

## Chemical physics and catalysis

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**Abstract:** The role of chemical physics in the science of catalysis and design of new catalytic technologies is discussed. As particular examples the role of chemical physics in the following areas is considered: homogeneous catalysis with metal complexes, heterogeneous catalysis with anchored metal complexes, heterogeneous catalysis with catalysts prepared via anchored metal complexes and organometallics, catalysis of olefin polymerization, catalysis by metals, catalysis by oxides, catalysis by zeolites, catalysis by heteropolyacids and biomimetic catalysis.

### INTRODUCTION

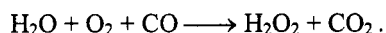
Within the last three decades in catalysis science and engineering a progressive shift was observed from phenomenological approaches to the studies at the molecular level (ref. 1). As a result, chemical physics, defined by Prof. N.N.Semenov as the mechanistic theory of chemical transformations at both microscopic and macroscopic scales, gradually became the theoretical basis of catalysis science and engineering. In this lecture the role of chemical physics in catalysis is briefly discussed with particular examples picked up from the works made at the Boreskov Institute of Catalysis.

### HOMOGENEOUS CATALYSIS WITH METAL COMPLEXES

Due to joint efforts of scientists from various countries the following key elementary steps were elucidated for the activation of small molecules ( $H_2$ ,  $CO$ ,  $O_2$ ,  $N_2$ , etc.) and activation of C-H and C-C bonds in organic molecules: (1) - oxidative addition of reactants to metal atoms; (2) - reductive elimination of reaction products from metal atoms; (3) - numerous, but what is important, well classified rearrangements of atoms and chemical bonds in the coordination sphere of metal atoms.

With a list of elementary rearrangements known for complexes of a given metal atom with particular ligands, and estimates of thermodynamic and kinetic characteristics for these rearrangements, it is possible nowadays to intentionally design new catalytic reactions or new catalysts for the known reactions.

A typical example of a new catalytic reaction that first had been designed on paper using this strategy, and then actually observed experimentally (ref. 2), is shown in Fig. 1. This is the reaction



The design of the catalytic cycle in Fig.1 was based on the well known ability of a hydroxyl ligand attached to Pd(II) atom, to oxidize olefins. Instead of using an olefin, V.A.Likholobov and Yu.I.Yermakov have suggested CO as an oxidized substrate (ref. 2). Indeed, in the first step of the reaction mechanism in Fig.1, the OH ligand oxidizes CO to  $CO_2$  forming in a reductive elimination process a Pd(0) complex. The second step is the oxidative addition of  $O_2$  molecule to Pd(0) complex, in which Pd(0) state returns to Pd(II) one, and simultaneously a coordinated  $O_2^{2-}$  ligand is formed. The latter is

actually already the backbone of a hydrogen peroxide molecule. Upon protonation with  $H_2O$  it forms  $H_2O_2$ . The latter molecule leaves the coordination sphere of Pd(II) in a sequence of ligand substitution reactions to close the catalytical cycle. Note, that reaction in Fig.1 presents an example of the homogeneous biphas catalysis, some stages of which proceed in the aqueous phase, while others - in the  $CH_2Cl_2$  phase.

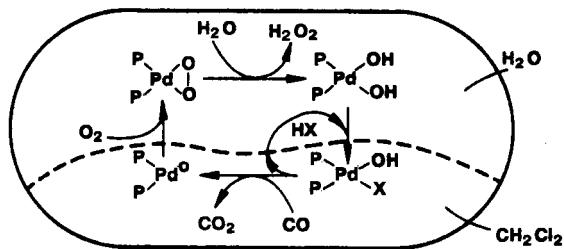


Fig. 1. The catalytic cycle for conjugated co-oxidation of  $H_2O$  into  $H_2O_2$  and  $CO$  into  $CO_2$  (ref. 2).

## HETEROGENEOUS CATALYSIS WITH ANCHORED METAL COMPLEXES

An important example of new catalytic systems created by molecular design is provided by catalysts formed upon anchoring of metal complexes to the surface of solid supports via chemical bonds (ref. 3). A spectacular example (ref. 4). of such a catalyst is presented in Fig.2. In Fig.2a a bimetallic Co—Pd carbonyl complex chemically anchored to the surface of silica is shown. Note, that such Co—Pd species are not formed in solutions. The bimetallic active site of Fig.2 was designed for the hydroformylation of olefins into aldehydes. The *a priori* expected catalytic cycle for this reaction over a Co—Pd bimetallic site is shown in Fig. 2b. The idea behind designing such a cycle was as follows. Pd atom is known as a better site for H<sub>2</sub> activation, while Co atom is known as a better site for CO insertion into the metal-carbon bond. When acting together, the Pd site provides a fast activation of H<sub>2</sub>, while the Co site provides the fast CO insertion. As a result, the combined bimetallic site in Fig.2 works much better in hydroformylation catalysis than each of the monometallic sites (Co or Pd), when taken separately.

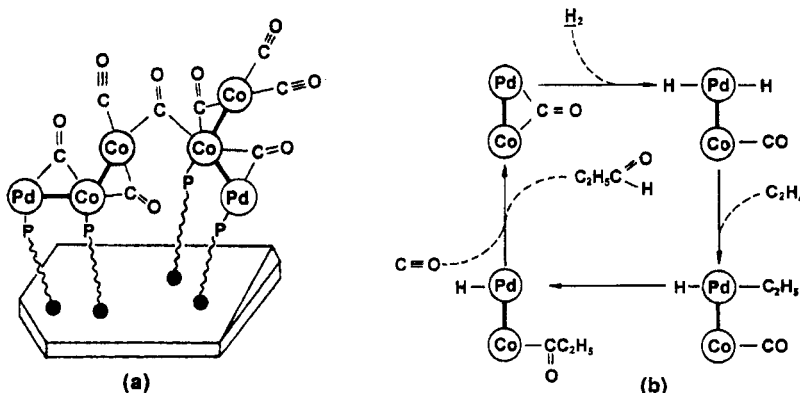


Fig.2. Active site of bimetallic (Pd + Co)/SiO<sub>2</sub> catalyst (a) and the mechanism of hydroformylation of ethylene over this site (b). ●—P denotes a phosphine ligand bound chemically to the surface of SiO<sub>2</sub> (ref. 4).

