Mechanism of the H_2–D_2 Exchange Reaction over ZnO—Dynamic Behaviour of Chemisorbed Hydrogen as a Reaction Intermediate during the Course of the Reaction

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The mechanism of the H_2–D_2 exchange reaction over ZnO at lower temperatures (from −70°C to room temperature) was studied by measuring the adsorption during the course of the reaction by the volumetric method as well as by the infrared spectroscopic technique.[1]

The zinc oxide employed was Kadox 15 and Kadox 25 of the New Jersey Zinc Company; it was evacuated for more than five hours at 400°C prior to the reaction. The infrared spectra of the adsorbed hydrogen and deuterium on ZnO were observed at 3490 (ZnOH), 2584 (ZnOD), 1712 (ZnH), and 1233 (ZnD) cm^{-1}, as has been reported by Eischens, Pliskin and Low.[2]

Below room temperature, the rate of hydrogen chemisorption over ZnO was rapid, while the rate of desorption was slow. No isotope effect was detected, within the limits of experimental error, in the rate of hydrogen and deuterium chemisorption or in the adsorption equilibrium over ZnO, as has been reported previously.[3]

When H_2 (9.4 cmHg) was pre-adsorbed over ZnO and D_2 (9.6 cmHg) was then added to the system, the pre-adsorbed H(a) was displaced by D(a) as the exchange proceeded. The rate of HD formation obeyed the first-order rate equation as to H(a), a uniform reactivity of H(a) being demonstrated. Similar experiments were carried out by the infrared technique. The rate of the total decrease in the ZnH and ZnOH-band intensities was equal to that of the increase in the ZnD and ZnOD-band intensities, and it was revealed that the rate of HD formation is proportional to the amount of exchangeable hydrogen chemisorbed which is observed by the infrared technique, and to the D_2 pressure in the ambient gas. At 0°C, the rate of HD formation in the volumetric experiment and the rate of the total decrease in the ZnH and ZnOH-band intensities in the infrared spectroscopic technique were in reasonable agreement. These results lead to the conclusion that the chemisorbed hydrogen observed by the infrared technique exhibits a behaviour similar to that measured volumetrically and that it is the real intermediate of the exchange reaction.

When a mixture of H_2 and D_2 (1 : 1) (total 22.2 cmHg) was introduced, the amounts of ZnH, ZnOH, ZnD, and ZnOD were equal at the beginning of the adsorption, but as the exchange reaction proceeded the amounts of ZnH and ZnOD increased at different rates, whereas those of ZnD and ZnOH decreased correspondingly; this demonstrated the rearrangement of the chemisorbed species through the exchange reaction. No such rearrangement was detected in the absence of the ambient gas, which shows no appreciable mobility to be involved between the hydrogen on zinc and that on oxygen. When one mixture of H_2 and D_2 (2 : 1) (total 24.2 cmHg) was introduced over ZnO, the rate of HD formation was about one and half times as great as that when another H_2 and D_2 (1 : 2) (total 24.3 cmHg) mixture was introduced. Consequently, though no isotope effect is involved in the chemisorption, as has been described above, a considerable kinetic isotope effect is observed in the rate of the exchange reaction.

As the behaviour of the four chemisorbed species, ZnH, ZnD, ZnOH, and ZnOD, may be separately examined by the infrared technique over a wide range of ambient pressures and chemisorbed amounts, and with various isotope contents, the exchange reaction through one of those species and ambient molecules, or through their recombinations, may be studied. It was, consequently, concluded that the rate of the HD formation from the recombination of the chemisorbed species (the Langmuir mechanism), which corresponds to the desorption rate, is at least one or two orders of magnitude slower than the exchange reaction between the molecular hydrogen in the ambient gas and the chemisorbed species (the Eley-Rideal mechanism).

If the repetition of the dissociative chemisorption and desorption of hydrogen results in the H_2–D_2 exchange reaction, as neither process has any kinetic isotope effect, the exchange reaction rate would exhibit no kinetic isotope effect. The marked isotope effect demonstrated in the exchange reaction proves this not to be the case.

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