humidity produces swelling in hydrated calcium silicates and portland cements. Bernal[13] suggested that swelling may be caused by entry of water between the layers of tobermorite, thus increasing the *c* spacing. Kalousek[24] determined the surface areas of various concrete specimens by nitrogen and water vapor adsorption, and he noted that the former was always smaller than the latter. He attributed the difference between the two to the ability of water and the inability of nitrogen to penetrate between the layers of the calcium silicate hydrate. The same explanation was used by the present investigators to account for the difference between the water and nitrogen surface areas of tobermorite.[2]

The investigations reported in this paper indicate that this explanation is not valid. The density experiments showed that tobermorite dried to an H_2O/SiO_2 ratio of approximately 1.0 does not swell in a saturated $Ca(OH)_2$ solution. Prior to surface area determinations, tobermorite is dried to this water content. The maximum relative humidity used in the surface area determinations was 33%; it seems, therefore, very unlikely that water vapor entered between the layers in the adsorption experiments. Yet, there was a fivefold discrepancy between the nitrogen and water surface areas of C-23. It seems that the rolling of the sheets of tobermorite or aggregation of the crystallites or both together produce surfaces inaccessible to nitrogen molecules, though accessible to water molecules.

The above evidence does not show that Bernal's hypothesis as to the swelling of tobermorite is incorrect. The tobermorites in C-18 and D-43, having an H_2O/SiO_2 ratio of 1.4, exhibited a slow swelling in a saturated $Ca(OH)_2$ solution. It is possible that water can enter between the layers of a less thoroughly dried tobermorite more rapidly and at relative humidities below 100%.

6. The average index of refraction of the tobermorite in hydrated β-Ca_2SiO_4 was 1.56 ± 0.01. The same value was found earlier for tobermorite in paste-hydrated Ca_3SiO_5.[2] Heller and Taylor[16] obtained the same value for tobermorite prepared by the hydrothermal reaction of $Ca(OH)_2$ and silica gel. A sample of the natural mineral tobermorite, investigated by McConnell,[25] had an average index of refraction of 1.57.

Acknowledgments.—The authors wish to express their indebtedness to Mr. E. E. Pressler for the chemical analyses, Mr. C. H. Weise for density, ignition loss and carbon dioxide determinations, Miss Edith Turtle for X-ray analysis, Dr. L. S. Brown for index of refraction determination and microscopic examination, and to Mr. William Gregory for water surface area measurements. Discussions with Mr. T. C. Powers and Mr. R. H. Bragg were very helpful in these investigations.

CHICAGO, ILLINOIS

---

[24] G. L. Kalousek, *J. Am. Concrete Inst.*, **26**, 233 (1954).

[25] J. D. C. McConnell, *Mineral. Mag.*, **30**, 293 (1954).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Nickel, Copper and Some of their Alloys as Catalysts for the Hydrogenation of Carbon Dioxide[1]

BY LELAND E. CRATTY, JR.,[2] AND W. WALKER RUSSELL

RECEIVED JULY 26, 1957

The activity of nickel, copper and some of their alloys as catalysts for the hydrogenation of carbon dioxide has been determined. X-Ray diffraction and magnetic measurements indicate that, although these catalysts were prepared by the reduction of oxides obtained from precipitated metal carbonates, they were essentially homogeneous, equilibrium solids. Alloying 11% or less of copper with nickel caused sharp parallel drops in both the magnetic susceptibility and in the power of the catalysts to hydrogenate carbon dioxide to methane rather than carbon monoxide. Alloys containing more than 50% copper behaved essentially like pure copper in that carbon monoxide but no methane was produced.

Introduction

Nickel and copper are completely miscible in the solid state and show an essentially linear lattice parameter relationship in their alloys, therefore any significant deviations of catalytic activity from such a relationship offer evidence of the importance of non-geometric factors such as the electronic factor. Since nickel is a strong methanation catalyst and copper a much weaker hydrogenation catalyst, yet active in the water gas shift, a study of the nickel–copper system employing the hydrogenation of carbon dioxide appeared to offer interesting possibilities. The catalysts used were prepared as in an earlier investigation[3] involving the hydrogenation of ethylene in which no simple relation was found between the activity of the catalysts and their metallic composition. Even though these catalysts were formed by reduction of oxides obtained from precipitated metal carbonates, X-ray measurements in the present work as in the earlier work[3] yielded lattice constants characteristic of equilibrium alloys formed by melting the components together. Recently, Hall and Alexander[4] have made careful X-ray diffraction measurements on nickel–copper catalysts, prepared according to Best and Russell,[3] both before and after reduction of the metal oxides. These measurements also confirm that normal alloying occurs between nickel and copper and is very complete. These authors[4]

---

[1] This paper is based on a portion of a thesis presented by L. E. Cratty, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1957.

[2] Dow Fellow, 1954–1955, and University Fellow, 1955–1956.

[3] R. J. Best and W. W. Russell, THIS JOURNAL, **76**, 838 (1954).