## HETEROGENEOUS CATALYSIS WITH CATALYSTS PREPARED VIA ANCHORED METAL COMPLEXES AND ORGANOMETALLICS

Anchored metal complexes or anchored organometallic compounds can be also used to prepare specially designed supported metal catalysts (ref. 3). In catalysts prepared via this route it occurs possible to well control the size of supported metal particle. A typical example is a family of Pd/C catalysts designed and commercialized by Yu.I. Yermakov, V. A. Likholobov and V. A. Semikolenov with co-authors.

Particles of different crystallite size demonstrate different activity and selectivity. As an example, see the data on trifluoromethylnitrobenzene (TFMNB) hydrogenation to the corresponding amine (TFMAB) in Table 1 (ref. 5). As seen from this Table, the activity referred to a gram of Pd atom, first increases, but then decreases with the increase of the particle size. The initial increase in activity reflects the intrinsically smaller activity of small Pd(0) clusters compared to the bulk Pd metal, while the subsequent decrease in their activity reflects the decrease of the fraction of the surface Pd atoms as a particle size increases. Only surface Pd atoms participate in catalysis. Therefore, the decrease of their fraction leads to the overall decrease of the activity referred to the total content of Pd in the catalyst.

TABLE 1. Catalytic Properties of Pd Particles with Different Size in Hydrogenation of Trifluoromethylnitrobenzene (TFMNB) to Trifluoromethylaminobenzene (TFMAB)

The size of Pd particle/Å	Activity $\frac{\text{g TFMNB}}{\text{g Pd min} \cdot \text{atm}}$	Selectivity (yield of TFMAB)
~ 10	6.9	99.98
10-30	12.0	99.8
60-120	3.0	99.0
~ 1000	1.3	~ 80

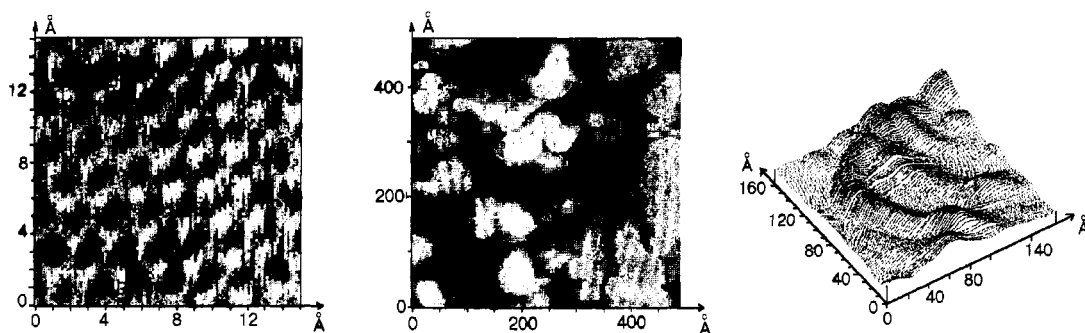


Fig.3. STM images of: (a) - the basal surface of graphite, (b) - the surface of Pd/Sibunit catalyst with highly dispersed Pd particles; (c) - the surface of a large Pd particle in Pd/Sibunit catalyst (ref. 6).

In contrast to the activity, selectivity of the reaction with respect to the desired amine decreases continuously with the increase of the size of the Pd particles. The reason for this can be understood from the data of Fig.3, where an STM (Scanning Tunneling Electron Microscopy) microphotographs of a big and small supported palladium particles are presented (ref. 6). As seen from Fig.3, the surface of the big particle is quite rough. It must contain Pd atoms in quite different coordination environment which implies their different chemical properties. Supposedly, some of the sites facilitate undesirable side reactions, thus decreasing the selectivity with respect to the desired TFMAB product.

On the ground of the data of Table 1, Pd/C catalysts with the 10-30 Å particle size were chosen for commercial production. They demonstrate the highest activity and still are selective enough.

### CATALYSIS OF OLEFIN POLYMERIZATION

One of the most spectacular examples, where studies at the molecular level carried out by scientists of different countries have already played a crucial role in a development of a new generation of catalysts and catalytic processes, is the area of catalytic polymerization of olefins (refs. 7,8). For both homogeneous and heterogeneous catalysis for olefin polymerization coordinatively unsaturated metal complexes with hydride and alkyl ligands were found to serve as the catalyst active sites.

The key elementary steps of catalytic polymerization have been determined (see Fig. 4).

Concentrations of active sites and rate constants of the key reaction steps have been measured for many practically important catalytic systems and used to design and optimize commercial catalytic reactors. These data are also widely used for the intentional control of physico-mechanical properties of commercial polymers obtained using catalytic technologies.

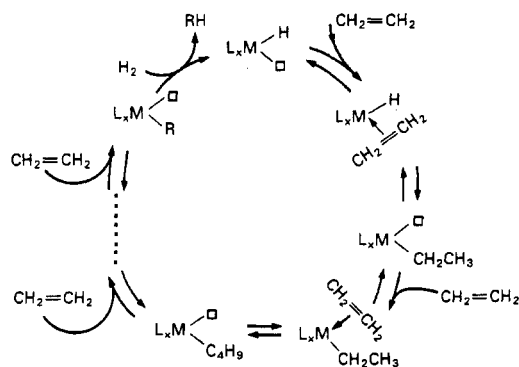


Fig.4. Key steps of the catalytic polymerization of olefins (refs. 1,7).

