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The Catalytic Hydrogen Exchange of Aniline on Supported Metal Catalysts[1]

By Hiroshi HAGIWARA* and Etsuro ECHIGOYA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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The hydrogen exchange reaction of aniline with deuterium was investigated on supported nickel, cobalt and platinum. The following results were obtained: 1) At 150°C, the hydrogen of the amino group of aniline exchanges at a higher velocity than the hydrogen attached to the benzene ring. At temperatures as high as 300°C, the hydrogen exchange in the benzene ring increases further. 2) The suggested hydrogenation mechanism obtained from the results of the exchange reaction can not be correlated with that obtained from the kinetic study. 3) The catalytic activity for the exchange reaction in the benzene ring is in the order $Pt > Co > Ni$. 4) The basic oxide support seems to suppress the adsorption of the amino group. 5) The relationship between the adsorption state of the aniline on the catalyst surface and the various reaction products, such as cyclohexylamine, benzene and dicyclohexylamine, has been well established.

[*1] Present address: Yoshitomi Pharmaceutical Co. Ltd., Yoshitomi, Fukuoka

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In experiments previously reported by the present authors,[2] it was observed that the hydrogenation of aniline to cyclohexylamine and to the secondary amines occurred in the temperature range from 150 to 250°C while the fission of the carbon-nitrogen bond (the hydrogenolysis) of aniline took place at temperatures above 250°C.

In order to understand this change in reactivity, it would be useful to know the adsorption state of the aniline molecule on the metal catalysts. Many reports have been published with respect to the metal-catalyzed exchange between aniline and deuterium oxide,[3-5] but few regarding the relationship between reactivities and the adsorption state. The aim of the present experiments was to investigate the catalytic activity of various kinds of catalyst in the hydrogen exchange reaction of aniline with deuterium, and then to deduce the relationship between reactivities and the adsorption state.

Experimental

Material.—Deuterium oxide obtained from the Showa Denko Co. (99.75% D_2O) was used without any additional purification. Deuterium was obtained from the electrolysis of deuterium oxide containing 20% sodium deuteroxide. The electrode was a nickel plate (see Fig. 1). Aniline (technical grade) was shaken with zinc powder and then purified by fractional distillation. The catalysts were prepared by the impregnation method.[6] Powdered support was added to a solution of metal nitrate. The slurry was stirred for some time, and then to it there was slowly added, at 20°C, a water solution of ammonium carbonate in a slight excess. After the precipitate had been filtered and washed, it was dried at 100°C and then calcined at 450°C for 2 hr.

Procedure.—*The Experimental Method of the Hydrogenation of Aniline and Benzene.*—The hydrogenation experiments were perforemed in a fixed-bed apparatus of the flow type. The products were analyzed by gas chromatography.

The Experimental Method of the Hydrogen Exchange of Aniline with Deuterium Oxide.—The metal catalyst was reduced by hydrogen inside the reaction tube, into which aniline and deuterium oxide were then introduced by distillation from their respective vessels.[7] The tube was kept at the reaction temperature in a thermostatic bath. After the reaction, both aniline and deuterium oxide were separated from the catalyst by distillation, and condensed in a cold trap. The aniline layer was treated with an amount of water about 20 times its volume in order to transform all the N–D bonds to N–H bonds. The aniline layer was then extracted with benzene, and the mixture of benzene and aniline was dehydrated by anhydrous sodium sulfate and separated by the gas chromatographic technique.

The Experimental Method of the Hydrogen Exchange of Aniline with Deuterium.—Figure 1 shows the flow diagram.[8] A mixture of aniline vapor and deuterium was introduced into a fixed-bed reactor. The reaction temperature was maintained by external electric heating. The gaseous products leaving the reaction zone were caught in a dry ice-and-methanol-cooled trap, from which condensates were drawn for the gas chromatographic analysis. The oxide catalysts were placed in the same fixed-bed apparatus used for the reaction, and reduced to the metal by a flow of hydrogen at the rate of 50 cc./min.* After the reduction procedure, the catalyst was cooled in a deuterium stream to the reaction temperature, and then a run of the hydrogenation of aniline with deuterium was carried out.

