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The role of adsorbed hydrogen species in the dehydrogenation and hydrocracking of saturated hydrocarbons on supported metal catalysts

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Abstract. The role of certain hydrogen adsorption complexes in the dehydrogenation and hydrocracking of hydrocarbons on low-percentage one-component, (Pt, Pd/Al_2O_3) and bimetallic (Pd – Co, Pd – Ce, Pt – Co, $Pt-Sn/Al_2O_3$) catalysts is discussed. It is shown that the combination of metals in reduced forms and forms oxidised to different extents on the catalyst surfaces is responsible for their high capacity for the chemisorption of hydrogen, the wide range of its energetic inhomogeneity, and the high activity of the catalysts in the conversion of saturated hydrocarbons. Catalysts containing on the surface mainly sites for the type $H^{\delta-}$ chemisorption are the most active in the dehydrogenation of hydrocarbons, whereas specimens chemisorbing hydrogen mainly in the $H^{\delta+}$ form are the most active in the hydrocracking of hydrocarbons. It is concluded that the strongly bound atomic hydrogen $H^{\delta+}$ plays a dual role, since it not only participates directly in the dehydrogenation reaction but also promotes the reduction of the electron-deficient surface centres, which optimises the number of centres for the activation of C – H bonds. The bibliography includes 75 references.

I. Introduction

Hydrogen strongly affects the course of the processes involved in the heterogeneous catalytic conversion of saturated hydrocarbons. It alters the capacity of hydrocarbons for adsorption, participates in the hydrogenation of highly dehydrogenated molecules, enters into the composition of intermediate adsorption complexes, etc.[1-3]

In the present review, attention is concentrated on the role of hydrogen in the dehydrogenation and hydrocracking of hydrocarbons on supported metal catalysts. Mainly platinum catalysts, including those modified by doping with other elements, containing both zerovalent and oxidised metals are used as dehydrogenation catalysts.[1] The participation of adsorbed hydrogen in dehydrogenation and hydrocracking and also the nature of the adsorbed state, which is determined by the composition and structure of the active centres on the catalyst surface, have been scarcely investigated hitherto.

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II. The mechanism of the activation of H – H, C – H, and C – C bonds in molecules of hydrogen and hydrocarbons

The mechanism of the chemisorption of hydrogen on the surfaces of Group VIII metals has been discussed in detail in a number of communications, in particular in reviews.[4,5]

In considering the mechanism of the activation of hydrogen on metal oxides, one should bear in mind that experimental estimation of the sorption state of hydrogen is possible only in the case of metal oxides which are difficult to reduce — those of molybdenum, zirconium, strontium, barium, and cerium.

As a consequence of the highly ionic character of such metal oxides, the interaction of hydrogen with the latter leads to the polarisation of the hydrogen molecule:

$$\begin{matrix} H^{\delta-} & \cdots & H^{\delta+} \\ \vdots & & \vdots \\ H^{\delta+} & \cdots & H^{\delta-} \end{matrix}$$

This is followed by heterolysis.[6-11] The existence of the $M^{m+}-O^{n-}$ pairs on the surfaces of the oxides of the metals indicated above[12-18] with different coordinative unsaturation of the metal and oxygen (surface defects) is responsible for the presence of several types of pairs of active centres differing in the strength of bonding of the chemisorbed hydrogen.[7,18]

The chemisorption of hydrogen on readily reducible metal oxides (including Group VIII metal oxides) and its energy characteristics have been investigated mainly by theoretical methods.[7,12,19-22]

Quantum-chemical calculations for the chemisorption of a hydrogen molecule on the (001) face of NiO indicate that the binding of hydrogen to Ni^{2+} ions is very weak in a perfect lattice (E_b = 0.65 eV).[19,22] Only a positively charged molecular form of chemisorbed hydrogen arises on a positively charged iron ion in the hematite (Fe_2O_3) lattice.[20] The presence of defects — cationic or anionic vacancies — on the oxide surface leads to strong binding of hydrogen (E_b = 4.5 – 7.7 eV).[7,19,22]

Calculations for the chemisorption of a hydrogen molecule on an oxygen ion of the Fe_2O_3 cluster showed that the H–H bond energy diminishes greatly on interaction with an O^{n-} anion.[20] When the hydrogen molecule is oriented parallel to the metal – oxygen bond, the interaction is repulsive, i.e. there is no chemisorption of hydrogen on Fe_2O_3 via a heterolytic mechanism.

Analysis of the H–H and C–H bond activation processes on metallic surfaces and on transition metal complexes showed that these processes proceed via similar mechanisms.[6,18,23,24] The activation of hydrocarbon molecules, like that of hydrogen molecules, involves electron transfer from the bonding σ_g orbitals of the H–H and C–H bonds to the metal and the reverse electron transfer from the occupied orbitals of the metals to the antibonding unoccupied σ_u^* orbitals of the molecule of hydrogen or the saturated hydrocarbon.[23] The electron-donating or electron-accepting nature of the interaction of metals with hydrogen or hydrocarbons is determined by the oxidation states of the metals, i.e. by the position of the Fermi level of the metal relative to the highest occupied or lowest unoccupied level of the reactant molecule, which is in fact the reason for the preferential charge transfer either to the adsorbed molecule or to the transition metal.[23]

In the case of zerovalent metals, the high energies of the highest occupied molecular orbitals (HOMO) of their surface atoms give rise to interaction involving mainly electron transfer from the metal to the σ_u^* levels of the hydrogen or saturated hydrocarbon molecule. Quantum-chemical calculations of the heats of chemisorption of saturated hydrocarbons (CH_4, C_2H_6) on 3*d* transition metals showed[24] that the difference between the energies of the Fermi level of the metal and the σ_g levels of the hydrocarbon molecules are fairly large for the majority of these metals. It is therefore evident that the electron-accepting properties of saturated hydrocarbons will predominate in the interaction with metals.

