The Structure and Properties of Supported Cobalt Catalysts

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In experiments previously reported by the present same authors[1], it was observed that the catalytic activity of supported metal catalysts in the hydrogenation reaction of aniline varied greatly for different types of catalyst. In order to understand this phenomenon, it is necessary to know the structure and properties of these catalysts.

Many reports[2-5] have been published with respect to the structure and properties of supported nickel catalysts, but few regarding supported cobalt catalysts. Anderson et al.[6] have reported on the structure and properties of the catalyst for Fisher-Tropsch synthesis. However, their study was restricted to the chêmical properties of a cobalt-diatomaceous earth system.

The present investigation has been undertaken in an attempt to obtain some information about the structure and properties of cobalt oxide as supported on various kinds of oxide carriers, and also on the relationship between the hydrogenation activity and the catalyst structure.

Experimental

The Preparation of Catalysts. — The standard procedures of catalyst preparation were as follows:

The Impregnation Method: The powdered support was added to a solution of cobalt nitrate. The slurry was stirred for some time, and then to it was slowly added, at 20°C, a quantity of dissolved ammonium carbonate in a slight excess. After the precipitate has been filtered and washed, it was dried at 100°C and then calcined at 500°C for 2 hr.

The Coprecipitation Method: The catalyst was prepared by coprecipitation, from a mixed solution of cobalt nitrate and aluminum nitrate or sodium silicate, by ammonium carbonate solution at 20°C with vigorous stirring. The slurry was stirred for some time, and then it was vacuum-filtered. The precipitate was washed with distilled water on the filter, dried in a drying cabinet at 100°C, powdered, and calcined at 500°C for 2 hr. in air.

The Hydrothermal Treatment: Basic cobalt carbonate (prepared from cobalt nitrate and ammonium carbonate solutions at 20°C) was mixed with silica gel or aluminum oxide gel, and then heated with water in an autoclave at 200°C for 25 hr. It was then cooled, filtered, washed with distilled water, dried at 100°C, and calcined at 550°C for 2 hr.

The Mixing Method: The powdered silica gel and cobalt basic carbonate were mechanically mixed in water in a beaker. The mixture was vacuum filtered, and then it was dried at 100°C and calcined at 500°C for 2 hr.

Surface Area Measurements.—The area of the samples was estimated by the BET method.

The Reduction of the Catalysts in Hydrogen.—*Hydrogen consumption measurement.*—The volumetric apparatus shown in Fig. 1 was used for this attempt. Hydrogen was continuously circulated through the catalyst at the flow rate of 100 cc./min., and the water produced by reduction was removed using a dry-ice methanol trap and a silica gel drier placed behined the catalyst bed. The pressure was held manually at one atmosphere by adjusting the leveling (L). Thus the pressure difference of the manometer showed directly the volume of hydrogen consumed; this volume was then plotted as a function of the heating-up temperature and of the time (Fig. 1). The apparent H_2 consumption as measured as described above was then corrected for the changes in volume caused by heating.

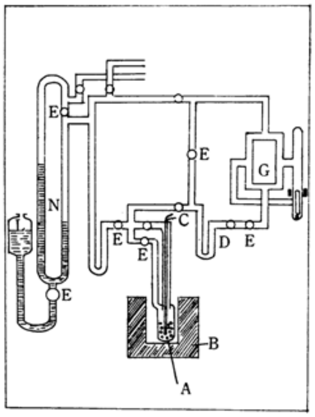

Fig. 1. Apparatus for hydrogen consumption measurements.

A: Catalyst bed   B: Electric heater
C: Themocouple   D: Drying agent
E: Stop-cock   G: Circulation pump
L: Leveling   N: Manometer

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[1] H. Hagihara and E. Echigoya, *Shokubai* (*Catalyst*), **6**, 345 (1964).

[2] J. J. B. van Eijk van Voorthujsen and P. Franzen, *Rec. Trav. Chim.*, **70**, 793 (1951).

[3] W. O. Milligan and L. Merten, *J. Phys. Chem.*, **50**, 465 (1946).

