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Behavior of Nickel–Copper Alloy in Hydrogenation, Orthohydrogen–Parahydrogen Conversion, and H_2–D_2 Exchange Reaction

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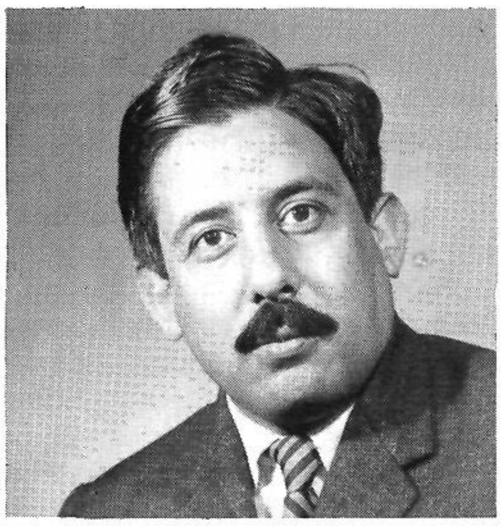
Contents

1. Introduction

The group 8 transition metals of the periodic table when combining with the group 1B metals generally form binary alloys (solid solutions of varying composition), which are commonly used as heterogeneous catalysts. Despite similarities in their composition and structure, the alloys exhibit a remarkable range of electronic and physical properties. The electronic properties are involved in the basic chemisorption processes that underlie their catalytic activity, but the measured activity patterns cannot readily be related to changes in their electronic structures. Copper appears to be practically inactive for hydrogenation unless some or other promoter is present. The mechanism by which nickel promotes copper is not clearly understood as yet. The activity patterns shown by the Ni–Cu alloy system in catalytic reactions are of great interest, and quite controversial results have been reported.

The Ni–Cu system is usually found to form a continuous solid solution with the lattice parameter exhibiting a near-linear relationship. Hence the significant deviations observed in the catalytic activity of this apparently ideal system would indicate the importance of nongeometric factors, such as electronic effects, in understanding the various patterns of catalytic activity. However, Sachtler and Dorgelo[1] found that the surface composition of evaporated Ni–Cu alloy films is not coincident with the overall composition of the bulk. They also confirmed the existence of a wide miscibility gap for the Ni–Cu films equilibrated at 200 °C. These results have also been supported by the work of others.[2,3] The purpose of this review is to discuss the results obtained in the past few years by various investigators when employing solid solutions of Ni–Cu alloys in the liquid- and vapor-phase hydrogenation of hydrocarbons, in orthohydrogen–parahydrogen conversion, and in H_2–D_2 exchange reactions.



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2. Preparation of Ni-Cu Alloy Catalysts

It was demonstrated by Long et al.[4] that a completely homogeneous Ni-Cu alloy solid solution could be formed by coprecipitation of the metals from solutions of the constituent ion hydroxides after reduction by hydrogen. Irrespective of whether the bimetallic catalysts (in nitrate form) are precalcined or not, both Cu and Ni exist in the zerovalent metal state and are engaged in alloying after a hydrogen treatment at 500 °C.[5] Best and Russell[6] used an alternative method to produce the alloy whereby ammonium bicarbonate was used to coprecipitate copper and nickel ions in the form of carbonates from a solution of the mixed nitrates, with subsequent calcination at 400 °C and reduction in a stream of hydrogen. X-ray diffraction and magnetic susceptibility measurements indicated that though the catalysts were prepared by the reduction of mixed oxides obtained from the precipitated metal carbonates, they were essentially equilibrium solids. Measurements of the lattice parameters showed Vegard's law to be obeyed quite closely and to have the same values for alloys produced by both of the above methods. The lattice parameters were also identical with those found for Ni-Cu alloys produced by melting the metals.[8] Takeuchi et al.[7] prepared granular alloys from mixed solutions of copper and nickel nitrates, which were evaporated to dryness and then ignited to metal oxides in a furnace at 500 °C. The oxides were then reduced at 200 °C in an atmosphere of hydrogen. The mechanism for the formation of Ni-Cu alloys by reduction of mixed oxides has been discussed in the literature.[8-14]

Massive alloys were prepared[7] from mixtures of electrolytic copper and nickel by completely melting the metals in a furnace. Crystals of Ni-Cu alloys have been grown by Cox et al.[15] using the Bridgman technique. Rods with varying composition over their lengths were produced by this method, and individual crystals of near-uniform composition were machined from them as small spheres. Studies of supported Ni-Cu alloys have been reported for kieselguhr,[16] alumina,[12,17,18] and silica-alumina.[19,20] The supported catalysts were prepared by impregnating them with aqueous solutions of copper and nickel salts to the point of incipient wetness, followed by drying and reduction with hydrogen. The reduced (500 °C) Ni-Cu, Si-Al system has revealed the presence of a Ni-Cu alloy which was identified by X-ray diffraction. In addition to the Ni-Cu phase, metallic Ni and Cu may be present on the catalyst surface.

Sachtler and Dorgelo[1] prepared Ni-Cu alloy films by (i) evaporation of an alloy wire from a supporting tungsten, tantalum, or rhenium filament, (ii) simultaneous evaporation of two pieces of the pure metals or an alloy in a tungsten cup which was heated by high-energy electron bombardment, and (iii) successive evaporation of the two metals from different sources, followed by heat treatment to homogenize the film. Gharpurey and Emmett[21] prepared Ni-Cu alloy films by evaporating nickel directly from a heated wire and copper from an electrically heated tungsten support. They deposited thin films of nickel in high vacuum and then superimposed thin films of copper. The films were homogenized by sintering for a few hours at 300 °C in a hydrogen atmosphere. The achievement of homogeneity was based on qualitative information such as color changes, and no X-ray analysis was reported. In later work on such films, Campbell and Emmett[2] performed X-ray studies and found that films homogenized at 500 °C appeared to favor the formation of a specific Ni-Cu phase.

3. Physical Properties and Miscibility Gap

The chemical and physical properties of Ni-Cu alloys[13,22-41] and their catalytic properties[42-48] have been described quite extensively in the literature. Nickel and copper both crystallize in the fccub lattice with lattice parameters of 3.517 and 3.608 Å, respectively. When the metals are melted together, it is found that they form a continuous solid solution of binary alloys within which the lattice parameter varies almost linearly. A small deviation from Vegard's law and Raoult's law is observed.[28] Similar deviations have been observed for Ni-Cu catalysts prepared by reduction of coprecipitated metal carbonates.[8] The maximum deviation from Vegard's law for Ni-Cu powder is 0.17%, and it occurs at a copper concentration of 65%. The Ni-Cu system also exhibits a number of deviations from ideal behavior with respect to such properties as magnetic susceptibility, electronic specific heat, thermoelectric power, and electrical resistivity.[27] These properties show a discontinuity or a maximum when the copper content reaches the vicinity of 60%. Low-temperature specific heat data of Ni-Cu alloys indicates that the energy density of electron states at the Fermi surface decreases sharply when the d band of nickel becomes nearly filled at a concentration of 60% copper. Measurements have been made of the ferromagnetism, saturation magnetization, and Curie temperature of Ni-Cu solid solutions and sintered alloys.[49,50] The saturation magnetization curves of the solid solutions were found to deviate from the adjusted normal curve in the temperature range of 500 to 1200 °C. The ferromagnetism at fixed magnetic field was found to diminish very rapidly at a composition of 60% copper.

Weiss and DeMarco[51] made X-ray measurements to determine the outer electron configuration of nickel and copper in the solid state and found the number of d electrons to be 9.7 ± 0.03 and 9.8 ± 0.3, respectively. X-ray studies of the Lα emission band in Ni-Cu systems indicate that the d-band holes in copper-rich alloys are associated with the nickel atoms.[52,53] An examination of the intensity-voltage curve for Lα emission in the alloys containing 40 and 25% nickel shows that the line for copper does not differ appreciably from that of pure copper but that it is much narrower than for nickel.