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

conclude that these catalyst alloys are essentially homogeneous and that "compositional variations, if present at all, cannot exceed 3%." In the present work measurements of specific magnetization and of magnetic susceptibility have been made both upon the active catalysts and upon annealed solid pellets obtained by melting the finely divided catalysts. These magnetic measurements agree, as well as could be expected, with literature values for these metals and alloys prepared by refined conventional methods. This is additional evidence for the homogeneity of the catalyst alloys. The magnetic measurements also yield information about the electronic structure of the catalysts and particularly about holes or unpaired electron spins in the 3d band in the nickel. Since chemisorption on nickel is thought to involve 3d band electrons[5,6] suitable magnetic measurements should yield information pertaining to catalytic activity. In this connection it is of interest to note that Reynolds found that the activity of Raney-type nickel–copper catalysts for the hydrogenation of benzene at 100° closely paralleled the measured magnetic susceptibility of the catalysts.[7] In the present work to account for the yields of methane and/or carbon monoxide obtained with the catalysts, it appears necessary to consider both the electronic and the geometric factors.

Experimental

Apparatus and Purification of Gases.—The reactant gases, hydrogen and carbon dioxide, of the same grade, and metered and purified essentially as already described[8,9] were in an all-glass system until they had passed out from the synthesis catalyst. The catalyst chamber consisted of a vertical Pyrex tube 15–23 mm. i.d., having an axial 8 mm. o.d. thermocouple well, placed in an electrically heated furnace and controlled by a potentiometric controller-recorder.[8,9] Wet test meters separately measured the two reactant gases before entering the catalyst bed and the dried exit gas mixture issuing therefrom. The exit gases were analyzed for water, carbon dioxide, hydrogen, carbon monoxide and saturated hydrocarbons as already described.[9]

Preparation and Reduction of Catalysts.—The catalysts were prepared by precipitation or coprecipitation, washing, drying, sintering and reducing as described elsewhere.[3]

Catalyst Activity Evaluation.—The volume and composition were known for the entering synthesis gas and also for the exit gas. Therefore, the contraction and also the hydrogen and carbon dioxide participating in synthesis could be determined. No oxygen, unsaturated and/or liquid hydrocarbons were detected in the exit gases. Runs were made at successively higher temperatures and between runs the catalyst was maintained in a stream of hydrogen at the temperature of the completed run. All gas volumes are at S.T.P. The synthesis gas consisted of hydrogen plus carbon dioxide always in a volume ratio of 2 to 1. This gas passed through the catalyst at a predetermined rate which was in the range of from 3 to 17 l. per hr. In order to compare the over-all hydrogenating activities of the catalysts, in the absence of surface area measurements, the percentage of the input carbon dioxide which reacted was plotted as a function of W/F, the ratio of catalyst weight to the rate of synthesis gas flow, for each run temperature. Using these plots extrapolation has been made where necessary to a W/F value of 0.5 since this value occurred most frequently in the experimental data.

Magnetic Measurements on Catalysts.—Measurements of specific magnetization and of mass susceptibility were made on the nickel and the nickel-rich alloy catalysts after reduction and also after melting and annealing at 900° for 5 to 7 hr. The melting in a high frequency induction furnace, the annealing and also the magnetic measurements were carried out while the sample was in an atmosphere of helium. The magnetic measurements, at temperatures ranging from −30 to 535°, were made on a modification of the magnetic torsion balance described by Buehl and Wulff[10] and used by them to measure the magnetic properties of steels. Constancy of field and the absence of heating effects were secured by replacing the electromagnet by a permanent magnet which, however, limited measurements to a single field strength.

The Fereday-type pole pieces[11] produced a field gradient which varied linearly from 2400 to 2100 gauss over a distance of 13 mm. along the axis of the circular pole pieces. In the middle of this axis of constant gradient the radial field was constant outwards 5 mm. from this axis. The sample was centered well within this right cylinder of constant field gradient. The planar pole piece diameter was 34.9 mm., that of the concave pole piece was 42.9 mm., while the radius of the concavity was 63.3 mm. The gap between the pole pieces was 25.5 mm. This gap width permitted the use of a non-inductively wound furnace for heating and of a cooling bath for the lower temperatures. A Pt–Pt, 13% Rh thermocouple in contact with the sample measured temperature during the magnetic measurements, except at the low temperatures where a copper–constantan thermocouple was used. The catalyst sample was securely held in a thin spherical glass bulb blown on the end of a Pyrex glass tube which was mounted in the torsion wire block of the magnetic balance. For the susceptibility measurements the balance was calibrated against Mohr salt ($\chi = 31.8 \times 10^{-6}$ c.g.s. units at 20°), and for the specific magnetization measurements against a nickel pellet made by melting a sample of pure electrolytic nickel.[12]

Evaluation of Other Catalyst Properties.—A small portion of catalyst fines was reduced, then photographed in a Debye–Scherrer type X-ray camera and lattice parameter computed, all as described earlier.[9] Duplicate samples of the alloy catalysts while still in the mixed oxide state were analyzed for both copper and nickel in order to establish the copper–nickel ratio.

Catalyst 2 composed of nickel, weighed 16.7 g. after reduction, possessed a cubic lattice constant $a_0 = 3.5226 \pm 0.0007$ Å., and had light gray color.

Catalyst 8 contained 3.71 atom % copper, weighed 6.9 g. after reduction, had $a_0 = 3.5279 \pm 0.0013$ Å., and was light gray color with some luster.

Catalyst 7 contained 11.33 atom % copper, weighed 6.4 g. after reduction, had $a_0 = 3.5307 \pm 0.0006$ Å., and was light gray color.

Catalyst 1 contained 32.93 atom % copper, weighed 14.6 g. after reduction, had $a_0 = 3.5504 \pm 0.0015$ Å., was of light gray color.

