Catalytic Activities of Copper-nickel Alloys for Hydrogenating Reactions

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The catalytic activities of copper-nickel alloys for hydrogenating reactions have been interpreted by Dowden and Reynolds[1] in the light of the modern electronic theory of metals. In their studies, massive copper-nickel alloys (foils) were employed as the catalysts. Since an early study by Schwab and Brennecke[2], many investigations[3-7] of hydrogenating reactions have been carried out employing granular copper-nickel alloys prepared chemically. However, no such obvious relation to the number of holes per atom in the 3d-band of these alloy has been found as Dowden and Reynolds found for the massive alloys. Moreover, the results are not in accordance with one another. The cause of this discrepancy in the results has not yet been explored. It was sometimes proposed that the granular catalyst might be joined with a homogeneous alloy as in the case of the massive alloys. As a result of previous studies[8,9] with an electron diffraction of the reactions between hydrogen chloride and the catalysts, the writers proposed that the concentration of nickel at the surface of the granular copper-nickel alloy differs from that of the interior of the composing particles. The present work is concerned with the catalytic activities of hydrogenations of ethylene and benzene over two copper-nickel series, i. e., granular and massive alloys, in order to make sure whether the discrepancy in catalytic activities between granular alloys and massive alloys can be explained by the nonuniform distribution of nickel in the granular alloys. In addition, the heat of the adsorption of hydrogen and the amounts of hydrogen adsorbed on granular alloys were measured in order to confirm the previous data reported by the writers[10] and to discuss the relation between the heat of adsorption and the catalytic activity of the copper-nickel alloy.

Experimental

The tests of the activity of two series of catalysts (granular and massive alloys) were made by a static method, using ethylene. The test of benzene was made only for granular alloys by a flow method.

Granular alloys were prepared from solutions of copper and nickel nitrates and their mixtures, by evaporating them to dryness and by igniting them to metal oxides in a furnace at 500°C, in a way which was described elsewhere[8,9,11]. Prior to use, the oxides were then reduced at 200°C for about three weeks in an atmosphere of hydrogen, which was replaced about five times. At the end of the reduction period, the catalysts were evacuated for several hours at 200°C to a pressure of 10^{-5} mmHg. Several samples of each catalyst were analyzed for total nickel and total copper to provide data for a study of the composition variable.

Massive alloys were prepared from mixtures of electrolytic copper and nickel by completely melting them in a furnace. The ingots containing less than 40% nickel were rolled in the form of a sheet 0.1 mm. thick, while those of 65% and 80% nickel were cut down in the form of a plate 1 mm. thick. These sheets and plates were polished with emery paper and washed by pure alcohol and distilled water; then they were reduced in an atmosphere of hydrogen.

The ethylene used was prepared by the dehydration of ethyl alcohol with sulfuric acid and was purified by vacuum distillation using a liquid oxygen bath. The benzene used was commercially available material which was purified by stirring it with sulfuric acid, with sodium hydroxide solution and then with water, and which was dried by contact with calcium chloride and then distilled.

The hydrogen used for the adsorption measurement or for the hydrogenation reaction of ethylene was prepared by the electrolysis of water and was purified by diffusion through a palladium thimble, preceded and followed by liquid oxygen traps. The commercial electrolytic hydrogen was used for the test of the activity of benzene. It was purified by

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copper wire at 350°C, followed by anhydrous calcium chloride.

The apparatus used for the hydrogenation of benzene was a modification of that of Ipatieff[4]. The diameter of the reaction tube was 20 mm., and the length of tube was 30 cm. In every experiment, 20 g. of oxide was mounted on a glass boat 25 cm. in length. After the end of the reduction of the oxide at 200°C with the stream of hydrogen, the mixture of hydrogen and benzene at atmospheric pressure was passed in a volume ratio of 8 : 1 at a flow rate 100 ml./min. over the catalyst at 190°C; then about 2 l. of hydrogen were used to sweep the catalysate which remained in the catalyst into the receiver. Three grams of benzene was used for each run. The composition of the liquid catalysate, a mixture of benzene and cyclohexane, was determined by means of the refractive index.

