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Comparison of dinitrodiamminepalladium with palladium nitrate as a precursor for Pd/SiO$_2$ with respect to catalytic behavior for ethane hydroformylation and carbon monoxide hydrogenation

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The catalytic behavior of the two kinds of Pd/SiO$_2$ catalysts prepared from dinitrodiamminepalladium and palladium nitrate are compared for ethene hydroformylation and carbon monoxide hydrogenation. The catalyst prepared from dinitrodiammine-palladium, on which very fine particles of Pd were observed, showed high activity for ethene hydroformylation. On the other hand, the catalyst prepared from palladium nitrate, on which relatively large particles of Pd were observed, showed high activity for CO hydrogenation.

KEY WORDS: Pd/SiO$_2$ catalysts; ethene hydroformylation; carbon monoxide hydrogenation.

1. Introduction

Effects of metal particle size on catalytic behavior of supported metal catalysts have been recognized to be one of the important subjects in the field of supported metal catalysts for a long time [1–6]. In general, the number of active sites is determined with the hydrogen chemisorption data. It has been commonly pointed out, however, that the distribution pattern of metal particle size should be clarified in addition to the adsorption profiles. We have previously reported that Pd/SiO$_2$ catalysts prepared from dinitrodiamminepalladium showed higher Pd dispersion than those from palladium nitrate [7]. The catalytic activity of the former for ethene (C_2H_4) hydroformylation was high compared with that of the latter. However, we did not clarify the details of the particle size distribution on them. In the present work, X-ray diffraction measurements and transmission electron microscope measurements were performed in order to clarify the particle size distribution. In addition, catalytic behavior of the two-types of Pd/SiO$_2$ for carbon monoxide (CO) hydrogenation has been compared with that for C_2H_4 hydroformylation.

2. Experimental

Catalysts, which contained 2.0 wt% of Pd as metal, were prepared by a conventional impregnation method from palladium nitrate (Pd(NO$_3$)$_2$, dissolved in H_2O) or dinitrodiamminepalladium (Pd(NO$_2$)$_2$(NH$_3$)$_2$, dissolved in aqueous ammonia). Four kinds of silica gel supports used were obtained from Fuji Silysia Chemical Ltd. Values for specific surface area and average pore diameter on them were as follows; No.1 (300 m^2/g, 10 nm), No. 2 (190 m^2/g, 15 nm), No. 3 (100 m^2/g, 30 nm) and No. 4 (90 m^2/g, 50 nm). All catalysts were reduced with hydrogen (100 cc(STP)/min) at 773 K for 3 h. In the following part, the catalysts prepared from Pd(NO$_3$)$_2$ on SiO$_2$ of Nos. 1, 2, 3 and 4 are represented by A-1, A-2, A-3 and A-4, respectively. In the same way, the catalyst B-1 was prepared from Pd(NO$_2$)$_2$(NH$_3$)$_2$ using SiO$_2$ of No. 1.

The apparatus used for C_2H_4 hydroformylation and for CO hydrogenation was a fixed-bed type reactor with a continuous flow at atmospheric pressure. The re-treatment of the catalyst with hydrogen-flow (50 cc(STP)/min) at 673 K for 3 h was followed by the reaction (C_2H_4 hydroformylation:with a mixture of He–C_2H_4(20%)–CO(20%)–H_2(20%) (flow rate = 100 cc (STP)/min) at 373 K, CO hydrogenation:with a mixture of He–CO(10%)–H_2(30%) (flow rate = 100 cc(STP)/min) at 623 K). The conversion of reactants was kept below 20% in every catalytic run by controlling the amounts of catalyst used. The concentrations of products in the effluent gas stream were determined by gas chromatography.

