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The Catalytic Hydrogenation of Ethylene on Nickel-Copper and Nickel-Gold Alloys

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The rate of ethylene hydrogenation on copper-nickel alloy films in the temperature range 0° to 21°C has been measured. The films were prepared by successive deposition of copper and nickel by the usual film-forming procedures followed by sintering the films in 5 cm of hydrogen at either 300° or 500°C. The activity per unit area of film increases to a value 7 to 15 times as great for a catalyst containing 10% to 20% Cu as for pure nickel. Similarly, catalysts containing 5% to 20% nickel are as much as eight times as active as pure nickel. A minimum of activity with composition is found in the 25% to 35% nickel region, where the activity is about the same as on pure nickel. X-Ray data show that films homogenized by heating to 500°C in a few cm of hydrogen form an alloy containing about 60% copper; the excess of nickel or copper present gives a diffraction pattern for the pure metal. Gold-nickel alloys containing 15% and 55% gold, respectively, have rates only about one-tenth as great as that of pure nickel. The apparent energies of activation for the reaction over the copper-nickel alloys vary with composition in the range 9 to 12 kcal/mole; those for the two gold-nickel alloys are about 4 kcal. The reaction rate is first order with respect to hydrogen and independent of ethylene for the copper-nickel alloys and for pure nickel; it is first order with respect to both hydrogen and ethylene for copper.

Alloy catalysts, particularly those of copper and nickel, have been studied for a number of years, with a view to confirming the proposals of Dowden (*1*, *2*) and of Schwab (*3*) relative to the influence of the electronic structure of solids on their catalytic activity. Dowden reported that the addition of 38% copper to nickel completely destroyed the activity of the latter for the hydrogenation of styrene, and suggested that *d*-band vacancies in the metal are essential for it to be active as a hydrogenating catalyst. Soon, however, experimental data on the hydrogenation of ethylene indicated that certain copper-nickel alloys were ten to a hundred times more active than nickel. Most recent work on ethylene hydrogenation has probably received its impetus from the observation by Best and Russell (*4*) that rates on catalysts containing 90% and 63% copper were higher than on pure nickel by factors of about 10 and 100, respectively. The enhancement of the activity of nickel for the hydrogenation of ethylene resulting from adding copper to form an alloy was confirmed by Hall and Emmett (*5*). These authors also observed that hydrogen adsorbed on copper-nickel alloy catalysts acted as a promoter whereas on pure nickel, it appeared to be an inhibitor for the ethylene hydrogenation reaction. In view of the fact that it seemed reasonable that catalysts reduced from metal oxides might retain small residual amounts of oxides which could act as possible promoters, it was decided to attempt to prepare alloy catalysts by a film technique. Characteristically, the preparation of metal films usually avoids contamination with oxygen. Measurements of such metal films should then either prove or disprove the capability of copper to enhance the activities of nickel as a hydrogenating catalyst for ethylene.

A start in the direction of alloy work from

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films was made by Gharpurey and Emmett (*6*). They deposited thin films of nickel in high vacua and then superimposed thin films of copper. Sintering the films for a few hours in 5 cm pressure of hydrogen at 300°C appeared to homogenize these alloys. It was definitely established that alloys of different composition had the same catalytic activity regardless of whether the nickel was deposited on top of the copper or the copper deposited on top of nickel. Furthermore, visual observations indicated that the appearance of the films by this alloying procedure was altered to something intermediate between that of metallic copper and metallic nickel. The results of Gharpurey and Emmett agreed in general with those obtained by Hall and Emmett, thought they were insufficient in number to give a detailed outline of the way in which the catalytic activity changed with the catalyst composition.

The present work was undertaken with a view to obtaining a number of additional experimental observations on the activity of copper-nickel alloys made by films. In addition, a few of the films were studied by X-ray technique to ascertain the extent to which homogenization occurred in the thin metal films. The X-ray results led to the astounding conclusion that homogenization at 500°C appeared to form a nickel-copper alloy containing approximately 60% copper and 40% nickel. The only other phases present were those corresponding to pure copper or pure nickel depending upon which metal happened to be present in excess of the 60–40 copper-nickel alloy. This X-ray observation was very baffling, and was partly responsible for causing the authors to delay publication of this work, which was completed 3 years ago. A recent publication by Sachtler and Dorgelo (*7*) has led to the conclusions that particular copper-nickel alloys, rich in copper, appear to be formed preferentially if complete equilibration of copper-nickel alloys is permitted to take place. The data here presented are of interest, therefore, both as an indication of the way in which the activity of nickel-copper alloys varies as a function of composition and also as a confirmation of the preferential formation of high copper alloys when these alloys are made by sintering thin films of the respective metals. A few runs were also made on nickel-gold alloys.

