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Gas Chromatographic Determination of Reversible Adsorption of Hydrogen

VI. The H_2–D_2 Exchange Reaction on a Copper Catalyst in Relation to the Reversible Adsorption of Hydrogen

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The H_2–D_2 exchange reaction on a copper catalyst was examined by means of a pulse flow technique in relation to the reversible adsorption of hydrogen. The Arrhenius plots of the exchange activity showed a break around 20°C at which the reversible adsorption of hydrogen reached a maximum. This result suggests that the exchange reaction at lower temperatures takes place on special sites of higher activity but of smaller number and other than those for the reversible adsorption at lower temperatures, and another type of site of lower activity but of larger number operates at temperatures higher than about 20°C, which are responsible for the reversible adsorption above 20°C.

1. INTRODUCTION

Since the initial studies with nickel catalysts (*1*, *2*), the determination of reversible adsorption of hydrogen by means of a gas chromatographic technique has been undertaken on metal catalysts such as iron (*3*), cobalt, copper, (*4*), platinum and palladium (*5*).

It has been confirmed that any one of these metals which are known as hydrogenation catalysts reversibly adsorbs hydrogen. The next step of this study should be to find a correlation of the reversible adsorption with the reaction rate of hydrogen on these metals. However, there is a difficulty which discourages the investigation of the correlation. That is, those catalysts of large surface area on which the reversible adsorption can be determined by the gas chromatographic technique are generally so active that the reaction rates are too high to be measured at the temperature at which the reversible adsorption is determined.

In this respect, a copper catalyst has been studied for its activity in the H_2–D_2 exchange, because a copper catalyst is admittedly less active than other transition metal catalysts (*6*). The H_2–D_2 exchange reaction has an advantage that the reaction conditions are completely identical with that of the determination of reversible adsorption.

2. EXPERIMENTAL

Catalyst. Copper: aluminum (1:1) alloy of grains of 2–3 mm in diameter was supplied by Kawaken Fine Chemicals Co. The alloy was treated by a sodium hydroxide solution of 5 wt% at room temperature for 2 hr and then at 100°C for 3.5 hr, and washed with distilled water. The surface area of the prepared catalyst was 10 m^2/g. The purity of the alloy was reported by the supplier as follows: copper, above 99.85%; aluminum, above 99.8%. The aluminum content remaining in the prepared catalyst was determined to be $0.4 \pm 0.1\%$.

Procedure. The Raney copper catalyst (23 g net) was packed in a wet state into a glass U tube 9 mm in diameter. The length of the packed part was 30 cm. The accompanying water was evacuated and replaced by hydrogen. After the catalyst was treated with flowing hydrogen at 270°C for 17 hr, the gas chromatographic determination of the reversible adsorption of hydrogen was made by the method reported previously (*1*). In the case of the exchange reaction small amounts of the catalyst were packed into glass U tubes of 4-9 mm diameter and treated with flowing hydrogen at 270°C for 5 hr. The determination of the exchange rate was made by a pulse flow technique. That is, a pulse of deuterium gas carried by hydrogen was introduced to the catalyst bed. The flow rate was 30.7 ± 0.5 ml STP/min and the effluent pulse was analyzed for HD and D_2 by a molecular sieve 5A column. The correction factor of peak area for HD was taken as one-half of D_2 as reported previously (*1*). In the examination of the effect of water vapor, the carrier gas was contaminated by passing over an ice trap at −20°C. The resulting hydrogen stream contained about 0.6 mm Hg of water vapor.

Determination of activation energy for the exchange. The rate of exchange V can be determined by the equation (when the concentration of HD at time zero is nil),

$$\ln \frac{[\mathrm{HD}]_e}{[\mathrm{HD}]_e - [\mathrm{HD}]} = Vt \qquad (1)$$

where $[\mathrm{HD}]_e$ and [HD] denote the concentrations of HD at equilibrium and time t, and t is the contact time. In the case of pulse flow techniques, the time of retention should be involved in the contact time. However, the retention volume due to the catalyst column was at most 0.55 ml STP/g at 20°C and nearly nil below −50°C, as shown in Fig. 2, and can be neglected from the contact time as compared with the size of pulse (at least 2.3 ml STP), either because the amount of catalyst used was so small or the amount of reversible adsorption per gram of catalyst was so small. Thus the contact time, t, may be simply expressed as CW/FT, where C is a constant; W, the amount of catalyst in the bed; F, the flow rate of carrier gas; and T, the column temperature. Equation (1) is rewritten as

$$V = \frac{FT}{CW} \ln \frac{[\mathrm{HD}]_e}{[\mathrm{HD}]_e - [\mathrm{HD}]} \qquad (2)$$

For runs with a common value of F, the term

$$\frac{T}{W} \ln \frac{[\mathrm{HD}]_e}{[\mathrm{HD}]_e - [\mathrm{HD}]},$$

is proportional to the exchange rate, V.

