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Hydrogen Spillover. Facts and Fiction

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CONTENTS

1. INTRODUCTION

In 1964, Khoobiar reported that WO_3 is reduced by H_2 to blue WO_{3-x} when it is in contact with a Pt catalyst.[1] The blue color appears because hydrogen atoms, which are created by dissociative chemisorption of H_2 molecules on the Pt particles, migrate from the Pt surface to the yellow WO_3 particles and reduce them to blue WO_{3-x} particles. Boudart et al. coined the word "spillover" to describe the migration of H atoms from the metal particles to the support, because the H atoms spill over, as it were, from a hydrogen-rich to a hydrogen-poor surface.[2] Spillover in general is defined as the transport of a species, adsorbed or formed on a surface, to another surface, which does not adsorb or form this species under the same conditions.[3] In catalysis, only the spillover of catalytically active species is important. Hydrogen atoms are not usually produced on the surface of a support. In hydrogen spillover, H atoms are created on a metal surface and migrate to the surface of the support. As early as 1963, Sinfelt and Lucchesi reported[4] that ethene can be hydrogenated by the spillover of H atoms from Pt/SiO_2 to Al_2O_3 and cited the experimental results of Khoobiar in an internal Exxon report of 1959. Thus, and because the results of Sinfelt and Lucchesi turned out to be due to impurities rather than to spillover (as we will see in section 8.1), Khoobiar's work represents the beginning of the spillover concept.

In 1971, Pajonk and Teichner made the next discovery, which enforced the idea of spillover. They found that a pure support, such as Al_2O_3 or SiO_2, can hydrogenate ethene and benzene when it is treated with H_2 for a number of hours at elevated temperature by means of indirect contact with a metal-on-support catalyst.[5] This they ascribed to the spillover of H atoms, produced during the prereduction step on the metal-on-support catalyst in a basket, onto the support outside the basket. I will discuss these experiments in section 4.2.1.

Ever since these observations, spillover has attracted the interest of many scientists, who have attempted not only to explain it, but also to use it as an additional hydrogenation method. Five international conferences on spillover have been held, but interest waned because there was no direct proof of spillover, a scientific basis for discussion was lacking, and applications were not developed. However, in recent years, new ideas and experimental results have been published, and there is a renewed interest in spillover. While spillover was formerly restricted to catalysis, applications of spillover in hydrogen storage have materialized in the past decade.

In this Review, articles on spillover published after 1996 will be discussed. Only some of the earlier articles will be mentioned, because two comprehensive reviews, published in 1995 and 1997, cover former studies.[3,6] As will be shown in section 3, spillover does not occur in all circumstances, and caution must be exercised before suggesting that spillover is the explanation of a scientific event. All too often scientists have proposed spillover as an explanation of scientific phenomena when further experimentation may have provided a more straightforward answer.

Before discussing recent results of hydrogen spillover in catalysis and hydrogen storage, I will first discuss in section 2 the latest developments with regard to Pt/WO_3, the starting point of spillover. In section 3, a new look will be taken at H−D exchange on the support of a metal catalyst, which is considered by many to be the best proof of hydrogen spillover. Thus, in a

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review it was stated in 1995: “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.”[3] I will show that hydrogen spillover onto the surface of a defect-free nonreducible support is energetically improbable and that H−D exchange of OH groups on such a support provides no proof of spillover. In section 4, I will discuss spillover from metal particles to insulating supports and to defects on such insulators. In section 5, spillover to carbon supports and its role in hydrogen storage will be reviewed. In sections 6−8, the role of hydrogen spillover in the synthesis of methanol, hydroisomerization, and the hydrogenation of alkenes and aromatics will be discussed, while in section 9 the application of spillover in isotope enrichment in organic compounds will be discussed.

2. Pt/WO_3 REVISITED, SPILLOVER TO REDUCIBLE SUPPORTS

WO_3 turns blue when Pt/WO_3 is exposed to H_2, and this is caused by reduction.[1] Hydrogen atoms, created by dissociative chemisorption of H_2 molecules on Pt particles, migrate (spill over) from the Pt surface to the WO_3 particles and reduce them to blue WO_{3-x} particles. Boudart and co-workers demonstrated that not only is a metal necessary to dissociate H_2 into H atoms, which reduce WO_3, but also a base such as water or an alcohol.[7,8] They ascribed this to the fact that the H atoms become protons and electrons when in contact with the WO_3 support. The electrons reduce W^{6+} cations to W^{5+} cations and move through the WO_3 lattice by W^{5+}−W^{6+} exchange, while the protons are solvated by water and move fast by hydrogen bonding. In this way, even W^{6+} cations that are not in the immediate neighborhood of the Pt particles can be reduced reasonably fast.

Recent density functional calculations (DFT) of the analogous spillover of hydrogen in Pt/MoO_3 confirm that H atoms do not migrate, but that protons and electrons do.[9,10] The path of a H atom from a Pt_6 particle to the (010) surface of MoO_3, the migration of the proton and electron on the surface and in the bulk of MoO_3, and the role of hydrogen bonding have been described in detail. Molybdenum bronze H_xMoO_3 is formed, and it was shown that the high mobility of protons is due to hydrogen bonding. A minimum energy path calculation of the migration of a H atom from the Pt_6 particle to the MoO_3 (010) surface showed that an O−H bond formed and that the barrier for metal-to-support migration is only 36 kJ/mol (Figure 1).[9] Charge analysis indicated that the electron of the H atom moved to a Mo atom next to this O−H bond and that the H atom became part of an OH group, conventionally called a proton. A hydrogen atom has a repulsive interaction with an oxygen O^{2-} anion, but when it transforms into a proton and an electron on the MoO_3 an attractive interaction between proton and O^{2-} anion develops. The H atom (proton plus electron) first moves to a terminal oxygen atom (t1), then to a second terminal oxygen atom t2, and finally to oxygen atoms in bridging positions (a1 and a2). The activation energies for these migrations are low (50−60 and 40−30 kJ/mol, respectively), and the final state is 44 kJ/mol lower in energy than the initial state (Figure 1). Migration of the proton and electron in the bulk of MoO_3 is easier than on the surface, with activation energies of 6−12 kJ/mol because of the more extensive hydrogen bonding of the proton with oxygen anions.[10] The DFT calculations thus confirmed that an H atom on a reducible support transforms into a proton and an electron.

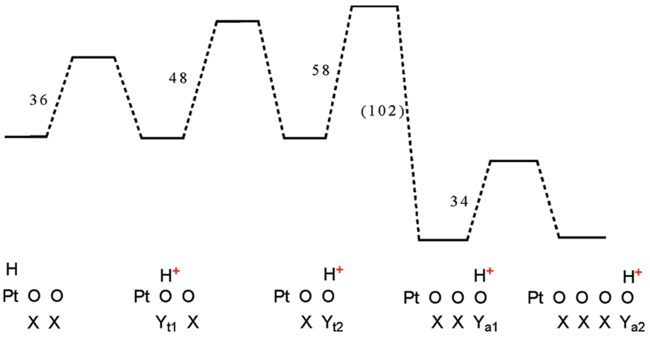

Figure 1. Spillover of a H atom from a Pt_6 particle to the MoO_3 (010) surface. X = Mo^{6+}, Y = Mo^{5+}, t1 and t2 are terminal oxygen atoms, and a1 and a2 are asymmetric bridging oxygen atoms at the MoO_3 surface. Numbers are activation energies in kJ/mol; the number in parentheses is an energy difference in kJ/mol. Adapted with permission from ref 9. Copyright 2008 American Chemical Society.

Triwahyono et al. studied the kinetics of the adsorption of H_2 on MoO_3 and Pt/MoO_3.[11] H_2 uptake on MoO_3 was very small, demonstrating that MoO_3 is hardly able to dissociate H_2. On Pt/MoO_3, on the other hand, H_2 uptake was about 200 times greater than that on MoO_3. H_2 uptake on Pt/MoO_3 was slow at 150 °C and even after 10 h had not reached equilibrium. At 200 °C, it was initially very fast (H/Pt ≈ 2.0 in 0.5 h) and reached equilibrium (H/Pt ≈ 2.5) in 2 h. The high final H/Pt ratio (much higher than 1.0) indicates that spillover of H atoms from the metal to the support, diffusion of these H atoms (as protons and electrons), and formation of H_xMoO_3 had taken place. The heat of H_2 adsorption on Pt/MoO_3 was 18 kJ/mol, and the $t^{1/2}$ dependence of the hydrogen uptake showed that the rate-controlling step was surface diffusion, with an activation energy of 83 kJ/mol. This is of the same order of magnitude as the value calculated by DFT.[9]

These recent studies of Pt/MoO_3 confirm that the proposals put forward in the 1960s to explain the color of Pt/WO_3 are true. Spillover of hydrogen does take place from Pt to WO_3. Hydrogen atoms are not produced when H_2 passes over pure WO_3 but are produced on the WO_3 surface when H_2 passes over WO_3 that is in contact with a metal such as Pt. The hydrogen atoms are formed by chemisorption of H_2 on the Pt surface and move to the WO_3 surface where they become a combination of protons and electrons. The electrons reduce the reducible cations of WO_3, and the protons bind to the surface oxygen anions.

Spillover of hydrogen from metal particles on a reducible M_xO_y support can lead to full or partial reduction of the support. After the initial reduction of a M^{n+} cation to a $M^{(n-1)+}$ cation at the metal−support interface, reduction can move over the surface or into the bulk of the M_xO_y. This has been proved by the calculations for MoO_3.[9,10] It means that the electron moves from the $M^{(n-1)+}$ cation to a neighboring M^{n+} cation by exchanging an electron, and that the proton moves at the same time to an O^{2-} anion attached to the adjacent M^{n+} cation. This coherent (because of charge balance) motion of the proton and electron can happen repeatedly, and, in principle, the proton and electron can move over the whole M_xO_y lattice. When the reduction moves away from the metal−support interface, the reoxidized metal cation at the periphery of the metal particle can be reduced by another H atom, and, with time, more and more M^{n+} cations are reduced. The extent of the reduction of the metal oxide depends on the activation energy of the proton−electron migration. The activation energy is low for MoO_3,[9,10] but proton−electron migration may be difficult for metal oxides with different crystal lattices and limited to the immediate environment of the metal particles, as observed for Pt/TiO_2.[12] The number of reduced Ti ions was similar to the number of Pt atoms present in the catalyst. This was interpreted as showing that only those Ti cations under and/or surrounding the Pt particles were reduced (Figure 2). Apart from the reduction of WO_3, MoO_3, and TiO_2 by H atoms spilled over from metal particles such as Pt, also the reduction of many other metal oxides in contact with metals or metal on support catalysts has been observed.[2,13]

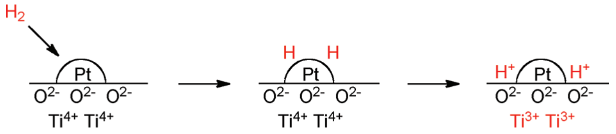

Figure 2. Adsorption of H_2 on Pt and spillover of H atoms to the TiO_2 support, producing protons and Ti^{3+} cations. Redrawn with permission from ref 12. Copyright 1981 American Chemical Society.

While spillover can totally reduce a reducible metal oxide particle that is in direct contact with a metal particle, it is an open question if remote metal oxide that is not in direct contact with the metal can be reduced as well. Probably it can, as long as all metal oxide particles are in good contact with each other. After reduction of a metal oxide particle that is in contact with the metal particle, contact between this reduced metal oxide particle and an unreduced metal oxide particle may then, without too much difficulty, lead to reduction of the unreduced particle through coherent proton and electron movement. If, on the other hand, particles of nonreducible metal oxides are situated between the reducible particles, then remote reduction of reducible metal oxide particles will be difficult if not impossible. This has consequences for TPR diagrams. When all particles of a reducible metal oxide make contact and a few are in contact with metal particles, then one should expect one TPR peak at not too high temperature. For isolated particles of a reducible metal oxide, the TPR peak will be shifted to higher temperature, similar to that of the pure reducible metal oxide.

When TiO_2 that is loaded with metal particles is exposed to H_2, the transmission of the IR spectrum decreases strongly, because a broad IR absorption band develops.[14] This band has been explained by spillover of H atoms from the metal particles to the TiO_2. The hydrogen atoms form electrons and protons on the metal oxide. The protons create charge carriers by forming M−O(H)−M moieties bound inside of the crystal, and the electrons are trapped at defect sites located slightly below the conduction band edge.[15,16] Electronic excitation from these shallow traps into the conduction band occurs by the absorption of IR radiation, giving rise to an intense absorbance over the range 1000−4000 cm^{-1} due to delocalization of the excited electrons in the conduction band. This band is therefore proof for shallow defect sites created by reduction of Ti^{4+} cations by H atoms.

3. SPILLOVER TO NONREDUCIBLE SUPPORTS

3.1. H−D Exchange Is Not Proof of Spillover

Inspired by the evidence of the spillover of H atoms from metals to reducible supports, many scientists assume that analogous spillover takes place from a metal to a nonreducible support such as alumina, silica, silica−alumina, and magnesia. On reducible supports, the H atoms transform into protons and electrons, and both have been detected (section 2). On defect-free nonreducible supports, this transformation and stabilization cannot take place, and only the presence of H atoms is evidence of spillover. H atoms, which spill over to nonreducible metal oxide supports, have not been observed directly, but Carley et al. claimed to have measured them indirectly.[17] They exposed a Pd/Al_2O_3 catalyst to H_2 at room temperature and then added a solution of *N*-benzylidene-*t*-butylamine *N*-oxide. This molecule traps H atoms, and ESR can unequivocally identify the resulting radical. The radical was observed only when both Pd/Al_2O_3 and H_2 were present, and this was considered to be direct proof of hydrogen spillover from the metal particles over the Al_2O_3 support to the organic molecules. However, the solution of *N*-benzylidene-*t*-butylamine *N*-oxide was brought into contact with the hydrogen-covered Pd/Al_2O_3 catalyst, and the molecules might just as easily have reacted with H atoms on the Pd surface as on the alumina. Thus, this ESR investigation does not constitute proof of spilled-over hydrogen atoms on the support.

Since the discovery of spillover, many authors hold H−D exchange between D_2 and hydroxyl groups on the support of metal-supported catalysts for proof of spillover.[18−20] Deuterium atoms, generated on the metal surface by dissociative chemisorption of D_2, are assumed to migrate over the support, where they exchange with the H atoms of the support OH groups (Figure 3). For instance, the disappearance of the OH bands and the appearance of OD bands in the IR spectrum of Rh/Al_2O_3 in contact with D_2 (Figure 4) were ascribed to spillover of D atoms from Rh to the support and to the diffusion of the D atoms over the support surface[19] (Figure 3). Similar observations and conclusions were made in IR studies of mixtures of metal-on-support catalysts and zeolites[18] and in NMR studies of the exchange of OH groups on SiO_2 with D atoms chemisorbed on Pt.[20]

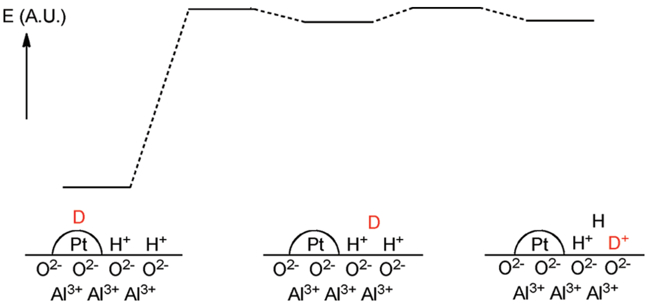

Figure 3. Energy scheme of spillover of a D atom from a metal particle to the support followed by H−D exchange on the support.

