Adsorption of Hydrogen on Copper-Magnesia Catalysts

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(Received August 27, 1956)

Most researches on copper-magnesia catalysts which have appeared so far in the literature are concerned with reaction kinetics¹⁾, and little is known about the physical properties of the catalysts. In the present paper are reported the adsorption characteristics of hydrogen on the copper catalyst containing 1% magnesia. The catalyst is treated at various stages of thermal sintering. The effect of sintering upon adsorption heat is primarily investigated and a tentative suggestion is made concerning the nature of the copper-magnesia catalyst.

Experimental

The copper-magnesia catalyst was prepared by dissolving copper oxide and magnesia in a molar ratio of 99 to 1 in extra-pure nitric acid. The mixture was dried gently on a water bath, and then ignited at 500°C in an electric furnace. The copper oxide was prepared from metallic copper supplied by Ishizu Chemical Co., in a manner as reported previously²⁾. Traces of Mg, Fe, Si, Mn and Pb were found in this oxide sample by a spectroscopic analysis.

The catalyst was reduced in an atmosphere of hydrogen for three weeks at 200°C, until no more decrease in hydrogen pressure was perceptible. Before adsorption measurement, the catalyst was evacuated at the reduction temperature (or sintering temperature) for six hours under 10^{-5} mmHg. Adsorption measurements were made at 100° and 160°C on this reduced catalyst as well as on those sintered at 400° and 500°C in an atmosphere of hydrogen. Much care was taken in attaining adsorption equilibrium, as has been done previously*.

The magnesia was supplied by Kanto Chemical Co. The sample was treated in hydrogen at 200° and 500°C for a week before adsorption

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1) R. Wynkoop and R. H. Wilhelm, *Chem. Eng. Progress*, **46**, 300 (1950) ; M. V. Sussman, *Ind. Eng. Chem.*, **46**, 457 (1954). M. Erlenbach and A. Sieglitz, *C. A.*, **48**, 2756e (1954).

2) T. Takeuchi and M. Sakaguchi, This Bulletin., To be published shortly.

* See Ref. 2) and also T. Kwan, "*Advances in Catalysis*", **6**, Academic Press, New York (1954), p. 67.

measurement. During this treatment, neither the adsorption nor any kind of consumption of hydrogen was measurable to any extent.

Results

Surface areas determined by the B. E. T. method, using ethylene at −183°C for the freshly reduced copper-magnesia catalyst and the sintered one as well are given in Table I, in which those for pure copper, copper containing 1% nickel (copper-nickel) and magnesia powder are also listed for comparison. The Table shows that the surface area of the copper catalyst increases by six times with the addition of magnesia, far more so than with the addition of nickel. Raising the sintering temperature decreases the surface area of the catalyst, this effect being pronounced on the unpromoted copper catalyst, less pronounced on the copper-nickel and least on the copper-magnesia catalyst. On the contrary, the surface area of the magnesia powder increases about twice as much when the sintering temperature is increased from 200° to 500°C.

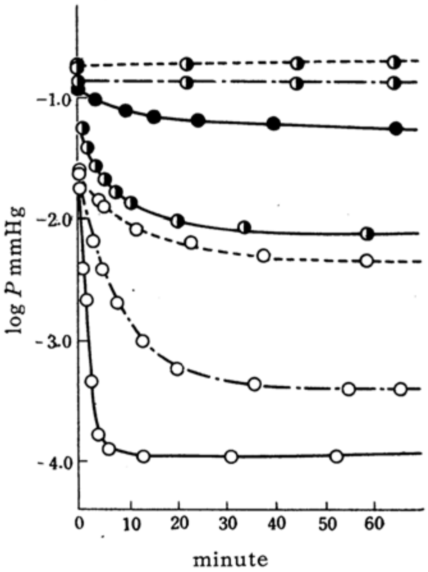

Fig. 1. Rates of adsorption of hydrogen at 160°C on Cu-MgO, Cu and Cu-Ni catalysts (5.0 g).

——○——	Cu-MgO reduced at 200° (initial pressure; 1.83 $\times 10^{-2}$ mmHg).
——◑——	Cu-MgO sintered at 400° (2.01 $\times 10^{-1}$ mmHg).
——●——	Cu-MgO sintered at 500° (1.21 $\times 10^{-1}$ mmHg).
- - -○- - -	Cu reduced at 200° (2.50 $\times 10^{-2}$ mmHg).
- - -◑- - -	Cu sintered at 400° (1.87 $\times 10^{-1}$ mmHg).
—·-○-·—	Cu-Ni reduced at 200° (2.66 $\times 10^{-2}$ mmHg).
—·-◑-·—	Cu-Ni sintered at 400° (1.40 $\times 10^{-1}$ mmHg).

