Rate of Hydrogen Adsorption on Reduced Copper

By Takao KWAN

(Received November 11, 1949)

As reported hitherto the adsorption of gas on metallic catalysts at ordinary or higher temperature is in most cases very rapid initially but slows 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 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 impurities contaminating the surface, or the heterogeneity of the surface, i. e., some surface of lower rate of adsorption. The present author actually observed⁽²⁾ that in the case of reduced nickel the rate of adsorption was considerably influenced by traces of impurities such as the vapor 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 usually been prepared by alternative oxydation and reduction⁽³⁾ at the temperature lower than 200° : it is hence doubtful if the reduction were complete or not.

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, in spite of exceptionally large heat of adsorption even exceeding 30kcal./mole⁽⁴⁾ which would definitely favor the opposite effect as inferred from the consideration from the standpoint of statistical mechanics in the foregoing work.

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

Experimental Procedure and Materials

The apparatus and the procedure for measurement of adsorption is quite the same as reported in the previous paper.⁽²⁾

Copper.—Copper carbonate of "Kojima Co." was heated at 450° for 65 hours and two grams of resulting oxide were reduced at 400° under several cm.Hg hydrogen pressure.

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

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

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

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

Experimental Results

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

The rate of adsorption was found considerably small even at the initial stage; for the pressure decrease it took two or three days below 300° to become measurable by McLeod gauge. The rate of hydrogen adsorption on Kojima's copper as well as on Kahlbaums observed at 400°, 350° and 300° is shown in Table 1 and Figure.

Table 1

Rate of Hydrogen Adsorption on Kojima's Copper

$T=300°\text{C}.\quad P_0=1.38\times10^{-1}$ mm.Hg

t, hr.	$P\times10^{-1}$ 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

---

(1) Ward, *Proc. Roy. Soc.*, **133**, 506 (1931); Melville and Redeal, *Proc. Roy. Soc.*, **153**, 77(1936); Iijima, *Sc. Pap. I. P. C. R. Tokyo*, **22**, 285 (1933); Morozov, *Trans. Far. Soc.*, **31**, 659 (1935).

(2) Kwan, *Journal of the Reseach Iust. for Catolysis*, Vol I, No. 2, 81 (1949).

(3) Ward, *Proc. Roy. Soc.*, **113**, 506 (1931); Melville and Redeal, *ibid*, **153**, 77 (1936); Beebe, Low, Wildner and Goldwasser, *J. Am. Chem. Soc.*, **57**, 2527 (1935).

(4) Ward, *Proc. Roy. Soc.*, **133**, 506 (1931).

$T=350°C.$ $P_0=1.6\times10^{-1}$ mm.Hg

t, hr.	$P\times10^{-1}$ 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.	$P=10^{-1}$ 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.	$P\times10^{-1}$ 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

$T=400°C.$ $P_0=5.90\times10^{-1}$ mm.Hg

t, hr.	$P\times10^{-1}$ mm.Hg	k, mm.Hg/hr.
18	1.4	0.015
24	1.0	0.014
41	0.19	0.016
45	0.12	0.016
51	0.058	0.016
	mean	0.0155

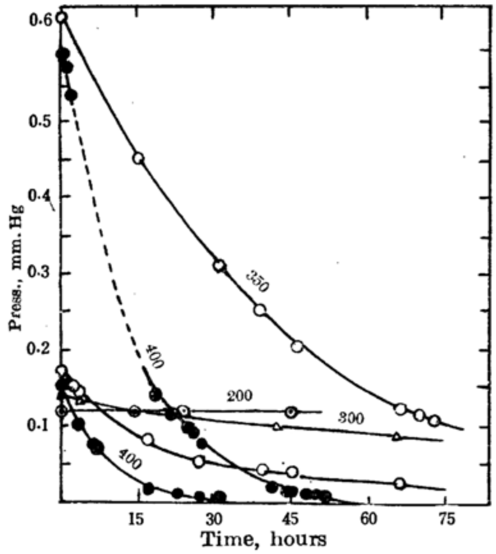

Fig.—Rate of hydrogen adsorption.

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 from that of the whole space preliminarily determined without catalyst.

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

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

derived from the proportionality of the adsorption rate to the momentary pressure, ignoring the minute equilibrium pressure ($<10^{-3}$ mm.Hg at 400°) finitely 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 that the measured pressure decrease was practically due to the adsorption and the solution of hydrogen into the bulk of the copper was negligible as calculated on the basis of the solubility data due to Sieverts(4).

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

$$E=RT^2\frac{d\log k}{dT}=20\ \text{kcal./mole.}$$

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

Adsorbed quantity for unit weight of copper, which was calculated from the initial pressure and the lowest pressure attained at 400° shown in Table 2 and the volume of the apparatus, is 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 gives the upper limit to the equiliblum pressure. This figure of adsorbed quantity is however exceedingly larger than any existing data,(1)(3) regardless of the higher temperature and the lower pressure in the present measurement, which favors 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°, the lower limit of the heat of adsorption may be calculated according to the statistical-mechanical expression Eq. (17) in the foregoing report that

---

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

$$\Delta\varepsilon > 35 \text{ kcal./mole.}$$

This figure is extremely larger than any data hitherto reported but it is in accord with that 47 kcal.⁽⁶⁾ derived from spectroscopic data for dissociation energy of CuH.

In conclusion, the present author wishes to express his sincere thanks to the Director of the Institute, J. Horiuti, for his kind and valuable direction given to this work. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

(6) Sponer, "Molekulspectren," Berlin (1935).

The Research Institute for Catalysis.
Hokkaido University, Sapporo