Spillover of H atoms to a nonreducible support is, however, energetically highly unlikely. Hydrogen spillover means that a hydrogen atom goes from the metal surface to the support surface and that a reasonably strong M−H bond is broken. The M−H bond strength is larger than one-half the dissociation energy of H_2 (436/2 = 218 kJ/mol), because otherwise the H_2 molecule would not adsorb dissociatively on the metal surface.[8] Indeed, the bond strength between a H atom and a Pt atom on the (111), (100), and (110) surfaces is about 260 kJ/mol.[21] Unless a new bond between the H atom and the support of about the same energy forms in the same elementary process as

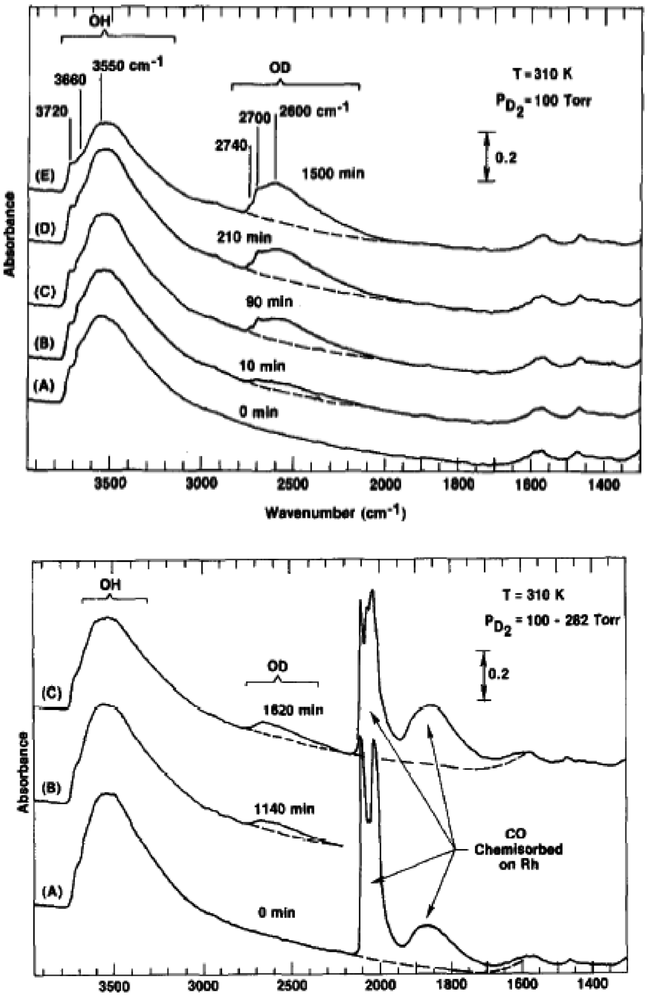

Figure 4. IR spectrum of Rh/Al_2O_3 after admission of D_2 for 0, 10, 90, 210, and 1500 min (top) and of Rh/Al_2O_3 after chemisorption of CO, evacuation, and admission of D_2 for 0, 1140, and 1620 min (bottom). Reprinted with permission from ref 19. Copyright 1981 Elsevier B.V.

the breaking of the M–H bond, the transport of a hydrogen species from the metal particle to the support surface is unlikely. However, according to valence bond theory, a hydrogen atom does not form a chemical bond with atoms with saturated bonds, and ab initio MO calculations indicate that H atoms are repulsed by the low index surfaces of solids with atoms (ions) that have all electrons in closed shells, such as MgO,[22] SiO_2,[23] and γ-Al_2O_3.[24]

Because H atoms do not bind to surface atoms that have saturated bonds, H–D exchange between a deuterium atom that moves as an atom to the support and a support OH group has a high activation energy of about 260 kJ/mol (Figure 3). Protons, on the other hand, have strong chemical bonds to oxygen anions.[23] H atoms can become protons by donating an electron to the support, but this is only possible when the support cations are reducible. In that case, the H atom becomes a proton, a metal cation is reduced, and the energy diagram has a low activation energy (Figure 5). For instance, H_2 reduces WO_3 in contact with metal particles by the reaction of the H atom on the metal with a water molecule, forming a hydrated proton, the H_3O^+ cation, and an electron in the conduction band of the metal.[8] This cation–electron pair moves to the support surface and, on reducible supports, the H_3O^+ cation protonates an oxygen anion and the electron reduces a metal cation.[25] For WO_3, it leads to the formation of H_xWO_3[8] and for TiO_2 to a hydrated surface with Ti^{3+} cations.[12]

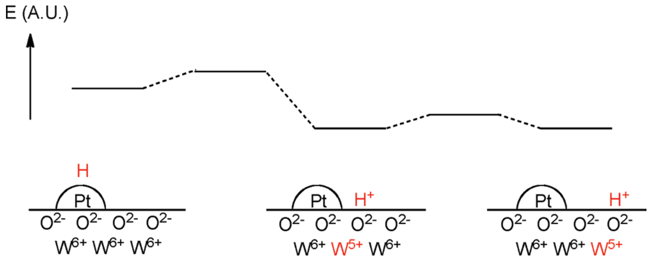

Figure 5. Energy scheme of spillover of an H atom in the form of a proton–electron pair from the metal particle to a support with reducible cations.

For supports with a wide band gap, the electron does not reach the valence band, and the cation–electron pair does not migrate to the support surface. In other words, H–D exchange between metal particles and the surface of SiO_2, Al_2O_3, and zeolites, as represented in Figure 3, is improbable. Dalla Betta and Boudart proposed a solution to this problem in 1976,[26] but this seems to have been largely overlooked in other publications, although Baumgarten and Denecke reiterated it in 1985,[27] without, however, referring to Dalla Betta and Boudart. Figure 6 presents the simple explanation proposed by Dalla Betta and Boudart for the H–D exchange of the hydroxyl groups of a nonreducible support. H–D exchange occurs, but spillover of a hydrogen atom (i.e., net transport of a hydrogen atom) does not occur. First, a D atom on the metal particle exchanges with the H atom of an OH group on the support at the perimeter of the metal particle. A water molecule speeds up this step. Water accelerates the H–D exchange of the support hydroxyls,[7,8,27] because the D–OH exchange at the metal–support interface and the OH–OD exchange on the support surface are aided by hydrogen bonding, which explains why the exchange of some OH groups is fast, while that of others is slow.[27] Apart from small energy differences between M–H and M–D bonds and between O–H and O–D bonds, the H–D exchange process is energetically neutral (Figure 6). The H atom of an OH group on a support is not a hydrogen atom, but rather a proton. Thus, a D^+ cation (deuteron), not a D atom, diffuses over the support by OH–OD exchange between the OD groups around the metal particles and OH groups on the support. Again, this diffusion is accelerated when water molecules are present. In this way, not only is the overall H–D exchange on the support energetically neutral, but also each of the steps along the way. In this H–D exchange, H atoms do not move from the metal particle to the support surface, and thus spillover does not occur (compare with the definition of

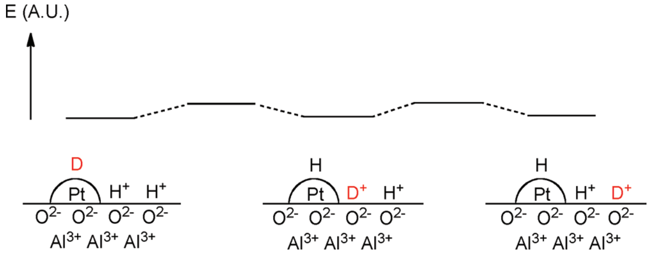

Figure 6. Energy scheme of the exchange of a D atom on a metal particle with a proton on the support followed by proton–deuteron exchange on the support.

spillover in the Introduction). This is the essential difference between Figures 3 and 6. In Figure 3, spillover of a D atom takes place from the metal to the support followed by diffusion of the D atom over the support surface and, finally, in D−OH exchange. Figure 6, on the other hand, shows exchange between a D atom on the metal and an OH group at the metal−support interface, followed by OD−OH exchange on the support surface. In both cases, H−D exchange occurs on the support surface, but in the former case this requires at least 260 kJ/mol (Figure 3), while in the latter case the activation energy is much lower (Figure 6). In analogy to the above explanation for the faster H−D exchange between D_2 and support OH groups in the presence of metals, the faster H−D exchange between silanol groups of SiO_2 and ND_3 in the presence of Rh was explained by the direct interaction of ND_3 adsorbed on the metal with support hydroxyls at the metal−support interface.[28]

An alternative explanation for the observed transfer of adsorbed hydrogen atoms from a metal to an oxide surface is given by H−D exchange with physisorbed species. For H_2O and metal M, the reaction $M{-}D + H_2O_{phys} \rightarrow M{-}H + HDO_{phys}$ followed by $HDO_{phys} + Si{-}OH \rightarrow H_2O_{phys} + Si{-}OD$ could occur. Levy and Boudart showed that water is essential for the transfer of H atoms from Pt to WO_3 and that solvated protons are responsible for the transfer.[8] Water also facilitates the H−D exchange on ZrO_2 in the presence of Cu.[29] The transport of HDO could take place by migration in physisorbed form from metal to support surface or through the gas phase. In both cases, traces of water would increase the H−D exchange rate very much. Gas-phase transport of traces of water would explain the observed H−D exchange between pressed disks of HNaY and Pt/NaY at a distance of several millimeters.[30]

Only when the support is reducible does a D atom move to the support, but spillover of the D atom only takes place at the perimeter of the metal particle. Once the D atom is on the surface, it donates its electron to a metal cation of the support and becomes a deuteron. The deuteron then diffuses over the oxygen anions of the support surface, while the electron moves by exchange between neighboring metal cations in different states of oxidation. For instance, in WO_3, a W^{5+} cation exchanges the electron with a W^{6+} cation. However, the D atom cannot donate its electron to a metal cation of a nonreducible support, and, thus, spillover does not occur. On the other hand, H−D exchange can still occur by the exchange of a D atom on the metal particle with an OH group on the support at the perimeter of the metal particle, followed by OH−OD exchange between the OD and OH groups on the support.

H−D exchange of support OH groups can take place by a reaction with a low activation energy and without net transport of H atoms to the support. H−D exchange of support OH groups by the transport of H atoms to the support is energetically impossible. However, a net transport of H atoms from the metal to the support is required if hydrogen spillover is to explain hydrogenation of molecules on the support. Thus, H−D exchange of OH groups on the support surface is not proof of hydrogen spillover. Nevertheless, a recent publication about the hydrogenation properties of Ag/SiO_2 catalysts stated "The rate of HD exchange of OH groups of the silica support in the presence of silver in comparison to the exchange of the pure support is an indicator for the availability of activated hydrogen on the entire support surface."[31]

3.2. H−D Exchange and Hydrogenation Are Not Correlated

Two publications showed that there is no correlation between H−D exchange and the hydrogenation of molecules adsorbed on a nonreducible support by spilled-over hydrogen.[32,33] Baumgarten et al. studied the H−D exchange of hydroxyl groups on the support and the hydrogenation of unsaturated molecules.[32] They mixed a Pt/Al_2O_3 catalyst with Al_2O_3, upon which unsaturated carboxylic acids were adsorbed to guarantee that the molecules remain on the support and do not migrate to the Pt surface. They did not observe a reaction of the unsaturated compounds with H_2 up to 350 °C. When H_2 was replaced by D_2, again there was no detectable reaction of the unsaturated compounds, but the OH groups of the support were extensively converted to OD groups at 200 °C. Because H−D exchange can be explained by an exchange of an H atom with a proton, but hydrogenation of alkenes needs H atoms, these results suggest that H atoms do not diffuse over the support surface at all.

Miller and Pei obtained results similar to those of Baumgarten et al. for the reaction of ethylbenzene and D_2 over a mixture of Pt@NaA and H-USY.[33] Pt@NaA, in which all Pt ions are supposed to be inside the sodalite cages, was prepared by adding $Pt(NH_3)_4Cl_2$ to the synthesis gel of zeolite NaA. After reduction, the Pt@NaA catalyst had a low CO chemisorption and high H_2 chemisorption. This indicates that the Pt particles were predominantly inside the sodalite cages of NaA, because CO cannot but H_2 can pass through the NaA windows. The Pt@NaA catalyst was mixed with H-USY zeolite, upon which ethylbenzene had been chemisorbed. Reaction of this mixture with D_2 at 75 °C resulted in isotopic H−D exchange of the H atoms of ethylbenzene but not in the saturation of the benzene ring. Because the Pt particles were inside the cages of NaA, which have windows with a diameter of only 0.41 nm, the D_2 molecules reach the Pt particles and produce D atoms by chemisorption, but the benzene molecules are too large to pass through the window and react on the Pt surface. The isotopic H−D exchange took mainly place with the five aromatic H atoms. Miller and Pei concluded that this isotopic exchange takes place by reaction of D atoms, which spill over from the encaged Pt particles to the protonated benzene on the acid sites of the H-USY zeolite. They did not consider the possibility that D atoms on the Pt particles may exchange with protons on the zeolite, and that the resulting deuterons are responsible for H−D exchange in ethylbenzene. This also explains how the D atoms diffuse from the NaA particles to the H-USY particles over a distance of several millimeters; for proton−deuteron exchange, this is no problem. They also reached the conclusion that there are no sites on the H-USY support on which spillover D atoms can hydrogenate benzene.

The results of Baumgarten et al. and Miller and Pei show that H−D exchange occurs even when hydrogenation does not occur. This means that either spillover of H atoms to a nonreducible support does not occur or that it does occur but that the spilled-over H atoms do not react with alkenes and benzene. The former possibility is in agreement with the theoretical prediction that a repulsive interaction occurs between H atoms and surfaces with atoms, the electrons of which are in closed shells.

3.3. No Spillover to Ideal Nonreducible Supports

Sachtler and co-workers demonstrated that H atoms do not spill over to a nonreducible support. They found that the reduction of Fe_2O_3 to Fe_3O_4 in the temperature-programmed reduction (TPR) of a mixture of Pt/zeolite and Fe_2O_3 was enhanced by the presence of the Pt-containing catalyst, but only when the catalyst had been oxidized (Figure 7).[34] TEM and X-ray energy dispersive spectrometry indicated that neither H nor Pt atoms migrated, but rather that Pt oxide (probably PtO_2) migrated from a nonacidic Pt/NaMOR catalyst, while Pt^{2+} cations migrated from acidic Pt/HMOR.[35] During the subsequent TPR run, these Pt species reduced to Pt metal particles on the Fe_2O_3. Hydrogen spillover then took place from Pt to Fe_2O_3, and the TPR peak of the reduction of Fe_2O_3 shifted to lower temperature. Similar results were obtained for mixtures of Pd/zeolite and Rh/zeolite with Fe_2O_3.[36,37] The TPR peak did not shift when reduced Pt/zeolite was mixed with Fe_2O_3. On the other hand, experiments with mixtures of Fe_2O_3 with Pt/TiO_2 or Pt/Fe_3O_4 did show a shift of the TPR peak of Fe_2O_3 to lower temperature. This means that H atoms on the surface of Pt, Pd, or Rh particles supported on a nonreducible support do not reach the Fe_2O_3 crystallites, while H atoms created on the surface of Pt, Pd, or Rh particles supported on a reducible support (such as TiO_2 and Fe_3O_4) do reach the Fe_2O_3 crystallites. In other words, the reducible support, but not the nonreducible support, functioned as bridge for the H atoms between the metal and the Fe_2O_3.

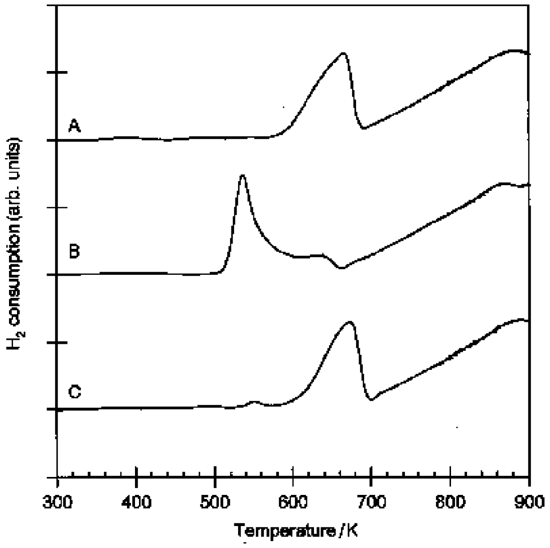

Figure 7. TPR profiles of a physical mixture of (A) Fe_2O_3 and prereduced Pt/Na-MOR, (B) Fe_2O_3 and Pt/Na-MOR after calcination at 400 °C, and (C) Fe_2O_3 and Pt/Na-MOR after storage in air for 6 weeks. Reprinted with permission from ref 34. Copyright 1998 The Royal Society of Chemistry.

The results of Sachtler et al. are in agreement with results of Van Meerbeek et al., who observed that metal oxides migrate easily.[38] When silica gel was treated at 800 °C in H_2 in the presence of a metal near to but not in contact with the silica, IR measurements showed that siloxane bridges were reduced to Si−H groups, and XPS measurements revealed traces of metal on the silica surface. The authors suggested that the metal was transported to the silica surface through the gas phase as an oxide, formed by interaction with traces of water, or as a metal carbonyl, formed by interaction with CO. Reduction by H_2 of the resulting metal compound on the silica provided sites for hydrogen spillover to the silica surface.

Earlier TPR studies indicated that contact or close proximity is required to catalyze the reduction of metal ions by Pt or Pd. This was done by comparing the results of TPR with the results of hydrogenolysis and H−D exchange of cyclopentane.[39] Hydrogenolysis of cyclopentane is much more severe over bimetallic Pt−Re clusters than over Pt or Re clusters. If during the reduction step in the preparation of Pt−Re catalysts spillover of H atoms from Pt to rhenium oxide were to occur, then one would expect almost pure Re particles, few bimetallic Pt−Re particles, and, consequently, weak hydrogenolysis. The opposite was the case, demonstrating that the majority of the reduced Re was present in bimetallic Pt−Re clusters and that migration of rhenium rather than of hydrogen had taken place.

The results of Sachtler and co-workers are in accordance with the theoretical prediction (Figure 3) that spillover of hydrogen atoms from a metal to a nonreducible support (insulator) is improbable. Nevertheless, hydrogen spillover is often evoked to explain catalytic hydrogenation reactions. In sections 5−7, I will show that spillover indeed may play a role in hydrogen storage (section 5), methanol synthesis over Cu/ZnO and Cu/ZrO_2 (section 6), and hydroisomerization over $Pt/SO_4{-}ZrO_2$ and $Pt/WO_x{-}ZrO_2$ (section 7.2), but is not required to explain hydroisomerization in general (section 7.1). First though, spillover to semiconductors and defective insulators will be discussed.

4. SPILLOVER TO SEMICONDUCTORS AND DEFECTIVE INSULATORS

4.1. Semiconductors

As discussed in section 2, a strong loss of IR transmission occurs for reducible metal oxides that are loaded with metal particles and are brought in contact with H_2. Spillover of H atoms from the metal particles produces electrons and protons on the metal oxide. The protons form M−O(H)−M moieties, and the electrons are trapped at defect sites located slightly below the conduction band edge.[16] Electronic excitation from these shallow traps into the conduction band gives rise to intense absorbance in the whole IR region. Also n-type semiconductors loaded with metal particles, such as M/ZnO (M = Cu, Ru, Pt)[15] and Pt/ZrO_2,[40] experience a strong loss of IR transmission upon exposure to H_2. As for reducible metal oxides, this has been explained by spillover of H atoms from the metal particles to the n-type semiconductor, leading to electrons and protons. M/ZnO and M/ZrO_2 catalysts might thus be able to spill H atoms over from the metal particles to the support surface. At elevated temperature, this might even lead to the formation of bimetallic M−Zn particles. As we will see in sections 6 and 7, M/ZnO and M/ZrO_2 catalysts are active in the hydrogenation of CO to methanol and in hydroisomerization, respectively.

