

# Formation of Active Sites for the NO + CO Reaction over Palladium Catalysts Supported on Mesoporous Silica

Aritomo Yamaguchi,<sup>1</sup> Takamitsu Hayashi,<sup>1</sup>  
Kenichi Oyaizu,<sup>2</sup> and Makoto Yuasa<sup>\*,1,2</sup>

<sup>1</sup>Department of Pure and Applied Chemistry,  
Faculty of Science and Technology,  
Tokyo University of Science, Noda 278-8510

<sup>2</sup>Institute of Colloid and Interface Science,  
Tokyo University of Science, Tokyo 162-8601

Received August 2, 2004; E-mail: yuasa@rs.noda.tus.ac.jp

The catalytic activities and structural changes of Pd containing mesoporous silica (Pd/MCM-41) catalysts for the NO + CO reaction were investigated. Pd/MCM-41 after calcination in air showed a very high catalytic activity for the NO + CO reaction because Pd metal particles with an appropriate size for the reaction were formed by the reaction gases.

Periodic mesoporous silicas have been of great interest since the discovery of mesoporous materials,<sup>1–3</sup> and they are promising materials for catalyst support because of their high surface area and uniform pore dimensions.<sup>4–8</sup> The removal of three toxic compounds, such as NO, CO, and hydrocarbons, in the exhaust gases from internal combustion engines is an important subject in order to reduce air pollution. Three-way catalysts (TWCs) have been developed to eliminate the three toxic compounds, and TWCs are typically based on Pt + Rh or Pd + Rh. Pd particles attract much attention of many researchers due to the high catalytic activity for the NO + CO reaction ( $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$ )<sup>9,10</sup> to simultaneously eliminate two compounds, NO and CO. However, Pd supported on mesoporous silicas have not been applied to NO reduction. The NO + CO reaction was found to be sensitive to Pd surface structures.<sup>11,12</sup> The Pd(111) surface showed higher activity of the reaction than the Pd(110) and Pd(100) surfaces. In addition, the reaction was supposed to be sensitive to the Pd particle size, although the effective particle size for the active site of the NO + CO reaction has been controversial.<sup>11,12</sup> Recently, Nishihata et al. reported that Pd species in Pd-perovskite were self-regenerated for automotive emissions.<sup>13</sup> The self-regeneration of the Pd species for the reaction becomes an interesting topic in the field of catalysis. Here, we report on the formation of Pd particles with a suitable size for the NO + CO reaction from Pd species supported on mesoporous silica.

The XRD pattern in the  $2\theta$  range from  $2^\circ$  to  $7^\circ$  has revealed that the prepared catalyst, Pd/MCM-41, retained its hexagonal structure of mesopore [XRD (100) 3.57 nm, (110) 2.09 nm,

(200) 1.81 nm]. A broad peak at angle  $2\theta$  of  $33.9^\circ$ , corresponding to palladium oxide (tetragonal PdO) particle, was observed in the XRD pattern of Pd/MCM-41 after calcination at 673 K. Broad peaks at angles  $2\theta$  of  $40.1^\circ$  and  $46.7^\circ$ , corresponding to palladium metal particles, were vanishingly observed. This result suggested that Pd/MCM-41 formed predominantly small PdO particles before the reaction. Fourier-transformed  $k^3$ -weighted EXAFS function for the Pd/MCM-41 catalyst before the NO + CO reaction is shown in Fig. 1 by the dotted line. Three peaks appeared at 0.17, 0.25, and 0.31 nm (phase shift uncorrected). The peak at 0.17 nm was assigned to Pd–O contributions, and the other two peaks at 0.25 and 0.31 nm were assigned to two kinds of Pd–Pd contributions. These three peaks were derived from PdO particles.<sup>14</sup> This result indicated that the PdO particles existed in Pd/MCM-41 before the NO + CO reaction, corresponding to the XRD pattern.

We investigated the catalytic activity for the NO + CO reaction with the catalyst Pd/MCM-41 after calcination at 673 K (open-circle plots in Fig. 2). Although NO was reduced to  $\text{N}_2$  and  $\text{N}_2\text{O}$ , in the temperature range of this study the conversion to  $\text{N}_2\text{O}$  was less than 20%. The conversion in the figure represents the percentage of the decrement of NO. NO conver-

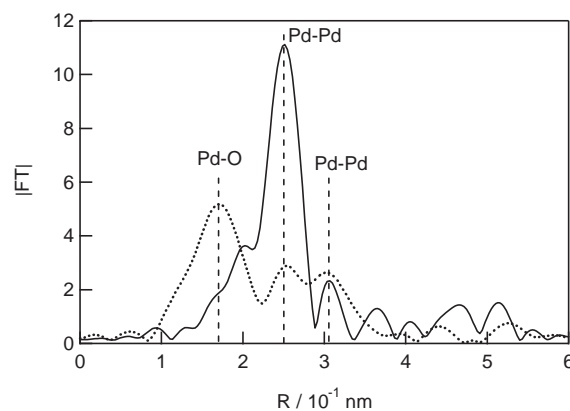


Fig. 1. Fourier-transformed  $k^3$ -weighted EXAFS functions for Pd/MCM-41 before (dotted line) and after (solid line) NO + CO reaction at 773 K.

