

## Thermal stability of Pt particles of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts prepared using microemulsion and catalytic activity in NO–CO reaction

Masanori Ikeda <sup>\*</sup>, Teruoki Tago, Masahiro Kishida, Katsuhiko Wakabayashi

*Department of Materials Process Engineering, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*

Received 6 June 2001; received in revised form 5 September 2001; accepted 5 September 2001

### Abstract

Sintering behaviors of the Pt particles of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst prepared using different preparation methods (microemulsion, sol–gel, and impregnation methods) were investigated. It was found that the catalyst prepared by microemulsion had a higher resistance to sintering than did the sol–gel and impregnation catalysts. To limit the sintering even more, the catalysts were pressed. The resistance to sintering in all the catalysts was improved by pressing. The pressed microemulsion catalyst was little deactivated in the NO–CO reaction by thermal treatment at 700 °C for 12 h, and had a high activity relative to that of the sol–gel and impregnation catalysts. © 2001 Elsevier Science B.V. All rights reserved.

### 1. Introduction

In supported metal catalysts, the phenomenon known as sintering occurs with use for long periods at elevated temperatures. The occurrence of sintering of metal particles decreases the exposed surface area of a metal, resulting in a decrease of the catalytic activity.

For automotive exhaust catalysts such as noble metal (Pt, Rh and Pd) catalysts supported on Al<sub>2</sub>O<sub>3</sub>, a high thermal stability with regard to sintering is necessary. In conventional impregnated (IMP) catalysts, however, the Pt particles are easily sintered [1]. In contrast, the catalyst

prepared by the sol–gel method has high thermal stability because the metal particles can be incorporated into the framework of the support [2–6] or partially embedded in the support [1,7,8].

We have developed a novel preparation method for supported metal catalysts using water-in-oil (w/o) microemulsion, an ME method. In this method, Rh particles are partially embedded in SiO<sub>2</sub> supports because the SiO<sub>2</sub> supports are formed by hydrolysis of TEOS around the Rh precursor particle before being synthesized in the reverse micelle [9]. Ruckenstein has reported that the increase in the area of the metal-support interface limits the diffusion of metal crystallites on the supports [10]. It is considered that the embedding of metal particles in the support is effective in limiting sintering because the area of the metal-support interface is large.

In this work, sintering behaviors of Pt particles were investigated in Pt/Al<sub>2</sub>O<sub>3</sub> catalysts prepared

<sup>\*</sup> Corresponding author. Tel.: +81-83-642-3505; fax: +81-92-642-3505.

E-mail address: kishida@apex.chem-eng.kyushu-u.ac.jp (M. Ikeda).

by different preparation methods (ME, sol–gel, and IMP). However, some extent of sintering occurred in the ME and sol–gel catalyst despite larger area of Pt–alumina interface relative to the IMP catalyst. Then, we pressed the catalysts to enlarge the interface area. The sintering behaviors of Pt particles of the pressed catalysts were also investigated. In addition, the catalytic activity of the pressed catalysts was examined in the NO–CO reaction.

## 2. Experimental

The microemulsion catalyst was prepared by the following procedure. The water-in-oil microemulsion composed of polyoxyethylene ( $n = 5$ )-*p*-nonylphenyl ether/1-hexanol/ $\text{H}_2\text{PtCl}_6\text{aq.}$  was used in this study. A microemulsion (100 ml) containing  $\text{H}_2\text{PtCl}_6$  ( $5.1 \times 10^{-4}$  mol) was mixed with another microemulsion (100 ml) containing cethyltrimethyl ammonium chloride ( $\text{CTA} \cdot \text{Cl}$ ,  $1.5 \times 10^{-3}$  mol) as a Pt-complex forming agent to form Pt-complex nanoparticles ( $(\text{CTA})_2\text{PtCl}_6$ ,  $\text{CTA} \cdot \text{HPtCl}_6$ ). Distilled water (15 ml) and aluminum tri-iso propoxide (40 g) were added to the microemulsion, followed by hydrolysis of aluminum tri-iso propoxide with stirring at 25 °C for 30 min. Then, precipitates of  $\text{Al}_2\text{O}_3$  gel involving Pt-complex nanoparticles were obtained. The precipitates were separated from the solution by centrifugation and were washed twice with ethanol. After the separation, the obtained gel was dried overnight and calcined at 600 °C for 2 h.

