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Preparation of Metallic Palladium Catalysts with Thermally Stable Surface Areas and Activities

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Pd metal catalysts were prepared by the reaction of palladium(II) chloride with sodium aluminate at pH 6—10. The Pd catalysts prepared at pH 10 contained only small amounts of Al (0.14 wt%), were the most thermally stable, and kept large specific surface areas and high catalytic activities in the hydrogenation of nitrobenzene even after hydrogen treatment at high temperatures up to 380 °C.

In the preparation of heterogeneous catalysts, attention has been focused on the catalyst's active life as well as its activity and selectivity in various catalytic reactions. For practical purposes, deactivation of the catalyst is one of the most important problems related to catalytic functions and is often observed with metallic catalysts in the sintering of a fine structure on the catalyst surface or in the agglomeration of particles caused by a large reaction heat or by a high temperature for producing the metallic surface. For instance, small amounts of alumina, magnesia, and silica as the stabilizers (the structural promoters) were contributed to prevent the agglomeration of magnetite. However no studies on such structural promoter effects have been done with noble metal catalysts for hydrogenation.[1)]

The sintering or agglomeration of a metallic catalyst takes place especially easily with Pd catalysts at high reduction temperatures or under vigorous reaction conditions because the Pd metal has a relatively low sintering point compared with those of other platinum metals.[2)] The sintered Pd metal catalysts generally lose their catalytic abilities.

Unsupported metallic Pd catalysts are prepared by several well-known methods.[3)] For instance, a Pd hydroxide-black catalyst is easily prepared by reduction of palladium hydroxide which is obtained, for example, by the reaction of caustic alkali and palladium(II) chloride.[4,5b)] The Pd hydroxide-black catalyst worked efficiently in the hydrogenation of various organic compounds under mild conditions.[5)] However, the catalytic ability of the Pd hydroxide-black catalyst, which provided excellent results in the hydrogenation of nitrobenzene to aniline, sharply decreased when the catalyst was treated with hydrogen or employed at high temperatures. Thus, a reproducible preparation of an effective catalyst which is stable at high temperatures is especially difficult with unsupported Pd metal catalysts.

We have recently found it possible to prepare highly stable Pd metal catalysts under a high reduction temperature by the reaction of palladium(II) chloride with sodium aluminate. The Pd hydroxide thus prepared was reduced with hydrogen at various temperatures and the activity of the resulting metal catalyst was investigated in the hydrogenation of nitrobenzene and *p*-cresol.

Experimental

Preparation of Catalyst: Pd hydroxide was prepared by the reaction of palladium(II) chloride with aqueous sodium hydroxide or with aqueous sodium aluminate. The reaction media were finally controlled to pH 6, 8, or 10 for each reaction. As an example, to palladium(II) chloride (2.0 g, 0.0113 mol) placed in a 1000 ml beaker were added 1—2 drops of 37% hydrochloric acid and 500 ml of distilled water. The mixture was stirred at about 80 °C until the palladium(II) chloride was dissolved. While the acidic palladium(II) chloride solution in the beaker was stirred mechanically, the pH of the stirred solution was brought to 6, 8, or 10 by slowly adding aqueous 1 M sodium hydroxide (1 M = 1 mol dm^{-3}) or sodium aluminate from a buret. The precipitates thus obtained were reduced in distilled water for 30 min at room temperature under 0.2—0.3 MPa of hydrogen pressure in a Parr hydrogenation apparatus. The metal blacks thus produced were washed with distilled water until the washing became neutral, and then dried in a desiccator under vacuum at room temperature. The catalyst was donated as Pd(N) or Pd(A), when sodium hydroxide or sodium aluminate, respectively, was used as precipitant. The small amounts of Na and Al contained in the Pd metals were determined by means of AAS (Shimadzu AA670) and ICP-AES (Kyoto Koken UOP-1 Mark II).

