Comparison with the experimental equation reveals that

$$2k_2K_1^{1/2} = \frac{2}{5}k_{\text{exp}}$$
$$k_7/k_8 = a = 2.0$$

It will be clearly understood that this correlation rests on the questionable assumption that the initial rate of pressure drop corresponds exactly to the over-all reaction

$$B_2H_6 + 6C_2H_4 \longrightarrow 2BEt_3$$

This assumption will obviously be in error to the extent that substituted diboranes accumulate as intermediates. Experimental determination of such accumulation poses a difficult problem owing to the interactions that are known to occur,[9] and has not been attempted. It is possible that the small apparent increase in rate with very large excess of ethylene in the one series at 154.5° may be accounted for in this way.

A final word may be added concerning the mild "explosion" which follows when the B_2H_6/C_2H_4 ratio is sufficiently large. The limit is, of course, to be identified with the denominator in the rate equation. Since the experimental constant, a, is taken as equal to 2.0, explosion should follow when the B_2H_6/C_2H_4 ratio exceeds 0.5. Actually, no good rate measurements could be obtained for initial values of the ratio greater than about 0.3 due to acceleration as reaction proceeded; and in early trials with a ratio of unity, the "explosion" followed immediately. The observed pressure increase under these circumstances is attributed to involvement of the excess of diborane in the process.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Nickel, Copper and Some of their Alloys as Catalysts for Ethylene Hydrogenation[1]

BY RICHARD J. BEST[2] AND W. WALKER RUSSELL

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The activity of nickel, copper and some of their alloys as catalysts for the hydrogenation of ethylene has been measured. These catalysts were prepared by the reduction of oxides obtained from the precipitated or coprecipitated metal carbonates. X-Ray examination of these catalysts indicates that they have the lattice constants of recorded equilibrium alloys. No simple relation is found between the activity of the catalysts and their metallic composition. A plausible explanation of catalyst activity appears possible in terms of the known electronic structure of the non-ideal nickel–copper system.

Introduction

Nickel, copper and their alloys have been studied by various investigators interested in the catalytic properties of these metals and their solid solutions. Thus Rienäcker and Bommer[3] studied the hydrogenation of ethylene over such catalysts in foil form between 400 and 500° and reported a marked drop in catalytic activity between alloy compositions of 80.2 and 80.8 atom % of copper, in which composition region the catalyst color changed from light grey to reddish. Using nickel, copper and mixed metal catalysts for the hydrogenation of benzene, Long, Frazer and Ott[4] on the basis of simultaneous X-ray diffraction studies showed that the reduction of the coprecipitated oxides produced active catalysts composed of the same substitutional type of solid solution obtained by melting the component metals together. Reynolds[5] studied the activities of a series of reduced carbonates of nickel and/or copper precipitated on kieselguhr for the hydrogenation of styrene, and also made magnetic susceptibility measurements upon these supported catalysts. In the present work the activity of reduced unsupported precipitated or coprecipitated carbonates of nickel and/or copper for the hydrogenation of ethylene has been studied. Also the surface areas and the lattice constants of the catalysts have been determined. The results appear to find adequate explanation in terms of the known electronic structure of the nickel–copper system.

Experimental

Apparatus and Purification of Gases.—Electrolytic hydrogen, and C.P. ethylene were metered and purified as already described.[6] The helium and likewise the nitrogen used in the adsorption measurements were purified essentially as earlier described.[6]

The catalyst chamber, which was placed in a bath of temperature-regulating liquid, consisted of a vertical Pyrex tube of 15 mm. o.d. in which was axially sealed a 5 mm. o.d. thermocouple well which extended about two-thirds of the way to the bottom of the catalyst bed. Catalyst exit gases passed through a three-way stopcock into a trap containing an aqueous acidified sodium sulfate solution[7] and to waste except when collected in an improved form of constant-head gas buret described elsewhere.[6] When the reaction velocity measurements had been completed upon a given catalyst, the catalyst chamber was sealed to a high vacuum adsorption apparatus generally similar to that described earlier.[8] This seal and the one closing the lower end of the catalyst chamber were made in a stream of purified nitrogen so as to protect the catalyst.

