Absorption Isotherm for Sintered Palladium Black-Hydrogen System

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Below a critical temperature, the absorption isotherm for metallic palladium-hydrogen system has a plateau at constant pressure where two phases of absorbed hydrogen coexist[1]. The value of this pressure depends only on temperature for a bulk metal[2]. One of the authors, however, found recently that the pressure, for a palladium deposited on glass, is lower than that for bulk metal such as wire and foil and that it is increased by sintering[3]. Further information about this phenomenon is reported here.

The absorption of hydrogen was accordingly measured at 0 and 30°C by means of a gas pipette with a Bourdon manometer and an absorption cell connected to the former through a trap maintained at liquid nitrogen temperature. Hydrogen was purified by diffusing through a palladium thimble. Fresh palladium black which was obtained from palladium chloride by usual procedure of reduction[4], was put into the cell in a wet state and was then dried in vacuo, reduced with hydrogen of 50 mmHg and was evacuated for several hours at 120°C.

The results of successive measurements for a sample are shown in the figure. The absorbent was sintered between the respective measurements by heating in vacuo for 0.5~3.0 hr. at 200~400°C. The BET area of the surface was determined at each step by the use of nitrogen at −195°C, of which value varied as 13.6, 11.7, 9.4, 8.1 and 6.6 m^2/g. Pd corresponding to the isotherms, A, B, C, D and E. The pressure which corresponds to the plateau was appreciably lower than those for bulk metal, 25.2 (wire)[3], 22.6 (foil)[3], 19.4 (wire, bead, foil)[5], 18.7 (sufficiently sintered black)[6] mmHg (30°C) and 3.95 mmHg (0°C)[6] and increased with decreasing area of the surface. The mean size of the absorbent particles which was deduced from the line-width of X-ray diffraction increased from 90 Å, the initial value, to 250 Å after all the heat treatments. This change in particle size was also observed by electron-microscope; the particles smaller than 400 Å in size, of which the major part of the aggregations of the sample is consisted, were turned into those of smooth shape which were several times larger than the former. On the other hand, the mean radius which was estimated from the BET area by assuming the particles to be spherical, increased as 180, 210, 270, 310 and 380 Å corresponding to the respective isotherms. Moreover, the micro-pore distribution obtained by Inkley's procedure[7] showed that the initial distribution having a sharp maximum at 30 Å was transformed into a

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6) L. J. Gillespie and F. P. Hall, *J. Am. Chem. Soc.*, **48**, 1207 (1926).
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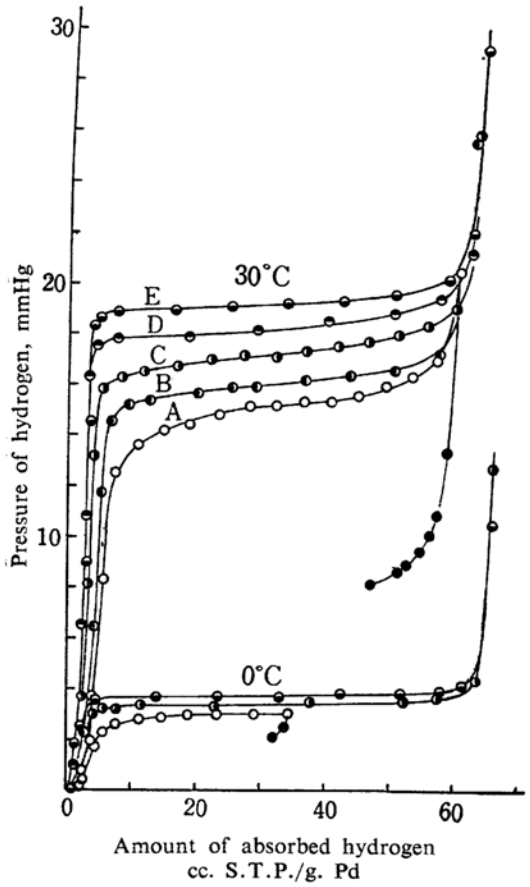

Fig. 1. Absorption isotherms for sintered Pd black-H_2 system. Every circles represent the values after standing for 20 min. Filled circles show desorption.

milder one with unchanged position of maximum.

The above information suggests that the pressure at the flat part depends on, even at the same temperature, the size and structure of particle of metallic palladium. The fact that the sigmoid isotherm is gradually deformed into that of folded-line type as the sintering proceeds, may be explained as that the particles distribute in various size and they grow by successive heating. The irregularities of structure, which may be the causes of this phenomenon, will disappear with the growth of particle and the equilibrium between gaseous and absorbed hydrogen may be sensitive to this change especially when the particle is sufficiently small. From the middle part of the isotherms the heat of absorption was estimated as 8.9 kcal./mol. which agrees well with those obtained hitherto[5].

It is to be suggested that this phenomenon will be available to elucidate the state of metallic palladium which is extremely dispersed on carriers.

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