The apparatus used for the hydrogenation of ethylene and for the adsorption of hydrogen was the same as that described in a previous paper[11]. In the case of the hydrogenation of ethylene, the apparatus was connected with a U-tube manometer of apiezon oil to facilitate the measurement of the pressure change in the reactions. The volume of the reaction vessel which included the U-tube manometer was 155 cc. For the test of activity, about 0.5 or 2 g. of granular oxide or about 0.2 m^2 (apparent area) of massive alloy were loaded in the vessel. Care was taken by using a liquid oxygen trap or a dry-ice trap, to prevent the contamination of the catalyst. A mixture of ethylene and hydrogen in a volume ratio of 1 : 1 and a total pressure of 20 mmHg was admitted into the reaction vessel; then the decrease in pressure was followed by the manometer, controlling the temperature of the reaction vessel at a constant value. The temperatures of the reaction were 100, 120, 140 and 160°C. In every interval of the test, catalysts were reduced afresh with hydrogen for two or three days at 200°C. The isotherms of the hydrogen adsorption on granular samples, i. e., 2.0 g. of 40% nickel and 0.5 g. of 86% nickel and pure nickel, were obtained at three temperatures, 100, 120 and 140°C, in the same way as has been described elsewhere[11]. The samples used for the adsorption of hydrogen were of 40% nickel, 86% nickel and pure nickel. After the catalyst testing had been completed, each sample was evacuated at 200°C for about three hours until a pressure of better than 10^{-5} mmHg had been attained. The B. E. T. area measurements were then made on each catalyst by ethylene, its cross-sectional area being taken to be 17.2 Å^2.

Results

In the hydrogenation of ethylene, both on the granular and the massive alloys, the relation of the logarithms of the rates to the time was represented by linear lines, except for a few minutes of the initial stage of the reaction. Figure 1 shows examples of the massive 80% nickel alloy. As can be recognized in the figure, the inclination of the linear part of the curve is not practically affected by the reaction temperature. In order to know the cause of the discontinuity in these curves, the adsorptions of hydrogen and ethylene were observed under the same initial pressures as in the hydrogenation, and a comparison between the two pressure changes was made. It was concluded after the comparison that the steep decrease in every initial stage of the hydrogenating reaction is probably due to the adsorption of ethylene on the catalyst. Figure 2 shows the relation of the activities in the hydrogenation of ethylene to the nickel percentage in the massive catalysts. The rates in the figure, at 120°C, were obtained from the inclination of each linear part of the curve. The figure shows that the pure copper was practically

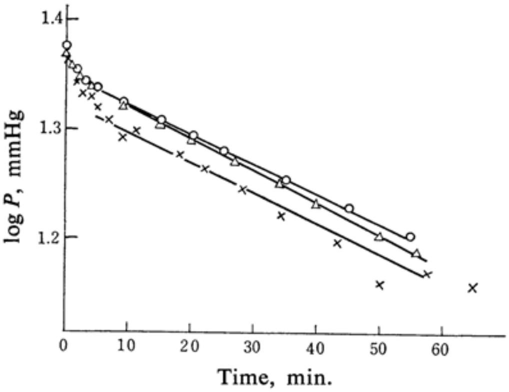

Fig. 1. Rates of hydrogenation of ethylene on massive 80% Ni alloy.
—×— 100°C, —○— 120°C, —△— 160°C

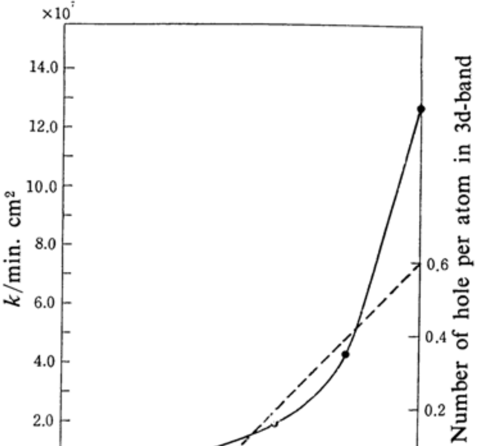

Fig. 2. Catalytic activities of massive Cu, Ni and Cu-Ni for the hydrogenation of ethylene at 120°C.
---- Number of hole per atom in 3d-band