### CATALYSIS BY METALS

In recent years considerable advances have been achieved in the study of the surface structure and mechanisms of action of metal catalysts. Many impressive examples from this area are cited in monograph (ref. 1). The results obtained in the fields of catalysis by single crystals and supported metal particles with a controllable size and surrounding should be noted especially.

#### Catalysis by Metal Single Crystals with Well Characterized Surfaces

Results of studies in this field have been summarized in excellent review articles by G.A. Somorjai, R. Madix, G. Ertl, D.W. Goodman (ref.9), M. Grunze P.R., Norton (ref. 10), V.I. Savchenko (ref. 11), as

well as in monograph (ref. 1). Therefore, here let us only note that the farther we advance in these investigations, the more our understanding of the mechanisms of catalysis by massive metals approaches the level, that has already been achieved for homogeneous catalysis by metal complexes. Although every step forward demands serious efforts, experience in homogeneous catalysis allows us to expect that future benefits will fully justify these efforts.

Among the data obtained in this field at the Boreskov Institute of Catalysis, let us first mention those of V.I. Savchenko and co-workers on the role of different states of adsorbed oxygen in catalysis of CO and H<sub>2</sub> oxidation by various surface faces of platinum, ruthenium, iridium and nickel single crystals (ref. 11). According to these data, oxygen adsorption is described by the scheme presented in Fig. 5. Oxygen is initially adsorbed in the molecular state (Fig. 5b), and then dissociates producing adsorbed atoms. The dissociation process occurs with a higher rate on structural defects (steps and microfacets) than on smooth planes. First, adsorbed atoms of type I are formed. This type of adsorption corresponds to the location of oxygen atoms above the metal surface (Fig. 5c). Oxygen atoms in this state possess the highest reactivity towards CO and H<sub>2</sub> molecules. The adsorbed oxygen atoms of type I can further transform to adsorbed oxygen atoms of type II. This adsorption state corresponds to oxygen atom insertion into the catalyst surface layer, in other words, to the formation of a two-dimensional surface oxide (Fig. 5d). The reactivity of oxygen of type II is far less than that of oxygen of type I. At elevated temperatures further transformations of the atomic state of type II to a 3-dimensional oxide several atomic layers thick are observed (Fig. 5e). Oxygen atoms of the oxide are also far less reactive towards CO and H<sub>2</sub> than oxygen of type I.

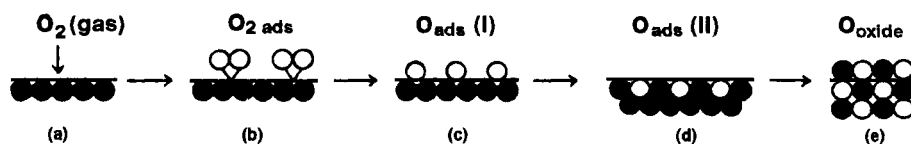


Fig. 5. Schematic representation of oxygen adsorption states on metals: (a) - free metal surface; (b) - molecular state; (c) - atomic state of type I; (d) - atomic state of type II; (e) - atomic state in oxide layer (according to ref. 11).

The formation of the adsorption state of type II is accompanied by reconstruction of the metal surface, which levels the initially different activities of different surface faces in oxidation reactions.

We may hope that the difference found between reactivities of the various states of adsorbed oxygen will be used in the future as an instrument for the intentional control of properties of metal catalysts in oxidation reactions.

The data obtained solve an old argument between G.K. Boreskov and S.Z. Roginskii on whether the specific catalytic activity, SCA (i.e. activity referred to a unit surface area), for catalysts with the same chemical composition of the surface, is constant or can vary from one catalyst to another. In 1953 G.K. Boreskov has formulated his rule about the approximate constancy of SCA for catalysts with the same chemical composition of the surface (ref. 12). This rule was substantiated with a series of very accurate experiments made for various reactions over a family of metal and oxide catalysts.

However, in the same year (1953) S.Z. Roginskii with co-workers in simple but very elegant experiments have observed a substantial difference between the catalytic activity of various surface faces of one and the same metal (ref. 13).

The reason for the deviation of the catalytic behaviour of different faces of the same metal from the Boreskov's rule, as well as the fulfillment of Boreskov's rule for the overwhelming majority of industrial catalysts is nowadays well understood.

Intrinsically various surface faces of the same metal have different catalytic activity. However, if the catalytic reaction occurs under such conditions that under the influence of the reaction mixture and/or elevated temperature the reconstruction of the catalyst surface to its new stable state under these conditions is fast enough, then the SCA will be constant; in other words, at a constant chemical composition of the catalyst surface and of the reaction mixture the SCA will be independent of the

catalyst prehistory. If such a reconstruction is impossible or occurs too slowly, the SCA may depend upon the catalyst prehistory.

