The Surface of Copper-Nickel Catalyst. II. Adsorption of Hydrogen on Copper, Nickel, and Copper-Nickel Catalysts

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In the previous paper[1] the authors reported their study of the surface of copper catalyst containing 1% nickel, a study carried out by means of the reaction of hydrogen chloride with the catalyst and through the use of an electron microscope; and they proposed that a small percentage of the total amount of nickel contained in the catalyst occupies a comparatively large proportion of the surface area of the catalyst, existing in the metallic nickel state.

The present work was undertaken to determine the heat of adsorption of hydrogen on copper, nickel, and copper-nickel catalyst at high temperature in order to obtain further knowledge of the structure of copper-nickel catalysts.

It is well known that the heat of adsorption of a gas on a metal at high temperature (heat of chemisorption) is greatly dependent upon the kind of metal as well as upon the gas adsorbed on it. If the metallic nickel particles supposed to exist in a large proportion on the surface of the catalyst is in an exposed state, it is expected that the heat of adsorption of the gas on the catalyst (copper-nickel) may be the same or nearly the same as that for a pure nickel catalyst. If the nickel particles are covered with copper, the heat of adsorption can be expected to be the same as that of a pure copper catalyst. If copper-nickel alloy is formed (contradictory to the conclusion of the previous paper), and is in an exposed state, the heat of adsorption can be expected to differ from both that for nickel catalyst and that of copper catalyst.

With a view to ascertain whether the surface of the copper-nickel catalyst is composed of nickel, copper, or alloy, the adsorptions of hydrogen on copper, nickel, and copper-nickel (copper containing 1% nickel) catalysts have been investigated, and the heats of adsorption given by the adsorption isotherms for these three catalysts have been compared with one another. Further, the effects of reduction temperatures upon the surface area and upon the adsorption velocity of hydrogen have also been investigated.

Experimental

The copper, nickel, copper-nickel, hydrogen, and ethylene which were used in this experiment were prepared in the same ways as in the experiment described in the previous report[1].

The apparatus used is shown in Fig. 1. In this figure, A is the reaction vessel of about 30 cc. volume. B is the U-tube which is cooled by liquid oxygen throughout the whole process of the reduction of the catalyst and the adsorption experiment, for the purpose of protecting the catalyst from being contaminated by grease or mercury vapor. C is the MacLeod gauge which can measure pressures as low as 10^{-6} mmHg. D is a 40 cc. messburette calibrated to 0.1 cc. E is the mercury reservoir connected to the burette and gas reservoirs. F and G are reservoirs for hydrogen and ethylene, respectively.

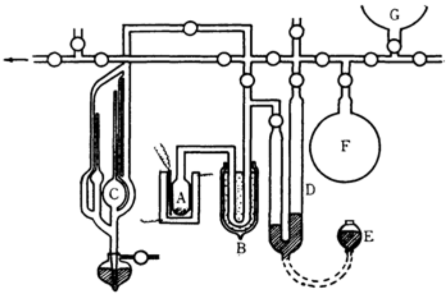

Fig. 1. Apparatus for adsorption of hydrogen on copper, copper-nickel, and nickel catalysts.

In the Knudsen pressure range, the relationship between the pressure P_1 of the reaction vessel A at the room temperature T_1 and P_2 at the reaction temperature T_2 is given as

$$P_1/P_2=\sqrt{T_1}/\sqrt{T_2}$$

In this experiment the corrected value of pressure P_2 was obtained empirically according to the method used by Kwan[2], because of the complexity of the temperature distribution of the apparatus, which was heated partially in the furnace and cooled partially by liquid oxygen.

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[1] Part I, preceding paper.

[2] T. Kwan, *J. Research Inst. Catalysis*, Hokkaido Univ., **1**, 81 (1949).

The quantities of the samples which were admitted into the reaction vessel were 2.0 g. for copper oxide and copper-nickel oxide, and 0.5 g. for nickel oxide. Reduction in hydrogen gas at a pressure of several cmHg was continued for three weeks at 200°C. In no case was there any decrease of hydrogen after about two weeks. Previous to the experiment of adsorption, the samples had been degassed at 10^{-5} mmHg for three hours at a constant temperature of 200°C.

The equilibrium pressure on each catalyst was determined as follows: After the admission of hydrogen into the reaction vessel, rapid decrease in pressure was observed with every catalyst. With nickel catalyst the pressure, after the first ten minutes of rapid decrease, was found to be constant for several hours, suggesting that the adsorption equilibrium had been rapidly attained; whereas with copper and copper-nickel catalysts, it took one or two days until the pressure became apparently constant.

