

On the nature of spilt-over hydrogen

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Abstract

Various experimental results on hydrogen spillover which have been obtained since the first evidence for this phenomenon are discussed concerning the nature of the activated hydrogen species. It will be demonstrated that the physical nature of the spilt-over species, especially their charge, can only be described by considering their interaction with the solid. A new model is proposed which is based on the description of spilt-over hydrogen as electron donor located at the surface. Consequently, H⁺ ions and H atoms coexist on the surface of the catalyst as also stated experimentally. Their ratio is determined by the electronic properties of the adsorbate/solid system. Considering atomic and recombinative desorption of spilt-over hydrogen, the adsorption isotherms are calculated exemplary for titania. The model is applied to interpret some experimental results related to hydrogen spillover, especially the partial electron transfer from the hydrogen species to the solid. © 1997 Elsevier Science B.V.

1. Introduction

Surface mobility of reactants and intermediates is a well-known phenomenon in heterogeneous catalysis. The corresponding mobile species are formed at surface sites which are distinct from sites where the reaction takes place. Very often, they may show a special type of activity and this can open new reaction pathways for the catalytic process. In some cases activation of species and reaction sites of the catalyst system are separated (even sometimes on separate phases) and active species formed on one surface site (e.g. on transition metal

clusters in the case of hydrogen) can diffuse to another surface site (e.g. to an acidic centre in zeolite catalysis) without the loss of their activity. This effect was called spillover and defined at the First Conference on Spillover (Lyons, 1983) as follows: *Spillover involves the transport of an active species sorbed or formed on a first phase onto another phase that does not under the same condition sorb or form the species. The result may be the reaction of this species on the second phase with other sorbing gases and / or reaction with, and / or activation of the second phase* [1]. Spillover effects have been observed for several small species such as hydrogen [2–7] (and its isotopes), oxygen [7,8], nitrogen [5,9], carbon monoxide [10,11], the isocyanate functional group [5,12] and organic species [5,13].

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The spillover (or more precisely back-spillover) phenomenon was found for the first time by Kuriacose in the late 1950's studying the hydrogen desorption from GeH_4 contacted with platinum [14,15]. He found that the formation of hydrogen was enhanced fourfold by the presence of platinum due to a facilitated recombination of atomic hydrogen at the platinum wire. This experimental result could only be explained by the diffusion of atomic hydrogen to the wire, i.e. backspillover, where it recombined to molecular hydrogen which could be desorbed more easily. The first direct evidence for spillover originates from Khoobiar who observed the formation of the hydrogen bronze H_xWO_3 from WO_3 at room temperature after the application of hydrogen in the presence of a platinum-containing catalyst [16].

Though spillover, especially that of hydrogen, has been continually studied in the last three decades, several questions in connection with the spillover phenomenon remained unanswered until now. Especially, the nature of the activated species and the way they interact with the support remained unsolved problems. For a large part, this is the consequence of failing to observe these species by spectroscopic methods in a direct manner.

2. Overview on literature and comparative interpretation of experimental results from a physical point of view

The physical nature of the hydrogen (and deuterium) spilt-over species has been comprehensively discussed already in the early publications about hydrogen spillover [16–19]. It should be mentioned that the subject of the following discussion will be the activated hydrogen and deuterium species (H^* and D^* , respectively) after the primary spillover step from the metal onto the support, e.g. at the reaction sites. These species may additionally diffuse onto another catalyst phase which does not contain an activating metal (secondary spillover step). In early

publications mostly H atoms were supposed to explain the phenomena occurring in connection with hydrogen spillover. However, a direct spectroscopic evidence of the presence of these atomic species in the spillover process, e.g. by ESR spectroscopy, has not been obtained yet. Consequently, the discussion concerning the nature of the diffusing activated hydrogen species is still continuing [20,21]: ionic, radical and bound species [5,6,22], ion pairs [4,23] and H_3 species [23,24] were considered in the literature.

2.1. Indications of the atomic nature of spilt-over species

The occurrence of hydrogen spillover has been demonstrated in the presence of several supported metals, e.g. Ni, Ru, Rh, Pd, Pt [2–6], which are known to adsorb hydrogen dissociatively. In particular, this has been shown for platinum by Pliskin et al. [25] using infrared spectroscopy. Only two bands were observed for the adsorption of a hydrogen/deuterium mixture on platinum corresponding to the Pt–H and Pt–D bonds whereas three bands corresponding to H_2 , HD and D_2 bound to Pt would be expected for molecular adsorption. This result was confirmed by NMR spectroscopy also indicating the presence of atomic hydrogen species [5,6,20]. Of course, the fact that hydrogen and deuterium formed in catalysts containing metals which adsorb hydrogen dissociatively are atomic species does not allow to extend this conclusion to the H^* and D^* species which have spilt over onto the support. Nevertheless, the necessity of dissociation on the metal strongly suggests that this is also *atomic* spilt-over species.

A further indication for *atomic* spillover species is the fact that they are able to enter metal oxide frameworks, e.g. WO_3 [16,17,22,26–29] and MoO_3 [28,29], to form hydrogen bronzes. This process takes place already at room temperature when a spillover source, i.e. an activating metal, is present. The colour change associated with the low tempera-

ture formation of bronzes can be used as a test for the presence of atomic hydrogen, because the bronze-forming reaction with molecular H_2 occurs only above ca. 670 K [28]. Several spectroscopic methods (IR, EPR, NMR spectroscopy) have been applied to show that in such bronzes atomic hydrogen is present on interstitial sites [30–33].

It was found that some effects which are related to hydrogen spillover in metal-containing catalysts do also take place after a treatment with hydrogen atoms formed externally in the gas phase. In the latter case atomic hydrogen can be produced either by a microwave discharge [34–36] or by a hot filament [37]. The formation of hydrogen bronzes from metal oxides such as WO_3 , MoO_3 and V_2O_5 was observed at low temperature (e.g. room temperature) via hydrogen spillover as well as under the action of hydrogen atoms formed in the gas phase [36,37]. The same similarity was found for the reduction of metal cations in metal oxides as detected by ESR spectroscopy [35,38–40].

Kramer et al. [34] compared the interaction of hydrogen with Al_2O_3 , Pt/Al_2O_3 and Ni/Al_2O_3 by means of temperature programmed desorption (TPD). They found that a characteristic desorption peak at 480°C corresponding to spilt-over hydrogen was present in the metal-containing samples. This peak was absent after hydrogen adsorption on pure Al_2O_3 . The TPD peak at 480°C was also observed for metal-free Al_2O_3 after a treatment with H atoms. This experimental result indicates that the species which was desorbed at 480°C could be formed either by hydrogen spillover or by the adsorption of H atoms.

The formation of catalytically active sites on initially inactive oxide surfaces by a treatment with spilt-over hydrogen was demonstrated by Pajonk et al. using an experimental setup that allowed to separate the spillover source (e.g. Pt/Al_2O_3) from the catalyst to be activated (e.g. SiO_2) [41]. An activation procedure including hydrogen spillover from Pt/Al_2O_3 to SiO_2

was necessary to initiate the hydrogenation of ethene on SiO_2 . It was shown that the spilt-over hydrogen itself was not active for this catalytic reaction. Its role consisted only in the formation of new catalytic sites on the SiO_2 surface [42–44]. The same activation of a solid surface leading to the creation of catalytic sites was achieved by a treatment with hydrogen atoms produced in the gas phase by a microwave discharge. The activation energy of the catalytic sites formed on SiO_2 was found to be the same for both activation procedures [45].

Maier et al. compared the isotopic distributions of various hydrocarbons after reactions either with deuterium on metal-containing heterogeneous catalysts or, in the presence of a solid surface, with D atoms produced by a microwave discharge in the gas phase. They also found a striking similarity for both reaction pathways [46,47].

The large number of effects corresponding to hydrogen spillover as well as to externally produced H atoms has often been interpreted by postulating H atoms as spilt-over hydrogen (H^*) species. As it will be shown in this work this straightforward conclusion is not completely true. Though after hydrogen spillover and after the application of H atoms the same effects are observed, the interaction of the H atoms with the surface can change their physical nature, especially their charge. Consequently, it can only be concluded that the dissociative adsorption on a metal and the external formation of H atoms in the gas phase are two ways to form an active *atomic* species and to let it come in contact with a surface. This species as existing on the surface is defined as H^* or spilt-over hydrogen. Therefore, the physical nature of the activated spilt-over species has to be considered by taking into account their interaction with the support.

A further clue for *atomic* H^* species was provided by electrical conductivity measurements studying the influence of hydrogen on the resistance of metal/semiconductor junctions of chemical sensors. Lundström et al. found a de-

crease of the interface barrier by 0.5 eV at the junction between Pd and SiO₂ in hydrogen atmosphere. This effect leading to a significant increase of the electrical conductivity was due to the ionization of atomic hydrogen. When Al was used instead of Pd hydrogen could not be dissociated and the conductivity effect of the hydrogen atmosphere was negligible [48,49]. The same influence of hydrogen was observed for other hydrogen-activating metal/insulator or metal/semiconductor systems such as Ni/SiO₂, Pd/GaAs and Pt/Si [50–52].

2.2. Indications for H₃ species

In contrast to the above studies favouring atomic spilt-over hydrogen species Bianchi et al. supposed the presence of H₃ species on the basis of kinetic results on the demethoxylation of methoxylated SiO₂ in the presence of an admixed Pt/Al₂O₃ catalyst [24]. According to their reaction mechanism hydrogen would be dissociated on platinum and the resulting H atom reacted with molecular hydrogen to form an H₃ species. Taking into account theoretical considerations an H₃⁺ ion was suggested [53].