Catalyst 6 contained 51.40 atom % copper, weighed 10.1 g. after reduction, had $a_0 = 3.5658 \pm 0.0017$ Å., was of a light gray color.

Catalyst 4 contained 68.54 atom % copper, weighed 12.1 g. after reduction, had $a_0 = 3.5802 \pm 0.0013$ Å., was of a light gray color.

Catalyst 3 composed of copper, weighed 14.8 g. after reduction, had $a_0 = 3.6155 \pm 0.0007$ Å., was of a brick red color.

Results and Discussion

Activities of the Catalysts in Synthesis.—The effects of temperature upon the distribution of products from the hydrogenation of carbon dioxide over two catalysts are shown in Figs. 1 and 2. This distribution is expressed as a carbon balance in terms of the volume percentages of the inlet carbon dioxide unconverted and converted to carbon monoxide and methane. The topmost curve

---

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

(6) D. A. Dowden and P. W. Reynolds, *Disc. Faraday Soc.*, **8**, 184 (1950).

(7) R. W. Reynolds, *J. Chem. Soc.*, 265 (1950).

(8) W. W. Russell and G. H. Miller, THIS JOURNAL, **72**, 2446 (1950).

(9) R. A. Stowe and W. W. Russell, *ibid.*, **76**, 319 (1954).

(10) R. Buehl and J. Wulff, *Rev. Sci. Instr.*, **9**, 224 (1938).

(11) R. A. Fereday, *Proc. Phys. Soc.* (*London*), **43**, 383 (1931).

(12) Furnished through the courtesy of Dr. E. Wise of the International Nickel Company.

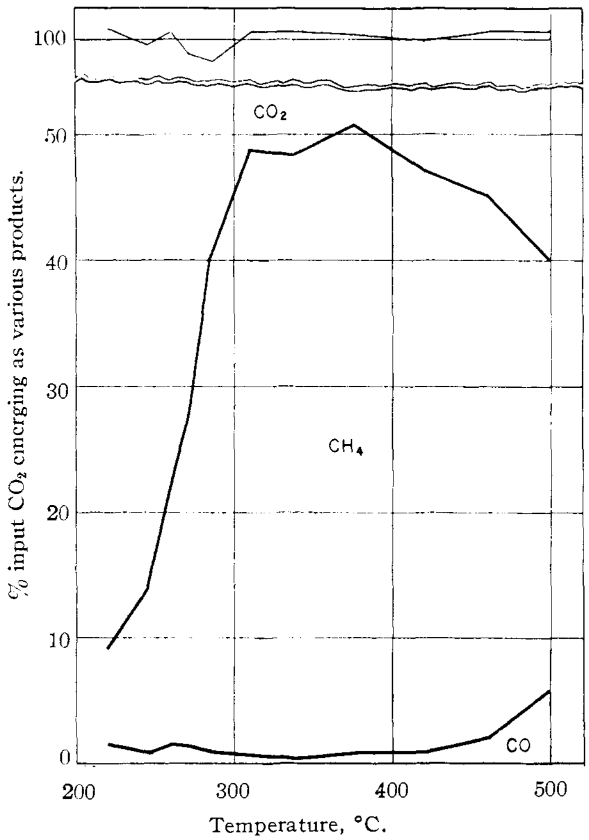

Fig. 1.—Effect of temperature upon product distribution in the hydrogenation of carbon dioxide over catalyst 2 (100% Ni). Carbon balance is in terms of input carbon dioxide.

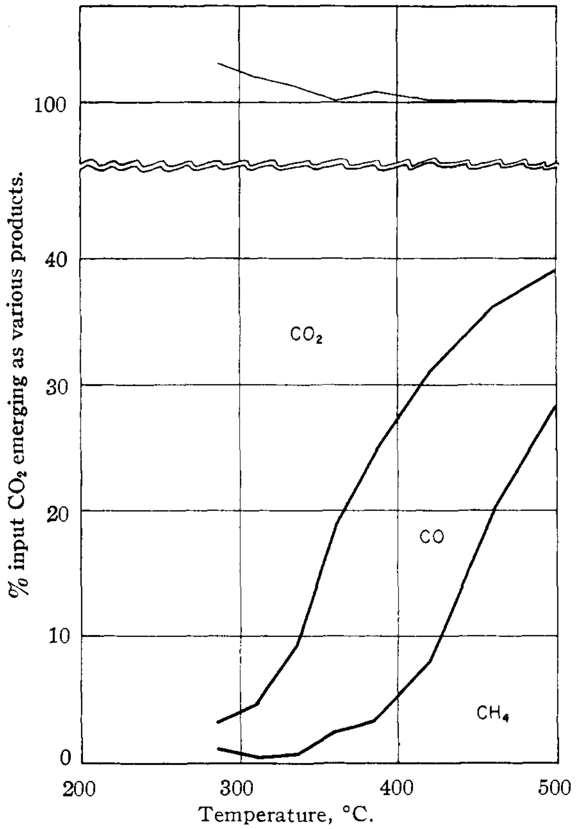

Fig. 2.—Effect of temperature upon product distribution in the hydrogenation of carbon dioxide over catalyst 8 (Cu:Ni, 3.7:96.3). The carbon balance is in terms of input carbon dioxide.

