

XAFS study on the active sites for NO + CO reaction over palladium catalysts supported on mesoporous silica

Aritomo YAMAGUCHI*¹, Takamitsu HAYASHI¹, Kazuki IWAOKA¹,
Kenichi OYAIZU², Makoto YUASA^{1,2}

¹Department of Pure and Applied Chemistry, Faculty of Science and Technology,
Tokyo University of Science, Chiba 278-8510, Japan

²Institute of Colloid and Interface Science, Tokyo University of Science,
Tokyo 162-8601, Japan

Introduction

Periodic mesoporous silicas have been of great interest since the discovery of the mesoporous materials and they are promising materials for catalyst support because of their high surface area and uniform pore dimensions. The removal of NO in the exhaust gases from internal combustion engines is an important subject in order to reduce air pollution. Palladium catalysts attract much attention of many researchers from high catalytic activity for the reaction of NO reduction. In this study, we attempted to synthesize Pd containing mesoporous silicas and investigated their structure and catalytic activity of NO reduction by CO [1].

Experimental

Mesoporous silica of type MCM-41 supported Pd catalysts (Pd/MCM-41) were prepared by impregnating MCM-41 with aqueous PdCl₂ solution. Pd/MCM-41 catalysts were calcined at 673 K for 2 h in air. Pd species before and after the NO + CO reaction was characterized by X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS). EXAFS spectra at Pd K-edge (23.3 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.

Result and Discussion

XRD pattern in the 2θ range from 2 to 7 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 2θ of 33.9 corresponding to palladium oxide (tetragonal PdO) particle was observed in the XRD pattern of Pd/MCM-41 after calcination at 673 K.

Fourier transformed k³-weighted EXAFS function for Pd/MCM-41 catalyst before the NO + CO reaction was shown in Figure 1 by 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. The other two peaks at 0.25 and 0.31 nm were assigned to two kinds of Pd-Pd contributions. This result indicated that PdO particle existed in Pd/MCM-41 before NO + CO reaction, corresponding with the XRD pattern.

Fourier transformed k³-weighted EXAFS function for Pd/MCM-41 catalyst after the NO + CO reaction was shown in Figure 1 by solid line. The large peak at 0.25 nm was assigned to Pd-Pd contributions of Pd metal particles. The coordination number and interatomic distance of Pd-Pd bond were 8.0 and 0.273 nm, respectively.

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 Pd species go to the outer surfaces during the reaction to form the large metal particles.

References

[1] A. Yamaguchi et al., Langmuir, submitted.

* aritomo@rs.noda.tus.ac.jp

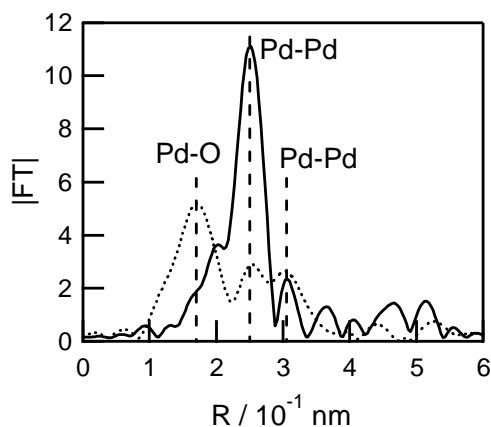


Figure 1 Fourier transformed k³-weighted EXAFS functions for Pd/MCM-41 before (dotted line) and after (solid line) NO + CO reaction at 773 K.