Memorial G.K.Boreskov Conference

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

ABSTRACTS

July 7-11, 1997
Novosibirsk - Russia

PART I

Open PART II

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Scientists from Independent States of the former Soviet Union (INTAS)

The Second International Memorial G.K. Boreskov Conference

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

ABSTRACTS

PART I

Novosibirsk - 1997

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PLENARY LECTURES

KINETIC COUPLING WITHIN AND BETWEEN CATALYTIC CYCLES

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Kinetic Coupling within Catalytic Cycles

The kinetic steady state of Bodenstein is generally applicable to catalytic reactions as a result of the much smaller amount of reactive intermediates in the reactor volume, as compared to the amount of stable reactants, intermediates, and products. A possible exception in practice deals with the tail end of environmental cleanup down to the last ppm quantities of pollutants. [1]

A consequence of the Bodenstein steady state is that all elementary steps in the catalytic cycle are kinetically coupled by the general relation:

$$v = v_+ - v_- = v_i = v_{+i} - v_{-i}$$

where v is the net turnover rate of the cycle and v_i is the net rate of the i'th elementary step suitably weighted with its stoichiometric number σ_i, namely the number of times that the step must enter into the cycle for each turnover. Subscripts + and - pertain to rates forward and reverse respectively.

As a result of kinetic coupling, a concept first introduced in 1983 [2], a thermodynamically unfavorable step in the cycle may yet move forward if a product of this step is removed by the following step, faster than it returns to reactants. This phenomenon follows directly from the principle of Le Chatelier and can be quantified by the relation of De Donder:

$$v_{+i}/v_{-i} = \exp(-\Delta G_i/RT).$$

In fact, as expressed by the equations of the steady state, no step in the cycle can be truly in equilibrium: even if v_{+i} and v_{-i} are both much larger than v_i, it is clear that $v_{+i} \neq v_{-i}$ as would befit a true equilibrium. Thus we can talk only of a step being in a quasi-equilibrium, and kinetic coupling is always present at the steady state.

For instance, in heterogeneous catalysis, we refer to a Langmuir-Hinshelwood mechanism when reactants and products are in equilibrium with their chemisorbed counterparts, with a surface step being rate determining in the true sense of the word [3]. But strictly speaking, in such a mechanism, equilibria are only quasi-equilibria.

More importantly, Langmuir-Hinshelwood mechanisms may well be the exception rather than the rule because kinetic coupling may shift a quasi-equilibrium to a position far from equilibrium [4]. At the extreme, an adsorption step or a desorption step may be practically *one way* steps, commonly called irreversible, namely when $v_{+i} >> v_{-i}$ so that $v_i \cong v_{+i}$. Thus it may occur that a reaction product does not inhibit the rate of a catalytic reaction because its desorption is one-way as a result of kinetic coupling. Such situations may not be readily apparent because the overall rate expression may be identical in two quite different situations. In the first situation, we deal with a Langmuir-Hinshelwood mechanism. In the second situation, we deal with a mechanism where the entry step of the cycle is one way and the same is true for the exit step, while the exiting surface species is the most abundant reactive intermediate [4]. Several examples of this situation will be discussed: the dehydrogenation of methyl cyclohexane to toluene on platinum [4], the decomposition of germane on germanium [5], ammonia synthesis on iron [6], and the aromatization of alkanes on zeolites [7]. In these cases the fugacity of an adsorbed species may be much higher than the fugacity corresponding to equilibrium between the gas phase species and its adsorbed counterpart. To describe such a situation, it is often said that the virtual pressure of the desorbed species is much larger than its real pressure at the steady state. A related example is the electrolysis of heavy water on palladium electrodes. In that case, very high expected values of the virtual pressure of hydrogen at moderate values of over potential led to the speculation that the corresponding very high concentrations of deuterons dissolved in the metal might lead to nuclear fusion [8]. Attempts at verifying the existence of such cold fusion have failed so far, but the idea of virtual pressure as a physico-chemical phenomenon related to catalytic coupling has been confirmed experimentally many times, for instance in the catalytic decomposition of ammonia far away from equilibrium [9].

Kinetic Coupling between Catalytic Cycles

When two or more stoichiometric reactions take place in parallel or in series on a homogeneous or heterogeneous catalyst, kinetic coupling between elementary steps taking place on identical sites at the steady state can lead to important and surprising changes in catalytic selectivity.

The most striking and best understood example is the hydrogenation of an alkene in the liquid phase of a chiral catalyst [10]. The effect of hydrogen pressure on the enantioselectivity to the R and S chiral isomers can be interpreted by catalytic coupling between both cycles [11]. In particular, it can be seen how by increasing the hydrogen pressure, the binding of the substrate can change from quasi-equilibrated at low pressure to one-way (i.e., irreversible) at high pressure because of a change in the catalytic coupling from loose to strong in both cycles. A similar perturbation from equilibrium adsorption of ethyl pyruvate on a dihydrocinchonidine-modified heterogeneous platinum catalyst accounts for the observed effects of hydrogen pressure on the enantioselectivity of the chiral hydrogenation [12].

Another example of kinetic coupling between catalytic cycles at the steady state is the isomerization of n-pentane to i-pentane on a bifunctional catalyst consisting of platinum clusters supported on an acidic alumina. The first cycle occurs on the metal and consists of the equilibrated dehydrogenation of n-pentane to n-pentene. The latter is then isomerized to i-pentene in a second cycle taking place on the Brønsted sites of the support. Finally i-pentene is hydrogenated on the metal to the final product, i-pentane [13,14].

A final example is catalytic cracking of alkanes on zeolites where catalytic coupling can be quantified by a detailed microkinetic analysis of the process that accounts for the yield of the various products from a single reactant [15].

Conclusion

Kinetic coupling within and between catalytic cycles at the steady state is a simple unifying concept that helps us understand why catalytic cycles turnover in spite of severe thermodynamic hurdles; how quasi-equilibrated steps can become one-way (i.e., irreversible); under what circumstances concentrations of reactive intermediates at the steady state become very different from the equilibrated values assumed in Langmuir-Hinshelwood mechanisms; the way in which process variables can modify selectivity in homogeneous and heterogeneous reactions; and the mechanism of bifunctional catalysis.

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PL-2

THE CLUSTER APPROACH TO MOLECULAR HETEROGENEOUS CATALYSIS

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Extended Abstract:

Heterogeneous catalytic reactions occur on solid surfaces. Hence it may seem that heterogeneous catalytic site models based on clusters cannot properly describe the surface chemistry that is the basis to heterogeneous catalysis. Clearly those aspects of the reaction that intrinsically relate to the presence of the extended lattice or micropore cannot be described by cluster models but require full consideration of the two-dimensional or three-dimensional geometry. Surface reconstruction and island formation belong to this category. In zeolites the shape and size of the micropore cavities may prevent particular reaction paths when transition states are too bulky.

Hence it is important to discriminate between those aspects of the reaction that depend on local properties, that often can be treated using a cluster approach and those aspects of the reaction that do not.

Here we will discuss this for examples from transition metal catalysis (1) and solid acid catalysis (2) by zeolites. In both cases we will use clusters to analyze the transition states of elementary reaction steps and we will demonstrate how this information can be used to predict the overall rate of a catalytic reaction. For the case of catalysis by a transition metal we will apply kinetic Monte Carlo methods (3) to analyze the occurrence of oscillations in the rate of CO oxidation.

In zeolite catalysis we will simulate the turn over frequency (TOF) of hexane isomerization in Mordenite and ZSM-5 (4). Here it appears essential to include the structure of the lattice that determines the difference in the heats of adsorption of the reacting molecules (5).

Clusters are useful in those cases where the surface-chemical bond is localized and where boundary effects are well understood.

Quantum-chemical research on clusters has become fruitful especially due to advances in the development of Density Functional Theory techniques and the incorporation of gradient correction terms to the exchange-correlation energy. Several computer programs now have efficient procedures to find the geometries that correspond to stationary points on the potential energy surface. Within the harmonic approximation the vibrational normal modes can be found, so that ground and transition state energies as well as entropies can be computed.

This enables the application of Eyring's transition state reaction theory to predict reaction rate constants (6).

We will start with an analysis of cluster size dependence and relaxation effects on Pd clusters (7). A comparison will be made with slab calculations using the Car-Parinello method (8).

After the discussion of transition metal catalysis, we will analyze methanol activation using protonic clusters (9). We will show how different reaction paths for dimethylether formation can be analysed.

Theory here appears to be essential for a proper understanding of carbenium and carbonium ion intermediates (10).

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MOLECULAR MODELS OF CATALYTICALLY ACTIVE SITES. QUANTUM CHEMICAL APPROACH

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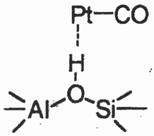
It is widely recognized that mechanism of catalysis depends intimately on the intermediate chemical interaction of reacting molecules with some groups of catalyst atoms usually considered as active site (AS) [1]. Investigation of AS structure and chemical properties has become the main objective of fundamental research in catalysis. AS molecular models can be justified by quantum chemical calculations of their structure and physical-chemical properties. As a rule, AS are some local structures on the surface of the catalyst. Therefore, it is reasonable to use the so called molecular cluster approach in quantum chemical calculations. According to the cluster approach, some finite fragment is cut off the lattice. The fragment choice is determined by features of process to be studied. The cluster approximation is rough since it is necessary to break the bonds between the cluster and the lattice. There are various ways to decrease the negative effect of the bond breaking. The saturation of dangling cluster bonds by some boundary monovalent atoms, for example, by hydrogens, or by atoms with specially fitted quantum chemical parameters ("pseudoatoms") is one of the simplest and most suitable ways to describe better the features of the system under study [2].

BROENSTED ACID SITES (BAS) IN ZEOLITES. Bridged hydroxyl group of a zeolite is a typical example of a BAS on the surface of a heterogeneous catalyst. The $(HO)_3SiOHAl(OH)_3$ cluster is the simplest model of a bridged hydroxyl group [2,3]. The deprotonation energy of a bridged hydroxyl was shown by semiempirical and *ab initio* calculations to be less than that of a terminal hydroxyl in silica and alumina [3]. Acidic properties exhibited by such structures may be considered to result from the OH group coordination by the neighboring electrophilic atom [1,4,5].

Zeolites often contain BAS of different acidic strength, that can be associated with a varying number of Al atoms in the second coordination sphere of the bridged hydroxyl group [3,6]. As a result, four main possible types of bridged hydroxyls can be specified in zeolites.

Usually the H-form of a zeolite is obtained via ammonium exchange. Calculations indicate that H^+ substitution for NH_4^+ is energetically preferential at sites with a higher concentration of Al atoms and show that the initial exchange stage yields the weakest BAS [7] in agreement with the experiment.

A number of different structures can be formed in zeolites by the interaction of chemically active bridged hydroxyl groups with some molecules and transition metal complexes. For example, alkoxide [8,9] and transition metal ionic forms can be mentioned [10]. Another interesting structure can be formed as a result of zeolite BAS interaction with a metal particle. The recent IR spectroscopy study of CO adsorption in mordenite [11] provides an evidence for the formation of stable electron deficient monoatomic Pt species. The proposition that this form can be assigned to Pt atom bonded to the proton of zeolite hydroxyl has been justified [12] by density functional calculation of the model cluster 1.

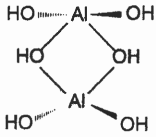


1.

The key role in the Broensted acid catalysis is played by the formation of protonated intermediates via chemisorption of reagent molecule on BAS. In liquids it is promoted by the additional solvation by polar molecules. In the case of the H-forms of zeolites, it was shown [1,13] that the surface basic centers (lattice oxygen ions) can serve as solvating agents during the NH_3 chemisorption providing a multi-centered (two or three) coordination of protonated NH_4^+ species.

The proton transfer in H-forms of zeolites may be considered as the most reliable path for the formation of electron deficient metal particles. The electron deficient state of the small Pd cluster in Pd/HNaY was deduced from the the IR spectroscopy study of adsorbed CO [14]. Density functional calculations of bare and protonated tetrahedral Pd_4 and octahedral Pd_6 clusters as well as their complexes with CO molecules [15] have justified such qualitative interpretation.

LEWIS ACID SITES (LAS). When considering the Lewis acid strength of transition aluminas and zeolites, it is common to differentiate between strong and medium LAS. These sites are assigned to three-coordinated (Al_{3C}^{3+}) and five-coordinated (Al_{5C}^{3+}) aluminium ions on the oxide surface, respectively. $Al(OH)_3$ and $Al(OH)_3(OH_2)_2$ are conventional cluster models for these sites [16-18]. The intrinsic design uncertainties of these cluster models have been analyzed in [19] using the density functional calculations of the Al_{3C}^{3+} and Al_{5C}^{3+}



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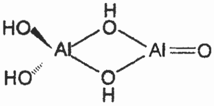


3.

interaction with a CO probe molecule. Comparison of calculated data with the results of experimental investigations gives the reason for a hypothesis on the existence of LAS in aluminas in the form of four-coordinated aluminium ions (Al_{4C}^{3+}) as well. Recently the density functional calculations of CO adsorption on Al_{4C}^{3+} sites have been performed using cluster model 2 [20]. The strength of these sites has been shown to be intermediate between Al_{3C}^{3+} and Al_{5C}^{3+}. Meanwhile, the cluster model 3 for LAS in zeolites has been considered. This type of LAS can be formed due to trapping of AlO^+ species by zeolite lattice. A similar suggestion has been made earlier for Ga/ZSM-5 [21].

ACTIVE SITES FOR METHANE ACTIVATION.

1. Selective oxidation of methane by dinitrogen monoxide on FeZSM-5 zeolites. FeZSM-5 zeolites exhibit extremely high catalytic activity in the selective oxidation of various compounds (alkanes, benzene, carbon monoxide) by dinitrogen monoxide [22]. These processes involve adsorption and decomposition of N_2O

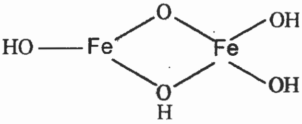
$$N_2O + Z \rightarrow N_2O...Z \qquad (1)$$

$$N_2O...Z \rightarrow N_2 + OZ \qquad (2)$$

where Z and OZ denote the active sites in FeZSM-5 and superactive oxidizing center, respectively. Methane, in particular, is converted to methanol with an almost 100% yield

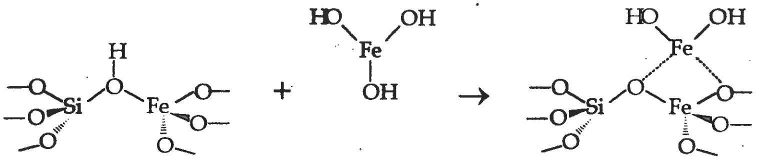
$$CH_4 + OZ \rightarrow CH_3OH...Z \qquad (3).$$

Knowledge of Z and OZ structure is the key for understanding this activity. The first molecular model of the Z center was suggested [23] in the form of the lowest-spin binuclear cluster 4. This structure was considered as a product of the partial dehydration of an extraframework Fe(III) hydroxide dimer. The formation of such extraframework compound was suggested by analogy with the formation of extraframework Al(III)-hydroxide dimers during dealumination of zeolites [7]. Another possible way of the similar dimer formation may be in the

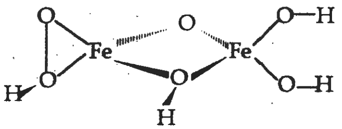


4.

chemical trapping of extraframework mononuclear iron species (e.g. $Fe(OH)_3$) by the lattice sites containing framework Fe(III) as it is shown in the scheme below.



Quantum chemical calculations (at the MP2 level) of stages (1) and (2) of the oxidizing center formation have given two possible stable structures of the OZ center [24]:



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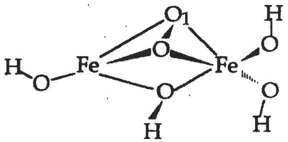

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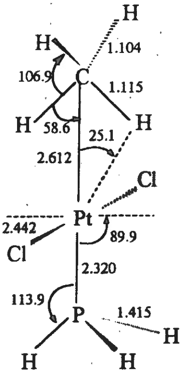
Oxygen O_1 in structure 6 was shown to be highly active in the activation of methane.

2. Oxidative addition of methane to Pt(II) and Os(II) complexes. The activity of $PtCl_2(PH_3)_2$ and $OsCl_2(PH_3)_2$ complexes in oxidative addition of CH_4 was studied using HF/MP2 technique. It was found that active state of the Pt(II) complex can be formed by elimination of one PH_3 ligand, what can occur in acid solution. The reaction path as well as the structure of the transition state (TS) and product (P) were calculated [25].



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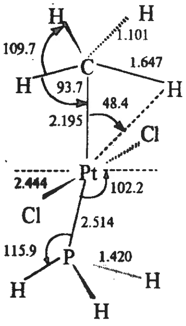
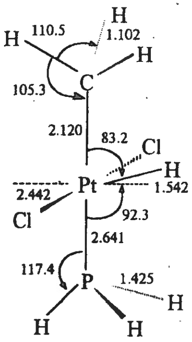


TS



P

Complex $Os(Cl)_2(PH_3)_2$ has a number of isomer structures having different activity in the oxidative addition of methane. In particular, the isomer with the tetrahedron structure is not active in this reaction whereas the isomer with the square pyramid structure shows very high activity in the oxidative addition of methane. If the electron correlation is taken into account the reaction heat and the energy of the transition state significantly decrease. The analysis of the reaction path and the transition state structure shows an important role of donor-acceptor ligands in the $Os(Cl)_2(PH_3)_2$ complex for synchronization of two processes: rupture of the C-H bond and formation of two Os-H and Os-(CH) bonds.

ACTIVE SITES OF Ni/MoS_2 HYDRODESULFURIZATION CATALYSTS.

Cluster $NiMo_2S_{10}H_{10}$ is suggested as a molecular model of active site of the Ni/MoS_2 catalyst. The electronic state of Ni atom in this complex can be considered as Ni(IV) state (d^6 configuration) with two d-orbitals, including d_{z2}, free for interaction with a sulfur-containing reagent (e.g. thiophene molecule). The higher activity of Ni(IV) compared to Ni(II) in activation of sulfur-containing compounds in the hydrodesulfurization reaction was demonstrated by the MP2 calculations of model complexes [26].

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IN SITU DYNAMIC STUDIES OF HETEROGENEOUS CATALYSIS

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A few years ago a small book, entitled "Catalysis Looks to the Future" was published by the National Academy Press. It was prepared by the Panel on New Directions in Catalytic Science and Technology, National Research Council. Almost all the top catalysis scientists in the U.S. participated in the preparation. In this book in the part of "research opportunities in catalytic science and technology" it is written as follows: "It is desirable to focus on areas in which the extensive scientific and technological resources of academy and industry may lead to the fastest practical results. In order of priority, these areas are:

1. in situ studies of catalytic reactions;
2. characterization of catalytic sites at atomic resolution (metals, oxides);
3. synthesis of new materials that might serve as catalysts or catalyst supports;
4. theoretical modeling linked to experimental verification."

Although the importance of "in situ studies" was pointed out, the ways how to study are not described in detail in the book. The catalyst surface during the course of reaction is, in general, covered by chemisorbed species, not only reactants and products, but also other species such as, for example, reaction intermediates and spectators, and the properties of the surface are, in most cases, markedly different from those of a clean surface under vacuum. It is, accordingly, of great importance to study the catalyst surface in its working state, and, in addition, the behavior of each of the chemisorbed species under the reaction conditions.

More than forty years ago I was studying the decomposition of germanium hydride on germanium surface in Princeton University in the laboratory of Sir Hugh Taylor. The reaction is zero order with respect to germanium hydride and, by using a catalyst with large surface area, I could estimate the amount of hydrogen chemisorbed on the catalyst surface during the reaction, which led to a conclusion that the rate determining step of the reaction is the desorption of hydrogen from the surface saturated with chemisorbed hydrogen. Various results by means of isotope tracer supported this conclusion. This catalytic system is the case in which adsorption was directly measured for the first time during the course of catalytic reaction.

Taking this opportunity, adsorption measurements during reaction were initiated. In my chapter in the Advances in Catalysis in 1964 I proposed what we call "isotope jump, or switch, method", which is a method to identify the reaction intermediates. Even if some adsorbed species are to be observed on the working catalyst surface, it does not follow that they are the reaction intermediates through which the overall reaction proceeds. According to the "isotope switch method", one of the reactants is replaced by its labeled species during the course of the reaction and then the behavior of each of the adsorbed species is observed. The labeled isotope may appear in one of the adsorbed species, then it goes to the next adsorbed species, and so on, finally coming into the reaction products. By measuring the rate of isotope transfer from one adsorbed species to another, we may not only find out the reaction path by following the behavior of the isotope tracer, but also estimate the rate of each of the steps in the reaction path. Under those circumstances, since just "in situ observation" without dynamic approach is far from enough, I purposely used the title "in situ dynamic studies". These dynamic approaches had been applied to various fundamental catalytic reactions, such as, for example, decomposition of ammonia, formic acid and methanol, H_2-D_2 exchange reaction, water gas shift reaction, hydrogenation of olefins and so forth by means of, in most cases, infrared spectroscopic techniques. In my talk recent results using laser Raman technique will be also presented in the catalytic system of, for instance, ozone decomposition on manganese oxide. In this case, the amount of chemisorbed species is in a dynamic equilibrium between chemisorption of reactant and desorption of the reaction product, just like in the case of ammonia decomposition on tungsten surface.

On the basis of such "in situ dynamic studies" new concepts in the field of heterogeneous catalysis had been obtained in recent years. One deals with "adsorption-assisted processes" and another with the way how "to identify the reaction sites on catalyst surfaces."

In the former subject, the results obtained by M. Kawai, Y. Iwasawa, X. Guo and their coworkers will be presented with introductory remarks of the works obtained in my laboratories. The rate of desorption of chemisorbed species used to be considered a function of its chemisorbed amount, being independent of the pressure of ambient chemisorbing gas. However, in the case of CO on transition metal surfaces, it was demonstrated that the rate of the desorption is markedly accelerated by the presence of ambient gas. It was, accordingly, demonstrated in some cases that the reactivity of chemisorbed species is influenced by the presence of ambient gases, which were called "adsorption-assisted processes".

As to the latter topics, recent observation of chemisorbed species by Tanaka and Sakurai by means of atomic resolution tunneling microscopy (STM) will be associated with the dynamic behavior of chemisorbed species, in particular, in the case of oxygen chemisorbed on silver and copper.

When oxygen is chemisorbed on Cu(110) surface at room temperature, (-Cu-O-) chains grow along the (001) direction, and the chains attract each other so that they coalesce to form islands. On the other hand, when oxygen is chemisorbed on Ag (110) surface at room temperature, one dimensional (-Ag-O-) chains grow along the (001) direction, but these chains repulse each other and the chains make the (n x 1) arrangement where the value of n changes sequentially from 7 to 2 as the amount of chemisorbed oxygen increases. In addition to such structure narrow out-of-phase domains with the wavering domain boundaries were observed. It is well known that silver is an essential catalyst for partial oxidation of ethene, which may be well correlated with such characteristic structure of chemisorbed oxygen on the silver surface. It is, accordingly, very interesting to study the behavior of the chemisorbed oxygen on copper and silver with different structure.

The kinetic behavior of the chemisorbed oxygen on copper and silver in the reduction with hydrogen was examined. A method to identify the reaction sites where the reaction takes place has been proposed, assuming that the reaction rate is proportional to the number of reaction sites on the catalyst surface. It is, accordingly, concluded that in the case of copper the reaction proceeds at the peripheral part of the chemisorbed oxygen islands with dissociatively adsorbed hydrogen, whereas, in the case of silver, molecular hydrogen attacks the linear chain of chemisorbed oxygen in the middle part of the chain, not at the end of chains. The reaction of hydrogen-oxygen mixture on these metals was also examined on the oxygen covered surfaces, what led to a conclusion that the reaction takes place between the chemisorbed oxygen and hydrogen gas.

In summary, the importance of "in situ dynamic studies of heterogeneous catalysis" has been emphasized, in particular, to elucidate the real nature of heterogeneous catalysis.

PL-5

VIBRATIONAL SPECTROSCOPIES IN CATALYSIS RESEARCH

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Vibrational spectroscopies, particularly Fourier transform infrared (FTIR) spectroscopy in transmission or diffuse reflectance (DRIFT), and laser Raman spectroscopy (LRS) are among the most versatile and flexible, non-destructive techniques for catalysis research. Both methods can be applied under in situ conditions over a wide range of temperatures and provide information on structures of the solid catalyst and of surface groups or compounds, on surface properties such as acidity and basicity when using appropriate probe molecules, and in favourable cases, on reaction intermediates. Several of the opportunities of vibrational spectroscopies in catalysis research will be discussed and demonstrated by selected examples.

A. Acidic and Basic Properties of Oxides

Surface hydroxyl groups can easily be detected by FTIR spectroscopy and their Brönsted acidity can be studied by their interaction with H-bonding probe molecules. CO and N_2 can be successfully applied for a ranking of the acid strength of OH-groups on several acidic solids. The same molecules can also coordinate to cus cation sites (Lewis acid sites), and a discrimination between Brönsted and Lewis acidity is possible. The use of H_2 as a molecular probe will also be discussed. The highly symmetric methane molecule is a promising probe since its adsorption structures can be elucidated relatively easily on the basis of symmetry considerations. It will be shown that methane may be used as a probe for surface basic sites. Other potential probe molecules for the characterization of basic materials such as halogenated methanes and unsubstituted and substituted acetylenes will also be discussed.

B. Multicomponent Oxidation Catalysts

The structures of multicomponent oxides that are frequently used as catalysts for selective oxidation can be studied by in situ Raman spectroscopy. For molybdate catalysts, this approach has elucidated the phase compositions of the catalytic materials under reaction conditions and isotope labelling experiments demonstrated the key role that is played by lattice oxygen.

It was shown recently that stoichiometric MoO_3 and Sb_2O_4 do not undergo oxygen exchange with gas phase $^{18}O_2$, while ^{18}O-incorporation into Sb_2O_3 was observed. Oxygen deficient MoO_{3-x} could be reoxidized with ^{18}O-incorporation. MoO_3 in physical contact with Sb_2O_3 was partially reduced with formation of Sb_2O_{4-x} and reoxidation led to ^{18}O-incorporation into the molybdenum oxide. These experiments emphasize the importance of oxygen vacancies for ^{18}O-incorporation from the gas phase in these oxide systems.

In situ laser Raman spectroscopy has been used to characterize peroxide species on catalysts for oxidative methane coupling, namely Na- and Sr-modified La_2O_3 and Ba/MgO. The presence of O_2^{2-}-ions on these catalyst surfaces has been proved by isotope labelling and their relevance for the activation of methane could be demonstrated by in situ Raman experiments on the working catalyst at temperatures up to 1070 K.

C. Supported Oxides

A technologically important class of catalysts or catalyst precursors are oxide overlayers supported on a second oxide. The structures of the surface oxides of many oxide combinations have been studied extensively by Raman spectroscopy. Sulfated zirconia as well as tungsten oxide supported on ZrO_2 and TiO_2 are presently discussed as strong solid acids (frequently claimed to develop superacidity). As an example, it will be demonstrated that the combined application of Raman and FTIR spectroscopy permits a detailed structure analysis of the surface groups (sulfate or tungstate), which can be complemented by studies of the acid properties using probe molecules. On the basis of such studies, one can attempt to establish structure - property relationships.

D. Supported Metal Catalysts

Supported metal catalysts and in particular, supported transition metal catalysts can be studied via the chemisorption of CO combined with FTIR. The surface chemistry of Rh/Al_2O_3 catalysts will be discussed briefly.

Silver catalysts are used for the epoxidation of ethylene and for the oxidation of methanol to formaldehyde. In situ surface-enhanced Raman spectroscopy (SERS) provided evidence for the formation of several surface, subsurface and bulk oxygen species and permitted to elucidate their respective role in the oxidation reactions.

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COMPUTER MODELLING AND CATALYSIS

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Computational techniques are having a growing impact on catalytic science owing to their unique ability to develop reliable models of complex materials and processes. In this lecture we will review recent progress in this field, concentrating on:

i) Modelling of complex structural problems, including crystal structures of microporous materials and oxide surfaces.

ii) Simulation of dynamic properties, including molecule docking and diffusion.

iii) Elucidation of reaction mechanisms in acid and partial oxidation catalysis.

We shall give strong emphasis to the use of modelling as a complementary tool to experimental investigation of catalytic systems.

NEW CATALYTIC TECHNOLOGIES IN JAPAN

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Recent trends in R & D of catalytic technology in Japan (cleaner and more efficient production, environmental catalysts and recycling processes) are overviewed first. Then, after some of recent achievements are listed, three remarkable examples, that is, hydration of cyclohexene, gas-phase Beckmann rearrangement of cyclohexanone oxime, and storage-reduction type 3-way automobile catalysts are described.

General Trends in R & D

The subject of this lecture given to me by late professor Zamaraev when he visited Japan in 1995 is very broad and large to cover satisfactorily. But I try to describe the general trends of catalytic R & D activities in Japan.

(1) Cleaner or more environmentally friendly production of materials and chemical energies is becoming more and more important as in other countries. Changes to solid acids from liquid acids, to catalytic oxidation from stoichiometric chemical oxidation etc. are keen issues with this respect.

(2) Catalytic process which make use of cheaper and more abundant raw materials in smaller number of reaction steps are always highly concerned. Recently, this is stressed particularly in the syntheses of fine chemicals.

(3) Productions of environmentally friendly materials and chemical energies (or clean fuels) as well as environmentally friendly disposal and recycling are the major targets of recent research. Although the economically acceptable recycling is very small in quantity at present, the importance of recycling will rapidly increase.

(4) Positive attempts to utilize new catalyst materials and to apply catalysts into a wide range of new applications are possibly good points of R & D in Japan.

(5) The examples of recent achievement in Japan are given in earlier reviews [1, 2], and also in

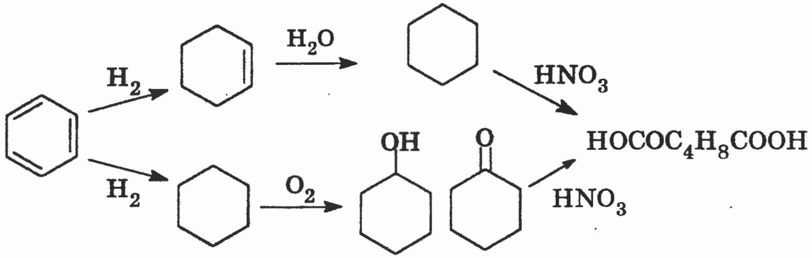
the recent articles [3]. Some from the latter are listed in Table 1 with a few additions. Three representative examples will be described below in more detail.

Table 1. New Processes and Catalysis

Process	*Comments (catalyst, etc.)*
Benzene to cyclohexanol	Partial hydrogenation (Ru cat.) and subsequent hydration (zeolite), 60,000 t/y (1990)
ε-Caprolactam from cyclohexanol oxime	Gas phase Beckmann rearrangement, silicalite, in the presence of alcohols (close to pilot)
DeNOx of lean-burn automobile exhausts	Storage-reduction type 3-way catalysts (1994)
Deep desulfurization of gas oil	Improved Mo-Co HDS catalysts (ca. 1994)
Aromatization of LPG or light naphtha	Metallosilicate, Z-forming (demonstration plant, 1990-1991)
Syndiotactic polystyrene	Metallocene, 5,000 t/y (1996)
cycloolefin copolymer	Metallocene, 4,000 t/y (1995)
MMA via methyl formate	New acetonecyanhydrin process, 41,000 t/y (1996)
γ-Butyrolactone from MAH	Ru-catalyst, 10,000 t/y (1997)
Acetic acid from ethylene	Pd + heteropolyacid, 100 kt/y (1997)
Aliphatic alcohols and amines	Utilization of vegetable oils
Phenol from toluene	Ni-Fe-Na oxide, Gas phase (pilot)
Pd-based automotive catalysts	Improved 3-way catalysts
Catalysts for living atmosphere	Many commercialized examples including photo catalytic self-cleaning tiles
Recycling of waste plastics	Several demonstration and pilot plants

Hydration of Cyclohexene in Slurry

Asahi chemical industrialized the production of cyclohexanol from benzene via partial hydrogenation and subsequent hydration. This new process is superior to the conventional two step oxidation process in several respects; selectivity, safety, corrosion, and energy-saving [4].



Here, the key points of the second step of the new process, hydration of cyclohexene, will be described.

A ZSM-5 type catalyst having a high Si/Al ratio and small particle size is used. High Si/Al provides hydrophobicity of pore wall to concentrate cyclohexene in the pore, and small pore to suppress the formation of bulky byproducts. Small particle size is essential for industrialization not only for releasing the diffusion problems but also for making the outer surface of particle hydrophilic. Due to this hydrophilicity of the outer surface, the catalyst powders of which the inside is hydrophobic become more stable in aqueous phase. This makes rapid the separation of oil and aqueous slurry phase in a settler and easy the following distillation of the oil phase to obtain cyclohexanol. If a liquid acid is used for the catalyst of hydration, cyclohexanol as well as cyclohexene is mainly distributed in aqueous acid phase and the distillation of this phase causes the reverse reaction, that is, dehydration back to cyclohexene.

The other important innovations in this process exist in the regeneration of catalyst. Wet oxidation with H_2O_2 successfully removes the organic deposits and the treatment in the controlled pH range returns the aluminum ion/back to the zeolite framework as revealed by the recovery of acid quantity. 60,000 ton/year of cyclohexanol has been produced by this process since 1990.

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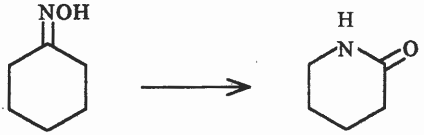
Gas-phase Beckmann Rearrangement of Cyclohexanone Oxime

There have been many attempts to replace the conventional process using fuming sulfuric acid with a gas-phase solid acid process. Sumitomo Chemical is about to succeed in this long desire by using a silicalite catalyst, which is almost non-acidic, in the presence of methanol in the feed [5].



A research group of Sumitomo Chemical found the rate and selectivity increased with a decrease in the acid amount or the Al/Si ratio. A constant selectivity of about 80% was obtained for Si/Al ratio greater than 1,000. The reaction appeared to proceed on the outer surface of particle as the rate increased with increasing outer surface area.

The group later made another important finding that the selectivity and life increased dramatically when alcohols such as methanol and ethanol were mixed into the feed; conversion > 99%, selectivity 92%. There is an optimum concentration of alcohol. Too high concentration of alcohol suppresses the rate, although the selectivity maintains a high level. The performance of this system is good enough to be considered for industrialization. Typical reaction conditions are: Si/Al = 147,000, 350°C, 1 atm, oxime/alcohol = 40, W/F =40 g-catmol^{-1}h^{-1}.

NOx Storage-Reduction Catalyst for Automotive Lean-Burn Engines

Abatement of dilute NOx in the exhaust gas from lean-burn and diesel engines are of great concern in advanced countries, since in spite of the application of the two established catalytic DeNOx technologies; NH_3-SCR and TWC, the NOx concentration still needs to be reduced. Reduction of NOx with hydrocarbons (HC-SCR) is a promising catalytic technology and much efforts have been devoted to it. However, there remain several serious problems to be solved.

Toyota group has recently succeeded (at least partly) in developing a new alternative catalytic system for the reduction of NO of automotive lean-burn engine. This engine is expected to save the gasoline consumption due to its higher fuel efficiency.

Three-way catalysts which contain basic oxide such as BaO in addition to precious metals and CeO_2 are used. Under oxidizing (lean) conditions, NO is oxidized by O_2 on the precious metal (PM) into NO_2, and then stored forming nitrate with the basic oxide. The nitrate is reduced to N_2 under reducing (or stoichiometric) conditions. The catalyst functions quite well by alternating between lean and stoichiometric operation.

$$NO \xrightarrow[PM]{O_2} NO_2 \xrightarrow[BaO]{} NO_3^- \qquad \text{(lean conditions)}$$

$$NO_3^- \xrightarrow[PM]{HC} NOx \xrightarrow[PM]{HC} N_2 \qquad \text{(stoichiometric conditions)}$$

High dispersion of basic oxide and its close contact with precious metal are very important, since these prevent the irreversible formation of sulfate and increase the durability. In case the particle size is very small, sulfate formed is relatively unstable and decomposes under reducing conditions. This reaction is probably catalyzed by precious metals. The performance at the initial stage is determined by the rate of storage, not by the subsequent reduction.

The fresh catalyst shows about 90% NO_X reduction on a vehicle test installed with a 1.8 l lean-burn engine (Japanese 10-15 mode with Japanese regular gasoline (S: 30 ppm)), and after durability test (corresponding to 100,000 km) more than 60% of NO_X is reduced.

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PL-9

STUDY OF OSCILLATING REACTIONS ON PLATINUM SURFACES ON AN ATOMIC LEVEL

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Introduction

In the late 1950s for the first time Prof. G.K. Boreskov stated a chemical approach to the kinetics of heterogeneous catalysis based on the effect of the reaction mixture and reaction conditions on the catalyst chemical composition and properties. The following principles were suggested: (i) steady state composition of the catalyst is dictated by the given reaction mixture and temperature; (ii) steady state composition of the catalyst and, hence, its properties vary with the composition of reaction mixture and temperature; (iii) effect of the reaction mixture on the properties of the catalyst is considered by incorporation of an additional factor in the rate constant [1]. A large body of research have shown that phenomena like hysteresis, metastability, kinetic oscillations, movable waves in the reactions of oxidative catalysis on metals are directly related to the effect of the reaction mixture on the catalyst. In heterogeneous catalysis the *kinetic oscillation phenomena* on platinum metals (Pt, Pd, Rh) in $CO+O_2$, $NO+H_2$, $NO+NH_3$ reactions have attracted considerable interest during a period of the last decade. In the oscillating regime the reaction mixture variously affects the properties of metals and can be accompanied by (i) surface phase transition {$CO+O_2$, Pt(100); 1x1 ↔ hex}; (ii) faceting of the surface {$CO+O_2$, Pt(210)}; (iii) formation of subsurface oxygen layer {$CO+O_2$, Pd(110)}; (iv) "explosive" nature of adsorbed particles interaction {NO+CO, Pt(100)} [2,3]. "Oxide" or "Carbon" models of kinetic oscillations become possible at high pressures of reactants [2].

In this work the mechanism of movable waves generation in oscillating $CO+O_2$, H_2+O_2 and $NO+H_2$ reactions was studied *in situ* on the Pt-tip 700 Å in radius by the Field Electron (resolution ~20 Å) and Field Ion Microscopies (resolution ~3-6 Å). Mobile reaction zone structure was analyzed by mass-to-charge resolved field-ion spectroscopy. A field ion microscope is simultaneously used as a catalytic flow reactor ($P_i \approx 5.10^{-4}$ mbar). The electric fields of ≈0,4 V/ Å in the FEM and of ≈ 1.5 V/ Å in the FIM appear to have a minor effect on the catalytic behavior of the platinum surface planes. The *nature* of reaction intermediates was studied by HREELS and TDS. On the basis of the data obtained, the kinetic oscillations and waves on the Pt(100) surface were simulated by the Monte-Carlo method.

Identification of intermediates

HREELS and TPRS methods were used to study the low-temperature O_2, H_2, NO, CO adsorption and $NO+H_2$, O_2+CO interaction on the Pt(100) surface. Coordination, thermal stability and reactivity of the adsorbed states of reactants were determined, reaction intermediates were identified. Hydrogen atoms are shown to be adsorbed on the *1×1* surface in bridge and 4-fold hollow sites. On the *hex* surface hydrogen adsorption induces a partial lifting of the *hex* reconstruction with the consequent appearance of the bridge and 4-fold hollow states on *1×1* patches. Additional adsorption states appear due to the population of structural defects and patches of the *hex* phase [4]. The 300 K reaction between 4-fold hollow H_{ads} and NO_{ads} in the mixed adsorption layer was studied by HREELS and TPRS on the unreconstructed Pt(100)-*1×1* surface. It has been found that the reaction results in the NH_{2ads} intermediate. Heating of the adsorption layer containing NH_{2ads} and H_{ads} leads to the ammonia evolution. NH_{2ads} intermediate was found to be N-coordinated to two platinum atoms, the molecular plane being normal to the metal surface.

The reactivity of molecular O^{2-}_{2ads} (peroxo) and atomic O_{ads} states towards CO was studied on the Pt(100) hex and 1x1 surfaces by HREELS and TDS. The reaction between the molecular state of oxygen {ν(OO) stretching band at 940 cm^{-1}} and on-top state of carbon monoxide {ν(CO) stretching band at 2100 cm^{-1}} proceeds under heating from T = 90 K up to 400 K. Reaction results in four peaks of CO_2-product evolution at 140, 190, 290 and 350 K. An atomic state of oxygen ("hot oxygen adatoms") with *extremely high* activity was found to be responsible for the lowest temperature desorption peak of CO_2 appeared at 140 K.

CO + O_2 reaction

The catalytic CO oxidation proceeds via a Langmuir-Hinshelwood mechanism:

1. $CO_{\text{газ}} + * <\!\!-\!\!-\!\!> CO_{\text{адс}}$
2. $O_{2\,\text{газ}} + 2\,* -\!\!-\!\!> 2\,O_{\text{адс}}$
3. $CO_{\text{адс}} + O_{\text{адс}} -\!\!-\!\!> CO_{2\,\text{газ}} + 2\,*$

For CO+O_2/Pt system, the experimental observations strongly suggest that the CO oxidation is a face-specific reaction; the kinetic oscillations are observed for (100), (110) and (210) but not for (111), (112) planes. Two spatially separated adlayers (O_{ads} and CO_{ads}) are formed on the Pt-tip surface under oscillating conditions [5]. The study with *atomic* lateral resolution of 3-6 Å has shown that the CO oxidation reaction is characterized by a sharp boundary between the movable waves of CO_{ads} and O_{ads} [6]. *A spatial profile of the reaction rate* was measured in detail using an *atomic probe method*. A reaction zone of 50 Å in width between CO_{ads} and O_{ads} layers has been found to exhibit the maximum productivity of CO_2. The initiating role of a reversible *phase transition* Pt(100)-*hex* ⇔ *1x1* was established for the generation of regular waves along certain crystallographic directions on the Pt-tip surface: (i) CO_{ads} wave follows the path in the direction (111) → (113) → (100); (ii) O_{ads} wave moves through (100) → (210) → (110) faces. The Pt(100) surface presented by *1x1* phase is catalytically active due to its ability to dissociate O_2 molecule; S_0 sticking probabilities are 0.3 and 10^{-3} for the 1x1 and hex phases, respectively.

Since the first discovery of correlation between reconstruction and kinetic oscillations in *CO* oxidation over *Pt*(100) by Ertl et al. [3] this surface has become one of the most extensively studied oscillatory systems in heterogeneous catalysis. The mechanism giving rise to oscillatory behaviour in the $CO+O_2$ reaction on a *Pt*(100) is attributed to a *hex* → (1×1) phase transition induced by adsorbed *CO*. The growth of (1×1)-*CO* islands on the extended *Pt*(100) plane has been recently studied by Hopkinson et al. [7]. It has been found that the rate of the *hex* →(1×1) transition strictly follows a nonlinear power law $\Theta_{1\times1} \sim (\Theta_{CO})^n$, with n ≈ 4.. This nonlinearity is also of key importance for the reported Monte Carlo model of oscillating $CO+O_2/Pt$(100) reaction. Our Monte Carlo simulations reproduce the synchronous variation of reaction rate, O_{ads} and CO_{ads} coverages and hex and 1×1 surface phases under conditions close to the experimental ones [8]. Self-oscillations of the reaction rate are accompanied by regular wave processes on the model platinum surface. The existence of the reaction *zone* between the moving adsorbate islands also has been shown.

NO+H_2 reaction

The 300 K NO+H_2 reaction on the Pt(100) hex surface reveals an autocatalitic behaviour. The reaction has been found to follow a Langmuir-Hinshelwood mechanism. The reaction results in N_2 and H_2O provided that the concentration of vacant adsites required for the NO and H_2 dissociation is high enough. On the Pt(111) surface NO molecule reacts with H_{ads} at 300 K to produce the HNO_{ads} intermediate. This is an example of the so-called "molecular catalysis". The rate determining step on the Pt(100) surface is an activated step of NO dissociation occurring at $T \geq 400$ K. N_{ads} atomic layer is highly active and readily reacts with hydrogen at 300 K, for example, on the Pt(111) surface giving rise to NH_{3ads}. The comparison of intermediate formed on different surfaces [HNO_{ads}/Pt(111), NH_{ads}/Pt(100)-hex, NH_{2ads}/Pt(100)-1x1] allows one to establish the features of molecular and dissociative mechanisms of catalysis in the NO+H_2 reaction.

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. $N_{ads} + N_{ads} \rightarrow N_{2gas}$

In the case of NO+H_2 reaction on the Pt-tip the oscillations were restricted only to {100} faces. The oscillations manifest themselves by regular changes in the electron emission intensity in FEM and appearance and disappearance of the surface waves in FIM.

H_2+O_2 reation

For H_2+O_2 /Pt system, the observed character of the H_2/O_2 oscillating reaction differs remarkably from that in CO oxidation: (i) product water molecules (H_2O^+/H_3O^+ ions) directly show the catalytically active sites; (ii) H_{ads} - and O_{ads}- fronts move in the reverse directions; (iii) hydrogen peroxy complex (HO...OH) is an intermediate in the H_2/O_2 reaction [9].

Conclusion

The regular waves appearance under the reaction rate oscillations is an amazing example of *a self-organization of catalytic reaction* when the size of active catalyst averages *some hundreds* Å. This result opens up new fields for the development of theoretical concepts of heterogeneous catalysis. It becomes possible to study the catalysis *on an atomic level* which is necessary for understanding of the mechanism of the action of high-dispersion supported metal catalysts having the metal microcrystallites 100-300 Å in size as an active part of the catalyst.

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CATALYSIS AND NONEQUILIBRIUM THERMODYNAMICS: MODERN IN SITU STUDIES AND NEW THEORETICAL APPROACHES

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Introduction

During the last two decades there were numerous brilliant break-throughs in understanding the detailed intrinsic mechanisms of the catalyst action in many model or practically important catalytic systems (see, e.g., recent reviews [1,2]). However, most of such studies were deeply mechanistic and restrict themselves with finding the most probable intermediates of the catalytic reactions as well as the relevant kinetic schemes of the surface reactions leading to the catalytic phenomena. For this reason, in spite of excellent results in a physico-chemical modeling the particular catalytic systems followed from the above considerations, these results could be typically applied to the very particular reactions only and thus, as a rule, made only a moderate promotion in a generalization of understanding the catalysis as a very specific but nevertheless general physico-chemical phenomenon.

Creation of the denoted general physico-chemical background of heterogeneous catalysis is known to be a field of very serious attention of G.K.Boreskov, thermodynamics being recognized by him as one of the most important whales of this background. A top issue of this recognition seems to be the well known and experimentally confirmed Boreskov's rule on an approximate constancy of the specific catalytic activity: "Upon the interaction of a catalyst with the reaction medium, the resulting stationary specific activity of the catalysts of the same chemical composition and at the same reaction conditions should be approximately equal, if only the catalyst maintains its phase composition" [3,4]. This rule is based namely on the thermodynamic considerations and results from nonevitable fitting the composition and thus the properties of the catalyst surface to external conditions regulated by the reaction medium.

However, there is a very serious obstacle for immediate implementation of conventional "equilibrium" thermodynamics for describing the state and behavior of **operating** catalysts since catalysis is principally a **nonequilibrium** phenomenon. A principal point of the nonequilibrium approach is that all the chemical transformations as well as other physico-chemical phenomena occurring with the catalyst in the course of its operation have to be considered as **being coupled with the main "coupling" reaction**. The latter is evidently the reaction to be catalyzed. Thus, the main driving force of all the chemical transformations of the catalyst that controls its state and, consequently, its catalytic properties, is the affinity of this latter coupling reaction.

In the last decade, a lot was done in order to approach nonequilibrium thermodynamics to consider the behavior of catalysts. The aim of this presentation is to summarize the current state of some ideas created in this area.

Recent in situ studies and nonequilibrium thermodynamics

Usually, a direct chemical kinetic approach is used to consider the state of the catalyst and the peculiarity of its behavior. Unfortunately, the direct chemical kinetics looks like a classic mechanics allowing to calculate a strict point of destination of a dynamic system if only strict starting conditions and concrete dynamic equations of the time evolution of the system are given. On the contrary, thermodynamics behaves here like statistical physics and gives a more suitable language for generalization of possible conclusions on the direction of the time evolution of complex chemical phenomena via elucidating the main **driving forces** of that evolution even in spite of only a little knowledge on the real mechanism of the process.

Note, however, that a direct application of the most elaborated **"linear" nonequilibrium (irreversible) thermodynamics** is unfortunately not possible for describing most of catalytic phenomena. Indeed, it deals only with the dynamic systems which are close to the thermodynamic equilibrium (for a reaction to be catalyzed this means that its current affinity A should be less than RT), while **typically the more realistic situation is that the system is far from the above equilibrium**.

In the last two decades, numerous in situ studies are accomplished over heterogeneous catalytic processes which gave, indeed, a lot of evidences of "nonlinear nonequilibrium" behavior of some catalysts during their operation. Among the phenomena typical for this "nonlinear" region of nonequilibrium thermodynamics is creation of the so-called "temporal dissipative structures" which are attributed to a **nonstable steady state** of the system and thus can be easily recognized due to their very specific behavior. For this reason the direct in situ studies of heterogeneous catalysts did evidence in the existence of namely these "nonlinear" phenomena like oscillations of the rate of catalytic reactions as well as chemical waves on the catalyst surface [2]. The both phenomena originate from a possible nonstability of the steady state of a catalyst.

On the contrary, till now much less is known on the "nonlinear" nonequilibrium phenomena related with the **stable steady state** of the catalyst. Note, that namely such phenomena lead, e.g., to a change in the catalyst phase equilibrium under the action of the reaction medium and thus are responsible for the validity of the Boreskov's rule.

Introducing the parameter of chemical potential in describing the state of operating catalysts

In this presentation we wish to draw an attention to few phenomena of general importance which can result from the nonequilibrium state of the operating catalyst being mostly in a stable steady state. As in any really thermodynamic considerations, the principal parameter here should be the **chemical potentials** of the catalyst and the reaction intermediates; note that we have to consider these parameters **under the operation conditions** rather than in an equilibrium.

According to our recent experience, the most suitable language for respective considerations could be a joint kinetico-thermodynamic analysis of chemical processes via a "thermodynamic form" of kinetic equations, which allows to discuss any chemical kinetic phenomena in terms of chemical potentials of the reagents involved [5]. According to this approach, the rate v of elementary chemical processes is expressed as a function of current chemical potentials $\mu_i = \sum_{\alpha} \nu_{i\alpha}\mu_\alpha$ of the "reaction group" "i" (a group of reagents involved into chemical transformations) rather than that of their concentrations. In the "thermodynamic" (or canonic) form, the overall rate v_{ij} of the reagents transition from reaction group "i" to reaction group "j" is expressed as

$$v_{ij} = \varepsilon_{ij}\left(\exp(\mu_i/RT) - \exp(\mu_j/RT)\right) \equiv \varepsilon_{ij}\left(\tilde{n}_i - \tilde{n}_j\right). \qquad (1)$$

A very important advantage of this approach is separation (in the parameters under use) of thermodynamic potentials of the "real" chemical structures like reagents or intermediates and of the transient states. Indeed it is easy to show that all the parameters of the reagents and intermediates appear to be accumulated inside the value of parameters $\tilde{n}_i$, while the parameter

$$\varepsilon_{ij} \equiv \frac{kT}{h}\exp\left(-\Delta G_{ij}^{\neq o}/RT\right)$$

appears to be a "reduced" rate constant depending, in contrast to conventional rate constants, on only the standard value $\Delta G_{ij}^{\neq o}$ of the respective transient state.

Application of joint kinetico-thermodynamic approach for analyzing both catalytic reactions and the nonequilibrium state of the catalysts

It is easy to show that for not very complicated catalytic reactions occurring in the steady state, the main driving force for the system evolution appears to be a difference in "thermodynamic rushes" $\tilde{n}_i \equiv \exp\left(\mu_i/RT\right)$ of the initial reaction group (or a reagent) and the final reaction group (or a product). This situation is principally advantageous for providing thermodynamic analysis since from the beginning it allows to analyze easily many systems **belonging to the "nonlinear" region of irreversible thermodynamics** and allows to operate not only in the neighborhood of the thermodynamic equilibrium, where $v_{ij} \sim A_{ij} \equiv \mu_i - \mu_j$.

