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Strong metal–carrier interaction and its role in catalysis

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ABSTRACT. The present state of the problem of the strong interaction of a metal with the carrier is analysed and the main causes responsible for the appearance of this effect are considered. Data demonstrating the influence of the strong interaction of a metal with the carrier on the absorption and catalytic properties of deposited metallic catalysts are presented.

The bibliography includes 175 references.

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I. Introduction

The term "strong metal–carrier interaction", which is so widely used nowadays to describe a wide variety of effects in reduced deposited metallic catalysts, was introduced by Tauster[1] to designate interactions whose essential feature involves the formation of a covalent bond between the atoms of the deposited metal and the cations of carriers such as TiO_2 [1] and vanadium, manganese, niobium, and tantalum oxides.[2]

A classification of metal–carrier interactions has been proposed;[3,4] a weak interaction (on non-reducible oxides of the type SiO_2, Al_2O_3, etc.), a moderately strong interaction (in zeolites), and a strong interaction (on oxides capable of being reduced at elevated temperatures). Without going into the details of the mechanisms, one can give the following phenomenological definition of the effect of the strong interaction of a metal with the carrier (SIMC): the SIMC effect is the term applied to the group of phenomena leading to the alteration of the electronic and structural properties of deposited metallic particles, which is accompanied by the corresponding changes in the absorption and catalytic (rate of reaction, selectivity) properties.

During the years which have elapsed since the publication of Tauster's study, a large number of studies devoted to the nature of the SIMC effect have been published. It was found that the phenomenon is much more complex than was suggested in the first investigations and the aim of the present review is therefore to compare the earlier data with the results published recently in order to understand more clearly the nature of the effect and the direction which will be taken by further studies.

II. Sources of the effect of the strong interaction of a metal with the carrier

In modern literature, the following sources of the SIMC effect have been specified:[3,5–10] electronic (collective and local) interactions, migration of the carrier on to the surface of the metallic particles and encapsulation of the metal in the carrier, the formation of alloys and intermetallic compounds, and thermodynamic factors.

1. Electronic interactions

The explanation of the SIMC effect in terms of collective electronic phenomena is based on Schwab's idea[11] that the Schottky theory is applicable to the metal–carrier interface in catalytic systems. If the catalyst contains an *n*-type semiconductor with an electron work function φ_n (on reduction, TiO_2 actually becomes precisely such a semiconductor) and a metal with a work function φ_m, where $\varphi_n < \varphi_m$, then electrons will migrate from the semiconductor to the metal until the chemical potentials of both solids (Fermi levels) are equalised. Under these conditions, the layer of the semiconductor adjoining the metal is depleted in current carriers and becomes positively charged, while the layer of the metal becomes negatively charged. A potential barrier, called the Schottky barrier, arises at the interface. If the Schottky theory is applicable to deposited metallic catalysts, then the change in the concentration of conductivity electrons does indeed influence the catalytic and adsorption properties, and this constitutes one way of explaining the SIMC effect, which has in fact been used in some studies.[12] However, the question arises of the meaning of the change in the concentration of conductivity electrons in the metal if their number in the latter is 10^{23} per cm^3. In order to determine from experimental data[13] the real concentration of electrons migrating from the carrier to the metal in conformity with the Schottky theory, the potential difference at the nickel–germanium interface was calculated. It was found that one electron is transferred from the conductivity band of germanium per 10^4 atoms. Evidently such a transition cannot alter in any way significantly either the concentration of conductivity electrons or the nature of the filling of the *d* band and it cannot influence greatly the adsorption and catalytic properties [of the metal]. This proof has been quoted also in other communications[14,15] in which deposited palladium catalysts were considered. Many investigators altogether cast doubt on such an approach, in which conductivity electrons are regarded as being responsible for the catalytic and adsorption properties of the metal. Furthermore, there is no certainty that the Schottky theory is applicable to the metal–carrier interface in real catalysts, because the potential jump at the interface may be due to the presence of extraneous poorly conducting layers between the metal and the semiconductors, for example layers of oxides as well as chemical impurities or lattice defects on the surface. Nevertheless, despite the clear deficiencies of the collective approach, some investigators[16,17] attempted in recent

years to use it to account for the mechanism of the influence of the carrier on the catalytic and adsorption properties of the deposited metal. For platinum deposited on TiO_2 to which Ta^{5+}, Sb^{5+}, or W^{6+} had been added to increase the electronic conductivity of the carrier, a model has been proposed,[18] according to which a platinum particle 20 Å in diameter creates on the carrier an electron-depleted semispherical zone with the radius r = 640 Å (Fig. 1). The authors suggest that electron transfer to platinum reaches an extent sufficient to alter the properties of the deposited metal compared with platinum on a non-doped TiO_2 after reduction at 473 K.

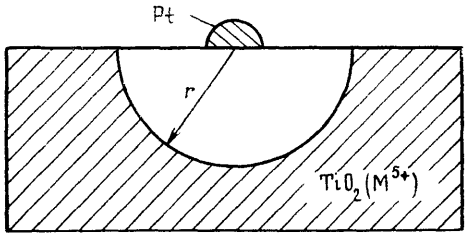


Figure 1. Model of the location of platinum crystals on the surface of modified TiO_2.[18]

Explanations associated with the local interaction of the metal atoms with a definite centre on the carrier surface are better founded.

TiO_2, which is reduced, losing O_2 on heating *in vacuo*, is the most typical carrier for the SIMC effect.[5] Hydrogen, dissociatively adsorbed on the deposited metal is capable of reducing TiO_2 at elevated temperatures. According to EPR spectroscopic data,[19] the deposited Ti/TiO_2 catalyst contains about 0.3% of Ti^{3+} ions after reduction in H_2 at 573 K. The ions are formed by the reaction

$$Ti^{4+} + O^{2-} + H = Ti^{3+} + OH^-.$$

Four different forms of Ti^{3+} have been observed for the same system,[20] two of which are on the surface and are sensitive to the adsorption of CO and H_2 and one form, with $g_\perp$ = 1.969 and $g_\parallel$ = 1.936, is present only on Pt/TiO_2 and is absent from reduced TiO_2. Reduction at 773 K leads also to the formation of anionic vacancies (Y) on the carrier surface:

$$2Ti^{4+} + 2O^{2-} + 2H = 2Ti^{3+} + O^{2-} + H_2O + Y.$$

Further, it has been noted in a review[5] and in a later study[20] that it is by no means always possible to detect the signal due to Ti^{3+} in the EPR spectra. Moreover, the ease of the migration of the anionic vacancies from the surface into the bulk of the carrier has been emphasised.[21] Thus reduced TiO_2 constitutes a mobile system with surface and bulk-phase anionic vacancies, OH^- anions, and Ti^{3+} cations in a state of dynamic equilibrium. We may note that, apart from isolated Ti^{3+}, the appearance of conducting Magneli phases (Ti_nO_{2n-1}) has been observed in deposited metallic catalysts reduced at 743 and 773 K.[22,23] The deposition of the metal (in the given instance Pd) reduces the electron work function of the Magneli phases and prevents their oxidation in O_2 at 300 K.[22]

Experiments using XPS, ^1H NMR, EPR, and the adsorption of H_2 demonstrated that at temperatures above 573 K the hydrogen adsorbed on the metal (Ni, Pt, Rh) spills over into the oxygen vacancies of the reduced TiO_2 with formation of the hydride-like forms $Ti-H^{3+}$.[24]

It is noteworthy that the relation between the SIMC effect and the anatase–rutile transition in deposited metallic catalysts reduced at 643–873 K has been emphasised in a number of recent studies.[25–27]

In the definition of the term SIMC,[1] it was postulated that a covalent bond is formed between the metal atom and the Ti^{3+} cation formed on reduction of the carrier. Quantum-chemical calculations for the interaction of platinum and TiO_2 using two cluster models (Fig. 2)[28] confirmed the validity of this hypothesis. The model (II) in which platinum atoms are inserted in the oxygen vacancies of the carrier with formation of a bond between Pt and Ti^{3+}, is more convenient. Not only a covalent interaction but also an ionic interaction involving the transfer of an electron from Ti^{3+} to a Pt atom takes place in this model. The disposition of the metal atoms outside the TiO_6 octahedron gives rise to only weak interaction as a consequence of the repulsion between Pt and the nearest O^{2-} ions. Indirect evidence for the metal–carrier interaction in highly disperse metallic systems has been obtained by spectroscopic methods. Thus it has been shown by the XPS method[29] that, after the reduction in H_2 at 773 K, the binding energy of the $4f_{7/2}$ level of Pt in the 5% Pt/TiO_2 system diminishes by 9.4 eV compared with the same specimen reduced at 473 K. Electron transfer from TiO_2 to Ni atoms has been observed by the XPS and AES methods in the Ni/TiO_2 system in which nickel was deposited in a thin layer on TiO_2 subjected to a preliminary vacuum treatment at 673 K.[30] The degree of electron transfer is 0.1 of an electron per Ni atom.[30] An increase in electron density on the Rh and Pt clusters as a result of their interaction with Ti^{3+} cations after high-temperature reduction has been observed by the XPS, AES, SIMS, and ISS methods.[31] Within the framework of this model, it is easy to explain the disruption of the SIMC effect by O_2, which leads to the disappearance of oxygen vacancies in the carrier and hence of Ti^{3+} cations.

