Russian Chemical Reviews **66** (2) 107 – 119 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 541.183 + 541.128 + 541.124

Hydrogen spillover in heterogeneous catalysis

V V Rozanov, O V Krylov

Contents

I.	Introduction	107
II.	Methods for the observation of hydrogen spillover	107
III.	The influence of various factors on hydrogen spillover	110
IV.	Kinetics of hydrogen spillover	111
V.	The mechanism of hydrogen spillover	112
VI.	Conclusion	116

Abstract. The phenomenon of hydrogen spillover (interphase diffusion of adsorbed hydrogen), the methods for its detection, and the factors influencing it are examined. The common occurrence of the spillover and its role in various adsorption and catalytic processes, particularly in reactions involving hydrogen on multiphase catalysts, are demonstrated. The possible mechanisms of the spillover are analysed. The bibliography includes 189 references.

I. Introduction

In heterogeneous catalysis, the term spillover is applied to the transport of active species sorbed or formed on one phase to another phase which does not sorb or generate these species under the given conditions.[1–7] The term 'spillover' (from spill over in English) was introduced by Boudart *et al.*[1] The phase generating the active species is called the initiator (or activator), while the phase providing sites for the adsorption of active species is known as the acceptor. If these phases are in direct contact, then the spillover is said to be primary, but when they are separated by an additional inert carrier, it is said to be secondary.

The first direct evidence for spillover was apparently obtained by Khoobiar.[2] WO_3 is known to be reduced by hydrogen at temperatures above 200 °C with formation of the blue oxide W_4O_{11}. On the other hand, when pure H_2 is passed over the 0.5% $Pt/Al_2O_3 + WO_3$ mechanical mixture, the colour changes already at room temperature. This effect is not observed on the $Al_2O_3 + WO_3$ mechanical mixture. This is explained by the fact that hydrogen dissociates on platinum and migrates via Al_2O_3 onto WO_3 in the form of atoms or H^+ ions.

$$H_2 \xrightarrow{Pt} 2H,$$

$$2H \overset{Al_2O_3}{\rightleftharpoons} 2H^+ + 2e,$$

$$2H + 4WO_3 \longrightarrow W_4O_{11} + H_2O,$$

$$H + H \longrightarrow H_2.$$

Measurement of the amount of adsorbed hydrogen showed that the $Pt/SiO_2 + WO_3$ mixture adsorbs several times more H_2 than Pt/SiO_2 without WO_3.[3] The blue colour of the tungsten oxide is due to the formation of the so called tungsten bronze under the influence of the hydrogen which has passed from Pt onto WO_3 via SiO_2 (or Al_2O_3).

The so called structural sensitivity, *i.e.* the dependence of the specific catalytic activity (calculated per unit surface or per active centre) on the particle size, is often observed in heterogeneous catalysis.[7] This leads to differences between the specific activities of supported and massive catalysts. One of the causes of this difference may be the involvement in the reaction of the initially inactive support surface as a result of the transfer onto it of active adsorbed species via spillover.

The spillover phenomenon is common in catalysis by supported metals and mixed oxides. The atoms of not only hydrogen but also of oxygen, as well as the N, CO, NCO, and certain other species may participate in spillover. The vast majority of the communications published hitherto on this topic have been devoted to hydrogen spillover. Since 1983, international conferences on spillover are being held regularly. The present review is devoted to studies on hydrogen spillover carried out mainly during the last 10 – 15 years.

II. Methods for the observation of hydrogen spillover

1. Chemisorption of hydrogen

The most common method for the determination of the surface area of a metal in supported catalysts, namely from the chemisorption of hydrogen, may be used for the observation of the spillover phenomenon.[3] H_2 is usually chemisorbed at 200 – 300 C°. Analysis of extensive experimental data showed that the number of metal atoms on the surface (N_M) usually corresponds to the number of hydrogen atoms adsorbed on this surface (N_H). The review of Sermon and Bond [5] contains tables for different supported metals (Pt, Pd, Rh, Re, Ru, Ni), from which it is seen that the ratio N_H/N_M varies in the range 0.5 – 2.0. With decrease in the metal particle size, the ratio becomes less than unity in most cases, although the opposite effects are also encountered. The deviations from unity are caused by the following factors: (1) the dissolution of hydrogen in the bulk of the

V V Rozanov, O V Krylov N N Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 117977 Moscow, Russian Federation. Fax (7-095) 938 21 56. Tel. (7-095) 939 74 49 (V V Rozanov), (7-095) 939 71 68 (O V Krylov)

Received 14 October 1996
Uspekhi Khimii **66** (2) 117 – 130 (1997); translated by A K Grzybowski

metal; (2) a change in the crystal system in small particles; (3) the presence of a relatively large number of low-coordinated atoms in small particles; (4) a change in the degree of oxidation of the metal; (5) the spillover phenomenon.

In order to elucidate the causes of the deviation of the ratio N_H/N_M from unity, hydrogen adsorption data are compared with results obtained by other methods: from the adsorption of CO, from the broadening of X-ray diffractograms, by electron microscopy, *etc*. If all the methods other than H_2 adsorption yield identical results, the possible cause of the discrepancy may be the flow of hydrogen onto the carrier. Thus the ratios $N_H/N_M = 5-10$ on the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts [8] and 75 on the Pt/C catalyst,[9] found by the H_2 adsorption method, have actually been explained by hydrogen spillover.

The additional chemisorption of hydrogen on platinum deposited on an activated charcoal, occurring with increase in the duration of exposure of the catalyst to a H_2 atmosphere, is also associated with the spillover of hydrogen from platinum to the charcoal.[10]

Spillover may also promote an increase in the rate of adsorption of hydrogen. This phenomenon has been observed, for example, in the adsorption of H_2 on a mixture of Co/C with activated charcoal.[11] On the other hand, the amount of adsorbed hydrogen is determined by the capacity of the acceptor and is independent of the concentration of Co or of another initiator (Ni, Cu, Fe).

The observation of spillover by the adsorption method is favoured by a high H_2 pressure and a high temperature.[5] Methods involving the measurement not of the amount but of the rate of adsorption of hydrogen on the support and oxygen – hydrogen titration are varieties of the adsorption method:[5]

$$Pt-O_x + (x + \tfrac{y}{2})H_2 = Pt-H_y + xH_2O$$

(water remains sorbed on the carrier). In the presence of hydrogen spillover, the number of adsorbed oxygen atoms N_O remains constant and N_H/N_O exceeds 2.

The surface hydrogen can also be titrated with olefins, which results in the formation of paraffins. It has been shown that at 100 C° the hydrogenation of pent-1-ene to pentane by the hydrogen adsorbed on Pt/SiO_2 is very fast in the initial period, after which the rate of reaction falls.[12] It has been suggested that in the first stage the hydrogenation is effected by the hydrogen adsorbed on Pt, whilst in the second stage it is effected by the spillover hydrogen adsorbed on SiO_2.

A gravimetric study of the adsorption of hydrogen and deuterium on the HNaY zeolite and on Pt/HNaY at room temperature showed that in the latter case hydrogen spillover from platinum to the zeolite takes place.[13] The amount of hydrogen adsorbed on the platinum-containing zeolite exceeds by more than an order of magnitude the amount of H_2 capable of being adsorbed on the supported Pt. As expected, the increment in the mass of the specimen in the adsorption of deuterium was twice as great as in the adsorption of protium.

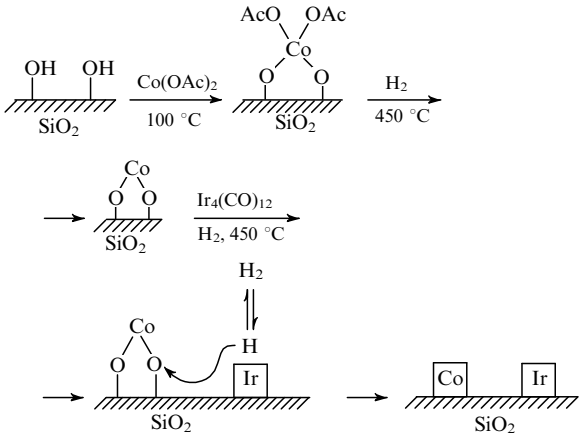
2. Reduction of oxides

In a mechanical mixture of a supported or unsupported metal with a reducible oxide (WO_3, MoO_3, Fe_2O_3, V_2O_5, Co_3O_4, CuO), the degree and rate of reduction may increase by virtue of hydrogen spillover:[4–6]

$$M^{n+} + O^{2-} + H \longrightarrow M^{(n-1)+} + OH^- .$$

As a result of spillover, the reduction temperature falls in certain cases by 200–400 °C. The studies have been carried out by gravimetric, differential thermal analysis, temperature-programmed reduction, microcalorimetric, *etc*. methods. Metals (Pt, Pd, Ni, *etc*.) are thus catalysts of the reduction of oxides. The degree of reduction can be determined from the amount of reacted hydrogen and also from the changes in certain parameters characterising the solid. In the reduction of, for example, V_2O_5 to V_2O_4, it is possible to measure the EPR signal due to V^{4+} or the area of the bands in the phase XRD spectra of the V_2O_4 phase.

In the presence of ruthenium or iridium carbonyls, the reduction of the Co/SiO_2 catalyst, obtained from cobalt acetate, *i.e*.



is accelerated by hydrogen spillover.[14] This results in the formation of a highly disperse catalyst which accelerates the hydrogenation of CO to oxygenates.

The carbide WC, the properties of which are similar to those of Group VIII metals, can also serve as the source of spillover hydrogen for the reduction of MoO_3.[15]

Sulfides can also be reduced by means of the spillover. When Ni or Co is added to WS_2, $H_{0.05}WS_2$ is formed.[16]

The adsorption of hydrogen on the Pt/WO_3 catalyst has been investigated.[3] It was found that WO_3 is reduced by virtue of the adsorption and activation of hydrogen on Pt and its subsequent diffusion to WO_3. On the other hand, on pure WO_3 the adsorption of hydrogen is not observed.

On platinum deposited on the CeY zeolite, Ce^{4+} was reduced to Ce^{3+} in the presence of adsorbed perylene, perylene serving as the bridge for the transport of active hydrogen from Pt to the zeolite.[17]

Hydrogen spillover has also been observed in the Pt/ZrO_2, Pt/SiO_2, and Pt/TiO_2 systems. In certain cases, spillover is promoted by the presence of water, the molecules of which may also serve as bridges for hydrogen.

When MnO_2 deposited on a SnO_2 film is heated, reduction does not occur in a H_2 atmosphere at 500 °C. According to EPR data,[18] the addition of Pd leads to the appearance of Mn^{2+} as a consequence of hydrogen spillover and the reduction of MnO_2. However, the effect of hydrogen spillover is not easy to estimate quantitatively for the examples quoted not only because of technical difficulties but also by virtue of the characteristic features of the topochemical process. Hydrogen spillover may prove to be an essential condition for reduction only in the nucleation stage, whilst in the phase growth process the reaction may be propagated by the hydrogen interacting directly with the oxide. The degree of reduction depends also on the extent of the interface between the metal catalyst and the oxide being reduced. The reduction of oxides can therefore be regarded as confirmation of the occurrence of spillover, but it does not allow quantitative estimates.

The apparent activation energy (E_a) for the reduction of oxides under spillover conditions does not differ from E_a in noncatalytic reduction. The presence of a metal apparently promotes an increase in the amount of reactive hydrogen or an increase in the rate of nucleation (in the pre-exponential factor).[6]

One of the products of the reduction of oxides is water. According to different data, it either accelerates or retards both hydrogen spillover and the reduction process itself. This also complicates the use of the oxide reduction process for the observation of spillover.

