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

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The activity of cobalt, iron and some of their alloys as catalysts for the hydrogenation of the oxides of carbon has been measured. These catalysts were prepared by the reduction of the precipitated or coprecipitated metal carbonates and/or hydroxides. X-Ray examination of these catalysts indicates that they possess the lattice constants of recorded equilibrium alloys. No simple relationship is found between the activity of the catalysts and their metallic composition. A tentative explanation of catalyst activity appears possible in terms of lattice parameter and atomic moment.

Introduction

The hydrogenation of the oxides of carbon over transition metals particularly iron and cobalt as is well known produces a wide variety of products including liquids. Thus in the Fischer–Tropsch synthesis carbon monoxide is hydrogenated to gaseous hydrocarbons and oil. Previous work[3,4] in this Laboratory has shown that carbon dioxide also can be hydrogenated to similar products using activated and/or beneficially poisoned cobalt catalysts. This reaction therefore appeared to offer the opportunity for studying the effect of alloy catalyst composition upon product distribution. Catalysts composed of cobalt, iron and their alloys were prepared by precipitation or coprecipitation of the metal carbonates and/or hydroxides, followed by reduction. Similar catalysts were prepared by Long, Frazer and Ott[5] and their activity for benzene hydrogenation determined. X-Ray diffraction measurements[5] on these precipitated, mixed metal catalysts showed the predicted substitutional type of solid solution found in equilibrium alloys. In the present work the lattice constants of the metal and alloy catalysts have been determined and found to be in agreement with recorded values for the metals, and alloys produced by mixing the molten metals together. No simple relation has been found between catalyst composition and catalytic activity. However, it appears that the values of such electronic structure parameters as atomic moment and lattice distance offer a reasonable explanation of catalytic activity observed.

Experimental

Apparatus and Purification of Gases.—The reactant gases hydrogen and carbon dioxide, of the same grade, and metered and purified as already described,[3] were in an all-glass system until they had passed out of the synthesis catalyst.

The catalyst chamber consisted of a vertical Pyrex tube 15–19 mm. i.d. having an axial 5 mm. o.d. thermocouple well, placed in an electrically heated furnace and controlled by a potentiometric controller-recorder.[3] The reactant gases passed down through the catalyst bed and upon emerging passed through cold traps and thence through a wet test meter, as already described.[3] The exit gases could be analyzed for carbon dioxide, oxygen, unsaturated hydrocarbons, hydrogen, carbon monoxide and saturated hydrocarbons, by means of a modified Shepherd[6] gas analysis apparatus.

Preparation and Reduction of Catalysts.—The catalysts were prepared from weighed portions of stock solutions of analytical reagent grade chemicals. The cobalt nitrate and the ferric nitrate solutions were in the range of 0.8–1.0 *M*, while the potassium carbonate solutions were in the range of 1–2 *M*; however, the concentration of each solution was always known. While the hot metal nitrate solution was vigorously mechanically stirred, sufficient hot potassium carbonate solution was added to precipitate completely the insoluble metal carbonate and/or hydroxide and then give a 10% excess. If the precipitate tended to "set up" during the precipitation, enough boiling water was added to prevent it. The precipitate was washed by decantation, using boiling water, until the diphenylamine test for nitrate was negative. The precipitate was now evaporated to extruding consistency on a steam-bath, then extruded onto glass plates from an all-glass syringe having a 2-mm. tip bore. After drying for 70 to 80 hours at 110°, the catalyst granules were cut into pellets about 1 × 2 mm. in size using a

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(1) This paper is based on a portion of a thesis presented by R. A. Stowe in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, September 1952.

(2) University Fellow, 1951–1952.

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

(4) R. N. R. Mulford and W. W. Russell, *ibid.*, **74**, 1969 (1952).

(5) J. H. Long, J. C. W. Frazer and E. Ott, *ibid.*, **56**, 1101 (1934).

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sharpened glass blade. After sifting to remove fines, the granules were placed in the catalyst tube, supported on a tuft of glass cotton.

During a period of three days the catalyst temperature was slowly raised to 500° in a stream of pure, dry hydrogen flowing at 5 l. per hour. On the fourth day, the hydrogen flow rate was increased to 20 l. per hour for intermittent two-hour periods, and until less than 0.1 mg. of water was collected per half hour at the 5 l. flow rate during the intervening periods.

