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Catalytic Hydrogenolysis and Dehydrogenation over Copper–Nickel Alloys

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The hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene were investigated over a series of copper–nickel alloys. The alloys were characterized by adsorption, X-ray diffraction, and magnetic measurements. The effect of adding copper to nickel was very different for the two reactions investigated. In the case of ethane hydrogenolysis, the catalytic activity decreased markedly and continuously with addition of copper to nickel over the whole range of alloy composition, although much of the activity decline was observed on addition of the first few percent of copper. With cyclohexane dehydrogenation, however, the catalytic activity increased initially with addition of small amounts of copper to nickel, and then remained insensitive to alloy composition over a wide range, finally decreasing sharply at compositions approaching pure copper. The effects of alloying are clearly very specific to the nature of the reaction.

INTRODUCTION

Studies on metal alloy catalysts constitute an important chapter in the history of heterogeneous catalysis. Much of the work has been done with the objective of investigating the relationship between catalytic activity and the electronic structure of metals, dating back to early ideas proposed by Schwab (*1*) and Dowden (*2*, *3*). Alloying provides a way of altering the electronic properties of a metal in a continuous manner. By studying the catalytic properties as a function of alloy composition, one then obtains information on the effect of varying electronic properties on the catalytic activity. Alloys of a Group IB metal with a Group VIII metal (e.g., copper–nickel) have received particular attention, principally for reactions such as the hydrogenation of benzene (*4*–*8*) and ethylene (*9*–*12*). It is widely suggested that the *d* electrons of a metal play an important role in determining catalytic activity for such hydrogenation reactions, whether one views the question in terms of the electron band theory or the valence bond theory of metals.

Although much research has been done on copper–nickel alloy catalysts for hydrogenation reactions of unsaturated hydrocarbons, very little attention appears to have been given to certain other hydrocarbon reactions, e.g., hydrogenolysis. We have for some time been interested in the catalytic hydrogenolysis of hydrocarbons on metals, with the objective of relating catalytic behavior to properties of the metals. In studies on the hydrogenolysis of ethane to methane, we have observed extremely wide variation in catalytic activity from one metal to another (*13*–*17*). The hydrogenolysis activities of the Group IB metals are much lower than those of the Group VIII metals (*17*), and alloy combinations of metals from these groups appeared to be good candidates for catalytic studies. Consequently, a study was made of ethane hydrogenolysis over a series of copper–nickel alloys. The dehydrogenation of cyclohexane to benzene was also investigated over these same catalysts. The results, coupled with previously published data on hydrogenation reactions on copper–nickel alloys, show clearly that alloying copper with nickel leads to catalytic effects in hydrogenolysis which are dramatically different from those observed for hydrogenation–dehydrogenation reactions. The effects of alloying thus appear to be highly specific to the nature of the reaction.

EXPERIMENTAL

Apparatus and Procedure

Adsorption measurements were made in a high vacuum apparatus, which has been described in detail elsewhere (*16, 18*). The catalytic studies were conducted in two separate flow-reactor systems, one for ethane hydrogenolysis and the other for cyclohexane dehydrogenation. The apparatus for the ethane hydrogenolysis studies has been described previously (*19, 20*). The reactor is a stainless-steel tube approximately 1 cm in diam and 8 cm in length, mounted in a vertical position and surrounded by an electrical heater. The catalyst is supported on a fritted stainless-steel disk located about half way down the length of the reactor tube. Quartz wool is packed on top of the catalyst to hold it in place. A 3 mm axial thermocouple well extends upward through the fritted steel disk so that the tip of the enclosed thermocouple is located at the center of the catalyst bed. The reactant gasses, with helium diluent, are first passed through a preheat coil and then downflow through the catalyst bed. The reactant gases, with helium helium are measured by simple constriction type flow meters (*20*). The total gas flow rate is maintained at 1 liter/min. Reaction products are analyzed with a silica gel chromatographic column connected to the outlet of the reactor. In the present work, a 1 g charge of catalyst, of 45–60 mesh particle size, was used. The reactor for the cyclohexane dehydrogenation studies was similar to that used for the ethane hydrogenolysis runs. Reactor dimensions were approximately 1 cm diam and 18 cm length. The fritted disk was located about 6 cm from the bottom of the reactor tube. A catalyst charge of approximately one gram was employed in the cyclohexane dehydrogenation runs. The catalyst was diluted with inert alundum granules to a volume of 5 ml. A layer of these same alundum granules was placed on top of the catalyst bed to serve as a preheat section. A measured flow of cyclohexane was delivered to the reactor with a motor-driven syringe. On entering the preheat section of the reactor, the cyclohexane was vaporized and brought to reaction temperature in admixture with hydrogen prior to passage down through the catalyst bed. The hydrogen flow rate was determined with a rotameter. The syringe was connected to the reactor inlet by a section of Teflon tubing. The reaction products were analyzed by a Perkin–Elmer Model 226 gas chromatograph containing a 300 ft squalane capillary column with a flame ionization detector. The chromatographic unit was connected to the reactor outlet.

X-Ray diffraction measurements on the copper–nickel alloys were made with a Phillips diffractometer employing copper $K\alpha$ radiation. Magnetic data on the catalysts were obtained by the Faraday method employing apparatus described in detail elsewhere (*21*).