Keren and Soffer compared spillover for reducible metal oxides and semiconductors with an electrochemical electrode−electrolyte system.[41] In both cases, H_2 is dissociated to protons and electrons, which migrate to the support surface by protonic and electronic conduction. Ionic and electronic conduction thus is a condition for the use of hydrogenation by spillover to semiconductors. Surface ionic conductivity is assured at sufficient density of surface OH groups and adsorbed water or other hydrogen-bonding molecules. Electronic conduction exists in many transition-metal oxides that are slightly nonstoichiometric or possess crystal defects. The difference between electrolyte system and gas−solid spillover system is that the electrolyte can support a substantial charging of the support surface by protons, because the compensating negative charge can be delivered by anions in the double layer at the surface. In the gas−solid system, however, this is not possible, and protons cannot diffuse over long distances, leaving the electron behind in the metal.[8] The amount of hydrogen that can be taken up must correlate with the “double layer” on the gas−solid interface. This explains the limited coverage of chemisorbed hydrogen, which amounts to only a few hundredths of a monolayer.[41]

Roland et al. proposed a model for hydrogen spillover in which H atoms on the one hand and protons and electrons on the other hand coexist on the surface.[42] With the aid of semiconductor theory and Fermi−Dirac statistics, they showed that at low coverages mainly protons are present at the surface, while at high coverages mainly H atoms are present. This is in accordance with the double layer arguments of Keren and Soffer.[41] The influence of the size of the semiconductor bad gap was not studied.

4.2. Insulators

4.2.1. Hydrogenation in the Absence of a Catalyst. In an unconventional experiment, Teichner and co-workers showed that ethene can be hydrogenated to ethane in the absence of a hydrogenation catalyst and ascribed it to the spillover of hydrogen.[5,43,44] A Pyrex bucket filled with Ni/Al_2O_3 was immersed in pure Al_2O_3 (Figure 8) and reduced with H_2 for several hours at 300 °C. Next, the reaction chamber with $Ni/Al_2O_3 + Al_2O_3$ was cooled in H_2, the Ni/Al_2O_3 bucket was pulled up by a winch mechanism, and a valve was closed, so that the reaction chamber contained only pure Al_2O_3 and H_2. Ethene was added to the chamber, and ethane formed slowly at 110 °C in the absence of a metal, with only Al_2O_3 present in the reactor. The formation of ethane was ascribed to the spillover of H atoms, produced during the prereduction of the Ni/Al_2O_3 catalyst, over the Pyrex surface of the bucket to the pure Al_2O_3 outside the bucket. The spilled-over hydrogen atoms apparently stayed on the Al_2O_3 when the bucket with Ni/Al_2O_3 was pulled up and had converted the alumina into a very unusual hydrogenation catalyst. The spilled-over hydrogen itself was not very reactive, however, and the true agent of hydrogenation was considered to be molecular hydrogen activated on the spillover-treated surface of the oxide.[44] This was deduced from the fact that the amount of ethane formed was much higher than the estimated amount of spilled-over hydrogen (1.5 $cm^3\ g^{-1}$). Furthermore, ethane was not formed in the absence of H_2. Evacuation of the alumina before the reaction suppressed the hydrogenation of ethene. This was ascribed to the removal of spilled-over hydrogen.

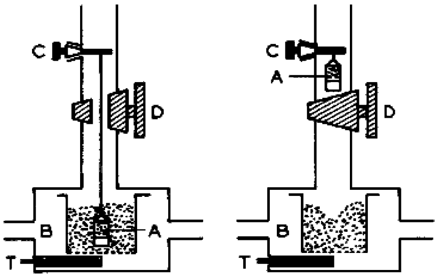

Figure 8. Reactor for measuring hydrogen spillover. On the left with bucket filled with Ni/Al_2O_3 catalyst surrounded by Al_2O_3 support and on the right with bucket pulled up. Reprinted with permission from ref 44. Copyright 1990 Elsevier B.V.

Similar experiments were performed with $Pt/Al_2O_3 + SiO_2$.[45,46] SiO_2 that had been in contact with a bucket filled with Pt/Al_2O_3 and treated with H_2 at 430 °C for 12 h hydrogenated ethene to ethane at 200 °C. On the other hand, neither SiO_2 that had been treated with H_2 at 430 °C for 12 h in the absence of a bucket filled with Pt/Al_2O_3, nor SiO_2 that had been in contact with a bucket filled with Pt/Al_2O_3 but treated with helium at 430 °C for 12 h, showed any hydrogenation activity. The number of sites accepting spilled-over H atoms was estimated to be 10^{12} cm^{-2}, that is, about 0.1% of the surface Si or Al atoms.[46] This means that surface defect sites are involved. Defects on the surface of alumina and silica, treated at high temperature for long periods of time, may be responsible for the hydrogenation activity, but their turnover frequencies are moderate.[47]

A possible explanation of the hydrogenation of ethene in the absence of a metal is that the high-temperature reduction created defects in the alumina, which then accepted H atoms (cf., section 4.2.2), and that the latter hydrogenated the ethene. Bianchi et al. proposed that the hydrogenation reaction proceeds through a radical chain mechanism,[43] analogous to the reverse radical chain formation of ethene in the industrial thermal cracking of ethane to ethene:

$$C_2H_4 + H^\bullet \rightarrow C_2H_5^\bullet \tag{1}$$

$$C_2H_5^\bullet + H_2 \rightarrow C_2H_6 + H^\bullet \tag{2}$$

Addition of NO, a radical chain inhibitor, inhibited the formation of ethane. The activation energy of both radical reactions 1 and 2 is low,[48] and the hydrogenation of ethene is feasible at around 100 °C.

Other groups confirmed that alkenes can be hydrogenated without direct contact of alkene and H_2 with a catalyst. Baumgarten et al. placed a sample of diphenylpicrylhydrazyl, anthracene, or anthraquinone below a Pd/SiO_2 catalyst and fed H_2 through the reactor at 60−100 °C. All three organic compounds could be hydrogenated, and the rate was faster when the distance between catalyst and organic sample was smaller.[49] The hydrogenation was ascribed to H atoms that migrated through the gas phase from the catalyst bed to the organic compound. Amir-Ebrahimi and Rooney placed a sample of Mn^{3+}/MgO below a Pt/SiO_2 catalyst and fed H_2 through the reactor at 380 °C. ESR showed that samples of the Mn^{3+}/MgO taken after reaction contained a high concentration of Mn^{2+} cations.[50] The authors suggested that H atoms that were formed on the Pt moved through the gas phase and reacted with the glass in contact with the Mn^{3+}/MgO, thereby creating new sites for dissociative adsorption of H_2. Spencer et al.[51] doubted the spillover interpretation of the experiments of Baumgarten et al.[49] because the equilibrium number of H atoms that can be produced below 100 °C is many orders of magnitude lower than needed for the observed hydrogenated organic compounds. They therefore suggested that very small traces of oxygen in the gas had provided the combustion energy to create the H atoms needed to explain the observed reductions. Baumgarten and Krupp therefore reinvestigated the influence of oxygen on gas-phase hydrogen spillover.[52] They led hydrogen over Pt/Al_2O_3 and brought it in contact with a stream of hexene below the catalyst bed. Also in this case, hydrogenation took place. Oxygen addition to the hexene increased the hexene conversion, NO addition lowered it, while water and nitrogen had no influence. The hydrogenation of hexene without contact with a catalyst was ascribed to the spillover of H atoms through the gas phase from the Pt/Al_2O_3 bed to the downstream zone and the positive influence of O_2 and negative influence of NO to a branched radical-chain reaction between H atoms and O_2 molecules.

4.2.2. Defects. Not only supports exposed to spillover H atoms, but also supports treated at elevated temperature can hydrogenate organic compounds. For instance, alumina hydrogenated ethene around room temperature after evacuation at 650 °C for 17 h,[53] and silica hydrogenated unsaturated molecules at 300 °C after activation in H_2 at 320 °C for 16 h.[54] Although no metal or metal/support catalyst was present during the activation, the treated alumina and silica could hydrogenate organic compounds. This is different from the experiments of Teichner c.s., in which the alumina or silica was in contact with a metal catalyst during treatment in hydrogen.[5,43−45] Like Teichner and co-workers, Rajagopal et al. explained their results by a radical chain mechanism (eqs 1 and 2) on active Si−H sites in $(SiO)_2Si(OH)-O-Si(H)(OSi)_2$ chains.[54] These sites were assumed to be formed by reaction of H_2 with $(SiO)_2-Si{=}(O)_2{=}Si(OSi)_3$, which formed by dehydration of silanol groups. It is well-known that defects are present on support surfaces, especially when they are heated to high temperature. For instance, three-ring aromatics and alkenes lose an electron and become cation radicals when adsorbed on zeolites that contain extra-framework alumina,[55] and zeolite H-ZSM-5 gives off H_2 when heated to high temperature.[56] Larson and Hall showed that H−D exchange occurred between CD_4 and CH_4 over Al_2O_3 that had been heated at 515 °C for 16 h and suggested that CH_4 may be activated to Al−CH_3 and Al−OH groups.[57] IR investigations by Joubert et al. confirmed that Al−CH_3 bonds are formed when γ-Al_2O_3, which had been calcined for 18 h and subsequently evacuated at 500 °C for 18 h, is exposed to CH_4. They also showed that Al−H bonds are formed when γ-Al_2O_3 was exposed to H_2.[58] Analogously, metal−hydride bonds were observed when ZnO and ZrO_2 were heated in H_2,[59] and Si−H bonds were observed when Ta and Zr hydride complexes, anchored to a SiO_2 surface, were heated under H_2.[60,61]

Temperature-programmed desorption (TPD) of hydrogen also provided evidence for spillover of hydrogen to Al_2O_3. Kramer and Andre observed a peak at around 450 °C in the TPD of hydrogen from Pt/Al_2O_3 and Ni/Al_2O_3 catalysts that had been reduced in H_2 at 400 °C.[62] A similar TPD peak was observed when Al_2O_3 was treated in hydrogen in a high-frequency discharge at room temperature. The authors therefore suggested that these peaks are identical and originate from atomic hydrogen in contact with the alumina. In the first case, the atomic hydrogen is generated by the metal and is spilled over to the support, while in the second case the atomic hydrogen is generated by the discharge and reaches the support through the gas phase. The number of the spilled-over H atoms was estimated to be in the order of 2×10^{12} cm^{-2}, that is, 0.1% of the surface OH groups.

As Kramer and Andre,[62] Miller et al. observed a peak around 400 °C in the TPD of hydrogen from Pt supported on SiO_2, Al_2O_3, and LTL and MAZ zeolites and originally concluded that this peak resulted from desorption of hydrogen that had been spilled over from the metal particles to the support.[63] However, in a follow-up study,[64] they withdrew this conclusion, because they did not observe the high-temperature TPD peak in a second experiment, after rereduction of the catalyst. Also, when they increased the calcination temperature of the catalyst, the intensity of the high-temperature TPD peak decreased. After pretreating the catalyst with N_2, the low-temperature peak disappeared, but the high-temperature peak did not (Figure 9).

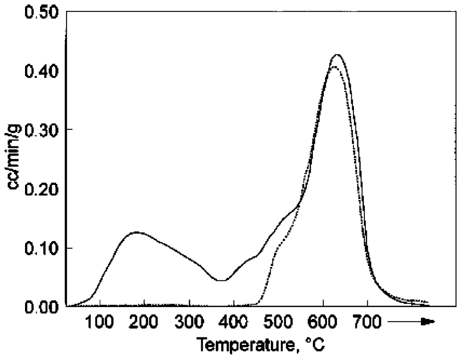

Figure 9. H-TPD of Pt/H-LTL reduced at 250 °C (−) and of Pt/H-LTL heated at 300 °C in N_2 (···). Reprinted with permission from ref 64. Copyright 1990 Elsevier B.V.

The latter experiment demonstrates that hydrogen is not the cause of the high-temperature TPR peak. Therefore, Miller et al. concluded that spillover hydrogen cannot explain this peak. Instead, they attributed it to the decomposition of NH_3 that had been adsorbed on the acid sites of the supports during catalyst preparation with $Pt(NH_3)_4Cl_2$. The chemisorbed NH_3 underwent isotope exchange with D_2. The authors explained this by spillover of D atoms from Pt to NH_3 molecules on the support, but it can also be explained by the formation of OD groups on the support surface by OH−OD exchange (cf., section 3.1, Figure 6), followed by NH_3−OD exchange on the support.

Neither the Pt@NaA catalyst nor a mixture of Pt@NaA and H-LTL catalyzed the hydrogenolysis of neopentane to methane and isobutene, $H_2 + (CH_3)_4C \rightarrow CH_4 + (CH_3)_3CH$, and the isomerization of neopentane to isopentane, $(CH_3)_4C \rightarrow (CH_3)_2CHCH_2CH_3$.[64] Thus, although H−D exchange of NH_3 took place, neopentane did not react. This is similar to benzene hydrogenation over Pt@NaA (section 3.2), in which H−D exchange of benzene occurred but not hydrogenation of benzene.[33] It again demonstrates that H−D exchange on the support does not have to be correlated with the reaction of a hydrocarbon in which hydrogen is involved.

Not only experiment but also theory indicated that H atoms can be present at support surfaces. H atoms are not stable at low index planes (section 3.1), but the reaction of H_2 with Al defect sites on the alumina surface is quite exoenergetic (−163 kJ/mol) for three-coordinated Al atoms (with high Lewis acidity) and four-coordinated Al atoms (−60 kJ/mol).[61] Similarly, Hartree−Fock[65] and DFT calculations[66] showed that defect sites on the silica surface (dangling sp^3 Si bonds, nonbridging Si−$O^\bullet$ radical centers, and neutral Si−Si oxygen vacancies) can react with H_2 to Si−H centers and H atoms, and that the reactions are exothermic with low activation energies.

Several theoretical studies have been carried out of the interaction of H_2 with MgO surfaces. They showed that H_2 molecules do not dissociate at (100) MgO surfaces,[22] but that exothermic dissociation is possible at surface defects. The reason is that defects have radical character and thus can bind (radical) H atoms. For instance, a self-trapped hole (O^- on the surface)[22] and a V center (two holes trapped in a cation vacancy, $O^-{-}V_{Mg}{-}O^-$) can dissociate H_2 and form two OH^- ions.[67] An OH^- anion and MgH^+ cation, a hydride anion bonded to a Mg^{2+} cation, can be formed when H_2 interacts with a V^- center (a hole trapped in a cation vacancy, $O^-{-}V_{Mg}{-}O^{2-}$),[22] with a double vacancy (V_{Mg}, V_O),[68] with neighboring Mg^{2+} and O^{2-} ions at a Mg_4O_4 cluster,[69] and with exposed edge and kink sites of a (100) MgO surface.[70] Because of the surface defects, MgO can equilibrate a $H_2{-}D_2$ mixture already at −196 °C. Boudart et al. ascribed the equilibration to V_I centers, consisting of three oxygen anions and a Mg cation vacancy $(O{-}V_{Mg}{-}O{-}O)^{4-}$, which are able to dissociate the H_2 molecule and form $(OH{-}V_{Mg}{-}OH{-}O)^{4-}$ centers at which H−D exchange occurs.[71] The number of defect sites is low, however, and the fraction of surface MgO sites that is able to split H_2 has been estimated as 0.6% after activation at 850 °C and orders of magnitude less after activation at 400 °C.[72]

It might well be that the hydrogenation of alkenes over pure supports, in the absence of a metal catalyst,[43−46,53,54] is due to surface defects. Defects are created by high temperature treatment during long time, and these are exactly the conditions used in the experiments of Teichner c.s. The presence of H atoms spilled over from a metal catalyst to the pure support might increase the number of defects on the pure support. The results of Baumgarten c.s.[49,52] are more difficult to explain. Maybe H atoms are indeed transported through the gas phase or along the wall of the reactor from the catalyst bed to the down-flow part of the reactor, where gas-phase hydrogenation took place. The thermodynamic objections of Spencer et al. remain to be answered, however.

Another question that is still unanswered is if the rate of hydrogen spillover and subsequent hydrogenation of the organic molecule on the support is competitive with hydrogenation directly on the metal surface. Spillover means that an H atom moves from the metal surface to the support surface and migrates over the surface until it finds a molecule that can be hydrogenated. The decrease in free enthalpy between initial and final state is the thermodynamic driving force of spillover. Before an H atom reaches the molecule that is to be hydrogenated, it must migrate over the support surface. Because H atoms are bonded strongly to the metal surface and very weakly to the support (section 3.1), there is a large positive enthalpy difference between an H atom on a metal atom and an H atom on a support atom (>260 kJ/mol).[21] On the other hand, at low temperature, there is a positive entropy difference, because diffusion on the metal is then limited by high H coverage, while on the support there is two-dimensional translational freedom of the H atoms. At 300 K, $T\Delta S$ is about 20 kJ/mol (the entropy of a hydrogen atom with three degrees of translational freedom is 0.11 kJ/mol·K at 300 K),[73] much smaller than ΔH. At higher temperature, $T\Delta S$ is even smaller, because, even though T is higher, ΔS is much lower due to the almost unrestricted diffusion of H atoms on the metal surface when the surface coverage becomes low. Thus, in all cases, the enthalpy change dominates, and the migration of an H atom from a metal atom to the support will constitute the rate-determining step in the spillover process.