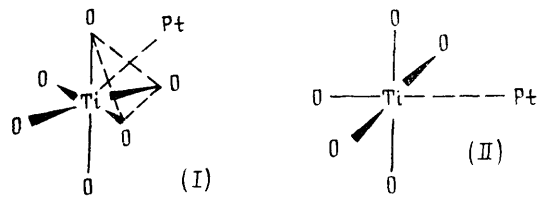


Figure 2. Cluster models for quantum-chemical calculations for the local interaction of a Pt atom with TiO_2.[28]

Direct evidence for the formation of a direct $Rh-Ti^{n+}$ chemical bond in the Rh/TiO_2 catalyst after reduction at 773 K[32] and of the $Rh-Ta^{n+}$ bond in the Rh/Ta_2O_5 catalyst after reduction at 858 K[33] has been obtained recently by the EXAFS method, the cation of the carrier being located in the first coordination sphere of Rh with a radius of 2.55 Å (2.68 Å in the Rh–Ti alloy) and about 1.7 Å

(2.73 Å in the Rh–Ta alloy) respectively. On the other hand, if the Rh/TiO_2 catalyst is obtained not by impregnation with a $RhCl_3$ solution but by the reaction of $Rh(\eta^3\text{-}C_3H_5)_3$ with the OH groups on the TiO_2 surface and subsequent reduction, then according to the EXAFS and electron microscopic data, thin three-layer positively charged Rh clusters are formed on the TiO_2 surface (Fig. 3) and interact strongly with the surface oxygen which remains in the catalyst even after reduction in H_2 at 773 K.[34]

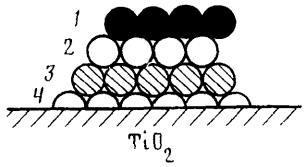


Figure 3. The structure of a Rh cluster fixed on the surface of TiO_2: *1–3*, upper, second, and first layers of rhodium atoms respectively; *4*, layer of oxygen ions of the carrier.[34]

An interesting approach to demonstrating the interaction of the Ni clusters with Ti^{3+} in the Ni/TiO_2 system has been used in a study[35] where the properties of the nickel deposited on the SiO_2 surface, modified by Ti^{3+} cations as a result of the attachment of $Ti(BH_4)_3$ and subsequent removal of the ligands *in vacuo* at 423 K, proved to be close to those of the Ni/TiO_2 catalyst reduced at 773 K. A similar result was obtained for palladium deposited on the SiO_2 surface and the surface of carbon doped with Pr^{3+} cations via organometallic precursors.[36] However, the SIMC mechanism examined above is not apparently the only one.

The possibility of a strong interaction of the deposited metal with the acid centres of the carrier has been frequently pointed out in the literature. For example, Zur Loye et al.[37] investigated the magnetic properties of the 1% Ni/TiO_2 catalyst prepared in different ways. It was then found that extrapolation to zero field of the specific magnetisation (σ) of the catalyst obtained by ion exchange and reduced at 773 K yields a value close to σ for the metallic nickel powder, while σ for the catalyst obtained by the impregnation method is diminished after reduction under the same conditions and corresponds to the reaction of 36% of the nickel with TiO_2. It has been suggested that the difference in the behaviour of the given system is due to the difference in the concentration of the surface OH groups, which is greatly reduced in the specimen obtained by ion exchange.

If one postulates the interaction of the metal with the acid centres, then the SIMC effect should be manifested on zeolites, aluminosilicates, Al_2O_3, ZrO_2, modified SiO_2, and other carriers with acid properties. The occurrence of electronic interaction between Ru clusters and Lewis and Brønsted acid centres has been demonstrated by IR spectroscopy and the thermoprogrammed reduction method in a study[38] of a series of ruthenium catalysts deposited on SiO_2, Al_2O_3, $SiO_2.Al_2O_3$, and an HY zeolite. The increase in acidity in the sequence $SiO_2 < Al_2O_3 < SiO_2.Al_2O_3 < HY$ is correlated with the increase in the electron deficiency on the Ru centres for the adsorption of CO. An XPS study of Ni, Pd, Re, Rh, Ru, and Pt, deposited on SiO_2, $\gamma\text{-}Al_2O_3$, and zeolites established that the metals interact to the maximum extent with zeolites, which is probably due to the presence in the latter of the strongest acid centres.[39] According to XPS, EXFAS, and electron microscopic data, the 6–7 and 11–13 Å Pt_{18} and Pt_{45} clusters located within the structure of the H-ZSM-5 zeolite are coordinated to the skeletal oxygen even after reduction at 773 K and exhibit an appreciable electron deficiency.[40] The interactions of platinum with the acid centres of L-zeolites modified by alkali and alkaline earth metal cations, after reduction at 623 K as a result of charge transfer, have been reported in a study[41] where the catalytic activity of the Pt/L-zeolite system was investigated in the hydrogenation of benzene and toluene.

Another example of the interaction of a metal with definite centres on the carrier is provided by the formation of paramagnetic Pt^{3+} cations on heating in O_2 of ammineplatinum deposited on Al_2O_3, which apparently takes place in the presence of a Lewis acid centre on the carrier surface:[42]

$$O^{2-}\text{—}Pt^{4+}\text{—}O^{2-} \xrightarrow{\text{reduction}} \square\, Pt^{2+}\text{—}O^{2-} + {}^1/_2O_2,$$
$$\square\, Pt^{2+}\text{—}O^{2-} + L\text{—}Al_2O_3 \xrightarrow{\text{heating}} \square\, Pt^{3+}\text{—}O^{2-} + L^-\text{—}Al_2O_3.$$

In general, the question of the relation between the SIMC and the acid properties requires a serious systematic study, which may yield interesting results when the acid carriers investigated in recent years (such as TiO_2, modified Al^{3+},[43] $\gamma\text{-}Al_2O_3$ treated with $SiCl_4$ [44] and tetraethoxysilane[45] vapours, the chemically mixed $TiO_2\text{–}SiO_2$, $TiO_2\text{–}Al_2O_3$, $Al_2O_3\text{–}SiO_2$, and $ZrO_2\text{–}SiO_2$ carriers,[46–48] and SiO_2 modified by the Sc^{3+}, Mg^{2+}, Fe^{2+}, Zn^{2+}, Al^{3+}, and Ga^{3+} cations[49]) are used for the preparation of deposited metallic catalysts.

Thus the explanations of the SIMC effect within the framework of local ideas reduce to a change in the electronic state of the metal atom and hence of the catalytic and adsorption properties under the influence of some kind of centre on the carrier surface. This is apparently true of an atomically disperse metal and small two-dimensional crystals and also of the atoms in larger metallic particles at the metal–carrier interface.[8]

2. Migration of the carrier onto the surface of metallic particles and encapsulation of the metal in the carrier

The appreciable changes in the properties of metallic particles whose size is 50 Å and more after high-temperature reduction cannot be explained solely by electronic effects. Several groups of investigators[50,51] put forward a hypothesis according to which part of the surface of metallic crystallites is shielded by the partially reduced TiO_2. A series of careful experiments carried out in 1984 confirmed the validity of this hypothesis.[52–54] It was found that TiO_x (where $x < 2$) has the surprising ability to migrate over considerable distances in a short time. For example, in an H_2 atmosphere at 698 K, TiO_x fragments appear on the surface of 120 Å thick nickel film deposited on TiO_2 after only 10 min, including the time necessary for the reduction of the TiO_2 surface.[54] The surface of platinum or rhodium film 30 Å thick on TiO_2 reduced beforehand are half-coated by a TiO_x monolayer after keeping the specimens in H_2 at 673 K for 2 min.[9] The mechanism of the migration of TiO_x is nevertheless not clear. On the one hand, in certain studies[54,55] the diffusion of TiO_x within the crystallites of the deposited metal has been demonstrated and, on the other, since the migration is frequently rapid it is logical to postulate that the carrier penetrates between the grains of the metal.[56] At any rate, the migration requires the dissociation of bonds in the crystal lattice of the carrier

and this can occur when the loss of the Madelung energy is made good by the stronger TiO_x–metal interaction. Thus the appearance of a TiO_x layer on the surfae of the metal supports the SIMC. We may note that not only the TiO_x phase can shield the surface of the deposited metallic particles. On the basis of the results of studies of the adsorption of H_2 and O_2, XPS, and electrical conductivity of the Ni/TiO_2 catalysts reduced at 623 and 773 K and having a nickel particle size of 100–200 Å, the following picture of the phase distribution has been put forward[57] (Fig. 4). Depending on the NiO content, on the surface of the initial catalyst there is either the nickel titanate phase (at a NiO concentration $\leqslant$ 35 mol%) or a mixture of nickel titanate and the NiO phase (at a NiO concentration > 35 mol%).[58] The reduction of 623 K is accompanied by the appearance of Ni crystals stabilised on the surface layer of the $Ni_\delta Ti_{1-\delta}O_2$ solid solution, which partly shields the Ni surface, and of the TiO_x bulk phase. The increase in temperature to 773 K leads to the decomposition of the $Ni_\delta Ti_{1-\delta}O_2$ solid solution and the formation on the surface of the conducting TiO_x of large nickel crystals, whose surface is shielded by the same TiO_x phase.