The impregnation catalysts were prepared by the following procedure. An aqueous solution of  $\text{H}_2\text{PtCl}_6$  was impregnated into alumina, which was prepared by the microemulsion method. The other preparation conditions were same as above. The sol–gel catalyst was prepared using the same starting materials of Pt and  $\text{Al}_2\text{O}_3$  as in the case of the ME catalyst. A mixture of aluminum tri-iso propoxide (40 g), ethanol (100 cc), and distilled water (20 ml) was stirred at 70 °C for 30 min.  $\text{H}_2\text{PtCl}_6\text{aq.}$  solution (0.42 M 1.2 cc) was added to the mixture and stirred at 70 °C for 1 h to obtain gel containing the Pt precursor. The gel was dried at 70 °C for 12 h and then calcined at 600 °C for 2 h.

To investigate the thermal stability of Pt particles against sintering, the Pt particle size of the catalyst was examined by powder X-ray diffraction (XRD) method before and after the thermal treatment, the air calcination at 700 °C for 12 h. XRD patterns were obtained using a Rigaku RINT 2500 instrument. The peak corresponding to Pt(111) was analyzed using Scherrer's equation,  $D_{\text{XRD}} = \alpha\lambda/B \cos \theta$ , to estimate Pt particle size. Here,  $\lambda$  is X-ray wavelength 0.14541 nm,  $B$  is a half of integral breadth, and  $\alpha$  was determined using a commercial standard Pt/ $\text{Al}_2\text{O}_3$  catalyst (Micromeritics, Pt 0.5 wt%, Pt dispersion  $30.6 \pm 5\%$ ) to be 0.9. The errors of Pt size determined by XRD were within 16%.

The morphology of the Pt particles and the alumina support was observed by transmission electron microscopy (TEM) using a JOEL JEM 2000FX. The amount of CO chemisorption to the Pt particles was also measured by CO pulse method.

Catalytic activity was measured using a quartz tubular reactor, and 0.2 g of catalyst was used. The reactant gas mixture was composed of 10 000 ppm NO, 10 000 ppm CO, and He as a balance. The gas-flow rate was  $100 \text{ cm}^3 \text{ min}^{-1}$  ( $\text{SV} = 30\,000 \text{ cc/g-cat h}^{-1}$ ). The effluent gas was introduced to gas chromatographs (Shimadzu GC-8A) for on-line analysis.

## 3. Results and discussion

We examined the sintering behavior of three different catalysts (ME, sol–gel, IMP) by thermal treatment at 700 °C for 12 h. Table 1 shows the Pt particle sizes determined by XRD before and after the thermal treatment. The Pt particle size of all the unpressed catalysts increased by the thermal treatment, but the Pt size of the unpressed ME and sol–gel catalysts did not increase much relative to that of the unpressed IMP catalyst. This result indicates that the sol–gel catalyst has more resistance to sintering of Pt than the IMP catalyst, which is in accordance with other reports [1], and that the ME catalyst also has more resistance to the sintering.

Table 1  
The levels of CO uptake and Pt particle sizes of the catalyst

	Catalyst	CO uptake ( $\mu\text{mol/g}$ )		$D_{\text{XRD}}$ (nm)	
		Before <sup>a</sup>	After <sup>b</sup>	Before <sup>a</sup>	After <sup>b</sup>
Before pressing	ME	6.2	4.1	5.8	13.1
	Sol-gel	10.7	2.7	7.1	14.8
	IMP	35.5	1.9	9.1	27.4
After pressing	ME	4.5	2.3	5.8	8.2
	Sol-gel	4.0	2.0	7.1	10.8
	IMP	36.0	1.5	9.1	17.9

<sup>a</sup>The value before thermal treatment.

<sup>b</sup>The value after thermal treatment at 700 °C for 12 h.