In oxides and metal complexes (in contrast to heterogeneous metal catalysts), the metal ions exhibit a higher coordinative unsaturation and the energies of their frontier orbitals are higher.[23,24] Thus the typical Fermi energies, established from the electron work functions of the reduced transition metals, range from −4.5 to −5.5 eV, while the ionisation potentials of the atomic *d* orbitals in complexes range from −8 to −12 eV.[23] As a consequence of the lower HOMO energies of the metals in complexes or oxides compared with H–H and C–H bonds, electron transfer from the σ_g orbitals of the H–H and C–H orbitals to the metal predominates in the early stages.[25,26]

The dominant role of electron-donating properties of saturated hydrocarbons in their interaction with metals in a high oxidation state, for example, with organometallic clusters, has been demonstrated.[24] The author[24] calculated a critical point $\varepsilon_d \approx -9.1$ eV on the energy scale. He showed that, when the HOMO energy of the metal is greater than this quantity, then the molecule, for example of CH_4, is an electron acceptor, whilst if it is lower than the critical point the molecule is an electron donor. Since the HOMO energies of the majority of transition metals are above −9.1 eV, the methane molecule is an electron acceptor in relation to them.

The frontier orbital energies of the molecules of hydrogen and the hydrocarbons involved in the chemisorption on the surface metal atoms determine the difference between the activations of the H–H and C–H bonds: the CH_4 molecule is a better electron donor, since its HOMO lies 2 eV higher than in hydrogen. The electron-accepting properties of hydrogen and methane molecules are similar, since the energy of the bonding σ_g hydrogen orbital is −17.56 eV, while that of the antibonding σ_u^* orbital is +4.17 eV; the energies of the corresponding orbitals in CH_4 are −15.4 and +3.6 eV.[23]

The deposition of the metal on a carrier exerts a significant influence on the donor–acceptor character of the interaction of the metal with hydrogen and hydrocarbons. According to Beran et al.,[27] the C–H bond dissociation energy in the CH_4 molecule on supported nickel catalysts diminishes with increase in the electronegativity of the carrier. The transfer of electrons from the carrier to the metal is hindered by the higher electron density in the latter (for example 10^{23} cm^{-3} in platinum and 10^{20} cm^{-3} in titanium dioxide).[28] However, in the case of highly dispersed particles of the deposited metal, which are electron-deficient,[29–31] paraffinic hydrocarbons exhibit electron-donating properties, coordinating very strongly to these particles, reducing catalytic activity in their reactions.[29,31,32]

In the reactions of hydrocarbons on the surfaces of heterogeneous catalysts, the C–C bond is activated together with C–H, which leads to a nonselective course of the reaction in the dehydrogenation of hydrocarbons. The ratio of the dehydrogenation and hydrocracking products is determined by the ratio of the energies of the bonds formed (M^+–H, M^+–C) and dissociated (C–C, C–H).[33]

It has been shown in a study of the hydrogenolysis kinetics of C_2–C_5 alkanes on supported rhodium and nickel catalysts and also on the surface of single crystal iridium[34–36] that the activation of the C–C bond is a structure-sensitive reaction. According to Dorfman,[37] because of symmetry considerations the dissociation of the C–C bond takes place on pairs of coordinatively unsaturated atoms of *d* metals located at the apices, on the edges, and in high-index planes of small crystallites.

Systematic data on the ability of metals to break the C–C bond as a function of their position in the Periodic System are not to be found in the literature; only isolated results have been published. Thus it has been shown[38] that the C–C and C–H bond dissociation energies decrease in the sequence Pt > Ni > Fe/W. The strength of the bond between the metal and carbon increases on passing from Pt to Ir and Os; the frequency of the C–C bond increases in the same direction.[34] It has been established for fission exchange involving deuteriated methane that cobalt and iridium preferentially form multiple bonds to a carbon atom, whereas on platinum the formation of single M–H bonds is preferred.[39,40] The ability of cobalt and iridium to form multicentre bonds explains their high activity in the hydrogenolysis processes.

Certain ideas about the mechanism of the fission of C–C bonds have arisen in the study of the high-temperature activation of saturated hydrocarbons by metal complexes.[33] Several C–C bond activation pathways are possible on coordinatively unsaturated transition metal (metals in the zerovalent or a low oxidation state) complexes. For example, activation takes place on direct insertion of the metal in the C–C bond via the oxidative addition mechanism or in the initial oxidative addition of a C–H bond to the metal complex and the subsequent cleavage of the C–C bond in the σ-alkylmetal hydride complex.

Thus the activation of hydrogen and hydrocarbon molecules on the surfaces of supported catalysts proceeds either via oxidative addition (the formation of negatively charged complexes) or via a donor–acceptor mechanism with charge transfer from the molecule to the metal (the formation of positively charged complexes) predominating depending on the degree of reduction of the metals on the surface.

