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# Cluster and Polynuclear Heterogeneous Metal Complex Catalysts

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The present state of the problem of catalysis by cluster and polynuclear transition metal complexes attached to the surfaces of mineral and organic polymers is analysed. The principal methods of preparation of heterogenised clusters and the possible ways of transforming them on the surfaces of carriers are examined and the influence of the nuclearity of the clusters on the catalytic activity and selectivity in the conversion of CO is discussed. The prospects for the employment of immobilised clusters in catalysis are considered.
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## I. INTRODUCTION

Heterogeneous metal complex catlaysis is a new rapidly developing field of catalytic chemistry. In the first review and monographs,[1-3] the likely usefulness of heterogeneous metal complex catalysts (HMC), containing cluster and polynuclear transition metal complexes attached to a carrier, was already pointed out. During the last 7–8 years, methods of synthesis have been developed and the properties of such catalysts have been investigated. It has been suggested that the cluster HMC manifest a high activity and selectivity in many-electron and multistage chemical reactions as a result of the activation of inert molecules on polynuclear active centres. It is therefore not surprising that the main tests for the catalytic activity of clusters have been reactions involving the simultaneous activation of CO and $H_2$. Some results of these studies are discussed in our previous review.[4]

Numerous investigations of the methods of synthesis of cluster HMC with different nuclearities and of the reactions of the clusters on the surfaces of carriers during catalysis have been published recently. A series of interesting results have been obtained in the investigation of the catalytic activities of these systems and of the influence of the nature of the carrier surface on their catalytic properties. This review is devoted to the analysis of these studies.

Since the terminology in the field of chemistry of cluster and polynuclear compounds has not as yet been finally formulated, we shall explain certain terms employed in this review. A transition metal cluster in catalysis is the name given to a group of $n$ metal atoms ($n \geq 2$) bound to one another. Polynuclear transition metal complexes are compounds whose composition includes two or more metal atoms not linked directly to one another. The nuclearity of the cluster is characterised by the number of metal atoms in its skeleton. The nuclearity of a polynuclear complex is determined by the number of metal atoms in its composition. Homonuclear complexes contain the atoms of only one metal, while heteronuclear complexes contain the atoms of several metals. The interaction of transition metal complexes with the surfaces of carriers, carried out in order to synthesise heterogeneous catalysts, is called heterogenisation. This process can include both pure adsorption interaction and chemical reactions on the surface.

## II. HETEROGENISATION OF CLUSTER CARBONYL COMPLEXES ON UNMODIFIED MINERAL CARRIERS

One of the simplest and most widely used methods for the heterogenisation of cluster and polynuclear complexes is adsorption from solution. Hydroxy-groups and acid and basic Lewis centres are distributed on the surfaces of mineral carriers, so that the interaction between the complex and the carrier may be due not only to weak adsorption forces but also to the formation of strong chemical bonds. The chemical interaction of the complex with the surface usually leads to one of three possible consequences: (1) the cluster skeleton and the oxidation state of the constituent transition metal atoms of the cluster remain unchanged; (2) the skeleton of the complex is preserved, but the oxidation state of the metal atoms changes; (3) the cluster skeleton breaks down. In the last case there is a possibility of both the dispersion of the cluster compound with formation of mononuclear centres on the carrier surface and of an increase in the nuclearity of the cluster up to the formation of the metallic phase. Unfortunately the possibility of the occurrence of the processes enumerated above on the carrier surface is by no means taken into account in all the studies devoted to catalysis by heterogenised cluster and polynuclear complexes. Since problems associated with the reactions of complexes on the surface are of key importance for the interpretation of the nature of the activity of heterogeneous cluster catalysts (HCC), studies in which the changes in the complexes on heterogenisation were investigated specially are considered below.

Carbonyl complexes, for example, $Mo(CO)_6$, can interact with the surfaces of mineral carriers in accordance with the following schemes:[5]

$$Mo(CO)_6 + |{-}O^- \rightarrow Mo(CO)_5(O^- {-}|);$$
$$[Mo(CO)_3]_{ads} + 2|{-}OH \rightarrow (|{-}O^-)_2Mo^{2+} + H_2 + 3CO.$$

Thus there is a possibility of the strong chemisorption of metal carbonyls on the carrier surface containing basic groups or acid Lewis centres.[6-8] In the heterogenisation of th iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ on $Al_2O_3$, analogous reactions were observed.[9] At 150 °C the so-called sub-carbonyl species $[Fe(CO)_2]_{ads}$ are formed on the surface.[9,10]

It has been suggested[11,12] that the carbonyl ligand may be attacked by the surface hydroxy-group in the first stage of the interaction of $Fe(CO)_5$ and $Fe_5(CO)_{12}$ with $Al_2O_3$ and MgO and the ionic hydride $[HFe_3(CO)_{11}]^-$ is formed:

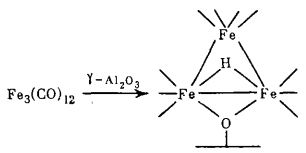
$$Fe_3(CO)_{12} + M-OH- \begin{cases} \longrightarrow (CO_2)_{ads}\ ; \\ \longrightarrow [HFe_3(CO)_{11}]^- M^+\ ; \end{cases}$$

$$3Fe(CO)_5 + M-OH- \begin{cases} \longrightarrow [HFe_3(CO)_{11}]^- M^+\ ; \\ \longrightarrow 3CO + (CO_2)_{ads}\ ; \end{cases}$$

$M=Al^{3+}, Mg^{2+}$.

The rate of reaction of the mononuclear complex with surface hydroxyls is lower than that of the cluster complex. The addition of HCl to the product leads to the regeneration of $Fe_3(CO)_{12}$ according to the authors' data.[11]

On the basis of EXAFS, infrared, and ultraviolet spectroscopic and thermal desorption data, Iwasawa et al.[13] arrived at conclusions differing somewhat from those of Brenner and Hucul[10] and Hugues et al.[11] They showed that a covalently bound $Fe_3$ cluster is formed when $Fe_3(CO)_{12}$ is adsorbed on the surface of $Al_2O_3$ at 40 °C:




$Fe_3(CO)_{12}$ does not interact with an $SiO_2$ surface.[13]

The anionic complex $[Fe_3(CO)_{11}H]^-$ is more stable on an $Al_2O_3$ surface than its covalently bound analogue, which is readily oxidised by atmospheric oxygen even at room temperature.[13] Presumably both structures considered may be formed on $Al_2O_3$ and the predominance of one of them depends on the acid–base properties of the carrier and the concentration of the surface OH groups.

This hypothesis has been to a large extent confirmed by the results of the study of the heterogenisation of $Fe_3(CO)_{12}$ on magnesium oxide dehydrated under mild and severe conditions.[12] The liberation of hydrogen and the appearance of $Fe^{2+}$ are characteristic of a carrier with a high concentration of OH groups on heating to a temperature above 80 °C. At 110 °C the cluster decomposes fully. The complex is fully decarbonylated without evolution of $H_2$ on the surface of MgO dehydrated at a high temperature, and zerovalent iron is oxidised to $Fe^{2+}$. It is assumed[12] that the $[HFe_3.(CO)_{11}]^-$ ions and possibly the compound $Fe(CO)_4(CO_2Mg)$ are formed on the surface with a low concentration of OH groups.

All three iron carbonyls have been heterogenised on the NaY and HY zeolites in order to synthesise catalysts of the Fischer–Tropsch reaction.[14,15] Behaviour analogous to that described above was then observed: when $Fe_3(CO)_{12}$/HY is heated to 60 °C, $H_2Fe_3(CO)_{11}$ is formed on the surface and decomposes on further increase of temperature to 200 °C giving rise to $Fe^{2+}$ ions attached to the zeolite.

The stabilisation of the metal in a low oxidation state has been observed on the NaY zeolite.[16]

The mononuclear carbonyl $Fe(CO)_5$ adsorbed on the HY zeolite is converted into cluster structures on heating:[15]

$$|\text{—OH} + Fe(CO)_5 \xrightarrow{25°C} [Fe(CO)_5]_{ads} + CO +$$

$$+ [|\text{—O}\cdots Fe(CO)_4] \underset{25°C,+CO}{\overset{60°C,-CO}{\rightleftharpoons}} [(|\text{—OH})_3\cdots F_3(CO)_{12}]\ ;$$

|—OH= zeolite HY.

Unfortunately specimens obtained to date by the interaction of iron carbonyls with zeolites are inferior as regards the selectivity of the formation of olefins in the Fischer–Tropsch reaction to the analogous HCC based on $Al_2O_3$.

In a study[17] of the heterogenisation of $Ru_3(CO)_{12}$ on $SiO_2$, it was established by the infrared spectroscopic, thermal desorption (25–170 °C), and radiochemical methods that the physical adsorption is followed by the formation of the subcarbonyl species:

$$|\text{—OH} + Ru_3(CO)_{12} \rightarrow (|\text{—O})_xH_yRu_3(CO)_5\ .$$

The resulting catalyst was active in the isomerisation and hydrogenation of olefins at 353–415 K.

On the other hand, Goodwin and Naccache[18] suggest that, although the cluster–carrier interaction, characterised by the appearance of new absorption bands in the infrared spectrum (2134, 2110, and 2119 $cm^{-1}$), is observed in heterogenisation of $Ru_3(CO)_{12}$ on $Al_2O_3$, $SiO_2$, and NaY, the composition and structure of the initial cluster do not change and hydride complexes are formed. The increase in sensitivity of the heterogenised $Ru_3(CO)_{12}$ to oxygen has been explained[18] by the ease of the oxidation reaction

$$Ru_3(CO)_{12} + 6O_2 \rightarrow Ru_3(O)_6(CO)_6 + 6CO_2$$

on the carrier surface.

In a number of instances a distinct tendency towards the formation on the carrier surface of clusters with a rigorously defined nuclearity, regardless of the nuclearity of the initial complex. Thus, when $Rh_4(CO)_{12}$ was attached to the $SiO_2$ and $Al_2O_3$ surfaces at room temperature,[19] a $Rh_6$ cluster was obtained:

$$3Rh_4(CO)_{12} \rightarrow 2Rh_6(CO)_{16} + 4CO\ .$$

The same cluster is formed on the $Al_2O_3$ surface from $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ when the latter are initially decarbonylated and then again brought into contact with CO.[20]

The high stability of $Rh_6$ structures on the carrier surfaces is indicated by the results of a study by Conrad et al.[21] It has been shown by infrared spectroscopy that $SiO_2$ has no influence on the structure of the cluster and that $Rh_6(CO)_{16}$ may be reversibly decarbonylated on the surface of this carrier.

According to spectroscopic data, the interaction of $Rh_6(CO)_{16}/SiO_2$ with water vapour or hydrogen and the adsorption of CO on metallic rhodium lead to the formation of identical structures on the surface:[22]

$$[Rh_6(CO)_{16}]_{ads} \rightarrow \left[\begin{array}{c} CO\ CO\ CO\ CO\ CO \\ |\ \ \ |\ \ \ |\ \ \ |\ \ \ | \\ -Rh- \quad Rh \quad -Rh- \end{array}\right],$$

When the $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ clusters heterogenised on $Al_2O_3$, $SiO_2$, and MgO are heat-treated, the polynuclear centre decomposes, the $[Rh(CO)_2]$ fragments are formed, and the metal is oxidised:[19,22,23]

$$Rh_6(CO)_{16} + 6X-OH \xrightarrow{100°C} 3\left[\begin{array}{c} (CO)_2\ \ (CO)_2 \\ Rh\ldots Rh \\ \diagdown\ \ \diagup\ \ \diagdown\ \ \diagup \\ O\ \ \ O\ \ \ O \\ |\ \ \ |\ \ \ | \\ X\ \ \ X\ \ \ X \end{array}\right] + 4CO + 3H_2\ ;$$

(A)

X=Al, Mg, Si.

Spectroscopic studies have shown that the metal–metal interaction in the dimer formed is very weak.[19,23]

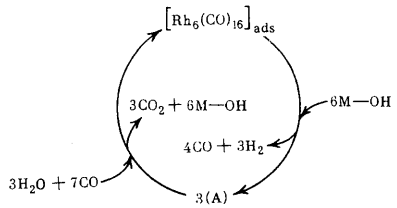
The initial cluster structures can be regenerated by a reductive treatment of the specimens with a mixture of water vapour and CO:[19]

$$2[Rh^I(CO)_2] \rightarrow 2[Rh^0(CO)_n] - \begin{cases} \longrightarrow Rh_x(CO)_y\ ; \\ \longrightarrow Rh_4(CO)_{12} \rightarrow Rh_6(CO)_{16}\ . \end{cases}$$

A highly dispersed metallic phase is formed in the absence of CO.

