catalysts

Review

The Hydrogen Spillover Effect—A Misunderstanding Study II: Single Oxide and Zeolite Supports

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Abstract: This investigation confirms that the existence of the hydrogen spillover effect (HSPE) in the case of metal catalysts supported on non-reducible monoxides or zeolites is based on a strong corpus of experimental studies, enlarging and deepening previous statements. The structure of hydrogen spillover consists of H/OH pairs conjugated with M^{m+}/O^{p-} pairs (p = 1 or 2). It is formed by dehydroxylation followed by OH/OH exchange or by the hydrogenation of conjugated pairs. Such a structure imposes the following chemical processes: (i) hydrogenations take place over OH Brönsted acid sites (BAS); (ii) they are excluded over M^{m+}/O^{p-} Lewis acid sites (LASs), which are deactivating or dehydrogenating; (iii) surface diffusion of hydrogen spillover proceeds through the migration of H/H pairs from LASs to LASs; (iv) the diffusion rates are determined by the oxide supports' basicity; and (v) H/D exchange is proof of the existence of hydrogen spillover. The nature of hydrogen spillover (radical/ionic) depends on the polarity of the H/OH pairs, which in turn, is determined by the basicity of the support. Our concept of conjugated active sites is a good descriptor of the reaction paths at the molecular level. The view of LASs bringing about additional activity to BAS is not pertinent.

Keywords: interface dehydroxylation; H/OH exchange; propagation; diffusion; oxides basicity/ionicity; H/D exchange; hydrogenation

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1. Introduction

Hydrogenation reactions are an important class of chemical processes in heterogeneous catalysis from an academic and industrial point of view [1–5]. They have attracted a great deal of attention in the particular domain of petrochemistry and organic synthesis [6,7]. Significant advances have been achieved since the beginning of the 20th century; however, some issues still remain unsolved. This is the case for hydrogenation reactions over oxide-supported metal catalysts. The chemical processes involved can take place on the metal or on the support; also, activity and selectivity are determined by the characteristics of the surfaces of the latter. This competition has been an important research topic since the discovery made by Khoobiar [8] in 1964 showing the reduction of WO_3 by H_2 through incorporation of H atoms in the presence of a Pt/γ-Al_2O_3 catalyst. The phenomenon was denoted as the hydrogen spillover effect (HSPE) [9] in which the H atoms stemming from the dissociation of H_2 on the metal migrated to the support where they were stored or reacted. The topic gave rise to debates and controversies, particularly as to whether or not it appears for non-reducible oxide supports [10–14]. Even though it is well established that hydrogen spillover forms and migrates as H^+/e^- pairs all over the surface of reducible oxide supports [11], there is still speculation on its existence for irreducible oxide supports.

Rejection of the HSPE is based on arguments like the absence of a correlation between the amounts of hydrogen spillover and catalytic activity, the presence of impurities (on the support or in the gaseous reactant flow), and gaseous transport of the metal active phase [15]. However, the most important and recurrent type of argument relies on thermodynamic considerations [11]. Certain authors concede that the phenomenon occurs at short distances from the metal particles only [16,17] and therefore, the support cannot contribute efficiently to hydrogenation reactions. For others, thermodynamic prohibitions apply to SiO_2, Al_2O_3, and MgO single oxides only and they propose an alternative mechanism [18]. This assumes that this could exist for zeolites, as well as irreducible supports. In the meantime, other authors [19] have claimed that the HSPE was prohibited for single metal oxide supports but allowed for zeolites, a statement based on their redox properties and opposite to what we previously suggested based on the acid–base properties of irreducible metal oxides [20].

In our preceding investigation [20], we demonstrated that the controversies were mainly due to misinterpretations or omissions in earlier works [21–27] and that the phenomenon does exist. For example, we showed that the absence of a correlation between amounts of hydrogen spillover and catalytic activity was simply due to the fact that all of the H spillover species formed were not involved in the hydrogenation processes; only those weakly adsorbed participated. We also proposed mechanisms of hydrogen spillover formation, diffusion, structure, and mode of action (see Scheme S1 and Schemes S2–S4 [20]), which still remain the opposite of common beliefs, however [3,11,17,19,28].

The persistence of beliefs as well as recent leading papers suggesting alternative mechanisms to the HSPE stimulated our thoughts on hydrogenation reaction paths and led us to closely revisit the literature data on this topic. The aim of this new investigation is to overcome prejudices and provide more insights on its comprehension. As shown below, this resulted in the strengthening and substantial enlargement of our previous claims.

2. Thermodynamic Considerations

In the literature, there still exists a strong conviction against the HSPE for non-reducible oxide supports based on the misreading of thermodynamics theoretical calculations [11,29].

According to DFT calculations, thermodynamic prohibitions do apply to defect-free irreducible oxides like silica, alumina, or magnesia where a hydrogen atom does not form a chemical bond with surface atoms with saturated bonds [29]. They showed that the binding energy of a hydrogen atom is small for MgO and even repulsive for SiO_2, while the bonding of a H atom to a metal atom of a Pt cluster situated on the support is strong [29]. These energy results led the authors to predict that the spillover rate is much lower than that observed for reactions that have been ascribed to spillover. Similar binding energies were obtained through MO calculations for the interactions between H atoms and the surfaces of MgO [30], SiO_2 [31], and γ-Al_2O_3 [32]. However, the authors specified that hydrogen spillover is possible at oxide surface defects and also from a metal particle to an oxygen-containing group on a carbon surface [29,33].

It was pointed out that these defects may be created after thermal treatment of non-reducible oxides under H_2 atmosphere [11]. They can act as receiving sites of H atoms, making hydrogenation processes possible. They could also be created by hydrogen spillover. As an example, the study of hydrogen thermal desorption for Pt(Ni)/Al_2O_3 catalysts or pure Al_2O_3 is cited, after activation by H_2 or by hydrogen spillover [34]. The results reported (Figure S2) clearly show differences in the temperature profiles: activation by H spillover species induced the formation of new active sites at higher temperatures, but this was not observed for the activation by molecular hydrogen, which is much less reactive. This behavior has been observed by other authors [35].

Furthermore, this new inspection revealed that the theoretical calculation misreadings in fact resided in the respective roles of heating and hydrogen spillover in the creation of active sites. The heating was favored [11], in contradiction with the hydrogen desorption study cited [34]. The authors argue that hydrogen spillover is thermodynamically permitted and not controversial, as is still commonly interpreted for metal catalysts supported on non-reducible oxides.

3. The Alternative Mechanism to Hydrogen Spillover for Single-Oxide Supports

For metal-based catalyst hydrogenation reactions, the HSPE takes place on the support or at the interface [20]. A bifunctional mechanism, as an alternative to the HSPE, was recently reported for the hydrogenation of toluene to methylcyclohexane (MCH) over a Pt/SiO_2 catalyst mechanically mixed with silica or alumina (magnesia or titania were also used) [18]. Dilution with alumina led to enhanced conversion of toluene, and this improvement increased with the increasing dilution ratio. Production decreased when propanoic acid (PA) was added to the reaction flow. PA is an inhibitor of H_2 dissociation over metal oxides [36] and, consequently, hydrogenation reactions. No effect of PA was observed with the catalyst diluted in silica. In a separate experiment, pure alumina activated by gaseous H_2 was shown to hydrogenate methylcyclohexene (MCHE) or methylcyclohexadiene (MCHD) but not toluene.

