is shown their key role in the formation of the epoxy intermediate product (perfluorinatedTPhPFe(III)OOH/Al_2O_3).

The elementary stages of the mechanism of the product's formation are proposed the simultaneous participation of the all catalitic groups (ironporphyrin,acid and basic active centers) in the catalitic action.

Experimental results is adequately described by the kinetic model composed on the base of the offered mechanism.

STUDY OF CATALYSTS FOR PROPYLENE POLYMERIZATION IMMOBILIZED ON THE SURFACE OF HIGHLY DISPERSED GRAPHITE OR BORON NITRIDE.

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It was found that under the fixing of the metallocomplex catalysts on the surface supports of layered type (graphite, boron nitride (BN)) a formation of high stereospecific active centres of polymerization of propylene takes place. A high catalytic activity was observed at strongly defined ratio Ti:support, which depends on the surface value of graphite or BN. Maximum stereospecifity corresponds to maximum of catalytic activity.

STM/ASM study of the interaction between the organoaluminium component and graphite and analysis of ESR data offer a conclusion, that electron properties of the supports determine the type of its interaction with the components of the catalytic systems. X-ray diffraction data confirms that the active sites on graphite or BN are formed at the defects of its crystal lattice. It was established, that the $Al(C_2H_5)_2Cl$ and $TiCl_4$ adsorb irreversibly on graphite and BN. Chromatographic, polarographic, ESR analysis of catalysts allows a conclusion that a stable metal complexes with $Ti(4)-(C_2H_5)$ groups are produced on the graphite surface and Ti(3) complexes are produced on the BN surface.

The nature of the catalytic centers in the presence of layered supports was found to depend on the procedure of the catalytic composite preparation. Nevertheless, the centers, formed from the wapor or in the presence of a solvent, are highly active isospecific centers of olefin polymerization.
The growth of the polymer chain in the presence of the investigated catalytic systems follows the enantiomorphic model, i.e the stereochemistry of isotactic growth is controlled by a chiral ligand environment of the transition metal catalytic complex.

MODELLING OF ETHYLENE CATALYTIC TRANSFORMATIONS BY AlO_4 CLUSTERS

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The AlO_4 tetrahedral units constitute important parts of many catalysts. Experimental studies show that in the presence of alumophenylsiloxane complex containing the AlO_4 fragment a variety of reactions occur requiring activation of the ethylene molecule. We report the results of modeling ethylene transformations on the AlO_4 clusters carried out with ab initio methods of quantum chemistry.

It is demonstrated[1,2] that the tetrahedral AlO_4 cluster with closing lithium or hydrogen atoms (which allows one to reproduce distributions of electron density in larger alumosilicate systems[3]) causes remarkable changes in the electronic structure of approaching it ethylene molecule. When moving along reaction paths dramatic reduction of population of either π(C-C) or σ(C-H) bonding orbitals of C_2H_4 from initial value of 2.0 occurs. We interpret this result as an indication of drastic weakening of the π(C-C) or σ(C-H) bonds due to cluster effect. In the latter case the conclusion is confirmed by direct quantum chemistry calculations of dissociative potential energy curves.

According to calculation results the reaction mechanism depends critically on orientation of reagents, however, in all cases creation of cation-radicals should be taken into account.

1. A.V.Nemukhin, I.M.Kolesnikov, V.A.Vinokurov, Mendeleev Communications, 1994, No4, p. 144.
2. I.M.Kolesnikov, V.A.Vinokurov, A.V.Nemukhin, Doklady RAN, in press.
3. A.V.Nemukhin, I.M.Kolesnikov, V.A.Vinokurov, Zh.Strukt.Khim. 1995, V.36, P.410.

INITIATION OF SOME REACTIONS BY MEANS OF PHOSPHORORGANIC ANODIC INTERMEDIATES.

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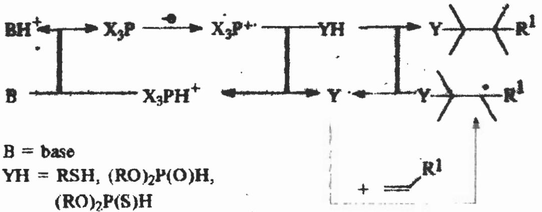
Electrochemical oxidation of threecoordinated phosphororganic compounds (POC) leads to formation of phosphorcentered radical cations. This particles react with initial POC in the course of electrolysis in absence other nucleophilic substrates, giving of biphosphonium salts:

$$X_3P \underset{}{\overset{-e}{\rightleftharpoons}} X_3P^{+\cdot} \xrightarrow{X_3P} [X_3PPX_3]^{+\cdot} \xrightarrow{-e} [X_3PPX_3]^{2+} \qquad (1)$$

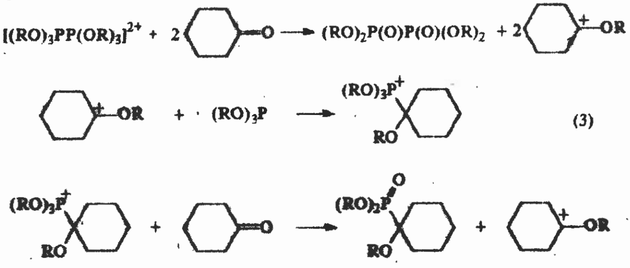
It was found that intermediates of anodic oxidation of POC may catalysed some reactions. For example, $X_3P^{+\cdot}$ are initiators of radical addition thiols, dialkylphosphites and dialkylthiophosphites to alkenes. Catalytic action $X_3P^{+\cdot}$ based on property radical cations react with substances possessing weak element-hydrogen bonds (YH) via mechanism of homolytic hydrogen abstraction. A general method of electrochemical catalysis of this reactions may be shown by scheme (2):



(2)

B = base
YH = RSH, $(RO)_2P(O)H$,
$(RO)_2P(S)H$

It was also established that other intermediates - hexaalkoxybiphosphonium salts, may electrochemically catalysed reaction of addition of trialkylphosphites to cyclohexanone via mechanism of formation alkoxycyclohexyl cations on reaction biphosphonium salts with ketone:



(3)

PPC-98 A

XPS STUDY OF Li/CaO CATALYSTS

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The catalytic activity of Li/CaO system in the oxidative coupling of methane is well-known to depend on the lithium concentration. However, the application of non-destructive physical methods of surface characterization to determine Li surface concentration is not a straightforward matter. For example, the drawback of X-ray photoelectron spectroscopy (XPS) originates from the low value of photoionization cross-section (σ) for Li1s core level on using traditional X-ray sources: AlK_α and MgK_α radiation. Indeed, $\sigma(Li1s)/\sigma(C1s)$ = 0.06 for MgK_α.

To tackle this problem we propose to use ultrasoft ZrM_ξ radiation which allows to increase the photoionization cross-section for Li1s level: $\sigma_{ZrM_\xi}/\sigma_{AlK_\alpha}=700$. Our previous study has shown that the XPS spectra of metal salts excited by ZrM_ξ are rather intensive. Indeed, the Li1s spectrum recorded at X-ray source power of 30 Wt (6 kV × 5 mA) and presented in Figure 1 is characterized by a high signal/noise ratio.

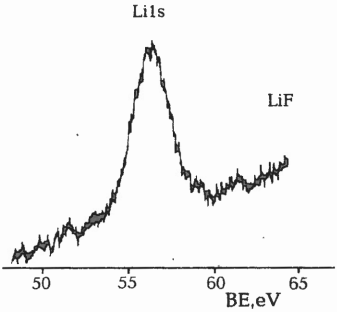

Fig.1. XPS spectrum of LiF in Li1s region under ZrM_ξ radiation

Ca3s and Li1s core level spectra of four Li/CaO catalysts containing Li 1.3, 1.8, 5.4 and 5.8 at.%. are compared in Figure 2. The bulk concentration of Li was measured by the atomic absorption method. All spectra were recorded using ZrM_ξ radiation. One can see, that the surface concentration of Li in the catalyst with the lowest Li content is much higher than the bulk one (σ(Li1s)/σ(Ca3s) =2.3). Li1s intensity for the sample containing 1.8 at.% of Li decreases essentially, while its back increase is revealed for the other samples.

Note that the sample containing 1.8 at% of Li has the higher (spectrum 2) catalyst activity. According to the EPR data, a solid solution originates in this sample. This is in good agreement with the XPS data obtained. For the other samples, the surface is essentially enriched with Li. Since the spectra of C1s region exhibit a peak characteristic of carbonate, we can suggest that either Li carbonate or hydroxide enrich the surface.

Thus, we come to the conclusion that the higher catalyst activity has Li/CaO sample, whose surface concentration is very close to the bulk one (1.8 at.%), otherwise the surface is blocked by the phase with an excess of Li.

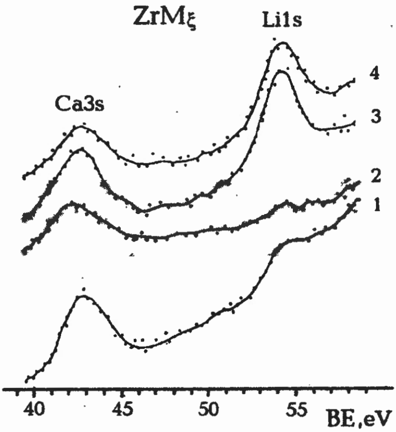

Fig.2. XPS spectrum in Li1s region of Li/CaO surface:
1 – 1.3 at.%; 2 – 1.8 at.%; 3 – 5.4 at.%; 4 – 5.8 at.%

In conclusion it should be said that this work demonstrates the advantage of ZrMξ radiation to study Li–containing systems.

The authors would like to acknowledge the financial support of the Russian Science Foundation, Grant No 93–03–4851.

PPC-99

HOMOGENEOUS HETEROBIMETALLIC CATALYTIC SYSTEMS FOR OLEFIN HYDROCARBOXYLATION, BASED ON PALLADIUM COMPLEXES.

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The catalytic reactions of olefin carbonylation with carbon monoxide are very important as a convenient method of synthesis of carbonic acids, esters, and aldehydes. Until recently, the homogeneous catalysts of these reactions was limited by mononuclear complexes of transition metals. Recently, the enhanced regioselectivity and/or enhanced activity have been observed for olefin hydroformylation, where heterobimetallic (Co/Rh and the like) catalysts were used [1,2]. We found that the selectivity (S) with respect to the linear product (I) of olefin hydrocarboxylation may be also enhanced if one adds Fe(III) or Co(II) chlorides (2.5 equivalents) to the catalyst precursor $PdCl_2L_2$ ($L = Ph_3P$) [3]. It is important that the high regioselectivity is achieved at lower L/Pd ratio than that in the case of the catalyst promoted with $SnCl_2$. The promoting effect observed may be due to activation of olefin or CO molecules by heterometallic complexes (or clusters), forming *in situ*. However, it is possible that the promoter is involved only in the key step of a catalytic process. Evidently, it is of fundamental interest to study the "synergism" of these heterobimetallic systems. For this purpose, we conducted the reactions of styrene and 1-heptene with CO and water in dioxane under low CO pressure (0.5 - 3 MPa), at 383K in the presence of the catalytic systems based on $PdCl_2L_2$ and various Co compounds.

$$RCH{=}CH_2 + CO + H_2O \xrightarrow{Pd/Co} \underset{(I)}{RCH_2CH2COOH} + \underset{(II)}{RCH(CH_3)COOH} \quad (1)$$

$R = C_6H_5$, $n\text{-}C_5H_{11}$;

It was shown that replacement of $CoCl_2$ by $Co(OAc)_2$ or $CoCO_3$ results in the decrease in the yield of both acids I, II ($R = C_6H_5$) and in the value of S. The latter is maximum (65%) in the case of $Co_2(CO)_8$ and $Co(acac)_2$, but both these Co compounds substantially reduce the activity of the catalyst as compared with $PdCl_2L_2/CoCl_2$. It is worth noting that $Ni(acac)_2$ does not affect the process.

The influence of $Co_2(CO)_8$ additives on the kinetics of reaction (1) ($R = n\text{-}C_5H_{11}$) has been studied at $PdCl_2L_2$ concentration 0.0065 M. The rate of alkene conversion lowers by on order magnitude when $Co_2(CO)_8$ concentration rises from 0 to 0.0065 M. The reaction order with respect to CO pressure decreases markedly in the presence of the promoter. Furthermore, in contrast to the unmodified catalyst, the value of S is slightly influenced by CO pressure and L concentration in the case of bimetallic system.

The data obtained were interpreted in terms of the scheme of mechanism of olefins hydrocarboxylation, involving three types of hydride complexes $HPdCl(CO)_mL_{2-m}$, whose selectivity with respect to product I decreases as m increases from 0 to 2 [4]. According to this interpretation, retardation of olefin carbonylation via hydride intermediates containing one and two CO ligands (m=1, 2) takes place owing to the promoter. It is possible that this effect is caused by the interaction between $Co_2(CO)_8$ and such active forms of Pd(0) as PdL_2 or Pd(CO)L, which are precursors of the aforementioned hydride intermediates. This hypothesis agrees the fact that, according to the data of IR spectroscopy *in situ*, study-state concentrations of Pd(0) complexes decrease in the presence of $Co_2(CO)_8$.

REFERENCES

1. Horvath I.T., Garland M., Bor G., Pino P. J.Organomet.Chem. 1988. V.358. C.17.
2. Garland M. Organometallics. 1993. V.12. No.2. P.535.
3. Noskov Yu.G., Terekhova M.I., Petrov E.S. Zh. Obsh. Khim. 1990. V.60. No.6. P.1336.
4. Noskov Yu.G., Petrov E.S. Kinetics and Catalysis. 1993. V.34. No.6. P.898; ibid., 1994. V.35. No. 5. P.728.

PPC-100

^{1}H AND ^{15}N NMR STUDIES OF SULFATE-PROMOTED ZIRCONIA CATALYSTS

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Sulfate-promoted zirconia have gained much attention due to their ability to catalyze the heterolytic reactions of paraffins at low temperature. At the same time the exact chemical nature and structure of the superacidic sites of these catalysts still remain unclear.

The aim of this work is to elucidate the role of proton donating (Bronsted) and electron accepting (Lewis) sites in isomerization and disproportionation of n-pentane catalyzed by sulfate-promoted zirconia by means of combined ^{1}H and ^{15}N NMR.

^{1}H NMR MAS of proton sites of a series of sulfate-promoted zirconia, ZrO_2 and $Zr(SO_4)_2$ has revealed a variety of surface OH groups that differ in their chemical shifts. Their amounts as function of sample preparation procedure and evacuation temperature have been measured. Occurrence in these systems of very acidic OH groups (^{1}H NMR MAS lines at ca. 8 and 11 ppm) provides a temptation to attribute the superacidic properties to formation of extremely acidic Bronsted sites. The obtained results show that the high catalytic activity of sulfated zirconia in paraffin isomerization cannot be only due to the formation of acidic S-OH groups.

^{15}N NMR of adsorbed N_2 was used for characterization of Lewis acidity. The interaction of N_2 with electron accepting sites change the chemical shift of ^{15}N NMR line due to the donation of the electron density from p-orbitals of nitrogen to vacant orbitals of Lewis sites in adsorption complexes [1]. The dependence of ^{15}N NMR chemical shift upon N_2 loading was used for determination of the complex formation constant K and of $\delta_c n_L$ values (n_L - number of Lewis sites, δ_c - chemical shift of N_2 in adsorption complex). It was found that the number of the most strong sites detected by ^{15}N NMR of adsorbed N_2 represent only a small part

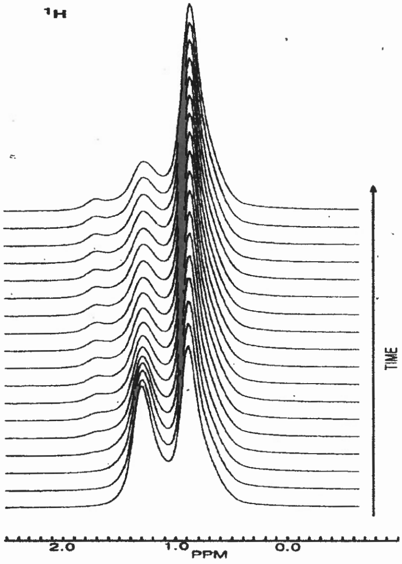

Fig.1. ^{1}H NMR MAS spectra illustrating kinetics of n-pentane conversion to i-pentane over sulfated zirconia catalyst. The time between recording spectra was 320 s.

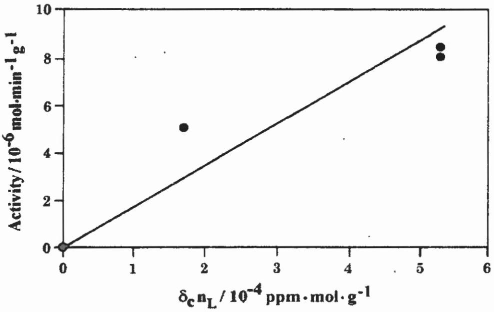

Fig.2. Correlation between the value of $\delta_c n_L$ (proportional to the number of Lewis sites), obtained from ^{15}N NMR of adsorbed N_2, and the isomerization activity, measured by *in situ* ^1H NMR at 20°C

of the total amount of sulfated Zr atoms on catalysts surface. The most active zirconia catalysts have very strong Lewis acidic sites with concentration of several μmole/g.

The numbers of Bronsted and Lewis sites have been correlated with the catalytic activity in reaction of n-pentane isomerization measured by *in situ* ^1H MAS NMR (Fig.1). Effects of catalyst treatment temperature and addition of CO and H_2O have been studied. No correlation between the catalyst's activity in reaction of n-pentane isomerization and the number and types of surface OH groups has been found. At the same time, the proportionality between the activity and the amount of the most strong Lewis sites detected by ^{15}N NMR of adsorbed N_2 has been revealed (Fig.2).

This conclusion is in a good agreement with a number of literature data that the active centers in sulfate-promoted zirconia are most strong electron acceptor (Lewis) sites associated with coordinatively unsaturated metal cations whose strength of acidity is strongly enhanced by electron induction effect of S=O bond.

[1] V.M.Mastikhin, S.V.Filimonova, I.L.Mudrakovsky and V.N.Romannikov, J.Chem.Soc. Faraday Trans., 87 (1991) 2247.

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PPC-101

NEW CATALYSTS FOR SELECTIVE CATALYTIC NOX REDUCTION WITH METHANE

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For the last years intensive research in the field of purification of exhausted gases from nitrogen oxides has been carrying out in Russia and abroad. Methane seems to be the most perspective reducing agent. But very quick deactivation of existing catalysts in the presence sulphur dioxide and especially in the presence of water vapour is the main problem [1,2].

Number of catalysts based on natural carriers has been studded. They were prepared via the incipient wetness technique and ion exchange method with Co (II) or Fe (III) ions. From the results presenting in the table 1 one can see that all the samples are active in the selective reduction of NO_x with methane.

Table 1. Catalytic Activity of Fe and Co containing Catalysts in Selective Reduction of NO_x with Methane. *

Sample	**Convertion,%. max.**	**T, K**	**Convertion,%. max.**	**T, K**
Fe 5%-F-160	40	903	40	903
Co 5%-F-160	70	650	70	650
Fe i.e. 5%-F-160	40	903	30	903
Co i.e. 5%-F-160	45	893	50	893
Fe 5%-KPP	40	883	50	883
Co 5%- KPP	60	673	55	673
Fe 10%- KPP	25	883	30	883
Fe 1%- KPP	10	893	10	893

* Conditions: $[CH_4]$=400ppm, [NO]=300ppm, $[H_2O]$=1%, space velocity 39000h^{-1}. F-160 and KPP are the natural carriers.

The obtained catalysts are stable below 873K in the presence of 1% water vapour and the convert ion slightly increases above 873K. The water conversion of methane to CO and hydrogen in the presence of Co and Fe ions is possible.

The catalysts provide high conversion of nitrogen oxide at high space velocities ($39000h^{-1}$). The possibility of creating honey-comb catalysts from the active component is an important advantage of them.

Literature.

1. Y.Li; J.N.Armor. //J.Catal., 150, 376-387, (1994).
2. A.Weda; M.Yaruta. 2-nd Tokyo Conference on Advanced Catalytic Science and Technology. Aug.21-26, 1994, Tokyo, Japan, 321-322.

PPC-102

Non-uniformity of Active Sites of Ziegler-Natta Heterogeneous Catalysts in Olefins Polymerization.

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The non-uniformity nature of active centres of heterogeneous metallocomplex catalysts in olefin polymerization, the distribution of active centres over the energy characteristics, the correlation of the last mentioned and the structure of surface catalytic complexes and their activity are curretly central problems in an investigation of Ziegler-Natta catalysis mechanism.

To obtain the information on the process of macromolecules formation an active sites of different energy state and aslo the early stages of macromolecules formation - of about 10-15 insertion of monomer links - the special experimental procedure using mass-spectrometric examination of the products of thermostimulated desorption (TPD) upon programmed linear heating of nascent sample "catalyst-polymer" in vacuum upto temperature of 500 °C .

In this work it was investigated by TPD method the ethylene polymerization in the early stages on supported catalyst Si-O-$TiCl_3$ + $AlEt_2Cl$ with registration of mass-spectrum over a range of m/e=10-400, that allowed to identify the desorption of polymer chains with -(-CH_2-CH_2-)- groups number in a range of 1-14. As it was shown [1], the catalyst used constituted the isolated Ti complexes covalently linked with SiO_2.

For samples of catalyst with nascent polyethylene prepared for a short time of polymerization and at low ethylene pressure two clear-out maxima were identified in the TPD curves over temperature interval of 180-320 °C, which were not observed in the TPD curves for samples of the catalyst before polymerization and the catalyst with nascent highmolecular polyethylene. This shows the maxima observed are unambiguously concerned with thermo-destruction of catalytic active sites Ti-C, formed in early stages of polymerization. The availability of two temperature maxima in the TPD curves indicates that at least two types of active sites which are distinguished by energy characteristics are present at catalyst surface. Based on the obtained results using mathematical simulation the bond energies of growing polyethylene macromolecules with active sites of marked types were assessed.

For analysis of non-uniformity of surface active centres the kinetics of gas-phase propylene polymerization upon stepwise poisoning of the catalyst based on $TiCl_3$ + $AlEt_2Cl$ by CO was investigated. The great non-uniformity of active sites on reaction with CO was shown under changes of CO concentration and contact duration. As a result of stepwise poisoning of the catalyst the decrease of chain propagation rate constant (Kp) on remainder of centres takes place.

The increasing of propylene polymerization activation energy upon permanent inhibiting of more active catalytic centres by carbon monooxide was shown.

Partial desorption of the cocatalyst from the titanium trichloride surface before monomer addition allowed to exclude less active centres and to study the properties of more active ones.

A correlation of time dependences of Mn of isotactic polypropylene obtained on the initial catalyst and on the catalyst subjected to a partial desorption of diethylaluminium chloride which enables to calculate corresponding Kp values points out once again substantial non-uniformity of active centres over Kp. An upper limit of Kp value for isotactic polypropylene obtained on system under investigation was assessed. It was shown that a sharp increase in rate constant of polymer chain termination was also observed in propylene polymerization on the separated more active sites hence a formation of most highmolecular part of the polymer is not connected with these high active centres.

REFERENCES

1. Kovaleva N.Yu., Krasheninnikov V.G., Gavrilov Yu.A., Novokshonova L.A. Polimery, v.34, N6-7, p.293 (1989).

PPC-103

GENERATION, IDENTIFICATION AND PHOTOCHEMICAL REACTIONS OF ALLYL RADICALS GRAFTED TO ACTIVATED SILICA SURFACE.

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Allyl radicals grafted to silica surface were obtained by interaction of buta-1,3-diene with silica structural defects such as $\equiv Si\cdot$ or $\equiv SiO\cdot$ obtained under photoactivation of silica surface and by a successive addition of formaldehyde, ethylene or acetone and buta-1,3-diene.

The structures of the allyl radicals ($\equiv SiCH_2\overline{C\dot{H}CHCH}_2$, $\equiv SiOCH_2\overline{CH\dot{C}HCH}_2$, $\equiv SiOCH_2CH_2\overline{CH\dot{C}HCH}_2$, $\equiv SiOCH_2CH_2CH_2\overline{CH\dot{C}HCH}_2$, $\equiv SiCH_2CH_2CH_2\overline{CH\dot{C}HCH}_2$, $\equiv SiOC(CH_3)_2CH_2\overline{CH\dot{C}HCH}_2$, I-VI respectively) were proved by comparison of their experimental and calculated ESR spectra of these radicals ; the latter was based on the first order perturbation theory and isotropy of g-factor and hyperfine coupling constants.

For the characterisation of free rotation of radicals grafted to silica surface correlation time τ (sec) for radicals with the structure $\equiv SiOCH_2\cdot$ through analysis of asymmetric broadening of width-lines of their ESR spectrum was estimated at $\lg\tau \approx -9{,}15$. Reactions of electronically-excited allyl radicals I-VI were investigated under irradiation at wave length $\lambda \geq 370$ nm (allyl radicals are known to have a long-wave symmetrical forbidden absorption band at $360 \leq \lambda$, nm ≤ 400). It was found that under the irradiation at room temperature allyl radicals III, IV, V photoconverted into alkyl radicals with the structure $\equiv Si(\text{or} \equiv SiO)\text{-}\dot{C}H\text{-}CH_2\sim$. The structure of the alkyl radicals was established through the comparison of their experimental and calculated ESR spectra based on axial symmetry of g-tensor and tensor of hyperfine interaction constants of α-hydrogen. The efficiency of photoconversion of allyl radicals IV into alkyl ones was estimated at ≈ 0,3. Under irradiation of radicals I at $\lambda \geq 370$

nm and room temperature concentration of structural surface defects ≡Si· increased. Under the same conditions concentration of radicals II and VI decreased without formation any paramagnetic centers which could be observed by ESR method under experimental conditions. It was established that under photoconversion of allyl radicals I-VI a total concentration of radicals considerably decreased (about 25-50%).

Under the irradiation at 77 K allyl radicals I converted into ones of cyclopropyl type, the last ones turned into radicals I at room temperature.

On the basis of estimation of average distances between neighbouring radicals, radicals and molecules adsorbed on silica surface under radicals generation and between radicals and surface hydroxyl groups it may be assumed that it is impossible for radicals grafted to silica surface to interact with each other and molecules adsorbed on silica surface (average distance is more than 10 nm) and that there is some probability of interaction between radicals grafted to silica surface and surface hydroxyl groups (average distance between them is about 1 ÷ 1,5 nm).

Probable reactions of destruction of radicals grafted to silica surface and possible mechanisms of photoconversion of allyl radicals into alkyl ones are discussed. The decrease of radicals concentration under photoirradiation at $\lambda \geq 370$ nm and room temperature is assumed to be a result of the rupture of the bond which is in β-position in relation to allyl part of allyl radicals (it seems to be more typical for radicals I and II) or hydrogen abstraction from surface hydroxyl groups (it seems to be more characteristic for radicals III-VI), with structural surface defects ≡SiO· obtained. It can't be determined by ESR method at the temperature more than 77 K. Migration of hydrogen atom from methylene group of alkyl part into allyl one of allyl radicals is likely to take place under photoconversion of allyl radicals into alkyl ones.

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PPC-104

Perspectivies of Application of Catalysts with Perovskite Structure on Metallic Substrates

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La-Sr-Cobaltate - based complex oxides $La_{1-x}Sr_xCoO_{3-y}$ having a perovskite structure are of scientific and applied interest as catalysts. These catalysts affects the oxidation reaction of carbon monoxide and the direct reduction of nitric oxides, and besides have the important ability to catalyse the following reaction:

$$NO + CO = 1/2N_2 + CO_2,$$

As our studies showed, this reaction can be used for purification of waste gases from nitric oxides, in particular, at heat power stations. In this case it is not necessary, to feed the purification zone by liquid or gaseous ammonia and carbon monoxide is a reducer.

As application practice shows the use of catalysts as coating on block-cell substrates is one of the optimum variants. The problem of preparation of complex oxides with the highly developed surface arises, because these compounds usually have relatively high temperature of synthesis, at which the sintering occurs. We have solved this problem by means of coating prepare by the method of spray-pyrolyses from salt solutions with special water-soluble polymer additions. Special conditions were chosen, when synthesis temperature of given phase in coating essentially decreased. Besides polymer additions improve film-formation and adhesion of coating. Additional increase of catalysts surface was achieved by with preliminary treatment of surface by sintering of metal powder with metal substrates.

One of the problems, solved in the present study - was the choice of cobaltate composition optimum for above-mentioned reaction catalysis: coefficient (x), and add the introduced doping d-elements. Comparable analysis showed, that perovskite $La_{0.8}Sr_{0.2}Co_{0.7}Fe_{0.3}O_{3-y}$ displayed high catalytic activity.