Reconstruction of surface layer under catalytic reaction conditions or at elevated temperatures has been observed also by many research groups (refs. 9, 10) and seems to be an intrinsic property of metal single crystals. This ability for reconstruction resembles the well known property of soluble metal complexes and metal clusters to become fluxional upon coordination of certain ligands and/or increase of temperature (ref. 14). *Reconstruction of the surface of heterogeneous catalysts under the influence of reaction mixture demonstrates that a rule resembling the third Newton's law in mechanics is valid for heterogeneous catalysis, namely, "the action is equal to the counteraction". If the catalyst is powerful enough to perturb the reaction mixture via intermediate chemical interactions to such an extent that it starts to react, then the reaction mixture must be equally powerful to perturb substantially the state of the catalyst surface via the same intermediate chemical interactions. Because of this the state of the catalyst surface in the process of catalytic reaction may be substantially different from its state before or after the reaction (ref. 15).*

The above statements have two important implications for the experimental studies of heterogeneous catalysis. First, for elucidating the correlations between the catalytic properties and the structure of heterogeneous catalysts, it is preferable to make structural studies *in situ*, i.e. directly under reaction conditions. Second, kinetic equations for reactions on solid surfaces can contain not only terms that reflect reaction mechanism itself, but also terms that reflect the change of catalysts upon interaction with the components of the reaction mixture (ref. 15). Appropriate taking in to account of the latter terms in certain cases may become quite essential for elucidating reaction mechanisms from kinetic data (ref. 15).

Note that reconstruction of the initial state of a catalyst to some new one which is stable under the reaction conditions, is typical not only for heterogeneous catalysis, but for homogeneous catalysis as well. A spectacular example here are Mo homogeneous catalysts for olefins epoxidation with hydroperoxides in solution (refs.16-18). As suggested earlier by Sheldon and co-workers (ref. 16) and verified recently with NMR by Talsi and co-workers (refs.17,18), two drastically different Mo complexes, namely  $\text{MoO}_2(\text{acac})_2$  (which contains Mo in the oxidation state +VI) and  $\text{Mo}(\text{CO})_6$  (which contains Mo in the oxidation state 0) under steady-state conditions of epoxidation reactions are both converted into the same set of three Mo(VI) complexes with diolo ligands.

### **Catalysis by Metal Particles with Controllable Size and Surroundings**

As a result of the investigations at the molecular level, important structural peculiarities of ultrafine particles of supported metals have been elucidated. Of special interest are the results obtained by EXAFS method, which permits one to measure interatomic distances and estimate coordination numbers for atoms of supported metals. Interesting work in this field was done by D.I. Kochubey (ref. 19).

In these studies it was found that distances between metal atoms in small metal particles on the support surface may appreciably (up to 0.2 Å) differ from the corresponding distances in massive metals.

Such particles are structurally nonrigid. It seems to be important for catalysis, since it should make more facile the formation of intermediate complexes between surface metal atoms and reacting molecules.

EXAFS studies suggest (ref. 19) that the so called effects of a "strong metal-support interaction", SMSI, (ref. 20), in some cases presents, from the chemical standpoint, the destruction of the metallic framework in the supported noble metal particle and formation of a ligand surrounding by oxygen anions (and, possibly, by atoms of the support metal) around the noble metal atoms.

For example, for the Rh/La<sub>2</sub>O<sub>3</sub> catalyst, for which the SMSI effect is observed, the number of Rh—O and Rh—La bonds considerably exceeds that of Rh—Rh bonds. In contrast to this, for Rh/SiO<sub>2</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> where SMSI effect does not occur, almost solely Rh—Rh bonds are observed. In accord with the observed difference in their local surroundings, rhodium atoms on different supports reveal essentially different catalytic properties in CO hydrogenation. For instance, for Rh/SiO<sub>2</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> the main reaction products are hydrocarbons, while for Rh/La<sub>2</sub>O<sub>3</sub> these are alcohols (ref. 21).

Recent breakthroughs in development of such instrumentation methods as Scanning Tunneling Electron Microscopy (STM), Field Electron Microscopy (FEM) and Field Ion Microscopy (FIM) allows researches to characterize the surface of metal catalysts and reactions on these surfaces at really atomic scale. An example of the Pd/C catalyst characterization with STM has already been presented (Fig.3). Note, that a special STM instrument, which provides catalyst characterization under the atmosphere of the reacting mixture starting from  $10^{-9}$  to 1 bar, has been designed at the Boreskov Institute of Catalysis for such studies (ref. 6).

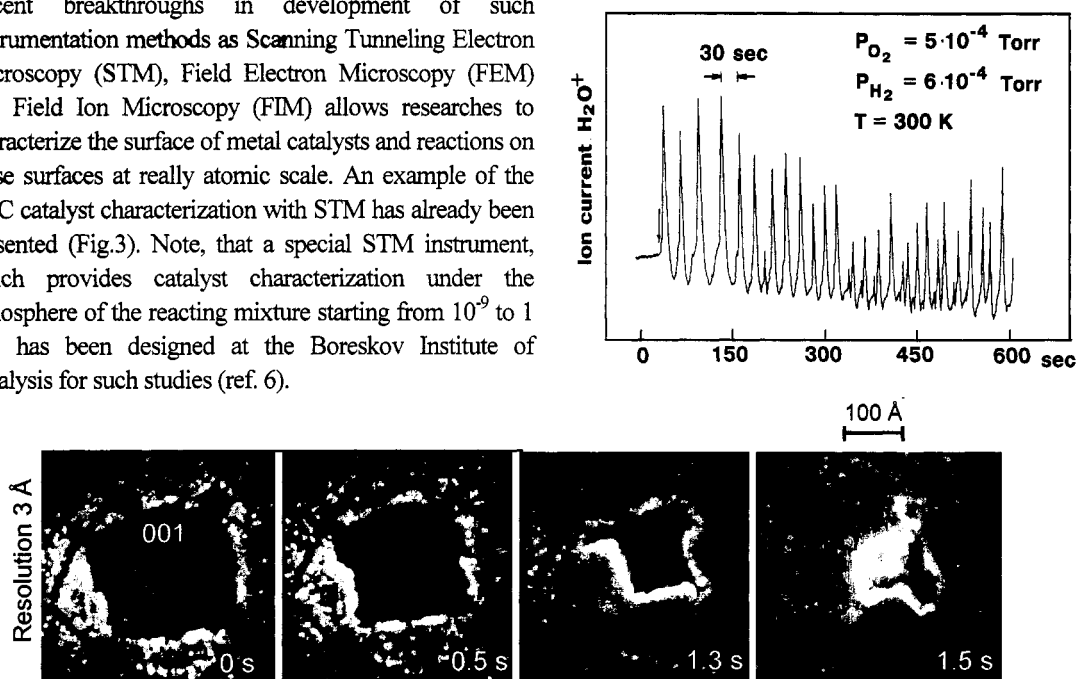


Fig.6. Kinetic oscillations and surface waves propagation in  $\text{H}_2 + \text{O}_2$  reaction on Pt according to Field-Ion Microscopy (ref. 22).

