The Hydrogenation of Aniline over Supported Rhodium-Palladium Alloy Catalysts

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The hydrogenation of aniline was investigated in the temperature range from 30° to 50°C over Rh-Pd alloy catalysts supported on activated carbon. The reactions were mainly carried out in acetic acid at an atmospheric pressure of hydrogen. The activity per unit weight of the catalysts was measured and plotted for the alloy composition. It showed a maximum at 75—85 wt% Rh. However, the activity per unit of surface area showed a maximum at about 25 wt% Rh, and the minimum activation energy of this reaction was observed at the same composition. The relationship between the selectivity and the alloy composition was also studied. The maximum selectivity to dicyclohexylamine was observed at 20—30% Rh, while the maximum formation of *N*-phenylcyclohexylamine appeared at 50—60% Rh. However, the selectivity to cyclohexylamine showed a minimum at about 25% Rh. The initial rates of the formation of cyclohexylamine and *N*-phenylcyclohexylamine were measured and plotted for the catalyst composition. The maximum activity was observed at about 85 wt% Rh for the formation of cyclohexylamine and at 50—60% Rh for the formation of *N*-phenylcyclohexylamine. Then the ratios of the two simple reaction rates were calculated. At a higher Rh content, (above about 25% Rh), the selectivity increased as the ratio increased. The reaction over the catalysts prepared by different methods and the hydrogenation of aniline in cyclohexane were also investigated.

Recently some interesting work with respect to the binary alloy catalysts of the platinum group metals have been reported.[1-7] However, there have been only a few reports on the Rh-Pd alloy system, and, moreover, these reports have shown two different tendencies for the catalytic activity change in this alloy series; on the one hand, a maximum activity was found for the hydrogenation of nitrobenzene and ethyl methyl ketone[4] at each certain Rh content, and on the other hand, the activity for CH_4+D_2 exchange and propane cracking [3a] changed smoothly with an increase in the Rh content.

Then we investigated the activity change for the hydrogenation of aniline with Rh-Pd alloy catalysts supported on activated carbon, in order to consider the contribution of any unpaired *d* electrons present in the metal and concerned with its magnetic susceptibility. The structure of the catalyst was studied by X-ray diffraction, and the surface area of the metal on the catalyst was measured by the CO adsorption method. The selectivity change in this series was of as much interest as the activity change. However, this subject was scarcely investigated. There has been one report showing that on Rh-Pt alloys of the Adams type, the catalysts containing 70 to 90 wt% Rh were the most active and selective for the hydrogenation of acetophenon.[1] In that report, however, the selectivity was not referred to any detail beyond the above description. Therefore in this report the selectivity change for the hydrogenation of aniline and the relationship between the selectivity and the activity were investigated with respect to the composition of the binary alloy catalyst.

Moreover, we studied how the activity and selectivity depended upon the catalysts obtained by the different method of preparation. The hydrogenation of aniline in a cyclohexane solvent with Rh-Pd alloy catalysts was also investigated.

Experimental

Procedure of Catalyst Preparation. The catalysts were prepared by the reduction of a solution of mixed Rh and Pd chlorides with formaldehyde, and by co-precipitation followed by reduction with hydrogen gas. Activated carbon was used as the carrier, and 5 wt% metal was supported on it.

Catalyst Preparation by Reduction with Formaldehyde: The method used as almost the same as that proporsed by Willstätter.[8] A given amount of the solution of mixed metal chlorides was added to the activated carbon. Then the metal chlorides were reduced with formaldehyde and sodium hydroxide at room temperature for 30 min and next at 100°C for 1 hr. It was left to stand overnight and then, after filtration, dilute hydrochloric acid was added until the pH of the solution went below about 3. After one day, it was washed fully with ion-exchanged water; a catalyst dried in the vacuum system was used directly for the reaction.

Catalyst Preparation by Co-precipitation: A given amount of the solution of the mixed metal chlorides was added at a stretch to the activated carbon, which was stirred at 40°C in a solution containing the calculated amount of sodium hydroxide. Then the metal hydroxide co-precipitated on the carrier was reduced to the metal by bubbling hydrogen gas into the solution and washed fully with ion-exchanged water. The dried catalyst in the vacuum system was used directly for the reaction.

