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Preparation of Highly Active Palladium Catalyst Supported on Silica by Ion Exchange Method

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Palladium catalyst supported on silica prepared by an ion exchange method using a low concentration of ammonia solution of $PdCl_2$ exhibited high and stable activity in the hydrogenation of benzene. It was found that the activity and stability of the catalyst were strongly dependent on concentration of ammonia of the ion exchange solution.

Supported palladium catalysts are usually prepared by an ion exchange method, when the hydroxyl groups present on the surface of the support such as silica gel. It is well known that an ion exchange is an effective preparation method in order to increase the dispersion of supported metal and the activity of catalyst.[1-3] The activity of the supported palladium catalyst, prepared by an ion exchange method, was gradually decreased with the process time in the hydrogenation of benzene. However, only a few investigations have been reported about the preparation method to suppress the deactivation of catalyst.[4] In this paper, we wish to report the effect of concentration of ammonia of the ion exchange solution on the catalytic activity. It was proved that the catalyst prepared using a low concentration of ammonia of the ion exchange solution shows high and stable catalytic activity in the hydrogenation of benzene.

The palladium catalysts supported on silica were prepared by the ion exchange method with various aqueous ammonium solution (28-0.5%) of $PdCl_2$ for 20 h. $PdCl_2$ was not sufficiently soluble in aqueous ammonium solution less than 0.5%. The support was silica gel obtained from Fuji Davison Chemical Co. (CARIACT-10). The ion exchange of the catalyst was done at 25 °C. After the ion exchange, the sample was filtered and then dried at 100 °C for 24 h. The catalysts were calcined at 200 °C for 2 h and subsequently reduced in a stream of hydrogen gas at 150 °C for 2 h. Over the all catalysts, palladium content was determined by chelate titration of the filtrate and palladium particle size was measured by CO pulse method. The catalytic activity was proved by the rate constant of benzene hydrogenation.[5)] The reaction was carried out by using a conventional flow micro reactor at 140 °C and 1 atm. The reactant composition was analyzed by gas chromatography with BX-10 column.

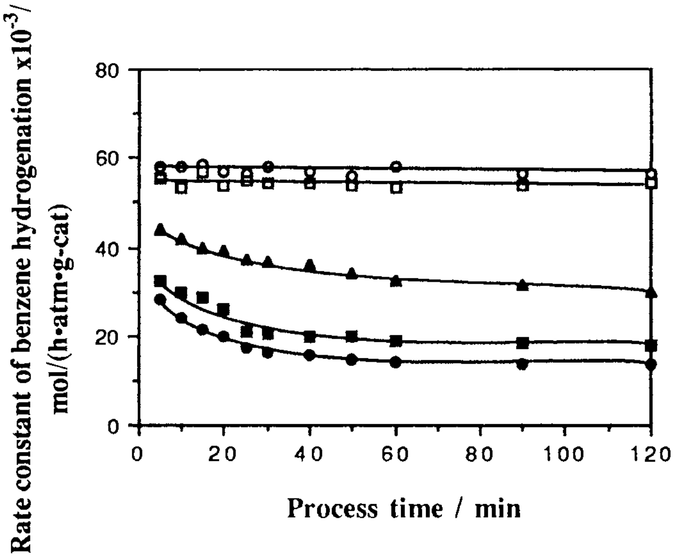

Fig.1. The effect of ammonia concentration of the ion exchange solution on the catalytic activity.
Catalyst weight; 0.8 g, Flow rate; 0.3 mol/h, Mol ratio of feed; H_2:C_6H_6 =10:1.
Concentration of ammonia of the ion exchange solution
—○— 0.5%
—□— 1.0%
—▲— 3.0%
—■— 14.0%
—●— 28.0%

Figure 1 shows the effect of ammonia concentration of the ion exchange solution on the catalytic activity. The activity of the catalyst prepared using 28% ammonia solution was decreased rapidly with the process time and the activity after 1 h reduced to one-half of its initial value. From CO pulse measurement, palladium particle size of the catalyst before the reaction was about 14 Å, which was unchanged after the reaction. It was found that the deactivation of the catalyst was independent on the palladium particle size. The initial activity of the catalysts were greatly increased with the decrease of ammonia concentration of the ion exchange solution. Further, the catalyst prepared using aqueous ammonia solution below 1.0% exhibited the high initial activity and it was little decreased during the reaction for 2 h. It has become apparent that the activity and stability of Pd/SiO_2 catalysts were strongly affected by ammonia concentration of the ion exchange solution. Figure 2 shows the DTA curves of the Pd/SiO_2 catalysts without calcination treatment. The catalysts prepared using 28% or 14% aqueous ammonium solution (a and b) show a peak at 300 °C when the DTA measurement were carried out in a stream of air, however, this peak disappeared in a stream of He as shown in Fig. 2 (e). This is the direct evidence that the peak at 300 °C was based on ammonia combustion.[3)] The catalysts prepared using a low ammonia concentration (below 1.0%) did not show a peak around 300 °C based on ammonia combustion. The amount of ammonia in the catalyst was strongly dependent on the concentration of ammonia of the ion exchange solution. Since the catalysts used for the reaction were calcined at 200 °C, a large amount of ammonia should remain in the catalyst prepared using a high ammonia concentration. It is worth noting that the catalytic activity and stability were strongly inhibited by ammonia remaining in the catalyst. However, this reason is not clear at present.