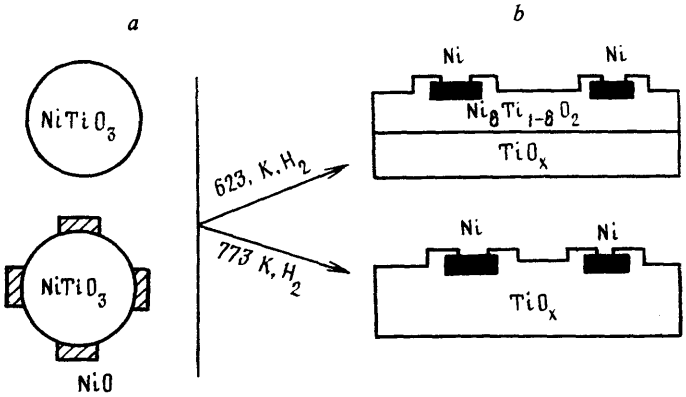


Figure 4. Distribution of the phases on the surfaces of initial (*a*) and reduced (*b*) nickel catalysts deposited on TiO_2.[57,58]

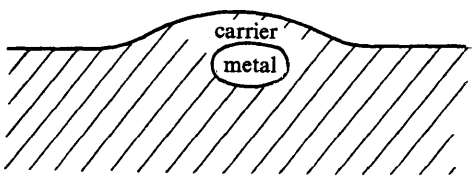


Figure 5. Model of a fully encapsulated metal particle.

The effect involving the spreading of the carrier on the metal surface during reduction is observed not only in metal–TiO_2 catalysts but also in the systems Ni/Nb_2O_5 at 773 K,[59] Ni/CeO_2 at 673 K,[60] and Pt and Rh/V_2O_3 at 773 K [61] and also for carriers which are difficult to reduce such as La_2O_3 in the Pd/La_2O_3 catalysts at 573 K,[29] ZrO_2 in the Rh/ZrO_2 catalysts at 873 K,[62] and SiO_2 modified with WO_3 in the Pt/WO_3–SiO_2 catalysts at 673 K.[29] In the last instances, the spill-over of hydrogen plays a major role in the reduction of the carriers to ZrO_x (with $x < 2$) and WO_2. Apparently even SiO_2 and Al_2O_3 exhibit some mobility in H_2 at high temperatures (about 1200–1300 K) and are capable of partially shielding the surface of the deposited metal.[4] On the other hand, there are carriers which migrate at an even higher rate than TiO_x. Thus an appreciable amount of MnO_x has been detected after heating for only 100 s *in vacuo* at 503 K on nickel films 150 Å thick deposited on MnO.[63]

We may note that the term "encapsulation", which means the immersion of the metallic particle in the carrier, is used fairly frequently in the literature.[64,65] Ultimately, the total encapsulation of the metal (Fig. 5) differs from the total shielding of the metal surface by the carrier perhaps only by the fact that the encapsulated metal does not recover its properties after oxidative treatment,[66] while in the case of the shielded metal in O_2 the carrier film becomes segregated and the metal surface is significantly freed with partial or complete removal of the SIMC effect after further mild reduction (Fig. 6).

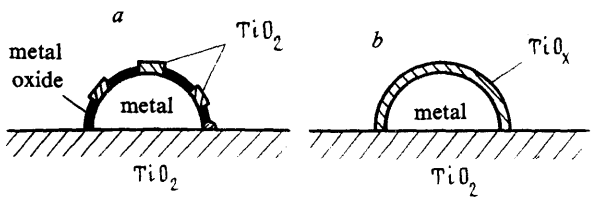


Figure 6. Model of the shielding of the metal surface by the carrier for different types of treatment: *a*, O_2, 673 K; *b*, H_2, 773 K.

Tauster, Vannice, Haller, Dumesic and over investigators,[9,24,29,31,67,68] who studied in detail the SIMC effect, frequently drew attention to the fact that often the carrier does not simply creep mechanically onto the metal, diminishing its surface area, but enters into electronic interactions with it, altering its properties. This can be seen particularly clearly in the study of metals coated by an incomplete TiO_x monolayer.[53,67]

The shielding of the metal surface by TiO_x combined with the electronic interaction is also observed when the metal is deposited on a support modified by TiO_2. Thus the study by XPS and Auger spectroscopic methods of platinum deposited on SiO_2 coated by 1–2 monolayers of TiO_2 showed that, apart from the partial shielding of the metal surface by the TiO_x oxide at high reduction temperatures, anionic vacancies and Ti^{3+} ions are formed and the platinum atoms interact with Ti^{3+}.[69] Admittedly, in contrast to the Pt/TiO_2 catalysts, in the Pt–TiO_2–NiO_2 system the TiO_2 phase exhibits a lower mobility and is more difficult to reduce as a consequence of the formation of strong linkages of the type Si–O–Ti.

3. Thermodynamic factors

In this section we shall consider the thermodynamic aspect of the SIMC effect. Theoretical calculations for the interaction of platinum with TiO_2 have led to the conclusion that, on strong interaction after the high-temperature reduction, the platinum crystallites should become lamellar.[16] This was indeed observed in an electron microscopic study of the Pt/TiO_2 catalyst in an H_2 atmosphere at 1075 K (Fig. 7), TiO_2 being reduced under these conditions to

Ti_4O_7, while the platinum particles on SiO_2 have a spherical shape.[70] Baker[71] showed that in H_2 at 875 K the spreading of platinum takes place after 10 s. Subsequent treatment in O_2 at 875 K of the Pt/TiO_2 catalyst reduced at a high temperature alters reversibly the morphology of the platinum crystals to the spherical form (Fig. 7).[71] From the thermodynamic point of view, this effect can be explained by the fact that platinum wets the surface of the reduced carrier phase more effectively than platinum oxide wets the TiO_2 surface.

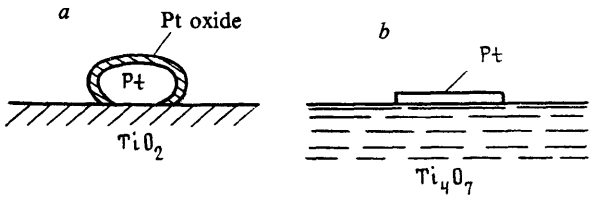


Figure 7. The change in the form of the Pt crystals deposited on TiO_2 and treated in a O_2 atmosphere at 875 K (*a*) and in a H_2 atmosphere at 1075 K (*b*).[70,71]

The spreading of the metal on the surface of the reduced TiO_2 has also been observed for nickel[72] and iron[73] but not for palladium[74] and rhodium.[75]

The existence of lamellar metal crystals is not an unambiguous demonstration of the SIMC. Firstly, this is associated with the experimental difficulty of identifying low-contrast images and, secondly, lamellar crystals have been observed on Ni/SiO_2,[76] Ru/SiO_2,[77] and Ru/Al_2O_3 [78] catalysts where there is apparently no SIMC effect. Evidently in certain systems weak physical forces are insufficient to alter the degree of wetting of the oxide surface by the metal.

The thermodynamic approach can explain also the high mobility of certain carriers coating the metal surface. Ko and Gorte[79] showed that TiO_x and NbO_x wet the platinum surface 5 times more effectively than Al_2O_3 and SiO_2. A comparative study of sorbed TiO_2 and Al_2O_3 layers on nickel yielded similar results. Under these conditions, the TiO_x monolayer occupying 0.1 of the nickel surface alters the catalytic and adsorption properties of the metal to the same extent as for coating by 0.7 of a Al_2O_3 monolayer.[67]

Finally, a thermodynamic model has also been developed for the encapsulation of the metal, according to which the free energy of the deposited system diminishes when the metallic particle is immersed in the carrier provided that the surface energy of the metal exceeds significantly the energy at the metal–carrier interface.[65]

4. The formation of alloys and intermetallic compounds

It was already noted above that the SIMC effect can be manifested also when a metal is deposited on SiO_2 and Al_2O_3. The reduction of the Pt/Al_2O_3 catalyst can be represented by Eqns. (1) and (2). It has been suggested[80] that the formation of a surface alloy via reaction (2) is a more realistic process:

$$Pt + Al_2O_3 \underset{\frac{1}{2}O_2,\ 723\ K}{\overset{H_2,\ 773\ K}{\rightleftharpoons}} Pt \cdot Al_2O_3, \qquad (1)$$

$$Pt + {}^1/_3Al_2O_3 \underset{\frac{1}{2}O_2,\ 723\ K}{\overset{H_2,\ 773\ K}{\rightleftharpoons}} Pt \cdot Al_{2/3}. \qquad (2)$$

The formation of the intermetallic compounds Pt_xAl_y has been observed for a platinum film 200 nm thick deposited on Al_2O_3 after reduction in H_2 at 1200 K [81] and also in a study of the Pt/Al_2O_3 catalyst under an electron microscope at a high temperature under the influence of an electron beam.[82] Magnetic measurements for the Ni/SiO_2 catalyst reduced at about 1180 K demonstrated the presence of the Ni–Si alloy.[83] If such surface alloys and compounds are formed, they can indeed explain the change in the adsorption and catalytic properties of deposited metals.

