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Poisoning by Carbon Monoxide in the Hydrogen Exchange Reaction between Deuterium Gas and Water Preadsorbed on a Platinum–Alumina Catalyst[1]

ITSUO IIDA

Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan

AND

KENZI TAMARU

Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Tokyo 113, Japan

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Poisoning by carbon monoxide in the exchange reaction between deuterium and the water preadsorbed on a platinum–alumina catalyst was studied, by measuring not only the rate of reaction but also its kinetic behavior and the adsorption of reactants on the catalyst surface. The shape of the poisoning curve is closely associated with the kinetic behavior and exhibited an abrupt change on freezing the adsorbed water below 273 K. When the rate is proportional to deuterium pressure and independent of the amount of water adsorbed, the exchange rate dropped sharply by carbon monoxide adsorbed of a few percent coverage without any marked changes in the amount and the rate of hydrogen adsorption on the platinum surface.

However, at temperatures lower than 273 K and at higher deuterium pressures, the rate depends not on the deuterium pressure but on the amount of water adsorbed. The migration of hydrogen in or through the adsorbed water is seemingly sufficiently suppressed by freezing to control the overall reaction rate. In this case, a small amount of adsorption of carbon monoxide did not show any toxicity, but then a steep poisoning started accompanying a change in the kinetic behavior.

It was accordingly demonstrated that the mechanism of the reaction may be better understood by studying poisoning and measuring adsorption, overall rate, and kinetic behavior.

INTRODUCTION

It was recently demonstrated that the exchange reaction between deuterium and water preadsorbed on platinum–alumina catalyst changes its kinetic behavior at different reaction temperatures and pressures (*1*). When the deuterium pressure is sufficiently high, the exchange rate drops abruptly at 273 K and the apparent activation energy changes from 38 kJ mol^{-1} to 54 kJ mol^{-1}. The drop at 273 K decreases as the deuterium pressure becomes lower, and, finally, such a discontinuous drop was not observed when the deuterium pressure was sufficiently low, but the slope of the Arrhenius plot altered below 273 K.

The dependence of the exchange rate on deuterium pressure and the amount of adsorbed water above 273 K is generally expressed by the following equation:

$$V \propto [P_{D_2}]^{0.9}[H_2O(a)]^0 \qquad (E_A = 38 \text{ kJ mol}^{-1}), \quad (1)$$

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where E_A denotes the apparent activation energy.

Below the freezing point of water, the kinetic behavior is rather complicated, and at 269 K, for example, the kinetic behavior is expressed as follows:

$$V \propto [P_{D_2}]^0[H_2O(a)]^{0.5-0.6}(P_{D_2} \gtrsim 27\ \text{kPa}) \quad (E_A = 54\ \text{kJ mol}^{-1}), \quad (2)$$

$$V \propto [P_{D_2}]^{1.1}[H_2O(a)]^{0.2}(P_{D_2} \lesssim 27\ \text{kPa}) \quad (E_A = 38\ \text{kJ mol}^{-1}). \quad (3)$$

These results were interpreted in a previous paper by the proposal that above 273 K the dissociative adsorption of deuterium from the gas phase onto the water-adsorbed surface would be the rate-determining step and that this is also the case at lower deuterium pressures below 273 K (cf. Eq. (3)) with equal apparent activation energy. However, at lower temperatures and higher deuterium pressures, the exchange rate is expressed by Eq. (2), mainly depending upon the amount of preadsorbed water, which is interpreted to demonstrate that the rate is controlled by the mobility of water molecules or its hydrogen over alumina through frozen water.

Since poisoning of metal catalysts is an important feature of catalysis, it has been widely studied by many workers, and various types of toxicity for metal catalysts have been investigated, especially by Maxted and his co-workers (*2*). As far as we know, however, the poisoning of a metal catalyst has never been considered in connection with the kinetic behavior and also the adsorption of the reactants during the course of the reaction over the poisoned catalyst. In this report, the poisoning by carbon monoxide of the isotope exchange reaction between deuterium and water preadsorbed on platinum–alumina catalyst has been studied measuring not only its kinetic behavior but also the adsorption of reactants over the catalyst poisoned to various extents.

METHODS

The rate of the exchange reaction between deuterium gas and the water preadsorbed on a platinum–alumina catalyst was measured in a closed circulation system with a dead volume of 340 cm^3. The initial decrease in the D_2 to form HD was taken as the initial rate. The isotope distribution in the gas phase was determined by gas chromatography at 77 K using a column filled with alumina and 5% manganese chloride. The catalyst was a platinum (0.5%) supported on alumina pellet of Lot No. 48-1-1 of Nippon Engelhard Company, Ltd. The catalyst was first evacuated at room temperature for 30 min and at 398 K for 30 min, and was then treated with hydrogen at 623 K overnight and evacuated at the same temperature overnight. The total surface area measured by the BET method with nitrogen adsorption was 92 m^2 g^{-1} and the amount of the catalyst used was 2.13 g.