(above break in figure) shows the experimental error in striking the carbon balance. As is shown in Fig. 1 methane formation predominated on the pure nickel catalyst at all temperatures studied, rising very rapidly between 200 and 300°, then falling more slowly between 400 and 500°. Whereas the carbon monoxide yield on pure nickel was small, alloying less than 4% copper greatly increased the carbon monoxide, as is evident in Fig. 2, while methane formation was largely suppressed below 400°. Alloying larger amounts of copper caused carbon monoxide to increase further at the expense of methane until the latter was no longer detectable above 50% copper.

Over all hydrogenation, expressed as the percentage of the inlet carbon dioxide converted at a constant ratio of catalyst weight to synthesis gas flow, *i.e.*, $W/F = 0.5$, was insensitive to changes in copper content of the alloy catalysts from about 4 to 70% copper. Thus at 420° as shown by curve H in Fig. 6 the total percentage of carbon dioxide converted in this composition range remained constant at 30 ±1. Although at certain other temperatures in this alloy composition region conversion was somewhat less constant no significant trend developed. Alloying more than 70% copper caused the over all hydrogenation to decrease little at 420° and above, but slightly more at the lower temperatures. The effect of alloying as little as 4% copper was to decrease the over all hydrogenation on nickel at all temperatures. This decrease at 420° is shown in Fig. 6, curve H. At higher temperatures this decrease was less but became progressively larger as the temperature was lowered.

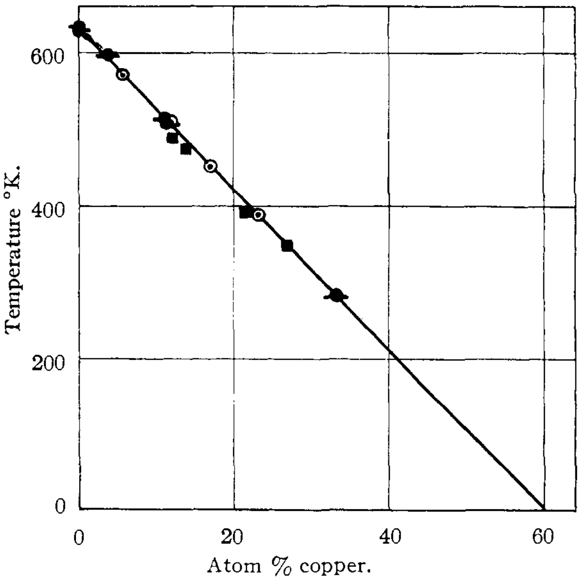

Fig. 3.—The linear relation between the ferromagnetic Curie temperature and catalyst composition. Present work: powders, -●; pellets, ●-; Wheeler, ■; Torkar and Mariacher. ⊙.

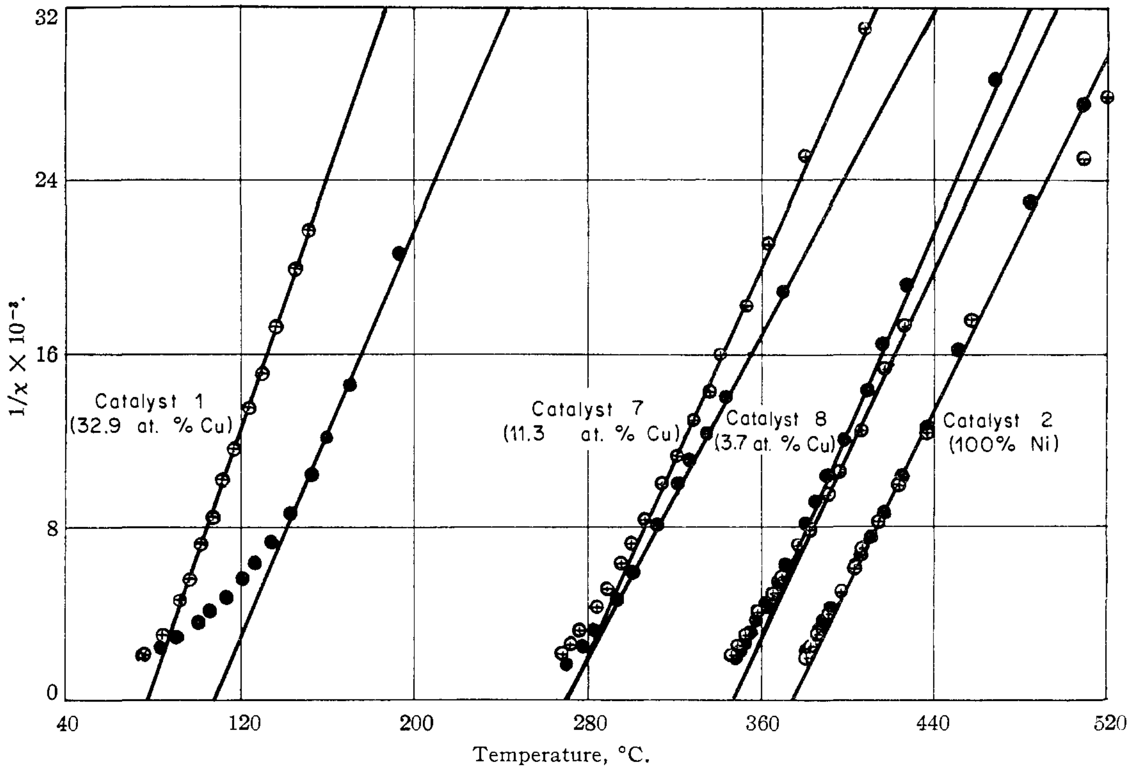

Fig. 4.—Curie–Weiss law plot. Reciprocal of the mass magnetic susceptibility per g. of nickel is plotted *vs.* temperature. Paramagnetic Curie temperatures may be read from abscissa intercepts: powder samples, ●; pellet samples, ⊕.