Hydrogenation of Aniline. The hydrogenation experi-

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[9] K. Ikedate, T. Suzuki, and S. Suzuki, *Nippon Kagaku Zasshi*, **88**, 972 (1967).

ments were carried out in the liquid phase at an atmospheric pressure of hydrogen in the apparatus described in a previous paper.[9] The rates of the hydrogenation of aniline were measured 2 or 3 times. When almost the same value was obtained in two measurements, that value was taken as the activity of the used catalyst. The method of the analysis of the reaction samples was the same as that already reported.[10] The surface area of the metal on the carrier was measured by the ordinary CO adsorption method.

Results and Discussion

X-Ray Diffraction of Rh-Pd Alloy Series. In order to examine whether or not, the catalysts prepared by reduction with formaldehyde were homogeneous, they were subjected to a X-ray diffraction. The X-ray diffraction angles observed for the Rh-Pd alloy catalysts are shown in Fig. 1. Since a linear relationship between these angles and the composition was observed, we considered that the catalysts prepared by this method formed homogeneous alloys.

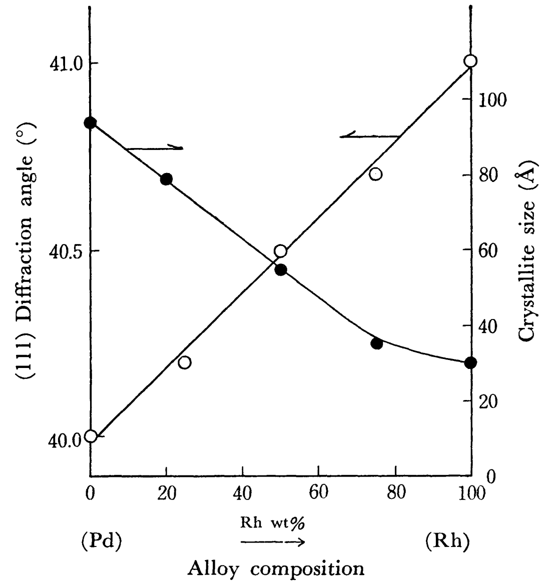

Fig. 1. X-ray diffraction angle and crystallite size of Rh-Pd supported on activated carbon.

The particle size, which was calcuated by the X-ray line-broaden method, changed smoothly in the range of about 30—100 Å. These catalysts were then used for the hydrogenation of aniline.

Hydrogenation of Aniline in Acetic Acid. The reaction was carried out in acetic acid at an atmospheric pressure of hydrogen in the temperature range from 30° to 50°C. The hydrogenation of aniline in this solvent over palladium supported on activated carbon, as has already been reported,[9] proceeded under a zero order of aniline concentration and one order of hydrogen pressure.

The influences of the hydrogen pressure on the reaction rates were investigated over a catalyst with a 15 wt% Rh content and over one with a 100% Rh content. The results are shown in Fig. 2. From this figure, it may be seen that over these catalysts the initial reaction rate was first order with respect to the hydrogen pressure. Since, in an initial reaction period, the aniline was consumed almost lineary for the reaction time, we consider that the reaction proceeds with zero order of the aniline concentration. Hence, we concluded that, over the Rh-Pd alloy series, the initial reaction rate may be expressed by the following equation, as on the Pd catalyst, when the constant weight of the catalyst is used: $V = kP_{H_2}$ Here, k denotes the rate constant.