Next, we examined the level of CO uptake, as also shown in Table 1. The level of CO uptake on the unpressed catalysts before thermal treatment decreased in the following order: the ME catalyst < the sol-gel catalyst  $\ll$  the IMP catalyst, which usually leads that the Pt particle size calculated from the amount of CO uptake decreased in the following order: the IMP catalyst  $\ll$  the sol-gel catalyst < the ME catalyst. However, the order of Pt particle sizes determined by XRD was almost the reverse: the ME catalyst  $\leq$  the sol-gel catalyst  $\leq$  the IMP catalyst. The Pt size observed from TEM images was the same order as in the case of XRD, as shown in Figs. 1(a)–(c). This discordance can be explained as follows. CO species cannot physically adsorb on the Pt surface in contact with the alumina support, that is, the interface between Pt particles and alumina supports. If the ratio of interface area to total Pt surface changes with the catalyst preparation method, the amount of CO uptake will change with the preparation method even at the same Pt size. In that case, the discordance can be caused by the difference in interface area: the area was larger in the following order: the IMP catalyst  $\ll$  the sol-gel catalyst  $\leq$  the ME catalyst. This order is also supported by the report that the metal particles of the sol-gel catalyst were incorporated into the framework of the support [2–6]. Furthermore, such large Pt–alumina interface area of the ME and sol-gel catalysts might contribute to lower incidence of sintering for Pt particles during the thermal treatment.

To limit the sintering even more, enlargement of the Pt–alumina interface area may be necessary.

Figs. 1(a)–(c) show TEM photographs of the unpressed catalysts before thermal treatment. Needle-like aluminas were observed in all the figures. It cannot be judged from these figures, but it is considered that the Pt particles were located in the aperture of the needle-like alumina, as illustrated in Fig. 2(a). In the sol-gel catalyst, it is well known that metal particles were incorporated with supports. In the ME catalyst, it is reasonable that the Pt particles are surrounded by the needles of alumina, since the alumina was formed in the solution containing the Pt-complex particles beforehand synthesized.

The Pt–alumina interface area shown in Fig. 2(a) should be smaller than in the case located in the bulk alumina. Then, we pressed the catalysts at 156 MPa to enlarge the area of the Pt–alumina interface, as illustrated in Fig. 2(b).

Fig. 3 shows the TEM photograph of the pressed ME catalyst before thermal treatment. In this figure, no needle-like alumina was observed after the pressing, which means that the alumina supports became compact by pressing the catalyst. Accordingly, it was confirmed that the interface between the Pt particle and the alumina support became larger, as shown in Fig. 2(b). Then the Pt particle size and the level of CO uptake of the pressed catalysts were examined. The Pt particle sizes determined by XRD and the level of CO uptake were shown in Table 1. The Pt particle sizes of all the pressed catalysts before the thermal treatment were the same as those of the unpressed catalysts. As can be seen in Table 1, however, the levels of CO uptake for the ME and sol-gel catalysts decreased by pressing them.

