[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Adsorption of Hydrogen by Copper Dispersed in Magnesia

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A few years ago it was observed[2] that hydrated magnesium oxide, although not itself active, is particularly effective in promoting the catalytic activity of hydrated copper oxide in the decomposition of sodium hypochlorite. Best promotion was obtained when the ratio was approximately 4 molecules of magnesium oxide to 1 molecule of copper oxide. It was also pointed out that the unpromoted catalyst's activity fell off rapidly due to the change (growth) in particle size. This change in activity was accompanied by a change in color of the catalyst from blue to dark brown or black. The co-precipitation of magnesium and copper hydroxides gave a product in which the copper hydroxide remained blue. These results suggested that magnesium oxide may serve as an excellent dispersion medium or support for metallic copper to be used as an adsorbent or as a catalyst in the many reactions in which copper is known to be particularly useful. Haygard found that copper, promoted with basic magnesium carbonate, is a better adsorbing[3] agent than the pure copper. His measurements were made at 20°.

Metallic copper is known to sinter[4] at temperatures near 450°. This has limited its usefulness. Will the addition of magnesia to metallic copper prevent its sintering at temperatures appreciably above 450°? Will copper dispersed in magnesia have a greater adsorptive capacity for hydrogen and other gases and also be more catalytically active than pure copper?

Recently Taylor and Joris[5] have shown that copper dispersed in magnesia is an excellent catalyst for hydrogenation reactions. For example, ethylene is hydrogenated rapidly at 0°. These authors also made X-ray studies of this catalyst the results of which will be published elsewhere.

This present paper presents the data for the adsorption of hydrogen on (1) pure copper, (2) pure magnesia and (3) copper dispersed in magnesia (2.02 g. copper in 5.125 g. magnesium oxide) at various temperatures.

Experimental

Apparatus.—The apparatus for this work was essentially the same as that used in Princeton for similar studies. The pressure was kept constant by an arrangement described by Taylor and Strother.[6]

Gases.—Hydrogen was prepared by the electrolysis of a 15% sodium hydroxide solution using nickel electrodes, and was passed over a glowing platinum wire and through a trap immersed in solid carbon dioxide and ether. Helium from a cylinder, used for determining the dead space of the adsorption tube, was first passed over freshly reduced copper at 500°, and then through a trap of activated charcoal immersed in liquid air.

Preparation of Adsorbents

Pure Copper.—To 0.5 mole of C. P. copper nitrate was added enough distilled water to give 2.5 liters of solution. To this was added dropwise, while stirring vigorously, 2 normal sodium hydroxide until precipitation was completed. The total volume of the solution containing the suspended copper hydroxide was about 3 liters. The precipitate was allowed to settle and the supernatant liquid removed by decantation. This precipitate was washed until the wash water gave no test for free alkali. Next the precipitate was filtered and dried at 120° for fifty hours. It was then placed in a tube and sealed to the apparatus where it was heated for one hour at 325° to remove the last trace of water. Finally, with the tube maintained at 140°, hydrogen was passed through at the rate of 15 cc. per minute for forty-eight hours. Reduction was assumed to be complete when a tared phosphorus pentoxide tube, attached to the tube through which the hydrogen escaped, did not gain in weight.

Magnesium Oxide.—This oxide was prepared in the same manner as the copper oxide. It was found that the last traces of water were removed with difficulty. For example, evacuation at 444° for fourteen hours did not remove all the water, but by raising the temperature to 570° and continuing the evacuation for another thirteen hours, a product was obtained that was free from water.

Metallic Copper Dispersed in Magnesium Oxide.—One-half mole of copper nitrate and 2 moles of magnesium nitrate were placed in a large glass cylinder and enough distilled water added to give 3.5 liters of solution. To this was added, drop by drop, while stirring, 2 normal sodium hydroxide solution until precipitation was complete. The total volume was about 6 liters. The resultant precipitate was washed, filtered and then dried at 120° for fifty hours. The temperature was raised to 325° and the drying process continued for an additional three hours. Reduction with hydrogen was then carried out. At temperatures of 150 to 190° the rate of reduction was so slow that the process was still incomplete after one hundred thirty hours. Consequently the temperature was in-

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(2) Lewis, *J. Phys. Chem.*, **35**, 915 (1931).