Materials

The ethane used in this work was obtained from the Matheson Company, and hydrogen from the Linde Company. Cyclohexane was obtained from Phillips Petroleum Company. As determined by chromatographic analyses, the ethane and cyclohexane contained less than 0.01% and 0.10%, respectively, of hydrocarbon impurities. The hydrogen was purified by passing it through a Deoxo unit containing palladium catalyst to remove trace amounts of oxygen as water, followed by drying with a molecular sieve.

The copper–nickel alloys employed in this work were prepared by a method described previously by a number of workers (*4, 7, 9, 10*). The method consists of coprecipitation of the metals as carbonates from an aqueous solution of copper and nickel nitrates. In the case of pure copper and nickel catalysts, the same procedure is followed except that the solution contains only one of the metal salts. In a typical preparation in the present work, a small amount of ammonium bicarbonate was added initially to a continuously stirred solution of the metal ions until a permanent turbidity just developed. An amount of 2.2 moles of bicarbonate per mole of metal ion was then added rapidly, and the suspension was stirred for 15 min. The precipitate which formed was allowed to settle overnight, after which it was filtered and washed several times with hot distilled water. After a final filtration, the precipitate was dried overnight at 110°C and then calcined in air for 2 hr at 400°C to convert the carbonates to the mixed oxides. The sample was then reduced in hydrogen in a heated quartz tube to form the copper–nickel alloy. The procedure involved initial heating of the sample to 150°C in a flow of 16 liter/hr of helium. A flow of 0.5 liter/hr of hydrogen was then introduced with the helium for 30 min and subsequently increased to 1.5 liter/hr for an additional 30 min. Much water was evolved during this treatment, but no marked temperature rise was observed. The flow of hydrogen was increased and the flow of helium decreased over a period of 3 hr, to a point at which the reducing gas consisted of a flow of 32 liter/hr of pure hydrogen. The temperature was then increased to 350°C, and the hydrogen flow was maintained overnight to complete the reduction. After the reduction, a flow of helium was introduced and the hydrogen flow discontinued. Helium purging was continued while the reduced metal granules were cooled to room temperature. The metal was then passivated by introduction of a small flow of oxygen into the helium stream with a gradual increase in oxygen concentration to 20%. The passivated metal was bottled and stored until needed for experiments. Prior to their use in catalytic, adsorption, and magnetic studies, the copper–nickel preparations were rereduced *in situ* in flowing hydrogen at 450°C for an additional 2 hr. The X-ray diffraction measurements were made on samples from adsorption runs. The samples were passivated *in situ* in the adsorption cells prior to discharge. In the adsorption and magnetic studies the samples were evacuated at 450°C after reduction.

RESULTS

The copper–nickel catalysts in the present investigation were characterized by adsorption, X-ray diffraction, and magnetic measurements. Data on surface areas determined by the physical adsorption of argon at 77°K and on lattice constants determined by X-ray diffraction measurements are summarized in Table 1. Interestingly, the surface areas of very dilute alloys on either the nickel-rich or copper-rich end of the composition scale were found to be lower than those of the pure metals or of more concentrated alloys. The highest surface areas were observed for the alloys containing roughly equivalent amounts of copper and nickel. A plot of the lattice constant vs the composition of the alloy is given in Fig. 1. The data on the present samples, represented by the circles, agree very well with the data of

TABLE 1
PROPERTIES OF COPPER–NICKEL CATALYSTS[a]

Composition, nominal % Cu	At. % Cu Chem. analysis	Surface area (m²/g)[b]	Lattice constant (Å)[c]
0	—	0.97	3.5237
5	6.2	0.63	—
10	10.3	0.83	3.5331
28	31.5	1.46	—
38	42.4	1.39	3.5560
48	52.7	1.24	3.5669
58	63.3	1.15	—
68	74.0	0.93	3.5879
95	95.6	0.64	3.6097
100	—	0.89	3.6152

[a] Properties determined on catalysts after re-reduction in flowing hydrogen at 450°C for 2 hr to correspond with the procedure employed in the catalytic experiments.

[b] Determined by physical adsorption of argon at 77°K.

[c] Determined by X-ray diffraction.

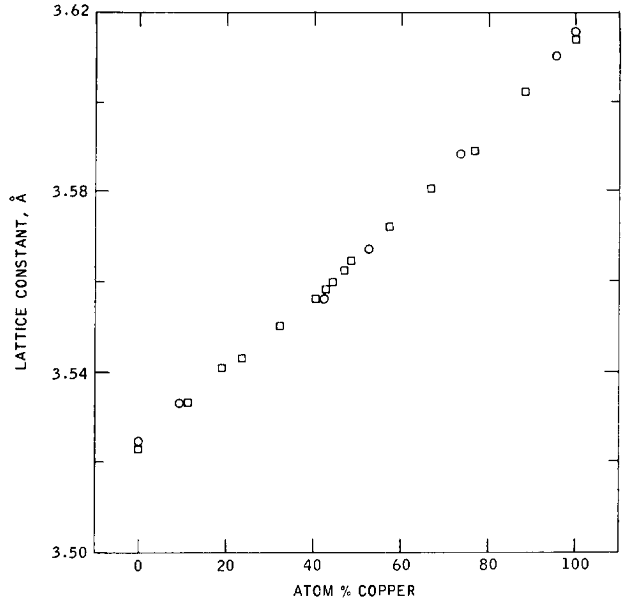

Fig. 1. Lattice constants of copper-nickel alloys as a function of composition: ○, data on copper-nickel catalysts used in the present work; □, data of Coles (*22*).

