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Author(s)	KWAN, Takao
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RATE OF HYDROGEN ADSORPTION ON REDUCED COPPER.

By Takao KWAN.

The adsorpion of gas on metallic catalysts at ordinary or higher temperatures as reported hitherto is in most cases very rapid initially, slowing down at later stage as referred to "secondary adsorption".

This effect is frequently attributed to some physical process such as the diffusion of gas along grain boundaries or solution into the lattice which governs of observed rate[1] at the stage. But the rate may equally be reduced by some other causes, for instance, the repulsion between the adsorbed atoms or traces of immpurities contaminating the surface or the heterogenity of the surface i.e. some surface of lower rate of adsorption playing the part. The present author has actually observed[2] that in the case of reduced nickel the rate of adsorption was considerably influenced by traces of immpurities such as the vapour of tap grease or of remaining oxide which could actually be removed by continuous reduction for a long period at relatively high temperature.

Copper powder used for the adsorption of hydrogen revealing the above mentioned features of adsorption process has now usually been prepared by alternative oxydation and reduction[3] at the temperature lower than 200°C ; it is hence doubtful whether the reduction were complete.

The latter question is further amplified by the experimental results that the adsorbed quantity of hydrogen per unit weight of the catalyst is exceptionally small compared with that of other metals[3] in spite of exceptionally large heat of adsorption even exceeding 30 Kcal/mole[4] which would definitely favour the opposite effect as inferred from the statistical mechanical consideration in the foregoing work.

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[1] WARD; Proc. Roy. Soc., 133 (1931) 506, MELVILLE and REDEAL; Proc. Roy. Soc., 153 (1936) 77, IIJIMA; Sc. Pap. I. P.C.R. Takyo, 22 (1933) 285, MOROZOV; Trans. Far. Soc. 31 (1935) 659.

[2] KWAN; This Journal. p. 81

[3] WARD; ibid. MELVILLE and REDEAL; ibid. BEEBE, LOW, WILDNER and GOLDWASSER; J. Am. Chem. Soc., 57 (1935) 2527.

[4] WARD; ibid.

In consequence the adsorption of hydrogen on copper was now observed with special stress on the thorough reduction of the adsorbent; the result was that on the contrary to the existing data as described below an exceptionally large quantity of hydrogen was adsorbed with a rate proportional to hydrogen pressure without any later slow stage mentioned above.

Experimental Procedure and Materials

The apparatus and the procedure for the measurement of the adsorption are quite the same as reported in the foregoing paper.

Copper; Copper carbonate supplied by "Kojima Co." was heated at 450°C for 65 hours and two grams resulting oxide was reduced at 400°C under several cm Hg hydrogen pressure.

Hydrogen pressure decreased within a first few hours but no more during the following one week. Throughout the latter period the catalyst was kept at the above condition of reduction but being occasionally evacuated and supplied with fresh hydrogen several times.

Five grams "Kahlbaum reduced copper extra fine" was similarly reduced as well for another sample for the adsorption measurement.

In any case copper was kept from grease or mercury vapour by means of liquid air trap directly attached to the reaction vessel. Copper thus prepared was evacuated at 400°C for one hour before use.

Hydrogen; Electrolytic hydrogen was passed over platinized asbestos at 300°C and then through a liquid air trap to remove the water vapour.

Experimental Results

Measured quantity of hydrogen gas was admitted into the reaction vessel containing the copper catalyst evacuated beforehand in a manner described above and maintained at any desired temperature.

The rate of adsorption was found considerably small even at the initial stage; it took two or three days below 300°C for the pressure decrease to become measurable by McLeod gauge. The rate of hydrogen adsorption on Kojima's copper as well as on Kahlbaum's observed at 400°, 350° and 300°C is shown in the following Table and Figure.

TABLE 1 Rate of Hydrogen Adsorption on KOJIMA's Copper

$T = 300°C$ $P_0 = 1{,}38\times10^{-1}$ mm Hg

t hr	$P\times10$ mm Hg	k mm Hg/hr
4	1,34	0,0012
21	1,20	0,00126
43	1,03	0,00127
66	0,89	0,00125
		mean 0,00125

$T = 350°C$ $P_0 = 1{,}6\times10^{-1}$ mm Hg

t hr	$P\times10$ mm Hg	k mm Hg/hr
4	1,43	0,0053
18	0,91	0,0059
27	0,68	0,0059
40	0,50	0,0055
45	0,45	0,0053
60	0,22	0 0056
		mean 0,0056