EXPERIMENTAL

Apparatus and Technique

An apparatus similar to that described by Kemball (*8*) was constructed. An additional dosing system was added in order to measure the surface areas of the films by the BET method.

Ethane and ethylene (Matheson, CP grade) were further purified by vacuum distillation, freezing, and pumping. The purity was checked by vapor pressure measurements. Hydrogen was purified by diffusion through an electrically heated palladium thimble; helium, by passage over freshly reduced copper wire at 400°C and then through activated charcoal at liquid nitrogen temperature. "Spectrographically standardized" nickel, copper, and gold wire were obtained from Johnson-Matthey Company, Ltd.; and tungsten wire and rod were supplied by A. D. Mackay, Inc.

The reactor chamber consisted of a 300-cc Pyrex balloon flask; the necessary electrical connections were made through a press seal by four tungsten rods. Experiments of temperatures greater than 450°C were carried out in a quartz reaction vessel attached to the press seal by means of a quartz-Pyrex graded seal. Nickel was evaporated directly from a heated wire (15 cm long, 0.5-mm diameter) since its evaporation temperature was lower than its melting point. Copper and gold, on the other hand, were evaporated by an electrically heated tungsten support (20 cm long, 0.2-mm diameter, copper or gold wire was wound over 10 cm of 0.3-mm diameter tungsten wire).

Before evaporation, the reaction chamber was evacuated at a temperature equal to or greater than 450°C for 24 hr, or until the pressure was much less than 10^{-3} μ. Simultaneously, the nickel, copper, or gold filaments which had previously been glowed at red heat in hydrogen to reduce any oxide layer were degassed just under their evaporation points. Evaporation was carried out with the reaction chamber cooled in ice at 0°C.

After deposition, the copper-nickel films were generally heated overnight at 300°C in 5 cm of hydrogen; the gold-nickel films were reheated overnight at 500°C in 5 cm of hydrogen. The films were cooled to room temperature and the hydrogen was pumped off. A standard reaction mixture of 2.5 cm hydrogen and 2.5 cm ethylene was then admitted to the reaction vessel through an acetone–Dry Ice trap. Before reaction, the reaction vessel contained 5.16×10^{20} molecules of ethylene. Reaction was initiated by heating the reaction vessel as quickly as possible from its initial temperature of −78°C to the desired temperature. The rate of reaction was followed on a mercury manometer isolated from the reaction vessel by means of an acetone–Dry Ice trap. The mercury level was measured by means of a traveling microscope.

Five of the nickel-copper films were homogenized by heating them to 500°C overnight in about 5-cm pressure of hydrogen. The catalytic activity of some of these samples and also the X-ray patterns were compared.

Generally, five reactions were carried out on each film, and after each reaction the film was reactivated by heating for 30 min at 300°C in 5 cm of hydrogen. The first and last reactions on each film were made under similar conditions in order to check for any variation in activity.

Film areas were determined by the BET method using ethane at liquid oxygen temperature. It was not necessary to pretreat the film with ethane as area measurements were always carried out after a reaction of ethylene and hydrogen to form ethane had occurred. The area of each ethane molecule was assumed to be 20.5 sq. Å units at liquid oxygen temperature.

RESULTS

The Homogenization of Copper-Nickel and Gold-Nickel Films

The extent of homogenization of these films at 300° and 500°C and in the presence and absence of hydrogen, was followed by X-ray diffraction. The results for copper-nickel system are summarized in Table 1. All the films were heated overnight in 5 cm of hydrogen except J, which was heated in the absence of hydrogen. No alloy formation was detectable by X-rays under the conditions described by Gharpurey and Emmett (overnight heating at 300°C in 5 cm of hydrogen).

As shown by samples B, E, and I in Table 1, alloying at 500°C appeared to occur with the formation in each case of a single alloy containing approximately 40% nickel. Samples B and I, which contained less than 40% nickel in the sample as a whole, therefore, contained the alloy plus lines corresponding to excess copper. Sample E, on the other hand, which contained more nickel than that of the 40–60 nickel-copper alloy, contained excess nickel, as judged by the diffraction pattern. The interpretation of these unexpected X-ray results will be referred to in the discussion further along in this paper.

It should, perhaps, be noted that the X-ray patterns obtained for all samples homogenized at 300°C and also for the sample homogenized at 500°C in the absence of hydrogen showed only the patterns of nickel and copper. This indicated that the 40–60 nickel-copper alloy, if present, was formed to such a small extent that it did not give any evidence of its presence by its X-ray pattern.