(3) Haygard, *J. Chem. Soc.*, 2055 (1932).

(4) Pease, THIS JOURNAL, **45**, 2296 (1923).

(5) Taylor and Joris, *Bull. soc. chim. Belg.*, **46**, 241 (1937).

(6) Taylor and Strother, THIS JOURNAL, **56**, 586 (1934).

creased to 375° and the hydrogen passed through for forty-four hours. Finally the temperature was raised to 444° and the flow of gas continued for one hour. At this point the effluent gas did not increase the weight of the phosphorus pentoxide tube, showing that all the copper oxide had been reduced. From results obtained, by evacuation at various temperatures and for different lengths of time, it appears that magnesia containing dispersed copper is more readily dehydrated than pure magnesia.

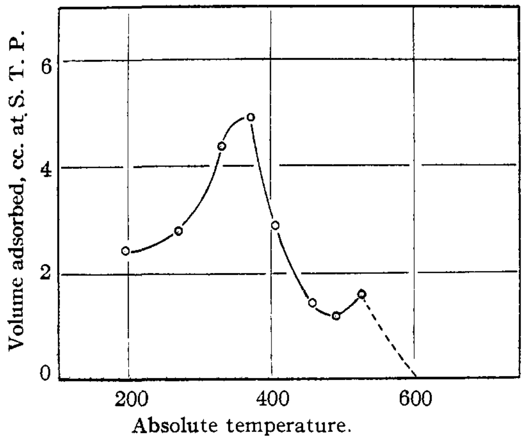

Fig. 1.—The adsorption of hydrogen at one atmosphere and at various temperatures on 14.31 g. of copper.

Experimental Results

The quantity of hydrogen adsorbed at 1 atmosphere pressure and at various temperatures is expressed in cubic centimeters, corrected to 0° and 760 mm. The data are summarized in tables and also shown graphically. Due to the extremely slow rate at which equilibrium is reached, the results reported are not necessarily the true equilibrium values. In most cases, however, the adsorption process appeared to have been completed. Some measurements extended over a period of eighty hours before readings became constant. Duplicate measurements were made. These checked the originals within 5%.

Table I

The Volume of Hydrogen Adsorbed on Pure Copper, Pure Magnesia and Copper Dispersed in Magnesia:[a] Cc. per Gram (S. T. P.)

Temp., °A.	Pure copper	Pure magnesia	Dispersed copper, uncorr.	Dispersed copper, corr.
80		1.46	7.92	4.18
195	0.17	0.077	2.66	2.24
273	.19	.084	3.26	3.15
298		.07	3.57	3.39
329	.30	.07	3.46	3.28
373	.34	.04	2.86	2.75
403	.20			
457	.10	.07	1.48	1.30
491	.08	.05	1.73	1.61
527	.11	.07	2.15	1.97
575		.26	2.47	1.79
717		.97	4.00	1.58

[a] The measurements were made on 14.31 g. of pure copper; 4.54 g. of pure magnesia and 2.02 g. of copper dispersed in 5.125 g. of magnesia. From these were calculated the data which are given in this table.

Table II

Energy of Activated Adsorption of Hydrogen on Various Surfaces

Adsorbent	Temp. range, °C.	Hydrogen adsorbed, cc.	Activation energy, kcal.
Copper	56–100	3	7.2
	218–254	0.8	11.5
Magnesium oxide	218–254	.3	34.1
	302–444	1.2	33.7
Copper in magnesium oxide	0–56	1.8	1.1
	−56	6.4	4.5
	56–100	1.8	1.0
	254–302	4.0	22.9