Catalyst Activity Evaluation.—The volume and composition were known for the entering synthesis gas and also for the exit gas. Thus the contraction and also the hydrogen and carbon dioxide participating in synthesis could be determined. No oxygen or unsaturated hydrocarbons were detected in the exit gases. The amount of oil, defined as hydrocarbons condensed by Dry Ice and not vaporized during rapid measurement at room temperature, was determined volumetrically. Oil samples were usually collected over an 8-hour period, the duration of the run. 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. Synthesis gas, consisting of H_2:CO_2::2:1, was passed through a catalyst at the rate of 6l./hr.

Other Catalyst Properties.—When filling the catalyst chamber with unreduced catalyst, a small portion of the catalyst fines was secured in the exit tube with a plug of glass cotton about an inch below the bottom of the main catalyst. After reduction this reduced catalytic powder was carefully removed, mixed with an equal volume of 50–50 sodium chloride–starch mixture, and sealed into an X-ray capillary tube, all while still under an atmosphere of hydrogen. This precaution was necessary to prevent any atmospheric oxidation of the catalyst, since all of the reduced catalysts were extremely pyrophoric.

X-Ray photographs were taken of each of the catalysts using a Debye–Scherrer type camera with nickel-filtered copper radiation. No $K\alpha_1$, $K\alpha_2$ splitting could be observed with the commercial film reader employed, so a weighted value[7] of 1.5418 Å. was used. The internal calibration provided by the sodium chloride was based on an a_0 value[8] of 5.64009 Å. The anticipated difficulty of excessive film background due to iron and cobalt fluorescence was not serious for an optimum time of exposure which was found by trial and error for each catalyst. The weights of the reduced catalysts could not be accurately determined at the end of the synthesis runs, except for the cobalt catalyst, because of carbon deposition on the iron containing catalysts. However, since the unreduced mixed catalysts were analyzed for both cobalt and iron, and also for the percentage of mixed oxides they contained, the weight of the reduced catalyst could be calculated. The mixed oxides were assumed to be CoO and Fe_2O_3. In the tabulation the weight of catalyst is given as that determined by weighing the nitrogen-protected catalyst plus any carbon after completion of the synthesis runs. The figure in brackets is the calculated catalyst weight. The difference between these two catalyst weights probably gives a rough value for the carbon deposition. The apparent volume of the catalysts was reduced by about 50% during reduction. After reduction the apparent density of the cobalt catalyst was only about a third of that of the other catalysts.

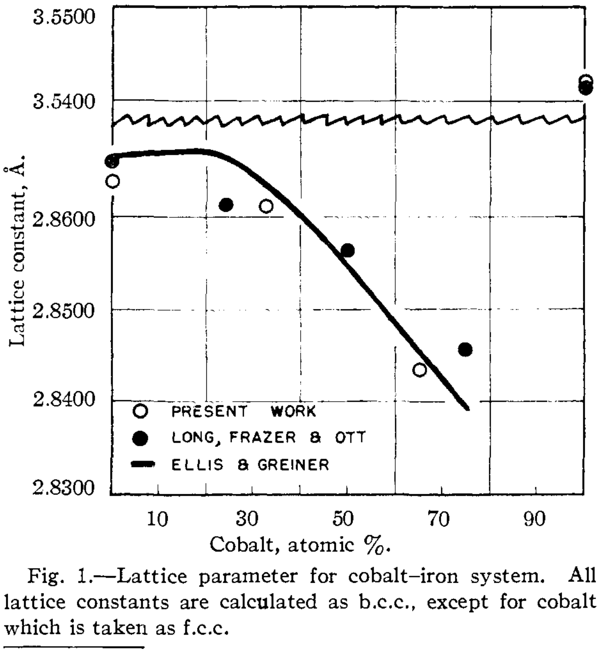

Fig. 1.—Lattice parameter for cobalt–iron system. All lattice constants are calculated as b.c.c., except for cobalt which is taken as f.c.c.

Catalyst A composed of cobalt, weighed 13.1 g. after reduction, and had a dull gray color.

Catalyst B contained cobalt and iron in atom percentages of 64.0 and 36.0, weighed 14.4 g. (13.0 g.) after reduction, and had a gray color with metallic luster.

Catalyst C contained cobalt and iron in atom percentages of 32.8 and 67.2, and weighed 13.0 g. (11.1 g.) after reduction, and had a shiny gray appearance.

Catalyst D composed of iron, weighed 14.8 g. (12.9 g.) after reduction, and had a dark gray color, without metallic luster.

