Preparation of size-controlled Pt catalysts supported on alumina

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It was found that Pt particles on Al_2O_3-supported Pt catalysts prepared using Pt complex nanoparticles formed in a water-in-oil microemulsion became very small and uniform compared to those prepared using reduced Pt metal nanoparticles or by an impregnation method. Moreover, the catalytic activity of the catalyst composed of very small Pt particles, which was prepared using the complex nanoparticles, was higher in the NO–CO reaction than those of the other catalysts.

Keywords: microemulsion, complex-forming agent, Pt particle size, NO–CO reaction

1. Introduction

We have developed a novel catalyst preparation method using a water-in-oil (w/o) microemulsion [1–6]. By this method we could control the rhodium particle size of Rh/SiO_2 catalysts in the range of 2–14 nm regardless of rhodium content [1–6]. Furthermore, we could immobilize rhodium particles with sharp size distribution onto the silica support [1,2]. The preparation procedure was as follows. At first we synthesized the Rh complex nanoparticles composed of rhodium and hydrazine in w/o microemulsion. Then we immobilized the Rh complex nanoparticles onto the silica support by hydrolysis of tetraethylorthosilicate. The Rh complex nanoparticles were so fine and stable that they could be immobilized uniformly onto the support at a high metal concentration ($\gg 10^{-5}$ mol-metal/l usually used [7–9]). The discovery of the Rh–hydrazine complex produced a good result for the control and uniformity of the particle size. Such a catalyst preparation method utilizing metal complex nanoparticles in microemulsion has been developed for the first time by our laboratory. Accordingly, the objective of this study is to prepare Pt/Al_2O_3 catalysts loaded with controlled and uniform Pt particles using Pt complex nanoparticles in w/o microemulsion. In addition, the performances of the catalysts for the NO–CO reaction were investigated.

2. Experimental

Pt/Al_2O_3 catalysts were prepared by two methods, namely the method using microemulsion (cats. A–D, F–J) and the impregnation method (cat. E). Reagents used in the preparation of these catalysts are shown in tables 1 and 2.

The method using microemulsion was as follows. A microemulsion system containing H_2PtCl_6 was mixed with another microemulsion system containing a complex-forming agent to form Pt complex nanoparticles. In this work, the microemulsion system was composed of polyoxyethylene(5)-*p*-nonylphenylether (NP-5)/1-hexanol. Quaternary ammonium salts such as cetyltrimethylammonium chloride (CTAC) were used as complex-forming agents. The reason why quaternary ammonium salts were selected was because we found through much investigation that H_2PtCl_6 formed Pt complex nanoparticles only with those salts. After Pt complex nanoparticles were formed in the microemulsion, aluminum isopropoxide was added into the mixture to be hydrolyzed into Al_2O_3 so that the Pt complex nanoparticles in the microemulsion might be immobilized onto Al_2O_3. The immobilized Pt complex nanoparticles were converted into Pt metal nanoparticles by air calcination at 500 °C for 2 h and successive reduction in hydrogen at 400 °C for 1 h. Any other catalysts prepared in this work were subjected to calcination and reduction under the same conditions. The catalysts prepared from $(CTA)_2PtCl_6$, $(TEA)_2PtCl_6$ and K_2PtCl_6 nanoparticles were denoted as cats. A, B and C, respectively. When hydrazine was used as a complex-forming agent, Pt metal nanoparticles were formed in the microemulsion instead of Pt complex nanoparticles. These Pt metal nanoparticles were immobilized in the same way as mentioned above. The Pt/Al_2O_3 catalyst thus prepared was denoted as cat. D. The detailed preparation procedure for cat. D was described previously elsewhere [3,4]. Catalyst E was prepared by impregnating Al_2O_3, which had been prepared from microemulsion with H_2PtCl_6 aqueous solution.

The sizes of Pt particles of Pt/Al_2O_3 catalysts prepared in this work were determined using the XRD broadening technique and the size distributions of Pt particles were determined by transmission electron microscope (TEM) analysis.

Catalytic activity was measured using a quartz tubular reactor. 0.2 g of catalyst sample was used. The reactant gas mixture was composed of 10000 ppm NO, 10000 ppm CO and He as a balance. The gas flow rate was 100 $cm^3\ min^{-1}$ ($SV = 30000^{-1}$).

Table 1
Pt particle size of Pt/Al_2O_3 catalysts.[a]

Cat.	Complex-forming agents	Particles in microemulsion	Mean Pt particle size (nm)	Side distribution
A	CTAC: $[CH_3(CH_2)_{15}N(CH_3)_3]Cl$	$(CTA)_2PtCl_6$	4.7	sharp
B	TEAC: $[(CH_3(CH_2))_4N]Cl$	$(TEA)_2PtCl_6$	17.6	sharp
C	KCl	K_2PtCl_6	34.3	broad
D	–	Pt metal	17.9	broad
E[b]	–	–	8.0	broad

[a] Pt content 1.0 wt%.
[b] Prepared by the impregnation method.