The regeneration of $Rh_6(CO)_{16}$ on the $Al_2O_3$ surface takes place simultaneously with the regeneration of the hydroxyl coating on the carrier with liberation of $CO_2$.[23]

The extremely high stability of the $Rh_6(CO)_{16}$ cluster makes it possible to set up a closed cycle for the Fischer–Tropsch reaction and the conversion of water vapour:[23]




The same behaviour has been observed for the $Rh_6(CO)_{16}$ cluster heterogenised on the NaY and HY zeolites and for the rhodium clusters immobilised on other mineral carriers.[24] Decarbonylation leads to the fragmentation to rhodium(I) complexes, but the initial structures may be subsequently regenerated.

As already mentioned previously,[12] the character of the interaction of the cluster with the carrier depends significantly on the properties of the surface, which are in many respects determined by the dehydration temperature the infrared spectra of $Rh_4(CO)_{12}$ on lanthanum oxide and $Rh_6(CO)_{16}$ on $\gamma$-$Al_2O_3$ (carriers dehydrated at 600 °C) corresponded to the spectra of the individual clusters.[25–27]

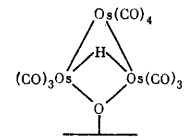
On the other hand, the adsorption of $Rh_6(CO)_{10}$ from solution in chloroform on $Al_2O_3$ dehydrated at a low temperature (200 °C) was accompanied by the partial oxidation of rhodium [the bands of the CO group at 2090 and 2015 $cm^{-1}$, characteristic of $Rh^I(CO)_2$, appeared in the infrared spectrum]. The more reactive $Rh_4(CO)_{12}$ is oxidised even on the carrier dehydrated at 600 °C.

It is essential to bear in mind that the chemical reactivity of the clusters may change on heterogenisation.[20] Thus, $Rh_6(CO)_{16}$, which is stable in air, decomposes partly on the $Al_2O_3$ surface even at room temperature, with evolution of $CO_2$:

$$Rh_6(CO)_{16}/Al_2O_3 + \left(m + n\frac{1}{2}\right)O_2 \rightarrow Rh_6(CO)_{16-n}(O_2)_m/Al_2O_3 + n\,CO_2 \ .$$

On the more inert $SiO_2$ carrier, this type of reaction does not occur.

Much attention has been devoted to the study of the sorption heterogenisation of osmium clusters differing in the nuclearity and nature of the ligands. In the study of the heterogenisation of the osmium clusters $Os_3(CO)_{12}$ and $Os_3(CO)_{10}(MeCN)_2$ on the $SiO_2$ surface at 150° and 25 °C respectively, Besson et al.[28] observed the formation of cluster structures having the composition



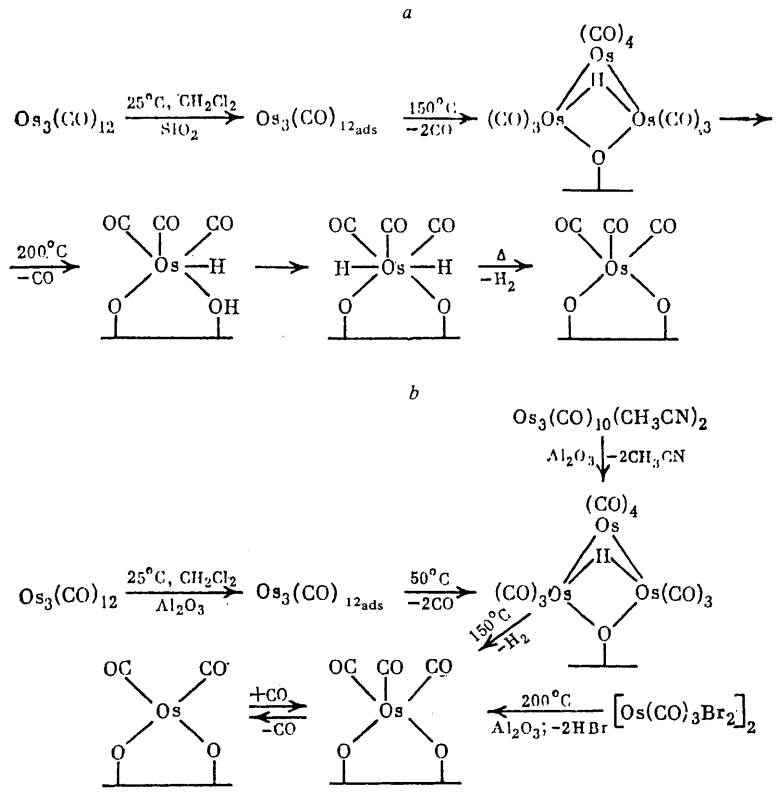
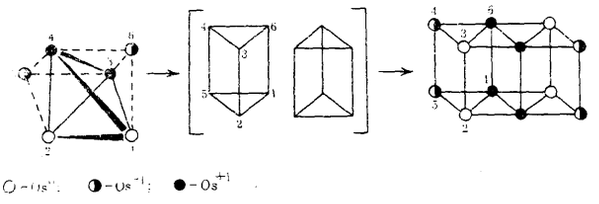




Figure 1. The transformations of the osmium clusters in the course of their heterogenisation on $SiO_2$ and $Al_2O_3$.[29]

The Os–Os distance in the immobilised cluster (2.68 Å) is shorter than in the initial $Os_3(CO)_{12}$ (2.88 Å). Fig. 1 presents the mechanism of the reactions of the osmium clusters heterogenised on $SiO_2$ and $Al_2O_3$ surfaces under the conditions of different types of treatment.[29]

Another rearrangement of the cluster structure has been suggested by Collier et al.,[30] who investigated the heterogenisation of $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ on the $Al_2O_3$, $SiO_2$, and $TiO_2$ surfaces.[30] When $Os_3(CO)_{12}$ is adsorbed, absorption bands at 442 and 595 nm, characteristic of the $Os_6(CO)_{18}$ cluster, are observed in the diffuse reflection spectra. Three bands in the region of the CO group vibrations have been found in the infrared spectra of the osmium complexes on all three carriers investigated. On the other hand, the spectrum of the initial osmium cluster contains 16 absorption bands in this region. It had been suggested earlier[31] that such simplification of the spectrum is associated with the formation of the mononuclear $Os(CO)_2$ and $Os(CO)_3$ complexes. However, it has been possible to demonstrate[30] that the three absorption bands mentioned above correspond to the vibrations of the CO groups bound to osmium atoms which are partly in negative (1950 $cm^{-1}$), partly positive (2120 $cm^{-1}$), and partly zero (2030 $cm^{-1}$) formal oxidation states. It has been shown for vanadium, chromium, manganese, iron, cobalt, and nickel carbonyls that a ±100 $cm^{-1}$ vibration frequency shift is characteristic of a ±1 change in the oxidation state.[32] Bearing in mind the weakly basic character of the carriers employed, the authors[30] suggested the possibility of the dimerisation of the $Os_6(CO)_{18}$ cluster:



○ – $Os^0$; ◑ – $Os^{+1}$; ● – $Os^{+2}$

The differences between the results of different investigations[29–31] can probably be explained by the fact that their authors used carriers differing in the degree of hydroxylation of the surface and in the reactivity of the hydroxy-groups. In addition, the surface concentrations of osmium were likewise not identical. Unfortunately it is not possible to take into account the effect of these factors quantitatively.

The study of the heterogenisation of clusters on the surfaces of mineral carriers has shown that the strength of the complex–carrier bond depends both on the nature of the transition metal atoms forming part of the composition of the cluster [for example, $Co_2Rh_2(CO)_{12}$, $Co_3Rh(CO)_{12}$, $Co_4(CO)_{12}$> $Ir_4(CO)_{12}$ > $Rh_6(CO)_{16}$ > $Ru_3(CO)_{12}$] and on the nature of the carrier (the adsorption on $\gamma$-$Al_2O_3$ is much stronger than on $SiO_2$).[33] It is significant that the adsorption of the molecules of cluster metal carbonyls containing bridging CO groups on $Al_2O_3$ is accompanied by the elimination of these groups. Decarbonylation is promoted by the dissolved oxygen. As a result, a stronger complex–carrier bond arises than might have been expected for adsorption heterogenisation via van der Waals forces.

The transformations of the clusters on the carrier surfaces are extremely complex. Thus, according to infrared spectroscopic data, the structure of the cluster does not change on heterogenisation of $Ru_3(CO)_{12}$ on the surface of $\gamma$-$Al_2O_3$.[34] On the other hand, two anionic complexes are formed on MgO:

$$3Ru_3(CO)_{12} + 2MgO \rightarrow [HRu_3(CO)_{11}]^-/MgO + [Ru_6(CO)_{18}]^{2-}/MgO \ .$$

In this case MgO exhibits "alkaline" properties.[35,36]

The dependence of the adsorption of the $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $Ru_6C(CO)_{17}$ on the $\gamma$-$Al_2O_3$ dehydration temperature has been investigated by infrared spectroscopy.[7] Under the conditions of weak dehydration (at temperatures below 300 °C), the absorption bands of the CO groups of the adsorbed $Ru_3(CO)_{12}$ undergo a bathochromic shift, which indicates the appearance of a negative charge in the cluster skeleton as a result of the interaction with the hydroxy-groups of the carrier:

$$Ru{-}CO + \begin{matrix}\diagdown\\ \\ \diagup\end{matrix}Al{-}OH \rightarrow \begin{matrix}\diagdown\\ \\ \diagup\end{matrix}Al^{\delta+}RuH^{\delta-} + CO_2 \ .$$

Under the conditions of vigorous dehydration (at temperatures above 500 °C), the fraction of adsorbed molecules of the complex varies in parallel with the concentration of the Lewis acid centres of the carrier, indicating an interaction of the type $M{-}C{\equiv}O \rightarrow Al^{3+}$. Similar surface compounds have been recorded by infrared spectroscopy in the adsorption of mononuclear nickel,[37] molybdenum,[38] and tungsten[39] carbonyls on $Al_2O_3$.

The hydride carbonyl clusters $H_4Ru_4(CO)_{12}$ [7] and $H_2Fe_3(CO)_{11}$ [40] also form surface anionic complexes by interacting with the hydroxy-groups on the $Al_2O_3$ surface. Some of them proved to be unstable, being transformed in accordance with the mechanism examined with the simultaneous oxidation of the metal and the evolution of CO and $H_2$.[23,25] The transformations of the clusters on $Al_2O_3$ examined above are characteristic also of other oxide carriers.[6,41,42]

In the examples presented above, the coordinated carbonyl ligand is attacked by surface OH groups. Clusters containing acid hydrogen atoms may be deprotonated. For example, the interaction of $H_4Ru_4(CO)_{12}$ ($pK_a$ = 11.7) with $Al_2O_3$ and MgO [43] results in the formation of the anionic cluster $[H_3Ru_4(CO)_{12}]^-$. However, the above feature is not general. In particular, the nucleophilic attack described above, leading to the anion $[H_3RuOs_3(CO)_{12}]^-$, is observed on heterogenisation of the mixed cluster $[H_2RuOs_3(CO)_{13}]$ on $Al_2O_3$.[44] It is noteworthy that the cluster skeleton of the complex obtained is not decomposed by the synthesis gas even at 200 °C.

Thus examination of the studies on the heterogenisation of the carbonyl clusters on the surfaces of mineral carriers leads to the conclusion that it is difficult to predict the state of the complex on the carrier. The composition and structure of the form stabilised on the surface depend on many factors, among which the following may be distinguished: (1) the nuclearity of a cluster; (2) its chemical nature: (3) the nature of the ligands in the coordination sphere; (4) the chemical nature of the carrier; (5) the density of the hydroxyl coating; (6) the heterogenisation conditions.

In addition, analysis of published studies has shown that, even when all the factors enumerated are virtually identical, results may be obtained which lead to different conclusions (see, for example, Refs. 29–31 and 45 and 46).