Coles (*22*), represented by the squares. Agreement with other data (*23, 24*) is also good. The data show a small but significant deviation from a Vegard linear relationship, as commonly observed with alloys of this type (*25*).

Magnetic data on a number of the copper-nickel catalysts are shown in Fig. 2

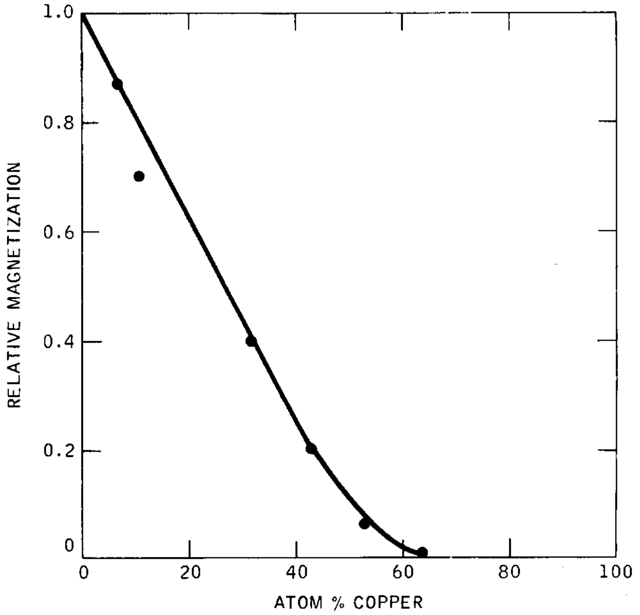

Fig. 2. Magnetization of copper-nickel alloys as a function of composition. The points are relative magnetizations at 77°K on the copper-nickel catalysts used in the present work, determined from data at field strengths of 1500–6500 oersteds. The curve is derived from values of the spontaneous magnetization at 0°K of copper-nickel alloys, reported by Ahern, Martin, and Sucksmith (*26*).

as a function of the alloy composition. The ordinate of Fig. 2 represents the magnetization relative to the magnetization of pure nickel. Data on the copper–nickel catalysts are represented by the points, and are compared with a curve representing the published data of Ahern, Martin, and Sucksmith (*26*). The curve is the ratio of the spontaneous magnetization of an alloy to that of pure nickel at 0°K, as determined by extrapolation of data on the dependence of the magnetization on field strength and temperature. The data on the copper–nickel catalysts were derived from magnetization values at 77°K determined at field strengths of 1500–6500 oersteds. At these conditions the magnetization was virtually independent of field strength for all the copper–nickel catalysts in Fig. 2. The ratio of the magnetization of a copper–nickel catalyst to that of pure nickel was therefore also essentially independent of the particular field strength at which the ratio was determined. In Fig. 2 each point represents an average value of the ratio over the range of field strengths employed. Clearly, the effect of composition of the copper–nickel alloys on the magnetization agrees very well with the previously published data, considering that the latter were obtained on alloys prepared from the molten metals. From Fig. 2, it is clear that the ferromagnetism of nickel disappears at an alloy composition of about 60 at. % copper, as shown by others (*3*, *6*).

The chemisorption of hydrogen on the various copper–nickel catalysts was also investigated. Typical adsorption isotherms at room temperature, expressed as volume adsorbed per unit surface area, are shown in Fig. 3. The three separate fields of