Since the directly observable quantity in this experiment is the relative amounts of HD and D_2, which can be obtained by gas chromatography, the value of $[\mathrm{HD}]_e/\{[\mathrm{HD}]_e - [\mathrm{HD}]\}$ can be calculated in terms of the conversion of D_2, X, which is expressed by

$$X = \frac{[\mathrm{HD}]}{[\mathrm{HD}] + 2[\mathrm{D}_2]} \qquad (3)$$

Then it follows that

$$\frac{[\mathrm{HD}]_e}{[\mathrm{HD}]_e - [\mathrm{HD}]} = \frac{X_e}{X_e - X} \qquad (4)$$

where X_e denotes the equilibrium conversion. X_e depends on the relative amount of light hydrogen in the deuterium pulse, the shape of which is subject to deformation during passage through the pathway including the catalyst column. Thus X_e depends on the amount of catalyst and the size of deuterium pulse. But they are held constant in a series of runs. The values of X_e can be obtained from the runs at higher temperatures, because the temperature dependence of X_e is negligible. Apparent activation energies can be obtained from the Arrhenius plots of $(T/W)[\ln X_e/(X_e - X)]$.

3. RESULTS AND DISCUSSION

The amount of catalyst was varied in order to obtain a proper conversion* to estimate the activity in different temperature ranges, as shown in Table 1.

The Arrhenius plots of $(T/W)[\ln X_e/(X_e - X)]$ are shown on Fig. 1. These plots were calculated from those conversions tabulated in Table 2. The values of the apparent activation energy obtained from the plots are given in Table 1. It can be determined from Fig. 1 and Table 1 that the apparent activation energy changes

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* Conversions less than 5% or more than 90% of X_e are inadequate for the estimation of the rate of exchange.

TABLE 1
EXPERIMENTAL CONDITIONS AND ACTIVATION ENERGIES OBSERVED IN DIFFERENT TEMPERATURE RANGES

	Series No.		
	(1)	(2)	(3)
Catalyst amount (g)	0.58	0.55	0.037
Length of the catalyst bed (mm)	5	13	2
Diameter of the catalyst bed (mm)	9	6	4
Temperature range (°C)	~−60–20°	~−100–60°	~60–140°
Amount of D_2 introduced (ml/STP)	2.6	4.6	2.4
Apparent activation energy (kcal/mole)	2.3	2.3–7.5	10

around 20°C from a low value of 2.3 kcal/mole to higher value of about 10 kcal/mole.

In Series (2) and (3) the effect of water vapor was examined. For the runs above 0°C, 0.6 mm Hg of water vapor was added to the carrier gas and was equilibrated with the catalyst column. The runs below 0°C were made with the catalyst column

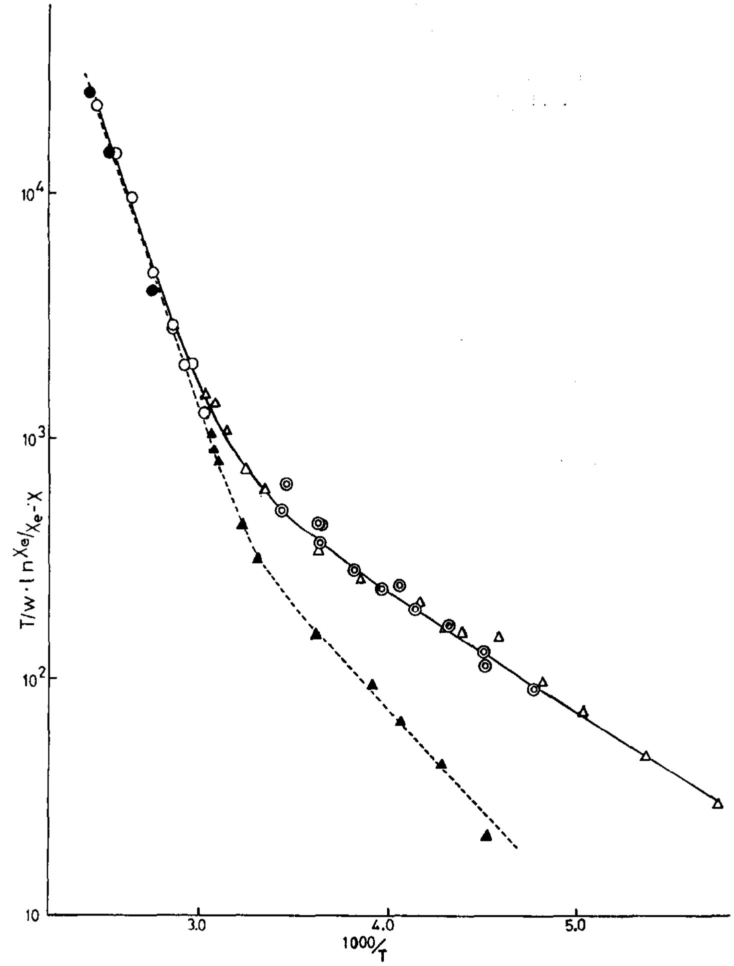

FIG. 1. Arrhenius plots of the exchange activity: series 1, (◎); series 2, △ ▲; series 3, ○ ●; ▲ and ● represent the runs with added water vapor.

TABLE 2[a]
CONVERSIONS OF DEUTERIUM.