The rate of spillover will thus be equal to the rate of the H migration step, and this rate can be estimated by transition state theory. In analogy to the desorption of a molecule from a surface, the rate of migration of a H atom from the metal surface to the support is $r = \nu \cdot \exp(-\Delta E/kT)$, where the frequency factor ν is dependent on the partition functions of the initial and transition state, and ΔE is the energy difference between initial and transition state.[74] For ΔE, one can take the Pt−H bond strength, which is about 260 kJ/mol.[21] In that case, even for a high frequency factor ν of 10^{16} s^{-1}, transition state theory predicts a rate of 2×10^{-7} s^{-1} at 600 K for the migration of a H atom from a Pt atom to the support. Thus, for nonreducible supports with a very low or even repulsive interaction between an H atom and the surface, the rate of hydrogen spillover is much lower than observed for reactions that have been ascribed to spillover.[3,6]

Also from another perspective it can be concluded that spillover of H atoms does not play an important role in the hydrogenation of molecules on the support. Spillover can be compared to the reaction sequence A ↔ B → C, in which two reactions take place on catalytic sites that are separated in space on the catalyst surface. The intermediate molecule B must diffuse from the site on which it is created to the second site on which it reacts further to C. As discussed by Weisz,[75] if the A ↔ B equilibrium is strongly on the side of A, the conversion of A to C depends on the distance between the two catalytic sites. If the distance is very small, the irreversible B → C reaction shifts the pre-equilibrium and all A molecules will react to C, even though at all times the concentration of B molecules is extremely low. On the other hand, if the distance is very large, then the conversion is determined by the A ↔ B equilibrium and low. Also in spillover there is a pre-equilibrium, between an H atom on the metal and an H atom on the support, which is strongly on the side of the initial state. The H atom then diffuses over the support surface until it encounters a reducible molecule A and reacts with it. This gives the sequence H−M ↔ H−S → HA. Full hydrogenation can be obtained if the distance between the metal site and the reducible molecule is small. If the distance is large, then the conversion is limited by the equilibrium H−M ↔ H−S and will be very low. Using the results of Weisz,[75] one can estimate that for $E(H{-}S) - E(H{-}M) > 140$ kJ/mol the distance between the H−M ↔ H−S site (metal particle) and H−S → HA site (hydrogenation site) must be smaller than 0.1 nm, otherwise the conversion is extremely small. That means that molecules that are to be hydrogenated must be in direct contact with the H atoms on the metal surface and shows that spillover of H atoms does not play a role in hydrogenation over defect-free supports of nonreducible metal oxides.

5. SPILLOVER FOR HYDROGEN STORAGE

5.1. Spillover to Carbon

Spillover has been reported to be important for hydrogen storage. Global warming has made us aware that an economy based solely on oil and coal as fossil fuels will lead to a strong increase in the concentration of CO_2 in the atmosphere. An economy based on hydrogen might alleviate this problem. However, before this is possible, several scientific problems must be solved. One of them is hydrogen storage for fuel cell applications. The aim is to develop a system that operates near room temperature and at moderate pressure and rapidly adsorbs and desorbs hydrogen. Porous materials such as zeolites,[76,77] metal−organic frameworks (MOFs),[78−81] and carbon materials, especially carbon nanotubes,[82−85] are under investigation for hydrogen storage. Storage of molecular hydrogen relies on weak physisorption (<10 kJ/mol) and, thus, must be carried out at high pressure and low temperature.

Some studies have cast doubt on the usefulness of carbon as a storage material for hydrogen. Tibbets et al. studied nine different carbon materials but did not observe any hydrogen sorption appreciably above background at room temperature, suggesting that the actual sorption for these carbon materials is very small.[84] The broad range of carbon materials evaluated, the very low values obtained for storage capacity, and possible experimental deficiencies in the papers, which claim high storage capacities, made Tibbets et al. skeptical of the claims for large hydrogen sorption at room temperature. They believed that claims of more than 1 wt % hydrogen sorption at room temperature are due to experimental errors. Hirscher and Becher came to similar conclusions.[85] They expressed serious doubt about several key experiments that had caused considerable controversy and concluded that high hydrogen storage capacities measured for carbon nanofibers had not survived cross-checking in different laboratories.

Hydrogen can also be stored as atoms by chemisorption and, thus, under ambient conditions. Metal particles can then be used as portholes for the formation of hydrogen atoms, which spill over to and spread over the carbon surface and increase the storage capacity.[86−88] As discussed in section 3, the transfer of H atoms from a metal surface to the perfect surface of a nonreducible material is improbable. Therefore, transport of H atoms across the surface of ideal zeolites and MOFs is not expected under ambient conditions. Nevertheless, a recent claim that atomic hydrogen (generated from the spillover of hydrogen from Pd particles) can penetrate the hexagonal openings of the zeolite Y framework and diffuse into the sodalite cages and affect the H_2 storage capacity of zeolite Y shows that some scientists still consider H−D exchange to be proof of spillover of H atoms.[89] On the other hand, transport of H atoms over the surface of zeolites and MOFs with defects and over carbon surfaces is, in principle, possible. Robell et al. studied hydrogen uptake on platinized carbon several years ago.[90] After initial fast adsorption on the Pt particles (0.1 cc/g), the uptake of hydrogen slowed and amounted to 1.4 cc H_2/g after an hour at 350 °C. The extra hydrogen uptake of 1.3 cc/g was much larger than the amount of hydrogen taken up by the carbon alone (0.3 cc/g) and increased with temperature. This was ascribed to the activated diffusion of H atoms away from the Pt particles. In subsequent work, Boudart et al. observed that cleaning Pt in oxygen at 350 °C slowed the further uptake of hydrogen.[91] They proposed that contamination of the metal particles by carbon provides bridges between Pt particles and the carbon support particles, which allow surface diffusion of H atoms from Pt to the support. Neikam and Vannice demonstrated that perylene, a pentacyclic aromatic molecule, considerably enhanced the adsorption of hydrogen onto a Pt/Ce−Y catalyst.[92] H_2 uptake was proportional to the amount of perylene, and more than 100 H_2 molecules were taken up per perylene molecule. The perylene molecules function as bridges for H atoms, which migrate from the Pt particles to the support where they reduce the Ce^{4+} ions. More recently, Lachawiec et al. used carbon bridges to improve the hydrogen storage properties of nanostructured carbon.[93] They took Pd/C as the source of the H atoms and single-walled carbon nanotubes as the receptor for the H atoms (Figure 10). By carbonizing glucose, a carbon bridge-forming precursor, in the presence of Pd/C and single-walled carbon nanotubes, the amount of hydrogen adsorbed increased substantially.

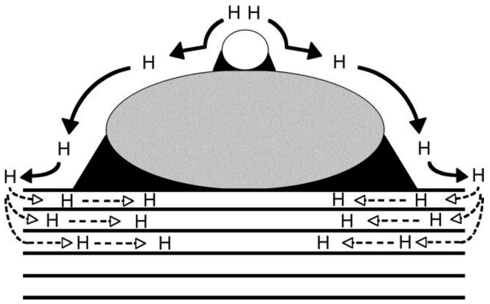

Figure 10. Primary spillover of hydrogen from the metal particle to the support (gray) and secondary spillover from the support to the receptor (graphene sheets) enhanced by carbonaceous bridges. Reprinted with permission from ref 93. Copyright 2005 American Chemical Society.

Three DFT studies and one MO study demonstrated that H atoms bind exothermally to single-walled carbon nanotubes, graphene, and coronene, a 7-ring aromatic hydrocarbon that is used as a model for graphite.[94−97] Chen et al. obtained binding energies of the H atoms of 80−140 kJ/mol,[94] Kayanuma et al. of 60−190 kJ/mol,[95] and Wang et al. of 66 kJ/mol.[96] Yet all H−C binding energies were smaller than 200 kJ/mol, which means that a H_2 molecule cannot split into two H atoms on a carbon support,[94−96] because 218 kJ/(mol·H) is needed to break the H_2 bond (436 kJ/mol). Molecular dynamics calculations therefore showed that physisorbed H atoms on fullerenes and graphene more easily react with each other to form H_2 molecules than with the substrate to form C−H bonds.[97] Only Yang et al. calculated high binding energies of 300−400 kJ/mol (Figure 11),[98] which may be due to the use of an SCF (ONIOM) method. DFT calculations by Psofogiannakis and Froudakis also demonstrated that H atoms do not migrate from Pt to graphite under normal conditions to any significant effect and that the spillover mechanism cannot operate in a system composed of metal particles and a carbon support.[99] While H atoms can chemisorb on coronene, they bind stronger to Pt atoms and clusters than to coronene by about 300 kJ/mol.

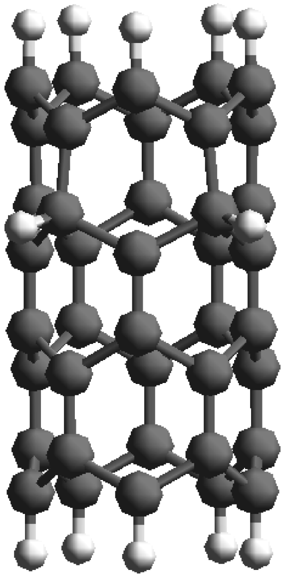

Figure 11. Single-walled carbon nanotube with two H atoms adsorbed at nonadjacent exterior positions. Reprinted with permission from ref 98. Copyright 2006 American Chemical Society.

Apart from binding to ideal carbon surfaces, hydrogen atoms can also adsorb at defect sites or armchair and zigzag edge sites of graphite crystallites. Defect sites may be created near metal particles by H_2 reduction during catalyst preparation as a result of the methanation of carbon catalyzed by the metal. The resulting C−H bonds may be strong enough to allow H spillover from metal to carbon. Inelastic neutron scattering of H atoms, spilled over from Pt and Ru metal particles to carbon black, provided evidence of the formation of C−H bonds at dangling bonds of carbon edge sites,[100] and thus of hydrogen spillover. Too strong C−H bonds may hinder hydrogen desorption from carbon materials, however, and would make spillover of little value for hydrogen storage. Yoo et al. observed that desorption of H_2 from carbon nanotubes, doped with Pd as well as with La to create defects, only began at 530 °C, indicating reasonably strong C−H bonds.[87] Others, on the other hand, observed that most of the hydrogen, which was adsorbed during adsorption isotherm measurements, was reversibly desorbed at 20 °C,[98] with only a fraction remaining at the carbon surface during desorption. This might suggest that most H_2 molecules are not taken up as H atoms during adsorption but as physisorbed H_2 molecules.

Not only defects, but also oxygen groups, may allow H spillover from metal particle to carbon support, as experimental and theoretical studies have shown. Thus, oxygen plasma treatment enhanced the hydrogen storage capacity of template carbon.[96] This was ascribed to semiquinone groups created at the carbon surface by the plasma treatment. MO calculations indicated H binding energies of 196, 164, and 263 kJ/mol(H) for semiquinone, carboxyl, and lactone groups, respectively.[96] These values are close to the 218 kJ/mol needed for spillover from metal to carbon. Psofogiannakis and Froudakis calculated that, when epoxide and hydroxyl groups are present on a graphitic surface, migration of a H atom from a Pt article to an epoxide group and forming an OH group was exothermic by 65 kJ/mol and that the energy barrier was only 39 kJ/mol.[101] Exchange of the H atom between an OH group and an adjacent epoxide group had an energy barrier of 32 kJ/mol. This easy migration of the H atom might explain why “carbon bridges” that contain oxygen functionalities enhance spillover capacity.[86,98]

The theoretical and experimental results of hydrogen adsorption on graphitic structures are of interest not only for hydrogen storage, but also for catalysis. While it was shown in section 3 that hydrogen spillover does not occur from a metal to a defect-free nonreducible support, the discussion in this section shows that spillover to a carbon support may be possible. Therefore, spillover to a nonreducible support may be possible when a graphitic type of carbonaceous material covers the support. Carbonaceous deposits are easily produced in reactions of unsaturated hydrocarbons and organic molecules. Fragments of such deposits may function as transfer agents in hydrogen spillover from the metal particles to molecules adsorbed on the support. The temperatures applied in catalysis are higher than in hydrogen storage and desorption. Thus, relatively strong C−H bonds are less of a problem in H-transfer catalysis than in hydrogen storage.

5.2. Spillover to MOFs

Metal−organic frameworks (MOFs) are promising candidates for hydrogen storage.[78−81] They consist of metal cations that are coordinated by multidentate organic ligands, and the size of the organic groups leads to a large distance between the metal cations and to a porous structure with wide pores. Because of the large surface area and pore volume, MOFs are investigated as possible storage materials for gases, for example, H_2. An often used MOF is IRMOF-1, that is constructed of clusters of four Zn^{2+} cations that are tetrahedrally coordinated by benzenedicarboxylate (terephthalate) anions. Li and Yang used spillover from a Pt/C catalyst to enhance the hydrogen uptake of MOFs at room temperature.[102] The H atoms move from the Pt surface to the carbon support and then to the MOF. The understanding of this spillover is limited, however. Whereas H atoms bind exothermally with graphite and other carbon structures, it is not clear how H atoms would bind to the organic units in MOFs. An MO calculation by Li et al. resulted in binding energies of an H atom to Zn, O, and C atoms of the benzene dicarboxylate unit of 3−50 kJ/mol.[103] These low values are insufficient for H spillover from metal to MOF. The MO calculations of Li et al. have been corrected by Mavrandonakis and Klopper.[104,105] By including zero-point vibrational energy, they obtained endothermic energies for the reaction of a H atom with the benzene dicarboxylate unit. On the other hand, reaction with H_2 gave exothermic reaction energies. Lee et al. also found that addition of one H atom gave endothermic binding energies, while exothermic values were obtained after addition of two H atoms.[106] The explanation is that the addition of one H atom disturbs the conjugation of the benzene ring and leaves an unpaired dangling bond. The addition of a second H atom passivates this dangling bond, thereby stabilizing the state with two added H atoms relative to that with one H atom added. Introduction of a hole in the benzene dicarboxylate (removal of an electron) makes the addition of one H atom exothermic.[106] Zinc vacancies in the MOF structure could be the source for the hole, but the hydrogen storage capacity of MOFs would be quite limited.

Recently, Luzan and Talyzin[107] and Hirscher c.s.[108,109] claimed that the spillover effect from Pt/C catalyst to MOF is below the detection limit. In reply, Yang and co-workers noted that the methodology to maximize spillover is still an art and that spillover depends on many experimental factors.[110,111] Luzan and Talyzin repudiated, however, that such factors could explain the absence of spillover in their experiments with Pt/MOF-5 materials.[112]

6. SPILLOVER ONTO ZnO AND ZrO_2. METHANOL SYNTHESIS

For decades, methanol has been industrially produced over a Cu/ZnO catalyst. Although intensive research has been carried out, several aspects of the mechanism of methanol synthesis, the nature of the catalytically active sites, and the importance of copper and zinc oxide are still the subject of much controversy. The most popular models are based on copper in the metallic state, either as pure Cu sites or as Cu−Zn alloy sites. It has been proposed that ZnO influences the dispersion and morphology of the Cu particles,[113] that ZnO provides Zn atoms for surface Cu−Zn alloy sites,[114] and that ZnO provides basic sites in a bifunctional catalyst.[115] In some bifunctional catalyst models, spillover of hydrogen is important. Burch et al. reported that a physical mixture of Cu/SiO_2 and Zn/SiO_2 had a much higher activity in the synthesis of methanol than the separate components. However, when separated from the mixture after reaction, Cu/SiO_2 had low activity.[116] These results showed that, even if Zn is transferred to the Cu/SiO_2, it would not be responsible for the synergy between Cu/SiO_2 and Zn/SiO_2. Transfer through the gas phase of reaction intermediates from one component to the other has been ruled out by experiments with beds separated by plugs of glass wool. These experiments with triple beds of $Cu/SiO_2//Zn/SiO_2//Cu/SiO_2$ and $Zn/SiO_2//Cu/SiO_2//Zn/SiO_2$ showed no synergy. TPD experiments showed two H_2 desorption peaks, attributed to H atoms on the Cu and the ZnO surfaces.[117,118] It was concluded that the H atoms on the ZnO were formed by spillover from the Cu to the ZnO surface. Burch et al. proposed two explanations for the synergy effect in the synthesis of methanol.[116] First, H atoms produced on the Cu surface spill over to the ZnO surface where they are trapped at surface defects and provide a reservoir of H atoms, which can migrate to other Cu particles and further the conversion of Cu formate to more fully hydrogenated species. Second, H atoms spilled over to the ZnO react with Zn formate to produce methoxy species on the ZnO.

From FT-IR and TPD experiments, it was concluded that methanol synthesis from CO_2 and H_2 occurred by the hydrogenation of formate species adsorbed on the Cu surface of Cu/ZnO.[118] Methanol synthesis from CO and H_2, on the other hand, proceeded by hydrogenation of formate on Zn cations to methoxide on Zn. Experiments over ZnO alone revealed formate but no methoxide on Zn cations. This suggested that hydrogen activated at Cu and spilled over to ZnO is responsible for the hydrogenation of HCOO−Zn to CH_3O−Zn over Cu/ZnO.

While some authors explain methanol synthesis by bifunctional catalysis and hydrogen spillover, others explain it by monofunctional catalysis on the copper surface, without hydrogen spillover. The state of zinc under industrial conditions is still being strongly debated. Opinions range from pure ZnO to the reduction of ZnO and the formation of a surface Cu−Zn alloy[114] and to the formation of a subsurface zinc hydride layer.[119] This does not help to reach a conclusion concerning the existence of spillover and its possible role in methanol synthesis over Cu/ZnO.