3. The influence of spillover on catalysis

Multiphase catalysts frequently possess an enhanced activity and selectivity. This can be explained by the fact that one of the stages of a complex process occurs on one phase whilst another occurs on another phase, spillover taking place between the phases (sometimes with participation of a third phase).[19] In the case of hydrogenation, the supported metal may adsorb and activate hydrogen, the support may adsorb the substance to be hydrogenated, and the reaction itself proceeds on the support surface as a result of hydrogen spillover.

For example, it has been found[20] that the specific rate of hydrogenation of benzene per unit mass of Pd increases by a factor of 3 when the Pd/Al_2O_3 catalyst is diluted with pure Al_2O_3. Hydrogen diffuses over distances up to 0.5 mm. At -52 °C, the degree of coverage of the Al_2O_3 surface by hydrogen may reach 3×10^{-2}.

In estimating effects of this kind, one should bear in mind that they may be accounted for by the 'trapping' by the diluent of the coke which poisons the catalyst.[5] This is also a kind of spillover but of the organic substance and not hydrogen. It has been shown[21] that the addition of Pt to the $Ni-Mo/SiO_2-Al_2O_3$ system ensures an appreciable decrease in the temperature corresponding to the removal of coke after the hydrocracking of heavy oils. When Pt was added to H–Ga silicate, an increase in the rate of aromatisation of propane and a sharp decrease in coke formation were observed.[22] A similar phenomenon has been noted in the alkylation of 1,2,4-trimethylbenzene and its disproportionation to durene after the addition of Pt to montmorillonite. It has been shown by IR spectroscopy that the Lewis acid centres are then converted into Brönsted acid centres.[23–25]

The increase in the rate of hydrogenation of ethene on the Pt/SiO_2 catalyst diluted with SiO_2 or Al_2O_3 has also been attributed to hydrogen spillover.[26] The use of Al_2O_3 as a diluent afforded a greater increment in the rate of hydrogenation than dilution with SiO_2.

As the Pt/C catalyst was diluted with pure carbon up to a ratio of 1 : 50, its activity in the hydrogenation of benzene initially rose and then became constant.[27]

The Pt/Al_2O_3 catalyst diluted with Al_2O_3 up to ratios ranging from 1:3 to 1:100 has been tested in the hydrogenation of benzene.[28] It was found that the specific activity of the catalyst per gram of Pt increases with increase in dilution up to 1 : 50. The activation energy for the reaction, which is 38.5 kJ mol^{-1}, did not change on dilution. The authors[28] assumed that the rate-limiting stage is not spillover but the interaction of benzene with atomic hydrogen. The rate of hydrogenation of benzene on the Pt/Al_2O_3 catalyst diluted with Al_2O_3 was equal to the sum of the rates of reaction on Pt/Al_2O_3 and Al_2O_3, but the reaction does not occur on pure Al_2O_3 in the absence of platinum.

The isomerisation of n-pentane to isopentane on the Pt/SiO_2 or H-ZSM-5 catalytic systems proceeds at a low rate, but when they are mixed an active and selective catalyst of the isomerisation reaction in the presence of hydrogen is obtained.[29] Oligomerisation predominates in the absence of H_2. It has been suggested that hydrogen spillover is necessary for the occurrence of hydroisomerisation.

The Pt/KA + NaY mixed catalyst exhibited a much higher activity in the hydrogenation of isobutene to isobutane than Pt/KA and NaY separately.[30] In this case too, hydrogen spillover accelerates the catalysis.

An appreciable increase in catalytic activity in the hydrodesulfurisation of thiophene was noted when MoS_2 (or WS_2) was mixed with $PtS/\gamma\text{-}Al_2O_3$, $PdS/\gamma\text{-}Al_2O_3$, or $Rh_2S_3/\gamma\text{-}Al_2O_3$.[31] It has been suggested that noble metals activate hydrogen, which then migrates via the spillover mechanism onto MoS_2 or WS_2, where it participates in the hydrogenation. The addition of Ru to the $Co-Mo/Al_2O_3$ [32] or MoO_3/Al_2O_3 [33] catalyst has the same effect.

The rate of hydrocracking of diphenylmethane also increases after the addition of sulfided $Co-Mo/SiO_2$ to an silica–alumina by virtue of hydrogen spillover.[34]

The mechanism of the cracking of n-hexane on the Pt/H-erionite bifunctional catalyst involves hydrogen spillover.[35,36] The hydrogen dissociated on platinum migrates onto the carrier, where a dynamic equilibrium is established between the atomic and protonated forms of hydrogen.

Organic deposits on the metal surface may also serve as a suitable 'phase' for the occurrence of spillover. It has been shown by LEED (low energy electron diffraction) that the hydrogenation of C_2H_4 on Pt and Rh single crystals takes place on top of an ethylidyne layer, which remains ordered under the reaction conditions.[37]

The hydrogen participating in spillover can also interact with organic deposits and can ensure the removal of coke.[38] The isomerisation of paraffins and aromatic alkyl-substituted compounds takes place on acid catalysts and the reaction stoichiometry does not require that hydrogen participates in it. However, the introduction of small amounts of Pt and H_2 into the system accelerates the process as a result of the hydrogenation of the coke which poisons the catalyst.

In a mechanical mixture of coke-saturated Al_2O_3 with $Pt-Re/Al_2O_3$, the hydrogenation of coke via the spillover mechanism begins at a Re concentration of 50%.[39]

4. Isotope methods

One of the commonest methods for the observation of hydrogen spillover is isotope exchange between D_2 and the OH groups of the carrier. An increase in the rate of isotope exchange between the OH and OD groups on Pt/Al_2O_3 compared with the rate of this process on Al_2O_3 was first observed by Carter *et al.*[40] Conner *et al.*[41] studied hydrogen spillover on Pt/SiO_2 with the aid of D_2 by FTIR (fourier-transform infrared) spectroscopy. Platinum was placed at the centre of pressed $Pt/Al_2O_3/SiO_2$ and Pt/SiO_2 discs in order to measure the concentration gradient during spillover. Experiments were carried out also in which the spillover initiator (Pt/SiO_2) was isolated from Al_2O_3.[42,43]

The isotope exchange between deuterium and the OH groups of a Y zeolite has been investigated by FTIR spectroscopy.[44] A two-component Pt/NaY–HNaY specimen was used for this purpose. The H–D isotope exchange on the surface of the HNaY zeolite was observed only when the latter was in direct contact with the platinum-containing component of the Pt/NaY specimen. At room temperature, the process was limited by the diffusion of deuterium and by the H–D exchange proper.

Tritium has also been used in the study of spillover.[45] Investigation of the interaction of $^{14}C_2H_4$ and $^{14}C_3H_6$ with T_2 on Pt/SiO_2 and Pt/Al_2O_3 showed that the OH groups of the support exchange with tritium under the hydrogenation conditions and that the degree of involvement of Al_2O_3 in this process is greater than that of SiO_2.

Transmission IR spectroscopy has been employed to investigate the exchange of the OH and OD groups of the Rh/Al_2O_3 catalyst in a stream of D_2.[46] The exchange of methoxylated OH groups with hydrogen on SiO_2 was observed when SiO_2 was mixed with Pt/SiO_2.[47,48] The formation of methane as a result of the interaction of the methoxy-groups with hydrogen (demethoxylation) via a mechanism involving spillover has been noted:

$$H_{sp} + OCH_3 \longrightarrow H \cdot OCH_3,$$

$$H \cdot OCH_3 + H_{sp} \longrightarrow OH + CH_4$$

(H_{sp} = spillover hydrogen).

5. The scavenger method

By adding to the system substances which interact quantitatively with hydrogen and by using sensitive methods such as, for example, EPR as indicators, it is possible to reduce greatly the threshhold in the observation of the spillover effect. This has been confirmed by the results of a study on the CeY zeolite + Pt black system,[49] where Ce^{4+} was reduced to Ce^{3+} in the presence of hydrogen. The adsorption of perylene or anthracene led to the

appearance of radicals, readily detectable by EPR. When spillover occurs, the radicals are hydrogenated and the EPR signal vanishes.

Weakly bound H atoms, participating in the hydrogenation of benzene, have been detected by depositing *N*-*tert*-butyl-α-phenylnitrone or 2,4,6-tri-*tert*-butylnitrobenzene, which served as 'traps' for H atoms, on Pd/Al^2O_3.[50]

6. Thermodesorption methods

The temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) methods can also be used to observe the spillover of adsorbed species.[51] The nonstationary temperature regime employed in these methods makes it possible to separate in time processes occurring on the surface at different rates, including processes involving the desorption of the initial substances, adsorbed in one form or another, and their conversion into other products via different pathways. In contrast to unsupported catalysts, on supported catalysts there is a possibility of the spillover of adsorbed species. This is manifested either by a simple increase in the areas of the TPD peaks due to the substances adsorbed beforehand or by the appearance of new additional peaks.

The TPD – TPR methods yield direct information about the amount of the substance which has diffused onto other phases and make it possible to calculate the coefficients of surface diffusion and the activation energy for the process.

The use of stable isotopes significantly expands the possibilities of the TPD and TPR methods in the study of the mechanism of the spillover of adsorbed species. These methods have been used to investigate hydrogen spillover on a wide range of supported catalysts: platinum,[52–57] palladium,[58] nickel,[52–57] and rhodium [52] on aluminium, titanium, and silicon oxides, cobalt and molybdenum on aluminium oxide [59] and activated charcoal,[69] and platinum on zirconium oxide.[61]

7. Reverse hydrogen spillover

This term is frequently used to designate the reverse migration of hydrogen from the support to the metal.

In the adsorption of an olefin on 0.03% Pt/H_xWO_3 at 100 °C, hydrogen is removed from the catalyst, its amount corresponding to the ratio $N_H/N_{Pt} = 277$.[5] Since H_xWO_3 is incapable of hydrogenating the olefin at this temperature, the participation of hydrogen in the hydrogenation can be accounted for by its reverse spillover from H_xWO_3 onto Pt. In $H_xWO_3 + Pt/SiO_2$ mixtures, where there is little contact between Pt and H_xWO_3, the reverse spillover was not observed.

The desorption of hydrogen from carbon [11,62,63] or from the H – ZSM-5 zeolite [64] is accelerated when platinum or a metal sulfide are deposited on them. The dehydrogenation of cyclohexane under these conditions (at 450 °C) is associated with the reverse spillover of hydrogen from the support to the metal. The catalytic activity increases with increase in the initiator concentration and reaches a certain limit, which is independent of either the amount or nature of the initiator. The reverse spillover may be the rate-limiting stage in the dehydrogenation reaction proceeding via the mechanism

$$C_nH_{2n+2} + 2X \longrightarrow C_nH_{2n} + 2X-H,$$

$$2X-H + 2M \longrightarrow 2M-H + 2X,$$

$$2M-H \longrightarrow 2M + H_2$$

(X is the carbon surface and M is the metal).

Ga^{3+} and Zn^{2+} ions may play the same role of accelerators in the recombination of H atoms, because the rate of aromatisation increases on mixing Ga_2O_3 or ZnO/Al_2O_3 with ZSM-5.[65–70] This entails the reverse hydrogen spillover from the aromatic compound, adsorbed on the zeolite, to Zn^{2+} and Ga^{3+}, which accelerate the recombination of H atoms.

III. The influence of various factors on hydrogen spillover

1. The influence of water, oxygen, CO, and other compounds

Many investigators noted a significant influence of water on hydrogen spillover.[1,3,5,71] Tungsten trioxide is reduced by hydrogen to the blue oxide at temperatures above 400 °C. If WO_3 is mixed with platinum black, the reduction temperature falls to 100 °C and, when water is adsorbed in addition, reduction begins already at room temperature. This effect can be naturally attributed to the positive influence of H_2O if, as stated above, hydrogen spillover occurs with participation of the OH groups of the support . In practice, both positive [71] and negative [72] effects of water have been observed. According to Cevallos-Candau and Conner,[73] water accelerates the exchange between the OH and OD groups on the support but not spillover as such.