The second simplification for our analysis should be a principal statement that for a stable stationary occurrence of a catalytic reaction, any reaction center of the catalyst could be considered as being in a steady state.

All the quite general conclusions discussed below are obtained for catalytic systems whose behavior is linear in respect to their active centra, i.e. for catalysts with a "single" active center. However, the validity of many of the presented conclusions can be extended to more complicated catalytic systems having stable steady state of the operating catalyst.

Some of the most interesting preliminary conclusions can be presented as follows:

(1) The steady state of catalysts with the noninteracting reaction centres under their operation is **stable** independently how complicated is the reaction to be catalyzed (it is assumed also that there is no coupling of these centres even through passing intermediates into the gas phase). It is of interest that for an arbitrary monomolecular (or reduced to such) path of dynamic evolution of the complexes "reagent-active center" this steady state refers to a minimum of an expression of the kind

$$\Phi \equiv \sum_{i,j}\varepsilon_{ij}\left(\frac{\tilde{n}_i}{\tilde{n}_K}-\frac{\tilde{n}_j}{\tilde{n}_K}\right)^2+\sum_i \varepsilon_{Ri}\left(\tilde{n}_R-\frac{\tilde{n}_i}{\tilde{n}_K}\right)^2+\sum_i \varepsilon_{iP}\left(\tilde{n}_P-\frac{\tilde{n}_i}{\tilde{n}_K}\right)^2.$$

Here the sum is made over the all possible intermediates "i", "j" of the catalytic transformations, while $\tilde{n}_R$, $\tilde{n}_P$, and $\tilde{n}_K$ stand for the "thermodynamic rushes" of the initial reagent, final product, and "free" (nonoccupied) state of the reaction center. The minimization should be made by varying the values $\tilde{n}_i$, $\tilde{n}_j$.

So, for any **"simple"** (i.e. undergoing only "monomolecular" transformations) **reagent complex** between the catalyst and the reagents, its dynamic evolution to the steady state of the catalyst is related with approaching of the catalyst to the state with a **minimum dissipation of energy** by the above complex.

This result corresponds well with the general statement of the main Prigogine's theorem on the direction of evolution of a system to the steady state [6] (being, nevertheless, much broader since our result is valid even for at least particular systems which are far from the thermodynamic equilibria).

(2) Since the equations of the type (1) are valid in a wide region of conditions including those far from equilibrium, it is easy to find that for many kinds of not very complicated catalytic systems, their stationary rate should obviously be proportional to the difference of "thermodynamic rushes" of initial reagents and final products. This gives directly the main Horiuti-Boreskov's rule [3,4] on the dependence of the stationary rate of most of catalytic processes on their deflection from thermodynamic equilibrium.

One can make a further generalization of the Horiuti-Boreskov's rule and show that in case of a set of parallel interacting catalytic reactions, their rates in the steady state should be expressed by the Onsager's types of equations. However, instead of affinities of the above reactions, which are considered to be the driving thermodynamic forces for the dynamic evolution of the system, in these equations one should use the respective differences of the "thermodynamic rushes".

In case of a vicinity of the catalytic system to the equilibrium, the stationary rate is evidently proportional to the affinity of the "coupling" reaction at any complexity of the catalytic scheme.

(3) The state of the catalyst substance at a steady occurrence of the process can differ significantly from conventional equilibrium states of the same substance, as it would be given by conventional equilibrium thermodynamics. For example, the catalyst substance can be in a **stable "metastable" state** (oversaturated, melt, etc.) or even create a "spacial dissipative structure". In some cases on the **"P-T diagrams"** one can foresee and experimentally observe a shift in positions of the "coexistence curves" for coexisting phases, etc.

An example of respective experimental in situ observations is melting of the active components of some metal (Fe, Ni, or Co) catalysts operating via formation of carbon-metal solutions. Such melting at extremely low temperatures has been observed in course of catalyzing of, e.g., a transformation "amorphous carbon → graphite" [7,8].

Copper-containing oxide catalysts for methanol synthesis and related processes give an evidence of reversible reconstruction of the catalyst under the action of the reaction medium via reversible migration of copper cations from the bulk of the oxide catalyst to the surface and their reduction to metal nanoparticles [9].

Quite recently we have observed a creation of a sort of spacial dissipative structures inside active components of metal cobalt catalysts carrying the reaction of CO disproportion [10].

(4) The notion of the current or steady "chemical potential" appears to be of a principal importance for analyzing the role of the reaction intermediates. Indeed, one of important but totally nonexpected conclusions is an **independence of the rate** of a catalytic reaction **on the standard thermodynamic characteristics of** these **intermediates** at low coverage of the catalyst. The reason of so "strange" behavior of catalysts is independence of chemical potentials of both intermediates and (at low coverage) of the "free" form of the active center on the same characteristics.

Indeed, in a steady state, the chemical potentials of all catalytic intermediates should drop stepwise to the direction of the final product and lie between those of the initial reagents and the final products. Thus, any chemical transformations of the intermediates occur namely from these energy levels. One can say that the intermediates are accumulating the Gibbs energy of the main reaction through increasing their stationary chemical potential (e.g., via an increase of their concentration) to the level controlled by the "reduced" rate constants ε_{ij} of the chemical reactions between the intermediates or, in other words, by the standard chemical potentials of the transient states only.

(5) From the above conclusion it follows immediately that the notion of the "transient state" in catalysis is much more sophisticated and broader than that in conventional "collisional" chemical kinetics. For example, in catalysis it may include a large set of intermediates allowing a complicated "monomolecular" dynamic evolution of the complex "reagent-active center".

The above extension of the notion "transient state" seems to be able to resolve some problems in receiving a quantitative, rather than a qualitative difference in traditional definition of "stepwise" and "coupled" mechanisms of catalysis as well as in an assumed necessity of different type of synchronizations in time evolution of the reaction complex.

(6) It is curious that till now there were only few discussions on a possibility **to change the selectivity** or even **the direction** of the catalytic "by-processes" in case when the "main" and "by-" reactions have the same catalytic intermediate. This possibility follows directly from analyzing the current stationary values of chemical potentials of the catalytic intermediates as well as the reagents, the products and byproducts of the overall catalytic reactions. Evidently, the mentioned phenomena have a "threshold" nature in respect to the concentration of the byproduct.

An evident particular importance of this conclusion is possibility to derive more correct, than simple "equilibrium thermodynamic", conditions for, e.g., protecting catalysts from coking as well involving methane molecules into direct reactions with larger hydrocarbons, etc.

Note also, that the above conclusions need a more accurate and sophisticated statement than the well known simple claim that "a catalyst is not able to disturb the thermodynamic equilibrium".

(7) An important remark is that in many cases the reversible dynamic evolution of the system to the real steady state of the catalyst accompanied by reversible reconstruction of the catalyst seems to follow in achieving the **minimum possible rate** of stationary catalysis at the given conditions. The "fresh" forms of the catalyst, which are achieving the thermodynamic equilibrium at both given temperatures and the **nonreacting** medium, are obviously more catalytically active than those resulted from the complete steady state. The reversible "self-inhibition" of the catalyst follows from the demand of the nonequilibrium thermodynamics to minimize the rate of the entropy production in the real steady state. The validity of this demand for many catalytic systems is easily demonstrated via analyzing the simple particular schemes of the reactions with participation of the catalysts capable of reversible phase transitions.

(8) The correct thermodynamic criteria can be easily obtained for the notion "kinetic irreversibility" of the steps in the catalytic reactions. These criteria demand, e.g., that for kinetic irreversibility of a stage in a consecutive chain of the catalytic transformations there should be a fall in the values of the stationary chemical potentials of the respective consecutive intermediates by more than RT value. Thus, the maximum number of the kinetically irreversible steps in this chain can not exceed the ratio of the total reaction affinity and RT.

Conclusion

The above discussion evidences that the role of thermodynamics in creating the physico-chemical background of heterogeneous catalysis is much more numerous and interesting than a "simple" Boreskov's rule or the statement on nonchanging the thermodynamic equilibra by catalysts.

To date, many of possible thermodynamic peculiarities of the nonequilibrium steady state, both stable and nonstable, of catalysts have been already observed via direct experimental in situ studies.

It is seen also how important for the occurrence of catalytic processes are the values of ε_{ij} (that is the properties of the transient states) between different catalytic intermediates which determine in fact the stationary values of the chemical potentials of the catalytic intermediates. One should expect that a systematization and analysis of possible transient complexes appear to be the main tool for further advances in a general theory of catalysts.

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NMR STUDIES OF SUPPORTED METAL CATALYSTS

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I. INTRODUCTION

Metal catalysts are widely used in the chemical and petroleum industries for the manufacture of products of great interest to everyone. Examples range from the classical iron catalyst which has been used for ammonia synthesis (1) to the more recent platinum-iridium and platinum-rhenium catalysts employed for the production of aromatic hydrocarbons for gasoline (2).

In addition to the chemisorption methods for obtaining information on metal dispersion (3,4), many physical techniques have been used to characterize supported metal catalyts : high resolution electron microscopy (5,6). Mössbauer spectroscopy (7,8), X-ray absorption spectroscopy EXAF (9-11), without forgetting much earlier applications of IR spectroscopy to the study of adsorption on these catalysts, which was also a source of considerable progress in this field (12,13).

Before the arrival of FT-NMR spectroscopy it was impossible, for reasons of sensitivity, to detect nuclei other than hydrogen, in particular metal nuclei, at the surface of clusters. Moreover, few metals lend themselves to NMR. For this reason Fraissard *et al* (14,15) proposed H-NMR to study hydrogen chemisorbed on metal as a probe. Since then technical progress has enabled Slichter and his group to carry out very original and interesting experiments on supported platinum and on molecules chemisorbed thereon (16). Finally ^{129}Xe-NMR of adsorbed xenon can be used to study the distribution of very small particles (a few atoms) difficult to detect by electron microscopy (17).

We summarize these various possibilities for investigating supported metals and chemisorbed phases.

II. ^{195}Pt-NMR STUDIES OF PLATINUM CATALYSTS.

II-1 GENERALITIES. KNIGHT SHIFT.

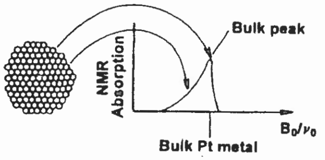
Platinum possesses desirable properties for the study of metal particles: the ^{195}Pt nucleus has sufficient natural isotopic abundance (33.7%), reasonably strong gyromagnetic ratio γ (9 MHz in 10 kG), and most important a spin I of 1/2 which eliminates the complexity of structure on the NMR line shape arising from electric quadrupole moment.

The NMR frequency ν_0 of a nuclear spin in a fixed external magnetic field B_0 varies for diamagnetic compounds, obeying a law for substance i:

$$2\pi\nu_0 = \gamma(1+\sigma_i)B_0 \qquad [1]$$

where $B_0/2\pi$ is the NMR frequency of a "bare" nucleus and σ_i is called the chemical shift. σ_i has its origin in magnetic fields produced at the nucleus by currents induced in the surrounding electrons by application of B_0. It is associated with the electron orbital motion induced by B_0. In metals, the conduction-electrons spins are polarised by B_0, giving rise to an additional shift in ν_0 called the Knight shift, which also obeys the previous relation [1]. In a metal σ_i is the sum of chemical shift and Knight shift. Usually, for a given nucleus, Knight shift is much greater in magnitude than chemical shift (18,19). For platinum, H_2PtH_6 is the reference compound most commonly used (19,20). Bulk Pt metal exhibits a large negative Knight shift (σ_i = - 3,4 %), which offers the possibility of resolving the Knight shift of atoms of surface layers (σ_i < 1.0 %) from that of atoms in the bulk.

(a) Clean particle



(b) Coated particle

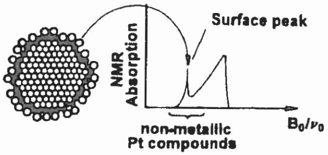


Figure 1. General form of line shapes expected for a sample of small Pt particles which are a: clean; and b: coated with adsorbed molecules.

○ Adsorbed molecule

● Surface Pt Atom

○ Pt atom

Consider a small particle of Pt atoms (Fig. 1). We would expect the Pt nuclei in the particle interior, far from any surface, to find themselves in an environment like that of a bulk Pt metal. On the other hand, Pt nuclei near the surface would certainly be in an environment different from that of a bulk Pt metal (since they lack neighbors on one side) and consequently exhibit different Knight shifts. Finally, atoms which are in interior layers near the surface would be expected to have shifts between those of bulk Pt and those on the surface (21). It should be pointed out that the chemical shift of surface atoms must depend on the nature of the adsorbed molecules.

II-2 EXPERIMENTS: SPIN-ECHO TECHNIQUE

Because of the large inhomogeneous broadening in these samples, free induction decay cannot be observed. Consequently Slichter *et al.* employed the spin-echo technique which essentially removes the effect of inhomogeneous broadening by refocusing the nuclear magnetization into an echo (18). The NMR lines are very broad. That is why the line shape has been obtained point by point, by measuring the area of the spin echo at different values of B_0, holding ν_0 fixed.

The dispersion of the Pt/γ-Al_2O_3 samples is given in table 1.

Table 1

Untreated SAMPLES	%DISPERSION, D, MEASURED BY			d(Å)
	Chemisorption	Electron Microscopy	NMR	(EM)
Pt-4-R	4		5	
Pt-11-R	11		8	
Pt-15-R	15	16	10	39
Pt-26-R	26	22	19	27
Pt-46-R	46	61	40	9
Pt-58-R	58		79	

II-3 RESULTS.

Figure 2 shows the line shape of untreated samples at 77 K. The curves have been normalized to have the same area since the samples contain equal numbers of nuclei. It is immediately obvious that the line shape is strongly dependent on particle size (21).

For the catalyst with low platinum dispersion (4-11%) there is a pronounced peak at B_0/ν_0 = 1. 138 kG/MHz, which is characteristic of the atoms in the deep interior of the platinum crystallites. The small peak at B_0/ν_0 = 1. 089 kG/MHz is identified with surface platinum atoms covered by chemisorbed species. The surface platinum atoms are therefore not metallic and do not exhibit a Knight shift. The intensity of this peak increases at the expenses of the previous one when the dispersion increases (fig. 2). The broad structureless region of the NMR line between the bulk and surface peaks is attributed to platinum nuclei near the surface, the environments of which are sufficiently different to produce a range of Knight shifts.

In general there is a fair agreement between the dispersion D obtained from the NMR data and from hydrogen chemisorption (Table 1).

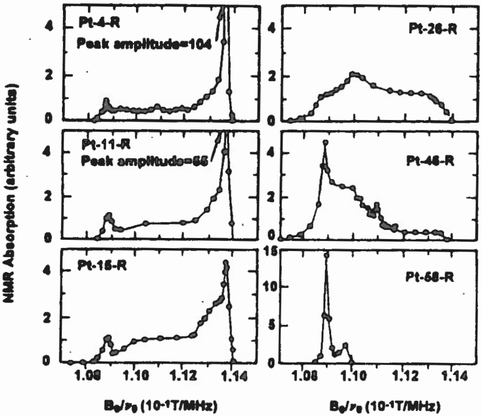


Figure 2. NMR absorption versus B_0/n_0 for untreated samples. Influence of the dispersion. Value of x in Pt-x is dispersion (in %). All samples were exposed to air before NMR measurement.

In order to prove that the resonance peak at 1. 089 kG/MHz arises from the surface layer of Pt atoms, the effect of some chemical treatments of the surface of Pt-46 has been tested (21,22): cleaning the sample, subsequent exposure to air, cleaned and then exposed to hydrogen.

These previous results show that the ^{195}Pt resonance of various coated samples occurs mainly in the vicinity of the ^{195}Pt resonance in diamagnetic compounds, but the surface NMR is not resolved from a near-lying peak due to the NMR of deeper layers. Using *spin-echo double resonance* (SEDOR) between ^{13}C and ^{195}Pt in samples of highly dispersed platinum catalysts covered with a layer of chemisorbed ^{13}CO, Makowka *et al* have completely resolved the NMR of surface ^{195}Pt (23).

III. ^{13}C-NMR OF MOLECULES ABSORBED ON METALS

We will report some applications of NMR to study the bonding of simple molecules (CO, small hydrocarbon molecules) to a metallic surface.

IV. ^{1}H-NMR STUDY OF HYDROGEN CHEMISORBED ON METALS - APPLICATION TO THE DISPERSION

NMR study of supported metals involves considerable theoretical and technical problems. In addition, it cannot be generalized to all metals used in catalysis. So the idea of studying metal surface by NMR using a gas, such as hydrogen, which could be chemisorbed by all metals and therefore be used as a universal probe. Hydrogen has also the advantage of being very sensitive to NMR detection and one of the gases most used in catalysis (14,15,24-27).

IV-1 HYDROGEN CHEMISORBED ON PLATINUM

After adsorption of a very small amount of hydrogen on the activated sample the NMR spectrum consists of 2 lines : one, a̲ , ($\delta_a \sim 0$) due to the OH groups of the support, and a second , b̲ , very much upfield shifted (δ_b negative) , which is characteristic of H_2 chemisorbed on Pt (26). When the number, N, of H_2 molecules/g increases, line b̲ grows but its chemical shift, δ_b, remains about the same up to a coverage, θ_H of the order of 0.45- 0.55 (depending on the techniques used for the determination of the monolayer) if the sample is monodispersed, that is if the particle size is homogeneous (segment AB, figure 3). Beyond this latter value, δ_b varies linearly with θ_H (segment BC, figure 3).

The Knight shift δ_b depends on θ_H but, for a given value of this latter, it also depends on the particle diameter, d, and on the chemisorption temperature. We will discuss the influence of these parameters on δ_b.

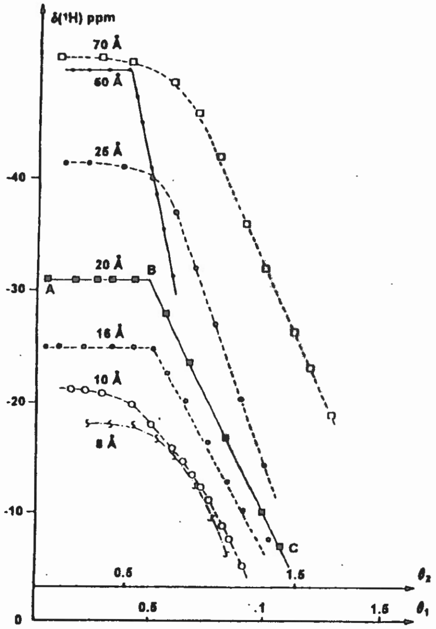


Figure 3. The ^{1}H chemical shift, σ (ppm), of hydrogen adsorbed on Pt at 26°C versus the hydrogen coverage. Influence of the particle size, q_1 refers to the total hydrogen adsorption; θ_2 refers to the chemisorption component. Reference TMS.

IV-2 HYDROGEN SORPTION ON PALLADIUM

The ^{1}H-NMR of hydrogen sorbed on supported palladium gives very different results which make it possible to identify several species in the presence of the metal: sorbed hydrogen, H_S, and hydrogen in α- and β-hydrides (28) (H_α and H_β, respectively).

The ^{1}H-NMR spectra of the Pd-H system show

- a signal S_1, with negative shift for low hydrogen concentration, due to rapid exchange between chemisorbed hydrogen H_S and the H_α hydrogen of the Pd-H_α hydride. At 26°C $\delta_1 = f(N)$ plot becomes horizontal for $\theta = 1$ and the maximum concentration of Pd-H_α (Pd-H_α = 0.035).

- a signal S_2, downfield, for hydrogen concentrations corresponding to a coverage greater than unity, due to Pd-H_β hydride in equilibrium with H_S.

In addition

- the $\delta_1 = f(\theta)$ plots are independent of the dispersion. The continuous variation of δ_1 with θ proves that the H_α and H_S concentrations increase homogeneously throughout all the particles.

- H_S concentration controls the formation of the Pd-H_α and Pd-H_β phases.

- The equilibrium $H_\alpha \Leftrightarrow H_S$ is displaced in the forward direction when the temperature is raised.

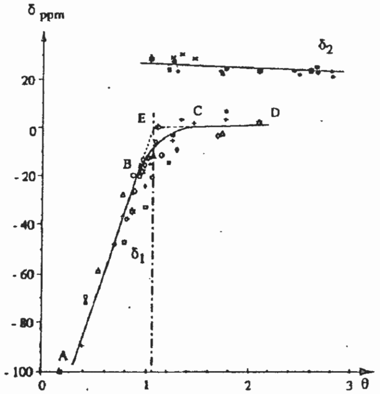


Figure 4. Palladium supported on NaY zeolite at 26°C. ^{1}H-NMR chemical shift dependence on the hydrogen coverage (θ). (θ is determined by chemisorption). D is the palladium dispersion. Reference TMS.

	δ1	δ2
1-D = 0,0492	☆	★
2-D = 0,145	◇	◆
5-D = 0,195	+	+
6-D = 0,24	o	●
7-D = 0,247	□	■
8-D = 0,5	△	▲

V. ^{129}Xe-NMR OF ADSORBED XENON FOR STUDYING THE DISPERSION OF METAL AND CHEMISORBED PHASE.

The chemical shift of physisorbed xenon, used as a probe, is the sum of terms corresponding to various perturbations to which it is subjected (29-30). In this case (31,32):

$$\delta = \delta_{ref} + \delta_S + \delta_{Xe} + \Sigma_i\delta_i \qquad [2]$$

δ_{ref} is the chemical shift of gaseous xenon extrapolated to zero pressure and used as a reference. δ_S corresponds to the chemical shift of xenon adsorbed on the support, extrapolated to zero concentration. δ_{Xe} expresses the influence of Xe-Xe interactions. δ_i corresponds to solid particles located on the support with chemically different surfaces S_i. The index i̲ denotes a particle type of population n, amongst the existing p types ($0 < i < p$).
Corresponding to each of these populations there is a shift δ_i characteristic of the Xe-S_i interaction, which is a product of two terms :

$$\delta_1 = \Big[\text{term for chemical nature of } S_i\Big] \times \Big[\text{term for frequency of Xe-}S_i\text{ collisions}\Big] \quad [3]$$

The spectrum depends on the lifetime of Xe on each adsorption site. Generally xenon has a very short lifetime at each adsorption site and can, moreover, diffuse rapidly on the solid surface. Then the spectrum consists of only one component whose position depends on the values of δ_i, each weighted by the probability α_i of Xe-S_i collisions. It is of course very difficult to get much information about this system from this single line. Fortunately the spectrum depends also on the distribution of different particles i, j... inside the sample.

In the case of supported metals, these different chemical surfaces S_i correspond to particles, M-iG, with a number i̲ of chemisorbed atoms or molecules of a gas G. For each number i̲ there is therefore a corresponding term $\delta_i = \delta_{M+iG}$ characteristic of the interaction between Xe and the particles M + iG.

The form of the spectrum of xenon adsorbed on such sample will depend on the Xe-(M + iG) interaction, on the numbers i, j... of atoms or molecules of G chemisorbed on various particles, and on the distribution of M + iG, M + jG... particles within the whole sample. We will give some examples of chemisorption on Pt-Y zeolite.

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BIOMIMETIC CATALYSIS

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Investigation of the structure of enzymes and development of the theory of catalysis allows to make sufficiently definite conclusions about the mechanism of catalytic processes.

Formulation of principally new mechanisms unknown in chemistry helps to use them to create new artificial catalysts.

Evolution of natural catalysts gives rise to optimal concerted mechanism with not only effective nucleophilic and electrophilic coaction but also reductive (or oxidative) coaction for catalytic redox processes. Modern methods of molecular design (molecular engineering) allow to increase the rate and selectivity following the principles of enzymatic catalysis.

PL-13

ADSORBED ALKYLCARBENIUM AND ALKYLCARBONIUM IONS AS TRANSITION STATES IN HETEROGENEOUS ACID CATALYZED TRANSFORMATIONS OF OLEFINS AND PARAFFINS

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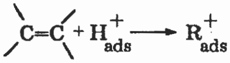
It is generally accepted that the role of active intermediates in heterogeneous acid-catalyzed transformations of hydrocarbons on zeolites and other solid acids is played by adsorbed alkylcarbenium and alkylcarbonium ions. For instance, it is believed that the catalytic transformations of olefins involve adsorbed carbenium ions, which are formed by proton addition to the double bonds:



$$>C=C< + H^{+}_{ads} \longrightarrow R^{+}_{ads} \qquad (1)$$

The consequent reactions of these species well explain the selectivity and composition of the final products of corresponding reactions.

In a similar way, the direct protonation of paraffins results in formation of adsorbed carbonium ions [1], which are then involved in reactions of protolytic cracking and dehydrogenation:

$$\begin{array}{l} RH + H^{+}{}_{ads} \rightarrow RH_2{}^{+}{}_{ads} \rightarrow R_1H + R_2{}^{+}{}_{ads} \\ RH + H^{+}{}_{ads} \rightarrow RH_2{}^{+}{}_{ads} \rightarrow R^{+}{}_{ads} + H_2 \end{array} \qquad (2)$$

These active species also well explain the composition of the final products of catalytic cracking of paraffins.

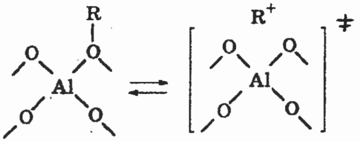
Until recently it was also generally accepted that both adsorbed carbenium and carbonium ions are the real short lived intermediates with the chemical properties similar to those of free carbocations. Therefore, when discussing the reaction mechanisms, the interaction of these species with the surface of the catalysts was neglected.

The account of chemisorption of carbocationic species on the surface of solid acids and discussion of the real nature of the resulting adsorption bonds of alkyl fragments with the surface was possible only recently due do development of modern "ab initio" quantum chemical computation facilities. Another important source of information about the nature of interaction of adsorbed carbocations with the surface is presented by IR spectroscopy and high resolution MAS ^{13}C NMR. The application of both these techniques allowed the study of proton transfer from the surface acid sites to adsorbed olefins or paraffins and presents a direct information about the nature of the resulting adsorbed active intermediates. These experimental results will be discussed below in parallel with conclusions drawn from quantum chemical calculations.

Both the spectral data and the theory indicated that the addition of surface protons to the double bonds of adsorbed olefins results instead of ion pairs in the covalent alkoxy groups. This follows from the analysis of the nature of chemisorption bond of resulting species with the surface oxygen performed by the electronegativity equalization method by Pearson [2,3], and was also confirmed by the "ab initio" quantum chemical calculations in [4-6]. This conclusion is also in agreement with numerous ^{13}C MAS NMR data, which never indicated formation of adsorbed carbenium from protonation of adsorbed olefins or alcohols [7-11].

Indeed, the alkylcarbenium ions are a relatively strong Lewis acids, whereas the surface oxygen ions of zeolites or some other solid acids should be considered as Lewis bases. Therefore, even if formed, the alkyl carbenium ions should rapidly convert into surface alkoxy groups, which are covalently bonded to the surface oxygen ions similar to the alkyl groups in oxonium ions in solutions.

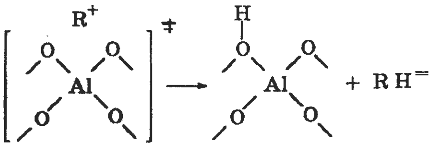
The quantum chemical calculations also indicated that the surface alkoxy groups could be considered as precursors of the carbenium ion-like transition states, resulting from vibrational thermal excitation or from stretching of carbon-oxygen chemisorption bonds:



(3)

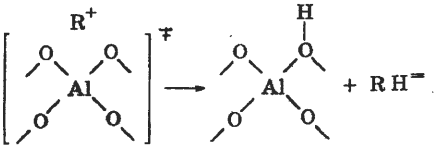
According to these calculations, the additional energy, which is required to form such transition states, is the lower, the more branched are the alkyl fragments or the higher is the acid strength of the surface hydroxyl groups from which these fragments were formed.

Such carbenium ion-like transition states can be involved in desorption of olefins from the surface:



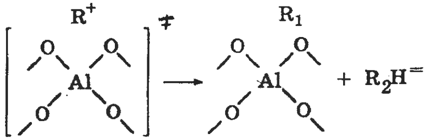
(4)

In the reaction of the double bond shift:



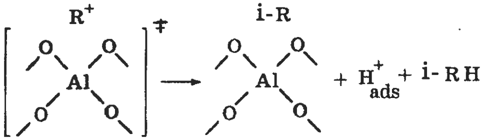
(5)

In cracking of olefins:



(6)

Or in skeletal isomerization of alkyl groups:



(7)

The calculated activation energies of these reactions are in a reasonable agreement with the corresponding values estimated from the study of the kinetics.

In a similar way, the quantum chemical calculations indicated that the adsorbed carbonium ions also are not the real reaction intermediates but the carbenium ion-like transition states [12,13]. This is quite natural, since the proton affinity of paraffins is considerably lower than for olefins. Therefore, the proton addition to paraffins (the formation of the adsorbed carbonium ions) is energetically much less favorable than for olefins. For instance, our "ab initio" calculations indicated that the proton transfer from the bridging hydroxyl groups of the high silica zeolites to isobutane requires an additional energy of about 40-50 kcal/mol. The geometry and the charge distribution in the resulting carbonium ion-like transition states really resemble those in free carbonium ions. However, these species are strongly bonded to the surface by the coulomb interaction with the surface oxygen anions. Therefore, the chemical properties of alkyl fragments in such energetically excited transition states are considerably different from those of free carbonium ions in the gas phase or from the reactivity of the weakly solvated carbonium ions in the solutions of super acids. Nevertheless, the quantum chemical calculations resulted in a reasonable estimation of activation energies of the reactions with participation of these species.

Thus, the obtained results indicated that the traditional discussion of the reaction mechanisms of heterogeneous acid catalyzed transformations of hydrocarbons via formation of quasi-free carbocationic intermediates is certainly a very rough simplification. In contrast, the adequate description of the carbenium-ion reaction mechanisms requires the account of adsorption, which strongly modifies the nature and the reactivity of carboanionic species.

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PL-14

THE GROWTH, STRUCTURE AND SURFACE CHEMISTRY OF OXIDE FILMS AS MODEL CATALYSTS

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ABSTRACT

"...the best long-range strategy (in all fields of catalysis research) is twofold: to carry out research for the discovery of new, advanced catalysts and catalytic materials, and to focus fundamental research on the elucidation of catalytic sites and catalytic reaction mechanisms at the atomic/molecular level" [Advanced Heterogeneous Catalysts for Energy Applications, G. A. Mills, *et al.*, DOE/ER-30201-H1, April 1994]. The present paper will describe recent results from our relatively new program to perform detailed studies of the catalytic properties of metal-oxide materials; in particular, to effect a determination of the active catalytic site(s) and the mechanism for reactions over this especially important class of heterogeneous catalysts. Issues of structure-sensitivity, poisoning and promotion, and competing reaction mechanisms are critical questions that need to be addressed in a detailed manner for catalysis by oxides. As just one important example, both surface (Langmuir-Hinshelwood) and direct (Eley-Rideal) reaction mechanisms have been proposed for the Selective Catalytic Reduction (SCR) reaction of nitrogen oxides (NO_X) over vanadia/titania catalysts. For this program we are using a number of unique, state-of-the-art capabilities available in the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory; for example, the first molecular beam epitaxy (MBE) system dedicated to the growth of model metal-oxide films, and a unique high-pressure catalytic reactor/surface science apparatus.. The research in the EMSL is specifically focused on DOE needs to cleanup and restore a large number of contaminated sites that are a legacy of 50 years of nuclear weapons production. It can be expected that catalytic processes will play a major role in the cleanup of DOE sites, and that oxide-catalyzed reactions are likely to be particularly important. Therefore, we have initiated EMSL research programs that are performing molecular-level studies of oxide-catalyzed reactions and we describe some of these in this paper.

I. INTRODUCTION

I.1. Catalysis by Oxides:

The critical role that catalysis plays in two of the largest US industrial segments, chemicals and petroleum processing, has been discussed at length in recent reports from the National Research Council [1] and the Department of Energy [2]. In these and other industries, catalytic processes are used as lower-cost, more energy efficient and/or pollution control technologies. Of these processes, a significant number are of particular interest to the missions of the Department of Energy (DOE), specifically with reference to energy production and efficient use, as well as the prevention or remediation of environmental insults. For the purposes of the present paper, three specific examples can be cited. Important examples in the environmental remediation area are the control of NO_X emissions derived from the processing of hazardous wastes from storage tanks at the Hanford site near Richland, Washington and elsewhere, and the problems of large quantities of chlorinated hydrocarbons in storage tank wastes and in contaminated soils and groundwater at a number of DOE sites around the country. Efficient processing of petroleum for fuels and other chemical feedstocks is of obvious relevance to the DOE's energy missions. These three examples are briefly elaborated on next with particular emphasis on the problem of NO_X emissions.

I.1.A. Gaseous emissions of NO_X from tank waste processing: Nitrogen oxides, NO_X (NO and NO_2), are some of the most common and most dangerous pollutants of the atmosphere. Stringent regulations have been and continue to be legislated to control these pollutants from stationary (*e.g.*, power plant) and mobile (*e.g.*, automobile) sources. Because of this situation, the need for stepped-up research efforts at both the fundamental and applied levels, with a goal to develop improved NO_X emission treatment technologies, has been emphasized in a number of places recently [1-4]. Gaseous NO_X emissions are of particular concern to the Office of the Assistant Secretary for Environmental Restoration and Waste Management (OEM) of the DOE in general, and the Hanford site in particular, because of the presence of large quantities of nitrite and nitrate anions in mixed wastes stored in underground tanks, as well as those discharged directly to the soils [5-6]. Treatment of these wastes will most likely involve the generation of gaseous NO_X emissions that will have to be secondarily treated to prevent their release to the atmosphere. Of additional concern to DOE and Hanford is the proposed utilization of a number of high-temperature processes for conversion and/or stabilization of much of the underground storage tank wastes, with high-level waste vitrification being just one example. Such processes have the potential to *generate* significant amounts of NO_X emissions by well-understood high temperature combustion reactions involving atmospheric nitrogen and oxygen [3]. These 'secondary' NO_X emissions will also need to be controlled. Presently, compliance with clean air standards is often accomplished by catalytically altering the exhaust emissions. It is quite clear, however, that the current catalyst technologies are insufficient for meeting future regulatory requirements [2,4].

The technologies for treating NO_X emissions are quite different for the two cases of mobile and stationary sources. In an automobile, NO_X is reduced by CO and/or unburned hydrocarbons over a three-way catalyst consisting of the precious metals Pt, Pd and/or Rh [4]. In contrast to the automotive (mobile source) case, NO_X emission control from stationary sources such as power plants is typically accomplished by selective catalytic reduction (SCR) with NH_3 over tungstate/titania or vanadia/titania catalysts [3]. However, a recent DOE study [2] specifically emphasized that "research is needed to understand better the fundamental nature of active sites and reaction pathways [of SCR] in order to make improvements in this developed technology". This is due, in part, to the fact that the standards regulating NO_X emissions from stationary sources have been, and are expected to continue to be made more stringent.

I.1.B. Chlorinated hydrocarbon wastes: A recent DOE study [8] has identified chlorinated hydrocarbons (CHCs) as one of the most commonly reported contaminants in soils and groundwaters surrounding its facilities, with concentrations of some of these CHC species exceeding existing regulatory guidelines by as much as 10^5. Among the technologies currently being considered for remediating large quantities of CHCs, heterogeneous catalytic oxidation processes and incineration are thought to be most effective at the present time [4c,9]. However, incineration in all likelihood will be a politically unacceptable technology [10] particularly for the mixed waste encountered in many DOE facilities, indicating an immediate need to actively pursue development of alternative catalytic processes. A number of recent reports in the patent literature and elsewhere describe new and promising catalytic materials and processes for the destruction of CHCs [4c,11]. Because these are very much developmental in scope at the present time, there are a number of technological hurdles to overcome, many involving the need for improved catalytic materials, before catalytic oxidation is a viable alternative for remediating large quantities of CHC wastes.

I.1.C. Oxide-catalyzed petroleum refining: Catalytic reforming is the second most important process for converting hydrocarbons in petroleum refining after catalytic cracking. Alkylation and transalkylation of aromatic compounds are also processes well known for their ability to produce products such as ethylbenzene, cumene, and linear alkylbenzenes, that are, in turn, important chemical precursors in the production of detergents and polymers. There has been recent renewed interest in replacing the conventional catalysts for these processes, sulfuric acid, phosphoric acid, hydrofluoric acid, and aluminum chloride, with novel oxide 'superacidic' catalysts because the former materials typically produce undesirable by-products such as oligomers and heavy polyaromatic compounds, as well as an extremely corrosive sludge by-product [2,12,13].

I.2. The Importance and Difficulty of Studying Oxide Surface Chemistry:

The three catalytic processes used as examples above have at least one important thing in common: they all currently use catalysts composed of oxide materials as in the case of SCR of NO_X [2,3,4c], or oxide catalysts are being developed for their use [2,4c,11-13]. Besides these, transition metal oxides have found numerous applications as heterogeneous catalysts for other industrially important processes such as the selective oxidation, isomerization and metathesis of hydrocarbons [2,14,15]. In spite of their importance, oxide catalytic materials and processes have received much less attention from a fundamental science point of view than have catalysis by metals [2,14-18]. This is particularly so for the use of sophisticated ultra-high vacuum (UHV) techniques to characterize the surface properties of oxide catalysts even though the recent NRC [1] and DOE [2] reports discuss at length the usefulness of such tools for determining critical information about catalyst composition and structure. UHV techniques have only recently begun to be utilized to study the structure and surface chemistry of oxide materials [16] owing, in large part, to the difficulty of experimentally applying such tools to insulating materials, not to mention the inherent complexity and diversity of possible surface structures on oxides [16,19].

I.3. Catalysis Studies in the EMSL at PNNL:

The work to be described here is taking place in the EMSL [20], a new DOE collaborative research facility at PNNL. The primary mission of the EMSL is to develop, refine, and use state-of-the-art research methods for investigating the molecular processes that underlie and control complex environmental processes. Four decades of production, testing, and operation of DOE nuclear weapons facilities have resulted in the interim storage of millions of gallons of highly contaminated radioactive, flammable and toxic wastes in hundreds of underground tanks, extensive contamination of the soil and ground water at thousands of sites within the U.S., and hundreds of buildings that must be decontaminated and decomissioned. The research in the EMSL is specifically focused on DOE needs to cleanup and restore these sites. As indicated above, it can be expected that catalytic processes will play a major role in the cleanup of DOE sites, and that oxide-catalyzed reactions are likely to be particularly important. Therefore, we have initiated EMSL research programs that are performing molecular-level studies of oxide-catalyzed reactions and we describe some of these in this paper.

II. EXPERIMENTAL

II.1. Synthesis of Model Oxide Surfaces:

As noted above, UHV spectroscopic techniques are well established for the study of metal and semiconductor surfaces, materials that are readily available as bulk single crystals. Oxides, on the other hand, have been much less studied by these techniques because they are insulators and hence, susceptible to surface charging [16,18,19]. In addition, many of the oxides of catalytic interest are not generally available as macroscopic single crystals of suitable size. Those that are available typically possess a plethora of surface defects from polishing and cleaning processes, as well as bulk impurities which typically segregate to the surface during cleaning in UHV. However, it is possible to avoid these problems by employing the techniques of epitaxial growth. By growing thin (<10 nm), insulating films on conducting substrates [21-26], or by doping these epitaxial films to increase conductivity [27,28], it is now possible to obtain sufficient conductivity to perform these measurements. In addition, epitaxial growth techniques have enabled crystalline materials to be synthesized in thin-film form with a level of structural quality and purity that is unprecedented in bulk crystal growth technology [29]. We are using plasma-assisted molecular beam epitaxy (MBE) techniques to grow oxide thin-films to use as model catalyst substrates.

II.2. Kinetic Studies of Model Catalysts:

We have constructed an apparatus that is capable of measuring reaction rates (using GC detection) under realistic, high-pressure (~1 atm.) conditions over these model, low surface area catalyst materials [30]. Details about studies of model catalysts with a combined catalytic reactor/UHV surface analysis apparatus are contained in a number of other places [1,2,31-33]. While such an approach has demonstrated utility for studying the catalytic chemistry of metal surfaces as described in some examples in the results section below, it has, at most, been used only a few times to address the catalytic behavior of oxide materials [34]. As with microreactor studies of realistic materials, reaction rates as a function of temperature and varying reagent partial pressures can be measured in this apparatus. From such data, a reaction mechanism can be proposed and a phenomenological kinetic model developed. In a few cases recently, high-pressure catalytic reaction rate data were successfully modeled using almost solely kinetic data for the elementary steps of the mechanism (*e.g.*, adsorption/desorption energetics) obtained in UHV measurements as parameters for the model [33,35]. In this way, a reaction mechanism is much more firmly established.

II.3. UHV Studies of Oxide Surface Structure and Chemistry:

Model studies such as those just described are extremely useful for inferring the identity of the catalytically active site(s) and of the various reaction intermediates, as well as in determining the overall rate of the catalytic process. This experimental information, when coupled with experienced chemical intuition, can provide invaluable clues to the underlying elementary processes involved in the catalytic reaction. These processes include reagent adsorption onto, diffusion to and reaction at the active site(s), and, ultimately, product desorption from the catalyst surface. Unfortunately, the microscopic details of the dynamics and energetics associated with these elementary steps are not provided by the microreactor measurements on the model catalysts. Detailed information regarding the geometric and electronic structure of reactive surface sites, and adsorbed reagent, intermediate and product species is similarly absent. This type of information can be usefully determined by a number of UHV spectroscopic tools. In the present work, we are utilizing low-energy electron diffraction (LEED), X-ray photoelectron diffraction (XPD), vibrational (high-resolution electron energy loss, HREELS, and FTIR) spectroscopies, and scanning tunneling/force microscopies

(STM/AFM) to determine the geometric structure of the substrate, and the adsorbate/surface complex formed by the chemisorption and surface reactions of the reactant molecules. Similarly, the electronic structure of the active surface site(s) and adsorbed species is being determined using XPS, ultraviolet photoelectron (UPS), and EELS spectroscopies. Temperature-programmed desorption (TPD) experiments are being used to determine surface coverages, reaction processes, and binding energies of adsorbed species.

III. RESULTS

In this section, we will briefly present some examples from our recent work that will demonstrate how we are using the above-described experimental approach to address a number of critical aspects of the surface chemistry and catalytic properties of transition metal oxides.

III.1. Synthesis of Model Oxide Surfaces:

We have used plasma-assisted MBE to synthesize a number of oxide thin films including MgO, TiO_2 (pure and Nb-doped), and the oxides of Fe [21-24,26-28], and have used them to study oxide surface structure and reactivity. Here we briefly give an example of this for the case of Fe_3O_4(001) grown on an MgO(001) surface (more details are contained elsewhere [26]). This substrate was chosen because of good lattice and crystal symmetry matching. The Fe_3O_4(001) film must be grown at a relatively low substrate temperature of 250°C to avoid interface reaction and Mg outdiffusion. The surface was found to display a $(\sqrt{2}x\sqrt{2})R45^\circ$ reconstruction. A model proposed to explain the observed diffraction pattern consists of a tetrahedrally coordinated Fe^{+3}-atom terminated surface with every other tetrahedral iron missing. These sites reside above a plane of octahedrally coordinated iron and oxygen atoms where every other iron atom is in either a +2 or +3 oxidation state. Thus, this surface can be expected to display a rich surface chemistry. We will discuss one example of this in the next section.

III.2. UHV Studies of Oxide Surface Structure and Chemistry:

We have recently been studying the adsorption and reaction of water and formic acid on a number of single crystal [36-40] and model thin oxide films [21,24,41] and have found that the surface chemistry of these species is strongly dependent on the atomic-level structure of the oxide surface. For example, the dissociation of water to hydroxyl groups on TiO_2 appears to require not only acidic cation adsorption sites, but also the close proximity of basic oxygen atoms in order for water O-H bonds to break [39]. Similarly, TPD results obtained on the reconstructed Fe_3O_4(001) described above contained three main chemisorbed states of water in the first monolayer, with TPD peak temperatures at saturation of 320, 280 and 225K, respectively [41]. We also found that each state is approximately equally populated with concentrations of around 1/3 ML. Recall from above that our proposed surface structural model, consistent with LEED results, consists of three distinct cationic iron sites, tetrahedral

Fe^{+3}, and octahedral Fe^{+2} and Fe^{+3} sites, with approximately equal concentrations. For this reason, we have tentatively assigned the three TPD states to desorption of water from these three distinct iron-atom sites on the surface [41].

III.3. Kinetic Studies of Model Catalysts:

The use of custom high-pressure catalytic reactor/UHV surface analysis instrumentation has provided significant new insights into the mechanisms of a number of metal-catalyzed reactions [30-33,35]. (Some recent examples of this from our work will be briefly described in the following sections.) However, we are aware of only two small recent efforts to apply such an apparatus to the study of the catalytic chemistry of oxide materials [34]. This is surprising considering its demonstrated utility to study metal-catalyzed reactions that are sensitive to surface structure [31,32,35]. Due to the fact that the electronic structure of covalent and ionic insulators is highly localized in comparison with conductive metals, one might expect that oxide catalytic chemistry would be rich with examples of structure sensitivity [14,15,19]. Correspondingly, metal oxides can be expected to show a much greater diversity of surface structures including varied defect types and geometries so that it will likely be more difficult to define structure/activity relationships in these systems. For these reasons, we have recently initiated studies of a particularly important oxide-catalyzed reaction, the SCR of NO_x by model single crystal vanadia/titania catalysts, using our catalytic reactor/UHV surface analysis system. The results to date are too preliminary in nature for this paper. Rather, in the following we present some recent results from our studies of Rh-catalyzed NO_x reduction to demonstrate the types of useful information that can be obtained in these experiments.

III.3.A. Structure sensitivity in Oxide-Catalyzed Reactions: The advantage of the catalytic reactor/UHV surface analysis apparatus is realized by the use of model catalysts, preferably single-crystalline in nature, that have a well-defined surface structure. On these model materials, the nature of the active site can be inferred and the relative activity of different sites assessed. This approach is particularly useful for addressing the origin of structure sensitivity in catalytic reactions [31,32,35]. For example, Figure 1 shows a recent measurement [32c] of the selectivity of the NO-CO reaction over two single crystal Rh surfaces. In this study, we found that the selectivity of two single crystal Rh surfaces displayed dramatically different selectivities for the two nitrogen containing products of the reaction, N_2 and N_2O, with the (110) Rh surface favoring production of the desired product, N_2, relative to the (111) surface under all reaction conditions studied.

III.3.B. In-situ and Post-Reaction Surface Analysis: Our catalytic reactor/UHV surface analysis apparatus also has capabilities for *in-situ* fourier transform infrared (FTIR) spectroscopy that can be used to identify both adsorbed and gas-phase chemical species present during reaction [42]. The presence or absence of various proposed reaction intermediates can be readily determined from the *in-situ* spectra [30,42]. The high-pressure reactor is directly coupled to an ultra-high vacuum (UHV) chamber that houses a variety of surface analytical probes, including Auger electron (AES) and X-ray photoelectron (XPS) spectroscopies, low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD). These various *in-situ* and *ex-situ* spectroscopies provide a fairly complete picture of the chemical state of the active catalyst surface. Notably, they provide information about the concentration of reaction intermediates, the oxidation state(s) of the constituents of the catalyst surface, and the structure of the active surface sites. Again using our recent studies of the NO-CO reaction over Rh single crystal surfaces [32c] as an example, Figure 2 shows XPS data obtained after high pressure reaction over Rh(111) and Rh(110). In the figure, it can be seen that reaction on the surface we found to be most selective for N_2, Rh(110), takes place at much higher steady-state concentrations of adsorbed N-atoms than does reaction on Rh(111).

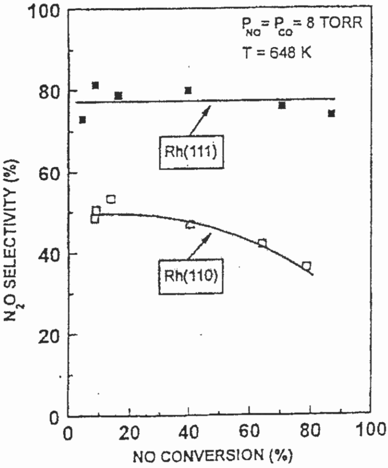

Figure 1: Selectivity for the undesirable product, N_2O, (relative to the total N_2 and N_2O production) of the NO-CO reaction as a function of NO conversion over single crystal Rh(111) and Rh(110) catalysts. From Reference 32c.

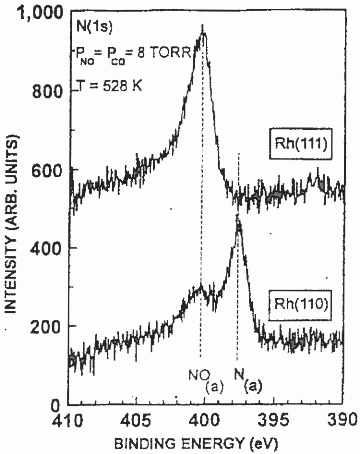

Figure 2: N(1s) XPS spectra obtained after NO-CO reaction ($P_{NO} = P_{CO} = 8$ Torr; T = 528K) on Rh(111) and Rh(110) single crystal catalysts. After high temperature reaction, the sample is cooled in the gas mixture, reaction rate measurements made, gases pumped from the reactor, and samples introduced into the UHV chamber for XPS analysis. From Reference 32c.

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[6] Consider that concentrations of nitrite and nitrate species in Hanford tank wastes are estimated to be about 1.1 x 10^8 kg, in addition to about 5.4 x 10^7 kg present in contaminated soils [5b]. Currently, all tank wastes are scheduled to be sent to

vitrification plants for final storage in waste-glass "logs". However, there are two major problems with this plan that are associated with the large quantities of nitrite and nitrate wastes; namely that 1) vitrification of *all* of the tank waste will be prohibitively expensive (current estimates suggest that about 40,000-60,000 glass "logs" will be required and each "log" is estimated to cost about $0.5 million to manufacture and an additonal $0.5 million to transport and store in a permanent repository), and 2) large concentrations of nitrite and nitrate species are incompatible with the current baseline waste-glass materials. For this reason, it is likely to be necessary that these species be removed from the waste stream prior to sending the feed to the vitrification plant(s). Unfortunately, current methods for denitrification of aqueous solutions result in the conversion of dissolved nitrite and nitrate anions into gaseous NO_x. (Even if a pretreatment for nitrate and nitrite destruction is not performed, exposure of the feed to the high temperatures of the glass melters will likely cause much of the nitrate and nitrite waste to be converted to gaseous NO_x.) Current U.S. and Washington state regulations effectively limit gaseous NO_x emissions to about 40 tons (or 3.6×10^4 kg) per year for any new "stationary source" on the Hanford site [7]. (Note that these regulations have become and are expected to continue to be more stringent over time.) With an expected 20 year lifetime for the vitrification plant(s), less than 1% of the total nitrate and nitrite inventory can then be emitted as gaseous NO_x. This level of destruction (> 99%) is well above the capability of current technologies that only remove at best 90% of NO_x (for the case of catalytic SCR, 60-90% efficiencies are reported, while other technologies are even less efficient and produce secondary waste streams [22]). Note that these reported destruction efficiencies are for gaseous feeds with much lower concentrations of NO_x (ppm levels) than is expected to be encountered in gaseous emissions from Hanford processing plants so that 90% efficiency using current SCR technology is likely to be an overestimate by a significant amount. However if 90% destruction could be achieved, a total of about 1×10^7 kg of NO_x would still be emitted. For this amount, over 300 years of emissions would be required to meet the present limitation of 3.6×10^4 kg/year. While purification and recycle of the nitrite and nitrate might be desirable as an alternative, it is unlikely that such a material would be acceptable for applications off the Hanford site so that it will ultimately need to be stored as mixed waste and/or destroyed. Furthermore, efficiencies for these technologies are currently less than that for SCR [3].

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PL-15

MECHANISM OF NEW OXIDATION REACTIONS OVER ZEOLITES

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Introduction: Due to fine operation of enzymes all oxidation reactions in the living nature proceed at ambient conditions by using the most common and readily available oxidant, i.e. O_2. Man-made catalysts are not so perfect as enzymes. One frequently needs several stages to accomplish a simple reaction, which nature does in a single move. In order to mimic nature more successfully, researchers try to use for the oxidation chemically premodified oxygen in the form of various oxygen-containing molecules. The present paper considers the mechanism of new reactions in the oxidation organic synthesis performed with nitrous oxide.