Zirconia (ZrO_2) is another effective support in methanol synthesis. As compared to ZnO, its chemistry is simpler and its chemical state in methanol synthesis is better understood. Its high catalytic activity in methanol synthesis and in hydroisomerization (section 7) has been attributed to hydrogen spillover. Like Cu/ZnO, $Cu-ZrO_2/SiO_2$ has been claimed to act as a bifunctional catalyst. When exposed to H_2 and CO_2 or CO,[120] the majority of the carboxylate, (bi)carbonate, and formate species were associated with ZrO_2. In the presence of H_2, these species became formate species, and subsequently methoxide species adsorbed on ZrO_2 (Figure 12). Cu greatly accelerated the hydrogenation of bicarbonate to formate species and the hydrogenation of formate to methoxy species: $HCO_3^* \rightarrow HCOO^* \rightarrow CH_3O^*$, where "*" denotes a site on the ZrO_2 surface. In the hydrogenation of CO_2, Cu promoted the reductive elimination of methoxide species as methanol, $CH_3O^{**} + H_2 \rightarrow CH_3OH + H^{**}$, where "**" denotes a site on the Cu surface, but the hydrolytic release of methoxide species from the ZrO_2 support, $CH_3O^* + H_2O \rightarrow CH_3OH + HO^*$, occurred much more rapidly. In the presence of Cu, spillover of absorbed CO from Cu to zirconia facilitated the formation of formate on zirconia at lower temperatures in the hydrogenation of CO. The reductive elimination of methoxide species appeared to be the slow step in methanol formation by CO hydrogenation.

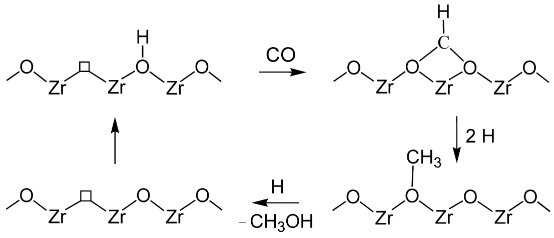

Figure 12. Mechanism of the synthesis of methanol from CO over Cu/ZrO_2. Redrawn with permission from ref 120. Copyright 1998 Elsevier B.V.

Thus, it was assumed that methanol synthesis over $Cu/ZrO_2/SiO_2$ occurs on ZrO_2, and that the primary role of Cu is to dissociatively adsorb H_2. The spillover of atomic H onto ZrO_2 provides the source of hydrogen required for the hydrogenation of the carbon-containing species. Cu and ZrO_2 were assumed to be in close proximity,[120] and CO molecules, adsorbed on coordinatively unsaturated Zr^{4+} ions, are hydrogenated in steps to methanol by H atoms that spill over from the Cu particles to the ZrO_2 support. Adsorbed water inhibited the rate of H−D exchange on ZrO_2, but increased it over $Cu-ZrO_2$.[29] Water is known to inhibit the dissociative adsorption of H_2 on ZrO_2;[121] this dissociation seems to be rate determining over ZrO_2. On the other hand, Cu can easily dissociate H_2, and water is not adsorbed strongly on Cu. Thus, for $Cu-ZrO_2$, the rate-determining step is the diffusion over the support surface by OH−OD exchange, explaining why water (through hydrogen bonding) enhances the rate of H−D exchange. The presence of formate groups on the ZrO_2 surface, formed primarily by the insertion of CO into HO−Zr bonds on the surface of ZrO_2 and also by the reaction on the Cu surface and spillover of formate onto the surface of ZrO_2, slowed the rate of H−D exchange,[29] probably because these groups block OH−OD exchange.

In the reverse reaction, that is, the decomposition of methanol over ZrO_2/SiO_2 or $Cu-ZrO_2/SiO_2$, the majority of the observed surface species were also associated with zirconia.[122] Methanol adsorption led to methoxide formation and in the presence of Cu methoxide species on ZrO_2 dehydrogenated to formaldehyde above 50 °C and decomposed to CO, CO_2, and H_2 above 130 °C. In the absence of Cu, methoxide species on ZrO_2 decomposed only very slowly at 250 °C. Methanol decomposition over $Cu-ZrO_2/SiO_2$ was assumed to occur primarily on ZrO_2, with the main function of Cu being a porthole for the removal of hydrogen by reverse spillover of H atoms from the support to the metal, combination to H_2, and desorption.[122]

Jung and Bell observed that the rate of H−D exchange on Cu/ZrO_2 was more than an order of magnitude faster than the rate of methanol formation.[29] Assuming that the rate of hydrogen spillover can be obtained from the dynamics of H−D exchange, they concluded that the rate of hydrogen spillover from Cu is not rate limiting in the synthesis of methanol over Cu/ZrO_2. However, as shown in section 3.2, H−D exchange is not related to spillover, and therefore this conclusion cannot be drawn. $Cu/m-ZrO_2$ (monoclinic, m) was 10 times more active for methanol synthesis than $Cu/t-ZrO_2$ (tetragonal, t) for the same Cu surface area.[123] This difference correlated with the stronger and higher CO adsorption of the $Cu/m-ZrO_2$, which was attributed to the presence of a high concentration of anionic vacancies on the surface of $m-ZrO_2$. These vacancies (coordinatively unsaturated (cus) Zr^{4+} cations) act as Lewis acid centers and increase the Brønsted acidity of adjacent Zr−OH groups. This in turn enhances the adsorption of CO as

HCOO−Zr groups, which are the initial precursors to methanol. Spillover of H atoms and the formation and reduction of formate and methoxide species proceeded more rapidly on Cu/m-ZrO_2 than on Cu/t-ZrO_2. Incorporation of Ce into ZrO_2 led to Cu/$Ce_xZr_{1-x}O_2$ catalysts with improved catalytic activity.[124] The maximum activity correlated with maximum H_2 adsorption due to reduction of Ce^{4+}−O−Zr^{4+} to Ce^{3+}−O(H)−Zr^{4+} centers formed by dissociative adsorption of H_2 on Cu particles and spillover of H atoms onto the support surface.

Spillover has also been proposed as an explanation for the promoting effect of basic metal oxides on the methanol activity of Pd/SiO_2 and Cu/SiO_2 catalysts.[125] Whereas the activity of a Pd catalyst supported on ultrapure SiO_2 was very low, the addition of basic oxides increased the methanol activity 10−40-fold in the hydrogenation of CO (Figure 13) and 30−60-fold in the hydrogenation of CO_2. This strong promotion effect indicates that the basic metal oxides are essential to catalysis and suggests that the promotion is due to bifunctionality of the Pd−M_mO_n/SiO_2 catalysts. Formic acid was once produced industrially from CO and methanol to give methyl formate over a basic catalyst, such as NaOH, and the methyl formate was then hydrolyzed to formic acid and methanol (which was recycled). Therefore, it was proposed that, over the Pd−M_mO_n/SiO_2 catalyst, formate groups are formed on the surface of the basic metal oxide, which are then hydrogenated by H atoms spilled over from the metal surface.

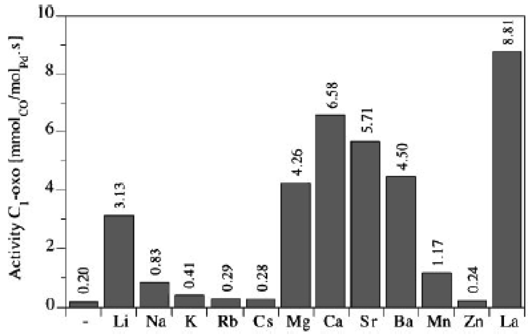

Figure 13. Methanol activity of Pd/SiO_2 promoted with the oxides of the indicated basic metals. Reprinted with permission from ref 125. Copyright 1998 Elsevier B.V.

While the addition of CaO to Pd/SiO_2 had a very strong promoting effect, it had a small negative effect when added to Pd/Al_2O_3.[125] Metal oxides interact strongly with Al_2O_3 and are, therefore, evenly distributed over the Al_2O_3 surface of Pd/Al_2O_3 and do not tend to become attached to the PdO particles. Metal oxides interact much more weakly with the SiO_2 surface, and the basic metal oxide crystallites end up on top of or near to the noble metal oxide particles.[126,127] The minor, negative effect of CaO on Pd/Al_2O_3 and its strong positive effect on Pd/SiO_2 therefore indicate that the basic metal oxide crystallites must be close to or in contact with the metal particles to have a catalytic effect. This is in agreement with the conclusion reported in section 3 that spillover does not occur over a nonreducible support. H atoms, created on the Pd particles, only reach basic metal oxide particles that are in contact with the Pd particles, and only these basic metal oxide particles will take part in the production of methanol from synthesis gas.

All three catalyst systems discussed in this section (Cu/ZnO, Cu/ZrO_2, and Pd−M_mO_n/SiO_2), have in common that the support or the basic metal oxide is not a promoter improving the function of the metal, for instance, by improving its dispersion or protecting it from sintering, but is essential for the catalysis. The support and basic metal oxides are cocatalysts and function through a bifunctional mechanism. In all cases, the transformation of the CO molecule to methanol occurs primarily on the support or metal oxide and not on the metal. The function of the metal is to supply H atoms to the support or to the metal oxide; actual spillover of H atoms takes place from the metal particles to the support or the metal oxide particles.

An open question remains as to the distance covered by the spilled-over H atoms. As the discussion in section 3 has shown, it is unlikely that the H atoms travel much further than the immediate interface between the metal particle and the metal−oxide particle. H atoms do not reduce the basic metal oxides, and, energetically, it would be a disadvantage for H atoms to leave the metal surface. Whether the whole surface of ZnO and ZrO_2 is utilized is unclear too. The interface between the metal particle and the metal−oxide particle may be the area where most of the H atoms react with formate groups, formed by the insertion of CO into OH groups on the support or the metal oxide, to methoxide groups. The entire surface of the ZnO and ZrO_2 can store formate and methoxide groups, when exchange of the HCOO−M and CH_3O−M groups with neighboring HO−M groups takes place. Contact of these methoxide groups with water molecules releases methanol and reforms surface OH groups. In this case, the mobility of the anionic groups (formate, methoxide, hydroxyl) rather than the mobility of the hydrogen atoms determines the rate of the reactions. Spillover then occurs only at the interface between the metal particles and the support, and there is no migration of H atoms over the support surface (ZnO, ZrO_2).

7. HYDROISOMERIZATION BY SPILLOVER

7.1. Mechanism

In the past decade, Pt/WO_3, the classic spillover system with a metal in contact with a reducible support, has attracted industrial as well as academic attention because of possible applications in the hydroisomerization of small alkanes. During hydroisomerization, alkanes are transformed into iso-alkanes. Because iso-alkanes have a much higher octane number than alkanes, hydroisomerization is used on a large scale in the oil industry to improve the octane number of gasoline. On a smaller but substantial scale, it is used to lower the melting point of mixtures of higher hydrocarbons and, thus, ensure that diesel and lubrication oil have good cold flow properties. The classic explanation for the hydroisomerization of alkanes is bifunctional catalysis, in which a metal functions as a dehydrogenation catalyst for the alkane RH_2 (eq 3) and as a hydrogenation catalyst for the resulting iso-alkene i-$R^=$ (eq 7), while the acid functions as a protonation catalyst for the alkene $R^=$ (eq 4), as an isomerization catalyst for the alkylcarbenium ion RH^+ (eq 5), and as a deprotonation catalyst for the resulting iso-alkylcarbenium ion i-RH^+ (eq 6):

$$RH_2 \rightarrow R^= + H_2 \tag{3}$$

$$R^= + H^+ \rightarrow RH^+ \tag{4}$$

$$RH^+ \rightarrow \text{i-}RH^+ \tag{5}$$

$$\text{i-RH}^{+} \rightarrow \text{i-R}^{=} + \text{H}^{+} \tag{6}$$

$$\text{i-R}^{=} + \text{H}_2 \rightarrow \text{i-RH}_2 \tag{7}$$

For instance, the reaction of hexane to 2-methylpentane would occur as follows: hexane → hexene → 2-hexylcarbenium ion → 2-methylpentylcarbenium ion → 2-methylpentene-2 → 2-methylpentane (Figure 14). When reaction 5 is rate determining, the rate r for the isomerization of the alkylcarbenium ion RH^+ is a function of the concentrations of proton H^+ and alkene $R^=$ at the catalytic site:

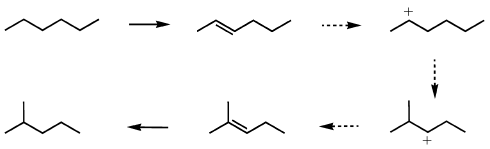

Figure 14. Transformation of hexane to 2-methylpentane over a bifunctional catalyst. Normal arrows indicate metal-catalyzed reactions, and hatched arrows indicate acid-catalyzed reactions.

$$r = k_5(\text{RH}^{+})_S = k_5K_4(\text{H}^{+})_S(\text{R}^{=})_S$$

In this equation, $(R^=)_S$ is a function of the alkene gas-phase pressure $(R^=)$, as described by a Langmuir isotherm $(R^=)_S = K_L(R^=)/[1+ K_L(R^=)]$ and by equilibrium 3 between alkane RH_2 and alkene $R^=$ to give $(R^=) = K_3(RH_2)/(H_2)$. This gives

$$\begin{aligned} r &= k_5K_4K_L(\text{H}^{+})_SK_3(\text{RH}_2)/[(\text{H}_2)[1 + K_LK_3(\text{RH}_2)\\ &\quad /(\text{H}_2)]]\\ &= k(\text{H}^{+})_S(\text{RH}_2)/[(\text{H}_2)[1 + K'(\text{RH}_2)/(\text{H}_2)]] \end{aligned}$$

and leads to the following approximate dependence on (RH_2) and (H_2):

$$r \approx [(\text{RH}_2)/(\text{H}_2)]^n \text{ with } 0 < n < 1$$

The same approximate dependence follows when a Freundlich isotherm rather than a Langmuir isotherm is assumed for the adsorption of the alkene on the acid site.[128] Indeed, for isomerization catalysts consisting of a metal on solid acid, the order in alkane is usually positive, and the order in H_2 is usually negative. The negative H_2 order is a consequence of the assumption that reaction 5 is rate determining and that, thus, reaction 3 is relatively fast and in equilibrium.

Spillover has been proposed as an alternative explanation of the hydroisomerization of alkanes over catalysts consisting of a metal on an acidic support.[129−132] In this explanation, H atoms, and not alkene molecules, initiate the hydroisomerization chain, and the only function of the metal is to provide H atoms to the support.[131] After spillover, H atoms and protons react by radical and carbenium ion chemistry on the acidic support:

$$\text{H}_2 \rightarrow 2\text{H}^{\bullet} \tag{8}$$

$$\text{H}^{\bullet} + \text{RH}_2 \rightarrow \text{H}_2 + \text{RH}^{\bullet} \tag{9}$$

$$\text{RH}^{\bullet} + \text{H}^{+} \rightarrow \text{RH}^{+} + \text{H}^{\bullet} \tag{10}$$

$$\text{RH}^{+} \rightarrow \text{i-RH}^{+} \tag{5}$$

$$\text{i-RH}^{+} + \text{H}^{\bullet} \rightarrow \text{i-RH}^{\bullet} + \text{H}^{+} \tag{11}$$

$$\text{i-RH}^{\bullet} + \text{H}^{\bullet} \rightarrow \text{i-RH}_2 \tag{12}$$

Zhang et al. mentioned three reasons why a spillover mechanism should be preferred over a bifunctional mechanism.[129] First, Pt/zeolite catalysts and mixtures of Pt/SiO_2 or Pt/Al_2O_3 and a zeolite showed good isomerization of pentane in the presence, but not in the absence, of H_2. Second, even a granular mixture had appreciable activity, and, third, the mixtures of powders of Pt/SiO_2 or Pt/Al_2O_3 and a zeolite were more active than a Pt/zeolite catalyst. These points, however, can just as well be explained by the bifunctional mechanism. First, although the authors noted substantial coke formation when N_2 rather than H_2 was present during the reaction, they did not consider that coke forms mainly on the acid part of the catalyst where it suppresses the isomerization reaction. Alkenes that form on the metal are basic compounds and adsorb strongly on the acid sites where they oligomerize to coke precursors and decrease the isomerization activity. This is in line with the interpretation given by Essayem et al. of their results in the hydroisomerization of pentane over mixtures of Pt/SiO_2 and several solid acid catalysts.[133] The high activity of a physical granular mixture of Pt on support catalysts and an acidic zeolite does not contradict the possibility of a bifunctional mechanism either. As long as the rate of hydroisomerization is not too high, the distance between the first catalyst component (metal) and the second (acid) can be rather large (100 μm) and still the rate of isomerization is high, as explained theoretically and experimentally decades ago by Weisz and Schwegler.[134−136] Third, the higher activity of a powdered mixture of Pt/SiO_2 and a zeolite than of Pt/zeolite is probably due to the imbalance between the functions of the metal and the acid in the Pt/zeolite catalyst. Pt particles in a Pt/zeolite catalyst are usually large and on the outer surface. Thus, the distribution of the metal sites and the acid sites is not optimal, leading to easy coke formation. Finally, Zhang et al. pretreated their catalysts in air at 550 °C for 2 h. It is plausible that, during this treatment, PtO_2 migrated from the Pt/SiO_2 to the zeolite, as shown by Sachtler c.s.[34−37]

Kusakari et al. showed that the rate of isomerization over a mixture of Pt/SiO_2 and zeolite H-Beta can be optimized by varying the pressures of hydrogen and pentane and the amount of Pt/SiO_2.[132] The results were explained by the above model (eqs 5 and 8−12), in which the only function of the metal is to provide H atoms, which spill over to the acid support and influence the acid-catalyzed reactions. However, Kusakari et al. did not discuss the possibility that the bifunctional catalysis model can also explain these results: At low H_2/alkane ratio, the alkene pressure is too high and catalyst deactivation occurs. At high H_2/alkane ratio, the high H_2 pressure suppresses the partial pressure of alkene and thus the rate of isomerization. The isomerization rate is the highest when the H_2/alkane ratio is moderate. The amount of metal catalyst regulates the alkene pressure in a similar way. Kusakari et al. also claimed that the low isomerization rate of pentane over zeolite Beta in the presence of H_2 and of a mixture of Pt/SiO_2 and zeolite Beta in the presence of helium can be explained only when spillover is taken into account.[132] Again, this is just as well possible with the bifunctional mechanism. The isomerization rate over zeolite Beta in the presence of H_2 is low due to the low pentene pressure, while the rate over a mixture of Pt/SiO_2 and zeolite Beta in the presence of helium is low because the high pentene pressure leads to quick coking of the catalyst.