III. The role of hydrogen in the reactions of hydrocarbons

In the numerous studies of the reactions of saturated hydrocarbons in the presence of hydrogen (dehydrogenation, dehydrocyclisation, hydrogenolysis, hydrocracking, etc.) published hitherto, it has merely been shown that hydrogen, without being a stoichiometric reactant, has a positive effect at certain concentrations both on the rate and selectivity of the process. Thus it has been observed[2,41] that the addition of hydrogen to the reaction medium suppresses the dissociative chemisorption of hydrocarbons on the surfaces of metals, which prevents self-poisoning of the catalyst surfaces and the deposition of carbon on the latter. On the other hand, at relatively high concentrations of the gas phase,

hydrogen promotes both the hydrogenation of the alkenes formed and the cleavage of the C–M bond, reducing thereby the fraction of the surface involved in the reaction of the hydrocarbons and lowering the overall degree of conversion.[2,41,42] The forms of hydrogen firmly retained on the catalyst surface insulate the surface metal atoms from direct contact with the reactant molecules,[43] which can alter the mechanism of their interaction.

The change in the size of the working metal assemblies, induced by the change in the amount of carbonaceous deposits, has also been explained[44] by the involvement of hydrogen in the reactions of alkanes on the surfaces of platinum catalysts. In the presence of a deficiency of hydrogen, the catalyst surface is largely covered by hydrocarbons, retained mainly on the platinum centres. The H–Pt–C system formed under these conditions breaks up the large platinum assemblies and the centres active in the dissociation of the C–C bond are blocked. In the presence of an excess of hydrogen in the mixture, whereupon the surface coverage by the hydrocarbons is low (the H–Pt system), the main reaction path involves the fragmentation of the alkane molecules.[44,45]

It has been established[46] that the reaction of n-hexane on the surface of a platinum–tin catalyst freed from adsorbed hydrogen proceeds nonselectively with formation of light saturated hydrocarbons. If the catalyst surface has been covered with hydrogen, then the selectivity with respect to alkenes increases.

The role of the energy characteristics of hydrogen, which influence the rate and mode of the reactions of hydrocarbons, have been discussed in a number of publications. Thus Volter and coworkers[47,48] observed a satisfactory correlation between the activity of platinum and platinum–tin catalysts in the dehydrogenation of cyclohexane and their content of hydrogen retained on the surface in the temperature range 0–300 °C.

The hydrogen initially adsorbed on the platinum/alumina catalyst can participate directly in the reactions of cyclohexane, effecting the hydrogenation of its extensively dehydrogenated strongly bound molecules with formation of a high-temperature form of benzene.[49] The chemisorbed hydrogen does not participate directly in the formation of the low-temperature form of benzene, but in the absence of hydrogen from the catalyst surface this form of benzene is not formed and the thermoprogrammed desorption (TPD) spectrum shows only the peaks of the strongly bound form of benzene.[49]

The direct involvement of atomic forms of hydrogen in the dehydrogenation of cyclohexane adsorbed on the surfaces of palladium or nickel catalysts has been demonstrated.[50] As a result of the study of the dehydrogenation of cyclohexane on specimens with preadsorbed deuterium, a reaction mechanism was proposed in which the adsorbed hydrogen and the hydrogen in the chemisorbed cyclohexane molecule recombine with elimination of a hydrogen molecule. Analysis of the activation energy for the reaction involving the deposition of carbonaceous deposits led Masai et al.[50] to conclude that the forms of hydrogen which can increase the activity of catalysts in the dehydrogenation of cyclohexane are also responsible for the high degree of carbon deposition on the surface.

The C_5-dehydrocyclisation reaction proceeds via a similar mechanism, presupposing the recombination of a hydrogen atom belonging to a hydrocarbon transition complex with a hydrogen atom adsorbed on the surface.[2]

It has been suggested in a number of investigations[51–53] that the C–H bonds in the cyclohexane molecule are activated on the centres for the adsorption of weakly bound hydrogen because the dehydrogenation reaction on the Pt/Al_2O_3 and $Pt–Sn/Al_2O_3$ catalysts begins at temperatures at which the surface of the specimens is freed from hydrogen (T_{des} < 350 °C).

A correlation between the content in the catalyst of the hydrogen desorbed in the temperature range 320–480 °C and the catalyst activity has been observed in a study of the dehydrogenation of n-dodecane on platinum catalysts promoted with indium and gallium.[54] The observed relation can be explained by the fact that the centres for the activation of the dissociatively chemisorbed hydrogen serve simultaneously as the sites for the adsorption of intermediate products formed on dissociation of a C–H bond.

Comparison of the reactivity of hydrogen in the dehydrogenation of cyclohexane and its thermodesorption characteristics in low-percentage promoted Pt and Pd catalysts on Al_2O_3 showed[55,56] that the most active specimens chemisorb two energetically different atomic forms of hydrogen—with T_{des} = 160–480 °C and 480–900 °C respectively. The weakly active catalysts are characterised by the absence from the surface of the form of hydrogen with a lower bond energy.

Thus analysis of the available literature data shows that hydrogen is an obligatory participant in the catalytic reactions of saturated hydrocarbons. However, as a consequence of the nonuniformity of the energy characteristics of the hydrogen chemisorbed on the surfaces of catalysts, it is necessary to discover the role of each form of hydrogen in the catalytic reactions of unsaturated hydrocarbons.

