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# Mechanism of the interaction between Group VIII metals and oxides of transition elements

O S Alekseev, Yu A Ryndin
Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk

ABSTRACT. The results of research into the chemisorptive and catalytic properties of Group VIII metals supported on oxides of transition elements are reviewed. The mechanisms put forward to account for the effects of a strong interaction between metal and support are discussed. The causes of the strong interaction between metal and support are analysed using the results of studies on the properties of $(M + E^{IV})/SiO_2$ model systems.

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## I. Introduction

Supported metal catalysts are being used to an increasing extent in large-tonnage industrial processes involving the chemical treatment of hydrocarbon raw materials (reforming, hydrogenation, dehydrogenation, etc.), and in the future they may also be used for the synthesis of a wide range of hydrocarbons and oxygen-containing compounds from CO and $H_2$. Therefore, extending the range of control over their catalytic properties is a vital task. Variation of the dispersity, the use of promoters, and varying the nature of the support constitute effective methods of controlling the activity and selectivity of a supported metal.

In the 1960s Schwab and Solymosi[1,2] called into question the generally held view at the time that an oxide support that prevented the sintering of a metal was inert. In 1978 Tauster et al.[3] discovered the effects of a strong metal–support interaction (SMSI) for metals that were supported on oxides of transition elements (TE). After publication of this pioneering work the number of studies in this area started to increase at an exponential rate (Fig. 1), and in 1982 an international conference devoted to the effect of supports and additives on the catalytic properties of metals was organised. It is worth noting that even at that time there was an intuitive understanding of the common nature of the mechanisms of the action of TE oxides as supports and promoters of active metals (also reflected in the name of the conference). To date more than 1000 studies on the problem of SMI have appeared in the literature. In correlating these studies it may be noted that the consequences of SMSI are: a) a reduction in specific chemisorption of CO and $H_2$ on a metal; b) a sharp decrease in specific catalytic activity of the metal in reactions involving hydrocarbons; c) an increase in specific catalytic activity and a change in selectivity in the hydrogenation of CO; d) an intensification of these effects with an increase in the temperature of reduction of the catalyst and their reversible disappearance after oxidation followed by treatment with hydrogen at a moderate temperature.

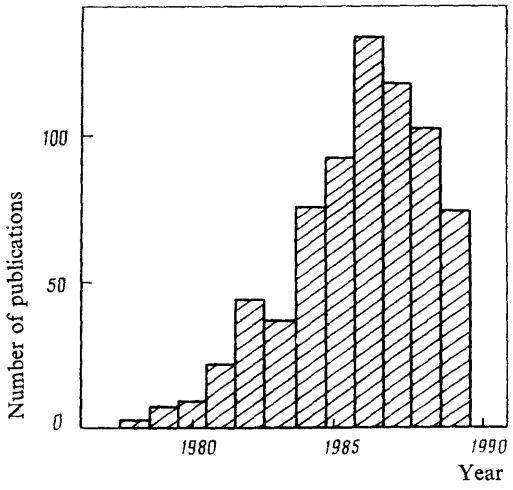



**Figure 1.** Growth trend for the number of publications on the problem of SMSI.[179]

It should be noted that effects similar to those of SMSI had previously been detected by Ermakov et al.[4–8] in catalysts prepared by fixing highly dispersed particles of Pd and Pt on low-valent surface Mo, W, or Re ions. In these studies the idea that the effect of the addition of an element that is difficult to reduce on the properties of Pd and Pt is caused by an interaction between the metal clusters and the surface ions of the promoter was first developed and confirmed experimentally. This interaction increases the stability of the dispersed metal towards sintering and is responsible for a change in its electronic properties, resulting in a change in its chemisorptive and hence its catalytic properties.

Despite the fact that at the present time a very large amount of experimental material on research into the properties of catalysts with SMSI has been collected, reviews concerned with classification

of the accumulated data are virtually absent from the literature. In the present review there is the task of analysing the results obtained by different research workers in the field of SMSI. At the same time particular attention is given to an analysis of models put forward to explain the effects of SMSI.

## II. Properties of Group VIII metals supported on oxides of transition elements

### 1. Chemisorptive properties

The first systematic study of the adsorption of CO and $H_2$ on different Group VIII metals supported on $TiO_2$ was undertaken by Tauster et al.[3] It was as a result of this investigation that the unusual phenomenon known as "a strong metal–support interaction" was observed. In fact, the reduction of Group VIII metals supported on $TiO_2$ at a low temperature (473 K) results in the formation of dispersed catalysts that are capable of the chemisorption of considerable quantities of CO and $H_2$. At the same time when the reduction temperature is increased to 773 K the quantity of chemisorbed CO and $H_2$ on all systems decreases almost to zero, while according to the data of electron microscopy and X-ray phase analysis such a significant change in the chemisorptive properties as this is not due to sintering of the supported metal.[3]

The range of supports on which the chemisorptive properties of metals are altered was considerably extended in subsequent studies.[9–12] Thus, on increasing the reduction temperature to 773 K for Ir supported on $Nb_2O_5$, $V_2O_3$, $Ta_2O_5$, almost complete suppression of the chemisorptive properties towards CO and $H_2$ was observed. It should be noted that treatment with oxygen followed by reduction at a moderate temperature (573 K) almost completely restores the chemisorptive capacity of the supported metals.

Water has a similar influence on the SMSI effect. It was shown by Duprez and Miloudi[13] that treatment of Pt, Ni, and Rh supported on $TiO_2$ with water vapour at 773 K completely eliminates the phenomenon of a decrease in chemisorption of $H_2$. At the same time, on a number of supports such as $SiO_2$, $Al_2O_3$, $Se_2O_3$, MgO, $ZrO_2$, $V_2O_3$, no perceptible changes in the chemisorptive properties of supported metals were observed over a wide range of reduction temperatures. On the basis of these results the authors[9–12] assumed that the SMSI effect is characteristic of readily reducible oxides of transition elements. In fact, it was demonstrated by Loye et al.[14] in a study of the chemisorption of $H_2$ on $Ni/Ti_nO_{2n-1}$ that the ratio of H:Ni decreases substantially on increasing the degree of reduction of the support. Beringhelli et al.[15] reported a decrease in chemisorption of $H_2$ on $Rh/ZrO_2$, although this had not previously been found for $Ir/ZrO_2$.[9] The patterns of variation in chemisorptive properties of Group VIII metals found by Tauster et al.[3] were confirmed in the studies of other authors.[16–22]

An interesting correlation between the chemisorptive properties of Pt and the heats of adsorption of $H_2$ and CO was found by Vannice et al.[23–25] It was shown that the heats of adsorption of CO and $H_2$ on Pt deposited on different supports ($SiO_2$, $Al_2O_3$, $TiO_2$) with low-temperature reduction of the catalysts did not depend on the nature of the oxide but were governed by the dispersity of the supported metal, being equal to 28 and 30 kcal $mol^{-1}$ for CO and $H_2$ respectively. However, the high-temperature reduction of $Pt/TiO_2$ in hydrogen (773 K) resulted in a substantial decrease in the heats of adsorption for CO to 10 kcal $mol^{-1}$ and for $H_2$ to 6–10 kcal $mol^{-1}$. Thus, for $Pt/TiO_2$ when the degree of covering the surface of Pt with CO and $H_2$ decreases, there is a reduction in the heats of chemisorption of these gases. Apart from that for $Pt/TiO_2$ no other similar correlations were found.[22] Despite the contradictory nature of the results of Vannice et al.,[22–25] a decrease in the heats of adsorption of CO and $H_2$ on the surface of the metal, resulting in a decrease in strength of the metal–adsorbate bond may be regarded as one of the causes of a reduction in the degree of covering the surface of the supported metal with a high reduction temperature.

### 2. Catalytic properties

#### a) Conversions of hydrocarbons

A change in the chemisorptive properties of metals supported on oxides of transition elements at high reduction temperatures must have a considerable effect on the properties of $M/E_xO_y$ systems. Thus, the activity of $Pt/TiO_2$ in the hydrogenation of benzene decreases after high-temperature reduction (793 K) by a factor of $10^{1.5}$ compared with a catalyst reduced at 473 K.[26] In the dehydrogenation of cyclohexane and the hydrogenation of ethylene the activity of $Pt/TiO_2$ decreases by a factor of 10. After reduction of $Ir/TiO_2$ and $Rh/TiO_2$ at 793 K a similar dependence occurs: in the hydrogenation of benzene the activity decreases by a factor of 10–100, in the dehydrogenation of cyclohexane it decreases by a factor of 5, and in the hydrogenation of ethylene it decreases by a factor of 10–100.[26] Oxidative treatment followed by reduction at a low temperature restores 80% of the original activity of these catalysts. A similar decrease in activity in the hydrogenation of benzene at a high reduction temperature (773 K) was observed for $Pt/TiO_2$,[27] (Ni, Pd, Ir)$/TiO_2$,[16] $Pt/TiO_2$,[28] and $Rh/TiO_2$ and $Pt/TiO_2$.[29]

In the hydrogenolysis of paraffins the activity of the catalysts is significantly affected by the temperature of their initial treatment in hydrogen. On increasing the reduction temperature from 523 to 773 K, Burch[30] observed a thousandfold decrease in the specific catalytic activity of $Ni/TiO_2$ in the hydrogenolysis of n-hexane. A similar dependence was found for (Ni, Pt, $Pd/TiO_2$) [16,31] and for $Rh/TiO_2$ [28] in the hydrogenolysis of ethane. At a reduction temperature of 773 K complete deactivation of the catalyst occurred in the same reaction for $Ir/TiO_2$.[26] Data on the effect of the reduction temperature on the properties of $M/TiO_2$ are given in five studies.[32–36] For all the Group VIII metals, except for Ru, when the reduction temperature is increased in the hydrogenolysis of ethane there is a sharp decrease in specific catalytic activity. At the same time, as for the hydrogenation of hydrocarbons, oxidative treatment followed by reduction under mild conditions restores the initial activity of the catalysts.[18,26,28,33,35]

It is interesting to note that the effect of the temperature of treatment does not manifest itself to an equal extent for all oxides of transition elements. Thus, in the hydrogenation of benzene on $Pt/CeO_2$ the activity decreases by a factor of 5 when the reduction temperature is increased, while in the hydrogenolysis of n-hexane there is no decrease in activity at all,[37] although the activity of $Pt/TiO_2$ in these reactions decreases by a factor of $10^{1.5}-10^2$.