Nickel and copper alloy catalysts have been studied for a number of years with the view of determining the validity of the proposals of Dowden[44,45] and Schwab[54] regarding the influence of the electronic structure of solids on their catalytic activity. According to Dowden, if a positive ion is involved in the catalytic mechanism then, for a series of Ni-Cu alloys, the frequency factor would be expected to fall as copper is alloyed with nickel, i.e., as the partially empty d band of nickel is filled. Hence at the critical composition of 40% Ni-60% Cu its value would be only a very small fraction of that of pure nickel. Because of the scarcity of holes the number of sites/cm^2 available for ion formation would be severely limited. Simultaneously, since the work function of copper is less than that of nickel, the activation energy would be expected to increase as copper is alloyed to nickel. The combined action of these two factors is such that the overall catalytic reaction rate would be expected to fall sharply at or near the critical composition. Dowden and Reynolds[55] observed that the addition of 38% Cu to nickel completely destroyed the activity of the nickel for hydrogenation of styrene, which suggests that the d-band vacancies in the metal are essential for it to be useful as a hydrogenation catalyst. However, the experimental data for the hydrogenation of ethylene[56] indicated that certain Ni-Cu alloys were much more active than pure nickel. In particular, the reaction rates of catalysts containing 63 and 90% Cu were higher than on pure nickel by a factor of 10 and 100, respectively. These results were also confirmed by others.[8] Dowden's theory is thus not a complete answer to the activity of Ni-Cu alloys. Beeck[57] has correlated catalytic activity vs. lattice parameter for the hydrogenation of ethylene over metal catalysts and has suggested that the increase in the specific activity of nickel is enhanced by the inclusion of copper because of the expansion of the lattice.

Sachtler and Dorgelo[1] measured the electronic work function and phase composition of Ni-Cu alloy films, prepared by suc-

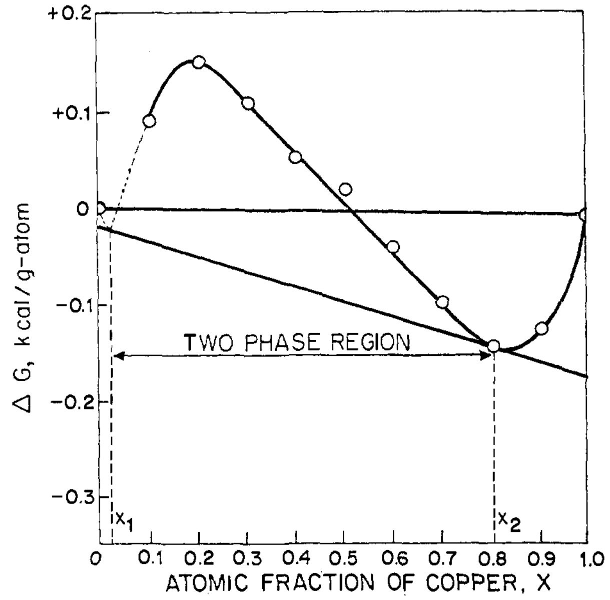

Figure 1. Free energy for Ni-Cu alloy formation at 200 °C.

cessive evaporation of the component metals and homogenization by heating in vacuum at 200 °C. The work function of the alloy films was found to be lower than that of the pure metals sintered at the same temperature. A thermodynamic analysis of the results,[58,59] as summarized in Figure 1, indicates that the alloy films annealed at 200 °C consist of two phases at equilibrium, one containing 80% and the other 2% copper. The electronic work function has a constant value of 4.61 eV within the two-phase region. From the work function study it appeared that the copper-rich phase existed on the film surface and the nickel-rich phase below the surface. The existence of a two-phase structure in Ni-Cu alloys at low temperature is expected on thermodynamic grounds. At high temperature the free energy of alloy formation is governed by the entropy term which favors a solid solution with random distribution of atoms. At low temperatures the entropy term is much smaller, and the free energy is determined by the enthalpy term. Consequently the Ni-Cu alloy at equilibrium should decompose into two phases. While the decomposition may be strongly inhibited in the interior of macroscopic crystals, it will take place more readily in a thin surface layer. Sachtler and Jongepier[58] inferred from diffusion data that within the two-phase region each crystallite consists of a kernel of almost pure nickel enveloped in a skin of alloy. The work of Pogorelov et al.[60] on the hydrogenation of nitrobenzene over Ni-Cu alloy foils suggested the constancy of Ni at the surface of the foils in the interval of compositions from 20 to 80 atomic % copper. Their work supports that of Sachtler and Dorgelo.[1]

Seib and Spicer[61] studied Cu-Ni alloys by ultraviolet photoelectron spectroscopy (UPS) and optical reflectance spectroscopy. They suggested that the surface electronic structure is entirely different from that of the bulk. It is also reported that the individual bonding sites (pure Cu, pure Ni, and mixed Ni-Cu) have different bonding energy on the alloy surface.[62,63] The surface composition would not be similar to that of the bulk, because of the difference in the volatility of copper and nickel as concluded by Burton et al.[10]

Robertson et al.[5] studied the reduction of Cu-Ni on silica catalysts by temperature-programmed technique. They reported that both Cu and Ni exist in the zerovalent metal state after a hydrogen treatment at 500 °C. These zerovalent metals are engaged in alloying. Further they proved that the surface of silica-supported Ni-Cu is formed on nonuniform alloys and the composition of the surface changed by the repetition of reduction and oxidation. The rates of reduction of metal oxides are also influenced by the impurities and by the supporting substance. The work of Takeuchi,[7,65] Frety et al.,[88,87] etc. shows that the relationship between reduction and the nonuniformity of powdered alloy is complicated. In general, both phases can coexist at the surface, and their relative properties depend on the heat treatment. The miscibility of nickel oxide for copper oxide and that of copper oxide for nickel oxide are ca. 5 and ca. 35%, respectively. Such poor miscibility of these oxides would be responsible for the formation of a nonuniform alloy. Dalmon[88] suggested that the metallic particle size depends on the temperature of reduction. By studies with volumetric hydrogen titration and the magnetic effects of hydrogen and oxygen chemisorption, it was observed that the surface composition was very similar to the bulk composition. But the surface is generally rich with Cu in Ni-Cu catalysts.

Campbell and Emmett[2] prepared their Ni-Cu alloy films by successive deposition of nickel and copper and then sintering them at either 300 or 500 °C in an atmosphere of hydrogen. It was observed in the 500 °C heat-treated samples that a homogeneous alloy developed containing approximately 60% Cu and 40% Ni. Excess copper or nickel was also found to be present, depending on the catalyst composition. In contrast to this the films, homogenized at 300 °C, failed to show such alloying effects. Byrne and Clarke[89] also produced such films annealed at 500 °C, but they found them to be single phased and homogeneous, irrespective of composition.

X-ray analysis of Ni-Cu alloy powders[70,71] showed the presence of only one phase, i.e., a solid solution. Electron diffraction studies[72-74] of granular Ni-Cu alloys revealed that the concentration of nickel at the surface differed from that at the interior. On the basis of heat of adsorption studies[75,76] it appears that the nickel particles on the surface of the Ni-Cu catalysts are covered with copper atoms. In the reaction of hydrogen chloride with the alloy, the composition of the surface was found to be independent of the overall alloy composition over a wide range of Ni-Cu compositions.[77,78] It was observed that the amount of nickel was greater on the surface layer than in the interior and that the amount in per unit area of the catalyst was less in the 12% nickel alloy than in the 1% nickel alloy. These results can explain the discrepancy in the catalytic activity of alloys with the same composition, but not the cause of activity increase in the alloy region.

Ono et al.[79] determined the change in the average Ni-Cu ratio of the alloy surface layer by using Auger spectroscopy. It was observed that while nickel became denser after argon ion bombardment, copper became denser after oxidation-reduction treatment. In both cases the activity was observed to increase severalfold due to the surface treatment. It was consequently suggested that the Ni-Cu ratio on the surface may not be the dominant factor in the catalytic behavior of the alloys. However, the Auger spectroscopy technique is favorable for evaporated films or sheets having flat surfaces.

4. Chemisorption on Ni-Cu Alloy Catalysts

While an amount of hydrogen equivalent to as many as 50 monolayers can be reversibly adsorbed or desorbed from Ni-Cu alloy catalysts, pure nickel and copper were found to adsorb hydrogen sufficiently for only one and two monolayers, respectively.[80] It was observed[81] that the ability of nickel metal to adsorb hydrogen increased with increasing copper content until a maximum of 80% Cu was reached, after which it decreased rapidly, as shown in Figure 2. Cadenhead and Wagner[3] reported different patterns of behavior for hydrogen adsorption on Ni-Cu alloy powders at −196 °C. Their results support Sachtler's predictions of a phase separation taking place and of the copper-rich surface composition being constant over a wide bulk compositional range. Similar results were also ob-

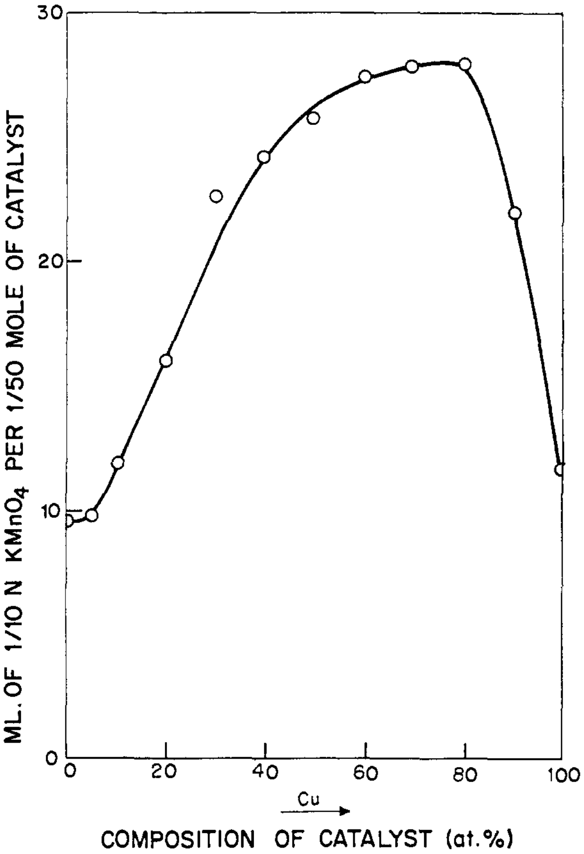

Figure 2. Hydrogen content of catalyst.