The nature of the adsorption complexes of hydrogen, determined by the state of the active centres of the catalyst surface, can be discovered from the relation between the oxidation state of the metals in supported low-percentage catalysts and the adsorption characteristics of the hydrogen on their surfaces.

IV. Relation between the adsorption characteristics of hydrogen, the state of the metals, and catalyst activity in the reactions of saturated hydrocarbons

It is essential to note that towards the beginning of the 1980s there had been virtually no experimental studies on the chemisorption of hydrogen and its energy characteristics on Group VIII metal oxides. The reason for this was the relative ease of the reduction of the oxidised metals in hydrogen.

The metals can retain their oxidation state during the reduction process if the oxides are part of the composition of low-percentage supported catalysts [in the presence of a strong metal–carrier interaction (SMCI)]. The H–H bond is activated via the heterolytic mechanism for high oxidation states or via the donor–acceptor mechanism for low oxidation states of the metal in the oxide and for chemisorption on highly dispersed electron-deficient particles of the metal on a carrier.[23,33,37]

It has been shown[1,57–61] that metals deposited on a carrier at low concentrations (0.02–0.1 mass% Pd; 0.5–1.0 mass% Co; 0.05–0.1 mass% Pt; 2.1 mass% Ce), corresponding to the SMCI region, are mainly in the oxidised state (Pt^{2+}, Co^{2+}, Pd^{2+}, Ce^{4+}) and in the case of Pd/Al_2O_3 partially in the atomically disperse[58,60] state after high-temperature (400–500 °C) treatment in hydrogen. The highly dispersed particles of the deposited metals with an increased concentration of the active phase are also electron-deficient.[29–31,62,63] In the above catalyst, virtually all the atoms of the deposited metal are on the surface and are accessible for chemisorption. Thus, according to data obtained by the paramagnetic probe method (PPM), after the deposition of 0.02–0.1 mass% Pd, 0.6×10^{13} palladium atoms cover 2×10^{13} Al^{3+} centres,[57] whereupon a sharp decrease (up to 50%) in the number of coordinatively unsaturated Al^{3+} atoms on the surface is observed (Fig. 1*a*, curve *1*).

The degree of coverage of the active phase of the catalysts by hydrogen in the SMCI region, determined by the TPD method,[57,58] is negligible: the ratio H : M $\leqslant$ 0.01 (M = Co, Ce, Pt) with the exception of Pd/Al_2O_3, for which H : Pd is somewhat higher—H : Pd = 0.01–0.2 (Fig. 1*a*, curve *2*; Fig. 2*a*, curve *1*). This is evidently induced by the presence on the catalyst surface of palladium in the atomically dispersed electron-deficient state.[58]

In catalysts with an active phase concentration higher than in the SMCI region (Pd $\geqslant$ 0.01–0.3 mass%; Pt > 0.1 mass%; Co > 1.0 mass%; Ce $\geqslant$ 2.1 mass%), the deposited metal is adsorbed on the previously occupied parts of the surface, because the number of coordinatively unsaturated Al^{3+} centres does not