#### b) Hydrogenation of carbon monoxide

An indication of the effect of the nature of the support on the properties of Group VIII metals in the hydogenation of CO was first given by Ichikawa et al.[38–40] In studying the synthesis of $CH_3OH$ on Rh, Pd, Ir, and Pt catalysts at atmospheric pressure, the authors[38–40] showed that the activity and selectivity of the catalysts

depended not only on the nature of the metal itself but also on the composition of the supported compound and the acid-base properties of the support. Thus, in the hydrogenation of CO on oxides with weakly defined basic properties such as MgO, $La_2O_3$, and $V_2O_3$, methanol is mainly formed, while on oxides with pronounced basic or acidic properties ($Li_2O$, $SiO_2$, $TiO_2$), methane is formed. A similar effect from the support on the properties of supported palladium in the hydrogenation of CO at a high pressure was observed by Ryndin et al.[41] However, in these studies[38–41] there is no analysis of the effect of dispersity on the activity and selectivity of the process. At the same time the dispersity of supported metal particles plays a significant role in this reaction. Thus, it was shown in two studies[42,43] that the specific catalytic activity of $Pd/SiO_2$ in the hydrogenation of CO to methane increases with an increase in dispersity of Pd, but it was found by Hicks and Bell[44] that the specific catalytic activity of $Pd/SiO_2$ in the synthesis of methane does not depend on the dispersity of Pd while the specific catalytic activity of $Pd/La_2O_3$ decreases with an increase in dispersity of Pd. In two other studies[45,46] it was shown that in the synthesis of methanol from CO the specific catalytic activity of $Pd/SiO_2$ and $Pd/La_2O_3$ catalysts increases with a decrease in dispersity of the supported metal. It was shown by Arkawa et al.[47] that for Rh catalysts the selectivity of the reaction with respect to oxygen-containing products increases with an increase in dispersity of Rh. On the whole the results given in the literature concerning the effect of dispersity on the activity of supported metals in the hydogenation of CO are quite contradictory.

The nature of the support affects the properties of a supported metal more significantly than a change in its dispersity.[48] It was shown in several studies[16,30,49–53] that at a reduction temperature of 723 K the specific catalytic activity of $Ni/TiO_2$ is higher than that of $Ni/SiO_2$, $Ni/Al_2O_3$, and Ni/C by a factor of 10–100. At the same time there was an increase in selectivity towards the formation of higher hydrocarbons.

Similar trends were found for other Group VIII metals.[54,55] Thus, Vannice[56,57] showed that the specific catalytic activity of platinum catalysts in the synthesis of methane was unchanged over a wide range of particle size (from 12 to 1000 Å), while the nature of the support had a considerable effect on their specific activity, which in $Pt/TiO_2$ was 10 times higher than in $Pt/Al_2O_3$ and $Pt/(SiO_2-Al_2O_3)$ and 100 times higher than in $Pt/SiO_2$. A constant value of the specific catalytic activity over a wide range of change in particle size of Pd in the hydrogenation of CO to $CH_4$ was established by Vannice et al.[58] However, as for Pt, the specific catalytic activity of Pd changed by a factor of 100 on varying the support (at the same time the activation energy of the reaction does not depend on the nature of the oxide).

An increase in activity of the supported metal also takes place on changing from $SiO_2$ and $Al_2O_3$ to oxides of transition elements. For example, the activity of $Ni/Nb_2O_5$ and $Ni/ZrO_2$ is considerably higher than the activity of $Ni/SiO_2$ and $Ni/Al_2O_3$,[59,60] and at the same time the selectivity towards higher hydrocarbons reaches 55%. It was shown by Szymanski et al.[61] that the specific catalytic activity of $Pt/ZrO_2$ in the synthesis of methanol at atmospheric pressure is higher than that of $Pt/SiO_2$ and Pt/C by a factor of $10^{1.5}$, and the selectivity with respect to $CH_3OH$ reaches 50%.

The effect of the reduction temperature on the properties of nickel catalysts in the synthesis of $CH_4$ from CO and $H_2$ was investigated in two studies.[59,62] When the reduction temperature of $Ni/ZrO_2$ and $Ni/TiO_2$ was increased from 543 to 973 K the activity per unit weight of nickel decreased more than ten times while the dispersity of the nickel did not alter significantly.[59] Fang[62] showed that on increasing the reduction temperature from 523 to 723 K the specific catalytic activity of $Ni/TiO_2$ decreased by a factor of 2, which was due to a decrease in strength of the Ni–CO bond, since there is a direct correlation between the decrease in activity and the reduction in strength of the Ni–CO bond. The reverse dependence occurs for Pt and Pd supported on $TiO_2$. At a reduction temperature of 773 K the specific catalytic activity of $Pd/TiO_2$ and $Pt/TiO_2$ is higher than at 573 K.[56,58,63]

An increase in the reduction temperature of $M/E_xO_y$ has only a slight effect on the selectivity for hydrogenation of CO to methane. It was shown by Turlier et al.[59] that the selectivity towards $CH_4$ for $Ni/TiO_2$ and $Ni/ZrO_2$ when the reduction temperature is changed from 523 to 923 K is virtually unchanged. It was shown by Anderson et al.[16] that the selectivity of a $Pd/TiO_2$ catalyst in the synthesis of $CH_4$ is virtually independent of the reduction temperature, but it is 20% higher than the selectivity of $Pd/SiO_2$.

Interesting results were reported by Kunimori et al.[21] in a comparison of the catalytic properties of Pd and Rh supported on $TiO_2$ and $Nb_2O_5$. When the reduction temperature for $Rh/Nb_2O_5$ and $Pd/Nb_2O_5$ was increased from 573 to 773 K, in addition to a decrease in chemisorption of CO by a factor of more than 10, there was a decrease in the specific catalytic activity of these catalysts in the synthesis of $CH_4$—by a factor of 100 for $Rh/Nb_2O_5$ and by a factor of 10 for $Pd/Nb_2O_5$. At the same time the activity of $Rh/TiO_2$ and $Pd/TiO_2$ remained constant on increasing the reduction temperature. However, prolonged experiments on the hydrogenation of CO on $Rh/Nb_2O_5$ and $Pd/Nb_2O_5$ catalysts showed that with the passage of time their activity increases to a value that is typical for samples reduced at 573 K. In the opinion of Kunimori et al.,[21] the increase in activity of $M/Nb_2O_5$ is due to disruption of SMSI by oxygen formed through dissociation of CO or by water formed as a result of reaction. At the same time the higher activity of $M/TiO_2$ catalysts compared to $M/Nb_2O_5$ (whatever the reduction temperature) is due to the readier disruption of the interaction between metal and support.[21] The true activity of $M/TiO_2$ catalysts at high reduction temperatures, according to Kunimori et al.,[21] must be lower than the observed value by a factor of 10–100.

It was found by Jackson et al.[64] that the specific catalytic activity of $Ru/TiO_2$ catalysts prepared from supported Ru carbonyl clusters decreased with an increase in reduction temperature, while raising the reduction temperature from 523 to 873 K had no effect on the activity of $Rh/ZrO_2$ catalysts.[65]

Thus, the data reported in the literature concerning the effect of the reduction temperature on the activity of Group VIII metals supported on $TiO_2$ and other oxides of transition elements in the hydrogenation of CO are contradictory in nature. However, the increase in specific catalytic activity of metals supported on $TiO_2$ or other oxides of transition elements compared to that of the same metals supported on $SiO_2$ or $Al_2O_3$ is not in doubt.[66]

## III. Models of the interaction between metals and oxides of transition elements

### 1. Direct interaction between metal atoms and low-valent ions of a support

A model which assumes direct interaction between the atoms of a supported metal and low-valent ions of the support was put forward by Horsley.[67] This model was based on theoretic calculations using

the method of the self-consistent field of dispersed waves of models of molecular clusters for a $Pt/TiO_2$ catalyst. Two different models were considered (Fig. 2). According to model (A) (Fig. 2*A*) a platinum atom interacts with an octahedral $(TiO_6)^{8-}$ cluster, while the metal atom is situated outside the octahedron. Model (B) (Fig. 2*B*) assumes that there is an oxygen vacancy in the $(TiO_6)^{8-}$ cluster that is occupied by a Pt atom. While in model (A) the closest neighbours of the Pt atom are oxygen ions, in model (B) direct coordination between the Pt atom and the titanium cation is assumed.