2.3. Indications for ion pairs

In addition to atomic and H₃ species Dowden discussed the possibility that *ion pairs* (H⁺–H⁻) would be the spilt-over hydrogen species [4]. This model has been taken up to interpret experimental results on the bifunctionally catalyzed conversion of hydrocarbons [54,55]. Particularly, in the case of the hydroisomerization of *n*-pentane on a platinum-containing ZSM-5 zeolite the proton was assumed to initiate the hydride abstraction from the paraffin whereas the hydride ion should stabilize the carbenium ion on the catalyst surface [55]. Investigations by Ebitani et al. [56] on a Pt/SO₄²⁻–ZrO₂ catalyst showed that the application of hydrogen in the presence of platinum led to the transformation of Lewis acidic sites to Brønsted acidic sites. The results were interpreted by a heterolytic

dissociation of molecular hydrogen on platinum leading to the formation of spilt-over H⁺ and H⁻ species on the surface [57]. Recently, Stumbo et al. [58] interpreted the enhanced diphenylmethane cracking activity after admixing sulfided CoMo/SiO₂ to a silica–alumina catalyst by the formation of additional Brønsted sites due to the presence of hydrogen spillover.

2.4. Indications for H atoms

Different spectroscopic techniques (e.g. NMR, ESR, IR spectroscopy) have been used in attempts to detect the spilt-over species in a direct manner, with the hope that this would also allow to answer the question of the physical nature of the H^{*} species [5,6,20,59].

An indication for the presence of H atoms was found by Lenz et al. [23] studying hydrogen spillover in a two-component Pt/Al₂O₃–SiO₂ catalyst by means of NMR spectroscopy. Further NMR studies on the adsorption of hydrogen at supported metal clusters have shown that in addition to the NMR-detectable amount of hydrogen on the metal other hydrogen species should be present at the surface of the support which could not be directly observed by NMR spectroscopy [60–63]. Additional evidence for a spillover of hydrogen onto the support could be provided by comparing the hydrogen species observable by NMR spectroscopy with the amount determined by gravimetric and volumetric adsorption measurements [64–67]. Root et al. [68] have indirectly shown by NMR spectroscopy that a spectroscopically non-observable amount of hydrogen is formed on the silica support of a Rh/SiO₂ catalyst. The longitudinal NMR relaxation time *T*₁ of hydroxyl protons can be significantly shortened by the presence of paramagnetic species. Since such an effect was observed for hydrogen spillover [60,65,67] it was concluded that the spilt-over species should be *paramagnetic H atoms*.

However, the attempt to investigate directly the paramagnetic H atoms supposed to correspond to the spilt-over species by ESR spec-

troscopy has not been successful until now. Even in catalytic systems where hydrogen spillover evidently occurred, H atoms could not be observed (e.g. [19,69,70]). But, on the other hand, reactions of spilt-over species with organic radicals could be monitored by ESR and IR spectroscopy repeatedly [19,69–72]. Particularly, Vannice and Neikam [19,69] studied the reaction of spilt-over hydrogen produced by Pt or Pd supported on or admixed to a Y zeolite with two organic radicals (anthracene and perylene ions) by means of ESR spectroscopy. The disappearance of the radicals was correlated with the reaction of what, as the authors proposed, to be H^* radical species (i.e. H atoms). The ESR technique was also used by Carley et al. [70] to detect the dissociation of hydrogen on a Pd/Al₂O₃ catalyst at room temperature. Atomic hydrogen reacted with the spin trap *N*-benzylidene-*tert*-butylamine-*N*-oxide (PBN) producing paramagnetic species up to a level detectable by ESR spectroscopy. However, there was no direct ESR spectroscopic evidence for H atoms. Taking into account these results, it seems very likely that the spilt-over hydrogen species is a radical but the activated hydrogen should not be considered as a stable H atom like, e.g. atomic hydrogen on an interstitial site in CaF₂ [73,74] or KCl [75] at low temperature. Similar experiments were carried out by Baumgarten et al. [71,72] who observed by infrared spectroscopy the reaction of spilt-over hydrogen with different reducible compounds, e.g. the 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical. In contrast to most of the other studies on hydrogen spillover Baumgarten et al. have proposed that the reactive hydrogen was diffusing in the gas phase (i.e. as uncharged H atoms). This conclusion was questioned especially by Spencer et al. [76] because of thermodynamical reasons.

2.5. Indications for H^+ ions

In contrast to the above results indicating the occurrence of paramagnetic H^* species, most

likely H atoms, a large number of studies led to the conclusion that H^+ ions should be present in the spillover process. Levy et al. [77] studied the influence of cocatalysts with different proton affinities on the formation of a hydrogen bronze from WO₃ in the presence of Pt black or a Pt/SiO₂ catalyst. They found a strong correlation between the reaction rate and the proton affinity of the cocatalysts with high proton affinities and concluded that the spilt-over species were H^+ ions. However, the conclusion of the authors that the electrons removed from the H atoms would remain on platinum is very unlikely, because H/Pt ratios of up to 35 were observed during a study of bronze formation via hydrogen spillover [26]. The accelerating effect of water which has also been observed before [7,26,29] was interpreted by postulating the diffusion of the spilt-over hydrogen as solvated proton.

The deuteration of surface hydroxyl groups can be considered as a model reaction for the investigation of hydrogen and deuterium spillover, because this can be easily monitored by IR spectroscopy. It has been frequently shown that the deuteration is markedly enhanced by the presence of platinum or another hydrogen-activating metal supported on Al₂O₃, SiO₂ and zeolites (e.g. [78–81]). Baumgarten et al. studied two different reactions of spilt-over H^* on alumina in the presence of a Pt/Al₂O₃ spillover source [82]: The hydrogenation of unsaturated carboxylic acids and the H–D exchange of surface hydroxyl groups. They found that no reaction of the activated hydrogen with preadsorbed unsaturated organic compounds occurred in spite of the fact that hydrogen spillover took place as indicated by the H–D exchange reaction. The authors concluded that hydrogen spillover does not necessarily lead to the formation of active hydrogen species which are able to hydrogenate unsaturated hydrocarbons. This observation is in agreement with results of Pajonk et al. [41–44], who described the H^* species themselves as relatively inactive with respect to the hydrogenation of ethene. Obviously, the spilt-over

hydrogen cannot be considered as a universally active species. Its activity is determined by the specific reaction and possibly by the (ionic or radical) nature of the H^* species on the catalyst surface. In the case of the H–D exchange on zeolites a correlation between the acidity of the OH and OD groups and the reactivity of the activated hydrogen and deuterium as experimentally found [81] could be an indication for an *ionic nature* of the spilt-over H^* species.

Our results on the influence of a homogeneous magnetic field on the H–D exchange in two-component Pt/NaY–HNaY zeolite samples led to the conclusion that the spilt-over hydrogen species should be electrically charged, most likely diffusing H^+ ions influenced by the Lorentz force [83,84]. This conclusion rests on the experimental finding that the exchange rate was decreased by a magnetic field directed perpendicularly to the main direction of diffusion (from Pt/NaY to HNaY) and was not influenced by a magnetic field parallel to this direction. This is what theoretical considerations predict when considering the diffusion constant of charged particles in a homogeneous magnetic field [85].

The assumption that the atomic spilt-over hydrogen species are H^+ ions is strongly supported by the results of electrochemical and electrical conductivity measurements on several catalysts. Keren and Soffer [86] proposed a mechanism for spillover that was adapted from the description of an electrode–liquid electrolyte system. They explained the observed long-range spillover by the following reaction steps: Dissociation of molecular hydrogen into H^+ ions and metal conduction band electrons, subsequent transfer of electrons through the metal/support interface and electronic and protonic conductance on the catalyst surface. Electrical conductivity changes due to the interaction of hydrogen with noble-metal-containing metal oxides exhibiting semiconductor properties were observed for different oxides such as TiO_2 [87–91], SnO_2 [92,93] and ZnO [94,95]. The increase of the n-type conductivity at low

temperatures, i.e. under conditions where no additional oxygen vacancies were formed by reduction, was interpreted by an electron transfer from hydrogen species to the metal oxide and the adsorption of the H^* species as *protons*. Alternatively, changes of the work function of the metal clusters and effects at the metal/support interface have been discussed to explain the cooperative conductivity effect between the metal, the semiconducting support and hydrogen [5,96–98]. In our recent studies on the influence of hydrogen spillover on Pt-containing TiO_2 we adopted a special geometry for our two-component sample in order to exclude such influences of the metal/semiconductor interface. By measuring the conductivity changes after exposure to hydrogen in the platinum-free TiO_2 component of two-component Pt/ TiO_2 – TiO_2 samples (pellets, thick-film and powder samples) we could demonstrate that the increase of the n-type conductivity was due to an electron transfer from the H^* species to titania. The diffusion of the spilt-over species occurred on the surface over a distance of some millimetres and gas phase diffusion could be excluded [90,99]. As already discussed for other effects related to hydrogen spillover the conductivity of metal oxides could also be increased by a treatment with H atoms externally produced in the gas phase [100–103]. An influence of hydrogen on the conductivity was observed even for an insulator like Al_2O_3 . Khoobiar et al. [104] showed that the dissociative adsorption of hydrogen on η - Al_2O_3 at 600°C led to an increase of the n-type conductivity whereas the adsorption of oxygen caused a switch from n- to p-type conductivity for oxygen pressures above ca. 100 Pa. In a way similar to the case of semiconductors, the authors proposed a protonization of the atomic hydrogen on the surface.