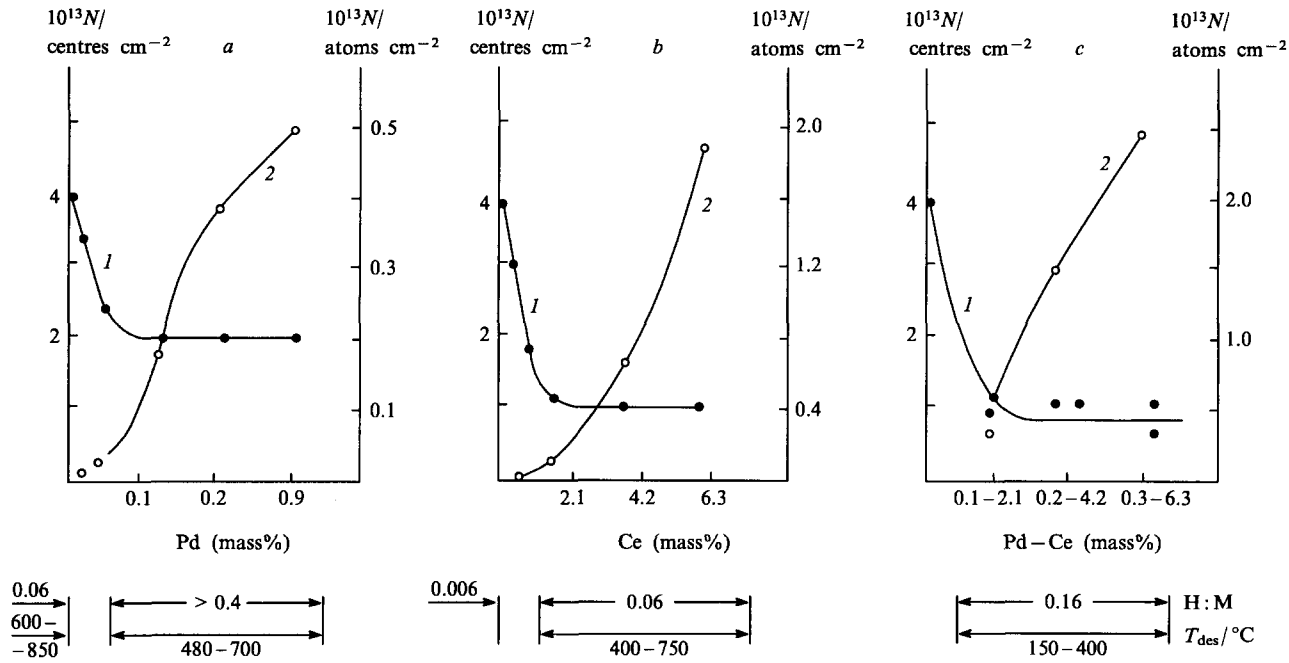


Figure 1. Effect of concentration of deposited Pd (*a*), Ce (*b*), and Pd–Ce (*c*) on the number of Al^{3+} acceptor centres on the Al_2O_3 surface (curves *1*) and on the overall content of the hydrogen adsorbed by the catalyst (curves *2*). The H : M ratios and the temperature ranges in which hydrogen is desorbed, corresponding to regions of strong and weak interaction of the metal with the carrier, are indicated on the scale parallel to the abscissa axis.

diminish with increase in the metal content, according to PPM data (Figs 1*a* and 1*b*, curves *1*).[57] After high-temperature reduction in hydrogen, metals in a more reduced form as well as highly dispersed metallic particles are detected in such specimens.[58,61,64–67] For example, it has been demonstrated by X-ray photoelectron spectroscopy (XPES) that in the 6% Co/Al_2O_3 and 0.35% Pt/Al_2O_3 catalysts 37% and 20% of the metal atoms relative to the overall content exist on the surface in the reduced form.[67,68] Catalysts of this type interact with H_2 and produce mainly strongly bound forms of the chemisorbed hydrogen ($T_{des} \geqslant 480-500$ °C; Fig. 2*a*, curves *2* and *3*), the ability of the specimens to chemisorb hydrogen increasing significantly with increase in the concentration of the deposited metal (from 0.1–0.3 mass% Pd, from 1.7–4.3 mass% Co, and $\geqslant$ 4.2 mass% Ce): the ratio H : M increases by a factor of 8–10 (Figs 1*a* and 1*b*, curves *2*; Fig. 2*a*, curves *1–4*; Fig. 3*a*, curves *1–3*) and hydrogen less strongly bound to the catalyst surface appears (Fig. 2*a*, curve *4*).[57–59]

For bimetallic catalysts, there is a mutual facilitation of the reduction of the metals.[56,58,64–72] Therefore in the platinum/alumina and palladium/alumina catalysts with the noble metal concentrations corresponding to the SMCI region ($\leqslant$ 0.1%) and promoted by the oxides of cobalt (1.0–1.7 mass%),[55,56] cerium (1.0–2.5 mass%; Fig. 1*c*, curve *1*),[56,57,59] and tin (2.0 mass%),[68] the degree of reduction of the metals is higher than in the corresponding monometallic catalyst. For example, the fraction of Pt^0 rises to 40% in $Pt–Sn/Al_2O_3$ compared with 20% in Pt/Al_2O_3. A characteristic feature is also an appreciable increase in the overall capacity for the chemisorption of hydrogen and the appearance of the form of hydrogen weakly bound to the surface (Fig. 1*c*, curve *2*; Fig. 2*a*, curve *5*; Fig. 4*a*, curves *2* and *3*).

Thus there is virtually no chemisorption of hydrogen on oxides of transition metals in a high oxidation state incorporated in the carrier matrix (in the SMCI region). Following the appearance in the specimens of weakly oxidised forms of the metal (highly dispersed electron-deficient metallic particles and the oxides of metals in a low oxidation state), the chemisorption of H_2 is observed with the formation of atomically adsorbed forms firmly bound to the surface (T_{des} > 480–500 °C). When the supported catalysts contain metallic bulk phases, the chemisorption of relatively weakly bound forms of hydrogen with $T_{des} \gtrsim 300$ °C is observed together with the chemisorption of the strongly bound forms.[56,58] This means that, as increasingly more reduced forms and bulk phases of the reduced metal appear in the catalysts, the energetic nonuniformity of the adsorbed hydrogen complexes increases as a result of the formation of the weakly bound $H^{\delta-}$ forms.

The absence of chemisorbed hydrogen from catalysts with the concentration of the active phase corresponding to the SMCI region, in which the oxidised forms of the metals are retained after the high-temperature treatment in hydrogen, may be a consequence of both thermodynamic difficulties induced by the greater difference between the energy levels of the oxidised metals and hydrogen and by the coordinative saturation of the metal oxides in the carrier matrix (Al_2O_3). The chemisorption of hydrogen on the more reduced metals can be regarded[23,33,37] as a result of the activation of hydrogen via the mechanism involving the donor–acceptor interaction with transfer of electron density in both directions $H \rightleftarrows M^{n+}$.