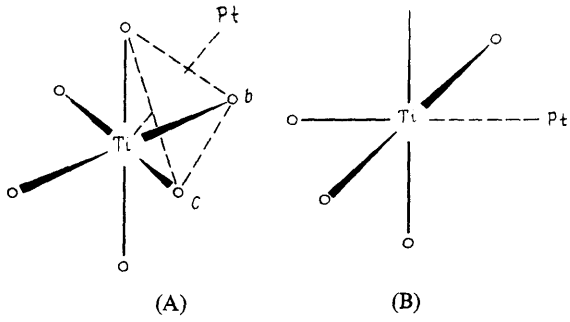



**Figure 2. Models of clusters in a $Pt/TiO_2$ catalyst.[67]**

Theoretical calculations show that for model (A) the platinum atom cannot lie sufficiently close to the $(TiO_6)^{8-}$ cluster because of strong repulsion between the Pt atoms and the adjacent oxygen ions, and the formation of a Pt–Ti bond is impossible.[67] For model (B) the Pt atom and Ti cation can lie sufficiently close to each other and the formation of a $Pt-Ti^{3+}$ bond is possible.[67] This bond is probably partly ionic with electron transfer from $Ti^{3+}$ to the platinum atom. According to the authors,[67–69] even a small transfer of electron density to platinum will produce a change in hybridisation of the metal–metal bonds, which assumes considerable changes in metal–metal distances. This may affect the population or change in symmetry of *d* orbitals in such a manner that they will not be able to interact with the molecular orbitals of $H_2$ and CO. As a result, a decrease in chemisorption and strength of the bond between metal and CO and $H_2$ will occur. It is clear that the interaction between metal atoms and $Ti^{3+}$ atoms is of a specific type and only occurs at the metal–support phase boundary, since the metal atoms and cations of the support are restricted in movement at the limits of the crystal lattice.[70]

The hypothesis put forward by Horsley was later supported experimentally in a number of studies. For example, Golodets et al.[71–73] observed a reduction in strength of the Ni–CO and Ni–H bonds on a $Ni/TiO_2$ catalyst as a result of the electronic interaction of $Ni-Ti^{3+}$. A similar trend was observed for a $Pd/La_2O_3$ catalyst.[74] However, the data from studies on the electronic state of metals are contradictory. Thus, in two studies[17,75] no significant changes occurred in $E_{bind}$ of the core levels of Rh and Pt supported on $TiO_2$ (X-ray photoelectron spectroscopy method), so the authors were able to conclude that electron transfer from $Ti^{3+}$ to the Rh and Pt atoms was negligible. At the same time, it was shown in several other studies[28,69,76–82] that reduction of (Rh, Ni, Pt)$/TiO_2$ catalysts with hydrogen at 873 K results in a decrease in $E_{bind}$ of the core levels of the metals, which suggests an increase in electron density on the metal atoms.

Experimental confirmation of an interaction occurring between $Ti^{3+}$ cations and Group VIII metals constituted important evidence in favour of the Horsley mechanism. A series of phyiscal methods (X-ray photoelectron spectroscopy, high-resolution electron energy loss spectroscopy, and UV photoelectron spectroscopy) were used to establish that when Ni,[76,83] Pt,[84] Pd,[85] and Rh [70] are deposited on the surface of a support containing $Ti^{3+}$ cations, the spectroscopic parameters that are characteristic of $Ti^{3+}$ cations either decrease or disappear. It was shown by means of Auger spectroscopy[70] that deposition of Rh on $TiO_2$ is accompanied by oxidation of the surface, and the changes in the UV photoelectron spectra are similar to those that occur when oxygen is adsorbed.

Direct experimental confirmation of the existence of a Rh–Ti bond was first obtained by Shpiro.[28,79] In a study of a $Rh/TiO_2$ catalyst reduced at 773 K using secondary ion mass spectrometry, mixed $RhTi^+$ clusters were detected together with $Rh^+$ and $Ti^+$, while at reduction temperatures of 473 and 573 K no $RhTi^+$ clusters were observed.

At the same time there is virtually no information in the literature about detection of a metal–$Ti^{n+}$ bond by means of the extended X-ray absorption fine structure (EXAFS). Only two examples of the detection of such bonds using the EXAFS method are known. Thus, Konigsberger[86] found the Rh–$Ti^{n+}$ distance to be 3.4 Å in length in a $Rh/TiO_2$ catalyst reduced at 773 K. However, this distance is too great for the formation of a chemical bond.[70] For a similar catalyst, Haller[87,88] demonstrated the existence of a Rh–$Ti^{n+}$ bond of length 2.55 Å, which is somewhat shorter than the length of the Rh–Ti bond in the majority of stable intermetallic compounds (2.68 Å). However, in more recent studies of $Rh/TiO_2$ catalysts using EXAFS it was not possible to detect a Rh–$Ti^{n+}$ bond.[68] The difficulties in attempting direct detection of a M–$Ti^{n+}$ bond arise because it is of a special type and is only formed at the metal–support interface. It is therefore to be expected that the coordination numbers for titanium may be low and lie outside the limit of sensitivity of this method.

## 2. Change in morphology of supported metal particles

The formation of flat metal particles (with a "pill-box" or "raft-like" structure) on the surface of partially reduced $TiO_2$ were first introduced by Baker[89] to explain the existence of SMSI. In a study of the sintering of Pt on different supports using high-resolution electron microscopy over a temperature range of 425–1075 K it was shown that the dispersity of Pt deposited on $TiO_2$ is higher than that on other supports. At the same time the Pt particles have a flat hexagonal form with uniform thickness, which indicates the formation of flat structures. Moreover, in the presence of Pt, $TiO_2$ was reduced to $Ti_4O_7$, being accompanied by a change in the lattice parameter (5.6 Å). In fact, Prins[90] showed by means of EPR that Pt catalyses the reduction of $TiO_2$. After treatment of a $Pt/TiO_2$ catalyst with hydrogen even at 573 K, the concentration of $Ti^{3+}$ ions is 30 times less than in the pure support.

It was shown by Baker et al.[91] that the formation of flat metal particles in an $M/TiO_2$ system is reversible. Thus, high-temperature treatment of $Pt/TiO_2$ with water vapour or $O_2$ results in the formation of globular Pt crystallites, while repeated reduction leads to the formation of flat structures.

A comprehensive scheme of the formation of flat particles is depicted in Fig. 3. As a result of high-temperature reduction, hydrogen atoms, diffusing from the surface of the metal to the support, reduce the $Ti^{4+}$ ions to $Ti^{3+}$. At the same time oxygen vacancies are formed in the surface layer through the elimination of lattice oxygen in the form of $H_2O$. The resulting oxygen vacancies can be compensated by the formation of a bond between the metal atoms and $Ti^{3+}$ cations. In fact, it was shown by Gingerich et al.[92] that the Pt–Ti bond is stronger than Pt–Pt. Thus, in their tendency to form a $M-Ti^{n+}$ bond, the metal atoms enter oxygen vacancies, and flat structures are formed on the surface, which was recorded by means of electron microscopy.[91] On oxidation by oxygen or $H_2O$ the $M-Ti^{n+}$ bonds are broken and $Ti_4O_7$ is oxidised to $TiO_2$. At the same time the metal particles change their structure, adopting an energetically more favourable spherical form. The metal acquires its normal chemisorptive and catalytic properties through cleavage of the $M-Ti^{3+}$ bonds.[90,91]

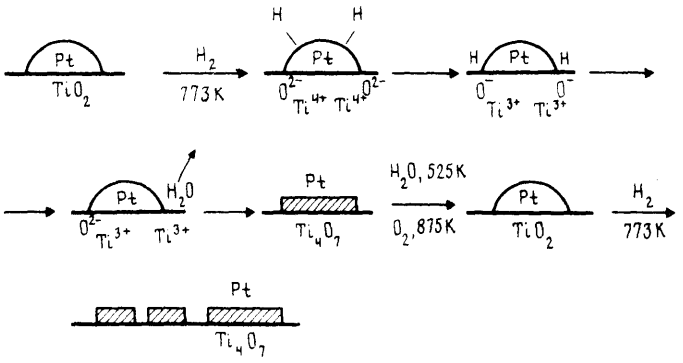



**Figure 3.** Scheme for the formation of flat metal structures in the system $Pt/TiO_2$.[90,91]

It should be noted that the unique flat structure of the Pt particles was not observed on oxides of nontransition elements ($SiO_2$, $Al_2O_3$) or on carbon. However, it was shown by Yates et al.[93] that flat Rh particles may also be obtained on $Al_2O_3$, while the shape of the particles does not affect the chemisorptive properties of Rh. Thus, the change in chemisorptive and catalytic properties of the metals in an SMSI state cannot be explained solely by a change in shape of the particles.

We should note that the existence of flat structures in other metals has not been clearly demonstrated. For example, the formation of flat particles of Ni in a $Ni/TiO_2$ catalyst was demonstrated by Mustard et al.[94] using electron microscopy, while flat structures were not detected by Baker et al.[95–97] in studies on similar catalysts. The formation of flat structures in $Pd/TiO_2$ was also not detected in another study.[98]

The results which suggest that partial reduction of $TiO_2$ occurs in the presence of Group VIII metals are not in doubt. The fact that the supported metal is localised on the reduced forms of $TiO_2$, namely, $Ti_4O_7$, suggests that the metal atoms form a chemical bond with the surface $Ti^{3+}$ cations. A change in the chemisorptive and catalytic properties of a supported metal also occurs because of the interaction between the metal atoms and the $Ti^{3+}$ cations.[89] The mechanism discussed in this section reiterates the assumptions made by Horsley.[67]

## 3. Formation of intermetallic compounds

The formation of intermetallic compounds was first proposed by Tauster as one of the mechanisms for interaction between a supported metal and a transition element oxide.[3] Experimental support for this hypothesis was obtained in two studies,[99,100] in which it was demonstrated that $Pt_{1-x}Zr_x$ intermetallic compounds are formed during the high-temperature reduction of $Pt/ZrO_2$ according to the reaction:

$$(1-x)Pt + xZrO_2 + 2xH_2 \longrightarrow Pt_{1-x}Zr_x + 2xH_2O.$$

In the case of $Pt/ZrO_2/C$ catalysts, intermetallic compounds are formed according to the reaction:

$$(1-x)Pt + xZrO_2 + 2xC \longrightarrow Pt_{1-x}Zr_x + 2xCO,$$

where C acts simultaneously both as a reducing agent and support. Appreciable formation of $Pt_{1-x}Zr_x$ compounds occurred at temperatures above 873 K. With an increase in temperature $x$ increases and reaches a maximum value ($x = 0.25$) at 1273 K.