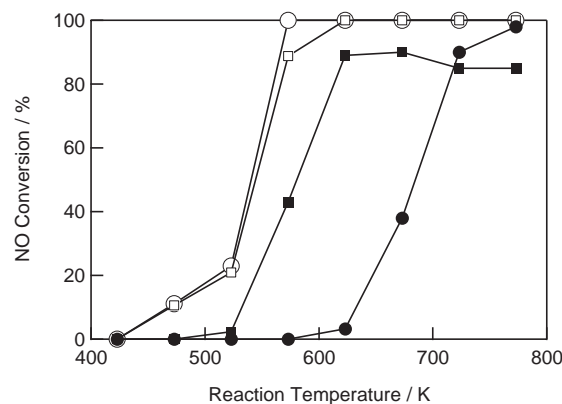


Fig. 2. NO conversion for the NO + CO reaction against reaction temperature. ○: Pd/MCM-41 catalyst after calcination at 673 K; □: Pd/MCM-41 catalyst after calcination at 673 K followed by reduction with  $\text{H}_2$ ; ●: Pd/SiO<sub>2</sub>; ■: Pd/Al<sub>2</sub>O<sub>3</sub>.

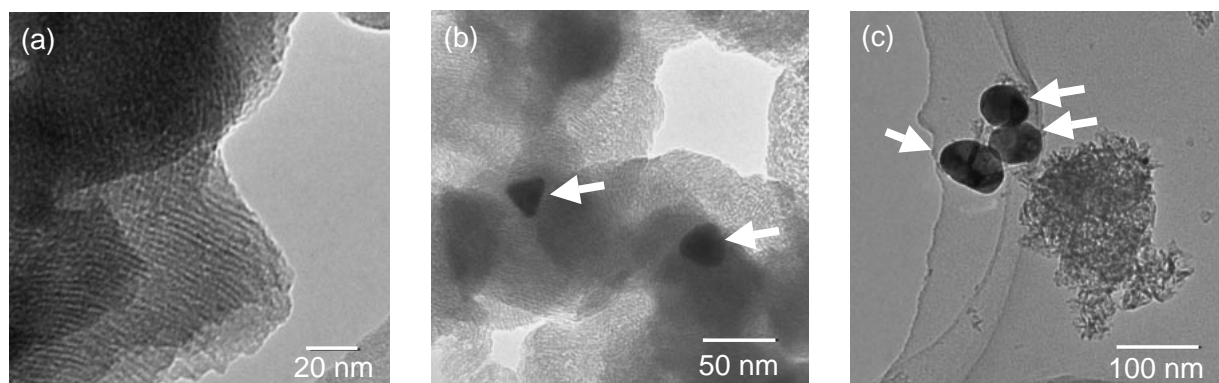


Fig. 3. TEM images of Pd/MCM-41 (a) before and (b) after the NO + CO reaction, and (c) Pd/Al<sub>2</sub>O<sub>3</sub> after the reaction. Arrows indicate Pd metal particles.