According to the authors, the reaction will occur on the metal phase only, directly and indirectly. They assumed that carbon deposits on Pt, which alter the conversions, could be depleted with the help of the support: metal–carbon adspecies would be desorbed as gaseous H-deficient intermediates (MCHE and MCHD) and then hydrogenated to MCH on the alumina diluent. This would have resulted in the liberation of active sites on Pt, bringing about additional conversion of toluene with rates much greater than on alumina. In the presence of PA, this route is prevented because $M^{m+}O^{p-}$ active sites of the diluent—on which H_2 dissociates—became contaminated, leading to decreased conversion. The influence of dilution was ascribed to a proximity effect between metal and support active sites: the shorter the distance, the higher the rate of enhancement. The reaction-transport model supported the chemical paths proposed.

These results call for comments.

If the experimental method and theoretical calculations used apparently corroborate the existence of the bifunctional process, they are not at all proof against the existence of the HSPE and this is for several reasons. First of all, contrary to the affirmation of the authors, bare alumina activated by hydrogen spillover is capable of hydrogenating the aromatic ring (see Section 3), and therefore, the test reaction with gaseous hydrogen is not pertinent and consequently the bifunctional mechanism is wrong. The bibliography of the authors on aromatics hydrogenation was incomplete, leading to the omission of important experimental results. On the other hand, PA was shown to chemically interact with amphoteric alumina but only physically with silica [36], explaining why this diluent was inactive in the hydrogenation of toluene. Moreover, silica is a support that is poorly reactive toward hydrogen spillover as compared to alumina or magnesia (MgO >> Al_2O_3 > SiO_2 [21–23]; also, it was not a good metal catalyst support nor a good diluent for the purpose of the demonstration. Finally, the proximity effect observed by the authors is also a characteristic of the HSPE. It is well known that dilution of a metal-based catalyst by the support increases its chemisorptive and catalytic properties up to a maximum, corresponding to the maximum distance between the metal particles and the hydrogen spillover-accepting sites, e.g., [16,37,38].

Furthermore, we noticed that the authors rejected the HSPE for silica, alumina, and magnesia but not for zeolites which are also non-reducible oxide supports widely used in catalysis. This meant that they implicitly admitted its existence for zeolites.

4. The Existence of Hydrogen Spillover on Single Oxide Supports

There is an important corpus of experimental evidence on the existence of the HSPE for SiO_2, Al_2O_3, and MgO non-reducible oxides, which are often ignored in the literature. It is therefore useful to keep in mind protocols and arguments supporting the reality of the phenomenon. We provide the essential features below.

4.1. The Experimental Proofs

Two types of catalytic systems have been used to prove the existence of the HSPE: metal-supported catalysts diluted by an oxide or an oxide activated by an external source of hydrogen spillover (metal catalyst immersed in the support).

The first type of experiment was described in the earlier works of Sancier [39] and Delmon et al. [40] for the hydrogenation of benzene with alumina-supported Pd or Pt catalysts diluted by the support. The catalytic activity increased with dilution, and it was demonstrated that the alumina diluent did not act as a trap for the removal of impurities from the hydrogen stream nor did the support metal impurities alter the activity measurements.

The most convincing proof of HSPE's existence was brought about by the Teichner group [21–23,41–44] using the second type of experimental protocol for silica, alumina, and magnesia. After activation, the oxides became hydrogenating (for ethylene, butenes, and benzene), isomerizing (for methylcyclopropane), aromatizing (for n-heptane), or cracking (for cumene) solids. The occurrence of one reaction or another depended on the nature of the metal, the nature of the oxide, and the activation or reaction conditions.

These results pointed out the existence of various hydrogenating–dehydrogenating and acidic centers induced by hydrogen spillover. For example, the hydrogenation of ethylene over alumina took place stoichiometrically in the presence of both hydrogen spillover and gaseous hydrogen after activation by Ni/Al_2O_3 but became catalytic (no need for hydrogen spillover) after activation by Pt/Al_2O_3. Silica is activated by Pt/Al_2O_3 hydrogenated ethylene and cracked cumene.

It is noteworthy that oxides activated by H_2 are always found to be much less active in ethylene hydrogenation than those activated by hydrogen spillover. In addition, the latter oxides were insensitive to reoxidation treatment, an indication that their hydrogenating properties were not due to the presence of metal impurities in the support nor to the migration of active metal particles onto the support [15], both arguments against the HSPE [11]. In contrast, oxides activated by gaseous H_2 became inactive after reoxidation by O_2. These results again indicated that molecular hydrogen and H spillover atoms gave rise to active sites of different types, as one expects [34] since the chemistry of single hydrogen atoms is different from that of molecular hydrogen.

4.2. The Hydrogenation of Benzene

In the specific case of benzene hydrogenation [43], the following was shown: in a flow reactor at 144 °C, alumina, activated at 300 °C by hydrogen spillover, catalytically gave cyclohexane and cyclohexene with a conversion of 1% and selectivity of 67% and 33%, respectively; in a static reactor, the performance at 115 °C was conversion of 2.5% with a composition of cyclohexane at 75% and cyclohexadiene at 25%; at 180 °C, the conversion was 30% with a composition of 68% in cyclohexane and 32% in cyclohexadiene and no traces of cyclohexene. The same alumina activated by H_2 was inactive in the reaction. Moreover, it may be remarked that the high selectivity into cyclohexene and cyclohexadiene (25–36%) again provides an argument against the migration of the metal from the catalyst to alumina, with the platinum exhibiting an aptitude for the total hydrogenation of benzene.

These results and observations strengthen the existence of the HSPE and the rejection of the bifunctional mechanism.

4.3. The Kinetics Studies

The HSPE for metal-based catalysts deposited on non-reducible oxides is supported by many kinetic studies. The most significant ones, in the context of this discussion, are those of the Vannice group [45–47]. They have described a great number of catalytic hydrogenation systems: benzene, toluene, or o,m,p-xylene reactant molecules associated with Pt or Pd metals supported on SiO_2, Al_2O_3, SiO_2-Al_2O_3, or TiO_2 oxides. On the other hand, the rate equations established took into account aromatic dehydrogenation reactions to various carbonaceous surface species which inhibited the principal reaction (as assumed by the authors of the bifunctional mechanism [18]). Moreover, the reaction was shown to occur on both the metal and the oxide support. For a given metal, the higher the acidity of the support, the higher its contribution to hydrogenation (e.g., SiO_2-Al_2O_3 >> Al_2O_3, SiO_2).

For the Vannice group, the Langmuir–Hinshelwood model was found to depict the kinetics of all of the catalytic systems considered. In addition, the isomerization of o-xylene was observed and the rate enhancements of this reaction were identical to that of the hydrogenation of o-xylene. The derived rate expression was computer fitted to the data and the obtained value of the adsorption equilibrium constants for H_2 and the aromatic compounds were consistent with assumptions in the model. They provided trends in agreement with results from the literature.