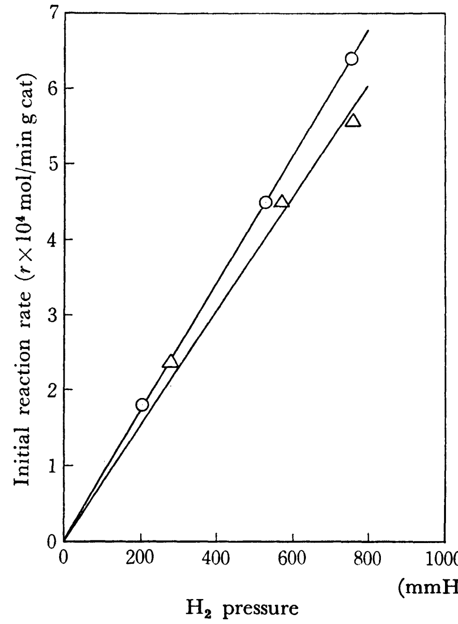

Fig. 2. Influence of the hydrogen pressure to the initial reaction rate.
—○— 15% Rh (at 50°C) —△— 100% Rh (at 40°C)

Then the initial reaction rate of the hydrogenation

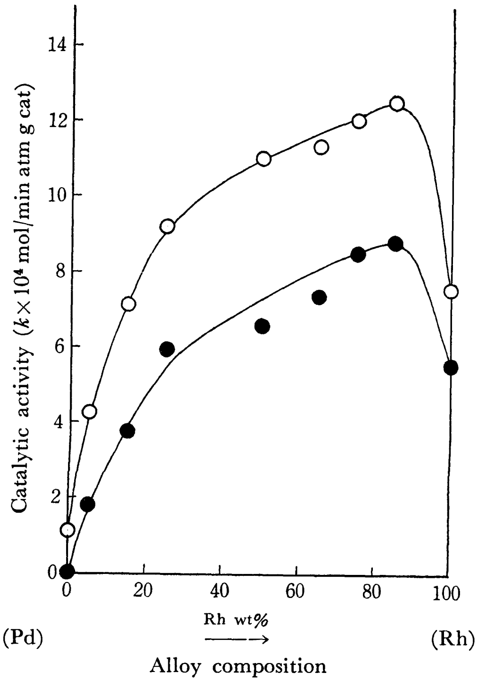

Fig. 3. Catalytic activity per g catalyst for the hydrogenation of aniline in acetic acid.
—○— at 50°C —●— at 40°C

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[10] K. Ikedate, T. Suzuki, and S. Suzuki, *Nippon Kagaku Zasshi*, **89**, 304 (1964).

was measured; the rate constant as a function of the alloy composition is shown in Fig. 3. In this alloy series the activity per unit of weight of the catalyst has a maximum at a 75—85% Rh content.

Since, in the last section, it was shown that the particle size of the metal on the carrier varied with the composition of the catalysts, it can be easily presumed that the active surface areas of the catalysts also vary with the composition. Therefore, the metal surface area on the carrier was measured by the CO adsorption method and the catalytic activity per unit surface area of the metal was calculated. The results, plotted in Fig. 4, show that the catalytic activity curve changed. The maximum of the activity shifted to about a 25 wt% Rh content, at that point the activation energy observed for this reaction had its minimum value.

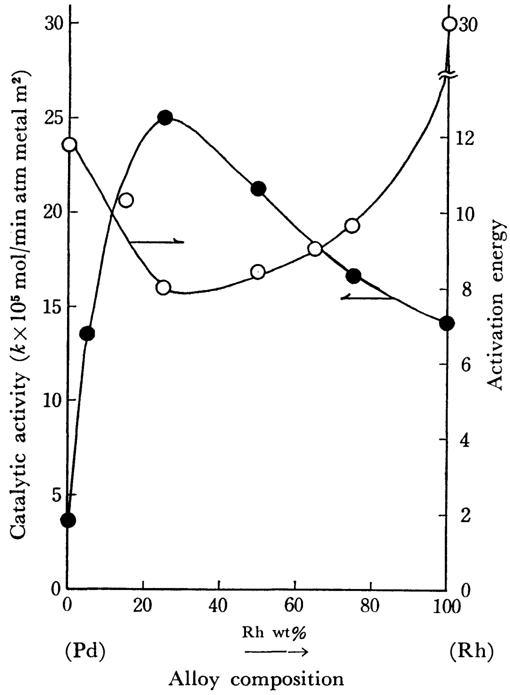

Fig. 4. Catalytic activity per unit surface area of metal on the carrier —●— and activation energy —○—.