## III. CATALYTIC ACTIVITY OF THE ADSORPTION-HETEROGENISED CLUSTER AND POLYNUCLEAR TRANSITION METAL COMPLEXES

A general characteristic of processes involving the participation of carbon monoxide (the Fischer–Tropsch reaction, hydroformylation, and carbonylation) is their relatively high exothermicity, i.e. the equilibrium in these reactions is strongly displaced towards the formation of products at room temperature. Nevertheless, real processes are carried out at elevated temperatures, since the activity of industrial catalysts is insufficient for reactions under mild conditions.

It is also known that the selectivity of these reactions is small. For this reason, the application of heterogenised transition metal clusters, which have a fairly uniform set of active centres and promote the many-electron activation of CO, has aroused interest. However, one should bear in mind that, under the conditions of catalysis, the heterogenised clusters as a rule undergo further transformations and their structure frequently differs from the initial structure.

Before being introduced into the catalytic reaction, the heterogenised clusters are usually activated thermally or chemically. The heat treatment is carried out both *in vacuo* and in an atmosphere of CO or the synthesis gas. We may note that even the rate of heating can influence significantly the degree of dispersion of the particles formed. Thus it has been established[47–49] that, on rapid heating (50 K $min^{-1}$) of $Co_2(CO)_8$ specimens on $TiO_2$, $Al_2O_3$, $ZrO_2$, and $SiO_2$, "superparamagnetic" cobalt species are formed and are characterised by a narrow signal in the ferromagnetic resonance (FR) spectrum. When the temperature is raised slowly, relatively large particles, giving rise to a broad signal in the spectrum, are produced.

Chemical activation usually reduces to the oxidation-reduction treatment of the heterogenised clusters. It has been noted[8] that preliminary oxidation of the carbonyl clusters or their decomposition in a stream of inert gas leads to the formation of more dispersed metal particles on the surface of the carrier than direct reduction with hydrogen.[50,51]

When heterogeneous catalysts are employed, it is essential to take into account the texture of the carrier. The effect of the carrier structure on the selectivity of the Fischer–Tropsch reaction has been noted.[52] The catalyst obtained as a result of the heterogenisation of $Co_2(CO)_8$ on $Al_2O_3$ and decomposed at 200 °C is active in the conversion of the synthesis gas into a mixture of linear $C_2$–$C_{20}$ paraffins ($CO:H_2 = 1:2$; 200 °C; 0.1 MPa). The average molecular weight of the paraffin fraction then depends on the effective radius of the carrier pores $r$: 80% of $C_3$–$C_{10}$ paraffins is formed on a narrow-pore carrier ($r = 65$ Å), whereas 80% of the $C_{14}$–$C_{21}$ paraffins are formed on the specimen with $r = 3000$ Å). It may be that the difference between the selectivities is caused by the different degrees of dispersion of cobalt on the two carriers.

The possibility of regulating the selectivity of the Fischer–Tropsch process by altering the nuclearity and composition of the cluster and also of the nature of the carrier has been examined.[53–58] An important result of these investigations is the direct preparation of ethanol from the synthesis gas under relatively mild conditions, which leads to the prospect for the synthesis of ethylene from coal via a process with a small number of stages. The dependence of the yield of ethanol (per atom of rhodium) on the nature of the cluster (with $La_2O_3$ as the carrier) can be represented by the series $[Rh_4(CO)_{12}] > [Rh_6(CO)_{16}] > [Rh_7(CO)_{16}](NEt_4)_3 > [Rh_{13}.(CO)_{23}H_{2-3}](NBu_4)_2$. The following rules have been established:[55] mainly ethanol is formed at temperatures above 200 °C, while at lower temperatures the product is methanol; highly basic carriers (ZnO and MgO) promote the formation of methanol, while basic carriers with weak acidity ($CeO_2$, $La_2O_3$, $TiO_2$, $ZrO_2$, and $ThO_2$) promote the formation of ethanol; weakly acid oxides ($\gamma$-$Al_2O_3$, $V_2O_5$, $WO_3$, and $Al_2O_3$–$SiO_2$) lead to the preferential formation of methane and higher hydrocarbons; the heterogenisation of the $Rh_2$–$Rh_6$ clusters leads to an increase of the selectivity of the conversion into ethanol, while in the presence of the $Rh_7$–$Rh_{13}$ clusters mainly methane and the $C_2$–$C_4$ hydrocarbons are formed.

The synthesis of methanol from CO and $H_2$ (mixture with the ratio $CO:H_2 = 1:2$) in the presence of catalysts obtained as a result of the adsorption heterogenisation of the platinum cluster $[Pt_{15}(CO)_{30}](NEt_4)_2$ on Group IIA, IIB, IIIA, and IVA metal oxides has been described.[54] The highest selectivity of the conversion into methanol, reaching 98%, has been observed for the catalyst on MgO.

Naturally, the process selectivity is greatly influenced also by the nature of the metal: the rhodium clusters immobilised on lanthanum and zirconium oxides promote the selective formation of ethanol, whereas only methane was obtained in the presence of platinum and iridium complexes under identical conditions.[53]

$Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $Ru_6C(CO)_{17}$, and $RuCl_3$ deposited on $\gamma$-$Al_2O_3$ have been used in the Fischer–Tropsch reaction.[59,60] It has been established that, with increase of the degree of dispersion of the metallic particles, the specific catalytic activity falls and the fraction of light hydrocarbons in the product increases. The authors explain this effect by the strong interaction of the metal with the carrier. It is believed[59,60] that only the centres coordinating one CO molecule are active. The surface subcarbonyl $Ru(CO)_2$ species are stable at the reaction temperature in an atmosphere of hydrogen, which is probably the cause of their catalytic inertness.

In the previous Section it was shown that the nature of the carrier can influence strongly the structure of the product of the heterogenisation of the clusters. It is therefore also not surprising that, when the same cluster complex is deposited on different carriers, active centres of different composition and structure are produced. Thus, when $Ru_3(CO)_{12}$ is heterogenised on $\gamma$-$Al_2O_3$, microcrystalline metallic ruthenium exhibits catalytic activity, which is confirmed by the composition of the products of the Fischer–Tropsch reaction.[34] The anionic complex $[Ru_6C(CO)_{16}]^{2-}$ proved to be responsible for catalysis on MgO. The same complexes were obtained also when $H_4Ru_4(CO)_{12}$ was heterogenised on $Al_2O_3$ and MgO. However, an active catalysis could not be synthesised by adsorbing $K_2[Ru_6C(CO)_{16}]$ on $Al_2O_3$. The authors[34] explained this by the fact that the interaction of $[Ru_6C(CO)_{16}]^{2-}$, formed when the neutral complexes $Ru_3(CO)_{12}$ and $H_4Ru_4(CO)_{12}$ are heterogenised on $Al_2O_3$, differs from the interaction of $K_2[Ru_6C(CO)_{16}]$. We may note that the compositions of the products of the Fischer–Tropsch reaction on $Ru_3(CO)_{12}/MgO$ and $Ru_3(CO)_{12}/Al_2O_3$ differ markedly. The experimental results described show that it is difficult to predict the catalytic properties of heterogeneous cluster catalysts.

Together with the cluster complexes of noble metals, catalytic activity in the Fischer–Tropsch reaction is shown also, as already mentioned above, by the cluster and polynuclear complexes of other Group VIII metals immobilised by adsorption on the surfaces of mineral carriers, for example by $Fe_3(CO)_{12}$ on a type HY or NaY zeolite.[56] The activity of this catalysis is relatively low: liquid hydrocarbons are formed only at 250 °C and 2 MPa (the degree of conversion is 85% after 15 h). The catalysts based on the dinuclear cobalt complex $Co_2(CO)_8$ immobilised on mineral carriers of different nature was active in the conversion of the synthesis gas into a mixture of liquid hydrocarbons only after reduction in a stream of hydrogen at 150 °C.[57,58] n-Alkanes are formed preferentially on the least active carrier, while isoparaffins are formed on strongly acid carriers. Although hydrocarbons ranging from $C_5$ to $C_{22}$ were detected in the mixture, the bulk of the latter consisted of $C_9$–$C_{13}$ paraffins. In analysing the results of this study,[57,58] one cannot rule out the possibility of structural isomerisation of hydrocarbons on a strongly acid carrier.

It is noteworthy that metallic catalysis obtained on the basis of heterogenised iron clusters are active in the hydrogenation of olefins.[61]

Linear hydrocarbons are mainly formed in the hydrogenation of CO on cobalt catalysis prepared by the thermal decomposition of $Co_2(CO)_8$,[62,63] the distribution of their molecular weights obeying the Schultz–Flory equation.[64] The catalysts obtained by the rapid decomposition of the deposited metal carbonyl are 2–10 times more active than the traditional cobalt catalysts.

The same rules hold for the heterogenised cobalt catalytic systems[65] as for the ruthenium systems:[59,60] an increase in the degree of dispersion of the metallic particles lowers the specific catalytic activity: with increase of the metallic particle size, the relative yield of higher hydrocarbons rises, the maximum yield being obtained using $TiO_2$ and $ZrO_2$ as the carriers.[63,66] The $Co_2(CO)_8$ clusters deposited on $SiO_2$ and $TiO_2$ showed the maximum activity.[65]

Pyrolysis of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ on the $\gamma$-$Al_2O_3$ surface yielded selective catalysts of the synthesis of light olefins.[67] However, in the course of the reaction the finely dispersed metallic particles increases in size and methane became the main product. By using the salt-like heteroatomic cluster $(NEt_4[[Fe_2Mn(CO)_{12}]$ as the initial complex, it is possible to increase the stability of the action of the catalyst and to reduce the yield of methane.[69] An attempt to synthesise an active and stable catalyst from the cobalt carbonyl and manganese compounds taken separately was unsuccessful.

In conclusion of this Section, we shall consider the catalytic properties of heterogeneous clusters in the hydroformylation and hydrogenation of olefins and in the dehydrocyclisation of alkanes and the hydrogenation of benzene. Ichikawa[70,71] hydroformylated ethylene and propene on $Co_4(CO)_{12}$/ZnO. Although this catalyst showed a lower activity than the rhodium and rhodium-cobalt clusters, the selectivity of the formation of the linear aldehyde proved to be higher.

The study of the dehydrocyclisation and the structural isomerisation of n-hexane on platinum clusters[72–75] showed that the reaction pathway depends on the number of transition metal atoms in the heterogenised complexes (Table 1). The complexes were deposited on $Al_2O_3$ and $SiO_2$ from solution in tetrahydrofuran. Stoichiometric amounts of CO and triethylamine were evolved on heat treatment of the heterogenised complexes *in vacuo*, in helium, or in hydrogen at 150 to 170 °C and platinum clusters, whose particle size did not exceed 1 nm, were immobilised on the carrier surface.

Table 1. The conversion of n-hexane on heterogenised platinum clusters.[75]

| Cluster | c**, wt.% | T, °C | Reaction products, mole % | | | |
|---|---|---|---|---|---|---|
| | | | 2-methylpentane | 3-methylpentane | methylcyclopentane | cyclohexane + $C_6H_6$ |
| $[Pt_{15}(CO)_{30}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.69 | 295 | 17.2 | 8.2 | 61.7 | 12.9 |
| $[Pt_{15}(CO)_{30}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.69 | 320 | 15.6 | 6.4 | 65.7 | 12.3 |
| $[Pt_{15}(CO)_{30}][NEt_4]_2/SiO_2$ | 0.15 | 320 | 21.4 | 12.5 | 58.5 | 7.6 |
| $[Pt_{12}(CO)_{24}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.54 | 275 | 1.25 | 6.8 | 64.1 | 13.9 |
| $[Pt_9(CO)_{18}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.26 | 320 | 9.6 | 6.4 | 72.8 | 11.2 |
| $[Pt_9(CO)_{18}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.50 | 320 | 11.4 | 5.2 | 74.4 | 9.0 |
| $[Pt_6(CO)_{12}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.18 | 320 | 5.4 | 3.7 | 83.6 | 7.3 |
| $[Pt_6(CO)_{12}][NEt_4]_2/\gamma$-$Al_2O_3$ | 0.25 | 325 | 5.2 | 2.6 | 87.0 | 5.2 |
| $[Pt_3(CO)_3(PPh_3)_4]/\gamma$-$Al_2O_3$ | 0.45 | 325 | 3.7 | 1.7 | 92.6 | 2.0 |

*After the heterogenisation of the complexes, the specimens were heat-treated at 350 °C (the last row—at 250 °C) in a stream of hydrogen for 5 h.
**The content of metallic platinum.

