

ANCHORED COMPLEXES IN FUNDAMENTAL CATALYTIC RESEARCH

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Abstract - The application of mononuclear and polynuclear species anchored on support surfaces reveals new possibilities for studying the theoretical problems of catalysis. Examples are given concerning a) elucidation of the type of the active species; b) study of the mechanism of catalytic reactions; c) active particles size effect; d) the influence of composition of active species on their catalytic properties.

INTRODUCTION

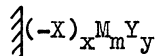
Two fields of research activity may be marked where new ideas for understanding catalytic phenomena are often produced. These fields are:

1. Use of new physical methods for catalyst investigation.
2. Use of new objects in catalytic research.

In the first area new approaches to explaining catalytic phenomena appeared every time a new physical method was introduced and its possibilities and limitations for catalysis were ascertained. In recent years we have witnessed the elucidation of the intimate mechanism of the interaction of reagents with active sites on metal surfaces by the methods of "ideal surface science" (Ref. 1 & 2). However the gap is evident between the conditions in which these studies are performed and those of application of real catalysts (Ref. 1). Apparently knowledge appropriated in this field is not as yet a basis for recommendations for real catalyst preparation.

In the second area the appearance of the new ideas in theoretical catalysis is caused by the discovery and the study of new catalysts. The study of stoichiometric and catalytic reactions of mononuclear transition metal complexes and organometallic compounds played an important role. The new ideas on the mechanism of catalysis were then disseminated in heterogeneous catalysis (Ref. 3, 4 & 5). Much may be expected from the studies of polynuclear (cluster) complexes for better comprehension of catalysis by metals (Ref. 6 & 7).

Fundamental studies in catalysis directly concerned with the preparation of practically important catalysts may be affected by the recent development of the methods of preparing systems containing surface complexes anchored in a non-active matrix. The composition of such complexes may be represented as follows:



where $\left\| \right.$ - matrix surface, M - a transition metal, X - an anchoring site (surface ligand), Y - outer ligands, x, m, y - stoichiometric numbers. In general surface species a) may be bi- or polynuclear ($m \geq 2$); in particular they may contain atoms of different transition metals; b) metal atoms may be bound with more than one anchoring sites and c) the composition of outer ligands may change during catalytic reaction. Systems containing anchored species as active centers may correspond to the concept of or "ideal" (or "precise") heterogeneous catalyst. Such catalyst have to contain uniform active species; all transition metal atoms have to be included in the composition of active centers. An active center can be defined as a surface compound conducting a catalytic cycle and restoring its composition after each cycle. Cer-

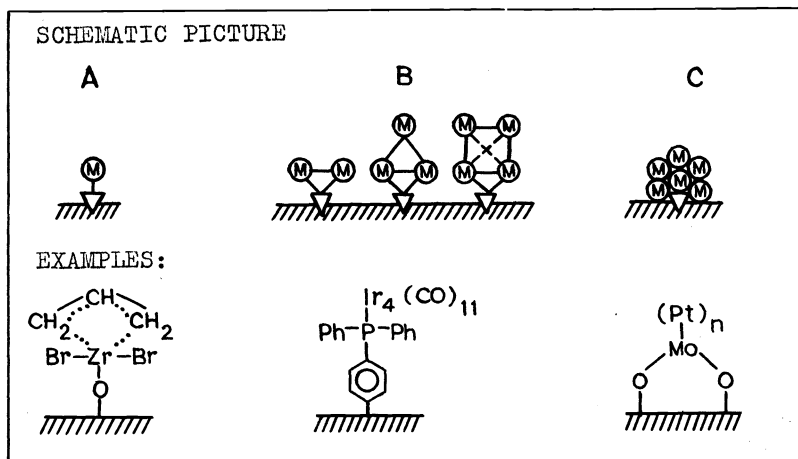


Fig. 1. Possible types of anchored complexes differing in nuclearity. A. Mononuclear complex. B. Bi- or polynuclear complexes (anchored clusters). C. Polynuclear center with indefinite number of metal atoms. - surface of matrix; ∇ - anchoring site (surface ligand); \textcircled{M} - complex (or atom) of transition element. Examples are taken from Refs. 8-10.

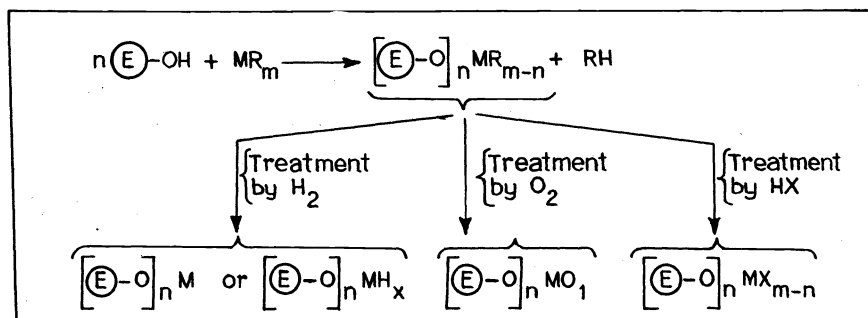


Fig. 2. Scheme of the preparation of various surface species via the anchoring of organometallic compound MR_m on oxide support. \textcircled{E} is adjacent to the surface atom of the element, forming oxide support; m, n, l, x are stoichiometric numbers.

tainly, it may be a matter of discussion whether the catalysts of this type have been prepared up till now by the synthesis of the anchored complexes. However, the elaboration of the methods of the preparation of such catalysts may be a challenging objective of catalytic research.