In the cases of nickel and copper catalysts each equilibrium pressure was determined by the procedure used by Kwan[2]. That is, when the pressure attained a constant value, the temperature was lowered or raised, then was kept constant until the pressure attained a constant value; then the initial temperature was restored. At this initial temperature the initial equilibrium pressure was reached rapidly on nickel and could easily be determined, but it took about one or two hours on copper.

In the case of copper-nickel catalyst, changing the pressure by raising the temperature was not so simple as in the cases of copper and nickel catalysts. When the temperature was raised from 100° to 130°C, it was found that the pressure increased for a time, then decreased gradually to a constant value; and when the temperature change was repeated, the pressure which had apparently become stable at each temperature, attained a constant value lower than the former one. The difference in pressures between the system immediately after the attainment of the temperature and that in the steady state was found to diminish gradually until it became hardly recognizable, as shown in Fig. 2. The authors define the equilibrium pressure with reference to this final state.

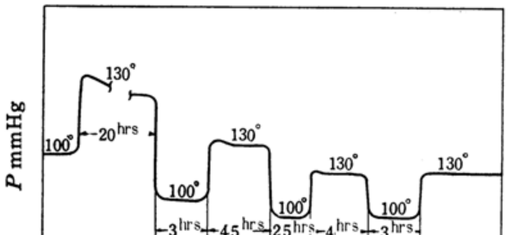

Fig. 2. Pressure change of hydrogen on copper-nickel catalyst on raising and lowering temperature.

After the adsorption experiment had been carried out, the surface area was determined from the adsorption isotherm deta of ethylene at -183 °C by the B. E. T. method. In the cases of copper and of copper-nickel catalysts, after the surface areas were determined, the temperature of the reaction vessel was raised to 400°C, and the catalysts were treated in hydrogen for a week. Then the same observations as those mentioned above were reported.

Results

The relationship between surface area and reduction temperature in the three catalysts is shown in the previous report[1]. From the result it is found that the surface area of nickel is remarkably larger than those of the others at every reduction temperature, and that of copper-nickel catalyst is a little larger than that of copper catalyst. On raising the reduction temperature from 200° to 400°C, each catalyst decreased its surface area, to about 30% of its original value for nickel catalyst, to 35% for copper catalyst, and to 45% for copper-nickel catalyst. This shows that the addition of nickel increases the surface area of the catalyst, and prevents the surface from shrinking with the increasing reduction temperature.

Fig. 3 gives the hydrogen adsorption isotherms on the catalysts, namely that on nickel catalyst determined at 100° and 120°C, that on copper catalyst at 100° and 130°C, and 160°C and that on copper-nickel catalyst at 100° and 130°C. The results are shown by a plot of the logarithm of the adsorbed quantity V in cc. N. T. P. per g. against the logarithm of the equilibrium pressure P_e in mmHg. The curves show that Freundlich's adsorption formula is not applicable to any of these catalysts, and that the amount of hydrogen adsorbed on nickel catalyst is by far the largest of the three, about ten times that of copper-nickel catalyst, while that of copper-nickel catalyst is about five times that of copper catalyst at 100°C. But when the adsorption amounts are represented as those per unit area, that of nickel catalyst is not larger than that of copper catalyst. Thus, the adsorption amount of copper catalyst is about 1.6 times larger, and that of copper-nickel catalyst is about five times larger than that of nickel catalyst, at the same equilibrium pressure of 10^{-2} mmHg.

From these isotherms, the differential heats of adsorption Δq were determined according to the usual equation

$$\Delta q = RT^2 (\partial \ln P_e / \partial T)_V,$$

where P_e denotes the equilibrium pressure, T the absolute temperature, V the amount adsorbed.

The results are shown in Fig. 4. These results show that the heat of adsorption of hydrogen on copper is remarkably smaller than that of nickel catalyst at the same coverage, that of copper catalyst being 10.6 kcal./mol., and that of nickel catalyst 24.2 kcal./mol. on each sparsely covered surface. The heat of copper-nickel catalyst may be the same as that of copper catalyst as presumed