Measurements of Surface Area and Particle Size: Prior to the determination of the specific surface area, each Pd metal was treated with hydrogen using a Shimadzu FLOW SORB II 2300 (SFS II-2300) instrument at 25—380 °C for 1 h, and then their specific surface areas were determined with the SFS II-2300 by the B. E. T. method using nitrogen at −195 °C as the adsorbate. In addition, the Pd metals prepared were sintered in a muffle furnace in the presence of air at about 650 °C for 1 h and the specific surface areas of the sintered metals were determined after reduction by hydrogen using the SFS II-2300 at 25 °C for 1 h. The distributions of the particle size of the type A and N catalysts obtained at pH 10 were determined by a Horiba LA-700.

In order to observe the state of the particles directly, the catalysts were examined by means of electron microscopy using a Shimadzu SEM Model 330.

The crystallite size of the Pd metal catalysts was calculated from the half-width of the Pd (111) plane in their X-ray (Rigaku Denki, RINT 2000) diffraction patterns.

Hydrogenation: Freshly distilled nitrobenzene (0.1 g) was hydrogenated in 20 ml of *t*-butyl alcohol (Guaranteed Reagent Grade) at 40 °C at a hydrogen pressure of 0.1 MPa over 3 mg of each Pd catalyst.

Freshly distilled *p*-cresol (1.1 g) was hydrogenated in 10 ml of *t*-butyl alcohol at 100 °C of a hydrogen pressure of 5 MPa over 30 mg of each Pd metal catalyst for 3 h.

Product Analysis: In the hydrogenation of nitrobenzene, the reaction mixture was analyzed with a gas chromatograph equipped with a flame ionization detector: a 3 m×3 mm i.d. column of 10 wt% PEG 20M on 60—80 mesh chromosorb WAW at 160 °C. In the hydrogenation of *p*-cresol, the products were analyzed on a gas chromatograph using a 25 m×0.25 mm i.d. capillary column (BP-1, correspondence to OV-1) at 50—200 °C.

Results and Discussion

The surface areas and the amounts of Na and Al of the catalysts are listed in Table 1 for the catalysts prepared from the solutions controlled at different pHs and treated at various reduction temperatures. The surface areas of the type A catalysts were increased by increasing the concentration of the sodium aluminate solution used to obtain a higher precipitation pH, whereas the surface area of the type N catalysts decreased with increasing concentration of the sodium hydroxide solution. The surface areas of the type N catalysts decreased markedly with an increase of the reduction temperature as Sermon stated previously,[6] but the surface areas of the type A catalysts scarcely varied with various reduction temperatures. Small amounts of Na and Na and Al were always contained in the type N or type A catalysts, respectively. The amount of Na in the type N catalysts increased considerably from 3.7 to 86.2 ppm with an increase in the precipitation pH from 6 to 10. The type A catalysts contained Al in greater amounts than Na. However, the greatest amount of Al found in the catalyst prepared at pH 10 was only 1400 ppm (0.14%) (See Table 1).

When they were treated under hydrogen at 25 °C, the median particle diameter was about 9.5 μm for both the type A and N catalysts. However, the median particle diameter in the type N catalyst increased to 17.4 μm on hydrogen treatment at 200 °C, while the type A catalyst held the small median particle diameter even after hydrogen treatment at 200 °C.

The relationship between the particle size and the reduction temperatures was further observed by means of electron microscopy. In the type N catalysts, finely divided particles were observed after treating with hydrogen at 25 °C. However, coarse particles resulted from treating with hydrogen at 200 °C (Fig. 1, a and b).

Table 1. Surface Areas and the Na and Al Contents of Pd Catalysts

Catalyst[a]	pH for Precipn.	Red. temp °C	Surface area $m^2\,g^{-1}$	Amount of Na and Al in catalyst (ppm)	
				Na	Al
		25	34.5		
Pd-N	6	100	13.8	3.7	
		200	2.0		
		25	26.6		
Pd-N	8	100	16.9	34.6	
		200	1.1		
		25	21.0		
Pd-N	10	100	10.5	86.2	
		200	3.0		
		25 (650[b])	1.0		
		25	43.2		
Pd-A	6	100	52.3	9.5	1360
		200	53.6		
		25	120		
Pd-A	8	100	114	8.9	1240
		200	116		
		25	141		
Pd-A	10	100	145	13.4	1400
		200	139		
		25 (650[b])	89.0		

a) Pd-type N and Pd-type A indicate the catalysts prepared with aqueous sodium hydroxide and sodium aluminate, respectively, as precipitant. b) The figure in parentheses indicates the temperature at which the catalyst was treated in a muffle furnace in the air.