Table 2
Particles formed in microemulsion and Pt particle sizes of Pt/Al_2O_3 catalysts prepared from different complex-forming agents.

Cat.	Complex-forming agents	Particles in microemulsion	Pt particle size (nm)
A	CTAC: $[CH_3(CH_2)_{15}N(CH_3)_3]Cl$	$(CTA)_2PtCl_6$	4.7
F	OTAC: $[CH_3(CH_2)_7N(CH_3)_3]Cl$	$(OTA)_2PtCl_6$	4.8
G	HTAB: $[CH_3(CH_2)_5N(CH_3)_3]Br$	$(HTA)_2PtCl_6$	5.3
H	TDAB: $[(CH_3(CH_2)_9)_4N]Br$	$(TDA)_2PtCl_6$	5.1
I	TPAB: $[(CH_3(CH_2)_2)_4N]Br$	$(TPA)_2PtCl_6$	5.5
B	TEAC: $[(CH_3(CH_2))_4N]Cl$	$(TEA)_2PtCl_6$	17.6
J	TMAC: $(CH_3)_4N{\cdot}Cl$	$(TMA)_2PtCl_6$	19.9

3. Results and discussion

The sizes of Pt particles of Pt/Al_2O_3 catalysts prepared in this work are listed in table 1. As can be seen from this table, the Pt particle sizes were varied with the type of particles formed in the microemulsion. The particle size of the catalysts prepared from $(CTA)_2PtCl_6$ was very small. On the other hand, the particle sizes of cat. B prepared from $(TEA)_2PtCl_6$, of cat. C prepared from K_2PtCl_6 and of cat. D from Pt metal were extremely large, and the cat. E prepared by the impregnation method had a comparatively small particle size, though it had a size distribution as broad as any other conventional impregnation catalysts. Figures 1, 2 and 3, for example, show the TEM photographs of cats. A, B and D, respectively. The difference in size and distribution can be seen from these three figures. These results suggest that the size of Pt particles of the catalysts could be controlled by the type of nanoparticles in microemulsion.

We succeeded in immobilizing Pt particles of small and uniform size by using CTAC as a complex-forming agent, as shown in table 1. Then we tried to control the Pt particle size of Pt/Al_2O_3 catalysts by adjusting the length of alkyl groups in the complex-forming agents from the viewpoint of the effect of the hydrophilic property on the stability of Pt complex nanoparticles in microemulsion. As shown in table 2, in cats. A, F, G and J, the complex-forming agents differed from each other in the length of only one alkyl group. On the other hand, in cats. B, H–J, the complex-forming agents differed from each other in the length of all the four alkyl groups. The Pt particle size of these catalysts is also shown in table 2. As can be seen from this table, the Pt particle size of the catalysts became smaller with increase in the length of alkyl group in the complex-forming agents. Accordingly, the longer the alkyl chains became, the more stable the nanoparticles became and the more difficult the Pt complex nanoparticles coagulated.

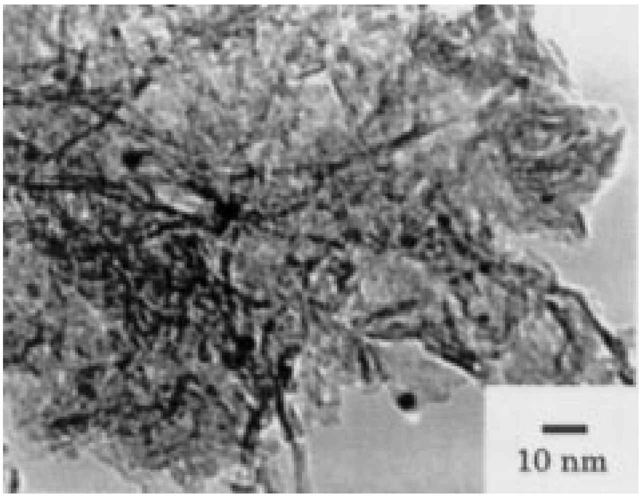

Figure 1. TEM photograph of Pt/Al_2O_3 catalyst prepared using $(CTA)_2PtCl_6$ complex nanoparticles in microemulsion (×600k) content 1.0 wt%.

