The Mechanism of Catalyzed Hydrogen-Deuterium Exchange on Gold Deposited over Poly(tetrafluoroethylene)

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The H_2–D_2 exchange reaction over Au(0.3%)/PTFE(poly(tetrafluoroethylene)) was studied. The apparent activation energy was found to be 29 kJ mol^{-1}. The dependence of the reaction rate on the total pressure was measured at 518, 432, and 393 K. It was found that the pressure exponent of the exchange reaction decreases with the increase in the total pressure and that in the lower pressure range, the reaction order is as high as 2. The rate equation obtained from the pressure dependence was $R=k\{KP/(1+KP)\}^2$. Accordingly, it was concluded that the H_2–D_2 exchange reaction over gold takes place between molecularly adsorbed hydrogen and deuterium through a dimeric intermediate. The heat of adsorption on the active sites in the gold surface was 5.9 kJ mol^{-1}.

The H_2–D_2 exchange reaction on metal catalysts has been extensively studied as a measure of hydrogen activation.[1,2] Transition metals are known to be effective catalysts for this exchange. By contrast, non-transition metals are notably less efficient than transition metals, due to their smaller ability to interact with hydrogen.

The earliest views on the mechanisms of this exchange were those of Bonhoeffer and Farkas,[3] who suggested the following steps:

$$\left.\begin{array}{l} H_2 + 2* \rightleftarrows 2H* \\ D_2 + 2* \rightleftarrows 2D* \\ HD + 2* \rightleftarrows H* + D* \end{array}\right\} \qquad (1)$$

This mechanism should operate when the adsorption-desorption process is rapid. Certain drawbacks to this mechanism soon, however, became evident. For example, Benton and White[4] showed that the desorption of adsorbed hydrogen from the surface of nickel powder only occurred above 173 K, although the H_2–D_2 exchange reaction proceeded measurably on nickel at about 83 K.

An alternative mechanism was therefore proposed as follows:[5,6]

$$\left.\begin{array}{l} H_2 + D* \rightleftarrows H* + HD \\ D_2 + H* \rightleftarrows D* + HD \end{array}\right\} \qquad (2)$$

This is called the Rideal-Eley mechanism.

It has been accepted that the Bonhoeffer-Farkas mechanism operates with transition metals above room temperature, where the adsorption-desorption process is fast. The Rideal-Eley mechanism is likely to apply to low-temperature reactions, where dissociated atoms are irreversibly adsorbed.

There have been many studies on the H_2–D_2 exchange reaction which attempted to distinguish between the Bonhoeffer-Farkas mechanism and the Rideal-Eley mechanism.[1,2]

On the other hand, Schwab and Killman suggested the following reaction mechanism for the exchange reaction over nickel foil, on the basis of the isotope effect of the reaction rate:[7,8]

$$\left.\begin{array}{l} H_2 + * \rightleftarrows H_2* \\ D_2 + * \rightleftarrows D_2* \\ H_2* + D_2* \rightleftarrows 2HD* \\ HD + * \rightleftarrows HD* \end{array}\right\} \qquad (3)$$

In this case, the isotope exchange takes place between molecularly adsorbed hydrogen and deuterium. However, A. Farkas made the criticism that their treatment on the basis of the isotope effect cannot provide proof for or against any mechanism.[8]

In this paper, we examine the H_2–D_2 exchange reaction on gold supported over poly(tetrafluoroethylene) (PTFE), which has already been proved to be a good support for platinum.[9] Although there are a few works on the H_2–D_2 exchange reaction over gold catalyst,[10,11] the kinetic behaviour of this exchange reaction has not yet been fully studied. In our study, the diagnostic test of a mechanism is based on the pressure dependence of the reaction rate.

Experimental

The rate of the H_2–D_2 exchange reaction was measured in a closed circulation system with a volume of 330 cm^3. Auxiliary equipment consisted of a mercury diffusion pump backed by a mechanical pump and isolated from the reaction apparatus by a liquid nitrogen trap. The pressure of the reaction system was measured with a mercury manometer which was covered with a small amount of silicone oil (Dow Corning 705 Fluid Lot. No. 33) at the top.

The isotope distribution in the gas phase was determined by gas chromatography at 77 K, using a column filled with alumina/5% manganese chloride. Prior to each measurement, the catalyst was subjected to heat-treatment *in vacuo* at 518 K.