Preparation and Reduction of Catalysts.—The catalysts were prepared by dissolving the calculated amounts of analytical reagent grade $Cu(NO_3)_2 \cdot 3H_2O$ and/or $Ni(NO_3)_2 \cdot 6H_2O$ in water then diluting to correspond to about 5 g. of NiO and/or CuO per 100 ml. To this solution, while rapidly stirred at room temperature, powdered reagent

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(2) Metcalf Fellow, 1950–1951, and University Fellow, 1951–1952.

(3) G. Rienäcker and E. A. Bommer, *Z. anorg. allgem. Chem.*, **242**, 302 (1939).

(4) J. H. Long, J. C. W. Frazer and E. Ott, THIS JOURNAL, **56**, 1101 (1934).

(5) P. W. Reynolds, *J. Chem. Soc.*, 265 (1950).

(6) W. W. Russell and L. G. Ghering, THIS JOURNAL, **57**, 2544 (1935).

(7) K. A. Kobe and F. H. Kenton, *Ind. Eng. Chem., Anal. Ed.*, **10**, 76 (1938).

(8) W. W. Russell and L. G. Ghering, THIS JOURNAL, **55**, 4468 (1933).

grade ammonium bicarbonate[5] was added until a permanent turbidity just formed, and then there was added fairly rapidly 2.2 moles of the bicarbonate per mole of metal ion. After stirring for 10 minutes the precipitate settled overnight, and was then washed by decantation with just enough hot water so that the washings were colorless and the nitrate ion was largely removed. Having decanted the last washing as cleanly as possible the precipitate was evaporated over a steam-bath to a pasty solid, then dried in an oven at 105° for 24 hours. The so dried precipitate was broken into small lumps and sintered for exactly 4 hours at a carefully controlled temperature of 400°. After crushing in an agate mortar so that the largest particle was not more than 4 to 5 mm. in diameter, and sifting to remove fines, a weighed portion of the oxides was sealed into the catalyst tube.

The catalysts were reduced in a stream of purified, dry hydrogen at a flow rate of about 22 ml. per minute, while the temperature was slowly raised over a period of some 8 hours to 500°. At 500° the hydrogen flow rate was doubled, and reduction was continued at this temperature until less than 0.1 mg. of water was collected in an Anhydrone tube in 15 minutes. Because the reduction temperature was lowered to 350° during the night, each catalyst was reduced about 10 hours at 500° and about 15 hours at a temperature above 350° but below 500°. After reduction the catalyst was cooled in hydrogen and maintained therein until reaction velocity experiments could be made.

Catalyst Activity Evaluation.—After each reaction velocity measurement, the catalyst was heated at 100° for an hour in a stream of hydrogen in order to condition the surface for the next run. During a run the temperature of the catalyst was obtained from the catalyst bath temperature and potentiometer readings which gave the difference in e.m.f. between the junctions of a calibrated copper–constantan thermocouple one of which junctions was placed in the catalyst chamber well while the other was immersed in the stirred liquid which surrounded the catalyst chamber. The catalyst was rather well insulated inasmuch as it had shrunk around the thermocouple well and away from the outside walls of the catalyst chamber during prior reduction. The temperature of the catalyst bath liquid was read from a calibrated thermometer whose bulb was placed close to the bath junction of the thermocouple. With hydrogen flowing over the catalyst the temperature of the latter was brought somewhat below that at which it was desired to start the run. The ethylene was now cut in with hydrogen always kept in excess. From periodic, timed collections of the exit gases in the gas buret, the rate of exit gas flow was determined, and knowing the inflow rate from the flow meter readings, the rate of ethane formation was easily calculated. Since it was found that a rather good correlation existed between the number of cc. of ethylene converted per minute (at least above one cc. converted) and the temperature rise in a given catalyst as measured by the thermocouple, it was possible to calculate a factor whereby amounts of hydrogenation too small to be measured accurately with the buret, *e.g.*, 5% or less, could be estimated from thermocouple readings.

