[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

The Adsorption of Hydrogen by Supported Copper Poisoned with Carbon Monoxide[1]

BY CARROLL W. GRIFFIN

In a previous study[2] sorption measurements were made at 0° for hydrogen and for ethylene on copper which had been poisoned with small amounts of carbon monoxide. It was found that a minute quantity of the poison gave rise to a low-pressure increase in the sorption either of hydrogen or of ethylene and that the increase gave way to a decrease at higher pressures. This behavior is quite different from that observed for the sorption of hydrogen on copper which has been poisoned with cyanogen[3] or with mercury[4] or which has been largely deactivated by heating to 450°;[4] in these cases the poisons and the heat treatment cause a decrease in the sorption of hydrogen at all pressures from zero to one atmosphere.

A possible explanation for this peculiarity in the sorption of hydrogen on copper poisoned with the monoxide has been suggested[2] by assuming that the sorption comprises a secondary action in addition to that of straight adsorption, and that this secondary action may be solution of hydrogen in the copper or that it may be diffusion.[3] As either solution or diffusion would affect the sorption significantly only at higher pressures, their absence, due to the lack of hydrogen dissociation centers when poison is present, would cause a decrease in sorption noticeable only at the higher pressures. Therefore, since the decrease in high-pressure sorption thus brought about is greater than the low-pressure increase caused by the poison, the isotherms for sorptions on the pure and on the poisoned copper previously have been found to cross one another.[2,3] It was thought that a different attack on the problem of distinguishing between sorption and adsorption might be pursued by employing a supported copper catalyst, since this should largely do away with all except surface adsorption.

Experimental Part

The apparatus, the method of preparation of the hydrogen, of the carbon monoxide, the limits of accuracy and the procedure for making a run have been described.[2] The method of measuring the smallest quantity of poison used has been explained.[5] Helium was used as a reference gas. The reversibility of high-pressure adsorptions was frequently confirmed by the absence of hysteresis. Between runs the catalyst bulb was evacuated at 150°.

As a support for the copper, diatomite brick, kindly furnished by the Armstrong Cork and Insulation Company, was used. The brick was broken up and sized to 8–20 mesh. It was then washed in hot, concentrated nitric acid for six days, after which it was thoroughly washed with water and dried for two hours at 105°. A sample of 41.8 g. of the brick itself at this point was tested for hydrogen sorption with a negative result. The granules were then impregnated uniformly with copper nitrate solution so as to obtain very close to one mole of copper per thousand grams of brick. After wetting with the copper nitrate solution the brick was dried at 105° and placed in a large Pyrex tube inserted in an oven where the temperature was increased to 500°. Eleven hours later the granules were removed, placed in a bulb and sealed to the apparatus. Reduction then was begin at 150° and continued until no more water was formed.

A sample of two moles of copper per thousand grams of brick was prepared by doubling the amount of copper on the above sample, and later, for runs on the sample of four moles of copper per thousand grams of brick, the quantity of copper again was doubled. However, in order to promote greater activity in these two samples, after heating the nitrate at 500°, alternate reductions and oxidations were carried out at successively lower temperatures as follows: reduction at 250°; oxidation (by drawing filtered air through the bulb) at 300°, reduction at 175°; oxidation at 200°, reduction at 150°; oxidation at 150°, reduction at 125°; oxidation at 125° (incomplete, but evenly distributed), reduction at 125°.

Results

Runs are numbered in the order in which they were made and the curves of the figures are numbered to correspond to the runs. Three runs were made with one mole of copper per thousand grams of brick. The isotherms for these runs are indicated by the broken curves, 2, 3 and 4 of Fig. 1. It is seen that the adsorptive activity fell off with each run. This behavior is similar to that found by Pease and Griffin[6] with their samples of massive copper and seems characteristic of copper of relatively few very active centers. It was to try to secure a catalyst of constant adsorptive power that the quantity of copper on the brick was now doubled. Following this, Runs 6 to 11 were made. There was a very

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(1) Presented before the Division of Physical and Inorganic Chemistry at the New York meeting of the American Chemical Society, April 23, 1935.

(2) Griffin, THIS JOURNAL, **49**, 2136 (1927).