The change in the properties of the Pt/TiO_2 system can also be due to the formation of surface intermetallic compounds because the reaction

$$TiO_2 + 2H_2 + 3Pt \rightarrow TiPt_3 + 2H_2O$$

is thermodynamically feasible at 773 K.[84] However, in this case it is not possible to observe a shift of the binding energy of the $4d_{5/2}$ level of platinum.[80] The formation of an alloy between a metal and titanium has been observed[1] at temperatures above 1120 K. In general, for metals deposited on TiO_2 the SIMC state is induced by reduction at lower temperatures than are required for the formation of intermetallic compounds such as Pt_3Ti, Ir_3Ti, and Ni_3Ti and, furthermore, metallic titanium could not be identified under any conditions.[85,86] Nevertheless, the presence of two types of Ni–Ti(Ni–Nb) distances has been established by the EXAFS method for the Ni/TiO_2 and Ni/Nb_2O_5 catalysts reduced at 773 K, the shorter distance of 2.62 Å (2.65 Å) being comparable to the distance characteristic of the corresponding alloys.[87] The structure of the carrier is apparently reorganised in the vicinity of the nickel particles. In a recent study[88] using high-resolution electron microscopy and Pt/TiO_2 and Pt/ZnO catalysts reduced at 773 K and above, the intermetallic compounds Pt_3Ti, PtTi, and PtZn were detected. Direct evidence for the formation of RhTi and especially Rh_3Ti after the reduction of Rh/TiO_2 catalysts at temperatures above 623 K has been obtained by the XANES method.[89]

Thus the question of the formation of alloys and intermetallic compounds and of their influence on catalytic and adsorption properties, especially at reduction temperatures in the range 700 to 900 K, remains controversial. However, for certain catalytic systems one must consider the possibility of the extensive reduction of the carrier. For example, the reduction of the Pt/GeO_2 catalyst even at 573 K is accompanied by the formation of the intermetallic compounds Pt_5Ge,[90] while in the case of the Pt–ZnO system, the compound PtZn appears at the metal–carrier interface after treatment in H_2 above 573 K.[91]

III. Manifestations of the effect in deposited metallic catalysts

1. The influence of the SIMC on chemisorption properties

A typical external manifestation of the SIMC effect is the suppression of the chemisorption of H_2 and CO after the high-temperature reduction of metallic catalysts deposited on TiO_2 with retention of the dissociative character of the chemisorption of H_2. Table 1 presents the literature data for the chemisorption of H_2 and O on various metals deposited on TiO_2. After reduction at 473 K, the ratio of the adsorbed H atoms or CO molecules to the total number of metal atoms characterises the dispersity of the metal on the carrier for Ir, Pt, Ru, Rh, and Pd. This ratio decreases sharply

by a factor of 4–7 and more if the catalysts are reduced in H_2 at 773 K. In the latter case, the metal particle size, calculated from the degree of chemisorption of H_2 or CO, does not correspond to the real particle size determined by the X-ray diffraction and electron microscopic methods. Consequently, the decrease in the degree of chemisorption of H_2 and CO is not associated with the increase in the size of the metal crystals during the high-temperature treatment.

Table 1. Chemisorption of H_2 and CO on metals (M) deposited on TiO_2 (50 $m^2\ g^{-1}$).

Metal	T_{red}, K	H/M	CO/M	Refs.
2% Ir	473	1.60	1.19	[1,92]
	773	0.00	0.00	
2% Os	473	0.21	—	[1,92]
	773	0.11	—	
2% Pt	473	0.88	0.65	[1,92]
	773	0.00	0.03	
2% Ru	473	0.23	0.64	[1,92]
	773	0.06	0.11	
2% Rh	473	0.71	1.15	[1,92]
	773	0.01	0.02	
2% Pd	448	0.93	0.53	[1,92]
	773	0.05	0.02	
1.01% Ni	573	0.102	—	[5]
	723	0.064	—	
4.67% Ni	573	0.086	—	[5]
	723	0.055	—	
10% Ni	573	0.099	—	[93]
	773	0.025	—	
15% Ni	725	0.043	—	[76]
	1023	0.001	—	
6.3% Fe	673	—	0.043	[94]
	723	—	0.026	
	773	—	0.012	
	873	—	0.002	
5.0% Fe	723	0.014	0.014	[95]

* T_{red} = reduction temperature.

Similar effects have been observed also for Ni, Fe, and Co deposited on TiO_2. However, a number of features should be noted. Firstly the dispersity of these metals on TiO_2 is usually low (5–10%). Secondly, the extent to which the degree of chemisorption of H_2 diminishes (by a factor of 1.5–2) after the high-temperature reduction is smaller. The clear effect for the 15% Ni/TiO_2 catalyst after reduction at 1023 K (Table 1) is evidently associated with the encapsulation of nickel in the carrier.

The adsorption of H_2 is suppressed after the high-temperature reduction of metals, which may also be deposited on carriers other than TiO_2. The chemisorption of H_2 on iridium-containing catalysts has been investigated.[2] The results are compiled in Table 2.

Tauster emphasised the correlation between the reduction temperature required for the appearance of the SIMC effect and the susceptibility of the oxide carriers to reduction. For the iridium systems, the following series of carriers can be formulated in terms of the decrease in the reduction temperature required to suppress the chemisorption of H_2: $ZrO_2 > Ta_2O_5 > TiO_2, V_2O_3 > Nb_2O_5$,[2,92] although the H/Ir ratios after reduction at 774 K are similar for all the catalysts, except Ir/ZrO_2, and are in the range 0.06–0.01.

Table 2. Chemisorption of H_2 on deposited Ir catalysts.[2]

Metal content, %	Carrier (S_{sp}^*, $m^2\ g^{-1}$)	T_{red}, K	H/Ir
2	TiO_2 (145)	393	1.17
		523	0.32
		774	0.02
1	V_2O_3 (11)	476	0.84
		624	0.11
		774	0.046
1	Ta_2O_5 (135)	573	1.01
		774	0.06
		976	0.015
1	Nb_2O_5 (26)	476	0.67
		724	0.04
		774	0.01

* S_{sp} = specific surface.

It is possible to quote examples also of other deposited metals. Thus the chemisorption of H_2 on 7.5% Ni/CeO_2 diminishes by a factor of 20 on raising the reduction temperature from 523 to 673 K, on the 3% Rh/Ta_2O_5 catalyst the decrease is by a factor greater than 15 after reduction of 858 K,[33] and on the 15% $Ni/TaO_2–ZrO_2$ catalyst the decrease is by a factor of approximately 8 after raising the reduction temperature from 573 to 793 K.[96]

The decrease in the capacity for chemisorption is frequently accompanied by qualitative changes. The decrease in the initial heats of adsorption of H_2 on the Pt/TiO_2 catalyst from 22.2 to 19.1 kcal mol^{-1} and in the average heats of adsorption from 14.9 to 12.9 kcal mol^{-1} on raising the reduction temperature from 523 to 773 K has been reported.[97] Using the thermoprogrammed desorption method and IR spectroscopy, Raupp and Dumesic[67] showed that, when TiO_x flows onto the nickel surface, the strong centres for the adsorption of CO (apical nickel atoms) with a desorption activation energy of about 134 kJ mol^{-1} are blocked and CO is then sorbed on weaker centres which are not occupied in adsorption on a clean nickel surface owing to the appreciable repulsion between the CO molecules. The long-range electronic influence of TiO_x is believed to be responsible for the decrease by 6 kJ mol^{-1} in the strength of the bonding CO for a degree of surface coverage of nickel by TiO_x of 0.1. The slow absorption of H_2 after the high-temperature reduction of the Ni/TiO_2 and Pt/TiO_2 catalysts, accompanied by a decrease in the strength of adsorption, has been observed.[98] The authors explain this by the slow binding of hydrogen at the metal–carrier interface or on the TiO_x coating of the surface of the metallic particles.

