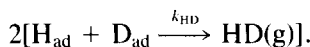
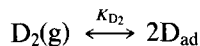
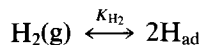


The H₂–D₂ Exchange Reaction over Pd

Several years ago it was reported that the apparent activation energy (E_{app}) for the H₂–D₂ exchange reaction on a Pd/C catalyst increased by about 30 kJ mol⁻¹ as the Pd crystallite size decreased below 2 nm (1), and over a Pd/mica catalyst E_{app} increased by 40 kJ mol⁻¹ as the Pd crystallite size decreased from 2.5 to 1 nm (2). Although a detailed reaction sequence was not presented, it was proposed that the adsorption energy of H₂ (and D₂) decreases along with the Pd particle size, and the conclusion that this increased E_{app} was caused by a decrease in the rate of dissociation of the adsorbed hydrogen (deuterium) (1) was reached. This implies that H₂(D₂) dissociation is a rate-determining step in this reaction; however, at the temperatures utilized in these studies (273–303 K), dissociative H₂ adsorption on Pd is very rapid and non-activated (3). It is the purpose of this note to provide an alternative explanation, based on new results, that is more consistent with the known behavior of H₂ and D₂ on Pd (3, 4).

We have recently reported in this journal isothermal, integral heats of adsorption (Q_{ad}) at 300 K for H₂ on Pd dispersed on a number of oxide supports (5). For crystallite sizes between 3 and 1000 nm, Q_{ad} remained constant at 63 kJ mol⁻¹ H₂ (15 ± 1 kcal mol⁻¹), a value in good agreement with those estimated from UHV studies. However, on crystallites smaller than 3 nm the Q_{ad} values increased with decreasing size to an upper value near 100 kJ mol⁻¹ H₂ (24 kcal mol⁻¹). This trend is opposite to that assumed by Takasu *et al.* (1), but it provides a simple explanation for their reported variation in E_{app} . Evidence strongly favors a Langmuir–Hinshelwood (L–H) model for this reaction on Pd (4):



The L–H rate expression at low conversions straightforwardly derived from this sequence is

$$r_{HD} = \frac{\frac{zL}{2} k_{HD} K_{H_2}^{1/2} K_{D_2}^{1/2} P_{H_2}^{1/2} P_{D_2}^{1/2}}{(1 + K_{H_2}^{1/2} P_{H_2}^{1/2} + K_{D_2}^{1/2} P_{D_2}^{1/2})^2},$$

where L is the number of surface Pd atoms, z is the number of nearest neighbors around a surface atom, and K_{H_2} and K_{D_2} are equilibrium adsorption constants for H₂ and D₂, respectively. At the pressures used in the two kinetic studies (2.7–6.6 Pa), the coverage of the Pd surface is very high; therefore, $K_{H_2}^{1/2} P_{H_2}^{1/2} \gg 1$ and $K_{D_2}^{1/2} P_{D_2}^{1/2} \gg 1$. Although a small difference of about 1.5 kcal mol⁻¹ is expected between the heats of adsorption for H₂ and D₂ due to the slightly higher zero point energy of the D₂ molecule (3), as a good approximation it can be assumed that $K_{H_2} \cong K_{D_2}$. The rate equation then simplifies to

$$r_{HD} = \frac{zL}{2} k_{HD} \frac{P_{H_2}^{1/2} P_{D_2}^{1/2}}{(P_{H_2}^{1/2} + P_{D_2}^{1/2})^2} = A e^{-E/RT} \frac{P_{H_2}^{1/2} P_{D_2}^{1/2}}{(P_{H_2}^{1/2} + P_{D_2}^{1/2})^2}$$

and the apparent activation energy is equal to the potential energy well associated with the desorption of the HD molecule. If adsorption is nonactivated, this desorption energy is equal to Q_{ad} . Consequently, the increase in the heat of adsorption of approximately 37 kJ mol⁻¹ for H₂ on small Pd crystallites would result in a concomitant

increase in E_{app} equal to the 30–40 kJ mol⁻¹ reported by Takasu *et al.* for the exchange reaction (making the reasonable assumption that Q_{ad} would vary similarly for D₂ on Pd).

In conclusion, it is proposed here that it is not necessary to postulate H₂(D₂) dissociation as the slow step in the H₂–D₂ exchange reaction on Pd, which is difficult to accept, but that the L–H model proposed by others appears very applicable and, in fact, predicts a variation in E_{app} consistent with the kinetic results of Takasu *et al.* and our heat of adsorption values for H₂ on Pd.

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REFERENCES

1. Takasu, Y., Akimaru, T., Kasahara, K., Matsuda, Y., Miura, H., and Toyoshima, I., *J. Amer. Chem. Soc.* **104**, 5249 (1982).
2. Takasu, Y., Kasahara, K., and Matsuda, Y., *Bull. Chem. Soc. Japan* **57**, 2313 (1984).
3. Conrad, H., Ertl, G., and Latta, E. E., *Surf. Sci.* **41**, 435 (1974).
4. Engel, T., Ertl, G., in "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (D. A. King and D. P. Woodruff, Eds.), Vol. 4, p. 195. Elsevier, Amsterdam/New York, 1982.
5. Chou, P., and Vannice, M. A., *J. Catal.* **104**, 1 (1987).

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