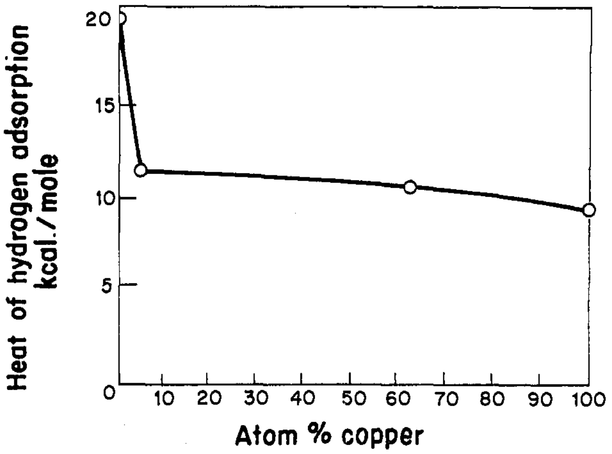

Figure 3. Effect of catalyst composition upon the heat of hydrogen adsorption.

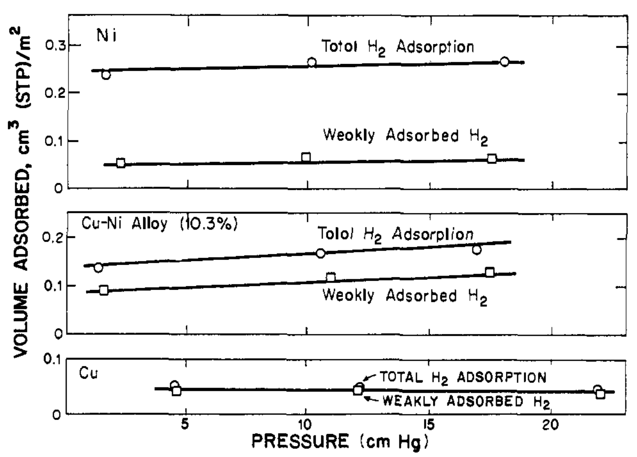

Figure 4. Hydrogen adsorption isotherms at room temperature on Ni–Cu catalysts of varying composition. The curves with circles are isotherms representing the total adsorption of hydrogen on the catalysts after reduction and evacuation at 450 °C. When these isotherms were completed, the catalysts were 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.

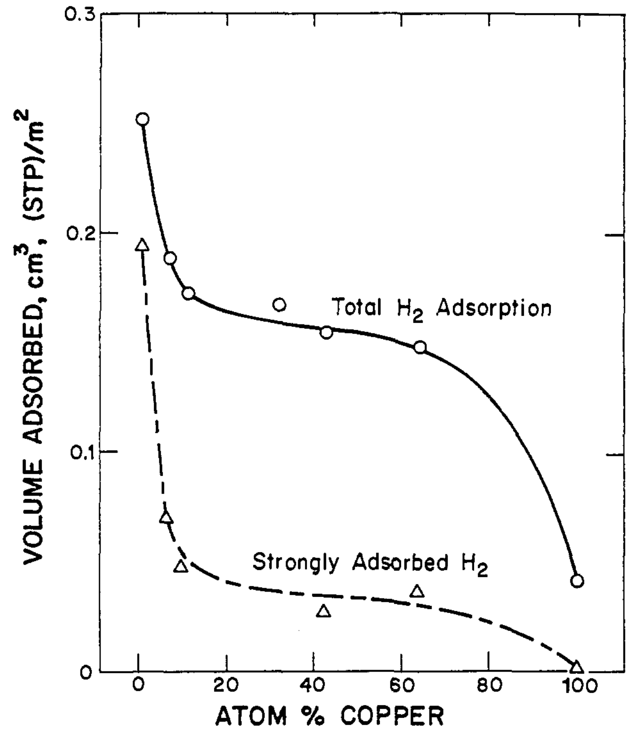

Figure 5. Adsorption of hydrogen on Ni–Cu catalysts as a function of copper content. The curve through the circles represents the total amount of hydrogen adsorbed at room temperature at 10-cm pressure. The curve through the triangles represents the amount of strongly adsorbed hydrogen, i.e., the amount 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.

tained by Shield and Russell[82] when plotting heats of hydrogen adsorption against catalyst composition (Figure 3).

Typical hydrogen adsorption isotherms at room temperature for nickel, copper, and Ni–Cu alloy catalysts[83] are shown in Figure 4. For the nickel catalyst it was observed that the amount of weakly adsorbed hydrogen (hydrogen which can be removed by simply evacuating the catalyst at room temperature) is small compared with the total adsorption. In contrast to this, the weakly adsorbed hydrogen accounts for essentially all of the adsorption on copper. The fraction of weakly adsorbed hydrogen increases markedly when a small amount of copper is added to nickel. Figure 5 shows the amount of strongly adsorbed hydrogen and total hydrogen adsorption as a function of catalyst composition at room temperature and an equilibrium pressure of 10 cm. 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 increments of copper until a composition of about 10% is attained. Though the effect of composition is relatively small for copper concentrations of 10–70%, it again becomes pronounced as the composition approaches that of pure copper.

Hall et al.[84,85] observed that the activity of Ni–Cu alloys for ethylene hydrogenation, parahydrogen conversion, and H_2–D_2 exchange was higher when the catalyst was cooled in hydrogen from a high reduction temperature (250–300 °C) to a subzero reaction temperature (−80 °C) than when they were outgassed at the reduction temperature before cooling. Pure nickel was affected in the opposite way, i.e., it was poisoned by the hydrogen. Shallcross and Russell[78] reported qualitatively similar results for the parahydrogen conversion over nickel and Ni-Cu alloys at -20 °C. Cooling in hydrogen at -196 °C reduced the activity of all the catalysts. The observations of Palczewska et al.[86-88] for the alloys confirm the poisoning effect on the surface by a special form of adsorbed hydrogen, namely the β-hydride state. Ni-Cu alloy films containing more than 60% copper do not form β-hydride.[89] The catalytic activity of evaporated nickel film was found to increase when the film was prepared in an atmosphere of hydrogen.[90]

Cadenhead et al.[91] studied the behavior of hydrogen adsorption on granular nickel powder, and when their results were compared with those obtained by Rideal and Swett[92] on nickel film it was observed that both the nickel film and the granular powder samples behave in a similar way. It was reported[93] for the alloy powders that water becomes trapped in pockets within the catalyst unless special precautions are taken during the critical initial stages of the reaction process. The water could not be expelled from the catalyst unless the reduction temperature was raised by 200 °C (to over 500 °C). On the other hand, when the partial pressure of hydrogen in contact with the catalyst was lowered sufficiently, the water was found to oxidize the nickel in the alloy to form nickel oxide with the evolution of hydrogen. A large amount of hydrogen was reversibly adsorbed and desorbed from the catalyst.

Takeuchi et al.[94] used the technique of autoradiography to investigate the reactivity of preadsorbed hydrogen or ethylene on nickel, copper, and Ni-Cu alloys prepared by various methods, using $^3H_2$ and [^{14}C]ethylene as tracers. The damage caused by the α rays and by the effect of sintering due to heat treatment was observed on massive alloys and evaporated films. A large difference was observed between the amount of hydrogen adsorbed on massive alloys and evaporated films. Although the adsorbed hydrogen was found to increase with increasing nickel content, the amount of adsorbed ethylene was not noticeably affected by the alloy composition. These results suggest that the catalytic activity of the metals depends mainly on structure factors rather than on electronic factors.