Hydrogen of seven nine purity (Nippon Sanso Co., Ltd.,) and deuterium of 99.5% purity (Showa Denko Co., Ltd.,) were passed through a liquid nitrogen trap before use.

Gold (0.3%) supported on PTFE catalyst was prepared as follows: PTFE (914J. Mitsui Fluoro Chemicals Co., Ltd.,) was soaked in an acetone solution of chloroauric acid and the solvent was evaporated; after evacuation at room temperature, the sample was heated to 463 K and evacuation was continued for 30 min at the same temperature, after which hydrogen gas (40 kPa) was circulated over the catalyst at 463 K for 3 h, followed by evacuation overnight at the same temperature. The amount of the catalyst used was 5.06 g.

For the blank test, an equimolar mixture of H_2 and D_2 at the pressure of 46.3 kPa was circulated over 5.26 g of PTFE at 503 K; it was found that no appreciable amount of HD was formed even after 140 min.

Results

The time course of the H_2–D_2 exchange reaction is described by the first order equation:

$$\ln \frac{\chi_e-\chi_t}{\chi_e-\chi_0} = -k_e t, \qquad (4)$$

where χ_0, χ_t, and χ_e are the fractions of hydrogen deuteride present at times zero and t and at equilibrium. The total rate of exchange, R (cm^3/min), is given by

$$R = k_e N \qquad (5)$$

where N is the total amount of hydrogen gas (H_2, D_2) introduced. We could not calculate the absolute rate (the exchange rate per unit metal surface area) since the surface area of gold was not determined.

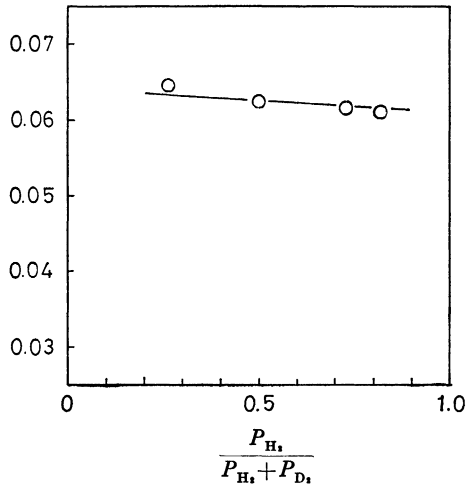

Fig. 1. First order rate constant (k_e) at 518 K against the fraction of hydrogen. Total pressure was kept constant at 24.9 kPa.

The dependence of the first order rate constant, k_e, on the composition of the mixture of H_2 and D_2 under the total pressure of 24.9 kPa was studied. The results (Fig. 1) show that there exists little isotope effect in the H_2-D_2 exchange reaction on Au/PTEE. Therefore, an equimolar mixture of H_2 and D_2 was employed in contact with the catalyst in all later experiments.

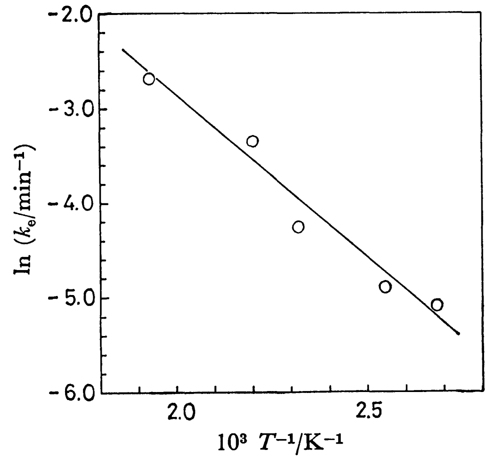

Fig. 2. Arrhenius plots for the H_2–D_2 exchange reaction on Au(0.3%)/PTFE. P=34.7 kPa.