At this level of the discussion, it is useful to mention another belief about the HSPE, its radical nature, expressed by several authors [11,17,21]. Based on the works of the Teichner group, this statement is inexact. In effect, the Teichner group mechanism was proposed (Scheme S5 [21]) in the following reaction conditions [21]: static reactor, hydrogen spillover produced by a monosource (immersion of a metal catalyst in alumina), alumina activation at 300 °C for 12 h, reaction temperature of 25, 110, or 300 °C. In comparison, usual kinetics studies are conducted with hydrogen spillover produced by a multisource (metal-supported catalysts) in a flow bed reactor at ~300 °C after activation at the same temperature.

The chemical properties of hydrogen spillover are obviously the same with mono- or multisource origins. Nevertheless, due to the differences in the number of active sites involved and in the mode of hydrogen supply (continuous/discontinuous), the reactive atmospheres are different and result in different kinetics and reaction paths. This could give rise to a radical chain process for oxides activated by H spillover species and to a Langmuir–Hinshelwood type process for supported metal catalysts. In other words, contrary to literature claims [11], *the radical mechanism is not intrinsic to the nature of the HSPE but to bare oxide catalysts activated by a hydrogen spillover monosource at high temperatures.*

5. Hydrogen Spillover and Experimental Protocols of Rejection

Close examination of the content of papers rejecting the HSPE showed that they used inadequate experimental protocols or unsuitable model catalysts or model reactant molecules. This is illustrated in the following examples [20].

Miller et al. [48] performed the hydrogenation/isomerization of ethylbenzene (EB) using a mixture of a pre-reduced Pt catalyst encapsulated in NaA zeolite and EB chemisorbed on the acid sites of ultra-stable Y (H-USY) zeolite. After flowing with D_2, it was submitted to thermal programmed desorption. The reaction gave rise to isotopic exchange on aromatic (~90%) and alkyl (~15–30%) hydrogens but not to saturation of the aromatic ring.

Pt/NaA is a non-hydroxylated catalyst and reported by the group to almost not incorporate hydrogen spillover, in contrast with the Pt/HA hydroxylated structure [49]. Moreover, Choi et al. [50] showed that Pt/HA hydrogenated benzene with high conversion via the HSPE whereas Pt/NaA was quasi-inactive. This explains why EB hydrogenation by Pt/NaA failed.

The same group [48] found that hydrogen spillover did not contribute to the hydroisomerization of neopentane over Pt catalysts encapsulated in hydroxylated zeolites. Neopentane is an archetypal hydrocarbon reactant for platinum-only-catalyzed skeletal rearrangements; it cannot form olefins or carbenium ions prior to isomerization, e.g., [51–53]. In addition, using neohexene (able to form carbenium ions and olefins) as the reactant molecule, Foger and Anderson [51] showed that, over Pt/zeolite catalysts, the rate-determining step occurred on the acidic sites whereas for neopentane, the reaction was entirely confined to the metal surface.

Various unsaturated carboxylic acids (benzoic, cyclohexene carbonic, acetylene dicarbonic, maleic, and acrylic) were adsorbed on γ-alumina and the covered oxide was submitted to hydrogen spillover supplied by an external source (oxide-immersed Pt/Al_2O_3) [54]. After flowing with D_2, H/D exchange occurred, not the hydrogenation reaction. In this case, the reason was that pre-adsorption of the carboxylic acids contaminated the potential active sites of hydrogenation (see Section 2 and ref. [36]) and only permitted H/D exchange to take place.

Primet et al. [55] reported an IR/UV study of the hydrogenation of benzene on 1%Pt encaged in Pt/NaY, Pt/HY, and Pt/CaY. Benzene was adsorbed on the catalyst after reduction and evacuation at 350 °C. Due to the low loading of platinum, benzene mainly adsorbed on the support. It was also found that there was stronger bonding of the benzene molecule on a surface of the platinum atom than on the support surface. During the reaction, conducted at 40 °C, the authors observed that the concentration of benzene adsorbed on the zeolite decreased whereas it remained constant on Pt for the three catalysts. They concluded on the occurrence of the reverse HSPE, that is, the migration of hydrogen from the support onto the metal where the reaction took place.

This conclusion is true for Pt/NaY and Pt/CaY catalysts because the absence of hydroxyls on the support surface did not allow for the occurrence of the HSPE and only permitted the reaction to occur on the metal phase [20,49,51].

To understand the results obtained with the hydroxylated Pt/HY catalyst, one has to keep in mind that hydrogen spillover exists as weakly and strongly held H atoms on the support, e.g., [20,27,35,48,49,56], and that the former species were the only active species [20,27]. Also, the harsh evacuation of the reaction cell at 350 °C before benzene adsorption would have led to the removal of effective hydrogenating H spillover species, those weakly adsorbed. This resulted in benzene adsorption on the remaining H spillover, those strongly bound to the HY support and non-reactive at the reaction temperature of 40 °C, and then to its migration to the metal nanoparticles where it reacted. This behavior is similar to the observations of the Teichner group [21–23] and Lenz and Conner [57] on ethylene hydrogenation by alumina activated by hydrogen spillover; the reaction did not occur when activation was followed by evacuation before the introduction of the reactant mixture.

6. The Existence of Hydrogen Spillover for Zeolite Supports

Many hydrogenation reaction studies claimed the occurrence of the HSPE on zeolite-supported metal catalysts.

The phenomenon has been widely demonstrated with encapsulated metal catalysts [12,58–61]. Choi et al. [50] used a 1.1%Pt model catalyst supported on Linde Type A (LTA) zeolite with a dense aluminosilicate matrix for the hydrogenation of benzene at 250 °C. The zeolite matrix allowed for the selective diffusion of hydrogen over the organic reactant, permitting hydrogenation or dehydrogenation on the support surface via hydrogen spillover. The results obtained showed that these reactions occurred with TOFs of substantial value, comparable to that of an open-structure Pt/SiO_2 catalyst of the same metal loading. In addition, dilution of the catalyst by the support led to substantial increased activity [61]. With Pd/SiO_2, the reaction occurred on the metal phase only due to the poor acidity of the silica support.

Semi-hydrogenation of alkynes to alkenes was similarly performed on sodalite zeolite encapsulated palladium nanoclusters [58]. The method was also used for the selective hydrogenation of crotonaldehyde to the unsaturated crotyl alcohol over a Sn-modified SiO_2-coated Pt catalyst [62].

The HSPE has been shown to also take place on more open zeolite supports. This is the case of toluene hydrogenation over catalysts based on Pt supported on large pore acidic HUSY and HBEA (Beta A) zeolites with different metal/acid ratios [63]. The electronic properties of Pt^0 clusters were similar for the different catalysts. The initial turnover frequency of fresh catalysts depended on both the metal dispersion and the support surface, indicating the contribution of zeolite acid sites to the reaction. The better activity of Pt/HBEA than that of Pt/HUSY was ascribed to the proximity effect between Pt clusters and acid sites.