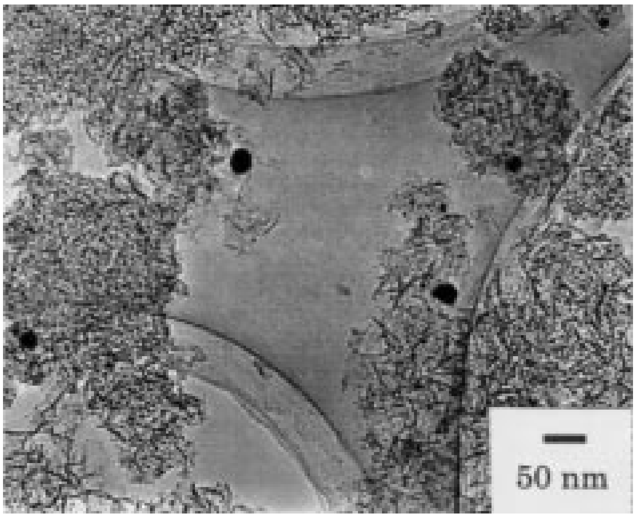

Figure 2. TEM photograph of Pt/Al_2O_3 catalyst prepared using Pt metal particles in microemulsion (×120k). Pt content 1.0 wt%.

Figure 4 shows the behavior of the NO–CO reaction over typical Pt/Al_2O_3 catalysts with 1.0 wt% loading. As can be

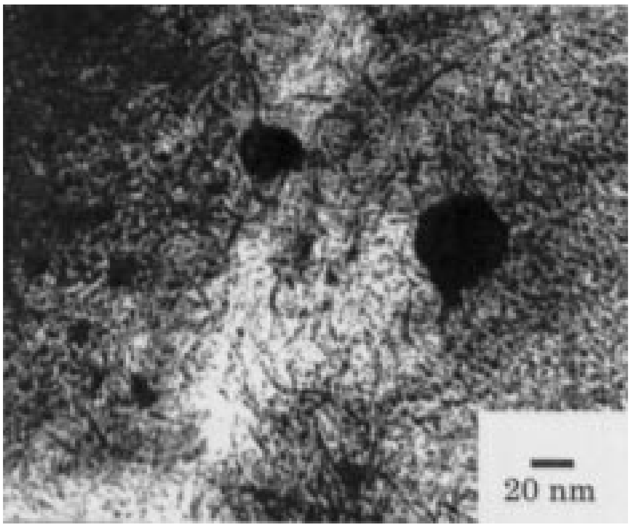

Figure 3. TEM photograph of Pt/Al_2O_3 catalyst prepared using Pt metal particles in microemulsion (×300k). Pt content 1.0 wt%.

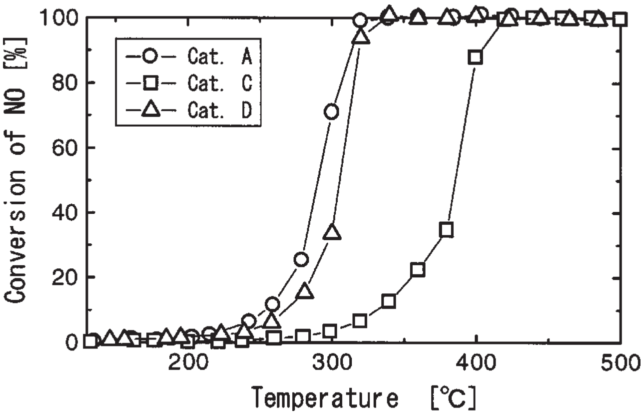

Figure 4. NO reduction by CO over various Pt/Al_2O_3 catalysts. Pt content 1.0 wt%.

seen from figure 4, the smaller the Pt particle size became, the higher the catalytic activity became, apart from the size distribution.

4. Conclusion

It can be concluded from the results obtained in this work that we have succeeded in preparing Pt/Al_2O_3 catalysts loaded with small and uniform particle size and in increasing the catalytic activity for the NO–CO reaction.

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References

[1] M. Kishida, K. Umakoshi, J. Ishiyama, H. Nagata and K. Wakabayashi, Catal. Today 29 (1996) 355.
[2] M. Kishida, T. Hanaoka, W.Y. Kim, H. Nagata and K. Wakabayashi, Appl. Surf. Sci. 121 (1997) 347.
[3] M. Kishida, T. Fujita, K. Umakoshi, J. Ishiyama, H. Nagata and K. Wakabayashi, J. Chem. Soc. Chem. Commun. (1995) 763.
[4] W.Y. Kim, M. Kishida, T. Hanaoka and K. Wakabayashi, Appl. Catal. A 155 (1997) 283.
[5] T. Hanaoka, W.Y. Kim, M. Kishida, H. Nagata and K. Wakabayashi, Chem. Lett. (1997) 645.
[6] W.Y. Kim, H. Hayashi, M. Kishida and K. Wakabayashi, Appl. Catal. A 169 (1998) 157.
[7] B.H. Robinson, A.N. Khan-Lodhi and T. Towey, in: *Structure and Reactivity in Reverse Micelles*, Stud. Phys. Theoret. Chem., Vol. 65, ed. M.L. Pileni (1989) p. 198.
[8] M. Boutonnet, J. Kiziling, V. Mintsa-Eya, A. Choplin, R. Touroude, G. Maire and P. Stenius, J. Catal. 103 (1987) 95.
[9] K. Kurihara and J.H. Fendler, J. Mol. Catal. 34 (1986) 325.