Results and Discussion

X-Ray Diffraction Measurements on Catalysts.—The following cubic lattice constants (a_0), based on averages of 4 to 5 measurements per catalyst except the cobalt catalyst, were obtained from catalyst A (Co, 100); B (Co:Fe, 64.0:36.0); C (Co:Fe, 32.8:67.2); D (Fe, 100), namely, 3.5420 ± 0.0006 Å.; 2.8435 ± 0.0006 Å.; 2.8613 ± 0.0009 Å.; 2.8638 ± 0.0007 Å. The precision of the data is expressed as the average deviation. The iron and iron-containing catalysts have been indexed as b.c.c. The cobalt catalyst, on which only duplicate measurements are available has been considered to be f.c.c. Long, Frazer and Ott[5] found their cobalt catalyst to be predominantly f.c.c. Hofer, Peebles and Bean[9] were able to find a complete set of arcs for neither the f.c.c. nor the h.c.p. structures for their cobalt catalysts, and so consider the catalyst structure disordered.

The X-ray data for the catalysts and for the cobalt–iron system are shown plotted against metallic composition in Fig. 1. The data for the present catalysts are shown as open circles. The data of Long, Frazer and Ott[5] are shown as solid circles. The solid curve in Fig. 1 is for the lattice constants of the corresponding equilibrium alloys of Ellis and Greiner.[10] For this comparison the earlier data[5,10] have been converted from what appear to be kX. units to Ångström units. From the foregoing it appears that the catalysts used in the present work had essentially the same lattice constants found for equilibrium alloys of the same composition.

Activities of the Catalysts in Synthesis.—The effects of temperature upon the distribution of products from the hydrogenation of carbon dioxide over the catalysts are shown in Figs. 2 to 5. This distribution is expressed as a carbon balance in terms of the volume percentages of the inlet carbon dioxide unconverted and converted to the various carbon containing products. The topmost curve (above break in figure) shows the experimental error

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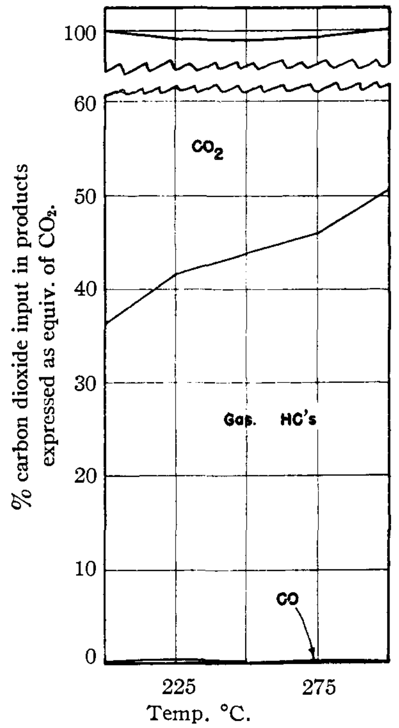

Fig. 2.—Effect of temperature upon product distribution in the hydrogenation of carbon dioxide over catalyst A (Co). The carbon balance is in terms of input carbon dioxide.

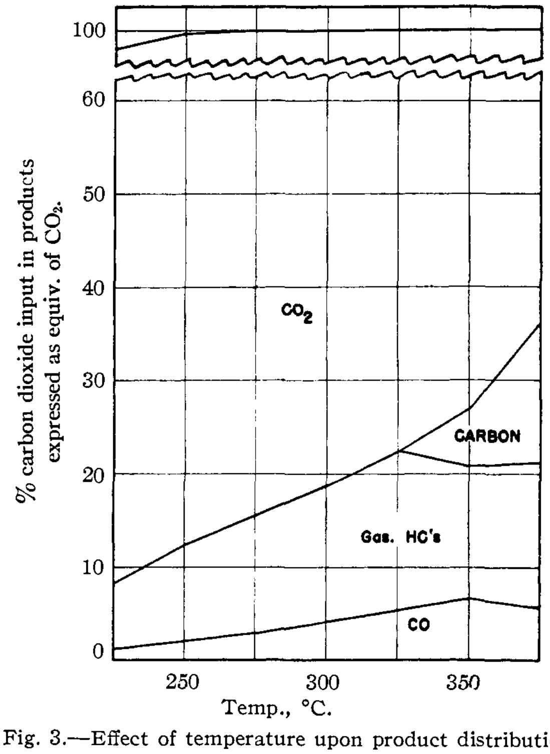

Fig. 3.—Effect of temperature upon product distribution in the hydrogenation of carbon dioxide over catalyst B (Co:Fe, 64.0:36.0). The carbon balance is in terms of input carbon dioxide.