In a study of the states of adsorbed CO on the Ni/TiO_2 surface (film 120 Å thick on a thin layer of TiO_2), reduced at 700 K, and on the surface of nickel single crystals, the high-resolution spectra of the

electron energy losses for the deposited nickel showed a faster decrease in the intensity of the 1910 cm^{-1} band (bridging form of CO) as a function of the duration of the treatment of the specimen in H_2 compared with the intensity of the 2020 cm^{-1} band (linear form) owing to the blocking of the surface nickel centres by the TiO_x phase similar to the cluster effect in the alloys.[54] A similar blocking of the nickel centres by the oxide MnO_x (where $x = 0.2-0.5$), whereupon the amount of chemisorbed CO decreases linearly with increase in the area of the shielded metal surface, has been observed after the reduction of Ni(III) single crystals coated by MnO_2.[99] In addition, the appearance of new forms of CO adsorbed at the sites of contact between the nickel particles and the MnO_x "islands", to which corresponds a peak at 305 K in the thermal desorption spectrum and a 1620 cm^{-1} band in the high-resolution electron energy loss spectra has been noted. Vannice et al.[68] state that the band in the IR spectra of CO adsorbed on the Pt/TiO_2 catalyst shifts from 2050 cm^{-1} to 2070 or 2080 cm^{-1} after high-temperature reduction and explains this by the weakening of the Pt–C bond as a consequence of the increase in the filling of the *d* orbitals of platinum in the SIMC state.

As a rule, in the SIMC state the CO/H ratio increases for platinum group metals approximately from 1 to 2 –3,[5] while for Ni, Fe, and CO the ratio CO/H usually changes to a lesser extent.

In the joint adsorption of H_2 and CO on the nickel surface partly coated by TiO_x, the bond between CO and nickel is weakened and the concentration of the strongly bound hydrogen increases by 1–2 orders of magnitude compared with the clean nickel surface, i.e. in this case hydrogen competes successfully with CO for the adsorption centres on nickel.[72]

One of the features of the SIMC effect is its partial or complete reversibility after treatment in O_2 at 673 K [100,101] and after the adsorption of O_2 at 298 K [5] with subsequent mild reduction in H_2 (Fig. 5), which leads to the recovery by the deposited metal of its normal adsorption capacity in relation to H_2 and CO.

At the end of the 1970s, it was believed that the chemisorption of H_2 and CO is not suppressed on metals deposited on SiO_2, Al_2O_3, and certain other non-reducible carriers. However, subsequent experiments showed a decrease in the degree of chemisorption of H_2 on Ni/SiO_2 (reduction temperature 1120–1180 K) by a factor of 3–7 compared with Ni/SiO_2 (920 K) [83] and on Pt/Al_2O_3 reduced at 773 K (the extent to which the degree of chemisorption diminishes depends on the form of Al_2O_3).[102] For the Ni/Al_2O_3 catalyst (873 K), the nickel particle size, determined from the degree of chemisorption of H_2, is greater than the value estimated from electron microscopic data and the strength of the adsorption of H_2 on nickel is diminished owing to the interaction of the metal with the carrier, while the CO/H ratio reaches 4.4.[103]

The introduction into SiO_2 of the TiO_2 or Nb_2O_5 additives in an amount corresponding to one monolayer leads to the SIMC effect in the Ni/TiO_2 (Nb_2O_5)–SiO_2 catalysts reduced at 673 K. In this case, the catalysts can be arranged in the following sequence in terms of the degree of suppression of the chemisorption of H_2: Ni/TiO_2 (Ni/Nb_2O_5) > Ni/TiO_2–SiO_2 (Ni/Nb_2O_5–SiO_2) > Ni/SiO_2.[104,105] A similar result has been observed of 1% Pt/Al_2O_3 after the introduction of 4% of Ti into the carrier.[106] In contrast to CO and H_2, the chemisorption of O_2 on deposited metallic catalysts, calculated per m^2 of the metal surface, does not change on raising the reduction temperature of the catalyst, while the size of the metal particles, determined from the degree of chemisorption of O_2 and X-ray diffraction and electron microscopic data, remains unaltered. A change in the stoichiometry of the adsorption of O_2 at room temperature on the Ni/TiO_2 catalyst prepared by impregnating TiO_2 with nickel(II) chloride (O/Ni_{surf} = 1),† compared with Ni/SiO_2 and Ni/Al_2O_3 (O/Ni_{surf} = 2) reduced as 773 and 573 K, and also on the Ni/TiO_2 obtained by impregnating TiO_2 with nickel(II) nitrate, has been noted[107] on raising the reduction temperature from 573 K (O/Ni_{surf} = 2) to 773 and 973 K (O/Ni_{sur} = 1). This conclusion is based on the comparison of the nickel particle sizes estimated from the degree of chemisorption of O_2 and X-ray and magnetic measurements. For the stoichiometries presented above, these dimensions agree satisfactorily. It is noteworthy that the nature of the carrier can influence not only the stoichiometry of the adsorption of O_2 but also the strength of its bond with the deposited metal. For example, the Ir–O bond strength is greater when iridium is deposited on the highly basic MgO surface than on deposition on Al_2O_3–SiO_2.[108]

Additional information about the SIMC states can be extracted with the aid of the adsorption of N_2. Resasco and Haller[109] reported that, on reducing the reduction temperature of the 2% Rh/TiO_2 catalyst, the degree of adsorption of N_2 at 523 K increases, while the degree of adsorption of CO at 298 K is suppressed (Table 3). These effects were not observed on the 2% Rh/Al_2O_3 catalyst.

Table 3. The influence of the catalyst reduction temperature on the adsorption of N_2 at 523 K and of CO at 298 K on the 2% Rh/TiO_2 catalyst.[109]

T_{red}, K	CO/Rh	N_2/Rh	N_2/CO
773*	0.01	0.023	0.032
473*	0.7	0.01	0.01
773*	0.01	0.024	0.034

* Repeated reduction after treatment in O_2 at 673 K.

Although Burch and Flambard[110] did observe an increase in the degree of adsorption of N_2 at 273 K on the 1% Ni/TiO_2 and 5% Ni/TiO_2 catalysts reduced at 723 K compared with the 1% Ni/SiO_2 and 5% Ni/SiO_2 catalysts, they concluded that the adsorption centres are the Ti^{3+} cations located next to the oxygen vacancies because reduced TiO_2 adsorbed more N_2 per unit carrier surface than the Ni/SiO_2 catalysts, while non-reduced TiO_2 altogether failed to adsorb N_2. In the presence of nickel, the adsorption capacity of TiO_2 increased by virtue of the ready reduction of TiO_2 by the atomic hydrogen formed on nickel. Thus the increase in the amount of N_2 adsorbed on deposited metallic catalysts with increase in the preliminary reduction temperature can be regarded as one of the signs of the occurrence of the SIMC, although its interpretation is controversial.

† Ni_{surf} represents nickel atoms on the surface.

2. Catalytic properties and the strong interaction of metal with the carrier

The SIMC effect is manifested not only in the adsorption properties but also in the catalytic properties of deposited systems. With increase in the temperature of the reduction of metals deposited on TiO_2, a decrease in their activity is observed in the hydrogenolysis of hydrocarbons, the hydrogenation of benzene, the dehydrogenation of cyclohexane, and the isomerisation of methylpentanes. On the other hand, an increase in activity in the D_2-H_2O exchange and in the H_2 + CO and NO + CO reactions as well as the change in selectivity in the CO + H_2 reaction had been observed compared with metals deposited on SiO_2 and Al_2O_3 or on non-deposited metals.

We shall consider initially the structure-sensitive (in terms of Boudart's classification[111]) reactions of hydrocarbons such as hydrogenation, dehydrogenation, and isomerisation.

The experimental data for the benzene hydrogenation and cyclohexane dehydrogenation reactions on Rh, Ir, and Pt deposited on TiO_2 (Table 4) indicate a decrease in the activity of the Ir and Pt catalysts by an order of magnitude with increase in their reduction temperature.

Table 4. The influence of the reduction temperature of the metals deposited on TiO_2 on their activity in hydrogenation and dehydrogenation reactions.

M, %	T_{red}, K	10^{-2} W*, molecules M_{surf}^{-1} s^{-1}	Initial reactants	Refs.
3.2% Rh	473	3.0	$C_6H_6 + H_2$	[112]
	793	2.4		
2% Rh	573	6.0	C_6H_{12}	[100]
	773	4.7		
2.7% Ir	473	1.2	$C_6H_6 + H_2$	[112]
	793	0.1		
6.8% Pt	473	3.68	C_6H_{12}	[113]
	793	0.24		
4.8% Pt	473	1**	$C_6H_6 + H_2$	[90]
	773	0.08**		

* W is the catalyst activity.