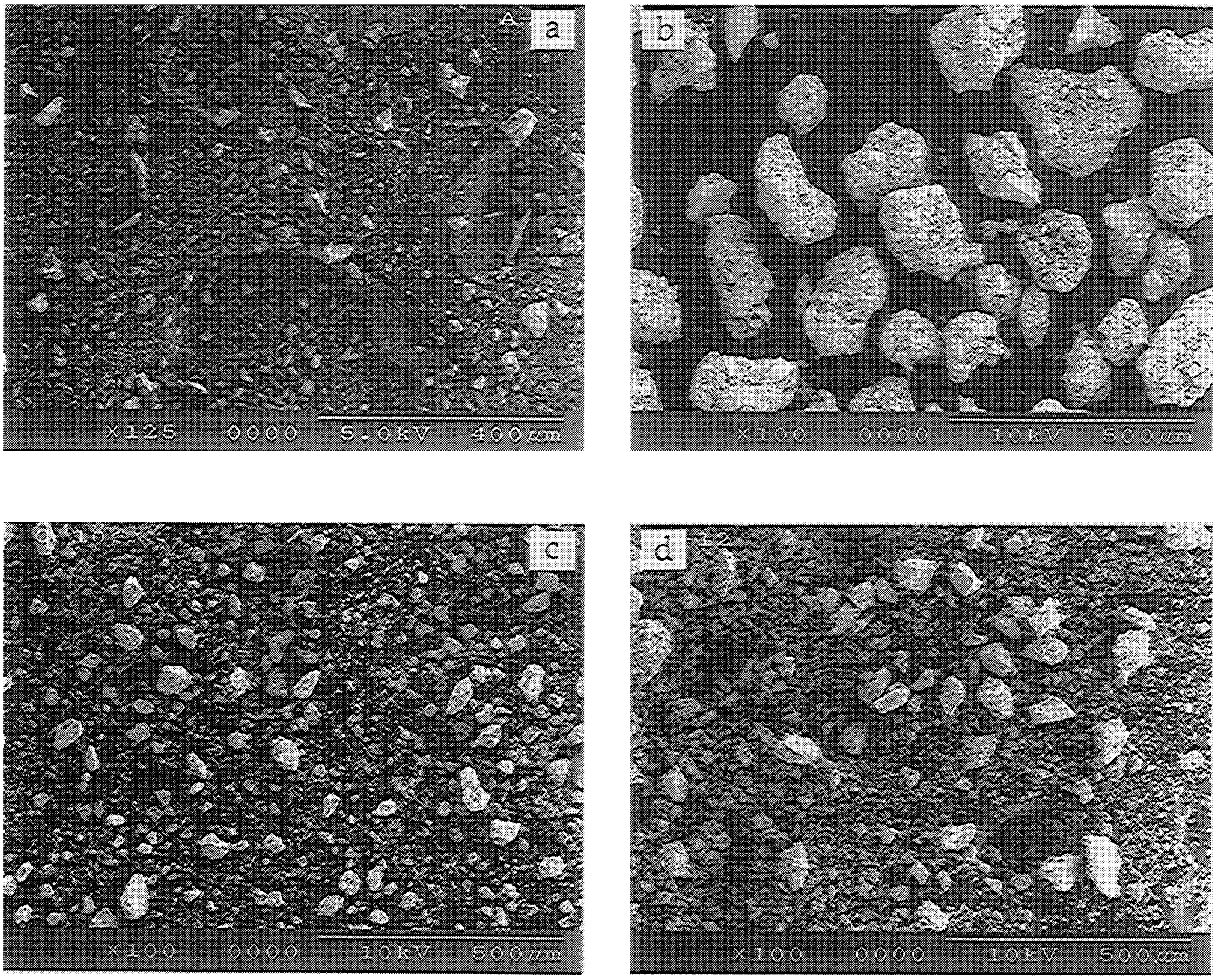

Fig. 1. Electron micrographs of Pd catalysts. a: the type N catalyst treated with H_2 at 25 °C; b: the type N catalyst treated with H_2 at 200 °C; c: the type A catalyst treated with H_2 at 25 °C; d: the type A catalyst treated with H_2 at 200 °C.