An electronic interaction due to an electron transfer from the spilt-over hydrogen to the surface region of metal oxides was also found by means of optical spectroscopy. Boccuzzi et al. have shown that the transparency of Cu/ ZnO

and Ru/ZnO catalysts in the infrared region was markedly reduced by a H₂ and D₂ atmosphere [105–107]. This loss corresponded to a broad absorption band in the spectral region around 1500 cm⁻¹ (independently, whether the sample was exposed to H₂ or exposed to D₂) and it was interpreted by the photoionization of oxygen vacancies producing two electronic donor states in the band gap of ZnO. Specifically, the photoionization process involved the singly ionized vacancies whose concentration was enhanced by a charge transfer from the adsorbed H* species. We obtained similar results by means of FT-NIR Raman spectroscopy studying Pt-containing TiO₂ [108,109]. The presence of H* species on the surface of TiO₂ was shown to result in a charge transfer to the defect states in TiO₂ leading to a diminution of the photoionization process which produces a broad fluorescence band in the FT-NIR Raman spectrum [109]. The corresponding results will be discussed in detail on the basis of the model we will propose in the following.

2.6. What is known about the nature of spilt-over hydrogen?

Different species have been discussed to describe the phenomena and spectroscopic results related to hydrogen spillover: H atoms, H⁺ and H⁻ ions, ion pairs, H₃ and bound species. A direct and unambiguous spectroscopic evidence for the H* species is still missing. A large number of experimental results and especially the similarities between effects due to spillover and due to externally produced H atoms indicate that the spilt-over species should be atomic. Concerning the physical nature of the H* species H atoms and H⁺ ions have been favoured. Surprisingly, experimental indications for both species were obtained in the same catalytic system (e.g. transition metals supported on silica and alumina) under similar conditions. Whether H atoms or H⁺ ions were observed seemed sometimes to depend on the test reaction or the spectroscopic method used

for the investigation. The conclusion is that the question concerning the nature of the H* species can only be answered by considering the specific interaction of these species with the support. Therefore, the consequence is that the definition of spillover as presently accepted [1] should not be understood as defining an invariable species which is formed on one phase and diffuses as such onto another phase while changing neither its nature nor the nature of its interaction with the support.

3. The new model for spilt-over hydrogen as adsorbed species

The objective of the model is to describe the nature of the active hydrogen species (H*) after the primary spillover step from the metal onto the support and, in certain cases, after the secondary spillover step onto another phase. The description will include the interaction of the spilt-over species with the solid. It has to be emphasized that the adsorption of hydrogen on the activating metal itself will not be considered here. Hydrogen adsorption on metals has been comprehensively described elsewhere and it has only a modest importance for the characterization of the *spillover* species.

The model is based on the hypothesis that the adsorbed atomic H* species produce an additional electronic state at the surface. Consequently, the assumptions leading to the Langmuir adsorption isotherm will have to be extended by the fact that *two states of the adsorbate* with different adsorption energies coexist at the surface. These adsorbate states correspond to two different atomic spilt-over hydrogen species: H atoms and H⁺ ions.

It will be shown later that new model allows to interpret a wide variety of catalytic and spectroscopic results on hydrogen spillover especially by considering the coexistence of both spilt-over species and the partial electron transfer from H* to the solid.

3.1. Chemisorption and charge transfer

3.1.1. Adsorbates as surface electron donors and acceptors

In contrast to physisorption where the structure and the electronic properties of the adsorbate remain nearly unchanged, chemisorption is characterized by an overlap of the electron wave functions of both adsorbate and solid [110]. Chemisorption is connected with a partial charge transfer between the adsorbate and the solid leading to a significantly larger adsorption energy in comparison to physisorption. Two states of a chemisorbate have to be generally considered [111]: the ionized state (positively or negatively charged; strong chemisorption) and the neutral state (weak chemisorption).

At low temperature the adsorption of molecular hydrogen occurs mainly as physisorption whereas the chemisorption of hydrogen at higher temperature usually requires the previous dissociation of H_2 . In that case the weak chemisorption, where the adsorbate remains neutral, is not identical to physisorption. In the case of hydrogen an activation energy for the transition from the physisorbed to the chemisorbed state is mainly due to the dissociation of hydrogen [112]. Weak chemisorption cannot be defined as the transition state leading to strong chemisorption. Taking into account the results already discussed there seem to be different possibilities to provide the atomic hydrogen species to be chemisorbed: the formation of H atoms in the gas phase and hydrogen spillover.

In principle, the chemisorption on semiconductors and insulators must be described by considering the electronic interaction between the electronic states of the adsorbate and the solid (especially, valence band, conduction band, additional electronic states in the band gap due to defects). One chemisorption model which was especially applied to describe the oxygen adsorption on n-type semiconductors was already proposed by Wolkenstein [111].

Obviously, there are two possible directions

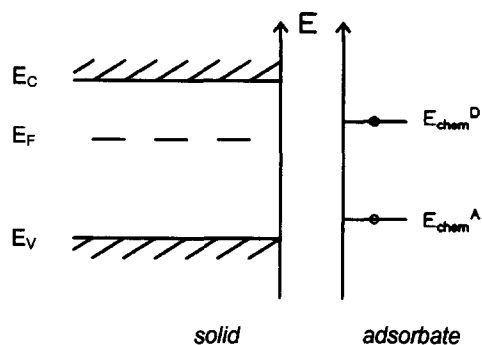


Fig. 1. Additional electronic state of a chemisorbate acting either as a surface electron donor or acceptor.

of an electron transfer between adsorbate and solid: to the solid from an electron donating adsorbate (D) and to the adsorbate for an electron accepting adsorbate (A). In these cases the electronic state of the adsorbate electron E_{chem} is situated above and below the Fermi energy E_F of the semiconductor, respectively, as represented in Fig. 1. (The band bending occurring due to a surface charge will be considered later.)

A typical example for an adsorption as an electron acceptor is the chemisorption of oxygen on metal oxide surfaces. The electron transfer from ZnO to O_2 leading to the formation of O_2^- as predicted by the Wolkenstein model [111] has been extensively proved [113–115]. The chemisorption of atomic hydrogen as a typical electron donor will be discussed later in connection with the model for hydrogen spillover.

The charge transfer between adsorbate and solid is connected with an increase of the adsorption energy in comparison to neutral adsorption: In the case of an electron donating adsorbate the electron has to be transferred back to the adsorbate state having a higher energy, before desorption (of the neutral species) becomes possible. The desorption of a negatively charged adsorbate (electron acceptor) requires the previous electron transfer to a higher electronic state of the solid, e.g. the edge of the conduction band (E_c).

3.1.2. Fermi–Dirac statistics of the adsorbate state

In the following only an electron donating adsorbate will be considered because of its importance for the description of hydrogen spillover.

The occupation probability of the additional electronic state at the surface which is produced by the adsorption has to be determined by applying Fermi–Dirac statistics involving all electronic states of the uniform quantum mechanical system adsorbate/solid. The corresponding occupation, or coverage when related to the number of adsorption sites, corresponds to the amount of neutral (weakly chemisorbed, $\theta_{\text{chem}}^{\text{w}}$) and charged (strongly chemisorbed, $\theta_{\text{chem}}^{\text{s}}$) adsorbate species. The total coverage involves the weakly and the strongly adsorbed species:

$$\theta_{\text{chem}} = \theta_{\text{chem}}^{\text{w}} + \theta_{\text{chem}}^{\text{s}} \quad (1)$$

The energy of the additional electronic state that is formed by the adsorbate is denoted by $E_{\text{chem}}^{\text{D}}$ for the non-charged surface, i.e. $\theta_{\text{chem}}^{\text{s}} = 0$. The occurrence of strong chemisorption is connected with a band bending in the surface region. Consequently, the adsorbate state is shifted by the surface value of the potential energy $V(x=0)$ which is defined as V_0 .

In order to simplify the expression of the equations, the notation often used in statistical thermodynamics will be adopted:

$$\beta = 1/kT \quad (2)$$

where k is the Boltzmann constant and T the (absolute) temperature.

The coverage for both types of chemisorption is calculated according to Fermi–Dirac statistics for an electron donor as usual in solid state physics (see, for example, Ref. [116]):

$$\theta_{\text{chem}}^{\text{s}} = \theta_{\text{chem}} \frac{1}{1 + 2e^{\beta(E_{\text{F}} - E_{\text{chem}}^{\text{D}} - V_0)}} \quad (3)$$

$$\theta_{\text{chem}}^{\text{w}} = \theta_{\text{chem}} \frac{2e^{\beta(E_{\text{F}} - E_{\text{chem}}^{\text{D}} - V_0)}}{1 + 2e^{\beta(E_{\text{F}} - E_{\text{chem}}^{\text{D}} - V_0)}} \quad (4)$$

3.1.3. Adsorption isotherm for the chemisorption of an electron donor

In Eqs. (3) and (4), the Fermi–Dirac statistics has been used to describe the relative amounts of neutral and charged adsorbate species depending on the electronic properties of the adsorbate/solid system and on the temperature for a constant coverage θ_{chem} . Now the influence of the gas phase pressure p at a constant temperature T shall be considered. Since the basic assumption of the model is that a charge transfer between adsorbate and solid takes place it is plausible to postulate a sub-monolayer adsorption with $\theta_{\text{chem}} < 1$. Additionally, distinct adsorption sites with a definite surface density will be assumed. Adsorption will only be possible when a species is striking an empty adsorption site. The adsorption sites are considered as energetically equivalent, the interaction between the adsorbate species is neglected. The further assumption of an adsorption from the atmosphere formed by an ideal gas leads to the well-known Langmuir adsorption isotherm [110,112] for the surface coverage θ without the consideration of a charge transfer:

$$\theta = \frac{bp}{1 + bp} \quad (5)$$

with

$$b = \frac{\alpha e^{\beta E_{\text{ads}}}}{\nu \sigma_{\text{sites}} \sqrt{2\pi mkT}} \quad (6)$$

The other parameters are the mass of the adsorbed species m , the adsorption energy E_{ads} , the fraction of species remaining adsorbed after contact with an empty adsorption site α , the rate constant for desorption ν and the surface density of adsorption sites σ_{sites} .