Evaluation of Other Catalyst Properties.—From nitrogen adsorptions at liquid nitrogen temperature, and helium dead space measurements, the surface area of each catalyst was determined immediately following the completion of the reaction velocity runs. Linear B.E.T. plots were employed and the cross sectional area of nitrogen taken as 16.2 Å.^{2}.

After the surface area measurements were finished, the catalyst was removed from the apparatus and weighed. Filings taken from several random catalyst particles were mixed with pure powdered sodium chloride and starch in a volume ratio of about 1:1:2 and introduced into a thin walled capillary tube for X-ray examination. After a 12 hour exposure to nickel-filtered X-rays from a copper target, and developing, film arcs were measured on a commercial film reader. The internal calibration provided by the sodium chloride was based on an a_0 value of 5.64009 Å. at 25°. This value was obtained from data of Straumanis and Ievins[9] by converting *kX*. units to ångström units. The catalyst films each showed two distinct regions. Up to about 60° Bragg angle only single lines could be detected, but beyond 60°, K_{α_1} and K_{α_2} splitting was observed. In the former region a weighted value for K_{α_1} and K_{α_2} of 1.5418 Å. was used, in the latter region separate calculations were made using 1.54051 and 1.54433 Å., respectively.

Duplicate samples of each of the reduced catalysts were analyzed by electro deposition of their copper. Nickel was calculated by difference. This was considered justified after analyses of a nickel–copper catalyst for both metals before reduction, and for copper after reduction gave results agreeing within 0.5%.

Catalyst 107 composed of nickel, weighed 1.87 g. after reduction, had a surface area per gram of 3300 cm.^{2}, and possessed a light gray color.

Catalyst 106 contained 63.1 atom % copper, weighed 1.37 g. after reduction, had a specific area of 6700 cm^2., and possessed a gray color.

Catalyst 108 contained 89.7 atom % copper, weighed 1.59 g. after reduction, had a specific area of 5300 cm.^{2}, and possessed a pink color.

Catalyst 109 composed of copper, weighed 1.50 g. after reduction, had a specific area of 2200 cm.^{2}, and possessed a typical clean copper color.

Results and Discussion

X-Ray Diffraction Measurements on Catalysts.—The film arcs were quite broad and diffuse indicating that the catalysts were composed of very small particles or crystallites, having diameters of 1000 Å. or less, and/or that there may have been a high degree of random disorder in the catalysts.

The following lattice constants (a_0) based on averages of from 6 to 9 measurements per catalyst were obtained: Catalyst 107 (Ni, 100), 3.5238 ± 0.0012 Å.; Catalyst 106 (Cu:Ni, 63:37), 3.5759 ± 0.0017 Å.; Catalyst 108 (Cu:Ni, 90:10), 3.6030 ± 0.0013 Å.; Catalyst 109 (Cu, 100), 3.6150 ± 0.0010 Å. The precision of the data is stated as the average deviation. These data are plotted in Fig. 1, as open circles whose size indicates precision, against catalyst composition. The solid line gives the measurements of Owen and Pickup[10] who found a discontinuity in slope at 66 atom % copper where the alloy shows a maximum contraction. The present work seems to confirm this discontinuity. The dotted line in Fig. 1 is the linear Vegard relationship. From the foregoing it appears that the catalysts used in the present work had the f.c.c. lattice constants found for equilibrium alloys of the same composition.

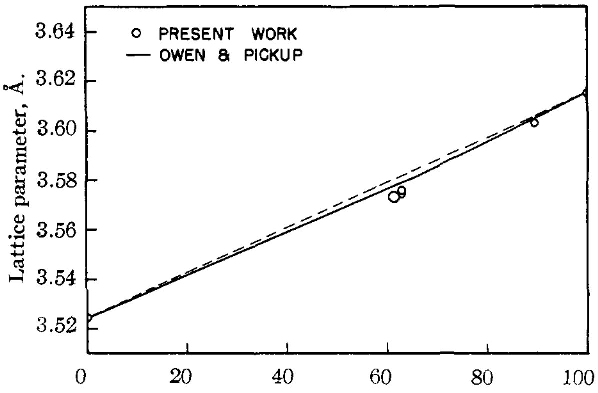

Fig. 1.—Lattice parameter for nickel–copper system. Experimental points from present work. Solid curve from Owen and Pickup.[10] Dotted curve is Vegard's law.

