the same amount (10 mg.) of catalyst in 50% ethanol solution the palladium-catalyzed reaction can be following the rate equation 10 whereas the rhodium-catalyzed reaction is following either equation 7 or equation 9. Such variation is consistent with the rate equation (equation 6) derived from this study. The effect of the substituents of nitrobenzene on the reaction rate exists in both the palladium- and rhodium-catalyzed reactions. Judging from the different orders of magnitude of b values for the same series of p-substituted nitrobenzene over different catalysts (Table VIII), one may conclude that the substituent group at the *para*-position may not only affect the true activation energy of the reaction

of the adsorbed reactants but also probably the adsorption coefficient of the reactants over the different catalysts.

Although this investigation gives a gross mechanism of the liquid phase hydrogenation of aromatic nitrocompounds, the detailed features about the stepwise reaction on the surface of the catalyst and the chemical structure of the adsorbed species such as whether the adsorbed hydrogen is in an atomic or ionic form still cannot be stated.

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Nickel, Copper and Some of their Alloys as Catalysts for Ortho–Parahydrogen Interconversion[1]

BY PHOEBE B. SHALLCROSS[2] AND W. WALKER RUSSELL

The activity of nickel, copper and some of their alloys as catalysts for the ortho–parahydrogen interconversion at $-196°$ and at several temperatures near room temperature has been studied. The dependence of catalyst activity upon catalyst composition is qualitatively the same for both the low temperature and higher temperature conversions. While alloying a few per cent. of copper or nickel with nickel or copper sharply decreases and increases catalyst activity, respectively, over the rest of the alloy composition range, catalytic activity changes relatively little. Experiments with preadsorbed hydrogen lead to the conclusion that in the alloy composition range from 5 to over 90% copper, compensation is operating between the effects of fixed hydrogen so that the reactivity of the adsorbed hydrogen which is more or less actively participating in the surface reaction remains little changed. The various types of adsorbed hydrogen must reflect in turn the influence of alloy composition.

Introduction

In a further study of the catalytic properties of the copper–nickel system the ortho–parahydrogen interconversion has been employed. The catalysts have been prepared by hydrogen reduction of the metal carbonate rather than the metal oxide precipitate[3] in order to avoid any separation of oxide phases.[4] However, X-ray diffraction measurements on the present catalysts show no significant differences from those on the earlier catalysts[3] or from careful measurements on massive nickel-copper alloys by others,[5,6] so it is concluded that the present alloy catalysts were well alloyed and highly homogeneous. This conclusion is supported by magnetic measurements made upon present catalysts both in the finely divided and in the massive state.

The ortho–parahydrogen interconversion appeared to be desirable as a measure of catalyst activity because only hydrogen is involved yet a magnetic mechanism[7] has been found operative

at very low temperatures while chemical mechanisms[7] prevail over a wide range of temperatures if suitable chemisorption occurs. Since in the temperature range here employed the nickel–copper system changes from ferromagnetic to paramagnetic to diamagnetic as copper concentration increases, further information about the importance of the magnetic properties of the catalysts was hoped for. However, it appears that adsorbed hydrogen, by modifying its own environment, can partially mask the effect of the electronic structure of the catalyst. Thus even for an apparently simple reaction the electronic structure of the catalyst appears to influence catalysis somewhat indirectly through several types of hydrogen adsorption, which largely dictate the rates of the ortho-parahydrogen interconversion.

Experimental

Apparatus and Purification of Gases.—The hydrogen, helium and nitrogen employed were very pure gases which were further purified by passage over Ascarite, reduced copper at 400°, an active nickel-kieselguhr catalyst at 350°, Anhydrone, and finally through a charcoal trap at liquid nitrogen temperature, except for the nitrogen for which this trap was cooled with Dry Ice. While this train was also suitable for preparing the liquid nitrogen temperature equilibrium ortho-parahydrogen mixture, the hydrogen was next passed over an active nickel catalyst at room temperature when the room temperature equilibrium mixture was required for the reaction velocity measurements. The all glass apparatus consisted essentially of the above purification system, catalyst tubes, thermal conductivity cell, flow meter, B.E.T. system, McLeod gauge, mercury diffusion pump, cold traps, etc. Two connecting, vertical

(1) This paper is based on a portion of a thesis presented by Phoebe B. Shallcross in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1958.