When the basic assumptions of the Langmuir adsorption model are supplemented by the fact that two states of chemisorption coexist a new dynamic equilibrium characterized by the fol-

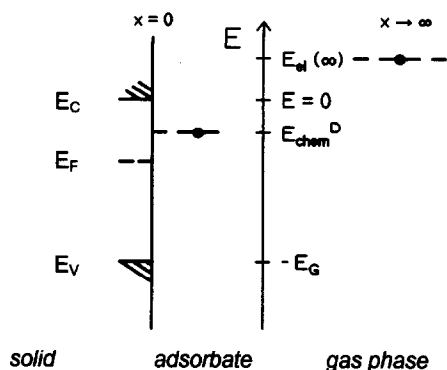


Fig. 2. Electronic levels of the uniform quantum mechanical system solid/adsorbate in comparison to the gas phase.

lowing equation for the adsorption and desorption rates is established:

$$P \frac{\alpha}{\sqrt{2\pi mkT}} (1 - \theta_{\text{chem}}) = \nu \sigma_{\text{sites}} \theta_{\text{chem}}^w e^{-\beta E_{\text{ads}}^w} + \nu \sigma_{\text{sites}} \theta_{\text{chem}}^s e^{-\beta E_{\text{ads}}^s} \quad (7)$$

The adsorption energies of the weakly and strongly chemisorbed states (E_{ads}^w and E_{ads}^s) have to be distinguished from the electronic energy E_{chem}^D . Their interdependence for an electron donating adsorbate will be discussed now on the basis of a consideration shown in Fig. 2.

In parallelism with the Wolkenstein model of chemisorption [111] it is assumed that the adsorption energies are determined by the *electronic* interaction between adsorbate and solid. The adsorption energy of the neutral state is the difference between the energy of the electron at the gas phase species at an infinite distance from the surface $E_{\text{el}}(\infty)$ and $E_{\text{chem}}^D + V_0$ corresponding to the energy of the electron at the adsorbate:

$$E_{\text{ads}}^w = E_{\text{el}}(\infty) - E_{\text{chem}}^D - V_0 \equiv E_{\text{ads}}^0 - V_0 \quad (8)$$

In order to describe the adsorption energy of the strongly chemisorbed state E_{ads}^s the electron transfer to the solid has to be incorporated in addition to E_{ads}^w . The calculation of E_{ads}^s can be simplified by the following consideration for the desorption process: Before the strongly

chemisorbed species can desorb into the gas phase, a hole (i.e. a defect electron) has to be excited from the adsorbate state $E_{\text{chem}}^D + V_0$ to the edge of the valence band $E_v + V_0$. Due to this transition the adsorbate species becomes neutral and its desorption requires the energy E_{ads}^w . Consequently, the adsorption energy of the strongly chemisorbed state can be determined according to the following equation:

$$E_{\text{ads}}^s = E_{\text{chem}}^D - E_v + E_{\text{ads}}^w \quad (9)$$

Usually, the energy at the edge of the conduction band E_c in the case of a non-charged surface is defined to be 0. The energy of the edge of the valence band E_v is then equal to $-E_G$ where E_G is the band gap of the semiconductor or insulator. This definition leads to

$$E_{\text{ads}}^s = E_{\text{chem}}^D + E_G + E_{\text{ads}}^w \quad (10)$$

The adsorption isotherm for the chemisorption of an electron donor can be derived from Eq. (7) by using the correlations 3, 4 and 8 to 10:

$$\theta = \frac{b_{\text{chem}}^D p}{1 + b_{\text{chem}}^D p} \quad (11)$$

with

$$b_{\text{chem}}^D = \frac{\alpha e^{\beta(E_{\text{ads}}^0 - V_0)}}{\nu \sigma_{\text{sites}} \sqrt{2\pi mkT}} \times \frac{1 + 2e^{\beta(E_F - E_{\text{chem}}^D - V_0)}}{2e^{\beta(E_F - E_{\text{chem}}^D - V_0)} + e^{-\beta(E_G + E_{\text{chem}}^D)}} \quad (12)$$

To understand the meaning of this equation let us consider a situation where E_{chem}^D becomes equal to $E_v = -E_G$. In such a case, an electron transfer from the adsorbate to the solid is not possible any more (since the electronic states in the valence band, i.e. below $E_v = -E_G$, are occupied). Thus, the strong chemisorption does not take place and the state of the strong chemisorption becomes insignificant now. Under these conditions b_{chem}^D (Eq. (12)) is equal to

b (Eq. (6)) and the isotherm (Eq. (11)) is transformed into the Langmuir isotherm (Eq. (5)).

3.1.4. Surface charge and band bending in the surface region

The electron transfer to the solid due to the adsorption of an electron donating adsorbate leads to a positive surface charge. The surface charge density σ_s can be calculated according to:

$$\sigma_s = e \sigma_{\text{sites}} \theta_{\text{chem}}^s \quad (13)$$

where e is the elementary charge.

The surface charge leads to a displacement of charges (electrons) inside the surface region of the solid (space-charge region) due to electrostatic interactions. In the case of an electron donor chemisorbed on the surface of a n-type semiconductor the concentration of electrons is increased. Therefore, the space-charge region represents an so-called *enhancement layer*. In contrast, the chemisorption of an electron acceptor (e.g. oxygen) would lead to the formation of a so-called *depletion layer* because of an electron transfer to the adsorbate.

For the idealized case of an infinitely extended surface with an isotropic charge distribution the problem can be treated one-dimensionally. In this case, the Poisson equation can be written only for the x direction perpendicular to the surface in terms of the potential energy $V(x)$:

$$\Delta V(x) = V''(x) = \frac{e\rho(x, V(x))}{\varepsilon} \quad (14)$$

The charge density ρ depends on the distance from the surface x and on the shift of the energy levels relative to the Fermi energy represented by the potential energy V ; ε is the dielectric constant of the solid. In order to calculate the charge density ρ for real catalysts, e.g. non-stoichiometric metal oxides, all charged defect states (vacancies, interstitials) have to be considered in addition to the electrons and holes.

The derivative of the potential energy at the surface $V'(x=0)$ is determined by the surface charge density according to:

$$V'(0) = \frac{e\sigma_s}{\varepsilon} \quad (15)$$

When the thickness of the solid is large in comparison to the Debye length (i.e. the thickness of the enhancement layer) the influence of the surface charge σ_s far from the surface (i.e. $x \rightarrow \infty$) can be neglected. Therefore, the solution of the equation must respect the following two boundary value conditions (representing a Neumann boundary value problem):

$$V(\infty) = 0 \quad (16)$$

and

$$V'(\infty) = 0 \quad (17)$$

Eq. (17) is also a direct consequence of the charge neutrality condition, i.e. the fact that the number of electrons transferred to the enhancement layer of the solid has to be equal to the number of elementary charges at the surface.

3.2. Application of the model to hydrogen spillover

The consideration of a large number of experimental results as discussed above led us to the conclusion that the spilt-over hydrogen should be described as a chemisorbed atomic species acting as a surface electron donor. In the frame of the corresponding model the experimental indications for H atoms as well as for H^+ ions can be understood by assuming two coexisting states of the adsorbate: weak (neutral) and strong (ionized) chemisorption. This assumption will in principle permit to calculate the partial electron transfer and to correlate the results with experimental data. Such results will be considered later and the new model will be used for interpretation.

For the description of hydrogen spillover the chemisorption model as discussed above has to be modified since the adsorption does not hap-

pen directly from the gas phase. Additionally, the desorption process has to be considered in more detail.

3.2.1. Adsorption rate

The adsorption isotherm should describe a steady state where the adsorption and desorption rates are equal. Therefore, a constant flow of spilt-over hydrogen species formed on the metal and diffusing to the adsorption sites has to be assumed in order to estimate the adsorption isotherm. The atomic species are provided by the remote hydrogen-dissociating metal. It will be assumed that a possible barrier for the diffusion of the spillover species from the metal onto the support can be neglected. The electron transfer process between the adsorbate and the solid is very fast in comparison to characteristic diffusion and adsorption/desorption times. As in the case of the Langmuir and Wolkenstein models the interaction between the adsorbate species is neglected. Taking into account these conditions an effective striking rate of the spilt-over species to the adsorption sites r_{eff} is defined. This value corresponds to the number of species being adsorbed per surface area and time. The adsorption rate u_{ads} depending on the coverage with spilt-over species θ_{spill} can be expressed by the following equation:

$$u_{\text{ads}} = r_{\text{eff}}(1 - \theta_{\text{spill}}) \quad (18)$$

As for the Wolkenstein chemisorption model (Eq. (1)) the coverage θ_{spill} is the sum of the coverages corresponding to strong ($\theta_{\text{spill}}^{\text{s}}$) and weak chemisorption ($\theta_{\text{spill}}^{\text{w}}$) representing the amount of adsorbed H^+ ions and H atoms, respectively:

$$\theta_{\text{spill}} = \theta_{\text{spill}}^{\text{s}} + \theta_{\text{spill}}^{\text{w}} \quad (19)$$

3.2.2. Desorption rate and isotherm

The desorption of the adsorbed spilt-over hydrogen can occur through four different pathways that may be significant (possibly simulta-

neously) according to the system and the reaction:

(i) By desorption as neutral atomic species from the surface into the gas phase (a desorption of charged species from the surface is very unlikely).