X-Ray Diffraction Experiments

X-Ray diffraction experiments were carried out using two different types of specimens. When possible, each metal film was washed off the walls of the reaction vessel with sterile water and benzene, dried, ground into a powder, and inserted into a fine capillary. Generally, however, it was impossible to detach the films from the walls of the reaction vessel and, therefore, before each experiment a thin Pyrex or quartz fiber was placed in the reaction vessel and the metal deposited on the fiber in order to form a specimen for the X-ray work. This type of specimen had an additional advantage in that the overall structure of each metal film was preserved for examination.

All X-ray patterns were obtained by the

TABLE 1

THE COMPOSITION OF COPPER-NICKEL FILMS "HOMOGENIZED" IN 5 CM OF HYDROGEN

Run Number	Metal deposited on top	Total film wt. (mg)	Composition by wt. (Atom % Ni)	Homog. temp. (°C)	X-ray data		
					Type of sample	Phases present	Composition
10	Ni	15.6	40	300°	Powder	Ni and Cu	100 %Ni 100% Cu
12	Ni	31.7	36	300°	Powder	Ni and Cu	100% Ni 100% Cu
B	Ni	26.3	21	500°	Quartz fiber	Ni-Cu Alloy and Cu	41% Ni 100% Cu
E	Cu	40.4	49	500°	Powder	Ni-Cu Alloy and Ni	41% Ni 100% Ni
I	Simultaneous	34.0	9	500°	Quartz fiber	Ni-Cu Alloy and Cu	38% Ni 100% Cu
J[a]	Simultaneous	16.2	33.8	500°	Quartz fiber	Ni and Cu	100% Ni 100% Cu

[a] Not heated in hydrogen.

Debye-Scherrer powder method using Cu-$K\alpha$ radiation. The composition of each phase present (atomic percent nickel) was calculated from the corresponding a_0 value. The data of Owen and Pickup (*9*) were used to estimate the composition of the copper-nickel alloys and those of Elwood and Bagley (*10*) for the gold-nickel system. These X-ray results are not accurate to better than 5% because the back reflections were too diffuse to measure due to the small crystallite size of the evaporated metal film.

Alloy formation was especially difficult with the gold-nickel system and X-ray diffraction showed that little or no alloying occurred at 500°C in 5 cm of hydrogen in 24 hr. The two metals were evaporated simultaneously. This contrasts with the results published by Belser (*11*), who reported gold and nickel alloy formations at temperatures as low as 190°C.

The Hydrogenation of Ethylene

Nickel. The activity found through pure nickel films was comparable to that determined by Beeck, Smith, and Wheeler (*12*) and by Crawford, Roberts, and Kemball (*13*). Plots of the logarithm of the ethylene pressure against time showed the reaction to be first order in hydrogen and zero order in ethylene. The temperature dependence of the initial rates (molecules per second per 1000 sq. cm of catalyst) was found to be given by the equation

$$\log_{10}(\text{initial rate}) = 25.5 - 10\,500/4.575\,T$$

with a temperature range 0° to 72°C.

Five runs were generally carried out on each film and an activity decrease occurred with each run. The decrease in activity was avoided by reactivating the films before each new run for half an hour in 5 cm of hydrogen at 300°C. Arrhenius plots were determined in two different ways. In one instance, the experimental points were obtained on films that had been reactivated prior to each run. In other instances, the fall-off in activity was corrected for by assuming a proportional decrease for each run and noting the final activity of the last run of a series. The Arrhenius plots arrived at by these two procedures were identical. This indicated a constant activity decrease on a sample with each run. The fall-off in activity was not due to sintering because the surface areas measured by ethane adsorption remained, within experimental error, constant. The surface area of the pure nickel films was generally in the range 800–1000 sq. cm or roughly up to four times the geometric areas.

The first order rate constant for the reaction over nickel at 0°C was found to be 0.196/min per 1000 sq. cm for a film cooled *in vacuo*. However, for a film cooled in hydrogen the rate constant decreased to 0.025/min per 1000 sq. cm surface. Thus, hydrogen adsorbed while cooling the film from 500°C acted as an inhibitor for the reaction, in agreement with the observations made by Hall and Emmett (*5*).

Copper. Over the temperature range 140° to 200°C, the temperature dependence of the initial rates of reaction in molecules per second per 1000 sq. cm was given by the equation

$$\log_{10} \text{(initial rate)} = 23.4 - 12\,000/4.575\ T.$$

At 200°C, the activation energy approached zero, and at the higher temperatures over the range 200° to 260°C, it appeared to become negative by approximately 2 kcal/mole. A similar phenomenon has been observed for the reaction on nickel at high temperatures and has been discussed by Twigg (*14*).