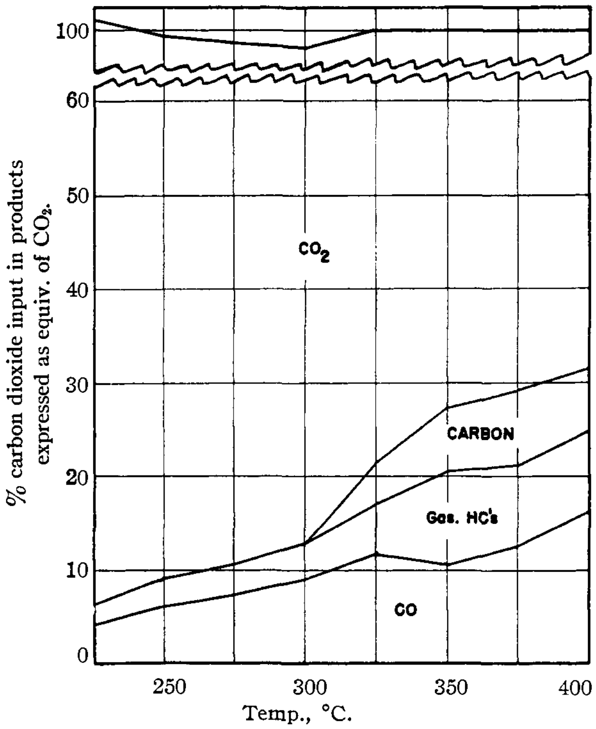

Fig. 4.—Effect of temperature upon product distribution in the hydrogenation of carbon dioxide over catalyst C (Co:Fe, 32.8:67.2). The carbon balance is in terms of input carbon dioxide.

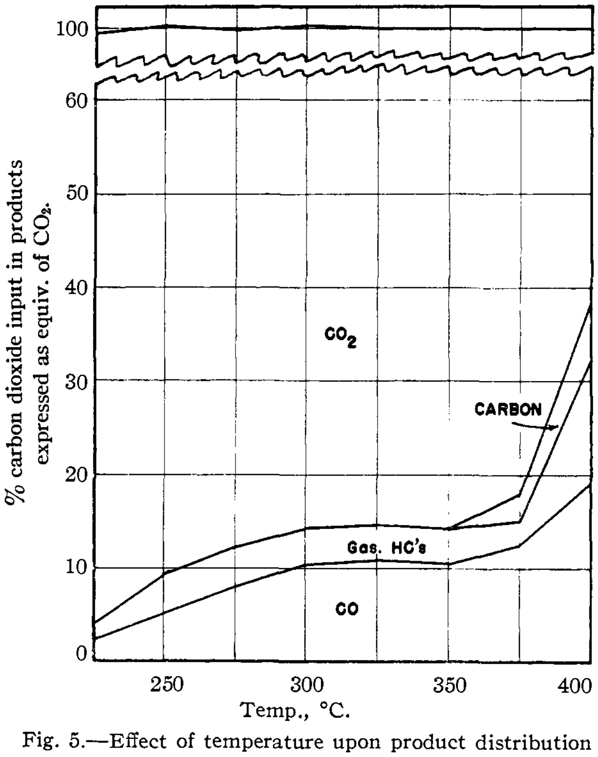

Fig. 5.—Effect of temperature upon product distribution in the hydrogenation of carbon dioxide over catalyst D (Fe). The carbon balance is in terms of input carbon dioxide.

in striking the carbon balance. The amounts of oil formed were too small to affect the carbon balance figures. Catalyst A (Co) gave no evidence of synthesizing oil but a kerosene-like odor in the cold traps was evident for the other three catalysts. Very small amounts of oil, *i.e.*, 0.002 to 0.012 ml. per hr., were collected with catalyst C (Co:Fe, 32.8:67.2) and also with catalyst D (Fe) at temperatures between 275 and 325°. No deposition of carbon could be detected on catalyst A. Carbon deposition, which was confined to the upper part of the catalyst bed, occurred on the other three catalysts. This carbon formation, which must have resulted from the decomposition of carbon monoxide, was greatest on catalyst C (Co:Fe, 32.8:67.2), starting at the relatively low temperature of 300°.