Activity Measurements on Catalysts.—Because of the great differences in activity shown by the

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[9] M. Straumanis and A. Ievins, *Z. Physik*, **109**, 728 (1938).

[10] E. A. Owen and L. Pickup, *Z. Krist.*, **88**, 116 (1935).

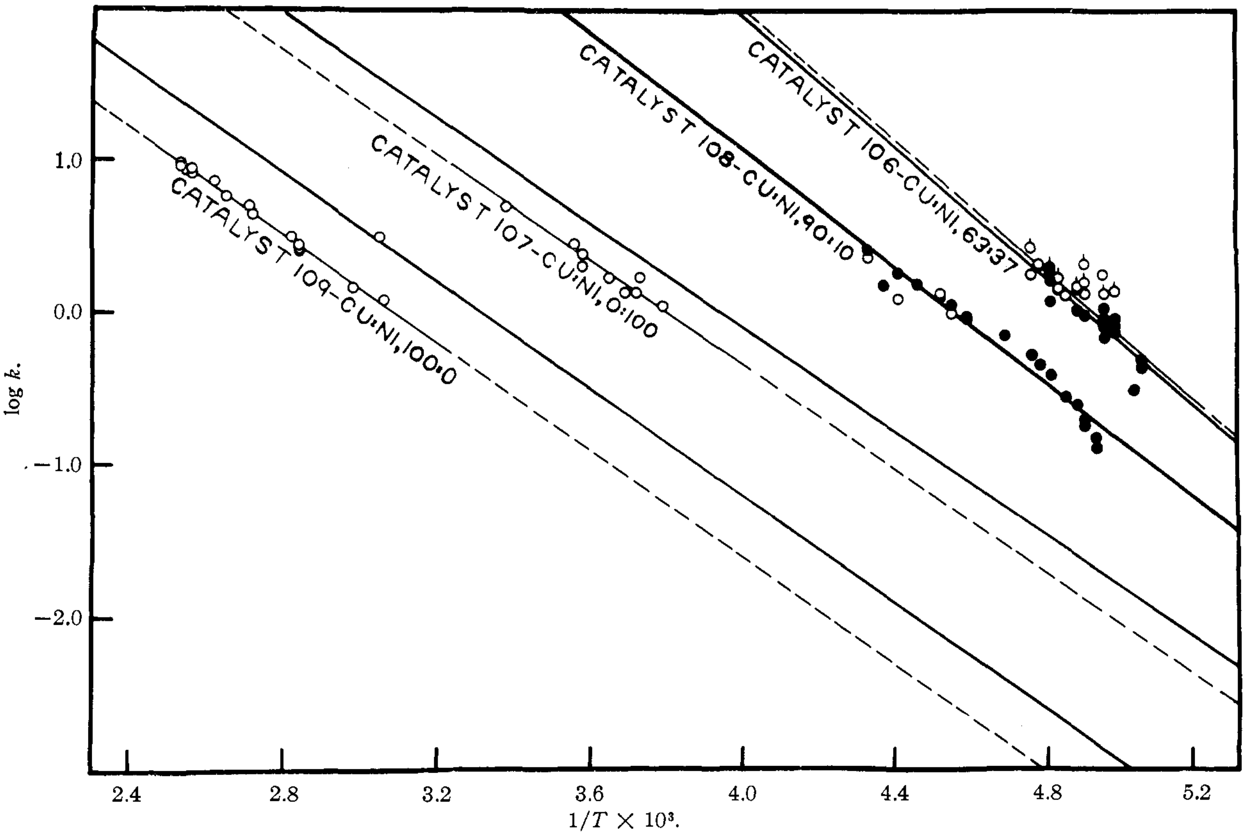

Fig. 2.—Reaction velocity curves for hydrogenation of ethylene over Catalysts 106–109. Solid curves calculated to same catalyst surface area as Catalyst 108.