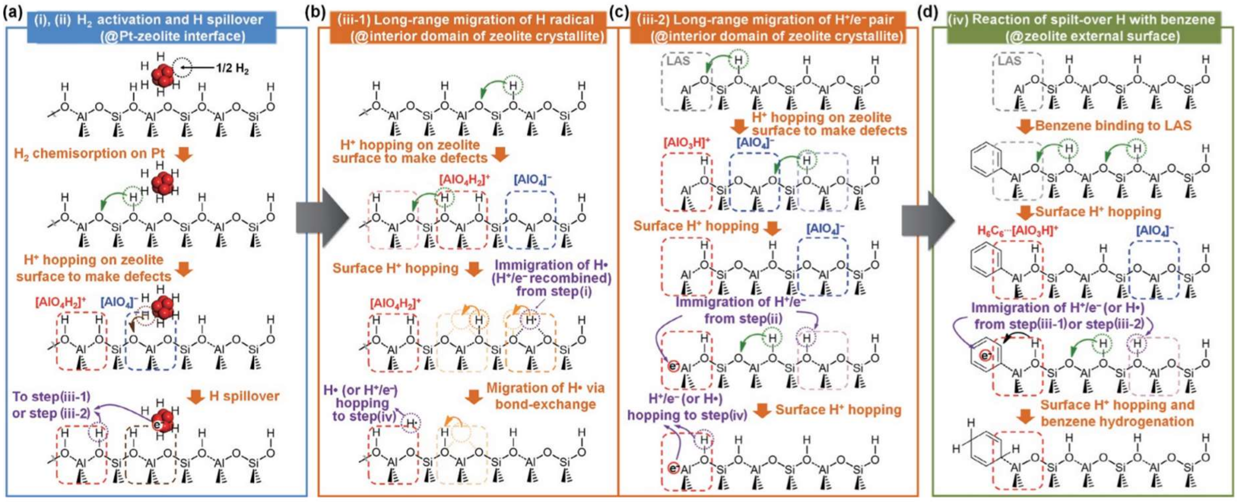
The influence of the metal/acid ratio has also been reported for the hydrogenation of benzene over Pt-loading dealuminated Y zeolite catalysts [64].

7. The Hydrogen Spillover Effect and the Redox Properties of Acid Zeolite Supports

We previously [20] considered that the HSPE held for irreducible supports whether they were single oxides or zeolites. Choi et al. [19] claimed that it existed for zeolites only and not for single oxides, considered to be controlled by the bifunctional mechanism [18]. This statement was based, on the one hand, on the assumption that the presence of an organic molecule induced the triggering of hydrogen spillover production and, on the other hand, on the redox properties of acidic zeolites [65].

The assumption meant that the HSPE holds for zeolites in a reactive atmosphere but not in a hydrogen atmosphere. In a hydrogen atmosphere, thermodynamic prohibitions apply like for irreducible single oxides: H atoms are repelled by the surfaces as the surface atoms have all electrons in the closed shell. In contrast, in a reactive atmosphere, the unsaturated molecules continuously consume H atoms stemming from sites far from the metal particles. This chemical process is denoted as "dynamic equilibrium" by the authors. As to the redox properties, they would allow hydrogen spillover to migrate over the support as $H^\bullet$ atoms or H^+/e^- pairs. The role of the support would therefore be to provide a migration pathway for $H^\bullet$ active atoms and sites for binding the organic reactant. Such a behavior is not possible for SiO_2, Al_2O_3, or MgO single oxides.

The mechanism proposed was simulated using DFT calculations where the model catalyst consisted of Pt_6 clusters encapsulated in a zeolite of NaA pristine type serving as an energetic reference state. The zeolite comprised an alternative arrangement of Si and Al and Brönsted acid sites (BAS) possessing a substantial radical character as the major mediator for hydrogen migration. The $H^\bullet$ atoms' migration took place from the interior of the zeolite to the exterior where organic molecules react (Scheme 1).



Scheme 1. Proposed H spillover pathways in Pt/HA (LTA) based on DFT calculations. (**a**) At the Pt_6–zeolite interface, H_2 is dissociated at the Pt_6 surface (step (i)) and then spilled over to the zeolite surface (step (ii)). (**b**) When H diffuses over the interior domain of the "defect-free" zeolite framework, H migrates in the form of an H radical (step (iii-1). (**c**) When the zeolite framework contains LASs, the H atoms migrate in the form of an H^+/e^- charge pair. (**d**) At the zeolite external surface, the LASs serve as catalytic active sites, and the LASs bind the organic molecule (such as benzene) at which the spiltover H^+/e^- pair is recombined and transferred to the benzene, yielding $C_6H_7^\bullet$ (step (iv)). Dashed squares represent Brönsted and Lewis acid centers. Reprinted from [19] with permission from Springer Nature 2022.

The results obtained showed that a series of rearrangements between OH groups on the zeolite surface can generate both H^+-deficient $[AlO_4]^-$ and H^+-rich $[AlO_4H_2]^+$ sites.

The H species chemisorbed on the Pt_6 surface can migrate to the zeolite surface only as H^+ while e^- remained on the Pt_6 cluster. Through further proton rearrangement between the OH surface groups, the spillover H^+ can move away from the Pt_6 cluster. When H^+ diffuses sufficiently far away from the Pt_6 cluster, H^+ and e^- can suddenly recombine to form $H^\bullet$, which is stabilized by $[AlO_4]^-$ by forming a three-centered O-H-O bond (change of the H^+/e^- pair to $H^\bullet$).

On the external surface of the zeolite, H^+/e^- migration becomes feasible due to the existence of terminal Lewis acid sites (LASs) (tri-co-ordinated Al sites). In addition, due to their ability to transfer H^+/e^- pairs, the LASs were also predicted to be binding sites for benzene, where hydrogenation takes place. The adsorbed benzene can accept an H^+/e^- pair to form $C_6H_7^\bullet$, which is again stabilized by the terminal Al sites with LAS characteristics for further hydrogenation. The reaction step between H spillover and LAS-stabilized benzene was expected to be almost barrierless. As a result, the rate-determining step of benzene hydrogenation via hydrogen spillover was predicted to be the surface diffusion of active H species.

These theoretical results call for the following questions: (i) in the absence of the unsaturated hydrocarbon, i.e., in a strict hydrogen atmosphere, what would the mechanisms of the formation, propagation, and storage of hydrogen spillover be? Hydrogen storage by zeolites is widely experimentally documented [10,48,49,66]; (ii) if the H migration process proposed works with pristine NaA-type zeolite with alternative Si and Al atoms, what would the mechanism in the case of a zeolite with Si/Al $\neq$ 1 be? In the same way, it is unclear as to why “far away from the nanoparticles H^+ and e^- suddenly recombine to form $H^\bullet$”. Is it a law? Is there a theoretical distance for this surface event?