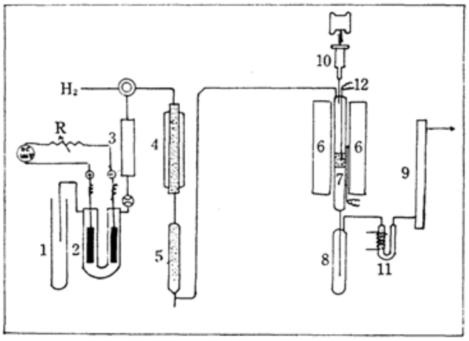

Fig. 1. Flow diagram.

1	Water head vessel for gas pressure regulation
2	Apparatus for electrolysis of deuterium oxide
3	Calcium chloride drying tube for D_2
4	Oxygen eliminator
5	Silica gel drying tube for D_2
6	Heater
7	Catalyst bed
8	Cold trap for gaseous products
9	Soap film meter for gas flow measuring
10	Aniline feeder
11	Nickel-kieselguhr catalyst
12	Thermometer

The Analysis of the Products.—The infrared, mass-spectroscopic and NMR methods were used. In addition, in order to determine the distribution of the deuterium in the aromatic nucleus, the aniline hydrobromide and the brominated derivatives of aniline (*p*-bromoacetanilide and 2, 4, 6-tribromoaniline) were prepared, and the percent-distribution of deuterium in the ring was determined by the calculation of the

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2) H. Hagiwara and E. Echigoya, *Shokubai (Catalyst)*, **6**, 35 (1964).

3) W. A. Sollich and J. L. Garnett, *Aus. J. Chem.*, **14**, 56 (1961).

4) R. A. Ashby and J. L. Garnett, ibid., **16**, 549 (1963).

5) C. G. MacDonald and J. S. Shannon, *Tetrahedron Letters*, **45**, 3351 (1964).

6) H. Hagiwara, E. Kojima and E. Echigoya, This Bulletin, **39**, 1800 (1966).

7) K. Hirota, K. Kuwata and T. Ueda. *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **81**, 362 (1960).

8) A. Ozaki, F. Nozaki, Y. Kawasaki and K. Morikawa, *Shokubai (Catalyst)*, **3**, 138 (1961).

* Nickel and cobalt catalysts were reduced at 450°C for 2 hr.; the platinum catalyst was reduced at 300°C for 3 hr.

peak height at $2260\ \mathrm{cm}^{-1}$** in the infrared spectra for each derivative. The estimation method was as follows:

$$D_{\mathrm{meta}} = \frac{\text{peak height of the 2, 4, 6-tribromoaniline}}{\text{peak height of the aniline hydrobromide}} \times 100$$

$$D_{\mathrm{para}} = \frac{\left(\begin{array}{l}\text{peak height of the } p\text{-bromoacetanilide} - \\ \text{peak height of 2, 4, 6-tribromoaniline}\end{array}\right)}{\text{peak height of the aniline hydrobromide}} \times 100$$

Results

The Catalyst Activity in the Hydrogenation of Aniline and Benzene.—The results of the activity test for the hydrogenation reaction are presented in Figs. 2, 3 and 4.

From these data, it can be concluded that:

1) For the nickel-magnesia catalyst, the hydrogenation reaction occurred above 120°C. for aniline, while benzene was hydrogenated at lower temperatures.

2) The platinum catalyst showed the same tendency in acting in the hydrogenation of aniline and benzene. With both catalysts, under the same reaction conditions, the rate of the hydrogenation of benzene was higher than that of the hydrogenation of aniline.

3) The hydrogenation of benzene on nickel or on the platinum catalyst was inhibited by the presence of aniline or cyclohexylamine.

4) The hydrogenolysis of cyclohexylamine on the platinum catalyst yielded benzene rather than cyclohexane at 170—200°C.