Analysis of the oxidation states of the metals and of the thermodesorption characteristics of the chemisorbed hydrogen permits a conclusion concerning the charge distribution in the adsorbed forms of hydrogen. Thus the chemisorption of hydrogen in the strongly bound atomic form (the $H^{\delta+}$ form with T_{des} > 480 °C), which occurs on electron-deficient metallic particles and on oxides of metals in a low oxidation state, may be associated with the activation of hydrogen via the donor–acceptor mechanism with the preferential transfer of electron density from the hydrogen molecule to the unoccupied *d* orbitals of the metal.[23,37] The presence of relatively weakly bound forms of hydrogen (the $H^{\delta-}$ form with $T_{des} \geqslant 300$ °C), which are characteristic of monometallic catalysts with a high metal concentration and of bimetallic systems containing bulk phases of the reduced metal, is due to the activation of hydrogen via a mechanism involving oxidative addition with electron transfer

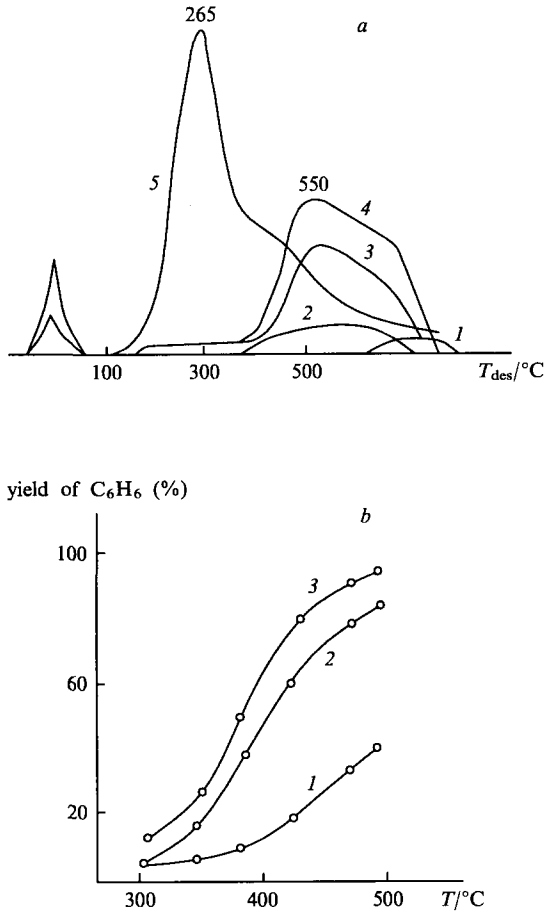


Figure 2. Spectra of the thermodesorption of hydrogen from catalysts on Al_2O_3 (*a*) and the activity of hydrogen in the dehydrogenation of cyclohexane when different catalysts are used (*b*). Metal concentration (mass%): (*a*) 0.04 Pd (curve *1*), 0.3 Pd (curve *2*), 4.2 Ce (curve *3*), 6.3 Ce (curve *4*), and Pd–Ce (curve *5*); (*b*) 0.05 Pd (curve *1*), Pd–Ce/Al_2O_3 (curve *2*); Ce content 1.0 mass% (curves *2*) and 2.5 mass% (curves *3*).

from the metal to the antibonding σ_u^* orbital of the hydrogen molecule.[23,27] The different degrees of dispersion of the reduced metallic particles create in their turn a set of energetically different desorption centres on the surface. Thus it has been shown[73] that, depending on their size, the monodisperse platinum particles on Al_2O_3 (23, 45, or 90 Å) chemisorb hydrogen with different bond energies (E_{des} = 204, 113.4, or 96.6 kJ mol^{-1}).

We shall consider the influence of the state of the metals and of the associated characteristics of the adsorption complexes of hydrogen on the activity of the catalyst in the hydrocracking and dehydrogenation reactions of hydrocarbons (cyclohexane[55,56] and n-propane[68]). In the cobalt/alumina catalyst with a low concentration of the deposited metal (1.7 mass%), containing cobalt mainly in the oxidised state (the SMCI region) and partly in the atomically disperse form, the amount of chemisorbed relatively strongly bound hydrogen in the $H^{\delta+}$ form is small. This catalyst exhibits a low activity in the hydrocracking of cyclohexane [~10% of C_1-C_5 hydrocarbons can be detected in the products (Fig. 3*b*, curve *1*)] and the parallel dehydrogenation reaction (~6% of benzene). The ratio of the yields of the hydrocracking and dehydrogenation products is 1.7. With increase in the cobalt content in the catalyst to 3.0 mass% – 4.3 mass% accompanied by a sharp increase, not proportional to the increase in the concentration of the deposited metal, in the amount of strongly bound hydrogen chemisorbed on weakly oxidised and finely dispersed particles of reduced cobalt, the hydrocracking of cyclohexane proceeds very readily (the yield of C_1-C_5 hydrocarbons is 95% – 99%; see Fig. 3*b*, curves *2* and *3*), while dehydrogenation is almost completely suppressed (the yield of benzene is 3.0% – 0.4%); the ratio of the yields of the hydrocracking and dehydrogenation products increases by a factor of 32 – 246 respectively.

The experimental data presented show that the hydrocracking reaction requires the presence of weakly oxidised forms of the metals on which hydrogen is chemisorbed with formation of strongly bound $H^{\delta+}$ complexes (E_{des} > 250 kJ mol^{-1}; Fig. 3*a* and 4*a*). With increase in E_{des} for the chemisorbed hydrogen, the ability of the catalyst to cleave the hydrocarbon molecule increases and the temperature corresponding to complete conversion diminishes (Fig. 3*b*, curves *2* and *3*; Fig. 4*c*).