Surface compounds prepared by fixation of transition metal complexes on supports may either directly serve as active catalytic centers or may be used as precursors in the synthesis of the surface species of various composition. Variation in the composition of the surface species prepared via complex anchoring may result in a whole spectrum of catalysts - from systems containing mononuclear centers to those containing dispersed particles (see Fig. 1). Here there is no space to mention all techniques of the synthesis of various anchored complexes. However, we will mention some approaches to the preparation of the surface species of different nuclearity.

Mononuclear anchored complexes are at present widely used in catalysis (see recent reviews 11-14). Different approaches to prepare such complexes have been developed. The application of systems in which the anchoring sites are surface hydroxyl groups is of interest for the study of traditional field of catalysis by transition metal compounds on oxide supports. The sufficiently versatile technique for the prepara-

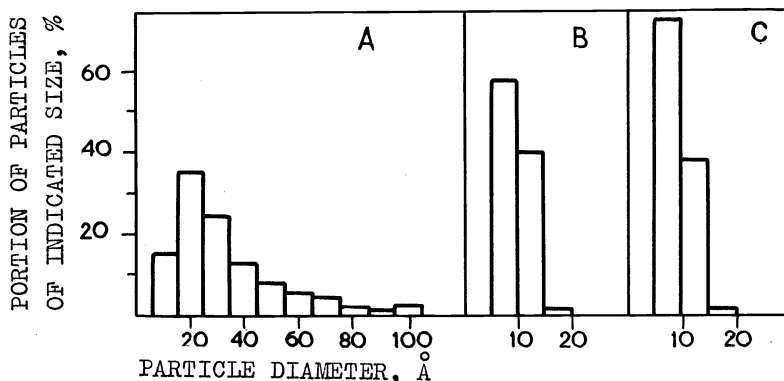


Fig. 3. Size distribution of metal particles on SiO_2 , according to electron microscopy data (Ref. 23). A. 3.6% Pt; sample prepared by supporting H_2PtCl_6 , reduced at 500°C . B. 1.4% Pt; sample prepared by supporting dimethylallylplatinum, reduced at 600°C . C. (2.8% Pt + 4.6% W); sample prepared by supporting diallylplatinum on SiO_2 containing anchored W(II) ions, reduced at 600°C .

tion of such systems is the use of transition metal organometallic compounds (Ref. 15) (see Fig. 2).

The study of catalytic properties of the surface polynuclear complexes containing a certain number of metal atoms (anchored clusters) (see B in Fig. 1) may be of great interest for fundamental catalytic research. They might be possibly obtained by supporting individual cluster complexes. However, fragmentation and agglomeration of clusters may take place during interaction of clusters with the oxide surface and especially, on heating in reaction medium. This may be exemplified by transformation of $\text{Rh}_6(\text{CO})_{16}$ and $\text{Ru}_3(\text{CO})_{12}$ on oxide supports (Ref. 16 & 17). Apparently it is possible to retain the structure of clusters by binding them with appropriate anchoring sites, for example, the known data on the fixation of rhodium clusters on polymer and oxide supports with phosphine ligands (Ref. 9, 18 & 19). These ligands have also been used for anchoring polynuclear complexes of palladium (Ref. 20).

The decomposition of anchored complexes results in the formation of dispersed surface particles, containing an indefinite number of metal atoms (see C, Fig. 1). By reduction of the anchored organometallic complexes of Ni, Pd and Pt metal particles are obtained in which the dispersion is essentially higher than that obtained by traditional techniques of the catalyst preparation (Ref. 15, 21 & 22) (see, for example, Fig. 3). Super-dispersed metal particles are obtained from organometallic species in the presence of bound to the surface transition metal ions which serve as anchoring sites (Ref. 10, 15, 22 & 24) (see C in Fig. 3).

The catalysts, containing active centers, obtained by anchoring complexes or by further transformation of anchored complexes may be applied to study many fundamental aspects of catalysis. Experimental examples considered below deal with the following problems (Note a):

1. The elucidation of the composition and the ways for the formation of active surface species. The intentional synthesis of the catalyst containing definite surface compounds implies formulation of the initial hypothesis what is the catalyst active center? Thus, the synthesis of potentially active centers via anchoring complexes with further examination of their catalytic properties is a direct experimental way to test the hypothesis concerning the essence of the catalytic behavior of the system under study.

Note a. Certainly not all possible applications are listed here. E.g., interesting application of supported complexes is described for studying problems of bi- or polyfunctional catalysis (Ref. 25 & 26).

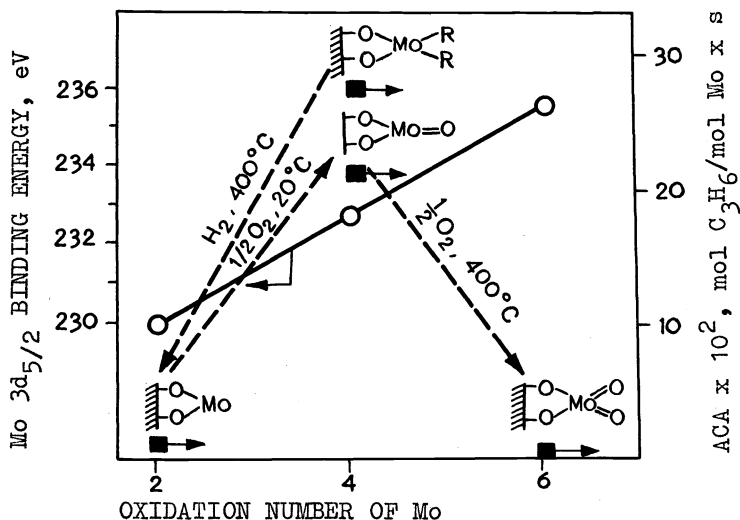


Fig. 4. Scheme showing the formation of anchored complexes containing molybdenum ions of different oxidation numbers. The energy of the Mo $3d_{5/2}$ level (\circ) and the atomic catalytic activity (Note a) (ACA) in propylene metathesis at 90°C (\blacksquare) are given. /// - surface of silica.