(ii) By desorption of neutral atomic species into an intermediate state with low adsorption energy and small coverage ($\theta_{\text{inter}} < 1$).

(iii) By recombination of the chemisorbed species on the surface and subsequent desorption as molecular hydrogen (recombinative desorption).

(iv) By a backspillover process, i.e. the diffusion of the spilt-over hydrogen back to the metal, recombination and desorption as H_2 from the metal into the gas phase.

The backspillover process has already been considered by defining an effective (net) striking rate for adsorption r_{eff} . In the following it will be assumed that other desorption pathways than (iv) predominate. The desorption mechanisms (i) and (ii) can be treated analogously where the desorption energy corresponds to the transition into the gas phase and the intermediate state, respectively.

3.2.2.1. Desorption of atomic hydrogen. For the cases (i) and (ii) the desorption process can be described as already done for the adsorption of an electron-donating adsorbate (Eq. (7)). The constant ν_{eff} can be assumed to be the same for the desorption of both species. An electron transfer back to the adsorbate is necessary before desorption can occur from the strongly chemisorbed state. This results in the larger desorption energy $E_{\text{ads}}^{\text{s}}$:

$$u_{\text{des}} = \nu_{\text{eff}} \sigma_{\text{sites}} \theta_{\text{spill}}^{\text{w}} e^{-\beta E_{\text{ads}}^{\text{w}}} + \nu_{\text{eff}} \sigma_{\text{sites}} \theta_{\text{spill}}^{\text{s}} e^{-\beta E_{\text{ads}}^{\text{s}}} \quad (20)$$

For the dynamic adsorption equilibrium

$$u_{\text{ads}} = u_{\text{des}} \quad (21)$$

the adsorption isotherm for the spilt-over hydrogen is obtained:

$$\theta_{\text{spill}} = \frac{b_{\text{spill}} r_{\text{eff}}}{1 + b_{\text{spill}} r_{\text{eff}}} \quad (22)$$

with

$$b_{\text{spill}} = \frac{e^{\beta(E_{\text{ads}}^0 - V_0)}}{\nu_{\text{eff}} \sigma_{\text{sites}}} \times \frac{1 + 2e^{\beta(E_{\text{F}} - E_{\text{chem}}^{\text{D}} - V_0)}}{2e^{\beta(E_{\text{F}} - E_{\text{chem}}^{\text{D}} - V_0)} + e^{-\beta(E_{\text{G}} + E_{\text{chem}}^{\text{D}})}} \quad (23)$$

3.2.3. Desorption of molecular hydrogen (re-combinative desorption)

The desorption of a hydrogen molecule from the surface into the gas phase necessitates the recombination of two atomic species being adsorbed at neighbouring sites. If one of the species is positively charged (H^+ ion) then additionally an electron has to be transferred to the adsorbate; the recombination of two H^+ ions requires the transfer of two electrons.

The desorption rate u_{des} is proportional to the square of the density of neutral atomic H species on the surface $\theta_{\text{ads}}^{\text{H}}$ which can either be present as weakly chemisorbed species or be formed from strongly chemisorbed species. Furthermore, the desorption rate depends on the recombination energy (E_{rec}) which is obtained by the recombination of two atomic H species at the surface and the energy $E_{\text{ads}}^{\text{H}_2}$ that is necessary for the desorption of a hydrogen molecule from the surface into the gas phase (where $E_{\text{ads}}^{\text{H}_2,0}$ is the value for the non-charged surface)

$$E_{\text{ads}}^{\text{H}_2} = E_{\text{ads}}^{\text{H}_2,0} - V_0 \quad (24)$$

Considering the three possibilities for recombination ($\text{H} + \text{H}$, $\text{H} + \text{H}^+$ and $\text{H}^+ + \text{H}^+$) and introducing a rate constant κ the desorption rate is expressed as:

$$u_{\text{des}} = \kappa \sigma_{\text{sites}} e^{-\beta(E_{\text{ads}}^{\text{H}_2} - E_{\text{rec}})} \times \left\{ \theta_{\text{spill}}^{\text{w}} + \theta_{\text{spill}}^{\text{s}} e^{-\beta(E_{\text{ads}}^{\text{s}} - E_{\text{ads}}^{\text{w}})} \right\}^2 \quad (25)$$

Defining

$$k = \kappa \sigma_{\text{sites}} e^{-\beta(E_{\text{ads}}^{\text{H}_2,0} - E_{\text{rec}} - V_0)} \quad (26)$$

and incorporating Eqs. (3), (4) and (10) leads to the rate of recombinative desorption of spilt-over hydrogen into the gas phase:

$$u_{\text{des}} = k \theta_{\text{spill}}^2 \left\{ \frac{e^{-\beta E_{\text{chem}}^{\text{D}}} (2e^{\beta(E_{\text{F}} - V_0)} + e^{-\beta E_{\text{G}}})}{1 + 2e^{\beta(E_{\text{F}} - E_{\text{chem}}^{\text{D}} - V_0)}} \right\}^2 \quad (27)$$

The adsorption isotherm is obtained by considering the dynamic adsorption/desorption equilibrium (Eq. (21)):

$$\theta_{\text{spill}} = \frac{r_{\text{eff}}}{2kB^2} \left(\sqrt{1 + \frac{4kB^2}{r_{\text{eff}}}} - 1 \right) \quad (28)$$

with

$$B = \frac{e^{-\beta E_{\text{chem}}^{\text{D}}} (2e^{\beta(E_{\text{F}} - V_0)} + e^{-\beta E_{\text{G}}})}{1 + 2e^{\beta(E_{\text{F}} - E_{\text{chem}}^{\text{D}} - V_0)}} \quad (29)$$

3.2.4. Calculated isotherms for the adsorption of spilt-over hydrogen on TiO_2

A calculation of the adsorption isotherms for spilt-over hydrogen has been carried out for both types of hydrogen desorption using electronic parameters typical for TiO_2 [109,113,117–119]: band gap $E_{\text{G}} = 3.05$ eV, $E_{\text{chem}}^{\text{D}} = -0.1$ eV, bulk density of intrinsic oxygen vacancies $[V_{\text{ox}}] = 4.27 * 10^{15} \text{ cm}^{-3}$, corresponding electron donor energies $E_{\text{D1}} = -0.8$ eV and $E_{\text{D2}} = -1$ eV, bulk density of electron acceptors $[A] = 6 * 10^{14} \text{ cm}^{-3}$, corresponding acceptor energy $E_{\text{A}} = -1.8$ eV, the adsorption energies for both types of desorption $E_{\text{ads}}^0 = 0.86$ eV, $E_{\text{ads}}^{\text{H}_2,0} = 0.86$ eV and $E_{\text{rec}} = 0.3$ eV and the density of adsorption sites $\sigma_{\text{sites}} = 1.48 * 10^{15} \text{ cm}^{-2}$ which corresponds to the surface density of titanium atoms. The calculations were performed for a temperature T of 300 K. The energy levels in the band gap of TiO_2 are schematically represented in Fig. 3. The charge density ρ in the space charge region was calculated numerically on the basis of Fermi–Dirac

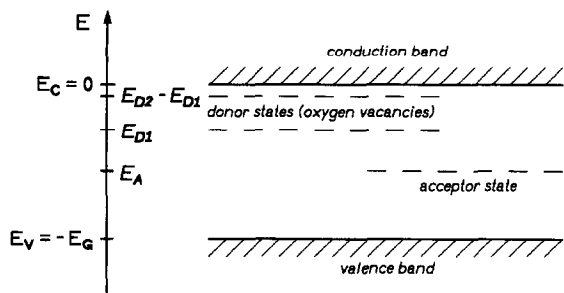


Fig. 3. Electronic states in the band gap of TiO_2 : activation energies of the two electrons at the oxygen vacancy and energy of the acceptor state.

statistics incorporating the concentrations of electrons n , holes p , singly and doubly ionized oxygen vacancies $[V_{\text{ox}}^+]$ and $[V_{\text{ox}}^{++}]$, respectively, and ionized acceptors $[A^-]$ according to the following equations:

$$n = N_c e^{\beta(E_F - V(x))} \quad (30)$$

$$p = N_v e^{-\beta(E_F - V(x) + E_G)} \quad (31)$$

with the constants N_c and N_v representing the density of electronic states at the band edges of titania (see [85,113,116]),

$$\frac{[V_{\text{ox}}^+]}{[V_{\text{ox}}]} = \frac{2e^{\beta(E_F - V(x))} e^{-\beta E_{D1}}}{1 + 2e^{\beta(E_F - V(x))} e^{-\beta E_{D1}} + e^{2\beta(E_F - V(x))} e^{-\beta E_{D2}}} \quad (32)$$

$$\frac{[V_{\text{ox}}^{++}]}{[V_{\text{ox}}]} = \frac{1}{1 + 2e^{\beta(E_F - V(x))} e^{-\beta E_{D1}} + e^{2\beta(E_F - V(x))} e^{-\beta E_{D2}}} \quad (33)$$

$$\frac{[A^-]}{[A]} = \frac{1}{1 + 2e^{-\beta(E_F - V(x))} e^{\beta E_A}} \quad (34)$$

and finally

$$\rho(V(x)) = p - n + [V_{\text{ox}}^+] + 2[V_{\text{ox}}^{++}] - [A^-] \quad (35)$$

The density of the electronic defect states is assumed to be constant throughout the hole bulk phase.