catalysts it became necessary to extend the temperature range of the reaction velocity measurements from −70° to over 100°. Therefore, to compare the relative activities of the catalysts at a common temperature, extrapolation is required. In Fig. 2 the experimental values for log *k* (the log of the number of cc. of ethylene converted per minute from a flow of 10 cc. of ethylene plus 12 cc. of hydrogen per minute) are plotted against the reciprocal of the absolute temperature of the catalyst. For the solid, heavier lines the values of *k* have been corrected, assuming a linear relation between catalyst activity and surface area, to the surface area of Catalyst 108 as standard. In this connection it may be noted that the specific surface area is smallest for copper, next for nickel, and largest for the alloy catalysts, with the 63 atom % copper catalyst being the larger of the latter two. In Fig. 2 there are three sorts of points. The open circles represent reaction velocities calculated from buret-measured exit gas rates. On Catalyst 106 the first two runs were made before the improved technique, employed in all subsequent runs was developed. Open circles with vertical tails mark these two somewhat less accurate runs. The solid circles represent reaction velocities calculated from the catalyst thermocouple readings, as already explained.

According to the literature[11] the apparent activation energy for the ethylene–hydrogen reaction appears to begin to decrease above room temperature. In the present work it has been necessary to measure reaction velocities above room temperature only on copper (Catalyst 109). The experimental points for this catalyst, however, fall on a fairly straight line. The loci of the points for all of the catalysts shown in Fig. 2 have also been considered as straight lines. These lines are approximately parallel to each other and deviations from parallelism are probably within the experimental error of the data. Therefore, the same sequence of relative activities for the catalysts is obtained by extrapolation to any of the reaction temperatures. In Fig. 3 is shown the effect of alloy composition upon the following alloy properties: curves A and A′, catalyst activity at −69 and −3°, respectively: curve L, lattice parameter; curve M, saturation magnetic moment[12]; curve S, magnetic susceptibility[13]; curve H, electronic specific heat coefficient[14] in arbitrary units. The data for curves A, A′ and L were obtained from the present work.

Discussion and Conclusions

Ideally alloy catalysts would probably be produced by thoroughly mixing the pure, molten metals, cooling without segregation, then subdividing to a submicroscopic powder, all without any contamination of the alloy. In practice the foregoing is substantially impossible. By coprecipitation to form suitable oxides, carbonates, or the like, with other products and any excess reagent being easily

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(11) G. H. Twigg, *Disc. Faraday Soc.*, **8**, 152 (1950).

(12) R. M. Bozorth, "Ferromagnetism," D. Van Nostrand Co., Inc., New York, N. Y., 1951, p. 440.

(13) B. R. Coles, *Proc. Phys. Soc.*, **387B**, 221 (1952).

(14) W. H. Keesom and B. Kurrelmeyer, *Physica*, **7**, 1003 (1940).

volatile, followed by reduction in situ, less contamination and large catalyst surface area should be possible. If in addition X-ray examination shows that either method leads to the same lattice structure, the coprecipitation method would seem to have marked advantages, and so has been used in the present work.

The hydrogenation of ethylene over the so-prepared catalysts of nickel, copper and alloys of these metals shows that no simple relation exists between catalyst activity and composition. The hydrogenation velocity constant increased more than 600-fold between copper and the nickel alloy containing 63 atom % copper. Although copper itself showed a very low activity in comparison to nickel, alloying copper with nickel produced a much more active catalyst than nickel alone. Thus copper has a marked promoter action on nickel for this hydrogenation.

In the field of metals and metallurgy the properties of the nickel–copper system have been carefully studied. Also ethylene hydrogenation has been intensely investigated. Although at first sight both the alloy system and the chemical reaction seem relatively simple, both have proved to be complex. In seeking an explanation for the present work several possibilities must be considered.