The reaction was found to first order in hydrogen and first order in ethylene at all of the temperatures studied, a result previously found by Pease (*15*, *16*) and his co-workers. Before each run, the films were reactivated in a manner similar to that described for nickel, though reactivation was more difficult with copper. In fact, it was necessary to heat the copper films for an hour in hydrogen at 300°C to completely reactivate them. The surface areas were generally just slightly greater than the geometric area (about 200 sq. cm).

Gold. Gold was the most catalytically inactive of all the metals studied. The initial rate of reaction at 486°C was found to be 5.6×10^{15} molecules/sec per 1000 sq. cm. The activation energy was not obtained because it was not possible to work at temperatures greater than 500°C as water tended to be desorbed from the walls of the reaction vessel at such high temperatures.

Copper-nickel and gold-nickel alloys. The Arrhenius plots for the initial rates of reaction at different temperatures were linear. The activation energies and frequency factors are given in Table 2 for the nickel-copper alloys. Those for the gold-nickel system are shown in Table 3.

Figures 1 and 2 show the initial rates of reaction at 21.2°C plotted against the atom percent nickel for the copper-nickel and the gold-nickel systems, respectively.

Effect of cooling samples in hydrogen. The variation in the activity of nickel films heated and cooled in hydrogen, and in helium or *in vacuo* was studied. The results are shown in Table 4. Two pairs of experiments were necessary and each pair was carried out on freshly prepared film. The ratio of the initial rate on the vacuum-cooled

TABLE 2

ACTIVATION ENERGIES AND FREQUENCY FACTORS (A) FOR INITIAL RATES OF HYDROGENATION OF ETHYLENE ON COPPER-NICKEL FILMS

Run Number	Mass evapd. (mg)	Atom % Ni	Metal deposited on top	Temp. range (°C)	$E \pm 0.5$ (kcal/mole)	$\log_{10} A \pm 0.5$[a]	Surface area (cm^2)	Homog. temp. (°C)
8	16.7	23.0	Ni	0.0° to 39.6°	10.5	25.6	998	300°
9	13.0	82.0	Ni	−12.0° to 24.6°	8.6	25.0	342	300°
10	15.6	39.7	Ni	−11.5° to 23.2°	10.5	26.2	442	300°
11	26.5	1.6	Ni	19.5° to 69.0°	9.8	25.3	210	300°
12	31.7	36.0	Ni	0.0° to 49.3°	12.8	27.3	282	300°
A	36.6	41.5	Ni	0.0° to 26.1°	13.3	28.4	259	500°
B	26.3	20.8	Ni	0.0° to 34.0°	9.2	25.2	331	500°
R	11.6	19.3	Cu	−9.0° to 29.0°	11.0	26.8	343	300°
S	44.4	3.7	Cu	0.0° to 35.6°	12.0	27.1	326	300°
T	33.4	10.6	Simult.	0.0° to 33.5°	9.8	24.9	442	300°
U	24.9	88.0	Cu	−10.0° to 22.5°	9.6	26.1	274	300°
Z	33.6	5.9	Cu	0.0° to 21.2°	10.5	26.5	345	300°

[a] A in molecules/sec 10^3 cm^2 of catalyst.

TABLE 3

ACTIVATION ENERGIES AND FREQUENCY FACTORS (*A*) FOR INITIAL RATES OF HYDROGENATION OF ETHYLENE ON GOLD-NICKEL FILMS

Run Number	Mass evapd. (mg)	Atom % Ni	Metal deposited on top	Temp. range (°C)	$E \pm 0.5$ (kcal/mole)	$\log_{10} A \pm 0.5$[a]	Surface area (cm^2)	Homog. temp. (°C)
W	47.2	45.3	Simult.	156° to 276°	3.6	19.4	485	500°
X	22.0	83.7	Simult.	114° to 202°	4.2	19.9	442	500°

[a] *A* in molecules/sec 10^3 cm^2 of catalyst.

film to that on a hydrogen-cooled film was about 8.0. It was clear that hydrogen strongly inhibits the reaction of nickel. Contrary to the results observed by Hall and Emmett (*5*), and Hall and Hassell (*17*), the cooling of the samples in helium produced less active catalyst than cooling in hydrogen. This apparent poisoning effect of helium in the present work is almost certainly due to small traces of impurity in the helium. The rates observed on the samples cooled in hydrogen are in good agreement with those reported above for pure nickel (first order rate constants 0.0570 and 0.0192/min per 1000 sq. cm of surface at 21.2° and 0°C, respectively).

