

Letter

‘On the nature of spilt-over hydrogen’

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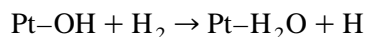
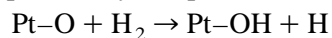
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In a paper under the above title, Roland et al. [1] propose a new model in which H^+ ions and H atoms (called together the H^* species) coexist at the surface of a metal catalyst, with subsequent transfer of H^+ to a metal oxide on which the metal is supported. A theory is developed to calculate equilibrium adsorption isotherms of spilt-over hydrogen on TiO_2 . There is no comparison between calculated and experimental values of these isotherms.

I am very receptive to the idea of a positively charged hydrogen species being of importance in hydrogen spillover in systems containing platinum in contact with yellowish WO_3 and exposed to H_2 . This system remains the best studied example of the phenomenon because of the rapidity of the spillover at room temperature, the very large amount of hydrogen tungsten bronze being formed H_xWO_3 with $x = 0.35$, and the visual impact of the blue color of the bronze. As recalled by Roland et al., this striking discovery was made by Khoobiar [2], who used WO_3 mixed with a standard Pt/Al_2O_3 catalyst and observed the blue color of the H tungsten bronze after exposure of the mixture to H_2 at room temperature. Khoobiar knew that WO_3 turned blue when exposed to H but not to H_2 at room temperature.

Hearing about the discovery of Khoobiar, we tried to repeat it. Dihydrogen was admitted to a reactor containing a mixture of WO_3 and Pt/Al_2O_3 , the same catalyst used by Khoobiar. But following reduction of the catalyst in H_2 with subsequent evacuation in a high vacuum system, no color change took place upon admitting H_2 . To bring about the blue reaction, it was necessary to introduce small amounts of O_2 into the reactor [3]. The Khoobiar reaction was explained by the processes:



Upon further examination [4], it became clear that the Khoobiar reaction took place only in the presence of water produced after exposure of the reduced catalyst to dioxygen. Water was identified as the necessary co-catalyst for the Khoobiar reaction. To avoid complications due to the hygroscopic alumina, most of the subsequent work in our laboratory was carried out with mixtures of WO_3 and platinum black, although Pd/SiO_2 was also used in later work.

In a subsequent publication on the subject, we coined the word *spillover* to denote the phenomena observed during the Khoobiar reaction [5]. We established the participation of water in spillover by measuring the kinetic isotope effects for the rate of spillover with H_2 , D_2 , H_2O , D_2O , in various combinations. The conclusion was clear: water was indeed the

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necessary co-catalyst for the Khoobiar reaction [5].

Finally, Levy and I were able to identify the nature of the species responsible for the water-assisted migration of H atoms adsorbed on Pt to the ultimate reduction site on and in WO_3 : the species is H_3O^+ [6]. Indeed, we measured the rate constant k , for the Khoobiar reaction bringing about the reduction of WO_3 by H_2 at 294 K in the presence of a Pt catalyst and various co-catalysts. A straight line over four orders of magnitude of k was obtained when $\log k$ was plotted against the known proton affinity of six co-catalysts, water and five different catalysts. These quantitative observations led us to a simple conclusion. As summarized by ourselves [7], “the co-catalyst is protonated at the surface of the metal with transfer of the valence electron of hydrogen to the conduction band of the metal. An ion-electron pair moves over to the surface of WO_3 where the protonated co-catalyst gives up its proton as hydrogen in a rate determining step which is the faster the lower the proton affinity of the co-catalyst.”

In their paper under discussion in this Letter, Roland et al. allude briefly to our paper with Levy. They write that we “found a strong correlation between the reaction rate and the proton affinity of the co-catalysts with high proton affinities and concluded that the spilt-over species were H^+ ions.” In fact, we proved that the diffused species was a protonated species. Roland et al. continue: “However the conclusion of the authors that the electrons removed from the H atoms would remain on platinum is very unlikely, . . .”. We never wrote such a statement or conclusion. The last sentence of our paper with Levy reads: “This solvated proton diffuses from the metal surface to the surface of WO_3 where the proton is released to the reduction site.” Released with what? With the associated electron at the reduction site, to produce the H atom and to make H_xWO_3 .

Spillover has been studied so much over 30 years with such different chemical systems that

it would be foolish to believe that our explanation of the Khoobiar reaction is generally valid for all systems. In connection with the paper of Roland et al. under discussion here, the important general point is that protons do not exist on a transition metal surface following dissociative chemisorption of H_2 . This is because the ionization energy of H is so much higher than the work function of metals.

There is an abundant set of surface science data on H chemisorbed on metals, as reviewed by Somorjai [8]. For different metals exposing different crystallographic planes, the sign of work function change upon dissociative adsorption of H_2 is always negative. This indicates that, if there is a partial charge on H chemisorbed on metals, it is negative and not positive.

By contrast, in the presence of water, H atoms at the surface of certain metals form stable hydronium ions H_3O^+ that are particularly stable in the presence of water in excess of a water monolayer because H_3O^+ is solvated. The relevant surface science data have been reviewed by Masel [9]. There H_3O^+ species have been identified on Pt(111), but not on Cu(110). Thus, observations confirm our mechanism proposed by us for the transport of H from Pt to WO_3 in the presence of proton acceptor molecules. But there is no evidence for the existence of H^+ on metals in the absence of proton acceptors, as postulated by Roland et al.

Our definitive work on the Khoobiar reaction was favored by luck: WO_3 is reduced by H atoms to H_xWO_3 without formation of water. Thus the necessity of water or other proton acceptors could be established in the case of the Khoobiar reaction. But in many other situations, the metal/oxide support combination is such that H_2 will reduce the support, generating water that permits hydrogen spillover to take place at lower temperatures as is the case for the Khoobiar reaction. Roland et al. use as their example the system $\text{H}_2/\text{Pt}/\text{TiO}_2$. In this system, TiO_2 is reduced to TiO_{2-x} with formation of water and TiO_{2-x} moves to the Pt surface, causing phenomena that have been attributed to

SMSI, or strong metal support interaction [10]. Clearly, Roland et al. ought to find a simpler system to compare results of their theory to actual experimental data. The work should include a quantitative kinetic treatment, as we have done in the case of the Khoobiar reaction.

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