sion in the effluent gas through the Pd/MCM-41 catalyst increased at ca. 473 K. On the other hand, those of reference samples, such as Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>, increased at higher temperature, as plotted in Fig. 2 by the closed circle and square, respectively. This result indicated that this Pd/MCM-41 catalyst had higher catalytic activity for NO reduction by CO than the reference samples. Two sharp peaks at angles  $2\theta$  of 40.1° and 46.7°, corresponding to Pd metal particles, were observed in the XRD pattern of Pd/MCM-41 after the NO + CO reaction at 773 K. The averaged size of the Pd metal particles was 17.1 nm, derived from Scherrer's formula.<sup>15</sup> The averaged size of the Pd metal particles for Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> after the reaction was more than 40 nm, calculated from the results of XRD measurements. Fourier-transformed  $k^3$ -weighted EXAFS function for Pd/MCM-41 catalyst after the NO + CO reaction is shown in Fig. 1 by the solid line. The large peak at 0.25 nm was assigned to the Pd–Pd contributions of the Pd metal particles. The coordination number (CN) and interatomic distance of the Pd–Pd bond were  $10.7 \pm 0.7$  and  $0.273 \pm 0.001$  nm, respectively. The CN of Pd metal particles having a diameter of 17.1 nm should be larger than 10.7, which suggested that a small part of the Pd atoms may not form Pd metal particles. The XRD and EXAFS results demonstrated that small PdO particles which existed before the NO + CO reaction were reduced to make larger Pd metal particles during the reaction. It seems reasonable to suppose that the PdO species before the reaction locates in the mesopore, but the Pd species go to the outer surfaces during the reaction to form large metal particles. The Pd metal particles had high catalytic activity for the NO + CO reaction, as indicated by the fact that NO reduction occurred at 473 K. The formation of Pd metal particles with a suitable size for the reaction from PdO species occurred during the reaction. The Pd/MCM-41 catalyst after the NO + CO reaction had the same temperature profile of catalytic activity for the reaction once again. This result also indicated that the size of the Pd metal particles formed after the reaction was suitable for the reaction. We measured TEM images of Pd/MCM-41 before and after the NO + CO reaction, and Pd/Al<sub>2</sub>O<sub>3</sub> after the reaction, as shown in Fig. 3. The Pd species were not clearly observed in the TEM photograph of Fig. 3(a) for Pd/MCM-41 before the reaction, because the PdO species in the sample were suggested to be dispersed in the mesopore of MCM-41. After the reaction, large Pd metal

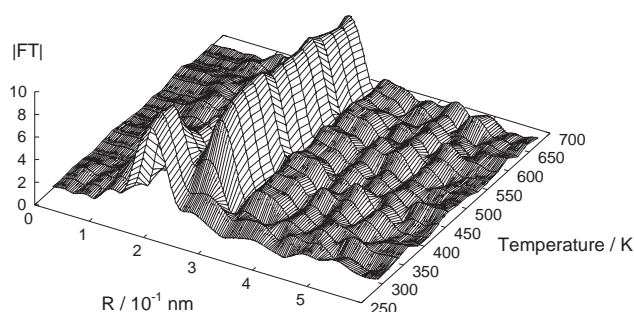


Fig. 4. Fourier transforms calculated from EXAFS spectra of the Pd K-edge during the temperature-programmed reduction of Pd/MCM-41 in H<sub>2</sub> from 293 K to 673 K.

particles (indicated by arrows) were observed in Pd/MCM-41 and Pd/Al<sub>2</sub>O<sub>3</sub>, as shown in Figs. 3(b) and (c), respectively, of which the size agreed with the size calculated from the XRD results. TEM images of Figs. 3(a) and (b) support that the PdO species before the reaction locates in the mesopore, and the Pd species go to the outer surfaces during the reaction to form the large metal particles.

Pd/MCM-41 calcined at 673 K in air was reduced in a flow of H<sub>2</sub> (3%)/He (97%) (50 cm<sup>3</sup> min<sup>-1</sup>) at 673 K for 2 h in order to prepare the pre-reduced Pd/MCM-41 catalyst. The reduction process of Pd/MCM-41 during temperature-programmed reduction (293–673 K) was studied by EXAFS spectra. The acquisition time of each spectrum was 4 min. After background subtraction,  $k^3$ -weighted EXAFS functions were Fourier transformed into R-space, as shown in Fig. 4. Phase-shift correction was not carried out in these spectra. A Pd–O peak was observed at 0.17 nm for the calcined Pd/MCM-41. During the reduction in H<sub>2</sub>, the intensity of the peak decreased at 373 K, and a Pd–Pd peak at 0.25 nm increased. The CN and interatomic distance of the Pd–Pd bond for the pre-reduced catalyst were  $10.6 \pm 0.7$  and  $0.273 \pm 0.001$  nm, respectively. This result revealed that PdO particles in MCM-41 were reduced to Pd metal particles in a flow of H<sub>2</sub>, and that the particle size was same as that of the Pd/MCM-41 catalyst after the NO + CO reaction. We also measured NO conversion of the NO + CO reaction with this pre-reduced Pd/MCM-41 catalyst (open square plots in Fig. 2). The pre-reduced Pd/MCM-41 catalyst had very high catalytic activity for the NO + CO reaction, and

had almost the same catalytic activity as the Pd/MCM-41 catalyst without the H<sub>2</sub> treatment. This result indicated that the active sites were Pd metal particles, and that PdO particles before the reaction without the H<sub>2</sub> treatment were reduced during the reaction by CO at the reaction temperature. Pd metal particles of the appropriate size for the NO + CO reaction were generated by the reduction of Pd/MCM-41 by H<sub>2</sub> before the reaction. In the case of Pd/MCM-41 without the H<sub>2</sub> treatment, Pd metal particles of approximately the same size were formed during the NO + CO reaction.