Active oxygen form: In 1988, three groups of researchers (including the authors' group) have independently found ZSM-5 zeolites to be the most efficient catalysts for direct hydroxylation of aromatic compounds. The simplest reaction of this type, i.e. oxidation of benzene to phenol

$$C_6H_6 + N_2O \longrightarrow C_6H_5OH + N_2 \qquad (1)$$

was demonstrated to proceed at 300-350°C with nearly a 100% selectivity. Recently, Monsanto announced a successful pilot-scale operation of a new one-step process for the manufacture of phenol from benzene according to reaction (1). Mechanistic studies showed that this remarkable activity of zeolites relates to Fe active sites (likely di-iron complexes) stabilized in the intercrystalline pore space of the zeolite matrix. During N_2O decomposition, these complexes generate new active form of surface oxygen (called α-form), whose participation provides unique oxidation performance to FeZSM-5 zeolites [1].

This mechanism reminds the features exhibited by enzyme monooxygenases (MO). The active sites of these enzymes also include Fe atoms and also generate a reactive oxygen form capable to selectively hydroxylate various organic molecules including aromatics.

Chemistry of α-oxygen: The following scheme of single-turn-over experiments was used to study the mechanism of N_2O oxidation:

1) α-Oxygen loading on FeZSM-5 surface from N_2O at 250°C;

2) Room temperature interaction of oxidized molecules with α-oxygen;

3) Product identification using both *in situ* spectroscopic techniques and extraction procedure followed by the NMR and chromatographic analysis.

Benzene interaction was the first to demonstrate the phenomenon of room temperature oxidation by α-oxygen resulting in a selective phenol formation [2]. Further experiments revealed an exceptional α-oxygen reactivity providing ready oxidation of alkanes, including the most inert CH_4 molecule, to produce alcohols [3]. Chromatographic data on the room temperature methane oxidation according to reaction (2):

$$CH_4 + (O)_\alpha \longrightarrow (CH_3OH)_\alpha \qquad (2)$$

are shown in Table 1, revealing nearly a 100% yield of the extracted methanol. Biomimetic type mechanism of this reaction is correlated with a high value of CH_4 kinetic isotope effect ($k_H/k_D = 2 \div 6$ depending on the temperature) typical for methane monooxygenase.

Further work on the reaction mechanism is in progress, in particular using Moessbauer spectroscopy and magnetic susceptibility measurements for studying the active state of iron.

Table 1. Room temperature methane oxidation by α-oxygen

Run No	CH_4 reacted (μmol/g)	CH_3OH formed (μmol/g)	CH_3OH yield (%)
1	20	19	95
2	23	21	91
3	18	18	100

Conclusion: At N_2O decomposition, Fe complexes stabilized in ZSM-5 zeolite matrix generate new form of surface oxygen. In contrast to O^- and O_2^- radicals, observed on the surface of some metal oxides, α-oxygen exhibits a pronounced similarity to the chemistry of active oxygen species of monooxygenases. This system imitates a remarkable strategy of biological oxidation and opens the way for developing new technologies in catalytic organic synthesis.

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PL-16

Giant Cluster Catalysis: possible intermediacy of carbene and nitrene species

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Catalysis with palladium metal is one of the oldest topics of catalytic chemistry. Traditionally, Pd-blacks, supported metal films, and colloidal palladium have been considered as variations of highly-dispersed metal containing no other components.[1] Little attention has been paid to the effect of the ligands on the size distribution and intrinsic structure of the metal particles. Changes in the catalytic properties of the "metal" by incorporation of organic molecules was treated as the catalyst "modification" or "gifting" on the level of the adsorption/desorption mechanisms. A realistic approach to understanding the chemical nature of the catalytically active metal species has come from cluster chemistry.[2-7] Due to similarities between metal skeletons of molecular clusters and submicroscopic fragments of a metal surface it became possible to have insight into a chemical nature of the metal catalyst and the mechanism of catalytic reactions proceeding on its surface. Moreover, cluster compounds, owing to the presence of metal atoms in uncommon oxidation states and metal-metal bonds were expected to display new chemical, particularly catalytic capabilities, distinguishing from mononuclear and bulk metal catalysts.

Clusters containing 4 to 38 palladium atoms have been synthesized and structurally characterized by single-crystal X-ray diffraction analysis.[8-16] So far all attempts to obtain larger palladium clusters in a single-crystal form have been unsuccessful. Meanwhile, a number of higher nuclearity low-valent palladium complexes, which displayed remarkable catalytic capabilities have been obtained as non-crystalline, highly-dispersed powders.[17-22] Their characterization was performed with the use of a series of indirect methods, *viz.*, HREM, electron diffraction, SAXS, NMR, STM, magnetic susceptibility, heat capacity measurements and EXAFS.[23-37] On the basis of these data, combined with those of elemental analysis, the compounds have been formulated as giant clusters[23,24] whose molecules consist of a positively charged, close-packed metal core (*e.g.*, containing 561 metal atoms in an idealized formula[23])* surrounded with coordinated (phen, dipy, O^{2-}) and outer-spheric (OAc^-, PF_6^-) ligands.[23-26] The concept of giant clusters[23] goes back to both a popular model of colloidal particles and the conjecture of P.Chini[38,39] on a "magic number" of metal atoms in the metal skeleton of large clusters. This approach appeared to be fruitful for chemical formulation of large metal clusters which amount from 55 to several hundreds and even thousands noble metal atoms ranging up to real colloidal metals.[7,26-30,40]

During the past decade, catalytic capabilities of palladium clusters were investigated. A large share of these studies have focused on these giant palladium clusters[22-26,31-37] by idealized formula $Pd_{561}phen_{60}(OAc)_{180}$ (I).

Oxidation of alkenes

Cluster I was found to be active in the catalysis of various reactions of organic substrates under mild conditions (293-363 K, 0.1 MPa). For instance, in acetic acid solutions of clusters I ethylene is converted to vinyl acetate

$$CH_2{=}CH_2 + 1/2O_2 + AcOH \rightarrow CH_2{=}CHOAc + H_2O\ , \qquad (1)$$

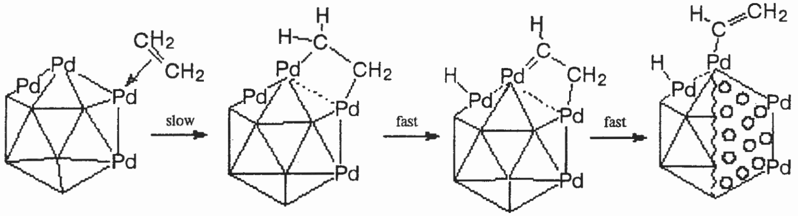
propylene to allyl acetate

$$CH_2{=}CHCH_3 + 1/2O_2 + AcOH \rightarrow CH_2{=}CHCH_2OAc + H_2O\ , \qquad (2)$$

and toluene to benzyl acetate

$$PhCH_3 + 1/2O_2 + AcOH \rightarrow PhCH_2OAc + H_2O\ , \qquad (3)$$

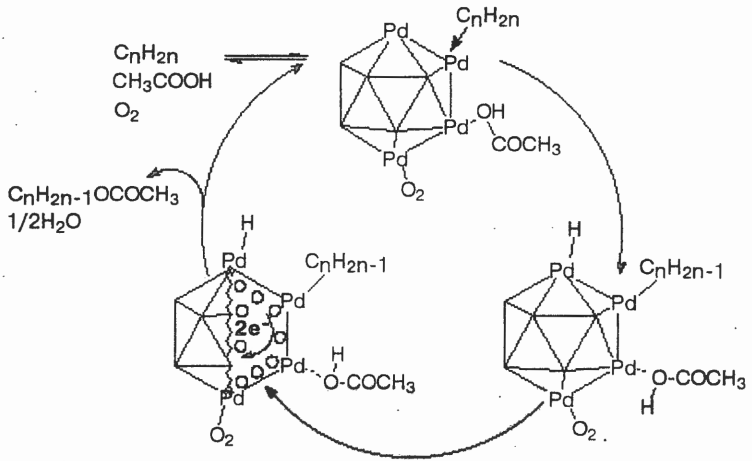
It was suggested that the rate-determining step is an oxidative addition (with opening the π-bond) of a π-coordinated C_2H_4 molecule to a Pd-Pd group of the cluster to form the σ,σ-coordinated $\cdots Pd\text{-}CH_2CH_2\text{-}Pd\cdots$ group. Subsequent splitting of the C-H bond with the elimination of a Pd-H fragment in this group is assumed to be a fast step, favored by the Pd=C multiple bond formation in the intermediate **2**:[25]



2

Evidence for the formation of σ,σ-coordinated ethylene and π,σ-coordinated vinyl groups on the palladium (100) surface were obtained by HREELS method.[41]

Subsequent reactions of the vinyl or allyl groups and H atoms coordinated at the surface of the cluster metal skeleton are assumed to proceed rapidly and exert no influence on the reaction rate. It is unlikely that all three molecules (alkene, O_2, and AcOH) can coordinate to the adjacent palladium atoms at the surface of the cluster core. The alkene molecule is more probable to bound at one site of the cluster surface, while the O_2 molecule is coordinated to another site, not necessarily next to the site where the alkene molecule is located. In this situation, electron transfer from the Pd-alkenyl or Pd-H surface group to the coordinated O_2 molecule can occur though the metal atom chain, the latter acting as an "electron transfer mediator"[25]



<u>*Oxidation of alcohols and aldehydes*</u>

In the presence of giant cluster **1** normal aliphatic alcohols are readily oxidized by dioxygen to form aldehydes and esters having the same carbon skeleton in both acid and alcohol components as the starting alcohol.[25,42,43]

Secondary alcohols are oxidized to ketons. In alcohol solutions both aldehydes and ketons readily form acetals (ketals), when the reaction is catalysed by giant Pd clusters (see below)[44].

The giant cluster-catalysed oxidation of acetaldehyde in water-free solvents (MeCN, EtOH, acetone) was found to afford acetic anhydride, along with ethyl acetate, acetic acid, and acetal.[45]

The addition of inhibitors, *e.g.*, hydroquinone, exerted no effect on either the reaction rate or products distribution of the oxidation of ethanol and acetaldehyde (including acetic anhydride), attesting to a non-radical mechanism of the reaction.[45]

Oxidation of formic acid

Formic acid is known to decompose over supported Pd catalysts to form CO_2 and H_2 at elevated temperature.[46] In the presence of dioxygen clusters **1** effectively catalyse the oxidation of formic acid at room temperature:

$$HCOOH + 1/2\ O_2 = CO_2 + H_2O$$

This reaction is also retarded by donor ligands with small in size molecules ($Et_2NCS_2^-$, SCN^-) rather than bulky ligands (PPh_3, phen). Using the poisoning technique, the number of the coordination sites in cluster **1**, which are accessible for the reagents of reaction under consideration, was found to be equal to ca.15, *i.e.* virtually the same as those for the oxidative acetoxylation of propylene (reaction 2).[46,47]

In this paper some new pathways involving intermediate formation of carbene and nitrene species for the reactions of nitro/nitrosoaromatics with CO [48,49] and nitriles with HCOOH[50] will be discussed.[51]

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PL-17

MOLECULAR DESIGN OF OXIDE CATALYSTS

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Oxides because of their ability to take part in the exchange of electrons as well as in the exchange of protons and oxide ions are used as catalysts in both redox and acid-base reactions. The use of oxides in catalysis may be classified into four groups: a) oxides of main group elements used as acid-base catalysts in the form of solid solutions, oxysalts, oxyacids or bases, in heterolytic reactions; b) oxides of transition metals used as redox catalysts in reactions, in which either electron transfer takes place across the reactant/catalyst interface (extrafacial reactions) or atom transfer occurs across this interface (interfacial reactions); c) oxides of main group elements, usually simple, used as supports; d) oxides of transition metals used as precursors for preparation of different active phases (e.g. highly dispersed metals, sulphides, etc.)

One of the most important classes of reactions catalysed by oxides is selective oxidation which is the simplest route to functionalise the hydrocarbon molecules. For catalysts to be active and selective in the oxidation of hydrocarbons, they must be able to perform complex multifunctional operations and therefore must conform to a number of conditions. Namely, active sites must be present at the catalyst surface, which: 1) activate the hydrocarbon molecule by abstraction of hydrogen from the surface intermediates by providing energy levels of appropriate redox potential; 3) properly orient the reacting molecule in respect to the surface; 4) perform a nucleophilic addition of a surface oxide ion which could be easily extracted from the surface in the desorption of the oxygenated intermediate; 5) activate the oxygen molecule and orient it properly at the surface in respect to the hydrocarbon molecule in electrophilic oxidation steps; 6) enable rapid diffusion of hydrogen by interaction with gas phase oxygen and show rapid diffusion of oxygen through the lattice to the reaction site; 8) all other active sites which could accelerate possible side reactions must be eliminated.

Activation and cleavage of the C-H bond at the surface of a semiconducting transition metal oxide starts with the polarisation of a hydrocarbon molecule in the electrostatic field stretching above the oxide surface. Quantum-chemical calculations show that then a carbon-surface oxide ion bond to form alkoxy group and a hydrogen-surface ion bond to form hydroxyl group appear so that both parts of the cleaved C-H bond become attached to surface oxide ions. Simultaneously, two electrons of this bond are injected into the conductivity band of the solid. The injection of electrons form an adsorbed redox pair into a semiconductor can take place spontaneously only if the redox potential of this pair is situated above the Fermi level and above the bottom of the conductivity band. The probability of this process is a function of the density of states in this band at the level of the redox potential of the adsorbed molecule.

The relative positions of the energy bands in the solid and the redox potential of the reacting molecule may be adjusted by: a) formation of one or more oxide/oxide interfaces with such values of the contact potentials that the conductivity band will shift to the optimum position; b) doping of the oxide with altervalent ions, which will shift the Fermi-level; c) generation of surface defects, which will create a broad distribution of surface electronic states participating in the exchange of electrons with the reacting adsorbed molecules.

Transition metal oxides used as catalysts in selective oxidation of hydrocarbons are non-stoichiometric compounds, their composition depending on the gas phase. Changes in oxygen pressure cause changes in stoichiometry of the oxide, which may be accommodated by the crystal lattice in two ways: either by generation of point defects or by alteration of the mode of linkage between the oxide polyhedrons, resulting in the formation of extended defects (crystallographic shear). When non-stoichiometry is introduced by the presence of point defects, a series of equilibria is established at the surface on the pathway of lattice oxygen being transferred into the gas phase or in the reverse process of reoxidation of the lattice. When the temperature increases, the equilibrium shifts in the direction of higher dissociation pressure of the oxide and the surface becomes more and more populated with electrophilic oxygen species. It should be borne in mind that in the case of those oxides, in which the transition metal cation is not in its highest oxidation state, chemisorption of oxygen takes place at low temperatures, electrons being transferred from the oxide to adsorbed oxygen molecules with formation of higher valent cations and electrophilic oxygen species. This may be followed by surface reconstruction and formation of a monolayer of high valent oxide at the surface of the lower valent oxide. Different behaviour is shown by oxides in which the change of stoichiometry is accommodated by the formation of shear structures. There is no vacancy formation on extraction of nucleophilic oxygen ion from the oxide surface by the hydrocarbon molecule, but instead a shear plane is formed or an existing one grows. This has a pronounced influence on the behaviour, the selectivity to partial oxidation products remaining very high because of the absence of electrophilic oxygen.

As the phenomenon of crystallographic shear appears in transition metal oxides with anisotropic lattices, pronounced structure-sensitivity of catalytic properties is observed and the habit of crystallites of the catalyst may have strong influence on the selectivity of the reaction. The polar crystal planes are usually much more active than non-polar ones. The latter can be either chemically saturated or show coordinative unsaturation.

The type of crystal face exposed may be controlled by depositing the transition metal oxide in form of a monolayer on another oxide serving as a support. The oxide monolayer catalysts are thus obtained, whose properties may be designed by selecting the appropriate active phase and the support, changing the surface coverage of the active phase, introducing co-deposited cations, doping the support and varying its dispersion.

Recent investigations showed that under ambient conditions the surface molecular structures of transition metal oxy-ions are directly related to the surface pH at point of zero charge of the aqueous film on the oxide supports and can be predicted from the corresponding aqueous transition metal ions chemistry. On heating, dehydration of the surface takes place and the transition metal polyoxy-anions decompose into molecularly dispersed oxy ions, but undergo reconstruction on exposure to water vapour. At higher temperatures thermal spreading may occur resulting in the formation of an oxide monolayer. Spontaneous spreading of one oxide over the surface of another oxide is a manifestation of the wetting of one solid by another solid due to the operation of forces of surface tension. It occurs when the free energy of adhesion of the mobile phase to the support is greater than the free energy of cohesion of the mobile phase and continues until the formation of a thermodynamically stable overlayer characterised by a surface free energy equal to that of the bulk of the active oxide phase. The rate of spreading is limited by surface diffusion described by a parabolic rate equation and depends strongly on the crystallinity of the support and type of the atmosphere. When the monolayer is deposited on a support which is not wetted, coalescence of the monolayer into crystallites of the deposited transition metal oxide takes place on annealing. As the free energies of cohesion and adhesion depend on the oxidation state of the oxide monolayer, reduction and reoxidation entail strong changes of the degree of dispersion. It should be also remembered that the surface free energy is very sensitive to the presence of additives (impurities). Therefore wetting of the surface of the support by the active phase may be controlled by the introduction of appropriate additives, which either remain at the surface or diffuse into the subsurface layer. The minority oxide (supported phase) can accumulate entirely at the surface of another oxide (support) when the temperature of annealing is low enough and the miscibility as well as chemical affinity of the two oxides are very limited. In the case of miscibility of the two oxide phases a solid solution may be formed at a high enough temperature and in the case of chemical affinity of the two oxides new surface or bulk compounds may be synthesised.

In recent years attempts are being undertaken to introduce the clusters of transition metal oxides into frameworks, which could control the spatial arrangement of molecules reacting at the active sites provided by the oxide. To this end pillared clays are synthesised, in which either the pillars are built of the active transition metal oxide phase, or this phase is deposited onto pillars composed of an inert material. Introduction of clusters of transition metal oxides into the zeolite framework has also been reported. Such "ship-in-the-bottle" catalysts are now a subject of considerable interest.

Application of the rapidly developing surface science techniques to the study of oxide surfaces and quantum chemical calculation of the interaction at oxide surfaces revealed that the surface of an oxide is not a rigid static structure, on which various phenomena involving molecules adsorbed from the fluid phase occur, but is always in dynamic interaction with the latter. The surface "lives" and adapts itself to the "living conditions". Adaptability to the change of these conditions is one of the most important properties of solid surfaces and is responsible for many phenomena of great theoretical interest and practical consequences. This is particularly important in the case of heterogeneous catalytic reactions on oxide catalysts, when continuous exchange of matter and energy between the catalyst and the reactants may result in many changes, which may be due either to the shift of chemical equilibria of defects or to kinetic effects. The oxide system may respond to the change of the composition of the reacting catalytic mixture in three different ways:

- defect equilibria at the surface of the oxide may be shifted and the change of the concentration of the given type of sites involved in the catalytic reaction may cause a gradual change of catalytic properties;

-when the concentration of defects at the oxide surface surpasses a certain critical value, ordering of defects or formation of new bidimentional surface phases may occur, resulting often in dramatic change of catalytic properties;

- in the case when a redox mechanism operates in the catalytic reaction, the ratio of rates of the catalyst reduction and its reoxidation may be different for various oxide phases and hysteresis of the dependence of catalytic properties on the composition of the gas phase may appear, these properties being therefore strongly influenced by the type of the pre-treatment.

A general conclusion may be thus advanced that heterogeneous gas/solid systems should not be treated as two phase systems but should be regarded as composed of the gas phase, the solid and the surface region. The surface region extends on both sides of the gas/solid interface. From the side of the solid the changes of surface free energy and the energy of interaction with adsorbed species may result in the enrichment of the surface layer of the solid in some constituents of the lattice (point defects, atoms of the solute, etc.) or may cause the surface reconstruction and formation of bidimentional surface phases. From the side of the gas phase the species in the adsorbed overlayer may aggregate to form bidimentional liquid domains or may undergo a long range ordering. The structure and properties of this region may be thus modified either by changing the composition of the gas phase or by introducing additives into the solid.

CATALYSIS BY CARBON-BASED MATERIALS WITH VARIOUS SURFACE AND POROUS STRUCTURE

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Porous carbon materials are widely used in various areas of chemical technology involving processes of adsorption and catalysis. Adsorptive and catalytic behaviour of these materials depend on a number of factors, among which the most important are both the elemental composition and structure of a non-carbon phase (for example, ash-forming impurities, supported components) and chemistry of the surface as it is. Specific features of porous structure of the carbon matrix and its microtexture should be also treated as the factors which have a noticeable impact upon the activity and, particularly, selectivity of the a porous carbon material for adsorptive and catalytic processes involving the molecules of the geometry complementary to the adsorption sites. Although enormous number of variations of porous carbon materials (prepared from practically any carbon-containing feedstock) can be used to study the contribution of each of these factors, problems of identifying the series which would follow changes in a sole parameter (a property of the carbon material) make it difficult to interpret the obtained data. A progress in revealing regularities of the influence of various bulk and surface characteristics of the carbon materials on their adsorptive and catalytic properties is possible if the studies are conducted with the carbon materials, whose preparation procedure allows the control of the process of formation of the carbon phase. Here the preparation of carbon materials from gaseous hydrocarbons by means of the so-called catalytic matrix synthesis is of some practical interest.

This approach was used at Boreskov Institute of Catalysis to synthesize a wide range of carbon materials and carbon-carbonaceous composite materials (CCM) of globular, filamentous, globular-filamentous textures. Among these CCM are: Sibunit produced by supporting pyrocarbon (PC) on carbon black granules (CB) followed by outburning the CB; carbon filaments (CFC) produced by decomposition of CH_4 over special catalysts allowing the yield of several hundred grams of carbon per gram catalyst; and the systems such as CFC/Sibunit, CFC/CFC, PC/CFC, etc. The CCM produced are differed by graphite crystallite sizes, their degrees of 3D-ordering, basal and edge contributions to porous surfaces. Specific procedures were used to make the surfaces of hydrophilic or hydrophobic nature.

A number of catalysts and catalytic processes based thereon were studied using physical methods such as HREM, EXAFS, NMR MAS, XPS, XRD techniques. Textural and substructural parameters of the carbon materials were shown to strongly effect the processes of formation and stabilization of catalyst active component particles and, finally, its catalytic behavior. The systems such as $PdCl_2/C$, PdO/C, Pd/C, Pt/C, Ag/C, Ni/C, Ru/C, $LiAlH_4/C$, HPA/C (where HPA is heteropoly anion), as well as bicomponent systems such $LiAlH_4/Pd/C$, Ru/HPA/C, etc. were examined. They were tested for the processes of hydrogenation, oxidation, hydrodechlorination, epoxidation. Some specific adsorptive features of filamentous and globular-filamentous CCM caused by a remarkable amount of slit-like pores built in their textures were revealed. The most spectacular effects of these pores are observed in the systems involving flat or spherical shape molecules, and can be employed to achieve both separation processes and specific catalytic ones.

Specific adsorptive and catalytic properties of CCM can arise upon eliminating or, *vice versa*, generating on their surface various oxygen-containing species. Available data demonstrate that the emergence of these properties is caused not only by the effects of plugging micropores and hydrophobic-hydrophilic interaction but also by considerable variation in electronic properties of the graphitized fragments of the CCM surface. The effects of the surface microtexture of small-size pores (supermicropores, small mesopores) on conformations of molecules sorbed in these pores are of practical importance for designing stereospecific adsorptive and catalytic systems. These effects are the most pronounced in the systems in which the molecular oligomers localised in the CCM pores behave as the active sorbing component: the conformations of these molecules in a supermicropore tend to be to a highest extent complementary to the surface structure of this pore. Another important display of the peculiarities of the surface structure of porous space of CCM and substructural characteristics of its microcrystallites is a propensity of CCM to epitaxial and intercalation interaction with a sorbate. For example, the epitaxial interaction makes it possible to transition metal (Co, Fe) particles to be stabilised in uncharacteristic crystal modifications on the carbon surface, and intercalation of atoms can generate "spatially extended active sites" with specific properties for, *e.g.*, reactions of polymerisation of vinylidene monomers.

PL-20

Catalysis by Solid Acids and Bases: Kinetic Coupling Between Dihydrogen Activation and Acid-Base Functions

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Introduction

An elementary step with positive standard Gibbs free energy (negative standard affinity) proceeds via kinetic coupling with other elementary steps within a catalytic sequence. These other steps either remove the products or increase the surface concentration of the reactants involved in the unfavorable step[1,2]. Kinetic coupling leads to an increase in the forward rate of chemical reactions by removing one of the products of an elementary surface step. In contrast, thermodynamic coupling removes a gas phase product of a reversible chemical reaction via a concurrent reaction and therefore influences only net reaction rates by decreasing the rate of the reverse reaction.

Propane dehydrogenation reactions on H-ZSM5 modified by Zn cations, n-heptane isomerization on zirconia modified by WO_x and Pt and alcohol condensation reactions on Cu-promoted Mg_5CeO_x oxides provide useful examples of the role of kinetic coupling between hydrogen adsorption-desorption sites and acid or basic sites in catalytic reactions involving the activation of C-H bonds. In each case, sites introduced by metal crystallites (Pt, Cu) or by isolated cations (Zn^{+2}) increase the rate of reactions typically occurring on acid or basic sites by introducing a "porthole" for adsorption-desorption reactions of H_2. These bifunctional pathways do not involve unsaturated gas phase intermediates such as alkenes or aldehydes. These catalytic sequences require, however, the activation of C-H bonds on acid or basic sites, the formation of mobile surface hydrogen species, and their spillover and surface migration to hydrogen activation and desorption sites.

Catalytic Reactions of Propane on H-ZSM5 and Zn/H-ZSM5

Propane conversion to aromatics on zeolitic acids requires sequential dehydrogenation steps and chain growth and cyclization reactions of propene intermediates[4,5]. Dehydrogenation reactions proceed via elementary steps that involve the activation of C-H bonds in alkanes and the disposal of the H-atoms formed in these reactions. C-H bond activation steps are quasi-equilibrated during propane reactions at 773 K on H-ZSM5 and the removal of the hydrogen formed in these steps limits dehydrogenation rates and selectivity. Hydrogen removal can occur via bimolecular or surface-mediated transfer to adsorbed hydrocarbons (hydrogen transfer) or by recombination to form H_2. Rate-determining hydrogen desorption steps create high hydrogen virtual pressures at catalytic surfaces and lead to unfavorable thermodynamics for surface C-H bond activation elementary steps and to "hydrogenation" surface reactions that form predominantly methane and ethane. The presence of exchanged Zn or Ga cations increases the rate of hydrogen removal by introducing "portholes"[3] for the recombinative desorption of H-atoms as H_2 and decreases the rate of formation of undesired light alkanes.[4,5]

The rates of C-H activation, recombinative hydrogen desorption, and propane chemical conversion have been measured simultaneously from isotopic redistribution and chemical conversion data using C_3H_8/C_3D_8 and D_2/C_3H_8 mixtures. C-H bond activation rates measured from isotopic scrambling rates in C_3H_8/C_3D_8 mixtures are similar on H-ZSM5, Zn/H-ZSM5, and Ga/H-ZSM5 and negligible on Na/ZSM5, suggesting that C-H activation requires Bronsted acid sites. C-H bond activation steps occur rapidly, but they are quickly reversed by recombination of hydrocarbon fragments with abundant surface hydrogen species. Zn and Ga cations prevent recombination reactions by removing the hydrogen atoms formed during C-H activation. Exchanged Zn and Ga cations increase the rates of propane aromatization, recombinative hydrogen desorption, H_2-D_2 isotopic exchange, and incorporation of D-atoms from D_2 into reaction products. These data are consistent with quasi-equilibrated acid-catalyzed C-H activation steps and rate-determining hydrogen removal steps. The kinetic coupling between Bronsted acid sites provided by Al sites within zeolite channels and dihydrogen activation sites consisting of isolated Zn^{+2} cations is consistent with measured kinetic rate expressions for propane dehydrogenation and aromatization reactions and with the observed correlation between dehydrogenation rates and H_2-D_2 isotopic exchange rates.

Stoichiometric hydrogen "acceptors", such as O_2, CO, and CO_2 also increase aromatics selectivity by coupling dehydrogenation steps with hydrogen removal via hydrogenation of these molecular acceptors. Typically, propane dehydrogenation reactions on Zn/H-ZSM5 are coupled thermodynamically with chain growth and aromatization reactions of alkenes; these reactions increase equilibrium propane conversion levels but lead to low propene selectivity.

This thermodynamic coupling can be intentionally disrupted by blocking cation exchange sites with alkali ions. Chain growth reactions required for the formation of C_6+ chains leading to aromatics can be modified by controlled titration of a fraction of the Bronsted acid sites. The selectivity to propene intermediates can be increased significantly by decreasing the density of protonic sites via selective titration with Na cations.

In-situ X-ray absorption studies have shown that Zn cations are present as isolated Zn^{+2} species at intrazeolitic exchange sites. Ion exchange synthesis methods lead to the direct introduction of Zn^{+2} cations onto those exchange sites. Bronsted acid site density measurements by NH_3 chemisorption suggest that Zn^{+2} cations replace two protons in H-ZSM5 and lead to the formation of Lewis acid sites that interact strongly with the nitrogen atom in NH_3. In contrast, $Ga^{+\delta}$ exchange occurs only after synthesis during treatment at 673-823 K in reducing environments. Zn ions do not reduce during reactions of propane at 773 K, but they undergo reduction-oxidation cycles during each hydrogen desorption turnover. In contrast with exchanged Zn^{+2} cations, ZnO clusters reduce to Zn metal and elute from the catalyst bed as Zn vapor at typical propane aromatization conditions. Zn^{+2} cations differ in reduction stability and in catalytic behavior from those present in ZnO clusters and in bulk Zn aluminate compounds. In ZnO, reduction occurs well below the reaction temperatures required for C-H bond activation; in Zn-AlO_x materials, hydrogen adsorption-desorption reactions occur only above 773 K.

Isomerization of n-Heptane on Pt/WO_x-ZrO_2 and Pt/SO_x-ZrO_2

Zirconia becomes a strong solid acid when modified by depositing WO_x species (10-15% wt. WO_3) on the surface of hydrous zirconium oxide[6]. When promoted with metals (e.g., 0.3% wt. Pt), these oxides catalyze the selective isomerization of C_7+ alkanes at 373-473 K without the extensive cracking observed on sulfated zirconia and zeolites promoted by metals[7,8]. Kinetic and isotopic tracer studies show that isomerization reactions proceed via chain reactions limited by the rate of hydrogen transfer from alkanes or H_2 to adsorbed isomerized hydrocarbons[8]. Hydrogen transfer steps decrease the surface lifetime of adsorbed hydrocarbons on acid sites and cause their desorption before undesired C-C scission occurs. Hydrogen transfer occurs primarily using H-atoms formed by H_2 dissociation on metal sites. On Pt/SO_x-ZrO_2, these hydrogen transfer desorption steps are slow because Pt surface atoms are poisoned by sulfur species. Slow desorption steps then lead to long surface lifetimes and to significant β-scission before desorption. On Pt/WO_x-ZrO_2, carbocation adsorption-desorption steps are quasi-equilibrated and surface isomerization steps limit the overall rates. As a result, desorption of isomerized surface species occurs before significant β-scission on Pt/WO_x-ZrO_2 [8].

On both types of materials, hydrogen species formed by H_2 dissociation on Pt sites participate in chain termination reactions of cationic or alkoxide intermediates adsorbed on acid sites and in the formation of Bronsted acid sites. The presence of dihydrogen increases the rate of o-xylene isomerization on WO_x/ZrO_2, even in the absence of a metal function, suggesting the activation and involvement of H_2 on WO_x/ZrO_2 during acid-catalyzed reactions. Reactions of o-xylene/D_2 mixtures show that dihydrogen participates in the formation of Bronsted acid sites but not in hydrogen transfer elementary steps during xylene isomerization. These Bronsted acid sites consist of H_xWO_3 species present at the surface of small octahedral WO_3 clusters and formed by hydrogen migration from H_2 dissociation sites.

n-Heptane and o-xylene isomerization rates on WO_x-ZrO_2 reach a maximum after oxide precursors are treated in oxidative environments at 1000 K. The strength of Bronsted acid sites, measured indirectly from the ratio of p-xylene to m-xylene among reaction products, also reaches a maximum value after oxidation at 1000 K. Isomerization activity is detected on WO_x/ZrO_2 only within a very narrow range of pretreatment temperatures (1000 K +/- 150 K) for both n-heptane and o-xylene reactants. As discussed below, oxidative treatments near 1000 K lead to small WO_x clusters that undergo reduction to form Bronsted acid sites in the presence of H_2 at relatively low temperatures.

High isomerization rates appear to require the presence of WO_x domains of intermediate size, which form after oxidation at 1000 K by controlled sintering of octahedral WO_3 clusters. This growth of WO_3 domains is aided by a decrease in ZrO_2 surface area and by the possible formation of a WO_3 tetragonal phase at temperatures near 1000 K. X-Ray absorption spectra at the W L_I and L_{III} absorption edges suggest the predominant presence of distorted octahedral WO_3 domains, even after dehydration, in all WO_x-ZrO_2 samples. Tetrahedral WO_x species are not detectable in any of these samples. UV-visible spectra show that the band gap in WO_x/ZrO_2 materials decreases with increasing oxidation temperature or increasing WO_x loading, suggesting the presence of larger WO_3 domains. These distorted octahedral domains differ markedly in electronic structure, reduction behavior, and isomerization rate and selectivity from previously reported isolated tungstate groups supported on Al_2O_3. Temperature-programmed reduction measurements show that small and large WO_x clusters reduce at higher temperatures than those of intermediate size. The unique acid properties of WO_x domains of intermediate size appear to be related to their ability to form W^{6-n}-O_x-(n-H^+) centers under reducing reaction conditions at low temperatures.

Aldol Condensation Reactions of Ethanol on Cu-Mg_5CeO_x Catalysts

Basic oxides catalyze the formation of higher oxygenates from aldehydes and alcohol reactants via aldol condensation chain growth pathways. Mg_5CeO_x oxides promoted with Cu and K catalyze the synthesis of isobutanol from CO and H_2 via bifunctional pathways requiring methanol synthesis and aldol condensation sites[9,10]. The Ce component increases the density and strength of basic sites in MgO and the rate of base-catalyzed chain growth reactions[10].

Reactions of ethanol on Cu-Mg_5CeO_x at 573 K lead to the formation of acetaldehyde, n-butyraldehyde and acetone as predominant products. The presence of Cu increases the rate of ethanol dehydrogenation to acetaldehyde. Dehydrogenation rates increase with the density of Cu surface atoms in Cu/Mg_5CeO_x catalysts; dehydrogenation turnover rates are independent of Cu crystallite size and much higher than on metal-free catalysts.

Acetaldehyde condensation reactions occur on basic sites, but condensation rates also increase with increasing density of Cu surface atoms. These condensation reactions require α-hydrogen abstraction steps for the formation of aldol-type chain growth intermediates. Hydrogen abstraction steps are limited by the rate of hydrogen removal via recombinative desorption, a process that occurs rapidly on Cu surface atoms but much more slowly on MgO. C-H bond activation steps on basic sites are kinetically coupled with hydrogen desorption steps catalyzed by Cu in order to increase the rate of formation of n-butyraldehyde and acetone during ethanol and acetaldehyde condensation reactions. Hydrogen migration and recombinative desorption on Cu sites increase the rate of aldol condensation by removing a surface bottleneck that tends to reverse the step that forms the unsaturated aldol-type species required for chain growth. This mechanistic proposal is consistent with the direct formation of aldol condensation products from ^{13}C-ethanol/^{12}C-acetaldehyde mixtures and with the increased rate of isotopic exchange in ethanol-d_0/D_2 mixtures as the density of Cu sites increases in Cu-Mg_5CeO_x catalysts.

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MECHANISMS FOR HYDROGEN ACTIVATION AND HYDROGENATION OF ACETONE TO ISOPROPANOL AND OF CARBON OXIDES TO METHANOL OVER COPPER-CONTAINING OXIDE CATALYSTS

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1. Introduction

Copper-containing oxide catalysts are active for hydrogenation reactions, including hydrogenation of carbonyl groups of organic compounds and carbon oxides to alcohols.

Two compounds were chosen for the investigations: copper chromite ($CuCr_2O_4$), which is the component of numerous industrial catalysts for hydrogenation, and solid solution of copper ions in anion-modified zinc oxide (hereinafter referred to as solid solution). According to some authors, the latter is the active component in the methanol synthesis catalyst.

Here the composition and structure of the catalysts after the reduction by H_2 were studied.

Kinetic methods, catalytic activity measurements, *in situ* XRD, neutronographic, IR spectroscopic and electron microscopic techniques were used for the studies.

2. The structure of reduced copper chromite

When the kinetic method was used to study the interaction of hydrogen with copper chromite at 220-350°C, only a portion of the reacting hydrogen, which corresponds to approximately a half of the oxygen monolayer at the chromite surface, was found to yield water, the rest of hydrogen is absorbed by spinel [1,2].

Copper ions are partially (50-60% from the total copper content) reduced with hydrogen to Cu^o and released as flat particles upon the surface of spinel crystals (Fig.1). These are well faceted particles 50×100×100 E in size which are bonded epitaxially to the spinel surface: compatibility between reciprocal lattice (111) planes of spinel and (111) planes of Cu^o is seen from superposition of spots (220) of copper and (440) of the chromite in the electron diffraction patterns [3-6].

A spinel phase is preserved in flowing hydrogen at temperatures as high as 400°C. At 250°C in hydrogen spinel acquires the cubic lattice with the lattice constant a=8.342 E. The diffraction pattern recorded for it is characterized by the line intensity distribution which is rather different from that of the chromite untreated with H_2. As temperature increases to 320°C, the difference in the line intensity distributions becomes even more apparent (Fig.2).

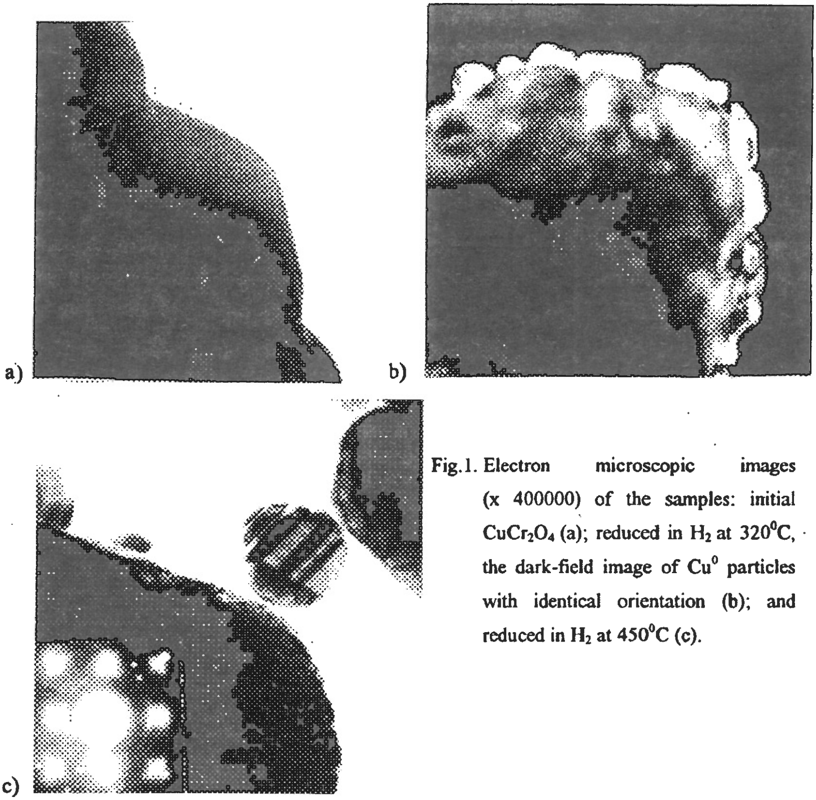

Fig.1. Electron microscopic images (x 400000) of the samples: initial $CuCr_2O_4$ (a); reduced in H_2 at 320°C, the dark-field image of Cu^0 particles with identical orientation (b); and reduced in H_2 at 450°C (c).

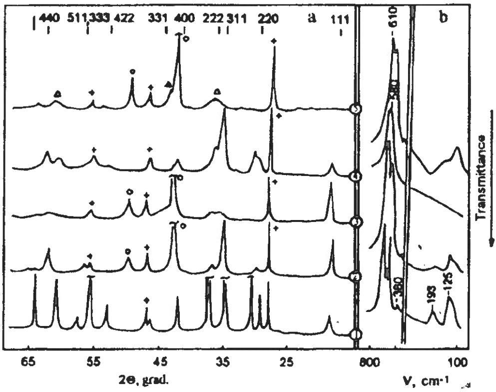

Fig.2. X-ray diffraction patterns (a) and IR spectra (b) of copper chromite: 1 - initial sample; 2, 3, 5 - reduced in H_2 at 250°, 320° and 450°C, respectively; 4 - sample 3 calcined in He at 320°C for 10 h.; (°), (+), (Δ) - reflections from the Cu^0, silicon and NaCl-type structures, respectively. Positions of the reflections from the cubic type $CuCr_2O_4$ spinel are marked on the top.

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The reduction at 250°C is seen from the IR spectroscopic data to result in a decrease in the intensity of the absorption bands assigned to oscillations of CuO_4 group of spinel, which practically disappear upon the reduction at 320°C. It means that the amount of copper ions occupying tetrahedral positions decreases with elevation of temperature and practically disappears when the reduction is conducted at 320°C. It should be pointed out, with the reference to the XRD data, that only a half of copper ions are released as metallic particles under these conditions.

In situ XRD technique was used to study the sample composition depending on the time of its exposure to hydrogen at 320°C. The study showed only scarce increase in the amount of copper metal formed (from 40-50 to 60%) against the time variation from 2 to 8 h, whereas a considerable redistribution of spinel lines intensity, i.e. a change in the spinel structure, was observed. Therefore, apart from the reduction of the surface to form water, which results in no structural change, two alternative processes take place in hydrogen. One of them is completed in the first 2-3 h; it is, apparently, the exchange interaction between hydrogen and copper ions: $H_2 \rightarrow 2H$; $2H + Cu^{+2} \rightarrow 2H^+ + Cu^o$. Another is completed not earlier than in 8 h of the exposure and can be assigned to the migration of Cu^{+1} ions, which are formed according to the reaction $H + Cu^{+2} \rightarrow H^+ + Cu^{+1}$, to the octahedral positions of spinel .

The states of dissolved hydrogen and their location over the structure of the reduced chromite were studied using a neutronogram recorded for the sample exposed to hydrogen at 320°C for 2 h. The obtained neutronographic data were analyzed to conclude about the interatomic distances [7]. For hydrogen of tetrahedrons, one H-O distance equal to 0.96 Å and three distances equal to 2.33 Å were shown, while for 16c positions all of six H-O distances are 2.12 Å. Hence, the proton formed as a result of exchange interaction with copper ion in tetrahedron reacts with one of the oxygen ions of the tetrahedron to form covalent O-H bond resembling the H-O-H bonds in a water molecule. Hydrogen of octahedrons can not be treated as a constituent of such groups as HO^-, H_3O^+, H_2O but represents the state similar to the atomic state in the oxygen octahedral surrounding (H*). A similar hydrogen state is discussed in [8].

Analysis of the data obtained allows the compositions of the sample exposed to hydrogen for 2 h to be described as follows:

$$Cu^{0}_{0.53} \| [Cu^{+2}_{0.33}]^{a} [H^{+}_{0.30}]^{e}_{4} [Cu^{+}_{0.07} H^{*\,*}_{0.38}]^{c}_{2} [Cr^{+3}]^{d}_{2} O_{4},$$

where a, c, d, e are crystallographic positions of ions in the spinel structure; H* - occluded hydrogen in octahedral positions.

3. Structure of reduced solid solutions based on anion-modified zinc oxide

The XRD data show that the phase of copper metal appears in hydrogen at 220-230°C (Fig.3). The microdiffraction data show the epitaxial junction of copper metal formed in hydrogen and zinc oxide growing along the direction of [001]ZnO|[111]Cu^0. The fragment of the diffraction pattern recorded in the 2Θ range of 108-119° (where the spots (300) and (213) of ZnO and (531) of Si reference were observed) was used to determine lattice constants. There is practically no change in the lattice constant *a* of the reduced sample, whereas constant *c* (5.217 - 5.194 - 5.202 Å) appears to be sensitive to the state of the solid solution (Table 1). Constant *c* of the solid solution is less than that for ZnO, however the constant for the sample upon the reduction is equal to that for ZnO and decreases again upon the reoxidation [9-11].

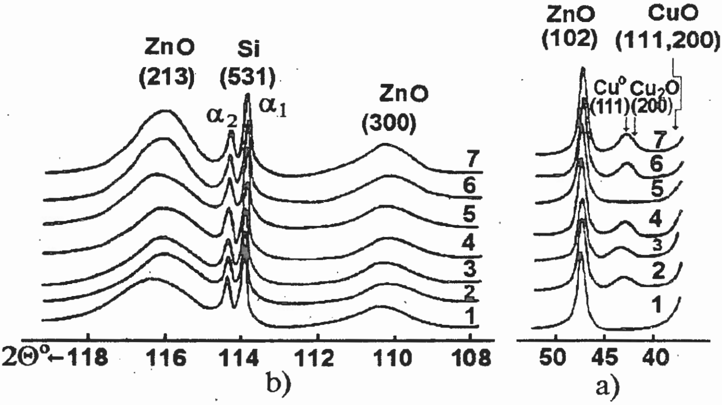

Fig.3. Fragment of *in situ* X-ray diffraction patterns: a) - 2Θ ~ 40-50°, b) - 2Θ ~ 108-119°; of the sample $Cu_{0.1}Zn_{0.9}O^{*1}$ after treatment: 1 - in air at 20°C; 2 - in hydrogen at 220°C; 3 - in helium at 220°C; 4 - in hydrogen at 220°C; 5 - in mixture H_2+CO at 220°C; 6 - in hydrogen at 420°C; 7 - in helium at 420°C.

Evidently, these processes are the consequence of the exchange interaction with protons involved:

$H_2 \rightarrow 2H$; $2H + Cu^{2+} \rightarrow 2H^+ + Cu^0$.

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[1] - anion modified oxide containing OH^- and CO_3^{2-} groups.

Table 1. Lattice constants forCu-containing ZnO after thermal treatment in various media

Thermal treatment conditions	a (Å) Δa=±0.002	c (Å) Δc = ± 0.003	Phase composition
Air, 350⁰ C	3.250	5.194	$Cu_{0.08}Zn_{0.92}O^*$
Hydrogen, 220⁰ C	3.254	5.217	$Cu_x^o + Cu_{(1-x)\,0.08}Zn_{0.92}O^*$
Helium, 220⁰ C	3.252	5.202	$Cu_{0.08}Zn_{0.92}O^*$

4. Mechanisms for hydrogenation of C-O bond in carbon oxides and acetone

To elucidate the mechanisms for hydrogenation of acetone to isopropanol and for synthesis of methanol from carbon oxides, the interaction of catalysts activated by hydrogen with the compounds to be hydrogenated was studied [12-14].

Hydrogenation of acetone to isopropanol. Catalytic properties of copper chromite were studied using a pulse flow installation at 75°C; the reaction products were identified chromatographically. This reaction temperature was chosen so that the effect of the back reaction would be negligible. A mixture of 10 vol. % acetone in hydrogen was examined. The catalyst was preactivated in hydrogen at various temperatures.

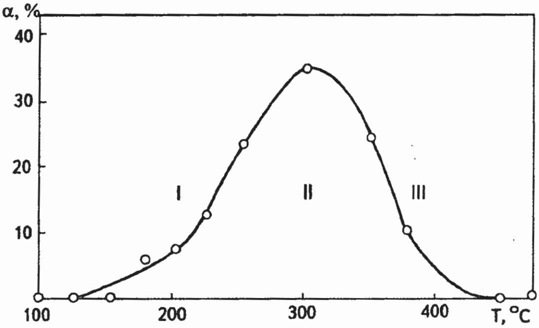


Fig.4. Conversion of acetone to isopropanol at 75⁰C *versus* the temperature of copper chromite pre-treatment with H_2.

Three activation temperature ranges in which the catalyst reveals different properties can be determined (Fig.4):

- 120-150°C - there is practically no conversion of acetone to isopropanol was observed;
- 150-420°C - conversion of acetone increases with the temperature, the maximum conversion being observed at 300-320°C; then it becomes very low;
- 420-450°C - the yield of isopropanol is brought to zero.

As mentioned above, the state of copper chromite in the hydrogen medium depends on temperature. The state reduced at 200-400°C is spinel with two above described types of hydrogen species dissolved in it; flat copper metal particles are formed on its surface. From the results described above it follows that this is the only state of chromite which catalyzes hydrogenation of acetone to isopropanol.

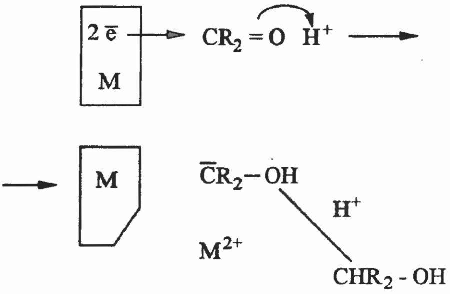
Next facts were obtained while studying the interaction of acetone and acetone and hydrogen with copper chromite in such state:

(1) In the hydrogen media bulk absorption of hydrogen in copper chromite takes place, at least a noticeable part of it (corresponding to approximately a half of the total copper in the chromite) is presented as protons, which makes it possible to consider the reduced chromite as a solid solution of chromic acid and copper chromite, i.e. "solid protonic medium";

(2) Formation of isopropyl alcohol occurs as a result of interaction of acetone with the reduced catalyst in the absence of gaseous hydrogen. The initial rate of alcohol formation coincides with the rate of the reaction between acetone and hydrogen.

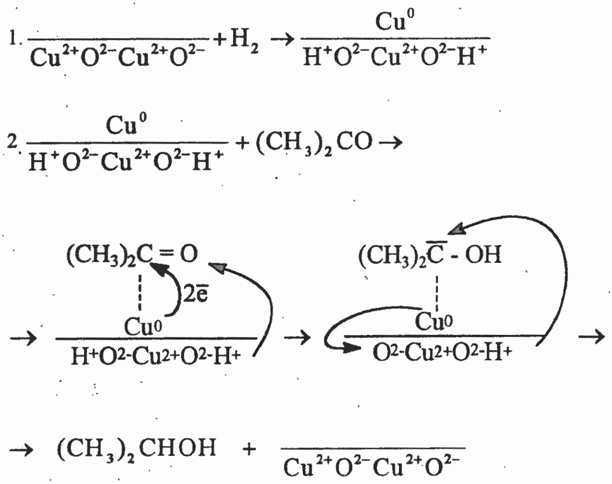
(3) Under acetone action transformation of the reduced catalyst to its oxidized state takes place.

We believe these facts allow us to discuss the mechanism of the reaction under study in terms of the ideas developed for liquid-phase reduction of ketones to alcohols with metals soluble in a "protonic medium" [15] (Scheme 1).



Scheme 1. Liquid-phase reduction of ketones to alcohols with metals soluble in a "protonic medium".

According to these ideas, the following scheme can be proposed for hydrogenation of acetone over copper chromite (Scheme 2):



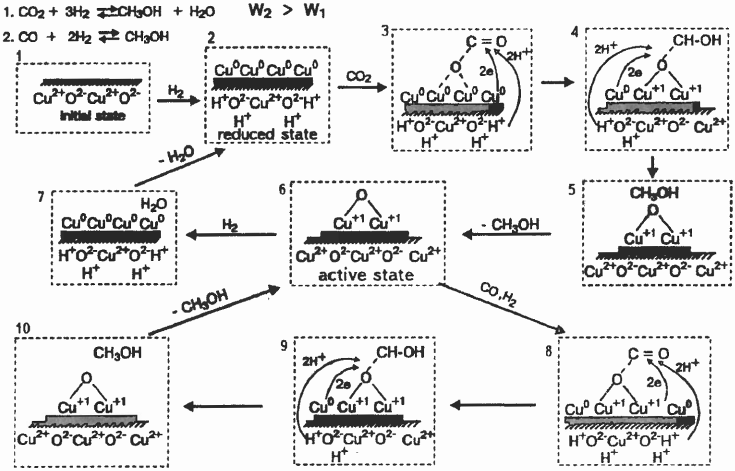
Scheme 2. Schematic presentation of acetone hydrogenation to isopropanol.