Since the magnetic susceptibility of the Rh-Pd alloys has a maximum value at 5 atm% Rh, as has been reported in the literature,[11,12] we considered that the unpaired *d* electrons concerned with the magnetic susceptibility might influence the activity of the catalysts, as Yoshida also pointed out in his report[5,13] on Rh-Pt catalysts. However, the composition at the maximum in the magnetic susceptibility of the Rh-Pd alloy series did not completely agree with that at the maximum activity observed in this reaction, and also in his data,[5] the composition at the maximum of the magnetic susceptibility of the Rh-Pt alloy series does not coincide exactly with that at the catalytic activity maximum based on the unit of the metal surface area for the hydrogenation of phenol and benzoic acid. Therefore, it may be considered that the catalytic activity could not be explained only in terms of the magnetic susceptibility of the metal used as the catalyst.

The Reaction Mechanism on Rh-Pd Alloys in Acetic Acid. Over the catalysts of the platinum-group metals, the hydrogenation of aniline proceeds through the reaction mechanism illustrated in Fig. 5, as has been shown in our previous reports.[10,14] When acetic acid was used as the solvent, over the Rh-Pd alloy catalysts dicyclohexylamine was formed from *N*-phenylcyclohexylamine (hereafter descrived as NPC) much as over other platinum metals,[14] and the hydrogenation of the NPC formed did not occur at the same time the hydrogenation of aniline was progressing. The hydrogenation of NPC began when almost all the aniline had been consumed. In acetic acid, then, the selectivity for the formation of cyclohexylamine in the hydrogenation of aniline was influenced by two steps in the reaction mechanism: namely by k_2 and k_3, and by k_5 and k_6. The former is named the first step, and the latter, the second step (Fig. 5).

Selectivity. The reaction was investigated in acetic acid at 50°C. Since the hydrogenation of aniline was finished, the yields of the cyclohexylamine and dicyclohexylamine formed express the selectivities for the respective amines. The selectivities at the end point of the reaction are plotted as a function of the alloy composition in Fig. 6. The maximum yield of the NPC formed, an intermediate, in the course of the reaction is also plotted. In this experiment the Pd-C catalyst prepared by the adsorption method reported previously[10] was used, because the palladium catalyst which was prepared by the reduction with formaldehyde was almost inactive and so, on this catalyst, the reaction proceeds scarcely not at all. A maximum of the formation of dicyclohexylamine was shown at 20—30

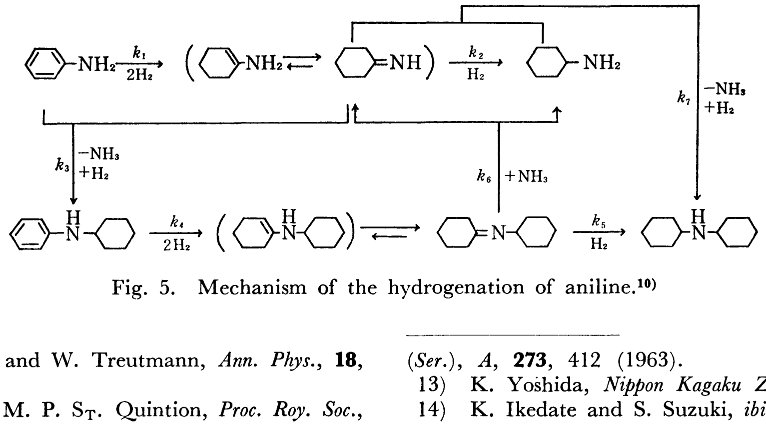

Fig. 5. Mechanism of the hydrogenation of aniline.[10]

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[11] E. Vogt, E. Oeholer, and W. Treutmann, *Ann. Phys.*, **18**, 168 (1966).

[12] A. J. Manvel and J. M. P. ST. Quintion, *Proc. Roy. Soc.*, (*Ser.*), *A*, **273**, 412 (1963).

[13] K. Yoshida, *Nippon Kagaku Zasshi*, **88**, 222 (1967).

[14] K. Ikedate and S. Suzuki, *ibid.*, **90**, 91 (1969).

wt% Rh. Then it greatly decreased beyond about 50% Rh. The formation curve of NPC showed a maximum at 50—60% Rh, but in the formation curve of cyclohexylamine a maximum was not found, while a minimum was shown at about 25% Rh.