(2) Jesse Metcalf Fellow, 1954–1955, and Edwin P. Anthony Fellow, 1955–1958.

(3) L. E. Cratty, Jr., and W. W. Russell, THIS JOURNAL, **80**, 767 (1958).

(4) W. K. Hall and L. Alexander, *J. Phy. Chem.*, **61**, 242 (1957).

(5) E. A. Owen and L. Pickup, *Z. Krist.*, **88**, 165 (1935).

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catalyst tubes 12 to 26 mm. and 4 to 6 mm. i.d., respectively, allowed an A and B portion of the same catalyst to be reduced simultaneously for reaction velocity measurements at liquid nitrogen temperature and at higher temperatures (controlled by a cryostat), respectively. After reduction the sealing off of appropriate connections not only allowed the A and B catalysts to be separately evaluated but finally permitted the A catalyst to be used for surface area measurements, all with no removal of catalysts from their original positions.

Preparation and Reduction of Catalysts.—The catalysts were prepared by precipitation or coprecipitation, washing and drying as described elsewhere,[3] but any sintering in air was omitted and the granulated precipitate after drying at 105° was reduced directly. When reduced in a stream of purified hydrogen most of the reduction occurred between 130 and 140°. Reduction was completed by about 25 hr. at 400° and 8 hr. at 500°.

Catalyst Activity Evaluation.—The rate at which hydrogen containing a fixed initial ratio of the para and ortho forms had to be passed over a catalyst to achieve an approach to equilibrium at liquid nitrogen temperature of 40%, or a 50% approach to equilibrium at reaction temperatures in the vicinity of room temperature, was used as a measure of catalytic activity. The thermal conductivity cell used to determine ortho-parahydrogen ratios contained a tungsten spiral (from a 100 watt light bulb) suspended axially in a 7 cm. glass tube of 10 mm. i.d. When connected to the circuit described by Stewart and Squires,[8] submerged in liquid nitrogen, and run at a filament current of 0.420 amp. this cell had a sensitivity $s = 0.08$. The cell was calibrated frequently during a reaction velocity run using as standards[9,10] hydrogen containing 50.4 and 25.1% para, respectively, corresponding to the equilibrium mixtures for -196 and 25°. A linear relationship was assumed between the per cent. of parahydrogen and the voltage drop across the cell filament in the 25 to 50% parahydrogen range, as was found by Stewart and Squires. In the present work, since catalyst activities were always compared at a constant parahydrogen content, any slight deviation of the calibration curve from linearity would introduce a negligible error. The extent of conversion to ortho- or parahydrogen occurring during a reaction velocity run is expressed as Y, the per cent. approach to equilibrium produced by the catalyst at the particular temperature.

$$\frac{Y}{100} = \frac{C_X - C_F}{C_T - C_F} = \frac{E_X - E_F}{E_T - E_F}$$

The term Y is defined above where C_X, C_F and C_T are the percentages of parahydrogen in the sample being analyzed, in the hydrogen feed and in hydrogen at equilibrium at the temperature T, respectively. The E quantities are the filament voltages corresponding to hydrogen compositions of similar subscript. To cover the range of activities shown by the catalysts the hydrogen feed flow rate had to be varied from 1 to 200 ml. per minute. All gas volumes reported in this work are reduced to S.T.P.

One of two alternate treatments always was given to each catalyst prior to determining its catalytic activity. One treatment consisted in heating the reduced catalyst in a stream of hydrogen while the temperature was raised slowly to 325°, then evacuating at this temperature to a pressure of 10^{-5} mm. or less. The catalyst was now isolated and cooled to a temperature at least as low as any to be employed in the subsequent reaction velocity run. In the other treatment the catalyst was similarly heated in hydrogen, but was not evacuated, but rather cooled to the run temperature in the presence of hydrogen.