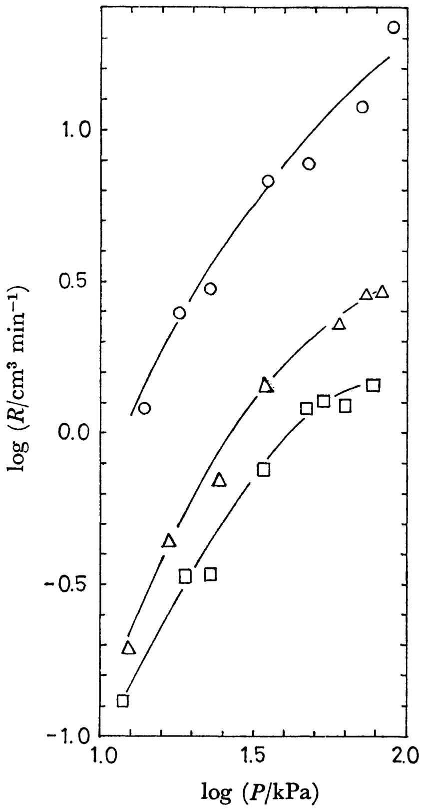

Fig. 3. Dependencies of the H_2–D_2 exchange reaction on the total pressure at 518, 432, and 393 K.
-○-; 518 K, -△-; 432 K, -□-; 393 K.

The temperature dependence of the first order rate constant, k_e, plotted in Arrhenius form is shown in Fig. 2. The apparent activation energy calculated from the slope of the line is 29 kJ mol^{-1}, which is the same as that over gold wire obtained by Avdeenko *et al.*[12]

The logarithms of the total rates of the exchange at 518, 432, and 393 K are plotted against those of the total pressure P of hydrogen in Fig. 3. It is shown in Fig. 3 that the pressure exponent of this exchange reaction decreases with the increase in the total pressure. For example, at 518 K, the pressure exponent decreased from 2 at pressures between 13 and 20 kPa to 1.0 at pressures between 50 and 70 kPa; at 393 K, it decreased from 2 at pressures between 13 and 20 kPa to 0.5 at pressures between 50 and 70 kPa.

It is surprising that the reaction order was found to be 2 in the lower pressure range, because neither the Bonhoeffer-Farkas mechanism nor the Rideal-Eley mechanism can explain such a high reaction order. For the Bonhoeffer-Farkas mechanism, where the exchange reaction proceeds by way of dissociative adsorption and desorption, the reaction order should vary from first at low coverages to zero at high coverages. For the Rideal-Eley mechanism, the order should be first, providing the atomic layer is complete and the molecular species only weakly adsorbed or not at all.

Consequently, we must consider the Schwab mechanism, in which the H_2—D_2 exchange reaction goes through an associative intermediate, as expressed by

$$H_2(a) + D_2(a) \rightleftarrows \begin{matrix} H\cdots H \\ \vdots \quad \vdots \\ D\cdots D \end{matrix} \rightleftarrows 2HD(a). \qquad (6)$$

In this case, the reaction velocity is proportional to the square of the coverage of the molecularly adsorbed hydrogen. Using the Langmuir equation, total rate of exchange is given by

$$R = k\left(\frac{KP}{1+KP}\right)^2, \tag{7}$$

where K denotes the adsorption constant.

By rearranging Eq. 7, we get the following equation:

$$\frac{P}{\sqrt{R}} = \frac{1}{\sqrt{k}K} + \frac{P}{\sqrt{k}}. \tag{8}$$

Therefore, it can be expected that when $P/\sqrt{R}$'s are plotted against total pressure, P, a straight line will be obtained.

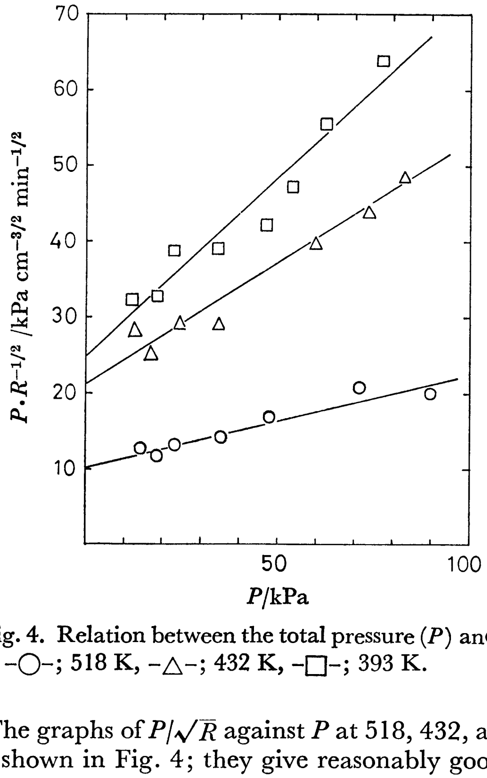

Fig. 4. Relation between the total pressure (P) and $P/\sqrt{R}$. -○-; 518 K, -△-; 432 K, -□-; 393 K.

