The Catalytic Hydrogenation of Aniline[1]

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A few reports and a number of patents have previously been published on the hydrogenation of aniline, but most of them have reported on the catalytic hydrogenation in the liquid phase.[2-4] The present authors have investigated this subject, using a number of types of catalysts, and this report will describe the development of the catalysts, and their selectivity in the vapor-phase hydrogenation of the benzene nucleus of aniline.

Catalysts consisting of single or mixed metals, or of supported metals, were used for this reaction. The catalyzed main reaction is the hydrogenation of aniline to cyclohexylamine:

$$C_6H_5NH_2 + 3H_2 \rightarrow C_6H_{11}NH_2$$

The side reactions of cyclohexylamine or aniline occur as follows:

$$2C_6H_{11}NH_2 \rightarrow (C_6H_{11})_2NH + NH_3$$

$$C_6H_{11}NH_2 + C_6H_5NH_2 \rightarrow C_6H_5NHC_6H_{11} + NH_3$$

Also, on a smaller scale, the hydrogenolysis reactions of cyclohexylamine to cyclohexane and ammonia, and of aniline to benzene and ammonia, took place under 250°C, as follows:

$$C_6H_{11}NH_2 \xrightarrow{H_2} C_6H_{12} + NH_3$$

$$C_6H_5NH_2 \xrightarrow{H_2} C_6H_6 + NH_3$$

Experimental

Procedure of Catalyst Preparation.—Reagents of a chemically-pure grade were used as starting materials in the preparation of the catalysts. The

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[1] Presented in part at the 15th Discussion Meeting on Catalysis of the Catalysis Society of Japan, Osaka, November, 1964.

[2] C. F. Winans and H. Adkins, *J. Am. Chem. Soc.*, **54**, 306 (1932).

[3] J. C. Jungers and G. Debus, *Chem. Abstr.*, **48**, 6975 (1954).

[4] H. Yamamoto and T. Kwan, presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

catalysts were prepared by co-precipitation, by impregnation followed by subsequent precipitation, by mixing, by impregnation, and by precipitation followed by hydrothermal treatment under pressure in an autoclave.

*The Catalyst Preparation of Single or Mixed Metal Oxide.*5)—Single or mixed metal catalysts were precipitated by slowly adding, with rapid agitation, a dissolved equivalent quantity of ammonium carbonate to a solution of nitrates at 20°C. After washing the filtered precipitates, they were dried at 100°C and calcined at 500°C, for 2 hr.

Catalyst Preparation by the Impregnation Method with Subsequent Precipitation.—The powdered support was added to a solution of nickel or cobalt nitrate. The slurry was stirred for some time, and then a solution of ammonium carbonate was slowly added to it until there was a slight excess at 20°C. After the precipitate had been filtered and washed, it was dried at 100°C and then calcined at 500°C for 2 hr.

Catalyst Preparation by the Co-precipitation Method.—The catalysts were prepared by co-precipitation with vigorous stirring from a mixed solution of nickel, or cobalt, and aluminum nitrate, or sodium silicate, and ammonium carbonate at 20°C. The precipitates were washed with distilled water, dried at 100°C, powdered, and calcined at 500°C for 2 hr. in an electric furnace.

Catalyst Preparation by the Impregnation Method.—The powdered support was added to a solution of nickel or cobalt nitrate and was in the solution for 5 hr. The slurry was then evaporated to dryness on a water bath, and the residue was dried in an oven at 100°C, washed with distilled water to remove nitrate ions, and dried again at 100°C. Then it was calcined at 500°C for 2 hr. in an electric furnace.

Catalyst Preparation by the Mixing Method.—The powdered support and the slurry of nickel or cobalt-basic carbonate were mixed mechanically in a beaker. The mixture was vacuum-filtered, and then it was dried at 100°C and calcined at 500°C for 2 hr.