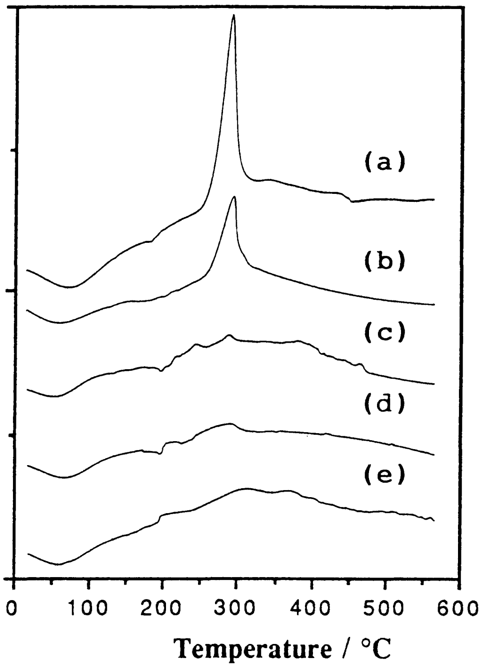

Fig.2. DTA curves of the catalysts. Concentration of ammonia of the ion exchange solution: (a):28%, (b):14%, (c):1.0%, (d):0.5%. (e) was mesured (a) in He Flow.

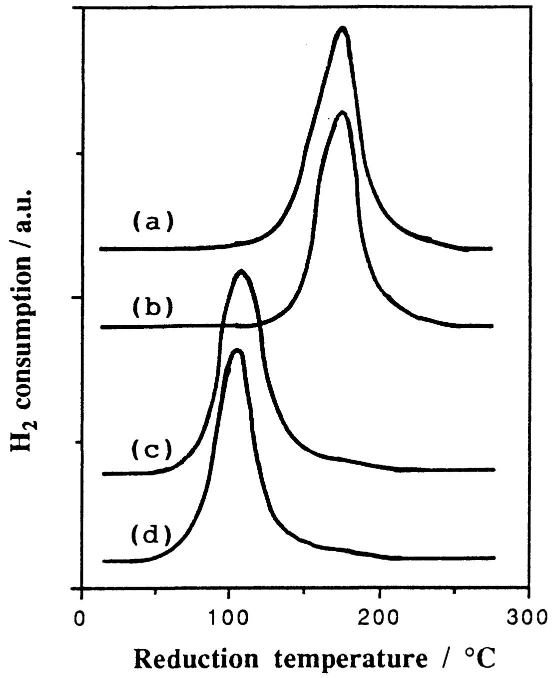

Fig.3. Temperature programed reduction patterns of the catalysts. Concentration of ammonia of the ion exchange solution; (a): 28%, (b): 14%, (c): 1.0%, (d): 0.5%.

Figure 3 shows temperature programmed reduction patterns of the catalysts calcined at 200 °C. The reduction peaks of the catalysts prepared using 28% and 14% aqueous ammonium solution were observed at around 180 °C. On the other hand, the palladium oxide of the catalysts prepared using aqueous ammonium solution below 1.0% were reduced at 110 °C. It might be the reason that the decrease of ammonia concentration of the ion exchange solution has considerably weakened the interaction between the aminepalladium complex and silica support. It is well known that the metallic palladium produced at low reduction temperature contains lattice defects which act as high active sites.$^{4,6)}$ The catalysts prepared using a low concentration of ammonia solution can be reduced easily at low temperature and contain a number of lattice defects.$^{7)}$ From this reason, they exhibited high catalytic activity. These results suggested that the state of aminepalladium complexes on the silica support were strongly affected by concentration of aqueous ammonia of the ion exchange solution. Bozon-Verduraz suggested that an exchange between NH_3 and H_2O ligands of aminepalladium complexes $[Pd(NH_3)_n(H_2O)_{4-n}]^{2+}$ $(n \leq 4)$ adsorbed on silica surface takes place during washing and drying.8) Furthermore, Summers and Ausene studied the exchange ligands of the noble metal complexes (Pt, Pd, Rh, Ru, Au, Ir) adsorbed on carrier surface.9) They suggested that the ion exchange process involves the reaction of the noble complex with surface site and a concomitant displacement of ligands from its coordination sphere when using complexes containing Cl^- ligands. Taking into account these suggestions, we considered that the exchange reaction between NH_3 and H_2O ligands of aminepalladium complex was promoted by the decrease of the ammonia concentration of the ion exchange solution. In conclusion, the catalytic activity and stability are strongly dependent on the concentration of ammonia of the ion exchange solution. Very high catalytic activity and stability in the hydrogenation of benzene can be achieved when the catalyst is prepared by an ion exchange method using a low ammonia concentration of the ion exchange solution.

References

1) H. Arai, Shokubai, 19, 365 (1977).
2) P. C. Aben, J. Catal., 10, 224 (1968).
3) E. Echigoya, I. Furuoya, and K. Morikawa, Kogyo Kagaku Zasshi, 71, 1774 (1968).
4) I. Furuoya, T. Shirasaki, E. Echigoya, and K. Morikawa, Kogyo Kagaku Zasshi, 72, 1431 (1969).
5) T. Fujitani, T. Kuroda, and E. Echigoya, Nippon Kagaku Kaishi, 1990, 12.
6) I. Furuoya and T. Shirasaki, Kogyo Kagaku Zasshi, 72, 1223(1969).
7) The lattice defects of the metallic palladium prepared using a low concentration of aqueous ammonium solution were confirmed by X-ray analysis.
8) F. Bozon-Verduraz, A. Escard, and B. Pontvianne, J. Catal., 53, 126(1978).
9) C. J. Summers and A. S. Ausen, J. Catal., 52, 445(1979).

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