The Surface of Copper-Nickel Catalyst. I. The Reaction between Hydrogen Chloride and the Catalyst

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Much work has been done by many researchers on the structure of copper catalysts containing a small amount of nickel as a component of the catalyst, prepared from copper and nickel salts, but much remains unexplored. Emmett and Skau[1], as the result of a study on hydrogenation of hydrocarbons, suggested that the nickel which was added to a copper catalyst might alter the crystal habit of copper, or collect preferentially on the surface of the powdery catalyst. From the results of measurements by Morris and Ross on magnetic susceptibility, Selwood[2] assumed that the surface of copper catalyst containing a small amount of nickel consists of microcrystals of pure nickel or of a nickel rich alloy. Recently, from a study by means of X-ray diffraction, Best and Russel[3] proposed that the catalyst should be an alloy.

The present investigation was undertaken to determine the state of the nickel which is contained in the catalyst — whether it exists as an alloy, or as microcrystals of pure nickel or as some other special form — by studying the reaction between hydrogen chloride and the catalyst, and also by the use of an electron microscope.

It is well known that hydrogen chloride reacts readily with copper and nickel, producing their chlorides, which are soluble in water. When hydrogen chloride is brought into contact with the copper-nickel catalyst, the reaction can be expected to start from the surface and extend to the interior of the catalyst. Two kinds of cations, Cu^{++} and Ni^{++}, will be found in the solution obtained by washing the catalyst with water; and from this solution the amount of nickel on the surface of the catalyst can be estimated. With this view in mind, the experiments were carried out on a copper catalyst containing 1% nickel (copper-nickel), and also both on copper and on nickel, for the purpose of comparison of their reaction rates.

1) P. H. Emmett and N. Skau, *J. Am. Chem. Soc.*, **65**, 1029 (1943).
2) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., N. Y. (1943), p. 257.
3) J. Best and W. W. Russel, *J. Am. Chem. Soc.*, **76**, 838 (1954).

Experimental

The copper catalyst was prepared from metallic copper supplied by Ishizu Chemical Co. by dissolving it in extra pure nitric acid, recrystallizing the copper nitrate thus obtained, drying the nitrate gently on the water bath, and finally igniting it at 500°C in air. The nickel catalyst was prepared from metallic nickel supplied by Kanto Chemical Co. in the same way as the copper catalyst. The copper catalyst containing 1% nickel was prepared by dissolving both nitrates in distilled water, then gently drying the mixture on a water bath, and igniting it at the same temperature as in the cases of the copper and nickel catalysts. The spectroscopic observation of the copper purified by recrystallization showed traces of Mg, Fe, Si, Mn, and Pb.

The hydrogen used for reduction was prepared by electrolysis of water, and purified by diffusion through a palladium thimble, preceded and succeeded by liquid oxygen traps. The ethylene used for the measurement of surface area was prepared by the dehydration of ethyl alcohol with sulfuric acid, and purified by vacuum distillation.

Hydrogen chloride was prepared from hydrochloric acid by heating it in a flask. The gas evolved by heating was condensed in a trap cooled by liquid oxygen, distilled in vacuum, and then dried by putting it in contact with phosphoric pentoxide for about two weeks.

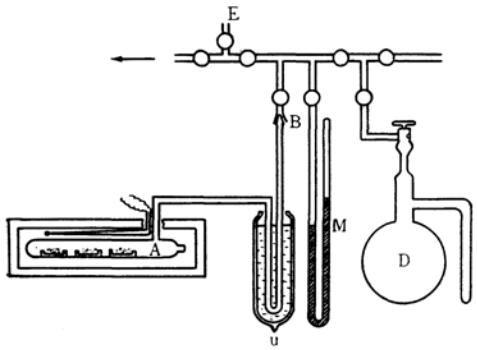

Fig. 1. Apparatus for the reaction between hydrogen chloride and catalysts.