[4] G. C. A. Schuit and L. L. van Reijen, *Adv. in Catalysis*, **X**, 242 (1958).

[5] K. Morikawa and F. Nozaki, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1568 (1962).

[6] R. B. Anderson, W. K. Hall and L. J. E. Hofer, *J. Am. Chem. Soc.*, **69**, 3114 (1947).

Table I. Samples

No.	Catalyst	Metal-content Wt.%	Metal-content Mol.%	Preparation method	Color	
1	Co-Al_2O_3	20	30	Impregnation	Black	20 Co-Al_2O_3-p
2	Co-Al_2O_3	49	64	Impregnation	Black	49 Co-Al_2O_3-p
3	Co-Al_2O_3	25	30	Coprecipitation	Black	25 Co-Al_2O_3-cp
4	Co-Al_2O_3	18	27	Hydrothermal treatment	Black-yellow	18 Co-Al_2O_3-ht
5	Co-SiO_2	20	21	Impregnation	Black	20 Co-SiO_2-p
6	Co-SiO_2	51	53	Impregnation	Black	51 Co-SiO_2-p
7	Co-SiO_2	26	27	Mixing	Black	26 Co-SiO_2-m
8	Co-SiO_2	20	21	Hydrothermal treatment	Blue	20 Co-SiO_2-ht
9	Co-Celite	50	52	Impregnation	Black	50 Co-Celite-p
10	Co-MgO	46	37	Impregnation	Black	46 Co-MgO-p
11	Co-ZnO	45	39	Impregnation	Grey	45 Co-ZnO-p

* The color is given for the catalyst which was calcined at 500°C for 2 hr.

The change in the X-ray diffraction pattern of the catalyst upon being reduced in a stream of H_2, using a high temperature X-ray camera. The heating unit of this X-ray camera consists of a Pt-Rh plate, which serves as a support for the powdered sample and also as a heating element by means of the passage of the electric current through it. The sample temperature was measured by a alumel-chromel thermocouple inserted in the center of the Pt-Rh plate. The whole assembly was placed inside a container, through which H_2 gas was then passed. The X-ray tube irradiates the specimen attached to the Pt-Rh plate, as in the ordinary powder method, and produces an overlapping X-ray pattern of the specimen and platinum. After a one-hour reduction with a 50 cc./min. flow rate of H_2 at a definite temperature, X-ray diffraction pattern was obtained. This technique was previously described by Kubo[7]; it was only slightly modified in this investigation.

Differential Thermal Analysis.—The differential thermal analysis was performed in air at a heating rate of 7—10°C/min. The reference junction of the differential couple was embedded in an inserted fused quartz. Fifty milligrams of the sample was sandwiched between two 200 mg. layers, of the fused quartz or α alumina, each in a platinum cell. The thermocouple employed was alumel-chromel.

Infrared Spectra. — The infrared spectra in the NaCl and KBr prism regions ($5000—600\ cm^{-1}$) were obtained by using a Hitachi EPI-2G infrared spectrophotometer. The wavelength calibration was made with polystyrene. Spectra were measured by the KBr disk and Nujol methods.

The Solubility of the Catalysts in 2 N Hydrochloric Acid.—0.2 g. of the powdered catalyst was added to 50 ml. of 2 N hydrochloric acid. The slurry was then stirred vigorously at 30°C for 8 hr. by a magnetic stirrer. The resulting slurry was decanted, and 50 cc. of 2 N hydrochloric acid was added to the remaining slurry. After this process had been repeated three times, the filtered solution was collected and the amount of cobalt oxide was determined by EDTA titration. The fraction dissolved was calculated as follows:

$$\text{Dissolved (\%)} = \frac{\text{the amount of Co in the soln. (g.)}}{\text{the initial amount of Co in the cat. (g.)}}$$

Activity Test.—The experiments were performed in a fixed bed apparatus of the flow type in the temperature range from 150 to 300°C.