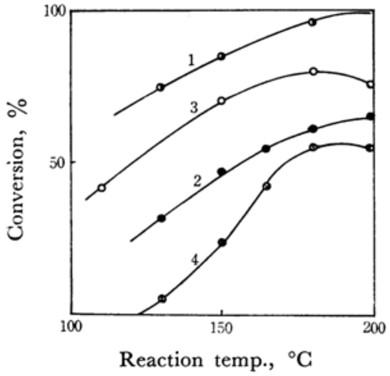

Fig. 2. The activity of $Pt\text{-}Al_2O_3$ and Ni-MgO for the hydrogenation of aniline and benzene.

1% $Pt\text{-}Al_2O_3$: 1, Benzene → Cyclohexane
2, Aniline → Cyclohexylamine
30% Ni-MgO: 3, Benzene → Cyclohexane
4, Aniline → Cyclohexylamine
Reaction conditions:
H_2/aniline feed mole ratio = 10
$SV \approx 1100\ \mathrm{hr}^{-1}$ (N. T. P.)

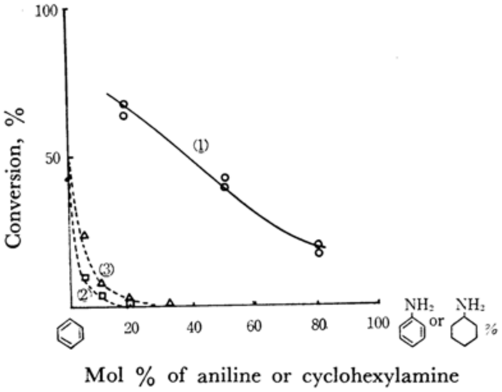

Fig. 3. The effect of aniline and cyclohexylamine on the hydrogenation of benzene over nickel-magnesia.

1 Aniline → Cyclohexylamine (Reactants: aniline + benzene)
2 Benzene → Cyclohexane (Reactants: aniline + benzene)
3 Benzene → Cyclohexane (Reactants: cyclohexylamine + benzene)
Reaction conditions:
180°C H_2/liquid mole ratio≈5
$SV \approx 1000\ \mathrm{hr}^{-1}$ (N. T. P.)

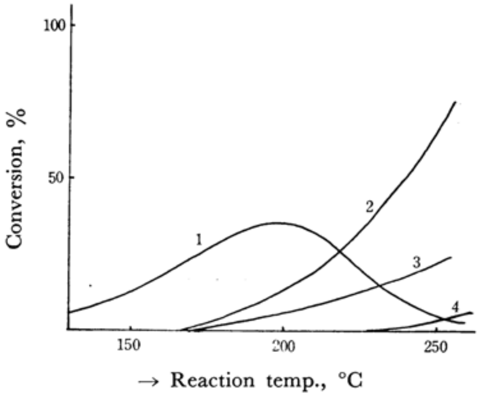

Fig. 4. The activity of $Pt\text{-}Al_2O_3$ for the decomposition of cyclohexylamine.

1 Yield of dicyclohexylamine
2 Yield of benzene
3 Yield of cyclohexane
4 Yield of aniline
Reaction conditions: H_2/Cyclohexylamine feed mole ratio = 10
$S_v \approx 1000\ \mathrm{hr}^{-1}$ (N. T. P.)

The Exchange Reaction of Aniline with Deuterium Oxide.—The results are shown in Table I. Examples of the NMR spectra and of the infrared spectra of the reaction products are shown in Figs. 5, 6 and 7. The data show that a little hydrogen-deuterium exchange occurs without the catalysts. It will be also evident

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** With deuterium, a new band appeared at $2260\ \mathrm{cm}^{-1}$ due to the C–D stretching vibration in the ring.

TABLE I. EXCHANGE REACTION OF ANILINE WITH DEUTERIUM OXIDE

Reaction conditions: Temp., 110—100°C; Residence time, 15 hr.;
Vessel volume, 20 cc.; Catalyst weight, 8 g.; Reactants (aniline 1 cc., D_2O 2 cc.)