It was established, that the substrate material has the very important effect on catalytic activity of coating . In particular, titanium substrates increase catalysts activity. Analysis of coating/substrate system promoted with taking of kinetics and thermodynamics of possible reactions into consideration. There possible ways of change of physico-chemical nature of cobaltate was selected from obtained data on structure of transient catalyst/substrate zone and from and phase equilibrium in this zone. It is There possible to change nonsoichiometry parameter (y) and hence, defect structure of cobaltate in adjacent to titanium zone because oxygen leares it in order to form TiO_2 transient film. Reaction process can have more deep character if heterophase zone of partly reduced cobaltate occurs. At least titanium can dope cobaltate and form appropriate solid solutions. All there possibilities don't each other exclude.

The dependencies of catalytic activity of coatings on temperature and oxygen pressure in gas atmosphere for above-mentioned reaction were obtained.

Preliminary laboratory and semi-industrial tests of these catalysts on gas boiler justified their perspectivity.

PPC-105

INVESTIGETION OF MECHANISM OF LIQUID-PHASE CLAUS CATALYSIS REACTION

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To elucidate the mechanism of sulphur dioxide interaction with hydrogen sulphide in aqueous medium is one of the most important problems of the chemistry of inorganic sulphur derivatives.

We have obtained data on the reactions of catalytic reduction [1] and decomposition of a thiosulphate ion; and reduction of a thiosulphite ion by hydrogen sulphide as the Claus process went in weakly acidic media (pH = 4-6). Kinetic studies were performed with the marked molecules method [4]. We have correlated our experimental results [4] with the data of [2,3]. The data on the quantitative analysis of reaction products and the sulphur activity distribution permit to suggest the reaction scheme of sulphite ions reduction.

We may consider, that during the initial stage of sulphite interaction with hydrogen sulphide, elemental sulphide and thiosulphate only are forming via two simultaneous reactions. During the second, more slow stage, thiosulphate formed at the first stage, is reduced by hydrogen sulphide.

The overall reaction should comply with the four experimentally obtained conditions:

1. $\alpha_S / \alpha_{Na_2SO_3} = 0.2$
2. $\Delta C_{Na_2SO_3} / \Delta C_S = 6.0$
3. $\Delta C_{Na_2SO_3} / \Delta C_{Na_2S_2O_3} = 1.4$
4. $\Delta C_{Na_2SO_3} / \Delta C_{H_2S} = 3.0$

where α_S and $\alpha_{Na_2SO_3}$ are specific activities of the sulphur formed and initial sulphite, respectively; ΔC - variations of components concentration.

The overall reaction:

$$41Na_2\overset{1}{S}O_3+\frac{48,5}{2}H_2\overset{0}{S}\rightarrow\frac{57}{2}Na_2\overset{1/3}{S}\overset{1}{S}O_3+\frac{3}{20}Na_2\overset{1}{S}_{10}O_6+\frac{49,4}{2}NaOH+\frac{23,8}{2}H_2O+\frac{3}{2}\overset{1}{S}+\frac{10,5}{2}\overset{0}{S}$$

Testing the conformity of 1-4 conditions towards the overall reaction, we see that they are performed accurately.

Note, the formation of a high polythionate, like $Na_2S_{10}O_6$, at 50°C and pH > 3 is highly improbable. So here decapolythionate should be recognized as a mixture of low polythionates (tri-, tetrathionates) with the overall sulphur content being equal to ten.

REFERENCES

1. Z.P. Pai, N.N. Kundo, Zh. Prikl. Khim., 4 (1989) 1702.
2. R. Stendel, H.J. Mausle, Z. fur Anorgan. und Algemein, 10 (1979) 165.
3. L. Korosy, H.L. Gewanten, F.S. Chalmers, S. Vasan, Sulfur Removal and Rec. Ind. Proces., Washington D.C., 1975, p. 192.
4. Z.P. Pai, N.N. Kundo, V.A. Kirillov, 11th Intern. Congr. Chem. Eng., Chem. Equipm., Design and Automat. (CHISA'93), Praha, 1993, vol. B, p. 37.

PPC-106

FLUORESCENCE STUDY OF SILVER CATALYSTS FOR ETHYLENE EPOXIDATION

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Silver catalysts exhibit unique performance in ethylene epoxidation. The recent years have provided data proving that defects of silver play the key role in the reaction. Thus, the XPS method has shown that defects in subsurface layers of silver (when the local environment of silver deviates from the perfect one) tend to increase in number as the size of particles decreases [1]. This phenomenon leads to the noteaceble change of electron states in the silver bulk. As a result, ^{109}Ag NMR line (the Knight shift) disappears, when particles become less than 500 A [2].

In this work we have studied the defect states of silver by the fluorescence spectroscopy and related techniques. A set of silver catalysts ($Ag/\alpha\text{-}Al_2O_3$, AgY zeolite, Ag powder) with particle sizes from tens to ten thousand angstroms were investigated. Fluorimeter SPEX-1600 used to register emission and excitation spectra at ambient temperature. Fluorescence spectra were registered from 450 to 800 nm at sample excitation at a wave length of 250 nm. Before spectra registering we exposed the samples to different redox treatments at 230°C, as well as calcination in hydrogen at temperatures up to 800°C.

The spectra of silver catalyst exhibit a typical band with a maximum at 497-535 nm, whose position depends on silver dispersity. As the silver particle size increases, the band shifts to shorter wave lengths and its intensity is decreased. The excitation spectra of supported silver exhibit three main bands: intensive at 250 and 330 nm and weak at 380 nm. Again, their intensity is decreased substansially with increasing particle size. Moreover, for silver powder two latter bands disappeared, so that weak band at 250 nm was observed only. Taking into account the above-mentioned XPS and NMR data we think that fluorescence is caused by the defects on the silver surface. These defects can represent as isolated atoms or clusters localized, e.g., near the intergrain boundaries. It counts in favour of this statement that excitation band at 330 nm in Ag catalysts and the emission band of silver clusters in the zeolite at 535 nm are close to the line of the most intensive electron transitions in Ag atoms. The bands at 380 and 250 nm are close to bands of planar and bulk plasmons in UV-VIS DR spectra, respectively.

Two types of fluorescence mechanism are possible for the samples studied. We can name the first one as local or pseudomolecular. In this case light excites electrons on the local defects (band at 330 nm) that most likely are the individual clusters of Ag. The processes of excitation and emission (band at 500 nm) occurs from the same defects. The second mechanism allows the energy of irradiation to excite the bulk and surface plasmons. Then energy scatters on the defects according to the theory of plasma resonance with emission at 500 nm. Local mechanism is typical likely for Ag catalysts with small (defect) particles (d ≤ 200 A). In this case the excitation bands at 250 and 330 nm are comparable and have maximum intensities. It means that energy exchange between the local and collective (bulk) electronic states is far slower. Second mechanism is exibited by bulk Ag powder (d~ 10000 A) predominantly. In this case emission and excitation band intensities are not high due to fluorescence is caused by the excitation of bulk plasmons and the following energy scattering on few surface defects.

Heating at 700°C decreases the intensity of excitation band at 330 nm, but only slightly alters the band at 250 nm. Only heating at 800°C makes excitation bands at long wave lengths disappear and band at 250 nm remains in the spectra.

To create the selective ethylene oxide catalyst we need an optimum ratio of defect and regular surface parts [3]. These data agree well with the present study. Indeed, for sample with small Ag particles the concentration of defects (band at 330 nm) is maximum, while for Ag powder it is minimum. The optimum ratio occurs in sample with particle size of 1000 A where we have enough defect parts along with regular parts (band at 250 nm).

ACKNOWLEDGEMENTS

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References

1.V.I.Bukhtiyarov, I.P.Prosvirin, R.Kvon, S.N.Goncharova, B.S.Bal'zhinimaev. J.Phys.Chem., accepted for publication.

2.V.M.Mastikhin,S.N.Goncharova, V.M.Tapilin, V.V.Terskikh, B.S.Bal'zhinimaev. J.Molec. Catalysis A, Chemica I96 (1995) 175-179.

3.S.N.Goncharova, E.A.Paukshtis, B.S.Bal'zhinimaev. Appl. Catal.,126 (1995) 67-84.

PPC-107

Homogeneous Catalytic Asymmetric Hydrogenation of N-t-Butylphenacylamine into (R)-2-tert-Butylamino-1-phenylethanol Modelling Approach to Medicine Salbutamol

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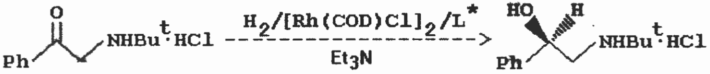
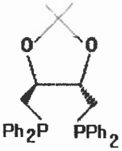
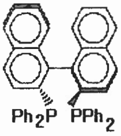
The asymmetric reduction of prochiral ketones to chiral alcohols is a pivotal reaction in organic synthesis. Catalytic homogeneous hydrogenation of ketones on chiral Ru [1], Ir [2] or Rh [3] complexes is more technologically attractive than reduction of CO group by chiral hydride reagents [4]. We describe herein an asymmetric catalytic hydrogenation of N-t-butylphenacylamine catalytic into (R)-2-tert-butylamino-1-phenylethanol. There is a clear analogy between chiral structure of this substance and medicine Salbutamol:



where L*:



1



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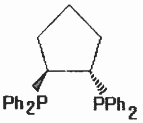

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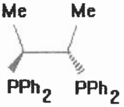

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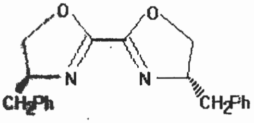

5

As it is shown in the table, the maximal conversion and optical yield were achieved on Rh/1 catalyst (entry 1 - 8). The optical yield of acetophenone hydrogenation is low in this condition though the product has the same configuration (entry 9). It's well-known [1] that chelate type coordination of functionalized ketones in the intermediate complex is of prime importance for high enantioselective hydrogenation in the case Ru/L*catalysts. The low optical yields in the presence of Rh/2 - Rh/4 (entry 10 - 13) catalysts probably indicate that there is no bidentante coordination of the substrate by Rh atom in the reaction conditions.

Table

Conditions[a]						Product[b]		
entry	catalyst	solvent	t°C	pressure atm	time, hour	conv. (%)	$[\alpha]_D$, grad	optical yield, %
1	Rh/1	MeOH/C_6H_6 (5 : 2)	50	100	4.5	100	-14.15	34 (R)
2	- " -	- " -	50	50	5.5	100	-14.60	35 (R)
3	- "-	- " -	50	30	4.5	100	-14.75	35 (R)
4	- "-	- " -	50	30	1.0	86	-9.13	21 (R)
5	- "-	- " -	50	17	4.5	100	-15.00	34 (R)
6	- "-	- " -	20	30	4.5	55	-11.36	26 (R)
7	- "-	- " -	50	30	4.5	100	-13.15	30 (R)
8	- "-	(4 : 3)	50	50	4.5	100	-15.30	35 (R)
9[c]	- "-	(5 : 2)	50	50	5.0	5[d]	-	8 (R)[d]
10	Rh/2	THF/C_6H_6 (4 : 3)	80	100	7.0	100	-2.75	6 (R)
11	- "-	- " -	50	100	9.0	0.1	0.0	0
12	Rh/3	MeOH/C_6H_6 (4 : 3)	50	50	4.5	65	-7.46	17 (R)
13	Rh/4	- " -	50	50	4.5	39	-1.80	4 (R)

[a] Hydrogenation was carried out in the presence of "in situ" complex in a glass ampule inserted into steel autoclave in purified hydrogen atmosphere, [Substrate (0.88 mmol)]/[Rh] =300, $[L^*]/[Rh] = 2.6$, $[Et_3N]/[S] = 0.01$, in 7 ml of dry solvents mixture.

[b] Conversion was determined by GLC analysis. Correlation of optical rotation and optical yield was deduced on the base of ee value of the product (entry 2), which was estimated by ^1H NMR with (S)-1,1'-binaphtyl-2,2'-diol as shift reagent. Configuration was deduced from the sign of the product optical rotation (entry 1, 3 in H_2O, others in MeOH) in comparison with halostachine ($PhCH(OH)CH_2NHCH_3 \cdot HCl$) [5] and related compounds [6, 7].

[c] Substrate - acetophenone.

[d] Conversion, ee and configuration was given by GLC analysis with β-cyclodextrine column.

Attempts of the asymmetric hydrogen-transfer hydrogenation of the substrate as a free-base on $[Ir(COD)Cl]_2/5$ catalyst (S/Ir/5/KOH(100:1:2.6:4) in 10 ml i-PrOH at 80°C) were hampered by the instability of the starting material in the reaction conditions.

References

1. R. Noyori, H. Takaya, Acc. Chem., Res., 1990, **23**, 345
2. Z. Xiaoyong et al, J. Amer. Chem. Soc., 1993, **115**, 3318
3. A. Roucoux et al, Tetrahedron: Asymmetry, 1993, **4**, 2279
4. M. Willis, J.R. Studley, Chem. Ind. (London), 1994, (14), 552
5. G.G. Lyle, J. Org. Chem., 1960, **25**, 1779
6. P. Pratesi et al, J. Chem. Soc., 1959, 4062
7. T. Hayashi et al, Tetr. Lett., 1979, 425

PPC-108

SYNTHESIS OF HETEROGENEOUS BIOCATALYSTS BASED ON SILICA

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Synthesis of silica-based heterogeneous biocatalysts may be fulfilled by the enzymes immobilization or by obtaining enzyme-modelling organic groups on silica surface. The success of this synthetic approach is possible if the three methods are used: molecular layering [1], solid phase peptide synthesis [2,3] and molecular imprinting method [4]. The first two methods allow to place on the surface of a matrix a great variety of oxide monolayers and organic functional groups, that may be used for enzymes immobilization and enzyme modelling. Additional opportunities for tuning a catalyst to a particular substratum are provided by the molecular imprinting method based on the forming of silica in the presence of susbstratum molecules. We revealed the possibility to regulate the catalytic properties of enzymes by synthesizing different number of titanium oxide monolayers of silica and by creating space organic groups of a definite size.

Synthesis of titanium oxide monolayers was carried out by alternating chemosorption of titanium tetrachloride and hydrolisis of the Cl-groups not having reacted with the support surface. The creation of space organic groups which served as centres for enzyme immobilization was carried out by processing of the silica surface with 3-aminopropyltriethoxysilane and 6 - (carbobenzyloxyamino) caproic acid using solid phase peptide synthesis.

For obtaining the substratum-oriented heterogeneous catalysts aerosil gel was formed in the presence of p - nitrophenilacetate. Silica produced by this method was then used for the synthesis of the titanium oxide layers with molecular layering method and for the creation of organic groups that form a part of active centres of serine protease. Synthesis of organic groups was implemented by a successive processing of the silica surface with β-phenilethyltrichlorsilane, water, chloromethyl methyl ether, imidazole, and N-protected amino acids. The properties of samples thus obtained were examined in the reaction of p-nitrophenilacetate catalytic hydrolisis. The investigation of the catalytic properties displayed a substatial excess of the activity of samples containing active centres on the substratum-present-formed surface over the activity samples obtained without the molecular imprinting.

Thus, the combination of molecular imprinting method with the molecular layering method and solid phase peptide synthesis is a promising way to synthesize heterogeneous catalysts based on silica. The synthetic methods used here could be employed for obtaining quite a number of catalysts when spatial correspondence between the substratum molecules and disposition of the active surface centres are essential.

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References:

1. Aleskovsky V.B. Chemistry of solids. Moscow, 1978.
2. Stuart B., Young D. Solid phase peptide synthesis. Moscow, Mir, 1971.
3. Postnov V.N., Makarov K.A., Aleskovsky V.B., Koltsov S.I. Doklady AN SSSR, 1977, v.235, N5, p.559-600.
4. Dickey F.H., J.Phys.Chem., 1955, p.695-707.

PPC-109

LEWIS ACID PROPERTIES OF α-;β-;γ-;δ- Ga_2O_3 SURFACES

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Ga_2O_3 is often used as petrochemistry catalysts component. It's catalytic properties supposed to origin from surface acid properties .

The aim of present work was to study acid properties of various Ga_2O_3 modifications. α-;γ-;δ- Ga_2O_3 modifications were synthesized after [1]. Oxides structure was determined by X-ray analysis. As well as DTA and DTG analysis of Ga_2O_3 polymorphic transformations have been studied. To study surface acid properties the method based on the formation of paramagnetic donor acceptor complexes between anthraquinone and Ga_2O_3 Lewis acid sites (LAS) has been applied. In ESR spectra of such complexes hyperfine structure corresponds to anthraquinone cation radical interaction with one (4 components) or two (7 components) equivalent gallium nuclei is observed. As it was detailed before [2] these spectra are of interaction between anthraquinone molecule and one or two nearby located coordinately unsaturated cations Ga^{3+}_{cus}.The results are in the Table .

n/n	modification	T pretreat,K	$[Ga^{3+}_{cus}]$ 10^{-16}, site/m^2	hyperfine structure	coordination number Ga^{3+} in Ga_2O_3	S,m^2/g
1	α(+γ ?)	728	9,7	7	6	87,0
2	γ+α	728	10,2	7	4,6	
3	β	728	12,2	7	4,6	14,1
4	δ	728	1,4	7+singlet	6	80,6
5	δ	473	0,4	7+singlet	6	80,6
6	β	473	0,08	7+singlet	4,6	14,1

The acidity of β-oxide surface correlates with those in [2]. The most probable way of strong LAS- three coordinated Ga^{3+} - formation is the dehydroxylation of Ga^{3+} ions in tetrahedral coordination. So that the acidity of γ-oxide and β-one are of the same value. The obtained γ-oxide sample has contained contamination of α-Ga_2O_3. This fact can be explained by easy transfer from γ- to α- under calcination. According to DTA data this transformation is an evolution type one and even prolonged calcination (5 hours,T=723 K) didn't resulted in pure α- Ga_2O_3 formation. It could be supposed that with α-oxide accumulation the surface acidity would become lower because of presence in α-oxide structure only 6-coordinated Ga^{3+}. However the sample 1 has demonstrated high acidity also. We assumed that due to high dispersity of sample 1 (S=87 m^2/g) its high acidity can be accounted for γ-oxide contribution. δ-oxide surface is one order magnitude less acid than β-one. Thus δ- Ga_2O_3 low acidity is probably due to the absence in its structure Ga^{3+} ions in tetrahedral coordination.

It should be noted that all ESR spectra of anthraquinone adsorbed on δ-Ga_2O_3 (with no dependence on temperature of preliminary treatment) contain single line, except seven component hyperfine structure. This spectrum as we supposed corresponded to anthraquinone anion-radical -anthrasemiquinone. Anthraquinone reduction process may occur on electron donor sites. On the rest Ga_2O_3 modifications such anthrasemiquinone single line didn't observed. The obtained data give evidence of higher donor and lower accepting ability of δ- Ga_2O_3 in comparison with the other oxides.

1.R.Roy, V.G.Hill, E.F.Osborn, JACS,74,719,(1952)
2. V.P.Galkin, E.V,Lunina, V.B.Golubev Zurn.Fizich.Khimii,48,1747, (1974)

PPC-110

OSCILLATING REACTIONS ON THE SURFACE OF Ag AND Ag-Pd NANOSTRUCTURES

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Nanostructures formed by the self-assembling from the electrochemically generated nonequilibrium metal nanophases on nonmetallic conducting substrates (glassy carbon, tin dioxide films, etc.) differ from bulk metals in the binding energies of core electrons and in the capacity to catalyze oscillating electrochemical transformations of the energy rich H-containing compounds (formaldehyde, hypophosphite-ions, etc.) [1,2].

In this work the mechanisms of the oscillating anodic reactions catalyzed by Ag and Ag-Pd nanostructures have been investigated in order to reveal the means of the self-ordering phenomena control in the electrochemical systems.

The oscillations of the electrode potential at a constant anodic current during the anodic oxidation of H-containing energy rich compounds have been found to result from the competition of two mechanisms with different dependencies of the reaction rates on the potential - a common mechanism with the exponential rate dependence and the specific mechanism characterized by high reaction rates at specific potentials and very low rates beyond the specific potential ranges. The latter mechanism is attributed to the non-electrochemical initiation of the anodic reaction followed by the electron injection from the unstable intermediate into the nanostructured electrode. The rates of the non-electrochemical stages are electrochemically controlled via the composition of surface layers dependent on the potential.

Computer simulation of the oscillating reactions kinetics based on our experimental results has revealed the necessity of the fits between the constants of electrochemical and non-electrochemical stages for nonlinear phenomena stimulation. These results have provided the design of the oscillating and bistable nanostructured systems with controllable behaviour.

1. G.A.Ragoisha, V.S.Gurin, A.L.Rogach, Microelectronic Engineering 27 (1995) 51.
2. G.A.Ragoisha, Interface, 3 (1994), No4, 58.

PPC-111

NEW REAGENT for the INVESTIGATION of ACTIVE OXYGEN in SOLID 2,2,6,6 TETRAMETHYL-1-HYDROXYPIPERIDINE.

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The importance of determination of active oxygen (AO) is connected with its influence on the properties of catalysts and superconductivity in HTSC. We proposed the reagent for this purpose - 2,2,6,6 tetramethyl-1-hydroxypiperidine (TMHP). This substance is able to react with various forms of AO, including molecular oxygen O_2: $2C_9H_8NOH + [O] - 2C_9H_8NO + H_2O$. This reaction results in the formation of stable nitroxide radical, which can be determined by ESR technique. The amount of AO reacted is found from the quantity of radical formed. We found, that the alumina and silica contain about $2 \cdot 10^{16}$ and 10^{15} atoms of AO per m^2, respectively. The TMHP was applied for extracting of active mobile oxygen (AMO) from superconducting perovskite-like copper oxides (at 290-330K) also. We studied the interaction of TMHP with phases of type A: $LnBa_2Cu_3O_7$ (where Ln=La,Pr,Nd,Sm,Gd,Ho,Yb,Y), $YBa_2Cu_4O_8$, $Bi_2Sr_2CaCu_2O_8$, $HgBa_2CaCu_2O_6$, and phases of type B: $La_{1,82}Sr_{0,18}CuO_4$, $HgBa_2CuO_4$. The phases of A and B types have different structural motives (one or two (CuO_2) layers per unit cell. The main effect of interaction of TMHP with "type A"-phases is a strong decrease of superconducting phase content when less than 0,08 a.u. of AMO (per unit cell) are extracted. Using our data on chemical and electrochemical behavior of AMO we proposed a hypothesis of its origin as a molecular oxygen.

PPC-112

COPPER CHLORIDE COMPLEXES WITH DIALKYL SULFIDES AS CATALYSTS FOR ISOMERIZATION OF CHLOROLEFINS

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The isomerization of 3,4−dichloro−1−butene (3,4−DCB) to trans − 1,4−dichloro−2−butene has been shown to be catalysed by polynuclear copper−dialkyl sulfide complexes [1,2]. Understanding of the formation mechanism of intermediate complexes and their role in the reaction is of great importance for development of new catalytic systems. According to our spectroscopic and kinetic data the maximum catalytic activity corresponds to the ratio Cu:L:D=3:2:2 (L=$(n-C_7H_{15})_2S$, D=3,4−DCB) which let us suppose that the complex of the same composition takes part in catalysis. The most active complexes can be obtained in dichlorobutene solution as by CuCl oxidation with O_2 as well by $CuCl_2$ reduction with dialkyl sulfide excess. Similar complexes have been identified in both cases.

Dialkyl sulfide (R_2S) complexes of $CuCl_2$ in chlorine−containing solvents (C_6H_5Cl) at the absence of chlorolefins presented parameters of the UV−Vis and EPR spectra (λ_{max}=308, 455, 710 nm; g_0=2,095, a_0=5.7 mT at 298 K, $g_\parallel$=2.180, $g_\perp$=2.060, $A_\parallel$ =14.2 mT at 77K) typical for tetragonal−bipyramidal structures with axial symmetry. Heating of the samples in C_6H_5Cl at 373 K leads to the reduction of Cu(II) complexes to CuCl, RCl and probably RSSR.

In the presence of chlorolefins, for instance 3,4−DCB, EPR−spectra of stable alkyl sulfide radicals ($RS^\bullet$) are observed superposing with a spectrum of Cu(II) complex with the spin−Hamiltonian parameters listed above. For R=$n-C_7H_{15}$ g= 2.032 and a^H=1.72 mT at 77 K. Two facts should be pointed out: 1) EPR−spectra at 298 K don't contain even traces of $RS^\bullet$ radicals; 2) the total amount of $RS^\bullet$ does not exceed 0.1−0.01% of the Cu(II) complexes' quantity.

Heating of the Cu(II)−R_2S solution containing 3,4−DCB leads to basic changes in the structure of copper complexes. A solution's colour becomes yellowish-brown instead of dark green ($\lambda_{max}=290$, 418, 900 nm), and the EPR-spectra indicate strong triaxial anisotropy of the Cu(II) ion's coordination sphere: $g_1=2.160$, $g_2=2.060$, $g_3=2.004$; $A_1=9.2$, $A_3=5.8$ mT. There are not any traces of the RS$^{\bullet}$ radicals. Computer simulation of the EPR-spectra together with analysis of the data published allowed to conclude that these very spectra are typical for trigonal-bipyramidal structure of Cu(II)-complexes with five ligand atoms. The same spectra have been obtained by heating at 373 K of the solutions containing CuCl with R_2S in the presence of 3,4-DCB and O_2.

Moreover, an EPR signal with $g=4.21\pm0.01$ has been seen at 77 K for the samples after heating; it indicates the presence of binuclear Cu(II) complexes in these samples.

The probable mechanism of the catalytic isomerization reaction of 3,4-DCB as well as structures of possible polynuclear mixed-valent intermediate copper complexes will be discussed in the paper.

1. T.N.Rostovshchikova, E.V.Vovk, E.N.Golubeva // Kinetics and catalysis. 1992. V.33. P.251, P.682.
2. T.N.Rostovshchikova, V.V.Smirnov, A.U.Bogomolov // Vestnik MGU. ser.2. Khimiya. 1995. V.36. P.145.

PPC-113

THE MECHANISM OF CIS-STEREOREGULATION IN THE POLYMERIZATION OF BUTADIENE IN THE PRESENCE OF LANTHANIDE CATALYSTS.

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Lanthanide catalysts, in particular $NdCl_3 \cdot 3TBP\text{-}Al(iC_4H_9)_3$ (TBP - tributyl phosphate), are highly *cis*-stereospecific in the polymerization of butadiene. However, the mechanism describing the behavior of the active centers in these systems is not completely clear.

To elucidate the reasons for high *cis* stereospecifity of lanthanide systems by means of guasi-relativistic extended Huckel theory, quantum-chemical calculatioins of the geometric and electron structure of $CH_3C^{\gamma}HC^{\beta}HC^{\alpha}H_2NdCl_2 \cdot Al(CH_3)_3$ as active center model of butadiene polymerization induced by $NdCl_3 \cdot 3TBP\text{-}Al(iC_4H_9)_3$ catalytic system have been carried out.

It is found that, as far as the total energy is concerned, the *syn*-structure of active center is more favourable than the *anti*-structure. This means that isomerization of the terminal unit from *anti*- to *syn*-structure is possible. From calculations it also follows that the *anti*- and *syn*-structures of active centers do not substantially differ in electron structure, providing the assumption that there is also a small difference in the reactivity of isomeric forms of active centers.

According to the results of our quantum-chemical calculations of model active center $CH_3C^{\gamma}HC^{\beta}HC^{\alpha}H_2NdCl_2 \cdot Al(CH_3)_3$, the terminal groups of growing polymer chains are connected to the Nd atom in the active centers via linkages of the π-allyl type. The chain growth proceeds via insertion of the monomer into the metal-carbon σ-bond. This means that for an effective chain growth event to take place, the coordinating diene molecule must in a some way stabilize the σ-structure of the terminal group $CH_3C^{\gamma}HC^{\beta}HC^{\alpha}H_2$. Further, it is also obvious that the coordinated molecule should be able to interact with the σ-bond Nd-C^{α} so that the insertion into this bond could proceed.

Quantum-chemical calculations for the active centers in model complexes with butadiene showed that the butadiene molecule is coordinated through its two double bonds in the *cis* or *trans* conformation. The essential feature of these complexes is that, regardless of its conformation, one of butadiene double bonds occupies the coordination place, which previously was occupied by the C^{γ} atom of the crotyl group. It is most important that, owing to occupation of this coordination place through one double bond, the *cis*-isomer of butadiene after slight changes in its orientation in the complex can interact through the other double bond with the active Nd-C^{α} bond in active center. The *trans*-isomer may be participate in interaction with the active Nd-C^{α} bond only after greate changes of its orientation in the complex. In this situation the stabilization of π-structure of center occurs and insertion reaction is stoped.

This result does not depend on the geometric structure of the active center as a whole (octahedral, tetrahedral, etc) and means that the delocalized π-allylic structure of the growing chain acts as a special lock which allows the insertion reaction only for the butadiene molecule in the *cis* conformation.