Magnetic Measurements on Catalysts.—Measurements of specific magnetization were made on the nickel and a nickel-rich alloy catalyst in the active, reduced, granular form, and also in the massive form obtained by melting the granular form in a high frequency induction furnace, then by annealing 12 to 16 hr. at 900°, finally slow cooling. These operations were carried out in an atmosphere of helium. The procedures used and the magnetic torsion balance employed were essentially the same as described elsewhere.[3] The magnetic balance was calibrated against a nickel pellet

made by melting a sample of pure electrolytic nickel.[11] The weights of the samples used in the magnetic balance measurements varied from 36 to 72 mg.

Evaluation of Other Catalyst Properties.—A small portion of catalyst fines was reduced along with the catalysts used for the catalytic activity measurements, then photographed in a Debye–Scherrer type X-ray camera and the lattice parameter computed, essentially as described earlier.[3] However, calibration for the X-ray measurements also was carried out by the Straumanis method.[12] Duplicate samples of the alloy catalysts while in the form of the dried, coprecipitated carbonates were analyzed for both copper and nickel in order to establish the copper–nickel ratio. From nitrogen adsorptions at liquid nitrogen temperature and helium dead space measurements, the surface area of the larger sample of each catalyst was determined immediately after 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] Since all of the nitrogen adsorbed at $-196°$ was removed during a brief outgassing at room temperature, it was assumed that no chemisorption occurred during the B.E.T. measurements, however, after this work was completed evidence[13] was published that some nitrogen is chemisorbed at $-195°$ on nickel.

Catalyst 2 contained only nickel, had a specific surface area $s = 0.65$ m.[2] per g.; a cubic lattice constant $a_0 = 3.5231 \pm 0.0003$ Å.: and the A and B portions after reduction weighed 1.99 and 0.0306 g., respectively.

Catalyst 8 contained 5.0 atom % copper; $s = 0.88$; $a_0 = 3.5277 \pm 0.0004$ Å.; $A = 2.73$ g. and $B = 0.0767$ g.

Catalyst 3 contained 24.8 atom % copper; $s = 1.37$; $a_0 = 3.5435 \pm 0.0003$ Å.; $A = 7.45$ g. and $B = 0.149$ g.

Catalyst 6 contained 62.1 atom % copper; $s = 0.97$; $a_0 = 3.5743 \pm 0.0005$ Å.; $A = 7.84$ g. and $B = 0.172$ g.

Catalyst 7 contained 78.6 atom % copper; $s = 0.75$; $a_0 = 3.5906 \pm 0.0003$ Å.; $A = 11.98$ g. and $B = 0.167$ g.

Catalyst 9 contained 91.7 atom % copper; $s = 0.40$; $a_0 = 3.6035 \pm 0.0004$ Å.; $A = 18.2$ g. and $B = 0.175$ g.

Catalyst 4 contained only copper; $s = 0.61$; $a_0 = 3.6140 \pm 0.0002$ Å.; $A = 8.75$ g. The precision of the lattice constant data is expressed as a mean deviation.

Results and Discussion

Activities of the Catalysts in Synthesis.—The catalytic activity of the catalysts was determined at $-196°$ by converting ortho- to parahydrogen, and by converting para- to orthohydrogen at higher temperatures in the range of -30 to 10°, except for the pure copper catalyst which was so inactive in the latter temperature range that temperatures from 60 to 110° were employed. Since it had been shown that the catalytic activity of nickel for converting ortho- to parahydrogen at $-190°$ could be poisoned by preadsorbed hydrogen,[14] as already noted reaction velocity measurements were made both on outgassed surfaces and on surfaces containing preadsorbed hydrogen. In Fig. 1 the dependence of the catalytic activity of previously outgassed surfaces upon catalyst composition is shown in curve I for the ortho to para conversion at $-196°$ and in curve III for the para to ortho conversion at $-20°$. The conversion by the pure copper catalyst at $-20°$ was far too small to measure directly and so has been estimated by extrapolation from the higher temperatures above noted. Catalyst activity is expressed as the rate of hydrogen flow over a square meter of catalyst surface necessary to secure a 40% ap-