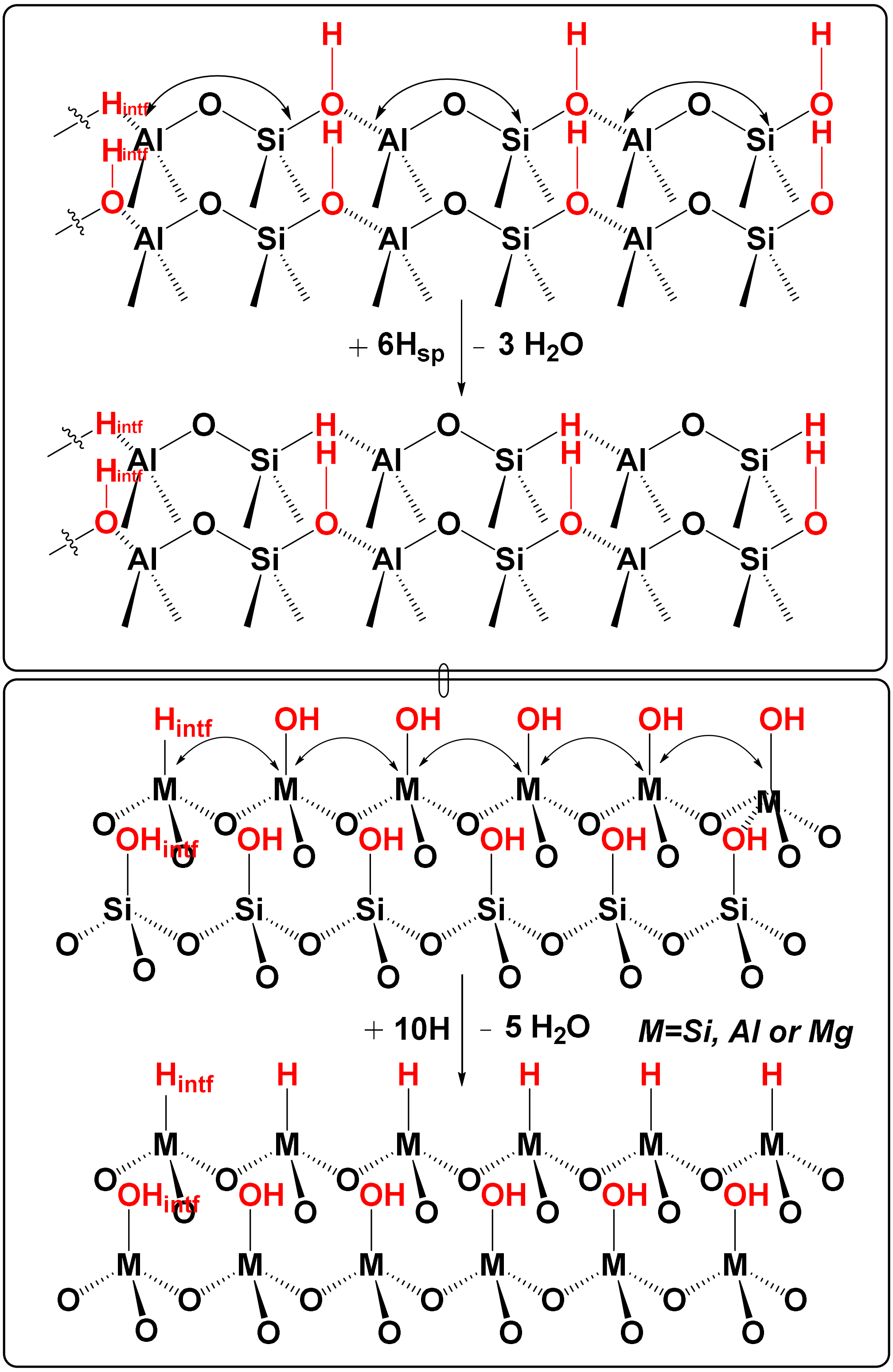
The mechanism proposed is based on the ability of the zeolites to spontaneously generate, in an inert atmosphere, radical cations upon adsorption of organic electron donors like unsaturated hydrocarbons [65,67–70]. Formally, the $[AlO_4]^+H^\bullet$ radical cation postulated par Choi group would be generated by the abstraction of a H atom from H_2 by the zeolite with the help of Pt_6 clusters. Such an interface reaction has not been reported in the literature. On the other hand, the occurrence of changes in the degree of oxidation of hydrogen spillover all along the diffusion pathway is intriguing. We are aware that it is accepted in the literature that acidic zeolites most likely contain a distribution of sites with a range of oxidizing abilities depending on the structure and chemical composition of the zeolite [65,71–74]. Nevertheless, it is hard to accept these changes for a given zeolite with a known structure and chemical composition. The reference of the authors to the same assumption by Roland et al. [75] is not proof. Finally, LASs are probably not likely the active sites since it is widely accepted that hydrogenation reactions mostly take place on BAS for zeolite supports (see Section 8).

8. The Hydrogen Spillover Effect and the Acid–Base Properties of Zeolites

The redox mechanism proposed is a refined chemical process, aiming in some way to mimic that accepted for reducible oxide supports where the H spillover atoms exist and rapidly diffuse over the surface as H^+/e^- pairs [11]. However, it suffers from some weaknesses, as highlighted in our analysis above. It is also very complex and not straightforward to understand.

8.1. The Dehydroxylation Process

We instead propose a mechanism based on the acid–base properties of zeolites, their classical and most important chemical properties, illustrated in Scheme 2. It is chemically similar to that we previously proposed for hydroxylated/acidic oxide supports (Scheme S2 [20]). It is much more plausible, simpler, and easier to understand and apply to Si/Al $\neq$ 1 (see Scheme S6). The acid–base properties are those widely admitted to work in the rich applied chemistry of zeolites (hydrogenation, isomerization, alkylation, aromatization, and cracking reactions). As to their redox properties, they may give rise to radical cation generation, the study of which rather enhances our academic knowledge. These entities have been invoked as intermediates in the hydrotreatment of hydrocarbons [76,77].



Scheme 2. Proposition of the mechanism of hydrogen spillover formation and propagation for single oxide and zeolite supports.

8.2. The Propagation of Hydrogen Spillover

The mechanism proposed for the formation and propagation of hydrogen spillover in the case of zeolites would take place through an hydro-dehydroxylation interface (where water molecules are formed) followed by H/OH exchange reactions. The H atoms incorporated would be stabilized by neighboring OH groups, where H and OH entities are close enough to hydrogen bonding [57]. As a result, the structure of hydrogen spillover for zeolite supports would consist of H/OH pairs which, after H_2 desorption or reaction, give rise to M^{m+}/O^{p-} pairs. These sites are denoted as conjugated pairs. The extent of propagation increases with zeolite hydroxyl concentration and activation temperature [48,49,56], up to a maximum where the hydroxyls are depleted from the surface.

Since OH and M^{m+} are Brônsted acid sites (BAS) and Lewis acid sites (LASs), respectively, we can say that BAS and LASs are conjugated sites interacting with H and O atoms, respectively.

We must underline that the dehydroxylation mechanism was experimentally proven for monoxide supports. Using silica activated by an external source of hydrogen spillover, Lenz and Conner [57] showed that catalytic activity in ethylene hydrogenation involved the previous dehydroxylation of the surface with the production of water. The number of water molecules formed equaled that of the H spillover species (Figure S1 [56]).