It follows from Table 1 that the last catalyst is characterised by a high selectivity in the dehydrocyclisation reaction. It may be that structural correspondence, as defined by Balandin, is manifested in this case and that the multiplet made up of three platinum atoms is the most suitable for this reaction.

An anlogous dependence of the selectivity of the reaction on the number of platinum atoms in the heterogenised cluster has been observed in antoher study by Ichikawa.[76] It was found that the catalysts based on the $Pt_{15}$ and $Pt_{12}$ clusters are active both in structural isomerisation and in hydrogenolysis of neopentane, while the $Pt_6$ and $Pt_5$ clusters lead mainly to hydrogenolysis products.

The influence of the nuclearity of the clusters on the activity and selectivity has also been demonstrated.[77] The complexes $Cp_2Ni$, $Cp_2Ni_2(CO)_2$, and $Cp_3Ni_3(CO)_2$ deposited on the silica gel surface from solution in THF showed different catalytic activities after heterogenisation on the carrier and heat treatment *in vacuo* or hydrogen at 120 °C. Thus it was found that acetylene was readily converted into benzene at room temperature (degree of conversion 75% after 2 h) on the nickel catalyst obtained from $Cp_2Ni$, whereas the cluster catalyst proved to be inactive. Under the same conditions, acetylene was firmly adsorbed on the latter (1 mole of $C_2H_2$ per mole of $Ni_3$ or $Ni_2$). On the other hand, the ethylene and benzene hydrogenation reactions, dueterium–hydrogen exchange, and hydroformylation of ethylene occurred only on the cluster catalyst.

## IV. HETEROGENISATION OF POLYNUCLEAR π-ALLYL COMPLEXES

The π-allyl complexes of transition metals are significantly less stable than the carbonyl complexes. Despite the difficulties arising from this fact, the heterogenisation of the π-allyl complexes has been quite widely investigated.[2]

This Section presents the results of the latest studies on the heterogenisation of polynuclear π-allyl complexes and the catalysts based on them.

Detailed studies have been made[78–83] of the heterogenisation of mono- and di-nuclear π-allyl complexes of molybdenum and chromium, which are of a similar chemical nature. The authors endeavoured to elucidate the following questions:

(1) is the structure of the dinuclear centre preserved on heterogenisation; (2) are there differences between the activities of the catalysts obtained by the heterogenisation of the mono- and di-nuclear complexes; (3) does the nature of the mineral matrix influence the character of the immobilisation. The authors established that the Mo–Mo distance in the complex $Mo_2(\pi\text{-allyl})_4$, which amounts to 2.183 Å, increases to 3.1–3.2 Å after heterogenisation. The bond between the molybdenum atoms in this structure is preserved, which has been confirmed by the study of the catalysts using the atomic radial distribution method. The average distance between the $Mo_2...Mo_2$ pairs in $Al_2O_3$ with a surface concentration of hydroxy-groups of 2.6 $nm^{-2}$ is 23 Å.

Figs. 2 and 3 present schemes for the heterogenisation of $Mo_2(\pi\text{-}C_3H_5)_4$ and $Cr_2(\pi\text{-}C_3H_5)_4$ on five carriers with different specific surfaces and different densities of the hydroxy-groups.

Comparison of the structures obtained by the heterogenisation of mononuclear complexes with the structures derived from their dinuclear analogues shows that the dinuclear molybdenum structures are produced with much more difficulty than the mononuclear structures (Fig. 4). Furthermore, whereas the reduction reaction proceeds in accordance with the scheme $Mo^{6+} \rightarrow Mo^{4+} \rightarrow Mo^{2+}$ for the mononuclear centre, in the case of the dinuclear centre it is possible to detect also the 5+ oxidation state. The $Mo^{3+}$ state was not observed in either case.[83] The variation of the stability of the surface dinuclear structures on $SiO_2$ with the surface

concentration of the immobilised complexes has also been noted: with increase of the concentration, the stability of the structures falls.[83]

The catalytic activities of the immobilised di- and mononuclear complexes differ appreciably. Thus in the oxidative dehydrogenation of ethanol the activity of the mononuclear catalyst is proportional to the concentration of the $Mo^{6+}$ centres, while that of the dinuclear catalyst is proportional to the number of $Mo^{6+}$ pairs (Fig.5). This makes it possible to speak of the cooperative effect of the $Mo^{6+}$ pairs in the catalyst obtained as a result of the immobilisation of the dinuclear π-allyl complex of molybdenum; in other words, this result agrees with Balandin's hypothesis that the dehydrogenation reaction proceeds via a doublet mechanism.

The catalytic properties of the mononuclear and dinuclear molybdenym complexes in a low oxidation state ($Mo^{2+}$) in the hydrogenation of butadiene also proved to be different[83] (Fig.6). Thus, in the presence of the catalyst obtained by the heterogenisation of the mononuclear cluster $Mo(\pi\text{-}C_3H_5)_4$, buta-1,3-diene is mainly converted into a mixture of *cis*- and *trans*-but-2-enes, while in the case of the dinuclear complex but-1-ene is formed in 60% yield. The hydrogenating activity of the dinuclear centre at 0 °C is 5 times greater than that of the mononuclear centre and 3280 times greater than the activity of the traditional impregnated catalyst.

By altering the nuclearity of the active centre and the oxidation state of the transition metal atom forming part of the composition of this centre, it is sometimes possible to

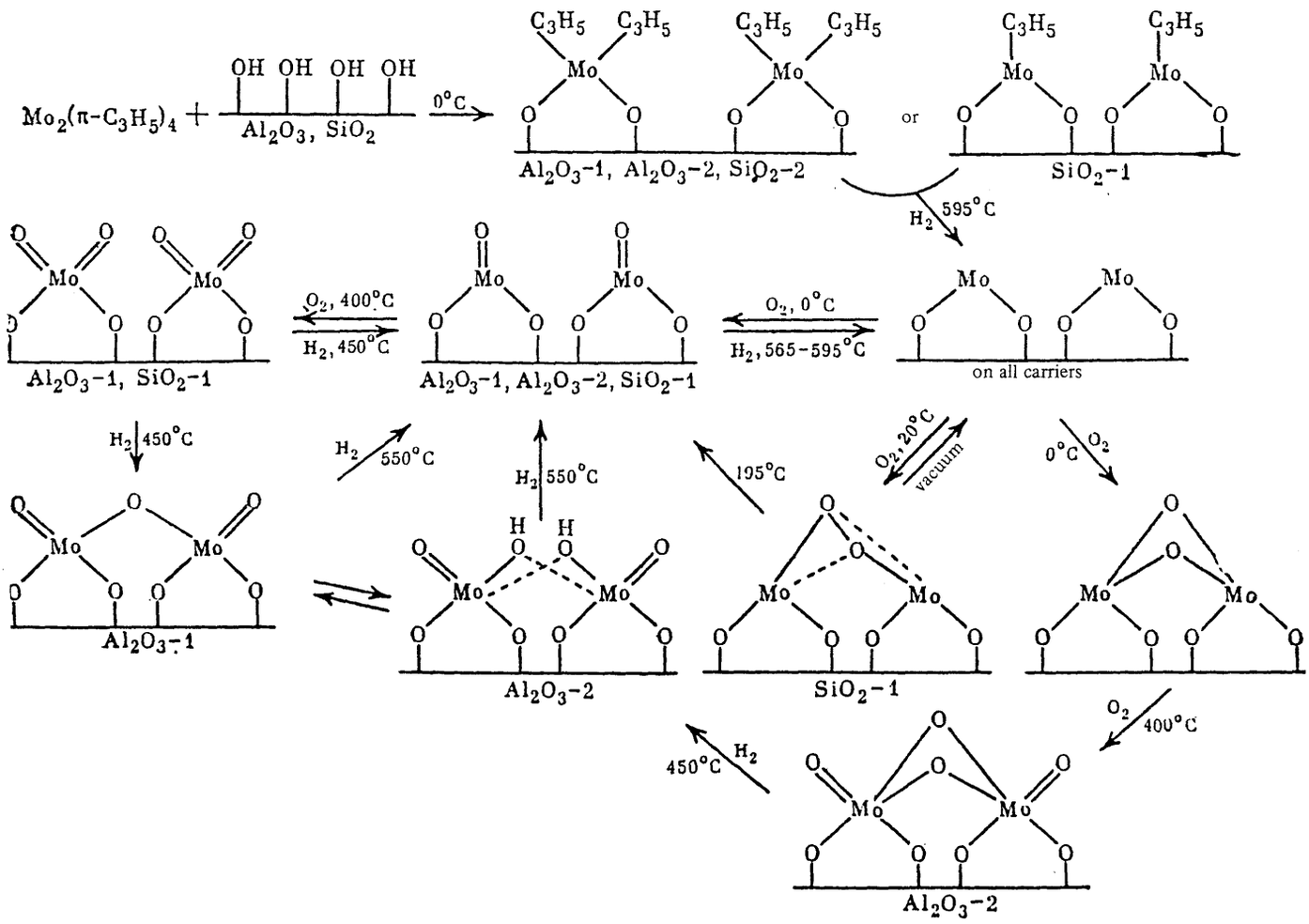
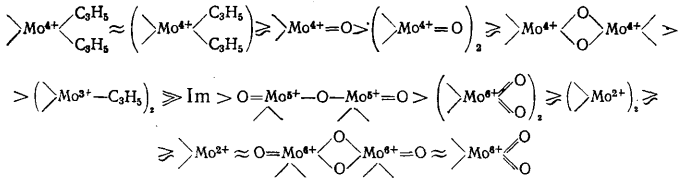
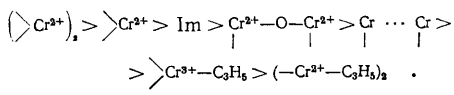



Figure 2. The structures of the surface centres formed as a result of the oxidation-reduction reactions of the dinuclear complex $Mo_2(\pi\text{-}C_3H_5)_4$ heterogenised on carriers of different nature. Carriers: $Al_2O_3$-1 (190 $m^2\ g^{-1}$, 2.6 OH group $nm^{-2}$); $Al_2O_3$-2 (385 $m^2\ g^{-1}$, 4.5 OH group $nm^{-2}$); $SiO_2$-1 (120 $m^2\ g^{-1}$, 3.5 OH group $nm^{-2}$); $SiO_2$-2 (285 $m^2\ g^{-1}$, 4.6 OH group $nm^{-2}$); $SiO_2$-3 (510 $m^2\ g^{-1}$, 1.3 OH group $nm^{-2}$).[78]

discover the structure of the centre which is optimal for the reaction of the given type. This problem has been solved[83] for the disproportionation of propene. The activities of different surface centres, illustrated in Fig.2, diminish in the sequence



where Im is the impregnated catalyst. The activities of the immobilised di- and mono-nuclear π-allyl complexes of chromium in the hydrogenation of propene at −35 °C vary in the analogous sequence:[83]



In this case too the dinuclear centre is more active than the mononuclear centre. This may be explained by the fact that the doublet (as defined by Balandin) is preferable for the hydrogenation reaction.