*Catalyst Preparation by Hydrothermal Treatment.*6)—Basic nickel carbonate or basic cobalt carbonate (prepared from a nickel or cobalt nitrate solution and an ammonium carbonate solution at 20°C) was mixed with silica gel or aluminum oxide gel and then heated in an autoclave to 250°C for 25 hr. with water. It was then cooled, filtered, washed with distilled water, dried at 100°C, and then calcined at 550°C for 2 hr.

Experimental Method of the Hydrogenation of Aniline.—The hydrogenation experiments were performed in a fixed-bed apparatus of the flow type in the temperature range from 150°C to 300°C. Figure 1 shows its flow diagram. The mixture of aniline and hydrogen was introduced into a reactor which was immersed in a fluidized thermal bath.

The gaseous products leaving from the reaction zone were caught in a condenser trap cooled with dry ice-methanol, from which trap condensates were drawn every thirty minutes for gas chromatographic analyses.

The oxide catalysts (5 ml.) were in the same fixed-bed apparatus used for the reaction, reduced to the metals in hydrogen according to a definite reduction schedule. The flow rate of hydrogen was 250 ml./min. The temparature of the catalyst bed was raised to 200°C in one hour, and then raised at the rate of 2.5°C per minute until 400°C or 450°C was reached. After the temperature had been held at 400°C or 450°C for two hours, the catalyst was cooled in the hydrogen stream to the reaction temperature, and then a run of the hydrogenation of aniline was carried out.

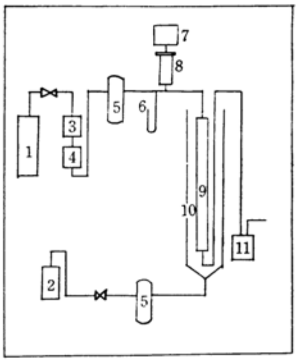

Fig. 1. Flow sheet for the hydrogenation reaction of aniline.
1. Hydrogen cylinder 2. Air compressor 3. Oxygen eliminator 4. Drier 5. Orifice flow meter 6. Manometer 7. Moter feeder 8. Feeder of aniline 9. Reactor 10. Fluidized thermal bath 11. Trap

After a steady state of activity was achieved, the activity of the catalyst was estimated as follows:

Conversion

$$=\frac{\text{The amount of reacted aniline (mol./hr.)}}{\text{Total aniline introduced (mol./hr.)}}$$

$$\text{Selectivity}=\frac{\text{Cyclohexylamine yield (mol./hr.)}}{\text{Reacted aniline (mol./hr.)}}$$

$$\text{Yield of benzene}=\frac{\text{Benzene yield (mol./hr.)}}{\text{Total aniline used (mol./hr.)}}$$

Yield of secondary amine

$$=\frac{\text{Secondary amine yield (mol./hr.)}}{\text{Total aniline used (mol./hr.)}}$$

Results

The Activity of Various Metals for This Reaction.—The catalysts were reduced by hydrogen at 400°C. The results of the activity tests are shown in Fig. 2. The single-metal catalysts are sharply divided into three classes. Ruthenium is active at low temperatures. Cobalt is more active than nickel. Iron and copper are inactive in this reaction.

It must be emphasized that the inactivity of iron or copper is not due to insufficient reduction or to the sintering of the metal. Especially in the case of copper, the reduction was carried out at a low temperature (about 200°C) to prevent it from sintering. It was found through experiments that the activity of a metal prepared by reduction

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5) G. Natta, "Handbuch der Katalyse", Vol. V, Springen, Wien (1957), p. 269.

6) J. J. B. van Eijk van Voorthuijsen and P. Franzen, *Rec. Trav. Chim.*, **70**, 793 (1951).