inactive for the reaction, and that alloying 60% or less of nickel with copper causes a gradual rise in the activity, while increasing the nickel content to over 70% causes a conspicuous rise in the activity, showing a maximum in pure nickel. Figure 3 shows the results of the hydrogenation of ethylene at 120°C and that of benzene at 190°C over the granular alloys. In the case of ethylene, the activity of pure copper is quite small, while it increases markedly on a slight addition of nickel (1%). The activity does not increase, but declines slightly on a further increasing of the nickel content ; it is

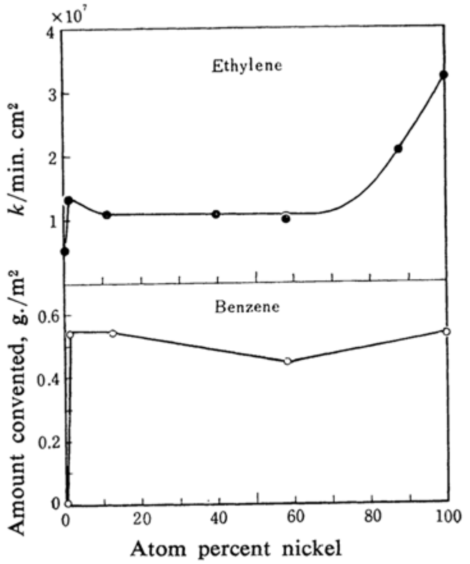

Fig. 3. Catalytic activities of granular Cu, Ni and Cu-Ni for the hydrogenations of ethylene and benzene.

—●— Ethylene, at 120°C by static method
—○— Benzene, at 190°C by flow method

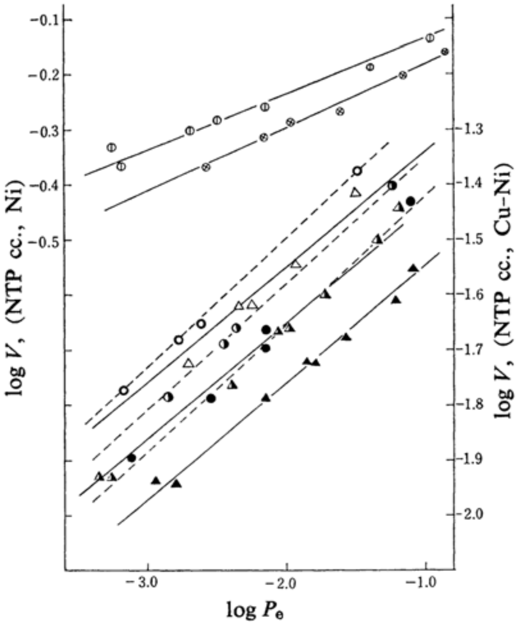

Fig. 4. Adsorption isotherms of granular Ni and Cu-Ni.

—⦶— Pure Ni {100°C
—⊗— (0.5 g.) {120°C
--○-- 40% Ni {100°C
--◐-- (2.0 g.) {120°C
--●-- {140°C
—△— 86% Ni {100°C
—◭— (0.5 g.) {120°C
—▲— {140°C

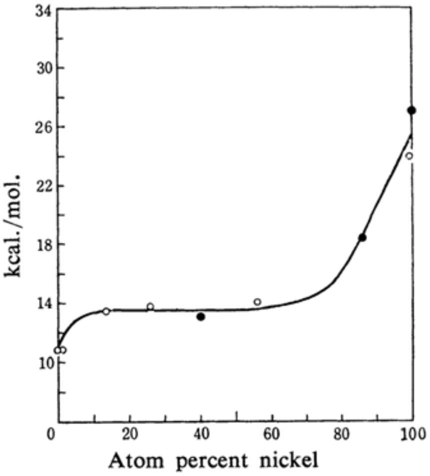

Fig. 5. Heats of adsorption of hydrogen on granular Cu, Ni and Cu-Ni.