Oxygen and CO inhibit spillover.[74,75] Oxygen interacts with hydrogen to form water, which lowers the rate of spillover.[6] However, the reduction of WO_3 was not observed in the WO_3 + Pt black mixture at room temperature in the presence of H_2.[76] On the other hand, the addition of oxygen to hydrogen or the adsorption of oxygen before the admission of H_2 alter the colour of WO_3, to blue, which may indicate the reduction of the oxide.

It has been shown [77] that mobile oxygen, adsorbed on the Pt/TiO_2 catalyst under the conditions of the oxidation of the latter, increases hydrogen spillover in this system.

The accelerating effect of water on the OH – OD exchange in the Pt/Al_2O_3 system in the presence of D_2 at 150 °C has been observed with the aid of chromatographic methods.[78] In the absence of platinum, no exchange was observed.

An increase in the rate of hydrogen spillover on the Pt/MoO_3 catalyst, obtained by impregnating MoO_3 with a solution of chloroplatinic acid,[79–81] promoted a decrease in the concentration of residual chlorine on heat treatment.

2. Spillover initiators

Hydrogenation catalysts are as a rule hydrogen spillover initiators: Pt, Pd, Ni, Rh, $CuCr_2O_4$, *etc*. The presence of even very small amounts (of the order of 10^{-4}%) of a metal (Ni, Pd, Pt, W) in SiO_2 may induce an appreciable absorption of H_2 at 1000 °C (the number of atoms of the absorbed hydrogen exceeds by a factor of 100 the number of metal atoms).[82]

The bond between hydrogen and the initiator metal should not be unduly strong and the catalyst must be sufficiently dispersed to ensure good contact between the metal and the accepting or transport phases. The activity of metals in the exchange between D_2 and the OH groups of pentasil varies in the sequence Pt > Pd > Ni, which is consistent with the greater strength of the Ni – H bond compared with the Pt – H and Pd – H bonds.[83]

In the mixed Co – Mo – S and Ni – W – S catalysts, the hydrodesulfurising initiators of hydrogen spillover are apparently Co and Ni sulfide phases. Rh_2S_3, PdS, and PtS_x mixed with MoS_2 or WS_2 can also serve as spillover initiators.[84]

The spillover initiators (donors of spillover species) do not necessarily have to be mixed with the acceptor; they can also be separated in space from the latter after the initial activation.

Special experiments have been carried out with separation in space of the source and acceptor of the spillover species.[6,85,86] The Pt/Al_2O_3 catalyst was placed in a bulb separated from the SiO_2 acceptor by a porous partition. After activation by heating in a hydrogen atmosphere at 430 °C, the bulb with the catalyst was removed from the activation zone and ethene, ethyne, heptane, benzene, or cyclohexadiene were hydrogenated on SiO_2 at a lower temperature (200 – 270 °C) with participation of spillover hydrogen. The amount of the latter was 10^{12} H atoms per gram of SiO_2. Such an activated SiO_2 specimen retained its activity in the $C_nH_m + H_2$ reaction for a long time, whereas on nonactivated SiO_2 the above mixture did not react. Hence it follows that

hydrogenation proceeds mainly with participation of hydrogen from the gas phase on centres created by virtue of spillover. Careful analysis demonstrated the absence of the Pt impurity in SiO_2 after spillover.

Cumene was cracked similarly on SiO_2 after its initial activation by the spillover hydrogen generated by the Pt/Al_2O_3 system.[87]

Similar results were obtained with the aid of Al_2O_3 activated by the spillover hydrogen flowing from the Pt/Al_2O_3 catalyst.[6,88] A similar activation but at a lower temperature may be ensured by Ni/Al_2O_3.

3. Hydrogen acceptors

In many cases, the final result of hydrogen spillover is the formation of new hydroxy-groups. Consequently oxygen ions may serve as acceptors of hydrogen atoms or ions:

$$O^{2-} + H^+ \longrightarrow OH^-$$

or

$$O^- + H \longrightarrow OH^-$$

or

$$O^- + H^+ \longrightarrow OH.$$

On oxides coated with a hydroxyl layer, structural defects serve as acceptor centres. Carbon is also a good acceptor.

It was already stated above that adsorbed unsaturated compounds and the metal oxides themselves may function as acceptors of H atoms. If protons participate in the spillover, then the effectiveness of the acceptors is determined by their proton affinity,[89] which varies in the sequence water = methyl alcohol > n-butyl alcohol > *tert*-butyl alcohol $\gg$ dibutylamine.

4. Promoting agents

Transport bridges or phases may serve as mediators for the transfer of H atoms from the donor to the acceptor. In one of the first studies on spillover,[9] it was found that the transport of hydrogen on the Pt/C catalyst is accelerated by carbon contaminations, which are produced after the isomerisation or hydrogenolysis of neopentane. The carbon contaminations act as bridge between Pt and C. Their combustion inhibits the spillover. Above it was already stated that perylene also serves as a bridge for the transport of H atoms between Pt and the CeY zeolite.[10,17] Such bridges may be water and the OH groups of the support. There are data showing that SiO_2 plays more effectively the role of a bridge for the transport of H atoms than Al_2O_3. In the hydrogenation of ethene on the $Pt/SiO_2 + H_xWO_3$ system, the WO_3 phase transfers hydrogen to C_2H_4. Carbon functions as a bridge in the Pt/C catalyst.

IV. Kinetics of hydrogen spillover

1. The number of hydrogen spillover adsorption centres

Measurement of the excess amount of adsorbed hydrogen compared with the amount necessary for monolayer coverage of the metal surface makes it possible to determine the number of support centres participating in spillover. The study of the adsorption of H_2 on Pt/Al_2O_3 at 250–300 °C by a volumetric method showed[90] that the number of spillover centres N_H is 10^{12} cm^{-2}. Data for the TPD of hydrogen on a similar catalyst yielded $N_H \approx 2 \times 10^{12}$ cm^{-2}.[57] A similar value (1.5×10^{12} cm) was obtained by NMR in experiments on the adsorption of H_2 on Pt/SiO_2 at room temperature.[91] Thus the number of centres N_H on oxides corresponds to $\sim$1% of the total number of surface centres, which is much less than the number of OH groups on the surface.[6]

On Pt/C, N_H is much greater — from 10^{13} to 10^{16} cm^{-2} (or from 0.01 to 10 formal monolayers).[9–11]

In experiments where the Pt/SiO_2 source of spillover was isolated from Al_2O_3, it was shown that, under the conditions of the OH–D_2 exchange, hydrogen is transferred over a distance of 1 cm in several minutes.[42] In the hydrogenation of C_2H_4 on the $Pt/SiO_2 + SiO_2$ system, the induction of activity on the SiO_2 surface requires prolonged exposure in H_2 (more than 17 h at 400–460 °C) and is characterised by an activation energy of 117 kJ mol^{-1}.[43]

2. Kinetics of catalytic reactions occurring under the conditions of hydrogen spillover

The kinetics of the chemisorption of hydrogen on Pt/Al_2O_3 have been investigated.[57,91] It was found that the amount of absorbed hydrogen is proportional to the square root of the adsorption time and that surface diffusion is apparently the rate-limiting stage.

When the hydrogenation reaction proceeds under stationary conditions, the overall activity of the supported metal greatly exceeds (by 1–2 orders of magnitude) the activity of the acceptor-diluent. Spillover should not therefore influence significantly the rate of hydrogenation. The situation is different when hydrogen and the substance hydrogenated are adsorbed on different phases. Spillover exerts a major influence on the kinetics also when the surface is reduced and the active centres are formed with participation of hydrogen arriving from another phase. Delmon[79] called this phenomenon 'remote control'.

It was found[92] that two kinds of spillover hydrogen exist on Pt/Al_2O_3 at 450 °C — irreversible and reversible. The rate of aromatisation of n-hexane is proportional to the surface concentration of irreversible spillover hydrogen, while the rate of hydrocracking and isomerisation is proportional to that of reversible spillover hydrogen.

A mathematical model of spillover has been examined by Edvinsson *et al.*[93] It was postulated that the reaction proceeds on the metal serving as the source of spillover species and that the carrier stores these species and interacts with the metal via the spillover and reverse spillover mechanisms. The application of the cyclic modulation method made it possible to discriminate between processes occurring with and without the participation of spillover.

According to a similar model proposed by Nam and Silverston,[94] there are two regions in the catalysts: active (metal) and inactive (carrier). Dissociative adsorption, the reaction, and recombination desorption take place in the active region. The dissociated species migrate to the inactive part, which serves as a reservoir for the latter, and conversely. The model predicts that, in the absence of spillover, the yield should monotonically decrease with increase in modulation frequency, whilst in the presence of spillover it should pass through a maximum.

Mathematical analysis of the overall kinetic model of a two-stage reaction at a surface incorporating sites of two types with different heats of adsorption showed that the spillover of the adsorbed species between these sites may lead to both an increase and a decrease in the rate of the chemical reaction.[95] In the oxidation of carbon monoxide on such a heterophase surface, the kinetic coupling of the reaction, induced by CO spillover, leads to an appreciable alteration of the temperature dependence of the reaction rate and also to the appearance of superadditive activity at low temperatures.[96]

3. Determination of diffusion coefficients

The TPD,[57] adsorption,[97] electron microscope,[98] and NMR[91,99] methods have been used to determine the diffusion coefficients of hydrogen. A table of the diffusion coefficients D_H for a series of oxides has been published in a review[5]. At room temperature, $D_H = 10^{-10}$ cm^2 s^{-1} on CeY.[17] At 50 °C, $D_H = 10^{-16}$ cm^2 s^{-1} on WO_3 and 10^{-13} cm^2 s^{-1} on MoO_3.[97] At 100 °C, $D_H = 10^{-14}$ cm^2 s^{-1} on carbon and SiO_2, while the activation energy is $E_D = 65$ kJ mol^{-1}.[98] At 400 °C, $D_H = 10^{-15}$ cm^2 s^{-1} and $E_D = 119$ kJ mol^{-1} on Al_2O_3 and diffusion takes place over a distance up to 200 nm from the Pt particles.[98]

According to NMR data, 10^{12} hydrogen atoms participate in the spillover on Pt/SiO_2 over each square centimetre of the SiO_2 surface[91] and, since the average distance between the Pt particles

on the catalyst is 180 nm, the spillover extends over a distance of at least 90 nm.

Data on the kinetics of the exchange between the OH groups of the support and D_2 are usually employed for the determination of D_H. For this purpose, it is necessary that the direct exchange without the participation of the metal should be negligible, that the migration on the support should be the rate-limiting stage, and that the surface diffusion should differ from the bulk-phase diffusion.[100]

If the surface concentration of H atoms on the initiator metals c_H is constant, then D_H can be calculated by the equation [57]

$$Q = c_H I_o \sqrt{\pi D_H t}\,,$$

where Q (atoms g^{-1}) is the number of species which have diffused onto the support during the time t and I_o (cm g^{-1}) is the perimeter of the metal particles. At 400 °C, $D_H = 9.3 \times 10^{-11}$ cm^2 s^{-1} on Rh/SiO_2, 1.7×10^{-10} cm^2 s^{-1} on Rh/Al_2O_3, 2.2×10^{-10} cm^2 s^{-1} on Rh/ZrO_2 and 8.0×10^{-10} cm^2 s^{-1} on Rh/CeO_2.[100]

Significantly higher hydrogen diffusion coefficients are also encountered. For example, it has been found [73] that $D_H = 10^{-3}$ cm^2 s^{-1} on Pt/SiO_2 at 200 °C. Such appreciable differences between the diffusion coefficients are most probably associated with differences not taken into account under the experimental conditions.