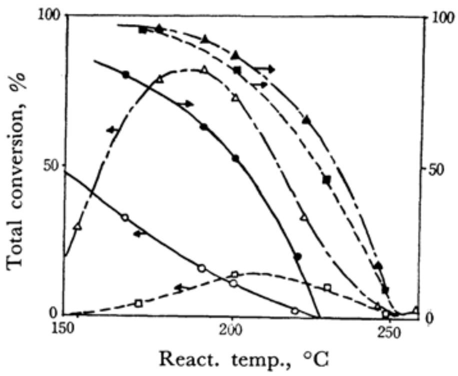

Fig. 2. The activity and selectivity of metallic catalysts in the hydrogenation.
—— Ru, –·– Co, ---- Ni
LHSV=1.0 hr^{-1}, H_2/aniline 10 (mole ratio)

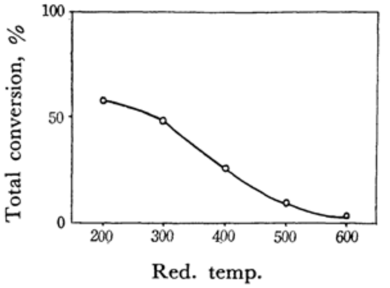

Fig. 3. Relative activity of Co vs. temp. of reduction.
LHSV=2 hr^{-1}, H_2/aniline 10 (mole ratio)

from the oxide is dependent on the length of the reduction time and on the temperature. The effects of the reduction temperature of cobalt on the activity were also investigated. The results are shown in Fig. 3.

The Activity of the Mixed Metal Catalysts.—The catalysts were reduced by hydrogen at 400°C. The results of the activity tests are shown in Fig. 4. The activity of the Co-Ni series showed a decrease as the nickel content increased. However, in the Co-Fe series, when the Fe content became 50%, the Co-Fe catalyst lost its activity almost completely. A similar results was obtained by Long et al.[7,8] in the hydrogenation of benzene.

Long et al. ascribed this to the different crystsl structures of mixed metal catalysts. They found that as the mixture becomes richer in cobalt, the more probable it is that the catalyst will have more of a face-centered cubic lattice, and will hence be active.

The Activity of Supported Metal Catalysts.—The activities of metal catalysts supported on the same oxide carrier, although prepared by different methods, show almost the same tendency in the relative abundance of the various products.

The activity of the catalysts prepared by the impregnation method with subsequent precipitation is shown in Figs. 6 to 9.

The Effect of the Reduction Temperature on the Activity of the Catalyst.—The catalyst

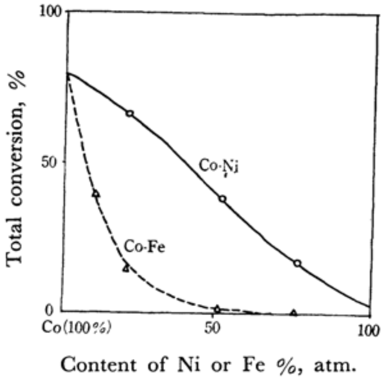

Fig. 4. The activity of Co-Ni and Co-Fe catalysts for the hydrogenation.
Reaction temp. 200°C
H_2/aniline 10 (mole ratio)

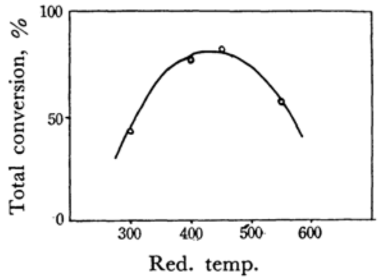

Fig. 5. Relative activity of Co-Al_2O_3 (50% cobalt) vs. temp. of reduction.
React. temp. 200°C, LHSV=1.0 hr^{-1}
H_2/aniline 10 (mole ratio)