The suggested mechanism of *cis*-regulation takes into account a energetically preferable π-structure of active center, as compared with σ-structure. In accordance with these results may be wait, that in the catalytic systems where π-structure of active centers has not the energetically predominance must be lowering the *cis*-stereospecifity. The theoretical and experimental investigation of diene polymerization in presence the $NdCl_3 \cdot 3TBP$-MgRR' confirm this conclusion.

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PPC-114

Strongly bound nitrite-nitrates in copper- and cobalt-exchanged ZSM-5 zeolites as intermediates in the reaction of NO_x selective reduction by hydrocarbons under oxygen excess: adsorption centers, structure, bonding strength and reactivity.

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Strongly bound surface complexes have long been proposed as intermediates in the mechanism of some important heterogeneous catalytic reactions such as methanol synthesis, methane reforming etc. However, up to now any reliable data relating reactivities of these species to their structure and strength of bonding with the surface centers are absent. In the work presented surface nitrite-nitrates were chosen as a typical heteroatomic oxidants of a rather high reactivity.

To analyse the effect of the coordination symmetry of adsorption center on the properties of nitrite-nitrates, samples of Cu-ZSM-5 (square planar coordination) and Co-ZSM-5 (octahedral coordination) with transition metal content from 0.2 to 2 wt.% were investigated. Broad range of concentrations allowed a smooth adjustment of the properties of adsorption centers by changing their degree of clustering. IR spectroscopy of adsorbed CO was applied to differentiate isolated cations (high-frequency bands in the carbonyls stretching region) and clustered oxidic species (lower-frequency bands).

To study the routes of nitrite-nitrate formation and their structure, Fourier-transformed IR spectroscopy combined with N,O isotopes substitution experiments was employed. At ambient temperatures, nitrite- nitrates formation via nitrosyls oxidation was found to accelerate considerably by oxygen addition. To a first approximation, discrimination between nitrites and nitrates were based upon the analysis of the shift coefficient $K=\nu_1/\nu_2$ when changing $^{14}N^{16}O$ for $^{15}N^{18}O$ as well as upon splitting of the absorption bands observed in some cases. For samples where isolated cations predominate nitrites are mainly presented with absorption bands at 1610-1620 cm^{-1}and K= 1,038 ($^{14}N^{18}O_2$). At high transition metal contents nitrates are more abundant having the next spectral appearance: absorption bands at 1570 and 1482 cm^{-1} , K= 1,053 for Co-ZSM ; bands at 1635 and 1490 cm^{-1} , K=1,020 for Cu-Z ($^{15}N^{16}O_2{}^{18}O$) . These results imply that nitrates are mainly stabilized on cluster centers.

By using on-line chemiluminescence analyzer, TPD peaks of NO and NO_2 evolved into the He flow due to nitrite-nitrates decomposition were obtained as a function of cation nature, transition metal content, type of pretreatment and parameters of the adsorption and TPD . The most strongly bound forms of nitrates are located on Co-ZSM-5 decomposing at ca 450 ^{0}C (heating rate 10 degrees/min) yielding both NO and NO_2. For Cu-ZSM-5 the temperatures of similar species decomposition are somewhat lower being around 390-400 ^{0}C. When cobalt content in zeolite is rather high, a new middle-temperature peak of NO evolution was detected at ca 200 ^{0}C assigned to nitrites disproportionation into nitrates and nitrogen monoxide. For both systems high-temperature peak of NO evolution was found to shift to lower temperatures with increasing metal content in the series while corresponding peak of NO_2 evolution was shifted in the opposite direction. These results were analyzed taken into account the molecular mechanism of the nitrites/nitrates decomposition and effect of the extralattice oxygen bonding strength on the mode of N-O bonds disrupture.

Interaction of nitrite-nitrate complexes with propane was studied by using both flow-type IR-cell (spectrokinetic method) and pulse/flow microcatalytic installation with chromatographic gas-phase analysis. IR-experiments in situ allowed to monitor the dynamics of the surface species transformation under the action of propane+oxygen mixtures at temperatures close to real temperatures of catalysis. Reaction orders, rate constants and activation energies of this surface reaction were determined as dependent upon the sample composition and found to afford steady-state activities. These results prove nitrite-nitrate to be true intermediates and exclude any possible participation of weakly adsorbed or gas-phase NO in the rate-determining step of the reaction of NO selective reduction by hydrocarbons.

Pulse experiments for titration of the nitrite-nitrates by mixtures of propane in He; propane +oxygen in He support this conclusion. In the absence of oxygen in the gas phase, a small part of the most reactive forms of these species reacts with propane to give NO and nitrous oxide with selectivity around 75%. The predominant part of nitrite-nitrates is rather selectively converted into the molecular nitrogen even in oxygen-free conditions. A detailed analysis of the dynamics of the surface reaction as related to the bonding strength and structure of nitrite-nitrates has been carried out. Comparison with the steady-state catalytic parameters allowed to explain some kinetic features such as existence of the operating temperatures windows, promoting effect of oxygen etc. In particularly, higher temperatures of the efficient action of cobalt-containing zeolites as compared with copper -based systems were explained by more strongly bound nitrite-nitrates.

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PPC-115

Defect structure of the surfaces of dispersed transition metal oxides as key factor in catalysis of the oxidation reactions.

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In recent years surface science studies of the metals and oxides single crystals have demonstrated atomic structure of the surfaces to be of crucial importance in governing their reactivity including catalysis. A special role of defect centers both biographic and generated by the action of reaction media is emphasized. However, for dispersed transition metal oxides such data are nearly absent. In the work presented are given the results of the experimental and theoretical analysis of the influence of defect structure of the surfaces of transition metal oxides with corundum (alpha-Fe_2O_3) and spinel (Co_3O_4) type structures on the catalytic properties in the reaction of carbon monoxide oxidation. A special attention was paid to a working hypothesis assigning the most active centers to outlets of the extended defects (dislocations, stacking faults etc) on the surface.

Genesis of the defect structure as influenced by the precursor nature, annealing temperatures and/or mechanochemical activation in high-powered ball mills was studied by using diffraction methods (TEM, XPD, X-Ray Small-Angle Scattering). The main types of bulk and near-surface point and extended defects are identified and their relative densities are estimated. Extended defects generated in the course of precursors topotactic transformations were found to dominate for samples annealed at rather low temperatures ($T_{ann.}$<600-700 ^{0}C), while at higher temperatures new types of defects appeared due to recristallization processes (sintering etc). For high-temperature samples ($T_{ann.}$ ca 1000 ^{0}C), surface extended defects - steps generated by reconstruction of the open faces dominate . In all cases a segregation of alkaline and alkaline-earth microimpurities in the vicinity of extended defects was found to play a decisive role in their stabilization. Density of near-surface extended defects changes considerably due to variation of the stoichiometry and degree of hydroxilation of the surface layer, that is of a special importance for spinel Co_3O_{4+x} where according to XPS-SR data mainly subsurface layers are nonstoichiometric.

By using IR-spectroscopy of adsorbed CO/NO combined with low-temperature isotope dilution experiments in the adlayer, both isolated and clustered coordinatively unsaturated cations were found to exist on the surface. The density of clustered centers was found to correlate with the density of bulk or near-surface extended defects estimated by diffraction methods. Hence, cluster centers can be assigned to surface steps including those at outlets of bulk extended defects. Based upon spectral data as well as upon theoretical considerations, models of these centers were proposed including surface cations in octahedrons and subsurface interstitial cations. Formation of the Me-Me bonds between these cations after their reduction and rupture of such bonds at oxygen adsorption decreases the energy of oxygen bonding with these centers. Regular centers are mainly covered by the tightly bound bridged oxygen forms nonreactive at the usual temperatures of catalysis. Catalytic activity in the reaction of carbon monoxide oxidation was found to correlate with the density of surface cluster centers, while isolated coordinatively unsaturated cations (surface point defects) appeared to be inactive. Since for the same oxide phase density of cluster centers broadly varies as dependent upon the preparation conditions, it explains structure sensitivity of CO oxidation reactions catalyzed by these systems.

The properties of these cluster defect centers as well as the heats of the oxygen, NO and CO adsorption and kinetic features of the CO oxidation reaction were studied as dependent upon the mean stoichiometry of the surface layer, its hydroxilation and the presence of carbonates on the surface. Surface reduction process has been demonstrated to be of a topochemical type and proceed via spreading of the reduced zone from extended surface defects accompanied by cations redistribution between the regular and interstitial positions. Reoxidation as well as hydroxilation/carbonization causes shrinkage of this zone and affects its adsorption and catalytic properties. Thus, on a thoroughly dehydroxilated and weakly reduced surface catalytic reaction of CO oxidation proceeds with a high efficiency via Langmuir- Hinshelwood -type mechanism including interaction of CO and oxygen adsorbed on cluster centers. For oxidized and hydroxilated surface the rate of reaction drastically declines and reaction mechanism is formally described by the impact-type scheme of interaction of gas-phase or physisorbed CO with a moderately reactive surface oxygen. Hence, real surface of the powdered transition metal oxides studied is of a partially flexible type due to its easily rearrangment in vicinity of the surface extended defects.

Isotope kinetics methods including analysis of the tracer transfer and redistribution of the isotope molecules in the low-temperature reaction of CO oxidation catalyzed by Co_3O_4 has revealed oxygen atom from CO molecule to incorporate into the molecule of CO_2 product while the second atom of this molecule is derived either from catalyst surface layer or from the O_2 molecule with a nearly equal probability. Existence of several forms of surface oxygen was confirmed by these isotope methods; surface densities of the active centers were estimated and reaction turn-over numbers were thus obtained and compared with the known values for catalysis by supported Pd clusters.

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PPC-116

VIBRONIC ASPECTS OF COORDINATION CATALYSIS.

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The foundation of modern views on chemical reaction paths is the second order Jahn-Teller effect proposed by Bader [1] and evolved in detail applying to the reactivity of coordination compounds by Pearson [2]. In catalysis these ideas have been successively developing in Bersuker's works [3].

Unfortunately these ideas have not found a wide development becourse of intricates of numerical calculations of electron, especially 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 simplest rules avialable for wide practical uses of them in describing coordination compounds as such are catalytic intermediates.

In this work we are suggesting and theoretically justifying the fundamental tenets in accordance with which a wide range of catalytic reactions proceeding with low symmetric active complexes which are, as a rule, variousligand, 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.

Initial antecedents:

1. Structures with the geometry of regular octahedron (Oh) and tetrahedron (Td) having the highest multiplicity of degenerated states were chosen as models.

2. Unequivalency of ligands was considered in terms of perturbation theory.

3. Only vibration coordinates displacement along which reveals to the change of the length of valent bonds M-L (in octahedron these are e-vibrations, in tetrahedron-t_2-vibrations) are taken into account.

Fundamental tenets of suggested concept:

1. Labile (potentially active) are the structures normal electron state of which correlates with E- and T-terms of initial octahedron and T-terms of initial tetrahedron.

2. 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.

Outcomes of theoretical model:

Vibronic model permits to reduce reactions proceeding with hydride and alkyl complexes (hydrogen exchange, isomerization, dimerization, hydrogenation et.al.) to reactions of intrasphere exchange. Experimental tests of concept:

In context of suggested concept the rule of "18 electrons" has been gained its theoretical justification and have been explained reasons for:

1. high stablity of octahedric polyhydride compounds of Co(3+) and Fe(2+).

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.

3. high activity of Ni(1+) cationic complexes in olefin dimerization.

4. existance of complexes of composition $(PR_3)_3NiCl$ in forms of three trigonal pyramides, quantum axes of which pass along Ni-P bond.

5. weak bonding of axial ligand in complexes $(PR_3)_3NiCl$.

6. existance of planar complexes of Cu(2+) and Ni(1+) in forms of tetragonal structures and of analogouis composition low spin complexes of Ni(3+), Co(2+) and Fe(1+) in forms of rhombic structures.

REFERENCES

1. Bader R.F.W.//Can.J.Chem.1962.V.40.No6.P.1164.

2. Pearson R. Pravila simmetrii v khimicheskikh reaktsiyakh.M:Mir.1979.592P.

3. Bersuker I.B.Effekt Jahna-Tellera i vibronnyje vzaimodeistviya v sovremennoi khimii.M:Nauka.1987.320P.

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PPC-117

REGIOSELECTIVITY OF OLEFIN INSERTION IN THE HECK REACTION

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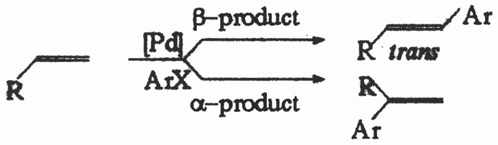
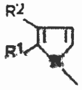
A number of olefins with substituents having various electronic and steric properties were tested to study factors, influencing on the regioselectivity of Heck arylation process. Particularly 1-vinyl-2,3-disubstitued pyrrols have been used as substrates for the first time.



(1)

R=CH_3, Ph, BuO, HOOC, C_4H_9, или  где, R^1=H, Me, Ph, R^2=H, Me, Pr, i-Pr, Ph

It was established that the type of addition of "Ar" in the absence of steric barrier is not dependent on the effective charge distribution of vinyl group carbons (which was evaluated by chemical shifts in ^{13}C NMR [1]) and has best correlation with their contributions in LUMO of olefin (MNDO, AM3, PM3 method calculations). It indicates the realization of the orbital control of regioselectivity and is in accordance with conclusions of authors [2] about the decisive importance of the transferring process of electronic density from HOMO of the metal complex to LUMO of olefin at the synchronic mechanism of insertion reaction.

In the presence of substituents at the β-carbon of vinyl group the steric factor seems to be dominating. So the appearance of methyl or phenyl group in position 2 of pyrrol ring actually influences on the regioselectivity of the reaction. Under these conditions α-product of Heck reaction firstly becomes practically unique.

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REFERENCES

1. B.A.Trofimov, A.I.Michaleva. N-vinylpyrroles,-Nauka, 1984, p. 260
2. I.I.Zacharov, V.A. Zacharov, G.M.Jidomirov. Kin. i Catal., 1994, T35,N1,p.74-82

PPC-118

KINETICS OF VARIOUS METAL CONTAINING COMPOUNDS SYNTHESIS BY REACTIVE METALS OXIDATION IN NON-AQUEOUS SOLUTIONS

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Reactions of metals with differen oxidizers in non-aqueous solutions have been known for a bond time. They are widely used or obtaining of organometallic and coordinated compounds. However, thermodynamic parameters and kinetic features of the summary process and its steps have not been studied. They've been no explanation of the role and mechanism of the action of coordinating solvent in those processes.

This paper is devoted to studying of kinetic laws of interaction between copper, silver, gold, magnesium, zinc, cadmium, tin and halogenes, quinones, different halocarbons in coordinatig solvent.

It was found out that: 1) rate of metal oxidation as a function of a donor number of the solvent has an extremum; 2) oxidation of metals in the solutions considered above proceeds according to the mechanism including equilibrium adsorption of reagents at adsorptions centers, which can be the same or different.

By using of the obtained experemental data it was possible to calculate rates of summary reaction at different couditions, equilibrium constants and enthalpies of adsorption of reagents on the metal survace.

Equilibrium constants and enthalpies of adsorption of some oxidezers and solvents used, as well as the number of adsorption centers per unit of the metal surface were found out by studying of adsorption of these compounds at metal surface by the method of quartz weighting.

Using the data obtained in experiments is possible to propose a scheme of synthesis of metal containing compounds by oxidation of corresponding metals in the presence of ligands.

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PPC-119

Engineering hammerhead ribozymes with high catalytic activity and exceptional stability to biological environment

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Hammerhead ribozymes are relatively small catalytic RNA molecules, which are accessible to mechanized chemical synthesis and, therefore, to structural engineering. For potential therapeutic applications ribozymes must be tailored to high stability in cells and body fluids, while retaining high catalytic efficiency and selective target recognition. Our principle is to achieve these goals with minimum deviation from the biological polynucleotide structure, in order to minimize the risk of toxicity and immunogenicity of the ribozyme analog and its putative biodegradation products. Therefore, we have introduced two structural alterations:

1. a 3'-terminal sense inversion (3'-3'-internucleotidic bond)
2. replacement of pyrimidine ribonucleoside units by 2'-deoxy-2'-fluoronucleoside units at a minimum number of intrachain positions previously identified from the cleavage pattern in human blood serum.

Following this route, we could obtain catalytic hammerhead RNA analogues with >2 days stability in human blood serum. Unmodified oligoribonucleotides will be fully degraded in 10 min. under these conditions.

Amazingly, the 3'-terminal inversion leads to an increased K_{cat} value versus unmodified ribozyme. The catalytic efficiency ($K_{cat/Km}$) is not much decreased by these structural modifications.

Aspects of the therapeutic application of synthetic ribozymes will be discussed.

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Photoassisted preparation of metal/oxide composites: towards the selective fixation of palladium on supported ceria.

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When studying the influence of metal-support interactions on the activity and selectivity of metal catalysts, the modification of the properties of the carrier need not be limited to changing the carrier itself; it can also be done through: (i) introduction of *additives,* an old practice;(ii) the use of *composite* oxides. The latter method has recently received increased attention by Schwarz et al (1) who have tried to carry out the *selective fixation* of a metal on just one component of the composite, through the different exchange abilities of the two oxide phases arising from their *different points of zero charge* (P.Z.C.). However, this method seems to be useful only when the disparity of the P.Z.C. is large. Moreover,while modifications in the catalytic behaviour have been established, the location of the metal in the composite has not.

We propose another approach to achieve the selective fixation of a metal on one component of a composite when that component is semiconducting (s.c.) and the other is an insulator. This approach exploits the differences in *electronic and optical properties* of each oxide, the semiconducting being susceptible to *photoactivation* . In the present work, two procedures are applied:

**Electroless plating* , an ancient procedure (2) which has lately received a renewed attention, in particular in the field of microelectronics. This method has been applied recently in the preparation of supported metal catalysts (3).

***Photoassisted reduction*, a well known process which has been applied to the preparation of mono-metallic and bi-metallic catalysts but, up to now, exclusively to *bulk* semiconducting carriers.

The composite oxides studied here are mainly ceria-silica but ceria-alumina and ceria-magnesia were also investigated.The composite were prepared by (i) anchoring cerium acetylacetonate on silica, alumina or magnesia (ii) calcination in air. Characterization of carriers and catalysts was achieved by several techniques : UV-visible, NIR spectroscopy (transmission and diffuse reflectance) XPS, HREM-STEM , X-EDS and X-ray line broadening measurements

It was observed that the grafting method employed leads to nanoparticles of supported ceria, in the 2-6nm range, which allows a quantum size effect to be detected. Palladium deposited via the *electroless procedure* is detected exclusively in the metallic form. On the other hand, the distribution of size of Pd particles is very large. Along with small particles (2-3 nm), there are also big ensembles (150-600 nm), Hence electroless deposition is not convenient to obtain narrow particle size distributions on dielectric particles. On the other hand, Pd deposition via *UV assisted photoreduction* is better suited for controlling the location of metal particle and their range of size. No Pd-free ceria particles have been found. Among the parameters governing the photoreduction of Pd, the pH value of the precursor solution seems to be the most important. Its control maintains the (Pd^{2+} / Pd) potential below the level of the ceria conduction band, a prerequisite to the photoreduction (5); it also precludes the precipitation of palladium hydroxide, taking into account the pH increase arising from the photoreduction of adsorbed H^+ ions. The best results are obtained in slightly acidic medium (pH ~ 3-5). *Such a selective metallization method may be extended to any composite system containing a semiconducting phase fixed on an insulating support.*

References

1) a)J.A. Schwarz, Catalysis Today. 15 (1992) 395.
b) R. Zhang, J.A. Schwartz, A. Datye and J.P. Baltrus, J. Catal., 135 (1992) 200.
2) M.Paunovic and J. Ohno, Proc. Sympo. Electroless Deposition of Metals and Alloys (The Electrochemical Society, Pennington, 1988)
3) A.Bensalem, G. Shafeev and F.Bozon-Verduraz, Catalysis Letters.18 (1993) 165.
4) A. Bensalem, F. Bozon-Verduraz, M. Delamar, G. Bugli, Appl.Catal A:, 121 (1994) 81.
5 M. Grätzel, *Photocatalysis, Fundamentals and Applications* (Serpone and Pelizzetti ed.) J.Wiley (1989) 123.

Scanning tunneling microscopy of the metal supported on carbon catalysts.

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Since its development a scanning tunneling microscopy (STM) as a powerful tool has been applied to many systems including metal single crystals and foils as a model catalysts. However, the STM studies of the highly dispersed catalysts are still at the starting point [1].

In this Communication, STM was used to study the morphology of the metal (Pt, Pd) particles supported on the various carbons, e.g. mesoporous carbon, filamenteous and porous carbons. In addition, the surface of the supports itself also have been investigated in detail.

The STM images were obtained with the home-built microscope in UHV chamber equipped with surface facilities (Auger spectrometer, ion guns and electron beam heater). Pd/C samples were prepared by impregnation of mesoporous carbon 'Sibunit' with palladium chloride. Pt/C catalysts were prepared by electrochemical deposition on porous carbon from platinum chloride solutions.

Generally, the surfaces of all the carbons studied were very rough. A large number of features looked as a semi-sphere particles of ca. 50 Å in diameter and 10-20 Å in height were revealed in the STM images. In 'Sibunit' they were attributed to the small crystallites covered by amorphous carbon. In the case of the filamenteous carbon the similar features are observed as well as irregular shaped (Fig.1).

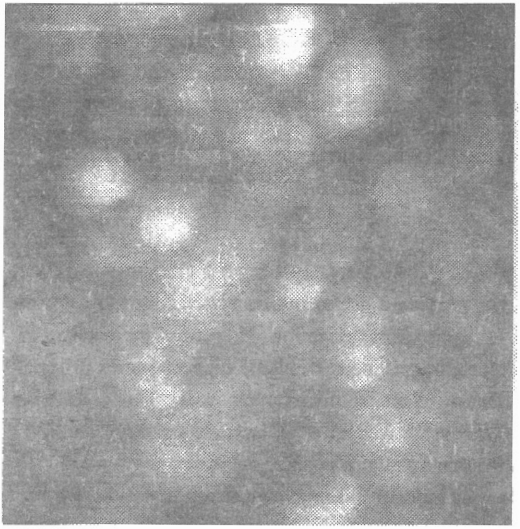
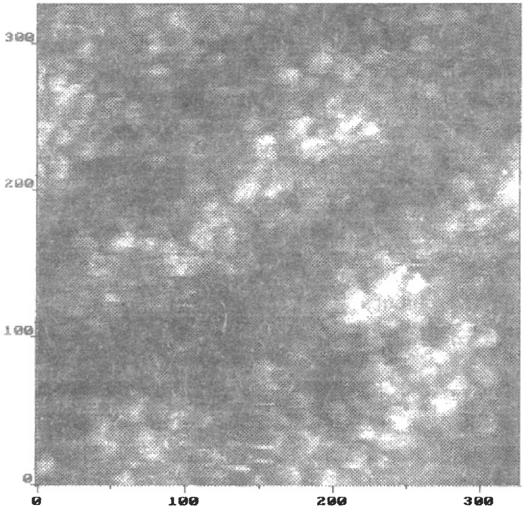


Fig.1 An 32x32 nm^2 STM image of the filamenteous carbon. Black-to-white gradation corresponds to 16Å.

It was suggested that the graphite layers on the surfaces of the filaments are forced to form a curved basal planes to diminish the total surface energy.

In the conditions when self-reduction of the Pd occurred on the carbon granules the STM images resolved a sphere-shaped particles ca. 20-50 Å in diameter. Despite the Pd particle size measured by X-ray diffraction were found ca. 300 Å, we never observed the large metal particles. It appears that the surface of larger particles is covered by smaller ones.



The Pt electrodeposition on porous carbon led to the formation of the ca. 40-100 nm metal particles. After the electrochemical oxidation of ethylene-glycol the STM images demonstrates very small ca. 10 Å clusters on the particle surface (Fig.2). The similar features was also observed on the Pt foil after identical treatments. Therefore, the changes of the metal surface morphology occurs during the electrocatalysis.

Fig.2 An 32x32 nm^2 STM-image of the Pt/C electrocatalyst.

Thus, the STM studies really can provide a useful information about the catalyst surface structure and can be used for their characterization. Note, that the surface of highly dispersed carbon supports and supported metal catalysts are sometimes differed from those proposed from transmission electron microscopy data. The combined studies when both microscopic techniques as well as other surface sensitive methods are used could propose the adequate models of the supported catalysts.

This work was supported by Russian Science Foundation (Grant 93-03-04754).

References.

[1] Sh.K.Shaikhutdinov, and D.I.Kochubey, Russ.Chem.Rev., 62(1993) 409.

PPC-122

CONTROL OF ELECTRONIC STRUCTURE OF METAL CLUSTERS BY VARIATION OF ACID-BASE PROPERTIES OF MOLECULAR SIEVES

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Two fundamental features in the behaviour of small metallic particles are related to both *intrinsic* electronic and structural properties and metal-support interaction which can significantly affect the effective charge of the cluster. The electron density of the small particles is directly related to the activity in the hydrogenation-hydrogenolysis reactions and to sulfur tolerance. However, the mechanism of this phenomenon is still a matter of great debates and controversy.

This work is addressed to the study of the electronic properties of small metallic clusters (Pt, Pd, Rh) in the range of 0.5-6 nm located within zeolite structures. in the dependence of the acid-base and polarization properties of zeolitic environment (NaX, NaY, HY, KL, Na-ZSM-5, H-ZSM-5) and comparison of these characteristics with reactivity in CO adsorption and sulfur tolerance.

The combination of the spectroscopes e.g., XPS, X-AES , FTIR of CO chemisorbed and HRTEM reveals intrinsic size-dependent effects as well as polarization and charge transfer for the metal particles caused by metal-support interaction. XPS core level and valence band spectra of rhodium in NaX show the considerable difference in the density of occupied d-states for small (1 nm) and large (>3 nm) particles due to spd-rehybridization..

Like XPS B.E., CO stretching frequencies are also size-dependent due to the different contribution of d-2p backdonation for small and large metal particles.

The data obtained by XPS and FTIR CO techniques demonstrate a strong dependence of the CO frequencies and the B.E. shifts on the donor-acceptor (acid-base) properties of the zeolite for clusters of similar size and serve as a very good guide for the identification of metal-support interaction (Table). The Pt interaction with protons in H-ZSM-5 results in the significant electron-deficiency manifested by a positive shift of the B.E. (1.4-1.6 eV) and a blue shift (20-

30 cm^{-1}) of CO stretching frequency. By contrast, platinum clusters of similar size in KL zeolite show anomalous low singleton frequency, 1925 cm^{-1} , which indicates the dramatic increase of d-2π backdonation due to higher electron density on the platinum cluster. In accordance with low CO frequencies the B.E. is shifted only by 0.3-0.4 eV for clusters containing 5-10 atoms.

The analysis of Auger parameter for Pd clusters in zeolites with different acidity (NaY, HY, Na-ZSM-5, H-ZSM-5, H-LTL, K-LTL) indicates that for cluster of similar size the effect of interaction with zeolitic support is predominant. Actually , genuine chemical shifts for metals on strong basic zeolite supports are negative indicating the increase of their electron density.

The mechanism of the interaction involves the formation of Me- framework oxygen bond which can be polarized in different direction in the dependence of the oxygen charge. The polarization properties of zeolite framework for strong acids and strong bases are also analyzed. They show that oxygen in KL can act as σ donor to donate negative charge to the Pt and Pd particles. Simple calculations of the effective charges on oxygen and platinum taken from the literature are in line with the experimental data (Table). The electron-deficiency of small particles found on acidic supports (HY, H-ZSM-5) is also related to the interaction between metal clusters and protons. Thus, the electronic properties of Pt and Pd, as any other metal can be varied by changing acid-base properties of the zeolite support without variation of the particle size which opens new possibilities for the activity control in such reactions as selective hydrogenation, dehydrogenation, NO reduction. The effect of electronic state of small Pt and Pd particles on CO chemisorption and sulfur tolerance has been demonstrated

Table. *XPS and FTIR CO data for nanoclusters in acidic and basic zeolites.*

Zeolite	Metal[a]	Acidity	Cluster size, Å	ΔE_b, eV	νCO,[b] cm^{-1}	The charge on Me[c]	The charge on oxygen[c]
H-ZSM-5	Pt	high	8-10	+1.4-1.6	2073	+0.1	-0.25
HNa-ZSM-5	Pt	moderate	10-15	+0.6			
HY	Pt	high	10-15	+0.8-0.10	2063	+0.13	-0.23
NaY	Pt	neutral	10-15	+0.6	2049		
KL	Pt	high basicity	<10	+0.3	1925	-0.03	-0.36
NaX	Rh	low	10	+0.7	2040		
NaX	Rh	low	30	+0.3			
NaX	Rh	low	60	<0.1			

a) determined at low CO coverage b) M.J.Kappers, Ph.D.Thesis, Utrecht University, 1993

PPC-123

New Photochemical Aerobic Oxidations of Saturated Hydrocarbons

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One of tempting tasks of contemporary chemistry is to develop new methods for the aerobic high selective oxidation of organic substances and especially hydrocarbons under mild conditions [1]. It seems that photochemical oxygenation with molecular oxygen (autooxidation) is a very perspective method of a chemical transformation because in this case, the process usually takes place at ambient temperature and atmospheric pressure of dioxygen (or often even air). Photoinduced catalyzed reactions of organic compounds with O_2 are very important as they are not only convenient synthetic routs to valuable products (peroxides, ketones, acids, *etc*), but also due to the fact that various biological systems apply light to stimulate the processes occurring in the living cell.