The amounts of hydrogen chemisorbed were measured at 298 K by a conventional static method using a glass-made apparatus connected to a vacuum line. The first measurement of H_2 adsorption was followed by the evacuation of the sample for 10 min at 298 K, and then the second measurement was performed. The sum of physical and chemical adsorption was estimated by extrapolating the flat part of the first adsorption isotherm to the zero of the equilibrium pressure for adsorption. The amount of physically adsorbed H_2 was

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estimated from the second isotherm in the same way for the estimation of total adsorption. The amount of chemically adsorbed H_2 (denoted by q_H) was estimated by subtracting the physical adsorption from the total adsorption. The values for %-exposed (denoted by D_H) were evaluated by $(2q_H/\text{total Pd-atoms}) \times 100$.

X-ray diffraction (XRD) measurements of the sample were carried out using a Rigaku RINT 1200 spectrometer. Transmission electron microscope (TEM) measurements of the samples were carried out using Hitachi H9000NAR electron microscope. X-ray absorption fine structure (XAFS) measurements were carried out using a TECHNOS EXAC 820 spectrometer with a transmission mode.

3. Results and discussion

Results of the H_2 chemisorption measurements were summarized in table 1. Both of palladium compounds, $Pd(NO_2)_2(NH_3)_2$ and $Pd(NO_3)_2$, showed the higher value for Pd-dispersion (D_H) on the support with the narrower pore size. Comparing two compounds on the same SiO_2, the D_H value on the sample prepared from $Pd(NO_2)_2(NH_3)_2$ was found to be higher than that from $Pd(NO_3)_2$.

In C_2H_4 hydroformylation, propanal (propionadehyde) and ethane were observed to be the reaction products. In CO hydrogenation, methane and H_2O were produced, whereas we did not measure the amount of H_2O formed. On both reactions, the catalytic activities gradually decreased with time-on-stream. In the present work, the activities were estimated from the reaction rates at time-on-stream of 5 h. Results on the catalytic performances are also summarized in table 1, where both of the values for the activity per unit gram of catalyst (*r*) and turnover frequency (TOF) are shown. It is noteworthy that the catalysts prepared from $Pd(NO_2)_2(NH_3)_2$ (catalysts of series B) showed much higher activity than those prepared from $Pd(NO_3)_2$ (catalysts of series A) in C_2H_4 hydroformylation. On the other hand, the activities for CO hydrogenation on A were observed to be much higher than those on B. Thus, the catalytic behavior on catalyst A was observed to be very different from that on catalyst B.

After the first catalytic run for 8 h, the catalyst bed was purged with He stream for 6 h. The re-treatment of the catalyst with H_2 (100 cc(STP)/min) at 573 K for 3 h was followed by the second catalytic run under the same reaction conditions. The catalytic activities on the re-used catalysts (A-1-(2), A-4-(2), B-1-(2) and B-4-(2)) are also shown in table 1. The differences between the activities on the first and the second run were observe to be very small in every case, indicating almost no appreciable changes in the oxidation states of Pd on the two kinds of catalysts during the reactions. XAFS measurements were performed on the catalysts of A-1

Table 1

Results of the H_2 chemisorption measurements and Catalytic activities of C_2H_4 hydroformylation and CO hydrogenation over Pd/SiO_2 catalysts

Catalyst	H_2-adsorbed	%-exposed	C_2H_4 hydroformylation				CO hydrogenation	
	q_H (10^{-6} mol g(cat)$^{-1}$)	D_H (%)	r(PA) (10^{-6} mol min^{-1} g(cat)$^{-1}$)	r(E) (10^{-6} mol min^{-1} g(cat)$^{-1}$)	TOF(PA) (10^{-2} min^{-1})	TOF(E) (10^{-2} min^{-1})	r(M) (10^{-5} mol min^{-1} g(cat)$^{-1}$)	TOF(M) (min^{-1})
A-1-(1)	18.4	19.6	0.82	41.2	2.23	112	2.59	0.70
A-1-(2)[a]			0.76	39.8	2.07	108	2.63	0.71
A-2	12.2	12.9	0.43	27.2	1.77	112	1.89	0.78
A-3	9.6	10.2	0.32	26.9	1.64	140	1.04	0.54
A-4-(1)	6.2	6.6	0.24	17.8	1.97	143	0.51	0.41
A-4-(2)[a]			0.25	18.2	2.02	147	0.48	0.38
B-1-(1)	35.4	37.7	11.4	403	16.1	569	0.62	0.09
B-1-(2)[a]			9.66	438	13.6	619	0.54	0.08
B-2	17.5	18.6	3.77	192	10.8	550	0.35	0.10
B-3	11.2	11.9	1.93	130	8.62	582	0.28	0.12
B-4-(1)	8.1	8.6	1.34	84.9	8.31	527	0.17	0.10
B-4-(2)[a]			1.13	83.2	7.02	517	0.16	0.10