In three studies[96,101,102] the formation of compounds of the type $M_3Ti$ was observed at 973 K for (Ni, Pt)/$TiO_2$. However, in two other studies[26,103] for $Ni/TiO_2$ there is no possibility of intermetallic compounds being formed even at 1073 K, since at this temperature $TiO_2$ cannot be reduced to metallic titanium.

A decrease in specific chemisorption of CO on $Ni_xZr_y$ was observed by Tomanek et al.,[104] and it was established that above 300 K carbon monoxide is mainly adsorbed in a dissociative form. It should be noted that after treatment of the $Pt_3Ti$ catalyst with hydrogen, the thermally programmed desorption (TPD) spectra indicated that desorption of $H_2$ did not occur. In the opinion of Bardi et al.,[105,106] either $H_2$ is not adsorbed at all on the surface or it is adsorbed sufficiently strongly for desorption not to occur up to 900 K. However, it is widely known that intermetallic compounds can form hydrides. Thus, it was shown in three studies[107–109] that Zn–Ni, Zr–Co, and Zr–Ni–Mo intermetallic compounds can dissociatively adsorb $H_2$ and contain it in bulk in the form of monoatomic species, which assumes that there is a high concentration of active hydrogen on the surface.

In the hydrogenolysis of ethane the activity of $Pt_{1-x}Zr_x/(ZrO_2, C)$ is 15–20 times lower than that of $Pt/ZrO_2$ and Pt/C catalysts.[99,100] It was shown in three studies[61,99,100] that in the hydrogenation of CO the specific catalytic activity of $Pt_{1-x}Zr_x$/support catalysts does not depend on the nature of the support, but their activity is higher than that of Pt/support catalysts by a factor of 10, and their selectivity towards $CH_3OH$ reaches 80%.

It should be noted that intermetallic compounds are stable towards oxygen and do not decompose at room temperature.[26,110,111] However, oxidation at temperature above 573 K results in segregation of the components and a decrease in the observed changes in chemisorptive and catalytic properties.[107,109–114]

## 4. Electronic interaction between a metal and transition element oxide

Schwab[1] and Solymosi[2] attempted to explain the change in catalytic properties of metals on varying the nature of the support in terms of an electronic interaction between the deposited metal and

support. Interest in these ideas grew again at the end of the 1980s. For example, it was shown in two studies[115,116] that electron transfer between the metal and support can play a substantial role in the catalytic reaction. It was first suggested by Meriaudeau[26] that electron transfer between metal and support is the main cause of the change in chemisorptive and catalytic properties of metals in an SMSI state. The model put forward by Meriaudeau[26] is based on the theory of semiconductors and is depicted schematically in Fig. 4.

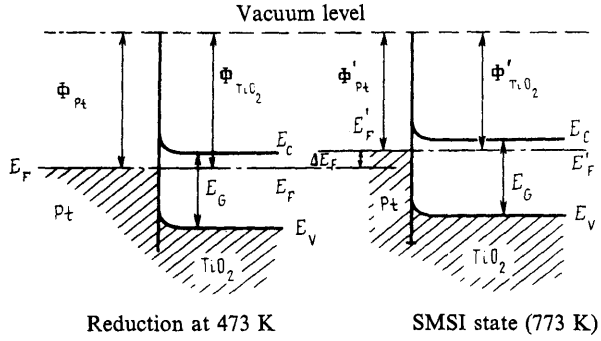



**Figure 4. Schematic depiction of energy diagram for the system $Pt/TiO_2$.[26] $E_F$ is Fermi level, $\Phi$ is electronic work function, $E_V$ is top of valence band, $E_C$ is bottom of conduction band, $E_G$ is width of forbidden band, $\Delta E_F$ is increase in Fermi level in the SMSI state.**

Since at a low reduction temperature the electronic work function ($\Phi$) for $TiO_2$ is 5.5 eV while for Pt it is 5.6 eV,[26] the Fermi level ($E_F$) of $TiO_2$ lies near $E_F$ for platinum. At high reduction temperatures, as a result of the high concentration of defects in $TiO_2$ (oxygen vacancies and $Ti^{3+}$) the electronic work function decreases to 4.6 eV, while the value of $E_F$ becomes higher than in Pt. At the points of contact between platinum and $TiO_2$ the values of $E_F$ equal out through the flow of electron density from support to platinum. The excess electron density on Pt will cause a modification of its electronic structure through a progressive filling of the $d$ orbitals and there is a transition from a $d^9$ configuration to $d^{10}$, i.e., to the same as in gold. Gold is known not to exhibit the chemisorption of $H_2$ and does not catalyse reactions involving the dissociative chemisorption of hydrogen.

When oxygen is added $TiO_2$ undergoes reoxidation. In this case the support becomes electron-deficient, which assist a flow of electron density from platinum to support. As a result Pt acquires a normal $d^9$ configuration and at the same time its normal chemisorptive properties restored.

The hypothesis put forward by Meriaudeau[26] has been supported experimentally in four studies.[117–120] Thus, it was shown by Herrmann et al.[118,119] that on reduction of $TiO_2$ in the presence of platinum, the electrical conductivity of $TiO_2$ increases by a factor of 100, which suggests that platinum plays a catalytic role in the reduction of $TiO_2$ and it confirms the results of Huizinga and Prins.[90] It was established[119] that evacuation of $TiO_2$ at 673 K increases the electrical conductivity by a factor of 100, and the subsequent deposition of Pt leads to a decrease in electrical conductivity of $TiO_2$ by a factor of 2. A decrease in the electrical conductivity of TiO and $Ti_2O_3$ on deposition of Pt was also observed by Chen and White.[117] These phenomena are due to the simultaneous occurrence of two processes:[117,119] 1) formation of anion vacancies through removal of lattice oxygen and the generation of free electrons; 2) migration of the free electrons from the bulk of the support to the metal, resulting in a decrease in electron density on the support and a decrease in its electrical conductivity. As a result of the latter process the chemisorptive properties of the metal must change, according to Meriaudeau et al.[26] In fact, it was shown by Loye et al.[14] for $Ni/Ti_nO_{2n-1}$ that with an increase in the degree of reduction of the support, a decrease in chemisorption of $H_2$ occurs. The change in chemisorptive properties of Ni through a change in electronic structure is supported by Longe and Stacy.[121] At the same time in a study by Fang et al.[62] on similar systems it was shown that an increase in bulk concentration of $Ti^{3+}$ has no effect on the catalytic properties of Ni in the hydogenation of CO. Using X-ray photoelectron spectroscopy, Huizinga and Prins[122] did not detect any change in the electronic state of Pt when the reduction temperature for $Pt/TiO_2$ was changed from 483 to 823 K.

An alternative explanation to that put forward by Baker et al.[89] concerning the formation of flat metal particles follows from the mechanism proposed by Meriaudeau.[26] Chen and White[117] assume that when transfer of electron density occurs from the bulk of $TiO_2$ to the metal, the negatively charged metal particle will tend to increase its surface area in order to reduce the surface charge density. Consequently, when electron transfer occurs the formation of particles with a flat shape becomes energetically more favourable.

Despite the fact that the mechanism proposed by Meriaudeau[26] accounts for the change in chemisorptive and catalytic properties of platinum, which has a $d^9$ configuration, it cannot be recognised as a fundamental principle since it does not explain why Ir and Rh, which have $d^7$ and $d^8$ electron configurations respectively, when supported on oxides of transition elements exhibit properties that are characteristic of systems with SMSI.

## 5. Interaction at the metal–support interface

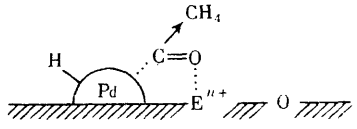
The existence of an interaction at a metal–support interface was first demonstrated by Burch and Flambard.[50] According to the model put forward by them, the formation of anion vacancies and $Ti^{3+}$ ions at the phase boundary can produce a change in the catalytic properties of a supported metal through direct and indirect participation of the support in the catalytic process. For example, $Ti^{3+}$ cations that are formed at the phase boundary can participate in the activation of CO molecules which undergo dissociative hydrogenation by hydrogen adsorbed on the surface. Furthermore, the support can form part of a heteroatomic adsorption site involving metal atoms and $Ti^{3+}$ cations on the surface of the support. It has been suggested that during adsorption to these sites a CO molecule forms a bond via its carbon atom with a metal atom while the oxygen atom binds to a surface $Ti^{3+}$ cation, resulting in a considerable loosening of the bond in the CO molecule and assisting its hydrogenation. Burch and Flambard[49,50] assume that in the interaction of metal atoms with $Ti^{3+}$ cations through the transfer of electron density to the metal atoms the electronic properties of the supported metal are modified. When excess electron density occurs on the metal it is to be expected, on the one hand, that there will be a decrease in the activity of the catalysts in reactions involving the conversion of hydrocarbons because of a reduction in the strength of chemisorption of reactants on the surface of the metal, while on the

other hand, an increase in activity is to be expected in the hydrogenation of CO through an increase in the rate of dissociation of a CO molecule or an increase in the rate of desorption of reaction products.[49,50]

The idea that the support participates in the catalytic process and that specific active sites are formed at the phase boundary has found further confirmation in several studies.[123–128] For example, it was shown by means of angular resolved X-ray photoelectron spectroscopy[125] that on treatment of $Pt/TiO_2$ with hydrogen, the resulting $Ti^{2+}$ and $Ti^{3+}$ cation sare localised at the metal–support interface. Stadler et al.[126] found that the high activity of a $Pd/TiO_2$ catalyst in the hydrogenation of 1,5-hexadiene is due to coordination of the olefin on the surface $Ti^3$ cations and to hydrogenation of the resulting complex by hydrogen that is dissociatively adsorbed on the surface of palladium.