Roessner et al. studied the hydroisomerization of hexane over H-erionite, pure and loaded with Pt, in the presence of H_2 or N_2 at 220 °C.[130] Over pure H-erionite, there was hardly any isomerization of hexane but substantial cracking to propane and butane. Similar results were obtained over Pt/H-erionite in the presence of N_2, while over Pt/H-erionite in the presence of H_2 the conversion was lower, isohexane formed, and the cracking to propane and butane was suppressed. These results were explained by the formation of a hexyl carbenium ion from the reaction of spilled-over H atoms with the hexane and the reaction of a proton with the resulting hexyl radical (eqs 9 and 10). The hexyl carbenium ion then isomerizes to the methylpentyl carbenium ion (eq 5) or undergoes β scission to an alkene and a smaller carbenium ion. Roessner et al. claimed that the small erionite pores prevent isomerization and β-scission of a tertiary carbenium ion, leaving the possibility of cracking hexane to smaller alkanes. The lower activity over Pt/H-erionite in the presence of H_2 than in the presence of N_2 and the transport of the alkene intermediate between the metal and the acid site were the reasons for supporting the spillover model rather than the classic bifunctional model. As explained above, both points can be explained just as well by the bifunctional model, which does not rely on spillover. A lower alkene concentration in the presence of Pt and H_2 explains the former point, and Weisz and Swegler explained the latter point years ago.[134−136] In conclusion, spillover is not necessary to explain hydroisomerization in catalysts consisting of a metal supported on an acidic, nonreducible metal oxide.

7.2. Pt/SO_4-ZrO_2 and Pt/WO_x-ZrO_2

The initial interest in applications of spillover in hydroisomerization focused on sulfated zirconia (SO_4-ZrO_2), which has a high acidity and can isomerize butane to isobutane and pentane to isopentane. These isomerizations are initially fast but are slowed by deactivation of the SO_4-ZrO_2 catalyst. Addition of Pt diminishes the deactivation. Heating a Pt/SO_4-ZrO_2 catalyst under H_2 increased the number of Brønsted acid sites and decreased the number of Lewis acid sites, while evacuation reversed these changes.[137,138] Li et al. showed that the Brønsted acid sites could be washed away from the surface of the SO_4-ZrO_2 catalyst and that they, and not the Lewis acid sites, are responsible for the isomerization of alkanes.[139] Ebitani et al. ascribed the increase in the number of Brønsted acid sites and the decrease in the number of Lewis acid sites (Figure 15) to spillover of H atoms from the metal to the support and the transformation of a Lewis site into a Brønsted site by the addition of a proton.[137,138] What happened with the concomitantly formed electron was not clear. Sato et al. proposed that the electron is trapped on a Lewis acid site and reacts with another H atom to a H^- hydride anion bonded to the Lewis acid site.[140] However, how a hydride anion is stabilized on a Zr^{4+} cation bonded to a sulfate anion is an open question. Probably the hydride anion reduces a sulfate group, as suggested by the shift of an S═O IR band to lower frequency upon reduction in H_2 and back upon evacuation. Large amounts of H_2 can be adsorbed on Pt/SO_4-ZrO_2 catalysts.[138,141] For instance, a 0.5 wt % Pt catalyst consumed an amount of hydrogen equivalent to $H_2/Pt = 65$, or $H_2/S = 3.4$, at 250 °C. The H_2 adsorption increased with increasing temperature (Figure 16), in contrast to usual adsorption, and suggests that reduction rather than adsorption had occurred. Sulfate can be reduced to sulfite and eventually to sulfide, consuming four H_2 molecules (eight reduction equivalents) per S atom. It seems highly unlikely that S═O bands are observed in the IR when six or seven reduction equivalents are taken up by each sulfate anion (formally in the S^{6+} oxidation state). The suggestion[137] that some H atoms will remain on the support surface does not seem plausible.

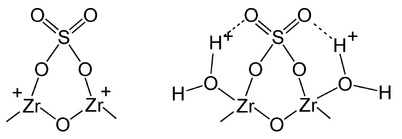

Figure 15. Possible structures of Lewis acid sites (left) and Brønsted acid sites (right) on the surface of SO_4-ZrO_2. Redrawn with permission from ref 141. Copyright 1993 Elsevier B.V.

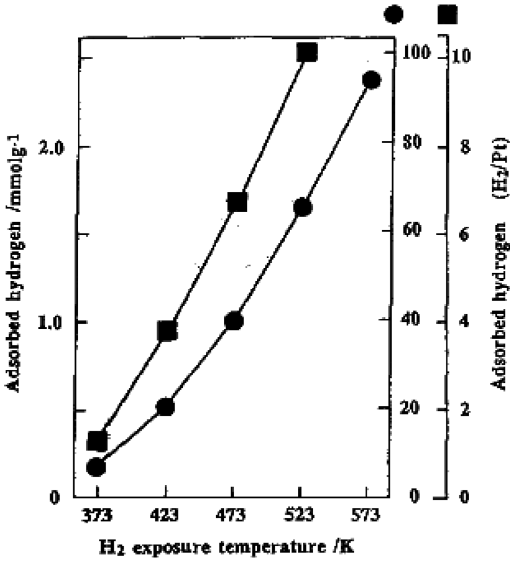

Figure 16. Amount of H_2 adsorbed on 0.5% Pt/SO_4-ZrO_2 (●) and 5% Pt/SO_4-ZrO_2 (■) while heating in H_2. Reprinted with permission from ref 138. Copyright 1992 Elsevier B.V.

Even Pt/SO_4-ZrO_2 deactivated fast during the isomerization of butane and pentane in the presence of nitrogen, but stable isomerization was attained under H_2.[137] Hydrogenolysis but not isomerization of pentane occurred over Pt/ZrO_2, while the reverse was true over Pt/SO_4-ZrO_2. Hydrogenolysis is probably suppressed, because the Pt surface of Pt/SO_4-ZrO_2 is sulfided by the reaction of the sulfate with hydrogen. This means that the actual catalyst consists of Pt particles covered with sulfur atoms on a ZrO_2 support that still contains sulfate groups. The Pt/SO_4-ZrO_2 catalyst shows similarities to the Pt/Al_2O_3 catalytic reforming catalyst, which requires a trace of sulfur in the feed to maintain the Pt surface mildly sulfided. On a mildly sulfided Pt surface, hydrogenolysis of hydrocarbons does not occur, but the hydrogenation capacity is maintained.

The order in H_2 in the isomerization of pentane over Pt/SO_4-ZrO_2 was about one, and in alkane it was close to zero.[141] These orders differ from those in the usual bifunctional hydroisomerization, where the order in H_2 is negative (more H_2 means fewer alkenes) and the order in alkane is about one. Addition of adamantane increased the rate of isomerization, indicating that hydride transfer limits the isomerization rate.[141] After the isomerization reaction, hydrogen transfer of the alkylcarbenium ion on the acid site takes place with a reactant molecule or with adamantane.

$$RH^+ \rightarrow i\text{-}RH^+ \qquad (5)$$

$$\text{i-RH}^{+} + \text{RH}_2 \rightarrow \text{i-RH}_2 + \text{RH}^{+} \tag{13}$$

The need for Pt sites and the first-order dependence on H_2 suggested that H_2 can also act as an H-transfer agent, just as adamantane:[141]

$$H_2 \rightarrow 2H^{\bullet} \tag{8}$$

$$H^{\bullet} + RH^{+} \rightarrow H^{+} + RH^{\bullet} \tag{11'}$$

$$RH^{\bullet} + H^{\bullet} \rightarrow RH_2 \tag{12'}$$

In this way, hydrogen decreases the lifetime of carbenium ion intermediates and enables their desorption before oligomerization and cracking occur. Farcasiu et al. suggested that initiation of the isomerization of alkanes over SO_4–ZrO_2 occurs by redox reactions,[142] and Li et al. showed that the reaction is initiated by small amounts of alkenes formed by oxidative dehydrogenation of alkanes by pyrosulfate groups (Figure 17).[143] In agreement with the assumed influence of redox reactions, oxygen decreased the induction period of the isomerization of butane.

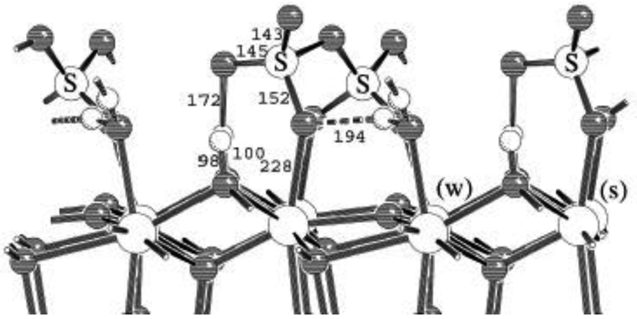

Figure 17. Structure of pyrosulfate on the surface of ZrO_2. Reprinted with permission from ref 143. Copyright 2005 American Chemical Society.

Despite its excellent intrinsic isomerization activity, the Pt/SO_4–ZrO_2 catalyst lacks stability and regenerability, because it loses sulfate groups during catalysis and regeneration due to the formation of volatile sulfur compounds by redox reactions. Attention has, therefore, shifted to tungstated zirconia (WO_x–ZrO_2), which also proved to be an excellent hydroisomerization catalyst, and more stable than the SO_4–ZrO_2 system. Reduction of WO_3 to $WO_{2.9}$ by alkanes or hydrogen occurs already at 80 °C in Pt/WO_3–ZrO_2 with the formation of tungsten bronze $(H^+)[(W^{5+})(W^{6+})_{n-1}(O^{2-})_{3n}]^-$.[144,145] The resulting proton explains the acidity, while the balancing negative charge is delocalized over several W cations in corner-shared WO_6 octahedra. W^{5+} centers were observed by electron spin resonance spectroscopy after reduction of WO_3–ZrO_2 at 200 °C[146] and of Pt/WO_3–ZrO_2 at room temperature.[147] Brønsted acid groups were directly observed by IR[146] as well as indirectly as pyridinium ions after pyridine adsorption.[148] Catalyst activity in the isomerization of pentane over WO_3–ZrO_2 decreased when Brønsted acid sites were neutralized with 2,6-dimethylpyridine.[149] In contrast to Pt/SO_4–ZrO_2, Pt/WO_3–ZrO_2 behaved like a normal bifunctional catalyst in the isomerization of heptane, with the order in heptane close to one, the order of −0.5 in H_2, and the order in adamantane close to zero.[144] Isotopic exchange between heptane and D_2 was rapid over Pt/WO_3–ZrO_2 but slow over Pt/SO_4–ZrO_2. On Pt/WO_3–ZrO_2, surface isomerization is thus the rate-determining step (reaction 5).

Isomerization activity had a maximum at WO_3 loadings in excess of monolayer coverage.[145,149] Raman and UV–vis diffuse reflectance spectroscopy showed that tungsten is present as isolated octahedral WO_6 units at low W loading, which are difficult to reduce, and as three-dimensional WO_3 at high W loading, the bulk of which is inaccessible to reactants (Figure 18).[150] At intermediate W loading, polytungstate units are present that can accommodate H atoms as protons and delocalize the electrons over the polytungstate unit, as in heteropolytungstate anions.[145,150−152]

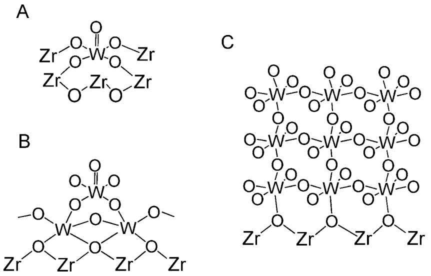

Figure 18. Increasing WO_x domain size with increasing WO_3 surface loading: (A) 0−4 W nm^{-2}, (B) 4−8 W nm^{-2}, (C) >8 W nm^{-2}. Redrawn with permission from ref 150. Copyright 1999 American Chemical Society.

These studies demonstrate that in Pt/WO_x–ZrO_2, too, spillover from the metal to WO_x takes place and that protons and electrons rather than hydrogen atoms are transferred. The protons and electrons end up in the WO_x phase on top of and in interaction with the ZrO_2 support (Figure 19). The same conclusions have been drawn for Pt/SO_4–ZrO_2, although the fate of the electron is unclear.

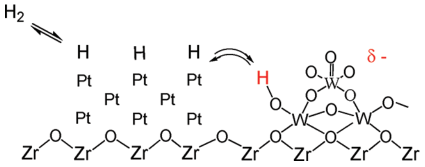

Figure 19. Scheme of Brønsted acid sites: reduction with H_2 and delocalization of negative charge in WO_x domains. Redrawn with permission from ref 145. Copyright 1999 Elsevier B.V.

8. HYDROGENATION BY SPILLOVER

8.1. Hydrogenation in the Presence of Impurities

As discussed in section 4, several publications indicate that organic molecules can be hydrogenated over pure supports. This aroused interest in the possibility to use the support as an extra channel for hydrogenation, in addition to the hydrogenation over the metal part of a metal-on-support catalyst. Thus, already in the beginning years of spillover, Sinfelt and Lucchesi found that a mixture of a Pt/SiO_2 catalyst and Al_2O_3 was 10 times more active in the hydrogenation of ethene at 100−150 °C than a mixture of Pt/SiO_2 and SiO_2.[4] They proposed that this is due to the spillover of H atoms, from Pt to silica and further to the alumina or silica, which react with ethene adsorbed on the silica or alumina. The higher concentration of ethene on alumina than on silica (due to stronger adsorption) would explain the higher activity of the mixture of Pt/SiO_2 and Al_2O_3.

However, Schlatter and Boudart discovered that the difference between the activities of Pt/SiO_2 + Al_2O_3 and Pt/SiO_2 + SiO_2, as observed by Sinfelt and Lucchesi,[4] was due to impurities.[153] They not only studied the effect of mixing Pt/SiO_2 with Al_2O_3 and SiO_2, but also the effect of a bed of Al_2O_3 or SiO_2 in front of the Pt/SiO_2 bed. The activities of a mixture of Pt/SiO_2 and Al_2O_3 and of Pt/SiO_2 and a prebed of Al_2O_3 were the same as that of the Pt/SiO_2 catalyst. However, mixing the Pt/SiO_2 catalyst with silica or using a prebed of SiO_2 lowered the activity substantially, while subsequent treatment with oxygen at 300 °C increased the activity to that of Pt/SiO_2. Briggs and Dewing confirmed the effect of carbonaceous contaminants on the rate of ethene hydrogenation as well as the importance of the cleaning treatments with oxygen.[154] Schlatter and Boudart concluded that the dilution of the Pt/SiO_2 catalyst with Al_2O_3 did not lead to an increase in the catalytic activity, as had been claimed by Sinfelt and Lucchesi,[4] but rather that dilution with SiO_2 decreased catalytic activity. Impurities deposited on the silica surface during pretreatment were transported to the Pt/SiO_2 catalyst, as a result of which the Pt surface became covered and the catalyst activity decreased. The higher the temperature is at which SiO_2 is treated, the greater is the number of impurities that desorb from its surface and reach the Pt catalyst. Short oxidation at 300 °C removes the carbonaceous residues. Al_2O_3 captures impurities, and the addition of a prebed of alumina to the Pt/SiO_2 catalyst or mixing it with Al_2O_3 thus has almost no effect on activity. The authors concluded that there was no evidence of spillover of hydrogen from Pt to Al_2O_3 in the hydrogenation of ethene.

While Baumgarten et al. concluded that spilled-over H atoms do not hydrogenate alkenes (section 3.2), Chen et al. concluded that spillover is important in the hydrogenation of hexene over a Pt catalyst supported on a carbon molecular sieve (CMS).[155] They found that the conversion of hexene to hexane after 6 h time on stream increased when the Pt/CMS catalyst was diluted with activated carbon (AC) and to an even greater extent when diluted with HY zeolite. Because AC and HY are inactive in the hydrogenation of hexene in the absence of Pt, the positive influence of dilution with AC and HY was ascribed to the spillover of hydrogen atoms from Pt/CMS to carbon or zeolite. Hexene molecules adsorbed on the added support could then be hydrogenated. Spillover to a carbon support is indeed possible (section 5), but that does not mean that spillover necessarily is the explanation. Plots of conversion against time on stream (Figure 20) show that the initial conversion was 100% for all three catalysts (Pt/CMS, Pt/CMS + AC, Pt/CMS + HY), but that the Pt/CMS catalyst deactivated fast, the Pt/CMS + AC slowly, and that the Pt/CMS + HY catalyst did not deactivate.[155] Catalyst deactivation is always a problem in reactions of alkenes because of oligomerization and coke formation. Dilution of Pt/CMS with an acidic support such as AC (which has carboxylic surface groups) and especially HY adds an adsorbent that traps these impurities and keeps the Pt surface clean. Similar to the results of Schlatter and Boudart,[153] the results of Chen et al. can also be explained by hydrogenation on the Pt surface alone.

