Spillover in Heterogeneous Catalysis

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I. Introduction and Background

Spillover involves the transport of active species sorbed or formed on a first surface onto another surface that does not *under the same conditions* sorb or form the active species.[1] Thus, the adsorbed species gain access to a different surface phase (accepting surface) that is in contact with the original adsorbing and activating surface. Diffusion across the first surface may proceed spillover and several processes may take place on the accepting surface

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following spillover: surface diffusion or transport, diffusion or reaction in the bulk, reactions on or with the surface, and creation of sites capable of adsorption or catalysis.[2] Spillover is important in adsorption and as a mechanistic step in heterogeneous catalysis.

Emmett discussed the possibility of spillover in 1940[3] when he noted that for NH_3 synthesis and decomposition, the rate increased as the catalyst particle size decreased, but only to a certain particle size. Below this size, the rate did not increase further. He concluded that below this particle dimension, "either the entire surface or a given fraction of it is active..." Emmett pointed out that these phenomena conflicted with theories that assumed only gaseous diffusion of reactants. He concluded that "some form of activated surface diffusion may easily constitute a major means by which gases reach the 'inner' surface of metallic catalysts...Final conclusions as to the part played by surface diffusion in catalytic reactions must await additional experimental results."

Experimental results of spillover did not come quickly. In 1957 Kuriacose observed that a Pt wire accelerated GeH_4 decomposition on a Ge film,[4] and Taylor proposed in 1961 that the wire was a "port-hole‘ for H atoms recombination to H_2.[5] In 1963, Sinfelt and Lucchesi postulated that activated species migrate from Pt/SiO_2 to Al_2O_3, where ethylene was hydrogenated,[6] and room temperature spillover was observed in 1964 when tungsten bronze formed for a physical mixture of WO_3 and Pt/Al_2O_3.[7] The word "spillover" was coined to describe the phenomena. Other early studies included isotopic exchange of OH groups due to spillover by Carter et al. in 1965,[8] and NiO reduction by H_2 in the presence of supported Pt or Pd by Verhoeven and Delmon.[9]

The first reviews of spillover were by Sermon and Bond in 1973[10] and Dowden in 1977.[11] These early reviews focused on H spillover that resulted in formation of bronzes, isotopic exchange of OH's, and enhanced adsorption. Several other reviews have appeared and the most recent was in 1986.[2]

The first international symposium on spillover was held in 1983[12] which sought a common definition of spillover.[13] Spillover was found to be involved in many surface reactions and transport phenomena, and to include other atoms (like O) and molecules or molecular fragments (like CO or NCO). Spillover was found to encompass not only adsorption but gasification of solids, creation of catalytically active sites, and reaction with adsorbed species. The second international symposium on spillover was held in 1989.[14] Considerable additional information was presented on spillover of non-hydrogen species, the mechanism and rate of spillover and surface diffusion, and the potential involvement of spillover in applied catalysis. The concept of remote control of catalytic activity was discussed.[15] The most recent international symposium took place in 1993.[16] The focus was on the broad extent of the applications of spillover in applied catalysis and the design of catalysts based on the phenomena associated with spillover. Many species were found to be involved in spillover, and that, even for a single molecule, different fragments, which also could be in various forms (charged, uncharged, or radical), could be involved in spillover.[17] Teichner forecast that there is "a very high probability... *(that)*-spillover does already exist in the mechanism of most catalytic reactions or may be introduced by a new design of catalysts."[18]

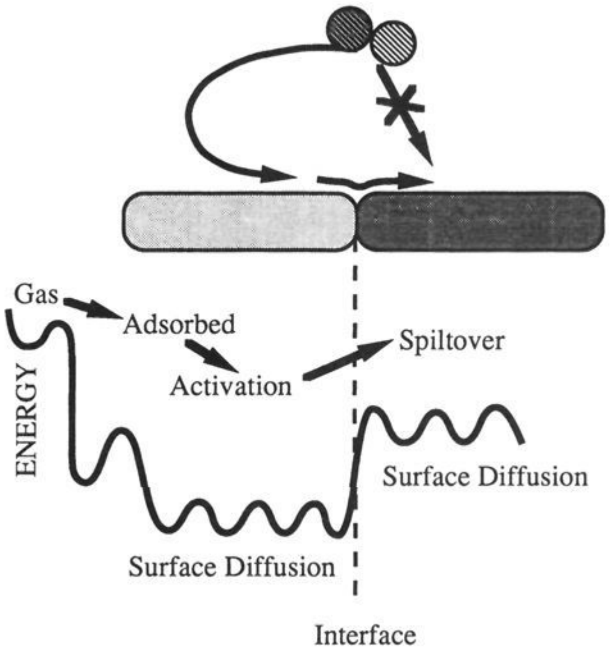

Figure 1. Schematic representation of spillover of a gaseous diatomic from an adsorbing onto a nonadsorbing surface. A reasonable energy level diagram for the processes is shown.[23]

The number of studies that have involved spillover is large and this review will emphasize work done in 1986 and afterward since spillover was extensively reviewed in 1986 by Conner, Pajonk, and Teichner.[2] It will also emphasize studies that have directly demonstrated spillover as opposed to those studies that have invoked spillover to explain their kinetic results. Many of these studies have used physical mixtures of catalysts, sometimes referred to as hybrid catalysts, to clearly demonstrate spillover.

II. Spillover and Associated Processes

Spillover is only one mechanistic step in a sequence that can occur in adsorption. There have been many polemics about spillover, e.g., does it exist, is it significant, what species are spilled over, or is spillover the rate-controlling step. Since no studies to date have been able to study the spillover step in isolation, all studies interpret experimental data for a combination of sequential steps. This may be the reason for the controversies. It is, therefore, necessary to define the process of spillover and the processes that are associated with spillover. Spillover will first be discussed followed by a discussion of surface diffusion as it relates to spillover. Finally, we will describe the reaction of spiltover species with the surface or adsorbed species.

A. Spillover

Figure 1 depicts spillover by showing adsorption and activation of a diatomic molecule onto a surface. The adsorbed species can then move across the surface to the interface with the second surface; the original diatomic cannot adsorb on the second surface. The spiltover species can diffuse across the nonadsorbing surface. For hydrogen spillover from a metal to an oxide, H_2 usually dissociates on the

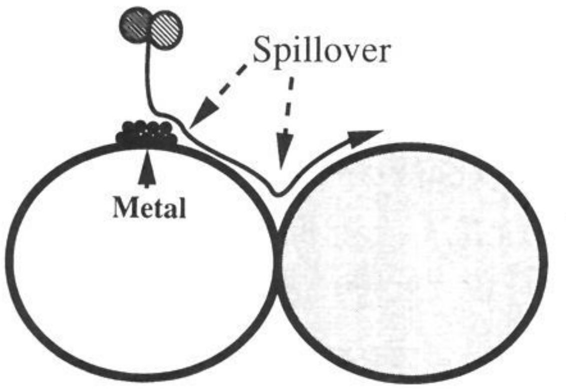

Figure 2. Schematic representation of spillover: from a metal adsorbing surface onto a support; and then onto another surface in contact with the support.

metal into atomic H, which then spills over onto the oxide support. Because most of the initial studies of spillover involved H_2, spillover was envisioned to involve spillover of atoms formed by dissociation of adsorbing molecules. However, adsorbing species can only partially dissociate or even retain their molecular identity during spillover. Movement across the surfaces can take place by forming equivalent bonds with similar neighboring surface atoms. This is effectively exchange of bonds between the adsorbed species and the surface, and allows the adsorbed species to reach an interface between the activating and the accepting surface. Spillover can take place from a metal to an oxide, from one metal to another,[19] from one oxide to another,[20] or from a metal oxide onto a metal.[21-23]

The energetics of spillover are also represented in Figure 1. Chemisorption on the original surface is exothermic, and the subsequent surface diffusion may have a small activation energy. Spillover at the interface between the two surfaces requires that bonds with the adsorbing surface are broken and new bonds are formed with the accepting surface. This is represented as an endothermic process that must then be facilitated by an increase in entropy for the spiltover species. The spillover species may bind strongly with the accepting surface, however, and spillover can also be exothermic. Diffusion across the accepting surface is expected to be a process with a low activation energy.[23]

Spillover is not limited to the surface immediately adjacent to the activating surface; it can extend to other surfaces in contact with the accepting surface. As shown in Figure 2, a diatomic molecule first adsorbs onto a metal surface (dark region), and the activated species then spills over onto the support (white sphere), where it can diffuse to the interface with another surface (darkened sphere). A second spillover onto the other surface can then occur, and if the second accepting surface is not the same composition as the first, a secondary spillover occurs. Whereas spillover from a metal to a support can be envisioned, transport to other noncontiguous surfaces is more difficult to accept. The experimental evidence is overwhelming, however, that spillover can extend from the initial accepting surface to adjacent surfaces in direct or indirect contact with the source of spillover or the surface that initially accepts the spiltover species. The mechanism of transport between surfaces that are in physical contact has not been studied extensively, although several authors suggested that additional surfaces, such as carbon between a metal and a metal oxide, may facilitate spillover.[24,25] The fact that spiltover species can be transferred over long distances has not been universally accepted, but some dramatic examples of spillover over millimeter or centimeter distances have been reported.[26-28]

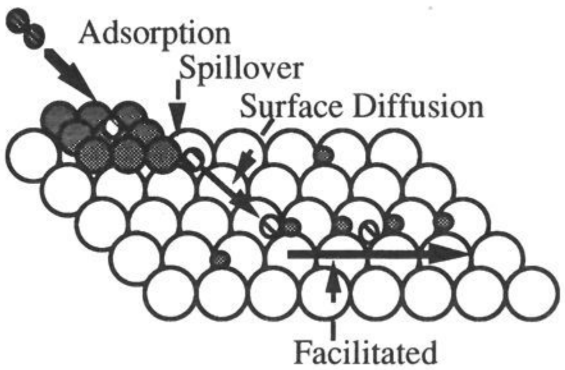

Figure 3. Schematic of hydrogen spillover from an adsorbing metal (medium-sized dark circles, upper left) and subsequent surface diffusion of atomic hydrogen (lined circles) across an oxide surface that is facilitated by the presence of hydroxyls (small dark circles).

B. Surface Diffusion

An adsorbed species can move across the surface on which it is first activated or across the surface onto which it is spilled over. Transport of adsorbed species across a chemically uniform surface is commonly referred to as surface diffusion. Surface *diffusion is not necessarily as simple as diffusion* through a fluid phase where the interactions between the diffusing species and its surroundings are constant (or increase or decrease progressively). The nature of the transport depends on the strength of the interaction between the adsorbed (or spiltover) species and the surface. This can vary from van der Waalls type interactions to more localized bonding between surface atoms and the species. Stronger interactions are better represented as activated exchange between adjacent adsorption sites. Thus, surface transport describes processes from two-dimensional diffusion to activated exchange.

Spillover occurs at the interface between the adsorbing and accepting surfaces. Surface diffusion to and from the interface between these surfaces can occur and the movement can be "activated" or "diffusive". Spillover can result in a long-range effect or one that is limited to the surface adjacent to the interface, depending on the relative energetics of transport (surface diffusion) on each surface. Activated surface translation of adsorbed species will differ from nonactivated diffusion in that there may be a bond between the adsorbed species and the atoms that comprise the surface. The energy of interaction will vary across the surface and so will the rate of transport. As an example, surface diffusion of hydrogen is facilitated by groups of hydroxyls on an oxide surface as a "bucket brigade".[23,29,30] This is depicted in Figure 3. This process is similar to the observations of Levy and Boudart who found that water or alcohols could assist in spillover and interphase transport.[31]

C. Reactions of Spiltover Species

Since the emphasis in this review is heterogeneous catalysis and spillover, the largest part of the review

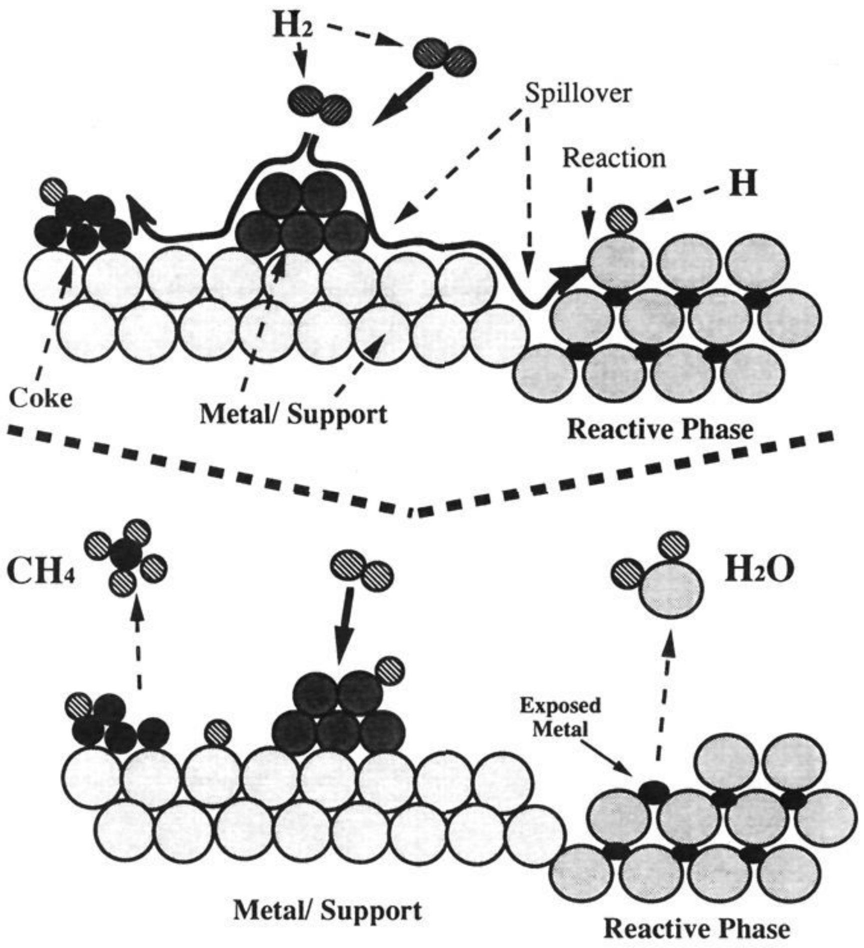

Figure 4. Schematic of spillover from a metal onto a surface possibly followed by spillover onto a second surface where it reacts. The lower figure represents the removal of hydroxyls (as H_2O) from a reducible metal oxide to expose underlying metal atoms on the right, and the removal of surface coke (as CH_4) from the support on the left.

will be on reactions of spillover species. This includes isotope exchange, reactions with solid phases, reactions of species adsorbed on different phases, and spillover of molecular species. Reactions of spillover species with solid phases can be important in maintaining catalytic activity. As examples, spillover of hydrogen or oxygen from a metal can react with surface carbon and remove it as CH_4 or CO_2.[32] This can be a mechanism for the cleaning of the surface by removing and controlling byproduct coke. Further, the spillover species can react with the support itself or even a second surface in contact with the accepting surface as depicted in Figure 4. In this example, hydrogen is represented to spill over from a metal onto its support. On the lower right of the figure, the spillover hydrogen spills over onto a second surface (in this case a reducible metal oxide) where it may then react with a hydroxyl to produce water, i.e., $OH + H \rightarrow H_2O$. This can expose the metal of the metal oxide and may create adsorption or catalytic sites. On the lower left of Figure 4, the spillover hydrogen reacts with coke and removes it as methane.

III. Spillover Processes in Catalysis

Several types of processes have been described that involve the participation of spillover in catalysis. The first systems where spillover was detected were supported metals with hydrogen spillover from the metal to the support. It was found that species could spill over from one metal onto another that does not independently adsorb the species. Other atomic species, specifically O, were also found to spill over from metals and other oxides. Finally, most of the processes associated with spillover are reversible. Each of these spillover processes on catalytic surfaces will be described in more detail.

A. Hydrogen Spillover onto Supports

Spillover of hydrogen from a metal to an oxide or carbon surface is important because most metal catalysts consist of small metal particles supported on either high surface area oxides or carbon, and many catalytic reactions involve hydrogen. Moreover, hydrogen spillover is the fastest spillover process, and H_2 adsorption is the most common method to measure the surface area of supported metal catalysts. If significant H spillover takes place during surface area measurements, then H/M ratios (number of adsorbed H atoms per total metal atoms) much greater than one can be obtained, and H_2 chemisorption is then not a useful method for surface area measurements. Indeed H/M ratios of several hundred have been reported as a result of spillover.[2,10] In addition, if H spillover is involved in a catalytic reaction, then the number of active sites on the surface is unknown, and thus turnover frequencies cannot be calculated for these reactions. Although H_2 does not readily adsorb or dissociate on most oxide surfaces, H_2 dissociates on group VIII metals readily even below room temperature. The resulting hydrogen atoms can then spill over onto oxide surfaces.

The presence of spillover hydrogen has also been detected by desorbing D_2 in TPD experiments in ultrahigh vacuum. Chen and White[33] observed four TPD states that were attributed to D_2 desorption from Al_2O_3 on a Pt/Al_2O_3 catalyst; three states were populated mainly by spillover and only one, the most weakly bond, was populated directly by D_2 adsorption in the absence of Pt. The spillover sites were also occupied by dosing atomic D onto Al_2O_3. For desorption of spillover hydrogen from Pt/Al_2O_3, the hydrogen was concluded to migrate back to Pt (reverse spillover). Eguchi et al.[34] saw a high-temperature TPD peak for H_2 on Ru/Al_2O_3 that was attributed to spillover hydrogen. Activated adsorption was required to create this peak. Similarly Kramer and Andre[35] observed a H_2 TPD peak at 753 K due to H on Al_2O_3 of Ni/Al_2O_3 and Pt/Al_2O_3. Activated adsorption at 673 K was required to occupy this spillover site that yielded the high temperature peak, but exposure to atomic H also created the peak and showed that it was due to hydrogen on Al_2O_3.

Miller et al.,[36] using TPD, related the quantity of spillover H on Pt catalysts to the number of OH groups on the support and the reduction temperature. Whereas no H_2 desorbed from the support alone, on Pt/H-LTL zeolite, the H/Pt ratio was 4.3 and a large H_2 peak due to spillover was observed during TPD. Figure 5a shows peak IV, which is near 873 K and is attributed to spillover. This peak is the largest for Pt on acidic supports. When a subsequent TPD was done (Figure 5b), peak IV was not present, and its absence was attributed to dehydroxylation of the support as a result of the high temperatures reached during TPD. Figure 5c shows the difference spectrum. Hydroxyl groups on the support were proposed to stabilize spillover H.

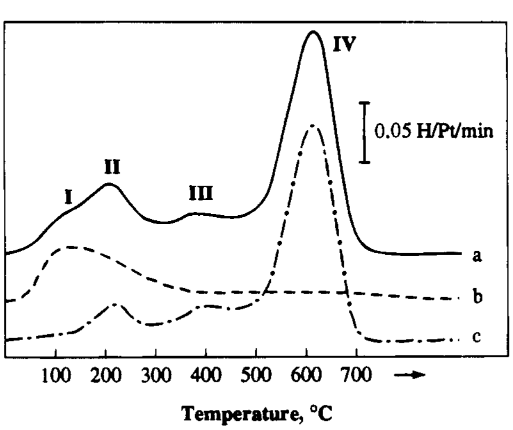

Figure 5. H_2 TPD spectra of Pt/H-LTL zeolite: (a) original TPD spectra showing spillover peak (IV); (b) TPD spectra after catalyst heated to higher temperature; (c) difference spectra a−b.[36]

Table 1. Chemisorption of H_2 and CO at 298 K on Mechanical Mixtures of C and Pt/C[38]

carbon to Pt/C ratio	amount adsorbed (10^{19}/g of sample) H atoms	amount adsorbed (10^{19}/g of sample) CO molecules	H/Pt ratio
0 (Pt/C only)	9.84	3.3	3.2
3:1	16.29	1.76	21
9:1	20.34	0.72	66
20:1	23.81	0.34	160
50:1	21.49	0.14	360
99:1	21.83	0.06	700

NMR was used by Chiaranussati et al.[37] to detect spillover H on a Pt/SiO_2 catalyst. Whereas no additional H adsorption was seen for Pt/Cabosil, two additional H adsorption sites were detected on Pt/sol-gel SiO_2. They concluded that radical spiltover hydrogen species interacted with the surface hydroxyl groups. Because of the different structures of Cabosil and sol-gel SiO_2, Chiaranussati et al. concluded that the spillover sites were strained siloxane rings present in sol-gel SiO_2.[37] The authors pointed out that the concentration of spillover sites could thus be controlled and optimized by controlling SiO_2 synthesis and processing.[37]

Chemisorption on mechanical mixtures of carbon and a Pt/carbon catalyst clearly demonstrates the ability of H_2 to spill over onto a carbon surface after dissociating on Pt.[38] As shown in Table 1, the amount of CO adsorbed per gram of total sample decreases as the Pt/C catalyst is diluted with carbon. That is, the CO adsorption tracks the amount of Pt on the sample mixture and thus CO is adsorbed only on the Pt. In contrast, the amount of H atoms adsorbed increases even though the number of Pt atoms in the sample decreases. The H/Pt ratio becomes large at the high dilution ratios because most of the H is on the carbon surface; the carbon surface appears to be saturated so that the H/C ratio is almost constant.