Results and Discussion

Surface Area Data.—The surface areas of the unreduced and reduced catalysts are given in Fig. 2 and in Table II. From these data, it can be seen that the surface area of all the catalysts studied decreased by upon reduction. The areas of the cobalt-silica, cobalt-alumina and cobalt-celite catalysts decreased to 90%, to 80—70% and to 60% of those before reduction respectively. It was shown, however, that the area of celite did not change appreciably when it was subjected to the usual reduction procedures[8]. From the data in Table II and Fig. 2, silica or alumina carriers appear to be more effective in preventing the sintering of Co during reduction than diatomaceous earth (celite). This may be attributed to the

Table II

Catalyst	Surface area $m^2/g.$
Co_3O_4	90
NiO	42
Co-Celite (50%)	140
Co-Celite 450°C, 2 hr. red.	95
Co-MgO (46%)	85
Co-ZnO (45%)	200
Co-SiO_2-ht (20%)	190
Co-Al_2O_3-ht (18%)	140

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[7] K. Kubo and M. Kato, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 63 (1961); **66**, 403 (1963).

[8] R. B. Anderson, W. K. Hall and L. J. E. Hofer, *J. Am. Chem. Soc.*, **70**, 2465 (1948).

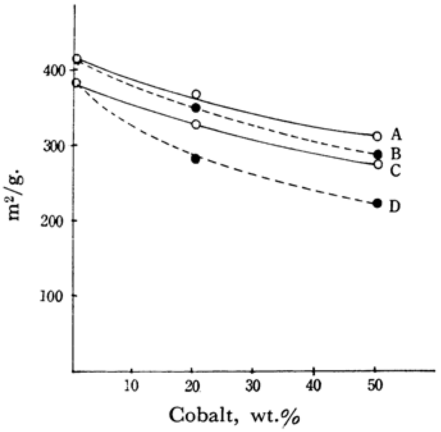

Fig. 2. Surface area of catalysts.
A: Co-SiO_2-p (unreduced)
B: Co-SiO_2-p (reduced at 450°C, 2 hr.)
C: Co-Al_2O_3-p (unreduced)
D: Co-Al_2O_3-p (reduced at 450°C, 2 hr.)

state of cobalt oxide on the carriers, i. e., to the oxide distribution on the carrier-surface and to the nature of the carrier-oxide bond. The decrease in the surface area of the catalysts produced by hydrothermal treatment during reduction was comparatively small. This may be caused by the low reducibility of cobalt oxide in the catalyst (i. e., the small fraction reduced to the metal.)

Reducibility by H_2.—The reduction curves are presented in Figs. 3, 4, and 5. The method of preparation bears a direct relationship to the reducibility of the supported cobalt oxide. For the cobalt diatomaceous earth system, Craxford⁹⁾ reported a decreasing reducibility as the formation of hydrosilicates progresses. The same phenomenon was reported for supported Ni-oxide by Van Eijk van Voorthujsen²⁾ and Morikawa et al.⁵⁾ Taking all these facts into consideration, it seems that an interaction has most probably occured between cobalt oxide and alumina or silica gel.

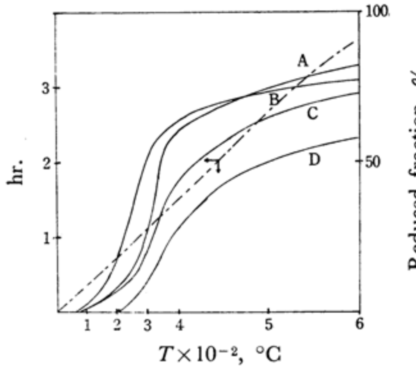

Fig. 3. Reduction curves of Co-Al_2O_3 catalysts.
A: 20 Co-Al_2O_3-p B: 49 Co-Al_2O_3-p
C: 25 Co-Al_2O_3-cp D: 18 Co-Al_2O_3-h

