

Letter

Reply to the Letter to the Editor of M. Boudart ‘On the nature of spilt-over hydrogen’

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The Letter of M. Boudart ¹ related to our publication [1] considering the nature of the spilt-over hydrogen species contains four main criticisms which we would like to discuss below.

(1) In the frame of the discussion of experimental results on hydrogen spillover, we also considered the extensive and expressive work of M. Boudart et al., in particular, his work with Levy on the role of co-catalysts acting as proton acceptors [2]. Without questioning the main ideas of this work, we mentioned that the *conclusion of the authors that the electrons removed from the H atoms would remain on platinum is very unlikely*. In fact, the discussion in Ref. [2] seems to us to be not completely clear in this point ([2], p. 311): *... the co-catalyst reacts with the hydrogen to form a solvated proton. The electron is left behind in the metal*. There is also another passage which does not make this easier to understand ([2], p. 313): *... the chemisorbed hydrogen loses its electron to the conduction band of the metal*. Actually, our moderate criticism is not new [3,4]. In another paper cited by Boudart et al. [5], the

interpretation is obvious and the transfer and the subsequent diffusion of an ion–electron pair is claimed. This assumption (which was also considered by Keren and Soffer [4]) is, in fact, close to our model where we described the adsorption of these species on the basis of solid state physics in a more dynamic manner (coexistence of H⁺, electron and H radical). Fermi–Dirac statistics allows to determine the ratio of these species in dependence on the properties of the support [1]. However, as discussed later, we think that the presence of a co-catalyst is not a necessary prerequisite for hydrogen spillover at low temperature, but its presence can accelerate transfer and migration [6,7].

(2) We clearly stated that our model is focused on the description of the activated hydrogen species after their diffusion from the activating phase onto the support phase ([1], p. 67): *The objective of the model is to describe the nature of the spilt-over 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. It has to be emphasized that the adsorption of hydrogen on the activating metal itself will not be considered here*. The only statement we made about the adsorption of hydrogen on the metal

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was that dissociative adsorption on activating metals can be understood as an indication for atomic H^* species. In fact, this assumption is not very speculative and commonly accepted. The argument of M. Boudart concerning the adsorption of hydrogen on metals is not directly relevant to our model. In detail, we did not claim the presence of H^+ on the metal as alleged in the comment.

We do not question the experimental finding of Boudart and others that water can favour hydrogen spillover, acting as a co-catalyst. Additionally, Levy and Boudart [2] have shown such a behaviour for other proton acceptors. However, we believe that we have clear experimental indications for the occurrence of hydrogen spillover in the absence of water or other co-catalysts even at ambient temperature. For example, we have gravimetrically measured the adsorption of hydrogen and deuterium on a platinum-containing zeolite after carefully removing water from the system [8]. As expected, we found the ratio of the mass gains to be 2, which would not be the case for water adsorption or the formation of water from oxygen traces. We carried out additional experiments on hydrogen spillover at ambient temperature: conductivity measurements on titania [9,10] and investigations on the H–D exchange of zeolitic hydroxyl groups [11–13] without water being present as shown by IR and NMR spectroscopy. Further examples are cited in our paper [1]. Of course, the migration of hydrogen from the metal onto the support requires an activation energy, which is likely to be higher in the absence of a co-catalyst. We found an indication for such a diffusion barrier in our adsorption studies [8].

(3) Of course, we took into account the possibility of the reduction of titania by hydrogen in the presence of a metal. We comprehensively discussed the conductivity effects of adsorbed hydrogen (H^*) in the two original papers [9,10] cited in Ref. [1]. Because we wanted to characterize the spilt-over hydrogen species interacting with titania, we made two significant choices of

experimental conditions. Firstly, to exclude effects at the interface between metal and support we used two-component samples consisting of a platinum-containing and a platinum-free component in contact. By studying the effects of H^* in the Pt-free sample part we could unambiguously correlate the conductivity changes with the H^* species. Secondly, the temperature range was chosen by bearing in mind that a decrease of the resistivity of Pt/TiO₂ upon hydrogen loading could be due to two effects: (i) the reduction of the titania surface (and, possibly, the bulk), leading to the formation of water and oxygen vacancies, and (ii) an electron transfer from H^* to titania. In the first case, the oxygen vacancies formed would act as electron donors, initiating an increase of the n-type conductivity. This process would not be reversible upon pumping off. In the second case, the titania phase would remain unchanged and the process would be reversible. We have chosen low temperatures (< 80°C) in order to exclude the first process. We could then prove our hypothesis of a charge transfer mechanism (H^* acting as surface electron donor) by showing the reversibility. Furthermore, a formation of oxygen vacancies and the occurrence of SMSI effects are unlikely at temperatures below 80°C [14–16]. The model calculations in Ref. [1] were made for a temperature of 300 K. Under the experimental conditions chosen, H₂/Pt/TiO₂ was shown to be a suitable model system to study hydrogen spillover. In particular, the application of a two-component sample geometry allowed us to unambiguously interpret the results as being due to the action of H^* .

(4) We are aware of the necessity, but also the difficulty, to prove our model in a quantitative manner and we expressed this in our paper where we stated *that much work has still to be done to quantify all the parameters whose contribution to the adsorption isotherms has been investigated* ([1], p. 82). Our intention was the development of a theory which can explain a wide variety of experimental results obtained during the last four decades. The quantitative

description of this model was consistently developed on the basis of solid state physics. The basic assumption, H^* acting as electron donor located at the surface, led to the coexistence of two spilt-over species (H^+ and H atom). In order to compare the calculated isotherms with experimental results, it is necessary to quantify the amount of H^* species on the catalyst surface (preferentially, separately for both types of H^* species). This leads to the serious problem of detecting these species spectroscopically in a direct manner, which could not be achieved until now. Kinetic studies as proposed by Boudart would not solve the problem because the isotherms represent equilibrium states. We discussed the possible origin of the difficulty to detect the H^* species directly by NMR and ESR spectroscopy in our paper. Probably, only experiments on single crystals would allow such a comparison. Besides spectroscopy, the measurement of work function changes due to the adsorption of activated hydrogen (corresponding to the band bending in the surface region of the solid) could be an expressive method. Bearing in mind these problems, our qualitative comparison represents the 'state of the art': further

studies are indeed required as we stated in the conclusion of our paper.

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