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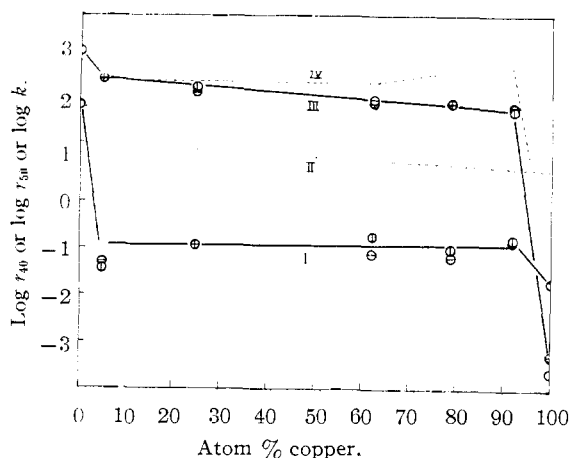
Fig. 1.—The effect of catalyst composition upon: (a) catalytic activity at −196°, curve 1; at −20°, curve III; ⊖, log r_{40} or log r_{50}; ⊙, log k; (b) catalytic activity per unit weight of nickel, curve IV; (c) % d-character. curve II.
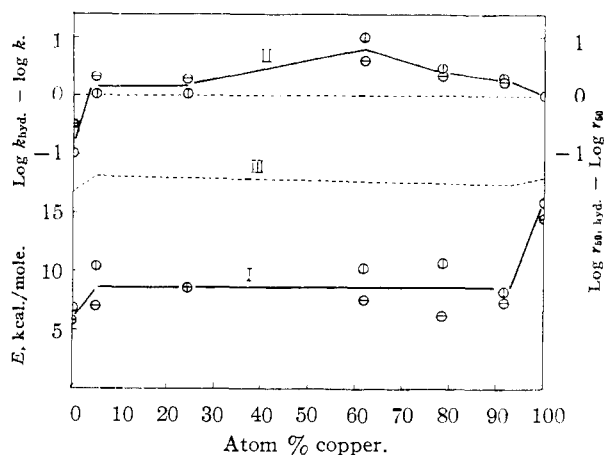

Fig. 2.—The effect of catalyst composition upon: (a) the apparent activation energy E. curve I: (b) the log of the apparent frequency factor B, curve III; (c) catalytic activity in the presence and absence of preadsorbed hydrogen, curve II; for initially outgassed catalysts, k or r_{50}; for catalysts containing preadsorbed hydrogen, $k_{hyd.}$ or $r_{50,hyd}$. Symbols ⊙ and ⊖ have same significance as in Fig. 1.

proach to equilibrium r_{40} at −196° and a 50% approach to eqilibrium r_{50} at −20°. Since the original rate data were obtained at several rates of hydrogen flow at each temperature, first-order rate constants also have been computed. When the curves for these rate constants are displaced vertically so as to make the log k value for the pure nickel catalyst equal to the log r_{40} or log r_{50} at −196 and −20°, respectively, it is seen from Fig. 1 that the two methods of evaluating catalytic activity give essentially the same results. Curves for the para to ortho conversion at 0 and 20° were of substantially the same shape as that for −20°. It is believed that the linear curves represent, within the experimental accuracy achieved, the relationship of catalytic activity at −20 and −196° to catalyst composition in the alloy range from 5 to 92% copper. The fact that the catalytic activity at −196° found for the 5% copper catalyst is lower than the activity of the other alloy catalysts at this temperature is probably to be attributed to some poisoning suffered by the portion of this catalyst used for the ortho to para conversion.

Curve I in Fig. 2 shows the relationship between catalyst composition and the apparent activation energy of the para to ortho conversion at −20° on initially evacuated surfaces. The apparent activation energies were calculated from the temperature dependence of both the log r_{50} and log k values. The scatter of the experimental values is such that only a linear relation appears to merit consideration in the alloy region from 5 to 92% copper. Activation energy values in the same range have been found by others[15] for this reaction on sheets of copper–nickel alloy, however, values of about 3 kcal. per mole were reported[16] on palladium and palladium–gold alloy filaments up to 60% gold, with the value finally rising to 17.5 for pure gold. The dotted curve III in Fig. 2 (ordinates in arbitrary units) shows the dependence of the log of the apparent frequency factor B upon catalyst composition as calculated from the

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data shown by curve III in Fig. 1 and by curve I in Fig. 2.