$T = 400°C$ $P_0 = 1{,}46\times10^{-1}$ mm Hg

t hr	$P\times10$ mm Hg	k mm Hg/hr
4	0,97	0,0193
17	0,73	0,0185
23	0,29	0,022
28	0,11	0,022
66	0,07	0,021
		mean 0,020

TABLE 2 Rate of Hydrogen Adsorption on Kahlbaum's Copper

$T = 350°C$ $P_0 = 6{,}26\times10^{-1}$ mm Hg

t hr	$P\times10$ mm Hg	k mm Hg/hr
14	4,50	0,0044
30	3,06	0,0044
38	2,50	0,0045
66	1,24	0,0046
		mean 0,00447

$T = 400^\circ\mathrm{C}$ $\qquad P_0 = 5{,}90\times10^{-1}$ mm Hg

t hr	$P\times10$ mm Hg	k mm Hg hr
18	1,4	0,015
24	1,0	0,014
41	0,16	0,016
45	0,12	0,016
51	0,058	0,016
		mean 0,0155

The first column of the Table shows the time measured from the admission and the second one the pressure at the moment. P_0 is the initial pressure calculated from the knowledge of the admitted amount of gas and of the whole space preliminarily determined without catalyst.

The third column shows constant k calculated from the observed data according to the expression,

$$k = \frac{1}{t}\log\frac{P_0}{P}$$

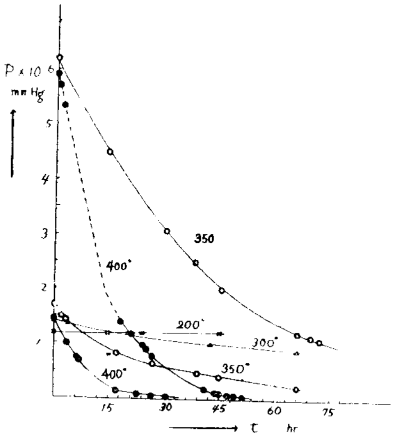

Fig. Rate of Hydrogen Adsorption

derived from the proportionality of the adsorption rate to the momentary pressure ignoring the minute equilibrium pressure ($<10^{-3}$ mm Hg at 400°C) finately attained compared with the working pressure $10^{-1}\sim10^{-2}$ mm Hg. The assumed proportionality is verified satisfactorily by the constancy of k.

It was shown thereby that the measured pressure decrease was practically due to the adsorption that to the solution of hydrogen into the bulk of the copper being negligible as calculated on the basis of the solubility data due to SIEVERTS[5].

From the rate constant at the different temperatures the heat of activation E was calculated according to the usual expression that,

$$E = RT^2\frac{d\log k}{dT} = 20\ \mathrm{Kcal/mole}$$

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5) SIEVERTS; Z. Phys. Chem., 60 (1927) 129. Pressure decrease as calculated by the data is only about 10^{-4} mm Hg at the temperature 400°C and at the pressure 10^{-1} mm Hg.

As regards to the adsorption equilibrium following may be inferred from the observation although the direct measurement has not been carried out.

Adsorbed quantity for unit weight of copper calculated from the initial pressure and the lowest pressure attained at 400°C shown in Table 2 and the volume of the apparatus are about 0,1 cc N.T.P. per gram which gives the lower limit of adsorbed quantity at the condition whereas the lowest observed pressure the upper limit to the equilibrium pressure. This figure of adsorbed quantity is however exceedingly larger than any existing data*), regardless of the higher temperature and the lower pressure in the present measurment, which favours the lower degree of adsorption.

On the other hand the surface area of the copper powder employed was observed by B.E.T. method, being found to be so small as almost within experimental error. Estimating from the latter the upper limit of the surface area and assuming that each hydrogen molecule occupied two copper atoms the lower limit of the covered fraction θ of the surface was calculated from the above lower limit of adsorption at 0,2.

From the upper limit of equilibrium pressure and the lower limit of θ at 400°C, the lower limit of the heat of adsorption may be calculated according to the statistical mechanical expression Eq. (17) in the foregoing report that,

$$\Delta\varepsilon > 35 \text{ Kcal/mole}$$

This figure is extremely larger than any data hitherto reported but in accord with that 47 Kcal**) derived from spectroscopic data for dissociation energy of Cu H.

In conclusion, the present author wish to express my sincere thanks to the Director of the Institute J. Horiuti for his kind interest and valuable discussion on this work, and also to Nippon Academy for financial grant.

The Research Institute for Catalysis
Hokkaido University
Sapporo, Japan

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*) Cf. ref 1), 3).

**) Sponer; Molekulspekren, Berlin 1936.