TABLE I

SURFACE AREA OF COPPER CATALYSTS (M^2/g.)

	Cu	Cu-Ni	Cu-MgO	MgO
Reduced at 200°	0.69	0.80	3.90	13.8
Sintered at 400°	0.25	0.34	2.70	—
Sintered at 500°	0.20	—	1.50	27.0

Fig. 1 shows the rate of the adsorption of hydrogen at 160°C on copper-magnesia, pure copper, and copper-nickel. As shown in the figure, the rate of adsorption on copper-magnesia reduced at 200°C is markedly greater than that on the others; more than ten times as great as that on pure copper, and three times that on copper-nickel. Of particular interest is the fact that the increase in the rate of adsoption by the addition of magnesia well exceeds the corresponding increase of the surface area. Raising the temperature of heat treatment considerably decreases the rate of adsorption, but it is less effective compared with that of pure copper and copper-nickel catalysts[2]. Thus, it becomes apparent that the promoting action of magnesia involves something more than maintaing the surface area.

Fig. 2 shows the adsorption isotherms per unit area of the catalyst**. It is found that the

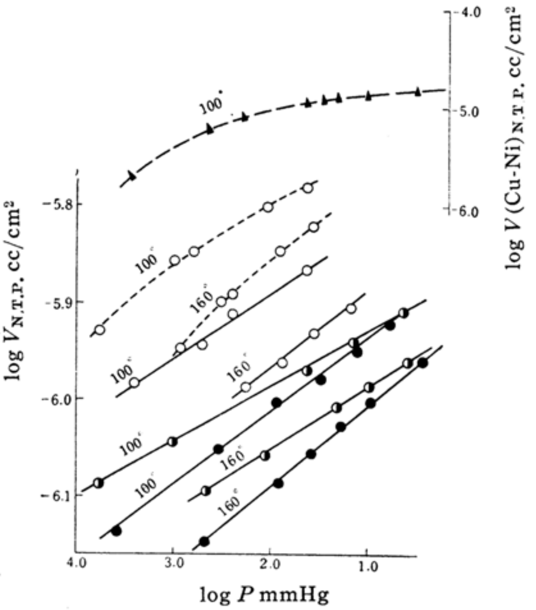

Fig. 2. Adsorption isotherms of Cu-MgO, Cu, and Cu-Ni catalysts.

——○——	Cu-MgO reduced at 200°
——◑——	Cu-MgO sintered at 400°
——●——	Cu-MgO sintered at 500°
- - -○- - -	Cu reduced at 200°
– –▲– –	Cu-Ni reduced at 200°

** The saturation value, as derived from the Langmuir plot of dissociative type, is 2.07×10^{-5}cc. N. T. P. per sq cm. on pure copper while 1.44×10^{-6}cc. N. T. P. on copper-magnesia. This indicates that the abundance of active site on the latter catalyst is only 7% of that on copper alone.

addition of magnesia decreases the amount of hydrogen adsorbed, while, on the contrary, the addition of nickel increases it. The heat treatment of copper-magnesia decreases the amount of hydrogen adsorbed.

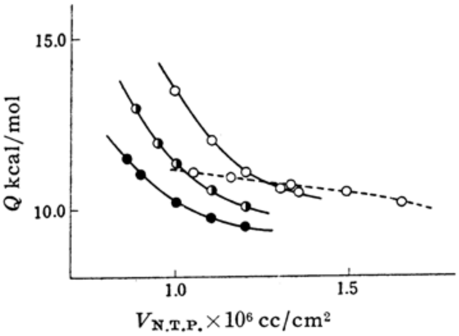

Fig. 3. Heats of adsorption of hydrogen on Cu-MgO and Cu catalysts.

——○—— Cu-MgO sintered at 200°
——◐—— Cu-MgO sintered at 400°
——●—— Cu-MgO sintered at 500°
- - -○- - - Cu reduced at 200°

Fig. 3 shows the relationship between the heat of adsorption and the amount adsorbed on the copper-magnesia catalyst. The broken line represents the heat of adsorption on pure copper. The heat of adsorption q was calculated by using Clapayron-Clausius' equation

$$(\partial \ln P/\partial T)_v = q/RT^2$$

where P is the equilibrium pressure and V is the amount adsorbed.

The heat decreases gradually as the temperature of heat treatment increases, as frequently happens on most reduced catalysts. A notable thing is that the decline of the heat curve is very steep on magnesia added to copper.

Adsorption measurement was carried out on a magnesia powder at 100° and 160°C, but the adsorption was too small to detect.