Series (1) X_e = 84.7% at 266°C		Series (2) X_e = 70.8% at 110°C		Series (3) X_e = 80.0% at 180°C	
Column temp. (°C)	Conv. (%)	Column temp. (°C)	Conv. (%)	Column temp. (°C)	Conv. (%)
−64°	18.7	−99.5°	7.9	59°	10.3
−52°	24.4	−87°	10.5	65°	16.0
−51°	24.3	−75.5°	14.3	70°	15.2
−42°	28.8	−66°	17.2	71°	14.9
−31.5°	31.0	−56°	22.9	78°	20.5
−27°	37.0	−46°	23.0	90°	31.1
−21°	35.5	−41.5°	23.7	106°	48.4
−11°	38.6	−33°	27.2	122°	60.4
1°	50.7	−15°	31.0	139°	70.1
2°	44.5	2°	35.7		
2.5°	51.5	25.5°	48.4		
16°	61.4	35°	51.9		
19°	52.9	45°	59.4		
		51.5°	64.3		
		56°	65.0		

[a] The runs were done in random order and it is shown that the data are independent of the order of temperature variation and are reproducible.

equilibrated with the water vapor at 20°C. Those results are shown by solid circles and triangles on Fig. 1. The added water seems to be harmless above 70°C but definitely decreases the rate of exchange below 20°C.

The retention volumes of deuterium pulses were separately measured with a longer catalyst column of 23 g (30 cm). They are shown on Fig. 2. The retention volume due to the catalyst column, V_R, increases with temperature from null at −78°C to a maximum of 0.55 ml/g at 20°C and then decreases.

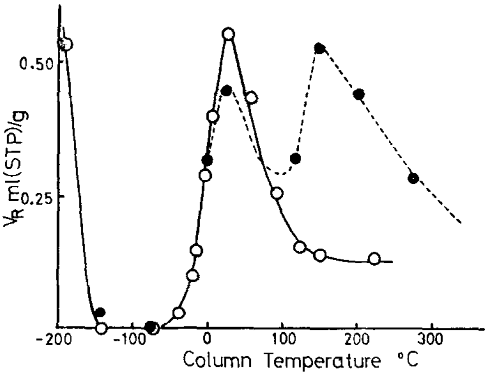

FIG. 2. Deuterium retention volume at different temperatures: ○, the runs with pure hydrogen carrier gas; ●, the runs with added water vapor.

The effect of water vapor on the retention volume was also examined. The results are shown by solid circles on Fig. 2. It was found that the added water does not affect the retention volume below 0°C, while it depresses the adsorption in the temperature range, 20° to 60°C, and it brings about another maximum of retention volume which can be ascribed to another reversible adsorption as well as the exchange with the adsorbed water (*4*).

The observed variation in the retention volume in the absence of water vapor has been interpreted as development of activated adsorption with increase in temperature (*4*). According to this interpretation, the rate of exchange between gas and adsorbed phases becomes rapid enough to realize an isotopic equilibration at around the maximum point of the isobar of retention volume. This isotopic equilibration made it possible to determine the reversible adsorption of hydrogen.

The variation with temperature of the activation energy for the exchange reaction of hydrogen should be consistent with the above interpretation. The lower value of the activation energy at lower temperatures is natural simply because a lower activation energy can be counterbalanced by a lower value of RT. However the increase in activation energy with temperature should be accompanied by an increase in the frequency factor, which will be discussed in the following.

As concluded in the previous paper for nickel (*1*), the active sites responsible for the hydrogen exchange at low temperatures seem to be few in number. It was observed in the present case that the eluted pulse of deuterium from the catalyst column of 23 g showed only 8% of conversion to HD at −195°C, while the retention volume at this temperature amounted to 12.3 ml (STP). The observed reversible adsorption did not necessarily cause the isotopic exchange at −195°C. Thus it is suggested that the exchange reaction at low temperatures takes place on special sites other than those for the reversible adsorption and fewer in number.

The remarkable decrease in the exchange rate at low temperatures caused by the added water, without an accompanying decrease in the retention volume, suggests that the active site for the exchange reaction at low temperature is a special site particularly susceptible to water poisoning, while the observed small effect of water on the exchange rate at higher temperatures is consistent with the view that the exchange reaction at higher temperatures takes place on the ordinary surface which is responsible for the reversible adsorption above 20°C. Although the exchange rate was partly decreased by the added water around 20°C, the reversible adsorption was also depressed.

It may be concluded that active sites of higher activity but of fewer number operate at lower temperatures, and that they are substituted for by another type of site of lower activity but of larger number at temperatures higher than about 20°C. The expected increase in the frequency factor accompanied by the alteration of activation energy amounts to 10^6 times. This would be reasonable if the reversible adsorption at higher temperature is dissociative and thus necessarily results in the exchange, while the exchange reaction at low temperature is catalyzed by some defects on the surface. Since the surface concentration of defects is usually stated (*7*) to be 10^8 to $10^{10}/\text{cm}^2$ as compared with $10^{15}/\text{cm}^2$ of lattice points, the larger part of the increase in the frequency factor may be ascribed to the increase in the number of sites.

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