2. Studies of mechanism of catalytic reactions. Due to a higher homogeneity of catalyst containing anchored complexes more reliable information about surface centers and their interaction with reagents may be gained using physical methods.

3. The study of the effect of the nuclearity of an active center. The study of the catalytic properties of the super-dispersed particles derived from anchored complexes is of interest for obtaining additional data on the "structural sensitivity" of reactions. The important further problem is the determination of the minimum number of metal atoms in an active center necessary to fulfill certain catalytic reaction.

4. The exploration of the dependencies of "catalytic properties vs composition". The use of anchored complexes permits us to get information at variation of the composition of active center (and not the bulk composition of catalyst).

ELUCIDATION OF THE TYPE OF THE SURFACE ACTIVE SPECIES

Oxidation state of molybdenum and tungsten ions in precursors of metathesis active centers

Anchored organometallic complexes of the VI Group elements may be transformed into surface species containing ions Mo with various oxidation numbers. The scheme of preparing anchored Mo(II), Mo(IV) and Mo(VI) ions on silica is given in Fig. 4. This scheme defined from chemisorption data (Ref. 15 & 28) is in agreement with the change of the energy of Mo $3d_{5/2}$ level (about 2 eV (Ref. 29) when the oxidation number changes by 2; see data in Fig. 4). The validity of this scheme is confirmed by the Iwasawa et al (Ref. 30 & 31) for the case when alumina was used as a support.

Methallyltungsten complexes anchored on silica undergo the similar transformations (Ref. 15).

In the metathesis of propylene at mild temperatures surface Mo(IV)

Note a. Here for characterization of the activity the concept of Borshkov (Ref. 27) on the atomic catalytic activity (ACA) assigned to one atom of a transition metal is used.

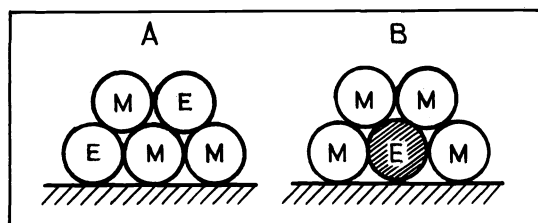


Fig. 5. Possible types of the surface species in supported metallic catalysts with promoters. (M) - atom of VII Group metal; (E) - atom of promoter element; (E) - ion of promoter element bound to the support surface.

(see data in Fig. 4) and W(IV) species play the role of precursors of active centers; surface compounds containing ions with other oxidation states appear to be inactive (Ref. 15, 30 & 32).

Polynuclear active species in promoted platinum catalysts

A very important problem is the elucidation of the role of promoters in so-called "bimetallic" catalysts for hydrocarbon reactions. Two extreme models of active species in such catalysts are under discussion (Ref. 22 & 24) (see Fig. 5). One model implies the formation of "bimetallic clusters" (Ref. 33) in which promoter atoms are in zero-valent state (see A in Fig. 5). Apparently, the formation of such alloyed particles is possible when supported compounds are easily reducible. The presence of the element E in the form of surface ions that perform the function of anchoring sites for dispersed particles of metal M is considered in another model (Ref. 15 & 22) (see B in Fig. 5). It is supposed that E and M are linked by metal-to-metal bonds E-M. As a result the particle of metal M may be strongly fixed on the support surface (Ref. 15 & 22). The interaction of the metal particles with promoter ions prevents metal sintering at conditions when bonds E-M are not destroyed.

Contradictory data regarding the state of a promoter element was obtained from the study of catalysts, prepared by traditional techniques. For example, the data are available which suggest that in (Pt+Re)/Al₂O₃ system rhenium may be either in the form of low-valent ions (Ref. 34) or in the metallic state (Ref. 35 & 36) (as "homogeneous bimetallic aggregates" or highly dispersed pure rhenium depending on the procedure of catalyst preparation (Ref. 36). According to the X-ray spectroscopic study using a synchrotron radiation (Ref. 37) these systems may contain rhenium differing in oxidation state.

The possibility of the formation of the surface type B species (Fig. 5) may be examined by special preparation of catalyst. The preparation comprises two stages:

1. Anchoring low-valent ions of promoter element E on support.
2. Supporting organometallic compounds of metal M (e.g., Pt) with further reduction treatment.

The use of silica as a support reveals an especially distinct difference between the samples prepared via anchored complexes and those prepared by traditional technique of supporting. For example, in the catalysts Re/SiO₂, prepared by reduction of anchored [Re(OEt)₃]₃ produced rhenium ions in surface species have an average oxidation number of about 2.5 (see Fig. 6) when rhenium being reduced to metallic state in the impregnation catalyst. The catalyst (Re+Pt)/SiO₂ prepared by the technique of anchoring after reduction retains rhenium ions as evidenced by the X-ray spectroscopy data (Ref. 38) (see Fig. 6 B). Platinum in this catalyst is in a super-dispersed state; the data of radial electron distribution indicate only the first coordination sphere of platinum (the particles of the size <10 Å (Ref. 39). Such samples exhibit an increased activity for benzene hydrogenation (see Table 1). On the contrary, catalysts prepared by conventional technique contain relatively large Re and Pt particles after reduction and rhenium exhibits no promoting effect.