Another direct method of detecting the effect of H spillover on a solid is by electrical conductivity measurements on Pt/TiO_2. Braunschweig et al.[39] used TiO_2 pressed samples, half of each sample was 0.5% Pt/TiO_2 and the other half was pure TiO_2. Electrical leads were then attached so that the electrical conductivity of each half could be measured independently as H_2 (0.4 atm) was exposed to the samples at 300 or 350 K. The conductivity on the Pt/TiO_2 part increased almost immediately after H_2 exposure, but the Pt-free half of the sample exhibited a slow increase and was still changing after 800 min. During H_2 exposure, H_2 adsorbed on the Pt, H spilled over onto the TiO_2, and H then diffused on the TiO_2. The increase in conductivity was slow in the TiO_2 half of samples because of the long diffusion distance. For a sample that contained no Pt, the conductivity of the TiO_2 did not change upon H_2 exposure. Barrett et al.[40] also observed that H_2 decreased conductivity of ZnO, but increased it for Cu/Co/ZnO below 500 K due to spillover.

The movement of H_2 through a microporous Al_2O_3 membrane can be accelerated by adding Pd, Ru, and Rh to the sol gel used in membrane preparation. Eguchi et al.[34] observed that rate of H_2 diffusion was larger than that expected for Knudsen diffusion alone because of H_2 chemisorption, spillover, and surface diffusion. The H_2/N_2 permeation ratio expected from Knudsen diffusion is 3.74, but for metal-dispersed membranes, higher H_2/N_2 ratios were observed, and they increased with temperature. Values of the H_2/N_2 permeation ratio as high as 7.0 were reported.

A difficulty in understanding H spillover arises if spiltover hydrogen modifies the oxide support so that the surface can subsequently adsorb H_2 directly. Teichner et al.[41,42] had shown that hydrogen adsorbed directly onto Al_2O_3 after activation by Pt/Al_2O_3 and removal of the source of spillover. Kim and Regalbuto[43] concluded this process also occurs on Pt/MoO_3. Hydrogen spillover reduces the MoO_3 so that H_2 can then adsorb directly on the reduced MoO_3 surface. However, even if hydrogen is spilled over onto an oxide, all oxide surfaces do not then adsorb H_2 directly or are not reduced by spiltover hydrogen at the conditions where spillover takes place.

Many studies have suggested novel phenomena involving hydrogen spillover that were not discussed above but which may give insight into spillover. Teichner has discussed photodissociation and photospillover of hydrogen and the contribution of spillover to the design of gas sensors.[18] Most intriguing were the results of Roland et al., that have shown the influence of an external magnetic field to hinder the spillover-induced exchange of hydroxyl for Pt on HNaY zeolites.[44] These studies also provide evidence for a reservoir of spiltover D on the zeolite adsorbent.

B. Metal to Metal Spillover

Many metals do not activate and adsorb molecular hydrogen or oxygen; however, atomic H or O can be adsorbed on their surface. A spillover source may be able to activate the adsorbing species, however. The atoms could then spill over onto the surface that does not adsorb the molecular species directly. Two types of hydrogen spillover will be discussed: from one metal to another on a single-crystal surface and from one metal to another in supported bimetallic particles. This is followed by an example where both hydrogen and oxygen are spilled over between metals, and finally an example is discussed briefly where nitrogen spillover between different metal phases has been found.

Copper metal does not adsorb molecular hydrogen at low temperatures and, indeed, Goodman and

Peden have shown that copper, evaporated to cover a Ru(0001) single crystal, will block H_2 adsorption.[19,45,46] If the copper covers only a fraction of the surface, the amount of adsorbed hydrogen decreases, but *not* in proportion to the amount of surface masked by copper. This is evident in the differences in the amounts of hydrogen adsorbed at 100 and 230 K. More hydrogen is adsorbed at higher temperature and it begins to desorb from the bimetallic surface at lower temperatures than for the pure Ru during TPD. The authors conclude that hydrogen is adsorbed on the Ru and then spills over onto the Cu. This spiltover hydrogen on the Cu then desorbs directly as the temperature is raised or it returns to the Ru, recombines, and desorbs. Crucq et al. studied Cu/Ni alloys[47] and Rodriguez et al.[48] studied single crystals of Re covered with Cu and came to similar conclusions, i.e., that hydrogen was adsorbing on the one metal and spilling over onto the other.

On et al.[49] studied bimetallic Pt−Re particles supported on γ-Al_2O_3 and found that hydrogen TPD reflected the surface composition of the uniform size particles due to differences in the hydrogen spilled over from the Pt onto Re or onto Pt−Re alloys. If the supported metals were first exposed to hydrogen at room temperature, Pt desorbed H_2 at around 470 K but there is little evidence for H_2 adsorption on Re. All of the samples were pretreated at 763 K in oxygen followed by hydrogen. If the samples were cooled in Ar, the 470 K desorption peak diminished and was finally suppressed as more Re was present in the samples. It was concluded that Re was able to block adsorption onto Pt. If, however, the samples were cooled in hydrogen from 763 K to room temperature and then flushed with Ar before reexposure to H_2, hydrogen desorption shifted to higher temperatures and was not suppressed. The authors concluded that hydrogen was adsorbing on the Pt and then spilling over onto the support and finally onto Re and Pt−Re particles. If instead of Ar flow, a 5% H_2 in Ar was used as the temperature increased (a temperature-programmed, adsorption−desorption experiment, TPAD), hydrogen was found to adsorb at $\sim$400 K, to desorb at $\sim$600 K, and to adsorb again at 870 K for a bimetallic system with $Pt/(Pt+Re) = {}^1/_3$. It was proposed that H_2 adsorbed on Pt surface clusters at low temperature (400 K) and then spilled over onto the adsorption sites on the Al_2O_3, Re, and Re-rich cluster sites. The spiltover hydrogen then desorbed from the Al_2O_3 at 600 K. At higher temperature, H_2 completed the reduction of the initial catalyst. These authors analyzed the sites required for H_2 dissociation on Pt and Pt−Re clusters for clusters of varying composition and found that differences in surface composition could explain the differences found in the TPD and TPAD profiles.[49] In this manner these authors were able to show that the desorption profiles for spiltover hydrogen were sensitive to the amount of metal suface segregation and/or the bimetallic nature of these supported particles.

The spillover of adsorbing species is neither restricted to metals in direct contact with each other nor is it limited to spiltover hydrogen. Nishiyama et al. employed X-ray photoelectron spectroscopy to study Rh and Sn supported on SiO_2.[50] They found that Sn suppressed the hydrogen adsorption ability for Rh on SiO_2 but enhanced the oxygen uptake of the system. They concluded that oxygen spilled over from the Rh to the Sn where $^{16}O_2$−$^{18}O_2$ isotopic exchange occurred. Also, H spilled over from Rh to Sn, effecting reduction of the Sn oxides. The Sn or its (reduced) oxides could block hydrogen adsorption on Rh, as proposed for reduced titania in the SMSI effect as discussed in section IV.B. Metal to metal spillover may also occur for metals on reducible transition metal oxides.

Hydrogen and oxygen are not the only atoms to spillover in bimetallic systems. Field ion microscopy was employed by Sotola and Knor to follow the spillover of nitrogen atoms between Mo and Pd on WO_x.[51] The spillover seems limited as the distance between the Mo and the Pd islands needs to be less than 1.5 nm to facilitate nitrogen spillover.

C. Oxygen Spillover

Although hydrogen spillover has been extensively studied because of its potential importance in many catalytic reactions, other atomic and molecular species also spillover. This section will briefly discuss oxygen spillover. Spillover of molecular species or fragments is discussed in section IV.D. Oxygen spillover is of interest both because of the large number of oxidation reactions and because surface carbon can be removed from catalysts by spillover oxygen (section V.C) . Surface carbon is a byproduct of many organic reactions and can cause catalyst deactivation.

Isotope exchange has been an effective means to demonstrate oxygen spillover as demonstrated by Duprez et al.,[52] who exchanged $^{18}O_2$ with ^{16}O in the Al_2O_3 support of a Rh/Al_2O_3 catalyst. The metal is necessary for $^{18}O_2$ exchange, and the exchange rate depends on the nature of the metal. Indeed, Rh is the most active metal in promoting exchange, whereas Pd is incapable of promoting oxygen exchange, even at 673 K.[53] At low pressure the rates of O and H exchange were similar on Rh/Al_2O_3 at 673 K, as if the H and O migrate together. The O and H exchange rates showed different dependences on OH concentration, however, and the rate of H exchange was more sensitive. The rate of each at 673 K was 500−1000 per metal site per hour. A slight dependence of O exchange on OH coverage was seen, where the OH coverage was changed by heat treatment. The rate-determining step for exchange on Rh/Al_2O_3 apparently changed with temperature. Below 593 K, the activation energy for exchange was 70−80 kJ/mol and adsorption−desorption of oxygen on Rh was concluded to be limiting. Above 593 K, the activation energy decreased to 19−22 kJ/mol and migration on the Al_2O_3 was concluded to be rate determining. In contrast, for Pt catalysts[53] the rate-determining step was concluded to be adsorption and desorption of O_2. It is also possible that the spillover may be rate controlling under some of the conditions.

Oxygen exchange has also been observed for SiO_2, ZrO_2, and CeO_2 supports with Rh used as the source.[54] Nakamura et al.[55] reported that $^{18}O_2$ exchange on Rh/SiO_2 was by spillover since they did

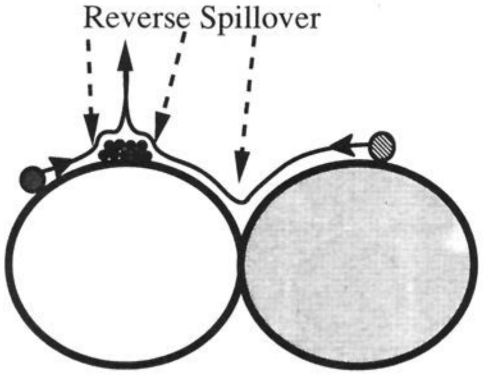

Figure 6. Schematic of reverse spillover from the accepting surface(s) back to the source of the original spillover.

not observe any exchange on SiO_2 alone. The rate of oxygen exchange was at least as large as the rate of CH_4 oxidation to CO and H_2 on their Rh/SiO_2,[54] so that CH_4 oxidation by $^{18}O_2$ resulted in ^{16}O incorporation from SiO_2 into products at 873 K. Similarly, lattice oxygen of Mn_2O_3 was easily removed at low temperature in the presence of Pd, and thus Pd/Mn_2O_3 has a higher activity than either Pd/Al_2O_3 or Mn_2O_3 alone for CO oxidation.[56]

Oxygen spillover has been used for the design of industrial oxidation catalysts.[57] For propylene oxidation to acrolein over multicomponent metal oxides, addition of Fe, Co, or Ni to bismuth molybdate improves performance. Tracer studies with $^{18}O_2$ showed that O_2 is activated on Fe or Co, and oxygen spillover proceeds mainly by bulk diffusion of oxide ions.

D. Reverse Spillover

Reverse spillover is when a spiltover species diffuses back to and moves onto the source of spillover. This is represented in Figure 6; the spiltover species moves back to the original porthole, where it can recombine (if dissociated), react, or desorb. Atomic species are depicted in the figure for simplicity, but nonatomic fragments or molecules undergo the same process. At steady state, spillover involves competition between forward and reverse steps. If a change is made in the gas phase such that the species spilling over is decreased in concentration or reacts with another species, then the concentration of activated species on the spillover source decreases, and the concentration gradient is reversed.

Reverse spillover assumes that the species under consideration cannot adsorb directly on the acceptor surface and only gets there by spillover. The term reverse spillover has not been used consistently with this definition, however, and has often been used to describe any transport from an oxide (or other nonmetal surface) to a metal. If the oxide can adsorb and activate the adsorbing species, this is not reverse spillover. It is spillover from an oxide to a metal if the metal is unable to adsorb the species directly, or it is exchange between the two surfaces if both are able to adsorb the species directly. For example, CO can adsorb on metal surfaces and it can also adsorb on oxide surfaces under certain conditions. If the CO adsorbs on the oxide and moves to the metal, it has been referred to as reverse spillover although it does not meet the strict definition. Because many papers have used a broader definition of reverse spillover, however, this section will include those studies. For example under some conditions, organic molecules adsorb on oxide surfaces, dehydrogenate to create H atoms, and the H atoms can then move onto a metal surface. Since H_2 is able to adsorb directly on the metal (but not the oxide) and spillover onto the oxide, the transport back to the metal is referred to as reverse spillover, even though the H did not originally get on the oxide by spillover from the metal.

Table 2. Effect of ZnO on Yield and Selectivity for the Aromatization of Cyclohexane on ZSM-5[59]

catalyst	aromatic yield %	aromatic distribution (%) benzene	toluene	xylenes
bentonite	0.1			
ZnO	0.7	99.3		
ZSM-5	48.3	23.5	41.4	23.6
hybrid (ZSM-5 + ZnO)	83	82.5	9.5	4

For oxide surfaces that do not adsorb H_2 directly, recombination of H atoms that form from reaction and desorption of H_2 may not take place or be very slow, according to microscopic reversibility. For example, Fujimoto[58] pointed out that during catalytic dehydrogenation on oxide surfaces, H atoms form and they must be able to recombine and desorb as H_2. The addition of a metal that provides sites for this recombination and desorption by reverse spillover can then accelerate the rate of dehydrogenation if either recombination or desorption is limiting. In the dehydroaromatization of paraffins on H-ZSM-5, small amounts of aromatics and large amounts of lower paraffins form.[58] The H that formed during aromatic formation stayed on the H-ZSM-5 surface and reacted with smaller olefins, which are intermediates to aromatic formation, to make smaller paraffins. When small amounts of Ga^{3+} or Zn^{2+} were added to the H-ZSM-5 catalyst, H_2 desorbed from these sites, and thus H_2 production increased. This increased the selectivity to aromatics and decreased paraffin formation. The Ga^{3+} was also effective when it was added by making a physical mixture of $Ga_2O_3/\gamma\text{-}Al_2O_3$ or Ga_2O_3 powder with H-ZSM-5 to create a hybrid catalyst, whereas $Ga_2O_3/\gamma\text{-}Al_2O_3$ alone was inactive. Thus, the H atoms were able to undergo spillover from the H-ZSM-5 onto the particles containing Ga^{3+} and then undergo reverse spillover to desorb.

Similarly, Van Mao et al.[59] reported that ZnO is not actively involved in any step of aromatization of alkanes, but when added to ZSM-5 zeolite, the ZnO helps to remove H that is released from zeolite acid sites. They demonstrated a dramatic effect by preparing hybrid catalysts of mechanical mixtures of ZSM-5 and ZnO, which were then extruded with bentonite clay. As shown in Table 2, conversion on ZSM-5 was increased by the addition of ZnO (which itself is almost inactive) and selectivity was also changed dramatically. The maximum aromatization activity was obtained for a hybrid catalyst with 5−15% ZnO. The oligomerization and aromatization take place in the zeolite and the H that is released migrates to ZnO, from which it can desorb into the gas phase.

For the hybrid catalysts, where ZnO and ZSM-5 are in close contact, aromatic yield was double that of a bed of physically mixed ZnO and ZSM-5. For beds of ZnO and ZSM-5 that were completely sepa-

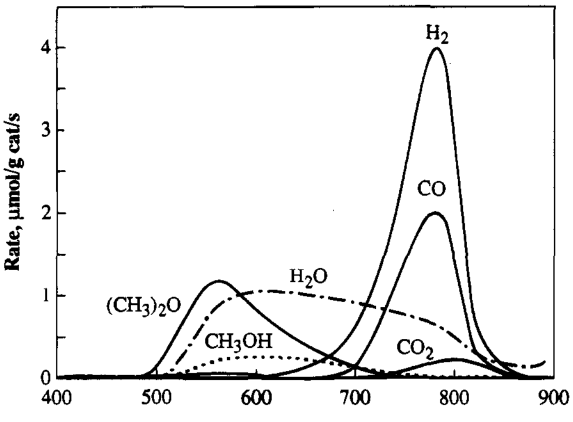

Figure 7. TPD spectra of CH_3OH (2 μL adsorbed at 300 K) on γ-Al_2O_3.[60]

rated physically, the conversion and selectivity were the same as obtained on ZSM-5. That is, the two catalysts must be in close contact for the best yield. Since the ZSM-5 particles were approximately 1 mm in size, that means that enhancement by ZnO, even in the hybrid catalyst, requires that H undergo reverse spillover over a distance of 1 mm.

Similarly, isopentane dehydrogenation to isopentenes or cyclohexane dehydrogenation to benzene on an active carbon surface can be accelerated by depositing a transition metal onto the carbon.[2] Since the rate of dehydrogenation can also be accelerated by adding a hydrogen acceptor (C_2H_4, NO) to the gas phase, the higher rate upon addition of a transition metal is due to desorption of adsorbed H by reverse spillover. A further indication that H_2 desorbs from the metal is the observation that H_2 adsorption on carbon is increased by the presence of a transition metal. Furthermore, a correlation was observed between the initial rate of H spillover at 673 K (during adsorption) and the rate of cyclohexane dehydrogenation at 673 K. The rate of desorption was also observed to increase directly by using TPD.[2]

A comparison of alcohol decomposition on Al_2O_3 and Ni/Al_2O_3 has shown directly that reverse spillover is important for decomposition on Ni/Al_2O_3.[60] TPD experiments show clearly that Ni dramatically increases the rate of methanol, ethanol, and 1-propanol decomposition. The alcohols adsorb on the Al_2O_3 surface, and thus, on a 5.7% Ni/Al_2O_3 catalyst where most of the surface area is Al_2O_3, most of the adsorption is expected to be on the Al_2O_3 surface. Indeed, the amounts of adsorbed alcohols were the same on Al_2O_3 and Ni/Al_2O_3. Essentially no alcohol was adsorbed on the Ni surface at room temperature. As shown in Figure 7, methanol decomposes above 700 K to form mostly CO and H_2. In contrast, CH_3OH decomposes much faster during TPD on Ni/Al_2O_3, even though essentially all the CH_3OH is adsorbed on the Al_2O_3 surface. The resulting TPD, in Figure 8, shows that decomposition starts below 450 K. That is, the presence of Ni increased the rate of CH_3OH decomposition by approximately 5 orders of magnitude. Similarly Ni increased the rates of decomposition of ethanol and 1-propanol adsorbed on the Al_2O_3 support by orders of magnitude. The increase in the rate was smaller as the number of carbon atoms in the alcohol increased, however. In order for the small concentration of Ni particles to have such a dramatic effect on the rate, the alcohol (or the species that form upon adsorption) must diffuse to the Ni crystallites. Decomposition on Ni/Al_2O_3 thus takes place by reverse spillover, either on the Ni surface or at the Ni–Al_2O_3 interface. An additional indication that decomposition took place at the Ni or Ni–Al_2O_3 interface is that dehydrogenation was the dominant reaction when Ni was present whereas C_2H_5OH and 1-C_3H_7OH dehydrate on the Al_2O_3 surfaces. On Pt/Al_2O_3, a similar enhanced rate of CH_3OH decomposition, relative to Al_2O_3 was observed.[61]

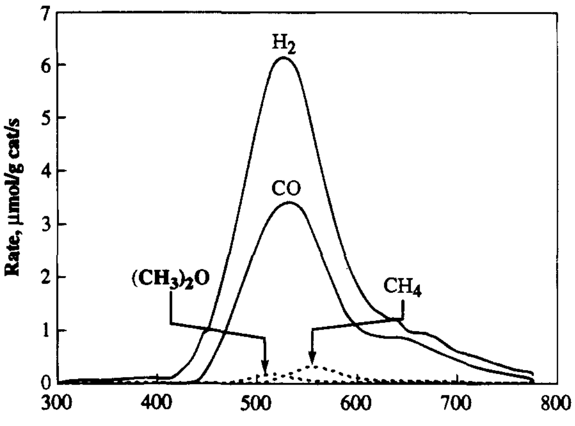

Figure 8. TPD spectra of CH_3OH (2 μL adsorbed at 300 K) on 5.7% Ni/Al_2O_3. [60]

An interesting aspect of these alcohol decompositions was that the rates of the C_1, C_2, and C_3 alcohols were quite different on Al_2O_3, but were similar on Ni/Al_2O_3.[60] Because CO and H_2 form simultaneously when the alcohols decompose, their formation was concluded to be limited by either the rate of reverse spillover or the rate of decomposition of the adsorbed species on the Ni or at the Ni–Al_2O_3 interface. Alternatively, the increased rate of alcohol decomposition could be due to the creation of active sites on the Al_2O_3 surface during pretreatment in H_2 at 773 K, similar to the creation of sites observed by Teichner on Pt/Al_2O_3.[62] However, a bed of Ni/Al_2O_3, placed on top of a bed of Al_2O_3 and pretreated in H_2 for various times exhibited TPD spectra that corresponded to two distinct processes: decomposition on Ni/Al_2O_3 and decomposition on Al_2O_3, Thus, pretreatment in H_2 did not appear to activate sites on Al_2O_3 for alcohol decomposition.