In a short publication, Ohgoshi et al. described similar hydrogenation experiments with mixtures of Pt@KA zeolite and NaY or H-ZSM-5 to hydrogenate isobutene.[156] Pt@NaA was prepared by adding $Pt(NH_3)_4Cl_2$ to the synthesis gel of zeolite NaA and was assumed to have all Pt ions in the sodalite cages. After Na−K exchange, the 8-member pore openings of the resulting zeolite are reduced from 0.41 nm for Pt@NaA to 0.3 nm for Pt@KA. The conversion of isobutene over Pt@KA was low, because the isobutene molecules are too big to penetrate the 8-ring zeolite windows and reach the metal particles inside the zeolite cages. On the other hand, high conversion of isobutene was obtained over the mixture of Pt@KA zeolite and NaY or H-ZSM-5. This was ascribed to spillover of H atoms from the Pt surface to the NaY or H-ZSM-5 surface where the isobutene was hydrogenated. TEM measurements showed, however, that some of the Pt particles were much larger than the zeolite cages and that part of the zeolite structure was damaged.

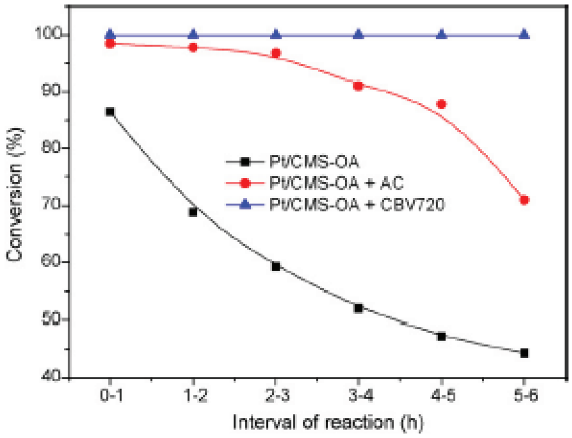

Figure 20. Catalytic activity of Pt/CMS and of Pt/CMS diluted with activated carbon (AC) and zeolite HY. Reprinted with permission from ref 155. Copyright 2007 Elsevier B.V.

That during the synthesis of Pt@NaA not all Pt becomes located in the NaA zeolite cages was demonstrated years ago by Juguin et al.[157] They carefully determined that 80% of the Pt particles was inside zeolite NaA, meaning that 20% was present in large intracrystalline pores. This explained why in their experiments thiophene and dibenzothiophene decreased the rate of hydrogenation of ethene by about 20%. Thiophene and dibenzothiophene cannot penetrate the NaA zeolite pores, but ethene can penetrate the pores and reach the Pt particles that are inside the micropores. On the other hand, H_2S completely poisoned the catalyst because it can penetrate the large pores as well as the micropores and sulfide the surface of all Pt particles.[157] The conclusion of Ohgoshi et al., that hydrogen spillover occurred from Pt@KA to NaY or H-ZSM-5,[156] therefore seems premature. Some of the isobutene may have been hydrogenated on the accessible Pt particles. As in the hydrogenation of hexene,[155] the higher conversion of the mixture containing a zeolite might be due to the trapping of oligomeric impurities.

8.2. Hydrogenation of Aromatics

Aromatic molecules are hydrogenated faster by metal catalyst particles when they are supported on an acidic support than when supported on a neutral or basic support.[158] This has been attributed to the fact that when metal particles are in contact with acid sites they become electron deficient and are more active. Another explanation is that hydrogen atoms spilled over from the metal particles can hydrogenate aromatic molecules, adsorbed on acid sites of the support. Lin and Vannice suggested that only the molecules adsorbed at the perimeter of the metal particles are involved.[158] Other authors claimed that benzene that is adsorbed further away on the support can be hydrogenated by spilled-over hydrogen as well.[159−163]

Sancier was the first to show that the dilution of a Pd/Al_2O_3 catalyst with Al_2O_3 increases the percentage of hydrogenation per mg Pd,[159] suggesting that the increase is due to hydrogenation of benzene adsorbed on the Al_2O_3. His experiments were performed in a pulse reactor, and Vannice and Neikam argued that a pulse reactor, in contrast to a flow reactor, leads to a distortion of the results of a zero-order reaction like benzene hydrogenation.[164] They also suggested that, because of the exothermicity of the hydrogenation reaction, the results obtained at high conversion are unreliable and that impurities might have distorted the results. Vannice and Neikam did not observe a dilution effect in a flow reactor. Moffat confirmed that benzene hydrogenation was zero order at 150 °C, both in pulse and in flow mode.[165] Broadening of a pulse will extend the contact between the reactant and the catalyst and will lead to an increase in the conversion of a zero-order reaction. Peak broadening and higher conversion of benzene was observed not only in pulse mode when a bed of Al_2O_3 was placed in front of the Pd/Al_2O_3 bed, but also when an empty reactor (10 cm^3) was placed in front of the catalyst bed. Placing the bed or empty bed downstream of the catalyst had no effect on benzene conversion. Like Vannice and Neikam, Moffat did not find a dilution effect in the flow reactor. Moffat's work demonstrates that it is impossible to study hydrogen spillover for a zero-order reaction in a pulse reactor.[165]

Studies in a flow reactor showed that dilution of a metal-on-support catalyst with a pure support increased the specific activity of benzene hydrogenation (mol converted/h·g metal). Antonucci et al.[160] and Ceckiewicz and Delmon[161] studied the effect of adding Al_2O_3 to Pt/Al_2O_3 on the hydrogenation of benzene, and Srinivas and Kanta Rao studied the effect of adding carbon to Pt/carbon in the hydrogenation of benzene.[162] Benseradj et al. investigated the dilution of Rh/Al_2O_3 with SiO_2, Al_2O_3, H-USY, and active carbon in the hydrogenation of toluene.[163] With the exception of Ceckiewicz and Delmon, none of these authors attempted to explain the positive effect of dilution by anything other than spillover. Ceckiewicz and Delmon confirmed that impurities in the feed influenced benzene conversion,[161] as suggested by Vannice and Neikam,[164] and as demonstrated by Schlatter and Boudart in the hydrogenation of ethene[153] (cf., section 8.1). Benzene conversion was higher when a bed of pure Al_2O_3 was placed upstream from a bed of Pt/Al_2O_3 than when the beds were stacked in the reverse order or when the same amounts of Pt/Al_2O_3 and Al_2O_3 were homogeneously mixed.[161] Benzene conversion was also higher when the benzene and H_2 were purified and when the catalyst was calcined before reduction. When Al_2O_3 was intentionally contaminated by coke and placed in a bed upstream from the Pt/Al_2O_3 catalyst bed, benzene conversion did not increase. All of these findings confirm that purification of reactant gases increases conversion and that experimental results obtained without purifying the reactants are unreliable. After taking precautions to remove the impurities, Ceckiewicz and Delmon still observed a synergetic effect after adding Al_2O_3 to Pt/Al_2O_3.[161] The activity of the mixtures was always higher than that calculated from the percentage of Pt/Al_2O_3. Normalized per milligram of Pt in the mixed bed, the conversion of benzene might be up to 4 times higher than that of undiluted Pt/Al_2O_3. This synergetic effect was ascribed to the reaction of H atoms, spilled over from Pt to the support, with benzene molecules on the support.

Addition of carbon to Pt/carbon[162] influenced the hydrogenation of benzene in the same way as the addition of Al_2O_3 to Pt/Al_2O_3.[160,161] Conversion decreased, and specific activity increased. Whereas CO chemisorption decreased when the Pt/carbon catalyst was diluted, hydrogen chemisorption increased. Thus, the number of CO molecules chemisorbed per milligram of Pt was constant, but the number of chemisorbed H atoms increased considerably. This was strong evidence for the spillover of H atoms from Pt to the carbon support. As shown in section 5, hydrogen spillover to a carbon support is energetically possible.

Whereas others observed only an increase in the specific catalytic activity in a flow reactor,[160−162] Benseradj et al. observed an increased conversion of the hydrogenation of toluene at 80 °C when Rh/Al_2O_3 was diluted by up to 50% with SiO_2, Al_2O_3, H-USY, and active carbon.[163] The specific activity increased strongly with increasing dilution level, especially when the catalyst was diluted with H-USY and active carbon. Because the stronger acidity of the added support gave higher conversion, protonated aromatic molecules were considered to be reaction intermediates in spillover hydrogenation. This conclusion disagrees with that of Primet et al.[166] They measured the concentration of benzene adsorbed in the pores of Pt/Y catalysts during hydrogenation by UV and IR spectroscopy and observed that the benzene concentration decreased linearly with time until very low benzene concentrations. If hydrogen spillover to the zeolite support, followed by hydrogenation, would have contributed to the hydrogenation, the hydrogenation rate constant should have decreased because the coverage of benzene on the zeolite surface decreased. The constant rate shows that migration of benzene from the zeolite to the Pt particles (because of the stronger bond of benzene to Pt than to the zeolite) ensures that during the whole hydrogenation the benzene coverage of the Pt surface is constant and complete.

All of the dilution studies were performed at high aromatic conversion (>20%),[159−163] sometimes even higher than 80% for the undiluted catalyst.[161,162] This must have led to nonisothermal behavior and a much higher catalyst temperature than assumed. Benzene hydrogenation is zero order below 150 °C, but at high conversion (low benzene pressure) it is first order. As a result, the activity of the undiluted catalyst would have been underestimated, due to a decrease in the surface coverage of benzene at higher temperature[159] or to deactivation after coke formation. This suggests that the reference state of the undiluted catalyst was not determined correctly and that all of the conclusions are unreliable. This is supported by the fact that Vannice and Neikam and Moffat did not find an effect of the diluent when the experiments were carried out under isothermal, differential conditions (low conversion).[164,165] Flores et al., too, found no effect of dilution of the Pt/Al_2O_3 catalyst with Al_2O_3[167] when they pretreated their Pt/Al_2O_3 catalyst with O_2 at 300 °C for 0.5 h to remove possible carbonaceous deposits, as suggested by Schlatter and Boudart, and when they limited the benzene conversion to 10% to guarantee isothermal behavior.[153] The increase in specific activity when diluting a metal-on-support catalyst with support[159−163] might be explained by spillover through carbonaceous products formed on the support. Such deposits can act as transfer agents of hydrogen and form more easily on acidic supports. In that case, hydrogen spillover would occur to the carbonaceous layer, not to the support. As explained in section 5.1, there is no theoretical objection against such spillover.

Not only have aromatic molecules such as benzene, toluene, and xylene been used in spillover hydrogenation, but also heteroaromatic molecules. Zhang et al. exposed pyridine, adsorbed on a physical mixture of Pt/SiO_2 and H-ZSM-5 zeolite, to H_2 at 200 °C.[168] Their IR measurements showed that the pyridine molecules adsorbed on the acidic Brønsted and Lewis zeolite sites and were hydrogenated to piperidine. They also demonstrated that the reverse reaction, the dehydrogenation of piperidine to pyridine, occurred. Their explanation was that pyridine adsorbed on a zeolite site is hydrogenated by hydrogen atoms that are generated on the metal surface and spilled over to the support (Figure 21). In the reverse case, it was assumed that piperidine dehydrogenates on the zeolite site and that the resulting hydrogen atoms migrate to the metal by reverse spillover. That would mean that strong C−H bonds (~400 kJ/mol) are broken without involvement of a catalyst! Three years later, however, Ueda et al. concluded that hydrogen spillover is not needed to explain the hydrogenation of pyridine on a physical mixture of Pd/SiO_2 and H-USY zeolite and that pyridine (or piperidine) molecules rather than H atoms migrate.[169] They deduced their conclusion about the migration of pyridine from the difference in behavior of the catalyst under high and low pyridine coverage.[169] IR measurements showed that pyridine molecules, which adsorbed at high coverage at Brønsted as well as at Lewis acid sites, were reduced to piperidine by hydrogen at 150 °C. At low coverage of pyridine, however, the pyridine shifted from the Lewis to the Brønsted acid sites, but hydrogenation did not take place. They proposed that, after saturation of the Brønsted acid sites with pyridine, additional pyridine molecules bind less strongly to the Lewis acid sites. These molecules can desorb and diffuse to the metal surface and become hydrogenated to piperidine. Because piperidine is more basic than pyridine, piperidine exchanges with pyridine on the surface of the acid support, and the reaction of pyridine on the metal surface continues until all of the pyridine is converted. Thus, hydrogen spillover is not required to explain the hydrogenation of the pyridine; pyridine and piperidine molecules rather than H atoms migrate. This conclusion is more logical and agrees with the conclusion of Primet et al. that benzene migrates from zeolite to metal in the hydrogenation of benzene over a Pt/Y catalyst.[166] Ueda et al. observed H−D exchange of support OH groups in the same samples,[169] demonstrating once again that there is no correlation between hydrogenation by spillover and H−D exchange of support OH groups (cf., section 3.2).

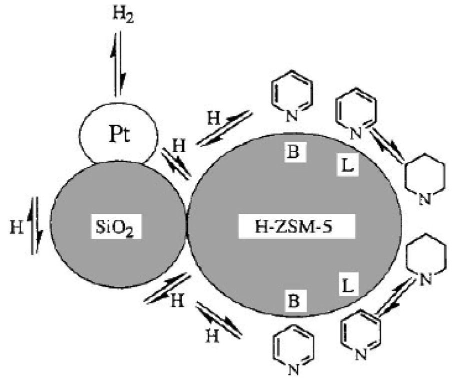

Figure 21. Hydrogenation of pyridine adsorbed on zeolite by H atoms spilled over from the Pt particle to the zeolite and dehydrogenation of piperidine adsorbed on the zeolite and reverse spillover of H atoms to the metal particle. Copied with permission from ref 168. Copyright 1997 Elsevier B.V.

8.3. Sulfur-Tolerant Hydrogenation by Spillover

Metal catalysts are responsive to sulfur, which quickly covers their surface when the catalysts are in contact with sulfur-containing molecules. As a consequence, hydrogenation activity decreases to a very low level. Even the most noble metals, Pd and Pt, are sensitive to sulfur, but this can be decreased by alloying and by putting them on an acidic support. The resulting increase in the sulfur tolerance of metal catalysts supported on acid supports has been ascribed to spillover. While adsorption and hydrogenation of aromatic molecules on metal particles is inhibited by the adsorption of sulfur, hydrogen might still adsorb on the sulfur-covered metal particles and dissociate. The resulting hydrogen atoms would then spill over to the support and hydrogenate the aromatic molecules adsorbed on the acid sites.[170] On the other hand, even bimetallic PtPd particles on acidic supports do not tolerate large amounts of sulfur. Song and Ma therefore proposed to use metal-on-support hydrogenation catalysts with a bimodular pore distribution to increase the tolerance of metal catalysts to sulfur.[171] Such supports have metal particles in small and large pores. When hydroprocessing heavy feeds, the large molecules can only penetrate the large pores and deactivate the large metal particles by sulfur coverage. The small metal particles in the small pores do not come into contact with the reacting molecules and are not contaminated by them. The small metal particles still dissociate H_2, and the resulting H atoms may spill over to the large metal particle in the large pores and recover the poisoned metal sites. A problem of this approach is that the sulfur-containing molecules release H_2S when they react on the large particles in the large pores and that the small H_2S molecules can penetrate the small pores and deactivate the small metal particles. Juguin et al. already demonstrated this years ago for Pt@NaA, in which most of the Pt cations are inside the zeolite cages. As discussed in section 8.1, they observed that thiophene and dibenzothiophene, which cannot penetrate the NaA zeolite pores with openings of 0.41 nm, decreased the rate of hydrogenation of ethene, which can penetrate the pores and reach the Pt particles inside the micropores, by about 20%.[157] H_2S, on the other hand, completely poisoned the catalyst because it can penetrate the micropores and sulfide the surface of the Pt particles.

To prevent the small H_2S product molecule from reaching the small metal particles in the small pores, Yang et al. used Pt@KA zeolite (with pore openings of 0.3 nm) and further narrowed the pores by chemical vapor deposition of tetraethyl orthosilicate (TEOS).[172] Reduction leads to Pt metal particles inside the cages, which can be reached by H_2 (which has a kinetic diameter of 0.29 nm), but not by H_2S (kinetic diameter of 0.36 nm). The TEOS-Pt@KA catalyst adsorbed 0.3 mL of H_2 per g catalyst (H/Pt = 0.69). After exposure to H_2S, it adsorbed 0.2 mL/g, showing that most of the Pt particles did not come into contact with the H_2S. The hydrogenation of naphthalene in heptane at 6.9 MPa H_2, 300 °C, and a LHSV of 2 h^{-1} over a mixture of TEOS-Pt@KA with HY zeolite and γ-Al_2O_3 gave a conversion of 10%, while in the presence of 3% H_2S the conversion was 4%.[172] The retaining of 40% of the hydrogenation activity in the presence of H_2S was ascribed to the hydrogenation of naphthalene molecules adsorbed on HY and γ-Al_2O_3 by hydrogen atoms spilled over from the Pt particles. This is in contradiction to the conclusion drawn in section 3 that spillover to a nonreducible support is not possible. It also contradicts the experimental result of Miller and Pei, that ethylbenzene could not be hydrogenated over a mixture of Pt@NaA and H-USY (section 3.2).[33] On the other hand, when the mixture of TEOS-Pt@KA with HY zeolite and γ-Al_2O_3 would be covered with a graphitic type of carbonaceous material, it is possible. Carbonaceous deposits are easily produced in reactions of unsaturated hydrocarbons and may function as transfer agents in hydrogen spillover between the metal particles and molecules adsorbed on the support (section 5). This might explain the retained hydrogenation activity in the presence of H_2S. Hydrogen spillover then would not take place over the surface of pure HY or γ-Al_2O_3, but over a graphitic layer on top of the surface of these supports.