** Relative to the activity of the specimen reduced at 473 K.

For the hydrogenation of benzene at 403 K, the activity of the 9.8% Ni/TiO_2 catalyst, reduced at 723 K, is 44 × 10^3 molecules s^{-1} Ni^{-1}, which is smaller by a factor of 4.75 than the activity of the same catalyst reduced at 523 K and by a factor of 3.61 than the activity of the 9.8% Ni/SiO_2 catalyst reduced at 723 K.[114] The decrease in the degree of conversion of benzene in hydrogenation at 393 K from 83 to 30% with increase in the catalyst reduction temperature from 673 to 793 K respectively has been observed on a catalyst containing 15% of nickel and deposited on a TiO_2-ZrO_2 mixed carrier (TiO_2/ZrO_2 = 1/1),[96] the SIMC state being abolished after the subsquent oxidation and reduction of the specimen at 573 K.

The relative probabilities of desorption and hydrogenation in the reaction of ethylene with deuterium have been determined.[115] It was found that the probability of the desorption of ethylene from Pt/TiO_2 is six times greater than from Pt/SiO_2. The authors explain this by the decrease in the strength in the absorption of ethylene on Pt/TiO_2 as a result of electron transfer from the carrier to the metal, although one should note that the catalyst was reduced at 573 K.

In the isomerisation of methylpentanes on the Pt/TiO_2 catalyst, the specific activity was smaller by a factor of 50 than on the Pt/Al_2O_3 catalyst, while the adsorption of hydrogen was suppressed slightly.[116] The isomers are formed mainly via the mechanism involving the migration of bonds in intermediate compounds.

The structure-sensitive hydrogenolysis reactions of saturated hydrocarbons and the interactions in the CO + H_2 reaction constitute a good test of the change in catalytic properties under the influence of the SIMC.

Table 5 presents data obtained[117] for the hydrogenolysis of ethane at 478 K on metals deposited on TiO_2 and SiO_2, reduced at 773 K for 16 h. It is noteworthy that the specific activity was calculated assuming 100% dispersity of the metal on TiO_2, which does not introduce serious errors for noble metals. However, this hypothesis is incorrect for Fe, Ni, and Co, because their dispersity is usually in the range 5–10%. Thus the real relative decrease in activity is greater by a factor of 10–20 than the values quoted in Table 5. Furthermore, iron in the SIMC state is almost inactive probably owing to the encapsulation effect. In terms of the decrease in the activity of the metal by the SIMC in the hydrogenolysis of ethane compared with the activity in the state of a weak interaction (M/SiO_2), the Group VIII noble metals can be arranged in the following sequence: Pt > Pd > Os, Ir > Rh > Ru, the activity of Ru remaining unchanged.

Table 5. The activities of deposited Group VIII metals, reduced at 773 K, in the hydrogenolysis of ethane at 478 K.[117]

M	W, mol h^{-1} m^{-2}		Relative specific activity of SiO_2/TiO_2
	SiO_2	TiO_2	
Fe	$1.2\cdot10^{-5}$	$<10^{-13}$	$>10^8$
Co	$3.4\cdot10^{-5}$	$1.0\cdot10^{-9}$	$3.4\cdot10^4$
Ni	$8.0\cdot10^{-4}$	$8.0\cdot10^{-7}$	10^3
Ru	$1.8\cdot10^{-3}$	$1.4\cdot10^{-3}$	1.3
Rh	$2.2\cdot10^{-4}$	$2.9\cdot10^{-5}$	7.6
Pd	$6.7\cdot10^{-10}$	$2.6\cdot10^{-13}$	$2.6\cdot10^3$
Os	$4.2\cdot10^{-2}$	$9.6\cdot10^{-5}$	$4.4\cdot10^2$
Ir	$1.1\cdot10^{-4}$	$3.0\cdot10^{-7}$	$3.7\cdot10^2$
Pt	$7.2\cdot10^{-10}$	$<10^{-13}$	$>7\cdot10^3$

A sharp decrease in the activity in the hydrogenolysis of n-butane and neopentane in the presence of Ir/TiO_2 in the SIMC state,[118] in the hydrogenolysis of n-hexane in the presence of Pt/TiO_2 [90] and Ni/TiO_2,[114] and in the hydrogenolysis of n-heptane in the presence of Ru/TiO_2 [119] has been noted.

On deposition of 9% of nickel on SiO_2 coated by a monolayer of TiO_2, the activity of nickel in the hydrogenolysis of ethane falls by 2–3 orders of magnitude compared with its activity on SiO_2.[104] A decrease in the activity of the 9% Ni/SiO_2-TiO_2 system from 5.6 × 10^{-5} to 9.5 × 10^{-6} molecules s^{-1} Ni_{surf}^{-1} with increase in the

specimen reduction temperature from 573 to 773 K has also been noted.

Such effects are not characteristic of catalysts with a TiO_2 carrier alone. Thus, on raising the reduction temperature of the 10% Ni/Nb_2O_5 system from 573 to 773 K, its activity in the hydrogenolysis of ethane falls by a factor of 35,[120] while the activity of the 9% $Ni/Nb_2O_5-SiO_2$ catalyst (Nb_2O_5 monolayer on a SiO_2 surface) diminishes under similar conditions by a factor of 14.[105]

The catalytic properties of deposited metals in the SIMC state have been studied in greatest detail in the CO + H_2 reaction, their activity being significantly higher than that of the metal single crystals and metals deposited on Al_2O_3 and SiO_2. Table 6 presents the activities for the Ru, Rh, Pt, and Ir catalysts.

Table 6. Specific activities of deposited Group VIII noble metals in the CO + H_2 reaction at 548 K and for the ratio CO/H_2 = 3.

M, %	T_{red}, K	$10^3 W$, $M_{surf}^{-1} s^{-1}$	Relative activity		Refs.
			$\frac{M/TiO_2}{M/Al_2O_3}$	$\frac{M/TiO_2}{M/SiO_2}$	
2% Ru	723	320	1	1	[95]
1% Rh	673	321	8.2	57	[121]
2% Rh	723	430	25	36	[95]
1.86% Pt	448	5.5	1	25	[122]
1.86% Pt	773	40	7	200	[122]
2% Pt	723	130	38	65	[95]
2% Ir	723	45	17	45	[95]

Evidently the specific activity of the M/Al_2O_3 catalyst is higher than that of the M/SiO_2 catalyst (the activity of the latter is comparable to that of the non-deposited metals). This is usually explained by the greater extent of the interaction of the metal with the carrier for the M/Al_2O_3 systems.[5] A strong interaction of the metal with the carrier does not affect the activity of Ru, which is correlated with the ease of the spreading of Ru on the surfaces of different carriers.[77,78] However, the selectivity of Ru/TiO_2 in relation to C_2 hydrocarbons and hydrocarbons with higher molecular weights is appreciably higher.[123] The specific activity of Rh, Ir, and Pt deposited on TiO_2 is higher approximately by 1 and 2 orders of magnitude than the corresponding values for catalysts deposited on Al_2O_3 and SiO_2, the fact that the activity of Rh/TiO_2 is highest being correlated with the highest reactivity of the CO adsorbed on it.[124] As regards selectivity, the latter does not change appreciably for Ir and Pt, whereas on Rh/TiO_2 and Rh/Al_2O_3 the main reaction product is methane and on Rh/SiO_2 it is methanol.[121,125] The data obtained by Japanese workers for the Rh/TiO_2 and Ir/TiO_2 catalysts[126] conflict with the above results, since the rate constants for the conversion of CO into methane hardly change on transition to the SIMC state. On the other hand, for Pt and Pd in the SIMC state, the rate constant is 10 times smaller than in the "normal" state.[127]

Deposited Fe, Co, and Ni apparently behave differently in the CO + H_2 reaction. Owing to the Fe encapsulation effect, it is difficult to observe the changes in catalytic properties on different carriers. Cobalt deposited on TiO_2, SiO_2, and Al_2O_3 has comparable activities.[4] On the other hand, the SIMC exerts an appreciable influence on the catalytic properties of the Ni/TiO_2 system. This system therefore merits greater attention.

Vannice[95] noted that the activities of various Ni/TiO_2 catalyst specimens, reduced at 723 K, in the CO + H_2 reaction at 548 K exceeds by a factor of 2–37 the activity of Ni/Al_2O_3 and Ni/SiO_2. In another study,[128] the ratio of the activities of the 5% Ni/TiO_2 and 5% Ni/SiO_2 catalysts, reduced at 723 K, was 33.8 at a reaction temperature of 553 K. The change in the activity of Ti in the SIMC state is as a rule accompanied by an improvement of selectivity in relation to higher hydrocarbons. Thus, whereas the selectivity of 9.8% Ni/SiO_2 (reduction temperature 723 K) was 9.3%, for 9.8% Ni/TiO_2 (723 K) it amounted to 27.7%.[114] At a reaction temperature of 600 K, the selectivity in relation to methane reached 99.82% for 9% Ni/Al_2O_3 (700 K), 54.6% for 13% Ni/TiO_2, and 68.1% for 12.5% Ni/Nb_2O_5 (700 K) (reaction temperature 503 K).[129]

The rate-limiting stage in the CO + H_2 reaction in the presence of deposited nickel catalysts is known to be either the dissociation of the adsorbed CO [130] or the hydrogenation of surface carbon.[131] A series of kinetic models have been proposed for the Ni/TiO_2 catalysts in the SIMC state,[132,133] according to which an increase in the fraction of hydrogen adsorbed on the surface, the weakening of the bond between CO and the metal, and other factors examined in detail above increase the rate of the rate-limiting stage. These conclusions have been confirmed by kinetic experiments on the hydrogenation of atomic carbon and the dissociation of CO on nickel-containing catalysts reduced in H_2 at 723 K. It was found that, while the activation energy remains unchanged, the specific rates of hydrogenation of carbon in the presence of nickel on different carriers differ by more than an order of magnitude, diminishing in the sequence Ni/TiO_2 > Ni/Al_2O_3 > Ni/SiO_2.[134] In addition, the order of the reaction with respect to H_2 is twice as great for Ni/TiO_2 as for other catalysts. The dissociation of CO on Ni/TiO_2 is also much faster.