The graphs of $P/\sqrt{R}$ against P at 518, 432, and 393 K are shown in Fig. 4; they give reasonably good straight lines. Accordingly, we get Eq. 7 as the rate equation for the H_2–D_2 exchange reaction on Au/PTFE.

From the slopes and intercepts of the graphs in Fig. 4, we can calculate the rate constant, k, for the surface exchange and the adsorption constant, K, at 518, 432, and 393 K; these are summarized in Table 1.

Table 1. Rate constant of the H_2–D_2 exchange reaction and adsorption constant of hydrogen molecule on Au/PTFE

T/K	k/cm^3 min^{-1}	K/kPa^{-1}
518	65.6	0.0122
432	9.66	0.0152
393	4.49	0.0190

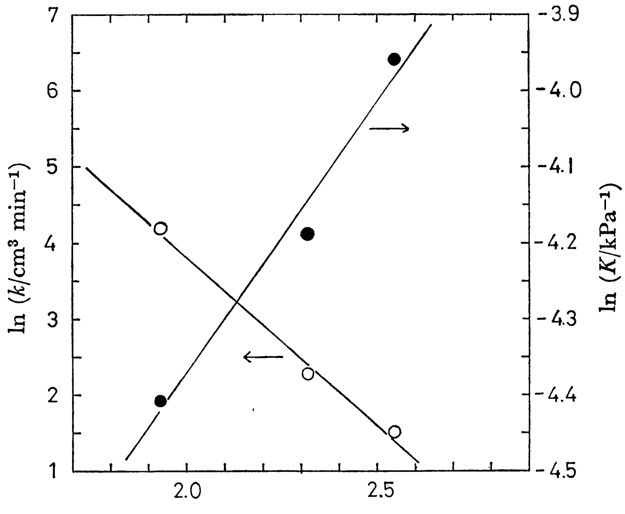

Fig. 5. Temperature dependencies of logarithm of rate constant (k) and that of adsorption constant (K).

In Fig. 5, ln k and ln K are plotted against $1/T$. The heat of hydrogen adsorption on the surface of gold and the activation energy of the surface reaction, given by the slopes of the lines in Fig. 5, are 5.9 kJ mol^{-1} and 37 kJ mol^{-1}, respectively. Although in the case of the H_2–D_2 exchange reaction on copper catalyst Kiyomiya *et al.* found a marked isotope effect,[13] we found little isotope effect for the reaction on gold. Therefore, the heat of adsorption obtained is not the average of that for hydrogen and deuterium. The heat of adsorption for hydrogen and that for deuterium are the same and are both 5.9 kJ mol^{-1}.

Discussion

Although Trapnell did not find chemisorption of hydrogen on the evaporated film of gold in the temperature range 293 K to 93 K,[14] there are a few reports on the H_2–D_2 exchange reaction on gold which indicate that the adsorption of hydrogen on gold does occur.[10,11] For example, Taylor and his coworkers[11] found the H_2–D_2 exchange reaction to take place on gold foil. They speculated that the hydrogen atoms were chemisorbed on the vacant d-orbital created by a promotion of a d-electron to the top of the s-band, since no d-orbitals are normally available in gold for surface bond formation.

On the other hand, Wise and Sancier found that after treatment of gold foil with hydrogen plasma, the rate of the H_2–D_2 exchange reaction on it became greater and that the activation energy was reduced from 90.0 kJ mol^{-1} over the untreated catalyst to 46 kJ mol^{-1}. Since the high activity of treated gold was reduced by evacuation at 615 K, chemisorbed hydrogen seems to have been formed, giving rise to the enhanced activity and presumably reacting with gaseous hydrogen (Rideal-Eley mechanism). However, they also paid attention to the fact that over gold foil treated with hydrogen plasma, another heterogeneous reaction of higher activation energy takes place which predominates at temperatures in excess of 450 K. They suggested that the reaction may proceed by the Bonhoeffer-Farkas mechanism in the higher temperature range.