[a] The results on the re-generated catalysts by the treatment with H_2 at 573 K for 3 h, after the first catalytic run.

and B-1, where the samples were treated with H_2 at 573 K in the XAFS cell and spectra were recorded in the presence of H_2. As shown in figure 1, Pd species on A-1 were observed to be Pd metal particles. Although small amounts of Pd species with Pd–O bond were present on B-1, the spectra showed that the predominant Pd species were Pd-metal particles even on B-1.

In order to clarify the difference between catalyst A and B, XRD measurements were performed on the catalysts prepared. As shown in figure 2, the peak intensity gradually increased with an increase in the pore diameter in the case of catalyst A, prepared from $Pd(NO_3)_2$. In the case of catalyst B, no appreciable diffraction peak was observed when SiO_2 with the narrow pores was used as a support (B-1), indicating that a large portion of Pd particles was present in a form of very fine particles. However, the diffraction peak clearly appeared on B-2 and it was much sharp compared with A-2. On B-3 and B-4 the similar tendency was observed. By applying Scherrer's equation, average particle sizes of Pd metal on catalyst A were estimated as 5, 7, 10 and 13 nm on A-1, A-2, A-3 and A-4, respectively. On the other hand, XRD measurements showed the presence of large particles of Pd more than 20 nm on catalyst B (20, 20 and 24 nm on B-2, B-3 and B-4, respectively) except for B-1.