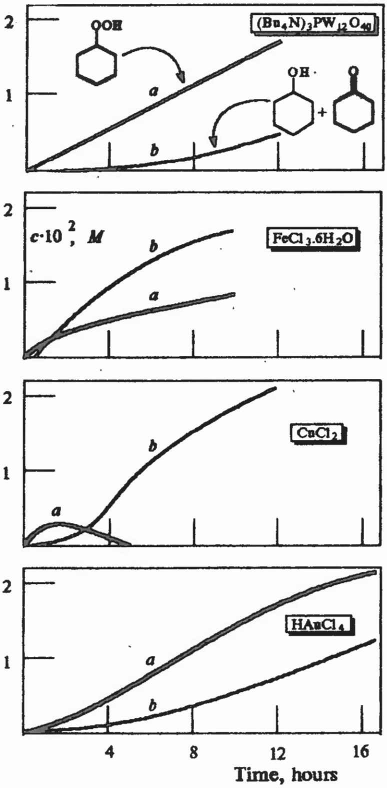

Figure 1. Kinetics of the cyclohexane (0.46 *M*) aerobic photooxygenation in the presence of various catalysts (5 · 10^{-4} *M*) in MeCN.

In recent years, we found that some inorganic complexes can efficiently catalyze aerobic photo-oxidation of alkanes and arylalkanes in solutions in MeCN or MeCOOH. The compounds $FeCl_3$, $CuCl_2$, $HAuCl_4$, polychromates, iso- and heteropolyoxometalates, uranyl chloride were used as photo-catalysts (see, *e.g.*, Fig. 1 and 2). Ketones (aldehydes), alcohols and alkyl hydro peroxides were formed as the main products in these reactions. It is interesting that light irradiation of emulsion of cyclohexane and aqueous solution of iron perchlorate (or chloride) in air produces exclusively cyclohexanone; no cyclohexanol or cyclohexyl hydroperoxide have been detected. In contrast to all these reactions, irradiation (long-wavelength light of incandescent lamps was used) of alkane solutions in MeCN in the presence of quinone and copper acetate causes smooth oxidation of the hydrocarbon by air to yield alkyl hydroperoxide which is stable under the conditions employed and is only very slowly decomposed to produce ketone (aldehyde) and alcohol. Alkyl hydroperoxide may be easily reduced by triphenyl-phosphine to alcohol and thus the reaction provides a convenient method of selective preparing alcohols from saturated hydrocarbons. The peculiarities of the reactions mentioned above and many other reactions developed by the authors will be discussed in the report.

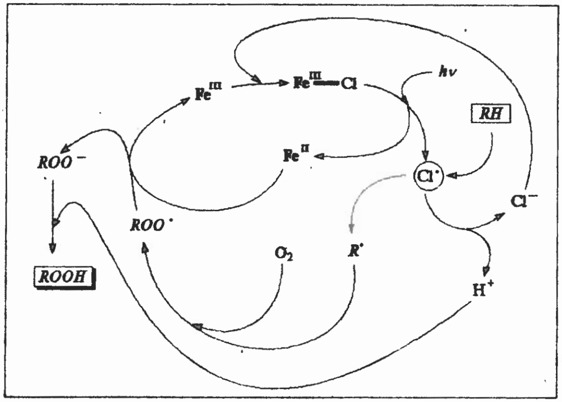

Figure 2. Proposed photocatalytic cycle of $FeCl_3$ - sensitized oxygenation of an alkane, *RH*.

This work was financially supported by the *International Science Foundation* (grants nos. MMS000 and MMS300), *INTAS* (grant no. 93-1226) and the *Russian Basic Research Foundation* (grant no. 93-03-5226). Some results have been published [2-7].

References

1. G.B.Shul'pin, *Organic Reactions Catalyzed by Metal Complexes*, Moscow: Nauka, 1988.
2. G.B.Shul'pin, A.N.Druzhinina, *Mendeleev Commun.*, **1992**, 36.
3. G.B.Shul'pin, A.N.Druzhinina, L.S.Shul'pina, *Neftekhimiya*, **1993**, *33*, 335.
4. G.Süss-Fink, G.B.Shul'pin, *Russ. Chem. Bull.*, **1994**, *43*, 1085.
5. J.Vicente, A.Arcas, D.Bautista, G.B.Shul'pin, *J. Chem. Soc., Dalton Trans.*, **1994**, 1505.
6. G.B.Shul'pin, M.M.Bochkova, G.V.Nizova, *J. Chem. Soc., Perkin Trans., 2*, **1995**, No. 7.
7. G.B.Shul'pin, G.V.Nizova, *Mendeleev Commun.*, **1995**, No.4.

PPC-124

BIOMIMETIC ALKANE OXIDATION. NEW CONCEPT OF METHANE MONOOXYGENASE MECHANISM.

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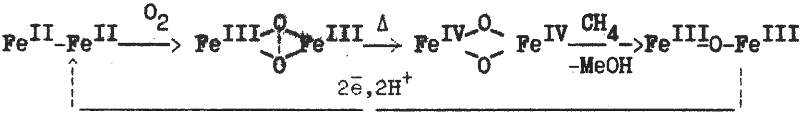
Binuclear μ-oxo iron complexes with terminal bidentate (bpy, phen or pyridine-carboxylate) and labile monodentate (H_2O, MeOH) ligands allow to model some structural, spectral and functional properties of Fe_2O enzyme methane monooxygenase (MMO) [1-3]. The study of biomimetic alkane (involving methane) oxidation mediated by these complexes and effect of substituents in terminal (bpy) and bridge ($RCOO^-$) ligands on their catalytic activity permit of some conclusions about the mechanism.

It is supposed that binuclear structure of the active center of MMO plays a determing role in dioxygen activation and in selectivity and specificity of alkane oxidation with this enzyme. New concept of MMO catalytic cycle involving the on-side coordination of O_2 and formation of bis-μ-oxo diiron (IV) complex, which is the active intermediate interacting with alkanes, has put forward and grounded [4].



Two centered mechanism of alkane activation and O-atom insertion into C-H bond, which explains the available results on selectivity of alkane oxidation by MMO much better, was suggested.

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1. A.A.Shteinman. *Dokl.Chem.*, 321, 775 (1991)
2. A.A.Shteinman. *Mendeleev Commun.*, 155 (1992)
3. A.A.Shteinman. *Russ.Chem.Bull.*, 42, 227 (1993)
4. A.A.Shteinman. *FEBS Lett.*, 362, 5 (1995)

PPC-125

Low-temperature Hydrodehalogenation of Polyhalogenated Aromatic Hydrocarbon Catalyzed by Me (0)/C.

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Halogenated hydrocarbons have found widespread use in all parts of sosiety, due to its well established excellent physical and chemical properties. Unfortunately these properties also leads to severe adverse effects, namely a lot of polychlorinated aromatic hydrocarbons are pollutants of the environment. Hydrodechlorination reactions compared to other detoxification methods are gaining importance because they allow the polychlorinated aromatics to be reduced to the parent hydrocarbons without the production of waster. Such reaction are very prospective for organic syntesis.

Liqued phase hydrodechlorination of 1,2,4,5 tetrachlorobenzene, hexachlorbenzene with Me (0)/C (where Me - Pd, Ni and C - carbon material - "Sibunit" or CFC - catalytic filamentouse carbon) have been studied at 20 -70°C. As hydrogen sourse was used hydrides ($NaBH_4$, $LiAlH_4$, $NaH(LiAlH_4)_{1/2}$). According to the studies catalytic composite 4% Pd/CFC - $NaH(LiAlH_4)_{1/2}$. This catalytic composite allowed to carry out effective dechlorination polychlorinated aromatic compounds at 70°C. Kinetic studies showed, that hydrodechlorination of these compounds to be concecutive reaction and under the conditions described may produce less-chlorinated compounds. In case of hydrodechlorination 1,2,4,5 tetrachlorobenzene the reaction path-way is: 1,2.4 trichlorobenzene and then, sequentially: the three dichlorobenzene isimers, chlorbenzene and benzene. Thus the method allows selectivity remove halogen from the aromatic ring.

In the case of hydrodechlorination of 1,2,4,5 tetrachlorobenzene in the presence Ni/CFC - $NaH(LiAlH_4)_{1/2}$ gives only 1,2,4 trichlorobenzene.

The formation of supported on C (Sibunit) metal particles (Pd) by chemical reduction metal salts with hydrides has been investigated. The particles size was characterized by X-ray phase analysis methods. Reduction of metal salts with hydrides resulted in the formation of metal particles with average sizes ~100 and 30 Å, depending on the reaction conditions. It was shown that catalytic activity (mg prod./g metal/min) depends on particles size. The 100 Å particles of metal were inactive.

The active component formation was studied using ^1H, ^{27}Al high-resolution solid state NMR spectroscopy of $LiAlH_4$ - Pd/C samples (where C - "Sibunit"). Pd complex hydrides were shown to form on the surface of the support.This methods provide important importation on the types of hydride species and their interaction with support surface. Supporting of $LiAlH_4$ - Pd/C samples results in formation of two hydride spesies, containing Pd and Al_xH_y in there there structure. Combination of results on hydrodechlorination of polychlorinated aromatic hydrocarbon with NMR date allows to one suggest that the formation of the mixed Pd - $LiAlH_4$ supported hydrides is may be responsible for the increase of the activity.

NONDIRECT INFLUENCE OF HETEROGENEOUS CATALYSTS ON SOLID WASTE PROCESSING

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We need to provide optimal conditions for catalyst action on a solid organic waste to make the catalytic combustion efficient. Using of a fluidized bed of dispersed catalyst allows to obtain a good mass exchange at considerably low temperatures (400-700°C) and efficient interaction of solid organic particles with air, while the intermediate products evolving due to this interaction are burnt on the catalyst surface. Meanwhile, nitrogen combined in the organic waste is oxidized mainly to molecular nitrogen. Sulfur compounds do not evolve into the gas phase due to the low combustion temperatures but remain combined in the mineral part of organic waste. The catalyst presence increases also the combustion degree. The similar dependencies were obtained upon the combustion of active sludge, micellar wastes from the production of drugs, city sewages and some agricultural wastes. After the catalyst bed the amount of nitrogen oxides does not exceed 150 mg/m^3, the amount of CO about 0,01% vol.. No sulfur oxides were registered after the catalyst bed.. Varying the stay period of particles in the catalyst bed via changing the bed height or fluidization rate, we can change the combustion degree, decrease the evolution of volatile components and increase carbonization of coke. The yield of solid product can attain 50-60% with respect to the sediment type. Investigation of the product texture shows, that we can obtain adsorbents with a high specific surface due to the low process temperatures. In the inert bed, where combustion proceeds in the diffusion region at 800-1000°C, micropores and mesopores are destroyed and a specific surface of products is decreased. Production of adsorbents via the catalytic processing of solid industrial wastes allows to combine efficiently utilization of sediments and purification of industrial effluents. Now, the scheme is implemented at "Grigishkes" (Lithuania) for purification of effluents provided upon fiber wooden plates and paper production. The industrial large scale tests have shown the possibility to implement the cyclic sediment treatment with a following utilization of solid product for adsorption/coagulation purification of effluents. In comparison to the known methods for detoxication of sediments and purification of effluents the new method allows to: reduce and size and metal weight of apparatus by factor 20; arrange an autothermal process at the wetness of sediments less than 75%; liquidate or reduce considerably gas ejections intoxicated with organics, oxides of carbon, nitrogen and sulfur; provide a high degree of effluent purification from the dissolved and condensed materials without expensive or deficit flocculants and coagulants.

PPC-127

INFLUENCE OF SUBSTRUCTURAL CHARACTERISTICS OF CARBON MATRIX ON CHEMICAL PROCESSES PROCEEDING ON ITS SURFACE

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Carbon materials are widely used as effective adsorbents or catalyst supports. It is well known that the nature of carbon used can strongly affect proceeding of processes of adsorption or catalyst formation. This is usually explained by differences in texture or surface chemical composition of carbons.

On the other hand, surface reactivity of solids may be governed by their dispersity as well as their structure imperfections. It is evident from the fact that work function and surface tension are size- and structure-dependent thermodynamical characteristics of dispersed solids.

Carbonaceous materials possess a huge variety of carbon matrix organization, as it follows from numerous studies involving X-ray scattering techniques (SAXS, WAXS, RDF). In this connection it is necessary to reveal and theoretically generalize correlations between thermodynamic or kinetic parameters of the chemical processes taking place on the carbon surface and the substructural characteristics of the carbon matrix derived from X-ray scattering spectra. The solution of the problem is a way of the evolution of scientific bases for production and use of carbonaceous materials which are optimal in a given process.

We had studied a set of commercial carbons by WAXS method. Their substructure properties can be ascribed by such characteristics as the interlayer d-spacing (d_{002}), the dimensions of quasi-graphitic crystallites (L_a, L_c) and relative integral intensities of X-ray diffraction signals from the (001) and (002) reflections (I_{001} and I_{002} respectively, the integral intensity of the 002-line for graphite being taken as a standard. Analysis for carbon substructure-dependence of work function [1,2], potentiostatic corrosion [3], H_2PdCl_4 adsorption equilibrium [4] and dispersion of Pd/C catalysts [5] was then performed.

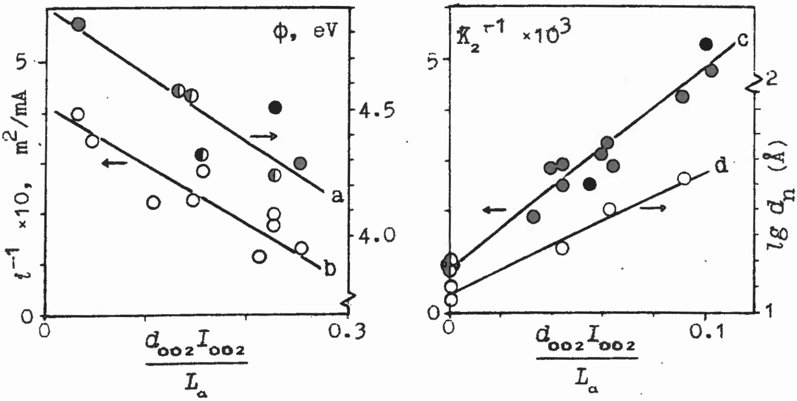

Fig.1. a) Work function (ϕ), b) specific corrosion currents (l) (H_3PO_4, 170°C, 1 V, 100 min), c) equilibria constants (K_2) of the strong adsorption of Pd/C catalyst precursor (H_2PdCl_4+C, 20°C) and d) mean diameters (d_n) of Pd particles in the final catalysts ($PdCl_2$/C + H_2, 1 atm, 250°C, 3h) as functions of the substructural characteristics of carbons.

The results are summarized on Fig. 1. These data show the surface processes involving charge transfer between carbon and reagents or adsorbed species to be substructure-dependent.

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REFERENCES

1. T.J. Fabish and D.S. Schleifer. *Carbon* 22, 19 (1984)

2. R.O. Loutfy. *Carbon* 24, 127 (1986)

3. P.L. Antonucci, F. Romeo, M. Minutoli, E. Alderucci and N. Giordano. *Carbon* 26, 197 (1988)

4. Yu.A. Ryndin, O.S. Alekseev, P.A. Simonov and V.A. Likholobov. *J.Molec.Catcl.* 55, 109 (1989)

5. P.A.Simonov, E.M.Moroz, A.L.Chuvilin, V.N.Kolomiichuk, A.I.Boronin and V.A.Likholobov. 6-th Internat. Symp. Sci. Bases for the Preparation of Heterogen.Catalysts. Sept. 5-8, 1994, Louvain-la-Neuve, Belgium. Preprints, Vol.3, 201 (1994)

PPC-128

ELEMENTARY STEPS OF RADICAL-SURFACE INTERACTIONS IN HETEROGENEOUS-HOMOGENEOUS PROCESS OF LOW PARAFFINS PARTIAL OXIDATION.

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A number of processes of catalytic oxidation are known to proceed via evolution of free radicals to the gas phase and their consecutive homogeneous and heterogeneous transformations. The new approach for kinetic modelling of such heterogeneous-homogeneous processes over oxide catalysts is suggested. It is based on the determination of the combination of elementary reactions taking part in overall process (including heterogeneous and gas-phase steps) and correlation between thermochemistry and kinetics of elementary radical reactions.

The processes of methane partial oxidation and oxidative dehydrogenation of ethane to ethylene over oxide catalysts were taken as the testing reactions for examination of the above mentioned approach. The model calculations are compared with experimental data. The following results were obtained:

- the difference of the rates in steady-state catalytic process and in separated redox cycles is caused by contribution of free radical processes in re-oxidation of the oxide and determined by water formation;
- the addition of peroxides to reaction mixture can lead to acceleration or inhibition of the process depending on relative contribution of homogeneous dissociation of ROOH molecules (into active RO and OH radicals) and their reaction with active sites on the surface leading to the formation of relatively inactive ROO radicals;
- the shift of selectivity in methane oxidation from oxidative coupling products (C_2-hydrocarbons) to oxygenates (HCHO) at temperature and $P(O_2)$ variations is caused by

(a) the equilibrium state in gas-phase reaction

$CH_3 + O_2 <=> CH_3O_2$

and

(b) the rates of radical-surface interactions such as

$[O] + CH_3O \dashrightarrow [OH] + HCHO$
$[\,] + CH_3O \dashrightarrow [O] + CH_3\ (\dashrightarrow C_2H_6)$

The main characteristics of the catalysts determining the rates of the processes and products distribution are H-atom affinity of the active surface oxygen and oxygen binding energy.

A model taking into account mass transfer in the pores of the catalyst was utilized to analyze the effects of addition of inert gas and total pressure on catalytic and non-catalytic methane oxidation. According to our experimental data, in absence of catalyst the addition of the inert gas leads to the sharp increase of selectivity towards oxidative coupling of methane (OCM) without any significant change of the rate of reaction due to contribution of inert gas as the third body in recombination of methyl radicals:

$$CH_3 + CH_3 <==> C_2H_6^*$$
$$C_2H_6^* + M ---> C_2H_6 + M^* \qquad (1)$$

Stabilization of exited ethane molecule $C_2H_6^*$ by collision with inert gas atoms M increases the number of CH_3 radicals transformed into OCM products decreasing the relative contribution of oxidation processes.

Addition of low surface area catalysts (<0.5 m^2/g) leads to increase of both reaction rate and C_2-selectivity increase, but the influence of inert gases is weak. We concluded that the surface of the catalyst is more efficient than monoatomic gases in removal of excess energy in recombination reaction (1).

In case of higher surface area catalyst (15 m^2/g) we observed the increase of the rate of reaction and C_2-selectivity when the pressure of inert gas was risen. This effect is more pronounced in case of argon compared to helium. It can be explained in the terms of heterogeneous-homogeneous mechanism of reaction including heterogeneous generation of radicals and chain reaction with branching in the gas phase. The contribution of surface-initiated gas reaction increases at decreasing rate of diffusion in case of the catalyst having relatively high surface area and more developed pore structure due to increase of the residence time in the interior gas space.

In general, the influence of catalyst morphology on the rate of heterogeneous-homogeneous reaction and products distribution can be described by taking into account competition of elementary processes of heterogeneous radicals formation, chain branching in the gas and heterogeneous termination complicated by mass transfer in the particles of the catalyst.

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PPC-129

NEW KINDS OF POLYNUCLEAR METAL-COMPLEX CATALYSTS IN REACTIONS OF HALOGEN DERIVATIVES

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Some principles of metal-containing enzyme action can be used to create a new type of polynuclear metal-complex catalysts possessing extreme efficiency. High activity of polynuclear catalysts is provided by the fact that oxidation-reduction centres and donor-acceptor groups present in catalytic complex at a time. Polynuclear complexes based on aluminium, copper and iron halogenides are highly active in the reactions of addition to olefins, isomerization and halogen exchange in allylic olefin halogenides. The reaction rates in the conditions of polynuclear catalysis are several orders higher than these with monomeric catalysts [1].

Stable polynuclear copper complexes with n-donors have been found to be the most active in isomerization of dichlorobutene [2,3]. Catalytic activity of complexes in series of donors increases in the following order: amine < phosphine < sulfide. The activity of dialkyl sulfide copper complexes increases in the following order: R= i-propyl < n-heptyl < n-butyl < ethyl < methyl. Process rate dependencies on donor concentration have a maximum at 1-3 ligand/copper ratio, corresponding to the highest concentration of an active polynuclear complex. The relationship between nuclearity and catalytic activity is shown below:

Copper compound	CuCl or $CuCl_2$	$CuCl_2$	CuCl	CuCl		$(CuCl+CuCl_2)$	
Donor	– – –	R_2S	R_2S	R_2S	PPh_3	PPh_3	R_2S
Complex nuclearity	– – –	1	1	2-3	4	4	3-4
Activity, rel.units	<1	1	2	6	8	16	20

Complexes containing 3-4 Cu atoms, substrate molecules and organic donor ligands have been isolated and studied by UV, IR and EPR methods. In the presence of oxygen these complexes are easily transformed into heterovalent ones catalytic activity of which depends on Cu(I)/Cu(II) ratio. The simultaneous presence of different oxidation states of copper in the catalytic complex may be explained by an electron transfer step in the isomerization mechanism. Features of the molecular structure of allylic chlorolefin ease one-electron transfer. The following scheme can be proposed:

$$\mathrm{Cu(I)} + \mathrm{RCl} \rightarrow \mathrm{Cu(II)} + \mathrm{RCl}^{\bullet -}, \qquad \mathrm{RCl}^{\bullet -} \rightarrow \mathrm{R}^{\bullet} + \mathrm{Cl}^{-}$$

$$\mathrm{R}^{\bullet} + \mathrm{Cu(II)} \rightarrow \mathrm{R}^{+} + \mathrm{Cu(I)}, \qquad \mathrm{R}^{+} + \mathrm{Cl}^{-} \rightarrow \mathrm{R'Cl}$$

In our opinion mixed copper complexes can be of use as catalysts for other similar processes of conversion of organic halogenides such as halogen exchange and addition to a multiple bond of olefins.

Kinetic regularities of reaction catalyzed by polynuclear complexes, i.e. hydrochlorination of olefins and isomerization of chloroalkenes, have been studied. The reaction kinetics strongly depends on stability of polynuclear catalyst. High reaction orders on a catalyst of 2 to 4 have been found in the case of $FeCl_3$ or $AlBr_3$ forming non-stable polynuclear complexes. High hydrochlorination rate in the case of non-stable Fe(III) polynuclear complexes is attributed to participation of tetrameric $FeCl_3$ complex with HCl in the catalytic reaction. H_2O and a number of organic n-donors (ethers, alcoholes, amines, sulfides) breaking polynuclear molecules were shown to be inhibitors of the processes. Reaction rate also decreases drastically at high olefin concentrations.

Preliminary conclusions about the mechanism of catalysis by polynuclear metal complexes have been made. Synchronous process realization and possibility of electron-transfer without considerable changes in the bond length between the centres fixed in one complex results in an essential decrease of activation energies.

1. T.N.Rostovshchikova, V.V.Smirnov, A.Yu.Bogomolov // Vestnik MGU. ser.2. Khimiya. 1995. V.36. P.145.
2. T.N.Rostovshchikova, E.V.Vovk, E.N.Golubeva // Kinetics and catalysis. 1992. V.33. P.251, P.682.
3. T.N.Rostovshchikova, V.I.Pergushov // Zhurnal obshchey khimii. 1994. V.64. P.12, P.985.

PPC-130

CATALYTIC SYNTHESIS OF ORGANIC MOLECULES IN GAS-CLUSTER SUPERNOVA REMNANTS

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Interstellar medium and molecular clouds contain various and rather complicated chemical compounds including organic ones, such as aldehyde, alcohol, esters, carboxylic acids, amino acids. The presence of organic compounds in an interstellar medium at low, practically cryogenic temperatures needs to be explained /1/. Previously, Gol'dansky with coauthors/2/ put forward a hypothesis about the tunnel reactions, which are enable to contribute to the synthesis of complex molecules in the cold molecular clouds. In the present work there is studied an assumption whether the expanding shells of supernova stellars represent a natural catalytic reactor, where the main synthesis of the complex organic molecules occurs.

Qualitatively the formation and functioning of such a reactor proceeds as follows. Stellar before its transformation to supernova has a structure with chemical elements arranged in layers, beginning with hydrogen and helium in the upper layers and ending with iron in the stellar center. During the explosion of the stellar with an intensive nucleosynthesis of the elements being more heavy than iron the surface hydrogen- helium layers cast out into the surrounding space forming a thin shell. The boundaries of such a shell are formed by two concentric shock waves. One of such waves, being directed from the stellar, compresses interstellar gas. Another shock wave, directed to the stellar, compresses the running on flow of the stellar substance. Due to gas dynamics expanding and substance radiation behind the shock waves fronts the thickness of the shell with respect to the distance from the stellar doesn't practically change. This structure is a stable one and ensures high substance concentrations at moderate temperatures. At the later stages of expansion the atoms and gaseous compounds of the carbon- oxygen layer arrive at the hydrogen shell and mix there. High-melting compounds of alumina, silicon as well as titanium, iron and other transition metals while expanding from the stellar form the clusters which become the base for interstellar dust grains.

Such clusters consisting of the catalytically active metals and compounds penetrate via a shock wave to the gas phase of the shell. As a result the conditions for heterogeneous catalytic reactions of the synthesis of complex organic compounds are created in the shell. The presence of carbon monoxide, a large excess of hydrogen, availability of the cluster phase catalytic activity, maintenance over a long period of time of a high reagent concentrations and temperatures being suitable for chemical conversion favor this process. The further expansion of the shell results in freezing of the reaction products. IC443 /1/ provides an example of such supernova remnants with shock waves structure.

Quantitative description of these ideas is performed by computer simulation on the basis of the dynamics equations of multi-phase, multi-flow medium/3,4/. They include:

- gas dynamic expansion of the supernova shell in the interstellar medium with the formation of a couple of shock waves, producing a region of chemical synthesis;
- coagulation of high-melting compounds;
- cluster's getting through with regard to gas component;
- change of the shell temperature owing to radiation, heat conductivity of electrons and contribution of chemical reactions.

/1/. B.E.Turner and L.M.Ziurys. Interstellar Molecules and Astrochemistry. "Galactic and Extragalactic Radio Astronomy". Eds. G.L.Verschuur and K.I.Kellermann. Springer-Verlag. 1988, p.200-254.
/2/ L.B.Goldanskii et al. Facts and Hypotheses of Molecular Chemical Tunnelling. Nature, 1979. V.279, p.109-115.
/3/. V.V.Maksimov, A.M.Orishich, A.G.Ponomarenko, V.N.Snytnikov. Effect of target geometry on compression of ions into a shell in a laser plasma expanding into vacuum. Sov.Phys.JETP 1989, 69(4), p.712-721.
/4/. L.B.Gavin and A.A.Shraiber. Turbulent flows of gas with particles. "VINITI. Ser. Mechanics of Fluids and Gases", 1991. V.25, p.90-182.

PPC-131

EPR and NMR Spectroscopic Study of Ferric Peroxide Species - Reactive Intermediates of the Iron Picolinate / Pyridine / Acetic Acid / HOOH Catalytic System for the Direct Ketonization of Methylenic Carbons

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Using EPR and ^1H NMR spectroscopy the high and low-spin iron complexes were characterized in the iron / picolinate / amine /acetic acid / HOOH (t-BuOOH) catalytic systems for the direct ketonization of methylenic carbons, the amines include pyridine or its derivatives [1]. The ferrous complex $Fe(PA)_2 \cdot 2H_2O$ (1) was used as a starting material for a catalyst (PA, anion of picolinic acid). The complex 1 rapidly reacts with H_2O_2 at room temperature. At the initial stage of this reaction the complex 1 converts into the mononuclear ferric complex 2 $Fe^{III}(PA)_2OH$ in amine/ acetic acid solvent systems.

When pyridine or pyridine/acetic acid solutions contain a great excess of water, the very unstable low-spin ferric complex 3 is observed besides the complexes 1 and 2. The observed EPR signal ($g_1 = 2.176$, $g_2 = 2.133$, $g_3 = 1.961$) of this complex and its unstability closely resemble end-on peroxo iron(III) complexes [2].