Another example of reverse spillover was reported by Li et al.[63] for a CeO_2 support. For CeO_2 alone, superoxide and peroxide IR bands were detected upon exposure to gas phase O_2, and these peaks were stable to 373 K (Figure 9). On Pt/CeO_2, however, these species were not detected by IR. They were concluded to be unstable because they migrate to the Pt where they desorb. Zafiris and Gorte[64] reported that CO adsorbed on Rh on CeO_2 films in UHV reacts to form CO_2 during TPD because of reverse spillover. The extra oxygen needed to form CO_2 was concluded to be from the CeO_2, and the region near the Rh particles could be depleted by multiple adsorption and TPD cycles. They concluded that oxygen migrates from the CeO_2 onto the Rh surface.

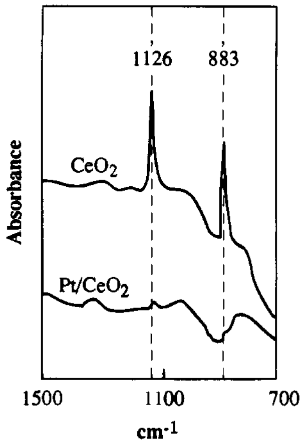

Figure 9. IR spectra of dioxygen adsorbed on reduced CeO_2 and Pt/CeO_2 at 273 K.[63]

In another example of CO oxidation, Ladas et al.,[65] using planar oxide surfaces onto which Pd particles were deposited, found that the reaction rate increased as the diameter of Pt clusters decreased, until the rate was greater than the collision rate of CO from the gas phase onto the Pd. Similar increases in the oxidation rate with decreasing Pd particle size were reported for Pd on mica.[66] Two pathways for CO adsorption were used to explain these results. In addition to CO adsorption on Pd, adsorption on the support, followed by diffusion and reverse spillover, provided additional CO on the Pd. A model incorporating reverse spillover and the existence of a collection zone around each Pd particle was used to account for the experimental observations.[67]

IV. Reactions of Spiltover Species

Spillover provides a mechanism by which activated species gain access to a new surface. The activation on the adsorbing surface can provide an indirect pathway for subsequent reaction on or with the accepting surface. Spiltover species provide a path for isotopic exchange of hydroxyls. These species can also react with the surface of the accepting solid to reduce or to oxidize an oxide or to gasify carbon. The spiltover species (which can be atoms, molecules, or fragments of molecules) can participate in catalysis on the accepting surface. Further, these spiltover species can maintain or induce adsorption or catalytic activity on the accepting surface.

A. Isotope Exchange

A direct measure of H spillover is exchange between species adsorbed on the support (including OH groups that are present on most oxide surfaces) and those in the gas phase. In contrast to H spillover studied by TPD, exchange hydrogen does not result in substantial additional hydrogen on the oxide support. It should be noted that exchange experiments in the presence of a hydrocarbon or water can differ from those in their absence because the hydrocarbon may provide a bridge for the spillover of hydrogen,[25] and water can catalyze direct exchange between $-OH$ and H_2.[68]

Isotope H$-$D exchange between the gas phase and species on the oxide surface have been studied by observing changes in the adsorbed species by IR spectroscopy and by observing changes in gas-phase species, either isothermally or during temperature programming. For example, Carter et al.[8] observed with IR spectroscopy that OH$-$OD exchange on Al_2O_3 was faster on Pt/Al_2O_3 than on Al_2O_3. Three types of OH groups were detected by IR and the high-frequency OH group was the most reactive for exchange. For example, after 10 min at 423 K, 30% of the OH at 3785 cm^{-1} had exchanged but only 9% of the OH in the bands at 3740 and 3710 cm^{-1} had exchanged. The D_2 was concluded to dissociate on Pt and migrate to OH on Al_2O_3. Ambs and Mitchel[69] observed with a chromatographic technique that no exchange took place between gaseous D_2 and OH groups on Al_2O_3 in the absence of Pt at 423 K. These authors concluded that H_2O adsorbs on Al_2O_3 and makes OH groups. The additional OH were assumed to provide bridges by which H atoms can migrate. Cavanagh and Yates[70] concluded from IR measurements on Rh/Al_2O_3 that D underwent rapid spillover from Rh to Al_2O_3, the diffusion was slow on Al_2O_3, and the exchange with surface OH was then rapid. This exchange was done at 310 K and thus exchange was still occurring after 1500 min on Rh/Al_2O_3. In contrast, no exchange was seen with pure Al_2O_3. Another indication of the role of Rh was obtained by first saturating the Rh with CO. The rate of exchange was then only 15% of that found in the absence of CO. Other studies[71] have also seen that CO preadsorption inhibits adsorption of spillover hydrogen.

Scott and Phillip[72] observed exchange by D_2 from 393 to 623 K that was attributed to exchange with H_2O, and exchange from 533 to 723 K that was attributed to OH exchange. In contrast, Chen and Falconer[73] observed more rapid exchange of both H_2O and OH on Ni/Al_2O_3 below 550 K. One complication in using exchange of OH groups on oxides to measure spillover is the influence of H_2O (or D_2O) and O_2. Bianchi et al.[68] observed that D_2O deuterates the surface without spillover and thus any O_2 in the D_2 stream must be eliminated since O_2 will react over transition metals to make D_2O. Infrared spectroscopy was used to study spillover from Pt/Al_2O_3 (a small spot on a SiO_2 pellet) onto SiO_2 and observed a concentration gradient in OD on SiO_2; however, when $D_2 + D_2O$ flowed, the OH exchanged and more exchange occurred as the D_2O concentration increased.

Exchange has also been observed for zeolite supports. When metals were placed on Y zeolite, the exchange temperature decreased by 300 K, and exchange was faster for supported Pt and Pd than for Ni.[74] Steinberg et al. found that hydroxyls on Pt/Y zeolite exchanged with D_2 at room temperature, and the exchange was complete in 2 h.[75,76] Even for mechanical mixtures, isotopic equilibrium was reached at 373 K. The authors concluded that spillover (and not surface diffusion of the spiltover D) was rate limiting for hydroxyl exchange. Similarly H$-$D exchange due to H spillover was observed in Pt$-$NaY/H$-$NaY, and exchange of OH groups took place at room temperature. Water was observed as a byproduct of spillover. Steinberg et al. monitored exchange of D_2 by IR of the H−NaY acceptor surface, at a location 0.5 mm from the interface to the Pt−NaY source. When HNaY zeolite was used alone, no exchange took place in 8 weeks.[76]

A direct measure of H spillover and surface diffusion has been obtained by FTIR measurements on SiO_2 wafers with a small spot of Pt on Al_2O_3 placed at the center.[26,27] As D spilled over from the Pt and diffused onto the oxide, a concentration gradient for the OD absorption band was observed on the oxide surface. The D concentration was measured as a function of time and distance, which enabled the diffusion coefficients to be calculated independent of the actual spillover process (see section VI). The saturation of the OD curves indicated that not all the OH groups on SiO_2 are available for exchange at the same rate. The "associated" (viscinal and geminal) hydroxyls exchanged first while the isolated hydroxyls exchanged at a slower rate. Thus, there are two mechanisms for exchange: one that involves rapid transport via the associated hydroxyls and one that involves diffusion across the bare oxide to exchange the isolated hydroxyls. They observed that if H_2O or O_2 (probably forming H_2O) were present in the gas phase, these species catalyzed OH exchange with gas phase D_2. Exchange occurred everywhere below 473 K if water was present at any concentration above 10^{-5} Torr, in confirmation of the results of Bianchi et al.[68] These results show that considerable care and fairly high vacuum ($<10^{-6}$ Torr) over the sample are required to assure that exchange can solely be attributed to spillover.

Similarly, spillover was studied using a wafer of SiO_2 and Pd in which Pd was in an outer ring and IR was only taken of the center SiO_2 region.[77] The IR results showed that a stable radical, diphenylpicrylhydrazyl, on the surface decreased and its hydrogen form increased due to spiltover hydrogen. Since the radical did not diffuse, this was direct evidence of hydrogen spillover at 338 K. The authors pointed out that H−D exchange probably cannot be taken as direct evidence of hydrogen spillover since nonspillover exchange is possible.

In what might be called temperature-programmed exchange (TPE), D_2 flowed over a catalyst while its temperature was increased at a constant rate.[11,78] The amount of displaced hydrogen was measured by a mass spectrometer for Pt on Al_2O_3, and exchange was complete by 300 K. The total number of H atoms exchanged was 249 μmol/g catalyst.[11] Similarly, on Ni/Al_2O_3, the D_2 uptake and HD and H_2 formation were observed with a mass spectrometer.[78] For example, a Ni/Al_2O_3 catalyst was pretreated at 775 K in pure H_2 and then cooled in H_2. The catalyst was then ramped in 10% D_2 flow, and as shown in Figure 10, D_2 was consumed between 440 and 550 K as HD and H_2 simultaneously formed. Since no molecules were adsorbed on the catalyst, this exchange was with the OH groups on the support. The large amount of H that exchanged (2900 μmol/g catalyst) shows directly that this was not exchange with H on the metal. Moreover, the concentration of OH groups estimated from TPE is 7.9 OH/nm^2. This is the total OH concentration expected for an Al_2O_3 surface dehydroxylated at 775 K.

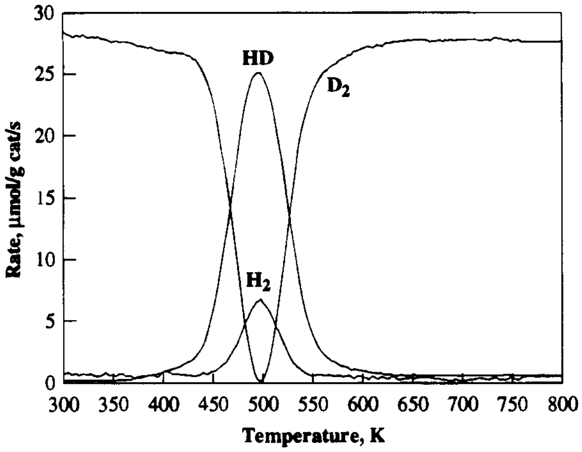

Figure 10. Temperature-programmed exchange spectra for 5.1% Ni/Al_2O_3. The catalyst was first pretreated in H_2 at 775 K and cooled in H_2. The spectra were then obtained by heating the catalyst in 10% D_2 flow.[73]

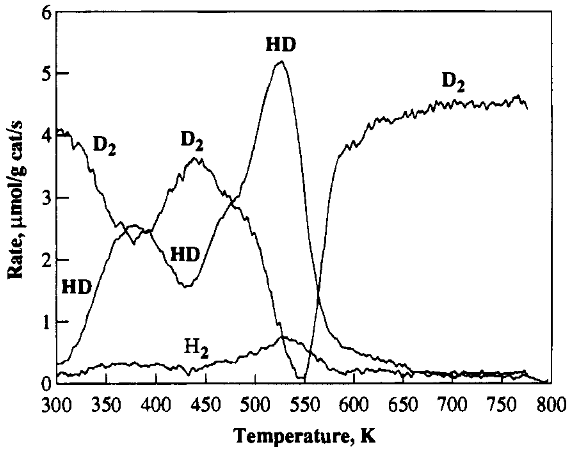

Figure 11. Temperature-programmed exchange spectra in 10% D_2 flow for 5.1% Ni/Al_2O_3 on which 1 μL CH_3OH was adsorbed at room temperature. The catalyst was cooled in 10% D_2 prior to adsorption.[73]

The rate that H atoms can move from the metal to the support is even faster than that observed in Figure 10, as shown by exchange with species adsorbed on the Al_2O_3 surface.[78,79] When CH_3OH, C_2H_5OH, and 1-C_3H_3OH were adsorbed on the Al_2O_3 surface, exchange from Ni started at room temperature and a large fraction of the H atoms in the alcohols had exchanged before the OH group started to exchange, as seen in Figure 11. To avoid confusing the OH exchange with alcohol exchange, the catalyst was pretreated at 775 K in D_2 flow and cooled in D_2 flow, so that OD groups were present on the surface before the alcohols were adsorbed. Exchange was inhibited by adsorbing CO on the Ni surface; this result demonstrated that spillover was necessary for exchange. As shown in Figure 12, exchange was even faster for H_2O adsorbed on Ni/Al_2O_3. A mass balance showed that all the H_2O had exchanged by 450 K.[78] Thus, it appears that exchange with the alcohols or OH groups is not limited by the rate of spillover, but apparently by exchange reactions on the Al_2O_3. Since H_2O may increase the rate of spillover,[32] however, it is difficult to separate these effects.

Baumgarten et al.[80] concluded that hydrogen spillover does not necessarily lead to formation of active hydrogen species on oxides, but that spiltover hydro-

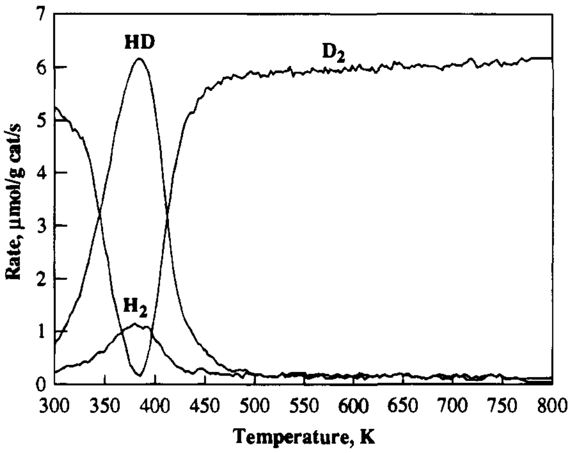

Figure 12. Temperature-programmed exchange spectra in 10% D_2 flow for 5.1% Ni/Al_2O_3 on which 1 μL H_2O was adsorbed at room temperature. The catalyst was cooled in D_2 from 773 K prior to adsorption.[73]

gen can exchange with OH groups on the oxide. That is, active hydrogen species for hydrogenation are not formed. They were able to show this by covering Al_2O_3 with unsaturated carboxylic acids and then pressing a wafer with Pt/Al_2O_3, In this preparation, no acid was in direct contact with Pt. The OH groups (as measured by FTIR) were extensively converted to OD after 20 min at 470 K but the acid groups did not change. That is, the spiltover hydrogen leading to HD exchange was not able to hydrogenate hydrocarbon on the support.

As the above survey shows, even for the same type of spillover measurements (H–D exchange) large differences are seen between different studies, different supports, and different metals. On some catalysts exchange takes place at room temperature, whereas for others it is only significant at elevated temperatures. On some samples all the OH groups can exchange, but on others only a fraction of them are able to exchange. The presence or absence of H_2O may be responsible for some of these differences, but this does not appear to be the complete explanation.

B. Reaction of Spiltover Species with Solid Phases

Spiltover species can react with an acceptor phase to reduce or oxidize it. Such reactions can be important steps in catalytic processes such as carbon gasification, coke removal from a catalyst support, reduction of oxides to suboxides, or reoxidation of the acceptor phase in order to maintain catalytic activity. Each of these types of spillover processes will be discussed in this section.

Catalytic reactions involving organic reactants can result in coke formation on oxide surfaces, and this coke can deactivate the catalyst. As examples, spillover of hydrogen or oxygen from a metal can react with surface carbon and remove it as CH_4 or CO_2.[33] For acid-catalyzed hydrocarbon reactions, for example, catalyst deactivation is caused by coke or coke precursors that deposit and block acid sites.[58] Transition metals on the oxide can serve as sources of hydrogen or oxygen atoms to hydrogenate or oxidize the coke or coke precursors to prevent accumulation. Thus, spiltover H in catalytic reforming and hydrocracking and spiltover oxygen in selective oxidation have been reported to remove coke from oxide surfaces.[20] For example, the rate that coke burned off an Al_2O_3 surface greatly increased when Pt was present to activate O_2. The O atoms that formed on Pt migrated onto the Al_2O_3 surface and oxidized the coke more rapidly than O_2 directly from the gas phase. Similarly, spiltover H was reported to stabilize the catalytic activity of H–Y zeolites and pillared monmorillonite against coke formation when these catalysts were used for disproportionation and alkylation of 1,2,4-trimethylbenzene.[81] Deactivation by coke formation on Lewis acid sites was completely prevented by using H_2 carrier gas and by adding small amounts of Pd onto the zeolite or by mixing the catalyst with Pd/Al_2O_3.

Weng et al.[82] demonstrated directly that spillover occurs in coke removal. They first deposited coke on MoO_3 and *then* mixed the MoO_3 mechanically with Sb_2O_4. The coke was eliminated faster by oxidation in air when the Sb_2O_4 was present. Thus, Sb_2O_4 served as the source for spiltover oxygen.

Metals and metal sulfides have also been shown to increase the gasification rate of carbon. A recent study by Rodriguez and Baker[83] used single crystal graphite and controlled atmosphere electron microscopy to provide direct evidence of spillover. Regions of the graphite surface in direct contact with metal sulfide powders (MoS_2, FeS_2, FeS) reacted at room temperature with H_2, but pits due to removal of carbon by gasification were also produced at locations remote from the catalyst. Pits also formed on the graphite at room temperature when the metal sulfide was separated from the graphite, and since the pit concentration decreased in regions further from the sulfide, they[83] concluded that H transported both on the surface and through the gas phase at the low pressure (0.2 Torr H_2) used. The possibility of spillover through the gas phase will be discussed briefly in section VI.F.