Recently, Calderone et al. proposed to prevent the poisoning of Pt hydrogenation catalysts by sulfur compounds by encapsulation of the Pt particles by silica layers.[173] Like Yang et al.,[172] they suggested that if the pores of the silica membrane would be small enough, only H_2 molecules but not H_2S molecules would be able to reach the surface of the Pt particles. The hydrogen atoms formed would spill over to the silica layer and hydrogenate toluene molecules, which cannot penetrate the silica pores, at the outside of the silica membrane. Several methods of silica encapsulation of the Pt articles failed. Only one sample, which had been calcined at 500 °C after encapsulation, showed an increased resistance against sulfur poisoning. However, the hydrogenation activity was much reduced, and after several hours the catalyst was completely deactivated.

8.4. Spillover between Stacked Beds

In a series of articles, Gil-Llambias and co-workers reported that spillover occurred between beds of catalysts that were stacked on top of each other but separated by a bed containing a pure support. These experiments were similar to the experiments with triple beds published by Burch et al.[116] but were carried out at high pressure. Gil-Llambias c.s. performed hydrodesulfurization (HDS)[174−179] as well as hydrodenitrogenation[180] (HDN) experiments with a bed of CoS/support or NiS/support above or under a bed of MoS_2/support, separated by a bed containing 5 mm γ-Al_2O_3, SiO_2, or SiC. The separator bed makes it impossible for a mixed Co−Mo−S or Ni−Mo−S phase[181] to form. I will refer to the sulfided Co and Ni as CoS and NiS, although the stoichiometries of these metal sulfides were unknown; they could just as well have been Co_9S_8 and Ni_3S_2, respectively. The total stacked-bed configuration was MS/support//separator//MoS_2/support or MoS_2/support//separator//MS/support (Figure 22). Industrial gas oil was the feed in most experiments, and the HDS was carried out under similar conditions as in industry, 3 MPa and 325−375 °C. While separate CoS/support and NiS/support catalysts showed no HDS activity, the combined MS/support//separator//MoS_2/support beds, with SiO_2[174] or Al_2O_3[175] as the support, increased the desulfurization conversion of the gas oil above that of MoS_2/support. When SiO_2 was the separator, the synergism was higher than with Al_2O_3, while there was no synergism with SiC.[175] The synergistic effect of CoS was higher at lower temperature, 38% at 325 °C and 6% at 375 °C.

When the order of the beds was reversed (MoS_2/support//separator//MS/support), synergy was not observed. The authors explained these results by the remote control model,[182−184] in which spilled-over H atoms migrate from a donor to an acceptor phase and influence the HDS of the acceptor phase. Co and Ni sulfides are considered to be donors and Mo and W sulfides acceptors of H atoms. H atoms will migrate from the MS/support bed to the downstream MoS_2/support bed, but will hardly migrate upstream from the MS/support to the MoS_2/support bed. An alternative explanation, that the MS/support bed functions as a guard bed, which prevents impurities in the gas oil from reaching the MoS_2/support bed, was not discussed.[174] Co sulfide was considered to be a donor and MoS_2 an acceptor of H atoms, although the activity of supported as well as unsupported Co_9S_8 is lower than that of MoS_2 in the hydrogenation of cyclohexene.[183,184] The HDS of dibenzothiophene (DBT)[177] and the HDN of pyridine and a gasoil spiked with pyridine[180] gave results similar to those of the HDS of gasoil.[174−176] In all cases, the activity of physically separated, stacked beds was higher than that of the sum of the separate beds, and this was ascribed to spillover of H atoms from the top CoS or NiS bed to the bottom MoS_2 bed.

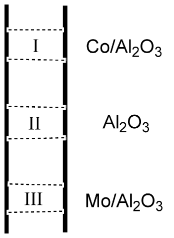

Figure 22. Stacked bed reactor with sulfided Co/Al_2O_3 in the upper bed, Al_2O_3 in the separator bed, and sulfided Mo/Al_2O_3 in the lower bed.

The experiments of Gil-Llambias c.s. with upstream and downstream catalyst beds have much in common with the experiments of Baumgarten et al. that were discussed in section 4.2.1.[49,52] Baumgarten et al. examined the hydrogenation of unsaturated molecules downstream of a metal-on-support hydrogenation catalyst, while Gil-Llambias c.s. examined HDS and HDN reactions on a supported MoS_2 catalyst downstream of a supported CoS or NiS catalyst. Both groups explained their results by spillover of H atoms from the upstream bed to the downstream zone.

Gil-Llambias c.s. considered their results proof of the remote control of the Co or Ni promoter on the Mo catalyst. Although the synergetic effect of Co in the stacked beds is much less (a factor of 1.5−2)[174−179] than that of Co in real Co−Mo−S catalysts (at least a factor of 10), the distance between Co and Mo atoms in stacked beds is 5 mm, while the distance in real catalysts is less than 1 nm.[181] Therefore, spillover might be much more efficient in real catalysts, because it depends on surface diffusion. The authors estimated that the main part of the promoter effect of Co in a commercial CoMo catalyst is based on hydrogen spillover.[178] The higher contribution of the hydrogenation reaction of DBT to cyclohexylbenzene than the contribution of the direct desulfurization pathway from DBT to biphenyl in the stacked bed reactor was considered to be further evidence of the remote control model.[177] If we use the same logic of extrapolating the distance in the stacked beds of 5 mm to atomic distances, then the hydrogenation reaction should dominate the direct desulfurization reaction in real catalysts. This is, however, not the case. On the contrary, the direct desulfurization reaction is strongly enhanced by the presence of Co in a sulfided CoMo/γ-Al_2O_3 catalyst, while the hydrogenation reaction is hardly enhanced.[185] Furthermore, not only the sulfides of Co and Ni, but also those of Mn, Cu, and Zn showed synergy in stacked bed experiments,[178] although Cu acts as a poison for MoS_2[186] and Mn and Zn hardly have a promoting effect on MoS_2.[186,187] Co showed a synergetic effect in the CoS/γ-Al_2O_3//SiO_2//WS_2/γ-Al_2O_3 stacked bed but does not act as a promoter in a Co−W−S catalyst.[188] These results indicate that it is not possible to extrapolate the results of the stacked-bed experiments to normal catalysts. It might well be that hydrogen spillover occurred in the stacked beds, but whether this can explain the promoter effect of Co and Ni in industrial Co−MoS_2 and Ni−MoS_2 catalysts has not been unequivocally demonstrated.

9. ISOTOPE EXCHANGE IN ORGANIC COMPOUNDS BY SPILLOVER

Zolotarev et al. have applied spillover to replace H atoms in organic molecules by deuterium (D) or tritium (T) atoms. The results of their extensive studies are described in two recent reviews.[189,190] They brought D_2 or T_2 gas in contact with a solid mixture of an inorganic support (such as barium sulfate or calcium carbonate), a Rh, Pd, or Pt salt, and a small amount of amino acid, peptide, carbohydrate, nucleoside, or heterocyclic acid at 100−240 °C during 20−200 min. An exchange of D or T atoms for H atoms took place in the organic molecule. The H atoms in the NH_2, COOH, and OH groups were easily replaced by tritium even at room temperature, but were exchanged back to the H form during work up of the product in ethanol-ammonia. Isotope exchange at the C−H bonds, on the other hand, only reached considerable rates above 100 °C and was almost complete in several amino acids. Below 180 °C, the label was incorporated in a selective manner; at higher temperature, uniform *T* distribution was observed. At lower temperature, aliphatic amino acids that contain no additional functional group (alanine, valine, leucine, and isoleucine) underwent isotopic exchange predominantly at the methyl groups. Hydrogen atoms at the tertiary and secondary (carrying the NH_2 group) carbon atoms reacted significantly slower. The isotope exchange occurred without appreciable hydrogenolysis or hydrogenation of double bonds and isotopic exchange at asymmetric carbon atoms proceeded with almost complete retention of configuration. The method of Zolotarev et al. is a valuable preparative method that allows the preparation of labeled amino acids and other molecules with a higher tritium inclusion than that obtained in traditional liquid phase exchange.

The hydrogen exchange pattern of spillover hydrogen is different from that of atomic tritium. Hydrogen atoms in amino acids can be exchanged under the action of thermally atomized tritium. Thermally atomized T atoms react as radical particles with the intermediate formation of amino acid radicals. In contrast to the spillover isotope exchange experiments, H atoms at tertiary carbon atoms are displaced more easily than H atoms of methyl groups, and the substitution takes place with substantial racemization of asymmetric C atoms. Therefore, Zolotarev et al. concluded that tritium in their spillover isotope exchange method does not react as an atomic particle.

Zolotarev et al. performed Hartree−Fock calculations of the interactions of a proton with amino acids. The electronegative N and O atoms of the NH_2, COOH, and OH groups had the largest proton affinities. This agrees well with the fact that the hydrogen at these positions is easily replaced by tritium in the spillover isotope exchange method. To explain the spillover isotope exchange reaction, HF calculations were performed for the interaction of organic molecules with a hydroxonium ion H_3O^+, the simplest representative of a Brønsted-type acidic center. The order of the theoretical activation energies for the exchange reaction of H_3O^+ with H atoms bonded to different carbon atoms correlated with the experimental exchange results. Therefore, it was concluded that the spillover isotope exchange reaction takes place on Brønsted-type acidic centers, formed by hydrogen spillover, according to a synchronous one-center mechanism. The transition state of this reaction is characterized by the formation of a penta-coordinated carbon (CH_5^+) and a three-center bond between the carbon and the incoming and outgoing hydrogen atoms.

The spillover of hydrogen from metal particles to organic molecules was explained by the simultaneous formation of H^+ and H^- ions, as proposed by Zhang et al.,[129] Ebitani et al.,[137] and Roland et al.,[42] who assumed that an equilibrium between charged (H^+ + e) and atomic (H) forms of spilled-over hydrogen exists on the support. Zolotarev et al. also pointed out that an investigation with Pt/SO_4−ZrO_2 had suggested that hydrogen spillover leads to the conversion of Lewis acidic centers into Brønsted acidic centers.[138] It is doubtful, however, if sites of sufficient acid strength for the protonation of aliphatic carbon atoms exist on the surface of $BaSO_4$ or $CaCO_3$, especially in the presence of molecules that contain N and O donor atoms. Another explanation for the observed H−T exchange may be that instead of migration of T atoms from metal to support surface, the organic molecules migrate from support to metal. After H−T exchange on the metal, the tritiated molecule moves back to the support by exchange with a neighboring unlabeled molecule on the support. The use of $BaSO_4$ and $CaCO_3$ as support may be crucial, as in the Lindlar catalyst. That catalyst is used for the hydrogenation of triple and conjugated double bonds to double bonds. The $BaSO_4$ is believed to not only act as support but also as modifier for Pt (by partly covering the Pt surface with S atoms), to suppress unwanted subsequent hydrogenation reaction of the double bond.

10. CONCLUSIONS

Spillover of H atoms from metal particles (or other sources of H atoms) to a reducible support is a fact; this was demonstrated by Khoobiar in the first publication on spillover.[1] Spillover of H atoms to a graphitic carbon has also been demonstrated (section 5). In both cases, energy arguments support the possibility of spillover. The situation is different for nonreducible supports. Spillover from a metal surface to the surface of a defect-free support such as Al_2O_3, SiO_2, MgO, and zeolites is energetically impossible, despite many publications to the contrary. In many publications, proof for such spillover is mainly or exclusively based on H−D exchange on the support, and in other publications a critical examination of possibilities other than spillover is lacking.

That does not mean that spillover can be disregarded. Spillover of H atoms from metal particles to a support with defects or to a contaminated support may be possible. If the defects bind H atoms and if the distance between the defects is not too large, then H atoms might diffuse from the metal particles to the defect sites. An order of magnitude estimate of the number of metal particles and defects shows that a 2 wt % Pt-on-support catalyst, with a support surface area of 100 m^2/g, has an average metal atom density of 0.6 atoms/nm^2. If each metal particle contains only 10 atoms (this corresponds to a 100% dispersion of the metal atoms), the average particle density is 0.06 particles/nm^2. This is of the same order of magnitude as the density of surface defects of MgO and Al_2O_3 powders (cf., section 4.2). If the metal particles and surface defects would be randomly distributed over the support surface, they would be $(1/0.06)^{0.5} = 4$ nm apart. However, it might well be that surface defects are not randomly distributed, because they will occur more often at high index planes and at edges than at low index planes. In that case, their average distance will be much smaller than 4 nm, and transport of H atoms from one defect to the neighboring defect may have much lower activation energy than calculated in section 3 for ideal low index surfaces. If furthermore metal cations are preferentially adsorbed on surface defects during wet catalyst preparation, the metal particles that are created by reduction may well be positioned at or close to surface defects. In that case, an energetically easy migration path for H atoms from metal particle to surface defects may be possible.

The theoretical and experimental results of hydrogen adsorption on graphitic structures (section 5) showed that spillover to a carbon support is possible. This suggests that spillover to a nonreducible support becomes possible when a graphitic type of carbonaceous material covers the support. Such carbonaceous deposits are easily produced in reactions of unsaturated hydrocarbons and may function as transfer agents in hydrogen spillover from metal particles to molecules adsorbed on the support. In hydrogenation catalysis in particular, this may be important, because before hydrogenation the molecules contain double or even conjugated double bonds, which easily lead to unsaturated coke. The results obtained for HDS over stacked beds might be explained in this way. Unsaturated molecules might form a thin coke layer on the surface of the separator bed. If the layer is graphitic, it may enable spillover from the upstream MS/γ-Al_2O_3 bed to the MoS_2/γ-Al_2O_3 bed. The higher synergism found for more acid supports[176,179] would then be due to their greater tendency to adsorb and polymerize unsaturated hydrocarbons.

In this review of literature published since 1996, the role of hydrogen spillover in four areas of applications was discussed: methanol synthesis, hydrogen storage on carbonaceous materials, hydroisomerization, and hydrogenation of alkenes and aromatics. The occurrence of hydrogen spillover has been demonstrated in the synthesis of methanol over Cu/ZnO and Cu/ZrO_2, but it is doubtful if it is of importance in the industrial process. In the area of hydrogen storage on carbonaceous materials, hydrogen spillover from metal particles to a carbonaceous support is energetically possible in some cases, but not in general, and its usefulness needs further study. Hydrogen spillover has been invoked to explain hydroisomerization, but the arguments opposing the bifunctional mechanism are based on a misinterpretation of the latter mechanism, which is still favored by most scientists. Evidence of spillover in the hydrogenation of aromatic and alkene molecules is often circumstantial or based on a wrong interpretation of H−D exchange of support protons of metal on silica, alumina, and zeolite catalysts. H−D exchange of support hydroxyl groups does not constitute proof of spillover. It can also be explained by exchange between M−D and S−OH species at the perimeter of the metal particles and then by OH−OD exchange on the support.

Hydrogenation by spillover of H atoms to molecules adsorbed on a defect-free nonreducible support cannot take place because migration of H atoms from a metal to such a support is strongly endothermic, but is possible when this support has defects or is covered by a carbonaceous layer. Such spillover could increase the hydrogenation capability of a catalyst or maintain hydrogenation activity in the presence of a poisonous gas such as H_2S. Yet even if hydrogen atoms were to migrate over a coked support surface, the ultimate question is what effect this will have on the hydrogenation capability of the metal on support catalyst.

Hydrogen atoms on a metal surface react with unsaturated molecules at relatively low temperature, but will a hydrogen atom on the support surface react nearly as quickly? The disadvantage of a reaction between a hydrogen atom and an organic molecule on the support is that, whereas the H atom is reactive, the molecule is not “prepared” for the chemical reaction by chemisorption. In the reaction between an H atom and an alkene, as in the reaction of ethene to the ethyl radical and then to ethane, this may not be a problem. Ethene reacts in the gas phase with an H atom with low activation energy.[48] Yet for aromatic molecules this may be a problem, because hydrogenated intermediates (radicals) have a high energy, unless stabilized by interaction with metal atoms. Surface science has shown that a bimolecular catalytic reaction is enabled by chemisorption of both reaction partners. For instance, in the hydrogenation of benzene, metal atoms split the H_2 molecule into H atoms and chemisorb the benzene molecule so that the electronic state of the carbon atoms changes. C−M bonds are formed and C−C and C−H bonds are elongated and weakened, so that they change toward the C−C and C−H bonds in cyclohexane.[191] Chemisorption does not occur when a benzene molecule adsorbs on a support surface, which can bind benzene only by weak van der Waals interactions. Thus, even if hydrogen spillover were to occur, its importance for catalysis is questionable. Nevertheless, some scientists maintain “Yo no creo en las meigas, pero haberlas haylas”.[192]

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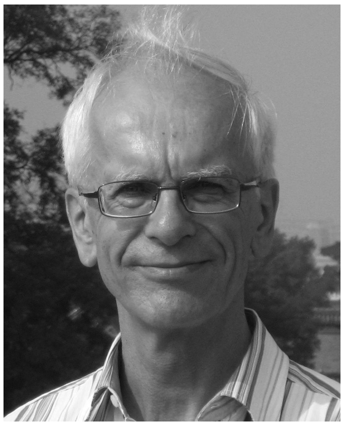
Notes

The author declares no competing financial interest.

Biography



Roel Prins (1941) received his Ph.D. degree in physical chemistry in 1967 at the University of Amsterdam. He then joined the Shell Co.

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