(3) Griffin, *ibid.*, **56**, 845 (1934).

(4) Pease, *ibid.*, **45**, 2296 (1923).

(5) Griffin, *Chemist-Analyst*, **19**, 21 (1931).

(6) Pease and Griffin, THIS JOURNAL, **49**, 25 (1927).

slightly smaller adsorption for Run 7 than for Run 6, but thereafter the adsorption was constant for hydrogen on the unpoisoned catalyst. Run 11 and check Run 15 give the isotherm for hydrogen on unpoisoned copper. Run 12 and check Run 16 show the effect of adding 0.039 cc. of carbon monoxide a half hour before beginning these runs. Run 13 shows the effect of 0.74 cc. of carbon monoxide poison.

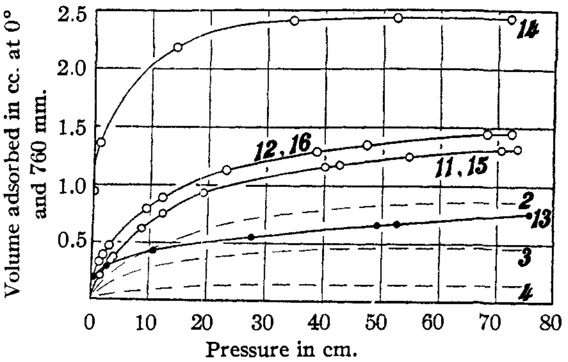

Fig. 1.—Adsorption of hydrogen on supported copper poisoned with carbon monoxide at 0°. Curves 2, 3 and 4, H_2 with no poison on one mole of copper per 1000 g. brick. All other curves for catalyst of two moles of copper per 1000 g. brick. Curves 11, 15, H_2 with no poison; 12, 16, H_2 with 0.039 cc. CO; 13, H_2 with 0.74 cc. CO; 14, pure CO.

In a like manner Fig. 2 shows the poisoning effects of the monoxide on hydrogen adsorption with the sample of four moles of copper per thousand grams of brick. Run 18 and check Run 22 were made with hydrogen on the unpoisoned copper, Run 19 with 0.039 cc. of carbon monoxide and Runs 20 and 23 with 0.72 cc. and 0.74 cc. of poison.

Discussion of Results

It is immediately apparent that, ignoring curves 2, 3 and 4, the isotherms of Fig. 1 and of Fig. 2 are qualitatively similar. Their quantitative differences are doubtless due to the fact that there were more centers of all degrees of activity when four moles of copper per thousand grams of brick were employed. The use of 0.039 cc. of poison on either sample causes an increase in hydrogen adsorption and this increase, it will be noted in contrast to results previously obtained with unsupported copper, continues by a nearly constant volume for all pressures up to one atmosphere. This result seems to indicate that the use of supported copper eliminates any secondary sorption factor. It will be noted further that this increase is approximately the same whether the 0.039 cc. of poison is used on the two mole or on the four mole sample.

When the larger amounts of poison are used the isotherms show a low-pressure increase in hydrogen adsorption equal in volume to the increase caused by 0.039 cc. of poison but which soon gives way to a decrease at higher pressures. However, the similarity between these curves and those previously obtained for this amount of poison on unsupported copper probably[2,3] is not so real as apparent. Judging from the 0.74-cc. poison curves alone it is possible that the explanation may be identical with that advanced for unsupported copper[2] with the added assumption that the brick itself, although showing no sorption of hydrogen before the copper was placed upon it, may dissolve hydrogen after the hydrogen-dissociating centers of copper are placed upon the brick. That is, at low pressures where the solution would be negligible we have the usual low-pressure increase due to the poison; but, as pressure increases and since the secondary factor is excluded by the poison preventing the formation of atomic hydrogen, a decrease in sorption is found.