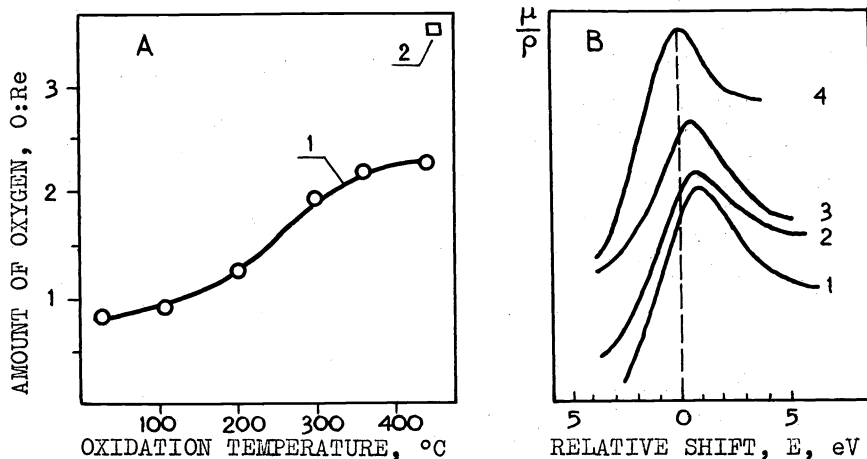


Fig. 6. Data on the state of rhenium in supported catalyst, prepared by different methods. A. Amount of oxygen consumed at oxidation of Re/SiO_2 catalysts preliminary reduced at 600°C . Oxidation by O_2 at $\geq 400^\circ\text{C}$ produces $\text{Re}(\text{VII})$ species. 1 - Sample prepared by interaction of $[\text{Re}(\text{OEt})_3]_3$ with SiO_2 ; content of Re 12.5 wt%. 2 - Sample prepared by impregnation of SiO_2 with aqueous solution of NH_4ReO_4 ; content of Re 4.0 wt%. B. L_{III} -adsorption spectra of Re measured using synchrotron radiation (Ref. 35). 1 - $\text{Re}(\text{OEt})_3$ anchored on SiO_2 . 2 - Sample 1 treated by H_2 at 600°C . 3 - $(\text{Re}+\text{Pt})/\text{SiO}_2$; prepared by supporting $\text{Pt}(\text{C}_4\text{H}_7)_2$ on sample 2; reduced by H_2 at 600°C . 4 - Re/SiO_2 , prepared with the use of NH_4ReO_4 ; reduced at 600°C , contains supported metallic Re.

TABLE 1. Properties of $(\text{Pt}+\text{Re})/\text{SiO}_2$ catalysts prepared by different methods

Catalyst composition (wt%)	Compounds used for catalyst preparation	State of supported elements	Activity in benzene hydrogenation	
			a)	b)
1.2% Pt, 3.6% Re	$\text{Re}(\text{OEt})_3$, $\text{Pt}(\text{C}_4\text{H}_7)_2$	Particles of Pt <10 Å, ions of Re	7.60	0.41
2.0% Pt, 3.4% Re	NH_4ReO_4 , H_2PtCl_6	Particles of Pt ~40 Å, particles of Re ~80 Å	0.27	0.08
2.3% Pt ^{c)}	$\text{Pt}(\text{C}_4\text{H}_7)_2$	Particles of Pt ~15 Å	0.70	0.06

a) Mole $\text{C}_6\text{H}_6/\text{g Pt} \times \text{h}$.

b) Atomic catalytic activity, molecules C_6H_6 per surface atom of Pt per s.

c) Nonpromoted catalyst; data given for comparison.

An essential difference in the state of supported elements is observed also for the reduced catalysts $(\text{Pt}+\text{Sn})/\text{SiO}_2$ prepared either by anchoring of complexes on silica (Sn is not reduced to metallic state) or by conventional impregnation technique (reduction of Sn is observed (Ref.40)

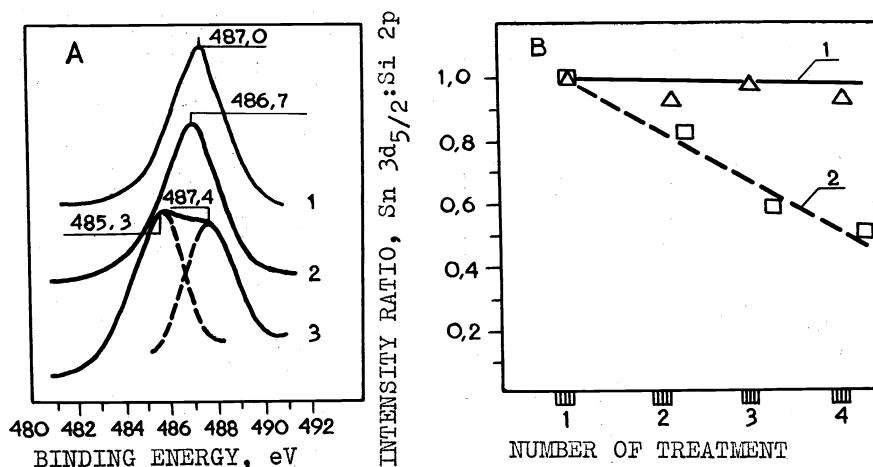


Fig. 7. Data on the state of tin supported on SiO_2 catalysts, prepared by different methods (Ref. 40). Content of Sn 1.6 wt%; content of Pt 2.0 wt%. A. XPS spectra of the region Sn $3d_{5/2}$.

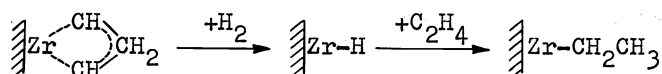
1 - Sample prepared by anchoring $\text{Sn}(\text{OAc})_2$ on SiO_2 ; then $\text{Pt}(\text{C}_4\text{H}_7)_2$ was supported. 2 - Sample 1 treated by H_2 at 600°C . 3 - Sample prepared by co-impregnation of SiO_2 with aqueous solution of SnCl_2 and H_2PtCl_6 ; reduced by H_2 at 600°C . B. Normalized intensity ratios Sn $3d_{5/2}$:Si 2p. 1 - The same sample as sample 1 in A. 2 - Sample prepared by co-impregnation technique. Treatment of samples: 1 - samples after supporting Sn and Pt. 2, 3, 4 - heating in H_2 at 200, 400 and 600°C , correspondingly.