Pliskin and Eischens[95] studied the infrared spectra of ethylene chemisorbed on nickel and observed that the adsorption can be either associative or dissociative depending on the experimental conditions used. The important variables are temperature, hydrogen pressure, and the presence or absence of a preadsorbed hydrogen layer. In some cases, especially after dehydrogenation of adsorbed ethyl radicals, the spectra obtained indicated that almost half of the carbons were unsaturated. McKee[96] studied the chemisorption and catalytic dissociation of ethylene on unsupported nickel catalyst in the range of -78 to 200 °C and observed the formation of ethane by self-hydrogenation. Morrow and Sheppard[97] obtained results in agreement with the self-hydrogenation phenomenon when they studied the species formed by 1-butene and ethylene over silica-supported platinum. It is possible that a similar phenomenon may also occur in Ni-Cu alloys. Dalmon et al.[98] performed magnetic and infrared studies of CO chemisorption on silica-supported Ni-Cu alloys and observed the surface complex to be sensitive to the electronic environment of the metallic atoms. When copper was added to nickel it did not act simply as a dilutent of the active phase, decreasing the relative abundance of the bridged species for purely geometric reasons, but also changed the electronic behavior of nickel by decreasing its acceptor properties.

5. Hydrogenation of Aromatic Compounds

Hydrogenation of aromatic compounds has been reported for benzene,[4,7,17,99-108] cinnamic acid,[16,109] styrene,[110] and nitrobenzene.[80] The activity of copper for benzene hydrogenation is found to be greatly dependent on the presence of impurities, especially that of nickel. Long et al.[4] studied the catalytic activity of pure nickel and copper metals as compared with three Ni-Cu alloy powders containing 28, 54, and 79 atom % copper, respectively. The highest activity was found for the pure nickel catalyst, and copper was found to be completely inactive. The alloy containing 28% copper was the least active of the alloys, and the activity rose slightly as the percentage of copper increased from 54 to 79%. No surface area measurements were reported for these catalysts. Hall and Emmett[101] determined the specific activities and apparent activation energies for several carefully characterized alloy powders in benzene hydrogenation. These results as a function of alloy composition are shown in Figures 6 and 7, respectively. Although the results are in qualitative agreement with those of Reynolds,[17] there are a few marked differences. Reynolds observed a sharp drop in the activity at about 70% nickel while Hall and Emmett found it to exist at a 40% concentration. The latter result is in agreement with the hypothesis that the activity should fall as the d holes are filled. The apparent activation energy is discontinuous with composition (Figure 7). As copper is alloyed to nickel, the activation energy increases at first and then remains constant up to a concentration of about 60% copper, after which it decreases. The results of Cadenhead and Masse[104] support these observations, but Lyubarskii et al.[105] have criticized the work of Hall and Emmett as being experimentally inaccurate due to the use of nitrogen rather than krypton in determining the surface areas. Surface areas determined by nitrogen may be 10-15% too high due to low temperature nitrogen chemisorption. Lyubarskii et al.[105] observed that the activity of the alloys for benzene hydrogenation was related to the unit weight of the samples as well as the surface area, and it passed through a maximum at 10-40% copper in the alloy. The specific activity, which is related to the unit surface area of the catalyst as well as the number of unpaired electrons, was found to decrease

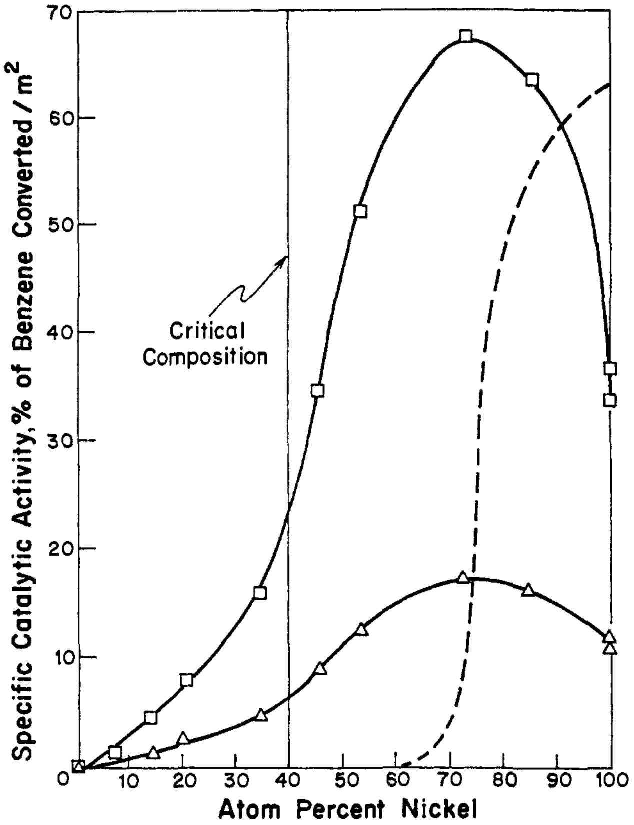

Figure 6. Catalytic activity of a series of Ni-Cu alloys in the hydrogenation of benzene: (□) data for 161.8 °C, (△) data for 135.0 °C. The dashed line is taken from the data of Reynolds.[17]

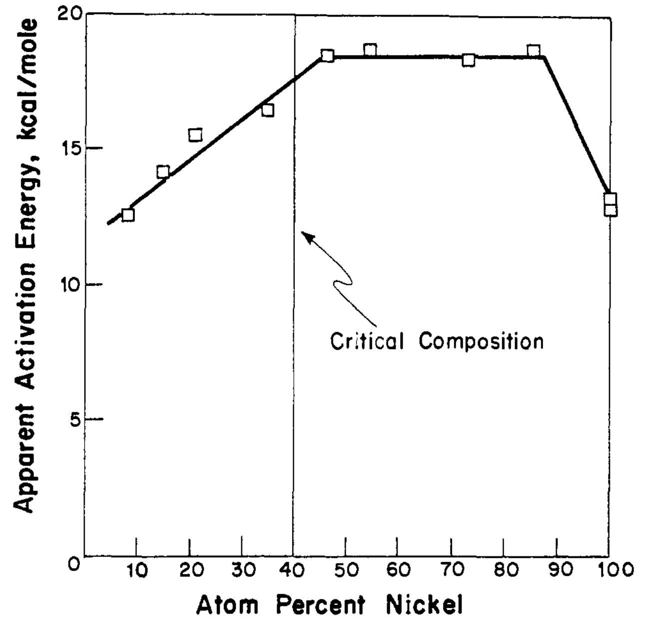

Figure 7. Activation energy for the hydrogenation of benzene for a series of Ni–Cu alloys.

almost linearly with increasing copper content and then to fall sharply at a copper content of about 80%.

Benzene hydrogenation has also been studied by Takeuchi et al.[7] on granular Ni–Cu alloys prepared in a different way from that of Hall and Emmett.[101] Their results for the activity pattern, shown in Figure 8, are entirely different from that observed by Hall and Emmett[101] and others[104,106] and support neither Dowden's view nor Sachtler's predictions. Van der Plank and Sachtler[111] studied the surface composition of equilibrated Ni–Cu alloy films and measured the catalytic activity by using benzene hydrogenation as a test reaction. They found that the catalytic activity of the two-phase alloy seems to be independent of the composition except for the nickel-rich side of the alloy where the enveloping of phase II by phase I may be incomplete due to the small quantity of phase I. It was also found that the catalytic activity of the sintered alloy films did not significantly depend on the order in which the metals were deposited. It was not clear as to why the catalytic activity of some reactions in their work changed so much over the composition range for which the work function did not change. The behavior predicted by Van der Plank and Sachtler[111] for Ni–Cu alloy films agrees well with the experimental results obtained by Cadenhead et al.[91] in powders. The hydrogenation of nitrobenzene over Ni–Cu alloy foils[60] supports the view of Sachtler and Dorgelo in that the Ni concentration remains constant at the surface, with a change occurring in the alloy bulk composition within the limits of 20 to 80% copper.

Schwab and Brennecke[109] studied the catalytic hydrogenation of cinnamic acid over Ni–Cu alloys and observed that the maximum activity lay in the nickel-rich region. Rienacker and Burmann[18] studied the cinnamic acid hydrogenation over unsupported and kieselguhr-supported Ni–Cu alloys. It was observed for the unsupported catalyst that a maximum in activity occurred at 40 atom % nickel, while for kieselguhr-supported alloys the activity decreased with increasing copper content until it became nearly zero at 60% copper. Dowden and Reynolds[55] and Reynolds[17] studied the hydrogenation of styrene in methanol solution over reduced Ni–Cu oxide supported on kieselguhr and on Ni–Cu foils between 20 and 80 °C and observed a parallel decline in the specific activity and magnetic susceptibility with increasing copper content in the alloy. It was observed that the specific activity and magnetic susceptibility both became very small or nearly zero at 50–60 atom % copper. Dupont and Piganol[112] observed that the addition of copper to nickel caused a decrease in the activity of the hydrogenation of allocinnamic acid.