Prior to the rate measurements, the catalyst was subjected to a heat treatment at 423 K, and then cooled to room temperature. In the study of the poisoning of the exchange reaction between deuterium gas and the water preadsorbed on the catalyst, 0.025 g of water was pre-adsorbed over the catalyst poisoned by carbon monoxide to various extents. If the area occupied by an adsorbed water molecule is 1.06×10^{-19} m^2 (*3*), a full coverage of the catalyst surface would require 0.055 g of water. Consequently, 0.025 g of water corresponds to 45% coverage of the whole catalyst surface. The equilibrium vapor pressure of the adsorbed water at 273 K was about 40 mPa. Oxygen treatment at 423 K overnight and hydrogen treatment at the same temperature overnight brought about the complete recovery of the catalyst activity for the D_2–$H_2O(a)$ exchange reaction.

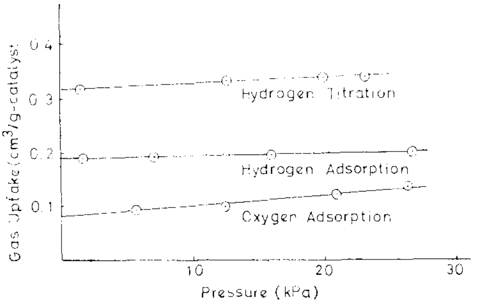

FIG. 1. Typical adsorption isotherms of hydrogen adsorption, hydrogen titration, and oxygen adsorption on platinum–alumina at room temperature.

RESULTS AND DISCUSSION

In order to estimate the number of the platinum atoms on the catalyst surface, hydrogen adsorption, oxygen adsorption, hydrogen titration, and carbon monoxide adsorption were performed. The typical adsorption isotherms are shown in Fig. 1.

The adsorption of hydrogen, oxygen, and carbon monoxide on the alumina support is throught to be of the Henry type (*4*). The linear portion of the adsorption isotherm at higher pressure was extrapolated to zero pressure to determine the saturated amount of adsorbed gas on the platinum surface. The stoichiometry of the adsorption of hydrogen, oxygen, and titration was first proposed by Gruber (*5*) and later Benson and Boudart (*4*) as follows:

$$Pt_s + \tfrac{1}{2}H_2 \rightarrow Pt_sH,$$

$$Pt_s + \tfrac{1}{2}O_2 \rightarrow Pt_sO,$$

$$Pt_sO + \tfrac{3}{2}H_2 \rightarrow Pt_sH + H_2O \text{ (support)},$$

where Pt_s denotes the surface platinum atom. Later, Wilson and Hall (*6*) showed that such stoichiometry holds only when platinum particle size is large, and when the platinum particle size is smaller than approximately 10 Å, the stoichiometry becomes as follows:

$$Pt_s + \tfrac{1}{2}H_2 \rightarrow Pt_sH,$$

$$Pt_s + \tfrac{1}{4}O_2 \rightarrow Pt_sO_{\frac{1}{2}},$$

$$Pt_sO_{\frac{1}{2}} + H_2 \rightarrow Pt_sH + \tfrac{1}{2}H_2O \text{ (support)}.$$

The former stoichiometry implies that the ratio of hydrogen adsorption, oxygen adsorption, and hydrogen titration is 1:1:3, whereas the latter stoichiometry gives 2:1:4. The results shown in Table 1 gives the stoichiometry 2.2:1:4.3, which agrees reasonably well with the stoichiometry proposed by Wilson and Hall for small particles; the number of surface platinum atoms was also calculated on the basis of the latter stoichiometry, and is shown in Table 1.

Using the results of hydrogen adsorption, the platinum particle size was calculated on the basis of the model of Hughes *et al.* (*7*) in which all particles are ideal cubes of uniform size with one face in contact with the support and the remaining five faces are exposed. The particle size thus estimated was found to be 14 Å. The particle size was also examined by electron microscopy. Photographic enlargement to $10^6\times$ was used to obtain a suitable image for the particles, which revealed that the mean particle size is 16 Å, which is almost in perfect agreement with that obtained by adsorption or titration technique.

