Catalytic Isotope Exchange Reaction between Deuterium Gas and Water Pre-Adsorbed on Platinum/Alumina

Itsuo Iida, Junko Kato, and Kenzi Tamaru*
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229
**Department of Chemistry, Faculty of Sciense, University of Tokyo, Hongo, Tokyo 113*

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The catalytic isotope exchange reaction between deuterium gas and the water pre-adsorbed on Pt/Al_2O_3 was studied. At reaction temperatures above 273 K, the exchange rate was proportional to the deuterium pressure and independent of the amount of adsorbed water, which suggests that the rate determining step is the supply of deuterium from the gas phase. Its apparent activation energy was 38 kJ mol^{-1}. Below freezing point of water, the kinetic behaviour was different from that above freezing point. At higher deuterium pressures the rate dropped abruptly at 273 K. Below the temperature the apparent activation energy was 54 kJ mol^{-1} and the exchange rate depended not on the deuterium pressure but on the amount of the pre-adsorbed water. At lower pressures, however, the kinetic behaviour was the same as that above 273 K, till the rate of the supply of deuterium from the gas phase exceeded the supply of hydrogen from adsorbed water to platinum surface.

These results suggest that below 273 K the supply of hydrogen is markedly retarded, the state of the adsorbed water differing from that above 273 K. It was also demonstrated that when the adsorbed water is in the state of capillary condensation, the exchange rate becomes very small.

The isotope exchange reaction between hydrogen and water is considered to be important in nuclear industry as a means of obtaining enriched deuterium, and the success of this process depends to a large extent upon the rate of isotope transfer between the two chemical species. The isotope separation is possible because the equilibrium constant K of the reaction, $HDO+H_2 \rightleftarrows H_2O+HD$, or the ratio of the isotope concentration in the reactants, is not equal to unity exactly, and the value of K depends upon the temperatures where equilibrium attained. In enriching the deuterium, different equilibration at different temperatures is employed. In principle, it is more effective if the temperature of the cold reactor is as low as possible, since the isotope effect is greater at lower temperatures.

Although platinum on an activated charcoal and nickel on chromium oxide were reported to be efficient catalysts for the vapour phase reaction, both catalysts lose their catalytic activities when condensed water film covers the catalyst surface at lower temperatutres,[1,2] which prevents these catalysts from being used in the lower temperature range.

The mechanism of the hydrogen exchange reaction catalyzed by transition metals at temperatures above the boiling point of water has been extensively studied.[3–5] Recently, Rolston and Goodale [6] studied the mechanism of this exchange reaction catalyzed by platinum supported on alumina and proposed that the rate determining step of the exchange reaction in the vapour phase consists of the hydrogen atom switch between chemisorbed hydrogen on platinum and physisorbed water on alumina. Sagert and Pouteau[7–9] also studied this reaction over various noble metals and reported that the exchange rate depended not on the hydrogen gas pressure but on the pressure of water vapour on platinum catalyst. They also supported the hydrogen switching mechanism proposed by Rolston and Goodale.

On the other hand, when the reaction takes place between liquid water and hydrogen gas bubble over suspended platinum charcoal catalyst at around room temperature, it was shown that the rate increases with stirring rate, which implies that the rate determining step consists of the hydrogen gas diffusion through the water to contact with the catalyst surface.[10] Since little is known of the chemical kinetic behaviour of this exchange reaction below room temperature, it is significant to examine the behaviour of each elementary step of the exchange reaction on the catalyst surface.

Experimental

The rate of exchange reaction between deuterium gas and the water adsorbed on platinum/alumina catalyst was measured in a closed circulation system, volume 340 cm^3, changing the amount of water adsorbed on the catalyst. The isotope abundance in the gas phase was determined by gas chromatography using 5% manganese chloride on an alumina column at 77 K. Prior to the measurements, the catalyst was subjected to heat-treatment *in vacuo* at 423 K, then cooled down to room temperature. The catalyst was 0.5% platinum supported on an alumina pellet (Lot No. 48-1-1 Nippon Engelhard Co., Ltd.,). Initial pretreatment of the catalyst consisted of evacuation at room temperature for 30 min, and at 398 K for 30 min. The sample was then treated with hydrogen at 623 K overnight and evacuated at the same temperature overnight. The surface area measured by the BET method was 92 m^2/g, the amount of the catalyst being 2.13 g. The adsorption isotherm of water on the catalyst in the temperature range 229—296.5 K was measured. Since the equilibrium pressure of the water at low coverage was very low, the pressure was measured with a Pirani gauge which was calibrated by a MacLeod gauge.