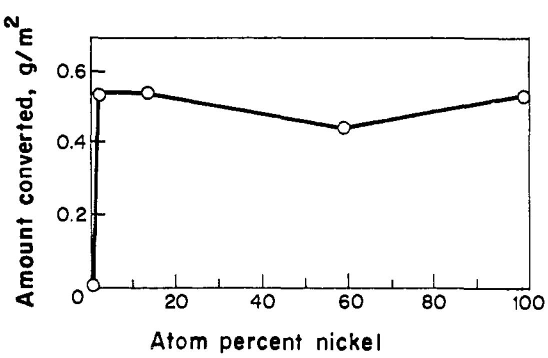

Figure 8. Catalytic activity of granular Ni, Cu, and Ni–Cu alloys for the hydrogenation of benzene at 190 °C.

6. Hydrogenation of Aliphatic Compounds

Hydrogenation of ethylene has been studied extensively over Ni–Cu alloys (see ref 2, 5, 7, 21, 55, 80, 84, 113–118). Studies have also been made on the hydrogenation of acetylene,[70,71,119,120] allyl alcohol,[80,100,121] acetone,[18,81,100,121,122] maleic acid,[100,122] allene,[123] and 1-butene.[124] Some of these reactions were also studied in the liquid phase. From the study of styrene hydrogenation over Ni–Cu alloys, Dowden and Reynolds[55] suggested that d-band vacancies were essential for the alloy catalytic activity. This was based on the observation of a complete loss of activity for styrene hydrogenation when nickel was alloyed with 3% copper. However, conflicting results obtained by using alloys prepared by different methods give rise to some confusion. Whereas Dowden and Reynolds[55] observed maximum activity at pure nickel for styrene hydrogenation over a series of alloy foils, Best and Russell[8] measured ethylene hydrogenation rates over alloy powders and found that the alloy containing 90 and 63.1% copper was 10 to 100 times more active than pure nickel alone. It is not possible to get an adequate idea regarding the dependence of catalytic activity upon catalyst composition between pure nickel and a 60% copper alloy from Best and Russell's work as they did not measure the activity as a function of catalyst composition. In the ethylene hydrogenation studies of Hall and Emmett[58] and Gharpurey and Emmett[21] it was confirmed that the activity of nickel was enhanced by the addition of copper. They also observed marked differences in the activity-composition patterns for Ni–Cu alloys which were cooled and treated with hydrogen or helium. It was observed in the hydrogen-treated studies that two maxima existed in the activity-composition diagram (Figure 9), one in the nickel-rich region and one in the copper-rich region. No such effect was observed in the helium-treated samples (Figure 10). It was observed further in the hydrogenation of ethylene that hydrogen adsorbed on Ni–Cu alloy catalysts acted as a promoter, while on pure nickel it acted as an inhibitor. The results do not appear to support the d-band theory of Dowden and Reynolds.

Campbell and Emmett[2] measured the rate of hydrogenation of ethylene on Ni–Cu alloy films prepared by successive deposition of the metal in the temperature range of 0 to 21 °C. They observed that the activity per unit area of film increased by 7 to 15 times for catalysts containing 10 to 20% copper, as compared to pure nickel (Figure 11). A minimum in the activity-composition diagram was found in the region of 25 to 35% nickel, where the activity was approximately the same as for pure nickel. The results obtained over massive Ni–Cu alloys[7] prepared physically and granular alloys prepared chemically, are quite different from those obtained by Campbell and Emmett[2] and Hall and Emmett.[58] It was suggested that the large increase

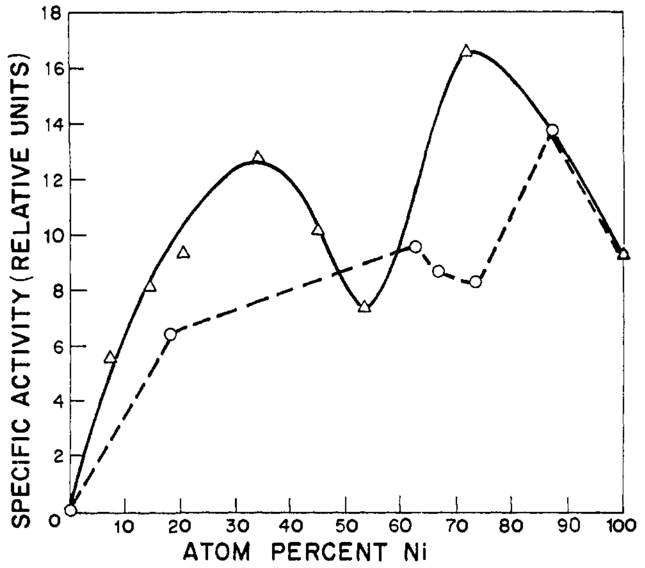

Figure 9. Hydrogenation of ethylene over Ni-Cu alloy films: (○) data at 0 °C, (△) data at 200 K. The activity units for the two sets of data have been made to coincide for nickel.

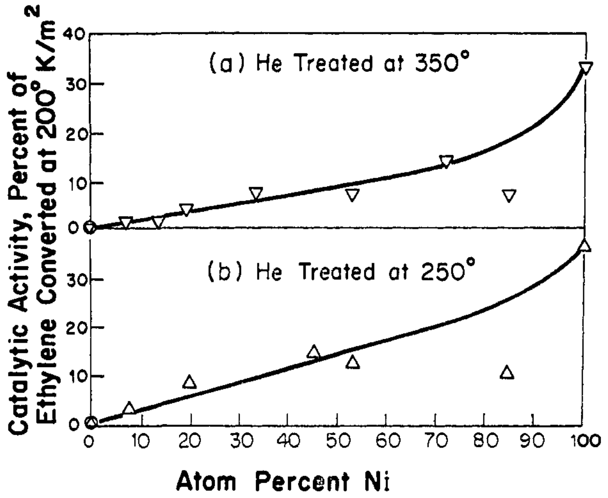

Figure 10. Catalytic activity of a series of Ni-Cu alloys at 200 K in the hydrogenation of ethylene.

in the activity for the hydrogenation of benzene and ethylene caused by a small addition (1%) of 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. A similar interpretation could be made for the heat of adsorption (Figure 12) and for the amount of hydrogen adsorbed (Figure 13) on the granular alloys.[7] It is observed in the figures that the activity remains constant over a wide range of nickel content from about 10 to 60% and then shows a maximum at pure nickel. These results support the view that the surface composition ratio of Ni/Cu remains constant over the 10-60% nickel range. The activity-composition pattern observed in granular alloys, however, could be interpreted in terms of the nickel concentration at the surface considered to be different from that of the interior. However, if the promotional effect of H_2 on the catalyst activity is due to increased Ni concentration on the surface, it is not clear why the enhanced activity is strongest in 80% Cu area. Moreover, pure Ni and other transition-metal catalysts are poisoned by the same treatment, indicating that a different explanation is required for these.

Several results show that the activity in heterogeneous catalysts is greatly affected by lattice defects and dislocations. It was observed that argon ion bombardment of nickel and platinum catalysts caused an increase in the activity of ethylene hydrogenation.[125,128] The effect of surface treatment on nickel and Ni-Cu alloys was observed to affect the activity and activation energy of the catalysts.[127] Yamashina and Farnsworth[116] bombarded Ni-Cu alloy sheets with argon ions and investigated the effect of Ni-Cu composition, bombarding current density, and thermal annealing on the catalytic activity of ethylene hydrogenation. While pure nickel was activated slightly by heating at red heat (800 °C), Ni-Cu alloys were found to be inactive until bombarded by ions. The activity of each alloy sample was found to pass through a maximum for ion current densities of between 120 and 200 μA (Figure 14). The activity of an alloy containing 60.5% copper was found to be a factor of 16 times greater than that of pure nickel for a bombarding current density of 160 μA. Annealing for a short time after ion bombardment produced an abrupt decrease in the activity at a critical temperature which increased with decreasing copper content.