Exp. No.	Catalyst	$\frac{D}{D+H}$ for the reacted sample	Number of Deuterium atoms per aromatic nucleus	Percent distribution of deuterium		
				ortho	meta	para
D_2O-6	20-Ni-Al_2O_3	0.39	2.73	70	$\doteqdot 0$	30
D_2O-7	20-Co-Al_2O_3	0.46	3.22	55	20	25
D_2O-9	1-Pt-Al_2O_3	0.62	4.4	45	20	35
D_2O-4	Without catalyst	0.075	0.5			

TABLE II. EXCHANGE REACTION OF ANILINE WITH DEUTERIUM

Reaction condition: Catalyst weight 0.4 g. (1—0.5 cc.)
Feed: Molar ratio of D_2/aniline$\approx$5
Space velocity: 1200—500 (N. T. P.) hr^{-1}

Exp. No.	React. temp. °C	Catalyst	Conversion of aniline				Deuterium distribution into the reacted aniline								$\frac{D_{amino}}{D_{total}}$**	Φ_D%*
			Aniline conver.	Yield of cyclohexylamine	Yield of dicyclohexylamine	Yield of benzene	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7		
D-3	150	20-Ni-Al_2O_3	17	8	3.5		58	32.2	8.6	1.2					0.94	7.6
D-9	150	30-Ni-MgO	21	18	1.0		46.2	40.3	10.4	2.6	0.5				0.90	10.1
D-11	150	20-Co-Al_2O_3	15	12	0.8		50.0	37.2	10.1	2.4	0.3				0.83	9.4
D-5	150	1-Pt-Al_2O_3	45	15	12		67.9	20.9	9.5	2.1	0.5				0.77	6.75
D-14	150	Alumina	0	0	0											
D-21	300	20-Ni-Al_2O_3	7	—		6	36.0	42.1	17.5	3.6	0.8				0.79	13.0
D-23	300	30-Ni-MgO	21	—		17	22.3	38.4	27.0	9.4	2.5	0.4			0.73	19.0
D-27	300	20-Co-Al_2O_3	15	—		12	26.9	35.6	27.1	7.5	2.4	0.5			0.66	17.8
D-15	300	1-Pt-Al_2O_3	32	2		26	44.8	34.0	14.1	6.0	1.1				0.50	12.1
D-19	300	Alumina	0.5	≈ 0		0	98	2								0.3

* $\Phi_D = \frac{1}{7}\sum_{i=1}^{7} i d_i$ (Average deuterium content %)

** Both fractions of N-D and C-D were determined by the IR absorption height compared to that of standard samples and by the mass spectrum analysis.

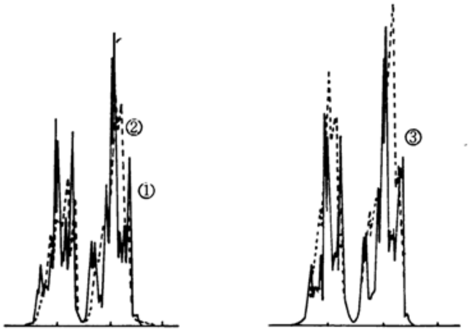


Fig. 5. NMR spectra for the reacted aniline.
1 Normal aniline (full line)
2 Deuterated aniline on Ni catalyst (No. D_2O-6) (dotted line)
3 Deuterated aniline on Pt catalyst (No. D_2O-9) (dotted line)

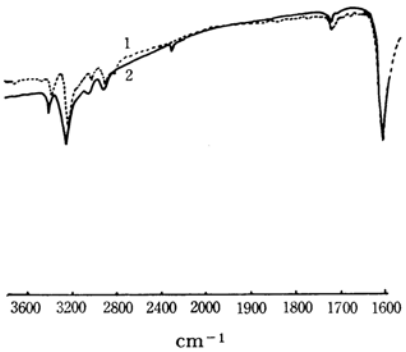


Fig. 6. IR spectra for 2,4,6-Tribromoaniline.
1 Normal aniline (dotted line)
2 Deuterated aniline on Ni-catalyst (No. D_2O-6) (full line)
KBr disc: NaCl prism