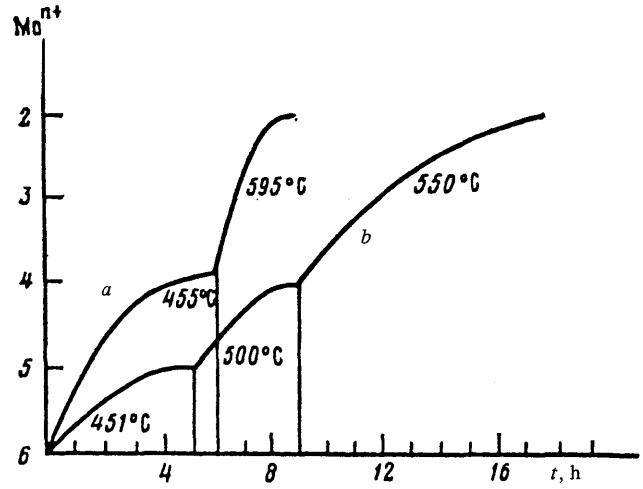



**Figure 4.** Kinetics of the reduction with hydrogen of immobilised mononuclear (*a*) and dinuclear (*b*) π-allyl complexes of molybdenum ($p_{H_2}$ = 64 mmHg).[83]

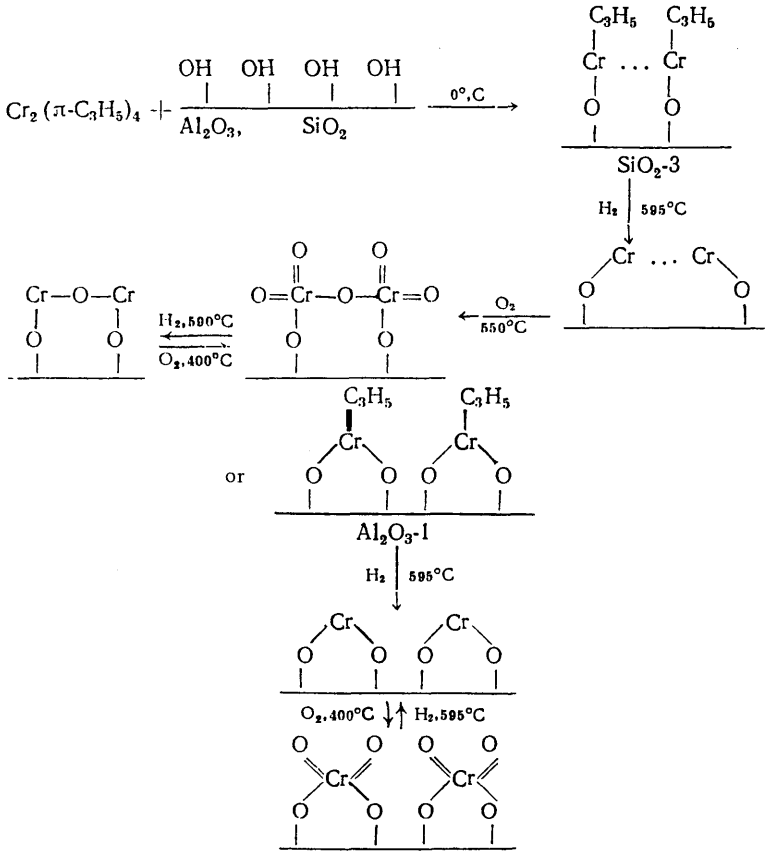



**Figure 3.** The structures of the surface centres formed as a result of the oxidation-reduction reactions of the dinuclear complex $Cr_2(\pi\text{-}C_3H_5)_4$ heterogenised on carriers of different nature; carriers—see the legend to Fig.2.[78]

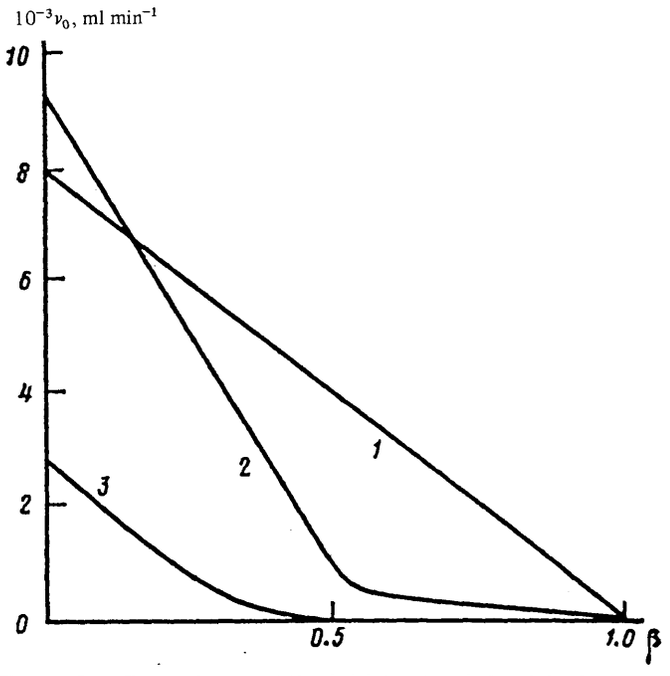



Figure 5. Dependence of the initial rate of the dehydrogenation reaction of ethanol ($v_0$) on the relative content of $Mo^{6+}$ ions ($\beta$) in the oxidised specimens of the immobilised $Mo(\pi\text{-}C_3H_5)_4$ (line *1*) and $Mo_2(\pi\text{-}C_3H_5)_4$ (line *2*) complexes; (*3*) impregnated catalyst based on $(NH_4)_2MoO_4$ ($7.85 \times 10^{18}$ Mo atoms, 148 °C).[83]

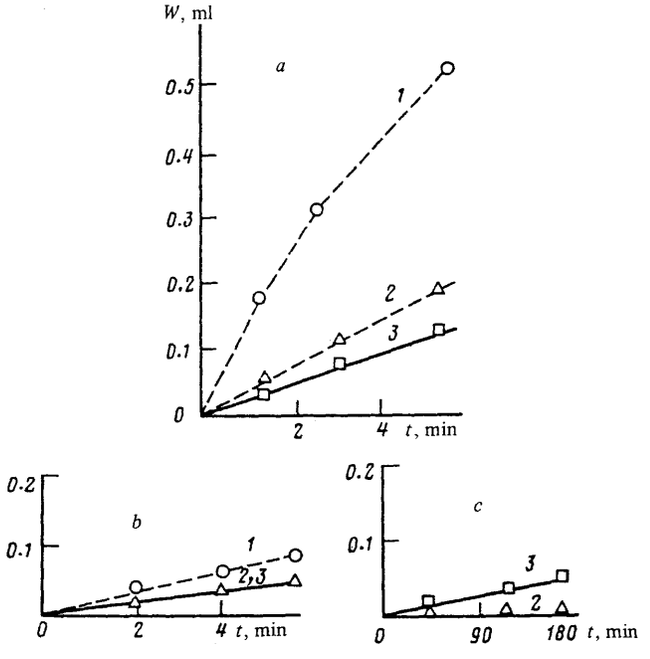



Figure 6. Hydrogenation of buta-1,3-diene on $Mo_2/Al_2O_3$ (*a*), $Mo/Al_2O_3$ (*b*), and the impregnated catalyst based on $(NH_4)_2$. $.MoO_4$ (*c*); molybdenum content (atoms): *a*) and *b*) $5.37 \times 10^{18}$; *c*) $3.16 \times 10^{19}$; 1) but-1-ene; 2) *trans*-but-2-ene; 3) *cis*-but-2-ene ($p_{C_4H_8} : p_{H_2} = 2:1$; 0 °C).[83]

An even greater difference has been obtained in the study of the catalytic activities of the mono- and di-nuclear centres based on the allyl complexes of molybdenum immobilised on the surfaces of aluminium and silicon oxides in the hydrogenation of ethylene (Fig.7).[83] It is of interest that, whereas no differences between the activities of the mono- and di-nuclear centres were observed on $Al_2O_3$, on $SiO_2$ only the immobilised dinuclear complexes were activie. The influence of the nature of the carrier is difficult to explain in this instance. The possible causes are the conversion of the dinuclear complexes into the monomeric form on the surface of $Al_2O_3$ and the lack of a difference between the structures of the mono- and di-nuclear centres. The significantly higher activity of the catalyst based on $Al_2O_3$ is also noteworthy.

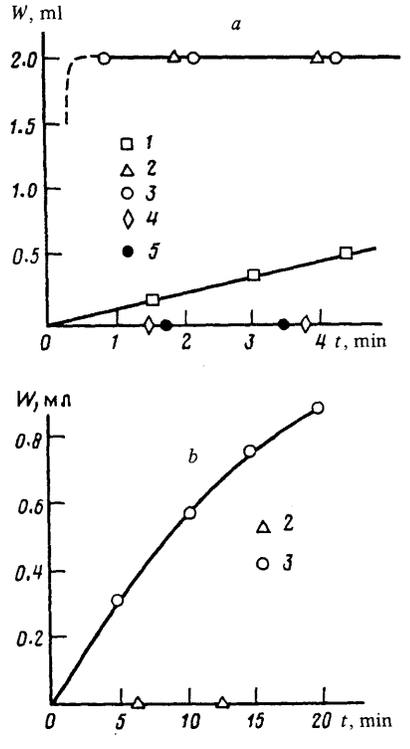



Figure 7. The influence of the structure of the surface centres formed in the oxidation-reduction treatment of the complexes $Mo(\pi\text{-}C_3H_5)_4$ and $Mo_2(\pi\text{-}C_3H_5)_4$, immobilised on $Al_2O_3$ and $SiO_2$, on the yield of ethane in the ethylene hydrogenation reaction ($p_{H_2} = 48$ mmHg; $p_{C_2H_4} = 12$ mmHg). Reaction conditions: *a*) for $TMC/Al_2O_3$, temperature 73 °C, sample size 0.1 g; *b*) for $TMC/SiO_2$, temperature 20 °C, sample size 0.28 g; 1) reduced impregnated catalyst based on $(NH_4)_2MoO_4$; 2) $(|\text{-}O)_2Mo$; 3) $[(|\text{-}O)_2Mo]_2$; 4) $[(|\text{-}O)_2Mo{=}O]_2$; 5) $(|\text{-}O)_2Mo{=}O$.[83]

Thus the nuclearity and the skeleton of the immobilised centre can be frequently preserved in the heterogenisation of transition metal complexes on mineral carriers. However, this does not guarantee that the immobilised structures remain unchanged under these conditions of the catalytic reaction. Unfortunately, very little attention has been devoted to this question in the literature.

## V. THE "ASSEMBLY" OF CLUSTER CENTRES ON THE SURFACES OF CARRIERS

All the methods of synthesis of cluster and polynuclear heterogeneous catalysts described above are based on the same procedure for the immobilisation of the complex obtained beforehand and containing several metal atoms. However, catalysts containing centres with a higher nuclearity can be synthesised also in a different way—from mononuclear complexes, i.e. by "assembling" the cluster or polynuclear active centres directly on the carrier surface.

Two main trends in the application of this method of synthesis of heterogeneous metal complex catalysts have come to be most widely used at the present time. The first may be referred to as the method of statistical assembly and the second the method of programmed assembly on the surface. The first method consists in the preliminary immobilisation on the carrier surface of mononuclear centres which can be converted by further chemical treatment into polynuclear formations stable under given conditions. Naturally, when this method is employed, the structure of the active centre is unknown and the species formed are non-uniform as regards size. This is caused by the statistical nature of the process involving the formation of the structure of the centres and the energetic and geometrical non-uniformity of the carrier surface.

The method of programmed assembly on the surface involves a series of consecutive chemical reactions leading to an increase in the complexity of the structures of the immobilised mononuclear complexes. In this case the degree of uncertainty in the structures of the centres formed on the surface is diminished but the element of uncertainty persists, because the number of different types of centre which may be superimposed on the surface is equal to the number of stages of the reaction occurring on the surface.

Examples of the employment of these two varieties of the surface assembly methods for the synthesis of polynuclear, cluster, and highly dispersed metallic catalysts are presented below. We may note that it is difficult to draw a clear-cut boundary between these types of catalysts, at any rate so long as the particle size does not exceed 30–50 Å.

### 1. Statistical Assembly

The statistical method of surface assembly of highly dispersed metallic catalysts consists in the preliminary immobilisation on the carrier surface of mononuclear complexes (for example, π-allyl complexes) which are reduced with hydrogen at elevated temperatures:

$$\left|\!-\mathrm{OH}\xrightarrow[-\mathrm{HL}]{\mathrm{ML}_n}\left|\!-\mathrm{OML}_{n-1}\xrightarrow{\mathrm{H_2}}\right.\right.\text{microcrystallites of the dispersed metal on the carrier surface.}$$

This method of synthesis of the highly dispersed catalyst as a result of the preliminary heterogenisation of π-allyl complexes of transition metals on $SiO_2$ and $Al_2O_3$ has been developed and studied in detail at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences.[2]

After the reduction of the immobilised π-allyl complexes of nickel, palladium, and platinum, it was suggested that the atomically dispersed metallic phase be produced on the surface. However, the low energy of the migration of atoms on the carrier surface (12.6 kJ $mol^{-1}$), which, amounts to half the energy of the interaction with the surface according to Anderson,[84] prevents the aggregation of metal atoms. The stabilisation of the highly dispersed state is achieved as a result of the preliminary immobilisation of Group VI metal ions in low oxidation states on the surface.[85,86] These atoms serve as "energy traps" and prevent the migration and the increase in the size of the surface particles as a result of the high energy of the $M^{VIII}$–$M^{VI}$ bond. It has been noted[87] that the increase in the interaction energy to 84 kJ $mol^{-1}$ increases the probability of the localisation of the surface atoms by a factor of $10^4$. The metal–metal bond energies in different complexes have been published;[88] these data make it possible to limit the range of atoms whose hydrogenation would promote the stabilisation of the state of the catalytic active centres based on noble and certain transition metals corresponding to the maximum degree of dispersion.