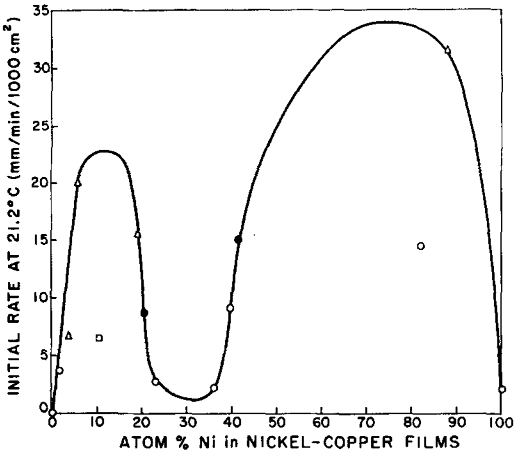

FIG. 1. The initial rates of reaction for ethylene hydrogenation in mm/min per 1000 sq. cm of surface. Open symbols are for samples pretreated by heating the alloy in 5 cm of hydrogen at 300°C; solid symbols are for samples homogenized by heating to 500°C in 5 cm of hydrogen. Triangles are for films 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.

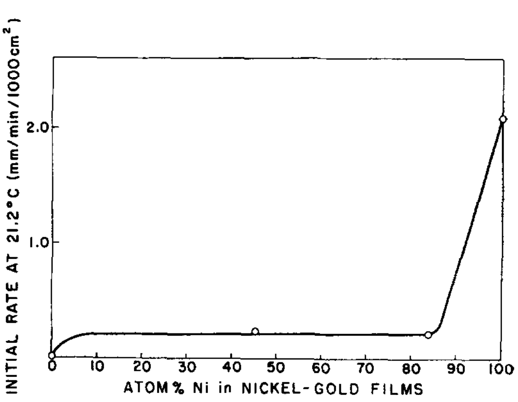

FIG. 2. The relative activities of pure gold, pure nickel, and two gold-nickel alloys for ethylene hydrogenation. For details see Table 3.

TABLE 4

FIRST ORDER RATE CONSTANTS ON HYDROGEN-COOLED, HELIUM-COOLED, AND VACUUM-COOLED NICKEL FILMS

Temp. (°C)	Type	Area (cm^2)	k [(min 30^3 cm^2)$^{-1}$]
0°	Vacuum-cooled	1000	0.198
0°	Hydrogen-cooled	1000	0.024
21.2°	Helium-cooled	1734	0.042
21.2°	Hydrogen-cooled	1734	0.066

The rates of reaction over a helium-cooled nickel-copper film were measured at 21.2° and 0°C, and were found to be slower by a factor of about 2 than those over the same film cooled in hydrogen. The composition of the nickel-copper film corresponded to 5.9% nickel. Copper was deposited on top of the nickel and the film was homogenized overnight in 5 cm of helium at 300°C. The temperature dependence of the initial rates under helium-cooled conditions was found to be given by the equation

$$\log_{10}(\text{initial rate}) = 26.2 - 10\,700/4.575\,T$$

Under hydrogen-cooled conditions, the reaction rate was given by the equation

$$\log_{10}(\text{initial rate}) = 26.5 - 10\,500/4.575\,T$$

over the temperature range from 0° to 21.2°C. These latter observations are consistent with the experiments of Hall and Emmett (*5*), in indicating that the absolute reaction rate on a catalyst containing 5.9% nickel was greater than the rate over pure nickel when both samples were cooled in hydrogen.

Attempts were made to measure the adsorption of hydrogen at 0°C on a copper-nickel film containing 12.9% nickel homogenized at 300°C and with the copper deposited on top of the nickel. No adsorption could be detected. It is impossible to say whether the hydrogen was adsorbed, or whether only 12.9% of the surface was covered since the latter quantity was just inside the experimental limit of the apparatus. In any event, a catalyst with this much nickel was severalfold more active than was a catalyst of pure nickel.

DISCUSSION

At the outset of the present discussion, it should, perhaps, be emphasized that in almost all of the work done on copper-nickel catalysts, there has been an uncertainty as to the composition of the surface of the alloy materials. Sachtler and Jongepier (*18*) imply that it is tacitly assumed by workers in this field that the surface composition is the same as the composition inside the alloy crystals. Actually, it is probably more nearly correct to say that most workers in the field recognize that it is never safe to assume that the surface composition of an alloy or a promoted catalyst is the same as the bulk composition but that they have found no means for assaying the surface composition. The adsorption of hydrogen suggests itself as a possible means but so far it has not been effective in determining the fraction of the surface covered by nickel. The chemisorption of carbon monoxide at low temperatures is of no value in the present instance in view of the fact that both copper and nickel chemisorb carbon monoxide at −195°C. This method was, as a matter of fact, explored in a paper by Skau and Emmett (*19*) in an effort to deduce the composition of the surface of alloy catalysts for the hydrogenation of benzene.