Results and Discussion

The adsorption isotherm of water on the catalyst at 296.5 K is shown in Fig. 1. If the area occupied by a water molecule is $1.06\times10^{-19}m^2$,[11] the monomolecular adsorption of water on the catalyst surface area corresponds to 0.054 g of water. In the standard run, the amount of pre-adsorbed water was fixed to 0.025 g and the pressures of the water vapour which were in equilibrium with the adsorbed water were below 40 Pa even at room temperature as given in Fig. 1. From the adsorption isotherm, the capillary condensation is considered to take place when the amount of adsorbed

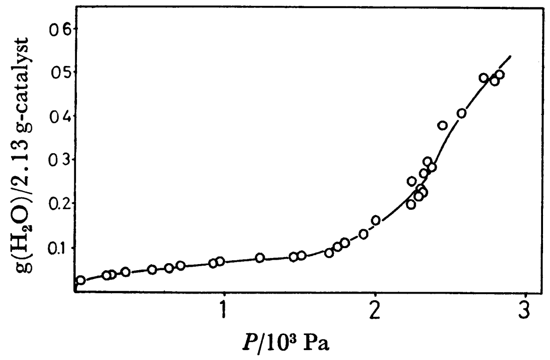

Fig. 1. Adsorption isotherm of water on 2.13 g of platinum/alumina at 296.5 K.

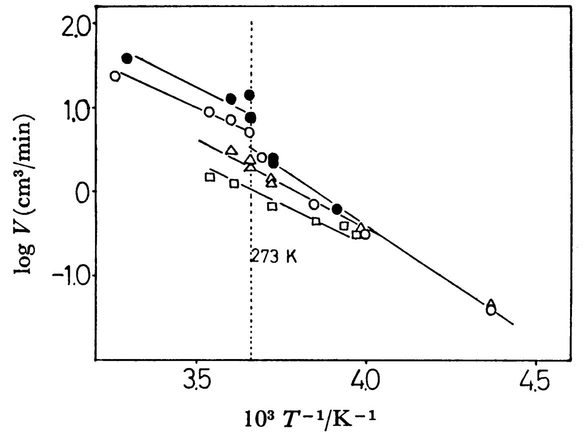

Fig. 2. Arrhenius plots for the exchange reaction between deuterium and water pre-asdorbed on platinum/alumina.
—●—; P_{D_2}=55 kPa, —○—; P_{D_2}=27 kPa, —△—; P_{D_2}=15 kPa, —□—; P_{D_2}=9.3 kPa, H_2O(a)=0.025 g.

water exceeds about 0.14 g.

The temperature dependence of the exchange rate between deuterium gas and the adsorbed water is given in Fig. 2 for several deuterium pressures in the Arrhenius form. Under deuterium pressures of 55 kPa and 27 kPa, the exchange rates dropped abruptly at 273 K, below which they fell to another temperature dependency. The apparent activation energies above and below 273 K correspond to 38 and 54 kJ mol^{-1}, respectively, which suggests not only an appreciable change in the rate determining step of the reaction at 273 K but also the possibility that the transport phenomena might be involved in a rate determining step which is markedly influenced by freezing the adsorbed water.

Under lower deuterium pressures such as 15 and 9.3 kPa, the Arrhenius plots exhibited no discontinuity at 273 K and the apparent activation energy was the same with 38 kJ mol^{-1}.

Consequently, the temperature dependence of the reaction rate revealed at higher deuterium pressures such as 55 and 27 kPa, the abrupt drop of exchange rate and the activation energy change could be observed, but at lower pressures such as 15 kPa and 9.3 kPa, the change of activation energy takes the form of a bent in the Arrhenius plots.

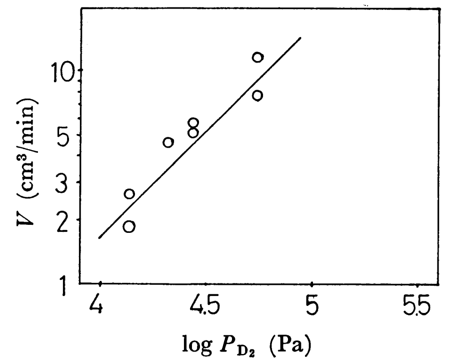

Fig. 3. Dependence of the exchange rate on D_2 pressure at 273 K.
H_2O(a)=0.025 g.