Of course, in order to correlate the calculated isotherms with experimental data or to predict the adsorption of activated hydrogen on a distinct catalyst the values for the electronic parameters would have to be estimated exactly for the system under study. Nevertheless, the main effects and a number of experimental results can be discussed in a qualitative manner on the basis of the model isotherms represented in Fig. 4 for atomic desorption and in Fig. 5 for recombinative desorption. For low spillover adsorption rates r_{eff} mainly H^+ ions were formed by adsorption and the total coverage θ_{spill} is almost equal to the coverage with strongly chemisorbed species θ_{spill}^s . The low rate region is shown in

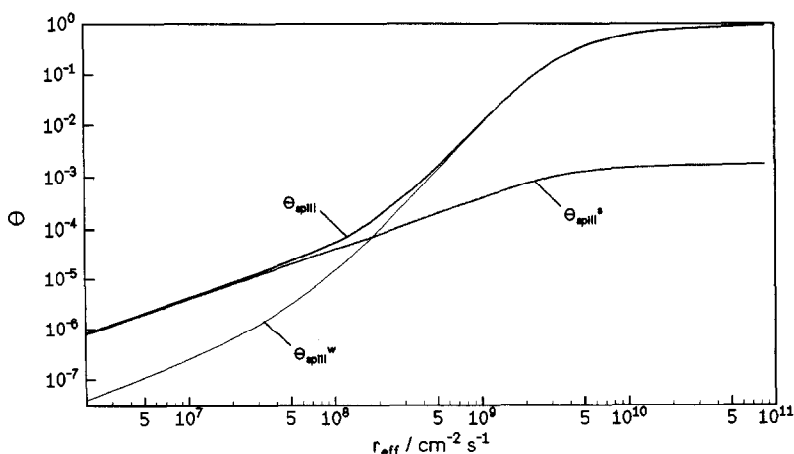


Fig. 4. Adsorption isotherm of spilt-over hydrogen on TiO_2 (atomic desorption).

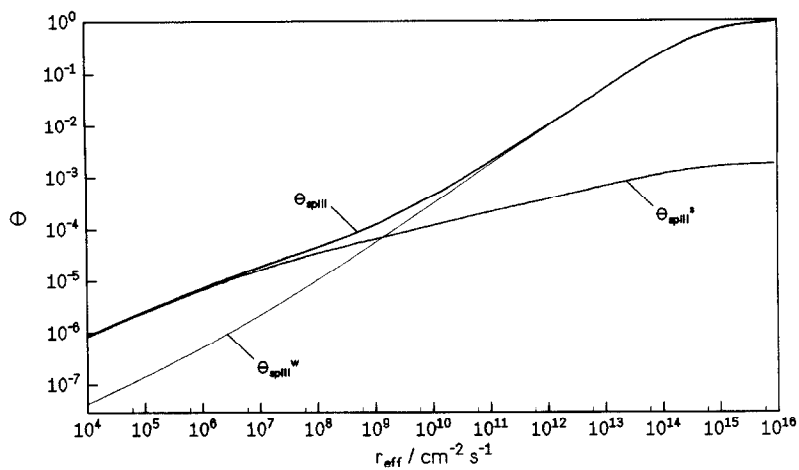


Fig. 5. Adsorption isotherm of spilt-over hydrogen on TiO₂ (recombinative desorption).

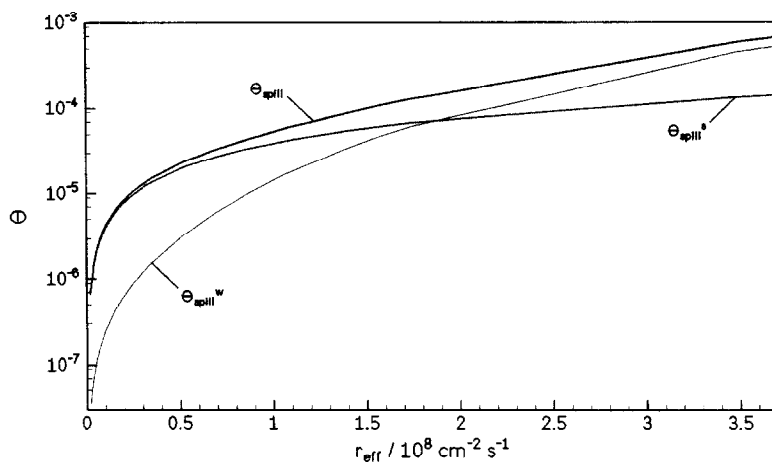


Fig. 6. Low striking rate region of the adsorption isotherm of spilt-over hydrogen on TiO₂ (atomic desorption).

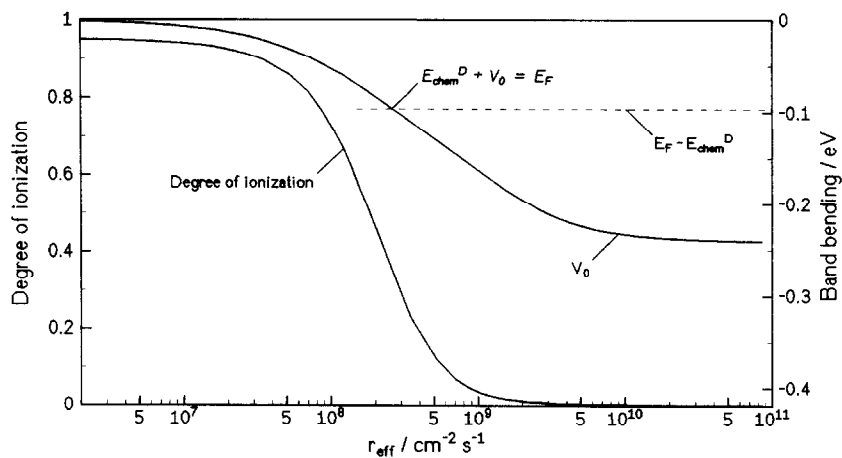


Fig. 7. Degree of ionization and band bending in the surface region for the adsorption of spilt-over hydrogen on TiO₂ as a function of r_{eff} (atomic desorption).

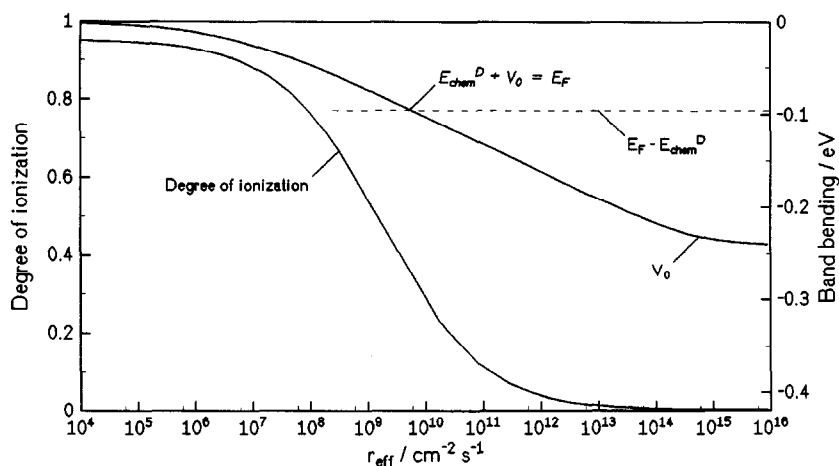


Fig. 8. Degree of ionization and band bending in the surface region for the adsorption of spilt-over hydrogen on TiO_2 as a function of r_{eff} (recombinative desorption).

more detail for atomic desorption in Fig. 6 (similar results are obtained for recombinative desorption). For high spillover rates r_{eff} the spilt-over hydrogen species are mainly adsorbed as H atoms since the electron transfer from the adsorbate to the solid is hindered by the large band bending due to the surface charge of the strongly chemisorbed species (H^+ ions). This effect is obvious from Figs. 7 and 8 for atomic and recombinative desorption, respectively. The transfer from strong to weak chemisorption (corresponding to a degree of ionization of 1/3)

occurs when the additional adsorption state $E_{\text{chem}}^{\text{D}} + V_0$ is equal to the Fermi level E_{F} ('Fermi level pinning'). The ratio between H^+ ions (the preferred adsorption state for $E_{\text{chem}}^{\text{D}} + V_0 > E_{\text{F}}$) and H atoms (preferred for $E_{\text{chem}}^{\text{D}} + V_0 < E_{\text{F}}$) strongly depends on the electronic properties of the solid and the total concentration of spilt-over species. Especially when assuming a recombinative desorption, there is a large range of spillover rates r_{eff} where significant amounts of H atoms and H^+ ions coexist on the surface of the catalyst (Fig. 8). This coexistence of two

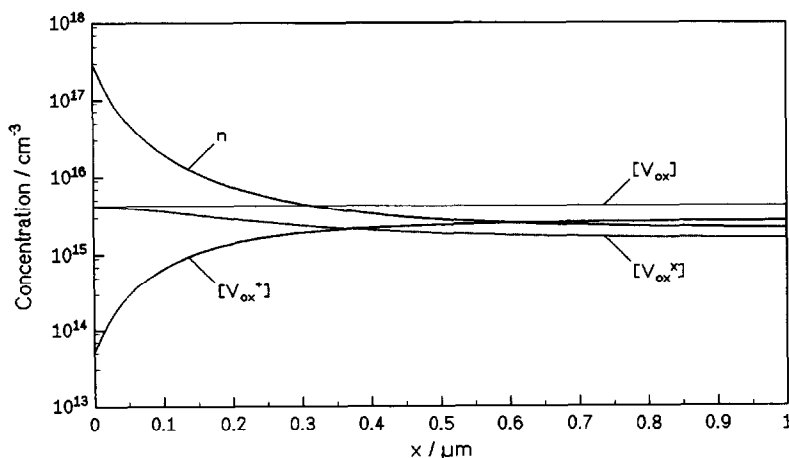


Fig. 9. Concentration of electrons and differently charged oxygen vacancies in the surface region of TiO_2 after the adsorption of spilt-over hydrogen.

hydrogen species is indicated by a number of experimental investigations as previously discussed in this work.