A method has been developed[89,90] for the preparation of highly dispersed palladium and platinum catalysts stabilised by the doubly charged molybdenum and tungsten ions previously immobilised:

$$2\left(\left|\!-\mathrm{OH}\right.\right)+\mathrm{MR_4}\rightarrow\left(\left|\!-\mathrm{O}\right.\right)_2\mathrm{MR_2}\xrightarrow[\mathrm{H_2}]{500\text{–}600^\circ\mathrm{C}}\left(\left|\!-\mathrm{O}\right.\right)_2\mathrm{M}\rightarrow$$

$$\rightarrow\xrightarrow{1)\ \mathrm{PtR_2};\ 2)\ \mathrm{H_2}}\begin{cases}\longrightarrow \underline{\mathrm{M}_x\mathrm{Pt}_n}\ (\mathrm{I})\ ;\\ \longrightarrow \left|\!\begin{matrix}-\mathrm{O}\\-\mathrm{O}\end{matrix}\right.\!\!>\mathrm{M}\!-\!\mathrm{Pt}_n\ (\mathrm{II})\ ;\end{cases}$$

$$\mathrm{R}=\pi\text{-}\mathrm{C_3H_5};\ \mathrm{M}=\mathrm{Mo},\ \mathrm{W}.$$

So far it is difficult to state that one of the proposed structures is preferable.[91]

The catalysts obtained by this method had a series of unusual properties compared with the unmodified molybdenum and tungsten catalysts: (1) a high thermodynamic stability of surface centres over a wide temperature range, which is characterised by the constancy of the ratio O : Pt = 1 (at 300–700 °C) in the chemisorption of oxygen; (2) a higher activity in benzene hydrogenation (by a factor of 2–5) and ethane hydrogenolysis (by a factor of $10^4$) reactions (Table 2); (3) a higher stability of the catalytic activity; (4) a change in the kinetic parameters of the hydrogenolysis of ethane (the activation energy is reduced and the order of the reaction with respect to hydrogen is altered).

**Table 2.** The activity of platinum catalysts in the hydrogenation of benzene (25 °C; $H_2 : C_6H_6 = 8 : 1$; 0.53 MPa).[91]

| Catalyst | $c$, wt.% | $T_r$, °C | $a$, mol $g^{-2}$ | $b$, $s^{-1}$ |
|---|---|---|---|---|
| $Pt/SiO_2$ | 3.5% Pt | 500 | 0.21 | 18 |
| $Pt/SiO_2$ | 3.1% Pt | 700 | 0.18 | 20 |
| $(Mo\div Pt)/SiO_2$ | 1.5% Mo; 4.4% Pt | 500 | 1.20 | 64 |
| $(Mo\div Pt)/SiO_2$ | 1.5% Mo; 4.4% Pt | 500* | 2.00 | 110 |
| $(W\div Pt)/SiO_2$ | 4% W; 2.9% Pt | 700 | 0.80 | 46 |
| $(W\div Pt)/SiO_2$ | 6% W; 3.0% Pt | 700 | 1.25 | 67 |

Notation: $c$ is the content of surface elements, $T_r$ the reduction temperature, $a$ the amount of benzene which has reacted per gram of platinum in 1 h, $b$ the amount of benzene (in moles) which has reacted per mole of the surface platinum atoms in 1 s (the turnover number).

*The catalyst was oxidised before reduction.

The study of platinum catalysts by X-ray photoelectron spectroscopy showed that the presence of a Group VI metal ion with a low charge leads to a redistribution of electron density and the appearance of an electron deficiency at the platinum atom. This entails an increase of the binding energy of the $4f_{7/2}$ level, which can be explained, according to the authors,[87] by the transfer of electrons to the oxygen atoms of the mineral matrix, the molybdenum and tungsten

ions with a low charge playing the role of a bridge. If this interpretation is correct, the active centre should have the structure (II) (see Scheme).

## 2. Programmed Assembly

A novel version of the method of the programmed surface assembly has been developed by Semikolenov and co-workers.[92,93] Its essential feature consists in the controllable growth of the catalytic centre, which is immobilised on $SiO_2$ by means of a chemically modified chelating ligand:

$$\equiv Si\begin{matrix}CH_2CH_2CH_2PPh_2\\ CH_2CH(CH_3)CH_2PPh_2\end{matrix}\ \left(\equiv Si-P_2\right):$$

$$\equiv Si-P_2 \xrightarrow[(a)]{Pd(OAc)_2} \equiv Si-P_2Pd(OAc)_2 \xrightarrow[(b)]{HCOOH}$$

$$\rightarrow \equiv Si-P_2Pd(OCOH)_2 \xrightarrow[-CO_2,-CO,-H_2O;(c)]{Pd(OAc)_2} \equiv Si-P_2Pd_2(OAc)_2 \xrightarrow[(b)]{HCOOH}$$

$$\rightarrow \equiv Si-P_2Pd_2(OCOH)_2 \xrightarrow[-CO_2,-CO,-H_2O;(c)]{Pd(OAc)_2} \equiv Si-P_2Pd_3(OAc)_2 \text{ etc.}$$

According to the authors' data, by alternating stages (*b*) and (*c*) several (*n*) times, it is possible to obtain a cluster containing $n + 1$ palladium atoms. In order to regulate the stoichiometry of the interaction and the degree of reduction of the $Pd^{2+}$ ions, the process leading to the assembly of the surface cluster was carried out in the presence of a ligand (the formate ion), which possessed, apart from reducing properties, also the ability to immobilise beforehand a new metal ion on the complex already immobilised, as a result of the formation of bridge bonds.

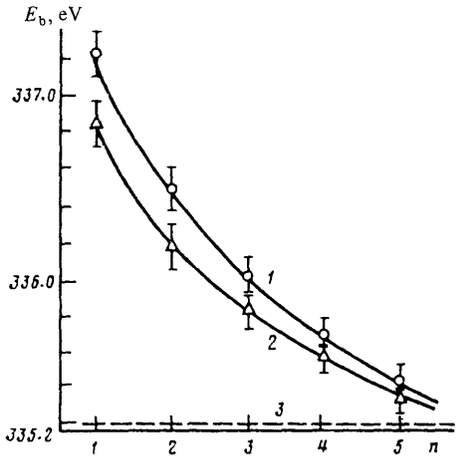



**Figure 8.** Dependence of the binding energy of the electrons of the Pd atom in the $3d_{5/2}$ level on the number of Pd atoms in the cluster: 1) initial $\equiv P_2Pd_n(OCHQ)_2$ specimens; 2) the same specimens heated *in vacuo* at 110 °C for 1 h; 3) metallic palladium foil.[92]

The successive formation of surface polynuclear structures with a nuclearity varying from 2 to 5 is demonstrated by the parallel decrease of the binding energy of the electrons in the $3d_{5/2}$ level and the increase of the number of palladium atoms immobilised on the surface of the matrix (Fig. 8).

We may note that the binding energy of the electrons in the $3d_{5/2}$ level for a pentanuclear cluster is very close to the binding energy of the electrons in the same level for the compact metal.

The catalytic properties of the cluster palladium catalysts with $1 \leq n \leq 5$ have been investigated in the cyclopentadiene hydrogenation reaction and in Zelinskii's irreversible catalytic reaction. The dependence of the catalytic activity on *n* has been demonstrated. Specimens with $n = 1$ or 2 did not exhibit activity in the disproportionation of cyclohexene. It is extremely probably that the surface of these catalysts contains no palladium microcrystals, because it is known that palladium on $SiO_2$ is an active catalyst in this reaction. For $n = 3-5$, cyclohexene is converted into cyclohexane and benzene with a high yield (Fig. 9). In the cyclopentadienes hydrogenation reaction the catalysts containing monatomic centres were inactive.

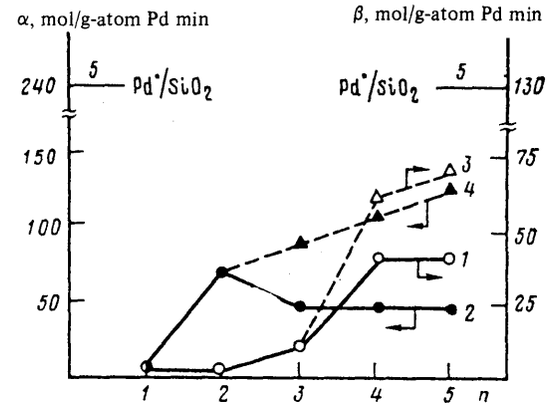



**Figure 9.** The influence of the nuclearities *n* of the palladium clusters on their catalytic properties: 1) disproportionation of cyclohexene (β); 2) hydrogenation of cyclopentadiene (α); 3) and 4) calculated dependences of the catalytic activity in the same reactions respectively plotted on the assumption that the active centres for the disproportionation and hydrogenation reactions are the $Pd_3$ and $Pd_2$ fragments respectively; 5) the level of activity of the impregnated $Pd/SiO_2$ catalyst in the same reactions.[93]

The results of the above studies[92,93] enabled the authors to conclude that the reactions considered proceed only on active centres with a definite structure: the hydrogenation reaction takes place on a diatomic active centre, whereas the cyclohexene disproportionation reaction occurs on a triatomic centre. These conclusions are consistent with the principle of structural correspondence in the multiplet theory of catalysis, to which this composition of the centres for the above reactions corresponds precisely.

Yet another version of the surface assembly method consists of the following operations:[94,95]

$$\equiv OH + SnCl_4 \rightarrow \left(\equiv O\right)_2SnCl_2 \xrightarrow{a\ NaML_n} \left(\equiv O\right)_2SnCl_x(ML_n)_{2-x}$$

$ML_n$=CpCr(CO)$_3$, Cr(CO)$_5$, CpMo(CO)$_3$, CpW(CO)$_3$, CpNi(CO); $x = 0, 1$.

The same approach can be used to synthesise heteroatomic dinuclear complexes:[96]

$$\left(\equiv SiO\right)_2 SnCl_2 \xrightarrow{1)\ Na[M'L_n];\ 2)\ Na[M''L_n]} \left(\equiv SiO\right)_2 \begin{matrix} M'L_n \\ M''L_n \end{matrix}$$

$M'L_n$=CpMo(CO)$_3$; $M''L_n$=CpNi(CO), CpFe(CO)$_2$

The Group IV non-transition element fulfills several functions: (1) it abolishes the non-uniformity of the carrier surface; (2) it serves as an "anchoring microsupport" for the transition metal atom (the fairly high $M^{VIII}$–$M^{IV}$ bond energy, amounting to 220–300 kJ mol$^{-1}$, gives rise to the hope that the atomically disperse metallic phase will be stable even under the conditions of a fairly high surface concentration of the complex); (3) it modifies the properties of the transition metal; (4) it makes it possible to obtain both homonuclear and heteronuclear immobilised active centres of different nuclearity.