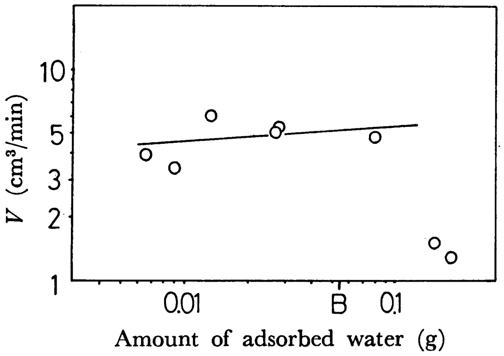

Fig. 4. Dependence of the exchange rate on the amount of adsorbed water at 273 K.
P_{D_2}=27 kPa.

The variation of the rate with deuterium pressure at 273 K is shown in Fig. 3. The reaction order with respect to deuterium pressure, given by the slope of line, is 0.9. The dependence of rate on the amount of the adsorbed water at 273 K is shown in Fig. 4. The amount of adsorbed water corresponding to that of monolayer full coverage is denoted by B. The results (Fig. 4) demonstrate that when the amount of adsorbed water does not much exceed point B, the reaction order with respect to the amount of the adsorbed water is zero. However, when the amount of the adsorbed water exceeds point B, the exchange rates decrease considerably. Judging from the results in Fig. 1, the amounts of adsorbed water in the range correspond to capillary condensation. It was accordingly suggested that when the adsorbed water is condensed in the pores of the catalyst, the diffusion of deuterium gas through the condensed water becomes the rate determining step.

The exchange rate is nearly proportional to the deuterium pressure, and is independent of the amount of the adsorbed water provided that the adsorbed water is not in the state of capillary condensation. It was suggested that the rate determining step of this exchange reaction above 273 K is the supply of deuterium from the gas phase to the active sites in the platinum surface.

In contrast to the kinetic behaviour above 273 K, the kinetic behabiour below 273 K is rather complicated. At 269 K, the order of the reaction with respect

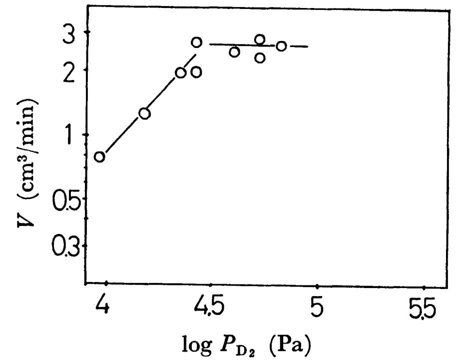

Fig. 5. Dependence of the exchange rate on D_2 pressure at 269 K.
$H_2O(a) = 0.025$ g.

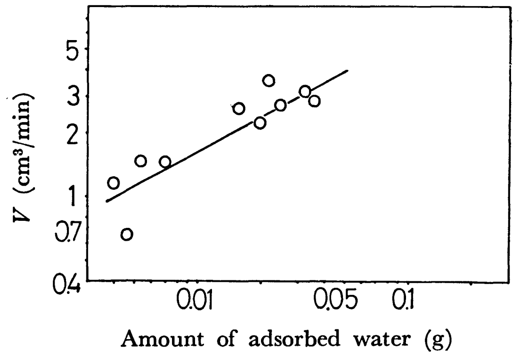

Fig. 6. Dependence of the exchange rate on the amount of adsorbed water.
$P_{D_2} = 55$ kPa.

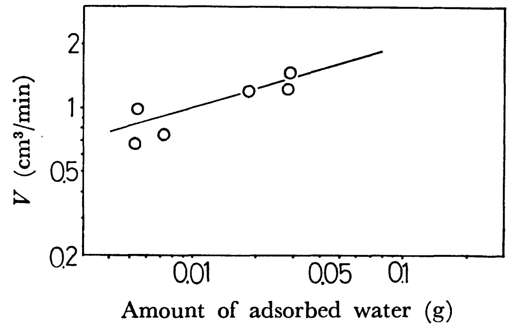

Fig. 7. Dependence of the exchange rate on the amount of adsorbed water.
$P_{D_2} = 15$ kPa.