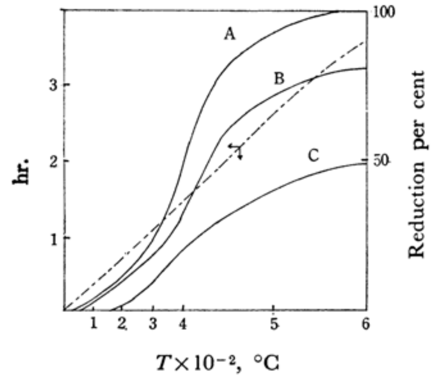

Fig. 4. Reduction curves of Co-SiO_2 catalysts.
A: 26 Co-SiO_2-m B: 51 Co-SiO_2-p
C: 20 Co-SiO_2-h

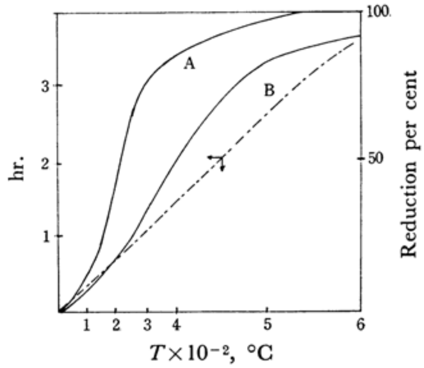

Fig. 5. Reduction curves of Co-MgO, Co-Celite.
A: 50 Co-Celite-p B: 46 Co-MgO-p

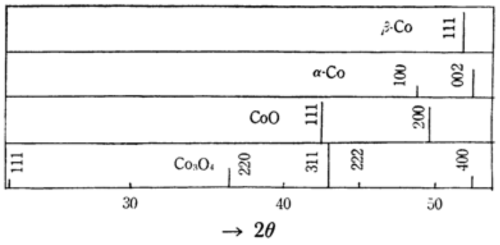

Fig. 6. The X-ray diffraction pattern of related materials.

In cobalt oxide - alumina catalysts,¹⁰⁾ prepared by the various methods described above, the degree of the formation of a complex structure was found to decrease in the following sequence: the hydrothermal>coprecipitation>impregnation methods. The same conclusion was obtained from a study of the effect of the hydrothermal treatment, which brought about an improvement in the complex structure. From the curves (Figs. 3 and 4), it is also apparent that the reducibility of cobalt oxide and the supported compounds decreases

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9) S. R. Craxford and A. Poll, *J. Chim. Phys.*, **47**, 253 (1950).

10) J. T. Richardson and L. W. Vernon, *J. Phys. Chem.*, **62**, 1153 (1958).

with an increase in the quantity of the carrier. This may be related to the high degree of dispersion and to the strong interaction between the metal and carrier used.

The Course of Catalyst Reduction in H_2, Seen by Using an X-Ray Camera.—As Figs. 7 and 8 show, the temperatures of the reduction to cobalt(II) oxide and cobalt-metal varied greatly with the cobalt oxide contents, the methods of preparation, and the kinds of carriers used. In cobalt-alumina catalysts, cobalt-metal was first observed in the temperature range from 300°C to 500°C. The different temperature of the formation of the cobalt-metal on the carrier is related to the structure and to the cobalt-oxide content of the catalyst. The preparation by the coprecipitation methods results in an improvement of the formation of the complex between cobalt oxide and the carrier. In the cobalt-silica system, the catalyst produced by impregnation and the coprecipitation method also showed a high resistance to reduction by H_2. The cobalt metal was first observed at 500°C. This phenomenon suggested a complex formation between cobalt-oxide and silica gel. In cobalt-celite, the temperature of the reduction to cobalt-metal was about 300°C. This may be related to the low degree of dispersion of cobalt oxide and to the less complex formation in this case. In the range from 200 to 300°C, the cobalt(II, III) oxide in the catalyst is mainly reduced to cobalt(II) oxide; later it is reduced to β-cobalt between 300 and 500°C (Fig. 9).