In Fig.6 the data obtained recently by the team of researches from the Fritz Haber Institute, Berlin, and the Boreskov Institute of Catalysis on studying at the atomic scale of the oscillating  $\text{H}_2$  oxidation reaction over Pt using FIM, are presented (ref. 22). From this Figure one can see how the oxidation reaction front (light areas in the Figure) is formed and moves in space as time goes. Note, that with the help of STM, FEM and FIM scientist can for the first time look at the kinetic behaviour of very small local spots of the catalyst surface. Thus, pictures which are not averaged over a large ensemble of catalyst surface sites and adsorbed species, can be obtained. This unique information, unavailable until recently, promises breakthroughs in understanding and describing at really atomic level of complicated kinetic behaviour for both model and practical reactions over heterogeneous catalysts.

In particular, it becomes possible to elucidate how in real macroscopic catalysts the kinetics typical for small local spots is statistically averaged to describe reactions at the macroscopic scale. Remind, that this is the latter kinetics that chemical engineers need in order to design catalytic reactors starting from the description of the catalytic process at the atomic level.

Small metal particles belong to the family of compounds which fill the gap between the world of metal complexes and that of bulk metals. Their sizes are such that their electronic structure is different from that of bulk metals. In particular, the number of atoms in very small metal particles is not big enough for the electronic bands and gaps (that are typical for bulk metals) to be formed. Therefore, it is not surprising that chemical properties of small metal particles are sometimes quite different from those known for bulk metals. Thus, we anticipate that further studies of catalysis with such particles indeed promise in the near future new unexpected exciting results.

One of such results obtained recently at the Boreskov Institute of Catalysis is illustrated in Fig.7 (ref. 23). This Figure demonstrates an unusual liquid-like behaviour of small iron particles supported over amorphous carbon at temperatures as low as 920 K. In the right-hand side of this Figure one can see how supported iron particles in a form of droplets move along the surface of amorphous carbon falling apart in some cases and merging together in other cases. The left-hand side of Fig.8 shows that upon their movement the iron particles catalyze transformation of the amorphous carbon into graphite. Their movement along the surface continues until they lose access to amorphous carbon and become trapped from all the sides by graphite. After that they freeze in the form of the iron carbide  $\text{FeC}$  species.

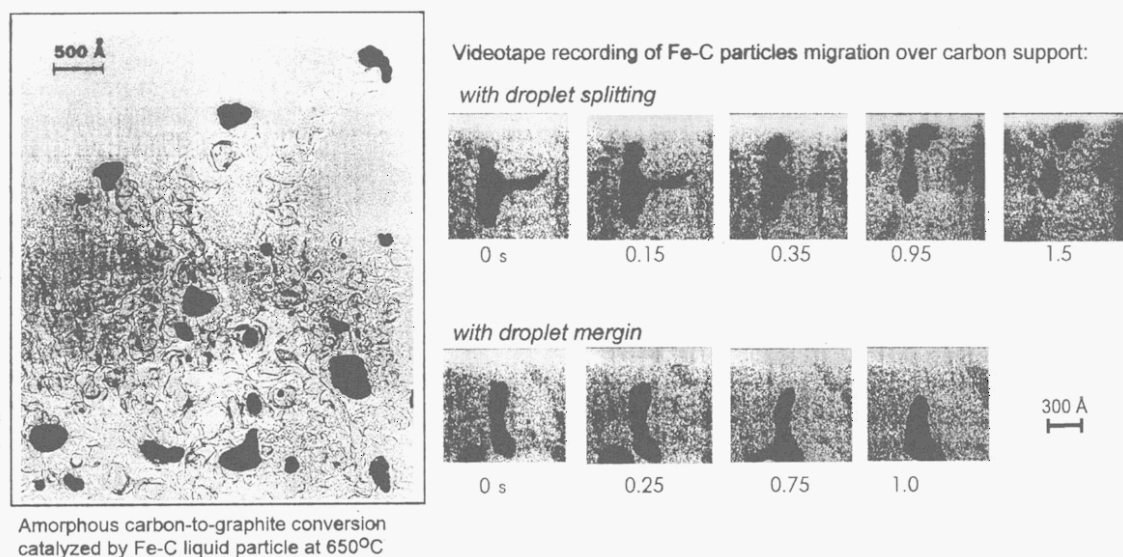


Fig. 7. Migration of liquid Fe-C particles over the surface of amorphous carbon in the course of its low temperature graphitization assisted by Fe catalyst (TEM data) (ref. 23).

According to ref. (ref. 23), the liquid iron particles are in fact very concentrated solutions of carbon in iron. The driving force for the formation of such "oversaturated" with carbon iron particles is the enthalpy of transformation of a less stable amorphous carbon to a more stable graphite (ref. 23). The catalytic properties of the unusual liquid iron-carbon particles are now under study at the Borekov Institute of Catalysis.