While analysing the relation between the state of the chemisorbed hydrogen and the activity of the catalysts investigated, it is essential to note that at 500 °C, where saturated hydrocarbons such as cyclohexane and n-propane react, only hydrogen with T_{des} > 500 °C remains on the surface according to data obtained by the stepwise thermodesorption method (Figs 2*a*, 3*a*, and 4*a*). The $H^{\delta+}$ form of hydrogen cannot evidently be displaced from the catalyst surface during the reaction by the organic component of the reaction mixture (H_2 + saturated hydrocarbon) as a consequence of the lower reactivity of the C–C and C–H bonds compared with the H–H bond.[33] Retained on the surface in this form, hydrogen promotes an increase in the degree of reduction of the weakly oxidised highly dispersed metallic particles, i.e. it behaves as a modifying additive able to alter the electronic properties of the catalyst surface.

Consequently the catalysts containing on their surface an appreciable amount of strongly bound atomic hydrogen in the $H^{\delta+}$ form exhibit an increased activity in the hydrocracking of cyclohexane. This agrees well with the finding that the structure-sensitive C–C bond dissociation reaction takes place readily on pairs of coordinatively unsaturated metal atoms via the

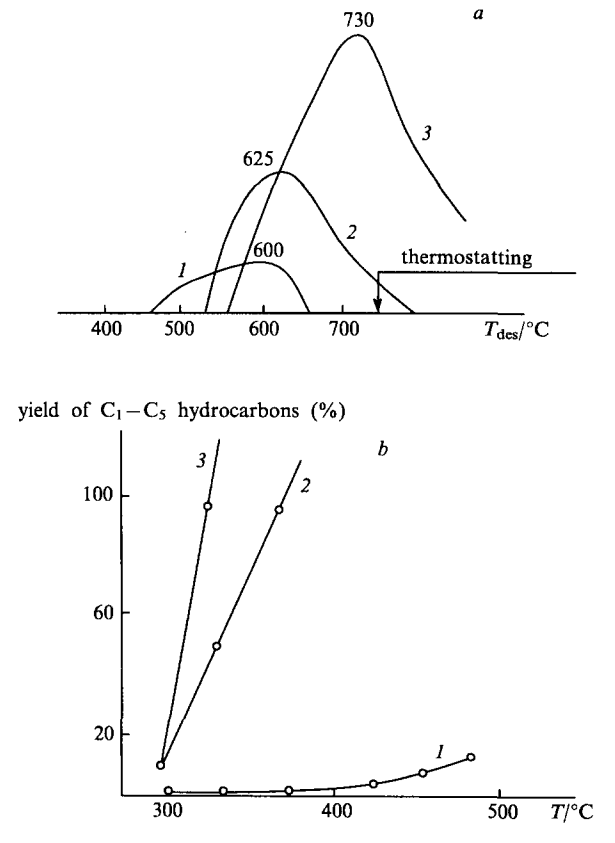


Figure 3. Hydrogen thermodesorption spectra (*a*) and the activity of the Co/Al_2O_3 catalysts in the hydrocracking of cyclohexane (*b*). Cobalt concentration (mass%): (*1*) 1.7; (*2*) 3.0; (*3*) 4.3.