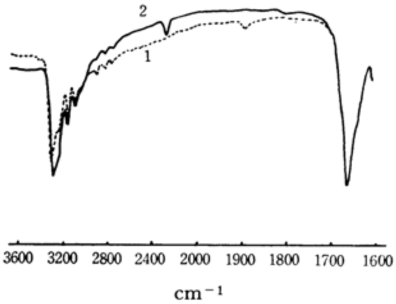


Fig. 7. IR-spectra for 4-bromoacetanilid.
1 Normal aniline (dotted line)
2 Deuterated aniline by Pt-catalyst (No. D_2O-9) (full line)

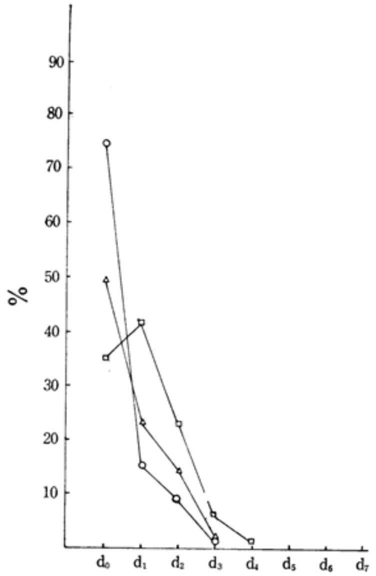


Fig. 8. Deuterium distribution in the exchange reaction of aniline with the deuterium at 300°C on $Ni-Al_2O_3$ at different space velocities.
D_2/aniline feed mole ratio≈5

	SV		SV
○	15000 hr^{-1}	△	7000 hr^{-1}
□	700		

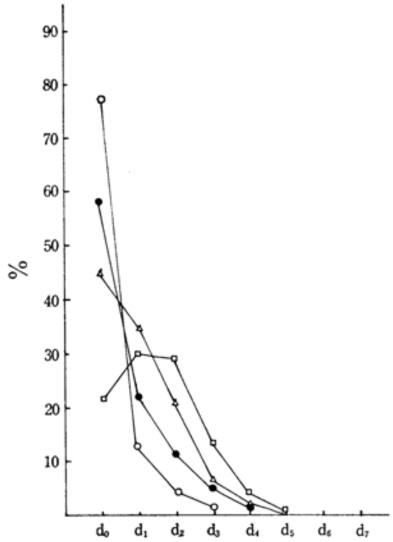


Fig. 9. Deuterium distribution in the exchange reaction of aniline with deuterium at 300°C on $Pt-Al_2O_3$ at different space velocities.
D_2/aniline feed mole ratio≈5

	SV		SV
○	20000 hr^{-1}	●	10000 hr^{-1}
△	1800	□	600

from an examination of Table I that the hydrogen atoms at the ortho and para positions of the benzene ring of aniline are catalytically exchanged by nickel, while over platinum, the exchange occurs in the ortho, para and meta positions. The existence of highly-deuterated aniline in the case of the platinum catalyst indicates that all the hydrogen molecules in aniline are exchangable.

The Exchange Reaction of Aniline with Deuterium.—The data on the activities of all the catalysts used are summarized in Table II. From Table II, the following conclusions may be drawn:

1) At 150°C, the exchange in the amino group predomoninated in the deuteration of aniline. These results can perhaps be accounted for by assuming that the aniline molecule is anchored to the catalyst through the electron pair of the nitrogen.

2) At 300°C, the amount of the exchange of hydrogen-deuterium had further progressed, and the d_3- and d_4- species increased in proportion. At temperatures as high at 300°C, the exchange in the benzene ring of aniline was found to occur at the ortho, para and meta positions.

3) The difference in the catalytic activities of nickel, cobalt and platinum were shown by the amounts of d_3- and d_4-species produced. The order of d_3- and d_4-species production capacity was platinum>cobalt>nickel (see also Figs. 8 and 9).

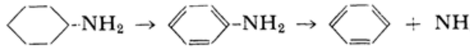
4) No definite difference in activity between nickel-magnesia and nickel-alumina catalysts was observed. However, the proportion of the d_3- and d_4-species increased when nickel-magnesia was used.