At the first stage the reduced state of chromite is formed upon the interaction with hydrogen that results in dissolving protons in the spinel. A corresponding amount of Cu^0 as epitaxially bonded flat particles is released at the surface.

The second stage is hydrogenation of acetone. It is known that acetone is adsorbed on Cu^0 atoms as π-complexes [16], electrons of the metal transfer to antibonding π-orbitals of the carbonyl group. Concurrently, a proton of the reduced chromite is inserted into an adsorbed acetone molecule. As a result, the organic molecule acquires a negative charge, and copper metal is oxidized and occupies the positions in the spinel structure it has left during the reduction. These transformations are followed by insertion of the second proton from the chromite and desorption of an alcohol molecule.

As shown, the catalyst is in its reduced state under the reaction conditions; hence, the second stage can be assumed to be the rate limiting. Under the conditions of catalytic hydrogenation, when there are both acetone and hydrogen in the reaction medium, it is most likely that only the protons located on the surface layer are involved in the transformations. Correspondingly, the reversible conversion of copper metal to its ionic state occurs only within the spinel surface layer.

Methanol synthesis. The investigation of interaction of reduced solid solution with CO, CO_2 and their reactions with H_2 allow to describe the mechanism of methanol synthesis by the next scheme (Scheme 3):



Scheme 3. Schematic presentation of the mechanism of the methanol synthesis.

1. Interaction of the solid solution of Cu^{2+} in a-m ZnO with hydrogen to generate the reduced state of the catalyst which is the solid solution with a proportion of copper ions substituted for protons and the corresponding amount Cu^0 located as an epitaxially bonded phase over the surface.

2. Adsorption of CO_2 on copper metal particles and its interaction with protons to produce methanol and oxygen-containing sites of the Cu^{+1}-O-Cu^{+1} type on the metal particle surface. Methanol is formed through a transfer of protons from the solid solution surface and electrons from Cu^o towards the adsorbed CO_2, like it was suggested for hydrogenation of acetone over chromite. Copper ions formed return in the solid solution.

3. Interaction of the oxygen-containing sites in the reaction medium proceeds along two paths:

a) CO is adsorbed on an oxygen ion as a fragment whose structure resembles the structure of the fragment formed upon adsorption of CO_2 on the metal ions. As a result, the CO molecule is rapidly hydrogenated to methanol as described above, the oxygen site being unchanged and capable again to activate CO molecules.

b) Oxygen ions interact with hydrogen to form water and Cu^0, the oxygen site disappearing.

The rate ratio for these paths determines the ratio of the rate of the formation of methanol from CO to that from CO_2. Apparently, the overall rate of methanol formation is to a great extent determined by the rate of CO hydrogenation; however CO hydrogenation is not possible but in the presence of CO_2 which provides generation of the oxygen-containing sites.

The catalyst in its reduced state, in which the metal particles have the oxygen-containing sites on their surface, should be discussed more carefully. This is an intermediate state formed during the reaction of methanol synthesis from CO_2 and H_2: the oxygen-containing sites appear during the formation of methanol and disappear at the interaction with protons or other activated hydrogen species to form water. However, this is the active state of the catalyst for synthesis of methanol from CO and H_2. The formation of water causes destruction of CO activation sites.

Based on the data obtained, it can be concluded:

Synthesis of methanol can be achieved with both CO_2 and CO as a feedstock, although the latter case needs the presence of CO_2, which provide the appropriate oxygen coverage of the surface.

Copper ions are active in oxide compounds in which they can be reduced to metal under the action of hydrogen to generate protons and be oxidized upon the interaction of protons with the molecules hydrogenated.

5. Conclusions

The results obtained allow the conclusion that two copper-containing oxides of different nature, copper chromite and anomalous solid solutions of Cu^{2+} ions in a-m ZnO, behave similarly for the interaction with hydrogen at temperatures below 400-450°C. The oxides dissolve hydrogen, which is partially consumed to reduce copper ions of the oxide and transformed to protons; the copper ions form a Cu^o phase epitaxially bonded to the oxide surface.

Hydrogenation of carbon oxides and acetone is the result of the ability of copper ions in copper containing oxides to generate copper metal and protons and to become back copper ions after completing the catalytic cycle.

Activation of acetone and CO_2 may occur by the interaction with copper atoms. Activation of CO may happen over oxygen-containing sites of the Cu^{+1}-O-Cu^{+1} type generated through oxidation of copper Cu^0 with CO_2.

Such mechanisms are practically identical to the mechanisms of C-O bonds hydrogenation in organics, which proceeds in acid medium in the presence of dissolving metals.

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AN ANALYSIS OF THE ASPECTS THAT AFFECT THE SELECTIVE OXIDATION OF C_1-C_5 PARAFFINS

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Abstract

This review examines some aspects in the development of heterogeneous catalysts for the oxifunctionalization of light paraffins. The state-of-the-art in paraffin oxidation and some aspects that affect the catalyst performance are discussed. The main aspects in the reaction network related to paraffins oxifunctionalization are also examined.

Introduction

Catalytic oxidation is a very important technology, widely employed for the functionalization of alkenes and aromatics, the most important raw materials for the petrochemical industry. In the future, however, the petrochemical industry will probably move towards the direct use of alkanes, which are more economical than the corresponding olefins, readily available raw materials with low toxicity as compared to aromatics.

The best known oxidation of a lower alkane is the selective oxidation of *n*-butane to maleic anhydride (1). This process is the only selective gas-phase alkane oxidation that has been commercialized. The apparent paradox of catalytic chemistry, that higher yield and selectivity to maleic anhydride are obtained in the oxidation of *n*-butane than in the oxidation of butenes, opens up the possibility that, with the choice of a suitable catalyst, experimental conditions and reactor technologies, it may be possible to obtain a better performance in the selective oxidation of other alkanes rather than in that of the relative olefins.

Over the past 15 years many examples of catalysts active in the selective oxidation and oxidehydrogenation of paraffins have been reported in patents and in scientific publications. However, low yields in the final product are frequently observed and, in almost all cases, the productivity of these processes is far from values of industrial interest. These low values may be due to different aspects, such as i) the low stability of the desired product, which under the conditions which are necessary for the activation of the paraffin may be more reactive than the reactant itself; ii) the nature of the mechanism of paraffin activation, which may lead to the presence of parallel undesired reactions of combustion over the paraffin, or of formation of other undesired products; iii) the steps involved in the mechanism of paraffin transformation to the products.

The present work is an attempt to analyze some of the chemical and technical aspects that affect the selective oxidation of paraffins.

State-of-the-art and challenges in the oxifunctionalization of paraffins

Table 1 summarizes the reactions of oxidation of alkanes which are actually employed in the petrochemical industry, as well as those that are under study and development (for the synthesis of intermediates and of base building blocks, i.e. olefins).

Table 1. Industrial processes and processes under study or development for the oxifunctionalization of light paraffins (C_1-C_6) in the petrochemical industry.

Raw material	**Product**	**Phase**	**Stage of development**
Methane	Chloromethanes	Gas, heterog.	Industrial
Methane	Methanol	Gas, het./hom.	Pilot plant
Methane	Syngas	Gas, het./hom.	Pilot plant
Methane	Ethylene	Gas, het./hom.	Pilot plant
Ethane	1,2-Dichloroethane, Vinyl chloride	Gas, heterog.	Research
Ethane	Acetic acid	Gas, heterog.	Research
Ethane	Ethylene	Gas, het./hom.	Research
Propane	Acrylic acid	Gas or liquid	Research
Propane	Propyl alcohol	Liquid, het. or hom.	Research
Propane	Acrylonitrile	Gas, heterog.	Demonstration plant
Propane	Propylene	Gas, heterog.	Research
n-Butane	Butadiene	Gas, heterog.	Industrial, abandoned
n-Butane	Acetic acid	Liquid, homog.	Industrial
n-Butane	Maleic anhydride	Gas, heterog.	Industrial
Isobutane	Methacrylic acid	Gas, heterog.	Pilot plant
Isobutane	Isobutene	Gas, heterog.	Research
Isobutane	*t*-Butyl alcohol	Liquid, het. or hom.	Research
n-Pentane	Phthalic anhydride	Gas, heterog.	Research
Cyclohexane	Cyclohexanol, one	Liquid, homog.	Industrial
Cyclohexane	Cyclohexanone	Liquid, het. or hom.	Research

Het./hom. indicates the likely presence of a mechanism initiated on the catalyst surface and transferred in the gas phase.

It is generally agreed that the possibility of wide industrial development of processes from light alkanes is strictly related to a profitable ratio between the costs of natural gas and of oil, and to the possibility of construction of the plant in a country where natural gas is available at low cost, or at least not far from the deposit, in order to lower the high penalty associated with transportation costs. From the process technology point of view, the least expensive solution is represented by the use of the same reactor and separation technology which are now used for the conventional process, with only minor expenses for revamping. This is the case of the ammoxidation of propane to acrylonitrile, where comparable reaction conditions might allow the use of the same reactor as for propylene ammoxidation, and a similar distribution of products might lead to only minor modifications in the separation section.

In some cases a solution can be represented by integration of the oxidation plant with a process that employs the product of partial oxidation itself, and that can operate without purification of the effluent stream of the oxidation reactor. This might facilitate the process flow-sheet, with less investment and operating costs. Different kinds of process integrations are under study or development; some examples are as follows:

1) Synthesis of 1,2-dichloroethane
$C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O$;
$C_2H_4 + 1/2O_2 + 2HCl \rightarrow C_2H_4Cl_2 + H_2O$

2) Synthesis of acrylonitrile
$C_3H_8 + 1/2O_2 \rightarrow C_3H_6 + H_2O$;
$C_3H_6 + 1/2O_2 + NH_3 \rightarrow C_3H_3N + 3H_2O$

3) Synthesis of methacrylic acid
$i\text{-}C_4H_{10} + 1/2O_2 \rightarrow i\text{-}C_4H_8 + H_2O$;
$i\text{-}C_4H_8 + 3/2O_2 \rightarrow C_4H_6O_2 + H_2O$

Sometimes the advantage in the development of a process of direct paraffin oxidation is not merely economic, but might be driven by higher process simplicity and safety, and by the use of less harmful raw materials and intermediates. This is the case of the synthesis of methyl methacrylate, which is actually produced at relatively low cost, with completely damped investment costs, but with a rather complex process, and with high negative environmental impact due to the use of toxic chemicals. The direct oxidation of isobutane to methacrylic acid might thus constitute a valid alternative to the industrial process (2).

From the catalyst point of view, the targets that if reached would allow transfer of the reactions actually under research to industrial exploitation are the following:

1) *Achievement of high productivity and/or high selectivity to the desired product.*
In most cases which are still at the research stage, the main problem is the development of a catalyst with good catalytic performance, in terms of both activity and selectivity to the desired product, in order to obtain acceptable levels of productivity and reduce the operating costs associated with purification of the product and possible recycle of the unconverted reactant.

2) *Development of stable catalysts*, which exhibit an overall industrially acceptable lifetime, and that can be easily regenerated. Necessity exists for the development of particularly active catalysts, able to activate the paraffinic substrate at relatively mild reaction conditions, under which the catalyst itself is structurally stable. This is the case of $(VO)_2P_2O_7$, the only catalytic

system active and selective in the oxidation of *n*-butane to maleic anhydride. The structural organization into a mixed oxide with a peculiar combination of acid and redox properties allows the paraffin to be activated selectively under conditions at which the catalyst is stable.

3) *Development of oxidation catalysts able to quickly furnish high amounts of oxygen* to the activated paraffinic substrates without undergoing structural collapse, and able to quickly recover the original oxidation state by contact with molecular oxygen. This would allow two-stage oxidation of the organic substrate (i.e., in circulating fluidized bed reactors), thus achieving better control of the selectivity (3).

From the reaction point of view, targets to be reached are the following:

1) *Absence of CO among the by-products.* In the oxidehydrogenation of light paraffins to olefins, the by-products CO_2 and CO can be easily separated from the paraffin/olefin mixture by absorption in basic water and in a demethanizer column under pressure, respectively. However, in the case of methane oxidative coupling or ethane oxidative dehydrogenation the separation of CO from the unreacted paraffin and from the produced olefins may become rather expensive.

2) *Absence of traces of corrosive by-products* (i.e. organic acids) when the reaction is aimed at the synthesis of products which are themselves non-corrosive, i.e. olefins. This might allow considerable savings in the cost of materials for construction of reactors and downstream apparatus.

Role of the stability of the product

There is no doubt that one reason why the only industrial process for selective oxidation of a paraffin is the synthesis of maleic anhydride from *n*-butane relates to the stability of the product. Notwithstanding the stability of maleic anhydride, many improvements in the process and modifications in catalyst composition have been aimed at lowering the extent of maleic anhydride decomposition. For instance the tuning of P/V ratio, the activation procedure and the addition of promoters operate to lower over-oxidation at high conversion.

The products obtained on V/P/O mixed oxides active and selective in *n*-butane oxidation are compared in Table 2 with those obtained in the heterogeneous oxidation of other paraffins in almost analogous conditions. These data indicate that V/P/O mixed oxides activate paraffins but some of the products formed can be easily oxidized to carbon oxides. Higher selectivities are possible only when products more stable against further oxidation are formed, such as anhydrides or nitriles. Thus, these results indicate that the drastic differences in the products obtained cannot be attributed to a different mechanism of activation of paraffins, but rather are due to the differences in the intrinsic sensitivity to further unselective oxidation of the reaction products. V/P/O catalysts can also be selective in the oxidation of ethane to acetic acid and of propane to acrylic acid, but only when very mild conditions are used, at which the products can be saved from consecutive unselective degradation. Under these conditions the conversion of the paraffin is usually very low, while in the case of the synthesis of anhydrides from C_4 and C_5 paraffins, very high conversions of the hydrocarbon can be reached.

Table 2. Type of products obtained on V/P/O catalysts in the oxidative transformation of various paraffins.

Paraffin	**Products**
ethane	CO_X > acetic acid
propane	CO_X > acrylic acid
propane + NH_3	acrylonitrile ≈ CO_X
n-butane	maleic anhydride > CO_X
n-pentane	phthalic and maleic anhydrides > CO_X
n-hexane	CO_X
cyclohexane	benzene

In the case of propane, research for the development of catalysts selective in the oxidation of this paraffin began long ago; however, because the oxygenated products, such as acrolein, are easily further oxidized once formed, sufficient yields of partially oxidized products have not been attained. Therefore, the catalytic ammoxidation of propane to acrylonitrile, which is more stable than acrolein against further oxidation, has been a main issue (4). For example, a comparison between oxidation and ammoxidation of propane on Sb/V/O-based catalysts shows that in the oxidation of propane only the formation of carbon oxides is detected, while in the ammoxidation reaction, acrylonitrile is selectively formed.

The same occurs in the oxidehydrogenation of light paraffins to olefins (5). Propane and butanes are more reactive than ethane because secondary C-H bonds are more reactive than primary ones, but due to the presence of allylic carbon atoms on the olefins formed, these products are also susceptible to oxygen insertion, resulting in the formation of co-products such as aldehydes, ketones, and acids along with the olefins. These may be precursors for the formation of carbon oxides, especially if hard reaction conditions are needed to activate the paraffin. Thus, high selectivities can be obtained only to ethylene from ethane and to butadiene from *n*-butane, while the lowest selectivity is obtained in isobutene production where two allylic hydrogen positions are present.

Reaction network in the oxidative transformation of saturated paraffins to unsaturated oxygenated compounds

At least two steps can be formally distinguished in the mechanism of the single-stage transformation of a paraffin to unsaturated oxygenated compounds: i) a first step of paraffin functionalization with hydrogen abstraction and formation of a double bond, and ii) a second step of transformation of this more reactive hydrocarbon to the final desired compound. The entire mechanism may occur on the catalyst surface, and it can be reasonably hypothesized that the first step is slower than the second one, on the basis of the lower reactivity of the paraffin with respect to the olefin (i.e., C-H bonds in allylic carbon atoms are more labile than C-H bonds in the corresponding paraffins). Therefore, assuming a slower rate for the first step, there is no desorption of the intermediate olefin because under the conditions at which the adsorbed olefin-like compound is formed, it is soon converted to the final product. This is the case of the oxidation of *n*-butane to maleic anhydride, where the reaction mechanism involves the likely formation of a butene- or butadiene-like intermediate compound, but no olefin is detected among the reaction products.

There are however some cases where this does not occur. For instance, in the case of the ammoxidation of propane to acrylonitrile, propylene is always obtained among the reaction products, and in the oxidation of ethane to acetic acid ethylene is also obtained in small amounts. While in the latter case the low reactivity of ethylene can be responsible for its desorption, in the former case it would be expected that propylene were completely transformed to acrylonitrile.

This aspect is very important because desorption of the intermediate olefin, and its low reactivity under the conditions employed, may constitute a limit to the maximum achievable selectivity to the desired product. Therefore, in addition to the problems associated with the presence of consecutive reactions of oxidative degradation upon the desired product (from this point of view the formation of stable molecules, such as anhydrides or nitriles, rather then aldehydes or acids, is a more favourable situation), and the undesired contribution of parallel reactions of paraffin combustion, the third aspect affecting selectivity is the desorption of the olefin-like intermediate.

The surface properties of the catalyst play an important role in affecting these aspects. For instance, an acidic surface may be important in the desorption of acids or anhydrides, while basic surfaces are necessary to accelerate the desorption of a nitrile and avoid its consecutive combustion. However, those properties that may favourably affect the final desorption of the desired product may also favour the desorption of the basic olefin, and avoid its further adsorption and conversion. This may justify the presence of propylene among the reaction products in the synthesis of acrylonitrile, and may explain the absence of olefins among the products in the synthesis of maleic anhydride from *n*-butane. The well known surface acid properties of vanadyl pyrophosphate, the active catalyst in this reaction, favour the interaction of the surface with the intermediate butene-like compound and its further evolution to the final product.

The need for multifunctional catalyst properties

Successful catalysts for the transformation of alkanes to unsaturated oxygenated compounds exhibit multifunctional properties, which are needed to activate the paraffin and perform multielectron oxidation. For instance, V/Sb/O-based catalysts, originally claimed by Sohio for the ammoxidation of propane, can be considered intrinsically multifunctional since both dehydrogenation and nitrogen insertion functions are present. The main problem of this type of catalyst is the low rate of the consecutive ammoxidation of intermediate propylene. Indeed, propylene is always present as a by-product. The same can be stated for catalysts disclaimed by Mitsubishi Kasei Company, consisting of Mo/V/Te/Nb mixed oxides (6). The catalytic system developed gives the highest yield to acrylonitrile to date.

Other examples of catalytic systems which are characterized by intrinsic multifunctional properties are vanadyl pyrophosphate (the industrial catalyst for the oxidation of *n*-butane to maleic anhydride), and transition-metal-modified 12-molybdophosphates (heteropoly-compounds) for the oxidation of isobutane to methacrylic acid (7). The multifunctional nature of the V/P/O system has been confirmed by the oxidation of model compounds where the different steps in the reaction pattern have been singled out. The high selectivity obtained for each reaction provides evidence of the multifiuctional nature of V/P/O catalysts. Heteropolycompounds are still far from industrial application for the oxidation of isobutane, but they are recognized to be the best system for the activation of this paraffin. In these cases, it is likely that a combination of properly tuned acid and redox properties are necessary in order to obtain active and selective catalysts.

The concept of multifunctionality is not enough to design optimal catalysts. Indeed, at present no adequate catalyst has been found for the oxidation of propane to acrylic acid and of ethane to acetic acid; also in the case of isobutane, too low yields are yet obtained for a commercial development. The multifunctionality must be accompanied by other properties, which allow multi-step transformation of the paraffin to be carried out i) without letting desorption of any intermediate occur, and ii) through the proper sequence of dehydrogenation and oxygen insertion reactions.

As mentioned above, in the oxidation of paraffins the slow step of the reaction must be the alkane activation or, at least the reoxidation of the catalyst. In other words, once the alkane has been adsorbed and transformed to the first intermediate species, the latter has to be quickly transformed up to the final stable product by neighbouring specific active sites. If this requirement is not met, the adsorbed intermediate (possibly an olefin-like species) may desorb; this leads to a lower selectivity to the final desired product, due both to the presence of unconverted olefin, and because the olefin may be readsorbed on non-specific oxidizing sites yielding other undesired products (aldehydes or acids), which can also be precursors for the formation of carbon oxides. For this reason, the multifunctional centers of the catalyst must be arranged so as to favour the quick transformation of intermediates, avoiding their desorption and the occurrence of undesired side reactions.

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PL-23

PARTIAL OXIDATION OF HYDROCARBONS. KEYS TO THE SELECTIVITY

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Partial oxidation of hydrocarbons is a route for direct synthesis of variety of important industrial products (aldehydes, acids, anhydrides, nitriles).Selectivity is the crucial parameter of the processes of partial oxidation, as it very often determines economical viability and environmental impact of the process.

The major difficulty to maintain a high selectivity during partial oxidation arises from the difference of the stability and the chemical reactivity of hydrocarbons and products of partial oxidation. As usually the latter are less thermally stable and more reactive, inclining to further oxidation into products of complete oxidation. Investigations of the mechanism of partial oxidation of hydrocarbons and catalysts properties controlling selectivity reveal, that two major routes exist to overcome this difficulty, which will be considered in this presentation.

1. First route involves a specific activation of hydrocarbon on the catalyst surface (predominantly on the acid-base sites) with the formation of reactive intermediates, which can be oxidized by electron - acceptor centers of the catalyst. Formation of oxy-product occurs as a results of incorporation of lattice oxygen in the intermediates. This route doesn't require a presence of active oxygen species neighboring to the adsorbed hydrocarbon, as it can cause a loss of selectivity. In order to provide a high selectivity, activation of hydrocarbon and oxygen must occur on separate sites on the catalyst surface. Experimental studies show that selective catalysts working by this way possess the ability to activate hydrocarbons and to transport effectively oxygen through the lattice (so, the oxygen activation can proceed on sites remote from the sites of hydrocarbon activation). This route is effective for the partial oxidation of hydrocarbons with relatively high C-H bond reactivity. So, the reaction can proceed at moderate temperature, when a product of partial oxidation is relatively stable.

2. Second route includes formation on the catalyst surface of highly reactive oxygen species, which can oxidize hydrocarbon even without their preliminary activation. The formation of these very active oxygen species can proceed on reduced sites on the catalyst surface (preferably, isolated sites in order to avoid fast complete reduction of oxygen into lattice ions). Experimental results confirm that this mechanism takes place for the partial oxidation of methane.

This way seems to be the only choice for partial oxidation of hydrocarbons with low C-H bond reactivity (as its activation which is necessary for the 1-st route can be effective at rather high temperature, where the reaction product is unstable). In this case catalyst must be able to perform partial oxidation at a very short residence time otherwise selectivity will be poor due to consecutive oxidation of the desirable product.

PL-24

Synthesis, Characterization and Catalytic Behavior of Vanadium Substituted Mesoporous Molecular Sieves (V-MCM-41)

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The selective catalytic oxidation of organic compounds by oxygen in the gas phase and by hydroperoxide in the liquid phase are reactions of practical significance. Among oxidation catalysts, zeolites and molecular sieves with transition metal incorporated into the lattice have attracted increasing attention in connection with their remarkable catalytic activity for partial oxidation of hydrocarbons under mild conditions. Incorporation of transition metal into the zeolite framework creates isolated active centers in an ordered matrix. Coordination and stabilization of the transition metal ion by the zeolite lattice can significantly affect its catalytic behavior and lead to catalysts with new and often improved properties. Vanadium silicalite is known to be an excellent hydrocarbon oxidation catalyst utilizing hydrogen peroxide [1,2].

While in the past, heterogeneous catalytic oxidation has been dominated by gas-phase reactions, recent developments have stimulated new interest in liquid phase reactions [3]. Large organic molecules are sterically hindered in medium-pore zeolites, and this limits the usefulness of these catalysts to the oxidation of small organic compounds. While there are available a large number of mesopore (20-200 Å) oxide catalysts and/or supports, these materials almost always have a wide distribution of pore sizes, relative to zeolites, which possess very uniform micropores (2-20 Å). It is generally presumed that a mesoporous material with uniform pores would have wide utility in catalysis.

Recently, a new family of mesoporous molecular sieves, designated as MCM-41, was discovered by Mobil scientists [4,5]. This material has a one dimensional, uniform hexagonal mesopore structure. It bridges the gap between amorphous materials and zeolites. Moreover, by using the liquid crystal template (LCT) mechanism, the pore size may be varied by changing the surfactant chain length. There is no doubt that there exists a strong incentive to synthesize metal incorporated zeolites with larger pores which can deal with bigger molecules.

Moreover, theoretically, the most important structural factor in zeolites is known to be the T-O-T angle. The effect of chemical factors may be tested with many conventional zeolites with different cations for a given structure. However, there is no simple way to vary the T-O-T angle without also changing the structure of the zeolite. MCM-41 may provide such an opportunity. In the current research, we have carefully characterized the structure of

V-MCM-41 and systematically investigated the catalytic behavior of these materials in both gas phase and liquid phase reactions.

Synthesis

The V-MCM-41 samples were synthesized by using surfactants of different chain length and also different loading of vanadium to systematically vary the pore size and metal loading of these materials. Moreover, they were synthesized by the so-called direct synthesis method under sodium free conditions. $VOSO_4 \cdot 3H_2O$ was used as the vanadium source, and it was added directly into the silica and surfactant mixture during the process of preparing MCM-41 materials as described by Beck et al. [5]. After hydrothermal synthesis, the materials were calcined at 540°C within a period of 26 hrs. The initial characterization was performed with small angle X-ray diffraction and argon physisorption to detect the uniform mesoporous structure. An intense peak in the low angle range of XRD profiles represents the regular spacing of hexagonal mesopores. By using the synthesis procedure described above, a slight decrease in the d spacing of V-MCM-41 is noticed as compared with siliceous MCM-41 counterparts prepared with the same surfactants. This is contrary to what would be expected because the V-O bond length is longer than that of Si-O. However, if the effect of local bond angle is considered, changes of these angles due to the incorporation of vanadium ion may compensate the increase of the bond length [6]. Furthermore, the XRD peaks are broader than those for the pure siliceous MCM-41 counterparts indicating a decrease in the structural regularity. Argon adsorption isotherms also confirmed the uniform mesoporous structure by a step increase of capillary condensation in the range expected for mesopores.

Characterization

In order to get information on V incorporation and the local structure around V, further characterization has been carried out on these samples. Vanadium model compounds which have well defined local symmetry are extremely useful for interpreting the results. They were also studied together with the MCM-41 samples by using diffuse reflectance UV-visible (DRUV) spectroscopy, solid state ^{51}V NMR and X-ray absorption spectroscopy.

Among the model compounds, V_2O_5 has a nearly square-pyramidal geometry around vanadium, consisting of four V-O bonds of similar length and a very short V=O bond. Alternatively, the environment could be considered as six-coordinate, if the very long second axial V-O bond is included. Metavanadates such as PbV_2O_6 or ZnV_2O_6, have a structure of strongly distorted octahedral pairs sharing corner oxygen atoms. Monomeric orthovanadates such as Na_3VO_4 and $Mg_3(VO_4)_2$ have a structure formed by isolated tetrahedrally coordinated V ions in nearly a symmetrical environment. Another type of metavanadates such as NH_4VO_3, KVO_3, $NaVO_3$, also have a tetrahedral environment but are strongly distorted and share two bridging oxygen with other polyhedra.

In DRUV characterization, most authors rely upon a relation between domain size and the optical bandgap energy of an insulator or semiconductor [7]. Theoretically, as in the case of a particle-in-a-box, where the separation between energy levels decreases with the increasing box size, the bandgap energy of a real system decreases as the domain size increases. The UV spectrum of vanadium consists of lower-energy charge-transfer (LCT) bands associated with an O to V electron transfer when the optical bandgap energy is represented by the energy edge. The edge position was determined in the classical fashion for allowed transitions [8,9] by finding the energy intercept of a straight line fitted through the low energy rise in the graphs of $[F(R_\infty) \times h\nu]^2$ vs. hν, where $F(R_\infty)$ is the Kubelka-Munk function for an infinitely thick sample and hν is the energy of the incident photon.

The domain size, or so called molecular cage size, could be defined by the nearest neighbor ligands (oxygen in this case) coordinating the vanadium center. Obviously the domain size is closely related to the local symmetry of vanadium. If we go further, the domain size can be described as an average bond distance, as proposed by Wong et al. [10]: $R=(1/n)\sum_i^n R_i$, where n is nearest-neighbor bonds. This size parameter is also calculated for all model compounds and listed with the local symmetry in Table 1.

Table.1 The relationship between domain size (local symmetry) and UV absorption edge & XANES pre-edge peak intensity on vanadium model compounds and V-MCM-41 samples.

Vanadium Model compounds and V-MCM-41 samples	Local Symmetry	Domain Size / Å	UV Edge Energy / ev	XANES Pre-edge Peak Intensity / a.u.
NH_4VO_3	Distorted Tetrahedra	1.735	3.30	0.720
Na_3VO_4	Distorted Tetrahedra	1.760	3.27	0.714
$Mg_3(VO_4)_2$	Distorted Tetrahedra	1.760	3.27	0.714
V_2O_5	Square Pyramidal	1.978	2.25	0.534
PbV_2O_6	Distorted Octahedra	2.075	2.00	0.376
V-MCM-41(C_8-C_{16})	Distorted Tetrahedra	< 1.735	3.35	0.676

As may be seen in agreement with the theory, the edge energy decreases monotonically with the increase of the domain size. In other words, the edge energy experiences a large shift (about 1.2 ev) as the local symmetry of vanadium changes from tetrahedra to octahedra. For real samples, this principle can easily be used to determine the local structure. Apparently, from Table 1, the vanadium ions in these calcined hydrated samples are tetrahedrally coordinated by oxygen, which is a strong indication of framework incorporation. On the other hand, the water ligands must not be attached directly to the vanadium center because this would affect the tetrahedral symmetry.

Vanadium is a favorable nucleus for NMR observation because it is % 99.8 abundant and has a large magnetic moment and a short spin-lattice relaxation time. The ^{51}V nucleus possesses a nuclear electric quadrupole moment (spin $I = 7/2$) in the medium quadrupole category ($0.1<Q<1.0$). Static wide-line ^{51}V NMR may provide further information on the local symmetry of vanadium through the line shape of the powder pattern. The two main interactions which affect the NMR line shape of vanadium species are quadrupolar interactions and chemical shift anisotropy (CSA). Fortunately, these interactions have opposite dependencies on the applied magnetic field strength. When the strength of the applied magnetic is increased, the CSA begins to dominate the quadrupolar interactions. At very high field, such as 11.7 T used here, the quadrupolar interactions are negligible, and the lineshape may be interpreted based on CSA of the central transition alone (+1/2,-1/2).

A large variety of vanadium model compounds have already been studied with ^{51}V NMR by [11]. The CSA value corresponds to different levels of electronic shielding, which is related to the local symmetry type. Usually octahedral structure has much higher value of CSA than the tetrahedral structure. The static and MAS ^{51}V NMR spectra of a series of vanadium samples with varied pore sizes were obtained. The spectra of V-MCM-41 samples are characteristic of a chemical tensor with axial symmetry. As the pore size becomes smaller, the ^{51}V powder pattern becomes broader, indicating a more distorted local environment. The CSA value may be either obtained directly from the powder pattern or can be calculated from the intensities of the spinning side bands in the MAS spectra [12]. Here MAS spectra not only serve this purpose, but are also useful to determine the isotropic chemical shift and to distinguish crystallographically different sites existing in the structure. By comparing the CSA value of V-MCM-41 samples with the model compounds, the vanadium in V-MCM-41 is mostly tetrahedrally coordinated with oxygen, obviously there is no separate phase of V_2O_5 outside the framework. This supports the conclusion obtained by DRUV. Moreover, from MAS NMR, only one unshifted peak is found after varying the spinning speed, indicating isolated equivalent vanadium sites in these samples.

The first row transition elements have well defined site symmetry spectra in the X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (XAFS). XANES spectra are sensitive to structural symmetry since XANES fundamentally originates from the transitions of a core electron to an empty state. In particular, features of vanadium K-edge XANES spectra vary significantly with geometry and valency of the vanadium present. The pre-edge peak is attributed to the so called 1s-3d transition, which is mainly caused by mixing of 2p orbitals of the oxygen with the 3dp orbitals of vanadium ions. It is proposed [13] that d-p mixing suggests the presence of terminal oxo group (V=O). The same series of model compounds were used as references in XANES for comparison. Empirically, the strength of the pre-edge transition is found to be dependent on the size of the "molecular cage" as well. Wong et al. [9] provided a theoretical basis for the correlation between the pre-edge intensities of different vanadium oxides and the domain size.

Among the model compounds, an almost linear decrease of the pre-edge peak intensity is found with the increase of the domain size. The results, including V-MCM-41 samples are summarized in the Table 1 also. Since XANES shows the overall features of the system, the difference in the pre-edge intensity between V-MCM-41 and tetrahedrally coordinated model compounds might be due to a small portion of octahedral species with water coordination, which has not been detected by the UV edge shift, in these hydrated samples. After dehydration, the pre-edge intensity becomes greater and approaches that of model compounds with tetrahedral symmetry.

X-ray absorption fine structure (XAFS) can offer quantitative information on local ligand environment. The XAFS was performed on one of the V-MCM-41 samples (C_{16}). The average bond length and coordination number were obtained by analyzing the spectra using a program package of the University of Washington: average bond length = 1.72 Å, CN = 4.39. This result agrees perfectly with the UV analysis.

Catalytic behavior in gas and liquid phase reactions.

Alcohol oxidation in the gas phase

First of all, in order to count the in-situ active vanadium sites in these mesoporous materials, the samples were initially reduced by one of the reactants (methanol or ethanol) instead of by hydrogen under reaction conditions. The oxygen uptake was then measured by sending pulses of oxygen over the sample and the oxygen uptake used as a measure of site density.

In the gas phase, catalysts were tested for both methanol and ethanol oxidation. The reaction was studied under different contact times, which were manipulated by changing the flow rate of reactants, at each temperature. As for methanol oxidation, the methanol (total) turnover frequency and turnover to the main product (formaldehyde) were calculated directly from the slope of the linear regime in the kinetic region to assure that the turnover frequency does not depend on the conversion or yield. Moreover, the turnover frequency was normalized by the active sites which were measured by the oxygen uptake.

The samples were investigated systematically with different pore size and metal loading. An effect of pore sizes and loading on catalytic activity were found on these materials. Figure 1 shows the correlation between turnover frequency to formaldehyde and pore size calculated from XRD d spacing. A strong effect of pore size on catalytic activity was found on the vanadium series samples, note that the turnover frequency increases with the increasing pore size to a maximum then decreases. If we consider this pattern as a volcano curve, then the activity must be affected by the metal oxygen bond strength, and further we assume that the bond strength is related to the change of local bond angles of O-V-O as the ring size changes. It is known that the most important structural factor in zeolites is the T-O-T angle. Another project from our group [6] demonstrated that the acidity of alumina incorporated MCM-41 was affected when the pore size was varied in the same range. In the case of Al, the pore size is an important variable because it is related to acidity through the effect of this structural parameter on the Si-OH-Al bond angle. A similar effect is expected for Si-O-V. When the T-O-T angle is varied, the fundamental chemical variable is the change in the relative participation of s, p and d orbitals in the bonding. In the case of Si-OH-Al, this is reflected in the acidity of the proton on the bridging hydroxyl; in the case of Si-O-V, this should be reflected in the oxidation potential of the vanadium which will quite naturally affect the activity of the V in the catalytic oxidation. We believe that the activity of these catalysts can be "tuned" by varying pore size. Thus we will take advantage of this effect and investigate the catalytic behavior of V-MCM-41 samples in liquid phase oxidation. On the other hand, the effect of metal loading on catalytic activity was also investigated and it is found that the catalytic activity decreases with increasing vanadium loading. The lower loading of vanadium produces samples with a higher fraction of isolated active sites.

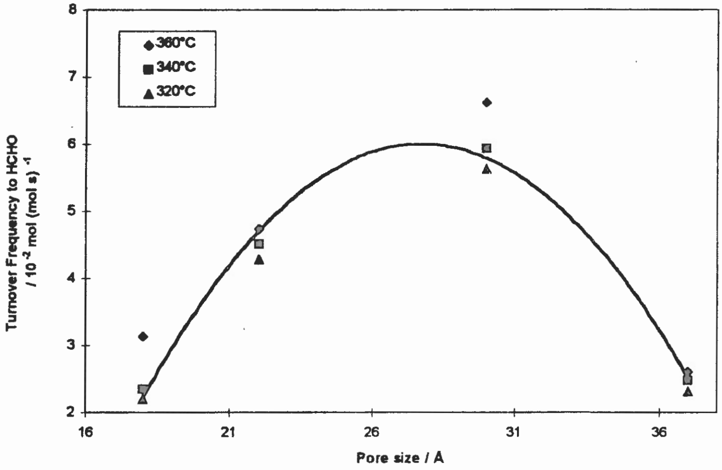

Fig.1 The effect of pore size on turnover frequency to formaldehyde (normalized by oxygen uptake) of methanol oxidation on V-MCM-41.

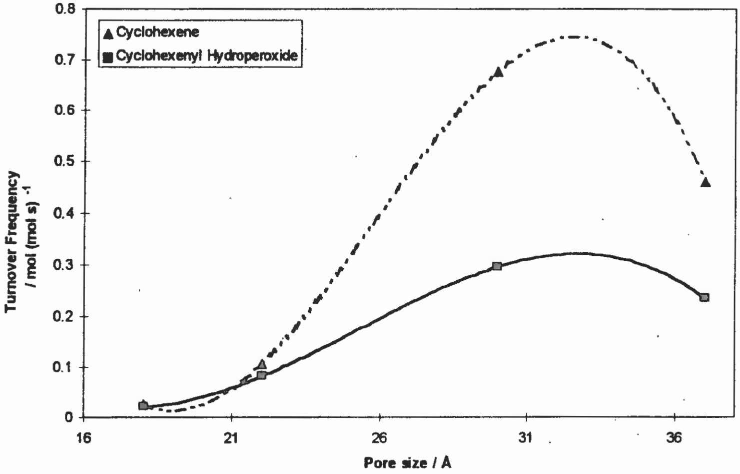

Fig. 2 The effect of pore size on cyclohexene turnover frequency (TOF) and TOF to cyclohexenyl hydroperoxide on V-MCM-41 at 60 °C

Liquid Phase Reaction

Liquid phase oxidation with H_2O_2 in the presence of V-containing silicalite have been investigated [1,2]. In the current study, reactions were carried out in a flask under reflux heated in a mineral oil bath.

Cyclohexene oxidation was carried out in acetonitrile at 60°C with V-MCM-41 of different pore sizes. The products have been analyzed by GC-MS and ^1H and ^{13}C NMR. The major product which is cyclohexenyl hydroperoxide has never been reported for this reaction. As might be expected, the cyclohexene (total) turnover frequency and turnover frequency to cyclohexenyl hydroperoxide follow the same trend as observed in the gas phase reaction for V-MCM-41 samples (shown in Figure 2). This indicates that the pore size also has a strong effect on catalytic behavior in liquid phase reactions.

The mechanism of cyclohexene oxidation proposed here is a free radical pathway. It is also found that the selectivity to epoxide increases if hydrogen peroxide is replaced by TBHP. This is consistent with the mechanism proposed since TBHP is more stable than H_2O_2. Furthermore, cumene oxidation was tested on V-MCM-41 samples since cumene hydroperoxide is an important industrial product. However, activity is quite low and the reaction conditions have not been optimized.

V-MCM-41 also catalyzes the phenol hydroxylation with hydrogen peroxide, the results show that the intrinsic activity is TS-1[14] > V-MEL [15]> V-MCM-41. It is difficult to explain these differences in view of the fact that TS-1 and V-MEL have a similar isolated coordination environment to that in V-MCM-41. It is probable that some of the vanadium sites are shielded and not accessible to reactants from the pore channels.

Conclusions

V-MCM-41 samples with different pore size have been synthesized. The vanadium ion was incorporated into the framework with tetrahedral symmetry. The pore size has a strong effect on catalytic activity of vanadium incorporated MCM-41. This may be related to the change of local bond angles of Si-O-V. The metal loading also has some effect on catalytic performance, lower metal loading produce samples with a greater fraction of isolated centers leading to higher activity. In the liquid phase oxidation, as expected, the pore size strongly affects the catalytic activity too.

Acknowledgment

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Direct Hydroxylation of Benzene to Phenol by Nitrous Oxide - From a Lab Curiosity to a Commercially Viable Process

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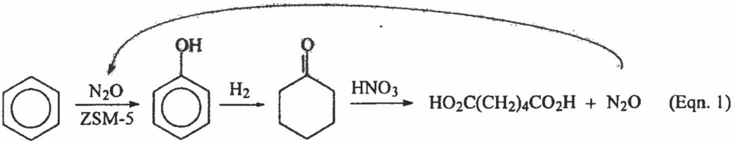
In the early 1990's, nitrous oxide was recognized as a greenhouse gas. It is co-produced in adipic acid manufacture in nearly an equimolar amount and much is emitted to the atmosphere. Several abatement technologies were sought and are in various stages of implementation by the major adipic acid producers. Monsanto chose to explore approaches more desirable than its current practice of reductive destruction of N_2O for this potentially valuable chemical.

Recent literature references to direct hydroxylation of benzene to phenol with nitrous oxide over a zeolite catalyst led us to an innovative adipic acid process concept in which the nitrous oxide could be fully utilized. Benzene could be hydroxylated to phenol with nitrous oxide; the phenol then reduced to cyclohexanone and cyclohexanol (KA); and finally the KA mixture would be oxidized to adipic acid with nitric acid and the co-product nitrous oxide could be recycled to the front end thereby closing the nitrogen cycle (Equation 1). If necessary, supplemental nitrous oxide could be deliberately produced. The phenol portion of the process concept offered significant safety and environmental improvements as well as cost advantages over the conventional cumene-based process.



The hydroxylation is a low pressure, vapor phase reaction with very short contact times. The process has outstanding safety features as it is maintained in the nonflammable region throughout. The benzene to phenol product molar selectivity is in the upper 90's. There are no large aqueous waste streams, inorganic salts or major co-products with which to contend. The productive use of the nitrous oxide waste from the adipic acid plant is another example of the green chemistry employed in the process.

In early 1994 Monsanto in cooperation with Boreskov Institute of Catalysis began commercial development and reached pilot plant demonstration stage by mid-1996.

The potential shape-selectivity of the zeolite framework plus the unique reactivity of the "alpha oxygen" show much promise for other applications.

PL-26

CONFINEMENT EFFECTS IN SORPTION AND CATALYSIS BY MOLECULAR SIEVES

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Molecular sieves, including zeolites, are distinct from other adsorbents and catalysts by the curvature at the atomic scale of the internal surface which they offer to the molecules they host.

Supramolecular interactions govern guest-host relationships between the molecular sieve framework and the substrate(s) in the free intracrystalline volume. By contrast to molecular shape selective effects which are mainly "negative" in their nature, imposing restrictions on sorbates, transition states, intermediates, or products, these supramolecular interactions lead to confinement effects of which the positive character favours adsorption of certain molecules vs. others, sometime at specific sites, stabilises transition states and decreases thereby activation energies for specific reaction pathways, and favours in some cases bimolecular reactions.

Confinement effects thus arise from the surface curvature of the zeolite pores and channels. The consequences of a quantitative model which we described in 1987-1988 are expanded in view of topics and examples selected from the recent literature dealing with sorption and catalysis by molecular sieves.

The following topics will be the backbone of this plenary lecture:

GENERALITIES
Guest-host interaction in zeolites: oxymoron or reality?
Molecular shape selectivity vs. confinement effects

PRINCIPLES

Van der Waals interactions as a source of confinement effects

Can physical confinement lead to electronic confinement

SORPTION AND ADSORPTION

Adsorption of hydrocarbons

Reasons for which the adsorption of ammonia and amines does not measure the real acid strength of molecular sieves

Confinement effects in the competitive adsorption of hydrocarbons

Use of confinement effects to tune the selectivity of zeolite membranes:

(i) reversing the selectivity, (ii) zeolite membrane switches

CATALYSIS

Testing zeolite catalysts: effect of the carrier gas

Zeolite acidity: strength or confinement effects?

Confinement effects explain reverse molecular shape selectivity

Confinement effects in zeolite catalysis for fine and specialty chemicals

VISTAS

New principles for zeolite catalysis in liquid phase

Assymetric synthesis with zeolites

Are zeolites solid pseudo-enzymes?

PL-27

STRUCTURE AND CHEMICAL TRANSFORMATIONS OF HETEROGENEOUS CATALYSTS UNDER THE INFLUENCE OF REACTION MEDIA

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Heterogeneous catalysts are formed usually with several components. Under the influence of the reaction media and reaction conditions significant changes of chemical and phase composition may take place in these multicomponent systems. As a result of this, the nature and structure of active centers of the catalyst can be changed too.

In the present report the following aspects of mentioned above problems are considered:

-the role of segregation processes in the creation of the active surface of the catalysts formed with intermetallic compounds and their hydrides;

-the oxide-oxide interactions influence on the structure and catalytic properties of systems containing iron, cobalt and nickel oxides;

-the reaction media influence on the composition, structure and activity of heterogeneous catalysts.

Isotopic Kinetics and Atomic-Molecular Mechanisms of Catalytic Reactions

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Abstract

Rigorous kinetic equations of isotope molecules distribution and redistribution due to chemical reactions are presented. This theory will allow to elucidate the atomic–molecular features of mechanisms of catalytic activation.

Isotopic methods play a great role in fundamental studies of catalytic reactions mechanisms (e.g. they are presented in 10–20% all of reports at International Congresses on Catalysis). G.K.Boreskov had made a outstanding contribution to development and application of labelled atoms in heterogeneous catalysis. Among more than 800 of his publications nearly 160 are devoted to the isotopic studies (see the bibliography in books [1,2]). This unique cycle of Boreskov's works that has no analogs in the world scientific literature, is an important part of his scientific heritage. Two main trends of Boreskov's scientific interests crossed here, namely catalytic reactions mechanism and isotopic methods. The result was the establishment of the well-known general regularities in heterogeneous catalitic reactions and the elaboration of the principal theoretical concepts concerning the nature of catalytic action. Author of the present report is related to the Boreskov's Isotopic School and is dedicating this work to the Memory of his Teacher.

The efficiency of isotopic methods in heterogeneous catalysis is well acknowledged. However up to now, traditional variants of methods did not allow to give a strong and complete description and interpretation of experimental data.

Character and quality of information obtained depend on used treatment of experimental data. Early complete and strict description of kinetics of distribution and redistribution of isotopic molecules was known for the simplest cases only:

a) heteroexchange in two component systems $X + RY = Y + RX$,

b) homoexchange of twoatomic molecules $X_2 + Y_2 = 2XY$,

where X and Y are isotopes. The isotopic exchange in both cases (**a** and **b**) is described with the only variable which depends on time exponentially (e. g. see [3]).

The rigorous isotopic–kinetical equations for hetero- and homoexchange of twoatomic molecules proceeding simultaneously were derived later [4–7]. There are two independent isotopic variables in this case and kinetical equations have more complex form.

Isotopic exchange of multiatomic molecules A_a $(a > 2)$ had no strict kinetic description up to now. The semiquantitative method proposed by Anderson and Kemball [8,9] is used to exchange of hydrocarbons C_mH_n with dideuterium D_2. The only attempt to describe redistribution of multiatomic isotopic molecules was made by Bolder, Dallinga and Kloosterziel [10,11]; however they considered some particular situations only and obtained very complex expressions.

Recently [12–15] the explicit system of isotopic–kinetic equations which describes the kinetics of redistribution of isotopes and isotopic molecules in general cases (without restrictions on molecule atomicity and reaction mechanism) was obtained. A crucially new feature in isotopic kinetics is concept of distribution atomicities for the quantitative characterization of atom rearrangement due to reaction [12]. Distribution atomicity a_{qp} is number of atoms of element A transited from initial molecule "q" to final molecule "p" by an elementary reaction act. These quantities and the principle of isotopic quasistationarity [15] form the basis for derivation of isotopic-kinetic equations of exchange of multiatomic molecules, e.g. methane [16,17]. It was shown [16,17] that kinetics of isotope redistribution is uniquely determined by the type of dissociation on catalyst surface. Thus proposed approach offers new possibilities for elucidation of catalytic activation mechanisms by isotopic methods — *methods of isotopic kinetics.*

The *usual* chemical kinetics deals with *chemical* molecules and describes their consumption and formation. Objects of isotopic kinetics are *isotopical molecules* and in addition to mentioned above it reveals such atomic–molecular features of reaction mechanism as a character of atoms rearrangements.

If atoms A of multiatomic molecules A_a (parts of molecules containing no A without limiting community have been omitted) are presented by two isotopes $A = X, Y$ we have $a + 1$ isotopic molecules $A_a = X_iY_{a-i}$

($i = 0, 1, \ldots, a$). Their mole fractions x_i are related by the normalisation condition (equation 1 in **Appendix**) so that number of independent variables x_i is equal to a. However isotopic–kinetical equations in terms x_i are too tremendous [11–13] and their application is very difficult. The analysis of the dependence between reaction mechanism and kinetics can be radically simplified if one substitutes variables x_i by new isotopic variables z_m determined by transformation presented in **Appendix** (eqs 3,4).

This transformations permit us to describe the kinetics of isotopic molecules redistribution due to any mechanism by a general set of equations in the simplest form:

$$N(dz_m/dt) = -A_m \rho z_m + f(s, z_{m-1}, \ldots, z_2),$$

where N — quantity of molecules A_a, ρ — exchange rate, t — time; $s = \alpha - \alpha_s$ — difference between fractions of isotope X in A_a (α, see Eq.2 in **Appendix**) and in exchange partner (α_s). The parameter A_m is determined by exchange mechanism type and may be called as *mechanism parameter*; other mechanism parameters are included in the second term of the right part of equation above.

Mechanism type corresponds to the variant of reversible fragmentation

$$A_a = \sum \nu_l A_{a_l},$$

by which exchange occurs. The fragments A_{a_l} are either individual species or parts accepted by other species taking part in elementary acts.

The simplest mechanism type

$$A_a = A_{a-1} + (A)$$

corresponds to *stepwise exchange* (according to Kemball [9]); here (A) denotes atom A accepted by exchange patner. In this case isotopic–kinetical equations have a very simple form:

$$N(ds/dt) = -A_1 \rho s,$$

$$N(dz_m/dt) = -A_m \rho z_m$$

$$(m = 2, 3, \ldots, a),$$

where $A_m = m/a$.

The present work involves both theoretical and experimental investigations.

Theoretical part of work includes the elaboration of theory and techniques of isotopic kinetics methods, especially the procedures for correct and complete interpretation of experimental information in respect to atomic-molecular mechanisms of catalytic processes on catalyst surface — nature of surface intermediates (atomicity, concentrations), kind of elementary steps (types of atomic rearrangement) and their rates (direct and backward).

In experimental part of work the studies mechanisms of activation of methane and some other light hydrocarbons (e.g. ethylene) on surface of catalysts are demonstrated [18–20]. Objects studied include range of catalysts — metals and oxides (supported, massive and films). The main aims of this part are to establish the regularities in the catalytic properties in respect to the features of atomic-molecular mechanisms (above mentioned) of reactions and to search for prediction of catalytic properties in heterogeneous catalytic conversion of hydrocarbons.

Appendix: Transformations of Isotopic Variables.