*It may be expected that further studies of ultrafine particles of supported metals will make it possible to develop in the future new types of industrial catalysts, which will combine a high activity and technological convenience typical for heterogeneous metal catalysts with a high selectivity typical for homogeneous metal complex catalysts.*

## CATALYSIS BY OXIDES

Due to the great variety of the chemical sites, present on their surface, oxide catalysts are typically more difficult to study at the molecular level than metallic catalysts. Nevertheless, in recent years serious advances in this field have also been achieved.

### Mechanism of SO<sub>2</sub> Oxidation over Supported Vanadium Catalysts

By the way of example let us consider the data on structure and mechanism of action of vanadium catalyst for SO<sub>2</sub> oxidation to SO<sub>3</sub> obtained at the Borekov Institute of Catalysis. These studies were carried out under the guidance and with active participation of Prof. G.K. Borekov (refs. 15,24). A distinct feature of this work is a combination of a detailed (at the level of elementary steps) investigation of reaction kinetics with the thorough examination with a set of spectroscopic methods of the catalyst states at various steps of its preparation and process performance. The insight into the mechanism of this heterogeneous reaction is now almost as deep as that traditionally available for only homogeneous catalysis. The results obtained in this field have been summarized recently in ref. 25).

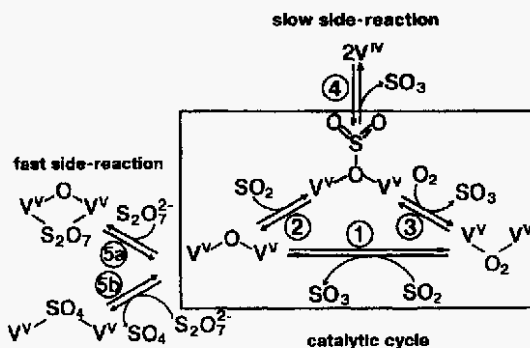


Fig. 8. The reaction scheme and kinetic equation for SO<sub>2</sub> oxidation (ref. 25).

The reaction mechanism identified from the set of spectroscopic, as well as steady state and relaxation kinetic studies for the reaction of SO<sub>2</sub> oxidation to SO<sub>3</sub>, is presented in Fig.8. These data are important not only from the scientific, but also from the practical point of view. First, they make it possible to optimize the operation of the industrial reactors on the basis of the reliable kinetic model that seems to reflect the real mechanism of the catalytic reaction at the molecular level. Secondly, they provided guidelines for further improvement of vanadium catalysts applied to particular conditions of their operation.

On the basis of deep insight into the reaction mechanism and kinetics of SO<sub>2</sub> oxidation, as well as heat transfer and mass transfer processes in catalytic reactors, a completely new process for SO<sub>2</sub> oxidation under forced unsteady-state conditions has been designed and commercialized (refs. 26,27).

Nowadays 6 reactor units for this process operate in Russia and licenses for the process have been sold to various companies all over the world.

### Hydrogenation of Organic Compounds and Methanol Synthesis over Cu-Containing Oxide Catalysts. Mechanism of H<sub>2</sub> Activation

Copper-containing complex oxides are important commercial catalysts for methanol synthesis and some other hydrogenation processes (ref. 28). Important data on the mechanism of H<sub>2</sub> activation over such catalyst were obtained recently at the Boreskov Institute of Catalysis by T. M. Yurieva and co-workers (refs. 29,30).

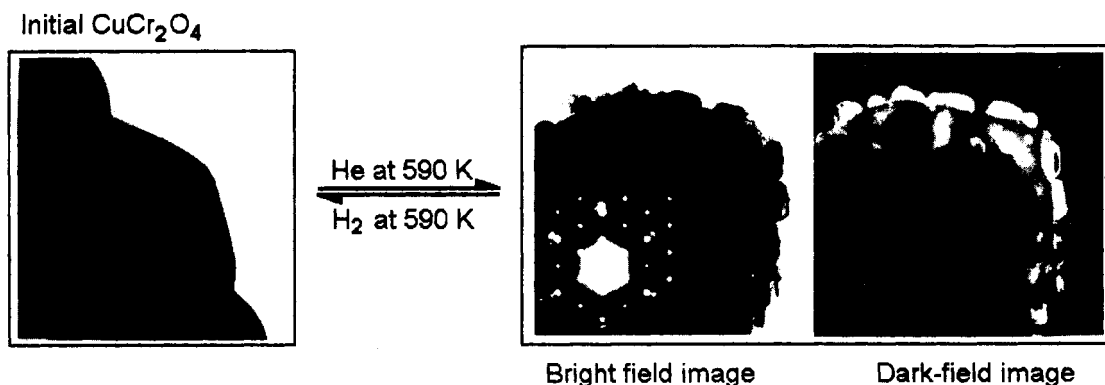


Fig.9. Changes in the structure of CuCr<sub>2</sub>O<sub>4</sub> catalyst upon alternating treatments in H<sub>2</sub> and He at 590 K (TEM data, ref.29).