The low-spin ferric peroxocomplexes similar to complex 3 were also detected in [py]/[AcOH] = 1:1 volume mixtures for the following catalytic systems:

$Fe^{II}(bpy)_2^{2+} + H_2O_2$ ($g_1 = 2.15$, $g_2 = 2.12$, $g_3 = 1.97$)

$Fe^{II}(bpy)_2^{2+} + Me_3COOH$ ($g_1 = 2.195$, $g_2 = 2.14$, $g_3 = 1.965$)

$Fe^{II}(phen)_2^{2+} + H_2O_2$ ($g_1 = 2.14$, $g_2 = 2.12$, $g_3 = 1.97$),

where bpy - 2,2′-bipyridine, phen - 1,10-phenanthroline.

The type 3-peroxocomplexes can be considered as possible reactive intermediates, which can abstract hydrogen atom at the initial stage of the methylenic carbon oxidation.

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References

[1] Hui-Chan Tung, Chan Kang, and Donald T. Sawyer, *J.Am.Chem.Soc.* **114** (1992) 3445-3455.

[2] A. Sauer-Nasarwa, N. Herron, C. M. Fendrick, D. H. Busch, *Inorg.Chem.* **32** (1993) 1086-1094.

"COLD" SYNTHESIS OF SUPPORTED CATALYSTS UNDER CONDITIONS, INITIATED BY A BEAM OF ACCELERATED ELECTRONS.

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Introduction.

It is well known, that the main stages of any conventional thermal synthesis catalysts (synthesis, modification, drawing of a active component, calcination and other) are carried out for a long (up to several hours) time at high temperatures. It is connected with diffusion processes - slowest stages of synthesis. Therefore thermal synthesis is accompanied by deterioration of catalysts quality: agglomeration, dehydration of a surface supports and etc.. Within the framework of conventional thermal synthesis it is impossible completely to exclude such negative phenomenon, remains only to determine conditions of realization of synthesis with a minimum collateral reactions. At radiation-thermal synthesis (RTS) it becomes possible to execute radiation stimulated reaction in the special conditions under the beam accelerated electrons, in essence excluding negative collateral processes, connected with high temperatures.

Results and Discussion.

The main idea of "cold" RTS of catalysts consists of replacement of slow diffusion-controllable stages of active metals salts decomposition on their radiolysis, proceeding on a radical gear. We determined realization conditions of reactions, this idea to become possible for real laboratory experience and industrial processes.

The method of "cold" RTS of heterogeneous catalysts is based on creation of reactions non-stationary conditions. Such conditions arise at continuous irradiation of catalysts by a beam accelerated electrons with energy up to 2,0 MeV. The electron's beam is formed on a powerful electrons accelerator. The processing by a electrons beam permits to execute synthesis at short-term (1-2 minutes) irradiation of initial reagents in conditions of the final active phase formation at very low (370-470 K) temperatures.

RTS is executed at the introduction of large energy density directly in to the volume of the irradiated material. The concept of " the gradient of temperatures on granule" loses significance, as far as the heating is accompanied by increase of temperature of the whole volume. In the surfaces layer large gradients of the electrical field, micro break-down and ionization of molecules are created. Emission (IR, visible, UV, soft characteristic X-ray emission, X-ray emission with energy up to 2,0 MeV) stimulates reactions on a radical gear.

Thus, non-stationary conditions of irradiation, parameters which are designed and checked by practice, permit to finish RTS and synthesize ready catalysts for very short period, when catalysts have no time to be heated (the "cold" synthesis).

Unsteady-state chemical processes of catalysts synthesis by powerful beam accelerated electrons have been investigated. RTS was conducted on a electrons accelerator with energy up to 1,6 MeV. A temperature interval from 373 K up to 1473 K was investigated. The time of irradiation was varied from 0,5 up to 40 minutes. Typical Ni-, Co-, Fe-, Pd-, Pt-containing supported catalysts were synthesized (Supports: γ-Al_2O_3, TiO_2, SiO_2). For RTS of particles on a supports the most favorable area of effect, enabling the generation of metals crystallites with minimum size and the temperature threshold irradiation have been determined. For the method of preparing catalysts by salts impregnating to the support from water solutions of, stage irradiation in a beam of accelerated electrons and subsequent reducing in a hydrogen was developed.

The effect of RTS catalysts consists of essential distinction of speeds of processes high-temperature radiolysis of active components salts and phase transitions of a supports structure at irradiation by a electron's beam, therefore:

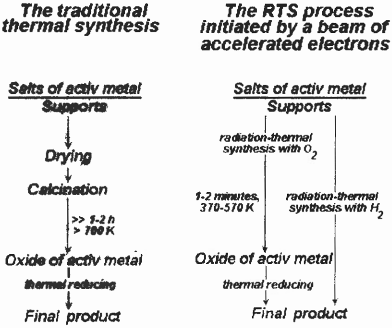

Fig.1. The scheme of carrying out of synthesis of catalysts in conventional conditions of thermal heating and unsteady state conditions of radiation-thermal synthesis

1) RTS of catalysts by a beam accelerated electrons at the expense of a small time of effect permits to avoid irreversible decrease of catalyst activity owing to phase transitions in a supports structure. All physical-chemical properties of a supports (porosity, specific surface area, phase structure, strength, density and etc.) are completely saved.

2) The decomposition of metals salts by a beam accelerated electrons effectively proceeds already at temperatures 320-370K during 1-2 minutes, that makes possible to exclude a calcination stage at catalysts synthesis (Fig.1.).

Computer calculations (the Monte-Carlo method) of the depth of effective distribution accelerated electrons with energy up to 1,0-1,6 MeV in a target show, that granules with the size up to 10 mm can be successfully used for synthesis of supported catalysts. The synthesis of supported catalysts is carried out practically lost-free in energy (up to 10 % at the charge of 0,5 kW/kg of a catalyst) down to 20-25 mass. % of a supported metals. Similarly the small losses of energy and of a penetration depth will be the same at any density of supports. Thus, for any catalysts with density, typical for porous oxides of Al, Ti and Si (and it's practically the whole spectrum of present known supports), radiation-thermal processing is applicable.

Technological applications.

RTS model conditions of supported catalysts is conducted for the first time. The data on scientific researches and laboratory experience are processed on a computer and are prepared for representation in the standard "engineering". The typical universal rules on designing of a technological line of "cold" catalysts synthesis are prepared on the basis of received scientific data.

THE EFFECT OF AMINS AND AMINOACIDS ON THE RATE STEROID OLEFINS DARK AND PHOTO OXIDATION CATALYZED BY Mn PORPHYRINATES

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Catalytical systems on base of metalloporphyrins (MP) are available to model the specific activity of hem containing oxidazes including Cyt. P-450 and to determine the main factors controlling that activity.

This report discusses the problems of modelling the influence of aminoacid residue of enzyme polypeptid chain on the catalytical activity of hem - Fe(III) protoporphyrin.

In vivo the high activity of hem in oxidation processes is basioly controlled by peptids surrounding the active center. In particular, His and Cys withdrawal from Cyt.P-450 active center leads to the enzyme desactivation [1]. And the substitution of Met-80, included in the Cyt. ?c active center, by the Cys results in the Cyt ?c showing properties similar to those of Cyt.P-450 [2].

However, in the modelling systems of metalloporphyrin - reducer[1], catalysing regio- and stereoselective oxidation of steroid olefins, Fe complexes with porphyrin (PFe) are considerably less active than Mn porphyrinates (PMn) [3].

To create adequate oxigenaze models we metalloporphyrins containing substitutors with various donor-acceptor properties. We showed thatsubstitutor effects on the catalytical properties of PFe and Pmn in the processes of dark nonradical olefin oxidation are different: PMn activity depends not only on substitutor nature but more on its position in porphyrin ligand. In particular, the including in mezo-positions of the cycle nitro-, amino-, metoxi-phenyl (mezosubstituted tetraphenylporphyrinates - TPhPMn), and pyridin groups leads to the increasing olefin oxidation rate by 1--20 fold comparing with Pmn containing substitutors in pyrrol cycles (hemato-, proto-, ethioporphyrinates). The number of mezopositions

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[1] In the native systems Cyt. P-450 functions in the presence of electronodor (NADF, ascorbic acid, flavinoids).

substitutors does not influence effect value. All the while, who is considerably less active than Pmn in such a processes, the PhPFe and hemin activities does not practically differ. However, the significant (5-10 fold) increase of catalytical activity of PFe was observed for hemin with di- and three- peptids [4].

This work shows, that cysteine and histidine participation in the reaction rises considerably (by 2 - 5 fold) the effective rate of cholesterol oxidation in the presence of Mn protoporphyrinate or Fe and Na borohyrid, and does not effect at the same time the rate of reaction with Mn and Fe tetraphenylporphyrinates participation. The cysteine gives the greatest effect in the rection. The dependence of reaction rate on aminoacid concentration is extremal, having maximum at molar ratio MP: aminoacid - 1 : 1. The presence of other aminoacid (leucine, serine) does not effects process rate.

The regularities observed can be explainde by the supposing that forming axial complexes MP - aminoacid facilitatete the pricess of bonding reduced MP with substrate.

The evidence of weak connected acxial complexes (amin containing electronodonors - MP) existance are experiments on photosensitized reduction of central ion in Pmn. After exitation of Pmn into Q - band in the presence of electronodonors of oxalic acid type the reduction of central ion are not observed, but in the presence of diaminobutan in the same conditions the process if inner molecular electrontransport from axially liganded diaminobutal takes place [5], leading to the reduction of Pmn.

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References

1. Metelica D.I., Uspehi khimii (russ) 1981.V.51, issue 11, p.2019.
2. Bren Kara L., Gray Harry B. J. Am.Chem.Soc. 1993 v.115, p.10382.
3. Enikolopjan N.S., Solovieva A.B. Zh. Fiz. Khim. (russ) 1988, v.62, N9. p.2289.
4. Lukashova E.A., Solovieva A.B., Zheltuhina G.A., Lubsandorzhieva L.K, Evstigneeva R.P. Zh.Fiz.Khim.(russ) 1995, in press.
5. Witten D.G., Wildes P.D., Derosier C.A. J Am. Chem.Soc. 1972, V.94, p. 7818.

STRUCTURAL REARRANGEMENT OF La-Mn PEROVSKITE DURING MECHANOCHEMICAL TREATMENT

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Complex oxide of perovskite-like structure are simular to Pt- and Pd-containing catalysts by the activity, thermal stability and poisons tolerance[1]. Development of the advanced technologies such as mechanochemical treatment and plasmochemistry allows to obtain dispersed oxide of high activity [2]. To understand the nature of the high activity of the perovskites prepared via these new routes one should study their real structure in details.

This paper reports on the results of X-ray powder diffraction and transmission electron microscopic invectigation of La-Mn- perovskites obtained via plasmochemical route followed by mechanochemical treatment for 5, 15, 30 and 60 min.

Usually La-Mn-oxides of perovskite structure my be considered as a complex row of non-stoichiometric compounds. As evident from the literature [3] $LaMnO_3$ of the stoichiomrtric composition has a orthorhombic structure whereas non-stoichiometric phase of $LaMnO_{3+x}$, where x is over 0.105, is characterized by a rhombohedral distortion.

In the initial sample of the seria to be investigated we observed a orthorhombic perovskite phase of variable composition and La_2O_3 (less then 10%). From electron microscopic micrographs it is evident that perovskite particles have a well-developed micrograined structure.

Mechanical treatment of the initial sample for 5 min leads to the disappearance of La_2O_3 phase. In X-ray spectra one can observe strongly broadened peaks corresponding to the cubic (pseudocubic) perovskite structure. Most of the peaks are asymmetrical. Structure of the sample mechanically treated for 15 min becomes more perfect: though peaks are still broadened, but their shapes are more regular.

In the specimen activated for 30 min MnO phase was found, the amount of which increases after mechanical treatment for 60 min.

In X-ray spectra of the activated samples it is observed halo lying in 2θ-range between 20 and 25 deg that seems to correspond to the amorphous phase, amount of which increases with raising the activation time. Electron microscopy revealed that particles of activated samples consist of crystalline grains of the perovskite-like structure distributed over amorphous material.

Using integrated intensities of the X-ray diffraction peaks the occupancy of the positions of lanthanium, manganese and oxygen in the cubic structure (Pm3m space group) of the sample mechanically treated for 15 min has been refined. Results obtained demonstrate that this phase has a non-stoichiometric composition and Mn cations should be mainly in bivalent state that appears to result in the cubic symmetry of the structure. The cubic structure of perovskite containing bivalent Mn ions is a new one from the row of La-Mn perovskite-like compounds.

Structural calculation was performed using a program complex POLYCRYSTAL [4].

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References.

1. Jamazoe V., Takaoka J. Cat.Today,1990, v.8 ,p.175-199.
2. Sadykov V.A., Isupova L.A., Tikhov S.F., Kimkhai O.N. Proc.MRS Fall Meeting, Boston, USA, Nov.28-Dec.2,1994, v.386.
3. Tofield B.C., Scott W.R. J.Solid State Chem., 1974, v.10, p.183-194.
4. Tsybulya S.V., Cherepanova S.V., Ovchinnikov A.V., Solovyeva L.P. Intern.Conf."Powder Diffraction and Crystal Chemistry", St.Petersburg, Russia, June 20-23, 1994. Absracts. St.Petersburg,1994, p.24.

Concerted mechanisms in heterogeneous catalysis: thiophene hydrogenolysis over sulfide catalysts.

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Concerted mechanisms in heterogeneous acid-base catalysis are well-known (see, e.g.,[1]). Recently this mechanism was proposed for HDS catalysis [2]. This paper presents new evidences of this mechanism in the C-S-bond hydrogenolysis reaction mediated by sulfides of various composition. The thiophene hydrogenolysis reaction was carried out on the following catalysts (both bulk and silica supported): M^1/WS_2 (where M^1- metal of the first transition row), Ni/NbS_2, Ni/ReS_2. As was shown in [3], the active component of these catalysts is crystallized in the structure which is typical for the sulfide HDS catalysts.

Synergism in thiophene hydrogenolysis was found for Ni/NbS_2, and antagonism for Cu/WS_2 and Ni/ReS_2. Despite of the low level of catalytic activity, the reaction is characterized with low activation energy (8-15 kCal/mol depending on catalyst composition) and absence of possible intermediates (tetrahydrothiophene (THT) or butadiene) in the reaction products. (THT was detected only on ReS_2, but it disappeared on bimetallic Ni/ReS_2 catalyst). This phenomenon is discussed in the frame of synchronous interaction of the reacting molecules in the coordination sphere of bimetallic active center: adsorption and activation of thiophene takes place on M^1 ions, while hydrogen activation occurs on the terminal sulfur atoms, enframed of the active component macromolecule. The detailed mechanism of the electron and proton transfer during catalysis is also discussed.

References

1. V.M.Nekipelov, K.I.Zamaraev, Coord. Chem. Revs., 61(1985)185.
2. A.N.Startsev, Russ. Chem. Revs., 61(1992)175.
3. A.N.Startsev, V.N.Rodin, V.I.Zaikovskii, A.V.Kalinkin, V.V.Kriventsov, D.I.Kochubey, K.I.Zamaraev., Kinet. Catal., to be published.

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Trapping of Alkyl Carbenium ions with Carbon Monoxide in Zeolite H-ZSM-5. A Formation of Carboxylic Acids from Alcohols and Olefins under Mild Conditions.

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The nature of the reactive intermediates in hydrocarbon conversion on acidic zeolites is still a challenge of high scientific interest. By analogy with reactions in acid solutions, it is generally agreed that hydrocarbon conversion on solid acids proceeds via the formation of intermediate carbenium ions [1]. However, due to high reactivity of alkyl carbenium ions, numerous attempts to detect these cations on zeolites by various methods were not successful.

In this paper we have presented an evidence for the formation of alkyl carbenium ions as intermediates in low temperature conversion of alcohols and olefins on zeolite H-ZSM-5. The evidence is based on the well-known reaction between alkyl carbenium ions and carbon monoxide in acidic medium affording oxocarbenium ions [2], the latter are easily converted into carboxylic acids under their interaction with water (the Koch reaction [3]).

Using ^{13}C CP/MAS NMR as the main analytical method we have shown that alkyl carbenium ions, which are expected to be generated at 296-373 K in zeolite H-ZSM-5 from alcohols (t-BuOH, i-BuOH, n-BuOH) and olefins (ethene, i-butene, octene-1) can indeed be easily trapped with CO to give carboxylic acids. The reaction occurs without excess of CO, just upon coadsorption of equal amounts of alcohol and CO or olefin, CO and water on H-ZSM-5.

t-BuOH, i-BuOH, i-butene have been found to transform selectively into trimethylacetic acid. n-BuOH gives rise to 2-methyl-butanoic acid. Ethene is converted into 2-ethyl-2-methyl butanoic acid. Interaction of octene-1 with CO and H_2O results to a mixture of C_9 ,C_{17} carboxylic acids. Thus, complete analogy is observed between our results and carbonylation of alcohols and olefins in solution of strong mineral acids via the Koch reaction [3]. The observed reactions clearly evidence for the formation of alkyl carbenium ions as intermediates inside H-ZSM-5 from alcohols and olefins at low temperature.

In addition, this study provides evidence that Koch reaction can proceed on zeolites not only at high pressure and high temperature [4], but also at low temperature and normal atmospheric pressure. The obtained results open up new possibilities in using zeolites for organic synthesis of carboxylic acids under mild conditions.

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References

[1] Jacobs, P.A. *Carboniogenic Activity of Zeolites*, Elsevier: Amsterdam, 1977.

[2] Hogeveen, H. in *Adv. Phys.Org.Chem.*, vol.10, London-New York, 1973, pp.29-52.

[3] Koch, H. *Brennstoff-Chemie* 1955, 36, 321; For review see: Bahrmann, H. in *New Syntheses with Carbon Monoxide*; Falbe, J., Ed.; Springer Verlag: Berlin, 1980, pp.372-413.

[4] Hoelderich, W.; Reuvers, J.; Kummer, R.; Hupfer, L. *Eur.Pat.* 249 976, Dec.23, 1987.

PPC-137

CATALYTICALLY ACTIVE SITES OF $Pd_{561}Phen_{60}Ac_{180}$ CLUSTER, THE STRUCTURE OF ITS SOLVATING SHELL IN ACETIC ACID SOLUTIONS

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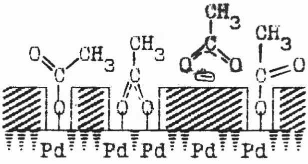
$Pd_{561}Phen_{60}Ac_{180}$ cluster (I) in acetic acid solutions (HAc) with and without water shows a high catalytic activity in partial homogeneous oxidation reactions [1]. For the solid phase in the absence of HAc, it has no catalytic activity.

We used the quantitative IR spectroscopy for studying the interaction between the Ac-anions and the core surface of cluster I in the solid phase as well as for determining the composition and structure of solvating cover formed by Ac-anions and HAc molecules around the nucleus of cluster I in its solutions in HAc. (According to the IR data, the phenanthroline molecules and Pd-core surface of I interact similarly in the solid phase and solutions).

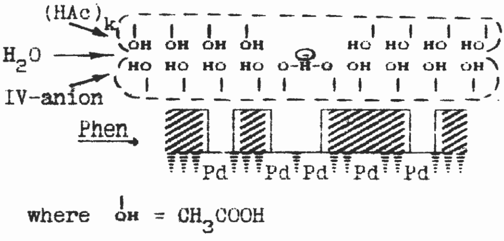
Solid phase. The IR spectra of cluster I in the solid phase exhibit three pairs of ν_{as}(COO) and ν_s(COO) bands, belonging to mono- and bidentatly bonded to Pd Ac-anions, as well as to outersphere Ac-anions.

Solutions in HAc. The IR spectra of suspension of I in HAc exhibit no absorption bands of COO groups, that are typical for the solid phase. There appear new strongly overlapped bands of COO oscillations, which coincide with those of acidic salts $R_3CH_3N^+(Ac \cdot nHAc)^-$ (II) and alkaline metals salts $M(Ac \cdot nHAc)$ (III) in a neat acetic acid solutions. It is impossible to interpret the IR spectra of cluster I in HAc medium without additional studies, taking into account, that the molecular state of salts II and III in acetic acid solutions is not studied yet. Thus, we have investigate $R_3CH_3N^+Ac^-$ solutions in CCl_4 + HAc [2]. As molar ratio HAc : R_3CH_3NAc increases to 4.7, the salts of II type formed with n grows successively to 4. On passing to the solutions of III with M = Li, Na, K, Cs in the neat acetic acid, n runs to 8-9. The detailed study of the molecular states of salts III in HAc and HAc + H_2O solutions as well using the complete coincidence of the IR spectra of acetate groups of these systems and the system of cluster I + HAc have enabled us to obtain the next data on the composition and structure of cluster I solvating shell in HAc.

Acetate anions interact with HAc molecules forming over the phenanthroline "surface" of a cluster nucleus complex chain anions $(Ac \cdot nHAc)^-$ (IV) with n = 8-9. These anions are extraspherically solvated by a variable k-number of HAc molecules, due to the dipole-dipole interactions of COO groups. Simultaneously these HAc molecules are bonded by Hydrogen bonds forming linear polymers $(HAc)_k$ (V). If we add some water into solutions, k increases, since H_2O molecules introduced between the COO groups of linear chains of IV-anion and V molecules, forming H-bonds. This process give extra stability to the ordered molecular structure (see the scheme). The latter is a prototype of liquid-crystal structures formed in alkaline metal carboxylate solutions in fatty(C_8-C_{18}) acids.



Three types of a COO group coordination in the solid phase of I



Solvating shell structure

Comparing how Ac-anions interact with cluster I core surface in the solid phase and how its solvating shell forms in solutions, we may deduced the next reasons of its catalytic activity in the neat acetic acid solutions. As I dissolves, COO groups of all three coordination types turn quantitatively into spatial outer sphere anions, which build an ordered structure over the "phenanthroline surface" (similar to the liquid-crystal one). The opened Pd-atoms become easy of access for other molecules, that is these particular Pd atoms are the catalyst active sites.

We understand now why cluster I is catalytically active towards small molecules, such as C_2H_4, C_3H_8 and HCOH. The larger the molecule, the harder its diffusion through the liquid-crystal solvating shell and only small molecules go easily into the "wells" formed by phenanthroline molecules reaching the "opend" Pd-atoms.

Acknowledgement. The research described in this publication was made possible in part by grant No NPK000 from the International Science Foundation.

REFERENCES

1. M.N.Vargaftik, V.P.Zagorodnikov et al., J. Molec. Catal., 53 (1989) 315.
2. E.S.Stoyanov, Yu.A.Chesalov, Zh. Strukt. Khim., (in press, 1996).

PPC-138

HYDRIDE SOLID STATE SYNTHESIS OF METALLIZED SURFACE LAYER ON SILICA

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Heterogeneous redox reactions of covalent element hydrides play important rôle in catalysis (for example in oxidation of CH_4 and NH_3 on oxides) [1], crystal growth [2] and atomic layer epitaxy [3] of semiconductor Si, Ge, binary compounds, including intermetallides. According to currently accepted conception the some synthesises proceed through intermediate stage of metal forming [2,3]. But the direct experimental registration of surface solid products "in situ" is practically impossible or very difficult to do by means of modern instruments [2]. One of the ways to study the chemical mechanism of such redox reactions on the monomolecular level may be in research of the those processes under hydride synthesis (HS) conditions on the sufficiently inert silica base. HS of metallic substances is based on reduction of solid metal compounds by gaseous element hydrides (E=N, C, Si etc.) or their derivatives in an open flow system at the temperatures below that of E-H-bond thermal dissociation [4]. The bulk metal products of HS are studied in [4,5] and are the dispersed solids of independent interest for the metal chemistry and material science because of their hot-and chemical stability.

In that work the systematic investigation of the structure of surface products reduced under HS conditions have been carried out. Initial samples were obtained by the molecular layering on the silica (from chlorides of Ni, Cu, Fe etc.) and by the gas-phase adsorption of the Fe-chloride on hydridpolysiloxane. By employing both the RPES, IRS, NGR, electronic transparence microscopy methods and the chemical analysis, it was established: a) metal-oxide bonds breakage (including thats on basic) on the silica and almost complete dechlorination of layered halogenides does occur (exepting reduction by CH_3SiHCl_2); b) surface nitrides, carbides or silicides of the metals were not formed, but the yielding of the ultradispersed metal on the basic takes place. It's founded that energy's value of the electron bonds (RPES) for metal (M) can be accurately regulated by employing the different covalent hydrides-reducers. Value of $M2p_{3/2}$ -level energy for solid products, which was reduced from both layered and bulk chlorides of the metals decreases in the row: SiH_4, CH_3SiHCI_2, NH_3, CH_4, H_2. It was shown, that during the obtaining of the metals on the silica basic in NH_3 or CH_4, the marked chemisorption of the elementhydrides does not occur rather than during the reduction by siliconhydrides. According to the IRS and NMR-methods results, the fixation on the N, C, Si in composition of the elementhydrogen compounds takes place in bulk products and that of Si-in layered metal. The oxidation degree of the element modifying the metal is similar to that of sorbed elementhydrides, in accordance with the energies of bond. The analysis of M-and E-bond energies and peaks form in the RPE-spectra including the compu - ter elimination of the Si2p-peak for layered samples evidences to the chemical interaction between M and E in the surface.

The two-stepped HS variant for Si-C-containing metallic layer (M=Ni, Co, Fe) on the silica has been elaborated. The synthesis consists in reduction of surface chloride by methyldichlorsilane and following action with simple hydredes (H_2, CH_4 etc.). It's uncovered that hydrophobic properties of the fer - ro-magnetic powders increase in depence of the metal nature - Fe, Ni, Co-and are such as well as that for polymethylsiloxane adsorbents. The analogous bulk HS-products are hydrophobic too [5], but their water-stability on the contrary grows from Ni-to Fe-sample. It's connected with more thick and compact SiC-film on the metallic particles than in the metal-ceramic systems on the silica base.

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1. Boreskov G.K. Catalysis. Novosibirsk: Nauka, 1971.
2. Goodman C.H.J. Crystal growth.Theory of growth and methods of crystal growthing. Moscow: Mir, 1977. P.11-14.
3. Proc.of the Third Symp.on Atomic Layer Epitaxy & Related Surface Processes/M.Ozeki e.a., ed. Elsevier. 1994.621p.
4. Syrkov A.G. Zhurnal obshchey khimii. 1994.64, N1, P.43-50.
5. Syrkov A.G., Mahova L.V.Proc.of Int.Conf.on Electronic ceramics-production & properties. Riga. 1990. P. 113-115.

PPC-139

Partial Oxidation of Ethane by Active Oxygen generated Electrochemically on Gold through Yttria-stabilized Zirconia

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An electrochemical reactor using yttria-stabilized zirconia (YSZ), Au|YSZ|Ag, has been constructed and used for the oxidation of ethane under the oxygen pumping through the YSZ. We found that propene was partially oxidized into acrylaldehyde over an inert Au anode film under the oxygen pumping: this suggests that oxygen species transported through YSZ onto Au surface was active for the selective oxidation of propene into acrylaldehyde.[1] In this paper, we report the selective oxidation of ethane to acetaldehyde by the same oxygen species.

When the ethane-nitrogen-helium mixture (5:5:90) was passed at a rate of 1.2 l/h over the Au anode at 475 °C, no oxidation of ethane occurred under open circuit conditions when no oxygen was pumped through the YSZ. The oxidation took place when oxygen was pumped under closed-circuit conditions, and an increase in the current by oxygen pumping resulted in an increase in the rate of ethane oxidation. No evolution of dioxygen was observed in this case. Selectivities of acetaldehyde and CO_2 were 45 and 55 %, respectively, based on converted ethane. When ethene (in place of ethane)-nitrogen-helium mixture (5:5:90) was passed at the same conditions, CO was substantially produced together with acetaldehyde and CO_2 and the rate of each production again increased with increasing the oxygen flux. However, ethene was also oxidized to acetaldehyde with the oxygen species adsorbed on the Au anode from gas phase.

The results obtained above clearly indicate no activity of an Au surface for the oxidation of ethane to acetaldehyde by surface oxygen supplied directly from the gas phase. It is likely that acetaldehyde production from ethane is achieved only by the 'active oxygen species' generated electrochemically on the Au anode surface through the YSZ and this oxidation does not proceed via ethene formation. When ethanol was passed over the Au anode, acetaldehyde was formed and its amount increased with increasing the oxygen flux. Atomic oxygen species may be formed over the anode surface by 4 electron oxidation of O^{2-} to O at the boundary between Au and ZrO_2 (YSZ). Ethane can be oxidized to form ethoxy intermediate on the surface, then oxidatively dehydrogenated to acetaldehyde, by the atomic oxygen species.