The most striking result in the present experiments was the observation that all three samples of a nickel-copper catalyst alloy heat-treated at 500°C in an atmosphere of hydrogen developed an alloy of a single composition containing approximately 40% nickel and 60% copper. In addition, of course, excess copper or excess nickel, depending on the catalyst composition, was found to be present. In contrast to this, all of the catalyst homogenized at 300°C failed to show any such alloying effect.

The formation of this alloy to a constant composition was very puzzling until the calculations by Sachtler and Jongepier (*18*) revealed that the free energy of formation of a catalyst containing 80% copper and 20% nickel at 200°C appears to be favored when the nickel-copper alloy has had an ample opportunity to establish the most stable state by diffusional processes. Specifically, in Fig. 3 is shown the curve representing the free energy changes for various copper-nickel systems as calculated from the early Russian cell measurements by Sachtler and Jongepier, and extrapolated down to a temperature of 200°C. On the same plot is a curve that we have calculated for 500°C. Clearly, the optimum nickel-copper composition for temperatures above 200°C corresponds to a lower copper content than at 200°C; the minimum at 500°C appears to be in the 60% to 70% copper range. It will be noted also that the calculations by Sachtler and Jongepier indicate that an alloy containing about 3% copper likewise is favored by the free energy calculations. They conclude that these two alloys are the ones present in a completely equilibrated sample. In line with this, they concluded that all alloys at intermediate compositions between 3% copper and about 80% copper will, if equilibrated at 200°C

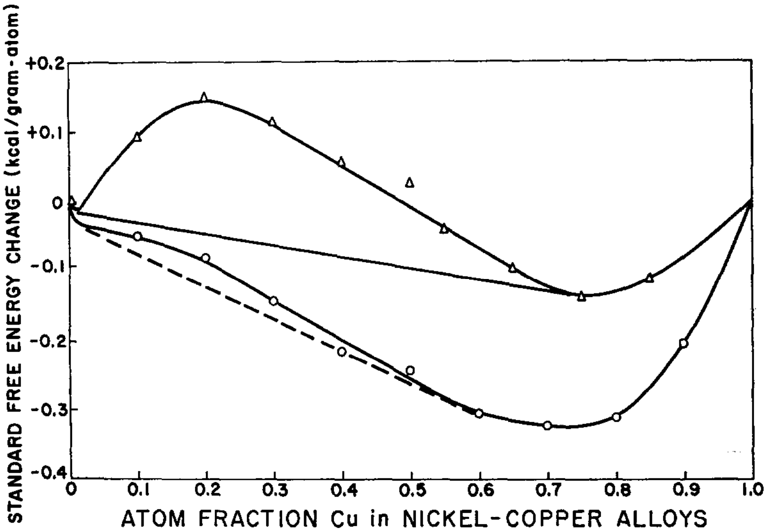

FIG. 3. A plot of the standard free energy change in the forming of copper-nickel alloys from the pure metals as a function of alloy composition. The triangles are for the calculations as made by Sachtler and Jongepier for 200°C; the open circles represent calculations for 500°C.

produce solids in which the high-copper phase of a given composition is exposed on the surface of a catalyst. The second phase (low-copper phase) presumably is buried within the catalyst and does not appear on the surface.

Sachtler and Dorgelo (*7*) obtained experimental evidence for the constancy and composition of the surface by photoelectric measurements of the work function of the alloy. They established specifically that whereas nickel has a work function of about 5.1 eV and copper has a work function of about 4.66 eV, the alloys over the range 3% to 80% copper had work functions of 4.61 eV. They conclude that just as the work functions do not seem to change much over the alloy samples made from thin films, so the catalytic activity of copper-nickel alloys does not appear to change much over this region. For example, in support of the approximate constancy of catalytic activity for alloys in the range of 3% to 80% copper they cite the measurements of Hall and Emmett (*5*) on ethylene hydrogenation and also the measurements on ortho–para hydrogen conversion published by Shallcross and Russell (*20*).