V. The mechanism of hydrogen spillover

1. The surface and gas-phase pathways to spillover

The question of the possible transfer of hydrogen atoms during spillover not along the surface but through the gas phase arose already in the first studies. According to the data of Dmitriev *et al.*,[101] in the isotope exchange between deuterium and surface OH groups of the HNaY zeolite the activated deuterium is transported not through the gas phase but along the surface of the support separating the spillover initiator (Pt) and the zeolite.

Gadgil and Gonzales [102] investigated the adsorption of the hydrogen atoms obtained in the high-temperature heating of tungsten in a H_2 atmosphere. It was found that the rate of adsorption is low and independent of the type of carrier, which most probably constitutes evidence against the transfer of H atoms through the gas phase. The study of the adsorption of hydrogen atoms generated in a microwave discharge [103] on Pt/TiO_2 showed that F centres, capable of effecting the hydrogenation of ethene, are formed in TiO_2 under the influence of these atoms. The low rate of adsorption of H atoms on the Pt/zeolite system is due to the fact that only the outer surface of the catalyst interacts with these atoms.[104]

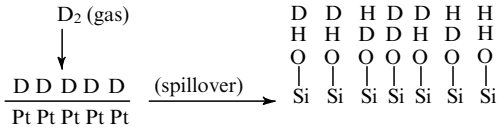
The conversion of CO into methane in a two-bed reactor, the lower section of which contained the Pt/zeolite X catalyst in a stream of H_2 in a stationary bed while the upper section contained the Ni/zeolite X in a stream of CO + H_2, occurred at a much higher rate than in the absence of platinum.[105] The authors did not reach a definite conclusion about the transfer of hydrogen atoms through the gas phase, noting the possibility of their diffusion through the glass lattice separating the two beds.

If SiO_2 is treated with hydrogen at a temperature above 800 °C in the presence of various metals but without being in contact with them, then the siloxane bridges Si–O–Si are converted into S–H groups.[106] This phenomenon has been explained by the transport of the metal on SiO_2 with participation of water vapour. In terms of their activities, the metals can be arranged in the sequence Ta > Ni > Pt > W.

Hypotheses concerning the gas-phase transport of H atoms at relatively low temperatures have been put forward in only a few investigations. In the study of Baumgartner *et al.*,[107] these hypotheses were based on experiments involving the reduction of anthracene and anthraquinone adsorbed on SiO_2 separated in space from the source of hydrogen — Pd/SiO_2. Rodriguez and Baker [108] concluded that at room temperature and a pressure of 0.2 mm Hg atomic hydrogen is transferred from metal sulfides (MoS_2, FeS_2, or FeS) through the gas phase onto a graphite surface separated from them. However, since the desorption of hydrogen atoms at low temperatures is thermodynamically unfavourable, one cannot rule out that hydrogen is transferred from the source to the acceptor not directly but in the form of other species (OH, H_2O, *etc.*) in these cases too.

2. The mechanism of the diffusion of hydrogen on an oxide surface

One of the first studies on the spillover mechanism was undertaken by Conner *et al.*,[41] who used for this purpose FTIR spectroscopy *in situ*. The diffusion of the deuterium adsorbed on Pt/SiO_2 from Pt to the carrier was followed from the exchange between D atoms and the OH groups of SiO_2. It was postulated that the process proceeds in accordance with the scheme



The heat of adsorption of H_2 on Pt was 115 kJ mol^{-1} and the activation energy was 67 kJ mol^{-1}. The heat of adsorption of H_2 on SiO_2 was smaller — 12.5 kJ mol^{-1}. Thus the transfer of deuterium from platinum to the support is an endothermic process and spillover occurs by virtue of the existence of a high deuterium concentration gradient at the interface between Pt and the support. However, it is possible that the heats of adsorption of H_2 on the real spillover centres greatly exceed 12.5 kJ mol^{-1}. Under the experimental conditions, the ratio of different forms of deuterium was

$$PtD : D_{sp} : OD = 1 : 5 : 600 \ (D_{sp} = \text{spillover deuterium}).$$

It has been postulated that the spillover on SiO_2 takes place via the formation of associative complexes with participation of pairs of OH groups (vicinal or geminal).[43]

Analysis of diffuse scattering IR spectra showed [109] that the adsorption of H_2 (D_2) on 10% Pt/TiO_2 at a low temperature results in the appearance of a new broad absorption band at $\sim$ 3000 (2300) cm^{-1}. The authors assigned it to the OH (OD) groups at the metal–support interface. This band is thermally unstable and at room temperature the OH and OD groups are readily involved in exchange with D_2 and H_2 respectively.

The involvement of the OH groups of the HNaY zeolite in the spillover of deuterium in the HNaY + PtNaY system has been demonstrated by FTIR spectroscopy *in situ*.[110, 111]

Under the conditions of the hydrogenation of ethene on Pt/Al_2O_3, the ethene reversibly adsorbed on the support reacts with the hydrogen arriving from platinum via the spillover mechanism.[112] Methylation of the support hydroxyls with diazomethane greatly reduces the rate of the reaction. The Pt/Al_2O_3–OCH_3 system formed after modification is at least ten times less active than Pt/Al_2O_3 and the hydrogenation reaction is propagated only by the metal on which ethene is strongly adsorbed. This demonstrates the need, in principle, for the spillover of hydrogen in order that the given reaction may be catalysed.

The majority of investigators hold to the view nowadays that hydrogen atoms participate in spillover.[17, 101, 113] It has been found [17] that the rate of disappearance of the EPR signal of perylene corresponds to the rate of adsorption of H_2 by the Pt/CeY system. We may note that the direct detection by EPR of H atoms on the majority of supports is possible only at temperatures below −170 °C. Careful analysis of the form and magnitude of the shift in the ^{1}H NMR spectra made it possible to establish [113] that hydrogen migrates on the SiO_2 surface in the form of the H$^\bullet$ radical species. The hydrogen radical species adsorption centres may be either F centres or the (SiO)- or Si-groups.

It has also been postulated that spillover proceeds via a proton mechanism.[71, 89, 114] This is indicated by the correlation between the rate of spillover and the proton affinity of the promoting agent,[71, 89] which may solvate the diffusing proton: $H_2O \gg CH_3OH > C_2H_5OH >$ n-$C_3H_7OH >$ n-C_4H_9OH. In the presence of all these promoting agents, the rate of spillover was independent of the specific surface of the supported Pt, while in the presence of CH_3COOH, which has a low proton affinity, such dependence was observed. In the latter case, the rate of reaction may be determined by the rate of solvation of the proton.

Bianchi *et al.*,[47] who investigated the hydrogen transfer from the Pt/Al_2O_3 catalyst to a methoxylated silica gel (Aerogel), even postulated the involvement of H_3^+ species in spillover on the basis of kinetic data.

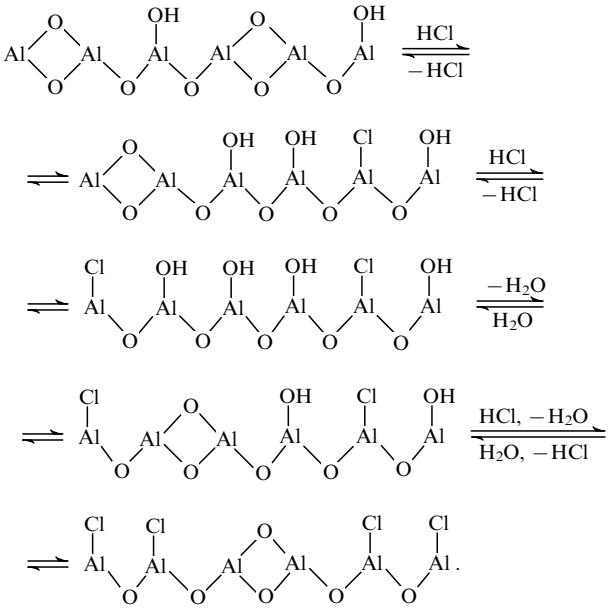
The adsorption of hydrogen on Rh/TiO_2 has been investigated by NMR.[74, 115, 116] Hydrogen was adsorbed in two forms: the reversible form bound to the support and the irreversible form bound to the metal. According to NMR data, hydrogen bound covalently to Pt is present at the Pt/SiO_2 surface.[91] Paramagnetic hydrogen, which reduces the relaxation time of the Si—OH bonds, participates in spillover. On Pt/SiO_2, two hydrogen NMR signals were also found: one corresponded to the Pt—H bond and the other to the spillover hydrogen located at the same sites as the hydrogen of the OH groups.[117]

The study of the exchange between D_2 and the OH groups of conducting supports on which platinum had been deposited failed to reveal appreciable differences between *n*- and *p*-semiconductors,[118] which permitted the conclusion that uncharged species are involved in spillover.

The rate of the $H_2 + D_2$ exchange on Pt or Pd, deposited on a zeolite with a modulus of 30, exceeded by several orders of magnitude the rate of exchange between D_2 and OH groups.[83] Thus the activation of D_2 does not limit the gas-phase exchange. Spillover of hydrogen should include the interphase transfer of the activated D_2, the migration of D on the surface, and recombination.

According to the data of Parera *et al.*,[38] the H – D exchange on Rh/Al_2O_3 proceeds in two stages: rapid spillover from Rh to Al_2O_3 takes place in the first stage, while the second involves a slow exchange between the spillover hydrogen and the OH groups of Al_2O_3.

Information about the number of spillover centres may be obtained from data [119] on the adsorption of H_2 on $Pt/Al_2O_3 - Cl$, Al_2O_3, and their mixtures at 500 °C. The presence of chlorine alters the rate of spillover. For a certain chlorine content, maximum spillover is observed:



The rate-limiting stage is the surface migration of H atoms. The above scheme shows that, in the presence of a low chlorine content, the number of spillover centres increases, diminishing in the presence of a high chlorine content. When all the OH groups have been replaced by Cl, the protons lose their mobility owing to the absence of surface OH groups.

According to NMR date, the hydrogen adsorbed on the $CuO + Cr_2O_3$ system is capable of hydrogenating isoprene to isobutene. This hydrogen does not enter into the composition of the OH groups and does not exist on pure Cr_2O_3. It apparently arises from the metallic copper formed under the reaction conditions.[120]

It is generally believed that the first stage of the process is the homolytic rupture of the H—H bond on the metal regardless of the involvement of hydrogen atoms or H^+ ions in the spillover.

Different investigators postulate that one of two stages may limit the spillover: either the surface diffusion on the acceptor or the transfer of species from the initiator to the acceptor. Since the activation energies for these elementary stages may be different, the variation of temperature may entail also a change in the rate-limiting stage of the spillover.[85] The cause of the change in the rate-limiting stage may be also the presence at the surface of spillover promoting or inhibiting agents. A more common view is that spillover is limited by the diffusion at the support surface.[6]

3. The mechanism of the diffusion of hydrogen into the bulk phase of oxides

When small amounts of Pt or Pd are added to the oxides WO_3, MoO_3, or V_2O_5, in the presence of hydrogen, tungsten (H_xWO_3),[5, 6, 121] molybdenum (H_yMoO_3),[6, 122–127] and vanadium ($H_zV_2O_5$) [128] bronzes are formed. They exhibit a catalytic activity in the hydrogenation of ethene, the rate-limiting stage of which may be the reverse spillover of hydrogen on Pt, where the hydrogenation reaction actually occurs.[6]

According to X-ray diffraction data, the initial monoclinic structure of WO_3 is converted into the cubic structure of $H_{0.4}WO_3$ as a result of hydrogen spillover. Hydrogen atoms occupy the hexagonal vacancies in WO_3. The diffusion coefficient of hydrogen in the tungsten bronze is $1 \times 10^{-7} - 7.9 \times 10^{-6}$ cm^2 s^{-1} at room temperature.[99, 122]

The study of the interaction of H_2 with the (100) face of MoO_3 at a very low pressure ($10^{-5} - 10^{-8}$ mm Hg) showed [123] that the monoclinic bronze $H_{1.6}MoO_3$ is formed in three stages: (1) initiation, (2) a stage characterised by a constant rate of absorption of H_2, and (3) the concluding stage of the formation of the new phase in which the rate of absorption of hydrogen diminishes. The spillover of H_2 from Pt is observed only in the first stage. Under these conditions, hydrogen permeates into the near-surface layers of the oxide. It then reacts with the oxide without the participation of Pt. The diffusion coefficient of H atoms in the second stage is 7–10 orders of magnitude higher than the coefficient usually observed in spillover.

