Preparation of Pt/SiO$_2$ Ultra-fine Particles in Reversed Micelles and Their Catalytic Activity

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(Received June 28, 1999; CL-990565)

Ultra fine Pt particles supported on SiO$_2$ was successfully prepared by the hydrolysis of tetraethoxysilane in the same reversed micellar solution of previously mono-dispersed Pt particles. Formed Pt/SiO$_2$ surface was partly covered with the residue of surfactant, which caused the inhibition of hydrogen adsorption as well as hydrogenation of propene.

In recent years, the preparation of ultra fine particles in a reverse micellar system has attracted great attention because of its possibility to obtain mono-dispersed particles in nm size. A wide variety of nano size particles has been synthesized by this method, including noble metals (Pt[1], Rh[1], Pd[2], Au[3]), metal oxides (SiO$_2$[4], ZrO$_2$[5]) and mixed oxides (ZrO$_2$-Y$_2$O[6]). In this connection, nano-sized metal/metal oxide particles prepared in the reverse micellar system could be excellent candidates for practical supported metal catalysts, but studies so far have been limited to only Rh/SiO$_2$[7] and Pd/ZrO$_2$[8].

This study is the first investigation of the preparation of Pt ultra fine particles successfully dispersed on SiO$_2$ by employing the reverse micellar system. The controlling factors to disperse Pt particles uniformly onto silica and their adsorption capacity for hydrogen were investigated in depth as well as catalytic activity for hydrogenation of propene.

The reverse micellar system used in this study composed of Aerosol OT (AOT)/heptane and polyoxyethylene-nonylphenyl ether (NP-6)/cyclohexane, whose concentration was 100 mmol/l in both solutions. The aqueous H$_2$PtCl$_6$·6H$_2$O solution (40 mmol/l) was added into AOT/heptane or NP-6/cyclohexane solution adjusting Rw= 5 (water to surfactant ratio), and stirred at 293 K for 5 h. The resulting micellar solution was reduced with NaBH$_4$, N$_2$H$_4$ or H$_2$, and a uniformly dispersed solution of ultra fine Pt particles was obtained. The formed Pt particle sizes were independent of the Rw value, but strongly dependent on the reduction methods and /or the properties of surfactants. To prepare Pt/SiO$_2$ particles, tetraethoxysilane (TEOS) and NH$_3$ solution was added successively into the dispersed solution of Pt particles, and the hydrolysis of TEOS was carried out at 293 K for 3 days. The particle sizes of Pt and SiO$_2$ thus obtained were determined by TEM measurement. The dispersion of Pt/SiO$_2$ after H$_2$ pretreatment at 573 K was determined by H$_2$ adsorption at 273 K. The catalytic activities for propene hydrogenation were tested in the closed circulation system at 293 K and 200 Torr of total pressure. The composition of the gas phase was analyzed by TCD gas chromatography.

In the case of AOT/heptane micellar system, mono-dispersed Pt particles were prepared by the reduction with NaBH$_4$ or H$_2$. Three different methods were employed to fix these Pt particles onto SiO$_2$ as follows; (1) conventional impregnation with commercial SiO$_2$ powder (Aerosil 300), (2) mixing two separately prepared micellar solutions of Pt and SiO$_2$ particles (3) hydrolysis of TEOS by ammonia solution in the same micellar solution of Pt.

As shown in Figure 1(a), Pt particles supported on SiO$_2$ by the first impregnation method were aggregated on the silica surface. During the impregnation in hydrophobic heptane solution, the Pt particles, which are also hydrophobic by surrounding alkyl chains of AOT, may aggregate on the hydrophilic surface of SiO$_2$ during evaporation. The second mixing method also gave the aggregate of Pt particles as shown in Figure 1(b). This suggests that the interaction between Pt and SiO$_2$ particles, which have been separately prepared in the reverse micellar solutions before mixing, is very weak because of the repulsion by the alkyl chains of the AOT molecule adsorbed on both the Pt and silica particles. In contrast to the above mentioned two methods, the successful dispersion of Pt on SiO$_2$ was obtained by the third hydrolysis method as shown in Figure 1(c). Since the hydrolysis of TEOS takes place at the interface of the water droplet in the reverse micelle containing Pt particles, the stronger interaction may be achieved between Pt and SiO$_2$ particles in this case. In the AOT/heptane system, it was difficult to use N$_2$H$_4$ as a reducing agent because of the polymerization of AOT, as reported by Clint et al.[9]

Figure 1. TEM images of Pt-SiO$_2$ (AOT / heptane, reduced with NaBH$_4$). (a) impregnation, (b) mixing after hydrolysis, (c) hydrolysis after dispersing Pt.

In the case of NP6/cyclohexane reverse micellar system, when H$_2$PtCl$_6$ was reduced with N$_2$H$_4$, aggregated particles were obtained as shown in Figure 2(a). These aggregated Pt particles were coated with SiO$_2$ after the addition of TEOS, followed by its hydrolysis with ammonia (Figure 2(b)). On the other hand, Pt particles reduced with NaBH$_4$ showed successful dispersion, and Pt/SiO$_2$ obtained after TEOS hydrolysis also showed good Pt dispersion as shown in Figure.2(c). To elucidate the different behavior of reducing agents, NaBO$_2$ was added to the dispersed solution of Pt particles prepared by the reduction with N$_2$H$_4$ and the hydrolysis of TEOS was carried out. The obtained Pt particles exhibited good dispersion on SiO$_2$, indicating that the presence of the ions like NaBO$_2$ formed during NaBH$_4$ decomposition may suppress the aggregation of Pt particles. For the preparation of Ag particles in reversed micelles[10], it is reported that by using N$_2$H$_4$ instead of NaBH$_4$, the size distribution of Ag particle obtained from the Ag salt broadened.

