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Interaction of Benzene with Protium and Deuterium on Copper-Nickel Films with Known Surface Composition*

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Copper-nickel films were prepared by successively depositing the two metals from the vapor and subsequently sintering the films under ultra-high vacuum at 200°C. The nickel content of the film surfaces could be "titrated" by selective chemisorption of hydrogen. In agreement with expectation all films with overall compositions within the miscibility gap of the copper-nickel system at 200°C possess an equal surface composition of 23 ± 4 at. % of Ni.

Benzene is hydrogenated at a constant rate at a given temperature over these films with equal surface composition, but widely varying overall composition. The activation energy over these alloys is $E_{\text{all}} = 25$ kcal/mole, while $E_{\text{Ni}} = 12$ kcal/mole. The rate of the exchange reactions between benzene and deuterium at 41°C is, again, constant for alloys of equal surface composition; it is by several orders of magnitude larger than the rate of hydrogenation at the same temperature. The exchange reaction displays a constant multiplicity over the alloys with equal surface composition. The totality of the results presented confirms the model proposed previously on the phase distribution of equilibrated copper-nickel films.

I. INTRODUCTION

Many scholars, including Rienäcker (*1*), Schwab (*2*), Eley (*3*), Dowden (*4*), Emmett (*5*), Hall (*5*), Russell (*6*), Takeuchi (*7*), Lyubarskii (*8*), Cadenhead (*9*), and Boreskov (*10*), agree that basic conclusions concerning the fundamental aspects of heterogeneous catalysis should be obtainable from reliable experimental data on Ib/VIIIb alloy catalysts such as Cu-Ni, Ag-Pd, and Au-Pt. In each of these pairs the Ib group metal is known to be a very poor hydrogenation catalyst, while its partner is a powerful catalyst for hydrogenation reactions. As the VIIIb metal is known to possess holes in the *d* band which are gradually filled by incorporating Ib metal atoms in the lattice, it is interesting to compare the filling of the *d* band in these alloys with their catalytic "activity pattern," i.e., the reaction rate of a test reaction, studied under standard conditions, expressed per unit of surface area and plotted versus the composition of these alloys.

While this seems to be a very obvious way to decide between conflicting theories on heterogeneous catalysis, the experimental results obtained in this way show a discouraging picture of mutually inconsistent data. Even the simple question whether the activity of an alloy remains within the limits set by the two parent metals has not been settled. Some authors report activity patterns with pronounced maxima exceeding the activity of the Group VIIIb metal (*5, 6, 11*), while other data fail to confirm such a behavior. Even the activity patterns reported at different periods by authors from the same school for the same test

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* This work has been described in greater detail in the thesis by P. van der Plank "Oppervlaktesamenstelling en katalytische activiteit van legeringsfilms van koper en nikkel," Leiden, 1968.

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reaction studied on alloy films of the same metal couple show pronounced discrepancies (*11, 12*).

Possible reasons for discrepancies in the experimental results reported for alloy catalysts can be classified in four groups:

(1) Different authors have used different test reactions.

(2) Alloys prepared by reducing mixtures of the oxides contain oxide pockets, or dissolved hydrogen, or are incompletely equilibrated, while the original oxides were not miscible in all proportions. The activity patterns then depend on the reduction conditions used and are different from the patterns obtained with clean alloy films.

(3) Some test reactions such as the hydrogenation of ethylene may cause a considerable self-poisoning by forming carbonaceous residues on the catalyst. The apparent activity pattern then is a superposition of the poisoning pattern and the intrinsic activity pattern.

(4) Alloys equilibrated at low temperatures where the $T\Delta S$ term in the free energy of alloy formation is very small should desegregate in two phases and indeed often do so (*13–17*). Depending on the conditions of preparations one or both phases may occur in the surface; the composition of either phase remains constant while the overall composition changes.

While this list is perhaps not complete, it is clear from it that meaningful data are only to be expected if care is taken that:

(a) the alloys are oxygen free, preferably prepared from the spec-pure metals under ultra-high vacuum;

(b) the test reaction is "innocent" as far as self-poisoning is concerned;

(c) the degree of self-poisoning is checked;

(d) the surface composition is determined.

Besides, an activity pattern, measured at one temperature only, provides less information than a complete set of Arrhenius curves measured on the pure metals and many of their alloys.