In conclusion, we reveal that Pd/MCM-41 catalyst has the high catalytic activity of NO reduction from low temperature because Pd metal particles with an appropriate size for the NO + CO reaction were formed by the reaction gases.

### Experimental

Mesoporous silica of type MCM-41 supported Pd catalysts were prepared by impregnating MCM-41 with an aqueous PdCl<sub>2</sub> solution. Pd/MCM-41 catalysts were calcined at 673 K for 2 h in air. Pd/SiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> were also prepared by the impregnation of an aqueous PdCl<sub>2</sub> solution, followed by calcination at 673 K for 2 h. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were JRC-SIO-6 and JRC-ALO-2, respectively, which were the reference catalysts supplied by Catalyst Society of Japan. The Pd loadings of all the samples were 1 wt %. Their catalytic activities were evaluated using a fixed-bed continuous flow reactor. A reaction gas mixture containing NO (3%), CO (3%), and He (94%) was fed through a catalyst (0.2 g) at a rate of 50 cm<sup>3</sup> min<sup>-1</sup> (SV = ca. 3100 h<sup>-1</sup> in the case of Pd/MCM-41). The effluent gas was analyzed by two on-line gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of N<sub>2</sub>, NO, and CO) and a Unibeads C column (for analysis of CO<sub>2</sub> and N<sub>2</sub>O). The reaction temperature was changed from 473 to 773 K in 50 K steps, and the steady-state catalytic activity was measured at each temperature. The Pd species before and after the NO + CO reaction was characterized by X-ray diffraction (XRD), extended X-ray absorption fine structure (EXAFS), and transmission electron microscope (TEM). EXAFS spectra at Pd K-edge (24.3 keV) of the catalysts were measured using a Si(311) channel-cut monochromator at BL-10B of KEK-PF. Data analysis was performed by UWXAFS package, and the backscattering amplitudes and phase shifts were calculated with FEFF8 code. The k range of the Fourier transformation and the R range used for fitting were 30–125 nm<sup>-1</sup> and 0.13–0.30 nm, respectively. The reported value of the coefficient of effective

amplitude reduction factor was 0.88 for Pd–Pd<sup>16</sup> and the Debye–Waller factor used in the fitting was calculated from EXAFS spectra at Pd K-edge of Pd foil. TEM images were measured using a Hitachi H-7650 electron microscope with a cold field-emission gun operated at 120 kV.

We thank Mr. Taku Ogura, Prof. Hideki Sakai, and Prof. Masahiko Abe of Tokyo University of Science, for measuring the TEM.

### References

- 1 T. Yanagisawa, T. Shimizu, K. Kuroda, and C. Kato, *Bull. Chem. Soc. Jpn.*, **63**, 988 (1990).
- 2 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
- 3 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
- 4 S. Biz and M. L. Occelli, *Catal. Rev.—Sci. Eng.*, **40**, 329 (1998).
- 5 D. T. On, D. Desplandier-Giscard, C. Danumah, and S. Kaliaguine, *Appl. Catal., A*, **222**, 299 (2001).
- 6 F. Schuth, A. Wingen, and J. Sauer, *Microporous Mesoporous Mater.*, **44–45**, 465 (2001).
- 7 A. Corma, *Top. Catal.*, **4**, 249 (1997).
- 8 X. S. Zhao, G. Q. M. Lu, and G. J. Millar, *Ind. Eng. Chem. Res.*, **35**, 2075 (1996).
- 9 V. I. Parvulescu, P. Grange, and B. Delmon, *Catal. Today*, **46**, 233 (1998).
- 10 P. Forzatti, *Catal. Today*, **62**, 51 (2000).
- 11 D. R. Rainer, S. M. Vesecky, M. Koranne, W. S. Oh, and D. W. Goodman, *J. Catal.*, **167**, 234 (1997).
- 12 J. H. Holles, R. J. Davis, T. M. Murray, and J. M. Howe, *J. Catal.*, **195**, 193 (2000).
- 13 Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, and N. Hamada, *Nature*, **418**, 164 (2002).
- 14 K. Okumura and M. Niwa, *J. Phys. Chem. B*, **104**, 9670 (2000).
- 15 D. L. Boxall and C. M. Lukehart, *Chem. Mater.*, **13**, 806 (2001).
- 16 E. D. Park, S. H. Choi, and J. S. Lee, *J. Phys. Chem. B*, **104**, 5586 (2000).