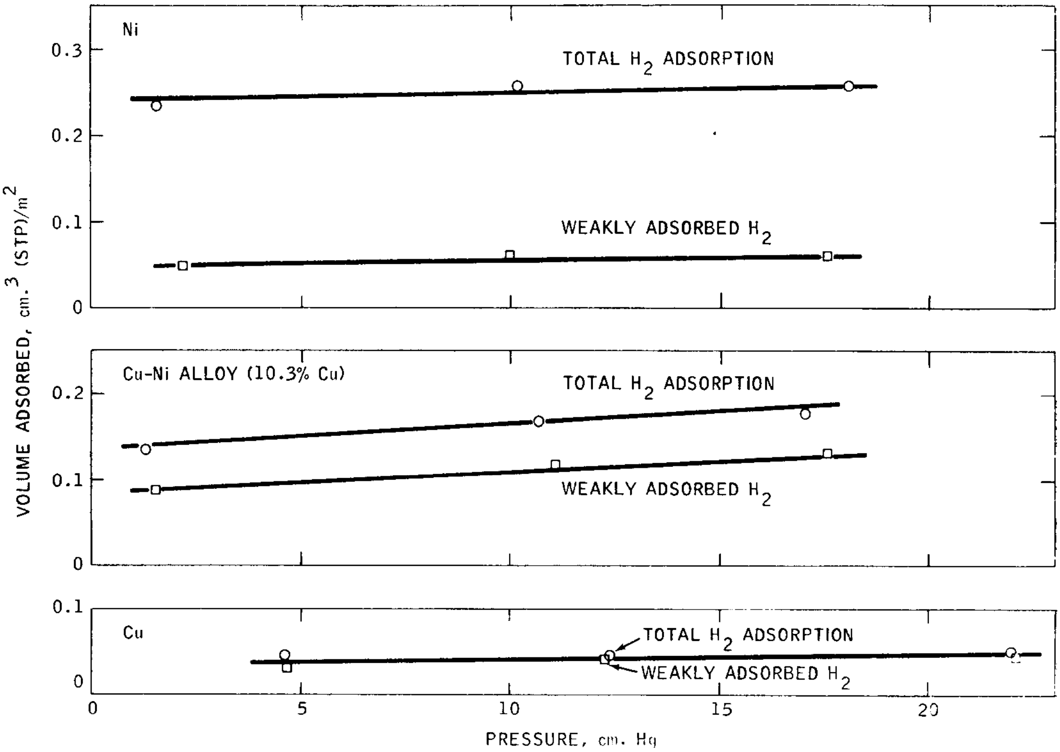

Fig. 3. Hydrogen adsorption isotherms at room temperature on copper–nickel catalysts of varying composition. The circles are isotherms representing the total adsorption of hydrogen on the catalysts after reduction and evacuation at 450°C. When these isotherms were completed, the catalysts were evacuated for 10 min at room temperature, after which the hydrogen isotherms represented by the squares were measured to determine the amount of weakly adsorbed hydrogen.

Fig. 3 show data for nickel, for a copper–nickel alloy, and for copper. Two isotherms are shown for each of the catalysts. In each case, the circles represent an isotherm obtained on the catalyst after reduction and evacuation of the catalyst at 450°C. After such an isotherm was completed, the catalyst was evacuated for 10 min at room temperature, and a second adsorption isotherm was determined. Isotherms obtained in this way are represented in Fig. 3 by squares for all three catalysts, and provide a measure of the amount of weakly adsorbed hydrogen, i.e., hydrogen which can be removed by simply evacuating the catalyst at room temperature. In the case of the nickel catalyst, the amount of weakly adsorbed hydrogen is small compared to the total adsorption. By contrast, the weakly adsorbed hydrogen accounts for virtually all of the adsorption on copper. The fraction of weakly adsorbed hydrogen increases markedly when a small amount of copper is added to nickel, as is evident from a comparison of the isotherms for nickel with those for the catalyst containing 10.3% copper. By taking the difference between isotherms for total adsorbed hydrogen and weakly adsorbed hydrogen, the amount of strongly adsorbed hydrogen is readily determined. In Fig. 4, the amount of strongly adsorbed hydrogen and the total hydrogen adsorption at an equilibrium pressure of 10 cm are shown as a function of the composition of the catalyst. The former is represented by the lower curve in Fig. 4, and the latter by the upper curve. Both the total hydrogen adsorption and the amount of strongly adsorbed hydrogen decrease when copper is added to nickel. The amounts adsorbed decrease markedly on addition of the first

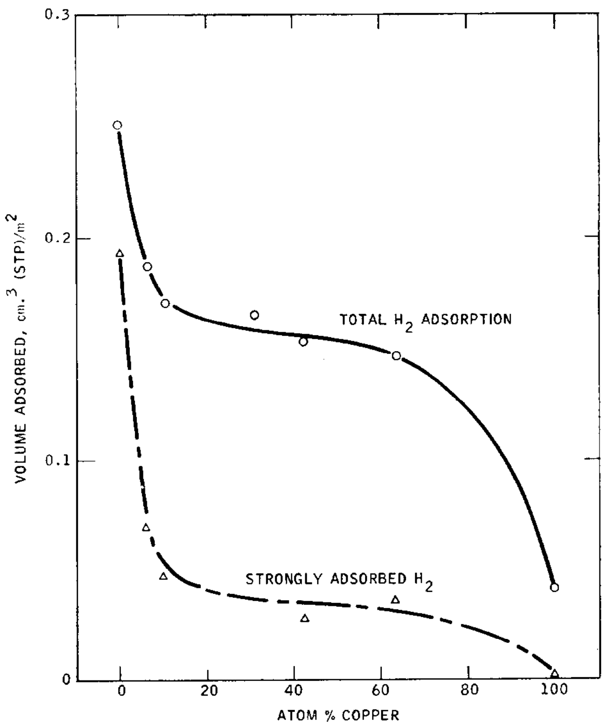

Fig. 4. The adsorption of hydrogen on copper–nickel catalysts as a function of the copper content. The circles represent the total amount of hydrogen adsorbed at room temperature at 10 cm pressure. The triangles represent the amount of strongly adsorbed hydrogen, i.e., the amount not removed by a 10 min evacuation at room temperature following the completion of the initial adsorption isotherm. The amount of strongly adsorbed hydrogen is determined as the difference between the initial isotherm and a subsequent isotherm obtained after a 10 min evacuation.

increments of copper until a composition of about 10 at. % copper is attained. The decrease at low copper contents is far more pronounced for the strongly adsorbed hydrogen. In the range of catalyst composition between about 10 and 70 at. % copper, the effect of composition is relatively small, but becomes more pronounced again as the composition approaches pure copper.

In the catalytic studies on the copper–nickel alloys, reaction rates were determined at low conversion levels: 0.1–2.7% for the hydrogenolysis of ethane to methane and 0.1–14% for the dehydrogenation of cyclohexane to benzene. Reaction rates per unit weight of catalyst were obtained using the relation,

$$r = (F/W)x, \tag{1}$$

where F is the flow rate of hydrocarbon reactant in moles per unit time, W is the weight of catalyst in the reactor, and x is the fraction of reactant converted (i.e., the fraction of ethane converted to methane or of cyclohexane converted to benzene). The catalyst surface areas in Table 1 were then used to calculate reaction rates in molecules/sec cm^2.