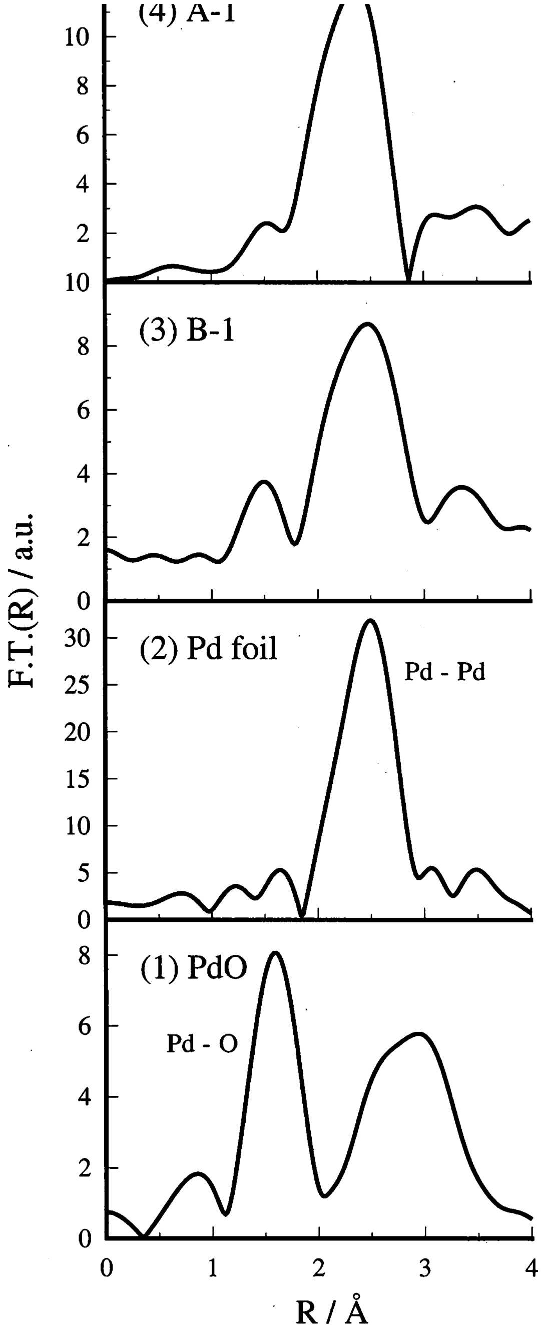

Figure 1. Fourier transforms of $k^3\chi(k)$ for Pd K-edge XAFS of Pd/SiO_2. (1) PdO mixed with SiO_2, (2) Pd metal foil, (3) reduce B-1, (4) reduced A-1.

Typical TEM photographs (magnification = 500,000) on A-1 and A-4 are shown in figures 3 and 4, respectively. Almost the same distribution pattern was observed. In the case of B-1, many fine particles of Pd were observed in addition to several large particles as shown in figure 5. TEM photographs obtained from B-4 were shown in figures 6 and 7. Both photographs were obtained on the same sample. As shown in figure 6, fine particles of Pd were observed, whereas the large particles were also observed. However, large particles were predominantly observed in figure 7. In the case of B-2, the formation of large particles became important compared to the formation of fine particles as shown in figure 8, where the increase in the number of large particles contributed to the appearance of the sharp XRD diffraction peak on the sample (figure 2).

XRD and TEM results are summarized as follows.

1. Catalysts A, prepared from $Pd(NO_3)_2$, showed the relatively narrow particle size distribution as the XRD results well agreed with the TEM results. The size of Pd particles was observed to be in the range of 5–13 nm.
2. On catalysts B-1, prepared from $Pd(NO_2)_2(NH_3)_2$, very fine particles of Pd less than 2 nm were almost predominantly present.
3. On B-2, B-3 and B-4, number of very large particles of Pd with the size of >20 nm remarkably increased besides the presence of fine particles.

On B-1, a very high activity for C_2H_4 hydroformylation was observed. This result shows the contribution of Pd fine particles to the high activity for C_2H_4 hydroformylation. The value for D_H on A-2 was found to be 12.9% and this value is close to that on B-3 (11.9%). Comparing the catalytic behavior of these two catalysts, B-3 was much more active for C_2H_4 hydroformylation than A-2. This is due to the presence of fine particles of Pd on B-3.. On the other hand, A-2 was much more active for CO hydrogenation than B-3, indicating the contribution of relatively large metal