Fig. 1 shows the main parts of the apparatus for examining the reaction between hydrogen chloride and the catalyst. In this figure, A is a reaction vessel of about 100 cc. in volume, and is made of pyrex glass. De Khotinsky cement was used to connect the reaction vessel and the part of the apparatus which is made of ordinary glass. U is a U-tube cooled by liquid oxygen or ice for the purpose of protecting the samples from being contaminated with vapors of grease and mercury. M is a mercury manometer, D a gas reservoir, and E a MacLeod gauge. 0.5 g. of nickel oxide, and 1.0 g. of their mixture were taken, and placed in pyrex boats side by side. The reduction of these oxides to corresponding catalysts with hydrogen was carried out at a constant temperature of 200°C for three weeks. After the reduction was completed, these samples were degassed at 10^{-5} mmHg at 200°C for three hours. Then the temperature was lowered to the reaction temperature of 150°C, the liquid oxygen bath of the U-tube was replaced with an ice bath, and a known quantity of hydrogen chloride was admitted into the reaction vessel. After a certain number of hours, the reaction was stopped by replacing the ice bath of the U-tube with the liquid oxygen bath to condense the residual hydrogen chloride.

The hydrogen chloride consumed by the reaction was determined by the measurement of the quantity of gas which was not condensed by the cooling with liquid oxygen, on the assumption that the gas was only hydrogen produced by the reaction.

After the reaction had been stopped, the vessel was cut open, and the samples were drawn out and were washed with distilled water until no chloride ion could be detected. To facilitate the analysis each solution was concentrated by heating on a water bath. Both metallic ions were analysed by means of the polarographic method, using ammonium chloride, ammonia, and tylose as supporting electrolytes. The suface areas of the catalysts were determined at −183°C by the B.E.T. method with ethylene using 17.6 Å^2/molec. as the cross-sectional area.

Results

Table I shows the results of the measurements of the surface area of the catalysts. In this table, the amount of sample is represented by the weight of each original oxide. In Table II are shown the conditions and the results of the experiment on the reaction between hydrogen chloride and the catalyst. In this table runs (8) and (9) represent the results of the experiments which were carried out to observe the effect of reduction temperature on the reaction. ΔP denotes the pressure decrease of hydrogen chloride in the reaction, and S and M denote respectively the single component catalyst (copper and nickel) and the mixed catalyst (copper-nickel).

Column 6 shows the number of ions produced by the reaction of one g. of each catalyst. Column

TABLE I

SURFACE AREAS OF COPPER, COPPER-NICKEL, AND NICKEL CATALYST, OBTAINED BY THE B. E. T. METHOD, USING ETHYLENE

Catalyst	Reduction temp. C°	Area $\times 10^4$ cm^2/g.
Cu	200	0.69
	400	0.25
Cu-Ni	200	0.80
	400	0.34
Ni	200	49.2
	400	16.4

TABLE II

DATA ON THE REACTIONS BETWEEN HYDROGEN CHLORIDE AND CATALYSTS

No.	Reduction temp. °C	Initial press. mmHg	Reaction time hr.	ΔP mmHg	Sample	No. of ion produced/g.	No. of ion produced/ No. of site	N_{Cu}/N_{Ni}
1	200	162.0	88	14.4	S Cu	1.1×10^{20}	15.6	14.2
					S Ni	7.1×10^{20}	1.1	1
					M Cu	1.5×10^{21}		
					M Ni	2.3×10^{19}		
2	〃	162.0	20	14.2	S Cu	2.4×10^{20}	33.6	15.3
					S Ni	1.4×10^{21}	2.2	1
					M Cu	8.0×10^{20}		
					M Ni	2.7×10^{19}		
3	〃	115.0	18	9.6	S Cu	5.8×10^{19}	8.0	13.3
					S Ni	3.6×10^{20}	0.6	1
					M Cu	5.3×10^{19}		
					M Ni	5.6×10^{19}		
4	〃	97.5	64	7.8	S Cu	4.4×10^{19}	6.0	12.0
					S Ni	3.5×10^{20}	0.5	1
					M Cu	2.7×10^{19}		
					M Ni	1.2×10^{19}		
5	〃	164.0	16	3.0	S Cu	7.0×10^{18}	1.0	16.6
					S Ni	3.9×10^{19}	0.06	1
					M Cu	1.2×10^{19}		
					M Ni	1.2×10^{19}		
6	〃	98.5	4	3.0	S Cu	1.3×10^{19}	1.8	20.0
					S Ni	5.4×10^{19}	0.09	1
					M Cu	2.3×10^{20}		
					M Ni	4.8×10^{19}		
7	〃	21.5	0.1	0.3	S Cu	2.2×10^{17}	0.03	15.0
					S Ni	1.4×10^{18}	0.002	1
					M Cu	2.3×10^{18}		
					M Ni	1.6×10^{19}		
8	400	81.0	15	1.0	S Cu	6.8×10^{18}	1.0	50.0
					S Ni	9.4×10^{18}	0.02	1
					M Cu	5.0×10^{19}		
					M Ni	6.3×10^{19}		
9	500	70.0	50	2.5	S Cu	4.0×10^{18}	0.5	50.0
					S Ni	7.1×10^{18}	0.01	1
					M Cu	5.1×10^{19}		
					M Ni	1.9×10^{19}		