It was established[127] that on addition of $Sb^{5+}$, $Ta^{5+}$, $W^{6+}$ ions to $Pt/TiO_2$ and $Pt/Nb_2O_5$, there is a decrease in chemisorption of hydrogen because of an electronic interaction at the interface between Pt and the introduced ions. When $Na^+$ ions were added to $Ni/TiO_2$, the selectivity of the catalyst increased and higher alcohols were formed from synthesis gas, which is attributed by Hayasaka et al.[128] to the participation of the $Na^+$ ions in the activation of CO.

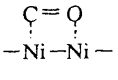
The high activity of $Pd/TiO_2$ and $Pd/La_2O_3$ catalysts in the hydrogenation of CO is attributed to participation of supports in hydrogenation.[21,45] In this case, as was suggested by Burch and Flambard,[49,50] the authors assume[21,45] that cations of the support can form part of a mixed adsorption site and participate in the activation of a CO molecule:



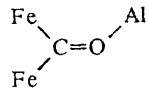

(I)

or take part in the adsorption of reaction intermediates.

Thus, the existence of active sites at the metal–support interface assumes that an unusual form of CO adsorption occurs parallel to the surface. The possibility of the planar coordination of CO simultaneously on Pt and Ti atoms was calculated theoretically by Mehandru et al.[129] According to Rice and Haller,[130] vibrations of the planar-coordinated form of CO should appear in the region below 1800 $cm^{-1}$ in the IR spectra. In fact, it was shown in two studies[131,132] by means of IR spectroscopy that when manganese, titanium, or zirconium ions are added to a $Rh/SiO_2$ catalyst, a new absorption band due to CO appears in the region 1800–1600 $cm^{-1}$. In this case its position depends on the metal–promoter ratio. We should note that in 1965 Garland,[133] when studying the adsorption of CO on Ni films, first detected an unusual absorption band of adsorbed CO at 1620 $cm^{-1}$, which was provisionally attributed to the coordination of CO on two nickel atoms:




It was only progress in the chemistry of cluster compounds that demonstrated the validity of assigning the absorption bands in the region below 1700 $cm^{-1}$ to vibrations of CO coordinated simultaneously through its carbon and oxygen atoms on metal atoms. For example, Nelson et al.[134] established the presence of




residues with a CO vibration frequency of 1527 $cm^{-1}$ for different Fe carbonyl clusters. It was shown by Sachtler et al.[135] that for different heteronuclear Mo, Fe, and Ru complexes the absorption bands of CO in M–C–O–M residues are in the region of 1700–1500 $cm^{-1}$.

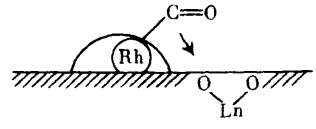
A considerable contribution towards proving that complexes exist at the metal–support interface in catalysts of the type $M/E_xO_y$ was made by Bredikhin et al.,[136–139] who demonstrated by means of IR spectroscopy that in the adsorption of CO, complexes are only formed at the metal–support interface for catalysts prepared by deposition of metals on oxides of transition elements ($TiO_2$, $ZrO_2$, $HfO_2$, $V_2O_5$, $La_2O_3$). At the same time for metals supported on oxides of *p*-elements (Al, Zn, Cd, Ga, Bi) and also for bulk metals or supports without metals, the formation of these complexes does not occur. Moreover, a systematic study of the chemical and spectroscopic properties of complexes formed at the metal–support interface was undertaken by Bredikhin et al.[136–139] It was shown in this case that they have a number of characteristics:

1) a broad absorption band in the region of 1800–1600 $cm^{-1}$, whereby its position depends on the nature of the metal and support used;

2) a low value of the isotopic shift ($^{12}CO \rightarrow {}^{13}CO$) and a lower value of the high-frequency shift with an increase in the degree of filling the surface compared to surface carbonyls, and the heat of adsorption of CO is similar to the corresponding value for carbonyl complexes;

3) they are oxidised by oxygen, in the same way as surface carbonyls.

At the same time the question concerning the type of CO adsorption at the sites formed at the metal–support boundary remains open. While Bredikhin et al.[136] give preference to complexes of the type

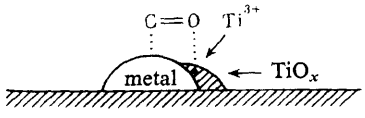



in several other studies[20,49,50,130,131,135] the authors assume that an adsorbed CO molecule forms a complex of the type (I).

Despite the difference in proposed forms for the coordination of CO at the metal–support interface, it may be assumed that the hydrogenation of CO on $M/E_xO_y$ catalysts occurs with the participation of novel complexes of adsorbed CO, which accounts for the unusual nature of their catalytic properties in the hydrogenation of CO. There is no doubt that further studies need to be carried out in order to verify this hypothesis, but the results already reported in the literature indicate the necessity for admitting the funadmental possibility of the coordination of molecules at the metal–support interface in representing the mechanisms of the catalytic reactions.[138]

### 6. Diffusion of $TiO_x$ to the surface of the metal

According to a number of published studies, one of the most widely recognised mechanisms introduced to account for the unusual properties of metals on oxides of transition elements is the diffusion of partially reduced residues of the support to the surface of the metal particles. This mechanism was first suggested by Meriaudeau et al.[37] and was further developed in three studies.[16,140,141] This mechanism essentially involves partial reduction of $TiO_2$ around the perimeter of the metal particles followed by migration of the $TiO_x$ residues to the surface of the particle. As a result the surface of the metal particle is obstructed by small islets of $TiO_x$, resulting in a decrease in the available surface of the metal for chemisorption of hydrocarbons and hydrogen, and hence to a decrease in activity of the catalysts in the conversion of hydrocarbons.[37,140] Furthermore, the total metal–support interface increases as a result of the migration of $TiO_x$ to the surface of a metal particle. At the same time, according to Anderson et al.,[16] there is an increase in the number of adsorption sites consisting of metal atoms and $E^{n+}$ cations that can participate in the coordination of a CO molecule according to the scheme:




Thus, on the basis of this mechanism participation of the support in the activation of CO explains the increase in activity of $M/TiO_x$ catalysts in the hydrogenation of CO.[16,142]

Experimental support for the mechanism involving decoration of the metal surface is provided in a number of studies.[143–160] At the same time the question regarding the migration mechanism of $TiO_x$ to the surface of the metal remains open. For example, in two studies[16,162] distortion of the crystal lattice of platinum was observed on reduction of $Pt/TiO_2$ above 673 K, which was attributed to diffusion of $TiO_x$ into the bulk of Pt. Diffusion of $TiO_x$ into the bulk of Pt over the temperature range 700–900 K was recorded in two other studies.[163,164]

It has also been thought possible that transport of $TiO_x$ to the surface of the metal occurs through the intermediate formation of metastable $M-TiO_x$ compounds which segregate on reduction to form $TiO_x$ residues on the surface of the metal. For example, the formation of $Ni-TiO_x$ structures was recorded in two studies.[121,165] The formation of $LaPd_xO$ structures on reduction of a $Pd/La_2O_3$ catalyst was demonstrated by Fleisch et al.,[166] and at the same time an increase in electron density on Pd was detected by X-ray photoelectron spectroscopy. On addition of $K^+$ ions to a $Pt/TiO_2$ catalyst, a decrease in chemisorption of $H_2$ occurred, which Spencer[167] related to the participation of potassium ions in the form of $K_2TiO_3$ in the transport of $TiO_x$ to the surface of Pt.

Furthermore, the counter-diffusion of metal atoms and resulting $TiO_x$ residues at the metal–support interface is not excluded. According to Spencer,[168] the mobility of the metal atoms is governed by the Hüttig temperature ($T_H$), which is equal to one third of the melting point of the metal. For example, $T_H$ = 700 K for Pt, 750 K for Rh, and 700 K for $TiO_2$ and TiO. It is to be expected that at reduction temperatures above 700 K the mechanism for transport of $TiO_x$ to the surface of the metal through the mutual diffusion of metal atoms and $TiO_x$ residues predominates.[97,168]

In order to confirm the hypothesis about decoration of the metal surface, a study was made of model systems obtained by depositing $TiO_2$ on the surface of different metals. It was shown by Gorte et al.[163,169] that when the content of $TiO_x$ on the surface of Pt foil is increased, the chemisorption of CO and $H_2$ is almost completely suppressed. The activity of $TiO_x/Pt$ catalysts in the synthesis of $CH_4$ from CO and $H_2$ is similar to that of $Pt/TiO_2$, while at the same time there is a decrease in the activation energy of reaction by 12 kcal $mol^{-1}$.

An increase in the activity of model $TiO_x/Rh$ catalysts in the hydrogenation of CO with an increase in the extent of surface coverage of Rh foil with $TiO_x$ particles was observed by Levin et al.[170] The maximum increase in activity in the synthesis of $CH_4$ occurred when the extent of surface coverage of the metal with $TiO_x$ was 15%, which is attriubted to an optimum number of Rh atoms being located along the $TiO_x$ boundary.[170]

The maximum activity for model $TiO_x/Ni$ catalysts in the synthesis of $CH_4$ occurred at 8% covering.[171] It was shown[172] that the chemisorption of CO on the surface of Ni(III) decreases in the presence of $MnO_x$, and the quantity of chemisorbed CO decreases linearly with an increase in coverage of the nickel with $MnO_x$ particles. Moreover, in the presence of $MnO_x$ a novel form of adsorbed CO occurs on the surface of Ni(III) with vibration frequency 1620 $cm^{-1}$, the intensity of this form reaching a maximum for average degrees of coverage with $MnO_x$.

