

## XAFS study on the local structure of zirconium containing mesoporous silicas

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### Introduction

Periodic mesoporous silicas have attracted attention since the discovery of the M41S family and they are promising materials for catalyst support because of their high surface area and uniform pore dimensions. Introduction of transition metals to silica framework of MCM-41 forms catalytic active sites for some reactions. Mesoporous materials containing zirconium have been applied to certain reactions, such as hydroxylation of 1-naphthol, photocatalytic generation of hydrogen and chiral alkene polymerization. In this study, we have synthesized Zr-MCM-41 by two different methods and characterized the product by X-ray diffraction, transmission electron micrograph and extended X-ray absorption fine structure (EXAFS) in order to reveal the effect of local structure of zirconium species on the catalytic activity for the peroxidative bromination of phenol red [1,2].

### Experimental

Zirconium-containing mesoporous silicas, Zr-MCM-41, were prepared by two different methods. In one method, we prepared Zr-MCM-41 by hydrolysis and condensation for the mixture of tetraethoxysilane and zirconium tetra-n-propoxide in aqueous cetyltrimethylammonium bromide solution. The product was denoted hereinafter as Zr-MCM-41-A. In the other method, ethanolic zirconium chloride solution and pure silica MCM-41 were used for impregnation. The product was denoted hereinafter as Zr-MCM-41-B. The EXAFS spectra at Zr K-edge (18.0 keV) of the catalysts were measured using a Si(111) double-crystal monochromator at BL-12C of KEK-PF. Data analysis was performed by UWXAFS package and the backscattering amplitudes and phase shifts were calculated with FEFF8 code. The  $k^3$ -weighted EXAFS functions were Fourier transformed and fitted in R space.

### Result and Discussion

Figure 1 shows the Fourier transformed  $k^3$ -weighted EXAFS functions (phase shift uncorrected) for Zr-MCM-41-A, Zr-MCM-41-B, and a reference sample  $ZrO_2$ , together with the calculated functions derived from the curve fitting analysis. The existence of Zr-(O)-Zr bonds at 0.29 nm demonstrated that zirconium species in Zr-

MCM-41-A aggregated each other because Zr atoms exist in the neighborhood of Zr atoms. Zr species in Zr-MCM-41-B were highly dispersed because no Zr-(O)-Zr bond was observed.

The results of catalytic activity revealed that Zr-MCM-41-B had the highest activity for the peroxidative bromination reaction of phenol red. As revealed in the results of EXAFS analysis, the aggregation of zirconium species caused reduces the catalytic activity for the reaction. We demonstrated in this study that highly dispersed zirconium species in mesoporous materials have a catalytic activity for the peroxidative bromination of phenol red.

### References

- [1] A. Yamaguchi et al., J. Jpn. Soc. Colour Mater. (Shikizai) 77, 57 (2004).
- [2] A. Yamaguchi et al., Physica Scripta, in press.

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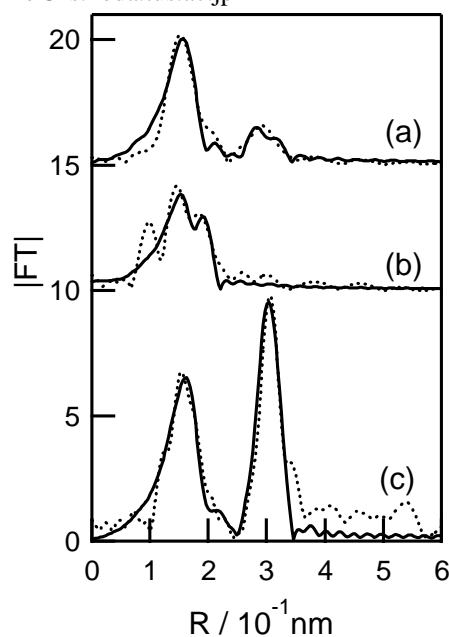


Figure 1. Fourier transformed  $k^3$ -weighted EXAFS functions (.....) for (a) Zr-MCM-41-A, (b) Zr-MCM-41-B and (c) reference sample  $ZrO_2$ , together with the results of curve fitting (—).