Doubt as to the general validity of the conclusion of Sachtler and Jongepier (*18*) as to constancy of activity of copper-nickel alloys arises from the fact that the experiments of Best and Russell (*4*) on ethylene hydrogenation showed that a copper catalyst containing 90% copper was approximately tenfold as active as a pure nickel catalyst and one containing 64% copper was approximately 100-fold as active as nickel. These results cannot be construed as indicating constant activity of the surfaces of copper-nickel alloy catalysts even though these catalysts were prepared by reduction of oxides in much the same way as the catalysts of Hall and Emmett were prepared. Furthermore, in the present runs on alloy catalysts prepared by sintering separate films of copper and nickel deposited on top of each other, the addition of copper clearly enhances the activity of nickel. The measurements as made indicate that a catalyst containing 88% nickel and 12% copper was as much as 15-fold more effective than nickel. Furthermore, catalysts containing 80% to 95% copper were all distinctly more active than nickel, the ratio of activity amounting to as much as a factor of 8 with a catalyst containing 94% copper compared to the pure nickel catalyst. It may also be noted that Alexander and Russell (*21*) recently found that a 54.6% copper–43.4% nickel alloy film catalyst made by induction evaporation and cooled in hydrogen was about eight times as active as nickel. This is in excellent agreement with our film results shown in Fig. 1.

The experiments on work function made by Sachtler and Dorgelo were apparently performed on an alloy the composition of which varied as a result of an increasing thickness of copper deposited on one end of the strip of nickel compared to the opposite end. In view of the fact that the total composition at any particular point along the sample would presumably vary with the thickness of the copper, the conclusion was reached that the work function was independent of the composition of the surface. In view of the rapid diffusion of copper on the surface of nickel, the question may well be raised as to whether the entire surface as subjected to the work function measurements may not have been uniform in composition rather than varying between 3% copper and 80% copper as assumed by Sachtler and his co-workers. Against this conclusion is the fact that the length of their sample was about 10^7 times the thickness. Therefore, lengthwise equilibration of the surface would perhaps be too slow to be noticeable. Certainly the two ends of their sample seem to correspond to pure Ni and Cu, respectively, and were not affected by diffusion lengthwise along the sample. In any case, the fact remains that at least three sets of experiments indicate that certain copper-rich catalysts are seven to one hundred times as active as nickel.

The data in Fig. 1 indicate that certain composite films made by depositing copper on top of nickel and then sintering the material at either 300° or 500°C in a few centimeters of hydrogen for a period of about 16 hr, results in an alloy surface a number of times more active than pure nickel. It is also surprising to note that the catalysts prepared by depositing copper on top of nickel seem to be more active than those prepared by depositing nickel on top of copper. The two catalysts made by sintering to 500°C seem to fall smoothly on the curve drawn through the other experimental points.

The question naturally arises as to whether the catalyst corresponding to an alloy of 40% nickel and 60% copper has either an unusually high or unusually low activity. Unfortunately, this is approximately the composition range in which the activity rises very rapidly with slight increases in the amount of nickel. Thus, a catalyst containing 58.5% copper and sintered at 500°C is approximately seven times as active as pure nickel, whereas a catalyst containing 64% copper and 36% nickel has about the same activity as a nickel catalyst. By contrast a catalyst prepared by Best and Russell containing 63.7% copper was some ten to one hundred times as active as nickel. If it were not for the observation of Best and Russell for a catalyst containing 63.7% nickel, one might well conclude that the nickel-copper alloy containing approximately 60% copper had relatively small activity and that increasing either the nickel content or the copper content caused an abrupt rise in activity. In other words, the high copper alloy might be a promoter for both nickel and copper. Definite conclusions in regard to this will have to await further work.

The reason why small amounts of nickel deposited on copper or large amounts of copper deposited on a small amount of nickel yield catalysts with an activity greater than that of nickel is not clear. One explanation that suggests itself is that although pure copper will adsorb molecular hydrogen with difficulty at room temperature, adjacent nickel-copper atoms on the high copper-nickel alloy might reasonably be expected to cause such adsorption. This follows from the fact that the heat of adsorption of hydrogen on nickel is sufficiently great that hydrogen sitting on a nickel-copper pair of sites would have a net heat of adsorption in excess of that necessary to dissociate the hydrogen. Adsorbed hydrogen atoms thus produced might very reasonably be free to migrate over the surface of copper. If now one assumes that the ethylene adsorbed on the copper surface is more susceptible to hydrogenation because of it being held with a lower heat of bonding than ethylene on nickel, one could have a system in which hydrogen atoms diffusing from the nickel-copper pairs could hydrogenate ethylene adsorbed primarily on a copper surface. Thus, the increase of nickel atoms on the surface of copper would, for a time, increase the activity. In line with this, Fig. 4 indicates that the A factor for an alloy containing 6% nickel is several orders of magnitude greater than that of pure copper. This could be consistent with an increase in the number of catalytically active sites with the addition of nickel to the copper.