A model has been proposed[114] for the Ni/TiO_2 system containing large nickel particles in which the specific influence of the carrier is restricted to the interface between the metal and the carrier. The increased activity of Ni/TiO_2 in the CO + H_2 reaction can be explained by the appearance of specific centres at the interface on which CO molecules are activated (Fig. 8*a*).

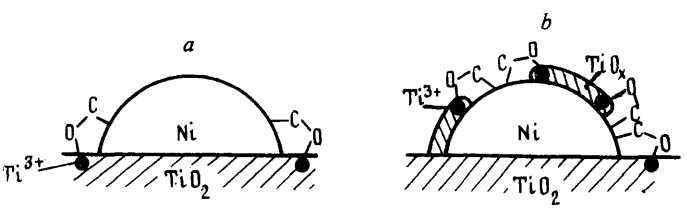


Figure 8. Model of the active centre in the CO + H_2 reaction at the interface between the Ni particle and the surface of the carrier after reduction at 573 K (*a*) and 773 K (*b*).[114]

Ponec[8] and Takatani and Chung[54] hold a similar view. In later investigations,[135] where an increase in activity in the CO + H_2 reaction was not observed for Ni, Pd, and Ir (deposited on TiO_2) in the SIMC state (suppression of the chemisorption of H_2 and of

activity in the hydrogenolysis of ethane), the model taking into account the phenomena at the interface was developed further (Fig. 8*b*). According to the authors,[135] the reduction of the catalyst at temperatures of about 723 K leads to the migration of TiO_2 onto the surfaces of metallic particles and the creation of new superactive centres at the interface. A significant proportion of the less active metallic centres are then shielded and ultimately the overall activity remains almost unaltered.

Chung et al.[136] rejected the model of Burch and Flambard on the grounds of data obtained for sputtered Ni/TiO_2 (100) specimens and for Ni (111) partly coated by TiO_2. They were treated in H_2 at 773 K. The authors believe that, if the active centres were located on the periphery of the nickel "islands", then the maximum concentration of such centres and hence their activity would have been observed for coverages corresponding to 0.6 of a nickel monolayer on TiO_2 or 0.6 of a TiO_2 monolayer on nickel. On the other hand, the highest experimental activity was shown by specimens containing three nickel monolayers on TiO_2 (100) and 8% TiO_x on Ni (111). Furthermore, their catalytic properties proved to be similar. It was concluded that the TiO_x diffusing onto the catalyst surface exerts a decisive influence on the activity of nickel. Similar conclusions (diffusion of CeO_x) have been reported[60] for the Ni/CeO_2 system.

In a number of studies,[129,137,138] the hypothesis was put forward that the changes in activity and selectivity following a change of carrier are associated with the presence of Ni^{n+} in Ni/Al_2O_3 and Ni/SiO_2 and its interaction with Ni^0. It has been suggested that the electron transfer from Ni^0 to Ni^{n+} increases the strength of the C–O bond in the adsorbed state, diminishing the probability of its dissociation. Thus the following series of specific activities (per m^2 Ni) in the CO + H_2 reaction on nickel in the "normal state", expressed in arbitrary units relative to Ni/SiO_2, has been explained[138] by precisely this factor: 14% Ni/TiO_2 (15) > 24% Ni/ZrO_2 (8) > 21% Ni/Al_2O_3 (2) > 24% Ni/SiO_2 (1); the same explanation was also used to account for the selectivity of the Ni/TiO_2 and Ni/ZrO_2 catalysts being higher by factors of 2 and 3 respectively compared with Ni/SiO_2. A decrease in the activity of nickel in the SIMC state has been noted for Ni/TiO_2 and Ni/ZrO_2. Treatment with O_2 and subsequent low-temperature reduction restore the initial activity to these catalysts.

Thus the question of the unique catalytic properties of metals deposited on TiO_2, Nb_2O_5, ZrO_2, and certain other carriers in the CO + H_2 reaction remains open and requires further studies.

Examples of other reactions in which the influence of the SIMC on the catalytic properties of deposited metals was investigated are fairly rarely encountered in the literature. These exist data on the catalytic activity of platinum deposited on TiO_2 doped with the Ta^{5+}, Sb^{5+}, and W^{6+} cations (to test the hypothesis concerning the nature of the SIMC involving electron transfer) in the CO + O_2 and CO + H_2O reactions.[139] Under these conditions, the activity of the doped catalysts in the first reaction is reduced by a factor of 3–5 and the activation energy is increased by 45%, while in the second reaction the activity falls by a factor of 80. An increase in the activity of the Rh/TiO_2 and Pt/TiO_2 catalysts in the SIMC state has been noted[140,141] in the CO + NO reaction. There are contradictory data for the acetone hydrogenation reaction as regards the SIMC effect. Thus a sharp decrease in the activity of the Rh/CeO_2 catalyst has been observed[142] after its reduction at 653 K, while the activity of Pt/TiO_2 in the SIMC state increased appreciably.[143] An elegant study of the catalytic properties of the Ir/Nb_2O_5 system reduced at 473 K ("normal" state) and at 773 K (SIMC state) in the acroleine hydrogenation and deuteriation reactions has been carried out by Japanese workers,[144] who established that mainly allyl alcohol is formed on the catalyst in the SIMC state at 353 K, and not propanol as on the catalyst reduced at 473 K. The activation energy for the formation of the main product falls from 12 kJ mol^{-1} (for the normal state) to 5 kJ mol^{-1}, while the activation energy for the formation of propanol increases from 12 to 35 kJ mol^{-1} respectively. Active centres of two types were identified with the aid of a kinetic study of the rate of formation of each product as a function of the catalyst reduction time in combination with the study of the distribution of the hydrogen isotopes in acroleine, allyl alcohol, and propanal. The formation of propanal, CH_2 = CDCHO, and of part of allyl alcohol and the dissociation of D_2 takes place on purely metallic centres, while CHD = CHCHO and the remainder of the allyl alcohol are formed on metallic centres adjoining the boundary of the NbO_x "islands", which appear on the catalysts reduced at 773 K.

IV. The apparent effects of the strong interaction of a metal with the carrier

It is frequently assumed nowadays that the change in the catalytic properties of deposited metals combined with the loss of ability to absorb H_2 and CO constitutes convincing evidence for the existence of the SIMC. It is therefore useful to examine certain effects erroneously interpreted as true manifestations of the SIMC.

In the first place, the sintering of metallic particles at elevated reduction temperature lowers the activity of the metal surface and hence diminishes its chemisorption capacity and alters the activity and selectivity of the catalyst. It is therefore essential to monitor the metal particle size at different reduction temperatures. Furthermore, the active surface of the metal can decrease as a result of the migration of the metal into the carrier, as in the case of the Fe/TiO_2 system. In this instance, comparison of the specific activities per gramme of the metal with those of other catalysts yields undistorted information only when additional data are secured by adsorption, X-ray diffraction, X-ray photoelectron spectroscopy, analysis of the extended fine structure of the X-ray absorption spectra, etc.

One must not forget that the surface of the metal contaminated in some way (poisoned, for example, by sulphur or iron impurities which may be present in the carrier[145] or the Cl^- anions remaining after the preparation of the catalyst from metal chlorides[107]) is incapable of adsorbing H_2 and CO or can adsorb them to a much lesser extent than the clean surface, and has significantly different catalytic properties. When catalysts consisting of a metal deposited on SiO_2 and especially on Al_2O_3 are obtained by impregnation with acid solutions, a very small proportion of the carrier can dissolve and ultimately, after reduction at elevated temperatures, can form a film or "islands" of oxygen-deficient SiO_x and Al_2O_x on the surface of the metallic particles, as a result of which the properties of the catalyst change qualitatively, as in the metal–TiO_2 system in the SIMC state.[146,147] Thus, on raising the reduction temperature of the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts from 523 to 773 K, their activity in the CO + H_2 reaction at 498 K increases by factors of 5.1 and 1.8 respectively.[146]

It is essential to recall that Group VIII metal cations exhibit a certain tendency to react with aluminium and silicon oxides to form aluminates and silicates, which are difficult to reduce, or solid solutions which are also not easy to reduce on heating.[137,148,149]

If the active specific surface of the metal and the degree of its reduction are known, this does not create serious difficulties in the study of the SIMC. However, account must be taken of the influence of the non-reduced cations on the behaviour of the reduced metal in view of the possible electron transfer.[138,150] There are data showing that certain carriers, especially alumina, can stabilise the metal in intermediate states such as Rh^+, Pt^{3+}, Re^{4+}, and Ni^+ and can thus inhibit their reduction.[151–153]

The energetic, electronic, and geometrical properties of deposited metallic particles can be simultaneously modified by the metal–carrier interactions and by changes in the properties of the metal—both bulk-phase and atomic. Both effects become very important when the size of the metallic particles is reduced and, as noted by Bond[4] and Ponec,[8] it is not always easy to separate the contributions of these two effects to the adsorption and catalytic properties of metals.