The surface area of the platinum catalyst calculated from the hydrogen titration was 0.8 $m^2\ g^{-1}$, assuming that each platinum atom has an area of 8.9×10^{-2} nm^2 (*8*). The saturated amount of carbon monoxide adsorbed was 5.9×10^{18} molecules/g, which is in reasonable agreement

TABLE 1

Amount of Adsorbed Gases and Number of Surface Platinum Atoms Calculated on the Basis of the Stoichiometry Proposed by Wilson and Hall (*6*).

	Amount of adsorbed gas (mole$\times 10^6$/g)	Number of surface Pt atoms ($\times 10^{-18}$/g)
Hydrogen adsorption	7.6	9.2
Oxygen adsorption	3.5	8.4
Hydrogen titration	15	9
CO adsorption	9.8	5.9

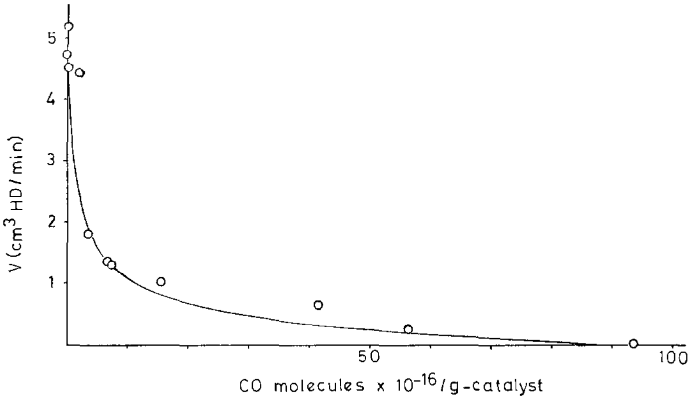

FIG. 2. Poisoning curve by carbon monoxide in D_2–H_2O(a) exchange reaction on platinum–alumina at 273 K; the rate of the exchange reaction in terms of that of HD formation is plotted against the CO preadsorbed on the catalyst; H_2O(a) = 0.025 g/2.13 g catalyst, P_{D_2} = 27 kPa.

if a considerable fraction of the carbon monoxide is in the bridged form.

The initial rates of the D_2–H_2O(a) exchange reaction were plotted against the amount of preadsorbed carbon monoxide at 273 K as shown in Fig. 2, which shows that 5×10^{16} carbon monoxide molecules/g, which corresponds to about 0.56% coverage of the whole platinum surface, caused the reduction of the initial rate of the exchange reaction by half, and with the adsorption of 9.3×10^{17} molecules/g, which corresponds to nearly 10% coverage, the catalyst lost most of its activity.

The rate and the amounts of hydrogen adsorption over the carbon monoxide poisoned platinum were studied. Table 2 shows that the saturated adsorption of hydrogen over the platinum surface with water and/or a small amount of carbon monoxide did not markedly decrease at both room temperature and 273 K. It is shown in Fig. 3 that the preadsorption of water and/or a small amount of carbon monoxide does not appreciably affect the rate of hydrogen adsorption and that 89 to 90% of hydrogen adsorption proceeds instantaneously and is followed by a slow uptake of a further amount of hydrogen.

TABLE 2

Hydrogen Adsorption on Platinum–alumina with Carbon Monoxide and/or Water at Room Temperature and 273 K

Temperature	Hydrogen uptake (atoms $\times 10^{-18}$/g catalyst)	CO preadsorbed (molecules $\times 10^{-18}$/g catalyst)	H_2O preadsorbed (molecules $\times 10^{-20}$/ g catalyst)
297 K	8.6	1.5	—
297 K	9.1	—	—
297 K	8.5	1.1	—
297 K	9.0	—	—
297 K	8.0	0.88	2.4
273 K	11	—	—
273 K	9	0.88	2.4
273 K	11	0.33	3.1

Accordingly, since preadsorption of a small amount of carbon monoxide brings about neither a marked decrease in the amount nor in the rate of hydrogen adsorption, it is suggested that in the beginning of the exchange reaction, most of the surface platinum atoms are saturated with deuterium atoms, which do not take part in the rate-determining step of the exchange reaction.