The effect of catalyst composition upon product distribution, rather than upon over all hydrogenating capacity, is considered more important in the present study. Although the heterogeneous hydrogenation of carbon dioxide is known to be complex, it appears to be consistent with the present results to consider that carbon monoxide initially formed *via* the water gas conversion reaction may be desorbed as such or undergo further hydrogenation to methane before desorption occurs. The specificity of a catalyst in forming methane may then be expressed as a specificity factor A.

$$A = \frac{\text{Volume CH}_4}{\text{Volume CO} + \text{Volume CH}_4}$$

The values for the volume terms in the formula were obtained directly from analyses of the exit gas. The factor A gives the fraction of the reacting carbon dioxide which yields methane. The term $(1 - A)$ then gives the fraction of the reacting carbon dioxide which is reduced only as far as carbon monoxide. As is evident from curves in Fig. 6, A is very sensitive to the presence of small amounts of copper in a nickel catalyst. Alloying less than 4% copper has caused A to drop at 420° from near unity to about 0.25, while at the lower temperatures the drop was from near unity to about 0.1. Between 460 and 500° alloying about 11% copper with nickel caused A to drop from about 0.9 to 0.2. At all temperatures following the initial sharp drop, A decreased more slowly with increasing copper content and became substantially zero at about 50% copper. The simultaneous changes in $(1 - A)$ can be inferred from the foregoing or seen as a curve in Fig. 6.

X-Ray Diffraction Measurements on Catalysts.—Even though copper and nickel both crystallize in a face centered cubic lattice and form a continuous series of solid solutions, some deviation from Vegard's law is found[13,14] in alloys made by melting these metals together. A similar deviation has been found[3,4] for copper–nickel alloy catalysts prepared by reduction of the sintered coprecipitated metal carbonates. Such catalysts have been employed in the present work and found to show a maximum deviation from Vegard's law, near 68 atom % copper, corresponding to 0.17% contraction. This is to be compared to values of 0.11 and 0.22 reported earlier.[13,14] Friedel[15] considers that deviations from Vegard's law may be due to a difference in compressibilities of two alloying elements. For copper and nickel he computed a value of 0.1 for his deviation parameter y which was found to be 0.2, in the region of highest contraction, for the present alloy catalysts. The present X-ray measurements appear to show, therefore, that alloy catalysts here studied possess the same lattice structures as annealed alloys prepared by melting the pure component metals together. Curve L in Fig. 6 is a plot of lattice parameter of the catalysts against catalyst composition.

Magnetic Measurements on the Catalysts.—Although numerous magnetic measurements have already been made upon the copper–nickel alloy system, it was considered important to make such measurements directly on the active finely divided catalysts and upon these catalysts after being

---

[13] W. G. Burgers and J. C. M. Basart, *Z. Krist.*, **75**, 155 (1930).

[14] E. A. Owen and L. Pickup, *ibid.*, **88**, 165 (1935).

[15] J. Friedel, *Phil. Mag.*, **46** [7], 514 (1955).

melted and so converted to the solid massive state to which state most of the literature magnetic measurements pertain. The magnetic measurements were confined to the four catalysts containing 33% copper or less. The specific magnetization measurements on these catalysts when plotted against temperature gave typical sigmoid curves.[16] Only the most copper-rich catalyst curve showed appreciable flattening prior to the Curie temperature. For a given catalyst the powder and pellet curves had a similar shape so that Curie temperatures calculated from the curve inflection points agreed rather well, *e.g.*, for the pure nickel catalyst: 358.9° powder, 358.0° pellet. These Curie temperatures, along with certain literature values, are plotted against catalyst composition in Fig. 3. It is seen that a linear curve results which extrapolates to zero Kelvin at 60% copper in the alloy. Since the catalytic activities of the catalysts studied were measured in the 300 to 500° temperature region, the magnetic susceptibilities measured in this region should be of more interest. When the reciprocals of these susceptibilities are plotted against temperature, the curves are essentially linear at the higher temperatures but become somewhat convex toward the temperature axis upon approaching this axis. Such a deviation from the Curie–Weiss law has been found by others.[17] Curie–Weiss plots are shown in Fig. 4 from which it is evident that both powder and pellet curves for a given catalyst extrapolate to essentially the same paramagnetic Curie temperature, except in the case of the 33% copper catalyst. As is usual[18] the paramagnetic is higher than the ferromagnetic Curie temperature. Figure 5 shows how the magnetic susceptibility decreased with increasing copper content for the finely divided catalysts at the temperatures employed in the synthesis runs. Also included are Wheeler's values[19] for massive copper–nickel alloys which are in reasonably good agreement with the present powder catalysts. Whereas susceptibilities per gram of nickel are employed in Figs. 4 and 5 and for the 420° curve of Fig. 5 which appears as the χ curve in Fig. 6, the χ' curve in Fig. 6 shows the susceptibility per gram of catalyst.