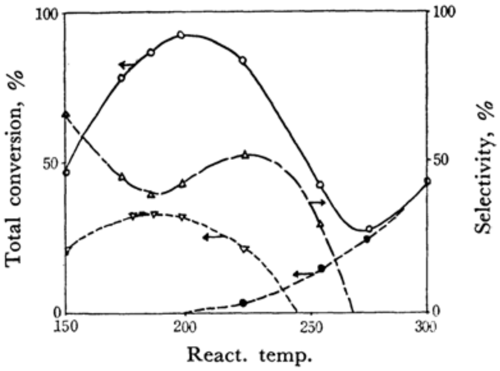

Fig. 6. The activity and selectivity of Ni-Al_2O_3 (30% nickel) for the hydrogenation.
LHSV=1.0 hr^{-1}, H_2/aniline 10 (mole ratio)
-▽- yield of dicyclohexylamine
-●- yield of benzene

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[7] J. H. Long, W. Frazer and E. Ott, *J. Am. Chem. Soc.*, **50**, 1101 (1934).

[8] F. Lihl, H. Wagner and P. Zemisch, *Z. Elek. Chem.*, **56**, 612, 619, (1952); **57**, 58 (1953).

samples were reduced for 2 hr. at various temperatures. Some of the results are presented in Fig. 5. Generally the catalyst which was reduced for 2 hr. at 400 to 450°C had the highest activity.

The Activity of Supported Nickel Catalysts.—The catalysts were reduced by hydrogen at 450°C. The results of the activity tests are shown in Figs. 6 and 7. From the results, it can be concluded that:

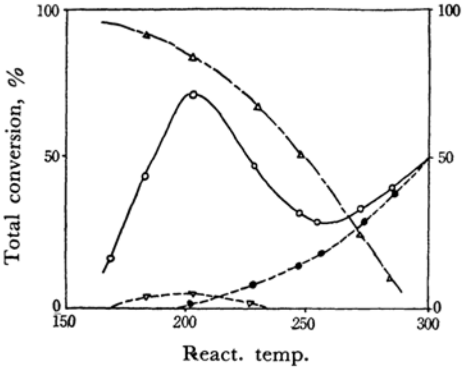


Fig. 7. The activity and selectivity of Ni-MgO (50% nickel) for the hydrogenation.
LHSV=1.0 hr^{-1}, H$_2$/aniline 10 (mole ratio)
-▽- yield of dicyclohexylamine
-●- yield of benzene

1) The maximum activity of catalysts for the hydrogenation reaction was obtained in the temperature range from 180 to 200°C, and 2) The production of secondary amine was affected by the kind of carrier-oxide used.

The Activity of Supported Cobalt Catalysts.—The catalysts were reduced by hydrogen at 450°C for 2 hr. The results of the activity tests are presented in Figs. 8 and 9.

From these data, it may be concluded that:

1) The maximum activity of catalysts for the hydrogenation reaction was obtained in the temperature range from 180 to 200°C, and 2) The production of secondary amine was less with a cobalt catalyst than with nickel catalysts. 3) The selectivity of this reaction was influenced by the kind of carrier-oxide.

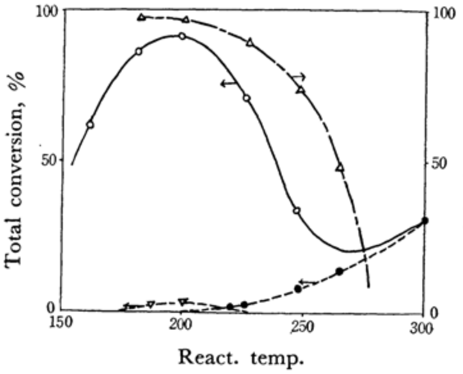


Fig. 8. The activity and selectivity of Co-Al$_2$O$_3$ (50% cobalt) for the hydrogenation.
LHSV=1.0 hr^{-1}, H$_2$/aniline 10 (mole ratio)
-▽- yield of dicyclohexylamine
-●- yield of benzene