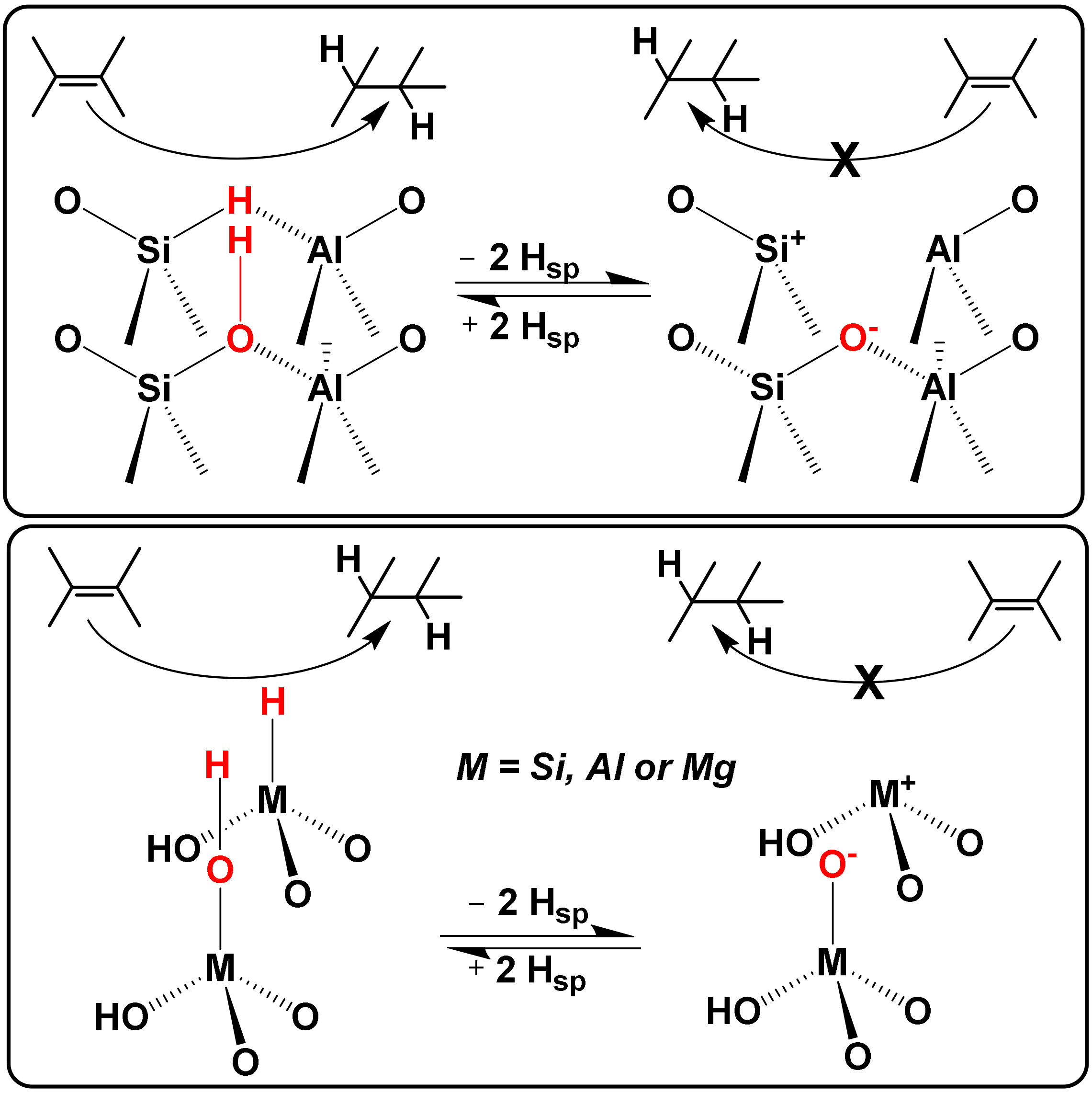
It is worth noting that water was formed only if oxide pre-treatment was conducted below 500 °C and not at higher temperatures [57]. The reason is that silanol groups exist as isolated and associated species (geminal or vicinal positions) below 500 °C and only as isolated species above this temperature. The associated groups permitted the stabilization of the H atoms incorporated. With zeolite supports, the hydrogen spillover amounts increased with that of hydroxyl groups up to a maximum temperature due to excess dehydroxylation [48,49,56]. This is the reason why the stabilization of H spillover species by hydroxyls can also be expected for zeolite supports.

8.3. Lewis Acid Centers Are Deactivating Not Hydrogenating Sites

We previously pointed out that the consequence of the H/OH structure of hydrogen spillover is that hydrogenation reactions necessarily occur through the anchoring of the unsaturated hydrocarbon molecule on BAS and are hydrogenated by the associated H atom (Scheme S4 [20]). The reaction cannot take place on LASs simply because no H atoms exist in the vicinity of the adsorbed unsaturated molecules. The same mechanisms would hold for zeolite supports (Scheme 3).

On LASs, both reactants, the organic molecule and the hydrogen, spillover completely. The adsorption of the hydrocarbon on these sites may be a source of deactivation or contamination. Contrary to that, dehydrogenation reactions may take place instead.

In the literature, LASs are believed to be involved in hydrogenation processes and could even improve the catalytic activity of BAS; however, the exact roles of these entities are unclear [61,63]. In contrast, our concept of conjugated BAS/LASs appears as a good descriptor of the reaction paths at the molecular level; catalytic activity would be correlated to hydrogenating BAS stemming from the hydrogenation of LASs. They would equally participate in the catalytic process.



Scheme 3. Proposition of the mechanism of a hydrogenation reaction over a H/OH site for single oxide and zeolite supports.

8.4. The Role of Brönsted Acid Sites

The role of Brönsted acid sites in hydrogenation reactions is widely accepted for zeolites as catalysts or as metal catalyst supports [78,79]. A linear correlation was shown to exist between the catalytic activity and the number of highly acidic OH groups ($H_0 < -10$) in benzene hydrogenation by steamed HY zeolites under the pressure of hydrogen [80]. Several zeolites (cubic and hexagonal faujasites, steamed or not) were tested as acid catalysts [81]. Direct benzene hydrogenation leading to cyclohexane was observed at low temperatures (230 °C, P_{H2} = 40 bars) with the less acidic zeolites ($H_0 = -8.5$). Side reactions grow progressively with the acid strength of the catalyst and coke is generated by the more acid hydroxyl groups ($H_0 = -12$).

Benzene as a probe molecule [82] has been widely used to characterize the sorptive properties of metal catalysts supported on acid zeolites [83,84]. Benzenium ions were postulated to form on BAS of Pt catalysts supported on zeolites. Benzene molecules were found firmly held on adsorption sites, cations, or protons, involving the π system of the aromatic ring in the case of exchanged zeolites [55]. It adsorbed in a direction perpendicular to the plane of the ring, i.e., the plane of the adsorbed molecules is parallel to the zeolite surface [85]. It interacted more weakly with the CeKY and HY zeolites than with CsNaY, RbNaY, KY, NaY, and LiY zeolites [83]. This interaction was also shown to be weak for benzene adsorption with the OH surface groups of silica-alumina solids [86].

The prevalence of BAS over LASs was brought about in the particular case of the hydrogenation of adsorbed pyridine into piperidine, using supported noble metal catalysts (Pt, Pd, Rh, and Ir)/SiO_2, physically diluted or not with zeolites (H-ZSM-5, H-USY, H–mordenite, and H–beta A) [87,88]. The reaction was conducted at 150–200 °C, after adsorption at the same temperature, and followed by IR spectroscopy. Pyridine was found to adsorb on the zeolites, not on the metal phases, due to its strong base character. Moreover, it adsorbed preferentially on LASs and, interestingly, under a hydrogen atmosphere, it migrated to a Brønsted acid site where it was hydrogenated. This suggested that spiltover hydrogen should enhance the desorption of pyridine on the LASs and that the possible state of spiltover hydrogen on this site should be hydride, which has strong Lewis basicity. It was concluded that the reaction took place due to the HSPE.