Discussion

In order to discuss the adsorption state of aniline on the surface of the catalyst on the basis of the experimental results, it is neccessary to check the partial pressure of deuterium in the reaction atmosphere. An evaluation of the fraction of deuterium in the reactant gases shows that the pressure of deuterium is predominant compared with that of hydrogen; thus it may be reasonable to assume that all the exchange occurring takes place through the adsorption of aniline on the surface of the catalyst with deuterium under the adsorption equilibrium conditions. The results show that, at 150°C the amino group strongly interacts with the metal surface. The formation of the strong nitrogen-metal bond may be considered to play an important role in the production of secondary amines (dicyclohexylamine and phenylcyclohexylamine). The experimental results of the hydrogen exchange reaction at 150°C cannot, however, account for the ring hydrogenation of aniline established by the kinetic study: a) judging from the results obtained by the hydrogen exchange reaction, it seems that the ring-hydrogenation of aniline proceeds via a step-by-step addition of adsorbed hydrogen atoms to the benzene nucleus of the adsorbed aniline but, b) judging from the kinetic study of the hydrogenation reaction, the ring hydrogenation proceeds via the addition of adsorbed hydrogen molecules to the benzene nucleus of the adsorbed aniline. This apparent contradiction seems to indicate that the hydrogenation reaction and the hydrogen exchange reaction proceed via different courses.

At temperatures as high as 300°C, the formation of the ring-metal bond or the formation of some dehydrogenated complex such as $C_6H_xNH_y$ on the surface (for instance, $C_6H_{11}NH_2 \rightarrow C_6H_xNH_y + (13\text{-}x\text{-}y)H$) was thought to take place.

The stronger the adsorption, the smaller the $(x+y)$ value will be. Hence the fission of the C–N bond will result. According to our experiments, the basic oxide support brought about a weak adsorption of amine, this effect will probably lead to the efficient hydrogenation of the ring, as was the case in the hydrogenation of ethylene on nickel.[9] Reference should be made here to the work by Morikawa et al.,[10] who found, studying the hydrogenolysis of ethane on nickel with or without added alkali oxides, that the addition of an alkali oxide to nickel causes the suppression of the stripping of hydrogen from the hydrocarbon. In the hydrogenolysis of cyclohexylamine over platinum-alumina between 170 and 200°C, the hydrocarbon product was mostly benzene, plus a little cyclohexane. It is thought that, before decomposing, some of the adsorbed cyclohexylamine loses hydrogen atoms from the ring. Hydrogenolysis then leads to benzene. This mechanism seems reasonable from the standpoint of chemical thermodynamic calculation. That is, in the following equations, the course of Eq. 2 is important.



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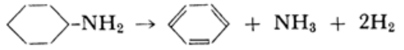

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Summary

The hydrogen exchange reaction of aniline with deuterium has been investigated on the supported nickel, cobalt and platinum. The following results have been obtained:

1) At 150°C, the hydrogen of the amino group of aniline exchanges more easily than the hydrogen in the benzene ring. At temperatures as high as 300°C, the exchange in the benzene ring progresses further.

2) The suggested hydrogenation mechanism obtained from the results of the exchange reaction could not be correlated with that of the kinetic study.

3) The catalytic activity for the exchange reaction in the benzene ring was in the order platinum>cobalt>nickel.

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[9] S. T. Thomson and J. L. Wishlade, *Trans. Faraday Soc.*, **58**, 1170 (1962).

[10] K. Morikawa, A. Ozaki and F. Nozaki, *Shokubai (Catalyst)*, **4**, 8 (1962).

4) The effect of basic oxide support seems to suppress the adsorption of the amino group.

5) The adsorption state of aniline on the catalyst surface is correlated with the variety in reactivity.

The authors wish to thank Professor Kiyoshi Morikawa for his useful discussion and guidance. Thanks are also due to Mr. Haruyoshi Sakurai for his kind assistance in the mass spectrum analyses.