The normalization condition of fractions x_i of isotopic molecules X_iY_{a-i} $(i = 0, 1, \ldots, a)$ —

$$\sum_{i=0}^{a} x_i = 1 \tag{1}$$

The fraction of isotope X in A_a —

$$\alpha = \frac{1}{a} \sum_i i x_i \tag{2}$$

The relative binomial moments β_k $(k = 2, \ldots, a)$ —

$$\beta_k = \binom{a}{k}^{-1} \sum_{i=k}^{a} \binom{i}{k} x_i \tag{3}$$

The isotopic variables z_m $(m = 2, \ldots, a)$ —

$$z_m = \sum_k \binom{m}{k} (-\alpha)^{m-k} \beta_k \tag{4}$$

The combination of k out of a —

$$\binom{a}{k} = \frac{a!}{k!(a-k)!} \tag{5}$$

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PL-30

MEMBRANE CATALYSIS

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Introduction

In 1866 T.Graham opened the area of palladium usage for hydrogen separation from gaseous mixtures and its catalytic activation for chlorine-water transformation into hydrochloric acid and liquid phase reactions at room temperature. In 1898 N.Zelinski at Moscow University combined the hydrogen evolution during hydrochloric acid reaction with zinc and hydrogenation by palladium sponge covered the zinc granules. It was the first composite membrane catalyst. W.Snelling in the USA patented in 1915 hydrogen removal through Pt or Pd tubes from the reactor with granular catalyst of dehydrogenation.

Twenty years later D.Dobichin and A.Frost in the USSR discovered an increase in catalytic activity of hydrogen evolved from Pd film in comparison with gaseous one. Hydrogenation on Pd and other metallic membrane by hydrogen electrochemically produced on the opposite surface of this membrane was investigated in 1935 at Moscow University by N.Kobosev and V.Monblanova and more extensively in 1949 in the UK by A.-R.Ubbelohde. C.Wagner and K.Hauffe in Germany in 1939, B.Wood and H.Wise in the USA in 1966 and later many other scientists studied the hydrogenation on palladium and palladium alloys membranes by hydrogen supplied as a gas to the other surface.

In 1964 a method was proposed [1] for carrying out simultaneously the evolution and consumption of hydrogen, which comprises conducting these processes in a reactor divided by a partition made from a material that is selectively permeable to hydrogen only and serves as a catalyst. A palladium tube electrolytically coated with palladium black has been used as membrane catalyst. Cyclohexane vapour was introduced into the tube, while the space between the tube wall and the reactor shell was filled with o-xylene vapour. At temperature of 703 K, the yield of benzene as a result of cyclohexane dehydrogenation was equal to 43%. The hydrodemethylation of o-xylene yields 6% of benzene on the other side of the membrane catalyst. Quite independently W.Pfefferle [2] performed ethane dehydrogenation into ethylene to the extent of 0.7% over a palladium - 25 wt.% silver tube, wherein the hydrogen evolved is oxidized on the other side of the membrane catalyst by oxygen diluted with nitrogen.

This paper presents some new data about membrane catalyst usage for selective hydrogenation, dehydrogenation and coupling of this reactions.

Selective hydrogenation

A hydrogen porous membrane catalyst provides independent control of surface concentrations of hydrogen and of hydrogenatable substance. It suppresses their competing adsorption which is harmful, but inevitable on conventional hydrogenation catalysts. The experiments with 100 micron thick foils of palladium binary alloy with 15% rhodium were performed at Topchiev Institute of Petrochemical Synthesis (TIPS). The foil was clamped between stainless steel end plates and separated the reactor in two chambers. Hydrogen was supplied into one of the chambers and a vapour of hydrogenatable substance and inert gas were introduced into another chamber. The reaction products were analyzed by GLC.

It was found that unlike the common catalyst this membrane catalyst converts olefins into paraffins in presence of aromatic hydrocarbons without hydrogenation of aromatics. This result is important for the upgrading of aromatic hydrocarbons because the selectivity of olefins admixture hydrogenation is 99.99%. The productivity of one square meter of the membrane catalyst per hour is 1.2 mole of olefins. The increase in aromatic hydrocarbons content from 25 to 52% in the mixture with paraffins and 3% olefins did not change the completeness of olefins hydrogenation.

Palladium - 9.8% ruthenium membrane catalyst proved to be selective for cyclopentadiene hydrogenation into cyclopentene - a synthetic rubber monomer. Cyclopentadiene is usually obtained by gasoline pyrolysis and includes admixtures of 1,3-pentadiene and isoprene. That is why the experiments were performed for elucidation of the influence of these admixtures on cyclopentadiene hydrogenation. The conversion and selectivity towards cyclopentene didn't diminish with increase in 1,3-pentadiene or isoprene content up to 20%.

A pilot-plant catalytic membrane reactor for liquid phase hydrogenation was constructed at TIPS and A.A.Baikov Institute of Metallurgy RAS, Moscow, Russia. Disks of mechanically strong and corrosion stable palladium-indium-ruthenium alloy foils 70 micron thick are used in a new construction of catalytic membrane reactor which may be used for ultra pure hydrogen production as well. Two specially corrugated disks are welded to a stainless steel ring. Such elements are combined in a series with gas distribution accessories. Hydrogen is fed inside the elements at pressure up to 10 atm and its outer surface is used as a catalyst for selective hydrogenation.

Liquid reactant is distributed uniformly along the membrane catalyst surface. The pressure drop across the membrane catalyst may be up to 5 atm. Hydrogen rich industrial gaseous mixtures may be used for hydrogenation instead of pure hydrogen. The reactor was tested in dehydrolinalool hydrogenation into linalool of parfumeric quality and in production of eatable hard fats from liquid plant oils. The aim substances are free of the products of thermal destruction because of atomic hydrogen participation in hydrogenation at lower temperature. Vitamins, dyes and other pure substances may be produced as well. The productivity of this reactor is 100 tons per year.

Composite nickel membrane catalyst promoted with rare earth oxides for selective hydrogenation of acetylenic hydrocarbons was prepared at TIPS. Also a composite membrane catalyst was prepared by coverage of one side of the porous stainless steel sheet by thin layer of titania and introduction of nickel ultradispersed powder with O.5 wt.% La_2O_3 or Ce_2O_3 powder. The electron microscopy study shows that titania coverage decreased the average pore diameter of the stainless steel sheet from 1.9 to 0.14 micron. The membrane structure did not change after heating at 673 K for 15 hours.

The composite membrane catalyst was inserted into the steel reactor as a partition between two chambers. Hydrogen flows through one chamber and hydrogenated hydrocarbon flows through the other chamber. The pressure drop between the two chambers may be up to 10 atm.

Dehydrolinalool hydrogenation into parfumeric quality linalool was performed on two membrane catalysts with different modificators. Ceria is twice more effective than La_2O_3 in productivity increase.

At Russian University of People's Friendship (RUPF) a method of porous supports coverage by a dense film of palladium alloy 1 or 2 micron thick was elaborated. One support was prepared by electrochemical oxidation of electropolished pure aluminium foil 100 micron thick in oxalic acid. The fresh prepared membrane was 135 micron thick and consisted of two phases - γ-alumina and boehmite. The cylindrical channels of 100 nm in diameter with regular distances 300 nm between each other crossed the membrane. The important forsake of such membrane is the metal aluminium frame along its contour which permits hermetic fastening of the membrane into diffusion cell or catalytic membrane reactor.

Other composite membranes were prepared on porous stainless steel sheets or on compressed refractory oxide plates. Introduction of ultradispersed powders of catalytically active metals into the porous volume of the above support permits one to prepare a composite two-layer membrane catalyst. The upper layer is a fine film of palladium alloy which is a source of atomic hydrogen. It participates in hydrogenation reaction after spillover along the metal powder surface in the porous volume of the second layer.

At RUPF and Lomonosov Moscow State University nitromethane (NM) reduction was performed by palladium foil 100 micron thick which divided two parts of electrochemical cell. Potentials of different sides of this foil were forced independently by two potentiostats. The membrane surfaces were covered electrochemically by palladium layers several microns thick. Their roughness factors changed from 50 to 130 for different membranes. For comparison NM reduction was studied on palladized platinum wire as well. The electroreduction rate by the membrane electrode is higher than by the common one probably because of the optimization of the surface concentrations of hydrogen atoms and NM. Adsorption of silver atoms on the membrane or on the wire electrode increases the reduction rate but copper or cadmium adsorption depresses this reaction.

Dehydrogenation with removal of hydrogen through membrane catalysts

Dehydrogenation of cyclohexanol (CHL) to cyclohexanone (CHN) was carried out at atmospheric pressure in an all-metal, flow-type, two-loop installation. Each loop contained one of the two zones of the reactor, separated from each other by the membrane catalyst and bubbler thermostat.

The main product of cyclohexanol dehydrogenation by palladium alloy membrane catalysts is cyclohexanone. At temperatures above 480 K cyclohexene or phenol is formed depending on the nature and the concentration of the second component of palladium-based alloy.

The rate of hydrogen removal from the cyclohexanol dehydrogenation zone of the catalytic membrane reactor is lower than the rate of hydrogen transfer through this membrane catalyst during passing the hydrogen-inert gas mixture at the same conditions. The ratio of hydrogen concentrations in both chambers of the catalytic membrane reactor proved to be a function of the membrane catalyst content. For example hydrogen concentration in the products of cyclohexanol dehydrogenation by binary alloys palladium with 10 % ruthenium or 5 % rhodium is higher than that in the hydrogen eluation chamber. The opposite situation takes place during cyclohexanol dehydrogenation by Pd-Ru-Pb and Pd-In-Ru membrane catalysts when cyclohexene is formed as side-product. Unlike the above catalysts, Pd-Ru and Pd-Rh catalysts give phenol as a side-product of cyclohexanol dehydrogenation. The mentioned difference in hydrogen concentrations at both surfaces of the binary and ternary membrane catalysts may be caused by diminishing of hydrogen atoms recombination rate and desorption of di-hydrogen molecules in the dehydrogenation zone in the presence of cyclohexene in comparison with the rate of hydrogen atoms diffusion through the ternary palladium alloys. Hydrogen desorbed in the dehydrogenation zone is slowly adsorbed on the surface covered by cyclohexene. That is the reason of hydrogen permeability decrease.

The amount of hydrogen diffused from the dehydrogenation zone may be increased by its usage in hydrogenation or oxidation on the other surface of the membrane catalyst. But the complete hydrogen removal was not succeeded even during hydrogen oxidation. It means that the limiting step of hydrogen transfer is hydrogen atoms recombination on the exit surface of the membrane catalyst.

Coupling of hydrogen evolution and consumption reactions on the monolithic membrane catalysts

Hydrogen transfer from the zone of its formation increases not only the equilibrium yields of this reaction, but its selectivity as well. For example, if, together with dehydrogenation, cracking of the initial hydrocarbon takes place, the removal of the hydrogen formed through a membrane catalyst facilitates dehydrogenation, but the cracking products remain in the same reaction space and retard the side reaction.

Table 1 summarizes the first applications of palladium and palladium alloys monolithic membrane catalysts for reactions coupling. The drawback of monolithic membrane catalysts is small catalytic surface area per unit volume of the reactor. The surface area may be increased by Raney type catalyst formation as a result of the introduction of chemically active metal into the surface layer of membrane catalyst and removing the introduced metal by acid. Another method of monolithic membrane catalyst surface increasing is the formation of the columnar structure layer of the same content on the surface by magnetron sputtering. The next step in the increasing of the surfaces of both sides of the membrane catalyst is coverage of porous refractory support by the layers of catalysts. The system of a support with two layers of catalytically active materials permits two reactions coupling. The examples of monolithic membrane catalyst with a columnar structure on one surface are given in paper [3].

Table1. Applications of palladium and palladium alloys monolithic membrane catalysts
for reactions coupling

Reactions	Catalyst	T, K	Authors
A: Dehydrogenation of cyclohexane; B: Demethylation of o-xylene	Pd, tube	703	Gryaznov, 1964
A: Dehydrogenation of ethane; B: Oxidation of hydrogen	Pd-25Ag, tube	625	Pfefferle, 1965
A: Coupling of dehydrogenation of trans-butene-2; B: Demethylation of toluene or hydrogenation of benzene	Pd, Pd-20Ag, tube	653-713	Gryaznov et al, 1966
A: Dehydrocyclization of undecane; B: Hydrodemethylation of dimethylnaphtalene	Pd-5.9Ni, foil	860	Gryaznov et al, 1968

Reactions	Catalyst	T, K	Authors
A: Dehydrogenation of isoamylenes; B: Hydrodemethylation of toluene or oxidation of hydrogen	Pd-5.9Ni, foil	723	Gryaznov et al, 1975
A: Dehydrogenation of isopropyl alcohol; B: Hydrogenation of cyclopentadiene	Pd-10Ru, foil	493	Mikhalenko et al, 1977
A: Borneol dehydrogenation; B: Cyclopentadiene hydrogenation	Pd-5.9Ni; Pd-10Ru; Pd-15Rh, foils	473-543	Smirnov et al, 1981
A: Butane dehydrogenation B: Hydrogen oxidation	Pd-9.8Ru; Pd-5.5Sn; Pd-23Ag, foils	753-823	Orekhova & Machota, 1981
A: Cyclohexanol dehydrogenation to cyclohexanon; B: Cyclopentadiene hydrogenation to cyclopentene	Pd-9.8Ru, foil	500-550	Basov & Gryaznov, 1985

The systems of monolithic membrane and granular catalysts have been investigated by many authors. Table 2 includes examples of such systems used for the coupling of hydrogen evolution and consumption reactions.

The increase in membrane catalyst surface per unit volume of the reactor shell was achieved by usage of thin-walled palladium alloy tubes in the form of plane double-start spirals. The spirals are stacked one on the other, the inlet and outlet ends of the tubes being secured in tubular headers positioned perpendicular to the plane of the spiral. This constructional arrangement enables the apparatus volume to be filled with tubes to a maximum. The blocks of spirals were mounted within the reactor shell and were joined in parallel to diminish hydraulic resistance to flow inside the tubes. Stainless steel reactor with 200 spirals with total length of tubes 400 m is used for hydrogenation of acetylenic alcohols into ethylenic ones. In TIPS a laboratory scale reactor of the same type was tested for selective hydrogenation of phenylacetylene into styrene.

Table2. The systems of metal-containing membrane and granular catalysts for reactions coupling

Reactions	Membrane	Catalyst	T, K	Authors
A: Borneol dehydrogenation to camphor; B: 1,3-pentadiene hydrogenation	Pd-5.9Ni, Pd-10Ru, Pd-10Rh, foils	Cu, wire; membrane catalyst	520	Gryaznov et al, 1977
A: Methane dimerization; B: Hydrogen oxidation	Pd, tube	Pt-Sn/Al_2O_3; Rh/SiO_2; membrane catalyst	630-710	Andersen et al, 1989
A: Butane dehydrogenation to butadiene B: Hydrogen oxidation	Pd-9.8Ru, foil	Cr_2O_3-Al_2O_3; membrane catalyst	723-823	Machota & Orekhova, 1981
A: Cyclohexane dehydrogenation to benzene B: Hydrogen oxidation	Pd, tube	Pt/Al_2O_3; membrane catalyst	470	Itoh, 1990
A: Butene-1 dehydrogenation B: Hydrogen oxidation	Pd, foil	Cr_2O_3-Al_2O_3; membrane catalyst	720	Zhao & Govind, 1990
A: Cyclohexane dehydrogenation to benzene B:1,3-pentadiene hydrogenation	Pd-6 Ru, foil	Pt-Re/Al_2O_3; membrane catalyst	490	Orekhova et al., 1991

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Catalytic Reactors Based on Porous Ceramic Membranes. Present Status and Future Opportunities

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Introduction

Inorganic membranes were industrially developed 5 decades ago, with the aim of separating UF_6 using gas phase diffusion processes. In the 80s, non-nuclear industrial applications were in place, mainly oriented towards microfiltration and ultrafiltration processes. A fast development ensued, which helped to obtain standardized processes for membrane production and control of the porous structure. The application of ceramic membranes as catalytic reactors also starts in the 80s. The driving force for this change was the possibility of integrating reaction and separation, which had already been achieved in the field of biochemical reaction engineering using polymeric membranes. These, however, were not applicable at the temperatures used in most of the processes of interest in the chemical process industry. The intense research activity that now takes place in the field of membrane reactors has been possible thanks to the availability of materials that can be used as membranes, while being able to withstand severe reaction conditions.

Commercial ceramic membranes currently in use tend to have an asymmetric structure, consisting of a support layer (generally alpha-alumina), with large pores and a low pressure drop, and a separation layer made of a different material (gamma-alumina, zirconia, silica, etc.), which controls the permeation flux. Since the materials used in the manufacture of ceramic membranes are also commonly used as conventional catalyst supports, there has been a strong interest in the development of membrane reactors by research groups previously working on heterogeneous catalysis, who adapted many of the preparation and characterization techniques used in this field.

In this work, some of the outstanding opportunities that catalytic reactors based on porous ceramic membranes present to the academic and industrial communities are presented.

It is not intended as a review of the field, which would exceed considerably the space allocated to this paper, but rather as a reflection on specific aspects of the interaction between catalytic reactor engineering and porous membranes.

Types of membrane reactors

Table I classifies inorganic membranes according to their nature and most important characteristics: Selectivity and permeability. Both are determined by the interaction between the membrane and the permeating molecules which gives rise to different transport mechanisms: Solution-diffusion and ionic conductivity in dense membranes, Knudsen diffusion, surface diffusion, capillary condensation, viscous flow and molecular sieving in porous membranes. It is commonly encountered that a trade-off exists between both characteristics, and thus the membranes with the highest permeabilities (porous membranes) have the lowest selectivities, while the opposite is true of highly selective dense membranes, such as metallic and solid electrolyte membranes.

Table I. Classification of inorganic membranes

Type of membrane	**Material**	**Selectivity**	**Permeability**
Dense	Metallic	Very selective (H_2, O_2)	Low to moderate
	Solid electrolytes		
Porous	Oxides, carbon, glass, metals	Low	High
	Zeolites	Can be very selective	Moderate
Composite	Glass-metal Ceramic-metal Metal-metal	Can be very selective	Moderate

The composite membranes in table I represent an attempt to simultaneously obtain moderately high fluxes and high selectivities. To this end, a porous substrate with a low mass transfer resistance is covered with a thin metallic layer which provides the selectivity. The methods used to attain this objective, such as electroless plating or ion sputtering (e.g. 1-3), are far from being fully developed, and the thin metallic layer on the composite membranes frequently develops cracks and pinholes that render it useless. However, composite membranes are clearly promising, and a good deal of research will undoubtedly be devoted to them in the near future. Another expanding area of research concerns zeolitic membranes. This field has barely begun to be investigated, albeit some very interesting results have already been obtained (e.g. 4,5), regarding the capability for selective transport of different zeolitic membranes. Finally, other porous ceramic membranes provide a very broad array of opportunities regarding the choice of materials for the membranes, their catalytic properties and possible applications. Some selected examples are discussed throughout this work.

Table 2. Classification of catalytic reactors based on ceramic membranes

Inert Membrane Reactors (IMR)	The role of the membrane is to remove products or to add reactants. The catalyst is located apart from the membrane structure.
Catalytic Membrane Reactors (CMR)	The membrane material itself is catalytic, or becomes catalytically active during preparation by the addition of active precursors.
Combined	There is catalytic material both inside and outside the membrane.

Table 2 gives a classification of catalytic reactors based on ceramic membranes, according to the role played by the membrane. When an Inert Membrane Reactor (IMR) is used, the catalytic material does not form part of the membrane (a typical configuration is a tubular membrane enclosing a fixed bed of catalyst). In this case, the membrane does not participate in the reaction directly, but it is used to add or remove selected species from the reactor. The most widely used application involves equilibrium displacement by removal of at least one reaction product (corresponding to configuration A of table 3). Product removal may be selective (i.e., H_2 permeation through a composite Pd-ceramic membrane), or preferential (i.e., preferential permeation of H_2 versus higher molecular weight products using a Knudsen-diffusion membrane). Equlibrium displacement can be enhanced through reaction coupling (configuration B in table 3). In this case, on both sides of the membrane run complementary processes that use either the permeated species (chemical coupling, e.g., dehydrogenation/hydrogenation reactions), or the heat generated in the reaction (thermal coupling, exothermic/endothermic processes).

A second broad application of IMRs consists in using the membrane to distribute a reactant in a series-parallel reacting network where there is a favorable kinetic effect regarding the partial pressure of the distributed reactant (configuration C). Thus, it has often been found in selective oxidation reactions that a low partial pressure of oxygen favours the selective oxidation reaction versus the deep oxidation to CO and CO_2. IMRs have been used successfully as oxygen distributors in a number of reactions (see Table 3), attaining not only greater selectivities with respect to conventional feed arrangements, but also a safer operation, with reduced formation of hot spots and a lower probability of runaway reaction. It is worth noting that sometimes obtaining a true IMR is not an easy task. Thus, the original membranes used in selective oxidation reactions often had to be significantly modified in order to reduce undesired catalytic activity (e.g., 13, 18). Finally, the membranes used in IMRs are not necessarily constrained to uniform permeabilities. On the contrary, the permeability can be tailored to suit specific permeation patterns (e.g., 15), as required by the reaction kinetics, heat transfer arrangements, etc.

As indicated in Table 2, with Catalytic Membrane Reactors (CMRs), the reaction (or at least part of it) takes place directly on the membrane. There is a strong ongoing research effort aimed to devise new preparation methods for catalytic membranes. In that respect, it should be noted that, during the preparation of a catalytic membrane, the catalyst precursors can be made to flow through the porous structure of the membrane, rather than diffuse into it. This opens up a whole new field of opportunities regarding the distribution of active components and of support material within the membrane, preparation of membranes with different catalytic layers, etc.

Reactant distribution can also be achieved using composite, catalytically active membranes (configuration D). However, there are few results reported to date, which is mainly due to the difficulties in attaining sufficiently high permeation fluxes (which is usually achieved by reducing the thickness of the dense layer), while at the same time maintaining the membrane properties during prolongued exposure at operating conditions.

Table 3. Some possible configurations of porous membrane reactors.

Configuration	Advantages sought	Type of membrane	Examples
A: Inert Membrane Reactor (IMR) - permeation of products	Increased reaction yield by equilibrium displacement.	i) Selective. Thin metallic layers (e.g., Pd or Ag-based alloys on ceramic substrates) ii) Nonselective. Porous membranes: Silica, alumina, titania, glass, etc. iii) Other: Zeolitic membranes	6-9
B: IMR-permeation of products plus reaction coupling	As above, although higher yields can be expected due to the thermal/chemical coupling of reactions.	As above	10,11
C: IMR-distribution of reactants	Increased selectivity through control of the concentration of selected species along the reactor. Increased reactor safety.	As above	12-19
D: Catalytic Membrane Reactor (CMR)- Mobile and active lattice oxygen	Control of the oxygen distribution in the reactor. In principle, it is possible to avoid the presence of gas phase oxygen.	i) Thin layers of Ag-based alloys on top of porous ceramic membranes ii) Thin layers of dense oxides on top of porous ceramic membranes	20,21
E: CMR-Segregation of reactants on both sides of the membrane	Confinement of reaction to a finite thickness zone inside the membrane. Reactant slip is avoided. Improved safety.	Porous catalytic membranes	22,23
F: IMR+CMR composite membrane	Control of the concentration of a reactant by means of mass transfer resistance in the IMR zone.	Composite membranes: Inert (diffusion) zone plus catalytically active zone	24,25
G: CMR-Segregation of liquid and gaseous reactants	Improved mass transfer in G-L-S reactions.	Porous catalytic membranes.	26,27
H: CMR- Joint permeation of reactants	Improved G-S contact, higher conversions.	Porous catalytic membranes.	28

Configuration F of table 3 represents an alternative form of reactant distribution. In this case, the concentration of a reactant is lowered by feeding it through a diffusion layer of sufficient resistance. This is followed by a catalytic layer, where the reaction takes place with the reactant permeated from the opposite side. The key to the success of such a configuration is the ability to obtain a sharp distribution of the active component across the membrane radius, which is not always achieved (25).

The last two configurations in table 3 use catalytic membranes to improve contact efficiency, with the objective of attaining higher conversion by decreasing mass transfer resistances. Configuration G aims to improve the contact in gas-liquid-solid systems by using a defined contact zone where the three phases are present. This does not require a permselective membrane and avoids the problem of catalyst recovery in slurry reactors. The concept has been demonstrated for hydrogenation reactions over Pt/Al_2O_3 catalysts (26,27). Finally, configuration F involves a different concept, which is briefly outlined below (Case 1).

Application of different reactor configurations. Case 1: Combustion of Volatile Organic Compounds (VOCs).

The combustion of VOCs represents a significant challenge to the present status of Chemical Reaction Engineering: VOCs are present in diluted streams, their production rate may change considerably with time and location in a given facility, and conversions higher than 95% are usually required. In addition, the catalytic system chosen should be able to handle mixtures, operate with a relatively low pressure drop, and avoid or minimise catalyst deactivation (by sulphur compounds, chlorides, silicon, polymerising materials, sintering processes, etc.).

A catalytic membrane reactor (configuration H) was selected to carry out VOC combustion (28). A Knudsen-diffusion membrane was obtained by deposition of γ-Al_2O_3 within the porous structure of a commercial microfiltration membrane, and Pt was loaded onto the membrane either by CVD or by conventional impregnation methods. Operation under the Knudsen regime provided an intimate contact between the VOC molecules and the combustion sites, which improved contact efficiency and decreased the diffusion resistances with respect to those present in other systems, such as fixed bed reactors or monolith reactors. As a consequence, low combustion temperatures were obtained, as shown in Table 4.

Table 4. Combustion of VOCs (toluene) in a flow-through membrane (configuration H).

Preparation method	γ-Al_2O_3 load (wt%)	Pt load (wt%)	C_7H_8 Conc. (ppm)	$T_{50\%}$ (°C)	$T_{99\%}$ (°C)
CVD	3.2	0.19	1030	161	177
CVD	3.2	0.19	1760	177	192
CVD	3.2	0.19	1200	175	199
Impregnation	2.5	0.17	2050	166	198
Impregnation	1.7	0.09	520	150	178
Impregnation	4.7	0.15	1850	175	185

Application of different reactor configurations. Case 2: Oxidative dehydrogenation of butane

Oxidative dehydrogenation of butane can be represented by a series-parallel network in which high oxygen partial pressures favour deep oxidation to CO and CO_2 rather than the production of the desired products (butene, butadiene). An IMR (configuration C) with a composite silica-alumina membrane was used to distribute oxygen to a fixed bed of V-Mg-O catalyst (18).

The membrane reactor (permeation of O_2) was found to be more efficient than a fixed bed reactor, under most of the conditions investigated, giving selectivities higher by ca. 10 percentage points in the 40-50% conversion range. In addition, it was found that the oxygen distribution arrangement had a direct effect on the average state of oxidation of the catalyst in the reactor, leading to a more favorable variation of the degree of reduction (φ) along the bed. The use of the membrane was also advantageous regarding the stability and safety of reactor operation. Thus, small temperature variations were obtained with the IMR under conditions in which the fixed bed reactor would give intense hot spots or even run away.

Conclusions.

The field of catalytic reactors based on porous membranes offers very attractive research opportunities to the scientific community working on catalysis. An important research effort is needed to develop new methods of preparation and characterization, new membrane materials and reactor configurations and new conceptual applications to different reaction systems. If successful, the research on membrane reactors will significantly change the current approach to Catalytic Reaction Engineering.

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DEVELOPMENT OF TECHNICAL CATALYSTS

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Chemical reactions are used to transform inexpensive raw materials into high value products. The whole chemical industry is based upon such chemical transformations. To carry out chemical transformations or synthesis we need a process and in more than 80 per cent of the cases we also need a catalyst. Catalyst and process cannot be seen independently of each other. The chemical synthesis can only be improved by optimizing the combined system process and catalyst.

The word catalysis is basically used to describe two distinct areas - homogeneous catalysis and heterogeneous catalysis. In homogeneous catalysis the catalyst is dispersed on a molecular level in a single liquid or gaseous phase. The dispersed substances are usually inorganic or organometallic complexes.

However, heterogeneous catalysts offer two major advantages. Not only are the catalysts relatively stable, but because catalysts and reactants are present in different phases, they also can be separated without difficulty from the products.

On the other hand, the homogeneous catalyst complexes are very sensitive to temperature, air and moisture and are often difficult to separate from the reaction products.

These properties are the reason why more than 80 per cent of all catalytic processes are carried out with heterogeneous catalysts.

Before attempting to develop or improve a heterogeneous catalyst, one must, of course, recognize what properties need to be improved or optimized. The most important of these properties are discussed.

In addition to activity and selectivity further important properties include suitable shape, chemical and mechanical stability and the resultant effective life time.

Also we can distinguish various structural types, namely carrier-free, supported and coated catalysts.

Heterogeneous catalysts can be manufactured in many different shapes: first of all the catalyst can be used as a powder, for instance suspended in a liquid. Other physical forms include spheres, pellets, rings, extrudates and honeycombs.

After we have recognized what properties and structural characteristics are required for a high performance industrial heterogeneous catalyst, it is possible to define the objectives, which must be met. When developing a catalyst for a particular chemical synthesis the aim is frequently not only to improve the activity and selectivity or space time yield, but also to increase the effective lifetime. In addition in many cases it is necessary to adapt the catalyst to modified process conditions. An important and often difficult step is the scale up from the laboratory scale to technical production.

The main objective of catalyst development is the optimisation of various different catalyst properties. A basic precondition for achieving such a goal is a close cooperation between experts working in very different branches of scientific research. The techniques of inorganic and solid state chemistry are used in the initial preparation of the catalyst in the laboratory. The physical methods of solid state and surface science are applied to characterise the bulk catalyst and the surfaces where the reactions take place. In order to assess the performance of new catalysts on a small scale or in a pilot plant one must take into account mass and heat transfer effects and also the reaction kinetics. Reaction engineering provides this information which is needed for the further optimization of the catalyst. Successful production of the catalyst on a technical scale requires comprehensive knowledge in the area of solids technology. This is particularly true during the scale-up from the laboratory to the technical plant. Finally, the experts in the field of reactor technology have to select the appropriate types of reactor, so that the technical process is correctly tailored to the catalytic reactions.

When developing an improved heterogeneous catalyst one needs to know not only the characteristics of the performance but also the factors which have the greatest influence upon the performance. Seven most important parameters are:

mass and heat transfer - both on the catalyst itself and also within the reactor, the kind of raw materials used in catalyst manufacture and also the structure of the solid, i. e. the pore structure of the catalyst. The chemical and mechanical stability are also important for the catalyst life. In addition, chemistry also plays a part, namely the composition of the active surface and of the bulk solid. Furthermore the stability of the active phase is also of particular significance.

The instrumental techniques available to us for investigating these different parameters are discussed:

The catalyst performance test in the laboratory or semi-technical reactor still remains to this day the most reliable method for evaluating a catalyst. These tests must frequently be supplemented by kinetic measurements in order to determine the optimum technical reaction conditions.

The physical structure, i.e. the pore structure of the catalyst is characterised using such techniques as BET-sorption, mercury porosimetry and scanning electron microscopy.

The mechanical and chemical stability of a catalyst are defined in terms of parameters such as abrasion resistance, crushing strength and solubility.

The chemical composition is normally determined by means of atomic absorption or ICP-spectroscopy and X-ray fluorescence.

Characterisation of the catalyst surface and bulk involves techniques such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Surface and solid state characterisation can also be carried out by EXAFS, IR-, Raman and NMR spectroscopy. These methods, in addition, have the advantage that the analysis can be done under in-situ conditions.

Analysis of the various crystallographic phases present in the solid is carried out using X-ray diffraction.

However the most important point during catalyst development is the correlation analysis, i.e. establishing relationships between preparation parameters, structural properties and performance data of the catalyst.

Four examples are presented to illustrate the relationship between the most important structure parameters and catalyst performance. First, the importance of the pore structure of the solid for the activity and selectivity can be demonstrated in the case of the styrene catalyst.

The next example, which is discussed in somewhat more detail, illustrates the drastic effect which mass and heat transfer phenomena can have upon the economics of a chemical synthesis, e.g. for the partial oxidation of propene to acrolein. In order to find out whether the acrolein synthesis can be carried out even more efficiently, it is necessary to study the influence of mass transfer effects in the acrolein catalyst. On the basis of the shown values it is evident that the conversion of propene on coated catalysts is strongly influenced by the coating thickness of the catalyst.

These measurements are valuable for an industrial company, because they enabled us to estimate what loss of yield we should have to expect on increasing the coating thickness in order to increase productivity.

X-ray diffraction can be used to identify the individual solid phases of which a heterogeneous catalyst is composed. Every crystalline solid possesses characteristic X-ray diffraction lines, with which it is possible to make an unambiguous identification. This is demonstrated for low temperature shift conversion catalyst. The catalyst precursors are produced by precipitation of copper, zinc and aluminium hydroxycarbonates. Depending upon the pH and temperature during the precipitation, various solid phases are produced which differ in their copper, zinc and aluminium content. Extensive X-ray studies revealed that precursors which consist mainly of mixed crystals of layered hydroxycarbonates of the hydrotalcite type lead to the most active catalysts.

Finally, the stability of the active phase is mentioned. In the case of the ethylene oxide catalyst, for instance, one recognises an initial formation phase during which a sintering of the active component, silver takes place. After three weeks this sintering process slows down considerably and gives the catalyst its desired long term stability.

After a heterogeneous catalyst has been developed in the laboratory it has to be produced on a technical scale. A manufacturing scheme for technical catalyst production is presented.

Following their technical production the catalysts are finally charged into the appropriate reactors of a production plant. According to the type of reaction and the behaviour of the catalyst, either a conventional fixed bed reactor is used or in the case of strongly exothermic or temperature-sensitive reactions a multi-tubular reactor can be employed. If the catalyst deactivates very rapidly during the reaction then a fluidised bed process with continuous catalyst regeneration is frequently chosen - as shown in the next diagram.

In conclusion we can summarize:

The development of technical catalysts is quite definitely an interdisciplinary task involving knowledge gained from numerous areas of chemistry, chemical engineering and process engineering.

Two major areas for future catalyst development can be anticipated. Firstly, there will continue to be a need for improving existing catalytic processes in terms of savings of energy and raw materials. In this connection increasingly strict environmental protection requirements will gain in importance.

Secondly, one can expect increased industrial exploitation of biochemical reactions, which are characterised by high selectivity and low energy requirements as compared to conventional processes.

THE MODERN PROBLEMS OF GAS PHASE ELECTROCATALYSIS AND ELECTROCHEMICAL PROMOTION

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The catalytic activity and selectivity of metals interfaced with solid electrolytes can be altered dramatically and reversibly via potential application. The increase in catalytic rate can be several orders of magnitude higher than that anticipated from Faraday's Law. This new phenomenon of electrochemical promotion is of considerable theoretical and potentially practical importance in heterogeneous catalysis.

During the last three decades solid electrolyte fuel cells, operating on H_2 or CH_2 fuel, have been investigated extensively in order to assess their technical and economic viability for energy-efficient power generation (1,2). The main commercial use of solid electrolyte cells is currently in sensor technology (3). Carl Wagner was the first to propose the use of solid electrolyte cells in heterogeneous catalysis in order to measure the thermodynamic activity of oxygen in oxidation catalysts (4). This idea was pursued experimentally to study the mechanism of several catalytic systems (5). It soon became apparent that solid electrolyte cells can also be used in an active mode to electrolyze molecules such as H_2O (6) and NO (7). Another potential application of solid electrolyte cells is electrochemical cogeneration, i.e., the simultaneous production of electrical power and useful chemicals in fuel cell electrochemical reactors (8,9). Such solid electrolyte fuel cells with modified anodes can be used, e.g., for the electrochemical oxidation of NH_3 to NO (8), H_2S to SO_2 (9), methanol to formaldehyde (10), or methane to ethylene (11) with simultaneous production (cogeneration) of chemicals and electricity.

In the course of chemical cogeneration studies a new and rather unexpected phenomenon was discovered, now known in the literature as non-Faradaic electrochemical modification of catalytic activity (NEMCA effect) or electrochemical promotion (12,13). The NEMCA effect quickly attracted attention (14) and its importance in electrochemistry, catalysis and surface science has been stressed by Bockris (15), Haber (16) and Pritchard (14), respectively.

In brief, it was found that the catalytic activity and selectivity of metal films deposited on solid electrolytes (e.g. Yttria-stabilized-zirconia (YSZ), an O^{2-} conductor, β''-Al_2O_3, a Na^+

conductor or $CaZr_{0.9}In_{0.1}O_{3-\delta}$, a H^+ conductor) can be altered dramatically and reversibly by applying an electrical current or potential between the metal catalyst film and a second film (counter electrode) also deposited on the solid electrolyte.

The induced reversible change in catalytic rate (expressed in mol/s) was found to be up to 100 times larger than the catalytic rate before current application, i.e., there is up to a 10,000% rate increase. Furthermore, this rate increase is typically 10-10^5 times larger than the rate, I/nF, of supply of ions (e.g. O^{2-}, Na^+, $Ç^+$) to the catalyst surface (where I is the applied current, n is the ion charge and F is Faraday's constant). This implies that <u>each</u> ion supplied to the catalyst can cause up to 10^5 adsorbed reactants to react and produce up to 10^5 product molecules: electricity acts as a powerful promoter rather than only an electrochemical driver of catalytic activity. Importantly, significant and reversible alterations in product selectivity were also observed for several reactions and it soon became apparent that the NEMCA effect is not limited to any particular metal catalyst, solid electrolyte or catalytic reaction. By 1992 when the NEMCA literature was first reviewed (17) more than 20 catalytic reactions exhibiting the novel effect had been studied. Today this number has exceeded 50 (18) and the effect has been demonstrated for several catalysts (Pt, Pd, Rh, Ag, Ni, Au, IrO_2, RuO_2) deposited on O^{2-}, F^-, Na^+ and H^+ conducting solid electrolytes. Recent demonstration of NEMCA using mixed ionic-electronic conductors (e.g. TiO^2) (19), Nafion (18) or aqueous alkaline solutions (20) is also noteworthy. In addition to the group which first reported on this effect (12,13,17,18), several other research groups at Novosibirsk (21), Yale (22), Cambridge (23), Tufts (24) and EPFL (25) have made important contributions in this area.

A NEMCA experiment

The experimental setup is quite simple (Fig. 1): The gaseous reactants (e.g. C_2H_4 plus O^2) are co-fed over the working electrode of a solid electrolyte cell:

gaseous reactants	Catalyst working electrode	solid electrolyte	counter electrode	auxiliary gas
(e.g. $C_2H_4+O_2$)	(e.g. Pt,Rh,Ag,IrO_2)	(e.g. ZrO_2-Y_2O_3)	(e.g. Au)	(e.g. O_2)

The working electrode serves both as an electrode and as the catalyst for the catalytic (no net charge transfer) reaction, e.g.:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

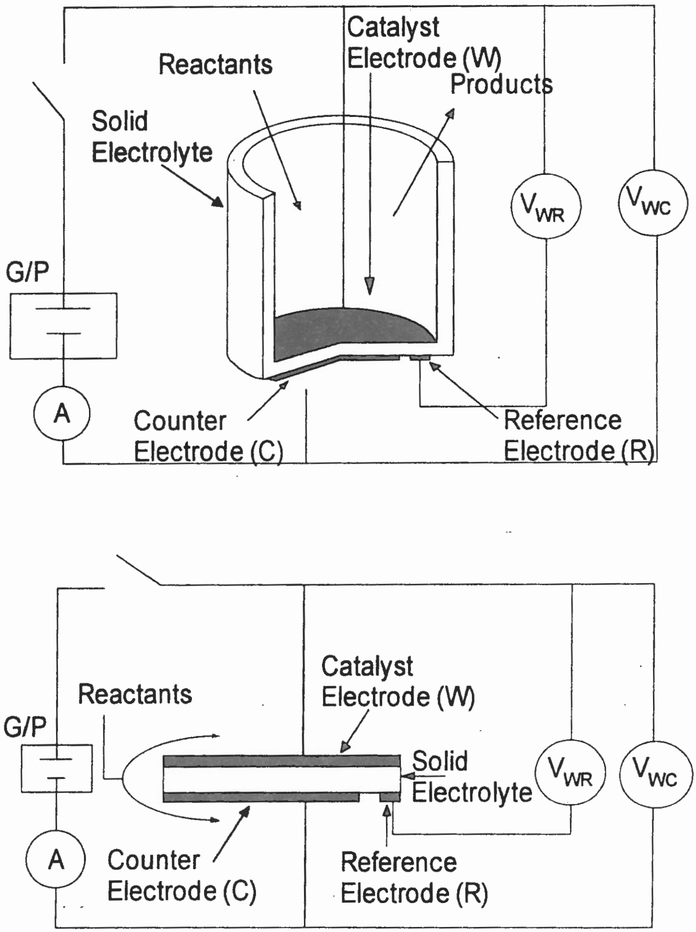

Figure 1: Electrode configuration for electrochemical promotion studies using the fuel-cell type (top) and single-pellet type (bottom) configurations; G/P, galvanostat/potentiostat.

The auxiliary gas can be ambient air when using the 'fuel cell' type design (Fig. 1, top) or the reactive gas mixture itself in the, so called, 'single pellet' design (17) (Fig. 1, bottom). A typical NEMCA experiment (17,18), carried out in the setup of Fig. 1, top, is shown in Fig. 2: Ethylene (at 0.36 kPa) and oxygen (at 4.6 kPa) are premixed and fed over the Pt catalyst electrode at 370°C in a continuous flow reactor. Initially (t<0) the electrical circuit is open (I=0) and the catalytic rate, r_o, is $1.5 \cdot 10^{-8}$ mol O/s. The corresponding turnover frequency (TOF), i.e., oxygen atoms reacting with C_2H_4 per surface Pt atom per s is 3.6 s^{-1}.

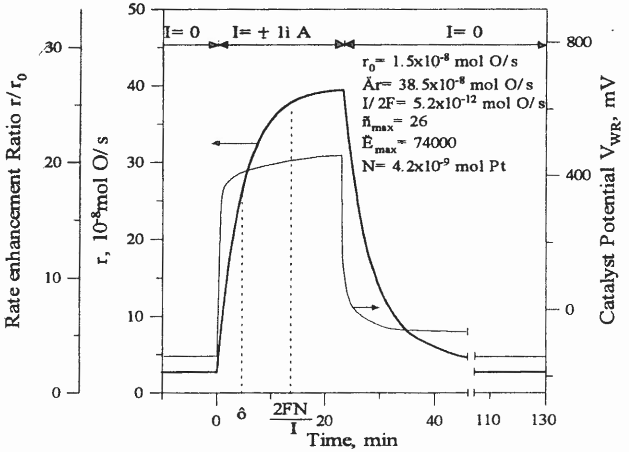

Figure 2: Electrochemical promotion: Catalytic rate and catalyst potential response to step changes in applied current during C_2H_4 oxidation on Pt (17). T=370°C, P_{O2}=4.6kPa, P_{C2H4}=0.36kPa. The experimental (ô) and computed (2FN/I) rate relaxation time constants are indicated on the figure

Then at t=0 a galvanostat is used to apply a constant current between the Pt catalyst and the counter electrode. In this way oxygen ions, O^{2-} are supplied to the catalyst at a rate $I/2F=5.2 \cdot 10^{-12}$ mol O/s, according to Faraday's Law.

The catalytic rate starts increasing and within 25 min gradually reaches a value $r=4.0 \cdot 10^{-7}$ mol O/s, which is 26 times larger than the initial value r_o. The new TOF is 95.2 s^{-1}. The increase in the catalytic rate is 74,000 times larger than I/2F. The latter is the maximum rate increase anticipated from Faraday's Law if all the electrochemically supplied oxygen were to react with C_2H_4 forming CO_2 and H_2O. Thus each O^{2-} supplied to the Pt catalyst causes at steady-state 74,000 oxygen atoms, chemisorbed on the Pt surface, to react with C_2H_4 and to form CO_2 and H_2O.

The Faradaic efficiency, Λ, defined from:

$$\Lambda = \Delta r/(I/2F)$$

has thus a value of 74,000 for the experiment of Fig. 2. A reaction exhibits the NEMCA effect when $|\Lambda| > 1$. Depending on the observed sign of Λ, catalytic reactions are termed electrophobic

($\Lambda>1$) or electrophilic ($\Lambda<-1$); Λvalues ranging from $3\cdot10^5$ to -10^{-4} have been measured for different catalytic reactions (18).

More importantly, relatively safe predictions can now be made about the order of magnitude of $|\Lambda|$ for any system from the expression $2Fr_o/I_0$, (17,18) where I^0 is the exchange current of the catalyst electrolyte interface. This parameter can be easily extracted from standard current-overpotential (Tafel) plots (17,18). The rate enhancement ratio, ρ, is defined from

$$\rho=r/r_o$$

For the experiment of Fig. 2, the maximum ρ value is 26; ρ values ranging from zero (complete reaction poisoning (18,26)) to 100 (18) or even higher (activation of a totally inactive catalyst surface (23)) have been obtained.

It is noteworthy in Figure 2 that the time, τ, required for the catalytic rate increase to reach 63% of its final steady-state value is of the order of (2FN/I), where N is the catalyst surface area, measured via surface titration (17,18). The parameter 2FN/I represents the time required to form a monolayer of oxygen on the catalyst surface when oxygen is supplied at the rate I/2F. This gave the first indication (12) that NEMCA is due to an electrochemically controlled migration of ionic oxygen from the solid electrolyte onto the catalyst surface.

Origin of electrochemical promotion

A key step in the elucidation of the origin of NEMCA was the experimental discovery (13) and theoretical confirmation (17,18) that solid electrolyte cells with metal electrodes are both work function probes and work function controllers for the gas-exposed surfaces of their electrodes.

Both Kelvin probe (13) and UPS, measurements (27) have shown that:

$$eV^\circ_{WR}=e\Phi_W-e\Phi_R$$

$$e\Delta V_{WR}=\Delta(e\Phi_W)$$

where V_{WR} is the working (W) electrode potential with respect to a reference (R) electrode, V°_{WR} stands for the open-circuit potential, and $e\Phi_w$, $e\Phi_R$, are the (average) work functions of the working and reference electrodes respectively. The first equation, valid when the same bulk material is used for the working and reference electrodes, shows that the EMF of solid electrolyte cells carries an important physical meaning, in addition to its usual Nernstian one. The second equation is even more important, as it shows that the work function of the gas-exposed, i.e., catalytically active, surface of solid electrolyte cell electrodes can be varied at will via current or potential application. Positive currents and potentials increase eF and negative ones decrease it.

It therefore becomes quite important to understand how this electrochemically controlled variation in catalyst work function is brought about at the molecular level, particularly since experiment has clearly shown the central role of catalyst work function in describing NEMCA: Catalytic rates and activation energies were found to vary exponentially and linearly, respectively, with catalyst work function (17,18).

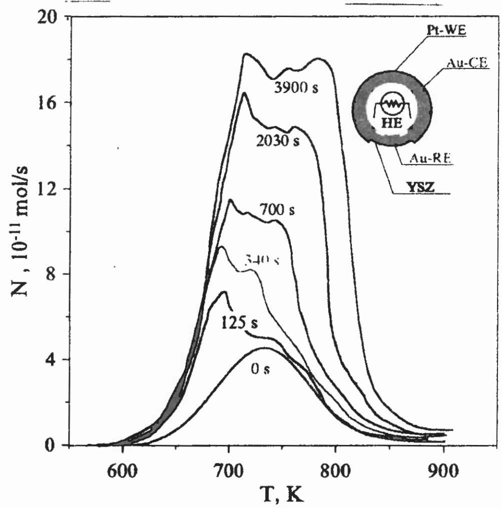

Figure 3: Schematic of the experimental (inset) and Oxygen TPD spectra after gaseous O_2 adsortion on Pt deposited on YSZ followed by electrochemical O^{2-} supply (I=15iÅ) for various time periods t/s comparable to 2FN/I(=2570s). Gaseous O_2 supply creates a single adsorption state (T_p=740 K), but additional electrochemical oxygen supply creates two adsorption states: The weakly bonded state (T_p≈680 K) is highly reactive (32), while the strongly bonded (backspillover) state (T_p≈750-780 K) acts as a sacrificial promoter for catalytic oxidations (32). Inset: Au counter and reference electrodes; HE: Heating element (32)

The unanimous answer came from a number of surface spectroscopic techniques, X-ray photoelectron spectroscopy (XPS) (23, 28-30), surface-enhanced Raman spectroscopy (SERS) (22,31), temperature programmed desorption (TPD) (32) (Fig. 3) in addition to high temperature cyclic voltamperometry (32) and scanning tunneling microscopy (STM) (33): Both the work function variation and the concomitant dramatic catalytic rate modification are due to an electrochemically controlled migration (backspillover in the catalytic terminology) of ionic species

($O^{\delta-}$ in the case of YSZ, $Na^{\delta+}$ in the case of β"-Al_2O_3) from the solid electrolyte onto the gas-exposed, i.e. catalytically active, electrode surface.

These ionic species, accompanied by their compensating charge in the metal, (thus forming surface dipoles) spread over the entire gas-exposed catalyst-electrode surface and establish an effective electrochemical double layer which affects the binding strength and thus catalytic activity of chemisorbed reactants and intermediates (Fig. 4). Recent ab initio quantum mechanical calculations have confirmed this picture and established theoretically the observed linear dependence of chemisorptive binding strengths on catalyst work function (34). It may thus be concluded that the origin of electrochemical promotion is now firmly established.

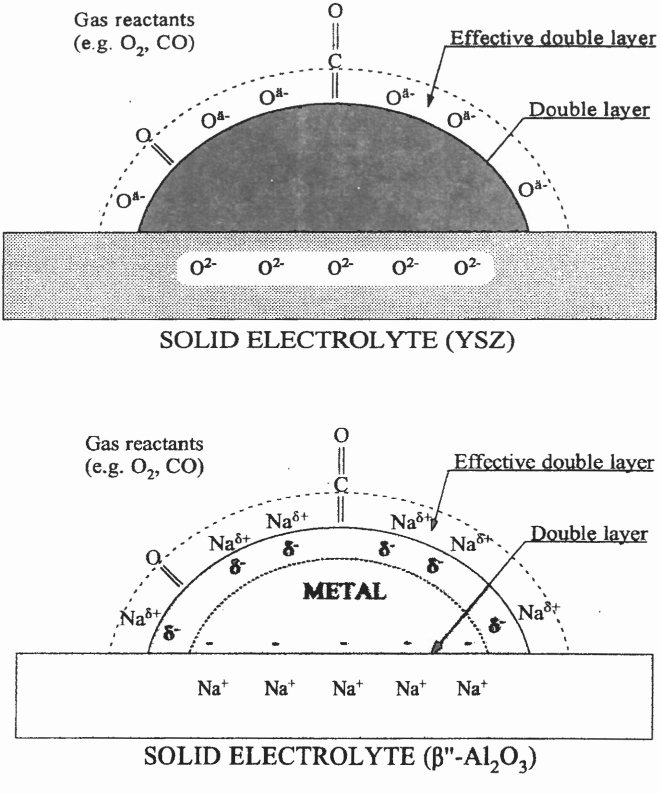

Figure 4: Schematic representations of a metal electrode deposited on a O^{2-}-conducting and on Na^+-conducting solid electrolyte, showing the location of the metal-electrolyte double layer and of the effective double layer created at the metal/gas interface due to potential-controlled ion migration (backspillover).

The non-Faradaic activation of heterogeneous catalytic reactions via the NEMCA effect is a novel and promising application of electrochemistry. There is a lot of new surface chemistry to be explored (14) with several promising technological possibilities, particularly in industrial product selectivity modification (18) and in exhaust gas treatment (30). There are still several unresolved scientific and mostly technical issues which will dictate the ultimate industrial usefulness of electrochemical promotion. One of them is the ability to induce NEMCA without external current application by utilizing the catalytic-reaction-driven potential difference between the catalyst and a less active counter electrode (35,36). Other issues include the ability to induce NEMCA on highly dispersed or on semiconducting catalyst surfaces. Research on these issues is needed to fully understand the technical potential of electrochemical promotion and to establish the basis for its technological utilization. At the very least, however, the new, electrochemically induced phenomenon will allow a systematic study and enhanced understanding of the role of promoters in heterogeneous catalysis.

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PL-34

New Approaches to Homogeneous Catalysis

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Homogeneous, transition metal based catalysis has seen a rapid growth in recent years mainly due to selectivity advantages. Many new processes emerged. The difficulties to recycle homogeneous catalysts have prevented even faster growth and have hindered more applications. To combine the advantages of homogeneous and heterogeneous catalysis two general approaches developed: immobilization of homogeneous catalysts via organic or inorganic solid supports and catalysis in two liquid phases (fluid-fluid-two-phase-catalysis).

The two-liquid-phase approach is based on the principle that the phase with the catalyst and the product-phase are immisible or that in two immisible phases (one containing the catalyst) the distribution coefficient of the product formed is high (Fig. 1).