In the present work the authors tried to fulfill these requirements by studying the hydrogenation of benzene with protium or deuterium over copper, nickel, and numerous copper-nickel alloys. All these catalysts were prepared as films by evaporation and sintering under ultra-high vacuum. The surface area of each film was determined by xenon adsorption. The reproducibility of the catalytic data was carefully checked and the surface composition of the catalysts used was determined by chemisorptive titration, i.e., the selective chemisorption of hydrogen. Some preliminary results of this work have been reported in a short note (*13*).

II. EXPERIMENTAL

The alloy films were prepared by successively depositing copper and nickel at a temperature of −196°C and in the pressure range of 10^{-10}–10^{-9} torr. Equilibrium was reached by sintering at 200°C during 18 to 20 hr. After this procedure the amount of hydrogen adsorbed on the films at room temperature and at saturation was measured. The hydrogen used was purified by diffusion through a Pd-Ag thimble. The sorption measurements were done with the aid of a dosing system between valves 5 and 6 shown in Fig. 1. The pressures in this volume (59 ml) were determined with a calibrated Pirani gauge. The pressures of hydrogen after saturation of the film surface were determined by means of a mass spectrometer (MS 10).

Subsequent to the chemisorption of hydrogen the physical adsorption of xenon at −196°C was measured, using the same dosing system. The xenon used was provided by L'Air Liquide in a very pure form. Before use it was further purified by sublimation. The xenon pressure above the film during adsorption was recorded, using an ionization gauge for the pressure measurements. The amount of xenon necessary for a monolayer on the film was determined according to the "point B" method.

After the sorption measurements most films were used for benzene hydrogenation. First benzene, purified by sublimation, was admitted and measured; subsequently the film vessel was cooled with liquid nitrogen to condense the benzene, and hydrogen was admitted. The quantities of both hydrogen and benzene were determined with a