Mechanically mixing a supported catalyst (Ni/Al_2O_3, Co/Al_2O_3, Ni/diatomite) with carbon loaded with iron increased the gasification rate in H_2 or in H_2/H_2O.[84] The H produced on the supported catalyst spilled over onto the support, then onto the carbon, and then onto the iron. The authors concluded that spiltover H increased the activity of the Fe by dissolving more carbon into the Fe because both hydrogasification and steam gasification rates were enhanced by the supported catalysts. Even placing a Ni/Al_2O_3 catalyst on the top or bottom of a bed of Fe-loaded carbon increased the conversion a factor of 3 at 1123 K. Mechanically mixing the two increased the gasification rate a factor of 11. Organic solids have also been hydrogenated by H spillover from a metal.[85]

Numerous studies have reported that the reduction temperature of metal oxides by H_2 can be lowered by the addition of transition metals, with Pt and Pd being the most efficient metals.[29] For example, surface hydrogen formed on Pt, Pd, Cu, and Ni can increase the rate of reduction of CuO, NiO, and Co_3O_4.[86] Similarly, reduction of metal oxides by hydrocarbons when transition metals are present occurs by spillover.[87] In many cases, reduction by

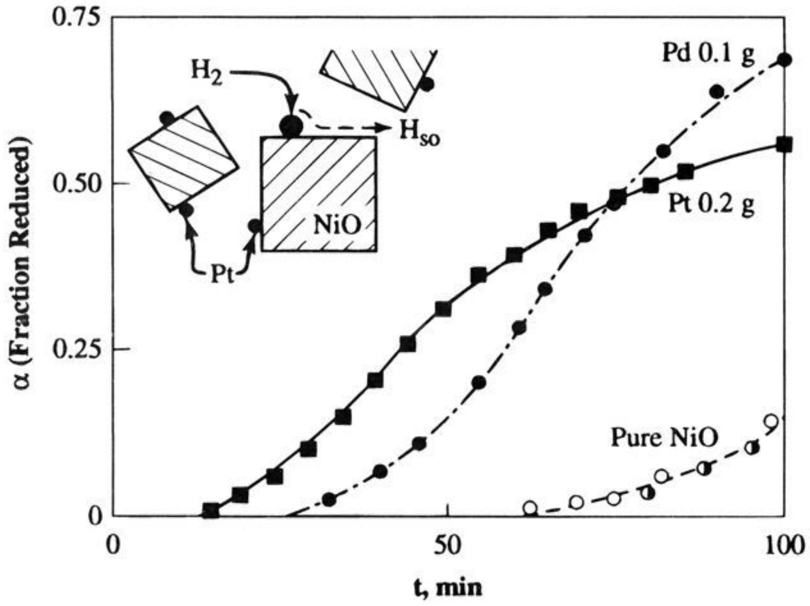

Figure 13. Influence of Pt and Pd added to NiO (1 g) on reduction by H_2 at 484 K. The fraction reduced is plotted on the *y* axis.[86]

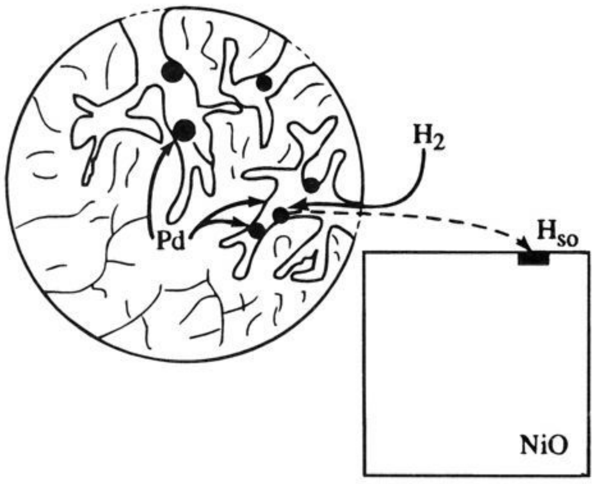

Figure 14. Schematic that shows how supported Pd catalyst increases the rate of reduction of NiO to Ni nuclei by spiltover hydrogen.[20]

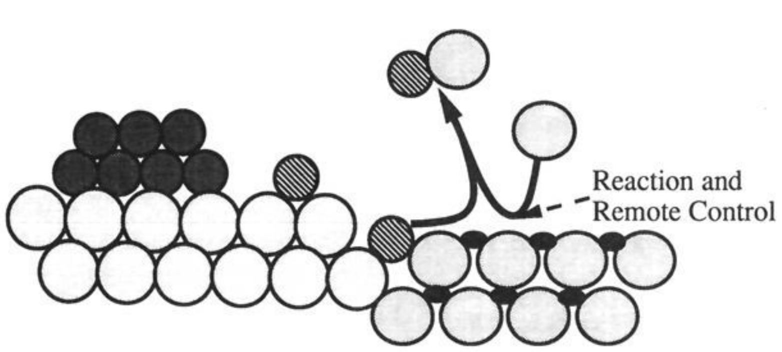

Figure 15. Schematic to illustrate remote control of the activity of a reducible oxide by spillover. In this representation hydrogen (lined circles) spills over from a metal (darkest circles) onto its support and then spills over onto a metal oxide. The spiltover hydrogen then reacts with the metal oxide to maintain it in an active state.

spillover may lead to reduced compounds that are not obtainable otherwise. The reduction of metal oxides by spiltover H is a catalytic process, but reduction of catalyst supports by H spillover can also create catalysts with unique properties. The phenomena of strong metal-supported interactions (SMSI) have been attributed to the reduction of support surfaces, e.g. reduction of TiO_2 to TiO_x. The resulting supported metal catalysts have different activities and selectivities than the same metals on nonreducible supports.[88]

Metal oxides are reduced more rapidly in the presence of transition metals because the oxides themselves are not capable of dissociating H_2 at a significant rate at the same temperatures where transition metals readily dissociate H_2. For example, TiO_2 alone is not reduced at 773 K in H_2, but TiO_2 in Rh/TiO_2 is reduced at 710−790 K.[89] The limiting step in this process was concluded to be spillover from Rh to TiO_2.

An example of the differences in reduction rates upon addition of Pt and Pd to pure NiO is shown in Figure 13. Note that at a time when $^1/_4$ to $^1/_3$ of NiO is reduced in the presence of Pt or Pd, the amount of NiO reduced in the absence of a transition metal is below the detection limit. Figure 14 presents a schematic that shows how a small amount of metal increases the rate that the NiO is reduced. The rate of NiO reduction increased even when the Pt or Pd was supported on Al_2O_3 or SiO_2 so that spiltover H must transport across the oxide support to reach the NiO.[20] Metals increase the H concentration on the oxide but usually do not lower the activation energy of reduction below that of the uncatalyzed reduction.

The starting reduction temperature for V_2O_5 by CH_4 was decreased from 773 to 453 K by the addition of 0.15 wt % Pt.[87] The CH_4 was concluded to adsorb and dissociate on Pt and fragments then spilled over onto the V_2O_5. Reduction to form tungsten and molybdenum bronzes (H_xWO_3, H_xMoO_3) from WO_3 and MoO_3 takes place when transition metals are added to the oxides, and numerous studies have observed formation of these bronzes as direct proof of spiltover H.[2,29,90]

C. Remote Control of Catalytic Sites

Delmon and co-workers have postulated a process in which spiltover species create or regenerate selective sites on a catalyst and named this remote control.[20,86] For example, a donor phase emits spiltover species that react with an acceptor phase to create active and selective sites on that phase. Thus, the donor phase, which is distinct from the catalytically active site (acceptor phase), controls the number or nature of catalytic sites. This spillover process has been used to explain the numerous examples of strong cooperation that exist between two phases even though no mutual contamination exists. As an example, the presence of a labile form of oxygen atoms can help to manipulate the metal−oxygen stoichiometry in the transition metal oxide. This is represented in Figure 15. Delmon and Matralis[86] pointed out that an important aspect of remote control is that a small number of spiltover species can produce an active site which transforms thousands of molecules. This concept of remote control does not appear to be universally accepted and remote control differs from activation of oxides by spiltover hydrogen or oxygen (section V). The concept of remote control implies that if the spillover of the species that provides the control ceases the catalytic activity will change and possibly disappear. Other explanations for enhanced catalytic activity for catalysts which contain several components are either bifunctional catalysis or the formation of new phases. In bifunctional catalysts, intermediate species are assumed to form on one phase, desorb, and then readsorb on the second phase where it reacts.[20]

Weng et al.[82] indicated that spiltover oxygen can improve activity, improve selectivity, or slow the rate

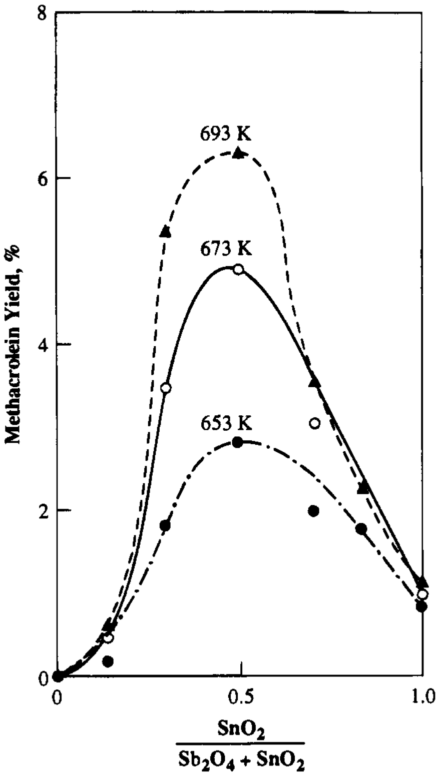

Figure 16. Yield of methacrolein dependence on the fraction of SnO_2 in the catalyst. This shows cooperation between SnO_2 and Sb_2O_4 in the oxidation of isobutene to methacrolein. The oxides, prepared separately, were suspended in *n*-pentane, mixed, and dried. All experiments were made with 0.75 g of the Sb_2O_4.[86]

of deactivation by remote control. The spiltover oxygen can do one or more of the following: prevent reduction of the surface of the active phase, inhibit coke formation, stabilize against segregation, promote solid-state reactions.

Note that inhibition of coke formation corresponds to the examples previously discussed in which coke from organic reactants is removed by spiltover hydrogen or oxygen.

Mechanical mixtures were used to demonstrate clearly that spillover takes place in remote control catalysts. The two solid components were added to pentane, which was then evaporated to yield a mixture with minimal mechanical damage.[82] Characterization techniques were not able to detect changes in the composition or texture of the two oxide phases as a result of mixing. A donor phase such as Sb_2O_4, $BiPO_4$, or Bi_2O_3 can protect phases that are active in selective oxidation from deactivation because O_2 dissociates on these donor phases to create spiltover oxygen.[86] Weng et al.[82] presented examples using mechanical mixtures for oxidation of isobutene to methacrolein and oxidative dehydrogenation of *n*-butene to butadiene. Oxygen migrates from Sb_2O_4 to the active phase, MoO_3, as shown by ^{18}O labeling. Spiltover oxygen reoxidizes the reduced MoO_3 faster than O_2 can directly.

A dramatic example of the remote control process is shown in Figure 16.[86] A mechanical mixture of Sb_2O_4 and SnO_2 was up to 11 times more active than the same weight of pure SnO_2 for oxidation of isobutene to methacrolein. The SnO_2 phase was the catalytically active phase and Sb_2O_4 was completely inactive by itself. Another example is isobutane oxidation to methacrolein; Sb_2O_4 caused higher yields and selectivities and less deactivation when added to a $Fe_2(MoO_4)_3$ catalyst.[82] The spiltover O prevented nucleation of reduced phases, which are nonselective. For $Fe_2(MoO_4)_3$ alone, MoO_2 and $FeMoO_4$ phases were detected, whereas for the mixture only $Fe_2(MoO_4)_3$ was observed. For oxidative dehydrogenation of *n*-butene, $ZnFe_2O_4$ is easily deactivated by reduction and both ZnO and a spinel phase were detected by XRD. For mechanical mixtures with Sb_2O_4, however, no segregation was detected by XRD and no deactivation was seen.[82]

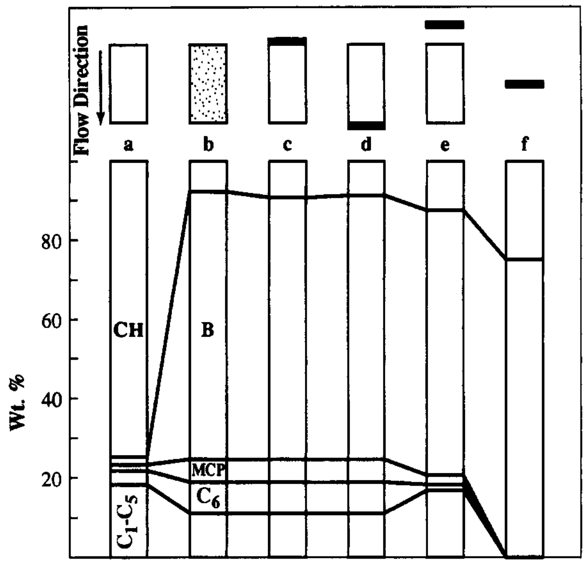

Figure 17. Bottom part of figure: Product distribution on various physical arrangements of H-ZSM-5 and Pt/Al_2O_3 after 5 h on stream in a recirculation reactor. CH = cyclohexane, MCP = methylcyclopentane, C6 = isomers from ring opening of cyclohexane, C1–C5 = hydrocarbon fragments. Top part of figure: The physical location in the reactor of the Pt/Al_2O_3 (dark region) and H-ZSM-5 (light region).[91]

Cyclohexane conversion on Pt/H-ZSM-5 has also been concluded to be governed by remote control.[91] In the presence of H_2, cyclohexane forms benzene, methylcyclohexane, and C_6 isomers. Much less reaction occurs in N_2. Methylcyclohexane is not formed to a large extent on either H-ZSM-5 or Pt/Al_2O_3 alone, but it is formed on mechanical mixtures of these catalysts. Since H_2 is not a stoichiometric reactant, its effect was explained in terms of hydrogen spillover. Hydrogen generated on Pt spills over to acidic sites and influences reaction (remote control) by controlling the concentration of intermediate carbenium ions. Experiments with various arrangements of catalyst beds (Figure 17) showed that spillover took place over significant distances. Similar product distributions were obtained whether a Pt/Al_2O_3 bed was placed on top or underneath a bed of H-ZSM-5. If the two catalysts were separated by gas phase (Figure 17e), the catalytic activity corresponds to that of both individual catalysts.

Other catalysts also exhibit improvements in rate, selectivity, or lifetime due to the presence of a second phase. For cyclohexane dehydrogenation and hydrogenolysis of the S–C bond of thiophene, a mixture of

$MoS_2 + Co_9S_8$ had a much higher activity than MoS_2 alone.[86] Similar synergistic effects were seen for the oxygen-aided dehydration of formamides to nitriles because degradation reactions were suppressed and the number of Brønsted sites on MoO_3 was increased.

D. Spillover of Molecular Species

Although most studies of spillover have focused on H and O species, multiatom species have also been detected on supports as a result of spillover from a metal catalyst, and species that adsorb directly on a support can react with H or O that adsorb on the metal. Examples will be presented of each of these types of spillover. The case where molecular species adsorb directly on the support but decomposes on the metal is presented in section III.D on reverse spillover.

The reaction of NO and CO on metal catalysts forms isocyanate (NCO), which can migrate from metal to support.[92] Infrared spectroscopy was able to distinguish between Pt−NCO (2180 cm^{-1}) and Si−NCO (2310 cm^{-1}) on Pt/SiO_2 catalysts. Isocyanic acid adsorption was used to help observe the decrease in the NCO on Pt and the formation of the NCO band on SiO_2. Isocyanate spills over onto SiO_2 at 373 to 425 K, while some of it also decomposes to form CO on the metal. On Rh/SiO_2, the Si−NCO species were studied in a wide variety of gases at 603 K. Spillover of NCO was concluded to occur by reaction of N atoms on Rh with CO, and the formation of NCO on Rh at 483−515 K occurred much more rapidly than the formation of NCO on SiO_2. Moreover, when gas phase NO and CO were no longer present, the Rh−NCO species disappeared but the Si−NCO species remained.

E. Spillover in Syngas Reactions

Because of the interest in methanation and Fischer−Tropsch synthesis, reactions of CO and H_2 to form adsorbed species have been extensively studied on supported metal catalysts. Infrared spectroscopy has been used to detect species, such as formate (CHOO)[93] and methoxy (CH_3O)[94] that end up on the support as the result of a spillover process when CO and H_2 are present. Temperature-programmed desorption (TPD) and reaction (TPR) have been particularly effective at demonstrating directly the location and stoichiometry of these spiltover species, and thus the formation and reactivity of CH_3O will be discussed in some detail to demonstrate spillover of molecular species.

The presence of CH_3O spiltover species and verification of their location on the support have been directly demonstrated by TPR in H_2 flow. Carbon monoxide, which readily adsorbs on metal surfaces at room temperature, reacts to form CH_4 when the catalyst temperature is raised in H_2 flow. On Ni/SiO_2 catalysts, a single, distinct and relatively narrow CH_4 peak forms as CO is hydrogenated during TPR.[95−97] In contrast, on Ni/Al_2O_3 two distinct CH_4 peaks are observed for the same TPR experiment,[95,98,99] and extensive studies have shown that one of these peaks is the result of spillover that forms CH_3O on the Al_2O_3 support. Figure 18 shows the CH_4 signal obtained during TPR on a 5.1% Ni/Al_2O_3 catalyst. The narrow, low-temperature CH_4 peak is from hydrogenation of CO adsorbed on the Ni surface. The broader, higher temperature CH_4 peak forms as CH_3O is hydrogenated.[99,100]

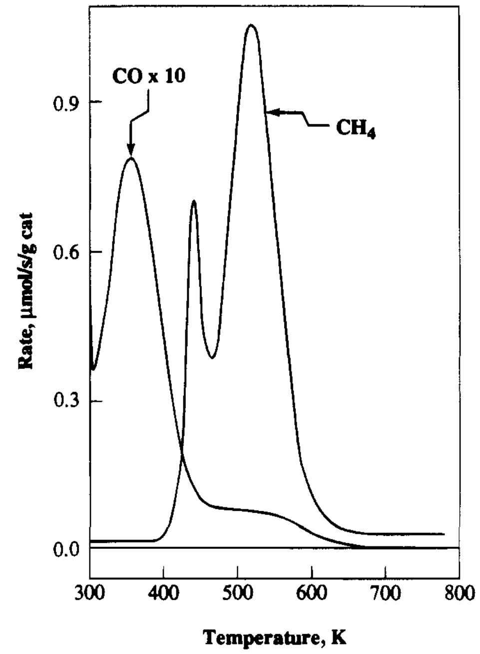

Figure 18. Methane and unreacted CO observed during temperature-programmed reaction (TPR) of CO adsorbed at 300 K on 5.1% Ni/Al_2O_3 catalyst after the catalyst was cooled from 775 K in H_2. The catalyst was heated in pure H_2 flow during TPR.[100]

The surface processes that take place during TPR were clearly elucidated by a number of variations on the TPR experiment. The steps that take place are as follows: (1) As the temperature increases during TPR, two competing processes take place on the Ni/Al_2O_3 surface, (a) CO reacts on the Ni surface to form CH_4 and (b) CO + H react to form CH_3O in an activated spillover process. (2) At an intermediate temperature, the Ni surface is depleted of CO and the Al_2O_3 surface is partially covered with CH_3O. (3) At higher temperatures, CH_3O is hydrogenated to CH_4. This hydrogenation may take place with spiltover hydrogen on the Al_2O_3 or at the Ni−Al_2O_3 interface.

Isotope labeling was used to verify these processes.[99] Interrupted TPR was carried out to a temperature where most of the CO was removed from the Ni surface. Isotopically labeled ^{13}CO was then adsorbed on the Ni surface. Any ^{12}CO remaining on the Ni was rapidly removed by isotope exchange at room temperature.[101] A subsequent TPR (Figure 19) showed the same $^{12}CH_4$ peak due to $^{12}CH_3O$ hydrogenation as would have been obtained if ^{13}CO had not been adsorbed. The $^{13}CH_4$ formed in two peaks because the Al_2O_3 surface was not saturated and $^{13}CH_3O$ formed from ^{13}CO and H_2 during TPR.

