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Raney Nickel–Copper Catalysts

II. Surface and Pore Structures

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Catalysts prepared by activating with aqueous NaOH a series of Ni–Cu–Al alloys, all containing about 50 wt% Al, were characterized by physical adsorption, chemisorption, and temperature-programmed-desorption experiments. The fraction of Al removed in the activation passed through minimum at about equal amounts of Cu and Ni in the alloy. Starting on the Ni side, the surface area, pore volume, and chemisorption of CO at − 195°C decreased, passed through a minimum at the equicomposition point for Ni and Cu, and increased again as the Cu content increased. Chemisorption of H_2 at −195°C decreased sharply from the Ni side to zero at about the equicomposition point. Temperature-programmed-desorption tests to 500°C were made on the activated samples. The H_2 evolved decreased with copper addition again to a minimum at the equicomposition point but the subsequent increase was small. This hydrogen seems related to the Ni part of the catalyst.

INTRODUCTION

Several studies have been made of changes in activity caused by the addition of copper to Raney nickel catalysts (*1–3*). However, little is known of the pore structure and chemisorption properties of catalysts prepared from Al–Cu–Ni alloys. Information on the pore structure of these catalysts seemed desirable for relating activity data to composition of the catalyst; however, incomplete activation of the alloy (*4*) and surface enrichment (*5*) are complicating factors. We have therefore examined the pore structure and surface areas of these catalysts, and have used the chemisorptions of H_2 and CO to provide a qualitative measure of the nickel and copper surface areas.

Raney nickel evolves large volumes of hydrogen when heated; these volumes usually exceed substantially the amount that can be attributed to chemisorption (*6*). The extra hydrogen has been postulated to be (a) held interstitially in the nickel, and (b) produced by the reaction of water with residual zero-valent aluminum, this water being trapped in the catalyst or part of alumina hydrates (*6*). Therefore, the ternary systems were examined to determine if these catalysts also evolve large quantities of hydrogen when heated.

METHODS

The studies were made on samples of the six catalysts used in a previous investigation (*4*). Each of the samples of original alloy contained about 50% Al by weight. Alloy 1 contained (in wt%) 41.2 Ni and no Cu; alloy 2, 38.4 Ni and 10.8 Cu; 3, 29.0 Ni

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[1] This work was conducted while M. S. Wainwright was on sabbatical leave at McMaster University.

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and 20.5 Cu; 4, 21.1 Ni and 29.2 Cu; 5, 9.4 Ni and 39.2 Cu; and 6, no Ni and 49.0 Cu.

ADSORPTION STUDIES

The adsorption of nitrogen at −195°C was studied in a glass volumetric apparatus. Samples were transferred to the adsorption vessel under water which was pumped off under vacuum. The samples were evacuated at room temperature for 8 h and then at 150°C for an additional 12 h. Samples were weighed by difference in the adsorption vessel on completion of each experiment.

In chemisorption studies, samples were evacuated by the procedure used for the adsorption of N_2. Separate catalyst samples were used for hydrogen and carbon monoxide chemisorption. The chemisorption of hydrogen was determined by measuring an isotherm on the original evacuated catalyst at −195°C; the sample was then evacuated for 2 h at −195°C and a second isotherm determined. The volume of strongly chemisorbed hydrogen was obtained by subtracting the second isotherm from the first as described by Freel and co-workers (*7*).

The chemisorption of carbon monoxide was determined in a similar way; the strongly adsorbed CO was taken as the difference of an original isotherm at −196°C and a second isotherm at −196°C following evacuation at −78°C for 2 h. Nitrogen isotherms at −196°C were also obtained on an original evacuated catalyst and on the sample used in the CO chemisorption sequence after a second evacuation at −78°C. Values reported subsequently for strongly chemisorbed CO were obtained by subtracting the original N_2 isotherm from the original CO isotherm, both plotted on a relative pressure basis. These values are within experimental error the same as those obtained from the two CO isotherms.