Data on the effect of temperature on the rates of ethane hydrogenolysis on the copper–nickel catalysts are given in Fig. 5. The data were obtained at ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively. Apparent activation energies and pre-exponential factors derived from the data in Fig. 5 are summarized in Table 2. Both of these kinetic parameters vary as the composition of the alloy is changed. The apparent activation energies are higher on the copper–nickel alloys than on the pure nickel catalyst, and the pre-exponential factors are generally lower.

The dependence of ethane hydrogenolysis rates on the partial pressures, p_E and p_H, of ethane and hydrogen, respectively, can be expressed by a simple power rate law:

$$r = kp_E{}^n p_H{}^m. \tag{2}$$

Values of the exponents n and m, and the temperatures at which they were determined, are given in Table 2. The exponent

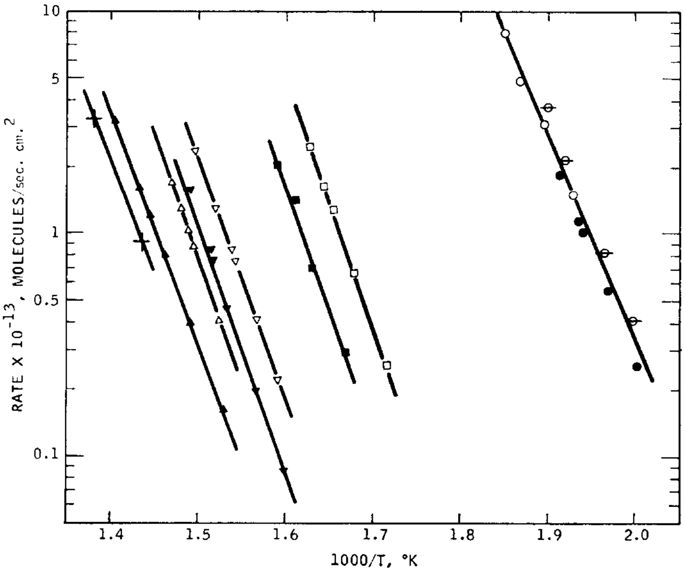

FIG. 5. Arrhenius plots for ethane hydrogenolysis over copper–nickel alloys: ●, ○, ⊘, 0% Cu (three different runs); □, 6.2%Cu; ■, 10.3% Cu; ▽, 31.5% Cu; ▼, 42.4% Cu; △, 52.7% Cu; ▲, 63.3% Cu; +, 74% Cu (the percentages are at. %). The ethane and hydrogen pressures are 0.030 and 0.20 atm, respectively.

TABLE 2

SUMMARY OF KINETIC PARAMETERS FOR ETHANE HYDROGENOLYSIS ON COPPER–NICKEL ALLOYS

Composition (at. % Cu)	Temp. range (°C)	E[a]	r'_0[b]	Reaction orders n[c]	 m[d]	 Temp. (°C)[e]
0	226–268	43	2.1×10^{31}	1.0	−2.1	238
6.2	308–339	51	3.2×10^{31}	0.9	−1.3	331
10.3	326–356	51	1.1×10^{31}	—	—	—
31.5	355–396	50	6.0×10^{29}	—	−1.3	377
42.4	352–395	51	5.2×10^{29}	0.9	−1.3	384
52.7	383–408	50	2.0×10^{29}	0.8	−1.2	399
63.3	383–440	48	1.8×10^{28}	0.8	−1.2	420
74.0	424–455	47	6.5×10^{27}	—	—	—

[a] Apparent activation energy, kcal/mole.

[b] Pre-exponential factor, molecules/sec cm^2, in the equation $r_0 = r'_0 \exp(-E/RT)$.

[c] Order with respect to ethane.

[d] Order with respect to hydrogen.

[e] Temperature at which the reaction orders were determined.

n was determined for ethane partial pressures in the range of 0.01–0.10 atm, at a constant hydrogen partial pressure of 0.20 atm. The exponent *m* was determined for hydrogen partial pressures in the range of 0.10–0.40 atm, at a constant ethane partial pressure of 0.030 atm. The data show that ethane hydrogenolysis is nearly first order in ethane partial pressure on all the catalysts investigated. The reaction rate

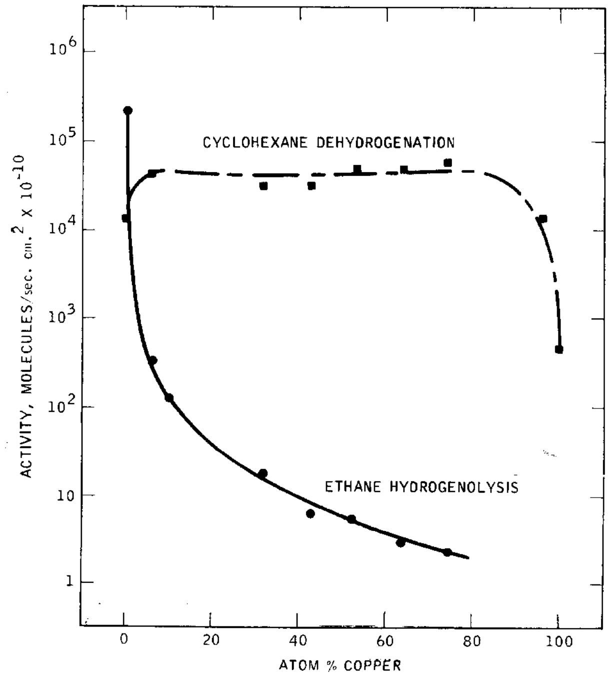

FIG. 6. Specific activities of copper–nickel alloy catalysts for the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene at 316°C: ●, ethane hydrogenolysis at ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively; ■, cyclohexane dehydrogenation at cyclohexane and hydrogen pressures of 0.17 and 0.83 atm, respectively.