The quantity of dicyclohexylamine formed was somewhat decreased when the reaction temperature went down. However, the formation curve observed at 40°C had a maximum at 20—30% Rh and showed almost the same shape as that observed at 50°C. Of course, the selectivity of the catalyst is influenced by the reaction temperature, but the formation curves may show almost the same tendency near 50°C.

From Fig. 6 it may be considered that the deviation between the curve of dicyclohexylamine and NPC shows the variety in the activity of each catalyst for the hydrogenating decomposition of NPC. This activity of the catalyst contributes to the second step and influences the selectivity. However, the change in the selectivity to cyclohexylamine can not be explained only this deviation.

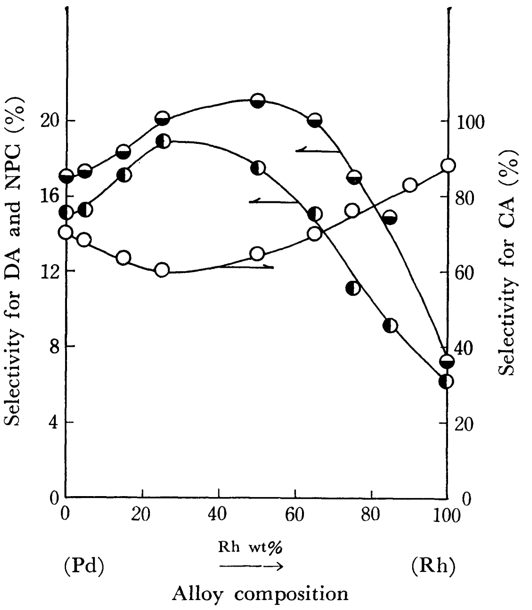

Fig. 6. Selectivity change for cyclohexylamine (CA) —○—, dicyclohexylamine (DA) —◑—, N-phenylcyclohexylamine (NPC) —◒— in acetic acid at 50°C.

The rates of the formation of cyclohexylamine and NPC, which influenced the first step, were measured. They are plotted in Fig. 7. The activity per unit weight of the catalyst for cyclohexylamine formation showed a sharp peak at about 85% Rh, while the activity for NPC formation showed a peak near 60% Rh and decreased in the region of Rh contents more than 75—85%. The activity per unit of weight of the catalyst for aniline had a maximum at 75—85% Rh, and it almost coincided with the maximum activity per unit of weight for the cyclohexylamine formation. Therefore, it was considered that, in this system, the total activity of this reaction depended mainly on the activity of the direct hydrogenation of aniline to cyclo-

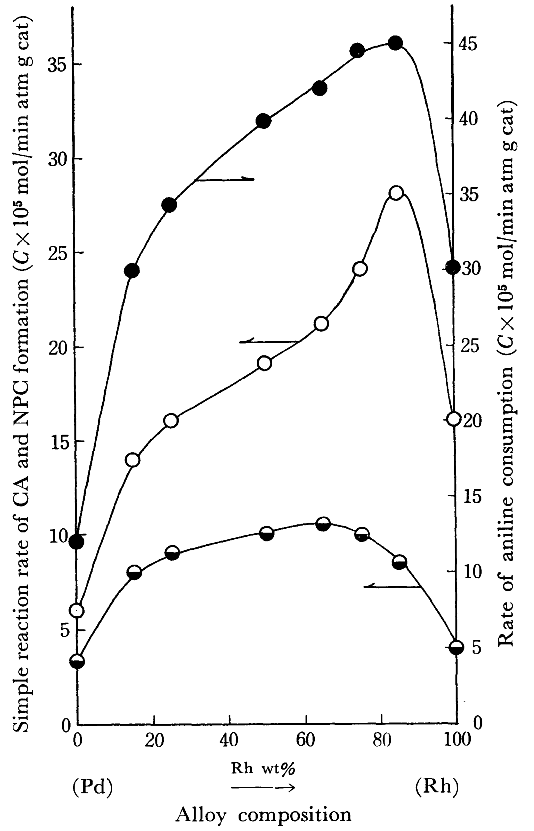

Fig. 7. Simple reaction rates of formation of cyclohexylamine —○—, N-phenylcyclohexylamine —◒—, and rate of aniline consumption —●— at 50°C, in acetic acid.