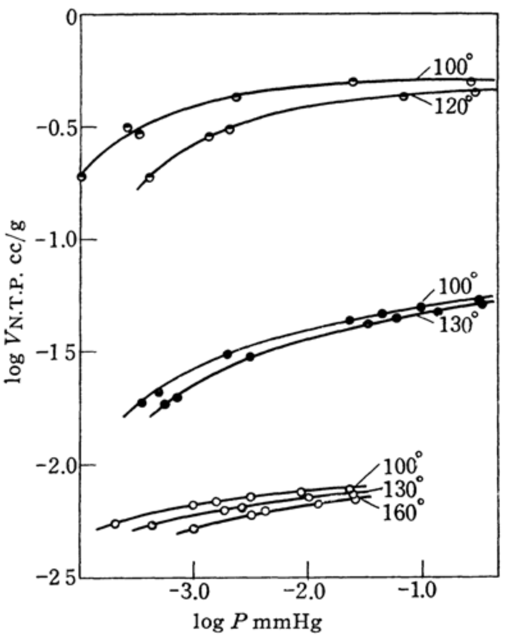

Fig. 3. Adsorption isotherms of hydrogen on copper, copper-nickel, and nickel catalysts reduced at 200°C.
○ Copper, ● Copper-nickel, ◓ Nickel.

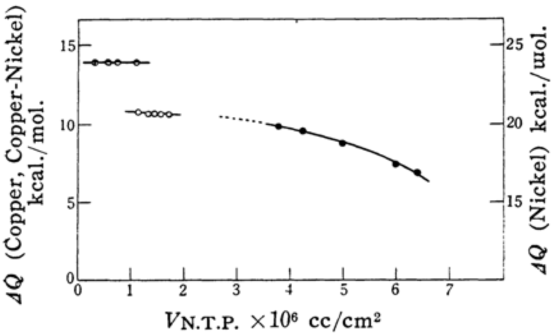

Fig. 4. Adsorption heats of hydrogen on copper, copper-nickel, and nickel catalysts reduced at 200°C.
○ Copper, ● Copper-nickel, ◓ Nickel.

by extrapolating the heat curve of copper-nickel catalyst up to its sparse coverage.

Fig. 5 shows the rate of adsorption of hydrogen on copper and copper-nickel catalysts, represented by a plot of the logarithm of the pressure P against time. The results show that the first-order equation can not be applicable to the rates contrary to the results of Kwan³⁾. The dotted line in the figure indicates the results obtained by Kwan, which are represented by a straight line. It is found that the rate of adsorption on copper catalyst in our experiment is far greater than that given by Kwan.

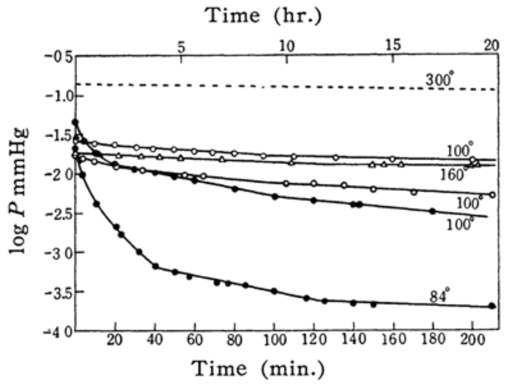

Fig. 5. Changes of hydrogen pressure with time on copper and copper-nickel catalysts.
● Copper-nickel reduced at 200°C,
○ Copper reduced at 200°C, △ Copper reduced at 400°C (time unit is hr.),
---- Copper reduced at 450°C (time unit is hr.), reproduced from Kwan⁵⁾.

In the case of the copper and copper-nickel catalysts reduced at 400°C, the rates of adsorption decrease markedly when compared with those reduced at 200°C; and the pressure decrease of hydrogen still continues after a week. Therefore, the isotherms of those reduced at 400 °C could not be obtained.

Discussion

The heat of adsorption of hydrogen on nickel has already been measured by many reseachers⁴⁾. However, the results of these measurements do not agree among themselves, and the value (26 kcal.) given by Kwan³⁾, who carried out his experiment very carefully, is nearest to the authors' value of 24.2 kcal. for a sparsely covered surface.

The reports on the heat of adsorption of hydrogen on copper are not so numerous as those on nickel. Kistiakowski et al⁵⁾ measured it by means of a glass vacuum calorimeter, and found a rise in the curve of heat of adsorption when plotted against the amount adsorbed; about 4 kcal. for a sparsely covered surface, 18 kcal. for a more densely covered surface, and 12 kcal. for a fully covered surface. The unusually low value and the sudden rise to the maximum value are unacceptable in the light of recent researches on the heat of adsorption on other metals, which invariably shows that the heat of adsorption gradually decreases as the amount adsorbed increases.

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3) T. Kwan, *J. Research Inst. Catalysis*, Hokkaido Univ., **1**, 95 (1949).