7 shows the ratio of ions to the number of atoms existing on the surface of the catalyst. In these calculations the numbers of atoms on the surface of the catalysts were determined by using the assumption proposed by Yamaguchi[4], that the surface of the copper catalyst is composed of (100) faces, and that of the nickel catalyst (100) and (110) faces in the ratio of 2 to 1. The lattice constants used in these calculations were 3.608 Å for copper, and 2.49 and 3.52 Å for nickel respectively.

This shows that the number of ions produced per unit site is conspicuously larger for copper than for nickel, irrespective of the reaction time, in the ratio of about 15 to 1 in the case of every run except runs (8) and (9), where the catalysts were reduced at 400° and 500°C, and the ratio is far greater (about 50 to 1)*.

Fig. 2 shows the plot of the logarithm of the number of the ions attacked per g. of the catalysts against ΔP. It is found that the amounts of the ions given by copper and nickel catalysts increase with ΔP. Of particuler note is the fact that the number of nickel ions gained from the copper-nickel catalyst is in the range of 10^{19} to 10^{20}, practically constant, independent of ΔP, while the number of copper ion increases with increasing ΔP as in the case of the copper catalyst. The experiment on the catalysts reduced at 400° and 500°C gives the same results.

Plate 1 contains the electron micrographs of copper and copper-nickel catalysts. It is found that the copper-nickel catalyst has a conspicuously rough surface, especially after being reduced at 200°C; and many small particles of several hundred Å in diameter adhere to it. The surface of the copper catalyst is not so rough as that of copper-nickel; and the small particles which are found in the copper-nickel catalysts can scarcely be found on the copper. The surfaces of both the copper and copper-nickel catalysts are less rough when reduced at 400°C.

Discussion

The results of the experiment on the reaction with hydrogen chloride show that

4) S. Yamaguchi, *Japan Chem. Meeting*, April (1949).

* The values of the surface area used in the calculation of the ratio on the samples reduced at 500°C were those reduced at 400°C, because the measurement of the area reduced at 500°C had not been carried out.

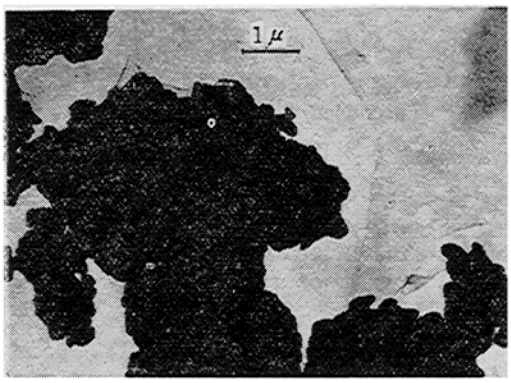

Photo. 1. Copper reduced at 200°C.

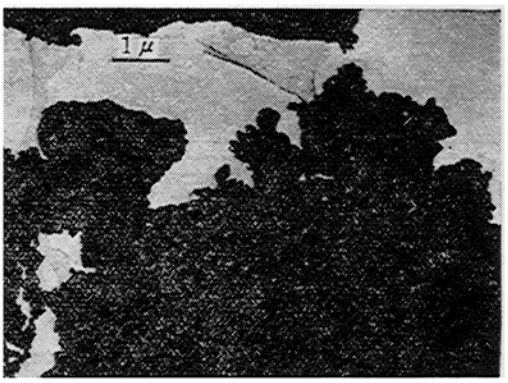

Photo. 3. Copper-nickel reduced at 200°C.