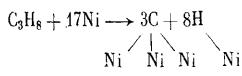
In the analysis of the dependence of the catalytic properties of deposited metallic crystals on their structure, it has been suggested[154] that three cases of structure-sensitive reactions be distinguished: (a) structural sensitivity for which the rate of reaction depends on the dispersity of the crystals which influences the number of specific centres in them (for example B_5 centres) is referred to as the primary structural sensitivity; (b) cases where the rate of reaction is independent of dispersity when the reaction is carried out under "clean" conditions but becomes structure-sensitive on partial poisoning of the surface of the catalyst (as already mentioned above) constitute a group of phenomena which are referred to as secondary structural sensitivity: (c) finally the third type of structural sensitivity may be due to the change in the electronic properties of crystals when their size is altered.

We shall now quote several examples. A study has been made[155] of the influence of the nickel particle size in the range 22–100 Å on selectivity of the propanol hydrogenation reaction at 473 K in the presence of Ni/SiO_2 catalyst. A sharp increase in selectivity with respect to propanol for a nickel particle size less than 50 Å was established. Taking into account the increase in the fraction of apical and edge atoms relative to the total number of surface atoms with decrease in crystal size, the authors concluded that the aldehyde is hydrogenated on edge and apical nickel atoms, while decomposition takes place on the planar surface of the crystal.

Apart from the number of edge and apical atoms and specific centres whose concentration is determined by the dispersity of the crystal, the ratio of different faces, whose activities in relation to the given reaction sometimes differ greatly, may vary on the surface of the crystal.[156] Thus, in order to account for the change in selectivity in the reaction of neopentane on platinum, it has been suggested[157] that neopentane isomerises via its three-point adsorption on atomic triplets located in the (111) plane and that the contribution of the isomerisation reaction increases with increase in the concentration of these faces on the surface. This result was confirmed in other studies.[158,159]

The Ni/SiO_2 catalyst containing nickel crystals oriented along the (111) plane and non-oriented crystals[160] exhibited different catalytic properties in the benzene hydrogenation and cyclohexene disproportionation reactions.[161] Whereas the rates of the first reaction were virtually the same on both catalysts, the second reaction was faster on the oriented crystals.

Analysis of the mechanism of the structure-sensitive and insensitive reaction involves directly the elucidation of the structure of the catalytically active centre, which may consist of a group of several atoms. Thus the hydrogenolysis of C_3H_8 can proceed on an assembly of 17 nickel atoms in accordance with the scheme[162]



A decrease in the rate of reaction is then observed for small nickel particles as their size diminishes further.

The influence of dispersity on the catalytic properties is manifested not only by a change in the rate and selectivity of the reaction but also by a change in the nature of the chemisorption bond in the adsorption stage as a function of the size of the crystals. For example, in a study of the adsorption of H_2 on nickel microcrystals deposited on SiO_2,[163] it was shown that the fraction of the irreversibly chemisorbed H_2 is related to the fraction of surface nickel atoms located on the edges and on the apices of the crystals. The different coordinative states of the surface metal atoms, which depend on the dispersity, influence significantly the form of the adsorption of CO, which was demonstrated[164] in relation to the Ni/SiO_2 and Ni/Al_2O_3 catalysts over a wide range of nickel crystal sizes and in another study[165] of the interaction of CO and H_2 on Ni/SiO_2 catalysts. It has been noted[166] that the form of the platinum particles themselves can change in the course of the adsorption of H_2 and CO on Pt/SiO_2 catalysts and hence their catalytic properties are also altered.

In a study of the adsorption of H_2 and CO on highly dispersed iridium deposited on Al_2O_3, it was shown that the H/Ir and CO/Ir ratios approach two and that this is not associated with the spill-over effect.[167] It has been established that such a high H/M ratio is characteristic of adsorption on atomically dispersed iridium and not on corner and edge atoms of small crystals because the stoichiometric adsorption on iridium crystallites smaller than 6 Å is approximately unity.

We shall now turn our attention to the electronic properties of the metallic crystals and clusters themselves as a function of their size without taking into account with the influence of the carrier. The general postulates concerning this problem have been described in another review:[10]

1. Depending on the number of atoms (n) in the cluster, the latter can have different structures (linear, two-dimensional, three-dimensional) and for $n > 10$ the three-dimensional crystals are probably more stable than the linear and two-dimensional structures. According to the results of calculations, among three-dimensional structures there may be a tetrahedron, a square pyramid, a pentagonal pyramid, a trigonal bipyramid, a triangular prism, or an icosahedron, i.e. structures which are not characteristic of massive metals. The icosahedral structures of small palladium and nickel clusters are apparently more stable than the face-centred cubic structures, which are in their turn preferred for copper and silver clusters.

2. The bond energy in the cluster calculated per atom is smaller than in the crystal, but increases with increase in n. The average bond energy in cubic and octahedral crystals with $n > 50$ does not differ very greatly from the energy of macrocrystals. In many cases, the equilibrium distances between atoms in the cluster are greater than in the metal lattice.

3. The ionisation potential of the cluster is greater than the electronic work function of the metal and diminishes with increase in the size of the cluster, approaching the electronic work function of the massive metal. Thus the electronic work function depends on the dispersity of the metal.

4. In the copper, silver, gold, and nickel clusters, the population of the *d* atomic orbitals is increased by virtue of the *p* atomic orbital [sic] compared with the $d^8s^1p^2$ configuration (the Engel-Brewer rule), while for the palladium cluster the population of thd *d* atomic orbitals increases with increase in *n*, approaching the value for the massive metal, i.e. the *d* character depends on the dispersity of the metal. It has been shown that for nickel the average magnetic moment per atom diminishes with decrease in *n*, amounting to 0.46 μ_B for Ni_{13} and 0.25 μ_B for Ni_8 compared with 0.54 μ_B for crystalline nickel.

5. With increase in the size of the cluster, the levels of the individual atoms are grouped into bands and the width of the *d* band increases with increase in the size of the cluster. The width of the forbidden gap then diminishes. It is of interest to note that all the possible features of the bulk-phase band structure are observed for the cubooctahedral Ni_{13} and Pt_{13} clusters.

In conclusion of this chapter, one should also mention a series of important factors which complicate the study of the SIMC effect. These are the reversibility of the SIMC as a function of the reaction conditions,[168,169] its sensitivity to the presence of water[169,170] and its relation with the spill-over of hydrogen,[171–173] the dependence on the way in which the catalyst is obtained,[34,37,174] and the presence of strongly retained forms of hydrogen.[175]

* * *

Summarising briefly the data presented above, one may note that the attention devoted by many investigators to the experimental and theoretical study of the SIMC effect has led to a sharp increase in the number of studies designed to elucidate the physicochemical and catalytic properties of deposited metallic catalysts. This fact is itself important because the above group of catalysts is of significant interest for industry. However, here one should note that the SIMC effect is frequently used to explain changes in adsorption and catalytic properties induced by completely different causes, for example by a change in the dispersity of the deposited metallic particles as a function of the nature of the carrier and the amount of the deposited metal, the complete encapsulation of the metal particles in the bulk of the carrier on sintering, the spill-over phenomena, etc.

Such a broad treatment of the phenomenon hinders to some extent its objective study and analysis and it is therefore useful, in our view, to restrict the consideration of the SIMC effect to the following phenomena, which influence the adsorption and catalytic properties: (a) the change in the electronic structure of the metal atoms or clusters located on the carrier and also in the electronic structure of the atoms at the metallic crystal–carrier interface; (b) the formation, as a consequence of the reduction of the carrier, of metal atoms doping the deposited crystals of the catalytically active metal; (c) partial shielding of the surface of the deposited crystals by a creeping film of the carrier accompanied by a change in the energetic, structural, and electronic properties of the surface.

Naturally, it is sometimes difficult to isolate these phenomena in a pure form and the application of a set of modern physicochemical methods and a wide variation of the procedures used to prepare the given deposited metallic catalysts are essential conditions for the understanding of the mechanism of the SIMC effect and for the synthesis of new effective catalytic systems.

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