The rate of hydrogenation of ethene on Pt/H_yMoO_3 increases with increase in the Pt concentration.[124] According to other data, the $H_{1.6}MoO_3$ bronze may catalyse the hydrogenation of C_2H_4 also in the absence of Pt.[125] The initial rate of reaction at 160 °C on $H_{1.6}MoO_3$ is approximately the same as on Pt/H_yMoO_3. In the course of the hydrogenation of C_2H_4 by the hydrogen entering into the composition of the $H_{1.6}MoO_3$ bronze, the latter is converted into $H_{0.9}MoO_3$, which has a different structure. In the presence of hydrogen in the gas phase, the bronze did not undergo structural changes. The activation energy for hydrogenation was 54 kJ mol^{-1} and was close to the activation energy for the diffusion of H atoms in the bronze.[125]

On $Pt/H_yVMoO_{5.5}$ with $2.85 < y < 3.31$, the spillover hydrogen forms with the surface a very weak, apparently physical, bond with $\Delta H < 12.5$ kJ mol^{-1} or is occluded between the oxide layers.[128] When $y = 5.85$, the heat of adsorption of hydrogen is 127.6 kJ mol^{-1}.

The vanadium bronze $H_{3-3.8}V_2O_5$ is X-ray-amorphous and, in contrast to the tungsten and molybdenum bronzes having metallic conductivity, exhibits a semiconductor conductivity.[129]

The reversible adsorption and removal of hydrogen occur also on heteropolyacids (HPA) and heteropolysalts formed from molybdenum and tungsten oxides. This process has been investigated by the temperature-programmed reduction (TPR) and IR spectroscopic methods in relation to the system $H_3PMo_{12-x}W_xO_{40} + Pd/C$.[130]

It was found that H_2 is absorbed already at room temperature, while water is evolved at a higher temperature. At 300 °C, the absorption of H_2 and the exchange between H_2 and D_2 take place also in the absence of Pt. The process includes two stages: (1) rapid dissociation of H_2 with the initial formation of atoms and then H^+ ions, diffusing into the bulk of the HPA, and (2) slow interaction of H^+ with the O atoms in the bulk phase . The rate of oxidation of H_2 depends little on the specific surface of the HPA.

The salt $Ag_3PW_{12}O_{40}$ exhibits an appreciably higher catalytic activity in the isomerisation of but-1-ene in the presence of hydrogen than the heteropolyacid $H_3PW_{12}O_{40}$.[131] It was also found that the reactivity of the salt increases with increasing H_2 pressure, whereas that of the acid is independent of this parameter. Protons of two types have been detected in the system by NMR: some of them are manifested only in the presence of H_2 in the gas phase, whilst others are present at the surface of the salt also when the system is evacuated. The reversibly bound hydrogen is evidently formed on silver and then diffuses to the organic molecule and participates in catalysis.

The oxidation of methane to CO_2 and H_2O on the Pt/V_2O_5 catalyst with a very low Pt content (0.15%) has been investigated by scanning calorimetry *in situ*.[132, 133] When Pt/V_2O_5 is heated to 550 °C, the stable V_2O_4 phase is formed, which can be detected from the heat of the reversible phase transition between the monoclinic and tetragonal forms of V_2O_4, occurring at 68 °C. The stable phase proved to be completely inactive in catalysis at 275 °C.

On the other hand, the reduction of the catalyst with methane at 275 °C leads to the formation of a metastable reduced vanadium oxide phase. Under these conditions, 20% – 25% of oxygen is removed from the specimen and the effective stoichiometric formula of the oxide becomes close to V_2O_4. However, the heat of the reversible transition from the monoclinic to the tetragonal form is not then observed. The stable catalytic activity of the metastable phase is retained when the specimen is cooled to 185 °C. The temperature of its reoxidation with oxygen is higher by almost 200 °C than for the stable phase. The low-temperature (50 – 350 °C) stage of the oxidation of the metastable phase is then characterised by an anomalously high heat of reaction (ΔH = 335 – 502 kJ mol^{-1}). On heating, the metastable phase is converted into the stable phase with evolution of a large amount of heat.

The study of the Pt/V_2O_5 surface by the XPS method showed that vanadium atoms in the V, IV, and lower valence states are present after catalysis at the surfaces of both the stable (weakly active) and metastable (highly active) V_2O_5 phases. The surfaces of the active and inactive phases differ little in composition. As regards the state of Pt, according to XPS data the appearance of catalytic activity in Pt/V_2O_5 after heating in methane coincides in time with the disappearance of the oxidised forms of Pt (the binding energy is $4d_{5/2}$ = 317.1 eV) and the appearance of metallic Pt (binding energy 314.1 eV).

Thus CH_4 dissociates on platinum particles in the course of its oxidation on the Pt/V_2O_5 catalyst.

$$2Pt + CH_4 \longrightarrow Pt-H + Pt-CH_3 .$$

Hydrogen atoms diffuse via the spillover mechanism to the V_2O_5 phase and reduce it to the nonequilibrium form V_2O_4.

$$Pt-H + V_2O_5 \longrightarrow Pt + V_2O_4 + OH(\rightarrow H_2O) .$$

The nonequilibrium V_2O_4 phase facilitates the transport of oxygen to the Pt/V_2O_5 interface, in the vicinity of which methane is oxidised. The O_2 and CH_4 adsorption centres are probably separated.

Similar processes occur in the oxidation of hydrocarbons on the $Pt/CeO_2/Al_2O_3$ catalyst used in automobile catalytic converters.[134] Hydrogen is split off from the hydrocarbon being oxidised, diffuses into the bulk of CeO_2, and reduces it to a lower oxide form. The reduction of CeO_2 in the Ni/CeO_2 system has been investigated in detail by the TPR, NMR, EPR, and IR spectroscopic methods.[135] At 400 °C, each gramme of CeO_2 is capable of absorbing up to 3.4×10^{20} hydrogen atoms (H/Ce = 0.1). This hydrogen hydrogenates isoprene at room temperature. Pure CeO_2 is inactive in hydrogenation, but the amount of hydrogen extracted by isoprene from the Ni/CeO_2 system is greater than would have been the case for the ratio H/Ni = 1. It is also possible that Ni^{2+} diffuses within the CeO_2.

The results of experiments on the synthesis of methanol on a mixture of Cu/SiO_2 with ZnO/SiO_2 suggested that hydrogen diffuses from the Cu to the ZnO phase under the reaction conditions.[136] It is postulated that H atoms are formed on decomposition of the HCOO complex on Cu and migrate to ZnO, which serves as a reservoir for the reverse hydrogen spillover. According to IR spectroscopic data, ZnO is partly reduced in the course of the hydrogen spillover from Cu to ZnO.[137] The electrical conductivity of ZnO in its mixture with Cu increases under these conditions, which, according to Barett *et al.*,[138] is associated with the intercalation of hydrogen and the formation of $ZnOH_x$. The diffusion of H atoms from the Cu to the ZnO phase has been demonstrated also by the direct neutron diffraction method.[139] A ZnO superlattice with an ordered arrangement of H atoms is then formed.

On the $Cu/SiO_2 + ZnO/SiO_2$ mixture, the yield of methanol from $CO + H_2$ was higher than on the separate components.[140] The authors explain such synergism by hydrogen spillover.

The study of the adsorption of hydrogen on the Cu/SiO_2, Ru/SiO_2, and $Cu-Ru/SiO_2$ catalysts led to the conclusion [141] that atomic-like hydrogen participates in the spillover from Ru to Cu through SiO_2.

TiO_2 is an effective hydrogen transferring agent. Its addition to the $CuO-TiO_2$ system greatly increases the activity and selectivity of the catalyst in the synthesis of methanol.[142] The addition of Pd has the same effect.[143]

Co^{2+} ions present in the NaY zeolite are reduced by hydrogen in the presence of Pd, provided that Co^{2+} and Pd^{2+} are in the same sodalite cavity.[144]

4. The strong metal – support interaction

The strong metal – support interaction (SMSI), inducing a change in the adsorption and catalytic properties of the carrier and the deposited metal, is as a rule observed in the reduction of an oxide carrier. This effect was named by Tauster and Fung,[145] who investigated the changes in the properties of TiO_2 on deposition of Pt. Under these conditions, the catalytic activity of the system in the Fischer – Tropsch synthesis is retained and even increases, although its adsorption capacity in relation to H_2 and CO falls.

The SMSI effect has been noted in the interaction of Pt, Pd, Ru, Rh, Ir, Ni Au, and Ag with TiO_2, TiO, Ti_2O_3, V_2O_5, V_2O_3 Ta_2O_5, Nb_2O_5, *etc*.[5] The mechanism of the effect has been usually investigated in relation to the Pt/TiO_2 system. It is generally believed that the SMSI effect is induced by the reduction of the carrier as a result of the spillover of hydrogen from the metal to the carrier.

In certain cases, the SMSI is accompanied by the formation of alloys or intermetallic compounds. Convincing evidence for the formation of the Pt_3Ti phase in the high-temperature reduction of Pt/TiO_2 has been obtained.[146] An electron microscope study of the Pt/TiO_2 system showed that the spillover of hydrogen entails the partial coating of the deposited Pt with titanium oxide. At temperatures above 550 °C, TiO_2 is reduced to Ti_4O_7. At a lower

temperature (300 °C), the formation of Ti^{3+} was observed.[147] The Ti^{3+} EPR signal vanishes on evacuation, but reappears after the admission of H_2 even at room temperature.

$$\tfrac{1}{2}H_2 \xrightarrow{Pt} H_{sp},$$

$$Ti^{4+} + O^{2-} + H_{sp} \longrightarrow Ti^{3+} + OH^{-}.$$

Thus at a low temperature the spillover results in the formation of the $Ti^{3+} + OH^{-}$ pair, whilst at high temperatures it gives rise to the bulk-phase reduction of the oxide.

In the spillover of hydrogen on Rh/TiO_2, the amount of adsorbed hydrogen corresponded to the ratio $N_H/N_{Rh} = 3$. According to NMR data, Ti^{3+} centres participate in the diffusion of H atoms.[148] The adsorption of H_2 on Rh/TiO_2 (rutile) has been studied by the TPR, IR spectroscopic, EPR, and NMR methods,[149] showing that hydrogen is adsorbed at room temperature in two forms — strong and weak. The weak form participates in the reverse spillover and in the reduction of the support surface:

$$\tfrac{1}{2}H_2 + Ti^{4+}-O^{2-} \rightleftharpoons Ti^{3+}-OH^{-}.$$

On anatase, such a process does not take place. The mechanism of hydrogen spillover is described by the following scheme:

$$[Ti-H]^{3+} + Ti^{4+}-O^{2-} \rightleftharpoons Ti^{3+}-[\,] + Ti^{3+}-OH^{-},$$

$$Ti^{3+}-OH^{-} \rightleftharpoons Ti^{4+}-O^{-} + H_{met},$$

where [ ] is a vacancy and H_{met} is metallised hydrogen. At 300 °C, hydrogen diffuses into the bulk of TiO_2. Similar processes have been observed also on Pt/TiO_2 and Pd/TiO_2.[150, 151]

The valence state not only of the carrier but also of the metal may change as a result of the SMSI.[152] In the Ni/TiO_2 system at 450 °C, large Ni particles interact with the carrier Ti^{3+} ions via spillover and the catalytic activity of such a two-phase system increases in the Fischer–Tropsch synthesis. However, at 650 °C a proportion of Ni migrates to the near-surface TiO_2 layers in the form of Ni^{n+} ions.