TABLE 1. RELATIONSHIP BETWEEN RATIO OF SIMPLE REACTION RATES AND SELECTIVITY FOR CYCLOHEXYLAMINE

Catalyst Ph-Pd-C (Rh content wt%)	$-\frac{dA^{b)}}{dt}\times 10^4$ mol/min atm gcat	$\frac{dNPC}{dt}\times 10^4$ mol/min atm gcat	$\frac{dCA}{dt}\times 10^4$ mol/min atm gcat	Ratio $\frac{CA}{NPC}$	Selectivity CA %
0% Rh (100% Pd)	1.2	0.33	0.60	1.8	70
15% Rh	3.0	0.80	1.4	1.8	64
25% Rh	3.4	0.90	1.6	1.8	60
50% Rh	4.0	1.0	1.9	1.9	64
65% Rh	4.2	1.05	2.1	2.0	70
75% Rh	4.4	1.0	2.4	2.4	74
85% Rh	4.5	0.85	2.8	3.3	80
100% Rh	2.4	0.40	1.6	4.0	88

a) The catalyst was prepared from H_2PdCl_4 adsorption on activated carbon.[9]
b) A: aniline

hexylamine.

In the Rh-Pd alloy series the selectivity to cyclohexylamine did not have a maximum and showed a minimum at about 25% Rh, as is shown in Fig. 6. Here, the selectivity can not be interpreted only on the basis of the activity of the catalyst. The ratios between the simple reaction rate of cyclohexylamine formation and that of NPC were then calculated; they are collected in Table 1. In Table 1 the rate of the formation of each substance is shown as an activity per unit of weight of the catalyst, but the ratio between the simple reaction rates does not have an order with respect to the catalyst. Therefore, it should be the same if it is obtained from the rates per unit of the surface area of the metal on the catalyst.

Beyond 25% Rh to 100% Rh the value of this ratio increased gradually with the increase in the Rh content. Between the selectivity to cyclohexylamine and this ratio, a good proportional relationship was observed. It was considered that, on these catalysts, the selectivity to cyclohexylamine was governed mainly by the first step under the present reaction conditions. For example, in spite of the lower activity over 100% Rh than over the other alloy catalyst, a better selectivity to cyclohexylamine was shown at 100% Rh. This can be explained on the basis of the fact that in the first step, the ratio for rhodium is the largest in the Rh-Pd alloy series. Therefore, it is clear that the selectivity did not depend only on the simple catalytic activity for the hydrogenation, but was also determined by the relative activity for the simple reactions which were concerned with the selectivity.

From 0% Rh (*viz.*, 100% Pd) to 25% Rh, the ratios between the rate of cyclohexylamine and NPC formation were almost constant. This signifies that, over catalyst in this composition range, the rate of the formation of cyclohexylamine increased to the same degree as that of NPC. However, the selectivity to cyclohexylamine decreased. Hence, it was considered that, in this composition range, the catalytic activity which was connected with the second step, mainly influenced the selectivity.

Influence of the Different Method of Catalyst Preparation. Changes in the selectivity and the activity were investigated over Rh-Pd catalysts prepared by two different methods: one was prepared by reduction with formaldehyde, and the other by the co-precipitation of these metals. A catalyst with a 25% Rh content was used, and the reaction carried out under the conditions described above.

The results are shown in Table 2. The total activity of the catalyst prepared by reduction with formaldehyde for the hydrogenation of aniline was higher than that of the catalyst prepared by the co-precipitation. Further, the activity for the hydrogenation of benzene had the same tendency as that described above. Hence, we expected that the former catalyst would have the higher activity for the benzene nucleous of aniline and would give the better selectivity to cyclohexylamine. However, the amount of NPC formed was almost the same in both cases; if anything, that of cyclohexylamine was somewhat lower on the former than on the latter. That the same amount of NPC was formed shows that, in the first step, the ratio between the simple reaction rates (*viz.*, k_2 and k_3) was almost the same over both the catalysts. Judging from the small difference in the amount of dicyclohexylamine formed, it was considered that, in this case, the preparation of the catalyst influenced the hydrogenating decomposition rate of NPC, although the difference between them in the amount of cyclohexylamine formed was not very large (about 6%).