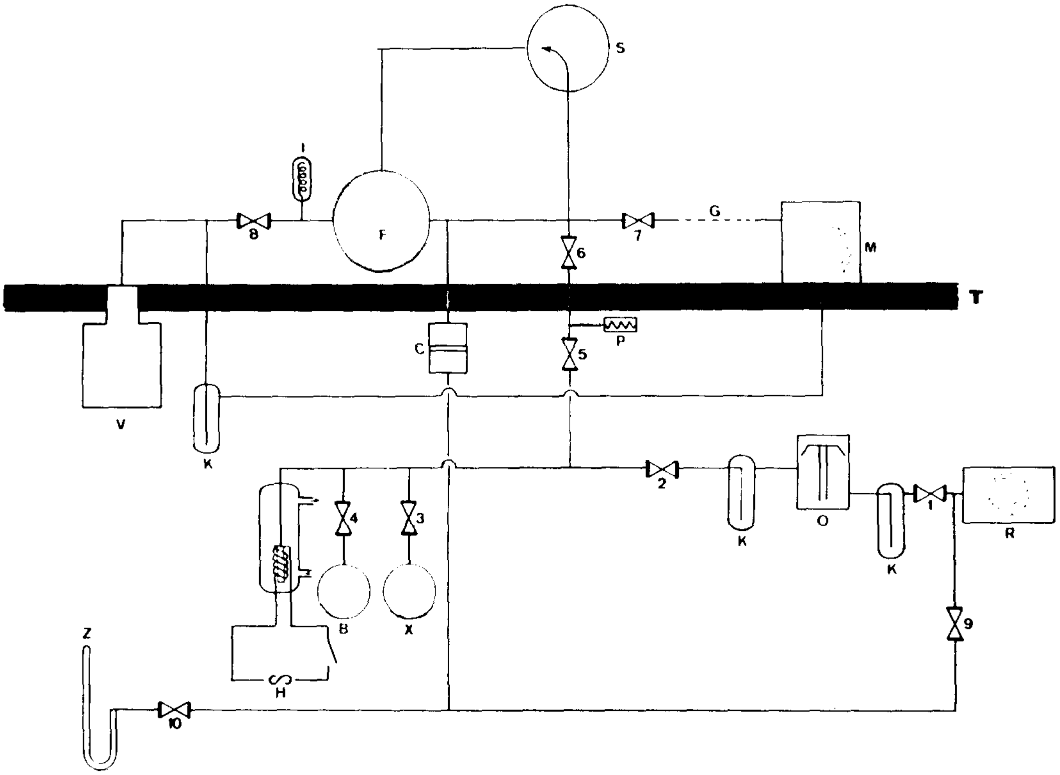

FIG. 1. Ultra-high vacuum apparatus for sorption and hydrogenation measurements on alloy films: 1 through 10, valves; R, mechanical forepump; O, oil-diffusion pump; V, ion getter pump; K, cold traps; B, X, reservoirs for benzene and xenon; H, Pd-Ag thimble; Z, mercury manometer; C, condensator (membrane) gauge; T, bakable table; I, ionization gauge; F, film vessel (reactor); S, gas circulation pump; G, capillary; M, mass spectrometer (MS 10).

membrane gauge. After mixing at room temperature with the circulation pump the reaction was started by bringing the reaction vessel to the desired temperature. From the pressure decrease the rate of hydrogenation could be calculated.

Some experiments were done with deuterium and benzene in an apparatus in which it was possible to admit benzene after deuterium. In this case the amount of benzene was determined mass spectrometrically, the MS now being connected to the dosing volume. In these experiments the dosing system was incorporated into the circulation system. The reactions (deuteration and deuterium exchange) started immediately when the gas mixture entered the reaction vessel which had already been brought to the desired temperature. The progress of the reactions was followed mass spectrometrically.

III. RESULTS

Sorption Measurements

The results of the sorption measurements are presented in Fig. 2 where the adsorption rate α, defined as

$$\alpha = \frac{\text{number of hydrogen atoms chemisorbed}}{\text{number of xenon atoms adsorbed}}$$

is plotted versus the atom fraction γ_{Ni} of the alloys. In these experiments hydrogen chemisorption was determined at room temperature and at a pressure of several microns.

In this range the adsorption isotherm of hydrogen has a horizontal slope. The physical adsorption of xenon was measured at 78°K as described in the experimental section.

As discussed in a previous note, the results show that alloys with overall com-

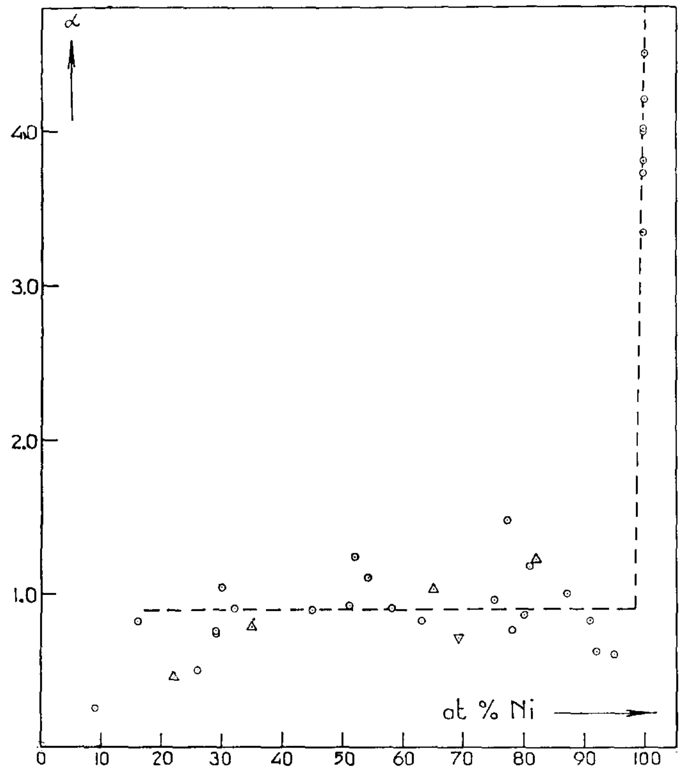

Fig. 2. Adsorption ratio α as a function of film composition: ⊙, Ni deposited on top of Cu, films sintered at 200°C during 18 to 20 hr; △, Cu deposited on top of Ni, films sintered at 200°C during 18 to 20 hr; ▽, Cu deposited on top of Ni, films sintered at 300°C during 14 hr.

positions in the range between 25% and 95% Ni have a constant surface composition. Its value is independent of the order of evaporating the two metals, as can be seen from Fig. 2. This strongly suggests that thermodynamic equilibrium has been reached.