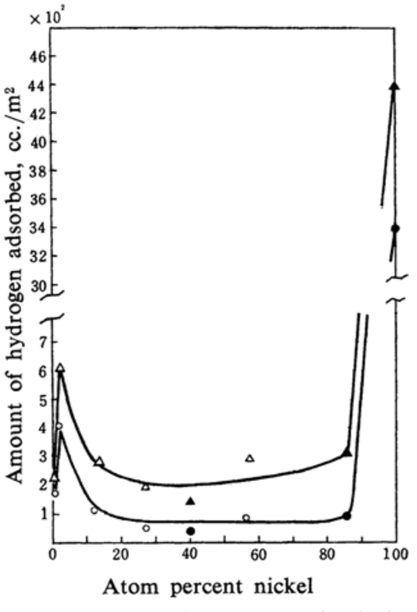

Fig. 6. Amount of hydrogen adsorbed on granular Cu, Ni and Cu-Ni.

-○- $P_e=10^{-3}$ mmHg, -△- $P_e=10^{-1}$ mmHg kept constant for the wide range of nickel content from about 10% to 60% and then increases again, showing a maximum in pure nickel. In the case of benzene, the activity is taken as the amount (in the unit, g.) of benzene converted to cyclohexane per unit area of the catalysts while 3.0 g. of benzene was being passed at a constant velocity over the catalysts. The figure shows that the activity of the alloyed catalysts is not substantially affected by the nickel content. Figure 4 shows the isotherms of the adsorption of hydrogen on 40, 86 and 100% nickel alloys of a granular form. Figures 5 and 6 show the relation of the heat of the adsorption of hydrogen at sparse coverage and of the amount of hydrogen adsorbed to the component of granular alloys findings which were given by the isotherms. The heats were calculated by adapting the Clausius-Clapeyron equation to the isotherms. The open circles and triangles in the figure show findings previously determined[10]. Linear relations can be found within the range of experimental accuracy over a wide range of alloy composition, except in the high-content range of both copper and nickel, as in the case of the hydrogenations of the same alloys. Table I shows the B. E. T. areas of the alloys used.

TABLE I. THE B. E. T. AREAS OF Cu, Ni AND Cu-Ni ALLOYS

Massive alloys reduced at 200°C (Total area)		Granular alloys reduced at 200°C	
Ni, %	m²	Ni, %	m²/g.
0	0.31	0	0.69
1	0.29	1	0.80
12	0.27	12	3.3
30	0.25	26	4.0
60	0.52	40	4.6
80	0.22	57	4.7
100	0.20	86	6.1
		100	3.0

Discussion

The results reveal that the activities of the massive copper-nickel alloys in the hydrogenation of ethylene may be interpreted by the Dowden theory. However, the activities of the granular alloys can not be interpreted simply by his theory.

The surface of the granular copper-nickel alloy has been discussed over a long period by many researchers[3,12-15]. Among them, Best and Russell[6] and Hall and Alexander[15] have proposed that the surface is composed of an equilibrium alloy. Their opinion were based on the coincidence of the lattice parameters given by X-ray diffraction with those of the equilibrium alloys. Problems will remain, however, in accepting their opinion inasmuch as the rather strong penetrating power of X-rays is not suitable for the investigation of the surface.