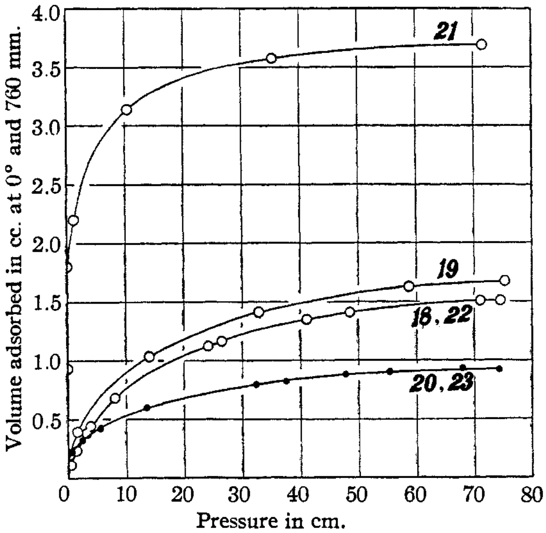

Fig. 2.—Adsorption of hydrogen on supported copper, four moles of copper per 1000 g. of brick, poisoned with carbon monoxide at 0°. Curves 18, 22, H_2 with no poison; 19, H_2 with 0.039 cc. CO; 20, 23, H_2 with 0.74 cc. CO; 21, pure CO.

However, there are at least two reasons why such an interpretation in the present case is unlikely. First, if such were true then 0.039 cc. of carbon monoxide, an amount of poison sufficient to occupy all the *very* active centers of copper, *also* should prevent or diminish or at least slow down the process of solution, or of diffusion, and these curves (12, 16 of Fig. 1 and 19 of Fig. 2) *also* should cross those for runs with no poison. Second, it is evident from both Fig. 1 and Fig. 2 that the decrease in adsorption for the runs with 0.74 cc. of poison soon becomes approximately constant, whereas, if solution or diffusion were a factor, the decrease should be greater the higher the pressure. It should also be noted that the decrease is roughly equal to the difference in the volume of poison employed and the low-pressure increase in adsorption. Equally important perhaps is the fact that the rate of adsorption with the supported copper was found to be much more rapid than with unsupported samples of earlier studies. In fact, even at atmospheric pressure, equilibrium was established within twenty or thirty minutes after hydrogen was admitted to the bulb, whereas under similar conditions two or three hours are usually necessary with unsupported copper.

From these observations it appears that there are a few very active centers which adsorb at least 0.039 cc. of the monoxide, which, in turn, causes the extra linkage of hydrogen to give the low-pressure increase in adsorption. As more hydrogen is admitted to the bulb it is adsorbed by centers of lesser activity. In the case of the larger amount of poison the monoxide, except for the very small quantity adsorbed on the few very active copper centers, is taken up by the centers of medium activity; thus as hydrogen is now added it is not adsorbed (*i. e.*, after the "extra" linkages, at low pressure, are satisfied) to the extent that it was when the copper was not poisoned or when only the few very active centers were utilized by carbon monoxide. Finally it happens then (at a pressure of 30 cm. to 40 cm.) that the decrease in adsorption due to 0.74 cc. of poison is less than 0.74 cc. by an amount roughly equal to the initial, low-pressure increase. This statement does not hold when dealing with unsupported copper where 0.74 cc. of the monoxide causes a decrease in sorption distinctly exceeding in some cases even the amount of poison employed. In brief, it seems that the smaller amount of carbon monoxide, adsorbed on the most active copper centers, assists in binding somewhat more hydrogen than normally would be held by the surface. The larger amounts of poison merely occupy, in addition to these few most active centers, many centers of lesser activity to the exclusion of an equivalent amount of hydrogen. The surface condition of the supported samples of copper, in so far as can be judged, is essentially the same as that of the unsupported copper already reported. It therefore appears that the difference in behavior in the two cases must be attributed to the absence of secondary factors of sorption where supported copper is used, this, in turn, being due to a lack of any subjacent action when the inert brick underlies the surface copper.

Summary

1. Adsorption measurements have been made at 0° for hydrogen on a supported copper catalyst poisoned with carbon monoxide.

2. A minute quantity of the poison causes an increase of hydrogen adsorption at all pressures up to one atmosphere.

3. A larger amount of poison causes a low-pressure increase and a higher-pressure decrease of adsorption.

4. An interpretation of the results has been outlined indicating the absence of secondary factors of sorption when supported copper is used.

POUGHKEEPSIE, N. Y. RECEIVED APRIL 25, 1935