On the other hand, it was previously demonstrated that the kinetic behavior changed on freezing the adsorbed water (*1*). The dependences of the exchange rate on the deuterium pressure and the amount of the adsorbed water at still lower temperatures such as 229 K were also studied. These data are presented in Figs. 4 and 5,

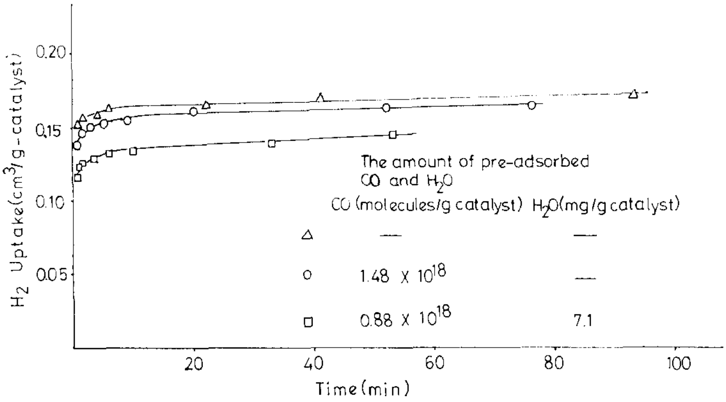

FIG. 3. Effect of the preadsorption of carbon monoxide and/or water on the rate of hydrogen adsorption on platinum–alumina.

respectively, and can be expressed by the equation

$$V \propto [P_{D_2}]^{0.1}[H_2O(a)]^{0.8}. \qquad (4)$$

With much larger amounts of adsorbed water the frozen water seemingly fills the pores of the alumina structure such that the rate of the exchange reaction decreases with the amount of adsorbed water.

The poisoning curves at lower temperatures such as 269 K, 255 K, and 229 K were studied under a constant deuterium pressure of 27 kPa. Below 273 K, as the dependence of the exchange rate on deuterium pressure and the amount of the adsorbed water changed as mentioned above, the poisoning curve was measured at 269 K under the deuterium pressure of 15 kPa as well as 27 kPa. The results are given in Fig. 6. Under such experimental conditions the rate equations are expressed by Eq. (1) or (3), and the exchange rate drops rapidly with a small amount of preadsorbed carbon monoxide. At lower temperatures and higher deuterium pressures, the exchange rate is expressed by Eq. (2) or (4). In such cases the poisoning of the D_2–$H_2O(a)$ exchange reaction was not appreciable with the adsorption of a small amount of carbon monoxide, but after adsorption of more than 11×10^{16} CO molecules/g a reduction of the catalytic activity was observed.

These results are interpreted as follows. On the free platinum surface water molecules are strongly held at a limited part of the surface where hydrogen dissociation takes place, and the hydrogen dissociation

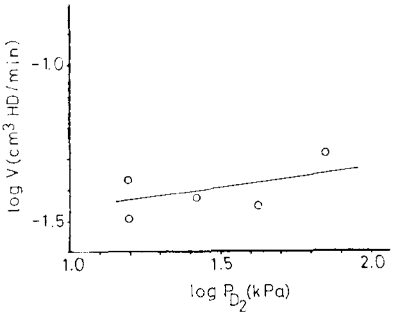

FIG. 4. Dependence of the exchange rate on the deuterium pressure at 229 K; $H_2O(a) = 0.025$ g.

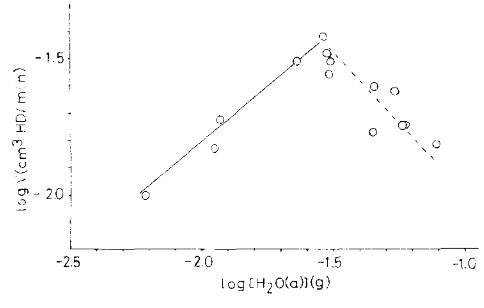

FIG. 5. Dependence of the exchange rate on the amount of the adsorbed water at 229 K; $P_{D_2} = 27$ kPa.

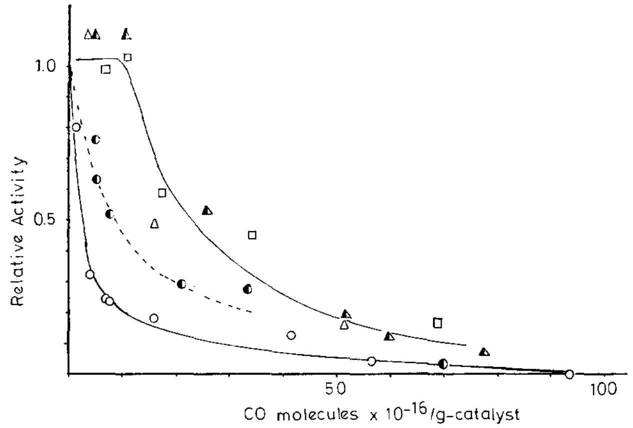

FIG. 6. Poisoning curve by carbon monoxide in D_2–H_2O(a) exchange reaction on platinum–alumina under various reaction conditions; relative activities are plotted against the amount of preadsorbed carbon monoxide. (○), P_{D_2} = 27 kPa, 273 K; (△), P_{D_2} = 27 kPa, 269 K; (□), P_{D_2} = 27 kPa, 255 K; (▲), P_{D_2} = 27 kPa, 229 K; (◐), P_{D_2} = 15 kPa, 269 K. In all cases H_2O(a) = 0.025 g/2.13 g catalyst.

is the rate-determining step for the exchange reaction. Accordingly the rate is first-order in hydrogen pressure and zero-order in the amount of water adsorbed on the catalyst surface. This active part is the region where carbon monoxide is preferentially adsorbed to exhibit a marked poisoning effect for the exchange reaction.