References

1 T. Hayakawa, T. Tsunoda, H. Orita, T. Kameyama, H. Takahashi, K. Takehira, and K. Fukuda, *J. Chem. Soc., Chem. Commun.*, 1986, 961; T. Tsunoda, T. Hayakawa, K. Sato, T. Kameyama, K. Fukuda and K. Takehira, *J. Chem. Soc., Faraday Trans.*, 91, 1111 (1995).

MODIFIED TIGHT-BINDING EQUATIONS FOR WAVEFUNCTION OF SEMI-INFINITE CRYSTALS OR INTERFACES WITH POINT DEFECTS

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A new approach for the calculation of one electron wavefunctions of crystal surfaces or interfaces with point defects in the tight-binding approximation has been developed [1,2]. This approach does not use structural simplifications of the system and besides electronic structures of a defect permit us to calculate its image in different experimental surface probes such as low energy electron diffraction, scanning tunneling microscopy, angle resolved photoelectron spectroscopy and so on.

The approach based on the representation of a wavefunction as a linear combination of localized basis functions of the perturbed crystal region and a finite number of waves existing in the perfect crystal and belonging to the same energy. In the case of a clean crystal surface or an interface these waves are the usual Bloch waves with the same parallel to the surface component of the electron wavevector and different normal to the surface components. The waves belong to the same energy and besides the non-localized Bloch waves contain waves decaying far from the surface. For a point defect in the crystal bulk, instead of the Bloch waves, a finite number of outgoing from defect waves constructed from the Bloch waves with wavevectors belonging to a constant energy surface in the reciprocal space are used. As for surfaces among outgoin waves there are ones decaying far from the defect. For a point defect near the surface both the Bloch and outgoing waves are used to construct the wave function. The coefficients of the linear combination satisfy to a finite algebraic set of equations named the Modified Tight-Binding Equations (MTBE). For energies in the band the MTBE is a non-homogeneous set of equation that solves the problem of scattering of an electron wave by the defect. For energies in the energy gaps the MTBE is a homogeneous set of equations the solutions of which, if they exist, gives the localized defect states.

Because the developed technique does not use structural simplifications of the system and gives us the wavefunction in the whole space we can construct an image of the surface electronic structure in various surface experimental probes. For example, the square of wavefunction on the surface of an analyzer gives us the distributions of intensity in electron diffraction experiments. The electric current can be expressed directly through the wavefunction and its gradient and will give us the image of the surface in scanning tunneling microscope or space distribution of the electron current in photoelectron emission experiments. The knowledge of the exact wavefunction of the whole system permit us to avoid a number of conventional approximations of the theory of these probes.

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References

1. V.M.Tapilin. Phys. Rev. B (1995). in press
2. V.M.Tapilin, Phys. Low-Dim. Struct.. submitted.

PPC-141

Olefin Metathesis on Supported Rhenium and Molybdenum Catalysts Activated by γ- and Photo-Irradiation in the Presence of Alkanes

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A new approach to the activation of Re_2O_7/Al_2O_3, $Re_2O_7/Al_2O_3{\cdot}SiO_2$, and MoO_3/SiO_2 catalysts for low-temperature olefin metathesis has been developed. The catalysts after pretreatment in oxygen and then in vacuum at 873 K (Re) or 1073 K (Mo) were subjected to g-irradiation at a 60°C source in the presence of gaseous alkanes (CH_4 or C_4H_{10}) at ambient temperature (total irradiation dose 100 MRad). IR and UV-Vis data revealed that, under γ-irradiation, reduced Re and Mo species were produced (metal ions in lower and zero oxidation states).

After evacuation at 293 or 423 K, catalytic activities of the γ-irradiated samples in propene and 1-hexene metathesis were measured at 293 K. For the gas-phase propene metathesis, TOF for irradiated 6% $Re_2O_7/Al_2O_3{\cdot}SiO_2$, 3% $Re_2O_7/Al_2O_3{\cdot}SiO_2$, and 6% Re_2O_7/Al_2O_3 were found to be 0.1, 0.07, and 0.14 mole C_3H_5/mole Re.s, respectively, that is approximately by one order of magnitude higher than TOF of the unirradiated catalysts. After thermal reduction in CO or H_2 at 623 - 723 K, the catalysts were much less active.

In the liquid-phase metathesis of 1-hexene, the following TON were obtained for the γ-irradiated catalysts (at hexene to metal ratios of 2000 - 3000):

1100 - 2700 mole C_6/mole Re for 3 and 6% $Re_2O_7/Al_2O_3{\cdot}SiO_2$ and 6% Re_2O_7/Al_2O_3 and 1200 mole C_6/mole Mo for 2.5% MoO_3/SiO_2. Unirradiated samples showed no activity in this reaction. The selectivities to C_{10} production in the 1-hexene metathesis were within 90-98%. In the case of $Re_2O_7/Al_2O_3{\cdot}SiO_2$, however, the selectivity decreased to some extent as the reaction proceeded due to double-bond shift in the reaction products and subsequent secondary metathesis reactions.

UV-irradiated 2.5% MoO_3/SiO_2 in the presence of gaseous CH_4 or C_4H_{10} were found to be very active in propene and 1-hexene metathesis (TON = 770 - 1000 mole C_6/mole Mo for the latter reaction). Photoirradiation of $Re_2O_7/Al_2O_3{\cdot}SiO_2$ and Re_2O_7/Al_2O_3 in the presence of CH_4 or CO did not result in the appearance of additional catalytic activity.

The catalysts activated by γ or UV-irradiation retain their activities when being kept at ambient temperature for a long time (at least, for several months). They do not lose much of their activity after heating in vacuum at 423 - 573 K and are rather tolerable to oxygen exposure.

It is suggested that γ- and UV-irradiation in the presence of alkanes induces a series of chemical transformations of the supported metal ions and can produce surface metal-carbene complexes which play the role of active intermediates in the metathesis reactions.

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Study of speciation in biological systems containing macromolecular ligands: application of new chemometric methods to the study of the effect of pH and metal compounds on the state of homopolynucleotides in aqueous solution.

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Results of the study of the effects of pH and copper(II) metal compounds on the state of homopolynucleotides poly(I)-poly(C), poly(A)-poly(U) in aqueous solution using Absorption Spectroctometry, Circular Dichroism, Fluorescence and Potentiometric experimental methods are presented. Hard-modelling least squares model based methods and Self-modelling curve resolution model-free methods are applied and compared in the study of the experimental data.

PPC-143

A NOVEL APPLICATION OF ^{129}XE NMR METHOD TO THE STUDY OF SILICA GELS AND SILICA-BASED CATALYSTS.

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^{129}Xe NMR of adsorbed xenon was found to be a useful tool for the characterization of the microporous solids (zeolites, clathrates, molecular sieves), which have pore sizes close to the xenon van der Waals diameter (4.4 A). It was demonstrated that different aspects of their structure can be investigated. Much less attention has been paid to the study of the porous solids with the pore sizes much larger than the diameter of xenon atom. In this work the method of ^{129}Xe NMR is proposed for investigation of the nonzeolitic mesoporous materials such as silicas and silica-based catalysts.

For xenon within silica pores, the observed ^{129}Xe NMR chemical shift, δ, is dependent on the probability for xenon atom to exist in adsorbed state on the pore wall (P_s) and in "free" gaseous state in the pore volume ($P_g=1-P_s$). Indeed, under the conditions of fast exchange of xenon between these two states the chemical shift δ can be represented as:

$$\delta=\delta_s P_s+\delta_g P_g \qquad (1)$$

where $\delta_{s(g)}$ is the chemical shift for s(g) state. Eqn.(1) is simplified since the experimental chemical shift is measured with respect to the gaseous xenon, i.e. $\delta_g=0$. The probability P_s is

$$P_s=n_s/(n_s+n_g)=\lambda S\exp(-\Delta G_s/RT)/[\lambda S\exp(-\Delta G_s/RT)+V_g] \qquad (2)$$

where $n_{s(g)}$ is the number of the xenon atoms in corresponding state, S - the surface of the pore wall. V_g - the volume of the pore, λ - the effective radius of action for a physisorbtion potential, ΔG_s - the change of free energy due to the adsorption of xenon on the wall. Denoting of a constant $K=\lambda\exp(-\Delta G_s/RT)$ we can rewrite eqn.(1) as:

$$\delta=\delta_s/(1+V_g/KS) \qquad (3)$$

The mean pore diameter is usually determined as $D=\eta V_g/S$, where η is dependent on the pore geometry. Changing the ratio V_g/S in eqn. (3) to D/η we obtain the relationship between the xenon chemical shift and the mean pore diameter of the silica sample:

$$\delta=\delta_s/(1+D/\eta K) \qquad (4)$$

For determination of the parameters δ_s and ηK, the number of silica gels well characterized by means of nitrogen adsorption and capillary condensation method (77 K) was used.

For used set of silica gels the correlation between the δ (ppm) and D (A) in the range 20<D<400 was found:

$$\delta=115/(1+D/131) \tag{5}$$

The proposed model describes the observed dependencies of the xenon chemical shift upon equilibrium pressure and temperature [1]. It also was used in the ^{129}Xe NMR studies of silica-based catalysts.

^{129}Xe NMR was applied for the investigation of the distribution of metal oxides (Al_2O_3, TiO_2, SnO_2 and ZrO_2) inside the pores of silica support. The value of the mean pore diameter D calculated from the xenon chemical shift using eqn.(5) reproduces the tendencies in variation of the pore sizes within our series of catalysts in agreement with the tendencies that follows from conventional porosimetry measurements. The ^{129}Xe NMR as well as nitrogen adsorption and capillary condensation (77 K) data reveal even and uniform distribution of the supported TiO_2 over silica surface for the 10% TiO_2/SiO_2 catalyst. Supporting of 10% Al_2O_3 results in formation of relatively large oxide particles and is accompanied with the essential change of the interior porous structure. The supporting of 10% SnO_2 does not perturb the porous structure substantially due to the uniform distribution of the active material. The increase of SnO_2 content up to 25% results in the filling of small pores by the tin oxide simultaneously with increasing of the mean pore diameter. For the ZrO_2/SiO_2 catalysts the formation of the species high-dispersed over silica surface is revealed.

The structure of heteropoly acid $H_3PW_{12}O_{40}$ (HPA) supported on silica also was studied by ^{129}Xe NMR method. The ^{129}Xe NMR spectral parameters (the number of the lines, their widths and chemical shifts) are strongly dependent on the HPA loading. From the xenon data three different types of surface HPA species can be distinguished: the isolated molecules at low HPA content (1-5%), surface HPA clusters (at 15-20% loading) and large crystalline HPA particles (at ca. 40%) in agreement with results of ^1H and ^{31}P NMR MAS [2] and electron microscopy. The microporosity accessible for xenon penetration was found for HPA/SiO_2 catalysts, in accord with conventional nitrogen porosimetry (77 K).

The possibilities of ^{129}Xe NMR method for testing of the silica gels and silica-based catalysts are demonstrated.

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[1] V.V.Terskikh, I.L.Mudrakovskii and V.M.Mastikhin, *J.Chem.Soc.Faraday Trans.*, 89 (1993) 4239.

[2] V.M.Mastikhin, S.M.Kulikov, A.V.Nosov, I.V.Kozhevnikov, I.L.Mudrakovskii and M.N.Timofeeva, *J.Molec.Catal.*, 60 (1990) 65.

PPC-144

NICKEL(1) CATIONIC COMPLEXES AS CATALYTICALLY ACTIVE INTERMEDIATES IN PROPENE DIMERIZATION

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Hydride complexes of Ni(II) are catalysts for a number of unsaturated hydrocarbon transformations including propene dimerization. We have been identified using NMR spectroscopy a Ni(II) hydride complex of composition $[HNi(PPh_3)L]^+BF_3OEt^-$, where $L=OEt_2$, among the products of interaction of $Ni(PPh_3)_4+4EtOH+2OBF_3OEt_2$. We are inclined to believe that similar complexes are responsible for the catalytic dimerization of propene under using systems of type $Ni(PPh_3)_4+HX+BF_3OEt_2$, where HX=HF, H_2SO_4, H_2O, ROH. Efficiency of similar systems in propene dimerization gets up to $8*IO^3$ mol C_3H_6/mol Ni*h. In that case the formation of active complexes consists from two basic steps: firstly the formation of structure $H^+[BF_3X]$ by equation $HX+BF_3OEt_2=H^+[BF_3X]+OEt_2$ and following oxidative addition of H^+ into Ni(0) complex. ESR spectroscopy studies of the interaction between the components of $Ni(PPh_3)_4+BF_3OEt_2$ type system including one in the presence of EtOH have been for the first time established the possibility of one-electron oxidation of Ni(0) to Ni(I) by boron fluorides [3]. A Ni(I) complex of composition $[(PPh_3)_3Ni(OEt_2)]BF_4$ has been isolated from interaction products of $Ni(PPh_3)_4+2BF_3OEt_2$ in toluene and identified by elemental analysis, ESR and IR spectroscopy data. The formation of Ni(I) cationic complexes in $Ni(PPh_3)_4+BF_3OEt_2$ system at ratio B:Ni=2-160 has been studied by ESR spectroscopy. The stepvise elimination of organophosphorus ligands from Ni(I) coordination sphere with increasing of ratio B:Ni has been shown. ESR spectra parameters of identified complexes are represented in the table. It was shown that Ni(I) complexes of $[(PPh_3)NiL_2]BF_4$, where $L=OEt_2$, C_3H_6, type are characterized by high activity in propene dimerization getting to $2.7*IO^5$ mol C_3H_6/mol Ni*h [4]. Ni(I) cationic complexes as potentially active in propene dimerization structures may be obtained also in systems of $Ni(Acac)_2+PR_3+AlEt_3+BF_3OEt_2$ type (Table). In that case both the nature of PR_3 and the ratio P:Ni may be varified in a wide range. Experimental data permitting to concluse that Ni(I) cationic complexes containing two or more organophosphorus ligands at Ni(I) do not exhibit activity in propene dimerization have been obtained. However, the activation of similar complexes with EtOH as the activation of Ni(0) has been followed by the formation of structures dimerizing propene with efficiency up to $2{*}IO^5$ mol C_3H_6/mol Ni*h.

ESR spectra parameters of Ni(I) phosphine complexes.

No	Complexes	$g_{(z)}$	$g_{(y)}$	$g_{(x)}$	$a^p_{(z)}$	$a^p_{(y)}$	$a^p_{(x)}$
1	$[(PPh_3)_3NiL]BF_4$	2.060	2.400	2.400			
2	$[(PPh_3)_2NiL]BF_4$	2.365	2.093	2.093	4.2	5.85	5.85
3	$[(PPh_3)NiL_2]BF_4$	2.275	2.128	2.032	5.0	5.9	5.5
4	$[P(o\text{-}MeOC_6H_4)_3NiL_2]BF_4$	2.254	2.129	2.042	4.8	6.5	5.3
5	$[P(p\text{-}EtOC_6H_4)_3NiL_2]BF_4$	2.283	2.125	2.029	5.0	6.8	5.7
6	$[P(n\text{-}Pr)_3NiL_2]BF_4$	2.270	2.134	2.027	4.9	6.0	5.3
7	$[P(n\text{-}Bu)_3NiL_2]BF_4$	2.271	2.130	2.025	5.0	6.0	5.3

*Hyperfine coupling constants are given in mT.

REFERENCES

I. G.Henrici-Olive. Coordination and Catalysis.New York: 1977.

2. C.Masters. Homogeneous Transition-Metal Catalysis. New - York, London: 1981.

3. V.S.Tkach, V.A.Gruznykh, N.A.Murasheva et.al.//React.Kinet.Catal.Lett.1991.V.43.No.2.P.431-437.

4. V.S.Tkach, V.A.Gruznykh, Gomboogiin Myagmarsuren et. al.//-Koord.Khimiya.I994.V.20.No.8.P.6I8-62I.

PPC-145

INFLUENCE OF NICKEL OXIDE ADDITION ON ACTIVITY OF CEMENT CONTAINING CATALYST GOPTALUM

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The Catalytic decomposition of ozone is one of the ways to solve the problem of converting the leftover quantities of ozone before releasing to the atmosphere. We have developed a mechanically strong and a heat resistant catalyst to decompose O_3 (GTT). It works stable in a damp stream and does not contain any expensive metals. It has oxides of manganese, copper and aluminates of calcium in its base [1].

In this particular job we investigated the influence of nickel oxide additions (from 0% to 60%) in the activity of the catalyst GTT in the ozone decomposition process.

The activity of the catalyst was tested for deferent concentrations of ozone, for dry and damp gas streams of deferent speeds.

It was found that the activity of the catalyst increases when nickel oxide is introduced into it. The maximum activity was noticed when there was 40% of NiO.

The research work showed that the activity of the catalyst heavily depends on the speed of the gas flow (W); when W is increased the activity increases. The reason for this, it seems, is the influence of diffusion in the process of ozone decomposition. The process of the heterogeneous decomposition of ozone was studied for deferent temperatures for deferent flow rates. It was found that in the area of low temperatures the activity of the catalyst for deferent flow rates overlaps; which means the process takes place in the kinetic region. In the region of high temperatures the activity of the catalyst for deferent speeds defers; which means the process progresses in the diffusion region. In room temperature the bend in the lnK against 1/T dependency curve serves as a confirmation of the fact that the reaction of ozone decomposition takes place in the transitional region.

[1] A. C. CCCP №1768274 A1, кл. B 01 I 23/84, B 01 D 53/36, 1992г.

PPC-146

New Chiral Pyrazole-Type Peroxo Complexes of Mo(VI) in Stereoselective Alkene Epoxidation.

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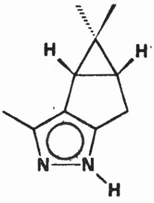
Formation of α-epoxides from the corresponding unsaturated hydrocarbons (and enantioselective variant especially) is one of the most important and being intensively studied reaction among the processes used in manufacture of fine chemicals. The most perspective processes seem to be those ones based both on catalytic and stoichiometric oxidative transformations under the action of chiral complexes of transition metal ions (Fe, Co, Ru, W, Mo, etc.). We have synthesized a number of novel fused heterocycles of the pyrazole type **1-4**, having 100% enantiomeric purity, and tested their peroxo complexes in catalytic and stoichiometric oxidation.



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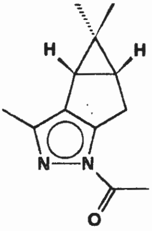

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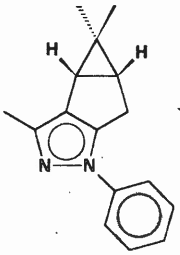

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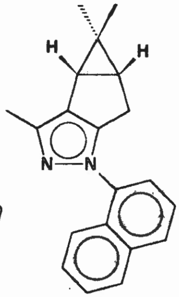

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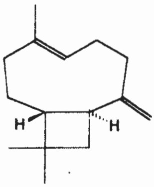
These amines were found to extract molybdenum diperoxo compound $MoO(O_2)_2$ (prepared from MoO_3 and 30% H_2O_2) from aqueous solutions to low polar organic solvents such as benzene, methylene chloride, chloroform, etc. The phase-transfer process in the case of pyrazole **1** is very rapid and is completed in a few seconds at room temperature, while the other compounds **2-4** "work" much slower (from several hours up to several days). Our attempts to isolate the complexes formed failed because they are extremely unstable and explosive solids. NMR study (^{14}N, ^{95}Mo) shows the formation of a peroxo complex that is quite stable for several hours at room temperature in diluted solutions. We have found that these solutions are able to oxidize certain organic compounds and tested them in the reactions of stereoselective epoxidation of prochiral and chiral alkenes: *trans*- and *cis*- 2-heptenes, *trans*- and *cis*- stilbenes, racemic and optically active natural compounds caryophyllene (**5**), limonene (**6**) and linalool (**7**), whose α-epoxy derivatives are of special interest.



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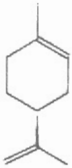

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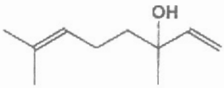

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In all the cases, except linalool and *trans*-stilbene, the reaction led to the corresponding α-epoxides whose formation was found to be stereoselective. The oxidation process is sensitive to steric factors: *cis*-2-heptene is oxidized faster than *cis*-stilbene in spite of higher nucleofilic ability of the double bond in the later alkene. Sesquiterpene hydrocarbon caryophyllene, having *trans*-carbon-carbon double bond in the nine-membered ring, is transformed to the single epoxide (caryophyllen-α-oxide) when treated with the peroxo complex, whereas usual epoxidation with peracids results in a *ca.* 80:20 diastereomeric mixture of α- and β-epoxides.

The research described was made possible in part by Grants RAU000 and RCS000 (the International Science Foundation), Grants RAU300 and RCS300 (the International Science Foundation, Russian Government and the Russian Fundamental Science Foundation), Grant 93-1588 (INTAS).

A NEW WAY TO ACTIVATE ORGANOTIN CATALYSTS FOR URETHANE FORMATION REACTIONS

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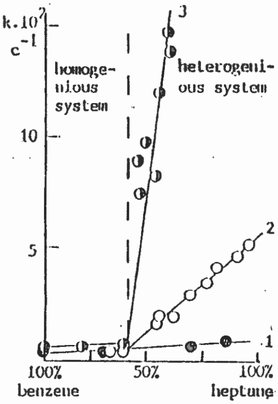
Organotin compounds are most active catalysts of urethane formation processes. When low molecular catalysts are used the non-linear dependencies of the rate constant on catalyst concentration take place as the result of formation of inactive associates including several organotin molecules incorporated into hydrogen-bonded structure of associated OH-groups. Immobilization of catalytic centers on polymer carrier is one of the ways of suppression of such heteroassociation.

The new soluble polymer supported catalysts based on polyethylene glycols (PEG) containing terminal tributhyltin carboxylate groups were elaborated. However the catalytic activity of the majority these catalysts exceeds only twice the activity of low molecular models. It is the result of low ability to complexation of catalytic centers with respect to reagents because of these centers are incorporated inside of polymer coil in solution.

The considerable increase of catalysts activity takes place when urethane formation is carried out in the binary system solvent-precipitator (for polymer chain of catalyst). By the precipitation of catalyst in form of fine dispersion phase its activity increases sharply as it is shown in the figure.

The reaction of 4(phenylaza)phenyl isocyanate with buthanol was used as model reaction of pseudo-first order.As it is seen from figure rate constants in benzene (good solvent for polymer chain of catalyst) are low. If polymer catalyst is soluble in binary solvent benzene-heptane (catalyst based on PEG-1000) the increase of rate constant up to 100% of heptane is not so high (1). If polymer catalyst is precipitated by the variation of solvent composition(PEG-6300, precipitation begins at the 40% of heptane) sharp increase of catalytic activity takes place (for examples 2 at the $[Sn]=1\cdot10^{-4}$ mol/l and 3 at the $[Sn]=1\cdot10^{-3}$ mol/l .



The reason of catalytic activity increase in heterophase system is going of catalytic centers from solution to the solid phase surface. As results of it polymer catalyst coil develops on the surface and active centers becomes approachable for reactive groups of monomers.

PPC-148

LEWIS ACID PROPERTIES OF π-Al_2O_3 SURFACE.

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Alumina is widely used catalyst and carrier. The data on preparation of amorphous modification of alumina - π-Al_2O_3, which can be used as a carrier with good thermostability, were recently appeared [1,2]. Lewis acidity of the alumina surface is very important for catalysis. This work is devoted to the investigation of the structure, strength and concentration of Lewis acid sites (LAS) of the surface of π-Al_2O_3. Comparison of π- and η-Al_2O_3 has been made too.

π-Al_2O_3 was prepared by calcination of the product of mechanochemical activation of the bayerite (π-Al_2O_3 (I)) and by calcination of the amorphous aluminium hydroxide (π-Al_2O_3 (II)). η-Al_2O_3 was received from bayerite. Composition of products was confirmed by DTA and X-ray diffraction. This data are in accordance with the literature.

For research of the surface we used the ESR method with paramagnetic complexes of the probe molecules: anthraquinone and 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) [3].

On the basis of anthraquinone spectra we conclude that the concentration of LAS on the π-Al_2O_3 surface is great and is about 2/3 of that for η-Al_2O_3, the shape of anthraquinone spectra (11 components of hyperfine structure) indicates the interaction with two surface LAS. The significant dipole-dipole broadening shows the high local concentration of paramagnetic complexes and, therefore, high local concentration of LAS.

Analysis of ESR-spectra parameters of TEMPO-LAS complexes revealed the differences between π- and η-Al_2O_3. For characterization of the strength of the LAS the parameter a_{Al} was used. a_{Al} is near to the hyperfine structure constant with ^{27}Al. The strength of LAS of the π-Al_2O_3 was found to be less than that of the η- Al_2O_3. The obtained data are presented in the table.

Sample	η-Al_2O_3	π-Al_2O_3 (I)	π-Al_2O_3 (II)
S,m^2/g	170	50	170
a_{Al},G	11.3	10.6	10.4
N*10^{-17},LAS/m^2	3.9	2.6	2.5

According to Knozinger et al [4], the alumina surface can be presented as a combination of the low-index planes of the spinel crystal. The regular disposal of LAS with high local concentration (as determined by ESR) is usual for the planes (111)A and (110)C. The decrease of the LAS concentration shows that the impact of these planes in overall surface decreases as a result of amorphisation. The decrease of the LAS strength shows that the relation between impact of low-index planes changes too.

The ordered local structure remains on the part of the amorphous alumina surface. This data may be important for the preparation of catalysts with desired surface properties.

1) S.M.Paramzin, B.P.Zolotovskii, O.P.Krivoruchko et al., Izv. SO AN SSSR, 1989, N2, ser. chim. nauk, p.33.

2) T.Tsuchida, N.Ichikawa, Reactivity of Solids, 1989, v.7, P.207.

3) E.V.Lunina, in O.A.Petrij and V.V.Lunin (Eds), Catalysis. Fundamental and Applied Studies, MGU, Moscow, 1987, p. 262.

4) H.Knozinger and P.Ratnasamy, Catal. Rev. Sci. Eng., 1978, v.17, p.31.

PPC-149

TRANSFORMATIONS OF THE RESIN ACIDS AS A BASE OF THE CHIRAL DIPHOSPHINE AND DIPHOSPHINITE LIGANDS SYNTHESIS FOR THE TRANSITION-METAL CATALYSTS OF THE ENANTIOSELECTIVE PROCESSES

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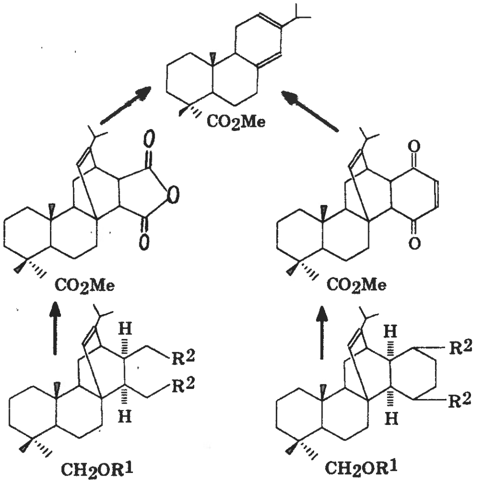
Using Diels-Alder adducts of levopimaric acid with maleinic anhydrite and p-benzoquinone we produced new homochiral diphosphine and diphosphinite ligands for the transition-metal complexes, catalyzing the enantioselective reactions of hydrogenation of carbon-carbon or carbon-oxygen double-bond, isomerization of prochiral allylamines, hydroformylation of alkenes and others.



R^1=Bn; R^2 = PPh_2, $OPPh_2$, $OP(C_6F_5)_2$

This work was financially supported by Russian Basic Research Fund
(project N 95-03-08517)

PPC-150

PROPERTIES OF COLLOIDAL PALLADIUM AND MECHANISM OF ITS FORMATION THROUGH REDUCTION IN AQUEOUS SOLUTIONS

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Metals in the colloidal state show increased catalytic activity. This paper is a study of the mechanism of formation and the properties of colloidal palladium.

Pulse radiolysis was used to study the mechanism of Pd^{2+} aqueous complex reduction in acid aqueous solutions (0.1- 1.0 M $HClO_4$) containing 0.1 M of isopropyl alcohol or some other organic compound. Pd^{2+} ions are reduced by organic radicals (R) to Pd^+ ions (λ_{max} = 290nm, ε^{290} = (5.7 - 0.3)$*10^3 M^{-1} cm^{-1}$), with PdR^{2+} complex as an intermediate product.

Further on, optic absorption could be observed which gradually shifts from 300 nm to 500 nm during 10^{-3} - 1 s. After 100 s, this is transformed into a fuzzy absorption band which expands over the whole of the UV and visible range. The transformations observed reflect the dynamic of formation and coagulation of Pd colloidal particles.