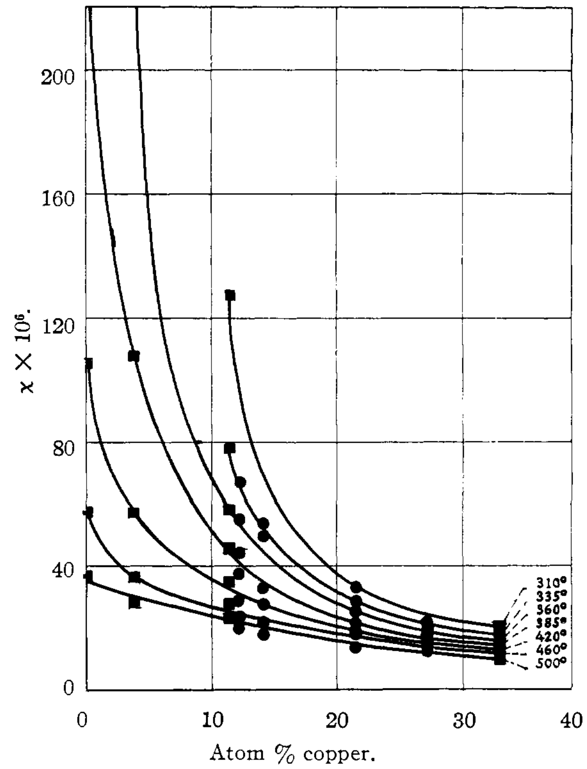

Fig. 5.—Effect of catalyst composition upon mass magnetic susceptibility per g. of nickel at various temperatures: present work, powder samples, ■; Wheeler, ●.

Discussion and Conclusions

Much of the more important experimental evidence is brought together in Fig. 6, in which at a reaction temperature of 420°, as a function of catalyst composition there are plotted total hydrogenating activity, catalyst specificity for methane and also for carbon monoxide production, magnetic susceptibilities and lattice parameter. At the other reaction temperatures the picture is qualitatively the same. It is immediately clear that lattice parameter alone allows no adequate interpretation of either the total hydrogenating activity or the specificity of the catalysts. However, the specificity of the catalysts for methane formation is closely paralleled by their magnetic susceptibilities. The magnetic susceptibilities of Wheeler[19] and of Kaufmann and Starr[20] have been used to extend the catalyst susceptibilities to pure copper in Fig. 6. Beyond about 50% of alloyed copper, methane was no longer detectable, and the magnetic susceptibility of the alloys is very small,[20] becoming zero then slightly negative beyond 95% copper. As already noted here and elsewhere[9] it appears consistent with the data to assume that the water gas conversion reaction occurs first on the catalyst surface and then that the adsorbed carbon monoxide formed is desorbed as such, or as methane if the catalyst surface possesses adequate activity. In terms of this concept all of the catalysts catalyzed the water gas conversion reaction, and at the higher temperatures with essentially the same efficiency. However, only nickel and the nickel-rich alloys produced methane. If a dissociative adsorption of carbon dioxide is assumed, then a water gas catalyst here is required to do little else than to adsorb oxygen in a form readily reducible to water at the reaction temperature and to desorb products. However, the conversion of adsorbed carbon monoxide to methane requires the participation of 6 hydrogen atoms, and at least some of this hydrogen must be available only through chemisorption. In terms of current theory[5,6] such hydrogen chemisorption is facilitated by holes or unpaired electron spins in the 3d band of the nickel. The number of spins per nickel atom at absolute zero may be estimated from the specific magnetization[21,22] as q_F and

---

[16] K. Torkar and H. Mariacher, *Metallkunde*, **47**, 260 (1956).

[17] W. Sucksmith and R. R. Pearce, *Proc. Roy. Soc.* (*London*), **167A**, 189 (1938).

[18] L. F. Bates, "Modern Magnetism," Cambridge Univ. Press. 1951. p. 304.

[19] M. A. Wheeler, *Phys. Rev.*, **56**, 1137 (1939).

[20] A. R. Kaufmann and C. Starr, *ibid.*, **63**, Sec. Ser. 445 (1943).

[21] E. C. Stoner, *Rep. Progr. Phys.*, **11**, 43 (1946–1947).

[22] R. M. Bozorth, "Ferromagnetism," D. Van Nostrand Co., New York, N. Y., 1951.