Lattice parameter has been considered important by many and especially by Beeck[15] in explaining the catalytic activity of metals for ethylene hydrogenation. As is clear from curve L in Fig. 3 the lattice parameter increases almost linearly from 3.52 Å. for nickel to 3.62 Å. for copper. This lattice region lies on a rapidly rising portion of Beeck's bell-shaped curve[16] ($\log_{10} k$ *vs.* lattice parameter) and, insofar as Beeck's data may be considered applicable to alloys, would predict a catalytic activity which steadily increased with the copper content of a nickel alloy. The sharp drop in catalytic activity found around a lattice distance of 3.60 Å. would not be expected from Beeck's work, although Beeck did find pure copper inactive. The present work gives no adequate idea of the dependence of catalytic activity upon catalyst composition in the region between pure nickel and a 60% copper alloy. Since lattice parameter increases linearly in this region, if catalytic activity also rises linearly here, a possible dependence would be indicated. Nickel–copper catalysts in this composition region must be studied in more detail before any real significance of catalyst interatom distances can be evaluated.

The composition of the nickel–copper system affects in an unusual manner not only the catalytic activity but also a number of other properties which may be considered dependent upon electronic structure. It is appreciated that an extrapolation is required in applying concepts of metal electronic structure, obtained from measurements of bulk properties, to catalytic phenomena which may be principally affected by the electronic structure of the metal surface. However, until the interrelations of bulk and surface electronic structures are better understood such an extrapolation appears inevitable.

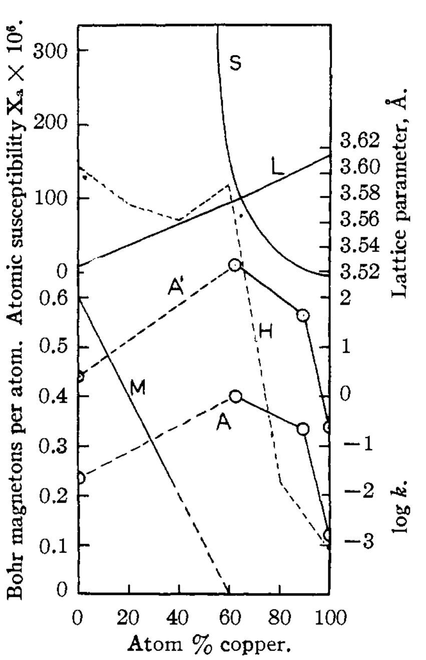

Fig. 3.—Comparison of several properties of the nickel–copper system as a function of catalyst composition: curves A and A′; catalytic activity at −69 and −3°, respectively; curve L, lattice parameter; curve M, saturation magnetic moment; curve S, atomic susceptibility; curve H, electronic specific heat coefficient in arbitrary units.

As is shown in curve M of Fig. 3 the saturation magnetic moment of 0.6 Bohr magneton possessed by nickel predicts that the holes in the nickel 3d-band should decrease as more copper is alloyed with nickel and be completely filled at a composition containing 60 atom % copper. Experimental confirmation of this appears to be based upon an extrapolation from measurements on nickel–copper alloys containing less than 38 atom % copper.[12] It recently has been emphasized[13] that the nickel–copper system exhibits a number of deviations from ideal behavior with respect to such properties as magnetic susceptibility, electronic specific heat, thermo-electric power, electrical resistivity, and the like. Of especial interest are the data on magnetic susceptibility and electronic specific heat, reproduced in Fig. 3, which while allowing the number of holes in the 3d band of a nickel alloy to decrease with increasing copper content, yet require some holes to persist up to very high copper concentrations, *e.g.*, 95% copper. X-Ray examination[17] of the L α-emission bands of the nickel–copper system indicates that d-band holes in copper rich alloys are associated with the nickel atoms. So the simple band theory does not account for the behavior of the nickel–copper system above 60 atom % copper. Thus it is probable that in the copper rich alloys the 3d-shell electrons of the nickel atoms cannot be regarded as belonging to a collective d-band of the whole alloy, but rather the dissolved nickel atoms may form a d-band of their own.[13]

Reynolds,[5] who studied the hydrogenation of styrene on supported nickel, copper and their alloys

[15] O. Beeck, *Disc. Faraday Soc.*, **8**, 118 (1950).