decreases markedly with increasing hydrogen pressure, with values of m ranging from —1.2 to —2.1 depending on catalyst composition and/or temperature.

Specific activities of the copper–nickel catalysts for both ethane hydrogenolysis and cyclohexane dehydrogenation are shown in Fig. 6 as a function of the catalyst composition. The specific activities are reaction rates at 316°C. In the case of ethane hydrogenolysis, the reaction rates were calculated using the apparent activation energies and pre-exponential factors in Table 2, which are applicable for ethane and hydrogen partial pressures of 0.030 and 0.20 atm, respectively. The temperature of 316°C represents an intermediate temperature in the range investigated on the various copper–nickel catalysts. In the case of cyclohexane dehydrogenation, the reaction rates on all of the catalysts were measured directly at 316°C, at cyclohexane and hydrogen partial pressures of 0.17 and 0.83 atm, respectively. The catalytic activity of nickel for ethane hydrogenolysis decreases markedly and continuously as copper is alloyed with it. The addition of 5 at. % copper to the nickel decreases the hydrogenolysis activity by three orders of magnitude. On further addition of copper, the hydrogenolysis activity continues to decline, although at a lower rate, over the whole range of composition investigated. The activity of a catalyst containing 63.3 at. % copper is five orders of magnitude lower than that of pure nickel. Attempts to measure the hydrogenolysis activities of catalysts containing 95–100 at. % copper were unsatisfactory, since the reaction rates were too low to measure in our apparatus, even at temperatures as high as the temperature of reduction of the catalyst. In contrast to the ethane hydrogenolysis results, the catalytic activity of nickel for cyclohexane dehydrogenation increases initially with addition of small amounts of copper, and then remains fairly insensitive to alloy composition over a wide range, finally decreasing sharply at compositions approaching pure copper. It is interesting that the activity of the catalyst containing 95.6 at. % copper is equivalent to that of the pure nickel catalyst, although the activity of the copper itself is roughly two orders of magnitude lower than that of the nickel.

DISCUSSION

The most interesting feature of the present work is the marked difference in the effect of copper on the catalytic activity of nickel for the ethane hydrogenolysis and cyclohexane dehydrogenation reactions. In the case of ethane hydrogenolysis, the activity of nickel decreases precipitously on addition of small amounts of copper, and continues to decrease with increasing copper content over the whole range of composition of the alloys. In the case of cyclohexane dehydrogenation, however, the activity of nickel is affected much less by the addition of copper, and actually increases slightly. As the copper content of the catalyst is increased to very high levels, the cyclohexane dehydrogenation activity remains virtually constant until the catalyst composition approaches pure copper. The promotional effect of copper on nickel is similar to previously reported results (*7, 9, 10, 12*) for benzene and ethylene hydrogenation on copper–nickel alloys.

In attempting to rationalize the markedly different effects of copper on the catalytic activity of nickel for ethane hydrogenolysis and cyclohexane dehydrogenation, it is of interest to consider effects of copper on the adsorption properties of nickel. The hydrogen adsorption studies of the present work indicate that addition of copper to nickel decreases markedly the average strength of adsorption of hydrogen, in the sense that the strongly adsorbed hydrogen becomes a much smaller fraction of the total. In general, this effect might be considered in terms of two factors, one being an electronic interaction between copper and nickel, and the other the structure or composition of the surface. The first of these factors would affect the strength of bonding of hydrogen to nickel, while the second would affect also the relative numbers of various types of sites available for adsorption, i.e., the number of surface Ni or Cu atoms, or the number of Ni–Ni, Cu–Cu, or Ni–Cu atom pairs in the surface. Other workers (*8*, *27*) have provided evidence indicating that the surface composition of copper–nickel alloys is quite different from the bulk composition, in that the surface of low copper content alloys contains very much more copper than the bulk. The marked effects of small amounts of copper on the adsorption properties of nickel in the present work are consistent with this. The conclusions of van der Plank and Sachtler (*8*) were derived largely from hydrogen adsorption data, and were based on the premise that nickel chemisorbs hydrogen while copper does not. These workers used the total hydrogen chemisorption at room temperature as a measure of the amount of nickel in the surface. However, in the present work it has been found that hydrogen adsorption on the copper catalyst, while small compared to adsorption on nickel, is not negligible. Thus, consideration of total hydrogen adsorption alone introduces complications in the determination of surface composition. It is clear, however, that the amount of strongly adsorbed hydrogen on the copper catalyst is negligible, and this may provide a better basis for an estimate of surface composition. However, there is still a complication, in that the amount of strongly adsorbed hydrogen on the base nickel catalyst was less than the total by about 20%. The nature of the weakly adsorbed hydrogen is not clear. For simplicity, we shall assume that consideration of only the strongly adsorbed hydrogen is necessary for a determination of the number of nickel atoms in the surface. For each of the copper–nickel alloys we can then calculate a quantity f, which represents the ratio of the amount of strongly adsorbed hydrogen per unit surface area on the alloy to that on the base nickel catalyst. This quantity is shown as a function of the catalyst composition in the lower curve in Fig. 7. In attempting to assess surface compositions we might simply take the quantity f to be equal to the atom fraction of nickel in the surface. However, if the strongly adsorbed hydrogen required surface sites consisting of Ni–Ni atom pairs, the concentration of such sites would not be simply proportional to the nickel content of the surface, but probably more nearly proportional to the square of the nickel concentration. In