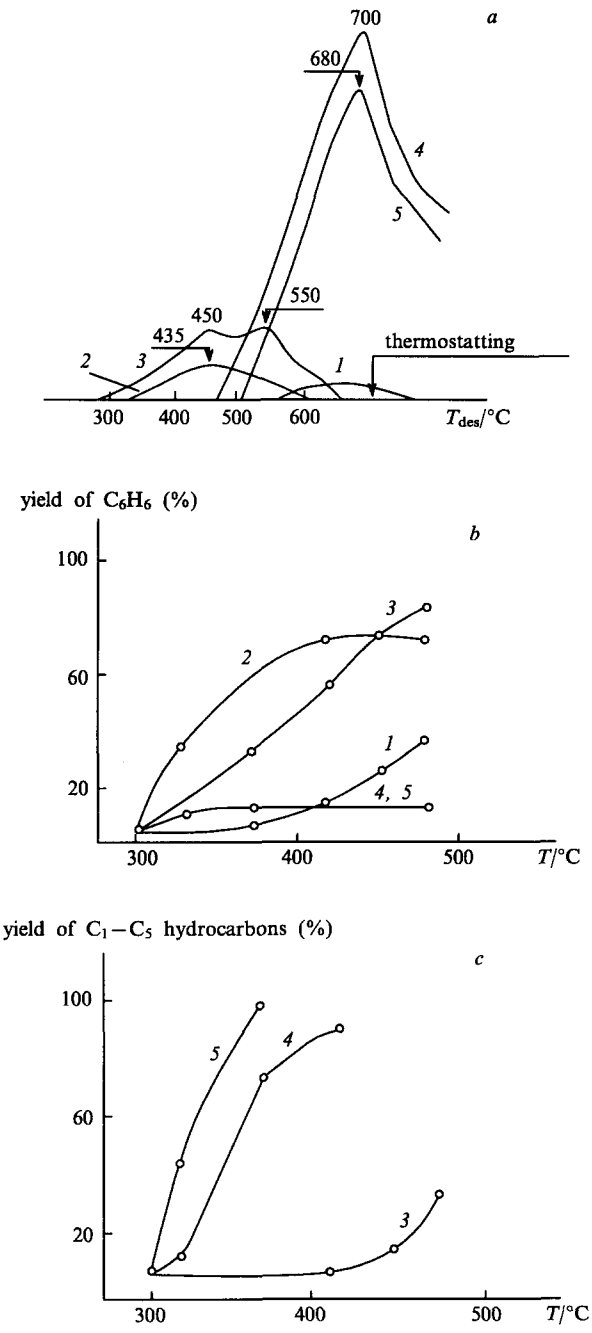


Figure 4. Hydrogen thermodesorption spectra (*a*) and activities in the dehydrogenation (*b*) and hydrocracking (*c*) of cyclohexane of the 0.1 mass% Pd/Al_2O_3 catalyst (curves *1*) and the $Pd-Co/Al_2O_3$ catalysts with various cobalt contents (mass%) [(*2*) 1.0; (*3*) 1.7; (*4*) 3.0; (*5*) 4.3].

oxidative addition mechanism with formation of negatively charged hydrocarbon fragments $(R_3C)^-$.[37] The hydrogen in the $H^{\delta+}$ form also promotes an increase in the degree of reduction of the coordinatively unsaturated electron-deficient metal atoms, accelerating thereby the dissociation of the C–C bonds in the hydrocarbon molecule. Furthermore, it evidently participates in the hydrogenation of the $(R_3C)^-$ fragments that are formed on cleavage of the C–C bonds. The possibility of the simultaneous activation of the H–H and C–C bonds on the same metal atom (centre) has been demonstrated.[37]

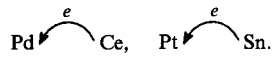
In the dehydrogenation reactions of cyclohexane and n-propane, the most active are bimetallic platinum/alumina and palladium/alumina catalysts containing low concentrations of the promoting agent [1.0–1.7 mass% Co (Fig. 4*b*, curves *2* and *3*), 1.0–2.5 mass% Ce (Fig. 2*b*, curve *3*), or 2.0 mass% Sn],[68] in which the degree of reduction of both the noble and nonnoble metals is higher. Their oxidised forms are less electron-deficient than in the corresponding monometallic specimens. These catalysts are characterised by the chemisorption of both the $H^{\delta+}$ form of the hydrogen and of the $H^{\delta-}$ form (Figs 2*a* and 4*a*).

In the dehydrogenation reaction, a significant fraction of the relatively weakly bound atomic hydrogen $H^{\delta-}$ in the modified catalysts is desorbed from the surface of the specimens, liberating the chemisorption centres on which the C–H bonds in the hydrocarbon molecules are activated. This stage is rate-limiting in the dehydrogenation reaction.[74, 75] The concentration of the centres for the activation of C–H bonds can be estimated quantitatively on the basis of the presence and content of the $H^{\delta-}$ form of hydrogen with E_{des} = 125–250 kJ mol^{-1}, which is chemisorbed on the most reduced surface centres of the catalyst, and the activity of the catalyst in the dehydrogenation of hydrocarbons can be inferred.

The hydrogen in the $H^{\delta+}$ form ($T_{des} > T$) chemisorbed on weakly oxidised and highly dispersed metallic particles is retained on the surface of the catalyst at the temperature of the dehydrogenation reaction. Evidently the hyrogen can participate directly in the catalytic dehydrogenation step, recombining with the atomic hydrogen $H^{\delta-}$ formed on dissociation of the C–H bonds as a result of their activation on the reduced surface centres via the oxidative addition mechanism.[37] Furthermore, the degree of reduction of the electron-deficient surface centres increases during the formation of the $H^{\delta+}$ form. Hence, the number of centres for the activation of the C–H bonds is increased.

V. Conclusion

The combination of reduced metals and metals oxidised to different extents in the bimetallic catalysts investigated, which chemisorb hydrogen via different mechanisms, ensures their high capacity for the chemisorption of hydrogen. The degree of reduction of the metals in bimetallic catalysts, which determines the strength of the bonding and the charge state of the different forms of chemisorbed hydrogen and hence the mode of the reactions of saturated hydrocarbons, depends on the chemical nature of the modifying additive (the electron work function, the oxidation-reduction potential, etc.) which weakens or intensifies the electron-donating properties of the noble metal, for example:



Catalysts containing on their surface centres for the chemisorption of complexes of the type $H^{\delta-}$ exhibit a fairly high activity in the dehydrogenation of hydrocarbons ($Pd-Ce/Al_2O_3$ with 2.5 mass% Ce). On catalysts containing centres for the chemisorption of both types, namely $H^{\delta+}$ and $H^{\delta-}$ (Pd–Co, $Pt-Sn/Al_2O_3$), alkanes react via two pathways: dehydrogenation and hydrocracking, whereas catalysts which chemisorb hydrogen only in the $H^{\delta+}$ form (Co/Al_2O_3) drive the process mainly along a single path — the hydrocracking of the molecule.

Chemisorbed hydrogen can be regarded not only as a participant in the dehydrogenation or hydrocracking reaction (hydrogenation of fragments of the hydrocarbon molecule in the hydrocracking process or recombination with the hydrogen atom formed on dissociation of a C–H bond) but also as a modifying agent, which gives rise to a definite degree of oxidation or reduction of the metals on the catalyst surface.

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