Our previous studies[16] of the granular copper-nickel alloys by an electron diffraction had led to the conclusion that the surface of copper-nickel powder is composed of microcrystals of various compositions. A more detailed conclusion could be derived from studies[8,9] of the reaction of the granular alloys (1 and 12% nickel) with hydrogen chloride gas. These results show that the amount of nickel was greater in the upper layer of the composing particle than in the interior and that the amount per unit area of the catalyst was smaller in the 12% nickel alloy than in the 1% nickel alloy. From these facts, it can be surmised that the great increase in activity caused by a slight addition of nickel (1% nickel) in a granular alloy depends upon the preferential aggregation of nickel on the surface and that the activity is determined mainly by the amount of nickel on the surface. The decline in activity caused by the increase in the concentration of nickel from 1 to 12% would be due to the decrease in the amount of nickel on the surface, and the extensive and essentially linear portion of the catalytic activity would reveal an invariablity in the concentration of nickel on the surface. Interpretations can be made in the same way for the heat of adsorption and for the amount of hydrogen adsorbed on the granular alloys. A discrepancy can be recognized, however, between the heat of adsorption and the amount adsorbed in the 1% nickel alloy. The heat seems to be quite small in the light of the great amount of hydrogen adsorbed. This would be due to the following troublesome fact which has been established by the present writers[11] concerning the adsorption of hydrogen on pure copper and on the 1% nickel alloy: the rates of the adsorption of hydrogen on these catalysts were too slow for it to be possible to find readily a distinct equilibrium pressure, because of the irreversibility of adsorption.

It has been recognized by many researchers[17]

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that the reaction is of the first order with respect to hydrogen and of zero order with respect to hydrocarbons. This would indicate that the amount of hydrogen adsorbed on a catalyst is far less than that of hydrocarbon. We can now understand the fact, established in our study, that the adsorbing ability of hydrogen is related to the catalytic activity.

Shallcross and Russell[18) have recently studied the ortho-parahydrogen interconversion over granular copper-nickel alloys prepared by a solution of ammonium bicarbonate. They found a constant activity in the alloy region from about 10 to 95% nickel. The shape of the curve for the activity of the reaction is substantially the same as those for the hydrogenation reactions of the granular alloys used in our study. In their report, they claimed that the catalysts were homogeneous both in bulk and on the surface. Very recently, Shield and Russell[19) have studied the heats of the adsorption of hydrogen on the same catalysts. In their paper, they ignored our results, which we had shown to them. Their scanty results are, however, quite similar to those measured by the writers. The agreement in both heats would indicate that the surfaces of the two granular alloys do not differ from one another.

In our study, the activity of granular pure nickel was the greatest for the hydrogenation of ethylene, but not for that of benzene. These results do not agree with those reported in other papers. Schwab[2) and Hall[7) found the maximum activity for the hydrogenation of cinnamic acid and benzene in a nickel-rich region, but Best and Russell[6) found the greatest for that of ethylene in a copper-rich region. The situation is very complicated. However, it can be noted that the results which gave the maximum activity in an alloy were obtained by the flow method. In the case of the flow method, the hydrogen used for the reduction of the catalyst occasionally remains in the catalyst because of the difficulty in evacuating sufficiently due to the characteristics of the apparatus. Attention should be called to the recent work of Hall[7). He has found that the hydrogen added in the temperature range 100 to 300°C acts as a promoter for copper-nickel catalysts but as an inhibitor for pure nickel. Although a theoretical interpretation of his results has not yet been established, it seems certain that the decrease in the activity found in the studies of the pure nickel and nickel-rich regions might be related to the hydrogen preadsorbed on (or dissolved in) alloys or pure nickel.

Many other factors might cause the decrease in the catalytic activity in the nickel-rich region and the disagreement in the relation of the activity to the composition of the alloy between studies. It should be emphasized, however, that the activity of the granular copper-nickel alloy may best be discussed by taking account of the non-uniform distribution of nickel on the surface.

Summary

The hydrogenation of ethylene and benzene on two series of copper-nickel alloys, i. e., massive alloys prepared physically and granular alloys prepared chemically, was carried out in order to determine the cause of the disagreement of the catalytic activities which have been found in these alloys. The adsorption of hydrogen on granular alloys was also examined to learn the heat of adsorption and the amount adsorbed; the results were compared with the activities of the alloys.

The activities of massive alloys may be interpreted by the Dowden theory, but those of granular alloys could not. The activities of granular alloys were interpreted in connection with the concentration of nickel at the surface, which can be considered to be different from that in the interior. It was concluded that the amount of hydrogen adsorbed, the heat of adsorption, and the catalytic activity of granular alloy are related to the concentration of nickel at the surface.

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