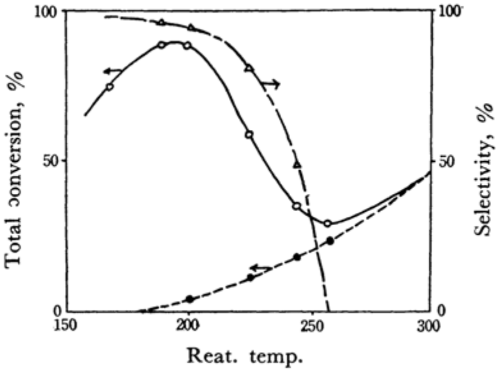


Fig. 9. The activity and selectivity of Co-MgO-Kieselguhr (45 : 10 : 45) for the hydrogenation.
LHSV=1.0 hr^{-1} H$_2$/aniline 10 (mole ratio)
-●- yield of benzene

On the basis of the above data, we have concluded that the kind of carrier-oxide used has an effect on the activity of nickel, as well as on the cobalt. The production of dicyclohexylamine is especially affected by the kind of carrier used.

The Activity of Catalysts Prepared by the Hydrothermal Treatment.—The catalyst were reduced by hydrogen at 550°C. The results are presented in Fig. 10. It may be concluded that the catalysts produced by the hydrothermal treatment are less active.

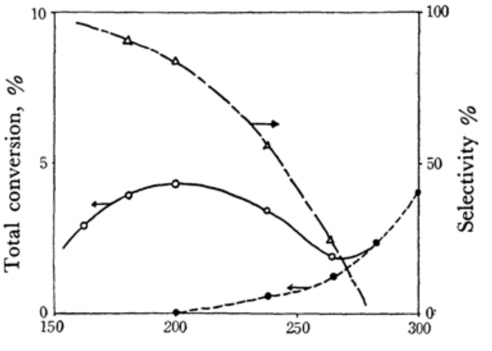


Fig. 10. The activity and selectivity of Co-SiO$_2$* cat. (20% cobalt) for the hydrogenation.
* The catalyst was treated at 250°C in an autoclave in the presence of water.
LHSV=1.0 hr^{-1}, H$_2$/aniline 10 (mole ratio)
-●- yield of benzene

The Effect of the Carrier-oxide Content of Metallic Catalysts on the Hydrogenation Reaction of Aniline.—The results are summarized

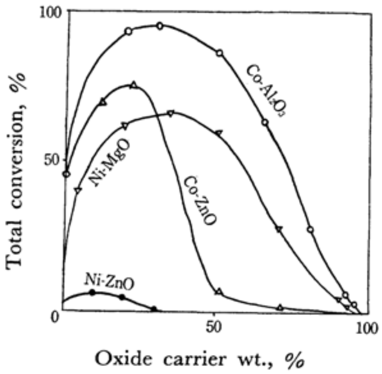


Fig. 11. Effect of the oxide carrier contents of metallic catalysts on the hydrogenation.
Reaction temp. 200°C
LHSV=1.0 hr^{-1}, H_2/aniline 10 (mole ratio)

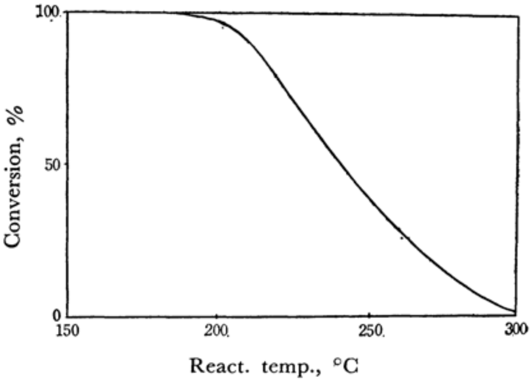


Fig. 12. Relation between temperature and equilibrium conversion.
H_2: aniline=10 : 1

in Fig. 11. The activity of the catalysts was found to be influenced by its carrier-oxide, and their activity is highest at a certain metal-to-carrier ratio.

In the Co-ZnO and Ni-ZnO series, the activity was found to be very low. This was attributed to the formation of a complex between the metal and its carrier. From X-ray analysis, it was concluded that $ZnCo_2O_4$ was formed.