At 385 K, spillover was much faster than methanation so that the Al_2O_3 surface could be saturated with CH_3O at this temperature. During a subsequent TPD of these saturated surfaces, CO and H_2 formed simultaneously as CH_3O decomposed.[100,102] Several experiments indicated that CO and H_2 for-

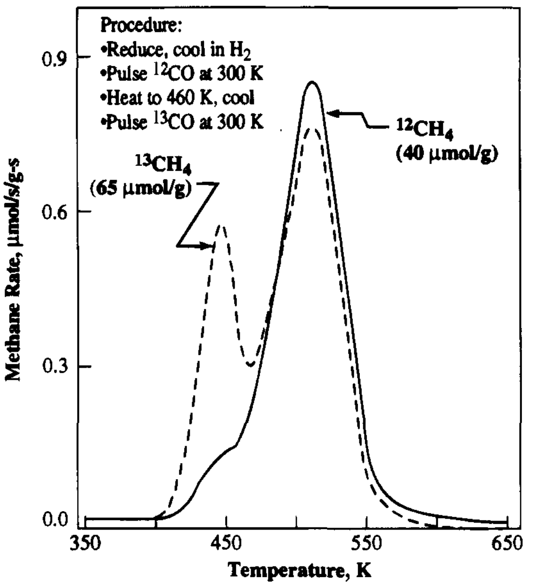

Figure 19. Methane ($^{12}CH_4$ and $^{13}CH_4$) TPR spectra for interrupted TPR on 5.1% Ni/Al_2O_3 catalyst. The surface was saturated with ^{12}CO at 300 K, and the low-temperature peak was reacted away by heating the catalyst to 460 K in H_2 before ^{13}CO absorption at 300 K. The catalyst was then heated in H_2 to obtain the resulting TPR spectra.[99]

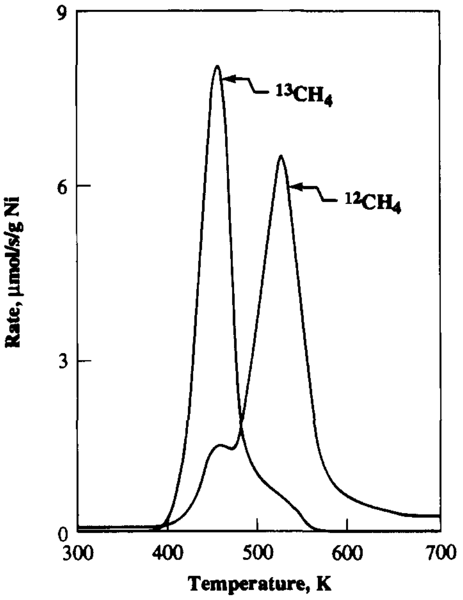

Figure 20. Methane ($^{12}CH_4$ and $^{13}CH_4$) spectra for interrupted TPR on a 5% Ni/TiO_2 catalyst. The ^{12}CO was adsorbed at 385 K in H_2, the catalyst was heated to 490 K to remove some ^{12}CO (as $^{12}CH_4$), and ^{13}CO was adsorbed at 300 K in H_2. The catalyst was then heated in H_2 to obtain the resulting TPR spectra.[106]

mation were due to CH_3O decomposition. Methanol TPD had the same peaks at the same location. Moreover, adsorbed CH_3OH hydrogenated to CH_4 during TPR at the same temperature as CH_3O did. Trapping experiments after adsorption of $^{13}CO + H_2$ on Ni/Al_2O_3 at 385 K were also used to verify $^{13}CH_3O$ formation on the support.[103] After ^{13}CO and H_2 formed $^{13}CH_3O$, C_2H_5OH was adsorbed on the support. A subsequent TPR detected significant amounts of $^{13}CH_3OH$, whereas none was detected for a normal TPR. An additional confirmation that CH_3O was adsorbed on the Al_2O_3 support was obtained by TPR on mechanical mixtures of $Ni/Al_2O_3 + Al_2O_3$ and $Ni/SiO_2 + Al_2O_3$.[104] The additional adsorption on the mixtures showed that the spiltover species could travel onto the Al_2O_3 surface across the SiO_2 or Al_2O_3 surface of the catalyst. This transport took place across the SiO_2 surface even though spillover did not form measurable coverages of CH_3O on the SiO_2 support of Ni/SiO_2.

Coadsorption of CO and H_2 also formed CH_3O on Ni/TiO_2, but the rate of spillover was much slower than on Ni/Al_2O_3.[105,106] As a result not much spillover took place during TPR, but as shown in Figure 20, CH_3O could be readily formed by CO and H_2 coadsorption at 385 K. This figure shows clearly that ^{13}CO on Ni and $^{12}CH_3O$ on TiO_2 existed simultaneously, and these adsorbed species could be labeled with different isotopes in order to study the rate of hydrogenation of each.

Spillover to form CH_3O has been observed for Ni/Al_2O_3 catalysts over a range of weight loadings and for various Al_2O_3 supports.[97,98,101,107-113] The formation of CH_3O by spillover is a general phenomenon that has also been observed for Ru,[114] Pt,[115-117] Pd,[118-120] and Co[121] metals, and for La_2O_3[115,119] and CeO_2[73] supports in addition to Al_2O_3 and TiO_2.

On Pt and Pd, the rate of spillover is fast relative to the rate of CO hydrogenation on the metals.[61,116,118-120,122] Robbins and Marucchi-Soos[116] clearly elucidated the spillover and hydrogenation steps on Pt/Al_2O_3 by combining TPR and IR spectroscopy. They observed the conversion of Pt−CO to Al−OCH_3 with FTIR as their Pt/Al_2O_3 was heated in H_2 flow. Two distinct CH_4 peaks were seen during TPR, and they showed with IR that in contrast to Ni/Al_2O_3 and Ni/TiO_2, the spiltover CH_3O species were more reactive in H_2 than most of the CO on Pt. A formate band was also observed, but it was the less-reactive surface species. The faster rate of CH_3O hydrogenation during these transient experiments indicates that for Pt catalysts the spiltover species may be important in steady-state reaction.

Flesner and Falconer[61] also observed for TPR of Pt/Al_2O_3 that CH_3O on the Al_2O_3 was more reactive than CO on the Pt. The same type spillover process was observed as on Ni catalysts, and mechanical mixtures of Al_2O_3 and Pt/Al_2O_3 showed that CH_3O was adsorbed on Al_2O_3. By varying the heating rate during TPR, the activation energy for spillover was shown to be lower than that for CO hydrogenation on Pt. Similar observations about activation energies were made on Ni/Al_2O_3.

Similarly, on Pt/TiO_2, Pd/Al_2O_3, and Pd/La_2O_3, the rate of CH_3O hydrogenation is faster than the rate of CO hydrogenation on the metal during transient experiments.[117-119,122] As a result, two distinct CH_4 peaks could not be distinguished during TPR. Dramatic differences were observed, however, between Pd/SiO_2 and Pd/La_2O_3 catalysts. Because CH_3O does not form at a significant rate on SiO_2, the methanation rate on Pd/SiO_2 is low during TPR and most CO desorbs unreacted.[119] In contrast, Pd/La_2O_3 and Pd/Al_2O_3 show high methanation activity during TPR. Palazov et al.[94] observed with IR the rapid spillover to form CH_3O on Pd/Al_2O_3 but not Pd/SiO_2. The same trend was seen during steady-state reaction: Pd catalysts that form CH_3O by spillover are more

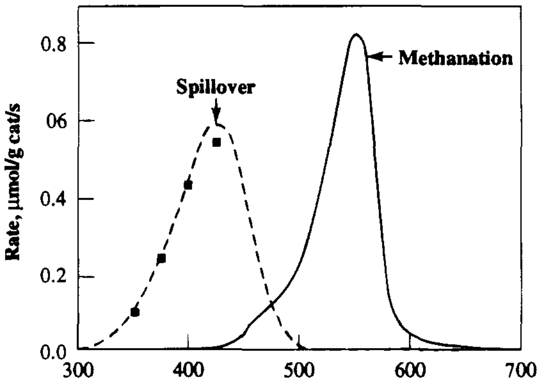

Figure 21. The spillover rate during TPR (dashed line) is compared to the methanation rate during TPR (solid line). The solid points correspond to the rates of spillover as measured from experiments using isotope exchange of CO to determine the amount of spillover after TPR in H_2 interrupted at various temperatures.[122]

reactive during steady-state reaction. Thus, spillover may be a factor in the strong dependence of methanation on the supports for Pd catalysts.[118]

The rapid rate of spillover, relative to CO hydrogenation on Pd and Pt catalysts, makes study of these processes more difficult, but isotope labeling combined with TPR was used to measure an activation energy of 43 kJ/mol for the spillover process.[122] Interrupted reaction of ^{12}CO followed by ^{13}CO exchange of any ^{12}CO remaining on the Pd was used to determine the amount of spiltover $^{12}CH_3O$ formed at a given temperature. These measurements were used to calculate the spillover rate, which is compared to the rate of methane formation in Figure 21. Note that spillover starts just above room temperature as CO and H_2 react to form CH_3O.

These studies show that molecular species can readily be formed by surface reaction of spiltover species. Exactly where CH_3O forms and what species move from metal to support have not been determined, however. Robbins and Marucchi-Soos[116] could not distinguish between CH_3O generation on Pt (and the Al_2O_3 support then acting as a reservoir for CH_3O) and CH_3O formation on the Al cation sites on Al_2O_3. Anderson and Jen,[123] using atom superposition and electron delocalization molecular orbital theory, concluded that CH_3O^- moves as an ion from one Al^{3+} site to another in conjunction with a proton that moves from one O^{2-} site to another.

F. Hydrogenation by Spiltover Hydrogen

Molecules that adsorb directly on supports can also be hydrogenated by spiltover hydrogen. Examples will be presented where the spillover effect is most clear: where two reactants were initially adsorbed on different phases of the catalyst or where hybrid catalysts were used.

An excellent recent example is the study by Ioannides and Verykios[124] of hydrogenation of aromatics. By comparison of supported Rh catalysts and the individual supports (SiO_2, Al_2O_3, TiO_2), they showed that benzene and toluene adsorb on the supports in weakly held molecular forms. During TPD these aromatic hydrocarbons desorb from the Rh catalyst in the same manner as from the support alone. Peak temperatures are below 403 K. The benzene or toluene that adsorbed on the Rh surface was a fraction of the total amount adsorbed and these species were more strongly held on Rh so that they did not desorb molecularly. Temperature-programmed desorption was used to determine how much molecularly adsorbed aromatics remained on the supports after exposure to H_2 at 298, 338, and 388 K. For Al_2O_3, TiO_2, and SiO_2, all without Rh metal, no reaction took place upon H_2 exposure, and instead benzene and toluene desorbed unchanged from the supports during subsequent TPD.

On the supported Rh catalysts, however, the results were quite different.[124] For all Rh catalysts, exposure to H_2, even at 298 K, resulted in hydrogenation of the weakly adsorbed benzene to form cyclohexane. That is, H_2 dissociated on the Rh, spilled over onto the support, and hydrogenated the benzene on the support. Cyclohexane readily desorbed from the support and appeared in the gas phase immediately upon introduction of H_2 to the catalyst. Benzene hydrogenation was sufficiently fast at 298 K, that on Rh/Al_2O_3 and Rh/TiO_2 all the benzene on the support was hydrogenated at 298 K. This experiment is a clear demonstration of spillover because no hydrogenation took place in the absence of Rh metal. Since the adsorption sites of the benzene (on the support) and hydrogen (on the metal) were known at the start of the reaction, reaction of these two species must involve spillover.

Similarly, toluene, which weakly adsorbs on the supports of Rh/Al_2O_3, Rh/SiO_2, and Rh/TiO_2 , was hydrogenated to methylcyclohexane at 298 K, but the hydrogenation rate was lower than that of benzene. The toluene that was strongly adsorbed on the Rh did not hydrogenate, even at 388 K. Ioannides and Verykios[124] carried out temperature-programmed reaction and observed toluene and methylcyclohexane as spiltover H hydrogenated toluene that was adsorbed on the support. Similar results have been obtained for a Pd/Al_2O_3 catalyst.[125] The weakly adsorbed benzene and toluene readily react to form cyclohexane and methycyclohexane, respectively, during temperature-programmed hydrogenation, with reaction starting below room temperature. When CO was adsorbed on the Pd, not much hydrogenation took place, showing that H spillover was inhibited because most of the H_2 adsorption sites were blocked by the strongly adsorbed CO. The weakly adsorbed benzene and toluene desorbed prior to their hydrogenation and prior to CO desorption or hydrogenation. This experiment also shows that hydrogenation was not due to the creation of active sites on the Al_2O_3 during the high temperature catalyst pretreatment.

Ioannides and Verykios[124] concluded that the rate of benzene hydrogenation at steady-state conditions and 303 K must be significantly influenced or even controlled by reaction on the support. Others have also made similar conclusions from steady-state measurements. Lin and Vannice[126] observed turnover frequencies for toluene hydrogenation that were 4 times higher with the most acidic support compared to the least acidic support they studied, and the difference was attributed to hydrogen spillover. Simi-

Table 3. Benzene Hydrogenation to Cyclohexane at 373 K on Mechanical Mixtures of Carbon and Pt/C Catalysts[38]

carbon to Pt/C ratio	percent conversion/ mg of Pt	turnover frequency (mol h^{-1}/g of Pt^{-1})
0 (Pt/C only)	8.6	0.55
3	16.8	1.08
9	26.1	1.68
20	37.9	2.45
50	56.4	3.64
99	59.4	3.64

Table 4. Isobutane Yield during Isobutylene Hydrogenation on Catalysts and Catalyst Mixtures[131]

catalyst	yield of isobutane (%)
Pt/KA	3
NaY	2
Pt/KA + NaY (physical mixture)	93
Pt/KA + H-ZSM-5 (physical mixture)	91

larly for benzene hydrogenation,[127] they concluded that benzene adsorbs on acid sites on the support and reacts with spiltover hydrogen. Reaction was thus due to the sum of the rate on the metal surface plus that on the support.[127] In particular, the interfacial region surrounding each metal particle was assumed to be where the spiltover hydrogen reacted. When the support plays such an important role in the reaction, a turnover frequency based on the metal dispersion is meaningless.[124]

Studies of benzene hydrogenation on mechanical mixtures of catalyst and support have further demonstrated directly that hydrogen spillover can hydrogenate benzene adsorbed on the support. For example, the catalytic activity, per milligram of Pd, increased when Pd/Al_2O_3 was diluted with Al_2O_3.[128] Similarly, the activity increased, per milligram of Pt, when Pt/Al_2O_3 was diluted with Al_2O_3.[129,130] Ceckiewicz and Delmon observed a 4-fold increase in the specific activity for benzene hydrogenation when Pt/Al_2O_3 was diluted with 20 times as much Al_2O_3.[129] Srinivas and Rao[38] observed that the total conversion for benzene hydrogenation decreased as a Pt/C catalyst was diluted with carbon, but the conversion per milligram of Pt, increased. The carbon alone was not active for hydrogenation. As shown in Table 3, conversion per milligram of Pt continuously increased with dilution and at a dilution ratio of 99, the turnover frequency was 6.6 times that of the Pt/C catalyst. Thus, for steady-state reaction, they concluded that part of the reaction occurs for benzene and H adsorbed on Pt and the rest occurs on carbon as H spills over from Pt and reacts with benzene adsorbed on the carbon.

A dramatic example of the effect of spillover in hybrid catalysts was obtained for isobutylene hydrogenation.[131] Table 4 shows the yield of isobutane for the individual catalysts and for the physical mixtures (hybrid catalysts). What makes these results particularly interesting is that isobutylene is too big to fit into the pores of the Pt/KA catalyst, and H_2 cannot be activated on NaY zeolite. Thus, in order for the hybrid catalysts to improve the yield so dramatically (from 2 or 3% for the individual catalysts to 93% for a physical mixture), H_2 is activated on Pt/KA, the resulting H atoms spill over onto the NaY zeolite, and isobutylene is hydrogenated on the NaY zeolite. The Pt was shown to be in the pores of KA zeolite because CO did not adsorb on the Pt but H_2 did. Thus, the hydrogenation reaction did not take place on the Pt surface. The procedure envisioned by Ohgoshi et al.[131] for this process is shown in Figure 22. As shown in Table 4, the same high conversion was obtained when H-ZSM-5 zeolite was used in the physical mixture instead of NaY zeolite. When a H-ZSM-5 zeolite that contained almost no SiOH groups was mixed with Pt/KA instead, the yield of isobutane was zero. Thus, the OH groups were concluded to be important for migration.

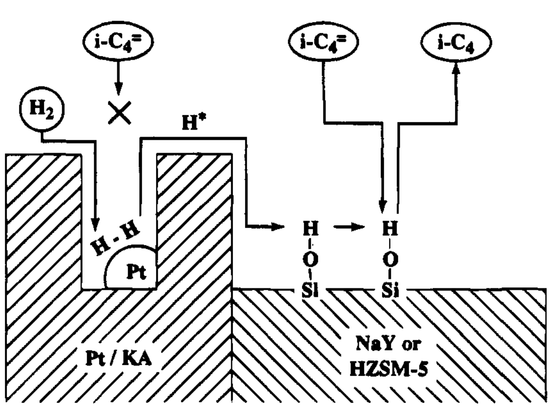

Figure 22. Model for isobutene hydrogenation on hybrid catalysts.[131]

Another example where transient measurements were used to show directly that spiltover species are involved in catalytic reaction is temperature-programmed reaction (TPR) studies of adsorbed oxygenates on Ni/Al_2O_3. Chen and Falconer[78,132] adsorbed methanol, ethanol, 1-propanol, dimethyl ether, formic acid, acetaldehyde, and acetone on the Al_2O_3 support of Ni/Al_2O_3 and then ramped the temperature in H_2 flow during TPR. The main hydrogenation product was CH_4. With the exception of formic acid, the organic molecules were only adsorbed on the Al_2O_3. H_2 only dissociates on the Ni surface and not on the Al_2O_3. These facts suggest that H spills over from the Ni to the support to form methane by reaction with the organics on the support. As shown in Figure 23, the alcohols all reacted at essentially the same rate to make methane and only small amounts of other products form. Since hydrogen can spillover onto Al_2O_3 to exchange with the hydroxyl groups of the alcohols[73,79] at lower temperatures then CH_4 formed, it was concluded that the limiting step was not H spillover. Instead, because the hydrogenation rates were similar to the decomposition rates during TPD, reverse spillover of the alcohol was concluded to be rate determining. Reaction could take place at the Ni$-Al_2O_3$ interface. The important aspect of these studies is that the two reactants (hydrogen and organic) were initially on different phases of the catalyst so spillover was necessary for reaction to occur.

When O_2 flow was used instead of H_2 flow for temperature-programmed oxidation,[133] the organics adsorbed on the Al_2O_3 support of Pd/Al_2O_3 catalyst were oxidized to CO, CO_2, and H_2O. When only the Al_2O_3 support was used, the oxidation was much

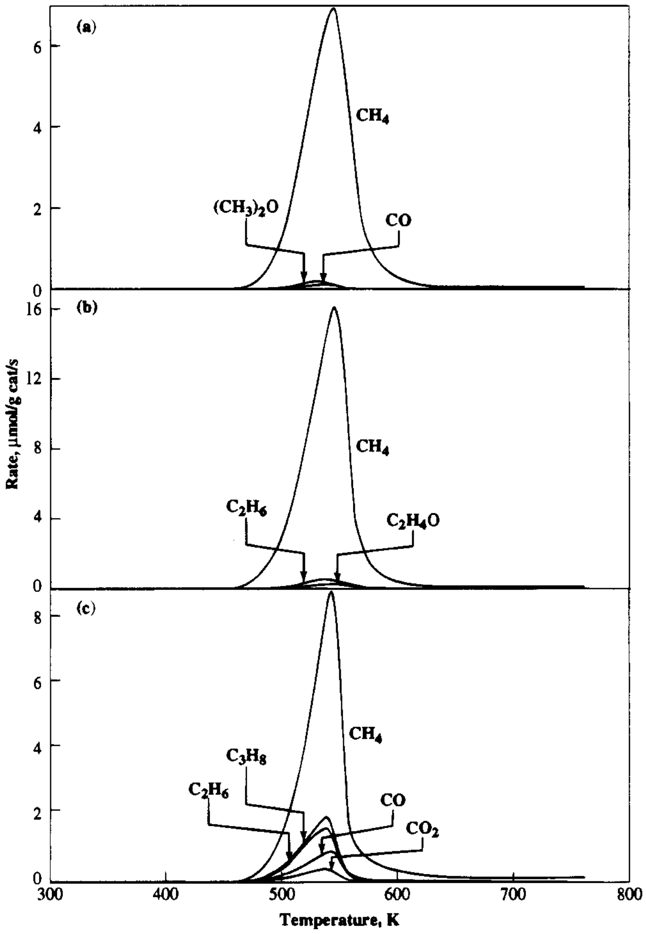

Figure 23. Temperature-programmed reaction spectra on 5.7% Ni/Al_2O_3 following adsorption at 300 K of 2 μL of (a) CH_3OH (b) C_2H_5OH, and (c) 1-C_3H_7OH.[133]

slower. That is, oxygen spilled over to oxidize the organics or the organics diffused back to the interface to be oxidized.