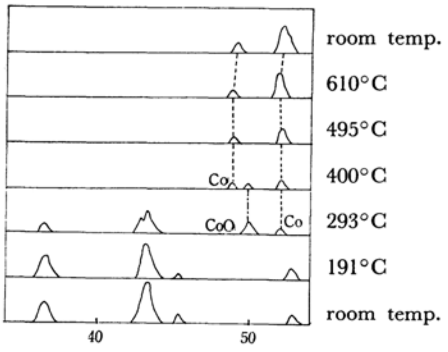

Fig. 7. X-Ray diffraction pattern in a stream of H_2.
Sample: 49% Co-Al_2O_3-p

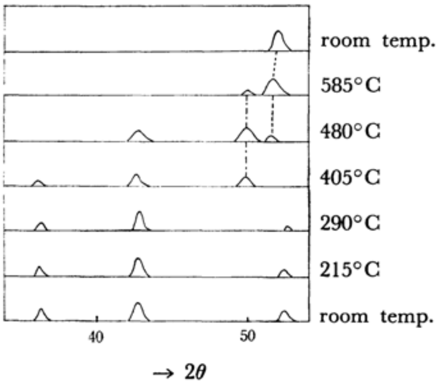

Fig. 8. X-Ray diffraction pattern in a stream of H_2.
Sample: 25% Co-Al_2O_3-cp

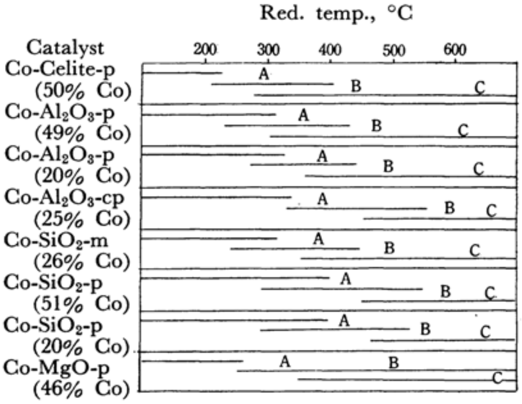

Fig. 9. Summary of the X-ray diffraction pattern of the catalyst being reduced in a stream of H_2.
A: Co_3O_4, B: CoO, C: β-Co

Differential Thermal Analysis.—All the thermograms of cobalt oxide catalysts are given in Fig. 10 for purposes of comparison. The basic cobalt carbonate exhibited two endothermal and one exothermal peaks. The endotherm at 100—150°C refers principally to dehydration, when most of the water is lost without any changes in structure. The endotherm at 250—350°C corresponds to the decarboxylation and dehydration which results in the change in structure from basic carbonate to cobalt monoxide. The exotherm at 350—400°C corresponds to the oxidation from cobalt(II) oxide to cobalt(II, III) oxide. Thus the changes in basic cobalt carbonate upon heating follow each other in the following manner:

$$\begin{tikzcd}
2CoCO_3\cdot 3Co(OH)_2\cdot nH_2O \arrow[rr, "100\text{—}150^\circ C"] & & 2CoCO_3\cdot 3Co(OH)_2 \arrow[d, "250\text{—}300^\circ C"] \\
CoO^{11)} & Co_3O_4 \arrow[l] & CoO \arrow[l, "350\text{—}400^\circ C"']
\end{tikzcd}$$

Except for the Co-SiO_2 catalyst produced by the coprecipitation method, the DTA curves exhibited by the various supported cobalt-oxide catalysts were almost identical with that of the basic cobalt-carbonate. For the Co-SiO_2 catalyst prepared by coprecipitation, however, only one broad endothermal peak was clearly observed between 500 and 700°C above the dehydration temperature. This may be attributed to the decomposition of hydrosilicate (orthotype) into cobalt oxide, silica and water.