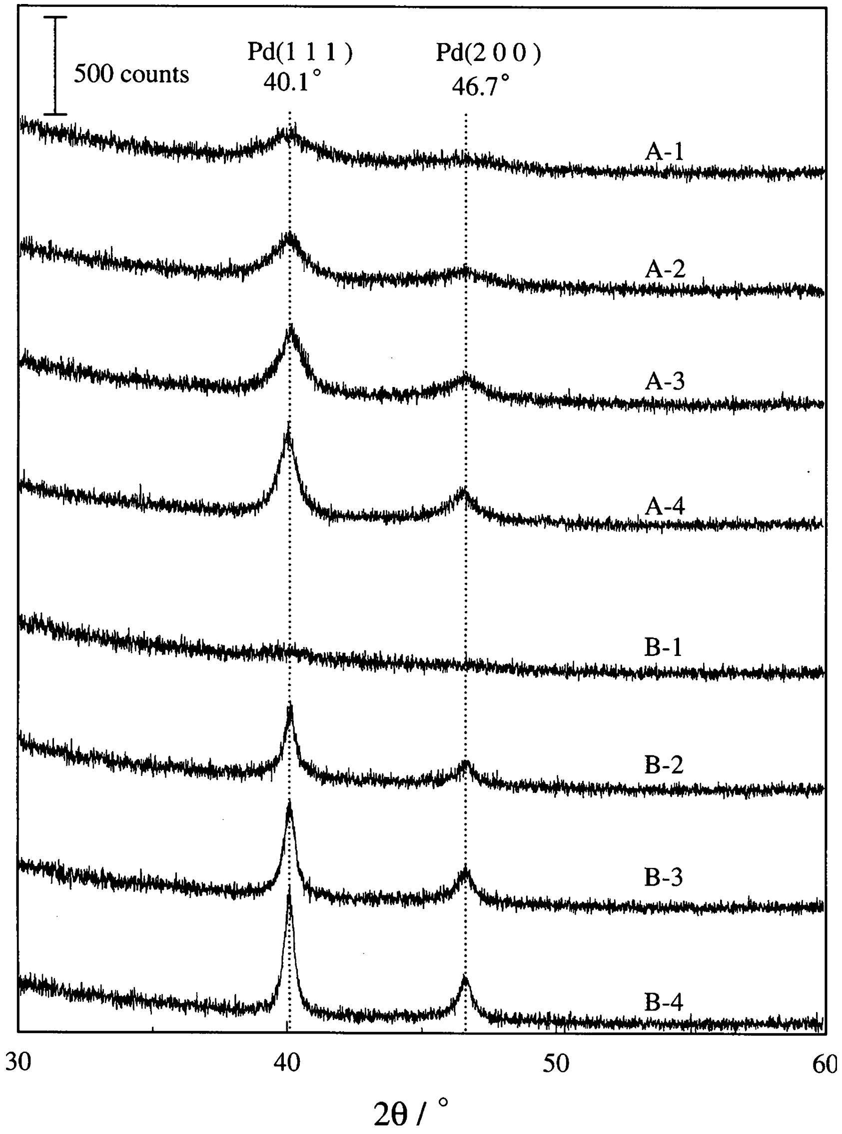

Figure 2. XRD spectra of Pd/SiO$_2$ catalysts.

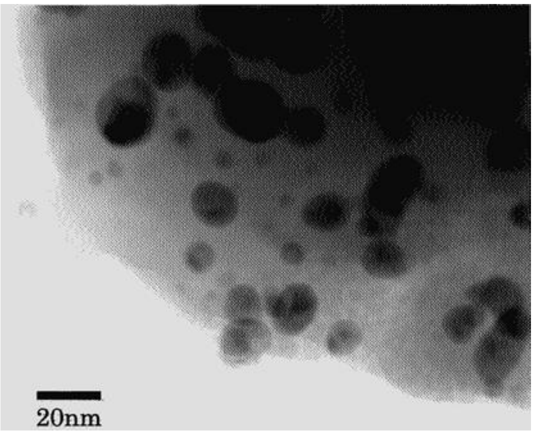

Figure 3. TEM photograph of Pd/SiO$_2$ catalyst A-1 (magnification 500 K).

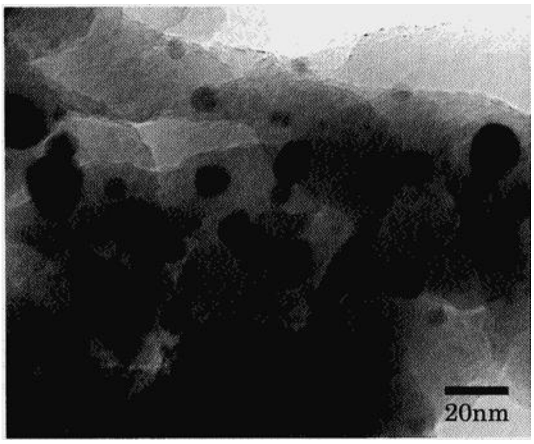

Figure 4. TEM photograph of Pd/SiO$_2$ catalyst A-4 (magnification 500 K).