The Relationship between the Activity and the Metal Content of the Catalyst in the Hydrogenolysis Reaction of Aniline.—Table I shows the relation between the conversion and the metal content of the catalyst in the hydrogenolysis reaction. From the data presented, it may be concluded that the rate of the hydrogenolysis reaction of aniline is related to the amount of metal on the oxide carrier, the activity of the catalyst was found to be proportional to the metal content of the catalyst.

TABLE I. THE RELATION BETWEEN CONVERSION AND THE METAL CONTENT OF THE CATALYST IN THE HYDROGENOLYSIS REACTION
Reaction temp. 300°C, LHSV=1.0 hr^{-1}
H_2/aniline 10 (mole ratio)

Metal content, %	Catalyst	
	Ni-MgO	Co-Al₂O₃
10	11%	14%
20	19%	17%
30	28%	24%

Discussion

The Relationship between the Activity and the Reaction Temperature.—As is shown in Figs. 6—9, in the hydrogenation reaction of aniline in the vapor phase the highest conversion of aniline into cyclohexylamine was obtained in the temperature range from 180 to 200°C. At high temperatures, the degree of hydrogenation decreased. This phenomenon of a negative temperature coefficient can be explained in terms of the thermodynamic chemical equilibrium calculated using the Nernst equation at the H_2 to aniline mole ratio of 10 to 1.

Since the hydrogenation is carried out in a dynamic (flow) system, the conversion is most probably controlled not only by the equilibrium constant, but also by the rate of the surface reaction. It was concluded from the kinetic study with cobalt and nickel of the vapor-phase hydrogenation of aniline that the results obtained may be expressed satisfactorily by the following rate equation in the 150—210°C temperature range.

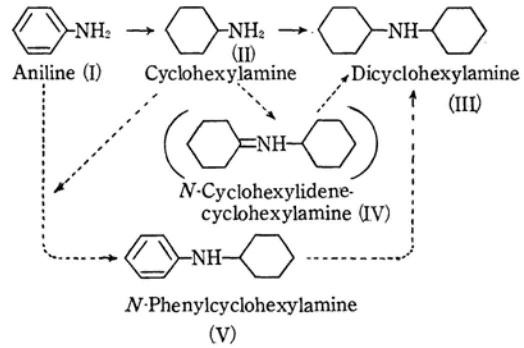
$$r=k\theta_A\theta_H{}^3$$

r: reaction rate
k: reaction rate constant
θ_A: the fractions of the surface covered by the aniline
θ_H: the fractions of the surface covered by hydrogen

A more detailed report of the kinetic study will be presented later.

A Relationship between the Activity and the Structrue of the Catalyst.—The chemical states of metal on the supported catalyst may be classified into two types. The one is the type in which the metal is not combined with the carrier but remains free on the surface of the carrier. In the other type, the metal oxide forms a complex with the carrier resists reduction by hydrogen. Generally speaking, catalysts of the first type (supported free metal) show a higher activity for the hydrogenation and hydrogenolysis reaction of aniline. A more detailed report on this will be presented in the near future.

The Mechanism of the Production of Secondary Amine.—In the course of the hydrogenation reaction, dicyclohexylamine and phenylcyclohexylamine are also found in the product. The course of the formation of those products may be described as follows.



(The main course is presented by a full line, the less important course is presented by dotted lines)

The cyclohexaneimine was not found in the product, but *N*-cyclohexylidene-cyclohexylamine could be isolated. However the quantity of IV found is small compared with that of III.

The main course of the production of dicyclohexylamine may consist of two paths, the one through *N*-cyclohexylidene-cyclohexylamine, and the other through the condensation of two cyclohexylamine molecules. We also found that the rate of the condensation of two cyclohexylamines into dicyclohexylamine is fast compared with the rate of the condensation of aniline and cyclohexylamine.

The Properties of the Carrier-oxides.—We have found that the properties of the carrier-oxides have a great influence on the selectivity of the catalyst.