If the assumption is made that for Ni and these alloys each surface Ni atom chemisorbs one H atom, the surface composition $\gamma_{\mathrm{Ni,s}} = 0.23 \pm 0.04$ results, which is in perfect agreement with predictions based upon the thermodynamic data of this alloy system (*17*, *18*). In these measurements the experimental scatter is considerable. Some of the deviations were larger than might be expected from the instrumental error. It appeared that in these cases other anomalies showed up too, e.g., the film separated from the glass when the vessel was cooled with liquid nitrogen for the xenon adsorption measurements. This caused an enlargement of the film surface registered by xenon adsorption but not paralleled in the preceding hydrogen chemisorption.

Hydrogenation of Benzene

Preliminary measurements on nickel and alloy films showed that hydrogenation of benzene is accompanied by poisoning of the catalyst surface. This is not surprising; in a recent publication (*14*) it was shown that self-poisoning on nickel and copper-nickel alloys is observed even with the hydrogen–deuterium exchange of propane as the test reaction.

In the present experiments it was found impossible to reproduce values for the catalytic activity on the same film. Therefore we decided to carry out only one hydrogenation experiment on each film and to use only the initial rates of hydrogenation for activity patterns and Arrhenius curves. Results obtained in this way are shown in Fig. 3 for nickel films. In view of the experi-

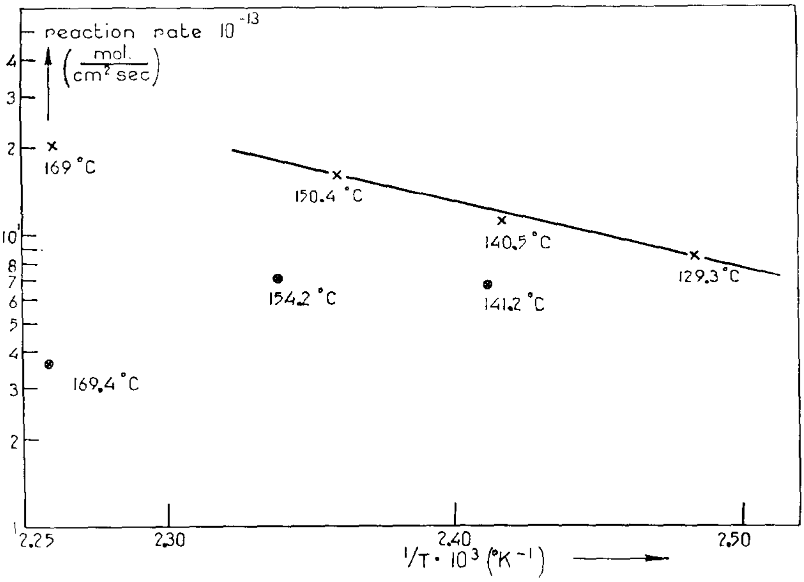

Fig. 3. Initial reaction rate for benzene hydrogenation on Ni films as a function of temperature: **X**, p_{H_2} = 322 torr, p_{benz} = 5.8 torr, E = 12 kcal/mole, log A = 20.4, ⊗, p_{H_2} = 145 torr; p_{benz} = 5.8 torr.

mental problems in this field it is satisfactory that for temperatures up to 170°C and a hydrogen pressure of 322 torr the initial reaction rates are found to obey Arrhenius' law. Furthermore, we notice from these points that the reaction order with respect to hydrogen is positive and that it increases with temperature. This was confirmed by more elaborate additional experiments.

Using a temperature of 150°C, a hydrogen pressure of 322 torr, and a benzene pressure of 5.8 torr as standard conditions, the initial activity was measured for copper, nickel, and several alloys. The resulting activity pattern is shown in Fig. 4. It strikingly resembles the chemisorptive titration pattern of Fig. 2; all alloys with compositions within the miscibility gap of the copper-nickel system display the same activity, which, at this temperature, is equal to about 20% of the activity of pure nickel. The alloys where nickel was evaporated first exhibit nearly the same activity as the alloys where the order of deposition was reversed.

The conclusion that the reaction rate be simply proportional to the nickel content of the surface is, although suggested, by no means proven by these results. The decisive question is whether the reaction on the alloys has the same activation energy as on nickel. If the activation energies are different, the value of r_{alloy}—0.20 r_{nickel} is a coincidental one and depends on the temperature used.