(see Fig. 7). The presence of Sn(II) ions on alumina according to chemisorption data was observed (Ref. 41) in the case of conventionally prepared catalysts after their reduction. The stabilization of the dispersed state of platinum was also established for catalysts containing ions of Mo, W or Pb anchored on silica (Ref. 22 & 24).

Provided that the model which considers stabilization of the super-dispersed platinum particles by interaction with the anchored to the support surface low-valent ions (see Fig. 5 B) is valid some recommendations for the choice of promoters may be formulated: promoter should be selected among elements capable to form hard-to-reduce compounds with a support; moreover the requirement of the formation of metal-to-metal bonds between promoter element and the atoms of catalytically active metal should be taken into account. The technique of catalyst preparation must ensure the formation of anchored to the support surface ions of the promoter.

STUDY OF THE MECHANISM OF CATALYTIC REACTIONS

Catalytic systems containing anchored complexes may be used to trace the conversion of the surface species into proper active centers and to study the steps of a catalytic reaction. As an example, we consider the data obtained at the studies of supported organometallic catalysts for ethylene polymerization. By IR-spectroscopy the reactions of the anchored allylzirconium complexes were studied (Ref. 42 & 43) (see Fig. 8). Anchored π -allyl complexes of Zr(IV) are the precursors of the active centers formed according to the scheme:



Zirconium retains the oxidation number IV in the active centers. This conclusion follows from the comparison of the concentration of active centers in such systems (as high as 40% of the total zirconium content

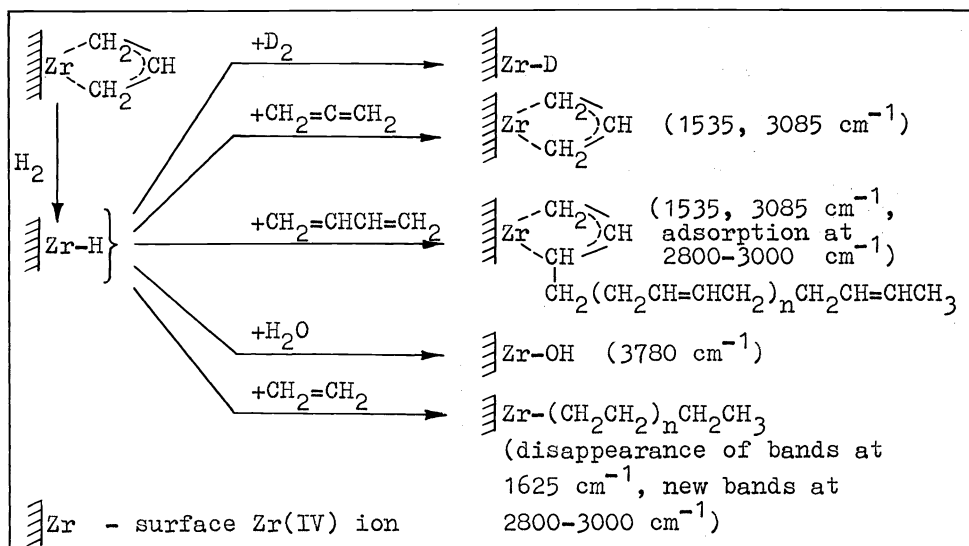
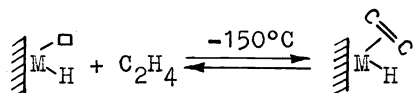


Fig. 8. Reactions of the anchored on silica complexes of zirconium according to IR-spectroscopy data (Ref. 42).

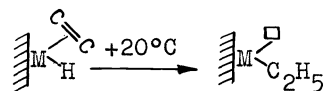
in catalysts) with the number of Zr(III) ions (less than 3% of zirconium (Ref. 43)).

Active centers containing Zr(III) and Ti(III) ions may be prepared by special treatment of the anchored organometallic compounds (Ref. 43). By the change of the ESR-spectra during interaction of these centers with reagents some elementary stages of the polymerization may be observed (Ref. 44):

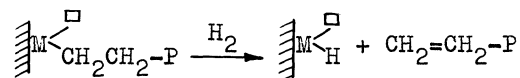
a) coordination of the monomer:



b) insertion into the M-H-bond (initiation reaction):

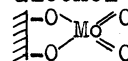


c) hydrogenolysis of the M-C-bond (chain transfer with H₂):



(M: Ti, Zr; P: polymer chain).