According to Sanderson,[9] oxides have thier own partial charge on oxygen and this value is an important parameter for determining the acidic character of oxides. We used the values given by Sanderson for Al_2O_3, SiO_2, MgO, CaO, ZnO, and K_2O and correlated these values with the $-\Delta H_0°$ values of the oxides given by Tamaru[10] (see Fig. 13).

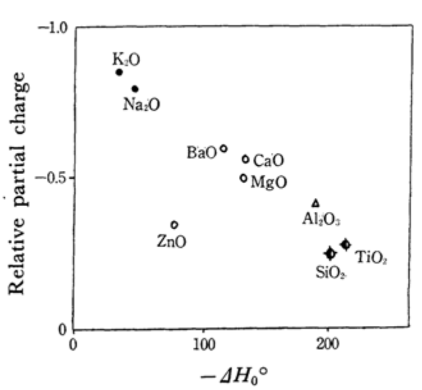


Fig. 13. Correlation between R.P.C. and $-\Delta H_0°$ of oxide.

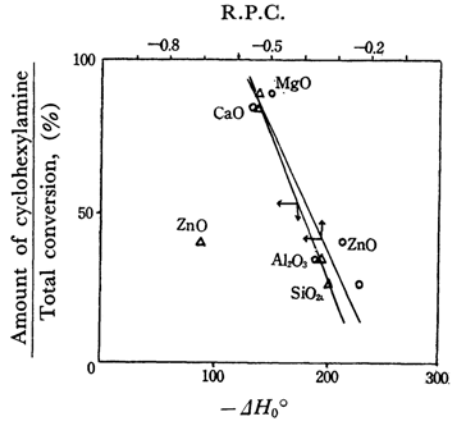


Fig. 14. Relationship between selectivity and oxide carrier of nickel catalysts (50% nickel). Reaction temp. 200°C, LHSV=1.0 hr^{-1} SV=3000 hr^{-1}, H_2/aniline 10 (mole ratio)

There is a relationship between the r. p. c. and $-\Delta H_0°$ values. As Fig. 14 shows, the selectivity of the catalysts was proportional to the value of $-\Delta H_0°$. Thus, we have concluded that the acidic and basic property of the carriers has a great influence on the production of secondary amine. The property of the oxide carrier is probably related to the elimination of ammonia from the cyclohexylamine and aniline molecules. The electron-donating property of the nitrogen of the amino group suggests that the amino group strongly interacts with the metal surface.[11] This effect may be considered to play an important role in the formation of the secondary amine. The adsorption of amine may be weakened on that metal which is supported by basic oxides.

Summary

1) The order of the activity of a metal catalyst for the hydrogenation of aniline is Co>Ni>Fe, Cu. The order of their selectivity is Co>Ni.

2) The activity of the mixed metals (Co-Ni, Co-Fe) is lower than that of a cobalt single catalyst.

3) The rate of hydrogenation increases with the temperature up to 180—200°C, and then decreases at higher temperatures. This phenomenon may be explained in terms of the kinetics of the reaction.

4) 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 almost completely loses its activity for the hydrogenolysis reaction.

5) The production of cyclohexylamine is affected by the property of the carrier oxide.

6) The main course of the production of dicyclohexylamine is considered to proceed through the

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[9] R. T. Sanderson, "Chemical Periodicity," Reinhold Pub. Comp., N, Y. (1960), p. 106.

[10] K. Tamaru and K. Tanaka, *Shokubai* (*Catalyst*), **4**, 328, (1962);

[11] Y. Y. Yao, *J. Phys. Chem.*, **67**, 2055 (1963).

condensation of two cyclohexylamine molecules and through *N*-cyclohexylidene-cyclohexylamine.

Notation: r. p. c. = relative partial charge on the oxygen of oxide (reported by R. T. Sanderson)

$-\Delta H_0{}^{\circ}$ = standard heat of formation of the highest oxide per metal g.-atm.

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