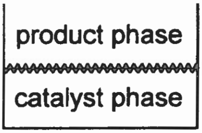


Fig. 1 Principle of two-phase-liquid catalysis

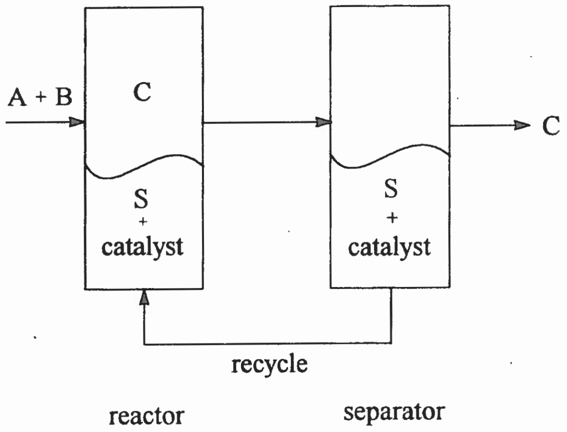
Three cases will be considered:

1. products separate during catalysis
2. catalysis is followed by extraction
3. solvent for extration is added during catalysis

1. Products separate during catalysis

The concept is illustrated in Fig. 2

$$A + B \longrightarrow C$$



S = solvent

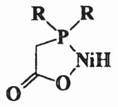
Fig. 2 Two-phase-liquid-liquid system (products separate)

The catalyst is dissolved in the solvent S (generally a polar organic solvent or even water). The products C formed „swim“ on S and can be „spooned off“. The reaction occurs in the reactor and product/catalyst separation follows in the separator. Easy catalyst recycle can be envisaged.

The first technical example operating by this principal is the SHOP process by Shell (eq 1) discovered by the author.

$$n\ C{=}C \longrightarrow \alpha\text{–olefins} \qquad (1)$$

cat.



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The catalyst is soluble in water, acetonitrile, 1,4-butanediol, glycol and other polar solvents. The α-olefins formed from ethene „swim up“ and can be separated easily thus enabling simple catalyst recycle. The proper choice of the polar solvents is crucial and is a chemical engineering problem such as solubility of ethene, distribution coefficient and so on. Fig. 3 shows a block scheme of the SHOP process.

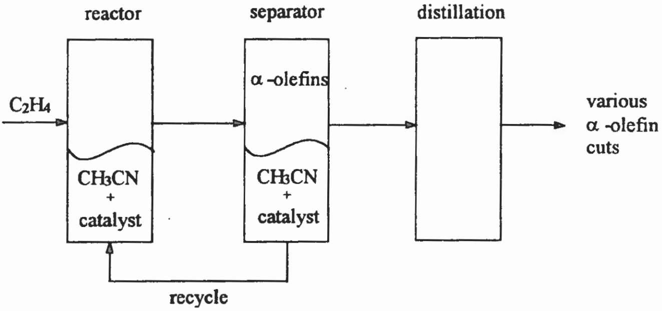
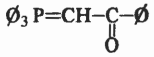
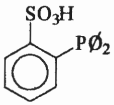


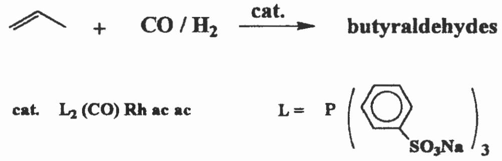
Fig. 3 Liquid-liquid-two-phase system in the SHOP process

Ligands active in SHOP are:

$\varnothing_2\ \mathrm{P\ CH_2COOH}$	soluble in	alcohols, ethers, nitriles, toluene, benzene
$\varnothing\ \mathrm{P\ (CH_2COOH)_2}$	soluble in	alcohols, ethers, nitriles, toluene
 $\varnothing_3\,\mathrm{P{=}CH{-}}\underset{\underset{\displaystyle O}{\|}}{\mathrm{C}}{-}\varnothing$	soluble in	alcohols, ethers, nitriles, toluene
	soluble in	water

Various processes based on the above principle are operated by industry.

In the Rhône-Poulenc-Ruhrchemie/Hoechst process propene is hydroformylated (eq 2).



(2)

The catalyst is soluble in water and the whole process is run in water.

Other processes carried out are: Synthesis of octadienols by Kuraray, isoprenylation (Rhône-Poulenc), synthesis of geranyl acetone (Rhône-Poulenc).

By using a fluorinated solvent (Hostinert 216 by Hoechst) we could oligomerize butene-1 as elucidated in Fig. 4 (M. Vogt, Thesis RWTH Aachen 1991).

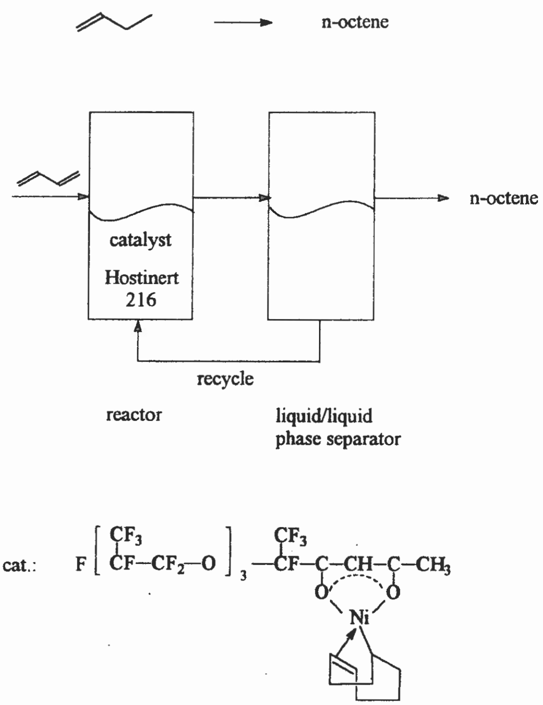
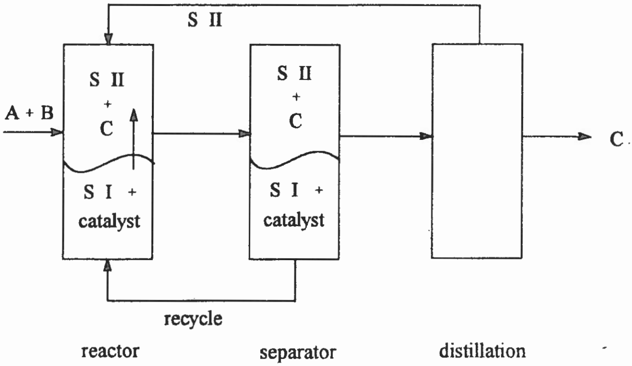


Fig. 4 Dimerization of 1-butene in a two-phase-liquid-system

2. Catalysis is followed by extraction

Fig. 5 demonstrates this approach

$$A + B \longrightarrow C$$



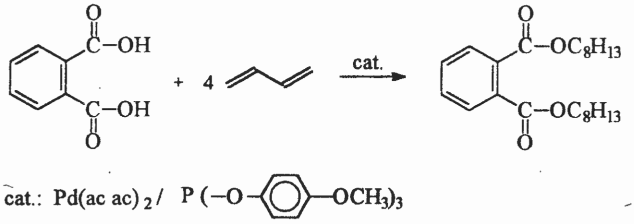
S I = solvent (polar)

S II = solvent (unpolar)

Fig. 5 Two-phase-liquid-liquid system applying extraction

The reaction is carried out in solvent S I, which contains the catalyst. An extraction of the products by the solvent S II is done in an extraction step. The catalyst phase S I is recycled. Products and solvents S II are separated in a distillation step.

As early as in 1976 (A. Durocher, Thesis RWTH Aachen 1976) we have demonstrated this approach in a system shown in Fig. 6, a self-explanatory way.



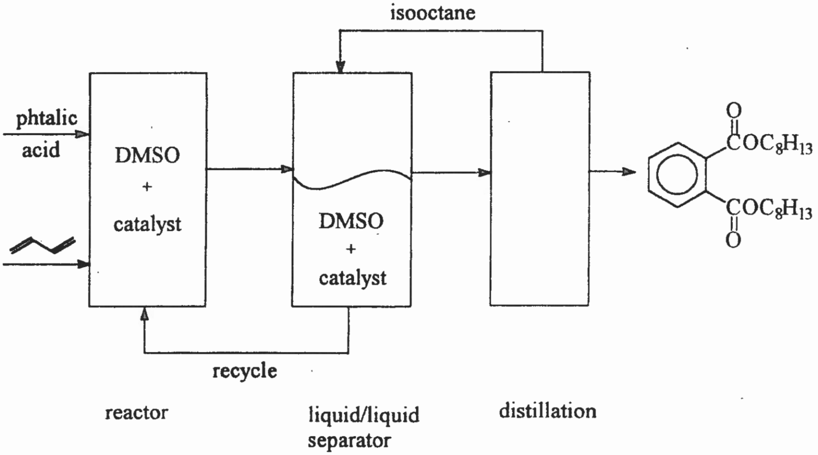
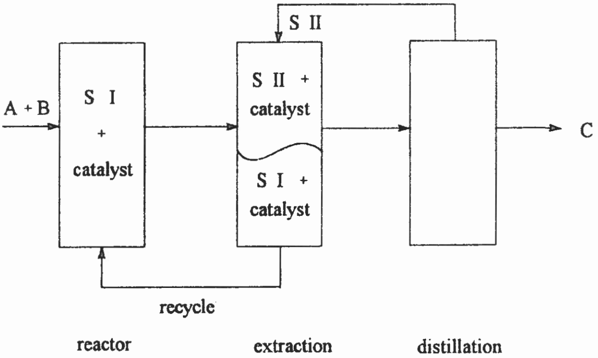


Fig. 6 Synthesis of octylphthalates in a two-phase system

3. Solvent for extraction is added during catalysis

In this approach a solvent S II is added already in the reactor to extract the products formed during catalysis (Fig. 7)

$$A + B \longrightarrow C$$



S I = polar solvent

S II = solvent for extraction

Fig. 7 Two-phase-liquid-liquid system with solvent for extraction added in reactor.

From a technical point of view this method is cumbersome, but offers the advantage to carry out reactions at low conversions. Normally in homogeneous catalysis high conversions and high selecticities are necessary to make the homogeneous process economic. High selectiviy and high conversion, however, are very demanding regarding the catalyst applied. Especially in processes where consecutive reactions occur, homogeneous systems are disadvantaged. Such a process is the telomerization of butadiene with ammonia (eq 3).

(3) n  $+ NH_3 \longrightarrow C_8H_{13}NH_2 + (C_8H_{13})_2NH + (C_8H_{13})_3N$

The product of technical interest is $C_8H_{13}NH_2$, but the latter one is very reactive entering consecutive reactions with butadiene yielding $(C_8H_{13})_2NH$ and $(C_8H_{13})_3N$. By adding toluene in

the reactor as solvent S II (Fig. 7) the initial product $C_8H_{13}NH_2$ is extracted and becomes the main product (T. Prinz, W. Keim, B. Drießen-Hölscher, Angew. Chem. 108, 1835, 1996).
Table 1 summarises some results obtained:

Table 1 Telomerization of butadiene by NH_3 in a two-phase-liquid system

Solvent S II of the second phase	**Selectivity %**		**yield %**
	$(C_8H_{13})NH_2$	**$(C_8H_{13})_2NH$ / $(C_8H_{13}N$**	
none	60,5	30	41
toluene	88	6	55
pentene	79	16	61

Obviously, the primary octylamine is the main product formed in a two-phase system. In this way it is feasible to run consecutive reactions at low conversions, a process route used frequently in heterogeneous catalysis.

PL-35

SELECTIVE HYDROGENATIONS IN LIQUID PHASE: DINITRILES TO AMINONITRILES ON RANEY CATALYSTS

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INTRODUCTION

Several hydrogenation reactions carried out in a liquid phase require high selectivity to a product that is an intermediate in a sequence of events leading to fully hydrogenated species. This is the case, for example, in conversion of dienes to mono-olefins, and dinitriles to aminonitriles. In general, the selectivity and activity can be affected by two approaches: modification of the catalyst properties, and modification of the medium of reaction. Thus, as examples of the first approach, borides of the Group VIII metals display higher selectivity in conversion of cyclopentadiene to cyclopentene than non-modified metals [1, 2]. A similar effect has been described for supported palladium catalysts partially poisoned with sulfur [3]. In nitriles hydrogenation the Raney catalysts have been modified by introduction of defects through a mechanical treatment [4], and by addition of other metallic components [5].

Hydrogenation of aliphatic dinitriles is used in industry mainly to produce diamines. In this sequence of series-parallel reactions aminonitriles represent the half-hydrogenated intermediates of the process. Maximum observed yields of aminonitriles are between 20 and ≤ 45% at incomplete conversion of dinirtiles (≤ 50%) in all cases. Higher selectivity to aminonitriles has been achieved by using catalysts containing rhodium deposited on high-surface MgO, and carrying the reaction in the presence of a large excess of NH_3 [6, 7].

The purpose of this work [8] was to define conditions resulting in the maximum yield of aminonitriles over commercial Raney catalysts. For the considered sequence of hydrogenation reactions

$$A + 2\,H_2 \xrightarrow{k_1} B$$

$$B + 2\,H_2 \xrightarrow{k_2} C$$

net rate of formation of the intermediate B is $dC_B/dt = k_1C_A - k_2C_B$. Thus the maximum yield of the aminonitrile (B) depends on the value of the k_1/k_2 ratio [9]. Phenomenological rate constants k_1 and k_2 may include adsorption components. Properly selected reaction medium can influence adsorption equilibria of species of interest by interaction with either the catalyst surface, or the adsorbate. It is the intention of this paper to show that the latter may be the case of observed enhancement of selectivity.

EXPERIMENTAL

Liquid phase hydrogenation reactions were carried out in a 300 ml autoclave equipped with a stirrer, provisions for heating and cooling, and a dip tube with filter. Samples of the reaction mixture were withdrawn periodically through the dip tube for gas chromatographic analysis, allowing for concentration profiles of components vs. time to be constructed. Reactions were carried out at temperatures from 40 to 120 °C, and hydrogen pressures from 15 to 100 bars. Commercially available Raney Ni (including catalysts promoted by the presence of Fe + Cr, Mo, and Co), and Raney Co catalysts were used in this work. Catalysts obtained from Degussa, W. R. Grace, and Activated Metals were tested. Typically 5 to 15 % (wt) of Raney catalyst was charged. Group VIII metals (Pd, Pt, Rh, and Ru) on various supports were also tested, but found less satisfactory, except for Rh/MgO (confirming the earlier work of Mares et al. [6, 7].

IR spectra of methanolic solutions, with and without NaOH present, were taken in transmission mode using conventional equipment. Spectra of aminonitriles in liquid ammonia, thus at elevated pressure, were obtained in internal reflection mode, using high-pressure attachment equipped with a sapphire rod.

RESULTS AND DISCUSSION

Hydrogenation of dinitriles containing from four (succinonitrile) to twelve (dodecanedinitrile) carbon atoms in the molecule was investigated. In the absence of solvents reaction leads to formation of diamines, and only low concentrations of aminonitriles are observed. For example, hydrogenation of neat adiponitrile (ADN) on Raney Ni catalysts gives the maximum yield of 6-aminocapronitrile (ACN) 2 50%, at ca. 70% ADN conversion. Thus interrupting the reaction at lower conversions of the dinitrile is not an efficient way to produce aminonitrile, because extensive separations and recycle would be required. But in the presence of 10-fold (molar) excess of MeOH (containing 1.5% (wt) NaOH) the [ACN]max > 75%, at ADN conversion ca. 85%.

A strong effect of the reaction medium on selectivity to aminonitriles was found. Good solubility of H_2 in the solvent is necessary, but not sufficient. The preferred solvents include simple aliphatic alcohols (with an inorganic base, for example 3 0.5% of NaOH or KOH (wt) added), or liquid ammonia. The effect of solvents is not additive, ie. addition of liquid ammonia to methanol does not further enhance selectivity. In general selectivity to aminonitriles increases with dilution by the above solvents. For example selectivity of conversion of ADN to aminocapronitrile increases with the amount of alcohol used, and reaches a plateau at ca. 10 mols MeOH per mol of ADN. Lesser excess of liquid ammonia solvent (5 fold molar, for ADN hydrogenation) is sufficient to achieve similar selectivity. It is interesting to note that the rate of dinitriles hydrogenation remains essentially insensitive to the amount of the solvent. Several other solvents, as ammonium hydroxide, hydrocarbons such as heptane and higher homologues, tetraglyme, several amines, and tetrahydrofuran (THF), were tested but found less satisfactory. Thus the enhanced selectivity to aminonitriles is not due to dilution alone.

Presence of an inorganic base, such as alkali metals hydroxides, methoxides or carbonates, is required when aliphatic alcohols are used as solvents. In the absence of a base in methanolic solutions of ADN the rate of hydrogenation decreases and byproducts (especially those formed by condensation) appear in excessive amounts.

Yield of aminonitriles decreases with increasing temperature of the process. Looking from the practical point of view, selective hydrogenation of dinitriles to aminonitriles can be operated in the range from 50 to 80°C. At lower temperatures the rate of hydrogenation becomes too slow, and temperature control of this exothermic process becomes too involved to be practical. At higher temperatures rates of hydrogenation of both the dinitrile and the aminonitrile are greatly accelerated, and selectivity decreases. In addition formation of products of condensation (bis-hexamethylenetriamine in the case of ADN hydrogenation) increases, resulting in a further decrease of selectivity.

Several Raney Nickel catalysts were tested. The best for our purpose, and about equivalent in performance, were Raney Nickels promoted with Cr + Fe, and with Mo.

Concentration profiles of the main components of ADN hydrogenation will be discussed in details. In general they follow the typical behavior of sequential reactions.

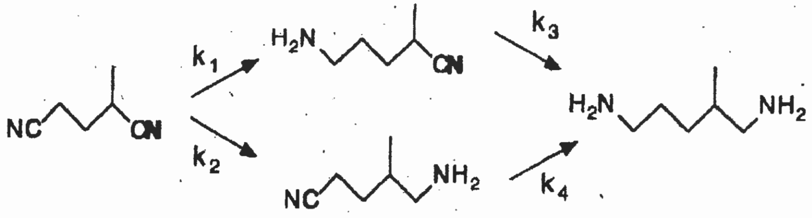
At 70°C and 34 bars H_2, in the presence of 5 mols of ammonia per mol of ADN, conversion of ADN is achieved within 180 minutes. Concentration of aminocapronitrile in the reaction mixture increases steeply, and reaches maximum of 72% at ca. 90% conversion of the dinitrile. At that time concentration of hexamethylenediamine, the final product of hydrogenation, is still below 10%.

The other way of looking on the same data is to plot the yield of ACN and HMD vs. ADN conversion. In such coordinates [9], the diagonal line indicates theoretical 100% selectivity of conversion of adiponitrile to aminocapronitrile. Data points corresponding to actual concentration of ACN in the reaction mixture show increasing deviation from this line with increasing conversion of ADN. A steep increase in hexamethylenediamine concentration can be seen above ca. 90% conversion of ADN.

Similar results were also obtained when 10-fold excess of methanol (containing NaOH) was used as a solvent. The high selectivity to ACN is not limited to liquid ammonia medium of reaction.

As will be demonstrared, the maximum yield of aminocapronitrile observed in this experiment exceeds 70%. Kinetic analysis [9] indicates that in order to reach such yield of an intermediate in series-parallel reactions under consideration, the effective value of the k_1/k_2 ratio (defined above) must be ca. 8. In the absence of one of the above solvents the k_1/k_2 ratio, measured in independent hydrogenations of neat ADN and ACN containing only aqueous solution of NaOH, has the value ≤ 2. The maximum yield of ACN found during hydrogenation of neat ADN is ca. 45%. Thus the observed enhancement of selectivity, associated with the presence of one of the preferred solvents, is accompanied by an apparent increase of the k_1/k_2 ratio by a factor of ca. four.

Effect of chain branching (linear ADN vs. branched methylglutaronitrile, MGN) was studied. The two CN groups in MGN are not equivalent due to the presence of the side methyl group in molecule. The steric hindrance of the methyl group favors formation of 5-amino-2-methyl-valeronitrile (later described as AN 1) over 5-amino-4-methyl-valeronitrile (AN 2).



Yield of the sum of both of these isomeric forms (Σ AN) reaches 80% at ca. 90% MGN conversion, while yield of the methylpentamethylenediamine (MPMD) remains below 5% up to ca. 95% MGN conversion. Thus, the steric factor in MGN is beneficial from the aminonitrile selectivity point of view.

The ratio [AN 1] / [AN 2] remains constant at ca. 2.75 until all the MGN is converted. Then this ratio increases steeply because the unhindered CN group of AN 2 undergoes further hydrogenation to MPMD, while the CN group of AN1 remains protected by the steric effect of the adjacent methyl group. Hence the relative concentration of the two isomers is not a constant, but varies with time on stream (MGN conversion). This indicates that, similarly as ADN, MGN is preferentially adsorbed on active sites of the Raney catalyst, and AN 2 can undergo hydrogenation only after exhaustion of the available MGN.

Hydrogenation of other members of the homologous series of dinitriles containing from four to twelve carbon atoms per molecule was undertaken, looking for optimization of aminonitriles formation. Selectivity to corresponding aminonitriles is lower for 7- and 8-carbon systems than that found for 6-carbons members, but higher than that for 12-carbon system. The behavior of sebaconitrile (C_{10}) during hydrogenation is similar to that of dodecanedinitrile (C_{12}).

Changes of selectivity to aminonitriles (at various dinitrile conversions) can be plotted versus the chain length of the starting dinitrile in the series. Selectivity decreases when the chain length of dinitriles increases from six to ten carbon atoms per molecule, but this relationship levels off at each extreme of the range. The decrease becomes steeper with increasing conversion of the dinitrile. For 90% conversion, the selectivity decreases from ca. 81% for five- and six-carbon species to ca. 25% for C_{10} and C_{12} molecules.

We propose to explain the above observations by invoking an intramolecular interaction leading to a heterocyclic (n+1) conformation, containing a solvated imino- form of the CN. Such ring structure would be in equilibrium with the linear form.

This equilibrium is driven to the right by the presence of a base: addition of an inorganic base (as NaOH or KOH) to the alcoholic solution, or by use of liquid ammonia as the solvent. Above hypothesis is supported by IR data. For solutions of aminonitriles in methanol alone there are two prominent lines observed: at 2248 cm^{-1} (CN group), and 1605 cm^{-1} (NH_2 group). On addition of NaOH to this solution the intensity of the CN band decreases, with a concomitant appearance of a new band centered around 1660 cm^{-1}, and assigned to vibration along the C=N bond. At room temperature ca. 25 to 30% of the adiponitrile undergoes such transformation (temperature dependence was not investigated.) Analogous changes were observed in liquid ammonia solvent. Such cyclic conformation would impede readsorption of the aminonitrile, necessary for its further hydrogenation, on the catalyst surface. [On the other hand no changes in the IR spectra were detected in solvents which do not enhance the aminonitriles selectivity. This was shown to be true for THF and heptane, with or without addition of aqueous NaOH solution.]

While 6- and 7- member nitrogen-containing heterocycles, postulated here to arise from five- and six-carbon aminonitriles, are common, increasingly more stress is involved in formation of higher-order rings. Thus the equilibrium will shift to linear form of aminonitrile (resulting in lower selectivity) with increasing number of carbon atoms in the chain. That is indeed the trend observed in this work. Maximum yield of the aminonitrile, and position of this maximum with respect to conversion of the starting dinitrile, depends on the ratio of rate constants k_1/k_2 (where k1 is the rate constant for conversion of the dinitrile to aminonitrile, and k_2 is the rate constant of further hydrogenation of that aminonitrile to the corresponding diamine). Change in the adsorptive properties of aminonitrile, associated with the existence of the cyclic form, results in lower effective value of the k_2, thus increasing the effective value of the k_1/k_2 ratio.

Another trend uncovered is the increasing tendency towards formation of dimers of aminonitriles with decreasing carbon chain length. Such dimers are formed during the course of reaction by coupling diamine-diamine, diamine-aminonitrile, and aminonitrile-aminonitrile, with elimination of one molecule of ammonia per created -bond. During hydrogenation of glutaronitrile (C_5) up to 15% of aminonitrile is found in the form of dimers, and is counted as aminonitrile in the data presented. But for hydrogenation of succinonitrile (C_4) more than 50% of the aminonitrile formed exists as dimers, and oligomerizatiion continues even on standing at room temperature. This is the reason why data for C_4 dinitrile hydrogenation will be not included in detailed discussion.

CONCLUSIONS

Relatively high selectivity to aminonitriles at high conversion of the starting material can be achieved when liquid-phase hydrogenation of dinitriles containing from 4 (succinonitrile) to 12 carbon (dodecanedinitrile) atoms per molecule over commercial Raney catalysts (as Ni/CrFe, and Ni/Mo) is carried out, at moderate conditions of temperature and pressure, in solvents such as MeOH + NaOH, or in liquid ammonia. Observed dependence of selectivity on the carbon chain length can be explained by invoking an intramolecular transformation of the aminonitrile molecules in the preferred reaction media to heterocyclic structures. Formation of such ring structures (existence of which is supported by IR results) should hinder readsorption and hence further hydrogenation of aminonitriles to diamines.

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REACTION MECHANISMS FOR PROCESSES OF IMPORTANCE TO ENVIRONMENTAL PROTECTION OCCURRING OVER ZEOLITE-BASED CATALYSTS

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INTRODUCTION

Increasing public concern with the effects of toxic chemicals on the environment has focused attention on finding means to produce the chemicals in an environmentally responsible fashion, and to destroy toxic substances before they can be released into the environment. Zeolite-based catalysts are promising candidates for the selective synthesis of chemicals, as well as destruction of toxic substances. Work on the first of these subjects has been reviewed by Holderich [see for example refs. (1a-c)] and will not be covered further. Instead, we shall focus on investigations conducted in our laboratory aimed at understanding the mechanisms of NO decomposition and reduction, and CH_4 oxidation.

NO DECOMPOSITION

Recent studies have shown that metal-exchanged zeolites can catalyze the decomposition of NO to N_2 and O_2 [see for example ref. (2) and references cited therein]. Copper-exchanged ZSM-5 is particularly attractive for the first of these reactions and Co-exchanged ZSM-5 is one of the most active catalysts for the second reaction. Our work has focused on understanding the structure of Cu-ZSM-5, and the manner in which this catalyst facilitates the decomposition of NO.

EPR studies demonstrate that immediately after exchange all of the copper in Cu-ZSM-5 is present as Cu^{2+}, presumably as hydrated $Cu^{2+}(OH)^-$ (3). Heating freshly prepared Cu-ZSM-5 in flowing He or in vacuum results in the autoreduction of Cu^{2+} to Cu^+ (3-5). This transformation was originally inferred from EPR (3-9) and photoluminescence (10, 11) observations and has now been confirmed by XANES (6, 12, 13). We have very recently shown by means of ^{65}Cu NMR and ^{27}Al-^{65}Cu SEDOR NMR experiments that all of the Cu+ species formed by autoreduction are associated with Al cation-exchange sites, and that the average Cu-Al distance is 2.3 ± 0.2 Å (14). We have also proposed that the autoreduction process proceeds via the reaction 2 $Cu^{2+}(OH)^{-}$ = Cu^{+} + $Cu^{2+}O^{-}$ + H_2O, since all of the copper can be transformed back to Cu^{2+} by exposing an autoreduced sample of Cu-ZSM-5 to water vapor (3). Density functional theory (DFT) calculations demonstrate that both Cu^{+} and $Cu^{2+}O^{-}$ are strongly bidentate coordinated with oxygen atoms bonded to Al in the zeolite framework, as shown in Figs. 1 and 2 (15). The distance of Cu+ from Al in a T12 site is 2.4 Å, in very close agreement with what is found experimentally. The DFT calculations also show that both Cu^{+} and $Cu^{2+}O^{-}$ have negligible net spin and hence should be EPR silent

Infrared studies show that NO adsorption occurs on both Cu^{+} and $Cu^{2+}O^{-}$ (16). The band observed at 1811 cm^{-1} is attributed to $Cu^{+}(NO)$ and a pair of bands at 1824 and 1733 cm^{-1} are attributed to $Cu^{2+}(NO)_2$. A band seen at 1906 cm^{-1} is assigned to $Cu^{2+}(O^{-})(NO)$. Additional bands observed below 1600 cm^{-1} have been attributed to nitrito and nitrato species. DFT calculations reveal that while NO adsorbed as $Cu^{+}(NO)$ and $Cu^{2+}(O^{-})(NO)$ is strongly bound, NO in $Cu^{+}(NO)_2$ is not (17). The heats of NO adsorption for the first two species are 43.3 kcal/mol and 53.7 kcal/mol kcal/mol, respectively, whereas the heat of adsorption for the third is 54.5 kcal/mol. These findings are consistent with experimental observation.

The nature of the species involved in NO decomposition over Cu-ZSM-5 is revealed by infrared spectroscopy. NO decomposition over Cu-ZSM-5 initiates above 573 K and reaches a maximum at about 523 K. In this temperature range, in situ infrared spectra show weak bands for only two species, $Cu^{+}(NO)$ and $Cu^{2+}(O^{-})(NO)$ (16). Several authors (11, 18-24) have proposed that Cu^{+} sites are essential for NO decomposition, and a correlation has been reported between the concentration of Cu^{+} sites and the activity of Cu-ZSM-5 for NO decomposition (11). While it has also been proposed (2, 25) that only Cu^{2+} sites are required for NO decomposition, the experimental evidence for this interpretation is not compelling.

To assess whether or not NO decomposition could occur over isolated Cu sites and the extent to which Cu^{+} and $Cu^{2+}O^{-}$ are involved, we have carried out a theoretical analysis of the Gibbs free energies of reaction for a sequence of steps comprising a mechanism for NO decomposition (17). Figure 3 illustrates a reaction mechanism based on choosing those elementary processes for which the change in the Gibbs free energy is most favorable. The numbers appearing in this figure give the change in the standard-state Gibbs free energy for each elementary step evaluated at 500 °C. Based on this analysis it is clear that NO decomposition could occur via a reaction sequence involving only Cu^+ and $Cu^{2+}O^-$ as the catalytically active sites.

The reaction mechanism shown in Fig. 3 is consistent with a number of experimental observation. As noted earlier, in situ infrared spectroscopy shows only two forms of adsorbed NO at temperatures in the range of 400-500 °C where the rate of NO decomposition is significant. While it has been suggested that N_2O could form via the decomposition of $Cu^+(NO)_2$, our calculations show that this species is not stable in the temperature range of interest (17). Thus it is far more likely that N_2O is formed via the reaction of NO with $Cu^+(NO)$. The decomposition of NO is known to be inhibited by O_2 (9). Figure 3 suggests that with increasing O_2 partial pressure, the rate of NO decomposition is inhibited by blocking the release of Cu^+ sites. H_2O is also known to inhibit NO decomposition over Cu-ZSM-5 (2). While the interactions of H_2O with Cu-ZSM-5 are not shown in Figure 3, we have calculated that the change in the standard-state Gibbs free energy for the reaction $Cu^+ + Cu^{2+}O^- + H_2O = 2\,Cu^+(OH)^-$ is -18 kcal/mol at 500 °C (15). From this we deduce that H_2O could inhibit the decomposition of NO by reducing the concentrations of Cu^+ and Cu^{2+}, both of which are envisioned to be essential species for NO decomposition.

NO REDUCTION

Studies by different investigators have shown that Co-ZSM-5 is not very active for the reduction of NO by CH_4 in the absence of O_2 (26-31). Introduction of O_2 into the feed stream greatly enhances the reduction of NO to N_2. This effect has been ascribed to the oxidation of NO to NO_2, which is then strongly adsorbed on the catalyst where it is attacked by CH_4. Direct observation of the reaction of NO_2 with methane has recently been obtained from infrared studies (32, 33). Figures 4 and 5 show spectra taken during the temperature programmed desorption of NO in either flowing He or CH_4 (33). Below 250 °C both sets of spectra are identical. Bands are seen at 2132 cm^{-1} due to $H^+(NO_2)$, 1941 cm^{-1} due to $Co^{2+}(OH^-)(NO)$, 1894 and 1815 cm^{-1} due to $Co^{2+}(OH^-)(NO)_2$, 1633 cm^{-1} due to nitrate species, and 1560-1530 cm^{-1} due to nitrito species. Above 250 °C the intensity of the nitrito band is significantly reduced by reaction with CH_4.

During steady-state reaction of NO with CH_4, two additional bands are observed at 2270 and 2173 cm^{-1}. These features have been assigned to $Al^{3+}(NCO)$ and $Co^{2+}(OH^-)(CN)$, respectively (33, 34). To assess whether these species might be reaction intermediates, experiments were carried out in which the isocyanate and cyanide species were prepared and then allowed to react with NO, O_2, or NO_2 at 450 °C and the rate of species disappearance was compared with that observed in flowing He. Significant acceleration in the rate of band attenuation was observed only in the case of the cyanide species, with the rate of consumption of cyanide species increasing in the order $NO_2 >> NO \approx O_2 > He$. In a complimentary set of experiments the products formed via reaction of NO, O_2 or NO_2 with cyanide species were followed by mass spectrometry. The dynamics of cyanide consumption determined by this means were virtually identical to those determined from infrared observations. Both N_2 and CO_2 were observed upon reaction of cyanide species with NO_2 and O_2, and the stoichiometric ratios in which these products were formed are consistent with assignment of the band at 2173 cm^{-1} to CN.

Based on the evidence presented above we propose the mechanism for NO reduction by CH_4 presented in Fig. 6. This scheme is based upon an amalgamation of elementary steps previously suggested in the literature (30-33, 35-37) and those deduced from the experiments presented here. The sequence begins with the adsorption of NO adsorption to form both mono- and dinitrosyl species (reactions 1 and 2). The later species undergo oxidation in O_2 (reaction 3) to form adsorbed and gas phase NO_2. The reaction of CH_4 with adsorbed NO_2 (reaction 4) is assumed to form a hydroxyl radical and adsorbed CH_3NO. Weiner and Bergman (38) have reported the formation of CH_3NO and other nitrosoalkanes by migratory insertion of coordinated NO into Co-C bonds of cobalt alkyl species. Subsequent reaction of adsorbed nitrosomethane with either OH radicals or O_2 (reactions 5) followed by the elimination of water (reaction 6) leads to the formation of adsorbed CN species. The nitrile species are hypothesized to react with NO_2 to form N_2 and CO_2 (reaction 7), or with NO to form N_2 and CO (reaction 8). The reaction of nitrile species with O_2 (reaction 9) could result in the formation of NO and CO. While not indicated, the CO released in reactions 8 and 9 is envisioned to undergo further oxidation to CO_2.

The reaction sequence presented in Fig. 6 is consistent with the mechanistic arguments given previously by Li et al. (36), who proposed that the first step in the reduction of NO by CH_4 over Co-ferrierite is the reaction of gas-phase CH_4 with adsorbed NO_2, but differs in regard to the sequence of reactions leading to N_2 and CO_2. It is noted that the possibility of CN serving as a precursor to N_2 and CO_2 was suggested recently by Li et al. (39), based on studies conducted with Cu/ZrO_2 and by Hayes et al. (40) based on studies conducted with Cu-ZSM-5.

The proposed mechanism is attractive in that it explains not only the manner in which NO_2 initiates the reaction of CH_4, but also the pathway to CO_2 and N_2. This mechanism would also explain why NO facilitates the combustion of CH_4 by O_2 (30, 32). TPD experiments conducted in our laboratory have shown that Co-ZSM-5 will not adsorb O_2, whereas it will adsorb NO_2. If the product of the reaction of CH_4 with NO_2 is retained as an adsorbed species,

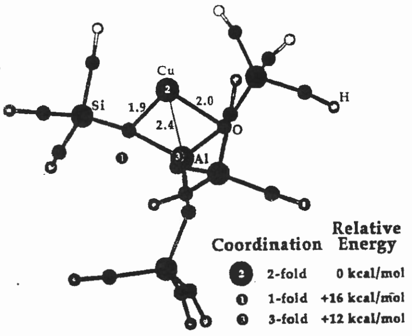

Fig. 1 Minimum energy structure of Cu+ in 1-fold, 2-fold, and 3-fold coordination sites in ZSM-5. Bond lengths are given in Å.

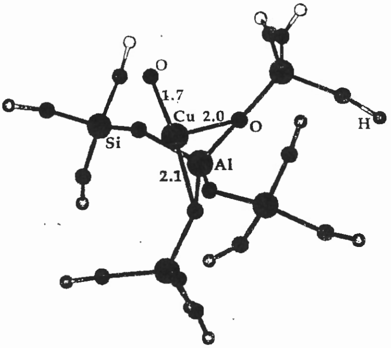

Fig. 2 Minimum energy structure of $Cu^{2+}O^-$ coordinated to two oxygen atoms in ZSM-5. Bond lengths are given in Å.

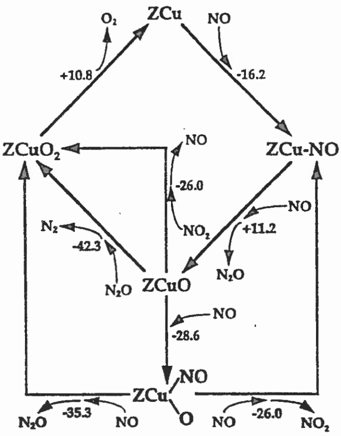

Fig. 3 Proposed pathway for NO_x decomposition over Cu-ZSM-5. Arrows in the diagram depict the progress of each reaction in the forward direction. Numbers are ΔG^o (773 K) in kcal/mol.

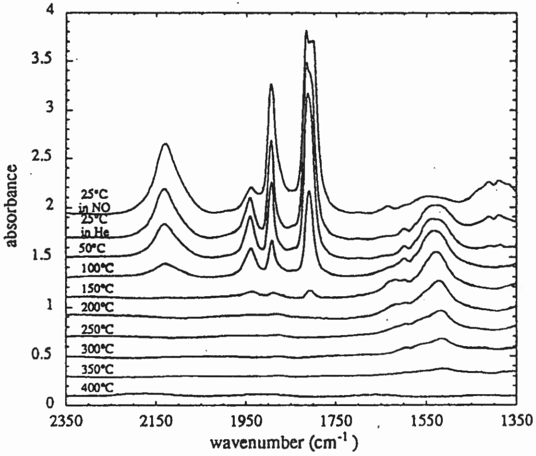

Figure 4. 6600 ppm NO was preadsorbed for 40 min at room temperature and desorbed in He, during temperature ramp.

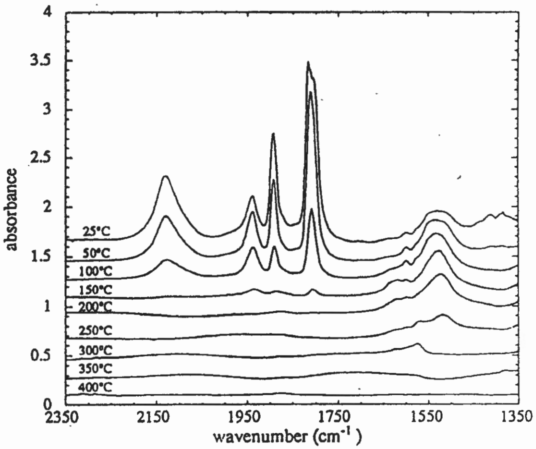

Figure 5. 6400 ppm NO was preadsorbed for 40 min at room temperature, and desorbed in 2.14% CH_4/He, during temperature ramp.

1 $Co^{2+} + NO \rightleftharpoons Co^{2+}(NO)$

2 $Co^{2+}(NO) + NO \rightleftharpoons Co^{2+}(NO)_2$

3 $Co^{2+}(NO)_2 + O_2 \longrightarrow Co^{2+}(NO_2) + NO_2$

4 $Co^{2+}(NO_2) + CH_4 \longrightarrow Co^{2+}(CH_3NO) + OH\cdot$

5 $Co^{2+}(CH_3NO) + O_2\ (OH\cdot) \longrightarrow Co^{2+}(CH_2NO) + HO_2\cdot\ (H_2O)$

6 $Co^{2+}(CH_2NO) \longrightarrow Co^{2+}(CN) + H_2O$

7 $Co^{2+}(CN) + NO_2 \longrightarrow Co^{2+} + N_2 + CO_2$

8 $Co^{2+}(CN) + NO \longrightarrow Co^{2+} + N_2 + CO$

9 $Co^{2+}(CN) + O_2 \longrightarrow Co^{2+} + NO + CO$

Figure 6. Proposed reaction mechanism for NO reduction by CH_4 in the presence of O_2.

then it is easy to see how NO_2 (derived from the oxidation of NO) could facilitate the oxidation of CH_4 by O_2.

CH_4 OXIDATION

Catalysts for the low-temperature (< 300°C) combustion of CH_4 are required for controlling the emissions of natural gas burning engines. Recent studies have shown that Pd-ZSM-5 is unusually active for this purpose (41, 42).

Work in our laboratory has demonstrated that ZSM-5 containing 0.4 % Pd exhibits a lower turnover frequency based on total moles of Pd than does ZSM-5 containing 4 % Pd. Raman spectra of the two catalysts were acquired after use, to determine the differences between these two catalysts. The catalyst containing 4% Pd exhibits a distinct Raman band at 650 cm^{-1} characteristic of PdO, whereas a similar feature was completely absent from the spectrum of the catalyst containing 0.4 % Pd. What this suggests is that PdO is the active phase required for the combustion of CH_4. This finding is in full agreement with studies of Pd dispersed on amorphous supports (43), and suggests that in the case of CH_4 combustion, the zeolite serves as an excellent means for dispersing small particles of PdO. Such particles are very likely trapped in the channel intersections and mesopores of the zeolites

In related investigations, we have investigated the behavior of PdO supported on ZrO_2 (44). This work has revealed that during the oxidation of CH_4, small particles of Pd nucleate on the surface of the larger particles of PdO. Methane adsorption occurs preferentially on the surface of the Pd particles and the fragments of dissociative adsorption rapidly diffuse to the PdO where they are converted to CO_2 and H_2O.

CONCLUSIONS

Considerable insight into the nature of adsorption sites and the mechanisms by which NO decomposition and reduction occur over metal-exchanged ZSM-5 can be gained by combining information obtained from experimental and theoretical studies. It is shown that NO decomposition over Cu-ZSM-5 requires both Cu^+ and $Cu^{2+}O^-$ sites. NO adsorbs on the first of these sites and then reacts with a second molecule of NO to produce N_2O and $Cu^{2+}O^-$. The latter species then reacts with either N_2O to form N_2 and $Cu^{2+}(O_2^-)$. O_2 is produced by decomposition of $Cu^{2+}(O_2^-)$. This process also restores the supply of Cu^+.

The reduction of NO over Co-ZSM-5 is greatly enhanced by oxidation of NO to NO_2, a species that remains strongly adsorbed even at elevated temperatures. Gas phase CH_4 reacts with adsorbed NO_2 releasing water and forming CN. The CN groups then react with gas phase NO_2 to form N_2 and CO_2, or with O_2 in a competing reaction to form NO and CO_2.

The oxidation of CH_4 over Pd-ZSM-5 takes place preferentially over small particles of PdO, rather than Pd cations. In this case the function of the zeolite is to maintain the PdO in a state of high dispersion. It is also found that under reaction conditions a small part of the PdO is reduced to Pd. CH_4 adsorption occurs preferentially on the small particles of Pd, and the fragments of such dissociative adsorption then diffuse to the PdO where they undergo complete oxidation.

Acknowledgment

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RECENT ADVANCE IN CATALYSIS FOR SOLVING ENERGY AND ENVIRONMENTAL PROBLEMS

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Abstract

Change in catalyst surface during the reaction is emphasized to investigate a suitable catalyst for solving energy and environmental problems. The rapid conversion and/or highly selective reaction are indispensable requisites for this purpose. By controlling the dynamic state during the rapid catalytic reactions, the effective syntheses of hydrogen by CO_2- reforming of methane and methanol by hydrogenation of carbon oxides is achieved. An autocatalysis is an also an important factor to realize a rapid reaction, and a typical example was shown in the case of gasoline synthesis from CO_2 or CO via methanol as the intermediate product. A non- linear reaction mechanism could rationally explain the elimination of NO under O_2-excess conditions.

1. Introduction

Adsorption and catalysis had particularly attracted attention from the last century to the beginning of this century as the most essential relationship to understand the catalytic phenomena. In the early part of this century, the adsorption phenomena could be systematized at the beginning by monolayer adsorption theory proposed by Langmuir. Langmuir-Hinshelwood reaction mechanism has then occupied the central part of the understanding and analysis of catalytic reaction kinetics. This theory is applicable under the conditions which afford the linear phenomena, in which adsorption rates of reactants are always beyond surface reaction rates or consumption rate of those reactants.

However, in recent years, never faced problems to be solved by the applications of catalysts have appeared. Namely, elimination of toxic materials which are present in the exhaust gases in extraordinary low concentrations, mitigation of carbon dioxide come from fossil fuel combustion, and new route syntheses of energy source and raw materials for chemical industries from alternative resources. These tasks need extremely more rapid conversion rate than the conventional conversion rate for the production of aimed compounds in usual industries, and the selective elimination of very dilute undesired compounds under the existence of high concentrated retarding compounds such as oxygen and water in the exhaust gas from diesel engine.

Merely with conventional linear phenomena in catalysis it is impossible to respond to those unusual demands, and in order to realize those novel phases in catalytic reactions, it is necessary to control non-linear phenomena were observed in catalytic reactions under special circumstances in both catalyst structure and reaction conditions. In this plenary lecture, recent advances in catalysis for solving energy and environmental problems are presented with typical rapid and effective catalytic reactions as examples.

2. Dynamic behaviors of catalytic surface and its control by applying spillover effect of adsorbed species

2.1 Change in oxidation states of metal oxide catalysts and its effect on the reaction rate

The oxidation-reduction state of metal and/or metal oxide catalysts is sensitively changed by the reaction environments, such as reaction-gas composition, temperature, pressure, conversion, and retardation by the reactants and products. However, in conventional analysis on catalytic surface reaction, these practical factors, which often belong to non-linear phenomena, are usually avoided or neglected for the sake of simplicity. The state of catalyst surface during the reaction under the zero-conversion level or differential reaction conditions, and too low temperature conditions as in a circulating reactor system, do not reflect directly the real state of the catalyst surface under practical reaction conditions in which the aimed reaction progresses actively. In catalytic combustion, exhaust gas purification in catalytic ways, catalytic reforming of methane, and methanation of carbon dioxide for examples, only the total conversion of the target reactants is significant, and their intermediate conversions have almost no meaning. Moreover, if the oxidation state of the catalyst surface changes so easily, it is rather difficult to maintain the intermediate conversion level stable.

For example, combustion of methane on a supported Pt catalyst was investigated by varying the composition of reactants as follows: (a) excess oxygen conditions (oxidative catalytic conditions), (b) stoichiometric conditions, and (c) excess methane conditions (reductive catalytic conditions) [1]. The hysteresis of conversion was measured, which is caused by elevating reaction temperature with a constant heating rate followed by descending the reaction temperature in the same way. This measurement method was named by us a forced-oscillating reaction method, by which hysteresis of oxidation-reduction state of the catalyst surface can be generally evaluated irrespective of the sort of catalyst. Under the oxygen excess conditions a minor hysteresis was observed as shown in Fig. 1 (a). At the stoichiometric conditions, the descending line was largely shifted to the lower temperature side (Fig. 1 (b)), and this tendency increased with increasing methane content in the feed. Under the CH_4 excess conditions, catalytic combustion of methane maintained even at one-hundred and several tens C with totally consumed oxygen (Fig. 1 (c)), even the heat supply from the electronic furnace was cut off. This kind of hysteresis reflects the oxidation-reduction states.

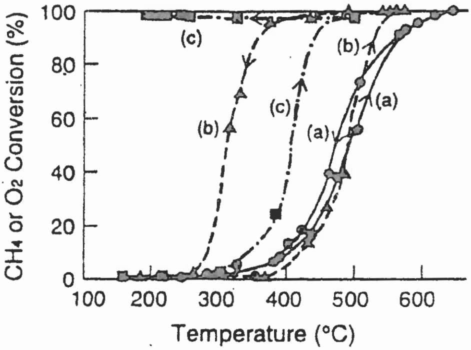
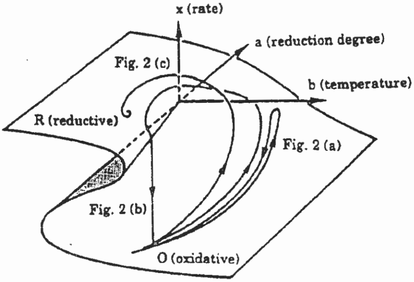


Fig. 1 Different hysteresis of the catalytic activity observed by the forced-oscillating reaction method. Catalyst:0.33 wt% Pt supported on a wash-coated ceramic form carrier, SV 14,000h^{-1}. (a) Oxidative catalytic conditions; (b) Stoichiometric conditions for complete combustion; (c) Reductive catalytic conditions.



Curved surface corresponding
to the cusp catastrophe
$f = x^3 + ax + b = 0$

Fig. 2 Cusp catastrophe depiction of hysteresis appeared in the catalytic combustion of methane with different reaction conditions corresponding to Fig. 1 (a) ~ Fig. 1 (c).

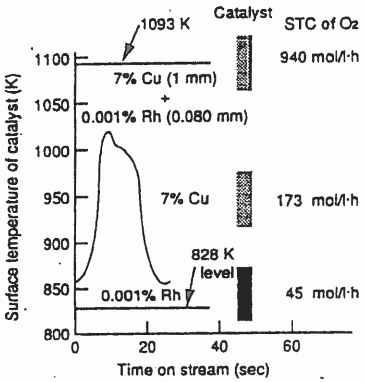


Fig. 3 A prominent effect of the contact Rh catalyst with the Cu catalyst in combustion of a city gas. Gas composition: city gas/air = 1/1.56.

In order to understand quantitatively these non-linear phenomena, lines appeared in Figs. 1 (a) ~ 1 (c) were fit to the curved surface corresponding to the cusp catastrophe, as shown in Fig. 2. It is well described in the figure that the hysteresis does not occur at the oxidative catalytic conditions, the sudden decrease of the activity occurs at an intermediate reaction condition, and at the reductive catalytic conditions, a high active level can be maintained.

This highly active level can be created also by the aid of catalytic structure. Figure 3 shows a typical example which could be realized by combination of a very diluted Rh catalyst with a supported Cu catalyst [2]. This jumping phenomenon in the catalytic activity is ascribed to the role of added Rh as a porthole of hydrogen spillover towards the main catalyst component - Cu oxide, and maintains the surface of Cu oxide in a very reduced state.

By application of this principle to accelerate catalytic activity, extraordinary highly active catalysts for catalytic combustion, methanation of carbon oxides [3], catalytic decomposition of methanol [4], and catalytic reforming of methane [5] could be developed.

As evidently shown in Fig. 4, the Rh-modified Ni-Ce_2O_3-Pt catalyst exhibited a very high activity, which approached near to the reaction equilibrium even at such a high space velocity (SV) as 730,000 h^{-1}, or a very short contact time of the reaction gas 4.93 m-sec. The activity of Rh-modified Ni-Ce_2O_3-Pt catalyst was much larger than sum of the activities of the component catalysts, Rh catalyst and Ni-Ce_2O_3-Pt catalyst [5]. This means that the modified catalyst involved two-step spillover, i.e., hydrogen formed was adsorbed on the Rh part very rapidly, faster than on the Pt part, and then the spillover hydrogen is abstracted by the Pt part followed by its diffusion towards the major catalyst component Ni part. Consequently, the Ni part can keep a reduced surface and the rapid reaction can progress on it. Ce_2O_3 would be not

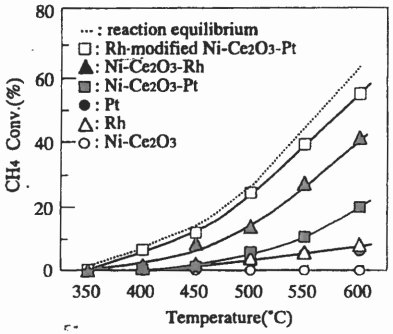


Fig. 4 Effect of Rh modification of the Ni-Ce_2O_3-Pt catalyst on CO_2-reforming of methane. Catalyst: 10 wt% Ni-5.6 wt% Ce_2O_3-10 wt% Pt-0.2 wt% Rh washcoated on ceramic fiber support of a shape of board with a 1 mm thickness, involving 86.3% voidness. Feed gas: 10% CH_4-10% CO_2-80% N_2, SV 730,000 h^{-1} or contact time 4.93 ms.

only the dispersing media for the Ni component, but also the transporting media for spillover hydrogen.