At lower temperatures when the adsorbed water is immobilized by freezing, the mobility of water or its hydrogen to and from the active region and the water condensed in alumina becomes rate-determining and the rate is expressed by Eq. (2) or (4). However, when it is poisoned by carbon monoxide, the mobility of water is not affected by the carbon monoxide adsorption, but the hydrogen dissociation is so much inhibited such that the hydrogen dissociation finally becomes rate-determining, thus exhibiting the rate equation (1) or (3) again.

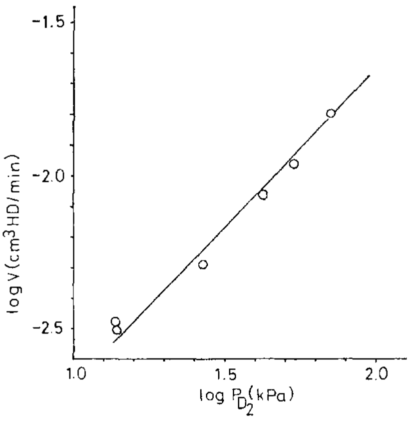

FIG. 7. Dependence of the D_2–H_2O(a) exchange reaction on deuterium pressure over CO poisoned platinum–alumina catalyst at 229 K; H_2O(a) = 0.025 g/2.13 g catalyst; CO preadsorbed = 34 × 10^{16}/g catalyst.

This is the reason why carbon monoxide poisoning is not distinctively exhibited in the first stage of the carbon monoxide adsorption. The exchange rate follows the behavior given by Eq. (2) or (4) until the reaction kinetics finally change to Eq. (1) or (3), hydrogen dissociation becoming rate-determining again, as is demonstrated in Figs. 7 and 8.

The speculation as to the mechanism of the exchange reaction itself is supported by the following results reported elsewhere (*9, 10*). When the exchange reaction was carried out on a platinum catalyst dispersed on hydrophobic supports, such as Porapak Q (copolymer of styrene and divinylbenzene) above 273 K, the rate ex-

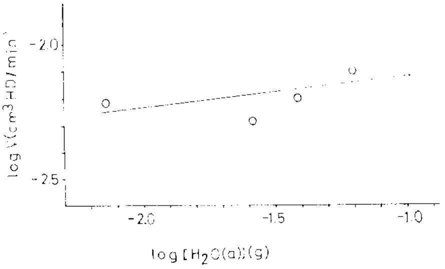

FIG. 8. Dependence of the D_2–H_2O(a) exchange reaction on the amount of water adsorbed on CO poisoned platinum–alumina catalyst at 229 K; $P_{D_2} = 27$ kPa; CO preadsorbed = 34×10^{16}/g catalyst.

pression was similar to Eq. (1) or (3), the rate being proportional to the pressure of deuterium and independent of water vapor pressure, and the shape of the poisoning curve was also convex from the beginning as in the case of platinum–alumina, although the slope was gentler.

The number of active sites and thus the turnover number can be estimated using the slope of the poisoning curve (*11*). The calculated ratio of the turnover number of the exchange reaction over platinum–alumina to that over platinum–Porapak-Q at 299 K was found to be 1.25. The adsorption of water vapor as well as hydrogen on the Pt–hydrophobic supports was separately measured under the reaction conditions, which revealed that hydrogen is adsorbed on platinum to saturation under normal hydrogen pressures, whereas water is adsorbed mainly on platinum surface depending upon the pressure of water vapor. The similar activity of the platinum catalysts dispersed on hydrophobic and hydrophilic supports strongly suggests that water adsorbed on the hydrophilic supports such as alumina does not play an important role in the exchange reaction, the reaction proceeding on the platinum surface. It is accordingly suggested that the adsorption of water and hydrogen on the platinum surface dispersed on alumina would be similar to that on the platinum dispersed on Porapak Q, the adsorption of water and hydrogen on platinum being directly measurable in the latter case.

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