Temperature-programmed desorption (TPD) was determined in an adsorption apparatus that is discussed in detail elsewhere (*8*). The Pyrex volumetric apparatus, equipped with a manostat and calibrated burette, was a constant-pressure, variable-volume system. It consisted of five calibrated bulbs, a calibrated graduated burette of 100-cm^3 capacity, and a mercury manometer all connected by capillary tubing and stopcocks to the sample tube and to a vacuum system and gas storage system. A liquid nitrogen trap was located between the sample tube and the volumetric apparatus to prevent water vapor from entering the measuring system. The volume in the burette could be altered continuously by the raising or lowering of a mercury leveling bulb. During hydrogen evolution experiments the leveling bulb was automatically lowered in small steps by a reversible 3-rpm motor which is activated when the mercury

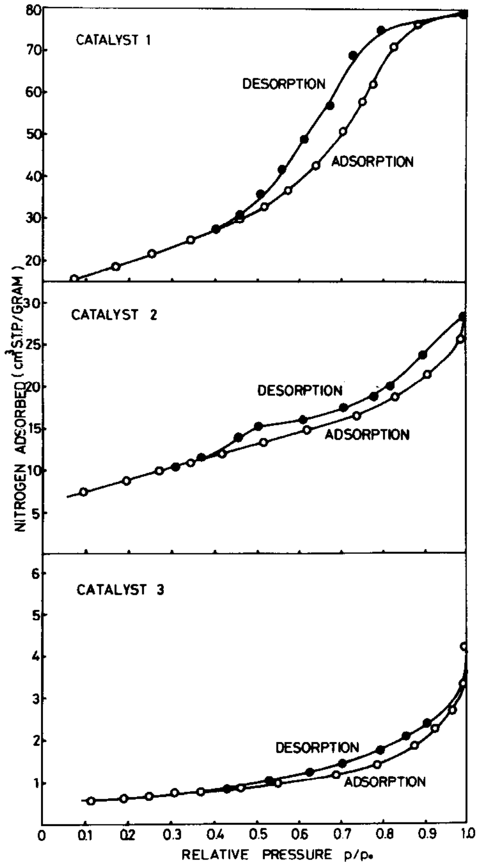

FIG. 1. Nitrogen isotherms at −195°C for catalysts prepared from Ni-rich alloys.

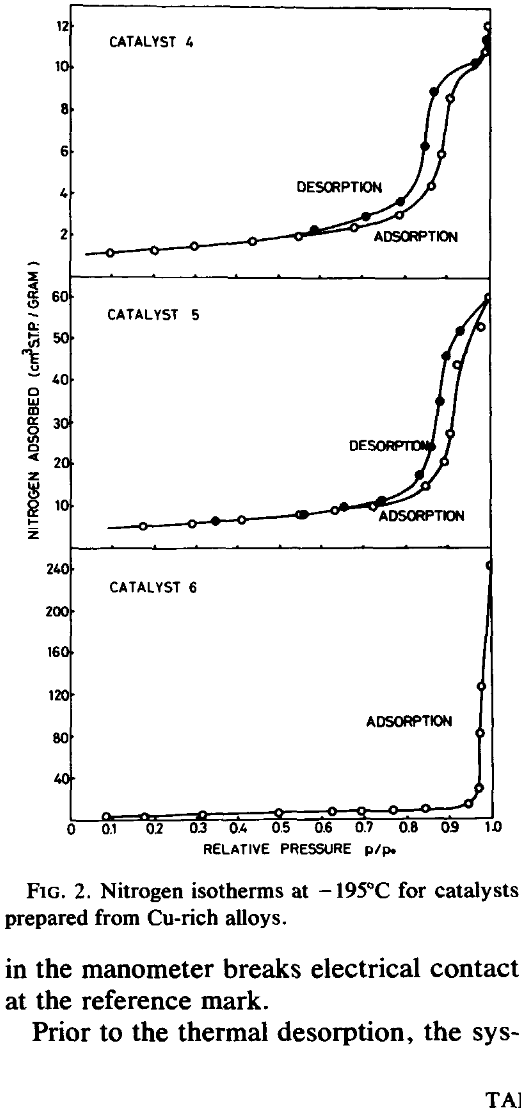

FIG. 2. Nitrogen isotherms at −195°C for catalysts prepared from Cu-rich alloys.

in the manometer breaks electrical contact at the reference mark.

Prior to the thermal desorption, the system was evacuated at 25°C until a vacuum of at least 10^{-5} Torr was indicated by a McLeod gauge. Then a small pressure of helium was admitted to the system and this pressure was maintained constant throughout the evolution experiment as described above.

The samples were heated in a tubular electrical furnace using a linear temperature program of 3.3°C/min for all catalysts. The hydrogen evolved was measured by noting the position of the Hg in the graduated burette frequently. Following the experiments the samples were weighed by difference in the desorption vessel.

RESULTS

Nitrogen isotherms for nickel-rich and copper-rich catalysts are presented in Figs. 1 and 2, respectively. Data derived from these physical adsorption isotherms are given in Table 1: the surface area by the simple BET equation and the pore volume estimated from the amount adsorbed at a relative pressure of 0.99, calculated as normal liquid. A mean pore diameter was calculated by the equation for nonintersecting cylindrical pores, $d = 4V_s/A$, where d is the mean pore diameter, V_s the pore volume, and A the surface area. The last two columns are calculated values for area and pore volume "corrected" to 1 g of Ni + Cu and complete extraction of Al.