It is noteworthy that this version of the surface assembly method also does not allow the preparation of a sufficiently homogeneous set of active centres on the surface. Thus, in the synthesis of heteronuclear dinuclear complexes, homonuclear as well as heteronuclear active centres may be formed on the surface. Furthermore, mononuclear active centres will persist on the surface, particularly at sites to which access is difficult (for example, within the narrow pores of the carriers). All these factors subsequently introduce an ambiguity into the interpretation of the results obtained. Despite these remarks, one should note that the required active centres are mainly formed on the surface, which is indicated by the almost complete identity of the infrared spectra of the heterogenised complexes and their low-molecular-weight analogues.[97]

The possibility of employing an analogous approach to the synthesis of heteronuclear surface complexes with a $M^{VI}$–$M^{VIII}$ bond has been demonstrated:[97]

$$|-OH \xrightarrow[-RH]{RLi} |-OLi \xrightarrow{CoCl_2} |-OCoCl \xrightarrow{Na[Mo(CO)_3Cp]} \rightarrow |-OCoMo(CO)_3Cp\ .$$

A method of synthesis of bimetallic cluster catalysts has been proposed by Ermakov et al.[98] It is based on the idea of the oxidative addition of a zerovalent palladium complex to the Co–Co bond by analogy with the reaction considered in the book of Nesmeyanov and Kocheshkov:[99]

$$Co_2(CO)_8 + M(PPh_3)_2 - (PPh_3)_2M[Co(CO)_4]_2\ .$$

The heterogeneous catalyst was synthesised in accordance with the scheme

$$|-Si-P_3 \xrightarrow[benzene]{Pd_2(DBA)_4} |-Si-P_3Pd^0 \xrightarrow[pentane]{Co_2(CO)_8} |-Si-P_3PdCo_2(CO)_x\ ;$$

DBA = dibenzylideneacetone and, $|-Si-P_3{=}SiO_2)-Si[(CH_2)_3P(C_6H_{11})_2]_3$ .

It was found that the infrared spectrum of the specimen obtained is analogous to the spectrum of the complex ($PPh_2$.$CH_2CH_2PPh_2$)$Pd[Co(CO)_4]_2$.[100] Together with the results of elemental analysis, these data show that the ratios P : Pd : Co = 3 : 1 : 2, and the results of the study of the heterogenised homonuclear palladium complex $Pd_2(DBA)_4$ and $Co_2(CO)_8$ on the analogous phosphinated $SiO_2$ [101,102] enabled the authors to suggest the formation of the heteronuclear complex $|-Si-P_3PdCo_2(CO)_x$, where $x$ = 6–8.

The heteronuclear HMC exhibits an appreciable activity in the hydroformylation of propene even at 40–60 °C, i.e. under conditions where homonuclear HMC are almost inactive. In the course of the reaction the activity of the heteronuclear catalyst fell and the relative yield of the products with the normal structure increased. Thus the introduction of palladium into the composition of the phosphine cobalt carbonyl complex leads to the appearance of a synergistic effect, which is most pronounced at 40–60 °C.

The heterogenisation of the mononuclear iridium complex [Ir(CO)$_2$ (*p*-toluidine) Cl] on polystyrene containing phosphine and diphosphine groups (DIOP) in the presence of zinc leads to the formation of surface clusters.[103–106] Thus the complex containing one phosphine group is formed on polystyrene with phosphine groups in the presence of a low phosphorus content (0.69 wt.%); at higher phosphorus concentrations (1.28 wt.%) the cluster centres linked to the carrier surface via monodentate and chelate bonds are superimposed. On polystyrene containing diphosphine groups, a set of surface compounds is produced. At a low phosphorus concentration in the polymer, $|-DIOP[Ir_4(CO)_{11}]_2$ is formed. With increase in the phosphorus concentration, the diphosphine groups begin to behave as chelating ligands and the surface complexes $|-DIOP[Ir_4(CO)_{10}]$ are produced. All the immobilised cluster structures exhibit a fairly stable activity in the hydrogenation of ethylene and cyclohexene under mild conditions (40 °C, $10^5$ N m$^{-2}$). Thus, under the reaction conditions mentioned above, the turnover number on the catalyst formed after the heat treatment of $|-PPh_2$.$Ir_4(CO)_{11}$ at 80 °C in helium was 5000. Heat treatment at higher temperatures (120 °C) leads to complete decarbonylation, aggregation of the metal, and an appreciable decrease in catalytic activity.[103,104]

The procedure examined above has been used[107] for the assembly of an iridium cluster on the surface of $SiO_2$ modified by phosphine groups. The reaction was carried out under the conditions of the synthesis of a cluster having the composition $[Ir_4(CO)_nPPh_3]$ from the low-molecular-weight complex [Ir(CO)$_2$ (*p*-toluidine) Cl] at 90 °C and a 5 atm CO pressure.[108] The authors suggested that the surface phosphine groups play the role of a monodentate ligand.[107]

After decarbonylation, the tetrairidium cluster heterogenised on $SiO_2$ proved to be active in the hydrogenation of ethylene at 30–90 °C. On the basis of the data obtained by Studer and Schrader,[107] one may postulate that the structure of the cluster breaks down in the course of the preliminary treatment and catalysis, and that the reaction proceeds on metallic microcrystals.

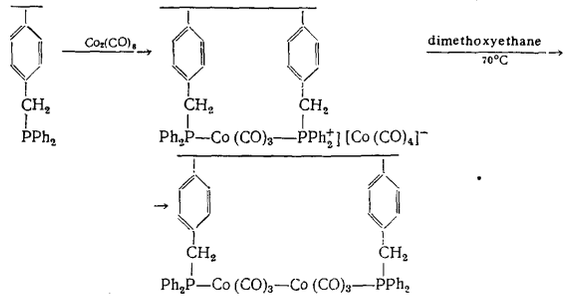
## VI. HETEROGENISATION OF POLYNUCLEAR AND CLUSTER COMPLEXES ON MODIFIED CARRIERS

The application of chemically modified carriers for the heterogenisation of complexes is based on the fact that with their aid it is possible to immobilise complexes on the surface via a chemical reaction specified beforehand, i.e. the use of modified carriers makes it possible to increase the probability of the retention of the initial structure of the transition metal complex. At the same time, chemical modification of the carrier constitutes an additional and frequently fairly laborious stage in the preparation of the catalyst.

### 1. Catalysts on Modified Organic Polymers

The synthesis of a cluster ruthenium catalyst on the surface of the phosphinated styrene–divinylbenzene copolymer, which is active in the hydrogenation of ethylene (52 to 95 °C), has been described.[109]

The heterogeneous metal complex catalyst, active under milder conditions than its homogeneous analogue, has been obtained in accordance with the scheme[110]




The catalyst exhibited a high stability in the hydroformylation reaction: after washing with a solvent, its activity hardly differed from the initial activity. The authors[110] believe that the active centre in this instance is not a dinuclear complex but a mononuclear hydride formed on hydrogenolysis of the Co–Co bond.

The reduction of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ heterogenised on phosphinated polystyrene yielded an active metallic catalyst for the hydrogenation of arenes at room temperature under normal pressure.[111,112] In contrast to the industrial $Rh/Al_2O_3$ catalyst, the rhodium deposited on the polymer is in a more dispersed state. The authors quote data concerning the extraction of rhodium from the catalyst with the aid of CO as evidence in support of this hypothesis. When the polymer catalyst is treated with carbon monoxide, it is possible to regenerate 50% of the rhodium, while the metal is hardly removed from the $Al_2O_3$ surface.[113]

It has been shown[114,115] that the olefin hydrogenation catalyst obtained by the heterogenisation of $Rh_6(CO)_{16}$ on phosphinated polystyrene contains no carbonyl ligands and the surface phosphine groups play the role of polydentate ligands stabilising the small rhodium clusters on the surface. Carbon monoxide poisons the catalyst and in the presence of traces of oxygen the surface phosphine groups are oxidised, which promotes the agglomeration of rhodium;[115] the activity of the catalyst remains stable at 75 h.

The heterogenisation of $Rh_6(CO)_{16}$ on polystyrene containing *NN*-dimethylbenzylaniline groups led to the synthesis of an active catalyst of the reduction of nitrobenzene and the conversion of water vapour.[116] However, it is somewhat less active and more sensitive to oxygen than its homogeneous analogue.

Studies of the heterogenisation of bimetallic clusters on the surface of phosphinated polystyrene established[117,118] that the clusters $[ClAuOs_3(CO)_{10}Ph_2P-|]$ and $[Co_2Pt_2(CO)_8.(Ph_2P-|)_2]$ with an open structure of the "butterfly" type are active in the hydrogenation of ethylene (<100 °C, $1 \times 10^5$ N $m^{-2}$) in contrast to polymers which contain clusters with a closed tetrahedral structure—for example, $[HAuOs_3(CO)_{10}.Ph_2P-|]$ and $[H_2PtOs_3(CO)_{10}(Ph_2P-|)_2]$.[115] This difference is due to the presence in clusters of the first type of coordination-saturated metal atoms. In order to impart catalytic activity to these clusters, it is essential to rupture the metal–metal bond.

The clusters $[RuPt_2(CO)_5(Pt_2P-|)_3]$ and $[Fe_2Pt(CO)_8.(Ph_2P-|)_2]$ immobilised on phosphinated polystyrene are active in the hydrogenation of ethylene (70–100 °C, $1 \times 10^5$ N $m^{-2}$). However, whereas the first complex is stable (turnover number ~4400), the second decomposes with formation of mononuclear complexes and the metallic phase.[118]

## 2. Catalysts on Modified Silicas

Bilhou et al.[119] heterogenised the rhodium cluster $Rh_6(CO)_{16}$ on the surface of phosphinated silica $\equiv Si(CH_2)_2PPh_2$ (grafting density 1.6 groups per $nm^2$) at room temperature and observed that the cluster is decarbonylated, which is characterised by the disappearance of the absorption bands of the carbonyl groups from the infrared spectrum. Treatment of the specimens with carbon monoxide is accompanied by the appearance of the corresponding bands in the infrared spectrum. This finding as well as the similarity of the stretching vibration frequencies for a series of rhodium carbonyl and phosphinerhodium clusters (Table 6) [Table 6 of Bilhou et al.[119]? (Ed. of Translation)] enabled the authors to suggest that the structure and skeleton of the cluster are retained after its heterogenisation on the mineral carrier.

The partly decarbonylated $Rh_6$ clusters exhibit a low activity in the benzene hydrogenation reaction at room temperature (25 °C). It has also been noted that phosphine-containing clusters, with the exception of that heterogenised on $SiO_2$, exhibit a higher (up to 150 °C) thermal stability than purely carbonyl clusters.

Other results have been obtained from the study of Thornton et al.[120] Two types of $SiO_2$ carriers were used as the matrix for the heterogenisation of the $Rh_6(CO)_{16}$ cluster: $SiO_2$ modified by a phosphine group $-(CH_2)_3PPh_2$ and $SiO_2$ modified by an amine group $-(CH_2)_3NHC_6H_{11}$. The density of the grafting of the functional group on the two carriers was the same (1.1 $nm^{-2}$) and the rhodium contents[119] were 0.24 and 0.66 wt.% respectively.

It has been shown that the interaction of rhodium clusters with aminated $SiO_2$ yields a specimen in the infrared spectrum of which vibrations appear at 2085 and 2003 $cm^{-1}$. These were characterised as symmetric and antisymmetric vibrations of the CO groups of a mononuclear rhodium carbonyl complex containing the $Rh(CO)_2$ fragment. The formula $L_nRh(CO)_2$, where $n$ is the number of amine ligands bound to the surface, may be attributed to this complex. The decarbonylation of the complex diminishes the intensity of the two CO absorption bands mentioned above and leads to the appearance of a new single absorption band at 1943 $cm^{-1}$, which can be assigned[121] to the vibration of the terminal CO group in the complex $L_nRhCO$. The decarbonylation–carbonylation processes

$$L_nRh(CO)_2 \underset{+CO}{\overset{-CO}{\rightleftharpoons}} L_nRhCO$$

are fully reversible up to 157 °C. At this temperature the amine ligand grafted to the surface begins to decompose. The reduction with hydrogen at the temperature above 117 °C is accompanied by the aggregation of the mononuclear rhodium centres, which is indicated by the darkening of the initial brown colour of the specimen and by the appearance in the infrared spectrum of an absorption band at 2020 $cm^{-1}$.

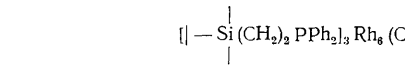
The same band has been observed after the adsorption of CO on the $Rh/Al_2O_3$ deposited catalyst and on thin rhodium films[122,125] (the CO group on 1.5–2.0 nm rhodium crystallites, formed as a result of the agglomeration of rhodium clusters immobilised on phosphinated polystyrene, absorbs at 2045 $cm^{-1}$ [113]). The hypothesis of the formation of the metallic rhodium phase has been confirmed by electron microscopy—the particle size is 1.6–1.7 nm.