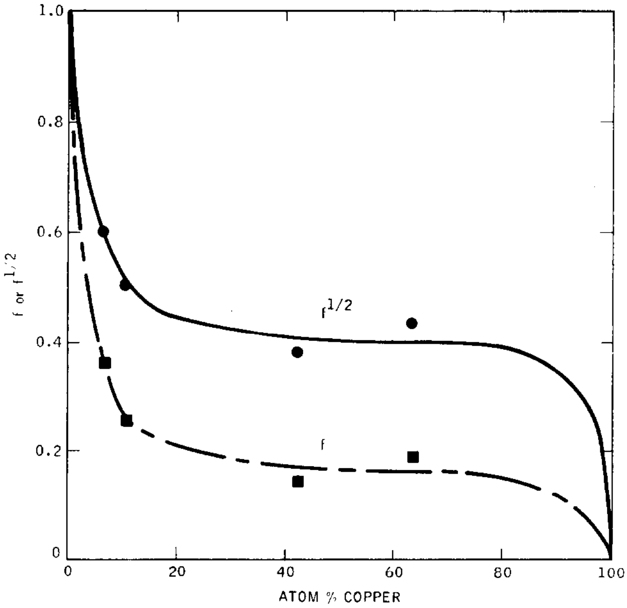

FIG. 7. Dependence of the quantities f and $f^{1/2}$ on the composition of copper–nickel alloys, where f represents the amount of strongly adsorbed hydrogen on an alloy relative to that on nickel.

this case the atom fraction of nickel in the surface would be equal to $f^{1/2}$, which is given in the upper curve of Fig. 7. This assumes that hydrogen chemisorption on Ni–Ni atom pairs, which is in all probability dissociative, is also immobile. If the adsorption were mobile, then hydrogen atoms formed on Ni–Ni sites could migrate on the surface to isolated Ni atom sites, in which case f rather than $f^{1/2}$ would be a better indication of the atom fraction of nickel in the surface. Thus, there is some uncertainty in the quantitative determination of surface composition from adsorption data. Nevertheless, it seems clear from the adsorption data that copper concentrates markedly in the surface of copper–nickel alloy catalysts of low over-all copper content. From Fig. 7 we would estimate that a catalyst containing 5% copper overall would have a surface composition in the range of 40–60% copper, depending on which of the curves in Fig. 7 is adopted as a measure of surface composition. Furthermore, for a broad range of alloy catalysts containing more than about 10 at. % copper, the variation in surface composition is small. As the over-all copper content approaches 100% copper, of course, the copper content of the surface increases correspondingly.

The conclusion that copper concentrates strongly in the surface of copper–nickel alloys of low over-all copper content would imply a much greater alteration of intrinsic metallic properties in the surface region than in the bulk. Thus, while the percentage *d*-character of the metallic bond (*28*) in copper–nickel alloys (*10*) decreases with copper content in the manner shown in Fig. 8, the value of this quantity in the surface region would decline much more sharply as small amounts of copper are added to nickel, because of the strong concentration of copper in the surface region. This point is particularly of interest in regard to the data on the effect of copper on the ethane hydrogenolysis activity of nickel. Previous work reported by us (*14–17*) has shown that the hydrogenolysis activity of metals varies in a manner that parallels the variation in percentage *d*-character of the metallic bond. Since copper has the effect of decreasing the percentage *d*-character of nickel on alloying, it would be expected to decrease the hydrogenolysis activity of nickel, as observed in this work. The particularly sharp

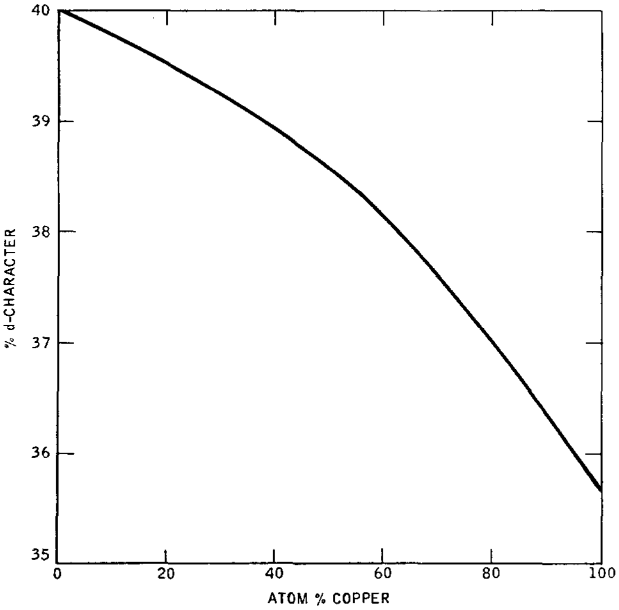

FIG. 8. Percentage *d*-character of the metallic bond in copper–nickel alloys as a function of composition (*10*).