We, therefore, measured Arrhenius plots for a number of alloys. Since only one point of the Arrhenius graph is obtained for each film it was necessary, ideally, to prepare a

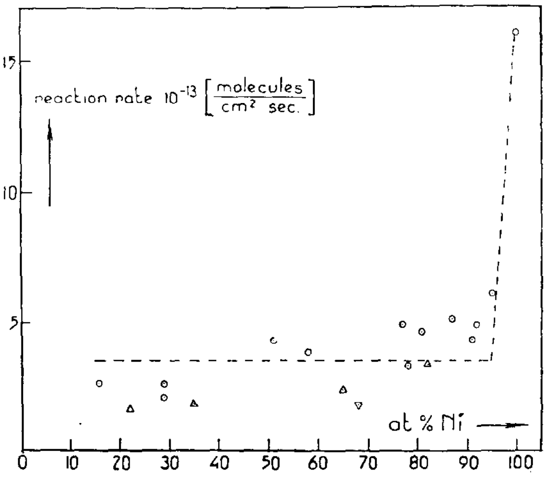

Fig. 4. Activity pattern for benzene hydrogenation at 150°C: p_{H_2} = 322 torr; p_{benz} = 5.8 torr. The symbols have the same meaning as in Fig. 2.

number of alloy films with equal composition in order to get the Arrhenius plot for this composition. This was, however, an impossible task with the apparatus described, but after gathering sufficient experience we succeeded in preparing alloy films with nearly equal compositions. The error made by the fact that the composition for the points used in one Arrhenius plot is not exactly equal, is, however, small, since we may rely on the evidence from Figs. 2 and 4 and previous publications (*15, 16, 17*), which show that the surface composition is constant for films with compositions within the miscibility gap of the copper-nickel system.

The resulting Arrhenius graphs for several alloys are shown in Fig. 5. The striking conclusion is that the activation energies are equal for all these alloys, but the derived value $E = 25$ kcal/mole is roughly twice as large as the value of $E = 12$ kcal/mole found for nickel. The pre-exponential factors ($\log A = 26.4$, 26.3, and 26.2, respectively) are only slightly different for the three sets of alloys, but differ markedly from the value of 20.4 found for nickel. An obvious conclusion from these results is that the ratio $r_{\text{alloy}}/r_{\text{Ni}}$ which was found from Fig. 4 to be equal to 0.2 at 150°C should have a much lower value at lower temperature.

Also, this conclusion was checked experimentally by using a temperature of 41°C. In these experiments deuterium was used instead of protium, so that additional information on a related reaction could be obtained viz., the H/D exchange between C_6H_6 and D_2. In these experiments a deuterium pressure of 13.5 torr and a benzene pressure of 0.2 torr were used. The exchange was studied by measuring the concentration