The effect of preadsorbed hydrogen on catalyst activity for the para to ortho conversion at −20° is shown in curve II in Fig. 2 calculated both from log r_{50} and log k values. At −196° preadsorbed hydrogen poisoned all of the catalysts for the ortho to para conversion. While the activity of the hydrogen poisoned catalysts at −196° was too small to measure accurately, it was observed that preadsorbing hydrogen decreased the catalytic activity from 40 to 80% on alloy catalysts containing more than 25% copper.

X-Ray Diffraction Measurements.—X-Ray diffraction examination of the present catalysts while still in the form of the dried carbonate precipitate indicated that the pure nickel carbonate lacked crystallinity but that crystallinity increased with increasing copper content. While a catalyst containing 25 mole % copper as carbonate still showed no crystallinity, many very diffuse lines and bands which could be attributed to cupric and nickelous phases appeared at the 62 and 79 mole % copper concentrations. Therefore, up to at least 25 mole % the coprecipitated carbonates appear amorphous, while in the higher copper range studied the diffuseness of the lines and bands made phase identification uncertain.

Because the sintering step was omitted here it was considered of interest to compare the lattice constants of the reduced metal catalysts with catalysts produced in this Laboratory by the reduction of oxides sintered at 400°.[3] However, no significant difference was found so it appears that omission of the sintering step has made no change in metal atom spacing detectable by X-ray diffraction. However, increasing the temperature of reduction of an alloy catalyst containing about 25 atom % copper from 400 to 500° caused the measured lattice parameter to decrease 0.005 Å.

Magnetic Measurements on the Catalysts.— Specific magnetization measurements made on the
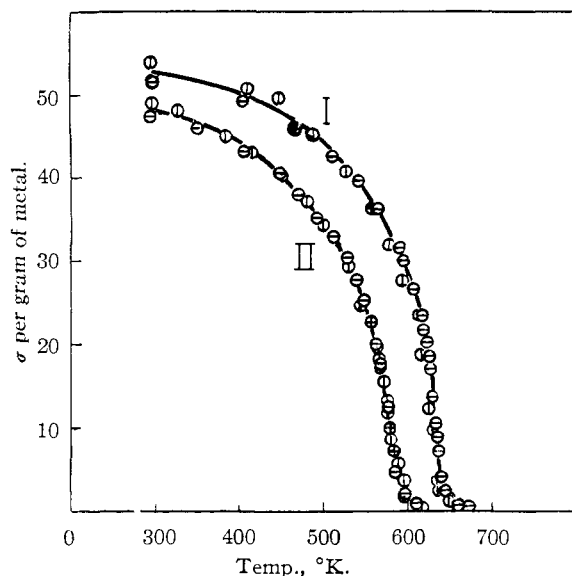
Fig. 3.—Specific magnetization curves: curve 1, pure nickel; curve II, 5 atom % copper; ⊖, powder samples; ⊙, pellet samples.

pure nickel and 5% copper alloy catalysts, both in the granular catalytically active form and after melting to a massive pellet and annealing in helium, are shown in Fig. 3 extending from room temperature to above the Curie points. Curie points taken from these curves are 360 and 354° for the pure nickel in granular and pellet form respectively, and similarly for the 5 atom % copper alloy 309 and 310°. The ferromagnetic Curie point of nickel is usually taken as 358°[17] and from this a value of 305° may be calculated for the Curie point of the 5% alloy.

Discussion and Conclusions

In the present work every effort has been made to prepare alloy catalysts which are homogeneous both in bulk and surface. Lack of homogeneity throughout an alloy may be detected by magnetic measurements and so it is of interest to compare the specific magnetization curves in Fig. 3. Although the pellet samples were subject to a considerable further annealing treatment, the curves for pellet and granular samples of the same catalyst coincide. Also the tail region of the 5% alloy catalyst is no more extensive than that for the pure nickel catalyst which involves no alloy formation. Thus there appears to be no evidence that alloys near the nickel-rich end of the alloy composition range lacked homogeneity and if alloys nearer the middle of the range were slightly less homogeneous. at least in the present work, this is less important since here catalyst activity has proved rather insensitive to large changes in catalyst composition. However, as is evident from Fig. 4 alloy catalysts possessing such insensitive regions of composition are by no means confined to alloys produced by the alloying technique here employed.