decline in the hydrogenolysis activity of nickel on addition of the first increments of copper is consistent with a much more marked decline in the percentage *d*-character in the surface region than in the bulk. The hydrogenolysis activities of copper–nickel alloys may also be considered from another point of view. In studies of the kinetics of ethane hydrogenolysis on nickel and other metals, it has been concluded that ethane is chemisorbed with extensive dissociation of carbon–hydrogen bonds leading to a highly unsaturated dicarbon surface residue as the reaction intermediate (*17*). It seems likely that such an intermediate would be multiply bonded to surface metal atoms. The amount of the intermediate could be very sensitive to restrictions in the number of multiple nickel atom sites available for chemisorption on a surface in which copper concentrates so markedly. The hydrogenolysis activity of the surface would clearly reflect this.

In returning to a consideration of the very different effects of copper on the catalytic activity of nickel for the ethane hydrogenolysis and cyclohexane dehydrogenation reactions, it will be helpful to consider a generalized, simplified sequence of steps involved in a catalytic reaction:

Here A represents a reactant in the gas phase, and D represents the final product of the reaction, also in the gas phase. The species B is a surface species formed from A on chemisorption, and C is another surface species formed from B. Desorption of the species C yields the product D. In general, any of the three steps shown could be rate limiting, and the effect of copper on nickel will clearly depend on which of the steps is rate controlling. If the product desorption step controls, the strength of adsorption of C is of prime importance. If the surface reaction B → C controls, then the strength of adsorption of B becomes important. It should be realized that the reaction rate in these two cases could be affected in directionally different ways by a change in the heat of adsorption of the surface species B or C. In proceeding with the discussion, we will assume that the strength of adsorption of hydrocarbons on nickel is affected directionally in the same way as the strength of adsorption of hydrogen when copper is added to nickel. If the surface coverage by the species C is very high, such that desorption of C controls the reaction rate, a decrease in the heat of adsorption of C would increase the rate. We suggest that this may be the case in cyclohexane dehydrogenation, i.e., desorption of the benzene product controls the reaction rate. Thus, on addition of copper to nickel the heat of adsorption of benzene would be expected to decrease, leading to a corresponding decrease in the activation energy of the desorption step. The suggestion here is prompted by previous work on the dehydrogenation of methylcyclohexane to toluene on platinum (*29*), where it was concluded that the reaction rate was limited by desorption of the toluene product. This reasoning would account for the initial enhancement of the rate of cyclohexane dehydrogenation observed on addition of the first increments of copper to nickel. The range of composition (6–74% copper) over which the rate was essentially constant is likely characterized by a somewhat smaller variation of the heat of adsorption of the hydrocarbon and by a gradual change in the rate determining step of the reaction, such that at very high copper content the reaction rate is limited by a step prior to the final product desorption step. It is entirely reasonable that the reaction rate could then be adversely affected by a decrease in the heat of adsorption of hydrocarbon intermediate B on the surface, corresponding to the observed decrease in rate as the catalyst composition approaches pure copper. In other words, there is an optimum strength of binding of surface intermediates corresponding to maximum catalytic activity. For the case of ethane hydrogenolysis, in which the reaction intermediate B is probably a highly unsaturated, dicarbon surface residue with both carbon atoms bonded to metal surface atoms, we can also rationalize the catalytic results in a general way. It seems reasonable that the strength of bonding between the two carbon atoms in the surface intermediate B would vary in an inverse manner with the strength of bonding of the carbon atoms to the surface. Consequently, the rupture of the carbon–carbon bond would be facilitated by an increase in the heat of adsorption, and inhibited by a decrease in the heat. If such carbon–carbon bond rupture is the rate limiting step in the reaction, the rate of reaction should decrease as the heat of adsorption decreases, corresponding to addition of copper to nickel. This would appear to be the case over the whole range of composition in the copper–nickel catalyst system. Presumably, the rate of rupture of the carbon–carbon bond (step B → C) would have to be even higher than that obtained on the base nickel catalyst to permit desorption of the methane product (step C → D) to be the rate controlling step.

In considering again the relation of catalytic activity to the percentage *d*-character of the metallic bond, we note that the situation for cyclohexane dehydrogenation on copper–nickel alloys is different from that already considered for ethane hydrogenolysis. In the case of cyclohexane dehydrogenation, the activity actually varies inversely with percentage *d*-character in the nickel-rich end of the composition range. This presents no anomaly. The role of percentage *d*-character would be fundamentally one of affecting the strength of adsorption, and we have just seen how catalytic activity can vary in different ways with the strength of adsorption of intermediate surface species, depending on the nature of the rate limiting step in a reaction.

In concluding the discussion, we wish to re-emphasize the major finding of the present investigation on catalysis by copper–nickel alloys, namely, that the effect of copper on the catalytic activity of nickel is strongly dependent on the nature of the reaction. Thus copper–nickel alloys exhibit a high degree of specificity in catalyzing certain types of hydrocarbon transformations.

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