4. Use of the new model to interpret experimental results

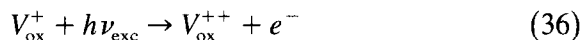
4.1. Conductivity measurements on TiO_2

The increase of the n-type conductivity of Pt-containing titania after an exposure to hydrogen as shown by different authors [87–91,96–98] could be clearly correlated with hydrogen spillover (in contrast to metal/solid interface effects) using a special two-component sample geometry [91,99]. The enhancement of electrons in the surface region is provided by the model calculations as represented in Fig. 9 (recombinative desorption, $r_{\text{eff}} = 10^8 \text{ cm}^{-2} \text{ s}^{-1}$, other parameters as denoted above) thus describing qualitatively the experimental results obtained for polycrystalline TiO_2 samples. The corresponding band bending $V(x)$ in the surface region of titania and the shift of the electronic states with respect to the Fermi energy E_F is shown in Fig. 10.

4.2. Influence of hydrogen spillover on the fluorescence of TiO_2

FT NIR Raman spectroscopic studies (using a Nd-YAG excitation laser with $\lambda_{\text{exc}} = 1064 \text{ nm}$) on the system Pt/TiO_2 have shown that the presence of oxygen vacancies in titania leads to fluorescence in the spectral region around 6450 cm^{-1} (corresponding to a Raman wavenumber of about 2940 cm^{-1}), i.e. an energy of ca. 0.8 eV [108,109]. The fluorescence process was proposed [109] to involve:

(i) The excitation of an electron from the electronic state of the singly ionized oxygen vacancy E_{D1} into the conduction band according to



(ii) The subsequent transition of the electron to the conduction band edge E_c .

(iii) The relaxation process



connected with the emission of a photon with the energy

$$E_{\text{emiss}} = E_c - E_{\text{D1}} = h\nu_{\text{emiss}} \approx 0.8 \text{ eV} \quad (38)$$

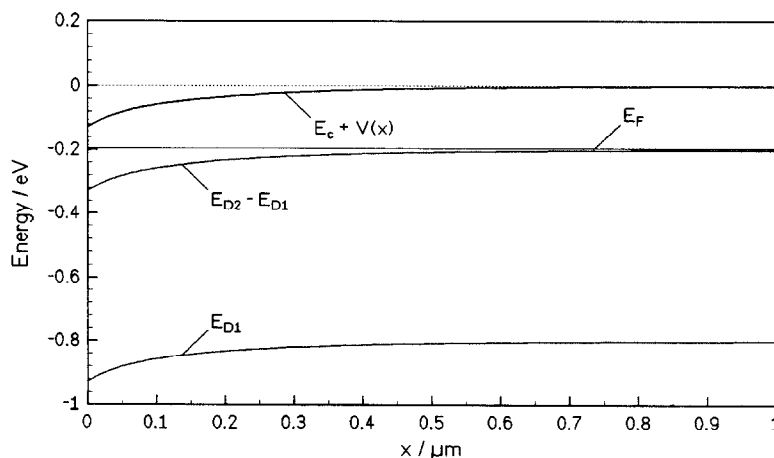
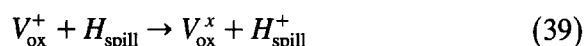


Fig. 10. Band bending $V(x)$ and shift of the electronic states with respect to the Fermi energy in the surface region of TiO_2 after the adsorption of spilt-over hydrogen.

The exposure of Pt-containing TiO₂ samples to hydrogen led to a marked decrease of the fluorescence. This was interpreted by the diffusion of atomic hydrogen onto the TiO₂ support. The chemisorption of these species was connected with an electron transfer to the solid leading to the formation of neutral oxygen vacancies (V_{ox}^x) from singly ionized ones (V_{ox}^+):

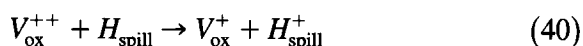


Consequently, the excitation process leading to fluorescence (Eqs. (36) and (37)) was diminished by the transformation of singly ionized to neutral vacancies due to the chemisorption of spilt-over hydrogen. This decrease of the V_{ox}^+ concentration in the surface region is obtained by the model calculations as shown in Fig. 9, too.

4.3. Influence of hydrogen spillover on the IR transparency of ZnO

The loss of transparency in the infrared region around 1500 cm⁻¹ (corresponding to ca. 0.2 eV) as observed by Boccuzzi et al. [105–107] after a contact of Cu/ZnO and Ru/ZnO with hydrogen or deuterium can also be interpreted by an electron transfer from spilt-over hydrogen

to ZnO. The enhanced absorption can be described according to Eq. (36). The origin is the formation of singly ionized oxygen vacancies (V_{ox}^+ ; $E_{\text{D1}} = -0.2$ eV [120]) from doubly ionized vacancies (V_{ox}^{++}) initially present in the surface region of ZnO, due to the chemisorption of electron-donating atomic hydrogen or deuterium:



This explanation is confirmed by the fact that the adsorption of hydrogen or deuterium on metal-free ZnO did not influence the infrared absorption.

A model calculation based on the chemisorption isotherm for recombinative desorption (Eqs. (28) and (29); $r_{\text{eff}} = 3.2 \cdot 10^5$ cm⁻² s⁻¹) is in agreement with this experimental result as represented in Fig. 11. The electronic and thermodynamic parameters for the calculation were obtained from the literature [106,120–123] as described in detail elsewhere [85]. The predicted increase of the electron concentration (Fig. 11) leading to an enhanced surface conductivity was experimentally found by Barrett et al. [124] for Cu,Co/ZnO and by Lobashina et al. [94] for ZnO with an admixed Pd/SiO₂ catalyst as the source of atomic hydrogen.

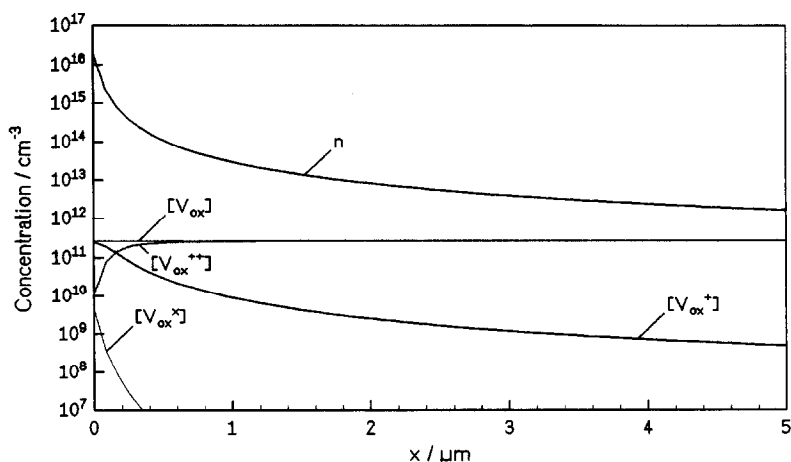


Fig. 11. Concentration of electrons and differently charged oxygen vacancies in the surface region of ZnO after the adsorption of spilt-over hydrogen.

5. Consequences of the new model

5.1. Coexistence of H^+ ions and H atoms

A main aspect of the model for the adsorption of spilt-over hydrogen is the introduction of an additional electronic state at the surface. This state may be occupied (i.e. the electron remains at the adsorbate, corresponding to the H atom) or empty (i.e. the electron is transferred to the solid leading to the formation of an adsorbed H^+ ion). The concentration ratio between both species which is represented by the degree of ionization depends on the electronic parameters of the system as shown in Figs. 7 and 8. A wide range of experimental conditions can exist where neutral and positively charged hydrogen species coexist on the surface (Figs. 4–6). This explains the disagreements concerning the nature of the spilt-over species when different detection methods are used. For example, a reaction specific for radical reactants may detect H atoms whereas other experimental techniques can provide indications for charged hydrogen species in the same system. The coexistence of both species in the same catalyst may have important consequences for the explanation of former experimental results. Particularly, both species were

proposed to take part in bifunctionally catalyzed hydroconversions on metal-containing zeolite catalysts [99,125]. Our model justifies this hypothesis.

Finally, it should be mentioned that the model could also explain the occurrence of H_3 and/or H_3^+ species during the spillover process as proposed by Bianchi et al. [24]. In this case, a reaction of H^* species with molecular hydrogen present in the gas phase may be assumed.