TABLE 1

Pore Structure of Raney Cu–Ni from Physical N_2 Isotherms at −195°C

Catalyst	Fraction of Al extracted	V_m (cm^3 STP/g)	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (Å)	Corrected surface area[a] (m^2)	Corrected pore volume[a] (cm^3)
1	0.88	16.80	73.4	0.124	68	103	0.173
2	0.52	7.43	32.5	0.045	55	96	0.133
3	0.26	0.49	2.2	0.007	123	15	0.047
4	0.39	1.04	4.6	0.021	184	19	0.086
5	0.67	4.25	18.6	0.096	206	38	0.194
6	0.98	3.51	15.4	0.378	982	16	0.396

[a] The corrected quantities are obtained by dividing the surface area and pore volume per gram of sample by the fraction of aluminum extracted and by the weight fraction of Ni + Cu in the catalyst.

TABLE 2

Chemisorption of H_2 and CO on Raney Cu–Ni

Catalyst	Metal composition (atom%)			V_m[a] (cm^3 STP/g)	Chemisorbed gas[b] (cm^3 STP/g)		V_{H_2}/V_m	V_{CO}/V_m
	Ni	Cu	Al		V_{H_2}	V_{CO}		
1	75.8	0.1	24.0	16.80	3.75	14.30	0.223	0.851
2	37.4	9.7	52.9	7.43	0.19	3.80	0.026	0.511
3	22.5	14.3	63.1	0.49	0.003	0.08	0.006	0.163
4	17.4	23.3	59.3	1.04	0	0.18	0	0.173
5	11.0	42.3	46.7	4.25	0	1.38	0	0.325
6	0.1	95.5	4.9	3.51	0	2.35	0	0.670

[a] Monolayer value for physically adsorbed N_2 at −195°C.

[b] Strongly chemisorbed H_2 and CO at −195°C.

Chemisorption data are given in Table 2 for the series of catalysts. In the last two columns the amounts chemisorbed are divided by the V_m value from the N_2 isotherm, so that the chemisorption data can be compared at the same surface area.

Cumulative temperature-programmed-desorption curves are presented for nickel-rich catalysts in Fig. 3 and for copper-rich catalysts in Fig. 4. Numerical differentiation of these data gave scattered rates. The main features of the TPD studies are the temperatures of the maxima of hydrogen evolution and the volume of gas evolved to 500°C; these are presented in Table 3.

DISCUSSION

Raney nickel, sample 1, had a pore structure somewhat different from that of the catalyst obtained by Freel and co-workers (*9*) for similar extraction conditions. For this reason nitrogen adsorption was repeated; the two isotherms were the same. The isotherm of catalyst 1 was almost identical to that of a commercial catalyst (*9*) which had been activated under more severe conditions.

The pore structure of Raney copper (catalyst 6) is of great interest because of the recent use of this catalyst industrially for the hydrolysis of acrylonitrile to acrylamide in the production of flocculants. The isotherm in Fig. 2 and the data in Table 1 indicate a low-surface-area catalyst with a mean pore diameter of 1 μm. The pore volume, 0.38 cm^3/g, equals the volume change for removing Al with a density of 2.7 g/cm^3 from the alloy.

Catalyst 3 had the smallest amount of aluminum extracted and the lowest surface area and pore volume either per gram or on the corrected basis. For alloys 2 to 5 the copper-enriched Ni_2Al_3 phase was insoluble in alkali. For alloy 3 the other component, the aluminum-rich material, was removed to produce only a small amount of high-area catalyst and large voids that probably would not fill with adsorbate in the usual physical adsorption experiment. Alloy 2 also contained $NiAl_3$ which reacted in the extraction to produce high-area catalyst. Alloy 4 was similar to 3 in its structure and activation except that Cu_4NiAl_7 was found in alloy 4 as well as in alloy 5. In alloys 4 and 5 this phase was insoluble in alkali. Alloy 5 also contained $CuAl_2$ and an aluminum-rich material; both of these vanished in the activation, presumably to produce a porous copper of moderate surface area.