Although the ortho–parahydrogen interconversion has been much studied,[7] it has often proved difficult to pinpoint its mechanism. Thus a

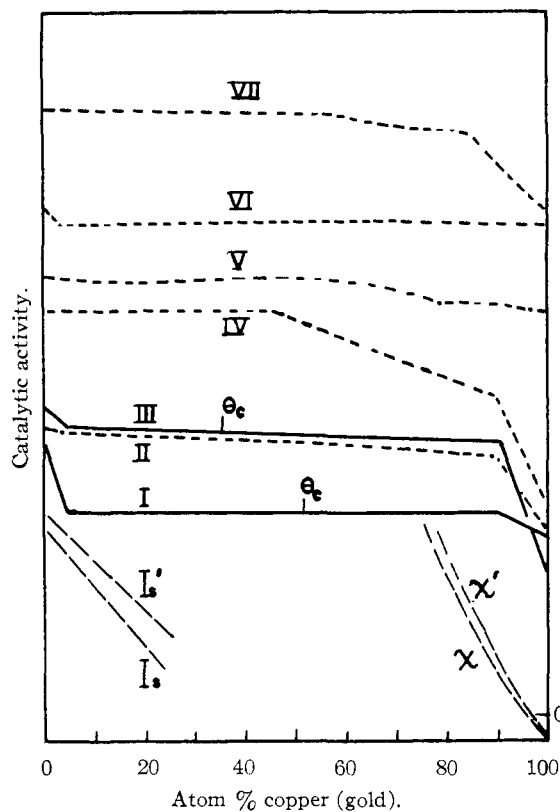(17) L. F. Bates, "Modern Magnetism." Cambridge Univ. Press, Inc., New York, N. Y., 1951, p. 317.

Fig. 4.—Comparison of alloy composition–catalytic activity curves, ortho–parahydrogen interconversion: present work at −196° curve I, at −20° curve III; on gold palladium alloy wires[16] at 227° curve IV: on copper nickel alloy sheets[15] at 350° curve V; on copper–platinum alloy sheets[20] at 150–580°. curve VII. Hydrogenation over copper–nickel alloy catalysts similar to those used in present work of: ethylene[18] at −73° curve II; carbon dioxide[8] at 420° curve VI. Specific magnetization: I_s' at −183°, I_s at 18°; magnetic susceptibility: χ' at −196°, χ at 22°. Ferromagnetic-paramagnetic transition composition is θ_0.

chemical mechanism has been found operable over a wide temperature range, yet a magnetic mechanism has also frequently been important at liquid air temperatures and below, especially in the presence of ferromagnetic or paramagnetic catalysts. As is clear from curves I and III in Fig. 1 both the conversion at −196° and the conversion at −20° respond to changes in alloy catalyst composition in a similar manner. The low temperature conversion remains substantially independent of alloy composition after the first few per cent. of copper or nickel is alloyed with nickel or copper, respectively, and the conversion at −20° changes relatively slowly at an essentially linear rate in this region. Alloying 5% or less of copper with nickel causes both conversions to fall sharply, especially at −196°. In this alloy composition region the specific magnetization both at 18 and −183° is also falling sharply as is shown in Fig. 4. Also alloying 8% or less of nickel with copper causes both conversions to rise sharply, especially at −20°. In this alloy composition region, as shown in Fig. 4, the magnetic susceptibility

both at 22 and −196° changes from slightly negative to positive. However, over more than 85% of the alloy composition range the rates of the ortho–parahydrogen interconversion change relatively much less. Lack of sensitivity of a catalyzed reaction to changes in alloy catalyst composition over considerable ranges of the latter frequently has been observed. Examples of this phenomenon are shown graphically in Fig. 4 in which in addition to curves I and III for the present work with the ortho-para interconversion at −196 and −20°, curves II and IV to VII are shown, arranged vertically in the order of increasing reaction temperature, for this reaction on copper nickel and other binary alloy catalysts containing a Group IB metal and a transition metal, also for two other reactions on such catalysts. Alloy catalysts in granular, sheet and filament form are represented in Fig. 4. Since for the copper–nickel alloys the lattice parameter changes nearly linearly with alloy composition, it is difficult to exclude the possibility that extensive and essentially linear portions of catalytic activity vs. alloy composition curves are related to inter-atom distances and electronic properties of these alloys related thereto. In this connection it is of interest that Hall and Emmett[18] have calculated that the percentage d-character of copper nickel alloys is essentially a linear function of alloy composition.