The increase in the electrical conductivity of TiO_2 in a hydrogen atmosphere after the deposition of Pt, Rh, or Ni was also accounted for by hydrogen spillover.[153–155] An increase in electrical conductivity initially of the TiO_2 bound to Pt and then also of TiO_2 without Pt was observed in the $Pt/TiO_2 + TiO_2$ mixture in the presence of hydrogen. It is postulated that hydrogen diffuses to TiO_2 in the form of protons.

After heat treatment in hydrogen, the $RhNb_2O_4$ phase is formed in the $Rh/SiO_2 + Nb_2O_5$ system.[156] Hydrogen dissociates on Rh also after spillover to the Nb_2O_5 phase , reducing the latter.

When TiO_2 or Cr_2O_3 is added to the Rh/SiO_2 catalyst, the oxides partly 'creep' onto the Rh surface. According to TPR data, spillover hydrogen is adsorbed on the oxides and partly reduces them. With increase in the coverage of the rhodium surface by the oxides, the catalytic activity of the system in the hydrogenation of CO also increases.[157] It has been suggested that the dissociation of CO with participation of hydrogen takes place on an active centre incorporating Rh and a partly reduced titanium or chromium cation.

Ni/Mo_x catalysts, in which Ni is in the form of very small clusters (less than 2 nm) and the Ti, Zr, and Nb oxides are partly reduced, have been obtained by sputtering mixtures of a nickel salt with titanium, zirconium, or niobium salts.[150] The SMSI effect, occurring with participation of spillover hydrogen, has been observed in the formation of such catalysts. The catalysts obtained exhibit a high activity in the hydrogenation of CO_2.

The SMSI effect has also been observed when Pt/TiO_2 was acted upon by hydrogen at 500 °C.[159] It has been suggested that a Pt–Ti alloy is formed in this system.

It has been demonstrated by the XPS method that heating of Ni/Al_2O_3 in a H_2 atmosphere leads to the SMSI, $(Al_xO_y)_n$ aggregates 'creeping' onto the surface of the deposited Ni.[160] Heating in O_2 or CO returns the metal to the initial state.

The coating of the catalyst by the carrier, accompanying the SMSI effect, has been noted in the interaction of methane with the $MoO_3 + SiO_2$, $V_2O_5 + SiO_2$, and $Fe_2O_3 + SiO_2$ systems subjected to a preliminary mechanochemical treatment.[161] Electron microscope and electron diffraction studies have shown that, as a result of such treatment, the particles of the reduced oxides MoO_x and VO_y and also of metallic Fe are enclosed within a SiO_2 shell. It may be that the increased mobility of hydrogen in the mechanochemical treatment leads to the appearance of effects resembling SMSI.

5. Synergism in catalysis

The phenomenon of synergism, *i.e.* of the non additive increase in activity in mixtures of catalyst components, has been often investigated in relation to the hydrodesulfurisation process on the Co(Ni)–Mo(W) catalyst. Delmon[162] gave the first explanation of this phenomenon, postulating that the Co–Mo–S catalyst consists of two phases. According to the model of contact synergism which he proposed,[163, 164] hydrogen is activated on the Co_9S_8 or NiS phase, while the sulfur compound being hydrogenated (for example, thiophene) is activated on the MoS_2 phase, hydrogen spillover occurring between the two phases. In a later model,[165] it was postulated that hydrogen spillover takes place between the CoS_2 and CoMoS phases.

The view that, whilst present in the real catalyst, the Co_9S_8 and NiS sulfide phases do not apparently play decisive roles in hydrotreating has predominated recently.[166–176] The formation of a 'Co–Mo–S' phase, in which the Co atoms are located on the side faces or edges of MoS_2 microplates, has been observed by various physical methods (EXAFS, NMR, XRD phase analysis, *etc.*). The coordination number of Co is IV or V according to EXAFS data. Such an optimum ratio is attained when the Co atoms are located on the edges of MoS_2 microcrystallites.

Data obtained by Mössbauer spectroscopy [177, 178] have shown that the same CoS species are formed under sulfiding conditions on the $CoMo/Al_2O_3$ catalyst as on Co/Al_2O_3, while on the CoMo/C catalyst the same CoS species are formed as on Co/C. This fact throws doubt on the hypothesis of the important role of the 'Co–Mo–S' phase. The MoS_2 phase is then regarded as a simple diluent. At the same time, it has been justly suggested that the CoMoS/C system may differ from $CoMoS/Al_2O_3$.[163] The Co/C catalyst exhibits an activity which is only three times lower than that of CoMoS/C.[179] The activities of the Co/Al_2O_3 and $CoMoS/Al_2O_3$ catalysts differ to a much greater extent.

As already mentioned, the Co atoms in the Co–Mo–S system are located on the edges of the MoS_2 microcrystallites.[180] The Co_9S_8 phase also exists, but its positive role is associated not with hydrogen spillover but with its additional function as a support for the Co–Mo–S phase.

The mechanism of the hydrodesulfurisation of thiophene on the Co/Al_2O_3, Mo/Al_2O_3, and $CoMo/Al_2O_3$ catalysts has been investigated by the TPD, TPR, and H–D exchange methods.[181] On Mo/Al_2O_3 and $CoMo/Al_2O_3$, the TPR spectra of thiophene, tetrahydrothiophene and butanethiol proved to very similar. At the same time, on the last catalyst the peaks due to the reaction products were displaced towards the region of low temperatures, which indicates higher rates of their formation. The TPR spectra of the same initial compounds on Co/Al_2O_3 differed sharply: no peaks corresponding to the majority of the main reaction products were observed on them. In contrast to Mo/Al_2O_3, hydrogen was present on the Co/Al_2O_3 and $CoMo/Al_2O_3$ surfaces in a weakly bound form.

The results obtained confirmed the view that thiophene (or its derivatives) are adsorbed on the MoS_2 anionic vacancies while hydrogen is activated on cobalt sulfide. Hydrogen may be transferred by means of spillover if the Mo and Co centres belong to different phases or via migration if these centres form part of the composition of a single phase. Presumably the hydrogenation–dehydrogenation reactions occur on centres of one type, whilst desulfurisation takes place on centres of another type.

Much interest has been shown recently in solid superacids of the type of $ZrO_2-SO_4^{2-}$, capable of catalysing a series of most important organic reactions of the acid type. The addition of Pt may improve the catalytic properties of superacids and, in particular, may increase their resistance to poisoning by coke, since the latter is hydrogenated by the spillover hydrogen.[182–184] Analysis of the IR spectra showed that new proton centres are formed in place of the acid Lewis centres under these conditions. Molecular hydrogen dissociates on Pt and the H atoms formed migrate via spillover to $ZrO_2-SO_4^{2-}$. It has been suggested that the H atom gives up an electron on Lewis centres, being converted into a H^+ ion, which is stabilised by the nearest surface $O^{\delta-}$ ion. The rate of the skeletal isomerisation of butane on such a catalyst is much higher than on the $ZrO_2-SO_4^{2-}$ catalyst without Pt.

Th hydrogenation of CH_3OH, $(CH_3)_2O$, C_2H_5OH, C_3H_7OH and HCOOH on the Ni/Al_2O_3 catalyst has been investigated by the TPR method.[185] It was found that the rate of formation of methane from all five compounds is the same and close to the rate of hydrogenation of the CH_2O fragment formed from the adsorbed CO and H_2. Thus in all cases hydrogenation has the same rate-limiting stage, which may be the spillover of hydrogen from Ni to the organic molecule adsorbed on Al_2O_3.

In the hydrogenation of CO on Ni/Al_2O_3 mixed with Pt/SiO_2 (or Ru/Al_2O_3), carbon monoxide is adsorbed on Pt, while hydrogen migrates via the spillover mechanism from Ni to Al_2O_3.[186] Data obtained by the TPD method have shown that the products are desorbed from the H_2CO complex. In the absence of the second component, such a complex is not formed on Pt/SiO_2. The independence of the rate of its formation of the Ni concentration indicates the formation of this complex on the support.

The H_2CO complex was also detected by the TPR method in the conversion of CO into methane on the $Ni/SiO_2 + Al_2O_3$ mixture.[187] The rate of spillover increased with improvement of the contact between the particles and with increase in the nickel concentration.

VI. Conclusion

Thus the phenomenon of hydrogen spillover, common in heterogeneous catalysis, has been observed mainly in multiphase systems. Hydrogen is activated on one of the phases, frequently the metallic phase (although this may occur also on certain transition metal oxide or sulfide phases) and then diffuses to the other phase, which in the absence of the activator phase is inactive or its activity is low in relation to the adsorption of hydrogen. The spillover hydrogen on the second phase may be detected by physical methods (EPR, NMR, neutron diffraction, *etc.*) and also from the change in the properties of the phase (for example, as a result of the reduction of oxides) or by virtue of the manifestation of new catalytic properties by the heterogeneous system.

The spillover phenomenon is not only of theoretical but also of considerable practical importance. The elucidation of the nature and rules governing spillover may promote a rational solution of the problem of the construction of multiphase catalysts. For this purpose, information is needed about the adsorption properties of each phase and also about the characteristic features of the interphase diffusion of hydrogen and its diffusion along individual phases. It appears that in catalysis different reactants are frequently activated on different phases and the catalytic reaction is effected as a result of interphase diffusion. It has been shown[19,188] that the high activity and selectivity of multiphase oxide catalysts in oxidation reactions can be explained precisely by the occurrence of individual stages on different phases and by the diffusion (spillover) of oxygen between the phases.

This claim is probably even more valid in relation to catalytic reactions with participation of hydrogen. Hydrogen atoms or ions are more mobile than oxygen and may diffuse more easily. The so called 'bifunctional' catalyst, consisting of the supported metal, on which hydrogen is activated, and an oxide (frequently with distinct acid properties — for example Al_2O_3 and zeolites), adsorbing or activating the component to be hydrogenated are widely used in catalytic reactions involving hydrogen. The role of interphase diffusion in such systems has been examined by Weisz.[189] Hydrogen spillover plays an important role in catalytic processes such as reforming, hydrogenation of unsaturated compounds, synthesis of methanol, isomerisation of hydrocarbons, and hydrodesulfurisation.

The mechanism of the hydrodesulfurisation reaction on the CoMo, NiMo, or NiW sulfide catalysts has been vigorously discussed in the literature. On the one hand, fairly numerous data indicate that multiphase catalysts are needed for the occurrence of this reaction. On the other hand, the idea that this requires not so much a multiphase system as the presence of centres with nonidentical functions, which can in general enter into the composition of the same phase, has been expressed recently with increasing frequency. However, in any variant it is essential to know the mechanism of the transport of hydrogen (or other adsorbed species) between such centres.

There is as yet no unanimous view about the mechanism of hydrogen spillover. The majority of investigators postulate that the initial stage of the spillover is homolytic dissociation of hydrogen on the metal phase (or an oxide or sulfide). However, the question in what form and by what mechanism hydrogen atoms pass from one phase to another remains controversial. It has been suggested that surface diffusion of the adsorbed species predominates, but in certain individual instances diffusion through the gas phase is not ruled out. The considerable scatter of hydrogen diffusion coefficients in spillover on various catalysts apparently indicates the diversity of the nature of the diffusing species and spillover mechanisms.