One of the simplest in the family is the spinel CuCr<sub>2</sub>O<sub>4</sub> catalyst for acetone hydrogenation to *iso*-propyl alcohol. Fig.9 demonstrates TEM data about the changes of the structure of this catalyst upon treatment in the atmosphere of various gases. Upon treatment in H<sub>2</sub> atmosphere at 590 K, tiny crystals of metallic copper grow epitaxially on the surface of the spinel oxide catalysts. Subsequent treatment of these samples with helium at the same temperature returns the catalyst to its initial form, that is the tiny copper particles disappear completely. This suggests that H<sub>2</sub> initially reduces Cu<sup>2+</sup> atoms of the catalysts surface to the Cu<sup>0</sup> state. At the same time, H<sub>2</sub> must, of course, be oxidized. However, the so formed states of hydrogen in the catalyst are quite unstable, and are easily blown out of it with the stream of helium, which is accompanied by the reoxidation of Cu<sup>0</sup> back to the Cu<sup>2+</sup> state. *In situ* X-ray and IR characterization of CuCr<sub>2</sub>O<sub>4</sub> catalyst also confirms that upon consecutive treatment in the atmospheres of H<sub>2</sub> and He, Cu<sup>2+</sup> is reversibly reduced to Cu<sup>0</sup> and then reoxidized back to Cu<sup>2+</sup> state. Neutron diffraction studies show the presence of two forms of atomic hydrogen in the reduced catalyst. The oxidized atomic forms of hydrogen which must be formed upon Cu<sup>2+</sup> reduction to Cu<sup>0</sup>, are responsible for the hydrogenation activity of the CuCr<sub>2</sub>O<sub>4</sub> catalysts (refs. 29,30).



## CATALYSIS BY ZEOLITES

Catalysis with zeolites and other molecular sieve catalysts is becoming progressively more and more important for industry. Several excellent reviews in this area (refs. 31-33) have been published recently.

To give the flavor of the mechanistic studies that are carried out in the area of zeolite catalysis at the Boreskov Institute of Catalysis, here we report two particular examples of such studies.

The first example refers to the acid catalysis of butanols dehydration over a family of well characterized ZSM-5 zeolites (ref. 34). The second example refers to a smooth redox catalysis of methane oxidation to methanol and of benzene oxidation to phenol over specially prepared iron-containing ZSM-5 catalyst (refs. 35,36).

### Mechanism of Butanols Dehydration on H-ZSM-5 Zeolite and Amorphous Aluminosilicate

The mechanism of dehydration of a family of butanols (*n*-BuOH, *iso*-BuOH, *sec*-BuOH and *tert*-BuOH) was studied recently jointly by the team of researchers from the Boreskov Institute of Catalysis (M.A.Makarova, A.G.Stepanov with co-workers) and from the Royal Institution of Great Britain (Prof. J.M. Thomas with co-workers). The reaction pathways were reliably elucidated by simultaneously using a set of steady state and transient GC-MS kinetic studies, IR *in situ* kinetic studies, and characterization of the reaction intermediates within the zeolites pores by IR and NMR methods.

The mechanism of the reaction that was found in ref. 34, is shown in Fig. 10. The key reaction intermediate is the OR species that is located in the center of the mechanism scheme presented in the Figure. This intermediate exists inside the zeolite pores in three rapidly interconverting forms, that is: a butyl-silyl ether, a carbenium ion and butanol molecule hydrogen bonded to the OH active in catalysis group of the zeolite (Fig. 10). Of these three forms, the alkyl-silyl ether prevails. Note, that this alkyl-silyl ether bears some peculiar features compared to its analogues in solutions. In particular, it demonstrates a remarkable fluxionality being able to convert rapidly enough into the carbenium ion state (Fig.10). This carbenium ion state seems in fact to be responsible for the remarkable catalytic properties of H-ZSM-5 catalysts in butanols dehydration.

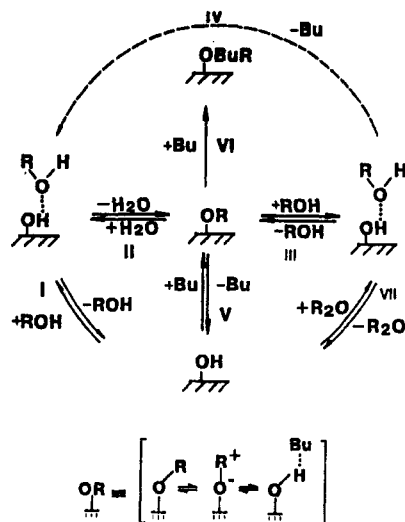


Fig.10. Mechanism of butanols dehydration on H-ZSM-5 zeolite and amorphous aluminosilicate (ref. 34).

### Selective Oxidation of Methane and Benzene over Iron-Containing ZSM-5: an Example of Biomimetic Heterogeneous Catalysis

Recently G.I. Panov and co-workers have shown that even such inert alkane as CH<sub>4</sub>, as well as benzene can be rather smoothly oxidized over a specially prepared iron-containing ZSM-5 catalyst, provided that N<sub>2</sub>O is used as an oxidant, rather than O<sub>2</sub> (refs. 35,36). As shown in refs. 35,36, the oxygen atom of N<sub>2</sub>O molecule is inserted with a remarkable selectivity into the CH bonds of CH<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> molecules forming methanol and phenol, respectively. Thus, iron-containing zeolite serves as an excellent model of the natural catalysts - monooxygenases that smoothly hydroxylate various hydrocarbons (ref.37).

According to refs. 35,36, an unusual weakly bound form of atomic oxygen is formed upon interaction of N<sub>2</sub>O molecule with the iron-containing sites of the zeolite. Note that in the future a remarkable hydroxylating ability of N<sub>2</sub>O with respect to alkanes and aromatic hydrocarbons, may occur of commercial importance.

## CATALYSIS WITH HETEROPOLYACIDS

Heteropolyacids exhibit a remarkable blend of the acid base and redox properties which make them unique catalysts for various reactions both in solutions (homogeneous catalysis) and solids (heterogeneous catalysis). Several excellent reviews are available in this field (refs. 38,39).

When located in a solution or on a solid surface, heteropolyacid molecules act as a polyfunctional catalytically active site. The origin of the polyfunctionality of the heteropolyacid catalysts is illustrated in Fig.11.