The chemisorption of hydrogen on Raney nickel was considerably smaller than obtained previously (*9*). However, this result was confirmed in a second experiment in

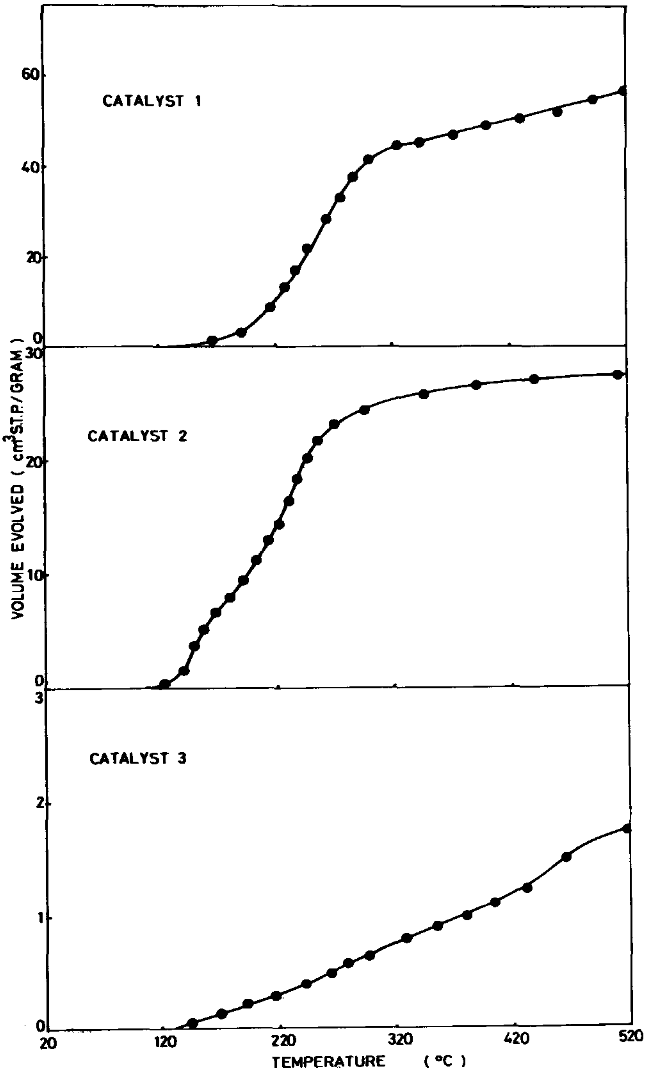

FIG. 3. Temperature-programmed-desorption curves for catalysts prepared from Ni-rich alloys.

the present system and a third in another adsorption apparatus. As shown in Table 2, the chemisorption of H_2 decreased rapidly to zero as the Cu content increased. Hydrogen was not chemisorbed on Raney copper at any temperature from −195 to 25°C.

Chemisorption of CO on Raney nickel was consistent with the values obtained by Freel and co-workers (7). Raney copper catalyst 6, which was almost pure copper metal (4), chemisorbed 2.35 cm (STP)/g of CO. The ratio V_{CO}/V_m is 0.67 for Raney copper, but this ratio drops to 0.33 for catalyst 5. A qualitative explanation of the data of Table 2 is that: (a) H_2 chemisorbs only on surface nickel, (b) CO chemisorbs only on surface nickel and surface copper, and (c) neither gas chemisorbs on binary or ternary alloys of the Ni–Cu–Al system or on alumina residues from the activation.

Hydrogen evolved on heating the catalyst to 500°C (Table 3), decreased rapidly as the copper content increased, and seems related to the nickel portion of the catalyst.