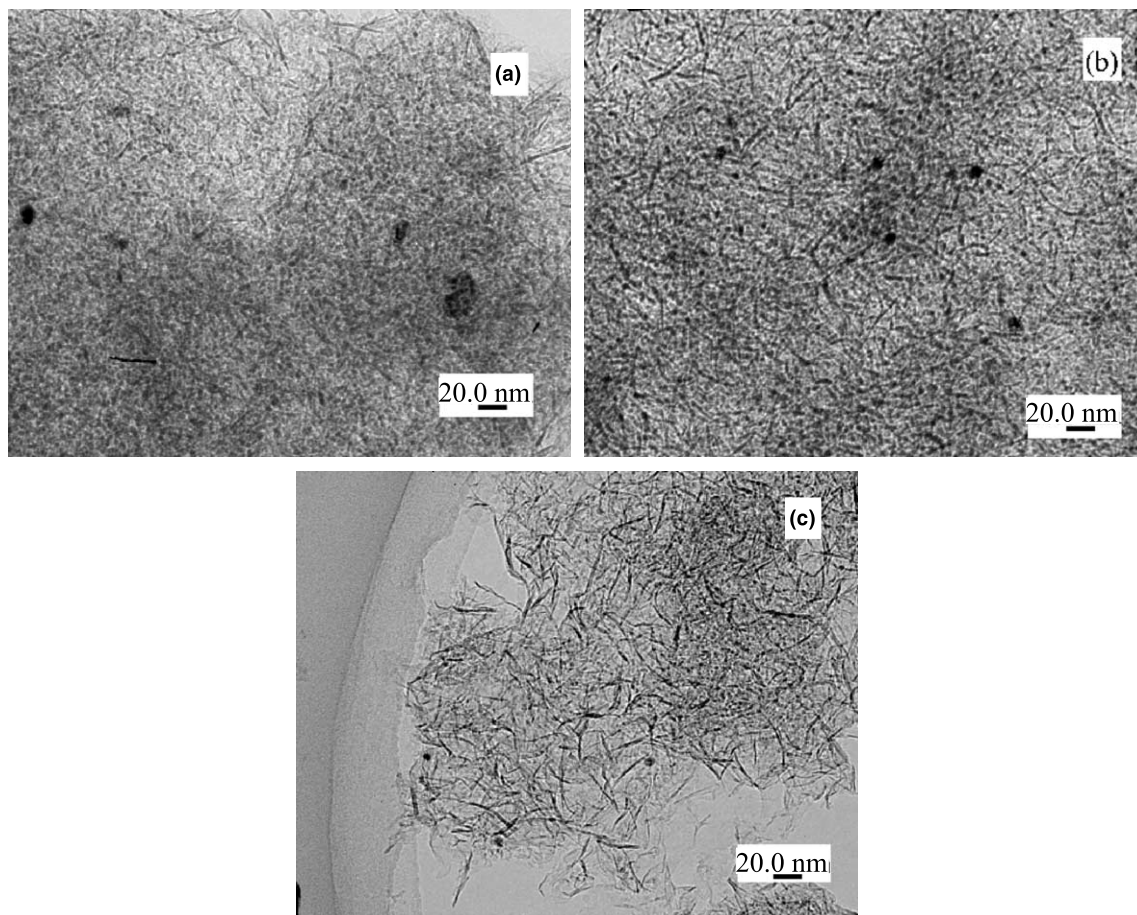


Fig. 1. TEM photographs of the unpressed Pt/Al<sub>2</sub>O<sub>3</sub> catalysts before thermal treatment: (a) IMP; (b) Sol-gel; (c) ME.

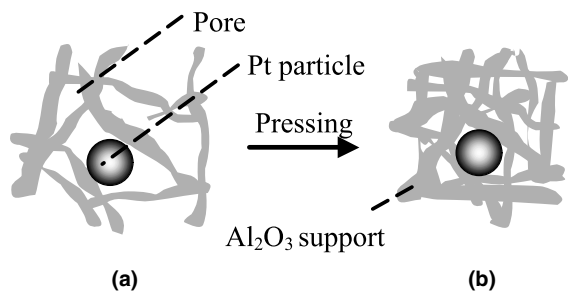


Fig. 2. A schematic representation of the configurations of (a) unpressed and (b) pressed catalysts.

These results suggest that the Pt–alumina interface area increased by pressing the ME and sol-gel catalysts.

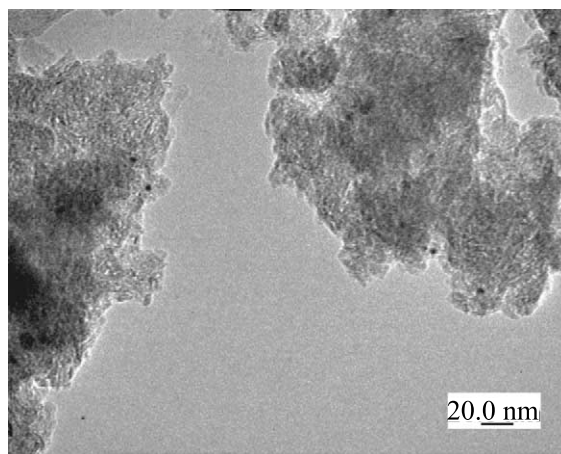


Fig. 3. TEM photograph of the pressed ME catalyst before thermal treatment.