Theoretical calculation has been performed of optical absorption spectra for ultrasmall Pd particles using Mi theory. The comparison between experimental and calculated absorption spectra shows that colloids with radii of 20 to 30 nm, 40 to 50 nm, and above 50 nm are formed at the intervals of 0.4, 5 and 100 s, respectively. The calculated values of extinction coefficient for particles with r = 40 to 50 nm is (4 - 6)$*10^3 M^{-1} cm^{-1}$ which is in fair agreement with experimental data.

A stable solution of colloidal palladium was prepared in the presence of polyacryl acid by radiation-chemical reduction of $Pd(NH_3)_4Cl_2$ or its reduction by molecular hydrogen.

Optical absorption of metal sols is represented by a wide band λ_{max} = 230 nm which slowly slants towards long waves $\varepsilon^{230} = 6.3*10^3$ $M^{-1}cm^{-1}$. Particle diameter increases with Pd(II) ion growth in a solution with 1 - 2 to 10 nm under complete reduction. Experimental spectra of colloidal palladium agree fairly well with those calculated according to Mi theory for spherical particles. The appearance of colloids is preceded by the formation of palladium clusters (a narrow band with λ_{max} = 205 and $\varepsilon^{205} = 2*10^4$ $M^{-1}cm^{-1}$) which are assumed to contain 10 to 14 atoms.

It has been established that colloidal palladium absorbs hydrogen. During the process, several minutes after the introduction of hydrogen, the absorption band gets considerably wider and shifts towards the red range as far as λ = 265 nm ($\varepsilon^{265} = 5.2*10^3$ $M^{-1}cm^{-1}$). The band shift observed seems to indicate a positive charge over the surface of colloidal particles due to the shift of electronic density from the metal towards the sorbate.

Metal-bound hydrogen is oxidized when the solution is exposed to oxygen or upon the introduction of other oxydizing agents. A study has been made of the reaction between hydrogen and methylviologen (MV^{2+}) catalyzed by colloidal palladium:

$$H_2 + MV^{2+} \xrightarrow{Pd_{coll}} 2H^+ + 2MV^+.$$

The reaction produces MV^+ cation radical with an intensive absorption band at 605 nm ($\varepsilon^{605} = 1.1*10^4$ $M^{-1}cm^{-1}$).

The introduction of air into palladium cluster and sol solutions gives rise to complete oxidation of clusters. Particles of colloidal metal is oxidized only partially. About 10 to 20% transforms into Pd(II). This seems to be caused by increased chemical activity of supersmall particles and their corrosion when exposed to oxygen.

STRUCTURE OF POLYNUCLEAR HYDROXOCOMPLEXES OF Pd(II) & THEIR ADSORPTION PRODUCTS

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The preparation of Pd/C catalysts often requires the synthesis of polynuclear hydroxocomplexes of Pd(II) (PHC) and their adsorption by carbon materials (CM). Using EXAFS we have studied the structure of PHC forming during the alkaline hydrolysis of the chloride complexes of Pd(II). We have found that in aqueous solutions the PHC particles are filaments rolled in balls. The filaments consist of flat coordination squares PdO_4. The latter are linked through one (O2, Fig.1) ore two (O1, Fig.1) bridge O atoms, bonds geometry being different. XRD patterns show the structure order of samples to differ a lot. A fresh suspension of PHC is completely chaotic (coherent scattering region (c.s.r.) is less than 10 Å). The PHC sorption and drying on CM produces highly dispersed particles of PdO structure (c.s.r. 15 Å and 25 Å , respectively). Elementary cell parameters were determined for the latter case. They are : a= 3.031 Å , c= 5.358 Å and somewhat differ from the standard parameters of PdO structure (a= 3.043 Å, c= 5.337 Å). Fig. 2 shows the model of PdO crystal fragment. Note the mutually perpendicular chains of coordination squares PdO_4. The shortest Pd-Pd distances exhibit two peaks in the RDF curves. One

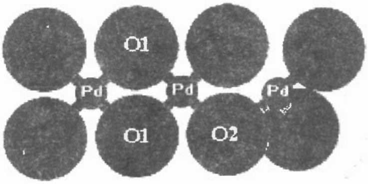


Fig.1

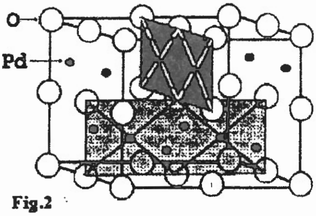
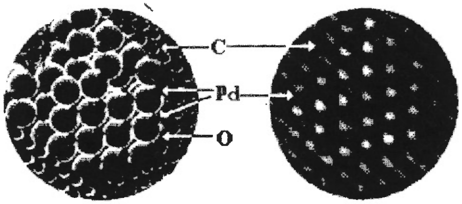


Fig.2

peak (r= 3,04 Å) characterizes the distances inside the same chain. Another (r= 3.43 Å) shows the distances between Pd atoms located in the mutually perpendicular chains. In a perfect PdO structure the ratio of peak areas is 1:2, while in the fresh PHC it is 1:1.18. This fact indicates that separate chains form predominantly. The RDF curve of dried PHC more resembles that of PdO: the contribution of peaks characterizing the interchain Pd-Pd distances increases (r= 3.43, 5.50 Å). Thus an ordered bulk structure of PdO forms.

We have also found that the PHC adsorption on CM from aqueous solutions does not change the chemical composition of complexes (reported in [1]) as well as the number of Pd atoms in a particle. PHC occupy the same adsites on the CM surface as mononuclear complexes do.

We have obtained the EM images of the sorbed PHC at atomic resolution. Simulating the EM images and modeling the crystal structure we confirm that PdO particles containing about 100 Pd atoms are the final product of sorbed PHC drying, since the simulated image of particle (Fig.3 b) built using PdO/graphite model (Fig.3 a) coincides with the EM image of this particle. At high coverages PHC tend to grow, since the complexes of low nuclearity can migrate over the surface.



a **Fig.3** b

The research in this publication was made possible in part by Grant N RP 5300 from the International Science Foundation and Russian Government and Grant N 93-03-483 from the Russian Foundation of Basic Research.

1. S.Yu.Troitski, M.A.Fedotov, V.A.Likholobov, Russian Chem. Bull., 1993, N4, 634.

PECULIARITIES OF METHANE DEEP OXIDATION ON MnO_X/Al_2O_3 AND Pt-BLACK-Al_2O_3 CATALYSTS

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Design of new catalysts is closely related to synergism effects in catalytic systems. New synergism effects in the deep oxidation of methane were observed for MnO_x/Al_2O_3 and Pt-black-Al_2O_3 catalysts. If MnO_x/Al_2O_3 catalyst is calcined at 900-1000°C, its specific activity (per 1 g) is 3 times higher than that observed at 500-850°C calcination. The specific activity of Pt-black-Al_2O_3 catalyst (per 1 g of Pt) increases, if Pt black and alumina powders are first mixed and then pressed at 50-600 MPa.

MnO_x/Al_2O_3

For this catalyst, the synergism effect of thermal activation is lower in methane oxidation at 500°C as compared to the model reactions of deep oxidation of butane, cumene, CO etc., proceeding at 250-350°C [1].

A combination of X-ray analysis, ESCA, EMHR, derivatography, titration of active oxygen and etc. allowed us to conclude that MnO_x/Al_2O_3, calcined at 900-1000°C comprises mainly -α-Al_2O_3 and manganese oxide particles, which are dispersed on the corundum surface. According to the X-ray analysis data, the size of manganese oxide particles is ~ 60 Å and it does not markedly change even after a 950°C calcination for more than 800 hours. Microdiffraction, EM techniques have shown that manganese oxide has a very defect spinel structure with the over-stoichiometric oxygen or iso-structural Mn(III) oxide, which lacks oxygen (according to the X-ray and chemical analysis). Oxygen titration data evidence that the increase of active oxygen amount governs the increase of the calcined catalyst activity. The higher the reaction temperature, the smaller amounts of weakly bonded active oxygen are on the catalyst surface, thus the smaller is the synergism effect.

In this case one can attribute the synergism effect to the catalyst new phase composition resulting from the high-temperature treatment.

A new thermally stable (to 1000°C) catalyst ICT-12-40, produced by AO "Katalizator" is based on the effect discovered.

Pt-Black-Al_2O_3

The activity of pressed mixed catalysts depends on the preparation, pressure and, correspondingly, its pore structure. Therefore, maximum catalyst activities in the deep oxidation of methane and butane were obtained, respectively, for pore sizes being > 10 nm and < 10 nm, i.e. at the maximum number of particle contacts per a grain volume unit [2].

If Pt-black is pressed with alumina containing radical traps on its surface, the increase in the synergism activity of the system drops sharply. Analyzing the data of X-ray analysis, H_2 chemisorption, optical microscopy, kinetics, etc., we attribute such synergism to the fact that radicals are born on platinum, then transfer onto alumina via the "jumpover" or "spillover" mechanism, and finally initiate unbranched chain reactions on the alumina surface.

REFERENCES:

1. P.G.Tsyrulnikov, V.S.Salnikov, V.A.Drozdov, S.A.Stuken, A.V.Bubnov, E.I.Grigorov, A.V.Kalinkin, V.I.Zaikovskii, Kinet.Katal., 32 (1991) 439-446.
2. V.S.Salnikov, P.G.Tsyrulnikov, Kinet.Katal., 29 (1988) 1117-1121.

The authors would like to acknowledge the financial support from Russian Science Foundation, Grant No 95-03-08915a.

ACTIVATION OF CO CATALYTIC OXIDATION BY OZONE

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With the purpose of improvement of a work efficiency of a catalyst at carbon monoxide neutralization of industrial gaseous waste is conducted by stronger and ecologically pure oxidizer — ozone. To accomplish this, the catalysts based on nickel, manganese, copper oxides and aluminium oxide modified by lanthanum and nickel oxides were investigated.

The activation of catalysts was achieved by means of preliminary ozone treatment and/or ozone activation, this preliminary treatment being performed at ambient temperature, while the oxidizer being added to reaction mixture at the temperature of the process of interest. Researches was conducted by the pulse technique.

Received results have shown, that the process is in direct dependence from both initial carbon oxide and ozone concentration. The ozone activation of a catalyst resulted in displacement of curve dependence of a degree of CO conversion from temperature in the area of lower temperatures. The activation energy and Habgood kinetic parameters were calculated.

Thus, ozone as activating agent promotes to increasing of intensity of carbon monoxide catalytic oxidation, that probably connect with its decomposition on a surface of a catalyst with possible formation of new active centers.

PPC-154

PROPERTIES AND ROLE OF CATALYSIS SPHERE IN HYDROCARBONS PYROLYSIS

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Analysing the kinetic model of radical-chain heterogeneous-homogeneous pyrolysis of hydrocarbons, we have found that surface affects the process in four ways. It inhibits, neutralizes and accelerates either heterogeneous or homogeneous component of the process rate [1]. In the latter case, the catalyst generates additional radicals into the bulk, thus providing a "superequilibrium" radical concentration around the catalyst granule. We consider it as "catalysis sphere". Here we shall discuss the size, properties and performance of this sphere in the catalytic pyrolysis of hydrocarbons.

We determined the sphere of radicals generated by the surface during the n-butane pyrolysis at T = 1000 K, P = 0.1 MPa. The life time of H, CH_3 and C_2H_5 were calculated as the function of number of active collisions with butane molecules. The diffusion coefficient was estimated by Hirshfelder. The Einstein-Smolukhovski equation $r^2 = 6\ Dt$ allowed us to calculate the distance of radical diffusion (r) into the bulk. r determines the sphere size.

R	H	CH_3	C_2H_5
r, cm	$1.56\ 10^{-4}$	$1.73\ 10^{-3}$	$6.7\ 10^{-3}$

The sphere imposes certain demands on the catalyst structure: the inner surface is not in use. The real pores are too small, thus the sphere can not develop.

The inner surface plays a negative part, since it accelerates the secondary processes. The outer surface of catalyst granules alone works in the radical-chain process.

The sphere requires optimum-size-catalyst granules. The reaction rate drops, if the granules are smaller than the optimum one, since the distance between its is too small for the sphere development. The top catalyst performance is observed when the free space volume between the granules approaches the sphere volume.

The catalysis sphere allows to estimate the optimum active sites concentration on the surface providing by their uniform distribution. The concentration of sites generating methyl radicals, equals 7.8 10^{-10} at.%. The kinetic model also recommends a low concentration of active sites [1].

The catalysis sphere depends on the reaction medium composition. We have established that the pyrolysis products - olefin hydrocarbons - quench the sphere. The catalyst layer at reactor inlet can solely generate such sphere and accelerate the reaction. The catalyst layer at reactor outlet is useless. The sphere responds to the feedstock dilution by an inert gas. As the dilution increases, the reaction rate first increases and then drops. Dilution prolongs the radical life. The rate increases as long as the growth of radical life time compensates the decrease of chain propagation. Then the rate drops. The process rate does not depend on the feedstock dilution in thermal pyrolysis.

We think, that the dependence of the process rate on the feedstock dilution my be experimental criterion of the catalysis sphere existence.

References

1. N.A.Vasilieva, R.A.Buyanov, K.I.Zamaraev, Khim. Phiz., 3 (1984) 688.

PPC-155

HIGHLY EFFICIENT CATALYSIS OF HALOGEN TRANSFER FROM POLYHALOGENOMETHANES $CH_{4-n}X_n$ (n = 4, X = Cl; n = 3, X = Br. I) TO ALKANES AND ARENES WITH HALOGENOPHOSPHINERHODIUM(I) AND HYDRIDOORGANYLPALLADIUM(IV) COMPLEXES

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Catalytic activation of alkane C-H bond with transition metal complexes is of great interest now [1]. Two major ways of hydrocarbon catalytic activation leading to organometallic intermediates have been demonstrated. They include electrophilic activation of substrate with highly oxidizing metal species as a key step, for example, with palladium(II) compounds [2] or oxidative addition of substrate to metal, for example, to rhodium(I) [3]. Catalytic hydrocarbon functionalization via hydrocarbon C-H bond oxidative addition to metal complexes is not so fruitful now as the former way. Only few examples of thermal catalytic reaction of this type such as alkane dehydrogenation are known.

In the presented work the first example of thermal functionalization of alkanes different from dehydrogenation is reported, which can be called metathesis of alkane / arene C-H bonds and polyhalogenomethane C-X bonds:

$$RH + CH_{4-n}(X)_n \xrightarrow{[M],\ 60\text{-}80^oC} R\text{-}X + CH_{5-n}(X)_{n-1} \qquad (1)$$

$n = 4$, X = Cl; $n = 3$, X = Br, I

RH = $n\text{-}C_6H_{14}$, cyclo-C_6H_{12}, C_6H_6, $C_6H_5CH_3$, CH_3CN

[M] = $RhCl(PPh_3)_3$ (**1**), $RPd(H)X_2(PPh_3)_2$ (**2**)

In absence of any additives the reaction of CCl_4 or $CHBr_3$ with alkanes proceeds very slowly even at 130° C and is not detectable in the case of benzene or acetonitril under the same conditions. Facts of hydrocarbon iodination with CHI_3 were not known.

The ability of complexes **1** and $PdX_2(PPh_3)_2$ which forms compounds **2** under reaction conditions [4] to add hydrocarbon C-H bond appears to form base for the metathesis (1):

$$R\text{-}H + [M] \rightleftharpoons \{R[M](H)\} \qquad (2)$$

Various factors which affect its rate do affect the rate of metathesis (1) either. Using palladium catalysts **2** with additives of acetonitril and potassium carbonate allowed us to reach preparatively high yields of chlorocyclohexane and to obtain high yields of chlorobenzene and chloroacetonitril on palladium. In contrast to compound **2** using rhodium complexes does not allow to get very high yields of metathesis product because of catalyst destruction in reaction mixtures. Physico-chemical characterization of reaction (1) catalyzed with both complexes **1** and **2** has been performed. It turned out that metathesis reaction is slightly inhibited with both benzo- and hydroquinone, though no significant amounts of radical dimers have been observed. Reaction is first order on both hydrocarbon and polyhalogenomethane. In order to clear mechanism of the reaction (1) substrate (toluene / cyclohexane competitive experiment) and regioselectivity for toluene and n-hexane metathesis were studied. Cyclohexane has showed higher reactivity per one C-H bond than toluene, especially using complex **1** as catalyst. Only traces of tolyl derivatives have formed. In the case of n-hexane secondary halides were dominant. Mechanism of catalytic metathesis is discussed which includes both C-H bond activation stage and C-X bond radical activation stage.

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1. Activation and Functionalization of Alkanes, Hill C.L. Ed., John Wiley, New York, NY, 1989. 2. Nakata K., Yamaoka Y., Miyata T., Taniguchi Y., Takaki K., Fujiwara Y., J. Organometal. Chem., 1994, **473**, 329. 3. Sakakura T., Tanaka M., J. Chem. Soc., Chem. Com., 1987, 758. 4. Vedernikov A.N., Kuramshin A.I., Solomonov B.N., J. Chem. Soc., Chem. Comm., 1994, 121

PPC-156

KINETICS, THERMODYNAMICS AND MECHANISM OF HYDROCARBON ACTIVATION VIA ALKANE AND ARENE C-H BOND OXIDATIVE ADDITION TO DIHALOGENOPALLADIUM(II) COMPLEXES

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New example of oxidative addition of alkane and arene C-H bonds to metal complex has been recently reported [1]:

$$\underset{\mathbf{1}}{PdX_2L_2} + R\text{-}H \rightleftharpoons \underset{\mathbf{2}}{Pd(R)(H)X_2L_2} \qquad (1)$$

where X = Cl, Br or I, and L = PPh_3;
RH = cyclo-C_6H_{12}, PhMe, C_6H_6, n-C_5H_{12}, n-C_6H_{14}, 2,2,3,3-tetramethylbutane, adamantane.

The first example of hydrocarbon oxidative addition to dihalogenopalladium(II) compounds (**1**) has turned out to be very attractive both from point of view of reaction mechanism and for application in catalytic hydrocarbon functionalization. Main features of this new hydrocarbon activating system are thermodynamic unfavorability of oxidative addition, unusual for oxidative addition selectivity and possibility to equilibrate hydridodihalogenoorganopalladium(IV) compounds (**2**) with reagents, that is complexes **1** and parent hydrocarbons. In the presented work we report results for kinetic, thermodynamic and mechanistic study of the reaction found.

Monitoring of palladation reaction (1) was performed using chemical tests (iodinolysis or brominolysis) followed with GLC analysis of volatile products. Halogenolysis is suitable method for quantitative determination of organopalladiums formed in reaction (1) as it has been shown by NMR spectroscopy. Effect of metal complex, hydrocarbon and triphenylphosphine concentrations on reaction (1) rate and equilibrium was determined. As a result kinetics of oxidative addition to palladium(II) complexes was analytically described. In the presence of large excess of free triphenylphosphine the reaction follows first order in both palladium complex and hydrocarbon, but in the absence of free ligand additive order on metal complex becomes two. Oxidative addition (1) is characterized with significant deuterium kinetic isotope effect (e.g. 4.4 at 120°C for cyclohexane addition to dibromocompound **1**). Activation enthalpies and enthropies of reaction (1) have been determined. Effect of non hydrocarbon co-solvents on reaction pathways and kinetic has been investigated. The results of kinetic study of the reaction have been interpreted in terms of reaction mechanism which include two ways, the slowest one via 16-electron compound **1** and more fast way via 14-electron species like PdX_2L or ion pair $PdXL_2^+$,PdX_3^-.

The reaction free energies, enthalpies and enthropies for hydrocarbons studied have been calculated. The obtained values allow to estimate palladium - carbon bond energies in compounds **2** using reasonable value of Pd-H bond enthalpy. Thermodynamic substrate and regioselectivity of the reaction (1) has been described using simple thermodynamic model based on Pauling bond energy - electronegativity relationship and Mullay's [2] model for metal electronegativity calculations. Role of both electronic and steric factors in determining thermodynamic selectivity of oxidative addition to metal complexes known including classic examples of cyclopentadienyliridium [3] and rhodium [4] compounds has been discussed.

Some new examples of catalytic alkane functionalization based on dihalogenopalladium(II) systems are reported.

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1. Vedernikov A.N., Kuramshin A.I., Solomonov B.N., J. Chem. Soc., Chem. Comm., 1994, 121; Zh. Org. Khim., 1993, **29**, 2129. 2. Mullay J., J. Am. Chem. Soc., 1985, **107**, 7271. 3. Buchanan J.M., Stryker J.M., Bergman R.G., J. Am. Chem. Soc. 1986, **108**, 1537. 4. Jones W.D.; Feher F.J., J. Am. Chem. Soc. 1984, **106**, 1650.

PPC-157

The application of Monte Carlo method for simulation of self-oscillations and autowaves on catalyst surface

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The imitation model of *CO* oxidation reaction on platinum metals in conditions of existence of oscillatory regime of reaction was studied *via* Monte Carlo method. Our model is based on the hypothesis about second form of adsorbed oxygen, that is less active in the reaction. The simulation was realized on the lattice, consisting from $N \times N$ square cells (N was varied from 128 to 512 cells).

The following reaction mechanism was considered:

1	$Z + CO \rightarrow ZCO$	2	$ZCO \rightarrow Z + CO$
3	$2Z + O_2 \rightarrow 2ZO$	4	$ZO \rightarrow ZO'$
5	$ZO' + ZCO \rightarrow 2Z + CO_2$	6	$ZO + ZCO \rightarrow 2Z + CO_2$

The intensities of stages 1)-5) were ajusted, that may be considered as the rate coefficients (realization of the stage 6 will be described below). These intensities were recalculated in the probabilities of realization of the processes. With help of random numbers generator, realization of one of the processes 1)-5) was chosen. Then we determine the coordinates of one cell (or two adjacent cells) of the lattice.

The realization of chosen stage was proceeded as follows:

1) Adsorption of *CO*. If the chosen cell is free, the cell was occupied by an adsorbed ***ZCO***. Otherwise, the attempt of *CO* adsorption was rejected.

2) Desorption of *CO*. If the chosen cell contains ***ZCO***, the cell was cleared. Otherwise, the attempt was rejected.

3) Adsorption of oxygen. The state of the two adjacent cells was checked up. If they are free, their states was changed on ***ZO***. If at least one of the cells was engaged, the attempt of adsorption was rejected.

4) Conversion of ***ZO*** to ***ZO'***. If the adsorbed ***ZO*** was found in the chosen cell, the cell state was converted to ***ZO'***. Otherwise, the attempt was rejected.

5) Interaction *ZCO+ZO'*. If the two chosen adjacent cells are engaged with ***ZCO*** and ***ZO'***, the cells are freed; and the reaction rate counter registers a new product molecule. Otherwise, the attempt was rejected.

After each process choice and its realization, the cycle of diffusion of CO_{ads} was processed. This cycle consist of ***M*** attempts of casual choosing of pair adjacent cells of the lattice. If such pair had the states ***ZCO*** and ***Z***, substances in these cells were exchanged, and thus the diffusion occurs. For all other pairs (except for pair ***ZCO*** and ***ZO***) attempt of diffusion was rejected. But if this pair had the states ***ZCO*** and ***ZO***, the both cells were marked as free; and the reaction rate counter increases by unity. Thus, in our model the rate of ***ZO+ZCO*** interaction depends on the intensity of the diffusion.

In accordance with the intencities of oxygen adsorption (at constant intensities of other stages), the three regions of adsorbate coverages self-oscillations attended by autowave behaviour of adsorbates on the surface were distinguished: 1) region of oscillations with irregular period and constant amplitude - at low oxygen partial pressure in the gas phase; 2) region of regular oscillations - at the middle intencities of oxygen adsoption; 3) region of chaotic oscillations of surface coverages and reaction rate - at the oxygen "excess" in the gas phase.

The analysis of local distribution of adsorbed substances shows, that the reasons of oscillations are the inhomogeneous distribution of the second form of adsorbed oxygen, the existence of slow stages of their formation and consumption and the competition of kinetic mechanisms of reagents adsorption. For adsorption of oxygen, the probability of successful adsorption attempt is higher in locations with minimum local concentration of ZO'. Namely in these locations the process of replacement of CO_{ads} on O_{ads} starts. That process is accompanied by growing of the reaction rate. Then, the diffusion of CO_{ads} induces the wave of the high local density of O_{ads}, that distributes on all the surface. In locations with the high local density of ZO', the process of CO adsorption dominates. In such locations, small clusters of CO_{ads} are formed, and their expansion in accordance with accumulation of ZO' results in the reaction rate vanishing. The chaotic regime of proceeding of the reaction is observed in "excess" of oxygen in the gas phase, i.e. at large values of summary ZO' concentration. As the result of its nonuniform distribution on the surface, the isolated areas of the active surfaces are formed, working as the independent oscillators. Synchronization of the reaction at these areas can not be carried out with the diffusion of CO_{ads}. At low partial pressures of oxygen in the gas phase, irregularity of oscillations till periods is determined by the distinction of time of the presence of the system at the condition with minimum reaction rate. In this condition, only CO_{ads} is on surface, and the moment of reaction ignition is defined by the probability of the formation of the surface spot with a low local concentration of CO_{ads}, sufficient for the excess of O_2 flow over flow of CO onto the surface.

The conclusions. The imitation model of CO oxidation reaction on platinum metals is constructed, that describes irregular till period, periodic and chaotic oscillations of the reaction rate. The model permits to explain both relaxational and harmonical oscillations. It is shown, that in the course of surface concentration oscillations, the movement of waves of the surface substances is observed. The initiation and propagation of these waves is induced by inhomogeneity of second form of the adsorbed oxygen on the catalyst surface, by difference of mechanisms of reagents adsorption, and by the process of CO_{ads} diffusion on the surface.

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PPC-158

KINETICS AND PRODUCTS OF ALKANES OXIDATION IN SYSTEM AT 105 - 220°C

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Homogeneous oxidation of saturated hydrocarbons (RH),excepting CH_4, by Pd(II) in acid media was discovered in our laboratory (1973). The reaction proceeds in 80-95 mass % H_2SO_4 solutions at 70-90 °C and is of first order by RH and by Pd(II). Cycloalkanes undergo oxidative dehydrogenation. Cyclohexane forms benzene, benzene sulfoacid. SO_2 and Pd(0) are formed in this reaction too. Reaction was occured as homogeneous non radical one by the stage dehydrogenation mechanism with formation of intermediates containing palladium in different degrees of oxidation (II,I,0).

We have found the heterogeneous analog $(PdSO_4-H_2SO_4)/SiO_2$ (ratio of components in moles is 1.8:42.5:100) of the homogeneous system $(PdSO_4-H_2SO_4)$ oxidates c-C_6H_{12} and other RH at 105 °C and CH_4 at 220°C. RH concentration in gas phase of static reactor is decreased according to eguation : $d[RH]/d\tau=-k[RH]$.The rate constant values $k \cdot 10^4$ (s^{-1}) ranged from 0.7 to 3 for c-C_6H_{12} at 105°C and from 0.4 to 1.5 for CH_4 and from 2 to 3 for CH_3OH amounting up to 30-40 for cycloalkanes, C_6H_6 and CH_3Cl at 220 °C, depending on the sample $(PdSO_4-H_2SO_4)/SiO_2$ and its storage time. However, the rate constant ratios $(k^r=k^{R_1H}/k^{R_2H})$ measured under similar conditions were reproduced within the limits of 10 to 20 % . The k^r values for oxidation of RH by $PdSO_4$ solutions in H_2SO_4 (A) at 90 °C ("Structure and reactivity of organic compounds and the reaction mechanisms". Nauk. dumka,Kiev.1980,P.69.) and in the system $(PdSO_4-H_2SO_4)/SiO_2$ at 105 °C (B) and at 220°C (C) are given below:

RH	CH_4	CD_4	C_2H_6	n-C_4H_{10}	i-C_4H_{10}	c-C_5H_{10}	c-C_6H_{12}	c-C_6D_{12}
A	–	–	0.01	0.2	1.4	1	2.8	1.3
B	–	–	–	–	0.6	1	2.8	1.5
C	0.02	0.01	0.2	0.5	0.5	1	1	0.9

The substrate selectivity of RH oxidation by A at 90 °C and by B at 105 °C are similar. According to (Kinetika i kataliz.

1989.v.30.N3.P.588) the KIE value for $c-C_6H_{12}/c-C_6D_{12}$ in solution $PdSO_4-H_2SO_4$ (94.3 mass %) decreases with the increase of temperature from 3.9 at 2 °C till 1.9 at 95 °C. Extrapolation up to 105 °C gives for solution A KIE value 1.8 which is in conformity with that for the system B at 105 °C. The lower k^r value of $i-C_4H_{10}$ oxidation by B at 105 °C as compared to $i-C_4H_{10}$ oxidation by A at 90 °C possible is connected with most steric difficulty in B. The low substrate selectivity of RH oxidation by C at 220 °C as compared to liquid-phase oxidation in A at 90 °C and with oxidation in B at 105 °C is apparently due to higher reaction temperature. Extrapolation up to 220 °C (referred above) gives the KIE value 1.1 for CH_4 which is in conformity with that for the system $(PdSO_4-H_2SO_4)/SiO_2$.