Although the copper–nickel alloy system is in many ways far from ideal,[19] saturation magnetization does change linearly with composition and simple theory predicts for example that d-band holes should be filled when about 60% copper or gold is alloyed, respectively, with nickel or palladium. However, in Fig. 4 breaks occur near this alloy composition only for the para- to orthohydrogen conversion at elevated temperatures on gold palladium wires[16] and copper–platinum sheets.[20] Even in these cases catalytic activity apparently is almost wholly independent of alloy composition while d-band holes are being filled. Alloy compositions having Curie points at the temperature used to measure catalytic activity are marked on curves I and III in Fig. 4 and there is no evidence of any significant change in catalyst activity in passing from ferromagnetic to paramagnetic alloys. Although in the present work changes in catalytic activity at the extreme ends of the copper–nickel alloy composition range are paralleled by changes in magnetic properties of the alloys, these magnetic properties continue to change rapidly long after catalytic activity ceases to change comparably. However, as is shown in curve II in Fig. 1 the percentage d-character (plotted with arbitrary ordinate units) falls linearly throughout the whole composition range with increasing copper in the alloy catalysts. Percentage d-character previously has been correlated with catalyst activity by others.[18,21] Therefore it is noted that the shape of the catalytic activity vs. alloy composition curves found in the present work would be obtained by a general pre-

dominance of percentage d-character except where ferromagnetic, or paramagnetic and diamagnetic properties predominate near the two ends of the alloy composition region.

Properties more directly related to the nature of a catalyst surface may also be considered in an endeavor to understand how catalyst activity can remain so relatively constant over wide ranges of alloy catalyst composition. To explain such relative constancy of catalytic activity while d-band holes are filling, it has been assumed by Couper and Eley[16] that the replenishment of the catalyst surface by such holes from the catalyst interior is permitted in the free electron theory or may result from the resonance of valence bonds. Also compensating changes in apparent activation energy and in frequency factor have frequently been observed in studies in heterogeneous catalysis and this phenomenon recently has been reviewed by Cremer.[22] In a recent study[23] of the hydrogenation of benzene over copper–nickel alloy catalysts similar to those here studied, Hall and Emmett found that catalytic activity and apparent activation energy rose together to a maximum and then fell as more and more copper was alloyed with nickel. This behavior was explained by assuming over-compensation by the apparent frequency factor. In the present work at −20° as is clear from Figs. 1 and 2, any substantial changes in apparent activation energy and frequency factor always were in the same direction, but the activation energy change predominated and accounts for the considerable changes in catalyst activity occurring near each end of the alloy composition range. Only the smaller change in catalyst activity over the remaining alloy composition range appears to reflect any predominance of the frequency factor.

The present work has served to emphasize the important effect of preadsorbed hydrogen upon the catalytic activity of nickel, copper and their alloys, with both poisoning and promoting effects being observed. It has been clear for some time that hydrogen may be adsorbed and held upon a catalyst surface in different ways. Recent studies by Singleton[24] of the para–orthohydrogen reaction over evaporated nickel films at −78° disclosed three types of adsorbed hydrogen, but only the loosely held hydrogen, whose adsorption caused an increase in the electrical resistance of the nickel film, participated directly in the parahydrogen conversion. In the present work at least for the orthohydrogen conversion at −196°, experiment showed that the poisoning of the nickel catalyst involved more than a simple blocking of a uniformly active surface, inasmuch as preadsorbing hydrogen equal to a tenth of a monolayer reduced catalytic activity by 75%. Preadsorbed hydrogen while poisoning pure nickel has enhanced the activity of all of the present alloy catalysts for the para–orthohydrogen conversion at −20°, as is shown by curve II in Fig. 2. These poisoning and promoting effects are in qualitative agreement with those found by Hall and Emmett[18] for the hydrogenation of ethylene over

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(24) J. H. Singleton, ibid., 60, 1606 (1956).

similar alloy catalysts. However, in the latter work[18] a sharp maximum in promoting effect occurred around 85% copper instead of near 60% as found in the present work. In the presence of preadsorbed hydrogen, the present work also confirms what was found earlier by Best and Russell,[25] with these alloy catalysts for the hydrogenation of ethylene, namely, that catalyst activity increased with copper concentration up to about 60% copper then fell as more copper was alloyed with nickel.