These results illustrate the role of BAS and LAS as conjugated/complementary actors in the case of a hydrogenation reaction induced by zeolite supports.

9. H/D Exchange Is Proof of Hydrogen Spillover

As an additional consequence of the H/OH structure of hydrogen spillover for irreducible single oxide supports, we previously suggested that its surface diffusion was necessarily carried out by the migration of H/H pairs (Scheme S3 [20]) and not by the hopping of single H atoms from OH to OH surface groups, as generally believed in the literature [11,17,34,89]. Since then, the article by Duprez and Martin [89] on this topic, which unfortunately escaped our attention, has strengthened this conclusion.

The authors studied the surface diffusion of H atoms over oxides and oxide-supported rhodium catalysts via temperature-programmed isotopic exchange. The coefficients of surface diffusion of hydrogen (D_s) obtained at 75 °C showed that the mobility of H spillover atoms decreased from ceria to silica supports for both catalyst series (Table S1 [88]):

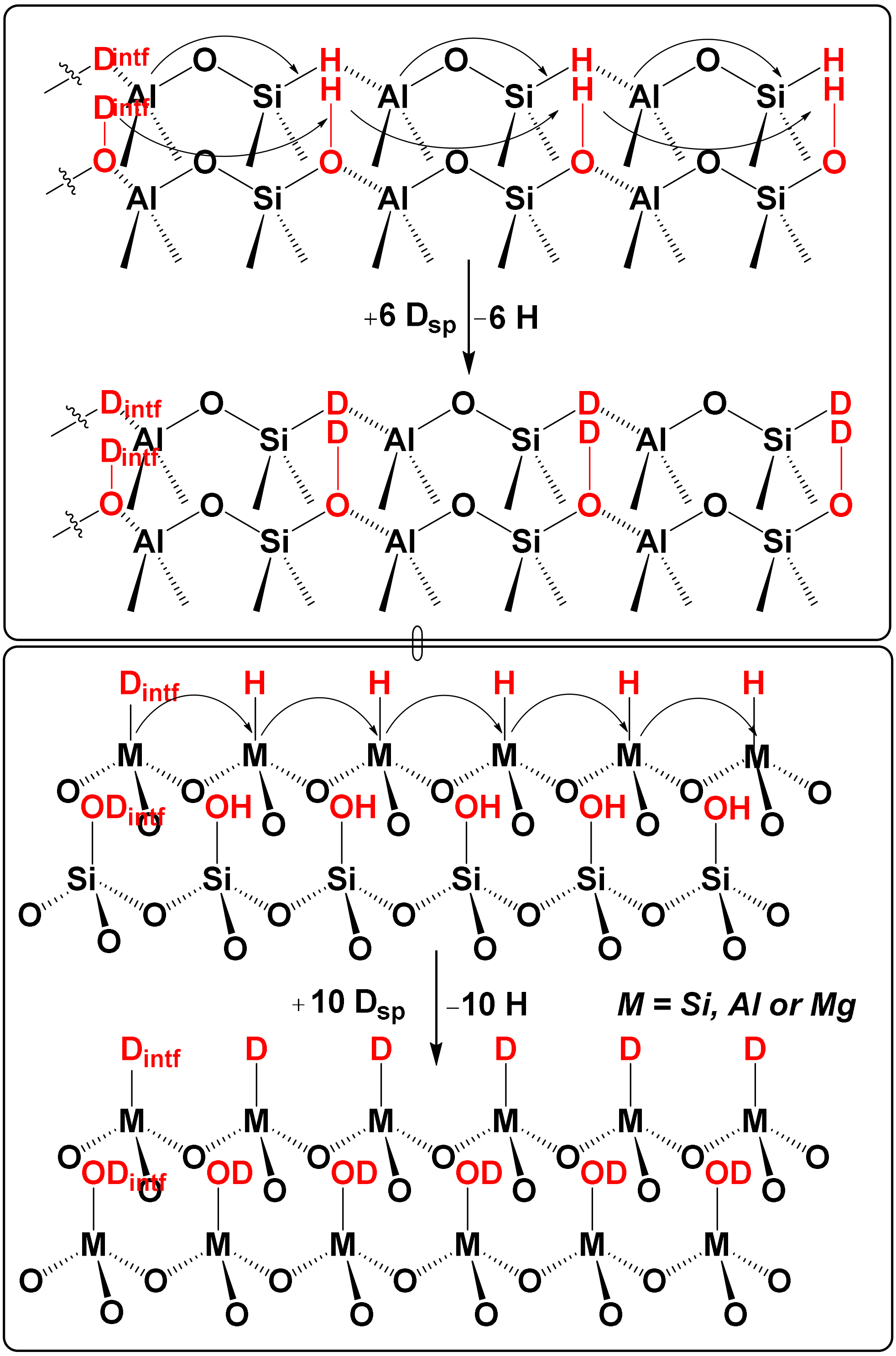
$$CeO_2 >> MgO > (ZrO_2) >> Al_2O_3 >> SiO_2{\sim}0 \quad (1)$$

Strikingly, this order followed that of pure oxide basicity, not of Brönsted acidity, clearly indicating that the diffusion of mononuclear hydrogen species does not apply. In contrast, the correlation with basicity indicated the intervention of both protonic and hydridic H species attached to the support. Diffusion of hydrogen spillover is thus controlled by the basic/ionicity properties of the oxide supports.

For the silica support, these results were confirmed by the work of Ni et al. [90] who studied the adsorption of H_2 and H/D exchange over Ru/SBA-15 catalysts using IRTF spectroscopy. The band observed at 1996 cm^{-1} was ascribed to the reversible formation of Si-H at the metal-support interface. The introduction of D_2 shifted this band to 1987 cm^{-1} with a very weak intensity. The red shift was ascribed to the deuterium isotope effect and the too-weak intensity to the lower stability of D species as compared to that of H species. This corroborated the very bad value of D_s for SiO_2 (Table S1 [88]), almost unable to dissociate the D_2 molecule.

A similar mechanism could be used for zeolite supports (Scheme 4). This is strengthened by an experimental and computational study showing that the H_2 molecule can be polarized in H-mordenite zeolites by simultaneous interactions with a bridged hydroxyl and a framework oxygen [91].

A consequence of this diffusion process is that *H/D exchange is proof of the existence of the HSPE*, in contrast with literature statements [11,17]. In effect, the energetics of the chemical process imply the intervention of both M-H and O-H bonds and not of the latter only.



Scheme 4. Mechanism of diffusion of hydrogen spillover over single oxide and acidic zeolite supports and H/D exchange.

The determination of the diffusion rates of hydrogen spillover using the H/D exchange method was carried out with metal catalysts supported on alumina [31,92,93] and with zeolites [94–96] through the use of infrared spectroscopy or NMR techniques. The disappearance of the signal of the OH group at the benefit of the OD group was ascribed to the migration of a D atom from the metal nanoparticles to the support followed by its hopping from OH to OH groups. The authors ignored the fact that the OD groups formed belonged to D/OD pairs.