The nature of the hydrogen acceptor centres on the surfaces of oxides has been little investigated. It was indicated above that the number of hydrogen acceptor centres is as a rule small (usually less than 1% of the total number of surface sites). In this case, the question arises what role is played in spillover by the remaining centres, such as O^{2-} ions or OH groups. What is the ratio of the heats of adsorption of spillover hydrogen on the activator and on the acceptor centres? How do the kinetics of the reactions change in the course of the migration or spillover of adsorbed species of one or several types?

These and many other questions concerning the spillover mechanism have so far not been analysed in depth either theoretically or experimentally.

Further detailed investigations of spillover with quantitative estimation of factors such as diffusion coefficients, the number of spillover initiator and acceptor centres, and the bond energies between hydrogen and these centres are needed.

This review has been written with support by the Russian Fundamental Research Fund (Grant No. 95–03–08429a).

References

1. M Boudart, M A Vannice, J E Benson *Z. Phys. Chem. New Folge* **64,** 171 (1969)
2. S J Khoobiar *J. Phys. Chem.* **68** 411 (1964)
3. J E Benson, H W Kohn, M Boudart *J. Catal.* **5** 307 (1966)
4. B Delmon, M T Pouchot *Bull. Soc. Chim. Fr.* 2677 (1966)
5. P A Sermon, G C Bond *Catal. Rev.* **8** 211 (1973)
6. W C Conner, G M Pajonck, S J Teichner *Adv. Catal.* **34** 1 (1986)
7. M Boudart *Adv. Catal.* **20** 153 (1969)
8. N M Popova, D V Sokol'skii *Tr. Inst. Org. Khim. Electrokhim. Akad. Nauk Kaz. SSR* **1** 1 (1972)
9. M Boudart, A W Aldag, M A Vannice *J. Catal.* **18** 46 (1970)
10. L E Hunt *J. Catal.* **23** 93 (1971)
11. K Fujimoto, S Toyoshi, in *Preprints of the 7th International Congress on Catalysis, Tokyo, 1980* A-14
12. P A Sermon, G C Bond *J. Chem. Soc., Faraday Trans. 1* **72** 745 (1976)

13. U Roland, H G Karge, H Winkler, in *Zeolites and Related Microporous Materials: State of the Art 1994, Vol. 84. Studies in Surface Science and Catalysis* (Amsterdam: Elsevier, 1994) p. 1239
14. Y Sugi, T Matsuzaki, H Arakawa, K Takeuchi, T Hanaoka, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 381
15. P Grange, T T Van, B Delmon *C.R. Hebd. Seances Acad. Sci., Ser. C* **229** 1007 (1981)
16. D Frazer, R B Moyes, P B Wells, in *Proceedings of the 7th International Congress on Catalysis, Tokyo, 1980* (Tokyo, 1981) p. 1424
17. W C Neikam, M A Vannice *J. Catal.* **20** 260 (1971); **27** 207 (1972)
18. S Sharma, K Nomura, Y Ujihara *J. Mater. Sci.* **26** 4104 (1991)
19. O V Krylov *Vestn. Akad. Nauk SSSR* (1) 26 (1983)
20. K M Sancier *J. Catal.* **20** 106 (1971)
21. S J Teichner, G M Pajonck, M Lacroix, in *Surface Properties and Catalysis by Non-Metals* (Eds J B Bonnel, B Delmon) (Dordrecht: Reidel, 1983) p. 457
22. T Inui, K Kamachi, Y Ishihara, Y Makino, H Matsuka, in *Proceedings of the 2nd International Conference on Spillover* (Ed. K H Steinberg) (Leipzig: Karl Marx University, 1989) p. 167
23. E Kikuchi, S Iwamura, T Matsuda, in *Proceedings of the 2nd International Conference on Spillover* (Ed. K H Steinberg) (Leipzig: Karl Marx Univesity, 1989) p. 187
24. E Kikuchi, T Matsuda, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 53
25. T Matsuda, H Seki, E Kikuchi *J. Catal.* **154** 41 1995
26. J L Carter, P J Lucchesi, H Sinfeld, D J C Yates, in *Proceedings of the 3rd International Congress on Catalysis, Amsterdam, 1964* (Amsterdam: North-Holland, 1965) p. 1
27. S T Srinivas, P Kanta Rao *J. Catal.* **148** 470 (1994)
28. P Antonucci, N van Truong, N Giordano, R Maggiore *J. Catal.* **75** 140 (1982)
29. K Aimoto, K Fujimoto, K Maeda, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 165
30. S Ohgoshi, I Nakamura, Y Wakashima, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 289
31. S Giraldo de Leon, P Grange, B Delmon, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 345
32. X S Li, Z S Hou, Q Xin, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 353
33. A Ishihara, M Nomura, M Azuma, M Matsushita, K Shirouchi, T Kabe, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 357
34. A M Stumbo, P Grange, B Delmon *Catal. Lett.* **31** 173 (1995)
35. F Roessner, A Hagen, R V Dmitriev, in *Catalysis by Microporous Materials, Vol. 94. Studies in Surface Science and Catalysis* (Amsterdam: Elsevier, 1995) p. 472
36. F Roessner, U Roland, T Braunschweig *J. Chem. Soc., Faraday Trans.* **91** 1539 (1995)
37. G A Somorjai, in *Proceedings of the 8th International Congress on Catalysis, West Berlin, 1984, Vol. 1* (Weinheim: Verlag Chemie, 1984) p. 113
38. J Parera, E Traffano, J Masco, C Pieck, in *Spillover of Adsorbed Species* (Eds G M Pajonk, S J Teichner, G J Germain) (Amsterdam: Elsevier, 1983) p. 101
39. E M Traffano J M Parera *Appl. Catal.* **28** 193 (1986)
40. J L Carter, P J Lucchesi, P J Cornell, D J Yates, J H Sinfelt *J. Phys. Chem.* **69,** 3070 (1965)
41. W C Conner, J F Cevallos-Candau, N Shah, V Haensel, in *Spillover of Adsorbed Species* (Eds G M Pajonk, S J Teichner, G J Germain) (Amsterdam: Elsevier, 1983) p. 135
42. J F Cevallos-Candau, W C Conner *J. Catal.* **10**6 378 (1987)
43. D H Lenz, W C Conner *J. Catal.* **112** 116 (1988)
44. U Roland, R Salzer, S Stolle, in *Zeolites and Related Microporous Materials: State of the Art 1994, Vol. 84. Studies in Surface Science and Catalysis* (Amsterdam: Elsevier, 1994) p. 1231
45. J A Altham, G Webb *J. Catal.* **1**8 133 (1970)
46. R R Cavanagh, J T Yates *J. Catal.* **68** 22 (1981)
47. D Bianchi, M Lacroix, G M Pajonk, S J Teichner *J. Catal.* **68** 411 (1981)
48. D Bianchi, M Lacroix, G M Pajonk, S J Teichner *J. Catal.* **59** 467 (1979)
49. W C Neikam, M A Vannice, in *Proceedings of the 5th Congress on Catalysis, Miami Beach, 1972, Vol. 1* (Amsterdam: Elsevier, 1973) p. 609
50. A F Carley, H A Edwards, B Mile, M W Roberts, C C Rowlands, T E Hanlock, S D Jackson *J. Chem. Soc., Faraday Trans.* **90** 3341 (1994)
51. M U Kislyuk, V V Rozanov *Kinet. Katal.* **36** 89 (1995) [a]
52. D Duprez, A Milondi, in *Spillover of Adsorbed Species* (Eds G M Pajonk, S J Teichner, G J Germain) (Amsterdam: Elsevier, 1983) p. 163
53. B Sen, J L Falconer. *J. Catal.* **117** 404 (1989)
54. B Sen, J L Falconer. *J.Catal.* **122** 68 (1990)
55. B Sen, J L Falconer, T-F Mao. *J. Catal.* **126** 465 (1990)
56. B Sen, J L Falconer, L Chang. *J. Catal.* **127** 732 (1991)
57. R Kramer, M Andre *J. Catal.* **58** 287 (1979)
58. B Chen, J L Falconer *J. Catal.* **134** 737 (1992)
59. V V Rozanov, Yamin Tsao, O V Krylov *Kinet. Katal.* **34** 131 (1993) [a]
60. K Fujimoto, A Ohno, T Kunugi, in *Spillover of Adsorbed Species* (Eds G M Pajonk, S J Teichner, G J Germain) (Amsterdam: Elsevier, 1983) p. 241
61. D-L Hoang, H Berndt, H Lieske *Catal. Lett.* **31** 165 (1995)
62. K Fujimoto, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 9
63. Y Ando, X Li, E Ito, M Yamashita, Y Saito, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 313
64. F Roessner, U Mroczek, A Hagen, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 151
65. R Le van Mao, L Dufresne *Appl. Catal.* **52** 1 (1989)
66. R Le van Mao, L Dufresne, J Yao *Appl. Catal.* **65** 143 (1990)
67. R Le van Mao, J Yao, L Dufresne, R Carli, V Ragaini, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 143
68. L A Dufresne, R Le van Mao *Catal. Lett.* **25** 371 (1994)
69. G Pop, D Ivanescu, R Ganea, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 137
70. E S Shpiro, D P Shevchenko, R V Dmitriev, O P Tkacnenko, Kh M Minachev, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 159
71. R B Levy, M Boudart *J. Catal.* **32** 304 (1974)
72. H Charcosset, R Frety, A Soldat, Y Trambouze *J. Catal.* **22** 204 (1971)
73. J F Cevallos-Candau, W C Conner, in *Proceedings of the 2nd International Conference on Spillover* (Ed. K H Steinberg) (Leipzig: Karl Marx University, 1989) p. 18
74. T M Apple, C Dybowski *J. Catal.* **71** 316 (1981)
75. Kh M Minachev, R V Dmitriev, N G Rassamakhina, A A Dergachev *Kinet. Katal.* **29** 174 (1988) [a]
76. H W Kohn, M Boudart *Science* **145** 149 (1964)
77. Xin Sheng Li, Wen Zhao Li, Yan Xin Chen, Hong Li Wang *Catal. Lett.* **32** 31 (1995)
78. W J Ambs, M M Mitchell *J. Catal.* **82** 226 (1983)
79. B Delmon, in *Proceedings of the 7th International Symposium on Reactivity of Solids, Vol. 1* (London: Chapman and Hall, 1972) p. 567
80. J-G Kim, J Z Shyu, J R Regalbuto *J. Catal.* **139** 153 (1993)
81. J-G Kim, J R Regalbuto *J. Catal.* **139** 175 (1993)
82. A Van Meerbeck, A Jelly, J J Fripiat *J. Catal.* **46** 320 (1977)
83. X M Minachev, R V Dmitriev, N G Rassamakhina, A A Dergachev *Dokl. Akad. Nauk SSSR* **291** 393 (1986) [b]
84. B Delmon, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 1
85. G C Bond, in *Spillover of Adsorbed Species* (Eds G M Pajonk, S J Teichner, G J Germain) (Amsterdam: Elsevier, 1983) p. 1
86. M Lacroix, G M Pajonk, S J Teichner *Bull. Soc. Chim. Fr.* 265 (1981)
87. S J Teichner, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 27
88. M Lacroix, G M Pajonk, S J Teichner *Bull. Soc. Chim. Fr.* 258 (1981)
89. R Levy, M Boudart *Ind. Chim. Belg.* **38** 506 (1973)
90. D Bianchi, G E E Gardes, G M Pajonk, S J Teichner *J. Catal.* **38** 135 (1975)
91. T C Sheng, I D Gay *J. Catal.* **71** 119 (1981)