There already exists much evidence that the electronic structure and catalytic properties of surfaces are modified by the presence of adsorbed gases. Studies of changes in work function and contact potential caused by adsorbates has led to the concept of an "induced heterogeneity" in surfaces[26] or a "work function effect"[27] which may either facilitate or hinder subsequent adsorption. Furthermore there is evidence that the distribution of lattice planes in a metal surface can be influenced by the presence of an adsorbed gas, especially at temperatures above about one third of the absolute temperature at which the metal melts.[28] Such adsorption-induced changes in the configuration of a metallic nickel surface recently have been considered pertinent by Roberts and Sykes[29] in explaining hydrogen adsorption on very carefully reduced nickel powders. It appears of interest that in the present work the deliberate preadsorption of hydrogen always occurred at 325°, which is well above the minimum temperatures for surface mobility of the catalysts studied.

Either deliberately preadsorbing hydrogen on pure nickel or alloying a few per cent. of copper with it reduced the catalytic activity of the nickel, and in both cases an increase in paired electrons in the 3 d-band of the nickel may be involved. Adding a few per cent. of nickel to pure copper always caused a marked increase in catalytic activity, and the activity at $-20°$ of the catalyst containing about 92% copper, per unit weight of nickel, was comparable to pure nickel as is clear from the dotted curve IV in Fig. 1. A similar curve with a maximum can be drawn for the reaction at $-196°$. The quite different dependence of the para-orthohydrogen conversion at $-20°$ upon catalyst composition in the presence of and in the absence

of the deliberately preadsorbed hydrogen, that is evident from a comparison of curves III and II of Figs. 1 and 2, respectively, indicates clearly the important role played by such hydrogen which presumably underwent little or no conversion itself. Whether the preadsorbed hydrogen acted as a poison, promoter or had little or no effect upon the catalytic reaction at a given temperature depended upon the catalyst composition. Even when no hydrogen was deliberately preadsorbed, there is no doubt that part of the hydrogen adsorbed at the temperature of the ortho-parahydrogen interconversion played a role somewhat similar to the former. This would be expected from earlier work with this reaction by Singleton[24] and from magnetic studies by Selwood,[30] who found chemisorption of hydrogen on supported nickel even at $-196°$. It appears that the dependence of the activity of the catalysts here studied upon catalyst composition could be strongly modified by the nature and extent of hydrogen so fixed or held to the catalyst surface that it participated in the catalytic reaction only indirectly. Such fixed hydrogen could act. depending upon alloy composition, as a promoter via the inductive effect or the work function effect or as a poison from such effects or by a simple blocking adsorption. The relatively small changes in catalytic activity of the alloys, as the copper content was varied from 5 to over 90% in the absence of deliberately preadsorbed hydrogen, is believed due to the effects of hydrogen fixed during the interconversion, further modifying the catalytic properties of the alloy surface upon which the hydrogen, actively participating in the ortho-hydrogen interconversion was adsorbed. It appears possible to consider that poisoning and promoting effects occur simultaneously and reflect the effects of factors such as gas pressure, temperature and catalyst composition. Poisoning effects appear to predominate on pure nickel in the vicinity of room temperature, but give way to promoting effects, which it is believed largely offset the effect of increasing copper concentration until the latter is over 90%. At $-196°$ a comparable compensation is not excluded, although promoting effect of fixed hydrogen at this temperature was not directly observed. A more complete understanding of the copper-nickel system as hydrogenating catalysts would seem to demand further study of the nature and effects particularly of such fixed hydrogen.

PROVIDENCE, RHODE ISLAND

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