to deuterium pressure is 1.1 under lower deuterium pressures below 27 kPa, whereas at higher pressures the rate is independent of the deuterium pressure (Fig. 5). The dependence of the rates upon the amount of adsorbed water was measured under deuterium pressures of 55 and 15 kPa at 269 K (Figs. 6 and 7, respectively). The reaction order with respect to the amount of the adsorbed water is 0.5—0.6 under the deuterium pressure of 55 kPa, and 0.2 under the deuterium pressure of 15 kPa. When the exchange rates are nearly proportional to the pressure of deuterium gas, the reaction order with respect to the amount of the adsorbed water is as low as 0.2 and when the exchange rates are independent of the pressure of deuterium gas,

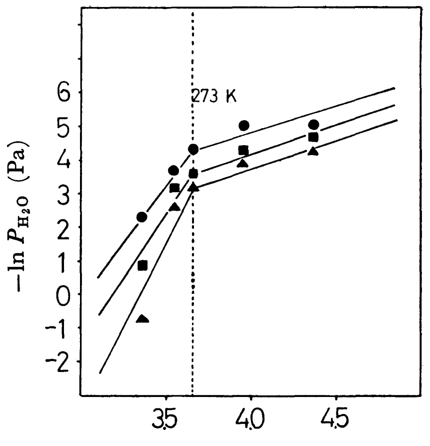

Fig. 8. Adsorption isoster of water on 9.44 g of platinum/alumina.
—●—; $H_2O(a) = 4$ mmol, —■—; $H_2O(a) = 5$ mmol, —▲—; $H_2O(a) = 6$ mmol.

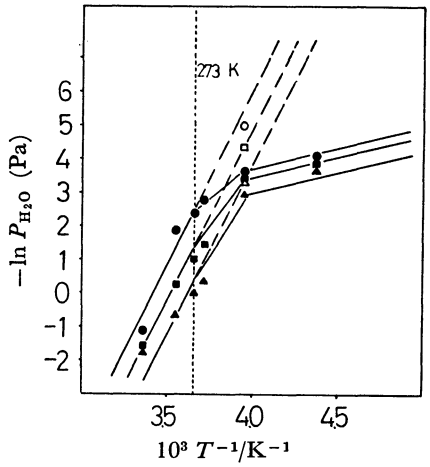

Fig. 9. Adsorption isoster of water on 9.44 g of platinum/alumina.
—●—; $H_2O(a) = 7$ mmol, —■—; $H_2O(a) = 8$ mmol, —▲—; $H_2O(a) = 9$ mmol, --○--; $H_2O(a) = 7$ mmol, --□--; $H_2O(a) = 8$ mmol, --△--; $H_2O(a) = 9$ mmol.
Broken lines are the plots for the second adsorption after the adsorption temperature was once raised.

the order is 0.5—0.6.

Consequently, the rate determining step at 269 K shifts from the supply of deuterium from the gas phase to that of hydrogen from the adsorbed water as the pressure of the deuterium gas increases.

The adsorption isosters of water over the platinum/alumina at lower and higher coverages are shown in Fig. 8 and Fig. 9, respectively, the slope of which is proportional to the heat of adsorption. We see that the adsorption isoster bent at 273 K.

Since the phase change of the adsorbed water from liquid to solid should cause an increase in the heat of adsorption below 273 K, it was interpreted that the equilibration of the adsorption of the water below 273 K is nearly apparent. In the experiments of water adsorption below 273 K, after the apparent equilibrium, the temperature of the adsorbate rose to room temperature, and after 12 h the temperature was lowered again. It was found that the additional adsorption (Fig. 9) and the plots of the equilibrium pressure of the water below 273 K come of the same line of the adsorption isoster above 273 K. The heat of adsorption of water on platinum/alumina was found to be 84 kJ mol^{-1}.

Thus, though the heat of adsorption of water on platinum/alumina is much greater than the heat of fusion of the water, the water cannot spread over the adsorbate easily and crystallizes on the surface of platinum/alumina.

Considering the results of the adsorption of water on the catalyst, it was concluded that the change in the kinetic behaviour at 273 K is due to the retardation of the supply of hydrogen from the frozen water. The apparent activation energy of the exchange reaction between deuterium and water below 273 K would be that for the transfer of adsorbed water. This activation energy might be measured above 273 K if the water coverage was very low. However, in such a case, the increase in the HD content of deuterium gas is not measurable.

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