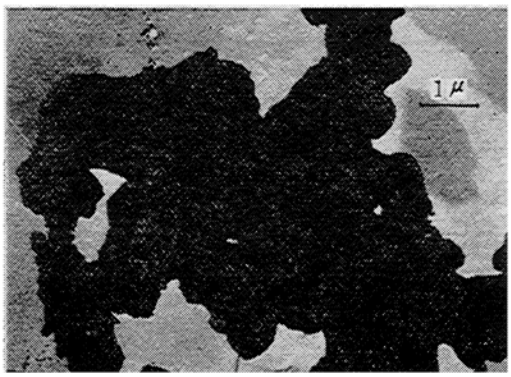

Photo. 2. Copper reduced at 400°C.

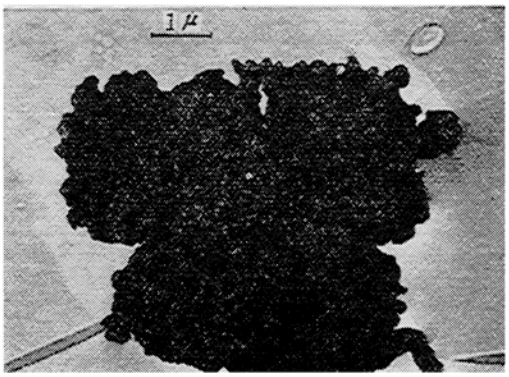

Photo. 4. Copper-nickel reduced at 400°C.

Plate 1. Electron micrographs of copper and copper-nickel catalyst.

the amount of copper ion obtained from the copper-nickel catalyst increases with the consumption of hydrogen chloride, whereas that of nickel ion remains roughly constant within the range 10^{19}—10^{20} ions, the average being 2.8×10^{19} ions/g., which is 3% of the total amount of nickel contained in the catalyst. This amount may be considered as that existing on the surface of the catalyst.

Masing[5] has recently reported that the copper does not dissolve so easily when combined with nickel, as has generally been believed. Kuczynski[6] has found that a particle of nickel of about 0.3 mm. in diameter placed on a copper plate sinters to the plate, forming a very deep groove in the copper around the place of contact, when heated in hydrogen. According to these facts and our study[7] on this catalyst by means of electron diffraction by changing the accelerating potential of electron, it can be said that the nickel in the copper-nickel catalyst does not compose an alloy.

In plate 1 the electron micrograph of a copper-nickel catalyst reduced at 200°C shows many indentations and small particles, similar in appearance to that observed by Kuczynski. Accordingly, the small particles seem to be composed of nickel, being sintered to the copper surface at the place of contact.

The ratio of the total surface area of nickel particles to that of the copper-nickel catalyst can be obtained by the following procedure, based on the assumption that the amount of nickel obtained by the reaction with hydrogen chloride is all that exists on the surface of the catalyst, and that the size of nickel particles is the same as that of the particles of a pure nickel catalyst. The average diameter $\bar{D}$ of the particles of nickel can be obtained as follows, when they are assumed to be spherical:

$$\bar{D}=6/\rho S \qquad (1)$$

where ρ is the density, and S the surface area of nickel powder per g.

5) C. Masing, "Grundlagen der Metallkunde," Springer-Verlag.. Göttingen (1951), p. 57.
6) Kuczynski, *J. Metals*, **185**, 813 (1949), Kuczynski, *J. Metals*, **187**, 169 (1949).
7) S. Yamaguchi and T. Takeuchi, in *Kolloid Zeit.*, accepted for publication.