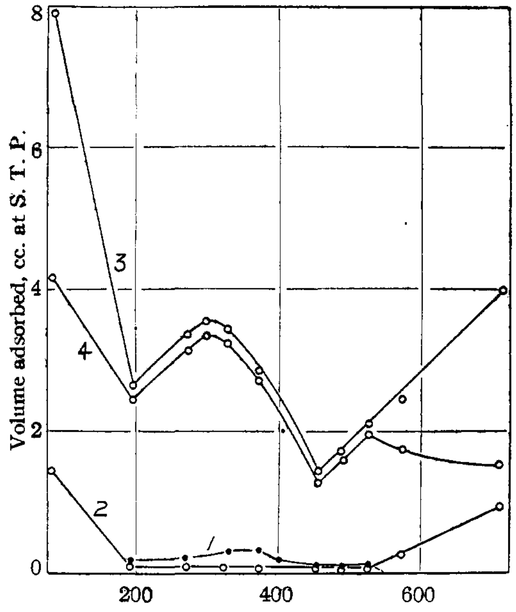

Fig. 2.—The adsorption of hydrogen on copper and on magnesia at one atmosphere and at various temperatures: Curve (1), cc. gas on 1.0 g. copper; curve (2), cc. gas on 1.0 g. magnesia; curve (3), cc. gas on 1.0 g. copper dispersed in 2.56 g. magnesia; Curve (4), cc. gas on 1.0 g. copper dispersed in 2.56 g. magnesia (corrected for the hydrogen adsorbed on the magnesia).

Discussion of Results

From an examination of the curve in Fig. 1 (and curve 1, Fig. 2) one sees that copper shows the ordinary physical adsorption (van der Waals) and also an activated adsorption. At a temperature of 525°A. the sintering process began and was completed at 717°A. It was noticed that there was a very marked contraction of the finely divided copper away from the walls of the container. Upon removal of this copper from the tube, the characteristic copper color remained indefinitely.

The curve for pure magnesium oxide, curve 2, Fig. 2, is very interesting. At low temperatures there is the ordinary van der Waals adsorption. From 200 to 500°A. the oxide is a very poor adsorbent. At 500°A. the curve turns up and continues to rise to 717°A., which was the highest temperature used in this study. These results agree qualitatively with those published by Hollings and Griffith.[7]

Curves 3 and 4, Fig. 2, show the adsorption of hydrogen on dispersed copper. In curve 3 the assumption is made that all the hydrogen is adsorbed on one gram of copper. Curve 4 is the same but corrected for the hydrogen that is adsorbed on the magnesia present. At temperatures between 200 and 450°A. it appears that copper is the active adsorbent. It is not excluded but improbable that magnesia (containing dispersed copper) is the effective adsorbent over this temperature range. Between these two temperatures activated adsorption takes place. The rise in the curve between 450 and 717°A. may indicate a second type of activated adsorption. In addition there may be some solution of hydrogen in copper. However, these data do not check the solubility data given by Sieverts[8] over the same temperature range.

There was no evidence of contraction of the powder away from the walls of the adsorption tube even though the tube had been heated to 800°A. The catalyst did not cake or form crusts as did the pure copper at this temperature. Further, upon exposure to air at room temperature, the dispersed copper soon changed in color from the characteristic orange-red to a dark brown or black.

From Table II one sees that the energy of activated adsorption is lower on the dispersed copper than on the pure copper or on the magnesium oxide. Since, however, the rate of adsorption is very rapid at first, it is difficult to measure the rate for the first gas adsorbed. The values given here merely indicate that the first molecules to go on the surface of the adsorbent require a lower activation energy than those which go on later. Also the activation energy is higher, the higher the temperature of adsorption. This is in agreement with the results obtained on zinc oxide and on zinc oxide–chromic oxide mixtures studied by Taylor and Strother.[6]

We wish to thank Professor R. N. Pease and also Dr. Nelson Trenner for helpful discussion of this problem.

Summary

1. The adsorption of hydrogen on pure copper, on magnesia and on copper dispersed in magnesia has been measured at one atmosphere and at various temperatures.

2. It has been shown that both physical and activated adsorption occur in each case.

3. Copper, when dispersed in magnesium oxide, is a better adsorbent for hydrogen and is also less likely to sinter than the pure copper.

4. The physical and activated adsorptions on magnesium oxide are separated by a wide temperature interval.

PRINCETON, N. J. RECEIVED JANUARY 3, 1938

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(7) Hollings and Griffith, *Nature*, **129**, 834 (1932).

(8) Sieverts, *Z. physik. Chem.*, **77**, 591 (1911).