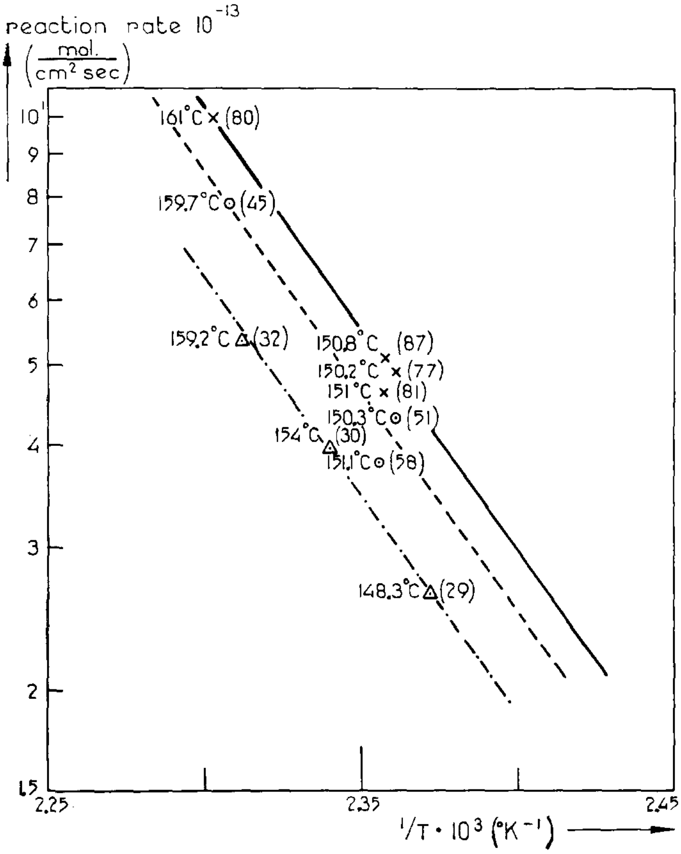

Fig. 5. Arrhenius' plots for benzene hydrogenation on various Cu-Ni alloys with compositions within the miscibility gap: X, ~80% Ni; o, ~48% Ni; △, ~30% Ni. The exact composition of each film is indicated in parentheses.

of the seven species $C_6H_{6-n}D_n$ as a function of time by means of the mass spectrometer. For the MS analysis it was assumed that isotopic effects are negligable in ionization and fragmentation.

In Table 1 the rates are listed both for the deuteration and the H/D exchange reactions. As to the deuteration the results confirm the expectation, based on activation energies and reaction orders, that the ratio $r_{\text{alloy}}/r_{\text{Ni}}$ is on the order of 10^{-4} at 41°C.

With respect to the H/D exchange between D_2 and C_6H_6 it was found that the rate is larger than the rate of deuteration by several orders of magnitude. Two rate constants can be defined for the exchange reaction. Following Kemball's (*19*) definition k_φ is the rate constant equivalent to the number of deuterium atoms entering 100 moles of benzene in unit time at the start of the reaction, while k_{d_0} represents the initial rate of disappearance of C_6H_6 in percentage per unit time. The ratio of both rate constants is unity only for a purely stepwise exchange process but

$$k_\varphi/k_{d_0} = M$$

is larger than unity if more than one hydrogen atom is exchanged per residence of a benzene molecule on the catalyst surface. In Table 1 the values of k_φ, k_{d_0}, and M are listed for some alloys. For nickel they could not be measured because the exchange rate is so high at 41°C that exchange equilibrium is already attained when the first gas sample is analyzed. The parameters could not be determined on copper either, because the exchange rate was too small at 41°C. In contrast to the measurements at 150°C it was possible to use a given film for several experiments below 55°C. Table 1 shows that for the alloys within the miscibility gap the ratio M of k_φ and k_{d_0} is constant and independent of the temperature used. These data, therefore, provide additional proof for the statement that the surface composition of all alloy films with compositions within the miscibility gap is essentially constant.

IV. Discussion

In previous papers we have shown that many experimental facts can be understood by applying the predictions from thermodynamics about copper-nickel alloys. From the known enthalpy and energy of alloy formation (*20, 21*) it follows that at 200°C the copper-nickel system has a miscibility gap with the limits $\gamma_{\text{Ni}} \sim 0.2$ and $\gamma_{\text{Ni}} \sim 0.95$, respectively (*15, 17, 18*). All equilibrated alloys within this range should consequently consist of two phases. Moreover, it was shown that for alloys prepared by vapor deposition of the two metals, followed by sintering at 200°C under ultra-high vacuum, the copper-rich phase with $\gamma_{\text{Ni}} \approx 0.2$ should

TABLE 1

Reaction Rates for Deuteration and H/D Exchange

Expt.	Film weight (mg)	At. % Ni	P_{D_2} (torr)	P_{benz} (torr)	Temp. (°C)	$k\varphi \times 10^3$ D atoms entering 100 mol./cm² min	$k_{d_0} \times 10^3$ percentage of benz/cm²/min	$\frac{k\varphi}{k_{d_0}} = M$	$r_D \times 10^{-12}$[b] $\left(\frac{\text{mol.}}{\text{cm}^2\,\text{sec}}\right)$
D3	12.3	100	14.4	0.19	41.0	Very large	Very large	—	5
D13a	18.7	83	13.5	0.11[a]	41.4	20.6	13.5	1.5	9×10^{-4}
D13b	—	—	13.5	0.07[a]	46.1	36.4	24.9	1.5	—
D13c	—	—	13.5	0.18	50.0	33.2	20.2	1.7	—
D11a	15.0	38	13.5	0.13[a]	41.0	27	16	1.7	6×10^{-4}
D11b	—	—	13.5	0.11[a]	46.0	33	19	1.7	—
D11c	—	—	13.5	0.10	51.9	38	25	1.5	—
D12a	18.4	21	13.5	0.18[a]	41.0	16.3	12	1.4	$\sim 10^{-5}$
D12b	—	—	13.5	0.17[a]	47.0	18	13	1.4	—
D12c	—	—	13.5	0.28	53.4	13.5	9.5	1.4	—
D5	14.1	0	13.6	0.18	41.0	Very small	Very small	—	—

[a] The accuracy of these benzene pressures, estimated from the MS data, is poor.