Hydrogen and CO were obtained equivalently by the reaction, and the space-time yield of CO obtained at 600°C was 3585 mol/l/h at a 55% methane conversion. Such an extraordinarily high space-time yield has been never realized till joining the spillover effect in the dynamic state of the reactions.

Furthermore, the limitation of the methane conversion owing to the reaction equilibrium at lower temperature range was overcome by supplying of more combustible light paraffins on the surface of the same catalyst. As a result, the catalyst temperature was kept at high temperature level around 200°C even at lower furnace temperature around 400~500°C [6].

2.2 Maintenance of optimum states of catalyst surface under the high reaction rates by a good balance between normal and inverse spillover effects

As mentioned above, the spillover effect is most effective in the kinds of extreme reactions such as complete combustion, complete hydrogenation, and decomposition reaction. On the other hand, in the reactions in which the purpose is to obtain selectively the intermediate oxidation or hydrogenation products, the optimum state of catalyst surface, in case of metal oxide catalyst for example, is an intermediate oxidation state. In order to increase the reaction rate, if the reaction conditions are shifted more radically, the spillover rate of adsorbed species is also markedly enhanced, and the catalyst surface inclines excessively to an undesirable reduced or oxidative one. As a result, the selectivity to objective product will decrease and/or the catalyst will be deactivated due to the segregation of catalyst components. Therefore, in order to maintain the optimum oxidation state of catalyst even under the conditions of high reaction rates, the catalyst component having an inverse spillover effect should be combined with the catalyst which involves the component exerting normal spillover effect, anticipating the rates of reduction and oxidation of the catalyst metal oxides show a good balance and a steady state. A typical example [7] is shown below. A Cu-Zn- Cr-Al mixed oxide catalyst prepared by the uniform gelation method and Ga oxide component, which has the inverse spillover effect, were mixed. The catalyst was used for a CO_2-rich syngas conversion, and yield of methanol increased while formation of CO as a by-product was suppressed. The reason of these reaction features would be ascribed to the retardation of excessive reduction of the catalyst surface. This was confirmed by temperature programmed reduction (TPR) experiment. As shown in Table 1, the catalyst was calcined at a considerably higher temperature, the BET surface area decreased to 1/2.5, however the reaction activity rather increased. Furthermore, activity of the Pd component, which has a hydrogen spillover effect, increased, particularly at a lower temperature. This effect was also confirmed by TPR measurement. The catalyst was then applied to syngas conversion, and unprecedented high synthesis rates were achieved. For example, space-time yield (STY) of methanol amounted 6,620 g/l/h and the summation of methanol and dimethylether was 8,210 g/l/h at 290°C at 80 atm.

Table 1 Effect of Ga and Pd combination on the Cu-Zn-based catalysts of methanol synthesis from CO_2-H_2 mixture

Catalyst	Calcination temp. (°C)	Surface area (m^2/g)	Cu dispersion (%)	Reaction temp. (°C)	CO_2 conversion to (%)			MeOH STY (g/l·h)
					MeOH	CO	H.C.	
1	350	114	5.4	250	13.7	2.7	0.0	810
				270	19.6	2.7	0.1	1158
2	600	46	4.3	250	12.8	3.3	0.0	756
				270	21.3	3.3	0.0	1261
3	Pd-modified catalyst 2	38	3.5	250	19.2	3.0	0.1	1135
				270	22.0	3.9	0.2	1300

Composition of catalysts 1, 2: Cu:ZnO:Cr_2O_3:Al_2O_3:Ga_2O_3 = 38.1:29.4:1.6:13.1:17.8 (wt%); Catalyst 3: catalyst 2 modified with 1 wt% Pd; 22 % CO_2 -3% CO - 68% H_2; 80 atm; SV 18,000 h^{-1}; calculated based on N_2O adsorption.

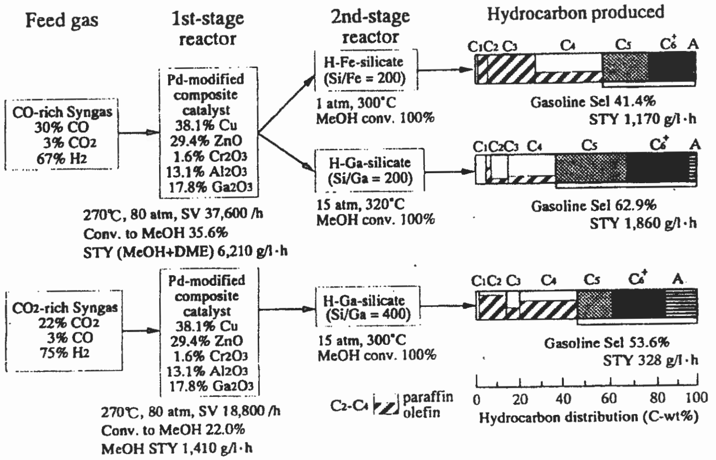


Fig. 5 Gasoline synthesis from a CO-rich and a CO_2-rich syngas via methanol by using a two-stage reactor packed with different function catalysts.

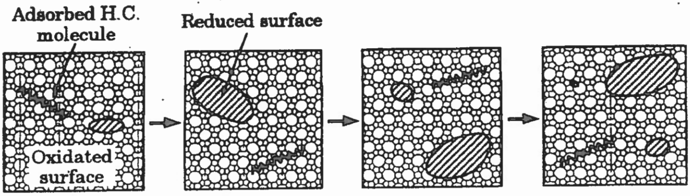
3. Autocatalysis and its application to the rapid catalytic reactions

Catalytic reaction processes, such as methanol to hydrocarbon conversion, and catalytic oligomerization of light olefins, involve autocatalysis. Coexistence of a very low concentration of alcohols and higher concentration of light olefins (above a certain critical concentration) markedly enhance the reactions, respectively. As a result, an extraordinary high reaction rate was observed. For example, on an H-Fe-silicate catalyst, propylene fed with a gaseous space-velocity 4,500 h^{-1} almost completely converted to gasoline-range liquid hydrocarbons, and space-time conversion amounted as high as 8.09 kg/l/h [8]. Moreover, the highly active methanol synthesis catalysts and the metallosilicate catalysts for methanol to gasoline conversion were packed into sequentially connected reactors, and as shown in Fig. 5, gasoline was obtained effectively from CO-rich or CO_2-rich syngases [9].

4. Application of non-linear catalytic phenomena to the elimination of NO under the extremely deviated conditions in a diesel exhaust gas

Recently, the catalytic reduction of NO in diesel exhaust gas has been investigated extensively. The key points of this technology are the addition of a small concentration of an appropriate kind of hydrocarbon or oxygen-involving compounds such as methanol and the use of well crystallized silica-rich zeolitic materials as the catalyst support.

Exhaust gases from diesel engine, components such as O_2, H_2O, and CO_2 which retard the reaction, exist in a large excess; on the other hand, both NO to be eliminated and the hydrocarbon to be added are present in extremely low concentrations compared with O_2 and H_2O. It seems to be very unnatural that NO can react with the hydrocarbons selectively by the bimolecular surface reaction as usually considered by adopting a linear reaction mechanism such as Langmuir-Hinshelwood bimolecular reaction mechanism. To the contrary, the following non-linear reaction mechanism rationally explained experimental facts. Since the catalytic combustion of hydrocarbon molecules easily causes the local reduction of a part of the surface of zeolitic catalyst, and on this reduced part NO decomposition can advance before oxidation by the excess oxygen at appropriate temperature range. Furthermore, the general experimental fact that above this temperature, NO conversion decreases whereas hydrocarbon added can undergo combustion, can be explained reasonably as follows: at higher temperature range, the local reduced part which forms by combustion of hydrocarbon is immediately oxidized by excess oxygen and there is no more chance to decompose NO. This kind of real heterogeneous reaction mechanism, expressed by the sequential reaction equations in Fig. 6, has been proposed by us as the Microscopic Sequential Reaction Mechanism (MSR mechanism) [10].



Oxidated surface

$$C_xH_y + nO_{ad}[S] \longrightarrow C_xH_{y\,ad}(nO_{ad}[S]) \tag{1-1}$$

$$C_xH_{y\,ad}(nO_{ad}[S]) + mO_{ad}[S] \longrightarrow xCO_2 + (y/2)H_2O + (2x+y/2)[S] + [(n+m)-(2x+y/2)]O_{ad}[S] \tag{1-2}$$

Reduced surface

$$NO + [S] \longrightarrow NO_{ad}[S] \tag{2-1}$$

$$2NO_{ad}[S] \longrightarrow N_2 + O_2 + 2[S] \tag{2-2}$$

$$O_2 + 2[S] \longrightarrow 2O_{ad}[S] \tag{3}$$

Fig. 6 Conceptional illustration of the Microscopic Sequential Reaction mechanism for deNOx reaction under the oxygen excess conditions.

The real heterogeneous reaction mechanism enables us to design a suitable catalyst for practical use from the view points of both hydrothermal stability and the catalytic activity to adjusting the medium temperature range around 400°C [11].

5. Conclusions

Dynamic states of catalyst surface during the reaction were demonstrated using the catalytic combustion reaction as a typical case. Oscillating reaction occurring in the rapid catalytic reaction was controlled by the combination of the catalytic components which can play the role of the porthole for hydrogen spillover. These controlling principles could be applied in many significant reactions related to solving energy and environmental problems. The important application of the function of autocatalysis to realize the rapid catalytic reaction was shown in the case of carbon oxides conversion to gasoline. The non-linear reaction mechanism enabled to understand the unique behaviors of reaction occurring in extremely deviated reaction conditions such as elimination of NO in exhaust gas from diesel engine.

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PL-38

CATALYTIC COMBUSTION IN FLUIDIZED BED, HONEYCOMB MONOLITHS AND FIBER MAT CATALYSTS

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Introduction

Ever-growing environmental problems of organic fuel combustion and considerable exhaustion of natural resources bring forth the problem of development of most efficient and environmentally safe fuel combustion technologies. One of the solutions of this problem is use of catalysts in fuel combustion.

Catalytic combustion of fuels is a special case of complete catalytic oxidation. Academician G.K.Boreskov initiated and accomplished a series of research projects in the field of total catalytic oxidation both over oxide and metal catalysts [1-2]. The distinguishing feature of catalytic combustion is the catalyst must ensure full conversion of stoichiometric fuel/air mixtures in particular conditions of high hydrocarbon concentration and heat evolution. Thus, combustion catalysts must have high thermal stability, mechanical strength and be resistant to catalytic poisons. Main results of recent research on catalytic combustion are summarized in reviews [3-7].

The works on catalytic combustion for home use, energy production and technological purposes are heading in several directions. Small catalytic heat sources for heating dwellings, industrial premises and means of transport are being created [8-19]. The studies on catalytic fuel combustion in gas turbines [20-26], catalytic combustion of low-calorific gases and gas exhausts from various industries [27] have been extensively started. In the above devices fuel combustion occurs at 1100-1600 K over a fixed bed comprised of catalysts based on noble metals deposited on fibrous, granulated or honeycomb supports. Catalyst makes it possible to increase the combustion efficiency and exclude the formation of CO and carcinogenic hydrocarbons formed upon flame combustion. The use of catalysts also provides the considerable decrease in nitrogen oxides emission.

For the last 20 years at Boreskov Institute of Catalysis extensive investigation of catalytic fuel combustion in apparatuses with different functions was carried out. Combustion catalysts and their supports were studied, and novel efficient catalysts were developed.

In this presentation the data on the development of three types of apparatuses for catalytic fuel combustion are summarized, namely: catalytic heat generators (CHG), catalytic air heater (CAH), catalytic space heater.

Catalytic heat generators

Fuel combustion in catalytic heat generators is based on four principles [28-31]:

- use of catalysts for complete oxidation;
- use of catalyst bed in fluidized state;
- combustion of nearly stoichiometric fuel/air mixtures;
- heat evolution and removal in the same catalyst bed.

In CHG flameless combustion of fuels occurs on the surface of oxide catalyst granules comprising a fluidized bed. CHG is a hollow apparatus with an air distributing grid situated at the bottom (Fig. 1.). The fluidization of catalyst occurs upon the upward flow of fuel, air and combustion products. Heat removal from the bed is performed either via heat exchangers immersed into the bed or by direct contact of the catalyst with a working body.

The principal advantage of this apparatus over those proposed previously for fluidized bed catalytic combustion of fuels is the presence of horizontal sectioning grid with a certain cell size. The sectioning grid constrains free circulation of catalyst particles and therefore serves as a non-isothermal packing. Owing to the use of non-isothermal grid the temperature of flue gases can be decreased to 420-450 K. In the apparatuses of this type various processes of heating, drying and thermal treatment of dispersed particles are successfully conducted.

Apparently, for catalytic fluidized bed processes the choice of catalyst and its support is of key importance.

The research intended for the creation of strong supports with high thermal stability was carried out. The results obtained made it possible to choose an appropriate support - γ-alumina prepared by the method of ammonia-hydrocarbon liquid phase molding [32-34]. Phase composition of supports prepared from various raw materials was studied using a complex of physico-chemical methods. Optimal temperatures of support drying and thermal treatment ensuring the requirements to mechanical strength and thermal stability were determined. The supports prepared had the following characteristics: specific surface area 150-200 m^2/g, mean pore radius - 40-50 Å, crushing strength - 25 MPa (Fig. 2).

The nature of active components of combustion catalysts was studied in detail using IRS, ESDR, XPA, and XPES. A number of active components based on mixed oxides of chromium, magnesium, copper and cobalt were proposed, and the genesis of catalyst phase composition was studied (Fig. 3.). The optimal conditions of support impregnation, catalyst drying and thermal treatment were determined. Support-active component pairs optimal for particular technological processes were selected. As catalysts are subjected to severe thermal, chemical and mechanical conditions, we have studied in detail catalyst deactivation using a complex of instrumental methods. The principal causes of catalyst deactivation during service in CHG are the reduction of cations in active components: Cu(II) → Cu(I) and Cr(VI) → Cr (III), and the formations of solid solutions of supports and active components with the composition $MeCr_{2-x}Al_xO_4$, where Me = Mg, Cu. The methods of catalyst regeneration based on additional deposition of dichromates on the surface of exhausted catalysts were proposed [35-37].

The results obtained allowed us to optimize the conditions of conducting various CHG processes and recommend definite types of catalysts for particular fuels and compositions of reaction medium.

The experience gained upon fuel combustion in a fluidized catalyst bed has shown that the most beneficial environmental effect of CHG is the reduction of nitrogen oxides emission. Figure 4 shows the comparison of nitrogen oxides emission in flame and catalytic fuel combustion. It is evident that fuel combustion in CHG ensures the decrease of emissions of both thermal and fuel nitrogen oxides.

Thus, the research into the nature of supports, active components and catalysts made it possible to recommend CHG apparatuses to be used in a number of technological processes, which are now being extensively introduced in industry.

Catalytic air heater

In Boreskov Institute of Catalysis a novel catalytic air heater for environmentally safe fuel combustion has been developed. It is the device for two-stage burning of natural gas

(Fig. 5.). At the first stage the gas is burned at the air/fuel equivalence ratio close to unity. Under these conditions the formation of nitrogen oxides is suppressed. Then flue gases diluted with air to necessary temperature enter the second chamber where catalytic cassette is installed. The cassette is a disk assembled of oxide catalyst units in the form of hexagonal honeycomb monoliths (channel density - 20-60 cm^{-2}) (Fig. 6). The temperature of flue gases at the cassette (650-1050 K) is sufficient for complete combustion of unburned organics and carbon monoxide, and nitrogen oxides reduction with excess carbon monoxide. The flue gases are further diluted with air behind the cassette and ejected from the apparatus to heat premises.

Obviously the crucial part of the heater is the catalytic cassette. The study of honeycomb catalysts revealed a number of strict requirements to both materials and structure of monoliths and the composition of active component. In particular the catalysts must be resistant to sharp temperature shocks which accompany fuel combustion in a fixed catalyst bed.

The research into the nature of active component, the genesis of catalyst phase composition and catalyst thermal stability allowed the determination of optimal composition of honeycomb support (cordierite or alumina, specific surface area 2-10 m^2/g, crushing strength - 10-12 MPa). Active components proposed are mixed oxides of cobalt, copper, magnesium and chromium. At present the catalysts for two-stage fuel combustion are manufactured on a small-scale commercial production line.

Catalytic air heaters successfully serve as mobile units for warming hothouses, repositories, production premises, as well as for feeding hothouse plants with carbon dioxide and creation of protective atmosphere in vegetable-storage cellars.

Catalytic gas-burning space heater

Catalytic heaters for home use are rather widespread in western Europe. However in Russia these devices were not produced until 1992.

In 1992 for the first time in Russia at Boreskov Institute of Catalysis the catalysts on fibrous supports have been developed which are used successfully in small space heaters intended for home use.

The catalyst supports are fibrous materials based on silica and alumina with specific surface area 50-150 m^2/g, fiber length 3-30 mm and diameter 3-30 μ.

The distinguishing feature of fibrous catalysts for environmentally clean gas combustion developed and studied at Boreskov Institute of Catalysis is the composition of the active component. Unlike noble metal catalysts used usually in devices of this type a novel mixed catalyst containing oxides of transition metals with the low content of platinum metals was proposed. The characteristics of this catalyst are just as good as those of foreign analogues, with thermal stability and resistance to catalytic poisons even superior to platinum catalysts.

Using a complex of instrumental methods, the catalyst phase composition, the nature of the active component and active component-support interaction were studied in detail in both catalyst synthesis and service. The results obtained allowed determination of optimal catalyst composition and organization of its serial production.

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CATALYTIC CONVERTERS: STATE OF THE ART AND PERSPECTIVES

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Introduction

In 1995 we celebrated the 20th year for which catalysts were widely used for the abatement of unburned hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NO_x) from the internal combustion engine. In 1975 the automobile manufacturers believed that catalysts would only provide a short term solution and would be quickly replaced with advanced engine technology. Now, over 20 years later, we continue the use of advanced catalysts in conjunction with sophisticated engine management systems and on board diagnostics. The application of catalysts in automobiles continues to expand into all parts of the world.

The demands of a catalyst to function in the hostile environment of the automobile exhaust has resulted in the development of materials never before needed in catalysis. We have seen the widespread application of ceramic and metallic monolithic substrates to support the catalytic washcoat. It allows high conversion efficiencies at high gaseous throughput, provides a high geometric surface area with low pressure drop, has excellent high temperature and thermal shock resistance and can be conveniently oriented in the exhaust train in any number of directions. The carrier material, most notably γ-Al_2O_3, has been modified by the use of oxide stabilizers to maintain high surface areas after experiencing temperatures up to 1100 °C in 10% H_2O present in the automobile exhaust. Similarly, the dispersion of the catalytically active precious metal components has been stabilized against sintering by incorporating metal oxides into the catalyst formulation. Other metal oxides play an integral role in providing oxygen storage to improve the conversion efficiency of the three way catalyst. This in turn provides the basis for the introduction of the O_2 sensor to aid in providing computer-controlled feed back to the combustion process. Truly, the automobile catalyst has resulted in the development of materials durable under extreme environments previously thought impossible in conventional catalytic processes. But still further improvements are required to meet ever more stringent emission standards world wide.

The value of the automobile catalyst experience extends well beyond the gasoline vehicle. The great success of this technology has provided a strong basis of confidence in using catalysts for many other applications in the vital role of cleaning our environment. Today we routinely use catalysts for abating emissions from diesel, natural gas fueled engines, small appliance engines, chemical manufacturing and power plants, restaurants and food processing facilities, commercial aircraft, and the treatment of pollutants in waste waters.

This paper will give an overview of the advanced technologies currently used for abating emissions from gasoline, diesel and natural gas fueled vehicles. The challenges for the late 1900's into the 21st century will also be presented.

A. Modern Three Way Catalysts

In the late 1970's it was discovered that certain precious metal combinations, most notably Pt and Rh, could simultaneously oxidize CO and HC and reduce NO_x, provided the air to fuel ratio in the combustion process was close to the stoichiometric point, or $\lambda = 1$ (lambda $= 1$). The key to advancing this new three way catalysis (TWC) technology was to control the air to fuel ratio at all times within a narrow "window" around the stoichiometric point of about 14.6 (wgt/wgt). This became possible by the development of the O_2 or lambda sensor which was positioned upstream of the catalyst. The oscillatory nature of the air to fuel ratio exposes the catalyst to slightly rich and lean conditions alternatively, i.e., approximately 2 or 3 times per second. Thus, when operating rich, there is a need to provide a small amount of O_2 to consume the unreacted CO and HC. This led to the development of the O_2 storage component which provides O_2 during the rich pulses and adsorbs it during lean perturbations. Reducible oxides such as CeO_2, NiO, Fe_2O_3 were found to have this property with CeO_2 (or CeO_2/ZrO_2) most commonly used.

Modern three way catalysts are primarily composed of about 0.1 to 0.15% precious metals at a Pt to Rh ratio of 5 to 1, and high concentrations of high surface area CeO_2 or CeO_2/ZrO_2 within the γ-Al_2O_3 washcoat. The γ-Al_2O_3 is stabilized against sintering with small amounts of La_2O_3 and/or BaO, and is deposited on a ceramic monolith composed of 400 cells per square inch. Metallic monoliths, with open frontal areas approaching 90%, are finding use for special applications where pressure drop must be kept to an absolute minimum, as for example, in high performance vehicles. Typically, the washcoat loading is about 1.5-2.0 g/in^3 or about 15% of the weight of the finished honeycomb catalyst.

Within the family of precious metals, Pd is significantly less expensive than either Pt or Rh. However it is poorly resistant to deactivation by poisons such as Pb and S. Therefore, research over the last few years has concentrated on preparation of poison-tolerant Pd containing catalysts. Base metal oxides in combination with Pd have found an important role in promoting the activity and stability of the catalyzed washcoat. In many instances Pd only can be used to accomplish what was previously done with Pt and Rh.

A-1. Challenges for the Gasoline Catalytic Converter

One of the major problems identified in the U.S. FTP and European (MVEG) test cycles is the inability of catalysts to oxidize the unburned non-methane hydrocarbons (NMHC) emitted during the cold start portion of the tests. The catalyst does not reach the HC light-off temperature (about 300 °C) until about 1 minute after the start of the test. Consequently, up to 50-80% of the total unburned hydrocarbons are emitted during this period resulting in a failure to meet future regulations, especially in California, for their ultra-low vehicle emission (ULEV) standards of 0.04 g/mile of NMHC.

The four approaches under intense investigation to address the cold start problem are; 1. closely coupled or manifold mounted catalysts, 2. electrically heated catalysts, 3. hydrocarbon traps, and 4. exhaust gas igniters.

Other requirements anticipated for automotive emission systems are 1. catalysts compatible with on-board diagnostics (OBD), 2. NO_x abatement catalysts for lean burn gasoline engines (see B-1 New Challenges for Diesel Exhaust Catalysts), and 3. catalysts for partial lean burn engines.

B. The Catalytic Converter for Diesel Engines

In the early 1990's the diesel engine manufacturers, being aware of the successes of the catalytic converter for the gasoline engine, considered a flow-through catalyzed monolith for controlling emissions from their engines. Diesel engines operate lean and their exhausts are much cooler than stoichiometric gasoline engines. The engine emits particulates composed of solid dry carbon and a liquid soluble organic fraction (SOF). Furthermore, the gaseous exhaust contains significant amounts of SO_2 which most oxidation catalysts convert to SO_3 (H_2SO_4), an unfavorable secondary emission. Thus, the challenges for diesel catalysts were quite demanding and different from that of its gasoline counterpart. The catalyst has to oxidize the SOF, CO and HC components to CO_2 and H_2O with minimum production of SO_3. Because diesel engines operate at low temperatures, the high surface area washcoat would have to store the liquids until the exhaust temperature increased sufficiently to initiate catalytic oxidation. Finally for such a system to function the dry soot has to be reduced to prevent plugging of the channels of the monolith. This is accomplished by advanced engine design.

Catalyst formulations having durabilities up to 180,000 miles for medium-heavy duty trucks have been successfully used in the U.S. since 1994. A $CeO_2+Al_2O_3$ formulation and Pd supported on ZrO_2 are two such catalyst materials. For diesel passenger cars in Europe, beginning in 1996, one formulation uses a small amount of Pt supported on γ-Al_2O_3 with additions of bulk CeO_2 and a zeolite. The zeolite effectively stores the unburned gaseous HC during cold conditions and releases them to the Pt for light-off. A second formulation utilizes a combination of Pt and V_2O_5 supported on TiO_2 where the V_2O_5 partially poisons the Pt to suppress the oxidation of SO_2 to SO_3. All formulations are deposited on ceramic monoliths.

B-1. New Challenges for Diesel Exhaust Catalysts

The desire for improved fuel economy and lower emissions of CO_2 is projected to increase the demand for diesel engines throughout the world. It is, therefore, of great importance to develop catalyst technology that will destroy NO_x in lean environments for truck and passenger car applications, preferably by decomposing NO_x directly into N_2 and O_2 or by reduction using on-board fuel-derived hydrocarbons.

Due to the lack of success in developing NO_x decomposition catalysts, the alternative approach of NO_x reduction using fuel-derived HC is now under intensive investigation. Catalyst formulations containing Pt are most active for HC/NO_x reduction between 200 and 300 °C, while Cu/ZSM-5 is active above 350 °C. The lean NO_x catalyst must have good low temperature activity and selectivity for NO_x reduction, high activity for SOF, CO and HC conversion but low activity for oxidation of SO_2 to SO_3 at elevated temperatures. The most serious limitation for Pt based catalysts is their narrow temperature range of activity. A serious disadvantage for Cu/ZSM-5 is its vulnerability to deactivation due to sulphur oxide poisoning and generally poor thermal stability of the zeolite. The origin of the sulphur is both from the fuel and the engine oil, and thus improvements in tolerance to poisons must be made.

The relatively low HC/NO_x ratio in the exhaust of a lean-burn engine requires the addition of fuel-derived hydrocarbons to permit adequate NO_x reduction. A sophisticated engine control strategy, working in concert with the catalyst, will be required for an effective system.

C. Catalysts for Natural Gas Fueled Vehicles

Commercial catalysts are now functioning in the exhaust of many lean burn natural gas vehicles, i.e. buses. They oxidize CO and NMHC and engine oil derived SOF. The catalysts are typically Pd and/or Pd/Pt with base metal oxide promoters on γ-Al_2O_3 deposited on ceramic monoliths with diameters and lengths of up to 7 inches.

C-1. Challenges for Natural Gas Fueled Vehicle Catalysts

Currently, methane emissions need not be abated since they are relatively unreactive towards photochemical smog generating reactions. They are, however, powerful contributors to the green house effect and thus their abatement would be welcomed, provided technology exists. The technical problems associated with abating methane will be discussed.

The other significant problem is NO_x abatement. This is especially difficult since natural gas has not shown high activity for NO_x reduction in real lean burn engine environments.

PROGRESS ON THE MECHANISTIC UNDERSTANDING OF SO_2 OXIDATION CATALYSTS

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For almost a century vanadium oxide based catalysts have been the dominant catalysts in the industrial processes for sulfuric acid production. Fundamental results in the understanding of the catalytic process was obtained by Academician G.K.Boreskov [1]. Last years these catalysts began to be also used to cleaning of flue gases and other SO_2 *containing industrial off-gases. In spite of the importance and long utilization of these industrial processes, the catalytic active species and the reaction mechanism have virtually been unknown until recent years.*

It is now recognized that the working catalyst is well described by the molten salt/gas system $M_2S_2O_7$-$MHSO_4$-V_2O_5/SO_2-O_2-SO_3-H_2O-CO_2-N_2 *(M = Na, K, Cs) at 400 - 600 °C and that vanadium complexes play the key role in the catalytic reaction mechanism.*

A multiinstrumental investigation that combined the efforts of the four groups from four different countries is carried out on the model system as well as on working industrial catalysts. Detailed information has been obtained on the complex and redox chemistry of vanadium. Based on this a deeper understanding of the reaction mechanism has been achieved.

The catalyst used for sulfuric acid production, catalyzing the reaction $SO_2 + 1/2\ O_2 \rightarrow SO_3$, is a supported liquid phase (SLP) catalyst, usually made by calcination of diatomaceous earth, vanadium pentoxide (or other V salts) and alkali salt promoters (usually in the form of sulfates) with the alkali-to-vanadium molar ratio ranging from 2 to 5. During the activation process, large quantities of sulfur oxides are taken up by the catalyst, forming molten alkali pyrosulfates [1-3] which dissolve the vanadium salts. Thus the above mentioned molten salt-gas system is considered to be a realistic model of the working industrial catalyst. A major problem in the SO_2 oxidation process is the sudden drop in activity which is experienced in all commercial catalysts at an operating temperature below 420°C. Interstage (and costly) absorption of SO_3 before the last catalyst bed has thus become unavoidable in order to attain low SO_2 content in the stack gas.

Previously [4, 5] very little has been known about complex and compound formation in the catalyst. However, this fundamental knowledge is essential for the understanding of the reaction mechanism and the severe deactivation of the catalyst below 420°C. Unfortunately, a direct study of the species formed in the liquid phase, which is dispersed in the small pores of the industrial catalyst, is very difficult and probably only methods like ESR and NMR can be applied. Progress in applications of magnetic resonance techniques to studies of vanadium catalysts is connected with Prof. V.M.Mastikhin's name [6, 7]. He was the first who directly showed that under reaction conditions, i.e. at 400-500°C the active component exists as a melt forming a very thin liquid layer on the surface of the support [8]. ESR spectra measured at temperatures up to 500°C revealed precipitation of V(IV) compounds causing deactivation of the catalysts [9, 10].

The present paper reviews an ongoing study dealing with (i) the complex and redox chemistry of vanadium; (ii) the formation of V(III), V(IV) and V(V) compounds; and (iii) the physico-chemical properties of the catalyst model system [11-13 and references therein]. The project strategy is to study both the working industrial catalysts and model systems in order to check if their chemistries can be linked together. In addition to ESR and NMR spectroscopy the study of the catalyst model system includes methods like UV/VIS-, FTIR- and Raman spectroscopy, electrical conductivity, potentiometry, EXAFS, XRD, neutron diffraction thermal analysis, differential enthalpic analysis and differential scanning calorimetry.

According to ^{51}V NMR various catalysts after treatment under reaction conditions become quite similar. This indicates that the active component in these catalysts is the same and is actually formed in the course of catalytic reaction. Initially, catalysts arising from different preparations contain a variety of V sites. On interaction with the components of the reaction media only the two V sites are formed. One of the sites belongs to V atoms in a slightly distorted tetrahedral coordination and can be attributed to vanadium bonded to the support. The second belongs to V atoms in distorted octahedral coordination typical for oxosulfatovanadates(V) (chemical compounds formed between V_2O_5 and $M_2S_2O_7$).

Measurement of the catalytic activity has shown tetrahedral vanadium species to be inactive in SO_2 oxidation. To elucidate V species which are active in SO_2 oxidation, ^{51}V, ^{17}O, ^{23}Na, ^{39}K and ^{133}Cs NMR were combined with catalytic activity measurements of the melts and of catalysts.

Multinuclear ^{51}V, ^{23}Na, ^{39}K, ^{133}Cs and ^{17}O NMR studies of V_2O_5-$M_2S_2O_7$ (M=K, Na, Cs) were carried out in the temperature range from 25 to 500°C. The data obtained show that the type of vanadium complexes in the melts depend on the total concentration of vanadium but does not depend on the type of alkali cation. At low vanadium concentration $VO_2SO_4^-$ monomeric complexes are most probable. The increase of the vanadium concentration above $X(V_2O_5)>0.3$ results in association of monomeric complexes with the formation of dimeric $(VO)_2O(SO_4)_4^{4-}$ and then oligomeric $(VO_2SO_4)_n^{n-}$ species. The following increase of vanadium concentration diminishes the number of sulphate or pyrosulphate anions coordinated to vanadium. In pure vanadium (V) oxide the chains of VO_4 tetrahedra bridged by common oxygen atoms are retained in the melt.

The catalytic active species have been proposed to be a dimeric V(V) oxosulfato complex [14]. Indeed recent investigations [15-17] of phase diagrams of the $M_2S_2O_7$-V_2O_5 systems (M=Na, K, Cs), XRD on isolated V(V) compounds [12], NMR measurements on melts [18] and ongoing Raman spectroscopic and potentiometric investigations show that the dimeric V(V) complex $(VO)_2O(SO_4)_4^{4-}$ seems to dominate in the catalyst melt.

The structure of this ion is shown in figure 1.

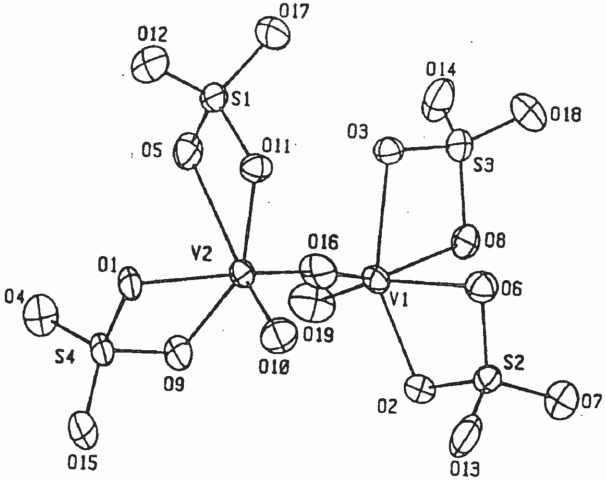

Fig.1. Structure of the $(VO)_2O(SO_4)_4^{4-}$ -ion

Reaction rates vs. temperature have been measured for industrial catalysts and silica supported model melts. Some examples are shown in figure 2. The Arrhenius plots show a marked break below which the catalyst looses the activity very fast. Similar treatment of catalyst model melts in the molten salt reactor cell leads to precipitation of V(IV) and/or V(III) compounds below he break point temperature.

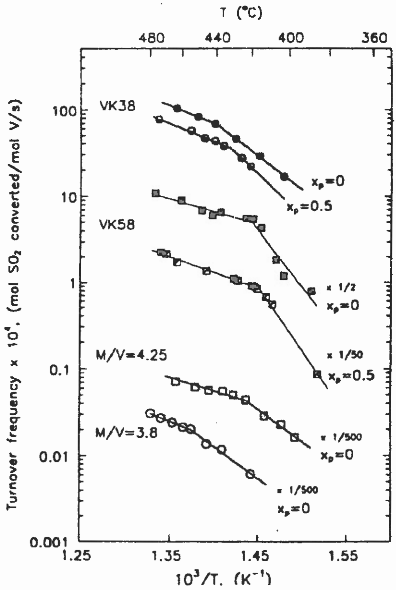

Fig.2. Arrenius plots of measured rates for the mixed alkali promoted industrial catalysts VK38 (Na, K) and VK58 (Na, K, Cs) and their model melts.

Feed gas: 10% SO_2, 11% O_2, 79% N_2 (x_p=0) or 5% SO_2, 5% SO_3, 9% O_2, 81% N_2 (x_p=0.5). Circles refer to VK38 and squares to VK58. The open symbols indicate the catalyst model melts, with the total alkali-to-vanadium molar ratios (VK58), respectively. For clarity some plots have been reduced by the indicated factor.

Thus the catalyst melt is depleted for the active component below this temperature leading to deactivation of the catalyst. Table summarises the type of compounds isolated from the catalyst model melts during deactivation.

Table. Possible Compounds Responsible for Catalyst Deactivation

V(IV)	V(III)
$Na_2VO(SO_4)_2$	$NaV(SO_4)_2$
$Na_3(VO)_2(SO_4)_4$[a]	$Na_3V(SO_4)_3K_4(VO)_3(SO_4)_5$
$KV(SO_4)_2$	
$K_3(VO)_2(SO_4)_4$[a]	
$Cs_2(CO)_2(SO_4)_3$	$CsV(SO_4)_2$
β-$VOSO_4$	
$VOSO_4(SO_2SO_3)x$[b]	

[a] Mixed valence V(IV)-V(V) compounds.

[b] $VOSO_4$ - like lattice with incorporated SO_2 and/or SO_3- molecules.

The compounds have been characterized by XRD and spectroscopic methods as recently described (19 and references therein). Based on the ESR spectra of the compounds, the in-situ ESR investigations on working industrial catalysts indeed reveal that similar compounds are formed in the catalysts during deactivation. An example is shown in figure 3 for 0% and 90% preconverted synthesis gas (19).

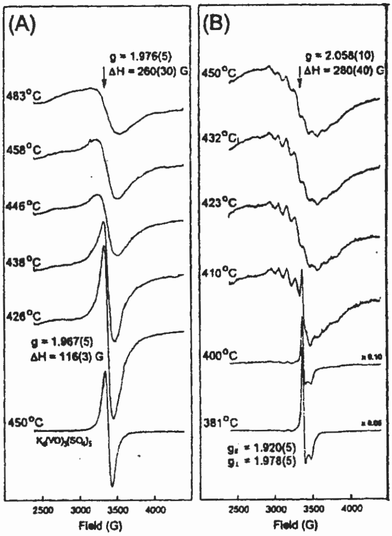

Fig.3. ESR spectra of the catalyst VK38 in (A): 10% SO_2, 11% O_2, 79% N_2 (x_p=0); (B): 1% SO_2, 1% SO_2, 9% SO_3, 7% O_2, 83% N_2 (x_p=0.9). The isotropic and anisotropic g components and line widths (ΔH) are as indicated. For comparison the spectrum of $K_4(VO)_3(SO_4)_5$ at 450°C is indicated. For convenience the signal intensity of the spectra measured at the lowest temperatures in Fig.3. (B) have been reduced by the indicated factors. In the series (B) the compound precipitated is most likely β-$VOSO_4$.

It is important to notice that the type of compound precipitated depends on the composition of the gas mixture. Thus the compound $K_4(VO)_3(SO_4)_5$ contains more sulfate per vanadium atom than β-$VOSO_4$. This is in accordance with the higher partial pressure of SO_3 in the latter case and that the melt equilibrium $SO_4^{2-} + SO_3 \rightarrow S_2O_7^{2-}$ accordingly will be shifted to a lower sulfate activity in the melt.

Very recently (20) modelling of the crystallization process in Russian catalysts by Monte Carlo calculations combined with ESR measurements supports the fact that catalyst deactivation indeed is caused by precipitation of V(IV) compounds. Furthermore, it has been found that the pore size of the carrier is an important parameter regarding the temperature of deactivation.

Earlier [14] and recent [20] ESR investigations have revealed clearly that vanadium remains in the oxidation state +V in the catalytic cycle. The reaction mechanism involving the dimeric V(V) complexes is proposed.

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DESIGNING OF COMMERCIAL CATALYSTS

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Designing of commercial catalysts is a continuation of the scientific fundamentals of catalyst preparation. Since the result (high activity) is more important than the process of its achievement, the main attention is paid to studies of the properties of empiric catalysts rather than to system analysis of their preparation methods. Nevertheless, recently a great success has been achieved in identification of active centers composition and molecular design of their structures. A deep insight into composition and action mechanism of catalysts has provided a theoretical base for changing a traditional heuristic approach to their preparation by a system approach - catalyst designing.

A system approach combines the fundamental and applied aspects of catalyst preparation. It may be used for generalizing experimental data on the scientific fundamentals of catalyst preparation and the composition of main types of catalytic systems as well as for estimating the optimal values of the parameters characterizing commercial catalyst quality.

Commercial catalysts should meet a set of requirements to their properties. The latter may be divided into three groups:

- chemical: composition, element state, nature and symmetry of ligand surroundings, etc.;
- physical: dispersity, morphology, texture, strength, bulk weight, etc.;
- service: activity, selectivity, service life, cost, regeneration ability, etc.

Designing of commercial catalysts is primarily based on the scientific concepts on the mechanism of conversion of initial material to active catalysts via numerous intermediates. Solution of technological problems requires both detailed knowledge of the physico-chemical methods of catalyst preparation (sorption, impregnation, precipitation, drying, reduction, etc.) and understanding of their effect on fundamental catalyst characteristics. The general chemical laws are fulfilled in all preparation stages. Nevertheless, there are only few scientific achievements in the field of catalyst preparation, as compared with those in recognition of catalytically active structures, and they are know-hows of companies. The matter is that the phenomena observed in various stages of catalyst preparation belong to different sections of chemistry and physics. Therefore a scientific aspect of designing requires knowledge from various, often bordering, fields of science.

Another peculiarity of commercial catalyst designing consists in taking some compromise settlements accounting for activity and deactivation rate, chemical composition and catalyst cost, efficiency factor and pressure loss in a catalyst bed, porous structure and granule strength, etc.

Consequently, realization of catalytic-system potentialities depends on both scientific and technical aspects. The former reflects our notions of catalyst composition, the latter shows what benefits can be gained from the achieved compromises. On progress of designing methods the relationship between these aspects changes in favor of system approach, i.e. scientific aspect.

Thus, designing implies a solution of multifactor problem in which scientific and technical aspects are closely interrelated. Catalysts designing includes a system solution of the following problems:

1. Synthesis of surface compounds (phases) in accordance with the notions of active-center structure.
2. Topography of active component distribution throughout granule and porous structure.
3. Optimization of porous structure and chemical (phase) composition of support (matrix).
4. Optimization of granule shape, size and strength.
5. Development of technologies to realize items 1-4.

The principle of system approach may be illustrated by the examples of designing of various catalytic systems: supported catalysts (for reforming), zeolite-containing catalysts (for cracking), and disperse oxides (for deep oxidation).

Supported systems. The principle of preparation of supported-systems consists in heterogenization of dissolved, rarely gaseous, precursors of active component over a support. The main purpose is to synthesize surface compounds with a specified coordination surrounding. Substitution of metal complex ligands for surface groups of support appears to be a general method of molecular design of anchored precursor.

Substituted metal complexes formation as products of their heterogenization under changes in the nature of complexing agent (Pt, Pd, Mo, Ni, Pt-Sn), surface ligand (Cl^-, Br^-, CNS^-, OH^-, $C_2O_4^{2-}$) and support (Al_2O_3, SiO_2, C) was observed [1-3].

Table 1

Composition of Pt(IV) and Pt(II) complexes anchored on Br/γ-Al_2O_3

(Br_2 content 3,6 mass %)

Initial Pt compounds	Pt cont., mass %	$[PtCl_{6-n}Br_n]^2$ and $[PtCl_{4-n}Br_n]^{2-}$ composition, %						Composition of adsorption center, n Br at.
		n=0	n=1	n=2	n=3	n=4	n=5	
H_2PtCl_6	2,0	-	-	-	35	38	27	4,1
H_2PtCl_4	2,2	-	13	27	32	27	-	2,7

Based on the established regularities of complexation via surface ligands, the following conclusions for acid complex anchoring by a ligand exchange mechanism were drawn:

1. A support serves as a three-dimensional ligand, forming multicenter bonds with anchored metal complexes.
2. According to the concept of "soft" and "hard" acids and bases [4], complexes containing ions of metals belonging to "hard" Lewis acids (Cr^{3+}, Co^{2+}, Fe^{3+}, etc.) and "soft" ones (Cu^{+}, Pd^{2+}, Cd^{2+}, Pt^{4+}, etc.) differ in anchoring on a surface. The former most actively interact with less polarized surface ligands, and the latter form strong complexes with readily polarized "soft" bases (S, J, Br, Cl, etc.).
3. Molecular design of the active-component precursor over a support surface can be performed using reference-book data on the reactions of ligand exchange as a base.

The active surface of supported systems is usually severalfold, and sometimes even hundreds-fold, lower than that of support. Therefore it can be selectively distributed throughout granule and porous structure of support. The mechanisms of precursor anchoring and transport during the supporting strongly affect the active-component topography on the inner support surface.

Systematic studies of isotherms and kinetics of precursor sorption in mono- and two-component solutions showed that distribution of active component throughout a support granule depends on three main parameters: sorption capacity of support (S), degree of its use (f), Henry's constant for isotherms of precursor (K^{AK}) and competitor (K^{KC}) [5]. To obtain a required distribution, the composition of impregnating

solution should satisfy the following inequality:

$$K^{AK} C_{AK} >> K^{KC} C_{KC} \quad \text{at } f<<1 \text{ - for catalysts of egg-shell type,}$$

$$K^{AK} C_{AK} << K^{KC} C_{KC} \quad \text{at } f<1 \text{ - for catalysts of ring and central type,}$$

$$K^{AK} C_{AK} \leq K^{KC} C_{KC} \quad \text{at } f \;\; 1 \text{ - for uniform catalysts,}$$

where C_{AK} and C_{KC} are the concentrations of precursor and competitor, respectively.

To govern active-component distribution in a porous structure, the main attention should be paid to choice of chemical modification, impregnating-solution temperature and impregnation duration. Varying these parameters, it is possible to localize a precursor in pores of particular size [6, 7].

Studies of many model and commercial reforming catalysts showed that after reduction at 300-500°C the surface platinum atoms in the catalytic Pt/Al_2O_3 system are present in two states:

1. Pt^{o} - high-dispersity (10-15 A) particles;
2. Pt^{σ} - Pt (II) complexes stabilized by interaction with a support [8].

These complexes are assumed to form chain structures [9]. Therefore they are called "few-ligand clusters" [10], which is the most apt name reflecting their main properties. These systems are intermediates between the compact metal and molecular clusters and differ from them by high content of surface atoms with low coordination numbers (almost all Pt^{σ} atoms are localized on the surface). The capacity of the complexes for oxidative addition of reagents defines their specific adsorption and catalytic properties (Table 2).

Table 2

Adsorption and catalytic properties of the surface Pt atoms in Pt/Al_2O_3

Specifications	Pt state	
	Pt^0	Pt^{σ}
Pt state distribution in per cents from the overall number of surface atoms in the catalysts:		
0.54% Pt/SiO_2	100	
0.36% Pt + 1% Cl/ -Al_2O_3	55	45
1.72% Pt + 1.3% Cl/ -Al_2O_3	74	26
Chemisorption stoichiometry:		
O/Pt	1	0.5
H/Pt	1	2.0
Bond energy for the level $4d_{5/2}$, eV	314.9	317.5
Atomic catalytic activity, molecules number/ at.Pt s., in the reactions:		
Benzene hydrogenation, 70°C	0.1	$<10^3$
Cyclohexane dehydrogenation, 300°C	10	~20
n-Heptane dehydrocyclization, 500°C	0.3	3-4

The relative part of the Pt^{σ} state can vary from 0 to 90%. Its value depends on the chemical composition of catalyst, the nature of precursor and its anchoring mechanism, and calcination and reduction conditions.

The above concepts were used for designing commercial reforming catalysts of practical importance. Selective aromatization of raw oil consisting of hydrocarbons of various classes and molecular weights requires active centers of different nature. Therefore the states of the surface Pt atoms in a commercial catalyst should be in balance. Using the above concepts on the structure of reforming catalysts and technologies of their designing, commercial polymetal catalysts based on Pt-Re-Cl/Al_2O_3- and Pt-Sn-Cl/Al_2O_3- were developed. These catalysts show high selectivity and operating stability when used in industrial reactors, compared with the similar home and foreign catalytic systems [11]. The new knowledge and developed technologies provide a firm basis to produce new, more perfect supported catalysts.

Cracking catalysts are composites consisting of zeolite component (Y or Y+ZSM-5 zeolites) and matrix including binding and filling agents. There is a great number of various cracking catalysts in the world. Their synthesis is the most progressively developed field of commercial catalysis. The methods of designing of cracking catalysts differ strongly from chose of supported systems. The technology for cracking catalysts designing includes two stages:

1) scientific ground on the requirements for physico-chemical properties of each component and development of the technologies of their attainment;
2) optimization of catalyst synthesis technology.

On studying of zeolite synthesis, the following conclusions were drawn:

- synthesis of zeolite Y starts when silicate monomers in initial silicate solutions disappear, and the concentration of branched polymers $(SiO_2)_n$ becomes maximal;
- optimal basicity should correspond to the ratio Na_2O/SiO_2=0.24-0.28. At higher ratios the groups with a great number of silicon tetrahedrons in the second coordination sphere of aluminium are broken, and neither nuclei formation nor completion of zeolite frame building occur;
- the best cracking catalysts should contain a zeolite component with 0.1-1.0 μm plate-shaped crystals.

Molecular design of active component is performed via several processes. Deep zeolite decationating providing Na^+ removal both from large and small zeolite cavities is a necessary condition for preparing a high-quality catalyst. Ion exchange ensures the compromise between activity and thermal stability of the catalyst. The optimal ratio between the contents of rare-earth elements (REE) and zeolite H-species is 1-3. Simultaneously, REE and H^+ should be localized close to each other. Localization depends on ion exchange consequence and conditions. Dealuminizing is the finest process of molecular design. The best results are achieved by simultaneous decrease of zeolite crystal size and steam treatment temperature.

According to the "accessibility" technology, designing of a catalyst grain requires using a porous-structure matrix. In this case the most high-boiling raw materials are cracked in macropores. Mezopores are necessary to crack large molecules before their entry into zeolite pores. Today there are many matrices involving aluminosilicate gel (small mezopores), aluminium hydroxide (large mezopores), alumina and kaolin (macropores). However, the experience in the improvement of catalyst production technology favored reducing matrix components number. The matrices of new-generation catalysts consist of only two components - aluminium hydroxide and natural clay treated according to a special technology.

Modernization of commercial production of catalysts according to the above concepts of their designing provided the increase in stable catalytic activity (referred to gasoline yield) from 29 to 52%. The activity of new-generation catalysts is 58-60%, which is higher as compared with the well-known catalysts produced by the leading companies all over the world. Thus, the results achieved confirm the fruitfulness of system approach to catalysts designing. A scientific concept of the approach opens new ways for further catalysts upgrading.

Of all stages of chemical conversions of initial compounds to their catalytically active forms, only one stage is often most important for active-component phase formation. Depending on the nature of active surface, such a stage may be:

- reduction - to obtain disperse metal and alloy particles (hydrogenation catalysts),
- sulfurization - to transform inactive oxides to active sulfides (hydropurification catalysts),
- calcination - to obtain high-dispersity oxide phases (deep-oxidation catalysts).

Understanding of the mechanism and kinetics of these processes specifies conditions of their performance. Taking into account that key stages are usually final in a preparation process, the technology of their performance affects the fundamental specifications of catalyst.

For example, the revealed thermal activation of manganese systems on high-temperature calcination [12] formed a basis for designing thermally stable deep-oxidation catalysts. The designing technology should ensure fulfillment of two necessary conditions:

- production of solid solution of Mn ions in γ-Al_2O_3 from initial materials,
- formation of high-dispersity manganese oxide particles in phase transition of γ-Al_2O_3 to its α-modification.

When the symmetry of support crystal lattice radically changes, a dissolved component is displaced to the outer surface of a new phase, thus forming high-dispersity oxide particles of active component [13]. Elucidation of the essence of the processes during calcination stage made it possible to choose the conditions for carrying out required conversions in the system. This comprised a scientific aspect of designing of thermally stable deep-oxidation catalysts.

A designing technology is not completed in catalyst preparation but also includes its practical application. Evolution of catalytic properties in the course of reaction and active means to govern the process are important designing stages closely related with the scientific aspects of the previous preparation stages.

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THE SINGLE EVENT APPROACH FOR THE KINETIC MODELING OF COMPLEX CATALYTIC PROCESSES

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The feedstocks processed in petroleum refining and in many petrochemical operations consist of a large number of components, each of which leads to complicated reaction pathwaths. In kinetic modeling the actual network is generally reduced to a small number of reactions between lumped species. Typical examples are the three lump model, involving four reactions, used in the simulation of the catalytic cracking of gas oil. The rate coefficients of this model depend on the feed composition, however, so that extensive and costly experimentation is required when the feedstock is changed. A second generation model was developed, containing 10 lumps involved in 17 reactions. Even then the question may be raised if the parameters are invariant and if 10 lumps or pseudo-components suffice to characterize in a satisfactory way the effluent composition and properties. The trend is clear: as the feedstocks considered for catalytic cracking (or hydrocracking) evolve to greater complexity, the reaction model will have to be more realistic, contain more lumps and more rate parameters ... Where is the limit? In this really the way to go?

The approach taken in the present paper is totally different. The model retains the full detail of the reaction pathways of the individual feed components and reaction intermediates. By expressing the kinetics of each reaction in terms of fundamental elementary steps, the number of rate parameters is kept within tractable limits. The values of these fundamental parameters are invariant, regardless of the feedstock composition. The approach has become possible through a better understanding of the underlaying chemistry, growing computational means and advances in instrumental analysis. The paper deals with the kinetic modeling of processes involving carbenium ion chemistry, as encountered in catalytic reforming, catalytic cracking and hydrocracking.