In Table 1, the Pt particle size for all the catalysts after the thermal treatment became smaller in response to pressing. Accordingly, it was found that pressing the catalysts is effective in limiting sintering of Pt. This effect was attributed to the increase in the Pt–alumina interface area by pressing the catalysts.

As can be also seen in Table 1, the pressed ME catalyst after thermal treatment had smaller Pt particles than the pressed sol–gel and IMP catalysts. Fig. 4 shows TEM photographs of the pressed catalysts after thermal treatment. It was confirmed from these figures that no large Pt particle was observed in the ME catalyst. Therefore, it was found that the pressed ME catalyst had a higher resistance to the sintering of Pt particles.

Finally, catalytic behaviors in the NO–CO reaction of these catalysts were examined. Table 2 shows the temperature of the 50% NO conversion in the NO–CO reaction, T<sub>50</sub>. The T<sub>50</sub> of the unpressed ME catalyst was the lowest of the three unpressed catalysts before thermal treatment, which means that the unpressed ME catalyst was the most active, although the CO uptake of the ME catalyst was the smallest in Table 1. The pressed ME catalyst was also the most active of the three pressed catalysts before thermal treatment. This result indicates that the Pt surface of the ME catalyst was more active than that of the sol–gel and IMP catalysts. In addition, the T<sub>50</sub>s of all the catalysts before thermal treatment decreased in response to pressing, the reason for which is not clear.