Thus, investigation of model $TiO_x/M$ catalysts shows that blocking the metal surface with partially reduced residues of support ($TiO_x$) and modification of the electronic properties of the metal through the interaction of metal atoms with $TiO_x$ results in a considerable loss of chemisorptive properties of these catalysts. However, the presence of residues of support on the surface of the metal leads to an expansion in the metal–support interface and an increase in the number of active sites consisting of metal atoms and support, which may be the cause of the increased activity of catalysts in the hydogenation of CO. We should note in conclusion that the model for decoration of the surface of the metal with $TiO_x$ residues is generalised model and incorporates the models put forward by Horsley, Baker, and Burch.

## IV. Study of the mechanism of the interaction between Group VIII metals and oxides of transition elements using $(M + E^{IV})/SiO_2$ model systems

It may be concluded from an analysis of the results given above that six basic mechanisms to account for the unusual properties of metals supported on transition element oxides have been discussed in the literature. However, the experimental data supporting a given mechanism are usually contradictory, and not one of these hypotheses has so far received conclusive experimental confirmation. We should note that research into the problems of SMSI is mainly being conducted in the following areas:

a) a study of real $M/E_xO_y$ catalysts using a range of physical methods;

b) the development and study of model systems (mainly catalysts obtained by covering the metal surface with $TiO_x$ residues);

c) theoretical calculations of the active sites in catalysts with SMSI.

It would appear that significant progress in solving the problem of SMSI could be achieved either by conducting more precise experimental studies of $M/E_xO_y$ catalysts using a range of physical methods or by developing fundamentally new model systems. In this regard the results of studies by Ryndin et al.,[173–184] in which the directed synthesis of $M-E^{n+}$ heteroatomic active sites similar to the active sites supposedly existing in real $M/E_xO_y$ catalysts on the surface of an inert matrix has been carried out using organometallic chemical methods, are of interest. The ideas developed by Ermakov[4–8] form the basis of the synthesis of the $(M + E^{IV})/SiO_2$ catalysts. As a result of a reaction between Group IV organometallic compounds with $SiO_2$, bonding of the surface hydroxide groups occurs, while treatment in $H_2$ results in the formation of fixed, coordinatively unsaturated $E^{IV}$ ions. When organometallic compounds of Group VIII metals are subsequently deposited, they interact with the coordinatively unsaturated $E^{IV}$ ions to form $M-E^{n+}$ bonds. With this method it is possible to obtain active sites directly by synthesis rather than as a result of high-temperature reduction as in the case of $M/E_xO_y$ catalysts.

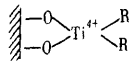
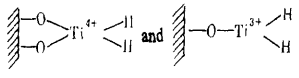
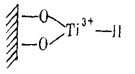
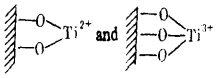
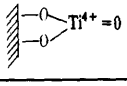
We shall briefly summarise the results obtained from the studies on model $(M + E^{IV})/SiO_2$ systems.

## 1. Information about the state of surface $E^{IV}$ ions

### a) State of $E^{IV}$ before deposition of a Group VIII metal

It follows from the chemisorption and TPD data of Ryndin et al.[180] that treatment of fixed Ti and Zr organometallic complexes with hydrogen either gives surface hydride complexes or leads to the formation of low-valent ions that are not bound to hydrogen. The composition of the surface compounds depends on the treatment conditions of the samples, principally on the temperature of treatment (Table 1). The presence of low-valent ions in $E^{IV}/SiO_2$ samples is confirmed by the X-ray photoelectron spectroscopy data.[180]

**Table 1.** Composition of the surface compounds for the system 1.1% $Ti/SiO_2$.[180]

| Activation conditions | Average degree of oxidation | H/Ti | Surface compounds |
|---|---|---|---|
| No treatment | 4.0 | – |  |
| $H_2$, 423 K | 3.4 | 2.3 |  |
| $H_2$, 573 K | 3.0 | 1.2 |  |
| $H_2$, 873 K | 2.7 | 0.1 |  |
| $O_2$, 673 K | 4.0 | – |  |

According to the electron microscopy data, disperse oxide phases or extended two-dimensional formations of $E^{IV}$ compounds are not formed in reduced $E^{IV}/SiO_2$ samples.[180] It follows from the data of EXAFS that the reduced $Zr/SiO_2$ catalysts mainly contain isolated Zr ions bound to oxygen of $SiO_2$.[179,180]

### b) State of $E^{IV}$ in the presence of M

This information may be obtained from data on the quantity of $O_2$ consumed in the oxidation of $(M-E^{IV})/SiO_2$ samples at different temperatures. For all the $(M-E^{IV})/SiO_2$ systems the quantity of $O_2$ consumed in oxidation was higher than that corresponding to the stoichiometry of O/M = 1 that is characteristic of $M/SiO_2$ (Table 2). These data indicate that in the model catalysts the promoter ions occur in a low oxidation state.[173–184]

**Table 2.** Quantity of $O_2$ consumed in the oxidation of $(M + E^{IV})/SiO_2$ samples at 673 K.[176,177,183,184]

| Catalyst, wt.% | $M_s/M_t^*$ | Atomic ratio | | $N^{**}$ |
|---|---|---|---|---|
| | | O/M | $O/E^{IV}$ | |
| 2.5% Pt | 0.66 | 0.97 | – | – |
| 0.9% Ni+1.1% Ti | 1.00 | 2.44 | 1.00 | 2.7 |
| 2.0%Pd+5.2%Zr | 0.84 | 1.35 | 0.12 | 3.8 |
| 3.2%Pt+1.1%Ti | 0.71 | 1.52 | 0.37 | 3.2 |
| 2.7%Pt+5.3%Zr | 0.79 | 1.31 | 0.11 | 3.8 |
| 2.0%Pt+4.0%Hf | 0.78 | 1.26 | 0.13 | 3.7 |

*Fraction of surface atoms of metal.
**Average degree of oxidation of $E^{IV}$.

## 2. Properties of the metal particles of $(M + E^{IV})/SiO_2$ catalysts

### a) Dispersity of metal particles

In all cases the introduction of small quantities of $E^{IV}$ into catalysts containing Ni, Pd, or Pt on $SiO_2$ results in a decrease in the metal particle size and a narrower distribution of particle size, while the stability of the metal particles towards sintering increases. This is suggested by the data of electron microscopy (Fig. 5), chemisorption (Table 2), and X-ray photoelectron spectroscopy.[176]

### b) Chemisorptive properties

Palladium and platinum catalysts on $TiO_2$ and $ZrO_2$ obtained from organometallic compounds contain dispersed metal particles (15 Å after reduction at 823 K). These catalysts adsorb virtually no $H_2$ (H/M = 0.01) or CO (CO/M = 0.05).[176,183,184]

Modified Pd catalysts are also characterised by a reduced chemisorption of CO and $H_2$. It follows from a comparison of the dispersity of Pd in (Pd + Zr)/$SiO_2$ and (Pd + Ti)/$SiO_2$ catalysts with a quantity of adsorbed $H_2$ and CO that the degree of coverage of the surface of Pd with these molecules is less than 50%. In the presence of Ti ions on the surface of $SiO_2$ platinum also exhibits

decreased chemisorption of $H_2$ and CO (H/Pt = 0.2, CO/Pt = 0.2).[176,183,184] Thus, the introduction of $E^{IV}$ ions on to the surface of $SiO_2$ leads qualitatively to the same effects relative to chemisorption on Group VIII metals as the deposition of these metals on $TiO_2$ or $ZrO_2$.

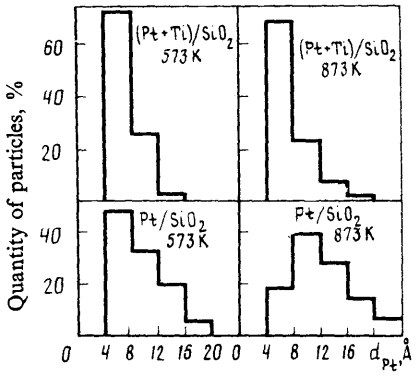



**Figure 5.** Dependence of the distribution of particle size on the temperature of reduction of the catalysts.[176]

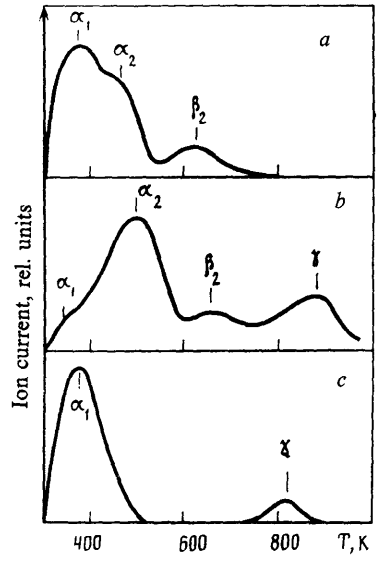
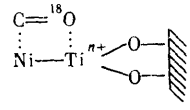



**Figure 6.** Thermal desorption spectra of $^{13}CO$ from nickel catalysts reduced at 823 K.[178] *a*, 0.72% $Ni/SiO_2$; *b*, (0.94% Ni + 1.1% Ti)/$SiO_2$; *c*, 0.47% $Ni/TiO_2$.

The nature of the adsorption of CO on Ni catalysts was studied by Alekseev et al.[178] by means of TPD. Three forms of adsorbed CO characterise the spectrum of the thermal desorption of CO from the surface of $Ni/SiO_2$ (Fig. 6). Two low-temperature molecular forms $\alpha_1$ and $\alpha_2$ occur with temperatures of the desorption maximum ($T_{max}$) at 370 and 450 K together with a medium-temperature form $\beta_2$ with $T_{max}$ = 620 K, which results from the recombination of C and O on the surface of nickel.