5.2. Dependence of hydrogen spillover on the electronic properties of the support

The probability of an electron transfer from spilt-over hydrogen and, therefore, the total amount of chemisorption strongly depends on the electron density in the solid which is closely connected with the Fermi energy E_F . It is obvious that the presence of electron acceptors in the bulk of the solid will enhance the electron transfer and, consequently, the amount of strongly chemisorbed species. According to the adsorption isotherms this corresponds to an increase of the average adsorption energy. In contrast, the presence of electron donors in the bulk will favour weak chemisorption and this corresponds to a lower average adsorption energy. A

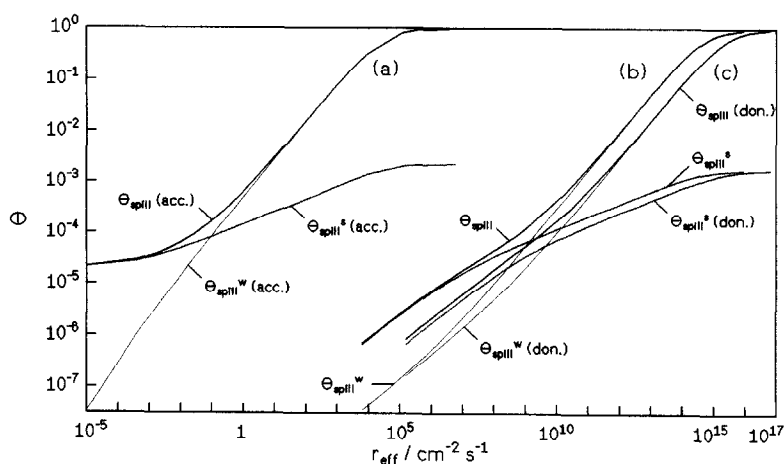


Fig. 12. Adsorption isotherms for spilt-over hydrogen on TiO_2 with different defect concentrations; the ratio between the acceptors and the oxygen vacancies is (a) 1.4, (b) 0.14 and (c) 0.014.

model calculation for TiO_2 at 300 K exhibiting different donor (oxygen vacancy) and acceptor densities is shown in Fig. 12.

The typical values for the defect concentrations which were used for the calculations above ($[A] = 6 \cdot 10^{14} \text{ cm}^{-3}$, $[V_{\text{ox}}] = 4.27 \cdot 10^{15} \text{ cm}^{-3}$, $[A]/[V_{\text{ox}}] = 0.14$) correspond to the adsorption isotherm (b). For these defect concentrations the Fermi energy E_F is situated 0.196 eV below the conduction band edge.

In the case where the acceptors dominate ($[A] = 6 \cdot 10^{14} \text{ cm}^{-3}$, $[V_{\text{ox}}] = 4.27 \cdot 10^{14} \text{ cm}^{-3}$, $[A]/[V_{\text{ox}}] = 1.4$) the Fermi energy E_F is shifted to a value of 0.808 eV below the conduction band edge E_c . The enhanced adsorption is obvious from the adsorption isotherm (a).

When the concentration of the oxygen vacancies as intrinsic donors is significantly larger than that of the acceptors ($[A] = 6 \cdot 10^{14} \text{ cm}^{-3}$, $[V_{\text{ox}}] = 4.27 \cdot 10^{16} \text{ cm}^{-3}$, $[A]/[V_{\text{ox}}] = 0.014$) E_F is located 0.155 eV below E_c and the adsorption of spilt-over hydrogen is suppressed as shown by the isotherm (c).

Previously, the described dependency of the adsorption properties on the concentration and the type of dopants had been qualitatively shown for the (as assumed, dissociative) chemisorption of hydrogen on differently doped ZnO [126–129]. Though investigations in connection with hydrogen spillover have not been described yet, experiments carried out by Hauffe et al. [130] may be interpreted as a first indication for the dependency discussed above. The authors studied the adsorption of hydrogen on NiO doped with an increasing amount of Ga_2O_3 and Li_2O forming electron donors and acceptors, respectively. They found that the hydrogen adsorption on Ga-doped NiO was very weak (below 10^{13} molecules/ cm^2 even for the lowest dopant concentration, i.e. 0.05 mol% Ga_2O_3). For comparison, the amount of hydrogen adsorbed on undoped NiO was about 10^{14} molecules/ cm^2 . Doping NiO with Li_2O led to a marked increase of hydrogen adsorption (to ca. $1.6 \cdot 10^{14}$ molecules/ cm^2 for 0.2 mol% Li_2O). The adsorption measurements were carried out at 373

K. The dependence of the hydrogen adsorption on the presence of donors or acceptors in the bulk of NiO strongly suggests that hydrogen acts as an electron donor at the surface. Taking into account the results of Delmon et al. on the reduction of NiO initiated by spilt-over hydrogen via the formation of metallic Ni sites [7,131,132] it is likely to assume the formation and adsorption of atomic hydrogen under the conditions applied for the adsorption measurements. In this case the results obtained by Hauffe [130] are exactly in agreement with the results of the model calculations (Fig. 12).

It should be mentioned that the activation conditions for oxidic catalysts (e.g. temperature and partial pressure of oxygen) can significantly influence the density of oxygen vacancies as intrinsic electron donors and, therefore, the adsorption properties especially for strong chemisorption. This effect has to be taken into account when investigating spillover and, more generally, chemisorption on oxide supported metals. In the case of the strong metal support interaction (SMSI) phenomenon [133–136] this influence on the adsorption behaviour should be considered in addition to changes of the metal work function, the modification of the metal/support interface or the coverage of the metal by TiO_x species connected with the formation of a ‘pillbox’ structure [5,6,136].

5.3. Consequences for the spectroscopic observation

The model that was proposed to describe the physical nature of the spilt-over H^* species may also explain the difficulties encountered in the attempts to investigate them directly by spectroscopic techniques.

Although the formation of additional OH groups acting as Brønsted acid sites due to hydrogen spillover has been described in some cases [56–58,137,138] a large number of H–D exchange experiments gave no indication of significant changes in the entire OH/OD concentration [5,21,79,83–85,139]. In both cases

the spilt-over species themselves cannot be identified with additional OH groups or specific bands detectable by infrared spectroscopy. This is logical when the delocalized character of the electronic interaction between adsorbate and solid in comparison to a chemical bond (e.g. between hydrogen and oxygen in a hydroxyl group) is taken into account. That is why IR spectroscopy seems not to be suitable to observe the spilt-over species directly. Nevertheless, it is undoubtedly a useful tool to investigate reactions specific for the H^* species.

Experimental results that were achieved by means of ESR spectroscopy have been already discussed. Using this method paramagnetic H atoms (even when coexisting with H^+ ions) should be observed when they are sufficiently stable (see [74]). However, when the degree of ionization is high (low spillover rates) then the concentration of paramagnetic H atoms is low and no ESR signal would appear. Additionally, there is another main problem: a fast exchange between both spilt-over species corresponding to a rapid electron transfer between adsorbate and solid would lead to a marked broadening of the ESR lines or even a diminishing of the ESR signal produced by the H atoms. Since electron transfer processes can be very fast, the existence of a rapid dynamic equilibrium between the two spilt-over species could be the origin of the difficulty to detect H atoms during the spillover process, even when test reactions (e.g. the H–D exchange or reactions with organic radicals [19,69,70,85]) provided unambiguous evidence for the occurrence of hydrogen spillover.

A further aspect has to be considered in the case of NMR spectroscopic investigations on hydrogen spillover: the NMR lines of paramagnetic species can be expected to be significantly shifted and/or broadened by hyperfine interactions [140]. The H atom exhibits an extremely large hyperfine coupling constant (corresponding to 1420 MHz) due to the intimate interaction of the nuclear spin and the spin of the 1s electron, a so-called Fermi contact interaction. That is why it is not possible to detect free H

atoms by means of conventional NMR spectroscopy [140]. A fast exchange between H atoms and H^+ ions in the time scale of NMR spectroscopy which is in the range of microseconds would lead to a line at a mean position. Because of the large NMR shift of the H atom this exchange signal could still not be observed. The situation would be the same for a moderate exchange rate leading to a broad and undetectable NMR signal. Only in the case of slow exchange the signal of the H^+ ion can be expected to be measured using conventional NMR spectroscopy. Summarizing, the coexistence of H radicals and H^+ ions, which is the main feature of our model, can explain the difficulties to detect the spilt-over hydrogen species in a direct way. This assumption is supported by the fact that some NMR investigations have shown that only part of the hydrogen adsorbed on supported metal catalysts is visible in the NMR spectra [64–68].

The consequences of a dynamic equilibrium between ionic and radical hydrogen species should be considered in spectroscopic studies investigating spilt-over hydrogen species. The model could help overcome the difficulties in the direct observation of spillover processes and permit more insight into the nature of the activated H^* species.

6. Conclusion

On the basis of a large number of experimental results it must be concluded that the nature of the spilt-over hydrogen species can only be understood by considering the electronic interaction of the adsorbed H^* species with the support. Consequently, the nature of activated hydrogen depends on the physico-chemical properties of the catalyst. A model is proposed that describes the spilt-over species as electron donors adsorbed at the surface. The additional electronic state may be occupied or empty, which corresponds to H atoms (weakly

chemisorbed) or H^+ ions (strongly chemisorbed) as H^* species. As an illustrative example the adsorption isotherms were calculated for semi-conducting metal oxides. In the frame of the model atomic as well as recombinative desorption were considered.

Although the relevant electronic states are rather difficult to describe for insulators and especially for microporous materials, e.g. zeolites, the model can be qualitatively applied also for such catalysts. However, much work has still to be done to quantify all the parameters whose contribution to the adsorption isotherm has been investigated. Especially, in order to confirm the calculated adsorption isotherms the dependence of the amount of adsorbed spilt-over species on the experimental and material conditions has to be estimated. The direct quantification by means of spectroscopic methods could become possible by considering the coexistence of both spilt-over species. This would allow a marked progress in the quantitative description of hydrogen spillover on the basis of the new model. Presently, it could be shown that various experimental results can be satisfactorily explained by the model. Apparently contradictory results concerning the nature of the spilt-over species can be understood by proposing the *coexistence of H atoms and H^+ ions* in agreement with the new model. The theoretical considerations presented here can contribute to the understanding of the influence of the material parameters on the catalytic properties and to the optimization of catalytic systems.

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