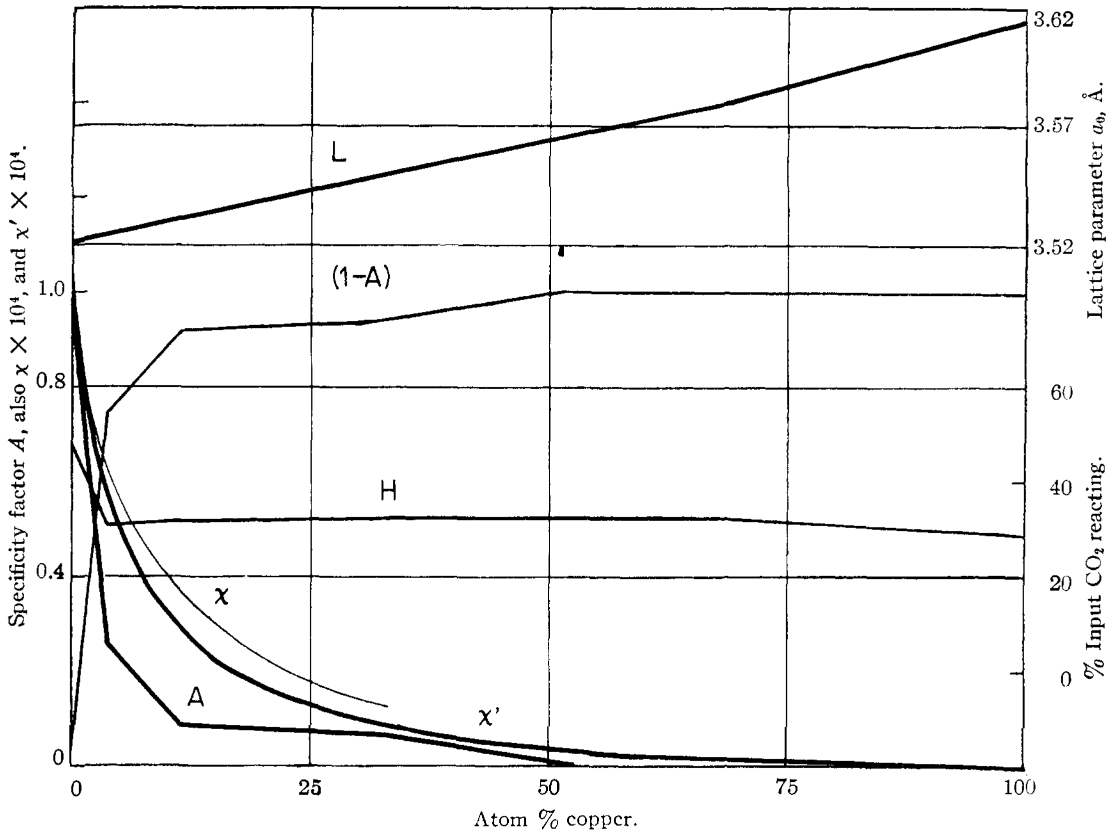

Fig. 6.—Comparison of several properties of the nickel–copper catalysts at 420° as a function of catalyst composition: curve A, fraction of reacting CO_2 converted to CH_4; curve χ', mass magnetic susceptibility per g. of catalyst (curve beyond 33 at. % copper from Wheeler, also Kaufmann and Starr); curve χ, mass magnetic susceptibility per g. of nickel; curve (1-A), fraction of reacting CO_2 converted to CO; curve H, % of input CO_2 which reacted; curve L, lattice parameter a_0 not corrected to 420°.

from the magnetic susceptibility measurements[21, 22] as q_P. For nickel and the nickel-rich catalysts the values of q_F and q_P decreased in a linear manner as copper content increased and extrapolated to zero in the vicinity of 80% alloyed copper. The persistence of holes in copper–nickel alloys above the classical limit of 60 atom % copper has been noted by others.[23] As usual[21, 22] the q_P values were larger than the q_F values being, respectively, 0.8 and 0.6 for nickel and 0.6 and 0.3 for the 33% copper catalyst. However, the magnetic susceptibility at the reaction temperature proved to be a better measure of the pertinent electronic factor for the catalysts than the estimated number of unpaired electron spins existing at absolute zero.

After an initial decrease in the percentage of carbon dioxide reacted, which decrease is especially small at the higher reaction temperatures, the carbon dioxide reacted changed little with increased alloyed copper. Up to at least 50% alloyed copper it appears that the decreasing number of holes in the catalyst *d*-band decreased the chemisorption of hydrogen with a comparable decrease in methane formation. While in the chemisorption of hydrogen on nickel, it is found that the electron moves from the adsorbate toward the adsorbent,[24, 25] with carbon monoxide the situation is more complex. When adsorption of carbon monoxide occurs on an unsupported copper–nickel catalyst at 270°, Morris and Selwood[26] found that the magnetic susceptibility decreased corresponding, as in the case of hydrogen, to an electron transfer from adsorbate toward adsorbent. However, when a transparent film of nickel is supported on glass[24] or a very dilute dispersion of small nickel particles is supported on silica,[25] the electron movement, at least at room temperature and below, appears to be toward the adsorbed carbon monoxide. Because of the nature of the structure of the carbon monoxide molecule and the fact that both one-site and two-site attachment[27] have been found necessary in order to explain carbon monoxide chemisorption on nickel, no easily predictable adsorption mechanism is to be expected for this gas. However, carbon monoxide adsorption must play a role in the present work. Unless compensating electronic factors make the carbon monoxide adsorption relatively independent of catalyst composition, alloying up to at least 50% copper with nickel should either enhance or diminish such adsorption. While the initial drop in carbon dioxide reacting may reflect one of the latter effects operating on the carbon monoxide adsorption and possibly on carbon dioxide adsorption

---

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

(24) R. Suhrmann and K. Schulz, *J. Colloid Sci.*, Supplement, **1**, 50 (1954).

(25) L. E. Moore and P. W. Selwood, This Journal, **78**, 697 (1956).

(26) H. Morris and P. W. Selwood, *ibid.*, **65**, 2245 (1943).

(27) P. M. Gundry and F. C. Tompkins, *Trans. Faraday Soc.*, **53**, Part 2, 218 (1957).

also, the relative constancy of carbon dioxide consumed over catalysts containing intermediate amounts of copper suggests the operation here of compensating electronic effects. Beyond about 50% alloyed copper the methanation reaction has disappeared and the carbon dioxide consumed soon falls slightly. In this region the alloy lattice parameter continues its nearly linear rise while the already small magnetic susceptibility of the alloys decreases only very slowly and it appears that the geometric factor may well be predominant here.