4) P. A. Beebe and H. S. Taylor, *J. Am. Chem. Soc.*, **46**, 43 (1924). C. F. Fryiing, *J. Phys. Chem*,, **30**, 818 (1926). O. Beeck, "Advances in Catalysis," Academic press. Inc., N. Y. (1950). p, 173.

5) Kistiakowski and Taylor, *Z. Physik. Chem.*, **125**, 341 (1929).

Ward[6] reported that the heat of adsorption on copper is within the wide range of about 80—9.8 kcal. In his report there is no detailed description of the process of reduction of the sample. It seems that the irreproducibility of adsorption, as well as the large value of the heat found after the initial treatment of baking of the sample, might be due to the reaction between hydrogen and the oxygen remaining on the surface of the sample. The value of 9.8 kcal. which was obtained after the last treatment of baking sample seems to be most reliable in his experiments, which agrees approximately with the value obtained in our experiment. Therefore, it is most probable to estimate the heat of adsorption on copper to be approximately 10 kcal. Thus, the heats of adsorption on copper and on copper-nickel coincide with each other, but they are both vastly different from the heat of adsorption on nickel. This suggests that the surface of copper-nickel catalyst is mainly composed of copper.

The error of the heat of adsorption is about 0.5 kcal. in this experiment. Using the heats of adsorption of hydrogen on pure copper and nickel catalysts at near zero coverage (24.2 and 10.6 kcal.), and the ratio of adsorption amounts per unit area at zero coverage $X_{\mathrm{Cu}}/X_{\mathrm{Ni}}$ (2.0), the proportion of the area of the exposed nickel on the copper-nickel catalyst to the total surface area—even if the exposed nickel particles exist on the surface of the catalyst—can be estimated as about 6% or less. This value is far smaller than that value of 17% estimated by the study reported previously[1]; and therefore, it is suggested that the nickel particles, which have been supposed to exist on the surface of the catalyst, are covered with films of copper which has a far lower melting point than nickel. It was found that the wall of the reaction vessel was colored by copper during the reduction of the copper-nickel catalyst. This facts shows that the copper vaporizes easily from the surface of the copper-nickel catalyst which is covered with copper atoms during the reduction.

It is quite plausible that the orientation of the copper films formed by the evaporation of the copper atoms was affected by the structure of the underlying metal face, and that the great activity of the copper-nickel catalyst was due to a special orientation of the copper atoms on the nickel particles of the surface of the catalyst, and to the electronic effect of nickel on copper. This is supported by Beeck[7], who pointed out that copper films prepared by the evaporation in hydrogen are far more active than ordinary copper films; and by Dowden[8], who electronically described the catalytic activity of copper-nickel alloy catalyst.

The decrease of the hydrogen adsorption activity of the copper-nickel catalyst with increase in reduction temperature may be due to the growth of the thick copper layer on the nickel particles, and consequently to the decrease of the electronic effect of the nickel on copper.

According to Kwan[3] the adsorption rate on copper is represented by a first-order expression throughout the adsorption process, while the results obtained in this experiment do not, and are far greater in value. Kwan carried out the reduction of the sample at high temperature (450°C), and measured a comparatively initial part of adsorption. We have found that the rates of adsorption on copper and copper-nickel catalysts decrease as the reduction temperature rises. It is doubtful whether his results could be represented by a first-order expression, if the pressure change due to adsorption had been measured until adsorption had practically ceased.

Summary

(1) The adsorption of hydrogen on copper, nickel and copper-nickel (containing 1% nickel) catalysts, prepared from the nitrates of copper and nickel were observed in the range of 100° to 130° or 120°C.

(2) The shrinkage of surface with increase of reduction temperature was smaller for copper-nickel catalyst than for pure copper catalyst.

(3) The rates of adsorption of hydrogen on copper and copper-nickel catalysts were far smaller than that of nickel; and the adsorption amount per unit area was the greatest for copper-nickel catalyst, while that of nickel catalyst was the smallest among the three.

(4) The differential heats of adsorption of hydrogen at near zero coverage were given as 10.6 kcal. both for copper and copper-nickel catalysts, and 24.2 kcal. for nickel catalyst.

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[6] A. F. H. Ward, *Proc. Roy. Soc.*, **A133**, 506 (1935).

[7] O. Beeck, *Discussion Faraday Soc.*, No. 8. 118(1950).

[8] D. A. Dowden, and P. W. Reynolds, ibid., No. 8. 184 (1950).

(5) On the basis of the coincidence of the adsorption heats of copper and copper-nickel catalysts, it is suggested that the nickel particles supposed to exist on the surface of the copper-nickel catalyst may be covered with copper atoms.

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