Therefore, it may be said that the selectivity of the catalyst does not differ much when the composition of the catalyst is the same. That is, this suggests that,

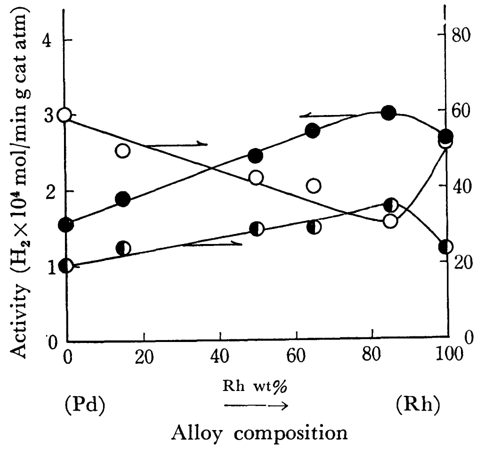

Fig. 8. Hydrogenation of aniline in cyclohexane at 50°C. —●— rate of hydrogenation, —○— cyclohexylamine, —◐— dicyclohexylamine.

TABLE 2. HYDROGENATION OF ANILINE AND BENZENE OVER THE SUPPORTED Rh–Pd CATALYSTS PREPARED BY THE DIFFERENT METHOD AT 50°C IN ACETIC ACID

Catalyst	Method of preparation	Rate of hydrogenation		Products in the hydrogenation of aniline		
		Benzene H_2 adsorbed $\times 10^4$ mol/min atm g cat	Aniline H_2 adsorbed $\times 10^4$ mol/min atm g cat	Intermediate[b)] NPC (%)	Final products[a)] DA (%)	CA (%)
25 wt% Rh	Reduction with formaldehyde	5.0	8.7	20	19	62
	Co-precipitation hydroxide	3.0	6.0	21	16	68

a) Mol. percent of DA and CA based on the moles of aniline consumed at the end point of the reaction.
b) Mol. percent of the maximum amount of NPC formed in the course of hydrogenation.

at a given composition of the catalyst, the ratios of the simple reaction rates are almost the same.

Hydrogenation of Aniline in a Cyclohexane Solvent. With the intention of considering the hydrogenation of free aniline over Rh-Pd catalysts, the reaction was carried out in a cyclohexane solvent. The results are shown in Fig. 8. The catalyst prepared by the reduction with formaldehyde was used. The catalysts were inhibited rapidly by the amine formed in the hydrogenation. The catalytic activity was then obtained from the initial reaction rate. The activity per g of catalyst showed a maximum at 75—85% Rh, the same composition as that observed in acetic acid.

The curves of the selectivity to dicyclohexylamine and cyclohexylamine in the non-polar solvent were different from those in acetic acid. The selectivity to dicyclohexylamine showed a maximum at the activity maximum. On the whole, the formation of dicyclohexylamine in cyclohexane was higher than that in acetic acid.

On the other hand, in a cyclohexane solvent the formation of NPC was extremely small as compared with that in an acetic acid solvent; at 15% Rh, the NPC formed was about 5 mol% of the material; at 85% Rh, NPC was barely perceived by gas chromatography with a thermal conductivity detector, and, as was reported in a previous paper,[14] at 100% Rh it was not found at all. Hence, it was clear that, in the hydrogenation of free aniline, dicyclohexylamine was formed mainly by the combination of imine and cyclohexylamine; this process is shown as k_7 in Fig. 5.

Thus, over the Rh-Pd alloy catalysts the process of the formation of dicyclohexylamine in cyclohexane was different from that in acetic acid. Therefore, the curves of the selectivity to dicyclohexylamine are different in the two solvents. From this, it was considered that the amine and imine which were formed in the hydrogenation, were in different adsorption states over the catalysts in the two solvents.