Discussion

On the basis of the fact that the amount of hydrogen adsorbed per unit area of the copper-magnesia catalyst is less than that on unpromoted copper and that hydrogen is scarcely adsorbed on the magnesia powder, it is suggested that the magnesia occupies a considerable portion of the surface. This is amplified by the study of electron diffraction as shown in Fig. 4; that is, diffraction pattern due to magnesia can be found together with that of copper, and no compound formation appears between magnesia and copper. The pattern also indicates that the magnesia exists in microcrystal particles on the surface. This was confirmed by Yamaguchi³⁾, who studied this sample by changing the accelerating potential of electron.

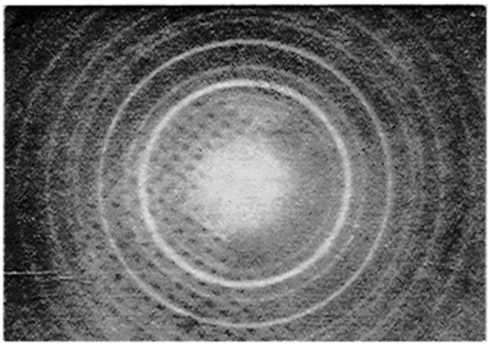

Fig. 4. Electron diffraction photograph of Cu-MgO catalyst: Wave length of electrons; 0.0306 Å, Camera length; 495 mm.

It is expected that copper in the catalyst may sinter upon heating and decrease its surface area, while magnesia, with a very high melting point, may not. Thus, the ratio of the surface area of the copper particles to those of the magnesia in the catalyst would decrease with increasing the reduction temperature of the catalyst. The B. E. T. surface area as given in Table I most probably includes the "dead area" which is inert toward hydrogen adsorption.

If the dead area is excluded for the adsorption of hydrogen, each of the three heat curves would shift parallel to the horizontal axis toward the right respectively according to the temperature of heat treatment. Thus the heat of adsorption of hydrogen on copper-magnesia catalyst well exceeds that on pure copper catalyst at a low coverage.

The greater heat value and the greater adsorption rate on the copper-magnesia catalyst would suggest that the physical property of copper in this mixed catalyst differs from that of pure copper.

How should the difference in the physical property of copper be explained? It has been proved by Willstätter⁴⁾ that the catalytic hydrogenation of phthalic anhydride and benzene over platinium or palladium is promoted by the presence of traces of oxygen, while it is often suppressed if the metallic catalyst is scrupulously freed from oxygen. Exhaustively reduced copper at 400°C, according to Kwan⁵⁾, shows an activation energy as high as 20 kcal. for

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3) S. Yamaguchi, *Z. Physik. Chem.*, **7**, 115 (1956).

4) R. Willstätter and D. Jacquet. *Ber.*, **51**, 767 (1918); R. Willstätter and E. Waldschmidt-Leitz, ibid., **54**, 113 (1921).

5) T. Kwan, *J. Res. Inst. Catalysis*, **2**, 95 (1949).

the chemisorption of hydrogen. The chemisorption rate is measurable only above 300°C. In view of these observations, it is impossible that the copper in the present catalyst is entirely freed from oxygen contamination. This must be a kind of contamination that would result in an increase in adsorption heat, and probably a decrease in activation heat for the adsorption.

According to Gwathmey[6], the small amounts of a metal or a metallic oxide added to a copper single crystal modifies the rearrangement of the surface either by controlling the development of certain facets, or by promoting the formation of copper powder at different rates on the different faces. Surface irregularities caused by the presence of magnesia might promote to an extent the adsorption of hydrogen on the copper-magnesia catalyst. It is hoped, however, that the effect of oxygen can be explained on the electronic basis. Possibly the copper in the copper-magnesia would lose electrons from its filled 3d shell by the interaction with the oxygen of magnesia, and Cu^{++} may act as an active site for the adsorption of hydrogen.

Summary

(1) The adsorption of hydrogen on a copper catalyst containing 1% magnesia sintered at various temperatures has been investigated at 100° and 160°C, and compared with that on copper alone. The addition of magnesia increases markedly both the surface area and the rate of adsorption. The latter increase, however, is far beyond the increase in surface area.

(2) The hydrogen adsorption per unit area of the copper magnesia catalyst is less than that on pure copper, and decreases with increasing heat treatment. The adsorption of hydrogen on magnesia powder is immeasurably small. The heat curves on differently heated catalysts do not agree with each other, but approximately do so if the effective area for hydrogen adsorption is taken into consideration. The adsorption heat for a low coverage is certainly greater on the magnesia added copper than on copper alone.

(3) By aid of the electron diffraction study, it is concluded that the magnesia in the catalysts exists on the surface and forms microcrystal particles. Presumably, copper in the magnesia added catalyst is modified by the oxygen of the magnesia and irregular defects are formed on the surface in the presence of magnesia.

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6) R. E. Cunningham and A. T. Gwathmey, *J. Am. Chem. Soc.*, **76**, 391 (1954).