Takeuchi et al.[113] studied the hydrogenation of ethylene over

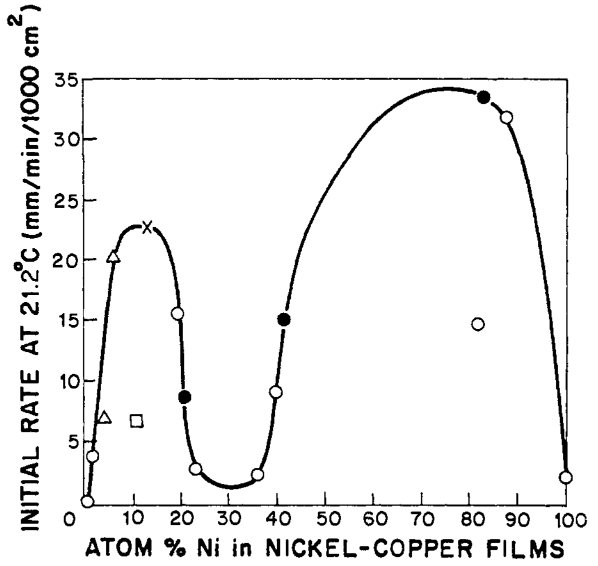

Figure 11. Initial rates of reaction for ethylene hydrogenation in mm/min per 1000 cm² of surface. Open symbols are for samples pretreated by heating the alloy in 5 cm of hydrogen at 300 °C. Solid symbols are for samples homogenized by heating to 500 °C in 5 cm of hydrogen. Triangles are for films in which the copper was deposited on the nickel. The open circles are for nickel evaporated on top of the copper. The open square represents a film in which the copper and nickel were deposited simultaneously.

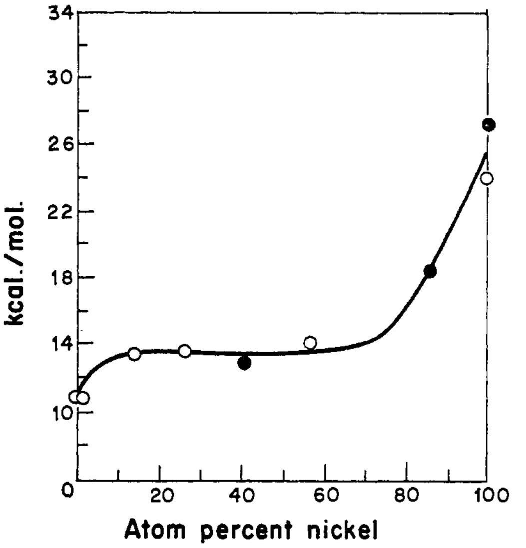

Figure 12. Heats of adsorption of hydrogen on granular Ni, Cu, and Ni-Cu alloys.

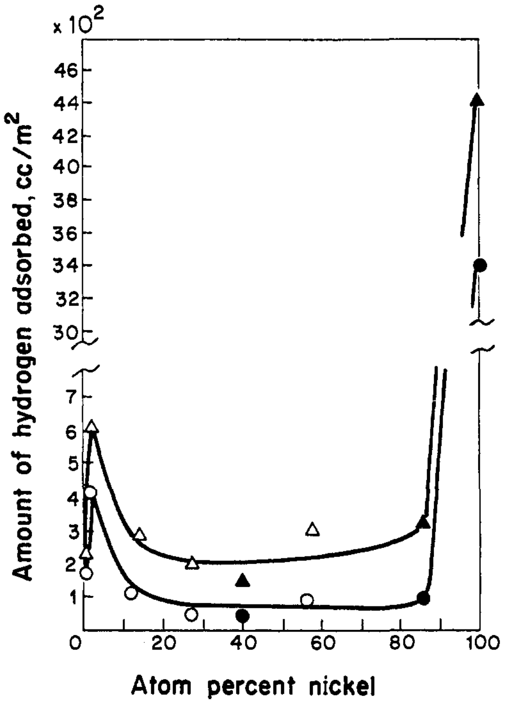

Figure 13. Amount of hydrogen adsorbed on granular Ni, Cu, and Ni–Cu alloys: (○) 10^{-3}-mmHg pressure, (△) 10^{-1}-mmHg pressure.

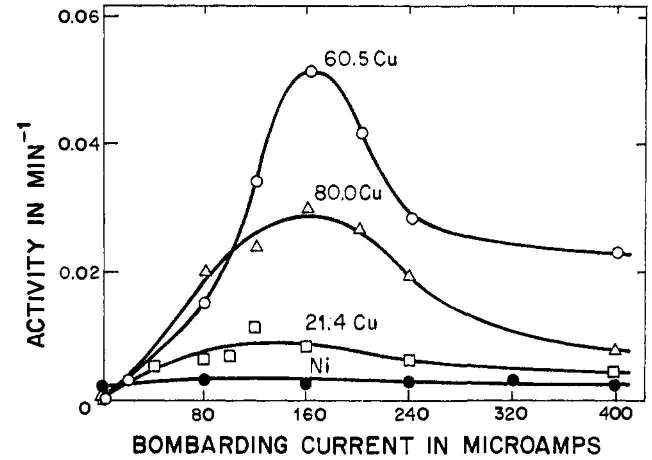

Figure 14. Activity as a function of bombarding current for Ni–Cu alloys of various compositions.

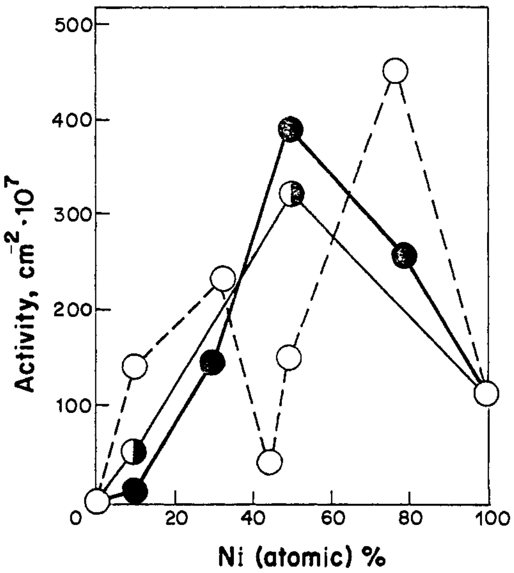

Figure 15. Catalytic activities of hydrogenation reaction of ethylene at 30 °C on Ni–Cu evaporated films treated at 30 °C: (●) films prepared from the alloy, (◑) films prepared from nickel on copper, (○) films prepared by the evaporation of copper on nickel.

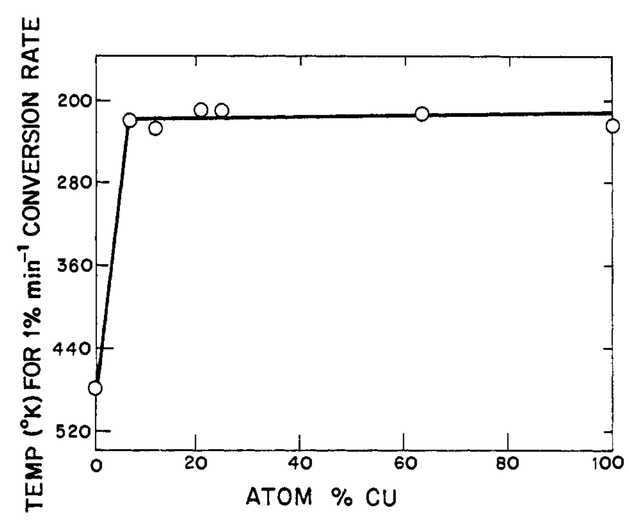

Figure 16. Activity pattern for the hydrogenation of 1-butene over Ni–Cu alloy films.

Ni–Cu films in order to determine the effect of resistance and catalytic activity as a function of composition. The films were prepared by evaporation of the copper and nickel metals or their alloys on a substance cooled by liquid oxygen and vacuum treated at 30 and 250 °C prior to use. For the films treated at 30 °C, maximum activity for the reaction was always found in the alloy region of the film, irrespective of the order of deposition of the two metals. Figure 15 shows the results of the film treated at 30 °C. The figure shows that films prepared from the alloy (●) and those prepared from nickel on copper (◑) give the maximum activity at a composition of about 50% nickel. The results for film (○) are similar to those obtained by Hall and Emmett,[56] who also found two large activities in the alloy region for films prepared by the evaporation of copper and nickel. For films treated at 250 °C it was found that the maximum activity shifted toward that of pure nickel. The increase in treatment temperature resulted in a marked decrease in electrical resistance, especially for the 50% nickel film.