During the ethylene hydrogenation reaction at 56 °C, the activity of the rhodium catalyst increased: the degree of conversion rose from 0.3% to 87% during 54 h; the authors explain this finding by the agglomeration of the metal in the course of the catalytic reaction.[120]

A more complex picture is observed in the heterogenisation of $Rh_6(CO)_{16}$ on phosphinated $SiO_2$,[121] but, as in heterogenisation on aminated $SiO_2$, it indicates, according to the authors,[121] the breakdown of the octahedral skeleton. As in the previous case, the surface mononuclear centres agglomerate during the catalytic process, which leads to the

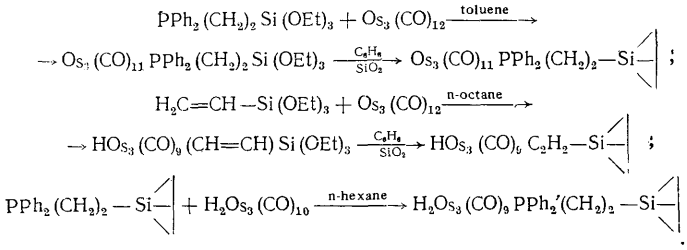
formation of 1.2–1.5 nm crystallites. The process is accelerated in a hydrogen atmosphere and on the phosphine-modified $SiO_2$ the rate of agglomeration of the metal is lower than on aminated $SiO_2$.

The heterogenisation of $Rh_6(CO)_{16}$ on $SiO_2$ modified by phosphine groups has also been investigated.[126;127] If the reaction is carried out at 80 °C in a boiling benzene solution, then, according to the authors, two types of complexes are formed on the surface. One complex contains structures of indefinite nuclearity comprising $Rh^+$ and two terminal CO ligands (in agreement with other data[121,128]). The second complex also consists of metal clusters whose nuclearity is unknown, but, after carbonylation, the infrared spectra of this complex correspond to those of $Ph_6(CO)_{16}/SiO_2$.[19] In the heterogenisation at room temperature hexa-atomic metallic clusters were formed on the surface.[127] The following structure was attributed to their carbonylation products:

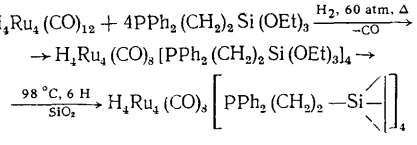


It has been noted that the catalysts obtained from boiling benzene solution are 10 times more active in the hydrogenation of aromatic hydrocarbons than those prepared at room temperature.

Several methods have been described for the heterogenisation of osmium clusters on chemically modified silicas:[128–130]



An analogous approach has been used also in the heterogenisation of the $H_4Ru_4(CO)_{12}$ cluster on $SiO_2$:[131]

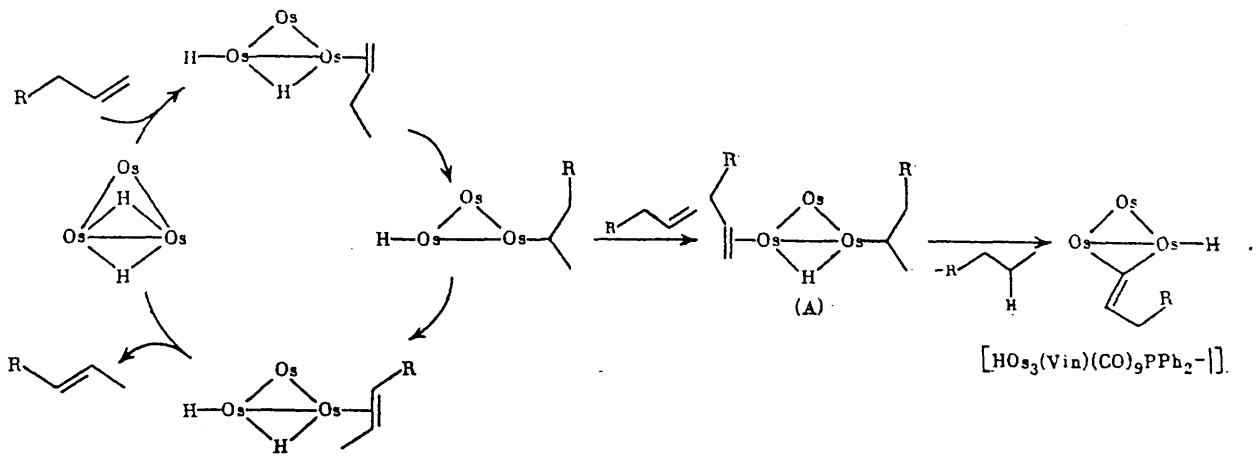


The activity of this catalyst in the ethylene hydrogenation reaction at 70 °C and a $C_2H_4$ and $H_2$ pressure of 100 mmHg is higher by an order of magnitude than the activity of the homogeneous complex $H_4Ru_4(CO)_{12}$ and the $H_4Ru_4(CO)_{12}/SiO_2$ catalyst. According to Doi et al.,[131] the cluster skeleton of the heterogenised complex is retained in the catalytic reaction and the cluster is not washed off into the solution, whereas in the case of $H_4Ru_4(CO)_{12}/SiO_2$ 30–40% of the clusters are transferred to the solution in heptane. This catalyst is regenerated by washing with heptane.

The preparation of heterogenised cluster catalysts by immobilising $[H_2Os_3(CO)_{10}]$ on the surface of $SiO_2$ modified with $[PPh_2(CH_2CH_2)Si(OEt)_3]$ has been reported.[130] An analogous system has been obtained also using phosphinated polystyrene cross-linked by divinylbenzene (3%). The results of an infrared spectroscopic study of the heterogenised clusters and their homogeneous analogues presented in the above communication indicate the retention of the cluster skeleton of the complex on heterogenisation.

The $[H_2Os_3(CO)_{10}]$ cluster is a 46-electron coordination-unsaturated complex, which exhibits a tendency towards conversion into a 48-electron complex in the presence of electron-donating ligands. Consequently, one might have expected that coordination-saturated complexes without catalytic activity would be formed as a result of immobilisation on a phosphinated matrix. A coordination-saturated catalytically inactive complex $[H_2Os_3(CO)_{10}PPh_2/carrier]$ was indeed obtained in the first stage as a result of immobilisation on a phosphinated matrix, which was demonstrated by the similarity of the infrared spectra of the homogeneous and heterogenised compounds.[130] Only after decarbonylation on boiling in hexane was a coordination-unsaturated cluster obtained, exhibiting catalytic activity in the isomerisation of pent-1-ene.

An important feature of the heterogenised clusters compared with the homogeneous analogue $[H_2Os_3(CO)_9PPh_3]$ is their high stability. Thus the homogeneous triosmium cluster decomposed during the reaction with formation of disproportionation products and mononuclear complexes, while the heterogeneous analogues promoted the isomerisation of pent-1-ene with an efficiency equivalent to $10^3$ moles of the olefin per mole of the cluster. The decrease of the activity of the cluster is attributed to the formation of a coordination-saturated complex containing a bridging vinyl ligand. The formation of the 48-electron vinyl cluster is reflected in the mechanism of the isomerisation reaction presented below (the carbonyl and phosphine ligands have been omitted):



It is noteworthy that the activity of the heterogenised triosmium cluster is twice as high as that of another homogenous analogue $[H_2Os_3(CO)_{10}]$. The authors[130] explained this finding by the steric hindrance arising at the stage involving the formation of the product (A), which requires the simultaneous coordination of two olefin molecules and this is responsible for the higher stability of the heterogeneous catalyst. The specific activities of the cluster heterogenised on $SiO_2$ and of its active homogeneous analogue proved to be identical. Bearing in mind the difference between the rate constants for the homogeneous ($k_1 = 0.026 \pm 0.005$ litre $mol^{-1}$ $s^{-1}$) and heterogeneous ($k_2 = 0.08 \pm 0.02$ litre $mol^{-1}$ $s^{-1}$) reactions, the authors[130] suggested that the promoting effect of the phosphine group on the surface is abolished by the influence of the carrier.

The complete analogy between the catalytic behaviour of the heterogeneous cluster and its homogeneous analogue is indicated also by the composition of the reaction products. Thus 19% of hexane and 79% of olefins with inner double bonds are formed in the presence of the triosmium cluster heterogenised on $SiO_2$ (in 45 h at 75 °C and a 4 atm $H_2$ pressure). Analogous results have been obtained[132] under the same conditions in the presence of the $[H_2Os_3(CO)_{10}]$ cluster (19 and 81% respectively).

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As can be seen from the literature data presented in this review, the heterogeneous cluster and polynuclear complex catalysts have attracted the attention of many investigators. However, despite the abundance of studies in this field, so far there have been no reports of qualitatively new results. Nevertheless data have been obtained which suggest that catalytic systems of the class considered are promising. In the first place this applies to cluster HMC for the selective synthesis of alcohols and ethylene glycol by the Fischer–Tropsch reaction.

The experience accumulated in the field of the synthesis, structure, and properties of cluster HMC has shown that these objects undergo changes during preparation, preliminary treatment, and catalysis. In the heterogenisation of cluster and polynuclear complexes, it is therefore necessary to pay special attention to the preservation of their structure.

As an example of an unsuccessful application of the immobilisation method in the preparation of cluster HMC, one may quote the study of Pierantozzi et al.[133] The heterogenisation of the cluster $[H_2FeRu_3(CO)_{13}]$ on phosphinated $SiO_2$ led, according to the authors' results, to the formation of mononuclear centres of the type $[Ru(CO)_4PPh_2-Si\equiv|]$ on the surface. The heterogenisation of the cluster $[Fe_2Pt.(CO)_8(PPh_3)_2]$ on the same carrier was accompanied by the decomposition of the cluster and the aggregation of the metal.

The complexity of the synthesis of the transition metal cluster and polynuclear complexes as well as their instability in the course of the preparation of heterogeneous catalysts necessitate the conclusion that in industrial analysis one should apparently favour the method involving the assembly of the cluster centres on the carrier surface, because relatively simple and accessible initial compounds are immobilised in this process.

For theoretical predictions of catalytic activity, important results can be obtained in the study of the influence of the nuclearity and the geometrical structure of the clusters on the catalytic activity and selectivity of the catalyst. Despite the large number of studies on catalysis by clusters and cluster HMC, many fundamental processes remain open. These include the influence of the nuclearity of the cluster on many-electron and structure-sensitive reactions, the synergistic effect in the above reactions on heteroatomic clusters, and the formation of cluster HMC with an asymmetric activity (both as a result of the presence of chiral ligands and the chirality of the cluster skeleton, arising either as a result of the asymmetry of the metal lattice or as a result of the skeletal asymmetry caused by the form of the cluster[134–137]). Presumably catalysts of the latter type will make it possible to synthesise selectively complex optically active compounds from CO and $H_2$.

During the preparation of the review for the press, a number of other review articles[138–145] and original papers[146–163] devoted to the preparation and application of catalysts based on heterogenised transition metal clusters were published.

Basset and Choplin[138] examined in detail the reactions of cluster compounds on the surfaces of mineral carriers. A mechanism has been proposed for the hydrogenation of olefins on the immobilised cluster $[HOs_3(CO)_{10}(O-|)]$. The results of an investigation of the Fischer–Tropsch reaction in the presence of carbonyl clusters on carriers have been described.[146,163] The reactions of clusters accompanying the Fischer–Tropsch reaction have been considered.

Another study has also been devoted to this topic.[147]

Using the EXAFS method, the interaction of the $[HFe(C).(CO)_{12}]^-$ cluster with the surface of a partly dehydroxylated alumina has been investigated.[148] A study has been made of the activity of the resulting catalyst in the CO and benzene hydrogenation reactions. The processes accompanying the heterogenisation of heteroatomic clusters on mineral carriers have been described in two communications.[149,150]

A simple geometrical model of the kinetics of the aggregation of clusters has been described.[151] Interesting results have been obtained in the study of the properties of catlaysts based on immobilised heteronuclear transition metal clusters.[152,153] Much attention has been devoted to the spectroscopic study of the products of the reaction of the clusters on the surfaces of carriers;[154–156,160,161] special mention should be made of studies[155,160] in which the EXAFS method was used to investigate the immediate environment of the metal ions.

Questions concerning catalysis by immobilised transition metal clusters have been considered at the IInd All-Union Conference on the Chemistry of Clusters (Odessa, May 1985). In addition they have been dealt with in a number of books.[164–166]

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