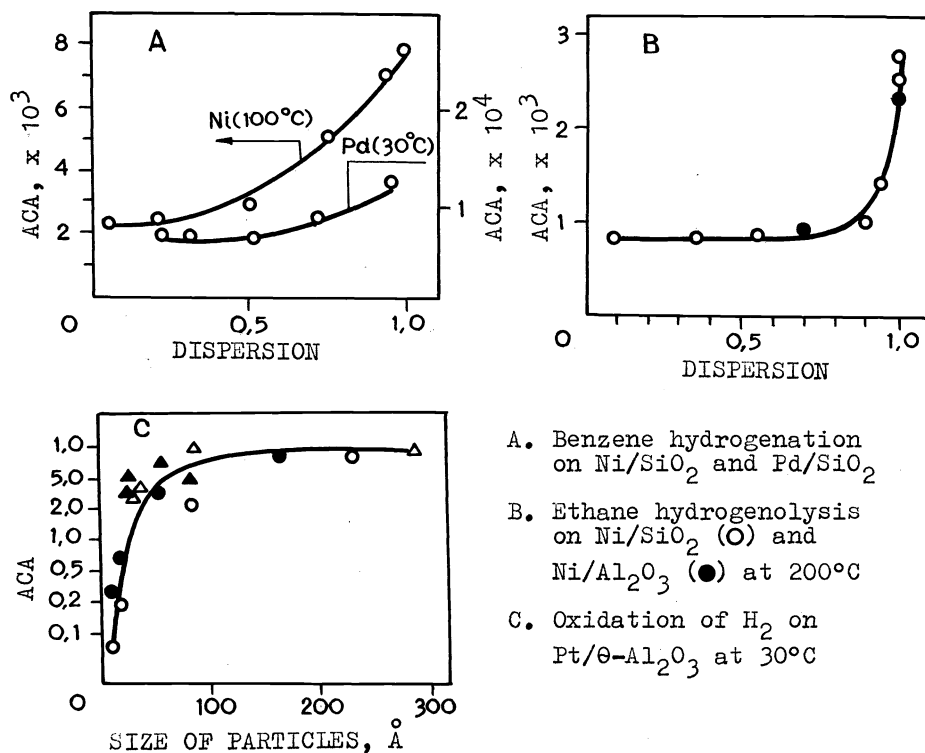
Note also that Mo(VI) complexes obtained via the interaction of Mo(C₃H₅)₄ with silica were used to the studies of the mechanism of alcohol oxidation (Ref. 45). In this reaction the surface compounds



containing Mo ions in tetrahedron environment play the role of active centers.

STUDY OF THE SIZE EFFECTS

The effects of the active particle size on catalytic properties are being widely discussed in literature. Additional data on these effects (especially in the region of super-dispersed particles) may be obtained using catalysts prepared by decomposition of anchored complexes. Figure 9

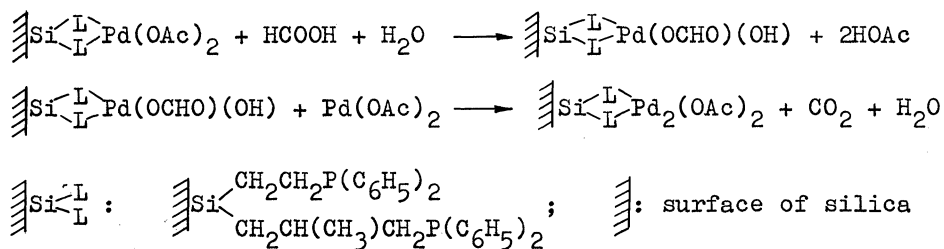


- A. Benzene hydrogenation on Ni/SiO₂ and Pd/SiO₂
- B. Ethane hydrogenolysis on Ni/SiO₂ (O) and Ni/Al₂O₃ (●) at 200°C
- C. Oxidation of H₂ on Pt/θ-Al₂O₃ at 30°C

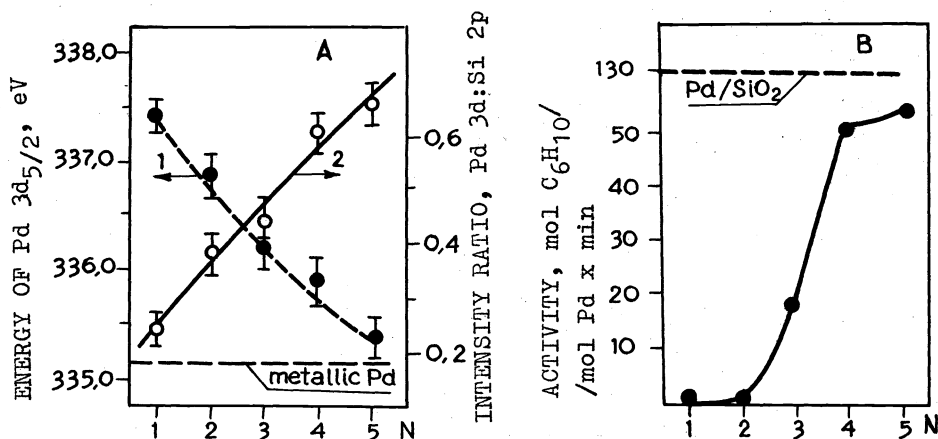
Fig. 9. Examples of the effect of metal dispersion on catalytic activity (Ref. 24). Catalyst are prepared by decomposition of anchored organometallic complexes. The size of the metal particles was varied by the change of the catalyst treatment by H₂. Atomic catalytic activity (ACA) in molecules of reagent per surface metal atom per s.

shows the change of activity in some reactions with metal dispersion. In benzene hydrogenation and ethane hydrogenolysis the change of activity is distinct in the region of small metal particles, but too slight to discuss the reasons for this firmly. An essential decrease of the activity was observed in hydrogen oxidation as the size of platinum particles on θ-Al₂O₃ diminishes from 100 till ~10 Å. Probably this is due to the intrusion of a part of platinum atoms into the lattice of θ-Al₂O₃ (Ref. 46).