[b] r_D = rate of deuteration.

envelop the granuli of the nickel-rich phase. For alloys prepared in this way, the surface properties should, therefore, be those of the copper-rich phase. All these properties should, hence, have a constant value for alloys with overall compositions within the miscibility gap and prepared in the same manner.

The prediction had been based on the phase diagram calculated from data of the enthalpy and energy published by Rapp and Maak (*20*), and by Vecher and Gerasimov (*21*). The data by these two groups differ somewhat; the two resulting phase diagrams are shown in Fig. 6. But for an equilibration temperature of 200°C, as used in the present work, the two sets of data give the same result for the miscibility gap. Besides these thermodynamic data, the model makes use of known facts concerning the mechanism of interdiffusion (*22*, *23*). The model had been confirmed experimentally by X-ray diffraction, by photoelectric data on the work function of the alloy films, and by surface potential data for adsorbed carbon monoxide (*16*). The same picture has now been confirmed by new independent experimental data reported in this paper for copper-nickel alloys within the miscibility gap, viz., (1) the constancy of the amount of hydrogen chemisorbed per unit surface area; (2) the constancy of the activation energy for benzene hydrogenation; (3) the constancy of the pre-exponential factor for this reaction; (4) the constancy of absolute exchange rates and *M* values characterizing the H/D exchange for $C_6H_6 + D_2$. Where explicitly checked, the results are found independent of the order of deposition of the two metals. Including the work function and the surface potential of adsorbed CO we now possess six independent parameters which are found constant for Cu-Ni alloy films with overall compositions within the miscibility gap and equilibrated at 200°C while these parameters are distinctly different from the corresponding parameters for pure Ni and pure Cu. Only one of these six parameters—the amount of hydrogen chemisorbed per unit surface area—has the value expected from linear interpolation; the alloy surface containing $\sim$20% of Ni chemisorbs $\sim$ 20% of the amount of hydrogen that is chemisorbed by pure nickel.

In a previous note (*13*) we had suggested that also the catalytic activity (for benzene hydrogenation) is as a first approximation proportional to the nickel concentration of the catalyzing surface $\gamma_{Ni,s}$. The data of the present article definitely disprove this suggestion. The activation energy of the alloys with $\gamma_{Ni,s} = 0.23$ is roughly twice as large as for pure nickel. The ratio of the rates on pure nickel and on the alloys therefore

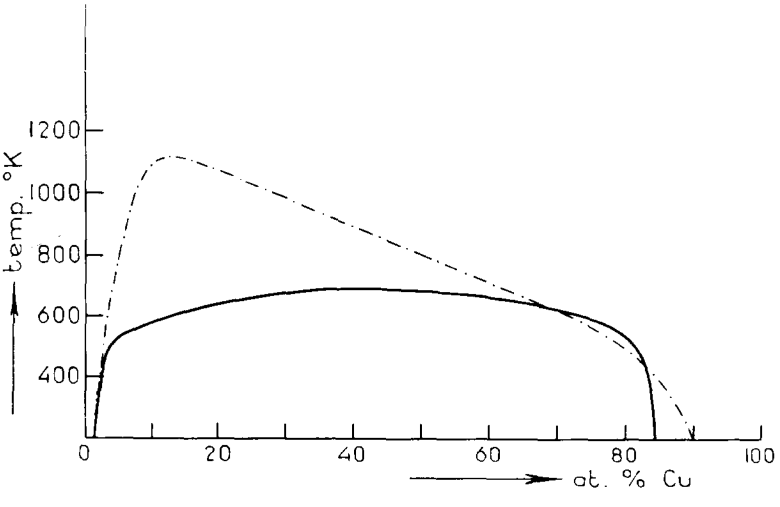

FIG. 6. Phase diagram for the Cu-Ni system, as calculated from thermodynamic data published in the literature: –.–.–, data by Vecher and Gerasimov (*21*); ———, data by Rapp and Maak (*20*).

depends on the reaction temperature. For the temperature range investigated it varies by four orders of magnitude.