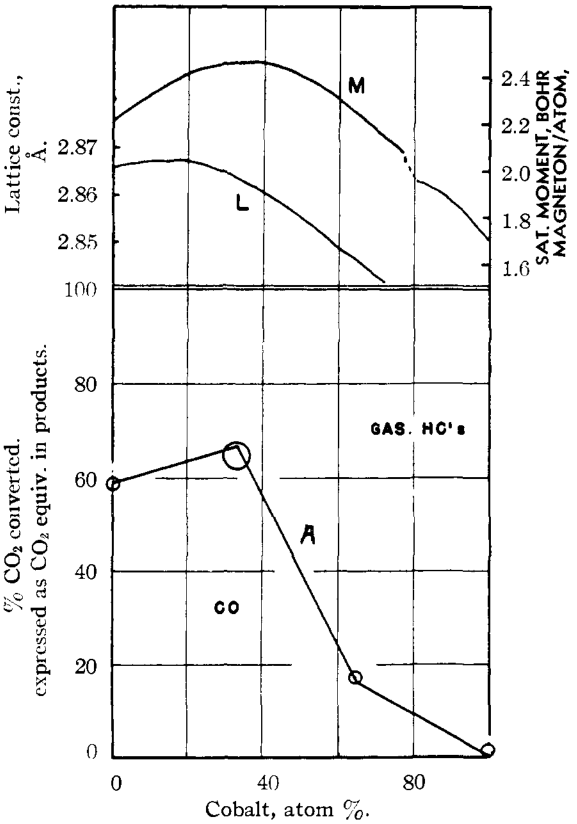

Fig. 6.—Comparison of some properties of the cobalt–iron system as a function of catalyst composition: curve A, catalytic activity at 250°; curve L, lattice parameter; curve M, saturation magnetic moment.

Although the surface areas of the catalysts are unknown, approximately the same weights of the various catalysts were employed and thus certain other synthesis characteristics of the catalysts appear clear. Although the amount of carbon dioxide reacting increased with rising temperature on each of the catalysts, catalyst A (Co) already converted at 200° about as much carbon dioxide as any of the other catalysts did at 400°, and at 300° converted more than 50% of the inlet carbon dioxide while no other catalyst converted as much as 20% at 300°. While the exit gases from catalyst A (Co) contained negligible amounts of carbon monoxide, on the other catalysts this gas increased in amount with increasing iron content of the catalyst and with rising temperature. The gaseous hydrocarbons from all of the catalysts were essentially methane, since their carbon number varied only from 1.1 to 1.4, the lowest values being obtained on catalyst A (Co). This catalyst converted the reacting carbon dioxide almost quantitatively to methane. On the other catalysts the amount of gaseous hydrocarbons produced decreased with increasing iron content of the catalyst.

Discussion

The effect of catalyst composition upon the distribution of the carbon-containing products at 250° is shown by curve A in Fig. 6. The shape of this curve was not much altered at the other synthesis temperatures up to 300°, except that with increasing temperature, on the pure iron the ratio of carbon monoxide to gaseous hydrocarbons increased so that the maximum in the curve had disappeared at 300°. Above 300° synthesis was complicated by carbon formation. In conformity with earlier work[3,4] the cobalt catalyst has hydrogenated carbon dioxide to methane with almost negligible production of gaseous carbon monoxide, or other carbon containing products. This may be attributed to the strong hydrogenating activity of unpoisoned or unmodified cobalt whereby any carbon monoxide formed on the cobalt surface is hydrogenated to methane before desorption. It is believed that the present work is consistent with the assumption that the water gas reaction occurs first upon the surfaces of the catalysts and is followed by hydrogenation of the carbon monoxide formed accompanied by a little polymerization. On this basis the ability of iron to hydrogenate carbon monoxide was at first somewhat reduced, and then increased rapidly as larger amounts of cobalt were alloyed with the iron. As a consequence methane formation was repressed as the iron content of the alloy catalysts increased and then increased slightly. This poisoning action of iron on cobalt was slightly beneficial in that very small amounts of oil were now formed.