Similar hydrogenation processes take place for CH_3O, formed by CO and H_2 coadsorption as discussed earlier, or when CH_3O was put on SiO_2. Bianchi et al.[134] used 500 mg of a hydrophobic SiO_2 (i.e., with methoxy groups substituted for hydroxyls) mixed with 20 mg of Pt/Al_2O_3. The methoxy groups were present because the samples were aerogels created from tetramethyl orthosilicate hydrolysis in methanol followed by hypercritical removal of the methanol. In the absence of the Pt/Al_2O_3 catalyst, no reaction was observed in H_2 at 703 K, but when the Pt/Al_2O_3 was mixed in, CH_4 formed as spiltover hydrogen reacted with CH_3O on SiO_2. A layer of catalyst on top of SiO_2 gave the same rate as the mixture of catalyst and SiO_2 so it was concluded that diffusion across SiO_2 is fast and the difficult step is the transfer of H from catalyst to SiO_2. Diffusion across SiO_2 was also shown to be fast by using a SiO_2 pellet onto which a small spot of Pt/Al_2O_3 was placed. IR spectroscopy was used to shown that the CH_3O^- had decreased at the same rate near the catalyst as far away, implying migration over SiO_2 at 703 K is fast relative to the hydrogenation step.[132]

Baumgarten and Dedek[135] observed that benzoic acid adsorbed on Al_2O_3 had an increased rate of oxidation when Pt/Al_2O_3 was added. The benzoic acid was adsorbed on the Al_2O_3 before mixing it with Pt/Al_2O_3 so that its initial location was known. Since the O_2 adsorbed on Pt, the two reactants started in separate phases and O spillover was required for oxidation. This system was a model of coke oxidation.

V. The Creation of Catalytic Activity Due to Spillover

Most catalytic systems are composites of several surfaces. Examples include metals (singly or as a combination of metals) on supports metal oxides, sulfides, and/or halides dispersed on supports, and mixtures of catalytic components formed into pellets or extrudates with binders. The surface of each component in the catalyst adsorbs the reactants and products with different bond strengths and at different rates when the component surfaces are studied separately. Thus, for example, any support that does not chemically adsorb a reactant in the absence of a metal is often assumed not to adsorb that reactant when a metal is present. This may not be a valid assumption as the surfaces may behave differently when part of the final composite catalyst.

Spillover of one species can induce adsorption and/or catalysis of species on surfaces that would not adsorb the species without the process of spillover. Thus, spillover of hydrogen from a metal under certain conditions can make silica or alumina active for olefin hydrogenation. Without activation by hydrogen spillover, neither silica nor alumina will adsorb hydrogen or ethylene and both are inert as hydrogenation catalysts.

At this time, only the spillover of hydrogen and oxygen have been shown to have these effects on oxide (support) surfaces. There is no reason that spillover of other species will not also react with the accepting surface and modify its sorption and/or catalytic activites. The surfaces that have been induced to possess unique sorption and catalysis include silica, alumina, other transition metal oxides, and zeolites. Thus, the combined system can exhibit sorption capabilities that are greater than the sum of those of the individual components. Furthermore, surfaces that are inactive as catalysts can become active after exposure to spiltover hydrogen or oxygen.

A. Hydrogenation Activity Created by Spiltover Hydrogen

Teichner developed a technique to study the activity of the support, after exposure to spillover by isolating the support from the source of spillover. In his extensive series of experiments, the source of spillover (typically supported Pt or Ni) was placed in a porous silica thimble supported by a string. This thimble was lowered to sit on the top of an inert oxide (e.g., SiO_2 or Al_2O_3) and was exposed to gaseous H_2 (or O_2) at elevated temperatures (typically >673 K) overnight. The string was then used to remove the thimble (and all the metal) through a vacuum stopcock, which was then closed to isolate the source of spillover from the treated oxide. In this manner SiO_2 and Al_2O_3 were found to become active catalysts for the hydrogenation of ethylene and acetylene and the

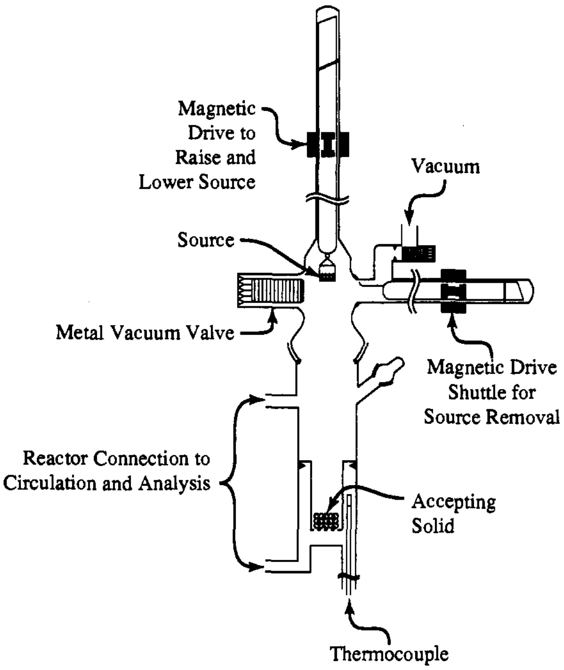

Figure 24. Schematic of the greaseless apparatus developed by Teichner et al. to study the effects of spillover onto a sample after isolation of the metallic source of spiltover species. The source is raised with a magnetically coupled lift and then transferred to a side chamber by a magnetically coupled shuttle where it is isolated by a metalllic vacuum valve.[42]

hydrogenolysis or cracking of benzene and cyclohexadienes. A schematic of this system is shown in Figure 24.

These results were disputed considerably when they were first disclosed. Many critics suspected that the Pt had migrated onto the oxide or that metallic impurities in the initial oxide were giving rise to the apparent activity. Teichner was able to show that impurities were well below the parts per million level and could not be responsible for the catalysis. Other investigators duplicated and built on these results.

The genesis of the active sites on silica was studied in the same manner by Lenz[136] and Lenz et al.[137-139] They found that the number of active sites increased with exposure to hydrogen spillover at 700 K up to a period of 12–14 h. The optimum activity was found for activation around 725 K and fell rapidly for activation above 750 K. The catalytic activity was found to be proportional to the amount of water produced during the exposure to spiltover hydrogen up to 725 K. If the silica was first degassed at successively higher temperatures prior to exposure to spiltover hydrogen, the eventual activity remained constant until the sample was degassed near or above 750 K, where the eventual activity decreased rapidly. Silica samples pretreated above 800 K were essentially inactive.

Since the activity was proportional to the water produced for pretreatment up to 680 K, dehydroxylation of the surface to create oxide defects would seem reasonable as a mechanism for the production of active sites (just as oxide defects are often perceived to give rise to active sites on many oxide catalysts). In this case, in contrast with many oxides, the active sites are created specifically from hydroxyls. Since the activity for samples pretreated above 750 K decreases, this suggests that certain hydroxyls are involved in the creation of active sites. A mechanism for this is shown in the first equation:

$$H_{sp} + -OH \rightarrow H_2O + -* \qquad \text{(denoting an active site)}$$

but

$$2Si-OH + \text{heat} \rightarrow H_2O + Si-O-Si \qquad \text{(not active)}$$

It is apparent that there is a difference between removal of hydroxyls by heating (presumably by condensation of hydroxyls, second equation above) and removal of hydroxyls by reaction with spiltover hydrogen. Further, it is apparent that the creation of catalytic activity is influenced by differences in the hydroxyls due to modifications at different temperatures. As silica is pretreated at successively higher temperatures (to $>$875 K), the surface area changes little; however, the surface chemistry is modified. Specifically, the density (initially $10^{13}-10^{14}/cm^2$) and nature of the surface hydroxyls change. Isolated hydroxyls and adsorbed water decrease progressively as the evacuation/pretreatment temperature is increased. The geminal and vicinal hydroxyls (associated hydroxyls) remain essentially constant up to near 770 K when they decrease dramatically until 875 K where only isolated hydroxyls remain on silica. Since silica samples pretreated at 875 K were then not able to be activated by spiltover hydrogen, Lenz et al.[136-139] concluded that the associated hydroxyls were the precursors of the active sites and that spiltover hydrogen reacted with the associated hydroxyls to create the sites active for hydrogenation and H_2-D_2 exchange on silica.

The number of active sites created can be estimated if we assume that one water molecule is produced during activation for each hydroxyl that reacts with spiltover hydrogen. The density of active sites created on silica is $\sim 2 \times 10^{12}/cm^2$ of silica surface. This corresponds to 0.1–1.0% of the total surface. The maximum turnover frequency for hydrogenation or H_2-D_2 exchange was 0.1/s. These trends in the turnover frequency with the temperature of silica activation (exposure to spiltover hydrogen) following evacuation at 703 K are shown in Figure 25.

The mechanism of hydrogenation of ethylene over silica activated by hydrogen spillover is similar to that found for other metal oxide catalysts and differs from hydrogenations on metals such as Pt or Ni.[136] Dideuterioethylene was the primary ($>$95%) product of the deuteration of ethylene on silica. The hydrogen isotopes apparently add molecularly to hydrogenate the adsorbed olefin and little isotopic exchange was found in the product.[136,137] The hydrogen isotopic exchange was inhibited by the presence of the olefin.

Silica and alumina are probably activated for olefin hydrogenation by similar mechanisms, i.e., active sites are created by the removal of hydroxyls (probably associated hydroxyls). Magnesia can also be activated by hydrogen spillover to hydrogenate ethylene. In this case, NH_3 poisons the reaction but O_2 does not.[2]

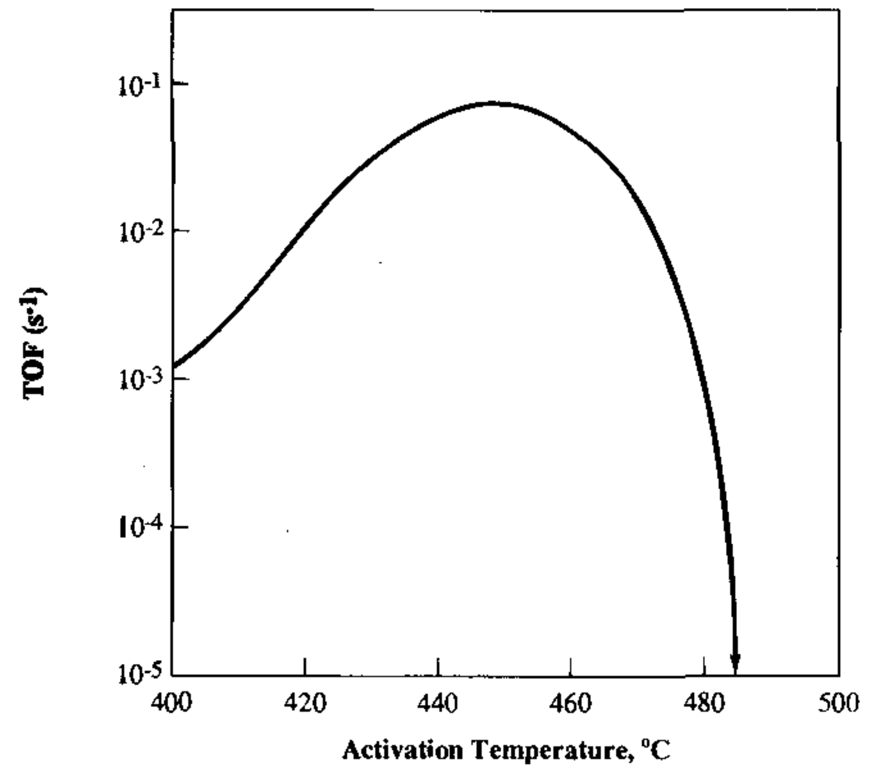

Figure 25. Ethylene hydrogenation activity of SiO_2 at 473 K following hydrogen spillover for 12 h from Pt/Al_2O_3 as a function of temperature at which the SiO_2 had been treated prior to spillover. The Pt/Al_2O_3 was removed after the pretreatment. Activity expressed as a turnover frequency calculated from the amount of water produced during the spillover at 703 K and assuming that one water is produced for each hydrogenation site[136]

The source of spiltover hydrogen giving rise to activation of these oxides can be a variety of supported metals (most notably Pt). However, the process is autocatalytic on alumina, which can form spiltover hydrogen, and thus, activated alumina can be a source of spillover.

B. Other Aspects of Catalysis Created by Hydrogen Spillover

Other catalytic reactions can be induced by spillover on different oxide surfaces. The activities for hydrocarbon cracking and isomerization differ substantially between oxides. Further, the ability to poison the reactions differs between oxides. It has also been found that not all forms of an oxide behave in the same manner due to activation by hydrogen spillover. Thus, δ-alumina, alumina aerogel, or α-alumina will exhibit different catalytic activities after exposure to spiltover hydrogen at high temperatures.

The section above primarily discussed catalytic activity induced onto an oxide due to exposure to spiltover hydrogen. The oxide is thus transformed to an active catalyst, and spiltover hydrogens are not necessarily present during the catalysis. Spiltover hydrogen has been shown to participate more directly in catalysis in four ways. Spiltover hydrogen can inhibit reaction, react with the surface, participate in the reaction as a reactant, or be part of catalytic sites created.

There is an induction period for the hydrogenation activity on silica or alumina activated by hydrogen spillover.[2] Only the hydrogenation of the first dose of ethylene exhibits an induction period. Subsequent doses show no induction period. If the hydrogen is evacuated prior to introduction of the ethylene, no induction period is found. Thus, the active sites created on silica or alumina can also adsorb spiltover hydrogen and this inhibits the initial adsorption of ethylene. However as this spiltover hydrogen adsorbed onto the active sites is removed in the production of ethane, ethylene can adsorb on the active sites and be hydrogenated.

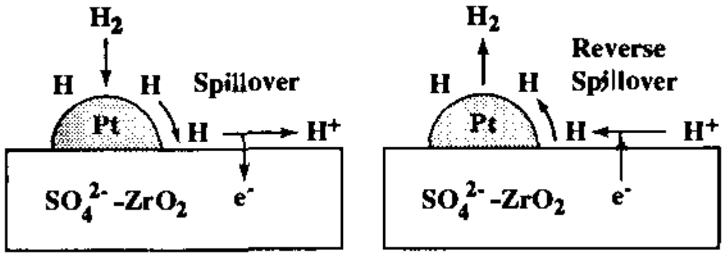

Figure 26. Schematic illustration for the formation and elimination of protonic sites for Pt supported on $SO_4^{2-}-ZrO_2$ due to H_2 adsorption on the Pt and spillover onto the support.[140]

Many other investigators have suggested that spiltover species can react with species adsorbed only on the accepting surface (as for an oxide support or for a metal that does not adsorb the spiltover species). This is the principal mechanism most often employed when spillover is invoked to explain the subsequent catalysis. The possibility that the adsorbing surface may have become catalytically active (without the need for the source of spillover still being present) has not always been considered.

Spiltover species also can become directly involved in the active sites. Many investigators have suggested that hydrogen spillover can give rise to protons, which can spill over to give rise to Brønsted acid sites on oxides. This creation of acidity has been proposed for oxide surfaces, including zeolites. Recall that the cracking activity of silica is induced by hydrogen spillover and it was proposed that this is due to Brønsted acidity since the sites were poisoned by NH_3. What is unclear is what becomes of the negatively charged species from the heterolytically activated hydrogen. The role and presence of H^- in the spillover-activated acid catalysis has not been discussed substantially. Hattori[140] suggests that H^+ is formed on the support with an electron being adsorbed into the bulk for $Pt/SO_4^{2-}-ZrO_2$. The proton can then recombine with the electron during the reverse spillover process as shown in Figure 26. Nakamura et al.[141] suggest that H^- is formed and can act as a reagent that eventually reacts with the positively charged hydrocarbon species to yield a hydrogenated product. The carbenium ion formed from the proton and hydrocarbon can undergo skeletal rearrangement and disproportionation. This is shown in Figure 27.

Figures 26 and 27 depict two mechanisms by which an acidic proton is created as a consequence of spillover. In the first case the proton is formed during spillover while an electron is adsorbed into the bulk, into ZrO_2 in Figure 26. In the second proposed mechanism, spiltover hydrogen is created as H^+ and H^- by a transition metal (Fe in this case with an apparent redox cycle). The spiltover proton then can participate as a Brønsted acid site on the zeolite or, in combination with the H^-, can lead to hydrogenation. It is apparent that the creation of

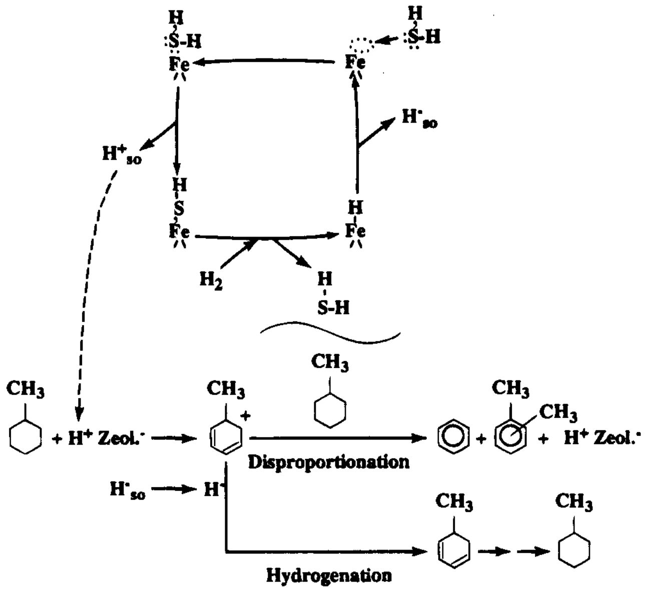

Figure 27. Schematic of the creation of spiltover protons on Fe via H_2S (above) and (below) the subsequent role of the proton on a zeolite to catalyze toluene disproportionation and hydrogenation.[141]

acidic sites to proton spillover is still speculative and requires further study.

Spillover does not create the same catalytic activity on all surfaces or even on all oxide surfaces.[2] The catalytic activities and selectivities differ as do the influence of potential poisons on the catalytic reactions that have been studied. Neither water, oxygen, nor NH_3 selectively poison hydrogenation activity over either SiO_2 or Al_2O_3.[142] However, silica also catalyzes the reaction of benzene to form acetylene and ethane (by sequential hydrogenation: acetylene → ethylene → ethane).[143,144] Spillover-activated alumina does not catalyze this reaction. Ammonia selectively poisons but oxygen only inhibits this hydrogenolysis of benzene over activated silica. These results suggest that at least two types of active sites are created on silica, e.g., those that hydrogenate and are insensitive to NH_3 and those that catalyze hydrogenolysis and are sensitive to NH_3. Silica is activated to create both type of sites, and alumina is activated to catalyze hydrogenation but not hydrogenolysis.

Alumina exposed to spiltover hydrogen exhibits catalytic activity not found for spillover-activated silica.[2] Alumina activated by hydrogen spillover was able to convert methylcyclopropane to *cis*-2-butene and 1-butene without the production of any *trans*-2-butene, the thermodynamically favored product. Further, the isomerization of *n*-heptane only occurs on activated alumina in the presence of both gas-phase hydrogen and spiltover hydrogen. The reaction is catalytic and forms heptene and heptadiene. On silica, the reactions of *n*-heptane produce considerable cracking to lower hydrocarbons at 543 K, but the reaction decreases in the presence of hydrogen gas. The reaction is limited as spiltover hydrogen is removed during the formation of smaller paraffins on silica. Further, the reaction on activated silica is selectively poisoned by O_2 and NH_3 but the reaction on alumina is not poisoned selectively.

C. The Creation of Catalytic Activity Due to Oxygen Spillover

Teichner et al. were the first to show that spiltover oxygen is able to activate oxides.[42,142] Oxygen spillover from Pt/Al_2O_3 activated alumina as a hydrogenation catalyst at lower temperatures than it can be activated in vacuum or in oxygen without the source of spillover. The rate of ethylene hydrogenation over δ-alumina at 453 K following activation by oxygen spillover is comparable to the rate at 673 K following activation without spillover at 773–1073 K in vacuum or in O_2. Oxygen spillover substantially enhances the ethylene hydrogenation activity. Several forms of alumina can be activated similarly, and the activity is not poisoned by NH_3. However, if the activated alumina is first exposed to H_2 at 703 K, the activity decreases to a level similar to that found for activation in vacuum or with O_2 (without spillover).

The mechanism by which alumina is activated by spiltover oxygen has not been well defined. Teichner hypothesized that excess oxygen on the surface as O^- or O^{2-} could give rise to the dissociation of H_2, and thus lead to hydrogenation of adsorbing ethylene. The activity is poisoned by NO, which would form inactive NO_2^- or NO_2^{2-}. These conclusions are inferential and no direct spectroscopic evidence has been presented (e.g., by electron spin resonance). It is not clear what happens to the other oxygen (or balance of charge) if, as proposed, O^- or O^{2-} is formed.