Table 1. Properties of Pt-ultra fine particles supported on SiO_2

Surfactant	Reductant	Particle size / nm[a]						
		SiO_2			Pt			
		TEM	(s.d.[c])	BET	TEM	XRD[b]	H_2 ads.	(H/Pt)[e]
AOT	$NaBH_4$	49.1	(25.1)	20.5	2.2	1.6	6.4[d]	(0.21)
AOT	H_2	-	(-)	-	4.4	1.7	-	
NP6	$NaBH_4$	85.5	(11.8)	-	3.2	-	-	
NP6	N_2H_4	34.8	(14.1)	14.0	4.8	2.1	-	
NP6[d]	N_2H_4	-	(-)	-	35.9[d]	-	57.9[d]	(0.03[d])

[a]as prepared, [b]estimated with Scherrer equation, [c]standard deviation(%), [d]after reduction at 573 K, [e]adsorbed at R.T. and atmospheric pressure.

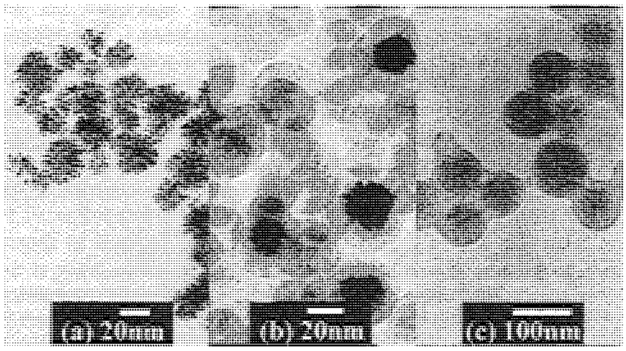

Figure 2. TEM images of Pt-SiO_2 (NP-6 / cyclohexane).
(a) Pt aggregates reduced with N_2H_4, (b) hydrolysis after dispersing Pt prepared with N_2H_4 reduction, (c) hydrolysis after dispersing Pt prepared with $NaBH_4$ reduction.

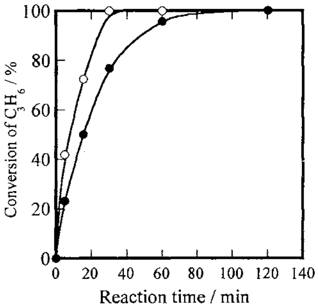

Figure 3. Hydrogenation of propene over Pt/SiO_2 catalysts prepared in AOT/heptane reverse micelles, at 293 K. Total pressure=20 Torr. (open symbol; after oxidation, closed symbol; after reduction)

Table 1 summarizes the particle sizes of SiO_2 support as well as dispersed Pt, determined by TEM and BET analyses. The particle sizes of Pt and SiO_2 prepared in the AOT/heptane system were smaller than those prepared in the NP6/ cyclohexane system. From the values of standard deviation in the parentheses, it is recognized that size distribution of the SiO_2 particles prepared in the NP6 system is narrower than that prepared in the AOT system. It is worth noticing that the particle size determined by BET analysis was smaller than that determined by TEM measurements, suggesting the porous structure of SiO_2 particles obtained by the reverse micellar system. It is possible that the AOT molecule adsorbed on the particle on which the hydrolysis of TEOS occured may inhibit the production of siloxane bonding from dehydration of silanol group.

To investigate the surface state and catalytic activity of Pt/SiO_2 prepared in reverse micellar system, H_2 adsorption capacity as well as propene hydrogenation were investigated after the pretreatment by H_2 at 573 K. As shown in Table 1, the particle size estimated from the amount of adsorbed hydrogen at 273 K was less than the TEM particle size, which suggests that Pt surface may be partly covered by residual carbon chains of surfactants and inhibit hydrogen adsorption. Figure 3 shows the catalytic activities for hydrogenation of propene at 293 K on the Pt/SiO_2 prepared by reverse micellar system. The rate of propane formation after H_2 pretreatment at 573K was less than that of after O_2 pretreatment at the same temperature. Over conventional Pt-group catalysts, their catalytic activities for alkene hydrogenation appear much higher in reducing state of metals compared to oxidized state. The opposite results in this study may be caused by the same reason as the inhibition of H_2 adsorption mentioned above. On the reduced surface, the alkyl chains of the residue of surfactant may adsorb to the Pt more strongly than on the oxidized surface and inhibit the propene hydrogenation. The inhibition was removed by the reoxidation of the reduced catalyst. To make this point clearer, temperature programmed desorption spectra of hydrogen over Pt/SiO_2 prepared in reverse micellar system were compared with those of conventionally prepared catalysts. In the desorption spectra over conventionally prepared catalysts, two distinct desorption peaks were observed at around 473 K and 673 K. On the other hand, from the desorption spectra over the reverse micellar catalyst, the only one peak at higher temperature was observed. The missing of the lower TPD peak of H_2 in the reverse micellar catalysts is consistent with the consideration mentioned above. Kishida et al.[11] reported that, on Rh/SiO_2 catalyst prepared by reverse micellar method and calcined at 773 K, the reaction rate of CO_2 hydrogenation was much faster than that on the Rh/SiO_2 catalyst prepared by conventional impregnation. Accordingly, in this study, higher temperature of calcination may lead to higher activities of the reduced Pt/SiO_2 catalysts prepared in the reverse micelles.

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