The present work shows that there is no simple relation between catalytic hydrogenation activity and catalyst composition for the cobalt–iron system. The X-ray diffraction measurements indicate that the mixed catalysts had the types of lattice and the lattice constants to be expected of equilibrium alloys[10] formed by admixture of the melted components. In the temperature range of synthesis, cobalt and iron form a complete series of b.c.c. solid solutions up to about 75% cobalt, above which additional phases intrude. No alloy catalysts in this latter composition region were studied. Also the reduction and synthesis temperatures were well below the critical ordering temperature range[10] of 678–732° found for iron–cobalt alloys containing from 35 to 67.5% cobalt. In the temperature region employed pure iron is also b.c.c. but pure cobalt may exist as a disordered array.[9] Because of this the other catalysts are more easily compared among themselves than with cobalt.

In seeking clarification of the present work the electronic structure-sensitive properties of the cobalt–iron system are of interest. The fact that the d characters of cobalt and iron are very similar, *i.e.*, 39.5 and 39.7%, respectively, probably makes this factor rather non-critical. Similarly the coefficients of the electronic specific heat terms have been found to be identical for cobalt and iron ($\gamma = 1.20 \times 10^{-3}$ cal./mole deg.^{2}).[11] However, as is shown in Fig. 6, the b.c.c. lattice constant (curve L) varies in a significant manner, showing a maximum for alloys containing about 20% cobalt. Interatomic distances have been considered critical by many, and especially by Beeck[12] in explaining the hydrogenating activity of metals. This author[12] finds a lattice distance of 3.75 Å. (Rh) to be optimum with hydrogenating activity falling off along a bell-shaped curve for either greater or lesser distances. Beeck[12] finds it necessary to use an interatomic distance of 4.05 Å. (distance between opposite corners of a b.c.c. face) in order to fit iron into his curve. Catalysts D (Fe), C (Co:Fe, 32.8:67.2), and B (Co:Fe, 64.0:36.0) would give corresponding distances of 4.050, 4.047, 4.021 Å., respectively, and in so far as Beeck's findings may be applied to alloy catalysts, would predict qualitatively the increase in hydrogenating activity found especially above 300°, in the present work with increasing cobalt concentration of the alloy catalysts. In the case of cobalt it appears necessary to consider the f.c.c. parameter of 3.542 Å. in order to reconcile its greater hydrogenating activity relative to that of the other catalysts even qualitatively.

Curve M in Fig. 6 indicates how the number of holes in the d-band (atomic moment), for metals and alloys having the same metallic composition as the present catalysts, changes with catalyst composition. Curve M shows at about 35% cobalt an atomic moment of nearly 2.5 magnetons,[13,14] the largest for any magnetic substance. Both catalytic activity curve A, and curve M exhibit a similar dependence upon catalyst composition, even to the extent that each exhibits a maximum in the vicinity of an alloy of the composition of catalyst C (Co:Fe, 32.8:67.2). This could mean that the activity of the catalysts for the hydrogenation of carbon monoxide is a function of the atomic moment of the catalytic metal or alloy. It seems probable that the catalytic hydrogenation of carbon monoxide on the catalysts here studied involves the chemisorption of hydrogen and presumably of both of these reactant gases. In accordance with current concepts[15,16] such chemisorption on transition metals may be considered to involve the partially filled d-band of the metal. Assuming the role of the atomic moment to be dominant, *e.g.*, that the energy density of electron levels[11] and their gradient, the work function, etc., remain constant, and further assuming that the chemisorption of hydrogen involves a 3d-band hole of the catalyst, the strength of chemisorption for hydrogen may then increase with increase in catalyst d-band holes, and *vice-versa.* In terms of such a mechanism catalyst C (Co:Fe, 32.8:67.2) should chemisorb hydrogen most strongly, while the reverse should be true on catalyst A (Co), with the indicated intermediate chemisorptions to be expected on the other catalysts. The dependence of catalyst activity upon catalyst composition here found would be understandable in terms of such hydrogen chemisorption on the basis of Beeck's findings, with ethylene hydrogenation on transition metals,[12] that hydrogenation activity varied inversely as the heat (strength) of hydrogen chemisorption.

Much more experimental evidence certainly now is necessary to assess the adequacy of atomic moments, measured as a bulk property, in accounting for hydrogenating activity on the surface of transition metals. Even in the present work the fact that catalyst B (Co:Fe, 64.0:36.0), which was prepared to have the same atomic moment as catalyst D (Fe), proved to be much the more active in hydrogenating carbon monoxide appears at least to require that not only the number but also the character of the catalyst d-band holes be important. Another factor which is critical in controlling the catalytic activity of the cobalt–iron system may well be interatom distance. In this connection it should be recalled that lattice distances and magnetic properties may not be unrelated.[17]

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