The TPD spectrum of the desorption of CO from the surface of a (Ni + Ti)/$SiO_2$ can be represented qualitatively as the sum of the TPD spectra of desorption from the surface of $Ni/SiO_2$ and $Ni/TiO_2$ catalysts. This phenomenon suggests that Ni particles of two types are present in the modified catalyst: 1) particles with chemisorptive properties that are similar to $Ni/SiO_2$; 2) those with properties that are similar to $Ni/TiO_2$.

The spectrum of the thermal desorption of CO from the surface of $Ni/TiO_2$ differs from that for the thermal desorption from the surface of $Ni/SiO_2$ by virtue of the presence of a high-temperature dissociative $\gamma$ form, which represents the dissociatively adsorbed CO at the metal–support interface. This assertion follows from the fact that for the $Ni/TiO_2$ catalyst the $\gamma$ form plays an active part in the heteroexchange of the oxygen in $C^{18}O$ with lattice oxygen. In the case of $Ni/SiO_2$ this reaction does not occur. The heteroexchange of $C^{18}O$ with oxygen of the support on a (Ni + Ti)/$SiO_2$ catalyst suggests that Ti ions in an oxygen environment form part of the active sites on which dissociative adsorption of $C^{18}O$ occurs:[178]




For Pd catalysts the nature of the activation of CO was studied by means of IR spectroscopy. In addition to the absorption bands corresponding to the linear and bridged forms of CO adsorption on metallic palladium, in the adsorption of CO on (Pd + Zr)/$SiO_2$ an additional absorption band appears at 1610 $cm^{-1}$, whose intensity increases, and which is shifted 10 $cm^{-1}$ to higher frequency with an increase in the CO pressure (Fig. 7).[184] From the results obtained and also the literature data the absorption band at 1600 $cm^{-1}$ can be attributed to the adsorption of CO on mixed active sites involving Pd atoms and Zr ions.

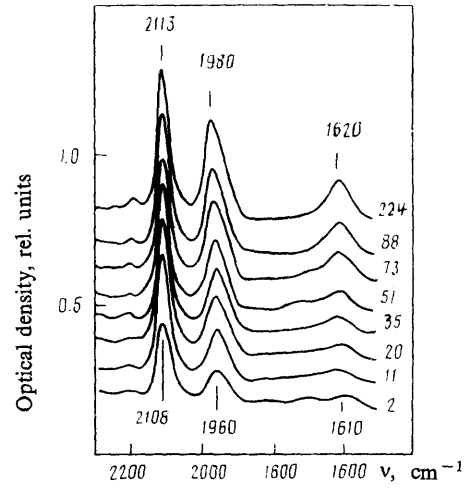



**Figure 7.** IR spectra of CO adsorbed on a (1.7% Pd + 5.2% Zr)/$SiO_2$ catalyst reduced at 573 K.[184] The figures by the curves correspond to the CO pressures (in Torr).

**c) Study of the electronic state of supported elements**

Information about the electronic state of Pd and (Pd + Zr)/$SiO_2$ systems was obtained by means of X-ray photoelectron spectroscopy. When Pd was supported on silica gel modified with Zr ions, there was an increase in $E_{bind}$ for the $3d_{5/2}$ level of Pd by 0.6–1.0 eV compared to $E_{bind}$ for this level in Pd/$SiO_2$, corresponding to a reduction in electron density on the Pd atoms in the presence of Zr ions. The electron-deficient nature of Pd in (Pd + Zr)/$SiO_2$ was also suggested by the IR spectroscopic data.[183,184] Since samples of similar dispersity were being compared, this positive shift could not be due to a dimensional effect but was caused by an interaction between supported components in the (Pd + Zr)/$SiO_2$. In the case of (Pt + Ti)/$SiO_2$ there was also a tendency for $E_{bind}$ of the $4f_{7/2}$ level of Pt to increase, but these changes were of the same order as the experimental error.[176]

After deposition of Pd and Pt on samples of Zr/$SiO_2$ and Ti/$SiO_2$ it was not possible to detect changes in the binding energies of levels in Ti and Zr. However, deposition of Pd and Pt results in a decrease in the relative intensity of the spectrum of the promoting element by 20% on average. These findings suggest that a proportion of the ions of the promoting elements is shielded by the metal particles.

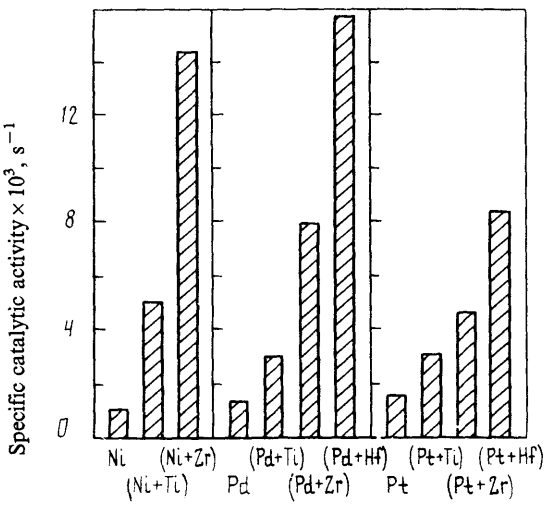



**Figure 8.** Effect of a Group IV element on the activity of a Group VIII metal in the hydrogenation of CO at 523 K.[176,177,183,184]

**d) Catalytic properties**

In all cases the presence of $E^{IV}$ ions in Ni, Pd, and Pt catalysts causes an increase in activity of the supported metal in the hydrogenation of CO. At the same time the selectivity of the process also varies—for Ni the yield of $C_2$–$C_3$ hydrocarbons increases to 30%, while for Pd and Pt the output of hydrocarbons decreases and the yield of methanol increases, reaching 95–99% at 523 K and a pressure of 10 atm. For all the Group VIII metals the promoting effect of the $E^{IV}$ ions increased in the series: Ti < Zr < Hf (Fig. 8).

In the hydrogenation of benzene a decrease in the activity of (M + $E^{IV}$)/$SiO_2$ catalysts compared to M/$SiO_2$ occurred by a factor of up to 10. At the same time the activity of the model systems was similar to that of M/$TiO_2$ and M/$ZrO_2$ catalysts.[173–184]

In the hydrogenolysis of ethane the activity of (M + $E^{IV}$)/$SiO_2$ systems, like that of M/$E_xO_y$ catalysts, decreases by a factor of 100–1000 compared to M$SiO_2$. It should be noted that after high-temperature oxidation the inhibitory effect of $E^{IV}$ ions on the activity of the model systems in the conversion of hydrocarbons disappears in a similar manner to that observed for M/$E_xO_y$ systems.

We should point out that the decrease in activity of (M + $E^{IV}$)/$SiO_2$ catalysts occurs even at low reduction temperatures (573 K). In this respect the model systems studied by Ryndin et al.[173–184] differ from metals on bulk oxides, where SMSI occurs after their reduction at high temperatures (above 773 K). This difference occurs because in the M/$E_xO_y$ catalysts the active sites that are needed for SMSI to develop are only formed during high-temperature reduction. At the same time formation of the active sites for the model systems actually occurs during synthesis of the catalaysts when the second component is deposited on the silica gel modified with $E^{IV}$ ions.[181,184] Therefore, high reduction temperatures are not needed for the effects of SMSI to be exhibited when model (M + $E^{IV}$)/$SiO_2$ catalysts are used.

## 3. Possible causes of the effect of Group IV elements on the properties of supported metal particles

Let us examine the possible models of surface formations in supported model (M + $E^{IV}$)/$SiO_2$ catalysts (Fig. 9).[179]

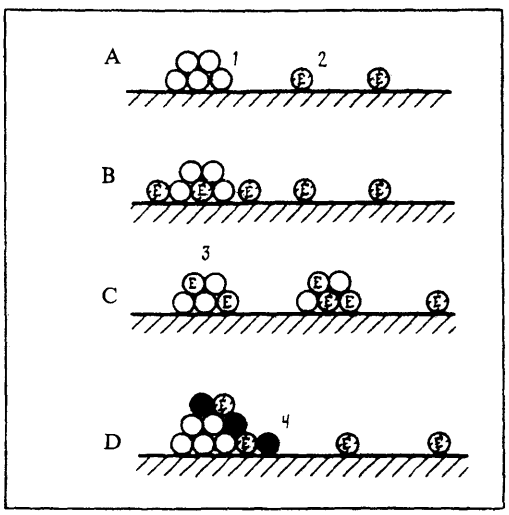



**Figure 9.** Possible models of surface formations in catalysts supported on $SiO_2$:[179] *1*, atom of Group VIII metal; *2*, surface ion of promoting element $E^{IV}$; *3*, atom of $E^{IV}$ element in a zero valence state; *4*, oxygen ion.

**Model A.** Metal particles that are not bound to $E^{IV}$ occur on the surface. This separate distribution of M and $E^{IV}$ does not explain the increase in dispersity nor the decrease in catalytic activity in the

conversion of hydrocarbons. However, it cannot be excluded that a proportion of the metal particles is located on the surface of $SiO_2$ without interacting with $E^{IV}$.

**Model B.** In this case it is assumed that the metal particles interact directly with the surface ions of the transition element in a similar manner to that previously proposed.[8]

**Model C.** This model assumes the formation of particles of an alloy of modified element and metal. Theories of this type have also been advanced to explain the properties of $M/E_xO_y$ systems.[3] However, for the model systems studied by Ryndin et al.[173-184] such a model is not consistent with the presence of $E^{IV}$ ions in an intermediate oxidation state in the catalysts.