A further stage in the study of the problem of the "size sensitivity" will, apparently, deal with the examination of the properties of the complexes containing a definite number of metal atoms. Ichikawa (Ref. 47) observed certain differences in catalytic properties of samples prepared by supporting mono-, bi- and trinuclear nickel complexes on silica. An attempt has been made to trace a change of catalytic properties of anchored complexes containing different number of palladium atoms (Ref. 48). Anchored palladium complexes were prepared according to the scheme:

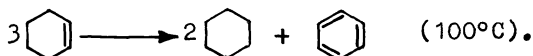


By repeating these reaction the surface clusters including upto 5 atoms



N: number of palladium atoms in the anchored complexes

Fig. 10. Change of the properties of the anchored polynuclear complexes $\begin{array}{c} \text{Si} \\ \diagup \quad \diagdown \\ \text{P} \end{array} \text{Pd}_n(\text{OAc})_2$ at variation of the number of palladium atoms in their composition. A. XPS data. 1 - Change of the energy of Pd 3d_{5/2} level. 2 - Ratio of intensities Pd 3d:Si 2p. B. Activity in disproportionation of cyclohexene:



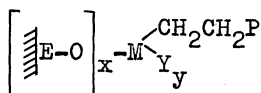
of Pd were prepared. As the number of palladium atoms N increases from 1 to 5 the energy of Pd 3d_{5/2} level approaches gradually that of the supported metallic palladium (Fig. 10 A). At the same time a linear increase of the intensity of X-ray photoelectron spectra of Pd 3d_{5/2} is observed with the increase of the number of palladium atoms in anchored complexes (Fig. 10 A). At N=5 the catalytic properties in olefins hydrogenation and cyclohexene disproportionation are close to that of supported metallic palladium. A fragment of 3 palladium atoms appear to be a minimum structural unit indispensable to the reaction of disproportionation of cyclohexene (Fig. 10 B). The study of anchored palladium complexes of different nuclearity gives a conclusion that catalytic properties of the surface species containing 4-5 atoms of palladium appears to be close to those of dispersed metallic particles (Ref. 48).

STUDIES OF THE CHANGE OF CATALYTIC PROPERTIES WITH THE VARIATION OF COMPOSITION OF ACTIVE SPECIES

One of the most important tasks of fundamental studies in catalysis is that of establishing and interpreting of correlations of "an active center composition vs catalytic properties". The advances in this field result in new approaches to control the catalyst properties. Examples of the studies with the use of catalysts prepared via supporting organometallic complexes are given below.

Ethylene polymerization

The composition of the active centers in supported olefin polymerization organometallic catalysts (Ref. 43) can be represented by



($\begin{array}{c} \text{---} \\ \text{---} \end{array}$ - surface of oxide support, P - polymer chain)

Intentional synthesis of the direct precursors of the active centers in these catalysts is accomplished by anchoring organometallic compounds.

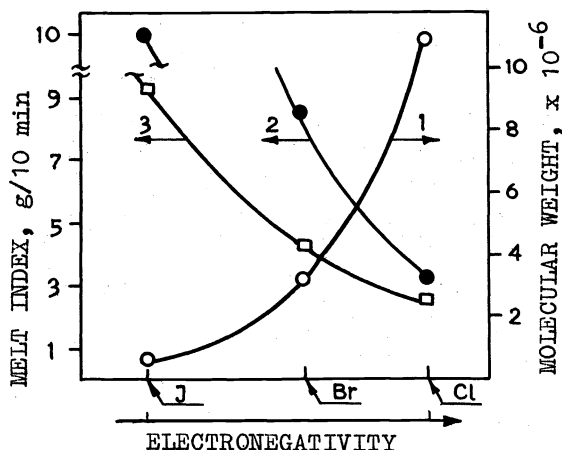
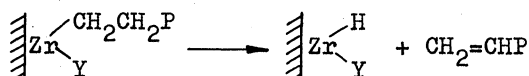


Fig. 11. The change of polyethylene properties with the change of ligand environment of the Zr(IV) ion in the active center. Curves 1 and 2: $Zr(C_3H_5)_2X_2 + SiO_2$ catalyst. Curve 3: $Zr(C_3H_5)_3X + SiO_2$ catalyst (Ref. 49). Polymerization at $80^\circ C$, pressure of C_2H_4 5.5 atm (4 atm of H_2 was in the system in the case of curves 2 and 3).

The correlations between the properties of active centers and their composition (metal M, the element forming the oxide support E, ligands Y) were studied (Ref. 43). The variation of E, M and Y involve the change of the rate constants of elementary steps of polymerization (e.g., propagation rate constant K_p , chain transfer rate constant with monomer K_m etc. (Ref. 43). As an example, we mention the influence of the ligands Y in series $Cl \rightarrow Br \rightarrow I$ when the catalysts were prepared by anchoring halide-containing π -allyl zirconium complexes (Ref. 43 & 49). In this series the molecular weight of the polyethylene drastically decreases (see Fig. 11). The molecular weight is proportional to the K_p/K_m ratio. Thus, a decrease in the electronegativity of the ligand Y results in the preferential increase of the chain transfer rate constant (K_m) due to the higher rate of β -hydrogen shift:



Reactions of hydrocarbons on promoted platinum catalysts

Though many researchers are attentive to the problem of "structural sensitivity" the change of the size of metal particles give no sufficiently effective possibilities to control the catalyst properties in practically important hydrocarbon reactions. An essential improvement of the supported metal catalysts for refinery processing is achieved by changing their composition. In this connection an influence of promoter elements in the active sites having presumably a similar structure (see Fig. 5 B) is worth regarding.

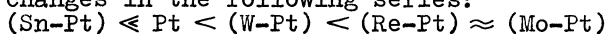
For platinum particles interacting with anchoring sites - low-valent ions of Mo, W, Re or Sn ions - a decrease of the energy of Pt $4f_{7/2}$ level by 0.5 eV is observed as compared to the Pt/ SiO_2 catalysts (Ref. 50 & 51). Thus the platinum atoms become less electronegative in bimetallic catalysts. The presence of a promoter essentially changes the electron levels in the valent zone also (Ref. 51). These data indicate the great changes in the chemical properties of platinum in dispersed particles anchored on low-valent ions. These changes manifest themselves in the variation of the adsorption and catalytic properties of platinum.

For the catalyst (Pt+W)/ SiO_2 the lowering of the heat of adsorption

of weakly bound hydrogen was established by a calorimetric method (Ref. 52). According to thermodesorption data the hydrogen becomes more strongly bound with platinum in the presence of tin ions (the desorption of hydrogen is observed mainly after 400°C (Ref. 24).