The Infrared Spectrum.—Several applications of this technique to the study of catalyst

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[11] K. Kubo and M. Kato, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **67**, 1502 (1964).

structures have been reported.[12-15] The results of our investigation are shown in Fig. 11. In the spectral region examined, three bands were found: near 3400 cm,$^{-1}$ 1600 cm,$^{-1}$ and 1000 cm^{-1}. The 3400 cm^{-1} and 1600 cm^{-1} bands are attributed to the O–H bond. The band near 1000 cm^{-1} may generally be attributed to the silicon oxide or aluminum oxide.[16] In the catalysts produced by hydrothermal treatment, these three bands diminished in intensity or were shifted compared with

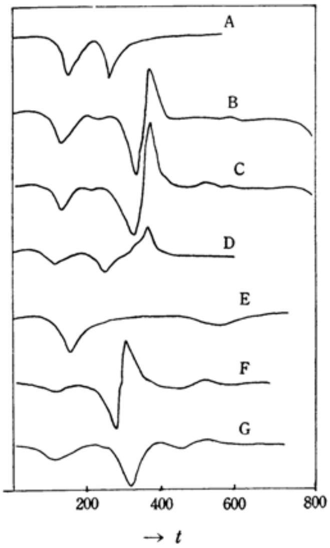

Fig. 10. DTA curves of dried catalysts.
A: NiCO$_3$·Ni(OH)$_2$ B: CoCo$_3$·Co(OH)$_2$
C: 49 Co-Al$_2$O$_3$-p D: 50 Co-Celite-p
E: 30 Co-SiO$_2$-cp F: 25 Co-Al$_2$O$_3$-cp
G: 18 Co-Al$_2$O$_3$-h

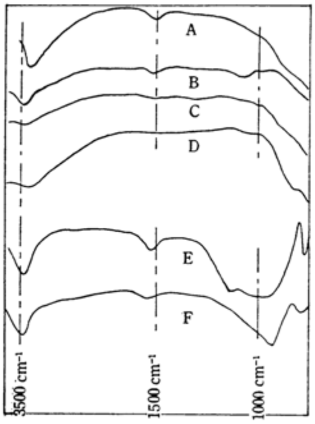

Fig. 11. IR spectra of catalysts.
A: 20 Co-Al$_2$O$_3$-p B: 49 Co-Al$_2$O$_3$-p
C: 18 Co-Al$_2$O$_3$-h D: CoAl$_2$O$_4$
E: 26 Co-SiO$_2$-m F: 20 Co-SiO$_2$-h

TABLE III. LIST OF PROPERTIES

Catalyst	Preparation method	Reducibility (at 500°C)	Main compound from X-ray (reduced at 500°C)	DTA main peeks		Solubility in 2 N HCl	Suggested structure after calcined at 500°C for 2 hr.
Co-Al$_2$O$_3$ (20%)	Impregnation	73%	β-Co	① 120°C ② 310 ③ 360	endo endo exo	60%	Co$_3$O$_4$ CoAl$_2$O$_4$
Co-Al$_2$O$_3$ (25%)	Coprecipitation	65%	β-Co CoO	① 120°C ② 290 ③ 310	endo endo exo	54%	Co$_3$O$_4$ CoAl$_2$O$_4$
Co-Al$_2$O$_3$ (18%)	Hydrothermal	50%		① 100°C ② 300	endo endo	38%	CoAl$_2$O$_4$ Co$_3$O$_4$
Co-SiO$_2$ (26%)	Mixing	93%	β-Co			100%	Co$_3$O$_5$
Co-SiO$_2$ (20%)	Impregnation	70%	CoO β-Co	① 150°C	endo	98%	Co$_3$O$_4$ Cobalt-hydrosilicate (ortho type)
Co-SiO$_2$ (20%)	Hydrothermal	40%				45%	Co$_3$O$_4$ Cobalt-hydrosilicate (meta type)
Co-Celite (50%)	Impregnation	96%	β-Co	① 120°C ② 250 ③ 360	endo endo exo	100%	Co$_3$O$_4$
Co-MgO (46%)	Impregnation	85%	β-Co CoO				Co$_3$O$_4$

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12) J. M. Hund, M. P. Wisherd and L. C. Bonham, *Anal. Chem.*, **22**, 1478 (1950).

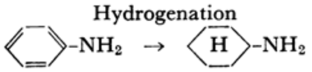
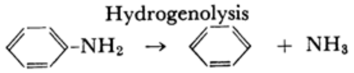
13) E. A. Miller and C. H. Wilkins, ibid, **24**, 1253 (1952).