**Model D.** Adsorption of $E^{IV}$ oxide occurs on the surface of a cluster of metal M. However, this model is at variance with the decrease in surface concentration of $E^{IV}$, as indicated by the data of X-ray photoelectron spectroscopy.

Thus, a model of the type B can explain the following results:

a) the increase in dispersity of metal particles in the presence of $E^{IV}$ through the stabilisation of metal clusters on fixed $E^{IV}$ ions;

b) the change in catalytic properties as a result of the change in electronic state of the metal cluster;

c) the effect of initial oxidation. Treatment of $(M + E^{IV})/SiO_2$ samples with oxygen at a high temperature leads to oxidation and segregation of the components (M and $E^{IV}$) followed by sintering of the metal;

d) the change in chemisorptive properties of the metal through a change in its electronic state.

At the same time the existence of $M-E^{IV}$ bonds was not revealed by the direct EXAFS method in these studies,[173-184] which would constitute the most important evidence in favour of model B occurring for the model systems. The absence of information about the existence of $M-E^{IV}$ bonds in the EXAFS spectra is evidently related to the reasons discussed in Section III. However, a set of evidence for the existence of an interaction between the metal and promoter in $(M + E^{IV})/SiO_2$ catalysts has been obtained.[173-184] Thus, it has been demonstrated that the following occur:

1) a change in the spectroscopic properties of $Ti^{3+}$ ions when an active metal is deposited (EPR data);

2) a change in the electronic state of the components in model systems and also shielding of a proportion of the ions of promoter by metal clusters (IR and X-ray photoelectron spectroscopic data);

3) the presence in the model catalysts of an additional absorption band due to CO in the region of 1600 $cm^{-1}$ (IR spectroscopic data);

4) the presence of a high-temperature $\gamma$ form of adsorbed CO in the TPD spectra of model systems as well as data on the heteroexchange of $C^{18}O$ with oxygen of the support (TPD data);

5) retention of a chemical bond with the surface of silica gel for $E^{IV}$ ions during reduction of the catalysts (IR and EXAFS spectroscopic data).

Thus, the data of TPD, EPR, EXAFS, and IR spectroscopy obtained from studies of model systems[173-184] in combination with chemisorption and catalytic electron microscopy data support the validity of model B for $(M + E^{IV})/SiO_2$ catalysts. This model does not exclude additional reasons (in addition to the change in electronic properties of a cluster of metal M) for the change in catalytic activity. For example, the increase in activity in the hydrogenation of CO may occur as a result of activation of CO on mixed active sites according to Scheme (I), as put forward in a number of studies.[18,49,130,131,135] At the same time the increase in activity of $(M + E^{IV})/SiO_2$ catalysts in the hydrogenation of CO in the promoter series Ti < Zr < Hf appears reasonable since the strength of the $E^{IV}-O$ bond increases in the same series.[185] Thus, by varying the nature of the Group IV ion in the chemisorption complex (Scheme I), the strength of the bond between the oxygen atom of the CO molecule and the $E^{IV}$ ion will increase in the above series. This may assist the addition of hydrogen adsorbed on the metal to the carbon atom to form a formyl complex, which acts as an intermediate in the synthesis of methanol from CO and $H_2$.[185]

## 4. Mechanism of the metal–support interaction in $M/E_xO_y$ systems

As has already been mentioned in Section III, in an examination of the effects of SMSI a considerable number of reasons have been suggested in the literature to explain the unusual properties of metals supported on $TiO_2$ and other oxides of transition elements. However, not one of these theories has received conclusive experimental confirmation. It is possible that for catalysts containing metal particles on transition element oxides there is no single cause of the effects of the so-called SMSI but the different characteristics of the metal properties have different causes. Let us examine the above mechanisms in terms of the results obtained by Ryndin et al.[173-184]

In one of the studies of Baker[89] it was found in a $Pt/TiO_2$ catalyst that Pt particles with a cross-section of several tens of Ångstroms had a flat, frequently hexagonal shape and were located on reduced sections of the surface of $TiO_2$ ($Ti_4O_7$ suboxide), which, according to Baker, gives rise to SMSI. The difference in shape and size of the metal particles in $M/TiO_2$ catalysts in this study[89] was due to the difference in the methods of preparing these catalysts. A study of $M/TiO_2$ catalysts prepared via fixed metal complexes showed that over a wide temperature range of reduction (573–823 K) the particles of supported metal retained a spherical form.[173-184] Furthermore, these catalysts exhibit all the catalytic and chemisorptive properties that are characteristic of SMSI. Consequently, the presence of flat metal particles located on the surface of suboxides such as $Ti_4O_7$ is not a necessary condition for the effects of SMSI to occur.

The results obtained in these studies[173-184] on $(M + E^{IV})/SiO_2$ catalysts suggest that intermetallic compounds and dispersed phases of $E^{IV}$ oxides are not present in these catalysts. Hence the common nature of the catalytic and chemisorptive properties of $M/E_xO_y$ and $(M + E^{IV})/SiO_2$ catalysts cannot be explained in terms of mechanisms that assume the formation of intermetallic compounds and the transfer of electron density to the metal particles from the bulk of the support.

In recent years in the literature there has been an increasing amount of publishd data to suggest that direct interaction between atoms of the active metal and low-valent surface ions of the transition element causes the SMSI effects.[67,161,186,187] Theoretical calculations of $PtTiO_5$ [67] and $Ni_3Ti_2O_5$ [187] clusters showed that in these cases a strong covalent bond exists between the metal atoms and the $Ti^{n+}$ ion. At the same time it appears that the metal atoms are positively charged as a result of the transfer of electron density from the Ni atom to the $Ti^{n+}$ ion. In an analysis of the properties of the model $(M + E^{IV})/SiO_2$ catalysts,[173-184] a model of the active sites involving interaction between the metal atoms and the promoter ions was put forward. Taking into account the similarity in the properties of $(M + E^{IV})/SiO_2$ and $M/E_xO_y$ systems, this model can be extended to $M/E_xO_y$ catalysts. In fact, $RhTi^+$ clusters were

detected in studies of a $Rh/TiO_2$ catalyst using secondary ion mass spectrometry[28,79] while the presence of $Rh-Ti^{n+}$ bonds in a $Rh/TiO_2$ catalyst was demonstrated by EXAFS in two studies.[86,87]

The idea that the reactants are activated at the boundary between the metal and support is a logical addition to the mechanism of Horsley,[67] since in its original exposition this theory[49,50] assumes that the catalytic and chemisorptive properties of $M/E_xO_y$ catalysts change both as a result of a change in the electronic properties of the metal and through the activation of the reactants at the metal–support boundary. In the opinion of Burch et al.,[20,45] participation of cations of the support in the activation of a CO molecule will assist the hydogenation of CO and thus permit an increase in activity of $M/E_xO_y$ catalysts. The existence of mixed active sites in $M/E_xO_y$ catalysts has been demonstrated experimentally by Bredikhin et al.[136–139] The existence of such sites in $(M + E^{IV})/SiO_2$ catalysts has been demonstrated in the studies by Ryndin et al.[173–184]

The mechanism which assumes the diffusion of reduction products of the support to the surface of the metal particles has gained the widest recognition in the literature.[16,37,140] According to this mechanism, the reduction in chemisorptive properties of the metal and also the decrease in activity of $M/E_xO_y$ catalysts in the conversion of hydrocarbons is due to blocking of the surface of the active metal with particles of the type $TiO_x$ while the increase in activity of these systems in the hydrogenation of CO is due to the expansion of the metal–support interface, which results in an increase in concentration of mixed active sites incorporating metal atoms and ions of the support.[16,140] Results that would exclude this mechanism were not obtained in studies of $M/E_xO_y$ catalysts.[173,184]

Furthermore, for the model $(M + E^{IV})/SiO_2$ catalysts the shielding of a proportion of the $E^{IV}$ ions occurs as a result of their interaction with the metal atoms. Thus, a situation occurs for the model $(M + E^{IV})/SiO_2$ systems which is the opposite of what is proposed in the mechanism put forward by Meriaudeau[37] and Haller.[140] Consequently, when there are no $E_xO_y$ residues on the surface of the metal (i.e., with no blocking of the surface of the metal), in the $(M + E^{IV})/SiO_2$ catalysts a reduction in chemisorption of CO and $H_2$ occurs as well as a decrease in activity of these catalysts in the conversion of hydrocarbons and an increase in their activity in the hydrogenation of CO. It may be assumed from these results and also the results of Burch and Flambard[50] which suggest that $M/TiO_2$ catalysts have high activity in the hydrogenation of CO even at low reduction temperatures, when the effect is absent that shielding of the surface of the metal with $TiO_x$ particles is not a necessary condition for SMSI to occur.

It should be noted that the origins of SMSI in $M/E_xO_y$ catalysts may be more complex than those in the model $(M + E^{IV})/SiO_2$ systems. Therefore, more rigorous arguments are required to prove the decoration mechanism for $M/E_xO_y$ catalysts.

Thus, the results of a number of studies[4–8,28,79,86,136–139,173–184] suggest that SMSI in $M/E_xO_y$ catalysts can be explained in terms of a mechanism which assumes a direct interaction between the metal atoms and low-valent ions of the support and the formation of mixed active sites involving metal atoms and support ions at the metal–support interface.

The above data show that supported metal catalysts obtained from organometallic compounds are convenient model systems for a study of the mechanism of SMSI. With the use of organometallic compounds it is possible not only to obtain highly dispersed metal catalysts but also to carry out the directed synthesis of active sites on the surface of supports and thus prepare catalytic systems with given chemical properties. From the synthesis and study of model $(M + E^{IV})/SiO_2$ catalysts obtained from organometallic compounds it is possible to make a critical investigation of the mechanisms that have been put forward in the literature to explain the effects of SMSI.

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