[16] O. Beeck, *ibid.*, **8**, 128 (1950).

[17] J. Farineau and M. Morand, *J. Phys. Radium*, **9**, 447 (1938).

as catalysts, measured also his catalysts' magnetic susceptibilities which decreased rapidly up to a copper content of about 50% and then more slowly to substantially zero for pure copper. However, the activity curve of Reynolds' catalysts followed rather closely the extrapolated saturation magnetic moment curve, shown as curve M in Fig. 3, both curves reaching zero near 60 atomic % copper in the nickel alloy. In this connection it is of interest to note that a recalculation of the previously mentioned data of Long, Frazer and Ott[4] yields results in agreement with the foregoing results of Reynolds. Thus at a temperature of 70° this early work shows that whereas pure nickel hydrogenated 76% of the benzene, nickel alloys containing 53.6 and 79.0% of copper, respectively, each gave only about a 1% conversion. Thus the two foregoing studies involving, respectively, the liquid phase saturation of an ethylenic side chain on a benzene nucleus, and the gas phase saturation of the benzene nucleus itself appear to find a possible explanation in terms of the atomic moments of the metals and alloys. However, the persistence of some d-band holes up to at least 90% copper appears necessary to understand the activities of the catalysts here studied for ethylene hydrogenation.

The present work appears to find a possible explanation in terms of the probable electronic structure of the non-ideal nickel–copper system and in terms of a mechanism of ethylene hydrogenation which requires the chemisorption of at least hydrogen and possibly both reactants. A suitable mechanism has been proposed by Twigg[11] in which a chemisorbed ethylene molecule reacts with a physically adsorbed hydrogen molecule whereby the latter is dissociated to form a chemisorbed hydrogen atom, and an adsorbed ethyl radical or half hydrogenated state is formed simultaneously. The latter then reacts with a chemisorbed hydrogen atom forming ethane. This mechanism thus requires that the catalyst be able to chemisorb both ethylene and hydrogen. In accordance with current ideas[18] such chemisorption involves the partially filled d-band of transition metals. For the chemisorption of hydrogen holes in the metal d-band appear necessary and it may be assumed that such is also true for ethylene chemisorption. Also the electronic work function, the energy density of electron levels, and the gradient may affect chemisorption.[18]

Many electronic structure sensitive properties of nickel–copper alloys show a discontinuity or a maximum when the copper content reaches the vicinity of 60%. To such of these properties as are already shown in Fig. 3 there may be added for example, density, electrical resistivity and thermoelectric power. Therefore, it is not surprising that the catalytic activity also appears to be a maximum for a nickel alloy containing near 60 atom % copper. As is clear from Fig. 3 the catalytic activity rises to a maximum while lattice parameter increases somewhat, the density of electron levels varies by a small amount, but the filling of the holes in the 3d-band of the nickel, by the valence electron of the copper, occurs rapidly yet not completely. If atomic moment is the controlling factor, this filling of the holes in the nickel d-band could cause a decrease in the strength (heat) of chemisorption of both hydrogen and ethylene. A decrease in heats of adsorption in accordance with Beeck's work[16] should be accompanied by a rising catalyst activity, as is found in the present work. As the catalyst activity falls beyond the maxima shown in Fig. 3, a slightly more rapid yet still small increase occurs in lattice parameter, but the density of electron levels and the holes in the nickel d-band both rapidly drop to very small values as the catalyst composition approaches pure copper. Too few d-band holes and the greatly diminished density of electron levels may adversely affect the chemisorptions of the reactants and catalytic activity correspondingly falls. It therefore appears that the activity of a nickel–copper catalyst for the hydrogenation of ethylene is a maximum for only certain critical values of the electron–atom ratio[19] of the alloy.

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(18) D. A. Dowden, *J. Chem. Soc.*, 242 (1950).

(19) W. Hume-Rothery, *J. Inst. Metals*, **35**, 309 (1926).