92. S Chen, Y Sun, S Peng, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 131
93. R K Edvinsson, R R Hudgins, P L Silveston, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 229
94. Y W Nam, P L Silveston, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 235
95. V I Savchenko, K A Dadayan *React. Kinet. Catal. Lett.* **55** 33 (1995)
96. V I Savchenko *React. Kinet. Catal. Lett.* **55** 143 (1995)
97. P A Sermon, G C Bond *J. Chem. Soc., Faraday Trans. 1* **72** 730 (1976)
98. T Fleisch, R Abermann *J. Catal.* **50** 268 (1977)
99. R F Taylor, M M Silva-Crawford, B C Gerstein *J. Catal.* **62** 401 (1980)
100. D Martin, D Duprez, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 201
101. R V Dmitriev, K H Steinberg, A N Detjuk, F Hoffmann, H Bremer, Kh M Minachev *J. Catal.* **65** 105 (1980)
102. R Gadgil, R D Gonzalez *J. Catal.* **40** 190 (1975)
103. M Che, B Canosa, A R Gonzales-Elipe *J. Chem. Soc., Faraday Trans.* **78** 1043 (1982)
104. H Jehan, H Zupei, S Yonzi, W Hanli, in *Spillover of Adsorbed Species* (Eds G M Pajonk, S J Teichner, G J Germain) (Amsterdam: Elsevier, 1983) p. 55
105. J Kapicka, N I Jaeger, G Schulz-Ekloff *Appl. Catal.* **A84** 47 (1992)
106. A Van Meerbeck, A Jelly, J J Fripiat *J. Catal.* **46** 320 (1977)
107. E Baumgartner, C Lentes-Wagner, R Wagner *J. Catal.* **117** 533 (1989)
108. N M Rodriguez, R T K Baker *J. Catal.* **140** 287 (1993)
109. V Yu Borovkov, L V Zaitsev, V B Kazanskii *Kinet. Katal.* **32** 772 (1991) [a]
110. G M Pajonk, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 85
111. U Roland, H Wincler, H Bauch, K H Steinberg *J. Chem. Soc., Faraday Trans.* **87** 3921 (1991)
112. G Lu, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 293
113. D H Lentz, W C Connor, J P Fraissard *J. Catal.* **117** 281 (1989)
114. E Keren, A Soffer *J. Catal.* **50** 43 (1977)
115. J Bonardet, J Fraissard, L DeMenoval, in *Proceedings of the 6th International Congress on Catalysis, London, 1976* (London, 1977) p. 633
116. T M Apple, P Gajardo, C Dybowski *J. Catal.* **68**103 (1981)
117. M Chesters, A Dolan, D Lennon, D Williamson, K Packer *J. Chem. Soc., Faraday Trans.* **86** 3491 (1990)
118. Kh M Minachev, R V Dmitriev, K Kh Shtainberg, A N Detyuk, Kh Bremer *Izv. Akad. Nauk SSSR, Ser. Khim.* 2682 (1978) [c]
119. J C Musso, J M Parera *Appl. Catal.* **30** 81 (1987)
120. C F Aissi, M Daage, M Guelton, J B Nagy, E C Derouanne *J. Catal.* **76** 231 (1982)
121. B Gerand, M Figlarz, in *Spillover of Adsorbed Species* (Eds G M Pajonk, S J Teichner, G J Germain) (Amsterdam: Elsevier, 1983) p. 275
122. R Erre, M H Legay, J J Fripiat *Surf. Sci.* **127** 69 (1983)
123. D Tinet, S Partyka, I Rouquerol, J J Fripiat *Mater. Res. Bull.* **17** 561 (1982)
124. J P Marcq, X Wispenninckx, G Poncelet, D Keravis, J J Fripiat *J. Catal.* **73** 309 (1982)
125. R Benali, C Hoang-Van, P Vergnon *Bull. Soc. Chim. Fr.* 417 (1985)
126. A C Cirillo Jr, L Ryan, B C Gerstein, J J Fripiat *J. Chem. Phys.* **73** 3060 (1980)
127. D Tinet, P Conneson, H Estrade, J J Fripiat *J. Phys. Chem. Solids* **41** 583 (1979)
128. X Lin, J F Lambert, J J Fripiat, C Ancron *J. Catal.* **119** 215 (1989)
129. J P Marcq, G Poncelet, J J Fripiat *J. Catal.* **87** 339 (1984)
130. M Misono, H Igarashi, K Katamura, T Okuhara, N Mizuno, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 105
131. T Baba, M Nomura, Y Ohno, Y Hiroyama, Y Ono, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 281
132. V Yu Bychkov, M Yu Sinev, B N Kuznetsov, E L Aptekar', V N Korchak, M G Chudinov, O V Krylov *Kinet. Katal.* **26** 665 (1987) [a]
133. V Yu Bychkov, M Yu Sinev, V N Korchak, E L Aptekar', O V Krylov *Kinet. Katal.* **27** 1190 (1986) [a]
134. T Yamada, K Kayano, M Funabiki, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 329
135. M P Sohier, G Wrobel, J P Bonnelle, J P Marcq *Appl. Catal.* **A84** 169 (1992)
136. R Burch, S E Golunski, M S Spencer *J. Chem. Soc., Faraday Trans.* **86** 2683 (1990)
137. F Boccuzzi, G Ghiotti, A Chiorino *Surf. Sci.* **183** L285 (1987)
138. E P S Barett, A J Blackburn, M A Yates, Y Wang, P A Sermon, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 207
139. O V Makarova, Candidate Thesis in Chemical Sciences, Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 1994
140. R Burch, R J Chappell, S F Golunski *Catal. Lett.* **1** 439 (1988)
141. X Wu, B C Gerstein, T S King *J. Catal.* **121** 271 (1990)
142. H Arakawa, K Sayama, K Okabe, A Murakami, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 389
143. K Fujimoto, Y Yu, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 393
144. Z Zhang, W M H Sachtler, S I Suib *Catal. Lett.* **2** 395 (1989)
145. S J Tauster, S L Fung *J. Catal.* **55** 29 (1978)
146. B S Beard, P N Ross *J. Phys. Chem.* **90** 6811 (1986)
147. T Huizinga, R Prins *J. Phys. Chem.* **85** 2156 (1981)
148. L Bonneviot, G L Haller *J. Catal.* **113** 96 (1988)
149. J C Conesa, P Malet, A Munos, G Munuera, M T Sainz, J A Sanz, in *Proceedings of the 8th International Congress on Catalysis, West Berlin, 1984, Vol. 5* (Weinheim: Basel, 1984) p. 217
150. J C Conesa, J Soria *J. Phys. Chem.* **86** 1392 (1982)
151. A R Gonzalez-Elipe, G Munuera, J P Espinoz, J Soria, J C Conesa, J A Sanz, in *Proceedings of the 9th Congress on Catalysis. Calgary, 1988, Vol. 3* (Ottawa: Chemical Institute Canada, 1988) p. 1392
152. R Burch, A R Flambard *J. Catal.* **78** 389 (1982)
153. J Herrman, P Pichat, in *Spillover of Adsorbed Species* (Eds G M Pajonk, S J Teichner, G J Germain) (Amsterdam: Elsevier, 1983) p. 77
154. Th Braunschweig, U Roland, H Winkler, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 183
155. U Roland, R Salzer, T Braunschweig, F Roessner, H Winkler *J. Chem. Soc., Faraday Trans.* **91** 1091 (1995)
156. K Kunimori, Z Hu, H Nakamura, A Maeda, T Uchijima, in *Proceedings of the 2nd International Conference on Spillover* (Ed. K H Steinberg) (Leipzig: Karl Marx University, 1989) p. 96
157. H Kato, T Mori, M Nakajima, Y Mori, T Hattori, Y Murakami, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 301
158. T Uematsu, M Fukuda, T Iijima, S Shimazu, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 397
159. K Kunimori, S Metsui, T Uchijima *J. Catal.* **85** 253 (1984)
160. Y L Huang, J A Schwarz, J P Diehl, J P Baltrus *Appl. Catal.* **37** 227 (1988)
161. O V Krylov, A A Firsova, A A Bobyshev, V A Radtsig, L Ya Margolis *Catal. Today* **13** 301 (1992)
162. B Delmon *Bull. Soc. Chim. Belg.* **88** 979 (1979)
163. B Delmon *React. Kinet. Catal. Lett.* **13** 203 (1980)
164. B Delmon *React. Kinet. Catal. Lett.* **22** 1 (1983)
165. M Karroua, H Matralis, P Grange *J. Catal.* **133** 371 (1993)
166. H Topsoe, B S Clausen, F E Massoth *Hydrotreating Catalysts. Science and Technology* (Berlin: Springer, 1996)
167. S I Kim, S I Woo *Appl. Catal.* **74** 109 (1991)
168. S I Kondrat'ev, S B Nikishenko, G V Antoshin, A A Slinkin, E A Fedorovskaya, Kh M Minachev *Kinet. Katal.* **25** 1168 (1984) [a]
169. M W J Craje, V H J de Beer, A M van der Kraan *Appl. Catal.* **68** L7 (1991)
170. R Candia, B S Clausen, J Bartholdy, N-Y Topsoe, B Lengeler, H Topsoe, in *Proceedings of the 8th International Congress on Catalysis, West Berlin, 1984, Vol. 2* (Weinheim: Verlag Chemie, 1984) p. 375
171. M J Ledoux, G Maire, S Hantzer, O Michaux, in *Proceedings of the 9th International Congress on Catalysis, Calgary, 1988, Vol. 1* (Ottawa: Chemical Institute of Canada, 1988) p. 74
172. H Topsoe, B S Clausen, R Candia, S Moing *J. Catal.* **68** 435 (1981)

173. R Candia, B S Clausen, H Topsoe *J. Catal.* **77** 364 (1982)
174. S M A M Bouwens, F B M van Zon, M P van Dijk *J. Catal.* **146** 375 (1993)
175. O Sorensen, B S Clausen, R Candia, H Topsoe *Appl. Catal.* **13** 363 (1985)
176. B Scheffer, E M van Oeri, P Arnoldy, V H J de Beer, J A Moulijn *Appl. Catal.* **25** 301 (1986)
177. M W J Craje, V H J de Beer, J A R van Veen, A M van der Kraan *J. Catal.* **143** 601 (1993)
178. A M van der Kraan, M W J Craje, E Gerkema, W L T M Ramselaar *Appl. Catal.* **39** L7 (1988)
179. J P R Vissers, V H J de Beer, R Prins *J. Chem. Soc., Faraday Trans. 1* **83** 2145 (1987)
180. K Imamura, R Prins *J. Catal.* **147** 515 (1994)
181. V V Rozanov, Yamin Tsao, O V Krylov *Kinet. Katal.* **37** (1996) [a]
182. H Hattori, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 69
183. T Tanaka, K Ebitani, H Hattori, S Yoshida, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 285
184. J C Yori, J M Parera *Appl. Catal.* **A129** 83 (1995)
185. B Chen, J L Falconer, in *New Aspects of Spillover Effect in Catalysis* (Amsterdam: Elsevier, 1993) p. 171
186. S Bishwait, J L Falconer *J. Catal.* **117** 281 (1989)
187. B Sen, J L Falconer, T F Mao, M Yu, R L Flesner *J. Catal.* **126** 403 (1990)
188. O V Krylov, B R Shub *Neravnovesnye Protsessy v Katalize* (Nonequilibrium Processes in Catalysis) (Moscow: Khimiya, 1990)
189. P B Weisz *Adv. Catal.* **13** 137 (1962)

[a] — *Kinet. Catal. (Engl. Transl.)*
[b] — *Dokl. Chem. (Engl. Transl.)*
[c] — *Russ. Chem. Bull. (Engl. Transl.)*