Bond and Mann[120] have examined the activity of unsupported Ni–Cu powder catalysts in the hydrogenation of acetylene. The activity patterns showed a significant dependence on temperature in the Ni–Cu series caused by variations in the activation energies. At 50 °C there was a fairly smooth decrease in activity with increasing copper content. A significant decrease in activity was observed at 60% copper, which is the point where the d band is thought to be filled. At 200 °C the activity initially increased with increasing copper content until a maximum at about 50% copper was reached. This result is similar to that observed by Best and Russell[8] in the hydrogenation of ethylene. Mann and Khulbe[71,128] also studied the hydrogenation of methylacetylene over Ni–Cu alloy powders and observed that the activity increased with small additions of copper and passed through a maximum at about 25% copper. Also, the activation energy decreased slowly with increasing copper content in the range 0–60%, reaching a minimum of about 6 kcal at 60% copper and then increasing to 21.5 kcal for pure copper. The selectivity of polymerization of methylacetylene was found to increase with increasing copper content in the catalyst. Mann and co-workers[123,128] also studied the hydrogenation of ethylacetylene, allene, and dimethylacetylene over Ni–Cu powders. They found that the activity was maximum for all reactions in the nickel-rich region of the alloys. Hence it appears that the preparation of the catalyst plays an important role in the activity of Ni–Cu alloy catalysts.

Hydrogenation of allyl alcohol, maleic acid, and acetone in the liquid phase has been reported[100,129] for the reactions over unsupported Ni-Cu alloys and alloys supported on alumina. The addition of small amounts of copper (0-5%) to nickel appeared to enhance the catalytic activity of the alloys for the hydrogenation of allyl alcohol and maleic acid, but in the case of acetone the hydrogenation activity usually showed two maxima with respect to composition. No simple relationship between the activity and composition could be found. It is suggested that this is due to the large composition difference at the surface of the catalyst as compared to the bulk. One might expect surface enrichment by nickel since hydrogen is strongly chemisorbed to nickel and only weakly to copper. Clark and Byrne[124] have offered evidence in support of this idea, based on 1-butene hydrogenation rates. The activity pattern observed by them (Figure 16) is consistent with the presence of a 2% Cu-98% Ni phase at the surface of Ni-Cu films annealed in hydrogen at 530 °C.

7. Orthohydrogen-Parahydrogen Conversion and H_2-D_2 Exchange Reactions

Shallcross and Russell[76] studied orthohydrogen-parahydrogen conversion at -196 °C and near room temperature over Ni-Cu alloy catalysts prepared by hydrogen reduction of metal carbonates. The dependence of catalytic activity upon composition was found to be qualitatively the same at both high and low temperatures (Figure 17). While the alloying of a few percent copper (5%) to nickel, or nickel (10%) to copper, sharply decreased or increased the catalytic activity, respectively, there was relatively little change over the rest of the composition. X-ray diffraction measurements, however, showed that all the catalyst samples were homogeneous and to be of a single phase. On the other hand, Rienacker and Vormum[129] studied orthohydrogen-parahydrogen conversion over Ni-Cu alloy powders and found that the catalytic activity decreased slowly with increasing copper content up to 60% and then more rapidly, supporting the views of Dowden. This behavior is also similar to that observed by Hall[130] in the hydrogenation of ethylene. Kummer[131] studied at 21 K the orthohydrogen-parahydrogen conversion and magnetic properties of Ni-Cu alloy catalysts prepared by reduction of the coprecipitated carbonates. The conversion rates over the alloys and copper and nickel are summarized in Table I, where it is observed that the rate over nickel is slightly higher than for pure copper and the alloys. It is not possible from these data to determine the activity pattern as a function of composition because the work has been reported for a small range of nickel concentrations.

Frackiewicz et al.[117] studied orthohydrogen-parahydrogen conversion over Ni-Cu alloy (3% Cu) evaporated films and observed a poisoning effect due to the adsorbed hydrogen. Hall et al.[85] studied the effect of chemisorbed gases on the rate of parahydrogen conversion and H_2-D_2 exchange over nickel and Ni-Cu alloy catalysts (72.4% Ni) prepared by reduction of the coprecipitated oxides. It was found that when the nickel catalyst was cooled in hydrogen from 350 °C to a subzero reaction temperature of -80 °C its activity for parahydrogen conversion or H_2-D_2 exchange was considerably less than when it was outgassed at elevated temperatures and cooled in He. The opposite was found for Ni-Cu alloys, where the hydrogen treatment caused a promotion effect. The rate of H_2-D_2 exchange was always slower than the orthohydrogen-parahydrogen conversion, under comparable conditions. While the rates of both of these mechanisms and the Arrhenius parameters for the alloy catalysts were in good agreement with those reported for nickel by Eley et al.,[132,133] the activation energy was nearly half of that reported by Shallcross and Russell[76] for orthohydrogen-parahydrogen conversion.

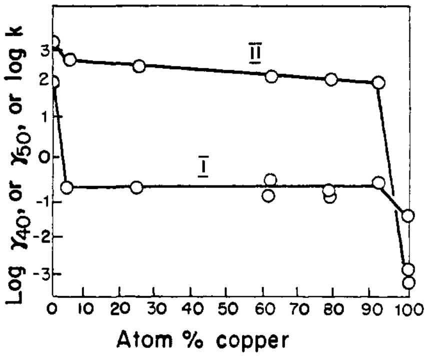

Figure 17. The effect of catalyst composition upon (a) the catalytic activity at -196 °C (curve I) and (b) the catalytic activity at -20 °C (curve II).

Table I. Orthohydrogen-Parahydrogen Conversion Data of Ni-Cu Alloys[131]

sample	redn temp, °C	surface area, m^2/g	conversion rate, R, cm^3 of para min^{-1} cm^{-2}
Cu	360	0.19	0.080×10^{-4}
Cu + 0.64% Ni	270	0.72	0.108×10^{-4}
	430	0.19	0.096×10^{-4}
Cu + 1.26% Ni	360	0.27	0.102×10^{-4}
	430	0.18	0.093×10^{-4}
	550	0.16	0.087×10^{-4}
Cu + 6.4% Ni	450	0.28	0.085×10^{-4}
Ni spec. pure	480	0.14	0.21×10^{-4}

The catalytic activity of Ni-Cu alloys (5 cm^2 area) was examined in H_2-D_2 exchange, after various surface treatments, by Takasu and Yamashina.[134] At 1.5-torr partial pressure of H_2 and D_2 it was found that the activity was greatest for pure nickel, gradually decreasing with increasing copper content, and becoming almost negligible for alloys containing more than 70% copper. The activity of the alloys was observed to be enhanced by an oxidation-reduction surface treatment. The activity after oxidation-reduction treatment was greatest for the alloy containing 85% copper, and to be 100 times that of pure nickel. Annealing for a short time in ultrahigh vacuum subsequent to oxidation-reduction treatment caused an abrupt decrease in the catalytic activity at 425 °C. The remarkable enhancement of the activity after oxidation-reduction treatment was attributed to the production of new active sites due to relocation of atoms on the surface. The effect of adsorbed hydrogen by the alloy surface may be important in accounting for the enhanced catalytic activity.

Byrne et al.[135] measured the equilibration rates of H_2-D_2 reactions on Ni-Cu alloy films and observed that irrespective of mechanistic complexity the activity was enhanced markedly (10^2 to 10^4 times greater than for pure copper) on the addition of nickel to copper, up to about 3 atom % nickel. The catalytic activity of the alloy consequently increased slowly with nickel content, reaching a maximum at about 40% nickel. In the region of pure nickel and at 40 atom % nickel in alloy the activity remained nearly constant.[136] Takasu and Matsuda[137] discussed the H_2-D_2 exchange reaction over Ni-Cu alloys. They concluded that the catalytic activities were related to the amount of strongly adsorbed H_2 which is bonded by the 3d band. No simple relationships were found between catalytic activity and electronic properties (work function, percentage of d character, and density of states at the Fermi level).

8. Miscellaneous Reactions

Cratty and Russell[138] studied the hydrogenation of carbon dioxide in the temperature range 200-500 °C over Ni-Cu alloy powders, prepared by the reduction of the oxides obtained from precipitated metal carbonates, and measured the methanation activity and magnetic susceptibility as a function of catalyst composition. It was observed that alloying with as little as 4% Cu caused a decrease in the overall activity of the hydrogenation of carbon dioxide. Between 4% copper alloy and pure copper the activity remained almost constant. Alloying with 11% or less copper with nickel caused a sharp parallel drop in both the magnetic susceptibility and the power of the catalyst for methanation. For alloys containing more than 50% copper, methane was no longer detectable, and the magnetic susceptibility was small. While in this region the lattice parameter of the alloy continued its nearly linear rise, the magnetic susceptibility decreased only very slowly. This effect appears to indicate that the geometric factor of the catalysts is of importance.