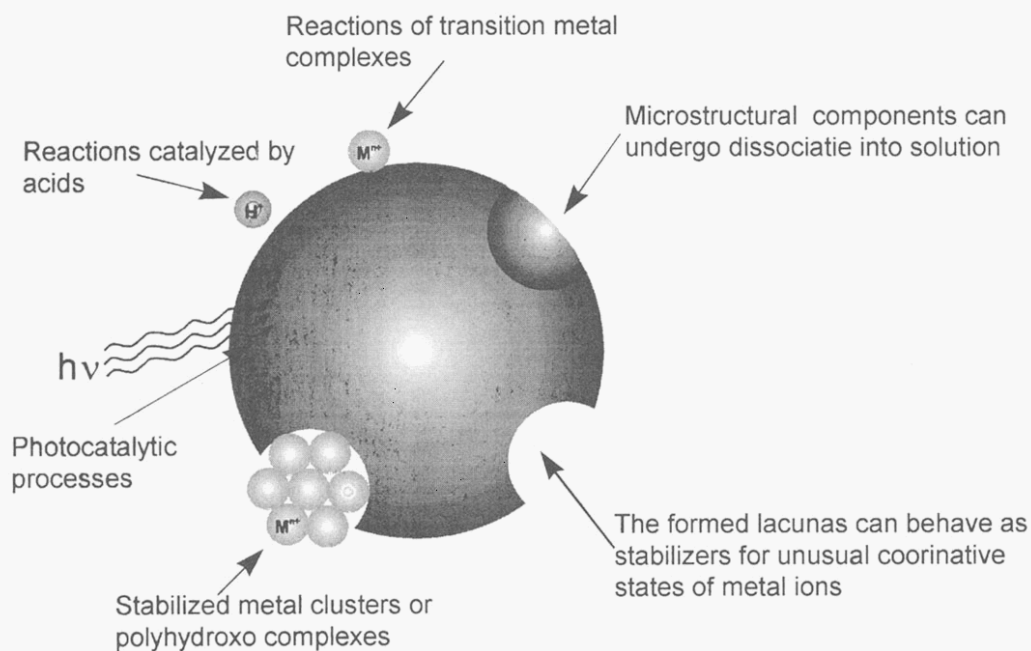
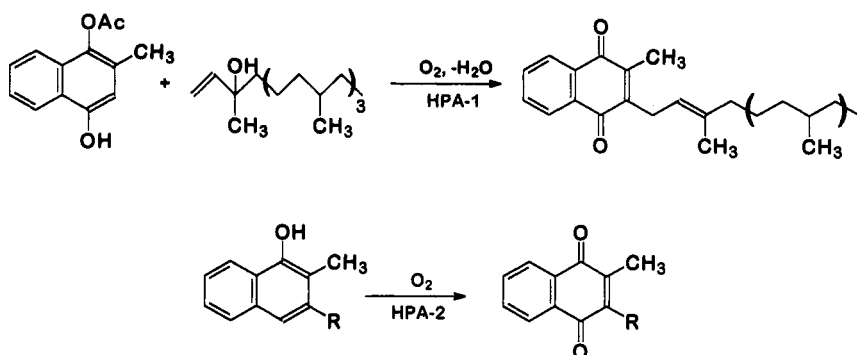


Fig.11. Schematic representation of the origin of polyfunctionality of heteropolyacids as catalysts.

First, HPAs are very strong acids in organic solutions. A reason for this is a very big size of an anion which is formed when a proton is detached from an HPA molecule. This makes HPAs very good acid catalysts. Moreover, the acidic catalytic properties of HPAs molecules can be monitored rather easily by changing the chemical composition of the skeleton of the heteropolyanion in these molecules. Second, transition metal cations can be easily substituted for protons in HPA molecules. Thus, metal complex catalysts can be prepared where the skeleton of HPA serves as a ligand.

Third, certain microstructural fragments of the HPA framework can dissociate in solutions, forming lacunas of different size. Into these lacunas various other catalytically active moieties can be inserted. Fourth, in many cases metal cations that compose together with oxygen anions, the skeleton of the HPA molecules, can be easily reduced or oxidized. Having in mind that the number of such cations is rather big, one immediately realizes that HPA molecules can work as multielectron reducing or oxidizing species. Note, that by varying the nature of metal cations in the framework of the HPA's polyanion, one can smoothly monitor the redox potential for various multielectron or one-electron transformations of HPAs molecules. This allows scientist to intentionally tune heteropolyacid catalyst to carry out particular redox reactions, they are interested in. Many heteropolyacid moieties have intense charge transfer absorption bands. Therefore, they can act also as efficient photocatalysts.

The reaction below illustrates the particular power of heteropolyacids to serve as catalysts for reactions of fine organic synthesis. One sees how over heteropolyacid catalysts vitamins K. can be synthesized (ref. 40):



## BIOMIMETIC CATALYSIS

Catalysis is a fundamental feature of life processes. Very complicated chemical reactions are carried out in living organisms with remarkable selectivity and at mild conditions with the help of special catalysts - enzymes. It is really a challenge for catalytic chemists to learn the principles that are used by enzymes in their operation and to utilize these principles for the design of new more efficient synthetic catalysts. This direction of catalysis is often called *biomimetic catalysis* (refs. 37,41).

A typical example of a biomimetic catalyst is the Fe-containing ZSM-5 zeolite described above. This catalyst remarkably mimics the ability of the enzymes - monooxygenases to smoothly insert an oxygen atom into carbon hydrogen bonds in hydrocarbons.

## CONCLUSION

The results presented in this lecture demonstrate that chemical physics, in meaning put into this term by Prof. N.N.Semenov, has indeed become the theoretical basis of catalysis. Particularly important have become the studies of catalysis at the molecular level using modern kinetic, spectroscopic and surface science techniques.

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