It is certainly a very complicated task to establish all reasons of the change of catalytic properties upon variation of the composition of polynuclear active centers. The accumulation of the experimental facts on the properties of the catalysts, containing active species of the same type is needed in this field. In principle, interaction of metal with a promoter element may cause both a decrease and an increase of the catalytic activity. This indeed was observed for catalysts prepared with the use of organometallic complexes.

Promoters influence the activity of platinum in such "structure insensitive" reactions as benzene hydrogenation or cyclohexane dehydrogenation. The activity of the samples prepared with the use of SiO_2 as a support changes in the following series:



In the case of $(\text{Pt+Sn})/\text{SiO}_2$ catalysts the catalytic activity in benzene hydrogenation below 200°C is totally inhibited due to the interaction of platinum with tin ions; the hydrogenation starts only at temperatures at which strongly bound hydrogen is removed from platinum. The effect of Re and Mo ions results in about ten times increase of the atomic catalytic activity in benzene hydrogenation on platinum.

In such "structure-sensitive" reaction as hydrogenolysis of ethane a more pronounced effect of promoting was observed. The presence of tin in this case also inhibits the reaction at temperatures till 400°C. The presence of W and especially Mo ions causes a drastic increase of the platinum activity (up to 10^4 times according to the reaction temperature); the properties of Pt become closer to those of its left neighbours in the periodic table namely Ir and Os (Ref. 10 & 53). A similar effect is observed in neopentane hydrogenolysis while the isomerization reaction is suppressed (Ref. 54). The change of kinetic parameters of hydrogenolysis - activation energies and frequency factors - is established. The change of catalytic properties may be attributed mainly to a decrease of heat of adsorption of the weakly bound part of hydrogen involved in the reaction; change of the metal electron properties apparently are predominant (Ref. 54).

It is of interest to examine the effect of promoters on the reactions of n-hexane, as the conversion of this hydrocarbon may be possible model of paraffin transformations in catalytic reforming. The influence of promoters - anchoring sites for platinum particles - manifests itself primarily in the rise of the catalyst stability. The interaction of platinum with non-transition elements (Sn, Pb) leads to some decrease in the over-all rate of n-hexane conversion (see Fig. 12). The influence of transition elements (Mo, W, Re) manifests itself in the increasing activity of platinum. Different promoters have a differentiating effect on the separate routs of n-hexane conversion, so the selectivity is changed (Ref. 24). For example, in the case of platinum catalysts whose activity in hydrogenolysis and C_5 -cyclization is suppressed by interaction with tin ions the dehydrogenation or aromatization (according to reaction conditions) of paraffins with a high selectivity may be performed.

Approximately the same high dispersion of platinum is attained in the case of all promoters studied (hundred per cent of platinum exposure) (Ref. 24). Considering this fact the conclusion may be drawn that the type of intermediates formed by the interaction of paraffins with promoted metal particles is determined primarily by the parameters of electronic state of metal. To obtain more detailed information concerning the mechanism of action of each promoter it is necessary to examine the types of adsorbed intermediates formed during interaction of hydrocarbons with the platinum clusters whose properties are modified due to the interaction with anchoring sites. It is a necessary task of further research.

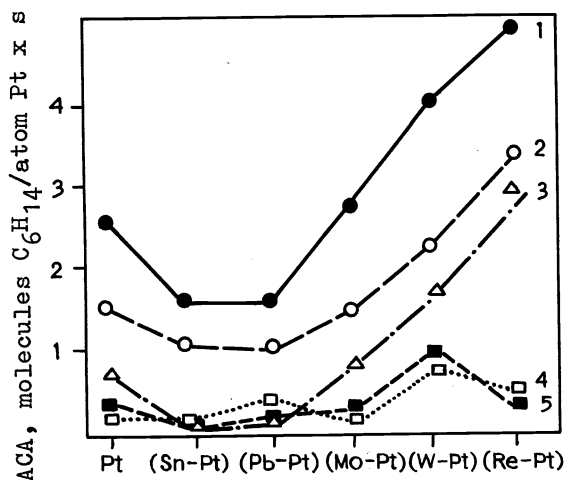


Fig. 12. The effect of promoters on the rate of n-hexane reactions at 500°C. Catalysts of the composition (Pt+E)/SiO₂ were prepared by fixation of the ions of promoter element E to the support surface with subsequent supporting Pt(C₄H₇)₂; content of Pt ~ 2 wt%; atomic ratio E:Pt ~ 2.5. The activity was measured in circulation-flow reactor; pressure of n-C₆H₁₄ 25 Torr; H₂:n-C₆H₁₄ = 30. 1 - Overall rate of n-hexane conversion; 2 - dehydrocyclization to benzene; 3 - hydrogenolysis; 4 - C₅-cyclization; 5 skeletal isomerization.

CONCLUSION

Initial progress of catalysis by anchored complexes is related mainly to heterogenization of complexes which were direct analogues of the known homogeneous catalytic systems. However, the new field of catalyst preparation begins to be orientated more to the synthesis of the surface active centers with no direct analogues among soluble catalysts. Further development of this trend may be expected including the preparation of catalytic systems useful for studies of problems of fundamental catalysis. The synthesis of the surface active centers may be based on the synthetic methods known in chemistry of coordination and organometallic compounds. Undoubtedly many difficulties are to be overcome in development of techniques for the intentional preparation of active centers for different reactions and their characterization; but the endeavours in this field will be rewarded. Preparation of catalysts using complicated and time-consuming procedures (and sometimes with application of reagents which are not conventional for experts in catalysts) can be justified if useful information about the composition of active centers and the ways of their formation is obtained. It is hoped that such information will permit available for practice recommendations concerning preparation of selective and active industrial catalysts.

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