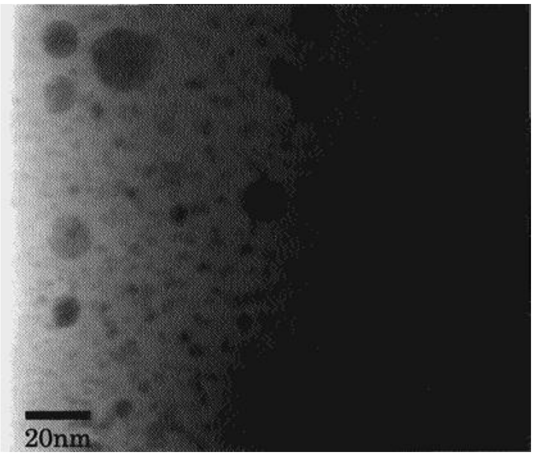

Figure 5. TEM photograph of Pd/SiO$_2$ catalyst B-1 (magnification 500 K).

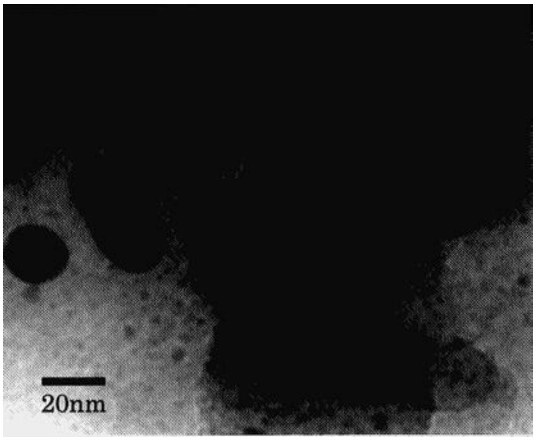

Figure 6. TEM photograph of Pd/SiO$_2$ catalyst B-4 (magnification 500 K).

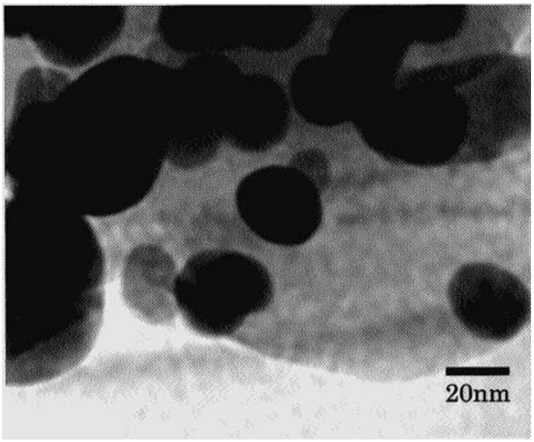

Figure 7. TEM photograph of Pd/SiO$_2$ catalyst B-4 (magnification 500 K).

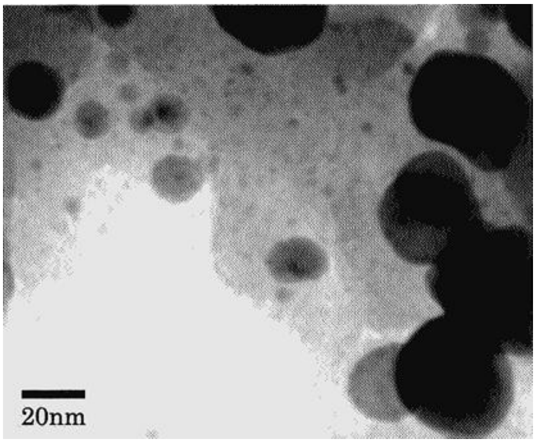

Figure 8. TEM photograph of Pd/SiO$_2$ catalyst B-2 (magnification 500 K).

particles of Pd to the activity for the reaction. In the case of C_2H_4 hydroformylation, the activation process of CO molecule with its molecular form would be required. However, the dissociation process of CO molecule has been suggested to be important in the case of CO hydrogenation [8,9]. Such difference in the CO activation process might relate to the difference in their catalytic activities.

In conclusion, the pattern of particle size distribution on catalysts prepared from $Pd(NO_3)_2$ was found to be very different from that on catalysts prepared from $Pd(NO_2)_2(NH_3)_2$. Comparing the particle distribution pattern with the catalytic activity profiles, C_2H_4 hydroformylation would be mainly catalyzed by the fine particles of Pd (<2 nm) and CO hydrogenation by the relatively large particles of Pd.

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