System B after reaction with c- C_6H_{12} was treated by acids-H_2SO_4, HCl and $c-C_6H_{12}$, H_2 also. Intensive absorbtion which is characteristic for Pd(I) complexes was found in H_2SO_4 solution by spectrophotometric method. Spectrophotometric analysis of cyclohexane solution points out to absence of any products in it. CO_2 is not detectable in the gas phase. The hydrogenation and treatment of catalyst by concentrated HCl leads to accumulation of $c-C_6H_{12}$ in gas phase of reactor. CO_2 (to 25% on CH_4 reacted), SO_2 (50%) were formed in the reaction of CH_4 with $(PdSO_4-H_2SO_4)/SiO_2$ at 220 °C. H_2SO_4 in A,B,C systems serves as oxidant and it, as strong Bronsted acid, increases electrophilic and oxidative functions of Pd(II).

The comparison of kinetics, products of RH oxidation by $(PdSO_4-H_2SO_4)/SiO_2$ and solution $PdSO_4-H_2SO_4$ permits to suppose C-H bond activation mechanisms in these systems are similar, but the differences have place at stage of products formation.

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PPC-159

Radical-Cation Intermediates in Aromatic Compounds Polycondensation on the Acid Catalysts.

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The role of radical-cations in the processes of adsorbed aromatic compounds polycondensation on different types of acid catalysts has been studied. It was shown that such reactions were important in low- temperature processes.

We have shown earlier that radical-cation mechanism of benzene polycondensation on ZSM-5 zeolites was the main in the range of temperatures up to 400 K [1]. In the present work radical- cation reactions for different types of acid catalysts have been studied.

Before the experiments the standard oxygen-vacuum treatment of catalysts at 773 K was carried out as described [1]. Then the adsorption of any chosen aromatic compounds (benzene, toluene, p-xylene) at the pressure of their saturated vapours (in some cases to the point of liquid phase appearence) was carried out at 243-293 K.

For such samples the EPR-spectra of appearing paramagnetic particles and their changes after heating of catalyst at fixed temperatures were recorded.

Following catalysts arranged in order of increasing their Lewis acid centres strength were used in this work: γ-Al_2O_3 ; F^-/Al_2O_3 ; SO_4^{2-}/Al_2O_3 ; H-ZSM-5; SO_4^{2-}/ZrO_2 .

It was show that for all investigated systems the same mechanism of primary radical formation during the adsorption of aromatic compounds on the surface acid sites (A_s) may be suppose:

$$Ar + A_s \rightarrow {}^{\bullet}Ar^+ + A_s^-$$

In many cases the primary radical-cations ${}^{\bullet}Ar^+$ themselves were observed during the adsorption [1,2]; in other cases secondary radicals were recorded.

It is essential that the investigated systems each is characterized by its temperature interval in which all chemical reactions proceed with retention of total radical concentration, as well as for the system benzene - ZSM–5 zeolites [1].

The polycondensation processes in this temperature interval can be expected to proceed by radical-cation mechanism. Their efficiency depends both on the strength and concentration acid sites (A_s) and donor properties (I_p) of adsorbed molecules.

On increasing the temperature higher certain critical point (T_{CR}), another mechanism of coke deposit formation results and radical concentration increases significantly.

Table shows characteristic temperatures (T_{CR}) and radical-cation concentration (N) for some investigated systems:

	F^-/Al_2O_3	H-ZSM–5	SO_4^{2-}/ZrO_2
	p-xylene	benzene	benzene
T , K	< 773 K	< 673 K	< 523 K
N, x10^{-16} spin/g	50	1.5	0.5

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References

1. V.A.Bolshov, A.V.Toktarev, A.M.Volodin Mendeleev Communs., 1994, N6, 212.
2. A.F.Bedilo, A.M.Volodin, G.A.Zenkovets, G.V.Timoshok React. Kinet. Catal. Lett., 1995, **55**, 183.

PPC-160

On the Interaction of a CO Molecule with an Electron-Deficient Pt Atom in Mordenite: A Density Functional Model Cluster Study

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Platinum is known to be one of the important catalysts. The interaction of extremely small metal particles with a zeolite support modifies the electronic structure of the metal. This can result in a different catalytic performance of highly dispersed platinum species supported on zeolites. Recently FTIR spectroscopy of adsorbed CO has been employed to study the state and dispersion grade of Pt in mordenite [1]. The results obtained are in line with the assignment of the IR absorption band at 2123 cm^{-1} to Pt carbonyl species anchored at zeolite protons in complexes like $CO\text{-}[Pt\text{–}H_z]^{z+}$ (z refers to the unknown number of acidic hydrogen atoms interacting with Pt, $z \geq 1$). This model is based on the findings that (i) the position of the band does not depend on the CO exposure and (ii) the intensity of this band depends critically on the presence of zeolite protons.

It is of interest to quantify the electronic state of monatomic platinum in zeolite using quantum-chemical methods as well as to verify the hypothesis about the possibility of the formation of extremely dispersed Pt species in mordenite. The aim of this work was to study the dependence of the adsorption-induced C-O frequency shift on the coordination and the electronic configuration of the platinum atoms in zeolites using the first-principles linear combination of Gaussian-type orbitals density functional (LCGTO-DF) cluster method [2]. For a heavy element such as platinum, it is of crucial importance to account for relativistic effects on various properties of the complexes under study. Therefore, a scalar-relativistic version of the LCGTO-DF method was employed [3].

The cluster model $(AlH_3)(SiH_3)OH\text{–}Pt\text{–}CO$, referred to in the following as Z-Pt-CO, has been designed to rationalize observed vibrational properties of adsorption carbonyl complexes. In order to investigate change of the CO stretching frequency with the number and the acidity of hydrogen atoms to which the platinum atom is anchored, the following simplified cluster models have been considered: Pt–CO, H–Pt–CO, $(HOH)_n\text{–}Pt\text{–}CO$ (n = 1, 2, 3), and ClH–Pt–CO.

Results obtained for the latter cluster models show that the C-O frequency increases in the series $(HOH)_n\text{–}Pt\text{–}CO$ with the number of water molecules to which Pt atom is attached (see Table). Similarly, the frequency increases with the Brønsted acidity of the substrates. Results for the more elaborate Z-Pt-CO model confirm the assumption that a larger acidity strength of the hydrogen atoms induces a higher C-O frequency. Local density functional (LDF) binding energies are known to often overestimate experimental values. For instance, for the Z-Pt-CO cluster, a Pt-H binding energy of 0.62 eV is computed at the LDF level of theory, but this value is reduced to 0.14 eV if a gradient-corrected energy functional is employed. This gradient-corrected result is more realistic and is in line with our previous study of weakly bound complexes in zeolite [4].

The calculated data support the suggestion [1] that the platinum atoms are electron-deficient in zeolites and that therefore a rather small red-shift of the C-O frequency may result.

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Table. Interatomic distances, R, C-O frequency shift relative to free CO, $\Delta\omega(CO)$, and the LDF Pt-H binding energy, E_b, corrected for the basis set superposition error.

System	R(C-O) [Å]	R(Pt-C) [Å]	R(Pt-H) [Å]	$\Delta\omega(CO)$ [cm^{-1}]	E_b [eV]
HOH-Pt-CO	1.146	1.76	1.97	-76	0.26
$(HOH)_2$-Pt-CO	1.149	1.76	1.97	-63	0.46
$(HOH)_3$-Pt-CO	1.146	1.77	2.06	-47	0.81
ClH-Pt-CO	1.150	1.75	1.94	-60	0.44
Z-Pt-CO	1.146	1.76	2.00	-43 (-20)[a]	0.62 (0.14)[b]

[a] experimental value [1]. [b] gradient-corrected value.

References

[1] V. L. Zholobenko, G.-D. Lei, B. T. Carvill, B. A. Lerner and W. M. H. Sachtler, J. Chem. Soc. Faraday Trans. **90**, 233 (1994)

[2] B. I. Dunlap and N. Rösch, Adv. Quantum Chem. **21**, 317 (1990)

[3] O. D. Häberlen and N. Rösch, Chem. Phys. Lett. **199**, 491 (1992)

[4] K. M. Neyman, P. Strodel, S. Ph. Ruzankin, N. Schlensog, H. Knözinger and N. Rösch, Catal. Lett. **31**, 273 (1995)

PPC-161

NMR STUDY OF SURFACTANT STABILIZED COLLOIDAL RHODIUM CATALYSTS

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Rhodium colloids with a very narrow size distribution around 2nm were recently prepared in organic solvents by hydrogen reduction of $RhCl_3$ in water solution in presence of tertiary amines or quaternary ammonium ions acting as phase-transfert agents. These colloids are quite active for the hydrogenation of aromatic compounds and are highly stereoselective in the hydrogenation of dibenzo-18-crown-6 ether [1]. It was postulated that rhodium colloids are stabilized in the organic phase by the surfactant molecules adsorbed on their surface. The aim of the present work is to characterize by NMR the adsorption on rhodium of tri-*n*-octylamine (TOA), tri-*n*-dodecylamine (TDoA), tri-*n*-decylamine (TDeA) and tri-*n*-pentylamine (TPA).

Whatever the surfactant/metal ratio, only one NMR peak is observed for each carbon atom indicating a rapid exchange between molecules adsorbed on the metal and those in solution. In the presence of rhodium the ^{13}C NMR peaks of the surfactant are shifted towards high magnetic fields, and the differences between the chemical shifts observed and those of "free" molecules depend upon the carbon position along the chain and upon the surfactant/rhodium ratio (Figure 1).

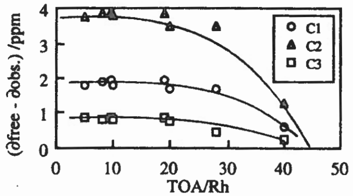


Figure 1 : Effect of the TOA/Rh ratio on the chemical shift difference

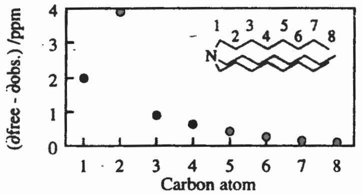
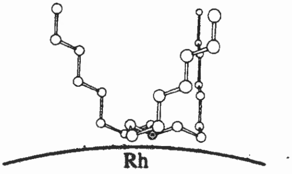


Figure 2 : Chemical shift difference of TOA

For the high values of the TOA/Rh ratio the chemical shifts observed tends towards those of the "free" surfactant. When the ratio decreases, the chemical shifts reach a plateau which means that only the adsorbed TOA molecules are observed for their relaxation is enhanced by the metal.

The chemical shift difference decreases along the chain with the exception of C2 carbon for which the highest value is observed (Figure 2 : TOA). This confirms not only that surfactant molecules are bonded to the Rh particle by their N atom but also that the C2 carbons are likely to be close to the metal surface (cf. scheme).



The results illustrated here dealt with the TOA, but similar ones are observed for the other trialkylamines (TDoA, TDeA, TPA), in particular the C2 shift difference is always the largest which indicates a similar structure of the surfactant adsorbed at the metal particle surface.

1. P. Drognat Landré, D. Richard, M. Draye, M. Lemaire and P. Gallezot, *J. Catal.* **147**, 214 (1994)

PPC-162

AB INITIO CHEMICAL REACTIVITY CALCULATIONS OF TI AND AL HYDRIDE AND ALKYL COMPLEXES AS MODELS OF ACTIVE SITES OF CATALYTIC POLYMERIZATION OF ALKENES AND ALKYNES.

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The addition of ethylene [1], propylene [3] and acetylene [2] to the metal-hydrogen and metal-methyl bonds in the complexes H_2MR (M=Ti, Al; R=H, CH_3) are investigated by ab initio SCF MO LCAO quantum chemical method. The geometries were completely optimized on the HF level with a double-ζ basis sets. The energy profiles of two-stage addition of monomers to the M-R bond were calculated. Energy minima on the potential surface and transition states (TS) were rigorously located and determined via diagonalizing the matrix of force constants. The electronic carrelation to the Moller-Plesset perturbation theory at the second order (MP2) was also taken into account. The role of electronic and steric factors in these reactious are analyzed. It is coucluded that the mechanism of the insertion of alkenes and alkynes into M-R boud is determined by the electron density transfer from the M-R bond to the π^*- antibonding orbital of monomers. Basing on the stability (aromaticity) of the transition state, we suggest that the relation between the reactivity in the reactions of growth of a chain is couuected with s-, p-, d-orbital coutributing to the bond formation. The activation energies of the insertion reactious are correspondinly insreased with increasing S-character of M-R bond. It was found that acetylene is more active thane olefins in the insertion reaction. The higher reaction activity of acetylene is caused by the formation of a more stable transition state during the coordinated monomer interaction. This fact can be attributed to a lower state of acetylene π^* - orbitals compared to that of ethylene. η^3 - allyl complex is the most stable product of the acetylene addition to the Ti-CH_3 bond. All of the results of the calculations are analyzed in relation to known experimental data.

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References:

1. Zakharov I.I.,Zakharov V.A., Zhidomirov G.M. Kinet.Katal. 1994.v.35, N 1, P.74.

2. Zakharov I.I., Zakharov V.A., Zhidomirov G.M. Kinet.Katal.1995.v.36, N 3.

3. Zakharov I.I., Zakahrov V.A., Zhidomirov G.M. Kinet.Katal., to be published.

PPC-163

MECHANISM OF SURFACE INTERMEDIATE FORMATION DURING THE NO+H_2 REACTION ON THE Pt(100) AND Pt(111) SURFACES: HREELS/TDS STUDIES

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A great deal of the detailed model studies of surface phenomena are required for an understanding the mechanisms of heterogeneous catalytic reactions. NO adsorbs on platinum molecularly or dissociatively depending on the surface structure. It is well known that this fact is determined by the details of the NO+H_2 reaction mechanism and the key products - N_2 and NH_3. This work presents some new results of the study of NO+H_2 reaction intermediate formation on two platinum surfaces: (111) and (100), using HREELS and TDS.

It has been shown that the topmost layer of Pt(100) exhibits two structures: the reconstructed (hex) phase and the unreconstructed (1×1) one, which have considerably different adsorption properties. The (hex) phase symmetry is similar to Pt(111) surface. Hence, the adsorption properties of the (hex) phase and the (111) surface would be expected to be similar in appearance. The HREELS and TDS data obtained after NO adsorption on the Pt(111), the (hex) phase and the (1×1) one are shown in Table 1. The ^{15}NO was used in our experiments.

Table 1. NO adsorption on the Pt(111) at 170 K and Pt(100) surfaces at 300 K

Platinum surface	(111)	(100)-(hex)	(100)-(1×1)
Molecular adsorption	+	+	+
Vibration band (cm^{-1})			
ν(N-O)	1720 (on-top) 1420 (bridge)	1620 1775	1590-1620[1]
Dissociative adsorption	-	-	+
ν(Pt-O)	-	-	540
ν(Pt-N)	-	-	(*)
Desorption temperature (K)	300-350	350-470	350-470

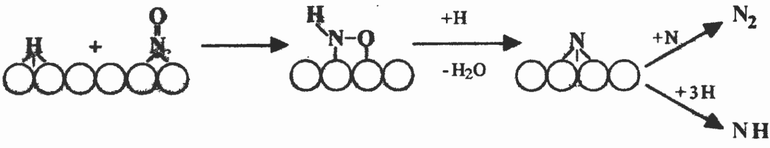
[1] ν(N-O) shifts to the red region as the NO coverage increases.

(*)ν(Pt-N) should be expected in the frequency range from 300 to 600 cm^{-1}. Probably nitrogen vibration is not distinguished with ν(Pt-O) and ν(Pt-NO) bands in our case.

NO adsorption According to the HREELS data nitric oxide adsorbs only molecularly on the Pt(111) and the Pt(100)-(hex) surfaces. By contrast, dissociation proceeds at the initial stage of NO adsorption on the Pt(100)-(1×1). Oxygen atoms appeared as a result of NO dissociation is characterized by the ν(Pt-O) band at 540 cm^{-1}. The molecularly adsorbed state appears as NO exposure increases. The nitric oxide adsorbs molecularly in island on the reconstructed Pt(100) inducing the back reconstruction of the topmost platinum layer from the (hex) phase into the (1×1) one. The NO adsorption occurs in two states. The molecules of the first state occupy the unreconstructed areas within NO_{ads}/(1×1) islands and exhibit the vibration band at 1620 cm^{-1}. The ν(NO) band at 1775 cm^{-1} testifies the formation of the minor adsorption state located in the vicinity of the island boundary.

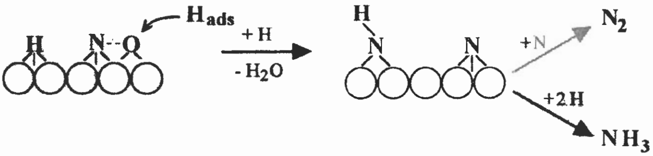
Desorption of the NO_{ads} layers from Pt(111) surface occurs without nitric oxide decomposition. Dissociation of nitric oxide molecules proceeds as a result of heating the NO_{ads} layers on the both phases of the (100) surface.

NO+H_2/Pt(111) It has been found that only the bridge NO_{ads} reacts with hydrogen at 300 K producing N_2 and NH_3 on the Pt(111) surface. Formation of HNO_{ads}-particles as a intermediate of NO_{ads}+H_2 reaction followed by their transformation into N_2 and NH_3 has been observed. This reaction is shown in Scheme I.



(I)

NO+H_2/Pt(100) The saturated NO_{ads} layers on both the (hex) surface and the (1×1) one cannot react with hydrogen due to absence of active (1×1) vacant site for NO_{ads} dissociation and H_2 adsorption. Indeed, preliminary heating at T≥375 K in vacuum provides room for hydrogen adsorption and nitric oxide dissociation. After heating the reaction exhibits autocatalytic behavior producing N_2 and H_2O on the original (hex) phase at 300 K. The appearance and subsequent disappearance of NH_{ads} as the reaction intermediate are observed by HREELS. This interaction is shown in Scheme II.



(II)

The reaction mechanism The differences of Pt(111) and Pt(100) surfaces in NO dissociation properties result in the dissimilar mechanisms of NO_{ads}+H_2 reaction. The titration reaction shows that the molecular mechanism via the HNO_{ads} intermediate formation proceeds on the (111) surface whereas the dissociative one is possible on the (100) surface. All attempts to registrate the NH_3 formation on the Pt(100) surface have failed that is most likely to be explained by the low rate of the corresponding reaction stage under low pressure conditions used in this work. The possible mechanisms of NO+H_2 reaction on the both surfaces can be present as follows:

Molecular mechanism, Pt(111)	Dissociative mechanism, Pt(100)
1. $NO_{gas} \leftrightarrow NO_{ads}$	1. $NO_{gas} \leftrightarrow NO_{ads}$
2. $H_{2gas} \leftrightarrow 2\ H_{ads}$	2. $H_{2gas} \leftrightarrow 2\ H_{ads}$
3. $H_{ads} + NO_{ads} \rightarrow HNO_{ads}$	3. $NO_{ads} \rightarrow N_{ads} + O_{ads}$
4. $HNO_{ads} + H_{ads} \rightarrow N_{ads} + H_2O_{gas}$	4. $O_{ads} + 2\ H_{ads} \rightarrow H_2O_{gas}$
5. $N_{ads} + 3\ H_{ads} \rightarrow NH_{3ads}$	5. $N_{ads} + 3\ H_{ads} \leftrightarrow [NH_{ads}] \rightarrow NH_{3gas}$
6. $N_{ads} + N_{ads} \rightarrow N_{2gas}$	6. $N_{ads} + N_{ads} \rightarrow N_{2gas}$

Acknowledgments

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PPC-164

STUDY OF SOLID-STATE CATALYTIC ISOTOPIC EXCHANGE WITH TRITIUM.

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New catalytic reaction between a solid bioorganic compound and activated spillover tritium (ST), based on High-temperature Solid-state Catalytic Isotopic Exchange (HSCIE) was examined. Only this reaction have been used for pertritiation of organic compounds for the first time [1]. A general description of the method which involves heating of solid-state mixture of organic compound and catalyst at elevated temperatures is shown below.

$$\text{Organic compound} \xrightarrow[\text{Catalyst, 40-240 C}]{\text{Tritium gas}} \text{Specifically labelled or per labelled compound}$$

The described process is based on the activation of hydrogen isotopes on platinum metals, activated hydrogen spillover in the organic compound layer and hydrogenolysis resulting in the formation of isotope-substituted compounds. The HSCIE mechanism and determination of the reactivity of hydrogen atoms in amino acids, peptides and proteins was investigated. Quantum mechanical calculations of the reactivity of hydrogen atoms in amino acids in the HSCIE reaction were done. The carbon atom with a greater proton affinity undergoes a greater exchange of hydrogen for tritium in HSCIE. The electrophilic nature of spillover hydrogen in the reaction of HSCIE was revealed. It was found that spillover tritium can migrate over considerable distances under conditions of spatial separation of the organic compound and the catalyst in the HSCIE reaction. The reaction with gaseous tritium was performed after the organic compound was placed on an inorganic support and mixed with solid catalyst. This version of the HSCIE reaction ensures a high chemical yield and an increase in specific activity. The effect of nature of the support on the reativity of amino acid was shown for L-Phe adsorbed on alumina, carbon and palladium catalyst. Adsorbtion of Phe on carbone leads to the close tritium distribution as for palladium catalyst. The reactivity of aromatic hydrogen atoms in o-Phe and p-Phe was close in both cases. The most active were aromatic hydrogen atoms in m-Ph. Quantum mecanical calculations showed that protonation of the m-Ph position was more preferable than of the o-Ph or p-Ph positions. On the contrary, in case Phe adsorbed on alumina, the reactivity of hydrogen at the alfa-carbon atom considerably increased. The cause of this alteration may be due to the interaction between the surface atoms of alumina and carboxyl grouping of amino acid. Quantum mecanical calculations showed that protonation of the alfa position was more preferable than of the beta position in this case. The reactivity of aromatic hydrogen atoms and protonation energy of this pozition were in good correlation. So, the main results of proton model of ST are in good correlation with the experimental data. In addition, the activation energy of proton spillover on a graphite layer calculated with quantum mecanical calculations was equal to 10 kcal/mol. This value was close to the activation energy of HSCIE of valine with ST [2]. The isotope exchange between ST and the hydrogen of the solid organic compound proceeds with a high degree of configuration retention at the carbon atoms. The application of the HSCIE reaction makes it possible to introduce the isotopic label directly into synthetic or natural peptides without modifying them, and minimum amount of the initial compound is necessary. The HSCIE reaction enables to synthesize tritium labelled proteins with a specific activity of 20-30 mCi/mg and kept biological activity. Examples of the application of the HSCIE reaction to the preparation of a wide range of hydrogen-isotope labelled compounds will be presented.

References:

1. Yu.A. Zolotarev , V.Yu. Tatur, D.A. Zaitsev, N.F. Myasoedov (1989) Method for Prepering Biologically Active Organic Compound Labelled with Hydrogen Isotope, US Patent No. 5 026 909

2. Yu.A. Zolotarev, V.S. Kozic, D.A. Zaitsev, N.F. Myasoedov, (1992) High-Temperature Solid-State Catalytic Isotopic Exchange with Deuterium and Tritium. J. Radioanal Nucl Chem. Art 162:3-14.

PPC-165

THERMOCHEMICAL ACTIVATION OF SOME LAYERED HYDROXIDE SYSTEMS.

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Manufacture of novel chemical products, demands for environmental protection urge on the development of the methods of solid state activation - up-to-date low waste technologies of the production of catalysts, supports and adsorbents. Among others thermochemical activation (TCA), the method of transformation of crystalline substances into the chemically active state, is now of increasing use in the synthesis of catalysts and supports.

At present, the regularities of TCA and the nature of resulting products have received the most study for gibbsite. As a result, a new low waste technology for production of a wide range of alumina supports, catalysts, adsorbents has been developed.

To extend the scope of chemical systems which may be subjected to TCA and to refine our understanding of this process, we have studied the regularities of TCA in two layered hydroxide systems - bayerite ($Al(OH)_3$) and Mg(II)-hydroxoaluminate (Al(III)-Mg(II) coprecipitated hydroxides).

We have identified parameters of TCA running for these two systems, so that resulting products are completely X-ray amorphous and chemically active. It was confirmed by means of electron-microscopy, differential thermogravimetry, XRD. According to ^{27}Al NMR the TCA product of bayerite exhibits new properties: its structure contains 5-coordinated Al. We have also paid much attention to examine the regularities of hydration process in two named systems. Crystallized bayerite yields the hydration of TCA product of bayerite at room temperature. If hydration runs at elevated temperature in weakly acidic medium, the TCA product of bayerite gives pseudoboehmite. At hydration of Mg(II)-hydroxoaluminate's TCA product the phase of Mg(II)-hydroxoaluminate forms, no matter what were the temperature (room, 80^oC) and acidity. So, the latter is completely reversible process. In order to elucidate common features and special peculiarities, we have made comparative analysis between properties of TCA products of bayerite, gibbsite, and Mg(II)-hydroxoaluminate. We explain determined peculiarities in the context of structural distinctions of original compounds.

The work is carried out under financial support from Russian Foundation of Fundamental Research (grant 94-03-08286).

PPC-166

THE PECULIARITIES OF ACTION OF FIXED COBALT PHTHALOCIANINES IN OXIDATION OF SULPHIDE SOLUTION

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Abbreviations:

functional polysiloxane matrices – FPS
cobalt phthalocianines – CoPc
poly(3–aminopropyl)siloxane – SAP
poly(3–aminopropyl, methyl)siloxane – SAPM

It is known that cobalt phthalocianines (CoPc) inserted and fixed on the surface of functional polysiloxane matrices (FPS) display a catalytic activity in an oxidation of S^{2-} ions [1]. In so doing, as follows from values of oxidation rates of sulphide solutions reported in the Table below, samples with supported CoPc possess a catalytic activity by one order of magnitude higher than samples with inserted CoPc.

Table

Values of oxidation rates of sulphide solutions
$t = 25°C$; $pH = 7.5$; $[S^{2-}]_o = 0.046$ M; $[S_2O_3^{2-}]_o = 0.027$ M

Catalyst	Matrix	$[Cat.] \cdot 10^6$, mol/g	W_{ox} , $l/mol \cdot s$
$CoPc(SO_3H)_4$	onto SAP	2.4	110
	onto SAMP	2.0	199
	into SAP	1.5	12
$CoPc(SO_3H)_2$	onto SAP	1.8	105
	onto SAMP	3.4	111
	into SAP	0.4	26
	into SAMP	0.6	37
CoPc x x $(3-NO_2)_4$ x x $(SO_3H)_2$	onto SAP	1.3	103
	into SAP	0.4	24
$CoClPc(SO_3H)_2$	onto SAP	2.0	78
	into SAP	0.6	24

It should be noted that a ratio of activities under homogeneous conditions does not correspond to heterogeneous ones. The nature of the matrix has an essential influence: thus, $CoPc(SO_3H)_2$ fixed onto the SAMP matrix has an activity which is practically equal to the activity of $CoPc(SO_3H)_4$ fixed onto the SAP matrix. But under homogeneous conditions, the latter is 2 times more active than the former.

Electronic spectrum of absorption and diffusion reflection showed the presence of a small amount of associated cop for the matrix – fixed complexes. For the complexes inserted in SAP or SAMP matrix, the bands observed have only been corresponded to monomeric form. According to [2], the capacity of complexes for aggregation influences strongly their catalytic activity under homogeneous conditions.

From this point of view, the above mentioned systems present an evident interest for next investigations.

New samples of CoPc have been fixed onto FPS matrices. The method of their obtaining differs from earliest ones by the way of CoPc fixing, as well as the ratio of functional groups on the surface. These new samples have been tested by various physical methods. The conclusions have been made concerning the state of Co onto the matrix surface , that is of great importance for the choose of suitable catalysts for HS–oxidation. It should be noted, that sulphide solutions practically always contain small amounts of thiosulphate ions. The ratio of fixed CoPc–complexes to the concentration of amino–groups on the surface of matrices is approximately of 1:1000 and "free amino–groups" can act as potential catalysts of the reaction between sulphide and thiosulphate to produce an elemental sulphur.

REFERENCE:

1. Yu.L.Zub, A.B.Pecheny, A.A.Chuiko, T.L.Stuchinskaya, N.N.Kundo, Catalysis Today, **17** (1993), p. 31.
2. T.L.Stuchinskaya, V.E.Maizlish, N.N.Kundo, R.P.Smirnov, J. Appl. Chem. (Russ.), 5 (1992), p. 1039.

CONTENT

SECTION CATALYSIS

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Part II (2)

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