The more significant role of oxygen spillover in catalytic activity is found for spillover onto metal oxides where the metal can be found in different oxidation states. The source of spillover may be a metal such as Pt or it could be another transition metal oxide such as Sb_2O_4.[20] Both can provide spiltover oxygen to an oxide for a physical mixture of the donor and accepting phases. Thus, spiltover oxygen can create or maintain activity (as discussed in sections V.C and IV.C) on reducible transition metal oxides.

In addition, spiltover oxygen may be a reagent for oxidation reactions. Thus, a mixture of Sb_2O_4 with MoO_3 can result in the spiltover oxygen (from Sb_2O_4) reacting with propylene (on MoO_3) to give rise to acrolein.[145]

VI. Quantification of Spillover: Rates, Concentrations, and Distances

The rates of spillover from metal to support, as measured by various techniques, have varied over a wide range. Spillover rates onto oxide surfaces appear to depend on whether spillover is measured by OH exchange, by the formation of spiltover hydrogen that can be detected by TPD, or by the rate of a reaction involving spillover. Direct measurements of surface diffusion on oxide surfaces have been made in some cases, and these provide the rate of one of the steps in the overall process. Similarly, a wide range of distances at which spillover can be effective has been reported. Although in catalytic reactions involving spillover the migration distance of the spiltover species is expected to be in the nanometer range, experiments to measure and understand spillover have reported the effects of spillover over distances that are many orders of magnitude larger. In this section, measurements of the rates of surface diffusion and of spillover, examples of the distances that spiltover species can migrate, and the concentrations of spiltover species will be presented.

A. Diffusion on Metal Surfaces

The rates of surface diffusion on metal surfaces have been measured directly by laser-induced thermal desorption by George and coworkers.[146-157] An initial laser pulse is used to heat a small, well-defined area on a surface so as to desorb adsorbates located in that area. After time is allowed for adsorbates to diffuse into that area, a second laser pulse heats the same area. The species that diffused into this region are desorbed by the laser heating and detected by a mass spectrometer. Surface diffusion coefficients are measured by carrying out these experiments with various delay times.[157] For H atoms on single crystal Ru(001), the diffusion coefficient was measured as 2.5×10^{-7} cm^2/s at 260 K and 1.3×10^{-6} cm^2/s at 330 K. The activation energy for diffusion is 4.0 ± 0.5 kcal/mol. Sladek et al.[158] also reported diffusion coefficients of 10^{-6} cm^2/s on Pt at 333–348 K and an activation energy of 5.7 kcal/mol.

Diffusion rates may be affected, however, by surface coverages, bonding energies of molecules to the surface, and surface contaminants. For example, carbon decreased diffusion rates, whereas oxygen increased them for H on Ru(001).[157] Coadsorbed CO on Ru(001) also decreased H diffusion by as much as a factor of ten at 280 K.[156] Carbon monoxide alone diffuses less rapidly than H; adsorbed H is 50–500 times more mobile than CO at 280 K, although CO diffusion has a higher activation energy (11 kcal/mol) on Ru(001).[155] The diffusion coefficient for CO also increases 2 orders of magnitude, to 1×10^{-6} cm^2/s at 290 K as CO coverage increases.[155] For neopentane, the opposite dependence on coverage was observed.[153] The diffusion coefficient decreased at 180 K from 5.5×10^{-7} cm^2/s at 0.1 of saturation coverage to 8.0×10^{-9} cm^2/s at saturation on Ru(001), and a carbon coverage of 0.6 monolayer also decreased neopentane's diffusion coefficient by a factor of 40. The effect of coverage on diffusion was more dramatic on a stepped surface Ru(S)-[15(001)×2(100)]. The diffusion coefficient increased by 4 orders of magnitude as coverage increased from 5% of saturation to saturation because the steps were trapping sites at low coverages but had minimal effect at high coverages.[149]

B. Diffusion on Oxide Surfaces

Because of the large diffusion coefficients, surface diffusion is probably not limiting on metal surfaces in most spillover processes. The technique of laser-induced thermal desorption has not been effective for measuring diffusion coefficients for species that are easily adsorbed directly on oxides; the time for desorption is shorter than the time required for the surface diffusion measurements. Thus, for NH_3 on MgO(100), the diffusion coefficient is less than 10^{-9} cm^2/s at 165 K; at higher temperatures, NH_3 desorbed.[150] Similarly, the diffusion coefficient is less than 10^{-9} cm^2/s for CO_2 on MgO(100) at 100 K.[146] The other difficulty with these measurements, which require ultrahigh vacuum (UHV), is that obtaining hydroxylated oxide surfaces is more difficult in UHV, and the laser beam can dehydroxylate the surface. The degree of hydroxylation can dramatically affect diffusion rates.[30]

Table 5. Summary of Hydrogen Diffusion Coefficients on Oxide Surfaces

accepting surface	diffusion coefficient (cm^2/s)	temp (K)	ref
WO_3 to make H_xWO_3	7×10^{-6}	300	186
Ce–Y zeolite	10^{-10}	413	160
Y-zeolite	10^{-15}	298	187
Al_2O_3	9×10^{-15}	673	35
exchange with OH on zeolite	10^{-10}	293	188
	10^{-6}	473	
SiO_2 in Pd/SiO_2	1.5×10^{-3}	413	189
SiO_2 (Pt/SiO_2 source)	10^{-4}–10^{-5}	473	26, 30

Diffusion coefficients have been measured on oxide surfaces by other means, however, and rates measured by reaction or by detection of spiltover species also provide a lower limit on the rate of diffusion. One concern with these results is the wide range of values measured for diffusion coefficients on oxides. For example, Kramer and Andre[35] created H atoms on Al_2O_3 by spillover from Pt and Ni. They used TPD to detect the presence of a H_2 desorption peak at 753 K; the same peak was observed for H atom exposure to Al_2O_3 alone and thus was attributed to spillover. This peak was not present following 3 h of H_2 exposure at 298 K, but it was observed after 3 h of H_2 at 673 K. The diffusion coefficient for surface diffusion, which they assumed to be the rate-determining step, was 0.9×10^{-15} cm^2/s at 673 K, and the activation energy was 28.5 kcal/mol. This diffusion coefficient is much smaller than the values measured by Conner et al.[26,27,30,159] who did not need to assume that surface diffusion was rate controlling in the combined processes. Table 5 provides a brief summary of diffusion coefficients that have been reported on oxide surfaces (a more extensive table is found in ref 29, Tables 2 and 3).

It is useful to understand the significance of diffusion coefficients. A diffusion coefficient of 10^{-6} cm^2/s corresponds to a surface diffusion distance of approximately 10 nm in 1 ms at low coverage. That is, diffusion from the center of a supported metal particle of 20 nm diameter to the metal–support interface or from the metal–support interface across a support surface for 10 nm would take only 1 ms. In 1 s, adsorbed species that diffuse with a diffusion coefficient of 10^{-6} cm^2/s can reach an area of greater than 10^8 nm^2 (10^{-6} cm^2). Thus, in 1 s the diffusing species could come in contact with approximately 10^9 surface atoms or 10^7 active sites (for 1% of the surface sites, 10^{13}/cm^2, being active for adsorption or catalysis). If the turnover frequency for a catalytic reaction were 1 (reaction/active site/second), such a diffusion coefficient would certainly suggest that surface diffusion would not be the limiting process by which spiltover species could influence the adsorption or catalysis on an accepting surface. The potential for influence varies in proportion to the concentration of active sites and the square of the diffusion coefficient, and inversely with the turnover frequency.

C. Spillover Rates

One measurement that demonstrates the speed of hydrogen spillover is the reaction of spiltover hydrogen with species adsorbed on an oxide support. The study by Ioannides and Verykios[124] that were discussed above showed that H_2 spilled over from Rh at room temperature to hydrogenate benzene and toluene adsorbed on Al_2O_3. All the benzene adsorbed on the support of Rh/Al_2O_3 was hydrogenated after 15 min exposure to H_2 at 298 K. Thus, hydrogen spillover from Rh to Al_2O_3 is also fast at 298 K. Many measurements of hydrogen spillover are slower than the rate of benzene hydrogenation. However, recall that in the presence of a hydrocarbon the rate of spillover may be increased,[25,160] and thus independent measurements of rates may not reflect the rates for the combined processes.

It should be noted that adding H atoms to a molecule adsorbed on the support or exchanging OH groups do not require a substantial net increase in the number of spiltover H atoms residing on the oxide surface. Exposure to H_2 at elevated temperature to create a H_2 TPD peak due to spillover, however, requires a substantial net increase in the number of spiltover species on the surface.

D. Spillover Distances

Cevallos-Candau and Conner[27,30,159] concluded that surface diffusion was not the controlling step but spillover from metal to oxide was controlling. They measured surface diffusion at 478 K by observing the exchange of OH by D_2. By having a small source of Pt on SiO_2 and then observing the OH and OD vibration bands with FTIR at various distances from the Pt source, they concluded surface diffusion was rapid because OD was detected 1 cm from the Pt source in a few minutes. Others have also reported spillover over large distances.

Studies on physical mixtures or on packed beds in which a donor phase is placed on top of an acceptor phase have reported spillover over long distances. Roland et al.[44] reported H spillover over several millimeters at room temperature for a two-component mixture of Pt/NaY and H-NaY. A dramatic example is presented for the system shown in Figure 28. The Pt/Al_2O_3 catalyst and the zeolite were located on top of each other instead of being mixed together. As shown in Figure 29, carbon (the dark regions in the A regions) was removed from the zeolite over a distance of 1 cm.[28] Although transport over such large distances is unlikely to be of significance in steady-state catalytic reactions, these measurements demonstrate how readily spillover can take place, and they allow the processes involved in spillover to be more accurately studied. Even longer spillover distances have been reported. Lenz et al.[38] studied spillover from Pt/Al_2O_3 to SiO_2 by NMR. In one experiment, the H had to diffuse 12 cm to reach the probe area of the NMR system. These authors came to the conclusion that spiltover hydrogen interracted with the surface hydroxyls as a radical even though the source of the spiltover hydrogen was not present in the NMR cavity.[139] A similar conclusion was reached by Chiaranussati et al.[37] (section III.A).

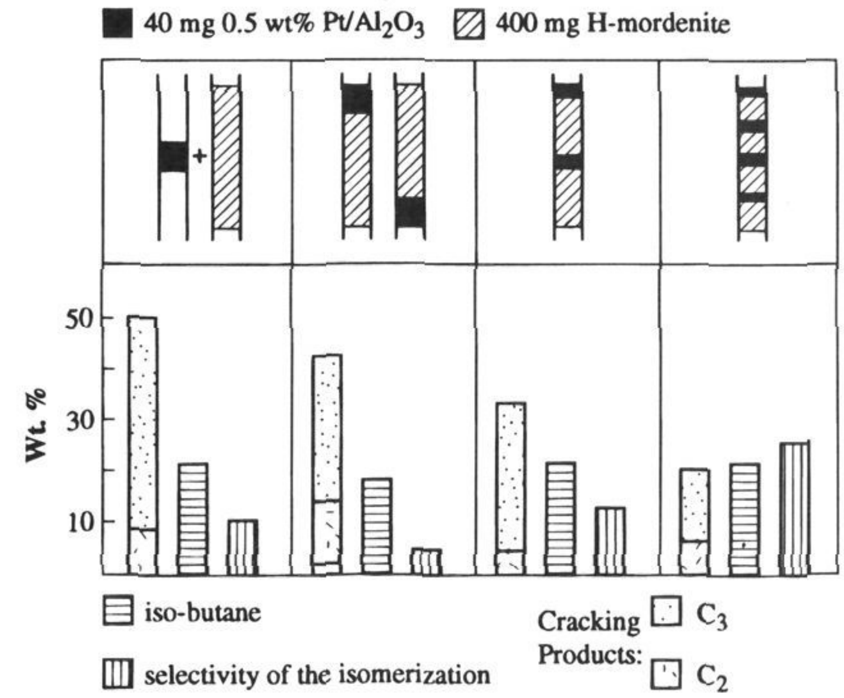

Figure 28. Influence of different arrangements of 0.5 wt % Pt/Al_2O_3 catalyst (dark regions) and H-mordenite (cross-hatched regions) on n-butane hydroconversion at 633 K. The arrangements are shown schematically above while the corresponding product selectivities are shown in Figure 29.[28]

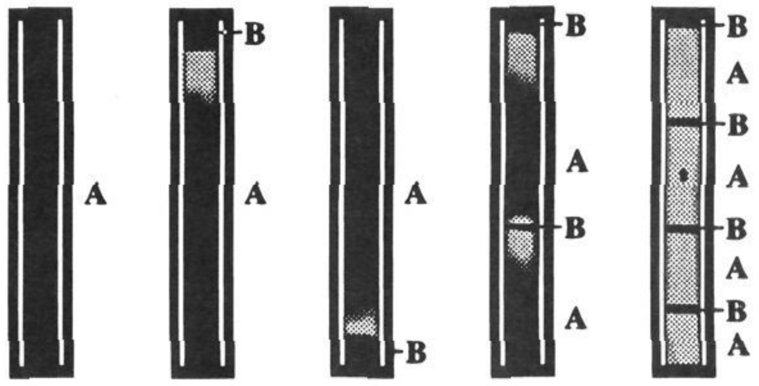

Figure 29. Photos of quartz glass reactor for catalyst arrangements shown in the top part of Figure 28 after 1.5 h hydroconversion of n-butane at 633 K. Reactant flow was from top to bottom: (A) H-mordenite; (B) 0.5 wt % Pt/Al.

E. Active Sites

The concentration of sites created by H spillover was only $10^{12}/cm^2$ on SiO_2, as determined by FTIR,[27] even though $10^{13}-10^{14}/cm^2$ OH groups exist on the surface. Kramer and Andre[35] reported similar value of $(1.4-2.2) \times 10^{12}/cm^2$ for Ni/Al_2O_3 and Pt/Al_2O_3. They indicated that 2×10^{15} OH groups/cm² were present on Al_2O_3, and concluded the spiltover H was adsorbed on surface defects, vacancies, and exposed Al^{3+}. Musso and Parera[161] also reported a concentration of spiltover H of 2×10^{12} H/cm². The concentration of sites to accept spiltover hydrogen on carbon supports is dramatically higher[162-164] where $10^{13}-10^{15}$ H/cm² have been estimated.

F. Surface versus Gas-Phase Diffusion

One of the fundamental perspectives concerning spillover is that it is a surface phenomenon. Baumgarten et al. have published a series of papers[77,135,165] wherein they have concluded that spillover occurs into the gas phase at low temperatures (<400 K). These authors observed hydrogenation of diphenylpicrylhydrazine, *DPPH*, promoted by the presence of

Pd/SiO_2 without any apparent contact between the Pd/SiO_2 and the surface containing the DPPH. Their explanation was that H_2 adsorbed on the Pd and then hydrogen atoms spilled over into the gas phase where they diffused to the surface containing the DPPH and hydrogenated the DPPH. It is difficult to accept that the concentration of hydrogen atoms spilled over into the gas phase would be sufficient to give rise to the hydrogenation activity claimed. Spencer et al.[166] calculated the maximum amount of atomic hydrogen that might be formed at equilibrium with gaseous hydrogen based on thermodynamics. They concluded that insufficient hydrogen could be produced by the proposed mechanism and suggested that some other ("parasitic") reaction must also be proceeding to provide the thermodynamic driving force for the observed reaction. Baumgarten et al.[167] disputed this suggestion but did not dispute their original observation that "It is not possible to explain the thermodynamics of the process completely."[165] They concluded that "desorption of hydrogen (*atoms*) into the gas phase, whatever the explanation of the source of energy, is at least one reaction path in hydrogen spillover."[167] A satisfactory explanation for these results is still needed before spillover of atomic species into the gas phase should be accepted as a significant mechanism associated with spillover. We agree with Dowden that many slow processes that may be associated with spillover "may not be relevent to practical catalysis."[168]

VII. Spillover in Applied Catalysis

Since its discovery, the significance of spillover in catalysis has been subject to much debate. At first spillover was considered a curiosity; however, soon it was invoked to explain many complex phenomena. Spillover is only one fundamental step in a series of mechanistic and kinetic steps that may take place on heterogeneous surfaces. Species activated by one surface can be transported onto a second surface where they may react with the second surface or with adsorbed molecules and atoms. The unanswered questions continue: What is the potential of spillover in catalytic process applications? Is spillover still only an interesting curiosity or does it play a significant role? Moreover, can insight into spillover help design new catalysts and/or improve current catalytic processes?

Spillover has been implicated in many aspects of a broad spectrum of catalytic processes. We will not attempt to review all the studies that suggest that spillover contributes to catalysis. Several examples will be discussed where there is strong evidence that spillover is involved. The focus in this section is on catalysts employed in industrial processes. The examples are chosen to demonstrate that spillover can contribute to substantially different reactions on different types of catalysts. Further, spillover may participate in several ways in the catalytic activity, i.e., in the activation of the catalysts, in the reaction mechanism, and/or in the maintenance of catalytic activity.

A. Petroleum Processing

Petroleum processing involves several catalytic processes: cracking, hydrogenation−dehydrogenation, skeletal isomerization, and aromatization. Prior to the manipulation of the octane by these processes, the crude oil may need to be purged of nitrogen- and sulfur-containing molecules. Hydrotreating is increasingly employed to remove the heteroatoms (N and S) from the crude feed. First we will consider the potential contributions of spillover to hydrocarbon rearrangement reactions (octane manipulation), and then, we will discuss the participation of spillover in hydrotreating. Catalysts deactivate in all of these reactions and its control and regeneration of the active catalyst will be discussed as it relates to spillover.

Reforming is a classical example of bifunctional catalysis where it is believed that acidity is responsible for the isomerization and a metal (often Pt) is responsible for the reversible hydrogen transfer. In addition, these catalysts may be deactivated by the formation of coke. As an example, the reforming of a saturated hydrocarbon is perceived to involve dehydrogenation on the metal followed by fluid-phase transport to the acidic site where isomerization occurs. This is possibly followed by fluid-phase transport back to the metal for subsequent hydrogenation to a saturated product or dehydrogenation to an aromatic. Extensive dehydrogenation on the metal could lead to coke formation.

Spillover could contribute to the storage of hydrogen removed from the hydrocarbon and recombination of hydrogen could occur on the metal by back spillover from the support. Spillover could also be involved in the creation of active sites during catalyst activation and/or the maintenance of catalytic activity by removing coke or coke precursors.

Parera et al.[32] were one of the first groups to recognize one of the major contribution of spillover to reforming. They showed that spiltover hydrogen and spiltover oxygen were effective in removing coke from Pt/Al_2O_3 naptha reforming catalysts. When Pt/Al_2O_3 reforming catalysts was mixed with a sample of coked alumina, the coke was removed by hydrogen or by oxygen at substantially lower temperatures than without contact with the reforming catalyst. The authors concluded that spillover is involved in the removal of coke and that "During naphtha reforming on Pt/Al_2O_3, coke formation is decreased by hydrogen spilt over from Pt... during the regeneration of this catalyst this coke is eliminated by the oxygen spiltover..."[32]

More recent studies have implicated hydrogen spillover more directly in the creation of active sites and as a reagent in the catalysis. The creation of Brønsted acidic sites from spiltover hydrogen (as H_{sp}^+) has been proposed.[140,141] The sites are proposed to be created on transition metal oxides as well as on zeolites. These are discussed in more detail in section V.B.

Steinberg et al.[28] showed that mechanical mixtures of Pt/Al_2O_3 and H-ZSM-5 catalyzed hydrocracking of *n*-heptane, whereas, separately, hydroisomerization and oligomerization of olefin intermediates are favored. This is discussed in section VI.D.