14) L. D. Frederickson, *Anal. Chem.*, **26**, 1883 (1954).

15) K. Morikawa and F. Nozaki, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **58**, 64 (1961).

16) K. Kumata and K. Aizawa, *Kagaku no Ryoiki*, Nankodo, (Tokyo) **40**, 21 (1959).

TABLE IV. ACTIVITY OF CATALYSTS

Reaction	Hydrogenation 		Hydrogenolysis 	
Experimental condition	Reaction temp. 200°C H_2/aniline mol. ratio 10 LHSV=1.0 π=1 atom.		Reaction temp. 300°C H_2/aniline mol. ratio 10 LHSV=1.0 π=1 atom.	
	Conversion	Yield of aniline	Conversion	Yield of benzene
20% Co-Al_2O_3 (Impreg.)	48%	42%	17%	15.5%
18% Co-Al_2O_3 (Hydrother.)	8.5%	5.5%	4%	2.8%
26% Co-SiO_2 (Mixing)	27%	22%	12%	10%
20% Co-SiO_2 (Hydrother.)	3%	2.5%	3.2%	3.0%
50% Co-Celite (Impreg.)	85%	73%	43%	35%

those of catalysts prepared by impregnation. These changes may also be due to the complex formation between cobalt oxide and the carriers.

Solubility in 2 N Hydrochloric Acid.—Applications of this test to the supported nickel catalysts have been reported by Morikawa and Nozaki. They found that only the free metal in the catalyst is soluble in 2 N hydrochloric acid. This technique was then applied to the supported cobalt-oxide in order to find the chemical state of cobalt oxide in the catalyst. The results are summarized in Table III. The catalysts which dried at 100°C were fully soluble in 2 N hydrochloric acid. In the cobalt-alumina system, when it was calcined at 700°C for 2 hr. the cobalt(II, III) oxide in the catalyst almost became insoluble. This shows that the interaction between cobalt oxide and alumina carrier progressed further as the calcining temperature was raised. The structure of the complex was probably that of cobalt aluminate ($CoAl_2O_4$) and a solid solution. In the cobalt-silica catalyst prepared by coprecipitation, the cobalt oxide was fully soluble in 2 N hydrochloric acid, even after calcination. This may be attributed to the formation of a soluble compound, like ortho hydrosilicate.[17]

The Relationship between Activity and Structure.—The results of activity tests are summarized in Table IV. From the data given above, generally speaking, the catalysts of the supported free-metal type showed a higher activity in the hydrogenation and hydrogenolysis reaction of aniline. For example, in the cobalt alumina series, the activity of the catalyst produced by hydrothermal treatment is about one-fifth that of that made by the impregnation method.

Summary

1) The chemical states of cobalt in the supported catalysts may be classified into two types. One is the type in which the cobalt is not combined with the carrier but remains free on its surface. In the other type, cobalt oxide forms a complex with the carrier and resists reduction by hydrogen.

2) The ratio of the amounts of the two types varied both with the kind of carrier and with the method of preparation used.

3) The hydrothermally-formed cobalt-alumina and cobalt-silica catalysts form $CoAl_2O_4$ and cobalt hydrosilicate compounds respectively.

4) The course of the reduction of cobalt oxide in the catalyst is as follows: In the temperature range from 200 to 300°C, the cobalt(II, III) oxide is mainly reduced to cobalt(II) oxide, and later cobalt(II) oxide is reduced to β-Co between 300 and 500°C. The reduction temperature of cobalt(II, III) oxide is different for the various types of catalysts.

5) The catalyst which consists of a complex between the metal and its carrier-oxide is less active than the free metal catalyst for the hydrogenation reaction, and it is almost completely inactive in the hydrogenolysis reaction.

6) The results of the various analyses of the supported cobalt catalysts are in good agreement with one other.

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[17] J. A. A. Ketelaar, "Chemical Constitution," Elsvier (1958), p. 61.