Some work over alloy catalysts has been reported on the decomposition of formic acid,[55,139-141] methanol,[110] hydrogen peroxide,[110] and carbon monoxide.[15] Quinn and Taylor[139] studied the kinetics of the heterogeneous decomposition of formic acid and of methanol over Ni-Cu alloys prepared according to the procedure of Best and Russell.[8] It was found that for the first 30-40% decomposition the formic acid was zero order. With the addition of copper to nickel the activity first decreased, up to about 30% copper, then rose to a maximum at about 70-80% copper. On further addition of copper to nickel the activity decreased to a minimum at pure copper. The activity of 70-80% copper in alloy was higher than for pure nickel. The methanol reaction rate followed the same trend as the formic acid reaction, with increasing copper concentration, but with the minimum and maximum being more pronounced. Reinacker and Bade[140] studied the decomposition of formic acid vapor between 120 and 200 °C using mixed alloy crystals and employing a static method. On addition of nickel to copper the activity was found to rise sharply for 10-30% nickel, and passed through a maximum at 18% nickel. Further addition of nickel caused the activity to increase gradually until it reached a maximum at pure nickel, which was three times more active than the alloy containing 18% nickel. Addition of nickel to copper caused a continuous decrease in the activation energy of the alloy from 22.3 kcal/mol for pure copper to 11.6 kcal/mol for nickel. Dowden and Reynold[55] concluded that the decomposition rates of formic acid and methanol vapors over Ni-Cu alloys decreased as the 3d band holes were filled and that the trend was similar to that for styrene hydrogenation.[17,55] On the other hand, the rate of hydrogen peroxide decomposition was said to fall as the 3d band began to empty, as was expected for a process controlled by the rate transfer of an electron from the metal to the substrate. Watanabe et al.[141] have reported results on the simultaneous measurement of Auger spectra and flash desorption spectroscopy applied to the decomposition of formic acid preadsorbed on clean Ni-Cu alloy surfaces. It was observed that the surface treatments of ion bombardment and annealing brought about a great difference in the decomposition process, which could be attributed to a change in the surface composition.

The hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene have been investigated over a series of Ni-Cu alloys.[83] The catalysts were prepared by coprecipitation of the metals as carbonates, followed by calcination and reduction. Very different results were observed for the two reactions investigated at 316 °C on addition of copper to nickel. In the case of ethane hydrogenolysis the catalytic activity decreased markedly and continuously with the 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. In the case of 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.

Ponec and Sachtler[142] studied the reactions of hexane isomers in an open flow reactor on Ni-Cu alloys prepared from coprecipitated carbonates. In the range of 0-23% copper it was observed that the activity of the catalysts decreased with increasing copper content and that the selectivity for C_6 products increased to a value previously found for active films.[143] While the activity remained almost constant for the catalyst containing 20-60% copper, the selectivity increased and reached a value of about 65%. Selectivity and fission parameter showed only a small temperature dependence. Sachtler et al.[144,145] reported results of studies on cyclopentane and methylcyclopentane reactions with deuterium at 0-200 °C on Ni-Cu alloy films and on methylcyclopentane reactions with hydrogen at 210-320 °C over Ni-Cu alloy powders. It was observed that, upon alloying copper with nickel, reactions with C-H bonds were influenced to a lesser extent than the reactions with C-C bonds (isomerization, cracking, etc.). The exchange reaction retained its high multiplicity also on alloys with high copper content while cracking is strongly suppressed. Alloying caused a change in the selectivity patterns of the C-C reaction in favor of nondestructive reactions. Besides the basic assumption that the metal adsorbate bond strength is weakened by alloying, the electronic effect (leading to the lowering of bond strengths) is also assisted by the geometric effect for the reaction of methylcyclopentane and hydrogen over Ni-Cu alloys. The size of Ni ensembles in alloys is smaller than in pure nickel, and this fact favors the reactions which need fewer sites (e.g., isomerization reactions) and makes the reactions which use more sites (e.g., cracking) less probable. Moreover, the cyclopentane-deuterium exchange reaction is accompanied by self-poisoning.

For Ni-Cu catalysts supported on η-Al_2O_3 the activity toward cyclohexane dehydrogenation passes through a maxima with increasing copper content whereas ethane hydrogenolysis activity drops sharply.[14] The first result is in agreement with the findings of Sinfelt et al.[83] for unsupported Ni-Cu catalysts, but the second result is not. It was suggested by Burton and Hyman,[10] on the basis of ethane hydrogenolysis data over Ni-Cu alloys, that the possibility of the active sites containing only one or zero nickel atoms is precluded, but the possibility that some copper atoms are also involved in the catalytic activity is not precluded. The catalytic activity occurs at a site containing two nickel atoms in the Ni-Cu alloys. Calculations showed that the nickel atoms would be a minority on the surface for all bulk concentrations.

Araki and Ponec[146] studied the methanation of CO and CO_2, disproportionation of CO, and hydrogenation of carbon deposited on the surface of Ni and Ni-Cu alloy film catalysts at low pressures and temperatures of 250-350 °C. It was observed that on the addition of copper to nickel the reaction rates were strongly reduced. Nishiyama and Tamai[147] studied the carbon deposited from benzene onto Ni-Cu alloy sheets at temperatures ranging from 570 to 700 °C in atmospheres of hydrogen and helium and their mixtures. The deposition rate onto pure nickel was higher in hydrogen than in helium whereas that onto 80% nickel alloy was higher in a helium-rich atmosphere than in hydrogen. The formation of ammonium cyanate and urea from NO over Ni-Cu catalysts has also been reported.[148] Hydrogenation of cottonseed oil was studied over the Ni-Cu-Al system,[18] and it was observed that the stability of the catalyst depended on the energy of bonding with H_2.

Studies have also been reported over Ni-Cu alloy catalysts for the hydrogasification of carbon,[149] the catalytic decomposition of ammonia,[150] the catalytic bond cleavage of long chain aliphatic alcohols and ω-phenylalkyl alcohols,[151] and the reduction of nitrogen dioxide.[152] The influence of alloying on the selectivity in Fisher-Tropsch synthesis by Ni-Cu alloys has also been reported.[153] However, no simple relation between catalytic activity and composition of the Ni–Cu alloy has been found.

9. Conclusions

From the foregoing discussions it seems that Dowden's electronic theory for catalysis is not true due to the following reasons. (a) Valency band theory of the solid state is applicable to the bulk alloys only and not to the structure of the bands at the surface. (b) Most of the catalytic data supporting Dowden's theory was obtained on Ni–Cu alloys. Later it was found that the alloys consist of two phases.

It has been found that the composition of alloy films differs greatly from the average composition of the bulk and that it remains constant over a wide range of compositions. This phenomenon has also been observed in granular alloys, reduced oxides, and massive alloys. Hence, surface composition plays an important role in alloy activity. It has also been determined that the activity of heterogeneous catalysts is greatly affected by lattice defects and dislocations.

Factors other than those discussed above may also affect the catalytic activity of Ni–Cu alloys. Although a theoretical interpretation of these results has not been completely established, it seems certain that the method of preparation of the catalyst and the reduction temperature can have a profound influence on the observed activity patterns. The promoting effect on the catalytic activity caused by cooling in hydrogen rather than under vacuum may be a significant factor. That is, it may be related to preadsorbed (or dissolved) hydrogen on the catalysts. The enhancement may also be due partly to a reaction with residual oxides in the powder.

The role of lattice vibrational effects is not usually mentioned when attempting to describe the chemical and physical behavior of the alloy catalysts. The importance of these effects and the nature of their behavior in the presence of impurities has been recently described in magnetic resonance studies of crystals[154] and in biological research on cell division.[155] Calculations[154] were made on the temperature dependence of the spin Hamiltonian parameter of Cr^{3+} impurities in axially symmetric sites of MgO. The Cr^{3+} ion in MgO is surrounded by six O^{2-} ions in a perfect octahedral arrangement. The axial symmetry occurs due to Mg^{2+} ion vacancies or unipositive ions such as Li^{+} in such vacancies, located in next-nearest-neighbor positions to the Cr^{3+} ion and acting as charge compensators. Experiments indicate[156] that the $Cr^{3+}\cdot 6O^{2-}$ complex with no local charge compensator vibrates with a single local mode frequency of 355 cm^{-1}, and the effect of a next-nearest-neighbor charge compensator[154] is to change the local mode vibration frequency to 562 cm^{-1}. Such changes in vibrational behavior may also be important in understanding the chemical and physical behavior of Ni–Cu alloys in the various catalytic reactions, the effect of alloy preparation and ion bombardment, and also the geometric and electronic behavior of the compounds.

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