Chen et al. found two types of spiltover hydrogen that they suggested are involved in catalytic reforming of *n*-hexane by Pt/Al_2O_3,[169] i.e., one is irreversible

Table 6. Toluene Disproportionation Conversions on Zeolites and Hybrid Catalysts[141]

catalyst	conversion (%)
Fe–KY	2.6
USY	4.6
Co–Mo/Al_2O_3	3.1
hybrid [Fe–KY + USY (50 wt %)]	8.2
hybrid [Co–Mo/Al_2O_3 + USY (50 wt %)]	25.3

while the other is reversible. They concluded that the reversible hydrogen is involved in hydrocracking and isomerization, and it is also involved in maintenance of catalytic activity (preventing coke formation). The irreversible hydrogen is associated with the aromatization activity. They point out that the amount and type of spiltover hydrogen is sensitive to catalyst preparation. This study mostly concerned hydrogen adsorbed during pretreatment of the catalyst and did not directly study hydrogen spilled over during reforming; however, the authors imply that their conclusions would also apply to reaction conditions.

Becker et al.[170] used pilot plant studies of the hydroconversion of *o*-xylene, ethylbenzene, and other C_8 aromatics, and the hydrocracking of middle distillates to conclude that hydrogen spillover from a metal to the zeolite contributed to the catalysis. Extruded physical mixtures of supported metal with hydrotreating catalysts were also shown to retain their activity for middle distillate feeds. They suggested that spiltover hydrogen controls the reactions at the acidic sites on the zeolite. Further, it can generate or consume intermediates and keep the acidic sites clear of poisons.

Nakamura et al.[141] showed that H spillover can promote acid-catalyzed reactions on zeolite. As shown in Table 6, conversions for toluene disproportionation are much higher for hybrid catalysts than for the individual catalysts. Both disproportionation activity and hydrogenation activity showed similar dependences on the USY content in hybrid catalysts (Figure 30a) but these activities did not correlate with the coke content (Figure 30b). Thus, disproportionation on hydrocracking catalysts in the presence of H_2 was promoted by spillover H to acid sites in the zeolite, and not by coke removal from acid sites. That is, Co–Mo/Al_2O_3 adsorbs H_2, which spills over onto the USY zeolite, where it promotes acid-catalyzed reactions.

Both conversion and selectivity can be affected by spiltover hydrogen. For *n*-pentane isomerization to isopentane, hybrid catalyst of Pt/SiO_2 + H-ZSM-5 showed both high selectivity and high conversion, equal to those obtained for a Pt/ZSM-5 catalyst.[171] In contrast, Pt/SiO_2 or H-ZSM-5 alone are not effective catalysts. Table 7 summarizes the kinetic results for Pt as well as Pd catalysts. The mixing state of the catalysts had a strong effect. A mixture of granules (20–40 mesh) to form a hybrid catalyst showed much less conversion (18.1%) than a powder mixture (71.5%), and a two-stage catalyst bed was even worse. This intimate contact that was needed indicated the mechanism for isomerization is not a bifunctional process. Instead, spiltover H was concluded to play a role in paraffin activation and stabilization of intermediates. The high isomerization activity was attributed to the generation of Brønsted acid sites by spillover.[58]

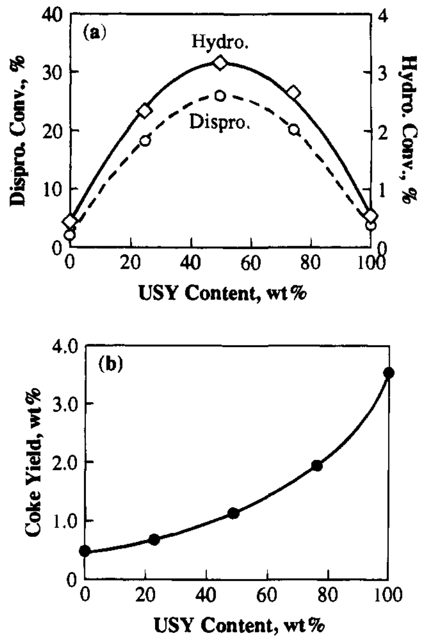

Figure 30. (a) Toluene disproportionation and hydrogenation conversions on hybrid catalysts of USY and Co–Mo/Al_2O_3 at 623 K, in H_2 + H_2S (0.2%) at 6.0 MPa and (b) carbon content of the same hybrid catalysts.[141]

Spillover has also been found to contribute to aromatization of smaller paraffins. Fujimoto et al.[172] found that physical mixtures of Ga/Al_2O_3 or Ga_2O_3 with H-ZSM-5 aromatized butane similarly to Ga supported directly on H-ZSM-5. They concluded that the Ga (on the zeolite, mixed as Ga_2O_3, or supported on alumina) provided a "porthole" for the hydrogen desorption. Inui et al.[173] suggested that hydrogen spillover from Pt also enabled a Ga/zeolite catalyst to be regenerated by oxygen spillover. Sites created by hydrogen spillover allowed oxygen to adsorb and to regenerate the catalyst. The composite catalyst was stable for over 1000 h on stream and subject to over a hundred regenerations by oxygen treatment, whereas a catalyst without Pt would have irreversibly deactivated much more rapidly.

Hydrotreating involves the reaction of hydrogen with hydrocarbons to remove the sulfur (hydrodesulfurization, HDS) or nitrogen (hydrodenitrification, HDN) often present in petroleum. The most active HDS catalysts are supported mixed-metal oxides (e.g., Co–Mo/Al_2O_3 or Co–Ni/Al_2O_3) that are sulfided with H_2S prior to reaction. The cobalt and molybdenum form alternate layers and are (or can be) exposed on different surfaces (edges vs planes).[174] Delmon et al.[175–177] have shown that physical mixtures of Co/Al_2O_3 and Mo/Al_2O_3 show an enhancement of HDS activity compared to the sum of the activities of the individual surfaces; although, the activity is not as high as that found for the Co–Mo/Al_2O_3 where the Co–Mo–S state is formed.[174] Delmon et al. concluded that the Co spilled hydrogen over to the Mo^{6+}, which was reduced to an active form. Interestingly, spillover was not deduced following hydrogen reduction of the precursor mixed oxides but only on the H_2S sulfided catalyst.[177] Physical mixtures of Mo/Al_2O_3 with platinum and

Table 7. Conversion and Selectivity for *n*-Pentane Isomerization on ZSM-5 Catalysts with and without Pt or Pd[a],[171]

	catalyst					
	H-ZSM-5	Pt-ZSM-5	Pt/SiO_2[b]	Pt/SiO_2 + H-ZSM-5[c]	Pd-ZSM-5	Pd/SiO+ H-ZSM-5[d]
conversion(%)	7.1	77.2	0.4	54.6	29.9	59.6
selectivity (C mol %)						
C_1-C_4	65.7	5.8	0	0.1	1.4	0.2
iso-C_5	15.2	93.9	49.6	99.4	96.8	99.2
C_6+ Aliphatics	10.1	0.3	50.4	0.5	1.8	0.6
C_6+Aromatics	9	0	0	0	0	0

[a] Reaction conditions: 523 K; *n*-C_5, 10 kPa; H_2, 90 kPa; H_2, 90 kPa; W/F = 10 g of cat h^{-1} mol^{-1}. [b] Pt/SiO_2 0.20 g. [c] Pt(2.5 wt %)/SiO_2:H-ZSM-5 = 1:4. [d]Pd(2.5 wt %)/SiO_2:H-ZSM-5 = 1:4.

rhodium sulfides on alumina were also able to effect an enhancement of HDS activity.[176] Direct participation of hydrogen spilled over from Co to react with the hydrocarbon adsorbed on the Mo has not been discussed; however, we infer that hydrogen spillover could be involved in the cleaning of the surface from deactivation by coke formation as in other processes. The main conclusions are that spillover of hydrogen from Co (or a donor) to Mo are involved in the activation of the samples and the maintenance of activity (by remote control) for HDS over biphasic catalysts.

B. Partial Oxidation Catalysis

Partial oxidation catalysis normally denotes the selective oxidation of a hydrocarbon. The hydrocarbon participates as a reductant on the catalytic surface. Partial oxidation is often catalyzed by mixed transition metal oxides where the oxygen often comes from the lattice. In mixed-metal oxides one metal is usually believed to adsorb and activate the oxygen and the other transition metals is believed to be involved in the adsorption of the hydrocarbon. Each of the transition metals (e.g., Bi and Mo in a bismuth molybdate) is thought to be exposed on different crystalline surfaces. The activated oxygen spills over onto the second phase, the oxide lattice, and is transported through the lattice toward the second metal where it adds to the activated hydrocarbon. These well-known phenomena have not been discussed as spillover; however, spillover (as defined above) is involved if one considers the different exposed surfaces (one to activate the oxygen and the other the hydrocarbon) as different phases. Since the mechanism of transport of the spiltover oxygen is not across the surface but through the bulk, physical mixtures of the individual components would not necessarily exhibit the same enhancement of catalytic activity, compared to sum of the activities of the individual components, found in other spillover phenomena. Mixed-metal oxides can contain oxide defects that can enhance transport of oxygen through the lattice. Moro-Oka has summarized the application of these concepts to the design of partial oxidation catalysts.[57]

Weng et al.[178] have shown that the oxygen spilled over from Sb_2O_4 can react with propylene on MoO_3 to form acrolein for physical mixtures of Sb_2O_4 and MoO_3. This is an example of the direct role of spillover in the formation of the partially oxygenated product where the two phases (donor and acceptor) are separated. The contribution of this form of spillover to partial oxidation appears to be minor. Zhou and Delmon[15] have shown that coke is effectively removed at a significant rate from the active MoO_{3-x} by spillover of oxygen from Sb_2O_4. In this manner, the mixed system can retain partial oxidation activity without deactivation by coke formation. Furthermore, the spiltover oxygen can react with Mo that becomes reduced by the hydrocarbon to maintain it in a partially oxidized, active state. This is a well-documented example[176] where spiltover oxygen is involved in the remote control of the oxidation state of an active transition metal oxide.

C. Methanol Synthesis

Spillover may be involved in either CO (or CO_2) as well as H_2 transport from the Cu or from the ZnO to the other surface in methanol synthesis catalysts. In addition it may be involved in the reduction of the copper or the activation of the ZnO surface by either CO or H_2. The conductivity of the Cu/ZnO increases in hydrogen at low temperature, whereas it decreases for ZnO alone.[40] At temperatures above 500 K in hydrogen, the conductivity increases for pure ZnO but it increases even more for the catalyst containing Cu. It is apparent that hydrogen spills over from Cu to the ZnO, which undergoes modest surface reduction. Boccuzzi et al.[179] studied Cu supported on ZnO. XRD and TEM did not detect a Cu phase being formed on reduction. The infrared transparency for Cu/ZnO was, however, decreased in the presence of gaseous H_2 at room temperature. They concluded that H_{sp} spilled over from the Cu onto the ZnO as H^+ and decreased the transparency of the supported system.

Burch[180] was one of the first to provide direct evidence of the influence of spillover in Cu/ZnO methanol synthesis catalysis. The methanol synthesis catalyst is understood to involve Cu sites in a reduced state (Cu^{1+} or Cu^0) present on a ZnO surface. Burch et al.[22] found that a physical mixture of Cu/SiO_2 and ZnO/SiO_2 was substantially more active than the sum of the individual solids for the reaction of H_2, CO, and CO_2. The activity approached the activity for a coprecipitated Cu/ZnO catalyst. When the Cu/SiO_2 was then separated, the activity was again low, indicating that the Cu was not just activated by the ZnO and the synergism was dynamic. In contrast, the reaction of CO and H_2 was not more active over the physical mixture. The enhancement of activity correlated well with the measured spillover of hydrogen. This is not "classical" bifunctional catalysis nor transport of intermediates through the gas phase as there is no enhancement if the Cu and ZnO catalysts are not well mixed.

The authors suggest that this effect is one of "synergy at a distance."

Burch et al.[22] further suggest that the CO_x is adsorbed onto the copper and is hydrogenated by a combination of hydrogen adsorbing on the copper and hydrogen present on the ZnO. This stored hydrogen may have spiltover from Cu or from sites on the ZnO. Methanoyl (HCO) species bound to Cu are proposed for well-reduced copper with either CO or CO_2 reactants. Formate species (HCOO) species may also be intermediates on partially reduced copper sites. Methoxy and formates species may also be formed on the ZnO but these authors suggest that they are less reactive than those on the copper; however, when hydrogen spills over from Cu to ZnO, these intermediates may form methanol. Surface species (not specified) formed from CO_2 and neighboring hydroxyls are proposed to facilitate the spillover of hydrogen.

Thus it is suggested that spillover of hydrogen from Cu to ZnO during reaction or activation will activate the ZnO by surface reduction. Spiltover hydrogen is also stored on the ZnO where it can react with formate or methoxyl species on the Cu. Formate and methoxyl species formed on the ZnO surface may also contribute to the formation of methanol under reaction conditions where spillover of hydrogen atoms from Cu becomes significant. Spillover is thus involved in the activation of the Cu/ZnO (or other) methanol catalysts, and spillover of hydrogen is also thought to participate directly in the mechanism by which methanol is formed over these catalysts.

D. Environmental Catalysis

Pollutants from industrial processes can be decreased first by improving the quality of the feed to the process and, "after-the-fact", by removing the pollutants from the effluent. Catalysts are employed in hydrotreating of petroleum feedstocks to remove hetroatoms that would result in "acid gas" from the petroleum processing industry (section VII.A) and contribute to the deactivation of petroleum processing catalysts. The contribution of spillover to hydrotreating processes is discussed above. The largest application of pollution control catalysis is certainly in automotive exhaust catalysis, an "after-the-fact" process involving further reaction of the reagents in the effluent. In addition, pollution may be decreased by reacting the pollutant with another reagent as in selective catalytic reduction (SCR) of NO_x to form N_2 and water by reaction with ammonia or hydrocarbons as hydrogen donors.

Recently the addition of ceria and other lanthanides has been shown to enhance the activity of automotive exhaust catalysts. The oxidation of CO and hydrocarbons is seen to commence at substantially lower temperatures if ceria is present.[181] Ceria is proposed to store spiltover oxygen and, thus, to enhance the catalytic activity of metals such as Rh.[64,182] The oxygen spiltover from Pt onto ceria provides a reservoir of oxygen for catalytic oxidation.[63] However, a physical mixture of of ceria (pure or supported on alumina) with Pt/Al_2O_3 does not show enhanced activity.[183] It is apparent that spillover does not occur between all surfaces and may be limited to the surface directly in contact with the source of spillover so that secondary spillover may not occur. Thus, as in SMSI (section IV.B) and partial oxidation (section VI.B), physical mixtures do not exhibit synergetic increases in activities.

Selective catalytic reduction of nitrogen oxide pollutants is now being employed to control their emission from stationary power plants. This reaction involves a hydrogen donor (NH_3 or a hydrocarbon) that reduces the NO_x to N_2 and H_2O. Most often a transition metal or metal oxide is employed in conjunction with an acidic zeolite for this reaction. The transition metal is seen to adsorb the NO_x, whereas the acidic sites on the zeolite are perceived to adsorb the hydrogen donor. Spillover should also play a part in this reaction. Spillover of hydrogen between sites may facilitate the combined reaction. In addition, the oxidation state of the catalytic transition metal (V or Cu) may be controlled remotely by spillover of O as well as H.[184]

VIII. Summary

Spillover is a phenomenon wherein the whole is substantially greater than the sum of the individual parts. Independent measurements of rates and selectivities of reactions or amounts of adsorption on isolated components do not always reflect the values obtained when the individual components are combined. This combination may be in a physical mixture or components may be in more intimate contact. In the past, various theories (e.g., the electronic theory or metal–support interactions) have been offered to explain the synergetic phenomena that are found when different components are combined in a catalyst. Most of these theories depend on direct contact between the components. Spillover is a documented phenomenon in which species activated on one phase are transported, usually across a surface, to another phase where they may then participate directly or indirectly in catalysis.

Spillover is only one step in a series of steps that results in catalysis. The spillover process can provide wider access to the total available surface than would be found for process studied over the individual surfaces. The spiltover species can simply exchange with other surface species, react with other species adsorbed on the surface accepting the species, react with and change the surface or the bulk of the accepting surface, and/or create sites for adsorption or reaction on the accepting surface. Thus, for example a metal can substantially modify the adsorptivity or reactivity on surfaces that would appear inert in the absence of the metal. For any catalyst with more than one component, spillover needs to be considered in parallel with electronic and other explanations for synergy. However, spillover does not contribute in all systems where the catalytic or adsorption properties are different for a combination of components than they are for the individual components.

This review has concentrated on studies that have demonstrated spillover directly by using (a) hybrid catalysts (physical mixtures of 2 types of catalysts), (b) oxide surfaces that are activated by spillover and then remain active after the donor is removed, (c) transient reactions in which the two reactants are initially adsorbed on different phases on the surface,

(d) direct detection by IR of adsorbed species on a accepting surface that is at a distance from the donor surface, (e) transient reaction techniques that eliminate gas-phase reactants so that adsorption sites are known, and (f) observation using two beds of catalysts to show spillover over large distances. Many other studies have used spillover to explain their experimental observations, and indeed it is likely that these studies also involve spillover, but these studies have in general not been included in this review. Some of the most compelling evidence that spillover contributes to catalytic reactions or to adsorption are the systems that exhibit synergy when combined in a physical mixture. Similarly, unique properties are evident for many systems after the source of spillover has been isolated from the accepting surface.

These approaches have demonstrated that many important reactions can involve spillover. These include hydrogenations, dehydrogenations, partial and total oxidations, hydrocarbon isomerization, HDS, HDN, gasification, and hydrocarbon synthesis from syngas. Spillover also has been implicated in the creation, maintenance, and regeneration of catalytic activity, including removal or control of coke formation. Indeed, coke removal was demonstrated in dramatic photographs to take place over a distance that is 1 cm away from the spillover source, and thus coke removal on the nanometer scale is certainly important in many reactions. In most cases the rates of reaction for physical mixtures are less than for the intimately combined system. However, the rates of processes that may be rate controlling in the physically mixtures could be substantially different in the combined system. More quantitative studies are needed to determine the potential for spillover to play a significant role in complex catalysts.

In addition to being important in catalytic reactions, spiltover hydrogen can also influence catalyst characterization and determination of turnover frequencies. For example, measurements of metal surface areas cannot be obtained by hydrogen adsorption if hydrogen spills over onto the support during the measurement. Similarly, turnover frequencies based on metal dispersion are meaningless when the support plays an important role in the reaction. The concentration of sites on the metal and on the oxide are both important in reactions on oxide or zeolite surfaces if reverse spillover of H atoms from the oxide back to the metal (where H_2 can desorb) is significant. Calculations of turnover frequency would not have a firm base. The influence of spillover can be indirect, as when hydrogen spillover from a metal can reduce oxides such as TiO_2. The reduced titania can then migrate back to the metal where it can decorate (cover) the surface and, thus, limit the ability of the metal to activate hydrogen at lower temperature (the SMSI effect). Thus, hydrogen spillover may directly increase the amount of hydrogen adsorbed per metal atom and indirectly it can lead to the masking of the metal for subsequent hydrogen adsorption.

This review has emphasized hydrogen spillover because hydrogen is involved is a large fraction of all catalytic reactions, and because the literature on hydrogen spillover is the most extensive. Many studies have been carried out for oxygen spillover, and recent studies of spillover of molecular species have also been presented.

Many studies of spillover show that spillover does not occur by a single mechanism involving a single species. Different sources of spillover and/or different accepting surfaces can result in different species being spilled over at substantially different rates. Molecules, fragments of molecules, or atoms in charged, neutral, or radical forms can be spilled over from one surface to another. The rates of the various processes involved in spillover can differ by orders of magnitude depending on the system and conditions. The important point is that spillover can be rapid. Many studies clearly show that hydrogen spillover takes place at room temperature and the spiltover hydrogen atoms can be involved in reaction at room temperature. A single mechanism for the spillover of a common species with fixed relative rates does not exist.

There are significant differences between the mechanisms by which spillover has been proposed to give rise to catalytic active sites on oxide surface. For the promotion of acidic catalysis, the spiltover species is proposed to be part of the active site, as H^+. The active sites for hydrogenation are proposed to result from reaction of spiltover hydrogen with specific surface hydroxyls. The spillover of oxygen or hydrogen has been proposed to be able to manipulate the surface stoichiometry for reducible transition metal oxides, i.e., by remote control of the transition metal oxidation state.

There is still much to be learned about spillover. Many spectroscopic techniques have been employed in studies of spillover[185] but these techniques have yet to provide *direct detection* of the species being spilled over for any system. Likewise, the mechanism of transport between surfaces that are in physical contact has not been studied directly. More quantitative studies are also needed to understand the relative rates of spillover and related phenomena for multiphase systems.

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