The absence of a correlation between H/D exchange and hydrogenation activity reported by Baumgartner [54] and claimed as a strong argument against the HSPE was actually due to an inappropriate experimental protocol (see Section 5).

10. Nature of H Spillover Species

Let us underline that the nature of hydrogen spillover has been at the center of HSPE controversies for decades: are H spillover species purely radical or ionic? [10,11,17,20,75,88].

The dissociation of H_2 is necessarily homolytic on metal nanoparticles, an intrinsic property of reduced metallic phases. On the other hand, on metal oxides, H_2 may be dissociatively adsorbed with charge separation or not, depending on the nature of the solid [97]. The higher the basicity/ionicity of the oxide, the higher the hydridic/protonic character of the resulting H atoms. The real question is then to know how charge separation proceeds when radical H atoms stemming from the metal nanoparticles adsorb on the support after crossing over the interface boundary.

Experimentally, Teichner et al. [23] showed that MgO treated with molecular hydrogen or with hydrogen spillover (from an external metal source) hydrogenated ethylene. Since H_2 is heterolytically dissociated on the bare oxide, this reasonably suggests the same nature for H spillover species. On the other hand, quantum calculations [98] have shown that, for the adsorption of H radical species on irreducible oxides like MgO, there might be the coupling of electrons to form two opposite ions (H^-/H^+) adsorbed on the two surface sites, involving an acid–base mechanism. In addition, it has been demonstrated by means of quantum calculations [98] that polar M−O bonds might favor the heterolytic dissociation of H_2 (e.g., for M = Mg or Al).

From these data, it appears that experimental and theoretical studies indicate that on the metal phase, H_2 is homolytically dissociated into $H^\bullet$ atoms which, after crossing the metal-support boundary, may become polarized or ionized species adsorbed on the oxide support. This is in good accordance with the diffusion of hydrogen spillover as H/H pairs with rates controlled by the dissociative power of single oxide or acidic zeolite supports. It can be concluded that hydrogen spillover sites exist as $H^{\delta-}/OH^{\delta+}$ pairs where $0 < \delta < 1$. In the particular case of zeolite supports, the strong base character of the hydridic species was shown to remove the organic molecule from LASs to BAS where the reaction took place.

11. Conclusions and Perspectives

This investigation shows that the HSPE for metal catalysts supported on non-reducible oxides (monoxides or acidic zeolites) is based on a strong corpus of studies. The active sites consist of conjugated H/OH hydrogenating and hydrogen-receiving M^{m+}/O^{p-} pairs (p = 1 or 2), with the latter entities being able to be converted to the former via interaction with H atoms stemming from the metal phase. In this configuration, BAS and LASs are stabilized by negatively charged H and O atoms, respectively. In the case of hydroxylated oxides (including zeolites), hydrogen spillover is formed by interface hydro-dehydroxylation and then H/OH exchange reactions. Its extent depends on the concentration of surface hydroxyls and activation conditions. For amphoteric or base oxides, the surface M^{m+}/O^{p-} pairs are able to directly form H/OH conjugated pairs with two H spillover species stemming from the metal phase.

As a consequence of the H/OH structure, for all oxide supports, hydrogenation reactions necessarily take place by the anchoring of the unsaturated hydrocarbon molecule on the BAS and hydrogenation by the associated H atoms. Hydrogenation over LASs is forbidden because of the absence of H atoms in the vicinity of the organic molecule adsorbed. A second structural consequence is that the diffusion of hydrogen spillover over oxide supports proceeds through the migration of H/H pairs from LASs to LASs and not by the hopping of single H atoms from BAS to BAS. The driving force of diffusion would be the basicity/ionicity for oxides and polarization power for zeolites. A third consequence is that the H/D exchange method for the determination of diffusion rates is proof of hydrogen spillover's existence, a statement also opposing common speculation.

The discussion on the nature of hydrogen spillover indicates that it exists as polarized $H^{\delta-}/OH^{\delta+}$ pairs where $0 < \delta < 1$. For zeolite supports, it was proven that the pyridine molecule was desorbed by H^- from LASs and directed onto BAS where it was hydrogenated. The discussion also showed that our concept of conjugated BAS/LASs, interacting with $H^{\delta-}$ an O^{p-}, is a good descriptor of the reaction paths at the molecular level. The view of LASs bringing about additional activity to BAS, invoked in many papers, is not pertinent.

This investigation confirms that the refutation of the HSPE relies on misreadings of previous works or thermodynamics studies and inadequate experimental protocols, unsuitable model catalysts, or model reactant molecules. The HSPE is thermodynamically allowed, with prohibition applying to defect-free irreducible oxides only and not to activated oxide supports. The alternative bifunctional mechanism for SiO_2, Al_2O_3, and MgO single oxides is not relevant because it is based on an erroneous catalytic system model. As to the hydrogen spillover mechanism based on the redox properties of zeolites, this is hard to accept because it is postulated to work in a reactive atmosphere only and not in a pure H_2 atmosphere. This means that the H spillover species could not be stored, in contrast with the experimental reality.

Obviously, the continuation of discussion on this important topic remains desired due to biases still encountered in the literature. From a fundamental point of view, our findings on the structure of hydrogen spillover could be improved by well-suited experimental protocols and physical tools of investigation. For hydroxylated supports, the precursors of the H/OH pairs need to be identified since the H species incorporated require stabilization by neighboring hydroxyl groups. In the particular case of zeolite supports, there is still work to be carried out on the formation and mobility of hydrogen spillover. A comparison of its surface diffusion rates with other oxides would be useful. The respective roles of BAS and LASs deserve to be further explored.

During our re-investigation, we found that beliefs also exist for metal catalysts supported on reducible oxides. This is striking, all the more as the occurrence of hydrogen spillover is widely accepted and its behavior has been thoroughly investigated for these supports. Thus, the correlation between the amounts of hydrogen spillover and catalytic activity (an argument against the HSPE for non-reducible oxide supports) has been hardly tackled in the literature and has been scarcely verified. In the same way, even if the mechanism of the formation and reactivity of oxygen vacancies are well documented, their exact role in hydrogenation or hydrodeoxygenation reactions, however, is still not as clear as generally asserted. As an example, no correlation has been observed between their concentration and catalytic activity, and, up to now, no rationale has been outlined for such an important observation. In support effect studies, reactivity orders including reducible and non-reducible oxides are empirically useful but are not very significant from a fundamental point of view. The reason is that the structure and electronic properties of the oxygen vacancies and surface cations involved are not comparable; also, the kinetics and reaction paths should be different. What would the effective role of hydrogen spillover be in the chemical processes involved? On the other hand, for reducible oxide supports, a certain level of confusion exists between the rate of propagation (which equals that of reduction) and the rate of diffusion of hydrogen spillover (determined by the reduced solid). This poses some problems regarding the methods of determination of hydrogen diffusion coefficients and the resulting values.

From the applied point of view, non-reducible oxide supports are highly valuable for industry because they are cheap materials, thermally stable, and have tunable acidity. Also, comprehending their role in hydrogenation reactions is of great interest. Better knowledge of the associated HSPE may have a positive impact on the improvement of catalyst design.

These considerations show that the chemistry of hydrogen spillover needs further investigation, and notably, comparisons between reducible and non-reducible oxide supports would be fruitful for its comprehension.

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