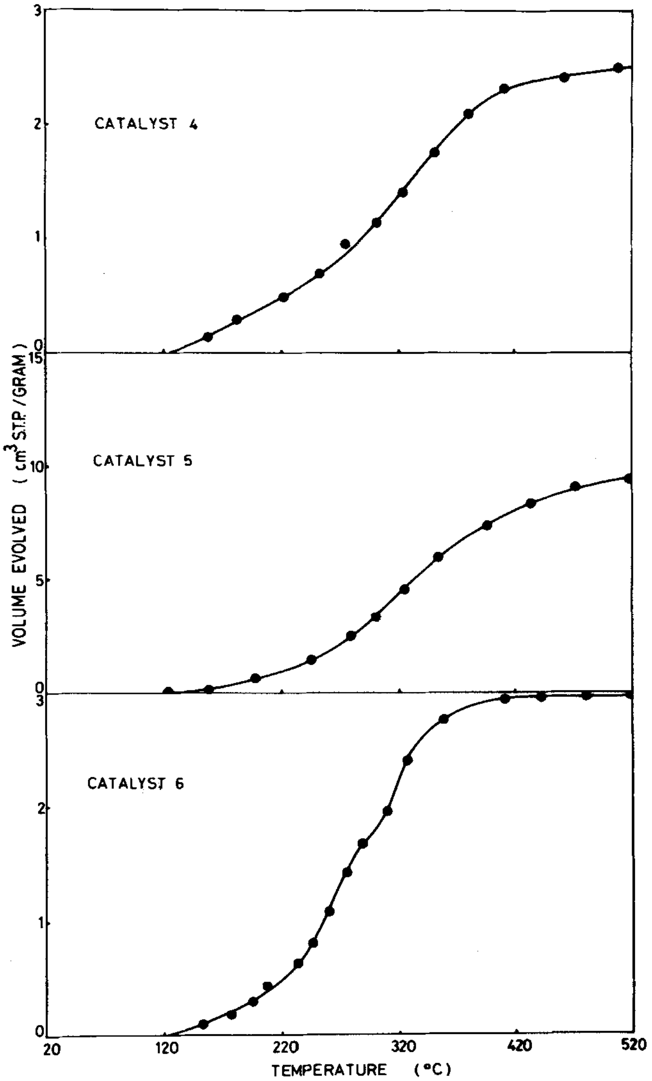

FIG. 4. Temperature-programmed-desorption curves for catalysts prepared from Cu-rich alloys.

The hydrogen evolved did not correlate well with the removal of aluminum in the activation or compositions of the alloys or catalysts. The H_2 evolved per unit area was 0.75, 0.85, 0.73, 0.54, 0.49, and 0.20 cm^3(STP)/m^2 for catalysts 1 to 6, respectively. Here the total surface area may be a measure of the catalyst generated in the activation. This ratio remained about the same for catalysts 1 to 3 and decreased slowly from catalysts 4 to 6.

The cumulative TPD curves (Figs. 3 and 4) changed slowly with temperature and the peaks in differential curves were broad as has been found for some Raney nickels (*8*). One or two maxima were inferred from the cumulative TPD curves.

The only comparable investigation of surface areas of this series of Raney catalysts has been by Reynolds (*3*) who used almost identical starting alloys. The conditions of extraction were much more severe than those used in the preparation of the present catalysts (*4*). These conditions are reflected in lower surface areas obtained for catalysts prepared from alloys corresponding to our samples 1 to 6: 34, 28, 6.6, 1.5, 3.0, and 2.8 m^2/g, respectively. The surface areas of Raney copper and the 4/1 copper–nickel catalyst are low compared with the results of the present study and may result from sintering of copper due to the severe extraction conditions.

Although we did not measure catalytic activity, discussing the results of previous workers (*1–3*) in the light of our results is worthwhile. However, the assessment of activity on the basis of hydrogenation of organic molecules may be of dubious value because the two metals are markedly different. For example, Reynolds (*3*) studied the liquid-phase hydrogenation of benzene on a similar series of Raney catalysts at 230 atm and 100°C. As the copper content was increased, the activity decreased to zero at the ratio of Cu/Ni = 0.67, and the activity remained zero to pure Cu. This drop in activity was greater than could be attributed to the decrease in specific surface area. However, Stanfield and Robbins (*2*) studied the hydrogenation of acetone over similar catalysts at 95°C and found that the addition of copper to Raney nickel decreased the activity, per unit weight, until the amounts of copper and nickel in the catalyst were equal, after which the activity increased slighly with decreasing nickel until pure Raney copper was reached. A recent study has investigated catalysts in the $NiAl_3$–Cu phase regions containing 1 to 30 atom% Cu (1). The rate of hydrogenation of dimethylacetylenyl carbinol in ethanol over catalysts made from alloys containing between 1 and 7 atom% Cu on $NiAl_3$ increased with copper content. At still higher levels of copper the activity, per unit area, decreased sharply. These three investigations indicate the large differences in behavior of the catalyst systems depending on the organic compound being hydrogenated. Another sample of the different behavior of Ni and Cu is the hydrogenation of CO. Raney nickel is very active for methanation (*12*), whereas Raney copper has been shown to be highly selective and moderately active for the methanol synthesis (*11*).

These Raney catalysts do not seem to be a good way of studying the Ni–Cu system because of the limited extraction of Al for some compositions and other complications described in the present and the previous (*4*) paper. For scientific studies the direct preparation of Ni–Cu alloys seems preferable; for example, Araki and Ponec (*12*) prepared evaporated Ni–Cu alloy films for methanation studies.

TABLE 3

Temperature-Programmed-Desorption Data

Catalyst	H_2 evolved to 500°C (cm³ STP/g)	Temperature for maximum H_2 evolution (°C)
1	55.0	255
2	27.5	230
3	1.6	285
4	2.5	330
5	9.2	323
6	3.0	265 and 313

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