It is interesting to discuss the present results in connection with several statements of the literature with respect to catalysis by alloys. One of the statements is Dowden's hypothesis (*4*) that holes in the *d* band are responsible for the hydrogenation activity of transition metals. As the present data show a considerable hydrogenation activity for a surface alloy containing 77% Cu in which all holes in the *d* band are supposed to be filled, this hypothesis cannot easily be reconciled with the present data.

A second point of interest concerns the activity patterns of copper-nickel with large pronounced maxima and minima published in the literature. The present authors feel that these activity patterns reflect poisoning or self-poisoning effects rather than true catalytic patterns. It has now been experimentally proven that even reactions such as benzene hydrogenation and propane–deuterium exchange (*14*) can cause irreversible poisoning at high temperature. The irreproducibility of the benzene hydrogenation experiments is indeed a great obstacle to gather reliable results which, as we found, can only be approached by exclusively using initial activities of virgin films at high hydrogen–benzene ratio. The formation of carbonaceous residues on the catalyst surface is a result of C–H bond cleavage. To a certain extent this process seems to be reversible according to

$$C_6H_6 \rightleftharpoons C_6H_{6-n,\,\mathrm{ads}} + nH_{\mathrm{ads}}$$

as was pointed out by Anderson (*24*). Both the high positive and temperature-dependent reaction order in hydrogen (see Fig. 3) and the large rate constant for the deuterium exchange reaction with benzene, which far exceeds the rate constant for benzene hydrogenation (see Table 1) are in agreement with this assumption of a partial dissociation of C–H bonds in adsorbed benzene.

When comparing the present results to those of other experiments it is obvious that there is a strong similarity with the results obtained by Cadenhead *et al.* (*25*) on the hydrogen adsorption on copper-nickel alloy powders. Also in their case the hydrogen chemisorption per unit of surface area is found constant for alloys with compositions within the miscibility gap. Also Rienäcker's data (*26*) on the activation energy of formic acid decomposition by copper-nickel alloys show a constant activation energy for these alloys, its value being intermediate between the activation energies observed on copper and on nickel. The structure of copper-nickel alloy films were also studied by Byrne and Clarke (*27, 28*) and by Zhavoronkova, Boreskov, and Nekipelov (*10*).

The former authors annealed their films at 500°C and the latter at 400°C. Consequently, the equilibrium phase distribution must be markedly different from the films studied in the present work, which were sintered at 200°C. Unfortunately, the two sets of thermodynamic data available from the literature strongly differ in their predictions of the miscibility gap above 400°C, as is shown by the curves in Fig. 6. According to the data of Rapp and Maak (*20*) no phase segregation is expected in equilibrium for copper-nickel alloys above 400°C, whereas the data published by Vecher and Gerasimov (*21*) predict a miscibility gap even at very high temperatures. As the X-ray diffraction results on films equilibrated at a temperature of 400° and 500°C do not reveal any phase separation they seem to favor the thermodynamic data by Rapp and Maak.

Takeuchi *et al.* (*7*) studied the heat of adsorption for hydrogen on nickel and some alloys. He found that the heat of adsorption per mole of hydrogen is considerably lower on the alloys than on nickel. This result is important in connection with the present finding that the apparent activation energy of hydrogenation on the alloys is nearly twice as large as on pure nickel. It seems thus that both the energy of the adsorbed state and of the transition state for hydrogenation are higher on the alloys than on nickel. While some data are known for the heat of adsorption of benzene on copper and nickel powders [Yu *et al.* (*29*)] there are, unfortunately no data available for the heat of adsorption of benzene on copper-nickel alloys, so that the complete energetic reaction scheme cannot be drawn for the alloys.

In conclusion, we feel that the catalytic activity patterns of alloys prepared under extremely clean conditions and studied by means of an "innocent" test reaction, can be rationalized, provided that the thermodynamic data of phase separation and the differences between surface and bulk compositions are properly taken into account.

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