In both of the works mentioned above, the pressure dependence of the exchange reaction was not studied

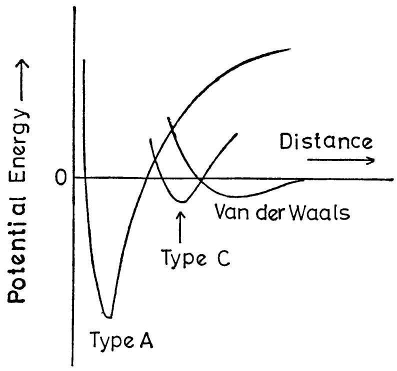

Fig. 6. Potential energy curves for Type A (M–H) and Type C ($M\cdots H_2$) chemisorbed hydrogen.

and the interpretations are not more than conjectures. It could be said that the results in these works do not exclude the possibility that the reaction goes through an associative intermediate.

As far as we know, we were the first to study the pressure dependencies of the H_2–D_2 exchange reaction on gold catalyst. We found that the pressure exponent of the H_2–D_2 exchange reaction was as high as 2 at the lower pressure range. Usually one cannot decide the mechanism of the H_2–D_2 exchange reaction only by measuring the pressure dependencies. In our case, however, the pressure exponent we obtained precludes mechanisms other than that proposed by Schwab and Killman. Moreover, the rate equation (Eq. 7) which we confirmed at 518, 432, and 393 K strongly supports the mechanism; the exchange reaction takes place between molecularly adsorbed hydrogen and deuterium.

At this stage, we consider the nature of the hydrogen adsorbed. Dowden[15] has pointed out that there is probably an initial state of chemisorption in many cases, named Type C chemisorption (molecular), on the empty atomic d-orbitals; this type is intermediate between physical adsorption and strong chemisorption, as shown in Fig. 6. Concerning this suggestion, Clark[16] commented that the potential energy curves of chemisorption of hydrogen on sp and d metals may be quite similar and that, for transition metals, the Type C potential curve may intersect the curve for strong atomic adsorption in such a way that very little activation energy is required for the hydrogen to transfer to the final atom curve, Type A, whereas in a nontransition metal, the crossing point may be located in a postition that requires a large activation energy for the transfer. Actually, preformed hydrogen atoms can be chemisorbed on Group IB metals,[17] which may indicate that chemisorption of hydrogen atom is limited by a large activation energy and not by the inability of gold to chemisorb.

Our results showed that hydrogen is adsorbed on a gold surface molecularly and that the heat of adsorption is as low as 5.9 kJ mol^{-1}, which seems correspond to Type C chemisorption.

On the other hand, it was shown by Hoffmann,[18] using arguments based on the conservation of orbital symmetry,[19] that in the gas phase reaction, the coplanar path proceeding through a square transition state is thermally forbidden. An approximate energy barrier for the process is that amount of energy necessary to raise two electrons from the bonding σ_g orbital in H_2 up to the non-bonding hydrogen 1s level, or 498 kJ mol^{-1}. In the study of the H_2–D_2 exchange reaction in the gas phase, Bauer and Ossa found that the activation energy was 177 kJ mol^{-1} and the possibility of an atomic exchange mechanism, *i.e.* $H_2 \rightarrow 2H$ followed by $H + D_2 \rightarrow HD + D$ was considered to be ruled out.[20] Various theoretical studies searching for a low-lying four-centre transition state have been, done but none of them has succeeded in explaining the low activation energy observed.[21]

On the other hand, in our study the activation energy for the surface exchange was found to be 37 kJ mol^{-1}. Therefore, a large amount of stabilization of H_4 intermediate does occur on the surface of gold. Although Mango and Schachtschneider pointed out that the reactions which are symmetry forbidden can become allowed by interaction with the d-orbital of a transition metal,[22] the argument cannot proceed in a similar fashion in the case of the reaction on gold for the lack of the vacant d-orbital. Nevertheless, there are various kinds of approaches for two hydrogen molecules to form a H_4 intermediate: *e.g.* an orthogonal approach passing through a tetrahedron, rectangle, and rhombus, and an allowed path suggested by Gimarc[23] passing through Y- and T-shaped transition states. Moreover, various kinds of sites differing in electronic or in geometric structure exist in the metal surface. Therefore, it seems that further theoretical studies will be necessary to understand the transition state of the surface exchange on gold completely.

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