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Primary Cobalt-60 Radiolysis Yields in Heavy Water[1]

BY H. A. MAHLMAN AND J. W. BOYLE

RECEIVED AUGUST 23, 1957

The cobalt-60 γ-ray decomposition of several heavy water solutions, 0.4 *M* in sulfuric acid, has been studied and the initial yields of D, OD, D_2 and D_2O_2 determined. The reactions investigated were the formation of D_2 in a degassed dilute bromide solution, the formation of D_2O_2 in air-saturated solution and the oxidation of ferrous ion in air-saturated solution. The yields for D, OD, D_2 and D_2O_2 were evaluated to be 3.99, 3.14, 0.38 and 0.81 in heavy water solution and the H, OH, H_2 and H_2O_2 yields in light water were 3.68, 2.96, 0.45 and 0.81. All yields are relative to the light water ferrous dosimeter value of 15.6 molecules oxidized for each 100 e.v. of energy absorbed.

Introduction

Heavy water, like light water, may be considered to decompose when subjected to ionizing radiations into the molecular products D_2O_2 and D_2 and the free radicals D and OD described by equation 1

$$-G_{D_2O} = G_{D_2O_2} + G_{D_2} + {}^1/_2(G_D + G_{OD}) \qquad (1)$$

In this paper the 100 e.v. yields of the primary heavy water radiolysis products will be denoted by G_{D_2}, $G_{D_2O_2}$, G_D and G_{OD}, and the yields of measured products will be denoted by G(product).

The 0.4 *M* sulfuric acid systems studied to determine the molecular and free radical yields were: (1) D_2 production in a degassed dilute KBr solution; (2) D_2O_2 production in an aerated solution; and (3) oxidation of ferrous ions in an air-saturated solution. The radiolysis mechanisms proposed for light water were used to calculate the heavy water yields.

Experimental

The γ-radiation was provided by either a 150 or a 1100 curie cobalt-60 source.[2] These annularly loaded cylindrical sources provided homogeneous irradiations of centrally placed samples. The rate of energy absorption was determined by the rate of ferrous oxidation in an aerated 0.4 *M* H_2SO_4 solution assuming 15.60 ferrous ions oxidized per 100 e.v. of absorbed energy.[3] Energy transfer from Co-60 γ-rays to the medium through which they pass is dependent upon the electron density of the medium. Since the molar volumes of light and heavy water are essentially the same, it was assumed that on a volume basis the rate of energy absorption was the same in light and heavy water.

All of the chemicals used were Baker and Adamson reagent grade except the reagent grade ceric acid sulfate which was obtained from the G. Frederick Smith Chemical Company. The heavy water was purified by distillation from an acid permanganate solution, from a basic permanganate solution and in an all-silica system. Storage was in a silica vessel. To minimize contamination with light water, the acid permanganate solution was prepared by treating SO_3 with D_2O and then adding potassium permanganate. The basic permanganate solution was prepared by dissolving Na_2O_2 in the distillate from the acid permanganate distillation and refluxing the solution until the D_2O_2 formed was thermally decomposed; potassium permanganate was then added. The purified heavy water was analyzed to be 99.74 mole % deuterium oxide. Further purification of selected 0.4 *M* sulfuric acid heavy water solutions was effected by irradiating with cobalt-60 γ-rays and then photolyzing with a mercury lamp to destroy the D_2O_2 formed.[4]

The solutions used for the hydrogen determinations were degassed and then irradiated in the 1100 curie source. The S.T.P. volumes of hydrogen were determined by ignition with oxygen on a platinum filament in a semi-micro Saunders-Taylor type apparatus.[5]

Hydrogen peroxide concentrations were obtained by reaction of aliquots of the irradiated solution with a known amount of ceric ion. The initial and residual ceric ion concentrations were determined on a Model 11 MS Cary Recording Spectrophotometer at 3200 Å. using a molar extinction coefficient of 5580[3] at 25°. The ceric ion molar extinction coefficients in light and heavy water were the same. Ferrous solutions were irradiated in non-coloring silica spectrophotometer cells and the amount of oxidation determined by measuring directly the ferric absorption at 3050 Å. The ferric ion molar extinction coefficient at 3050 Å. and 25°, relative to the ceric molar extinction coefficient of 5580, was found to be 2358 in light water and 2195 in heavy water.

Results and Discussion

It is assumed in this paper that the mechanisms postulated for light water are also valid for heavy water and that the only difference between light and heavy water radiolysis is the difference in free radical and molecular yields.

Hydrogen Yields in Degassed Dilute KBr Solutions.—The production of hydrogen in a dilute degassed KBr solution is assumed to be equal to the primary molecular hydrogen yield

$$G(H_2)_{Br^-} = G_{H_2} \qquad (2)$$

The average $G(D_2)$ for three 10^{-4} *M* KBr, 0.4 *M* D_2SO_4 samples irradiated 45, 60 and 75 minutes at a dose rate of 7.88×10^{20} e.v., $l.^{-1}$, $min.^{-1}$ was 0.38 with a standard deviation of ±0.01. The $G(H_2)$ was determined for five similar light water samples and found to average 0.45 with a standard deviation of ±0.01.

---

(1) Presented at the Fifth Annual Meeting of the Radiation Research Society, Rochester, New York, May 13–15, 1957. This paper is based upon work performed at Oak Ridge National Laboratory which is operated by Union Carbide Nuclear Company for the Atomic Energy Commission.

(2) J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instr.*, **22**, 473 (1951).

(3) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

(4) A. O. Allen and R. A. Holroyd, THIS JOURNAL, **77**, 5852 (1955).

(5) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).