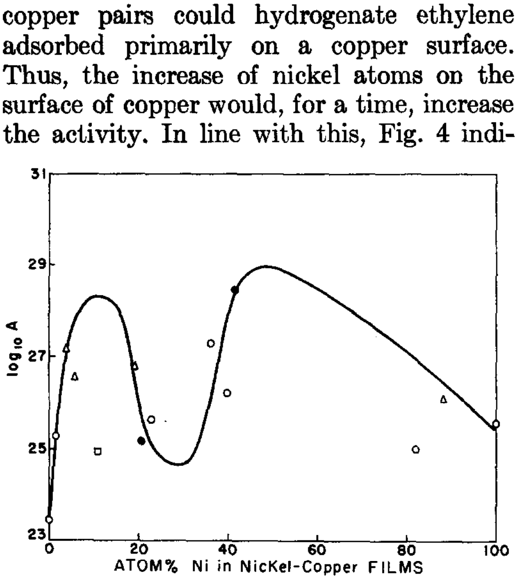

FIG. 4. Variation of the pre-exponential constant, A, with alloy composition for the hydrogenation of ethylene over nickel-copper films. Symbols are the same as for Fig. 1.

The high nickel catalysts appear to have obtained the enhancement in activity on adding copper from a slight lowering in the energy of activation for the reaction (Fig. 5). The A values are approximately the same for a catalyst containing 82% and 88% nickel as for pure nickel (Fig. 4). A reason for copper thus lowering energy of activation compared to nickel is not evident; perhaps the copper in some unexplained way tends to counteract the poisoning effect of hydrogen on nickel.

The general relationship between the change in the energy of activation in the nickel-copper alloy series and the change in the A factor becomes clear from Figs. 4 and 5. The reason, however, for the change in the values for energy of activation or the change in A factors throughout this nickel-copper alloy system is still obscure and must await further experimental measurements.

The gold-nickel system appears to behave very differently from the copper-nickel system. As shown in Fig. 2, the activity of both of the catalysts containing gold is about one-tenth as great as that of nickel. The lowering of the energy of activation from about 10.5 kcal to about 4 kcal by halving gold seems to be more than compensated for by the change in the A values as indicated in Table 3. The explanation for the

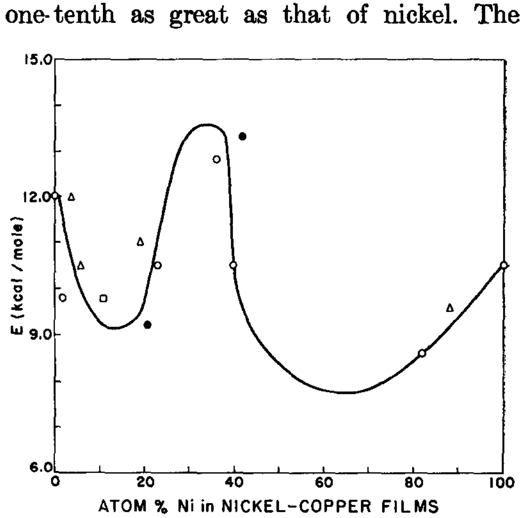

FIG. 5. Variation of the apparent energy of activation with alloy composition for the hydrogenation of ethylene over nickel-copper films. Symbols are the same as for Fig. 1.

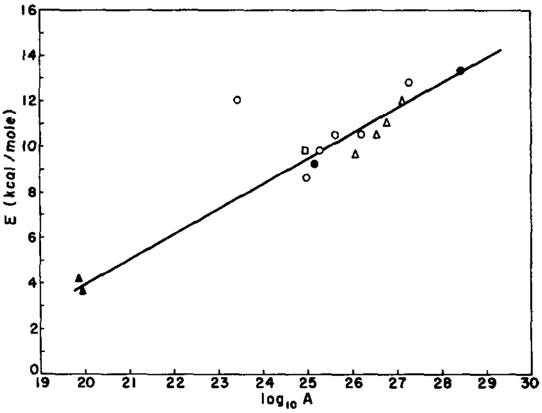

Fig. 6. Plot of the apparent energy of activation against the $\log_{10} A$ for the copper, nickel, and copper-nickel alloys (open circles, triangles and square, and solid circles as described for Fig. 1) and for the two gold-nickel alloys (solid triangles). The point for copper is off the curve.

difference between the gold-nickel system and the copper-nickel system is, at present, not clear.

Finally, in Fig. 6, is shown a plot of the logarithm of the A factor against the energy of activation for the entire copper-nickel system and for the two gold alloys. It appears that within experimental error almost all of the data fall on a linear plot, indicating a tendency for increased energies of activation to be compensated by increases in the pre-exponential A factor.

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