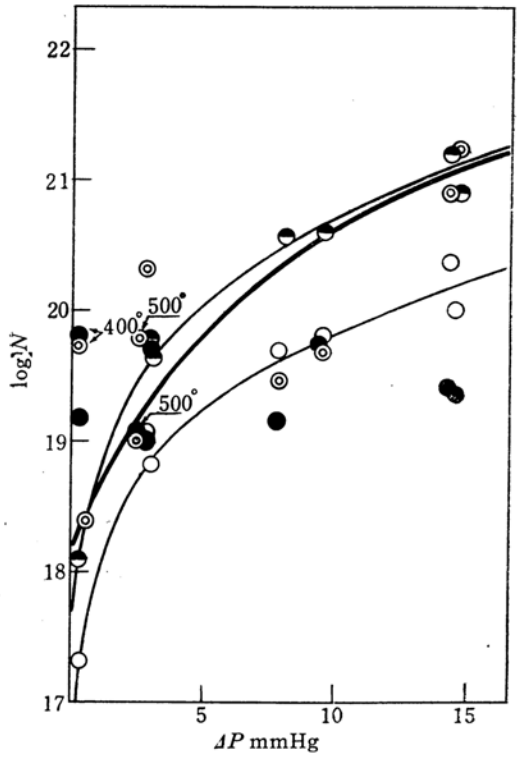

Fig. 2. Numbers of copper and nickel ions given by the reaction of hydrogen chloride with copper, nickel, and copper-nickel (per g.) as a function of ΔP.
○ Cu-ion from Cu Catalyst.
◎ Cu-ion from Cu-Ni Catalyst.
◓ Ni-ion from Ni Catalyst.
● Ni-ion from Cu-Ni Catalyst.

The number of nickel atoms $\bar{n}$ in one particle is given as

$$\bar{n}=\pi\rho\bar{D}^3N/6M \qquad (2)$$

where N is Avogadro's number, and M the atomic weight of nickel.

The number, A, of particles of nickel on a surface per g. of the catalyst is given as

$$A=n/\bar{n} \qquad (3)$$

where n is the total number of nickel atoms on a surface per g. of the catalyst.

The ratio γ of the total surface area of nickel particles to the total of the catalyst is given as

$$\gamma=A\pi\bar{D}^2/S' \qquad (4)$$

where S' is the specific surface area of copper-nickel catalyst. Assuming the value 62.4×10^4 cm.^{2}/g. to S, 8.85 to ρ, $\bar{D}$ is given as 1.1×10^{-6} cm. from equation (1). Assigning the value 2.8×10^{19} to n, and 1.0×10^4 cm.^{2}/g. to S', γ is given as 0.17 from (4)**.

According to the electron micrograph, the diameter of the particles on the catalyst can be estimated as 5×10^{-6} cm. or less. This size is roughly in accord with the calculated value $\bar{D}$ mentoined above. This corroborates the supposition we have made on the structure of the copper-nickel catalyst.

The amount of nickel obtained from the catalyst remains constant, independent of the reduction temperature. This suggests that the nickel on the surface of the catalyst has already settled on the surface before the reduction of the catalyst set in ; and the amount of nickel on the surface might depend mainly on the way in which the mixture of copper and nickel nitrates is prepared.

Summary

(1) The reactions of hydrogen chloride with copper, nickel and copper containing 1% nickel, and the observation by means of an electron microscope were carried out to determine the state of the nickel contained in the copper-nickel catalyst.

(2) The numbers of copper ion gained from the copper-nickel catalyst per g., after the reaction with hydrogen chloride, increase with the amount of consumption of hydrogen chloride used, whereas that of nickel ion is in the range of 10^{19}—10^{20}/g., practically constant, independent of the amount of the consumption of hydrogen chloride.

(3) The electron micrograph shows that the copper-nickel catalyst has a conspicuously rough surface, and many particles of several hundred angstroms in diameter are scattered on the surface of the catalyst.

(4) The results of the hydrogen chloride reaction experiment suggest that about 3% of the total amount of nickel contained in the catalyst exists adhering to the surface of the catalyst, in the state of metallic nickel particles.

(5) The ratio of the total surface area of nickel particles on the surface of the catalyst to the total surface area of the copper-nickel catalyst is given as 17%, by the calculation using the assumption that the size of the nickel particle is the same as that of the pure nickel catalyst prepared in the same way.

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** The values of S and S' used in the calculation were obtained as follows, from Table 1 ; $S=49\times10^4 M_{NiO}/M_{Ni}$ cm^2, $S'=8.0\times10^3 M_{CuO\text{-}NiO}/M_{Cu\text{-}Ni}$ cm^2, where M denotes atomic or molecular weight of material represented by the suffix.