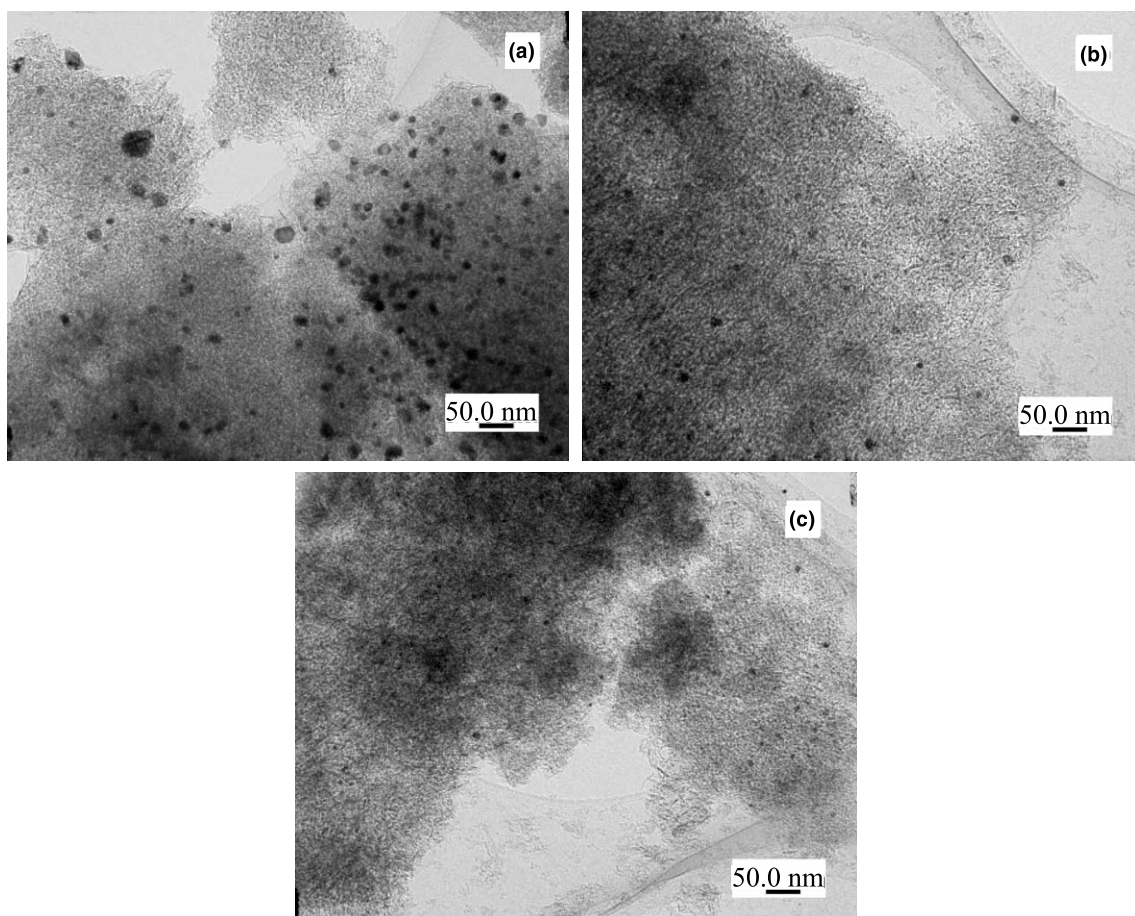


Fig. 4. TEM photographs of the pressed catalysts after thermal treatment at 700 °C for 12 h: (a) IMP; (b) Sol–gel; (c) ME.

Table 2  
T50 of the catalysts in NO–CO over 1 wt% Pt/Al<sub>2</sub>O<sub>3</sub> catalysts

	Catalyst	T50 (°C)		ΔT50 (°C)
		Before thermal treatment	After thermal treatment at 700 °C for 12 h	
Before pressing	ME	294	316	22
	Sol-gel	316	341	25
	IMP	307	332	25
After pressing	ME	285	296	11
	Sol-gel	302	324	22
	IMP	290	325	35

All the unpressed catalysts were deactivated remarkably in response to thermal treatment as can be seen in Table 2. This result is primarily attributable to the sintering of Pt particles. The T50s of all the pressed catalysts after thermal treatment also became lower than those of the unpressed catalysts. It was noteworthy, however, that the increase in T50 by thermal treatment, ΔT50, of the ME catalyst was the lowest of the three catalysts, and that the T50 of the pressed ME catalyst was the lowest after thermal treatment. Fig. 5 shows the NO conversions over the pressed catalysts after thermal treatment. At any temperatures, pressed ME catalysts exhibited the highest activity after thermal treatment of the three catalysts, as can be seen in Fig. 5. In conclusion, it was found in the present study that the pressed ME

catalyst has high activity and maintain this activity after thermal treatment.

#### 4. Conclusions

Resistance to the sintering of Pt particles was improved by pressing the catalysts at 156 MPa. For the endurance test under air flow at 700 °C for 12 h, the catalyst prepared using microemulsion and then pressed, the pressed ME catalyst, had greater resistance to the sintering of Pt particles than the sol-gel and impregnation catalysts. The pressed ME catalyst exhibited higher activity in NO–CO reaction and maintain the high activity even after the endurance test, in comparison with the sol-gel and impregnation catalysts.

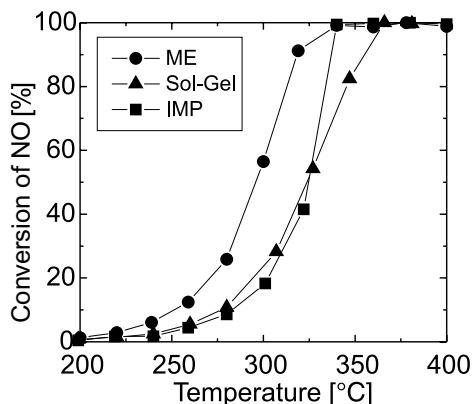


Fig. 5. Relative activity curves for NO–CO reaction over pressed Pt/Al<sub>2</sub>O<sub>3</sub> catalysts after thermal treatment at 700 °C for 12 h.

#### Acknowledgements

We would like to thank the research laboratory of the High Voltage Electron Microscope, Kyushu University, for the transmission electron micrographs, and we also thank the Center for Advanced Instrumental Analysis, Kyushu University, for the XRD measurements. The present work is partially supported by a Grant-in-Aid for Scientific Research (B) (No. 12450328) from the Ministry of Education, Science and Culture.

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