MULTIFUNCTIONAL REACTORS

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ABSTRACT

Chemical reactors are important energy consumers in case of endothermic processes, whereas energy is produced in exothermic processes. Therefore the efficiency of chemical reactors strongly influences the energy consumption in the world. The principle of the multifunctional reactor promises to improve very much the chemical reactors efficiency.

Multifunctional reactors are single pieces of equipment in which, besides the reaction, other functions are carried out simultaneously. The other functions can be a heat, mass or momentum transfer operation and even another reaction. Multifunctional reactors are not new, but they have received much emphasis in research in the last decade. A survey is given of modern developments and the first successful applications on a large scale. It is explained why their application in many instances is still far-away from large scale introduction. The first major successes have been achieved in the reduction of energy losses or increasing specific energy production.

INTRODUCTION

A large research effort is put into the development of chemical reactors. In the last decade the demand for better selectivities and higher conversions has increased more than ever to ensure prevention of the release or removal of products - often in very minor quantities - that would otherwise harm our natural environment. Also, energy saving considerations have strongly influenced the choice of type and design of a reactor and have also led to new, ingenious configurations and designs.

Also, in the last decade the so-called "multifunctional" reactors have received a strong developmental push, see Westerterp (1992). We owe the word "multifunctional reactor" to Agar and Ruppel (1988), who, in a pioneering paper, have given a survey of the possibilities and some practical examples of the application of the principle of multifunctionality. Its meaning is very simple: in a single piece of apparatus used for reaction, more than one function is executed. The other functions can be: mass, heat and momentum transport operations or even other, independent reactions.

Of course the principle of multifunctionality is not new and has been applied in many instances. Historically the oldest reactors were stirred pots, and for catalytic processes adiabatic beds. A retort was a multifunctional reactor combining reaction with mass transfer, distilling off a product. As soon as a cooling jacket or cooling coil was installed in a stirred pot we combined reaction with heat transfer. Also in our combustion engines, reaction and momentum transport are executed in the same cylinder. But today the degree of sophistication in using multifunctionality has increased by an order of magnitude.

We are not going to give a complete survey of the literature on multifunctional reactors nor a full outline of all the possibilities. We will only give a few examples to demonstrate the possibilities and challenges in the use of the principle of multifunctionality. We will discuss practical examples that are still at the research stage, or have already reached commercial application on an industrial scale. We will also, now and then, give a warning not to be over-optimistic; the reality of process economics puts strict limits on new developments. In placing limits we do not want to stop the researcher in his endeavours, but intend rather to stimulate him to make his invention even more efficient so that in the long run it can compete with existing reactors and eventually replace them.

REACTOR CAPACITIES

Reactor capacities, of course, vary widely. However, if one studies reactor capacity in certain branches of the process industries, some approximate ranges can be found. Thus, for the **bulk chemical** and oil industries capacities almost always vary between 4 to 50 kmoles produced per m^3 reactor volume per hour. The lower value relates to an economic boundary where reaction volume becomes too large and therefore uneconomical. The upper boundary refers to a technical limit: it becomes impossible to adequately withdraw the heat produced. For **fine chemicals**, where we mostly use batch processes, capacity levels are much lower and range from 0.1 to 1 $kmol/m^3$ hr. For **biotechnological processes** capacities are also much lower and range from 1 $kmol/m^3$ hr for the low cost products to very low values of say $500 * 10^{-6}$ $kmol/m^3$ hr for high cost chemicals like penicillin. In such processes heat removal rates cause no problems, but other operations may be limiting, e.g. oxygen supply may be the dominating factor determining capacity.

In nature, processes are even many decades slower, e.g. in petroleum geology, production rates range from $10 - 200 * 10^{-12}$ kmols converted/m^3 hr.

In our discussion we are primarily interested in reactors for bulk chemicals and will now have a further look at multifunctional reactors, where reaction and heat transfer are combined.

SIMULTANEOUS REACTION AND HEAT TRANSFER

Historically we see that soon the kettle type reactors were equipped with cooling equipment, such as coils and wall jackets, in order to cope with the heat effects of chemical reactions. Temperature rises in adiabatic catalyst beds were kept generally under control by dividing the bed into several parts and installing coolers between them. Then injection of cold feed gases between catalyst beds was practised. For reactions with very high heat effects, a (cooled) tubular reactor was soon developed, despite mechanical difficulties in coping with thermal expansion of the apparatus during operation. Early applications of these reactors were oxidation and hydrogenation reactions, which are highly exothermic. A major progress has been achieved, since for the first time a tubular reactor has been cooled by boiling water, so combining cooling and steam production. For energy saving this has become almost common practice in modern plants. We should note that in the oil industry, the tubular reactor for endothermic reactions had been introduced long ago: in thermal cracking furnaces the endothermic heat of reaction required was supplied directly in a furnace by combustion flames.

Later good heat transfer and temperature equilibration properties of the fluid bed reactor were recognised and since then many fluid bed systems have been installed. Agar and Ruppel (1988) describe a clever use of the principle of multifunctionality, in which an inert fluidizable powder is blown through a stationary catalyst bed and there absorbs the reaction heat. After leaving the catalyst bed the heated powder is cooled and returned to the bottom of the bed, where it is again carried through the catalyst bed by the fresh feed gas. With high circulation hot spots can be suppressed effectively and the reactor operates almost isothermally, see also Saatdjian and Large (1985).

The removal of reaction heat by evaporation of a solvent is another technique, which has been applied several times and is used, e.g. in the oxidation of para-xylene using homogeneous catalysts in the well-known Amoco process. The solvent is condensed outside the reactor and recycled. Due to mixing by the gas flow, these reactors behave like a tank reactor. Van Gelder et al. (1990a, 1990b) have discussed a more sophisticated application of cooling by evaporation, this time in a packed bubble column, which is packed with solid catalyst particles. The gas and liquid flow upward through the column, at the top the liquid and vapour-gas mixtures are separated. The principle of multifunctionality here gives us several significant advantages: 1) No expensive or elaborate cooling systems are required in the catalyst bed, 2) the reactor pressure can be set and hence, the maximum temperature is easily controlled, 3) temperature runaways are impossible because further heat production only increases the evaporation rate, 4) because of the packing, axial dispersion is suppressed, so that plug flow is approached in longer, slender columns. They recommend the method of hydrogen starvation in cases where hydrogenation has to be carried out to produce selectively an intermediate product in a consecutive reaction system. This combination of reaction with evaporation also can easily cope with a deactivating catalyst and Westerterp et al. (1988, 1996) specially recommend this reactor type with evaporative cooling for application to catalytic hydrogenations in the fine chemicals industries. Compared with a more classical reactor, the partial pressure of hydrogen, and therefore the reaction rate, is reduced due to the vapour pressure of the solvent, but this is more than offset by the ease of heat removal and temperature control.

Adiabatic bed reactor with periodic flow reversal

About 25 years ago in Novosibirsk, Boreskov et al. (1979) started the development of an adiabatic bed reactor with periodic flow reversal (RPFR) and its development was brought to completion by Matros (1985, 1989) during the eighties. Later, it was recognised that the RPFR had great advantages in better pollution control and so Eigenberger and coworkers (1988a, 1988b, 1991) started to develop this multifunctional reactor for the catalytic combustion of volatile organic compounds in exhaust air.

The RPFR works as follows. If the catalyst mass is hot, a cold air stream, containing some combustibles, will be heated up by the hot catalyst. Simultaneously the catalyst mass is cooled down. The air stream being heated up at some place in the catalyst bed will reach the temperature at which the combustibles ignite and the combustion reaction starts. Now, the combustion heat liberated will heat up the solids phase. If in the area of the catalyst bed outlet there is a zone where the catalyst is cold, the hot gas will heat up this cold catalyst. So in this part of the bed a heat wave will travel through the bed towards the outlet. And simultaneously near the inlet, where the hot bed is being cooled down, a cold wave is generated. In the zone between the two waves the bed is hot and here the combustibles are burnt.

By periodically reversing the direction of flow, see Fig. 1, heat can be kept in the reactor and by so doing the temperature in the middle zone will remain high and above the ignition temperatures. To reach a steady state after many flow reversals, the exit gas must be so much higher in temperature than the feed gas that the time-

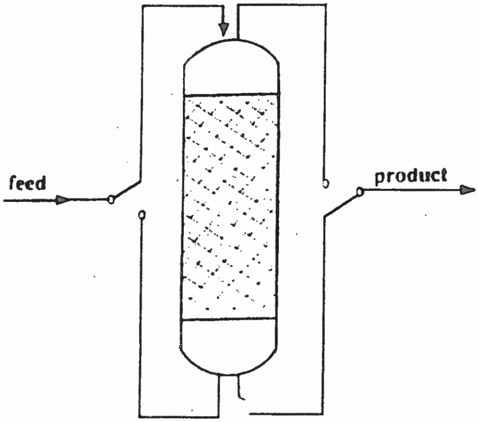

Fig. 1. The adiabatic bed reactor with periodic flow reversal

average liberated reaction heat will be carried away by the exit gases.

With mathematical modelling an understanding has been obtained of the operation of the RPFR, see Van de Beld and Westerterp (1996). In Fig. 2, two calculated temperature profiles are shown at the moment just before flow reversal of the flow direction. A plateau temperature established and the temperature difference between the inlet and outlet streams can be observed. **No energy at all is supplied to the process.** It is kept going by the combustion of the combustibles which are to be removed. The packed bed works partially as a heat exchanger, to heat up and cool down contaminated air, and partially as a combustion reactor. The plateau temperature of the hot zone is influenced by many variables. The concentration of combustibles in the air must never be so high that the oxidation catalysts become overheated and loose their activity. The RPFR has great promises in **the protection of the environment** in the removal of volatile organic compounds from polluted air by catalytic air oxidation **without external energy supply**: only the control problem for variations in composition and concentration of pollutants still has to be solved.

The RPFR therefore operates under dynamic conditions. The hot and cold fronts move back and forth with cycle time an important operating variable in preventing blow out of the reactor. The inlet and outlet zones act as heat exchangers and even at very low adiabatic temperature rises, ΔT_{ad}, due to very low concentrations of combustibles, heat exchange is so effective that the actual temperature rise is many times higher than ΔT_{ad}. Further, the switch valves operate at low temperatures, which increases the service life. For expensive catalysts the parts of the bed in heat exchange service can be replaced by inert material. We observe that in the RPFR expensive gas-gas heat exchangers are replaced by an additional layer of inert material installed in the same reactor shell.

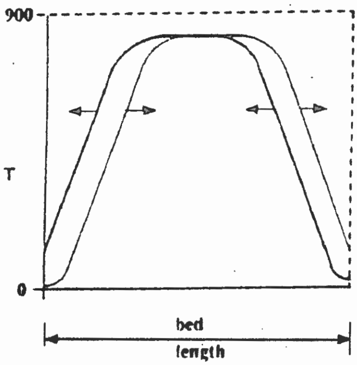

Fig. 2. Temperature profile just before reversal of the flow

In the two given examples, of combined reaction and heat transfer in a multifunctional reactor, with either an evaporating solvent or with periodic flow reversal, both will have the same or higher reactor capacity than their classical counterparts, provided that also the volume of the heat exchange equipment is taken into account.

After these examples we will now refer to multifunctional reactors which incorporate mass transfer in the reaction zone.

SIMULTANEOUS REACTION AND SEPARATION BY MASS TRANSFER

The combination of reaction and separation by mass transfer is not new and many lucid examples can be found in the history of chemical engineering. We do not mean heterogeneous reactions, where mass transfer and reaction are combined in a multiphase reactor system, but refer to reactors in which in the same apparatus one of the reaction components is removed or supplied by a mass transfer separation process. We will consider two older examples of combinations with extraction and distillation.

Schoenemann and Hofmann (1957) elaborated a process to make furfural from xylose in aqueous solution containing HCl. The furfural, which is produced in a combination of parallel and consecutive reactions, can decompose into resins and condensation products, so that yields of only around 10% can be expected. Now, by adding tetraline as an immiscible solvent phase they extracted the furfural as it was produced and obtained xylose yields of over 60%!

Geelen and Wijfels (1965) studied the equilibrium transesterification of vinyl acetate and stearic acid to vinyl stearate and acetic acid. As a by-product ethylidine acetate was formed. By executing this reaction in a distillation column they removed acetic acid selectively as soon as it had been formed, and by doing so suppressing the formation of the by-product almost completely. Moreover, by removing the acetic acid, they could bring the equilibrium reaction to completion with a very high selectivity!

We now will discuss more recent developments in the field of multifunctional reactors, namely the chromatographic reactor, catalytic distillation reactors, membrane reactors and the application of multifunctionality to the methanol synthesis.

The chromatographic reactor

The chromatographic reactor has already received attention for several decades, see Coca and Langer (1983). It is well known that e.g. in an equilibrium reaction such as $A \rightleftarrows B$, where the two components are adsorbed with differing strengths, a pulse of A injected into an inert carrier stream flowing over a catalytically active adsorbent will result in conversion to B beyond the equilibrium position. This occurs if A is strongly adsorbed and B is not, the column is long enough and the reaction is slow. As soon as some adsorbed A is converted, the B produced is carried away by the inert gas, so keeping the concentration of B low in the vicinity of adsorbed A.

Aris and coworkers, see Fisch et al. (1986) and Ray et al. (1990), have adapted this principle very elegantly to a continuous process. Pure A is injected somewhere in the middle of a column, through which a solid adsorbent-catalyst moves slowly downwards and an inert carrier gas flows upwards. A (in an equilibrium reaction) is converted into B which is less strongly adsorbed. Now the downward flow rate can be adjusted so that B moves upwards and A downwards. Experimentally they studied the hydrogenation of mesitylene to trimethylcyclohexane (TMC). Under their conditions they obtained a top product of 90% TMC, which was above the equilibrium composition.

The operation of a moving bed reactor is delicate and advantages must be sufficiently great to have an incentive for developing a moving bed chromatographic reactor for large scale operation. Agar and Ruppel (1988) in an elegantly novel approach used the principle of the periodic flow reversal to avoid the moving bed operation. They applied the principle to the removal of nitrogen oxides from combustion gases:

$$NH_3 + \text{adsorbent} \longleftrightarrow NH_{3\,\text{ads}}$$
$$NH_{3\,\text{ads}} + NO + 0.25\,O_2 \rightarrow N_2 + 1.5\,H_2O + \text{adsorbent}$$

In commercial steady state processes it is impossible to supply the correct stoichiometric amount of NH_3 to remove NO. NH_3 is not allowed into the atmosphere and therefore only 80 - 90% of the required amount is fed to the reactor to allow fluctuations in concentration and flow rates. Agar and Ruppel feed combustion gases to the Denox reactor and periodically give a large shot of NH_3 to the feed stream. The overdosed NH_3 reacts with the NO and the large excess is adsorbed on the Denox catalyst. An adsorption wave thus will travel through the catalyst bed in the direction of flow. After a certain period, the supply of NH_3 is stopped and the reaction continues, consuming the adsorbed NH_3. So a reaction wave also travels through the reactor. Before the NO breaks through, the direction of flow is reversed, and a new pulse of NH_3 is supplied at the inlet, again increasing the amount of NH_3 absorbed. The adsorption front now travels in the other direction, and as soon as the NH_3 pulse is stopped, a second reaction front will also follow. By periodically changing the direction of the flow, NH_3 is kept within the reactor and break-through is prevented. Furthermore a **complete conversion of NO** is now achieved and fluctuations in the concentrations are now coped with, by the buffering capacity of the catalyst. In the work of Matros periodic flow reversal is applied to a heat transfer situation, whereas in the work of Agar and Ruppel it is a mass transfer application. Their process promises to become the first large scale application of the chromatographic reactor.

The catalytic distillation reactor

The combination of reaction and distillation over a catalyst bed has been introduced to the large scale manufacture of methyl-tertiary butyl ether MTBE, see Smith and Huddleston (1982). To produce MTBE, isobutylene is reacted with methanol, see Fig. 3. The separation is improved by forming a methanol-MTBE azeotrope. Pure MTBE leaves from the bottom of the reaction-distillation column. From the top, a methanol-C_4 azeotrope is distilled. The catalyst used is an ion exchange type resin, which requires low reaction temperatures.

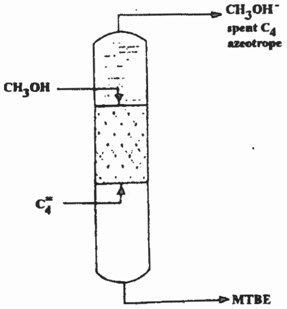

Fig. 3. Catalytic distillation.

Several advantages are apparent. The heat of reaction is used completely in the distillation, so **saving on steam consumption** is achieved. The methanol is fed to the top of the catalyst bed, where the isobutylene concentrations are low, and the high CH_3OH concentration pushes the equilibrium towards MTBE. Further, MTBE is removed more or less directly after it has been formed. So the MTBE concentration is kept low and the reverse reaction hardly occurs. Because of the distillation, almost all isobutylene can be converted into MTBE despite the unfavourable equilibrium, provided the catalyst bed is high enough. So by applying the principle of multifunctionality an equilibrium reaction can be forced to near completion in one pass.

Cumene has also been made by catalytic distillation, see Shoemaker and Jones (1987). Many aspects of the relevant vapour-liquid equilibria, the reaction and its kinetics have to be favourable in order that catalytic distillation can be applied successfully. Due to the presence of the vapour phase, the concentrations of some of the reactants in the liquid phase will be lower, thus reducing the reaction rate. For all but expensive catalysts and equipment, this reduction is more than off-set by the deletion of the separate separation step. Some more niches will be found for catalytic distillation, however, many preconditions have to be fulfilled, see also Mayer (1980):

- Temperature ranges for the distillation and the reaction must coincide.
- The reaction has to be fast enough so that the total residence time in the packed catalyst bed is sufficient.

- The reaction can not be so fast that the reaction occurs only in a small part of the bed, otherwise the reaction heat liberated only enhances the distillation locally.
- One of the desired products has to be either the highest or lowest boiling compound in the system, in order that by its separation, the equilibrium shifts in the desired direction, and of course, the reaction must be exothermic. An endothermic reaction would be quenched.

This process has also been recommended for the production of propylene glycol, see Kinoshita (1983) and for the separation of m- and p-xylene, see Saito (1971).

Membrane reactors

Membranes were originally developed for filtration. Dense non-porous membranes for hyperfiltration, also called reversed osmosis, and porous membranes used for ultrafiltration, with pore diameters of 3-200 nm, and for microfiltration, with pores of 0.2-10 microns. Polymeric membranes were almost exclusively limited to biotechnology, see e.g. Belfort (1989). We will restrict ourselves to inorganic membranes.

A distinction can also be made between dense and porous inorganic membranes. Foils of palladium or its alloys are permeable only to hydrogen and silver on dense zirconia is permeable only to oxygen. The selectivity of these dense membranes is, of course, very high, but permeation rates are very low. Costs limit the general application of these membranes.

Commercially available porous membranes are mostly based on alumina or zirconia. The membrane is at least 5 micron, but more usually 10-20 microns thick and placed on some intermediate support layers several mm thick. Diffusion through the pores is of the Knudsen type, hence separation factors are related to the permeabilities of the diffusing compounds and to the square root of the ratio of their molar masses. Sometimes for very narrow pores separation factors are much higher, what usually is called capillary condensation.

In the case of reactions, use is made of the membrane properties are used in several ways: In the case of equilibrium reactions, by removal of one of the products, so shifting the equilibrium in the desired direction. Side reactions can be suppressed by removal of products subject to decomposition. In cases where we wish to dose reactants slowly, membranes can give more precise control of the reaction. We will give a few examples of applications of inorganic membrane reactors, which, although receiving much attention, but have not yet passed beyond the research and development stage. For a recent survey e.g. see Hsieh (1991).

In 1966, the first patent was granted for the use of Pd as a **dense membrane** reactor, in which hydrocarbons were dehydrogenated and the reaction rate increased by removal of hydrogen, since then a great number of applications has been explored. For a recent survey, see Shu et al. (1991). A small scale pharmaceutical application was the synthesis of vitamin K in one step from a mixture of quinone and acetic anhydride in a Pd-Ni membrane reactor with a yield of 95%. This should be compared to the classical multistep synthesis with a yield of 80%, see Gryaznov (1986). Itoh et al. (1988) dehydrogenated cyclohexane in a Pd membrane reactor at 200°C. At that temperature the equilibrium conversion of cyclohexane would be 19%, but by continuous removal of H_2 conversions above 99% were reached. Many applications have been tried. Selectivity is very high, but success on a large scale is hindered by the low fluxes through the dense membranes.

Porous membranes exhibit low selectivities but have much larger permeabilities. A recent survey was given by Armor (1989). A distinction should be made whether the membrane is only a part of the reactor e.g. surrounding a catalyst bed or that the reaction takes place in the membrane itself. In the latter case the membrane is in most cases impregnated with a catalyst. Three examples follow.

Wu and Liu (1992) studied the dehydrogenation of ethylbenzene to styrene over a bed of catalyst pellets, surrounded by a ceramic membrane. H_2 diffused more rapidly through the membrane than the aromatics. Usually this reaction is a.o. accompanied by hydrocracking of ethylbenzene to toluene and methane. By applying the membrane separation this side reaction was strongly suppressed and the styrene yield increased due to reduced H_2 concentration in the reactor. Fluxes were however low.

Champagnie et al. (1990) used Pt impregnated alumina membranes to increase the conversion of ethane to ethylene in the temperature range of 450-600°C. They achieved conversions six times higher than the equilibrium conversion due to the selective removal of hydrogen. In catalyst-impregnated membranes reaction times are very short, hence only reactions with fast kinetics can be executed. Furthermore a typical problem emerges, namely the balance between reaction rates and diffusional permeation rates. The permeation rate of H_2 in the above example must be larger than the dehydrogenation rate of ethane, in order to reduce local hydrogen concentrations and so force the equilibrium in the desired direction. At the same time the permeation rate of ethane must be lower than the reaction rate. Usually there is a relatively narrow window of operation where conditions are favourable. This dehydrogenation of ethane was taking place with high fluxes.

For **control of a reaction** a membrane can be used to keep reactants separated, e.g. for partial combustion reactions in a porous ceramic membrane. Reactants are fed to different sides and diffuse from either side into the membrane. A catalytically active material has been deposited in the pores. There is no pressure difference over the membrane. For fast reaction rates the permeation rates are limiting resulting in a small reaction zone somewhere in the membrane. For instantaneous, irreversible reactions the zone reduces to a reaction plane. Product(s) diffuse out of the membrane to both sides. The location of the reaction zone inside the membrane is such that the molar fluxes of the reactants are stoichiometrically equal. After an increase in the concentration of a reactant on either side of the membrane, the reaction zone will shift in such a way that the stoichiometry is again met Sloot et al. (1990) proved this experimentally for the Claus reaction:

$$2H_2S + SO_2 \rightarrow 3/8\ S_8 + 2H_2O$$

The drift of sulphur to both sides of the membrane could be prevented by applying a pressure difference, so forcing the product in one direction. Fluxes were low.

Much work has also been done in the mathematical description of the behaviour of membrane reactors. Mohan and Govind (1986, 1988a, 1988b) published a set of papers in which, by simulation, they analyzed the influence of important parameters, including: membrane characteristics and dimensions, reactor geometry and heat transfer rates, the pressures on both sides of the membrane, flow rates of the feed and the sweep gas, temperatures and concentrations in the feed, kinetics, equilibria, and reaction heats. Also permeability variations, recycle streams, and direction of the flow (being co- or countercurrent) were taken into account.

Membrane reactors are still under development and many **problems** still have **to be solved**. These include: the geometry of the reactor, the sealing and packing of the individual units -e.g. in the case of tube shaped membrane in a large array and under greatly varying thermal stresses, and the fouling of membranes, e.g. by coke, for which steam has to be added. From the reaction engineering point of view major obstacles to their commercial introduction are:

- the low permeation rates. In most experimental studies until now the fluxes are still 10-1000 times too low to give a reactor volume with an acceptable capacity.
- the need for a sweep gas to remove the component(s) at the permeate side in order to keep concentrations low and consequently concentration differences over the membrane high, involves an additional separation step.
- the lack of an efficient method to supply or withdraw heat to or from membrane reactors on a large scale.
- the difficulty of keeping pressure differences across a membrane to almost zero, if desired, in large scale industrial reactors.

Much work still has to be done to tackle all these problems and we still have a long way to go. Some niche applications for membrane reactors surely will be found, the example mentioned for the vitamin K synthesis gives confidence. In view of the low capacity of membranes, more large scale applications should be sought in the fine chemicals industry.

Gas-Solid-Solid Trickle Flow Reactor (GSSTFR) and Reactor Section with Interstage Product Removal (RSIPR)

Equilibrium processes like the syntheses of ammonia and methanol require a cumbersome system to separate the product from the unconverted reactants and to recirculate these reactants to the reactor. **Much energy is wasted** in these separations and recirculations. Moreover, the feed preparation for these plants is complicated because a very pure feed of a stoichiometric composition is required. Any impurity or reactant in excess would accumulate in the recycle loop and slow down reaction rates and lower conversions. To overcome these problems Westerterp and Kuczynski (1987a, 1987b) developed two processes to achieve complete conversion in one pass through the reactor. In the gas-solid-solid trickle flow reactor (GSSTFR) they trickled a solid adsorbent countercurrently to the methanol synthesis gas through a fixed catalyst bed. The adsorbent selectively removed the methanol as it was formed. At high production rates they achieved 100% conversion and they ran a miniplant for 100 hours on a stoichiometric feed with the gas outlet closed and only a stream of solids, loaded with methanol leaving the reactor section.

To realise a process based on the GSSTFR on an industrial scale requires a cumbersome system for methanol desorption and solids recirculation. Therefore Westerterp et al. (1989) also developed a reactor section with interstage product removal (RSIPR), based on absorption of methanol in a liquid solvent at the reaction temperature. Also this process was operated successfully on a miniplant scale. In four sets of reactors and absorbers 97-98% conversion can be achieved in a once-through operation without recycle, see Fig. 4. This RSIPR principle is based only on proven technology.

Although much energy is saved by applying the RSIPR process, its main strength lies in the fact that it **can** also **handle non-stoichiometric feeds**. Any reactant in excess will pass through the reactor section as an inert material. An excess CO or H_2 leaving the RSIPR can be used as a fuel or for further processing in carbonylation, Fischer-Tropsh or hydroformylation processes and hydrogenations respectively. In Fig. 5 a block diagram shows the plants combined in a large methanol manufacturing unit. In the steam reforming unit, an excess of hydrogen, and in the partial oxidation unit, a feed stream deficient in hydrogen are produced, and by careful balancing an exactly stoichiometric feed can be made.

Now in the case, where the stoichiometric requirement can be dropped, as in the RSIPR, we obtain the following simplifications, see Fig. 6. First no recycle is required anymore in the synthesis unit.

Secondly the expensive steam reforming can be left out. As the partial oxidation is not an equilibrium process it also can be executed at higher pressures, say at synthesis pressure. Thirdly the expansion turbine and recompressor can be skipped and the natural gas, at proper pressure, can be fed straight to the oxidation and synthesis unit. The excess CO can be used for other purposes, e.g. in a Fischer-Tropsch unit. The oxidation unit delivers a stoichiometric ratio of 1.6 - 1.7, for the methanol production we require 2.0 and for Fischer-Tropsch a ratio of 1.0.

We observe that great savings can be obtained with the RSIPR principle applied to methanol synthesis, see also Westerterp (1992). The GSSTFR and RSIPR approaches can also be applied to consecutive reactions, by removing the desired product within the reactor.

COMBINATION OF REACTIONS

The combination of reactions in one single piece of equipment is also not new. In 1746 in England the so called lead chamber process was introduced to make sulphuric acid. In this process the oxidation of sulphur dioxide, according to $2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$ was carried out simultaneously with the reduction: $2NO_2 \rightarrow 2NO + O_2$ and later in the process the NO was reoxidized to NO_2 by air. We will present two examples of the application of multifunctionality to modern reactors.

Gryaznov et al. (1973) were the first to propose the coupling of two reactions in a **membrane reactor**, in which a hydrogenation and a dehydrogenation are carried out separated by the membrane. The exothermic reaction enthalpy of the hydrogenation reaction is used in the endothermic dehydrogenation. In a simulation study Itoh and Govind (1989) combined the dehydrogenation of butene-1 with a (more obvious) combustion of hydrogen, which has permeated through a dense palladium membrane. In tubes which were coated with a palladium membrane dehydrogenation catalyst pellets were placed, around the tubes air was supplied to burn the hydrogen. They demonstrated that such a reactor can be operated autothermally and that reasonable conversion rates can be obtained. Maybe the combination of endo- and exothermic reactions can solve the problems of heat supply or withdrawal in membrane reactors? At least, in reactors with dense membranes, it must also be possible to balance locally the heat absorption and production.

Recently Blanks et al. (1990) discussed the use of the adiabatic bed **reactor with periodic flow reversal** for a combination of an endo- and an exothermic reaction. Methane combustion with air $CH_4 + 0.5\ O_2 + 1.88\ N_2 \rightarrow 0.75\ CH_4 + 0.25\ CO_2 + 0.5\ H_2O + 1.88\ N_2$ was combined with the endothermic steam and CO_2 reforming process, $0.75\ CH_4 + 0.25\ CO_2 + 0.5\ H_2O \rightarrow CO + 2H_2$, yielding a synthesis gas claimed to be suitable for Fischer-Tropsch syntheses. Of course, the water-gas shift reaction $CO + H_2O \rightarrow CO_2 + H_2$ also occurred. They operated a miniplant and a pilot plant with a cylindrical reactor of 4 m length and diameter of 0.57 m. For a catalyst, they employed a nickel reforming catalyst. Zones of inert material at inlet and outlet were used for the heating and cooling. Natural gas conversions from 85-97%, and CO yields of 75-95%, were obtained. Reactor capacities were around 2.5 kmol/m^3 hr and the process could be run autothermally, without external energy supply. Again this is a very promising result employing the principle of multifunctionality.

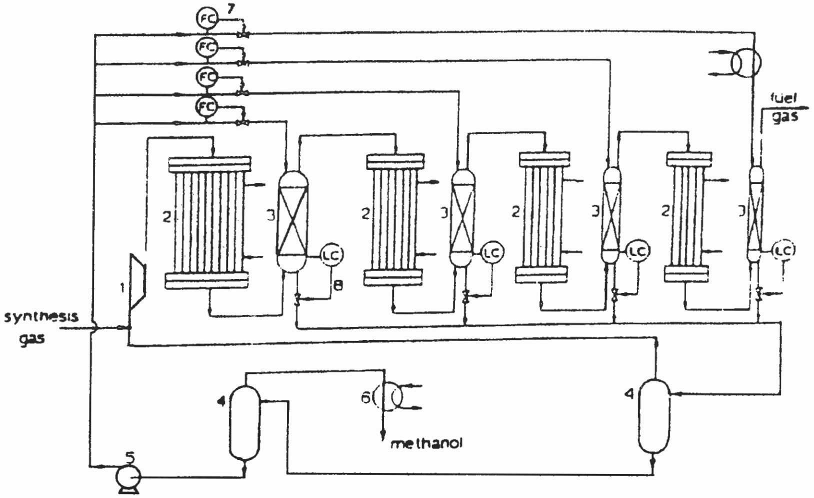

Fig. 4. The reactor section with interstage product removal for the methanol synthesis.

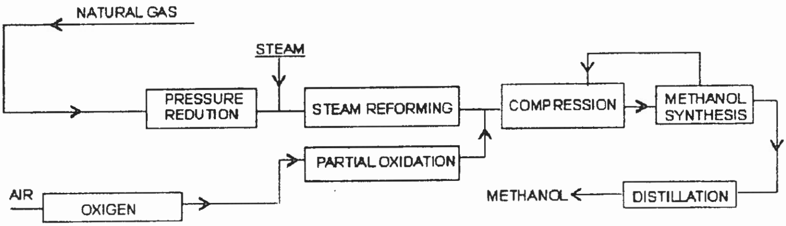

Fig. 5. The line-up of the units in a classical large scale methanol plant.

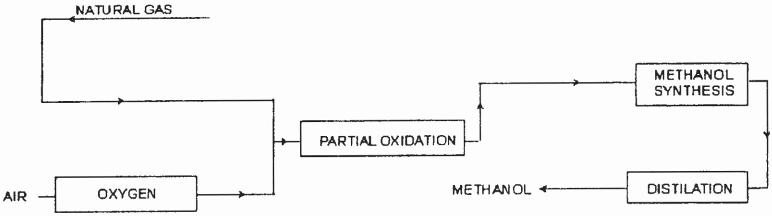

Fig. 6. The line-up of units in a methanol plant with a reactor section with interstage product removal.

CONCLUSIONS

Few large scale applications of multifunctional reactors and their consequences for energy savings could be reported in the outline above. This should not discourage the reaction engineer nor make him pessimistic. Rather it should stimulate him to increase his endeavours to make them successful. The reactor with periodic flow reversal and the catalytic distillation reactor, have already found large scale applications. Dense membrane reactors may be the next. The application of the reactor section with interstage product removal to the methanol synthesis has shown us what great impact the application of the multifunctionality principle can have on energy saving. Other multifunctional reactors are still rather far from large scale introduction.

We should realise that the more exotic our reactors become, the more delicate and difficult their construction and operation are. This implies that an operator will not change to a more complicated machinery for just minor savings in investments. Large advantages in operating costs and energy savings must be envisaged. This will limit a rapid introduction of multifunctional reactors, despite their scientific and technological challenges. Last but not least we acknowledge the appeal for working on new, alternative and surprising concepts, yet want to stress that for many years much more our efforts in science must still be directed to a better and more profound understanding, and further development, of existing methods and technologies.

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PL-46

ADVANCES IN UNSTEADY STATE CATALYTIC TECHNOLOGIES

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When the composition and/or temperature of reaction mixture entering the catalyst bed periodically changes, the catalyst surface also changes in order to adapt to new conditions. The adaptation may last from several seconds to dozens of minutes depending on reaction type, catalysts used and reaction conditions. Such catalyst surface properties allow new engineering solutions providing a purposeful catalyst maintenance at required activity level [1].

The practical application of unsteady state catalyst surface in process engineering is being intensively developed in the recent years. Let us briefly discuss some peculiarities of such processes.

I. Energy consumed on the process performance is considerably lower (by an order of magnitude).

II. In reversible reactions it is possible to provide product yield higher than the equilibrium one.

III. In catalytic processes reagents conversion is maintained constant at considerable oscillations of the inlet reaction mixture composition.

Let us exemplify above statements with some particular catalytic processes.

I. Energy consumed on gas purification from aromatics in the adsorption-catalytic method is 10-fold reduced [2].

In the deep oxidation of alkylaromatics up to 300°C the process occurs through the chemical adsorption of organic compounds (I) followed by the adsorbed species oxidation by oxygen (II):

$$C_n H_m + [\,] -> [P] \qquad (I)$$

$$[P] + O_2 \rightarrow CO_2 + H_2O + [\,] \qquad (II)$$

The adsorption-catalytic method bases on a periodic alternation of stages (I) and (II). At low temperatures the purified gases are purged through the catalyst bed, where admixtures adsorb, and reaction (I) occurs. Then at a given time the inlet bed temperature is risen to some definite value. Simultaneously, a wave of reaction (II) propagates along the catalyst bed, oxidizing the adsorbed admixtures. The oxidation increases the catalyst bed temperature. If in the course of catalyst recovery (admixture oxidation) gas flow reversal occurs, energy consumption is reduced considerably [3].

Figure 1 shows the typical experimental temperature profiles along the catalyst bed of demonstration plant during the oxidation of the adsorbed admixtures.

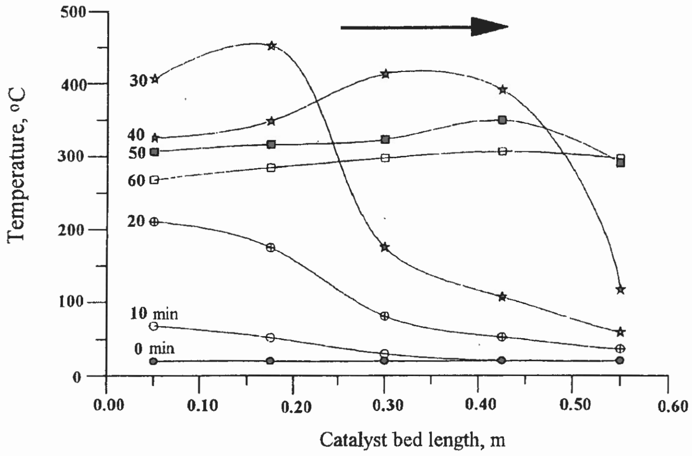

Fig. 1. Evolution of a temperature profile along the catalyst bed during incineration in a pilot experiment.

In 30 min after the recovery starts the catalyst bed temperature attains 300-450°C, which is enough to cause a spontaneous oxidation wave propagation along the catalyst bed. Then we can stop the heating at the bed inlet. During the adsorption outlet styrene concentration was below 1 mg/m^3 and thus could not be detected by chromatography. In the course of catalyst regeneration, the maximum concentration of styrene vapors did not exceed 10 mg/m^3, while its average concentration was less than 5 mg/m^3.

The adsorption-catalytic method of gas purification is characterized by extremely low energy consumption that is less than 2 MJ/1000 m^3 of purified gas [3].

II. Let us exemplify the overequilibrium conversion under unsteady state by the Dicon reaction and SO_2 conversion to SO_3.

The unsteady state of catalyst surface in the SO_2 oxidation to SO_3 bases on a periodic alternation of "adsorption-oxidation" and "desorption-reduction" stages [4]. The process flow sheet looks as follows:

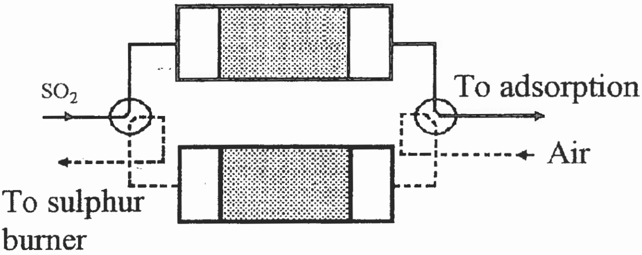

Fig. 2. Flow sheet of SO_2 oxidation to SO_3 under periodic catalyst activation by oxygen [5].

In the first half-period initial reaction SO_2-containing mixture passes through the catalyst bed. After the SO_2 oxidation to SO_3 the mixture goes to the absorber. In the next half-period air is purged through the bed but in the opposite direction, and then it passes to sulphur combustion.

A two-phase adiabatic bed model was used to simulate the process. Unsteady state kinetic model was used to describe the processes occurring on the catalyst surface. The model considered SO_2 dissolving in the melt, as well as active sites reduction and oxidation.

Figure 3 shows the average calculated SO_2 conversion at the bed outlet, when initial reaction mixture is supplied.

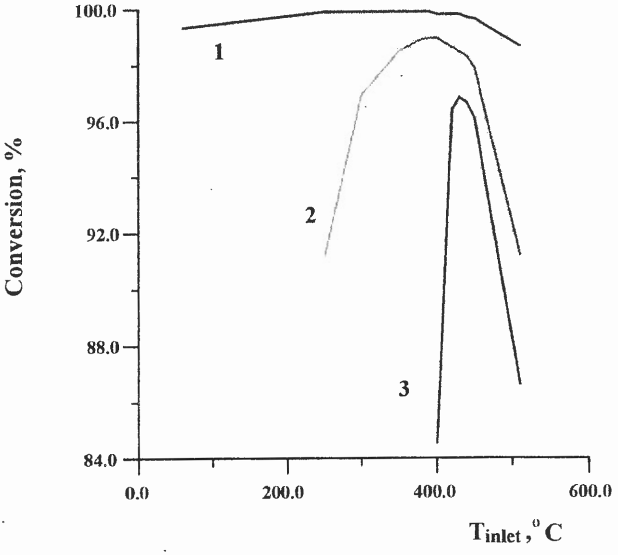

Fig. 3. Average conversion versus inlet temperature at various half-periods: $t_{c/2}$ =2.5 min (1), 5 min (2), 10 min (3). Inlet concentrations are $C_{SO_2} = 1\%$, $CO_2 = 3\%$.

(All calculations are done by N.V. Vernikovskaya, Boreskov Institute of Catalysis).

Figure 3 shows that at short half-periods (curve 1) conversion slightly depends on the inlet temperature. As the half-period increases, the temperature range where conversion is maximum, narrows and shifts to higher temperatures. Conversion attained at short half-periods ($t_{c/2}$ = 2.5 min) far exceeds the equilibrium value. Thus, beside oxidation SO_2 dissolves in the active component melt. In order to maintain the catalyst at such active state, hot air is periodically purged through the catalyst bed. This allows SO_3 desorption from the melt and high concentration of V(V).

In order to check the calculations we performed pilot tests. On the whole experiments agreed well with the calculations. The outlet residual concentration of SO_2 ranges from 30 to 60 ppm during the half-period.

According to [6] the Dicon reaction performance by conventional method does not allow reagents conversion higher than 84% due to reaction reversibility:

$$2HCl + 1/2O_2 \Leftrightarrow Cl_2 + H_2O$$

The authors of [6] suggest to separate the chlorination and oxidation stages:

$$2HCl + CuO \Rightarrow CuCl_2 + H_2O$$

$$CuCl_2 + 1/2O_2 \Rightarrow Cl_2 + CuO$$

Chlorine obtained by this method is pure, and production rate is higher than 100 kg per catalyst ton per hour.

III. Unsteady state catalyst surface phenomenon finds its application in gas purification from nitrogen oxides by their reduction with ammonia [7, 8]. The following reactions occur:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

The simplified mechanism of reaction occurrence on industrial vanadium-containing catalysts is the following:

$$NH_3 + [\ ] \Leftrightarrow [NH_3]$$

$$[NH_3] + NO + O_2 \rightarrow N_2 + H_2O + [\ ]$$

$$[NH_3] + O_2 \rightarrow N_2 + H_2O + [\ ]$$

Such a mechanism allows to estimate ammonia adsorption capacity of vanadium catalyst surface regarding experimental data obtained. For typical catalysts this capacity range from 3 to 10 ammonia volumes per catalyst volume.

Gas purification from nitrogen oxides proceeds as presented in Fig. 4 [8, 9]. Gases are purged through the inert and catalyst beds, where they are heated, then ammonia is introduced, and nitrogen oxides react with ammonia in catalyst bed 1. Simultaneously ammonia excess adsorbs in the same bed. At a given time (usually 5-60 min) the direction of filtered gas flow is changed to the opposite one. The purified gas passes inert and catalyst bed 1, where nitrogen oxides interact with ammonia adsorbed in the previous half-period. Then NH_3 is once again introduced into the partially purified gas, and the mixture comes onto catalyst bed 2, where nitrogen oxide reduction and ammonia adsorption occur. Then the cycle is once again repeated.

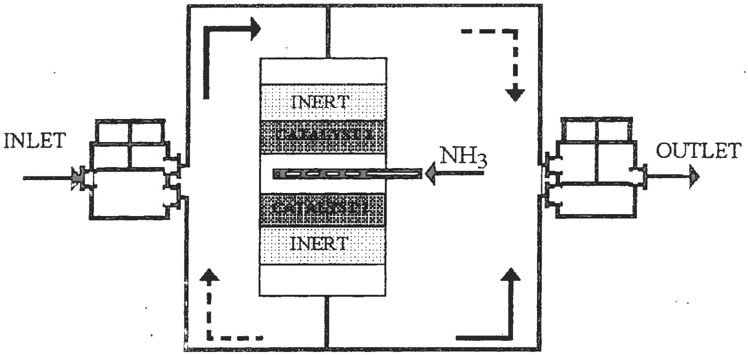

Fig. 4. Flow sheet of SCR process with a periodic gas flow reversal in the catalyst bed:

··········→ gas flow direction in the first half-period;

———→ gas flow direction in the second half-period.

Cyclic temperature changes occur provided for the reverse-process properties. Theoretical calculations of SCR on the catalyst grain show that, as the rate of temperature growth on the catalyst grain surface increases, the portion of adsorbed ammonia (used to reduce NO_x) decreases. Simultaneously, the portion of ammonia oxidized by oxygen increases. The calculations allowed to make an assumption about the optimum rate of temperature rise in the bed.

By the expense of periodic gas flow reversal the unsteady state catalyst helps to improve purification and decrease ammonia slip (see the Table) if compared to the steady state SCR process. This advantage is provided by ammonia adsorption on the catalyst bed.

Table

EFFICIENCY OF GAS PURIFICATION FROM NITROGEN OXIDES

$T_{in} = 260^0C$, $C_{NO_x}^{in} = 0.2$ vol.%, $\tau_k = 0.4$ s, $t_{c/2} = 5$ min

	Purification efficiency, %		Ammonia slip, ppm	
	REVERSE-PROCESS	Steady state	REVERSE-PROCESS	Steady state
$C_{in}^{NH_3} = 0.2\%$ vol	98.0	94.0	5	100
$C_{in}^{NH_3} = 0.18\%$ vol	90.0	88.0	2	28

The operation of industrial gas purifying plant, working under the reverse-process regime at the Buisk oleum plant, confirms the calculations. The plant used the process flow sheet presented in Fig. 4. As the oscillation of inlet NO_x concentration was from 2 to 11 g/m^3, the day slip of NO_x did not exceed 70 mg/m^3. There was no ammonia at the outlet in 90% of all control tests.

The recent papers report about the syngas composition stabilization at a partial oxidation of methane occurring by the expense of oxidized carbon deposited on the catalyst surface [10, 11]. Beside conventional reaction of CH_4 oxidation to CO and H_2 oxidation to H_2O on the catalyst surface the following reactions can take place [11]:

$$CH_4 = C + 2H_2 \qquad \text{(III)}$$

$$C + H_2O = CO + H_2 \qquad \text{(IV)}$$

$$C + O_2 = CO_2 \qquad \text{(V)}$$

Thus carbon produced in reaction (3) is gasified by the products via reaction (4) or by oxygen via reaction (5). The gas flow reversal in the catalyst bed will help catalyst maintenance in the active state by the expense of carbon deposits on the catalyst surface.

Conclusion

The above examples show that the artificial maintenance of the catalyst surface in unsteady state opens new ways of catalytic process engineering. Reaction product yield may be higher than the equilibrium one, and process efficiency remains the same at variable inlet conditions. Moreover, the processes are energy saving. The next step in the process development will be their introduction into industry.

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METATHESIS OF ALKANES CATALYZED BY SILICA SUPPORTED TRANSITION METAL HYDRIDES: A NEW CATALYTIC REACTION

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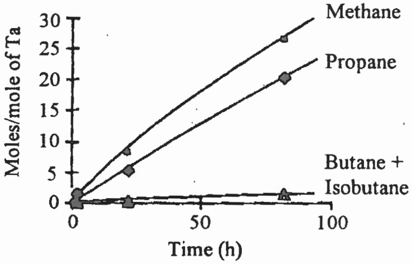
We have reported recently [1] that $Ta(-CH_2CMe_3)_3(=CHCMe_3)$**1** reacts with the OH groups of a silica dehydroxylated at 500°C to form a mixture of two surface species: $(\equiv Si\text{-}O\text{-})_xTa(-CH_2CMe_3)_{3-x}(=CHCMe_3)$ **2a** (≈65%; x=1) and **2b** (≈35%; x=2). Upon treatment under hydrogen at 150°C overnight, these two complexes lead mainly to a surface tantalum (III) monohydride $(\equiv Si\text{-}O\text{-}Si\equiv)(\equiv Si\text{-}O\text{-})_2TaH$ **3** (noted $[Ta]_s$-H] which has been fully characterized by IR spectroscopy, EXAFS, microanalysis and quantitative chemical reactions [2].

The $[Ta]_s$-H complex **3** reacts at room temperature with cyclic alkanes (cyclopentane to cyclooctane) [2, 3], via a C-H bond activation to form stoichiometrically tantalum (III)-cycloalkyl species with evolution of one equivalent of hydrogen:

$$[Ta]_s\text{-H} + (\text{cyclo-RH}) \longrightarrow [Ta]_s\text{-(cyclo-R)} + H_2 \qquad (1)$$

The $[Ta]_s$-H complex **3** catalyzes at moderate temperature (25-200°C) the metathesis reaction of acyclic alkanes, to form the higher and lower homologues. For instance, ethane was transformed at room temperature into propane and methane in comparable amounts with some traces of n- and isobutanes (Fig.1).



Higher and lower homologues were also obtained from propane, butane, pentane as well as from branched alkanes such as isobutane or isopentane. The mechanism of the step leading to C-C bond cleavage and formation very likely involves a four-centered transition state between a tantalum-alkyl and a C-C σ-bond of a second molecule of alkane.

To our knowledge, the alkane metathesis is a new unprecedented catalytic reaction which can be described by the general equation:

$$2C_nH_{2n+2} \rightarrow C_{n+i}H_{2(n+i)+2} + C_{n-i}H_{2(n-i)+2} \qquad (2)$$

where i = 1,2,...n-1, but with i = 1 generally favored.

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PL-28

METHANOL REFORMING FOR FUEL CELL APPLICATIONS

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No Abstract received.

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CATALYSIS FOR FINE CHEMICALS: TOWARDS SPECIFICITY WITH POLYPHASIC MEDIA

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No Abstract received.

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NEW CATALYTIC TECHNOLOGIES DEVELOPED AT STATE RESEARCH CENTER OF APPLIED CHEMISTRY

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RSC "Applied Chemistry", St. Petersburg, Russia

No Abstract received.

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"INTELLIGENT" CATALYSTS AND AN ENVIRONMENTALLY FRIENDLY CATALYTIC TECHNOLOGY TO CONVERT WOOD INTO PAPER

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Emory University, Atlanta, USA

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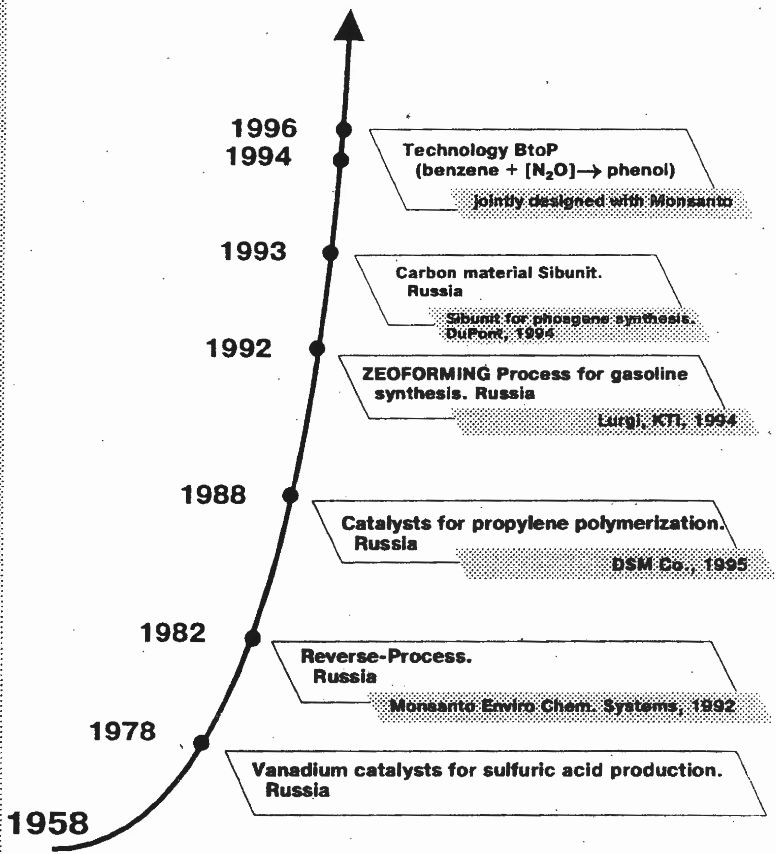

1996
1994

Technology BtoP
(benzene + [N_2O] → phenol)

Jointly designed with Monsanto

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Carbon material Sibunit.
Russia

Sibunit for phosgene synthesis.
DuPont, 1994

1992

ZEOFORMING Process for gasoline synthesis. Russia

Lurgi, KTI, 1994

1988

Catalysts for propylene polymerization.
Russia

DSM Co., 1995

1982

Reverse-Process.
Russia

Monsanto Enviro Chem. Systems, 1992

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