On the other hand, such a detectable particle size growth was not observed after hydrogen treatment at 200 °C for the type A catalyst (Fig. 1, c and d).

In Fig. 2 the crystallite size of the N and A catalysts is plotted against the reduction temperatures for the catalysts prepared at pH 10. It is seen that, compared with the type A catalysts, the type N catalysts are remarkable for the growth of their crystallite size at high temperature reductions.

The catalytic activities in nitrobenzene hydrogenation of these catalysts are shown in Fig. 3 for the catalysts prepared at pH 10. The type A catalyst treated at high reduction temperatures did not lose any appreciable activity in the hydrogenation of nitrobenzene to aniline, compared to the catalyst treated at 25 °C. In contrast, the activities of the type N catalysts decreased markedly with the increase of the reduction temperature.

High pressure hydrogenation of *p*-cresol with the type N catalyst (treated with hydrogen at 25 °C) afforded about 15% of 4-methylcyclohexanol after 1 h, whereas the 4-methylcyclohexanol was formed in a 60% yield with the type A

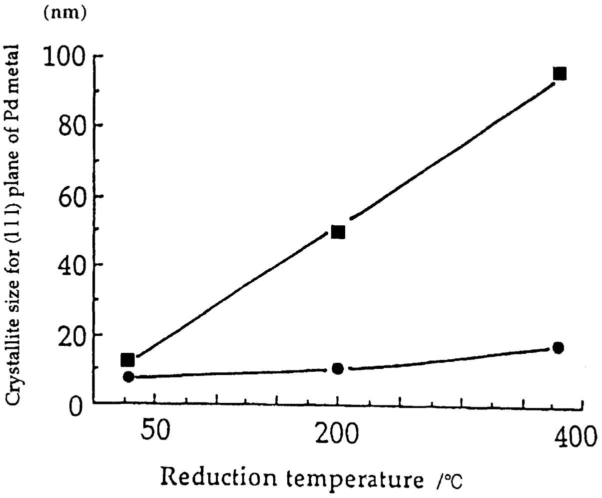

Fig. 2. Influence of reduction temperature on the crystallite size of type N and A catalysts. ■: Type N catalysts, ●: Type A catalysts.

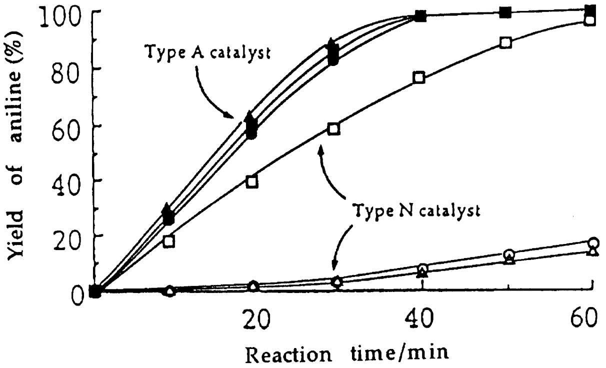

Fig. 3. Hydrogenation of nitrobenzene to aniline[a)] over type N and type A catalysts prepared at pH 10. a) Nitrobenzene (0.1 g) was hydrogenated in *t*-BuOH (20 ml) at 40 °C under hydrogen pressure of 0.1 MPa over each 3 mg of Pd catalyst. ■, □: reduced at 25 °C, ▲, △: reduced at 200 °C, ●, ○: reduced at 360 °C.

catalyst (treated with hydrogen at 25 °C) under the same conditions.[7)] The type A catalyst was approximately 4 times as active as the type N catalyst.

Thus, the results described above show that the small amounts of Al contaminating the type A catalysts acted to retain large surface areas and high catalytic activities at a high reduction temperature. We are currently researching the function and the state of Al in the Pd metal catalysts.

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7) *p*-Cresol (1.1 g) was hydrogenated with 30 mg of type A or type N catalysts in *t*-butyl alcohol (10 ml) at 100 °C and 5 MPa of initial hydrogen pressure.