

***In-situ* XAFS characterization of Mo/MCM-41 catalyst during CO photo-oxidation reaction**

Nobuyuki ICHIKUNI*¹, Takahiro AKITA¹, Kyoko K. Bando², Shogo SHIMAZU¹ and Takayoshi UEMATSU¹

¹Chiba University, Inage-ku, Chiba 263-8522, Japan

²National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8585, Japan

Introduction

Many investigations were performed for the highly dispersed Mo species since they possessed the photocatalytic activities. It was reported that the isolated molybdenum ions on silica support, which possess Mo=O bonds, exhibit a higher photoactivity [1]. Mo⁵⁺ species were produced from Mo⁶⁺ at Mo=O site under UV irradiation and stoichiometrically reacted with CO to produce CO₂ [2]. Thus, the proceeding of the CO photo-oxidation reaction is expected to lead the structural change in Mo site.

Highly ordered mesoporous silica MCM-41 has the specific surface area more than 1000 m²·g⁻¹. Thus, it seemed to be good support to prepare the highly dispersed catalysts. In this study, we observed the structural change in the active site in the course of CO photo-oxidation reaction using *in-situ* XAFS technique.

Experimental

5wt% Mo/MCM-41 catalysts were prepared by immersing MCM-41 with MoCl₅ cyclohexane solution under N₂.

Transmission Mo K-edge XAFS measurements were performed at BL-10B (PF) with a Si(311) channel cut monochromator. *In-situ* XAFS spectra under CO photo-oxidation reaction were collected using specially designed T-shaped SUS cell with a quartz window and two acrylic windows. The catalysts were pressed into 20 mm diameter self-supporting disks and settled in the cell. The number of disks was determined to regulate the edge jump to 0.5. The reaction was carried out with 50 cm³·min⁻¹ flow of 20% CO/Ar under irradiation by using a 75 W high-pressure Hg lamp. The curve-fitting analyses for Mo-O coordination in the *k*-space were performed by using K₂MoO₄ as reference.

Results and discussion

Figure 1 shows the EXAFS Fourier transforms for the pretreated catalysts and those under UV-irradiation with CO flow condition. The strong peak was attributed to Mo=O bond (0.160 nm), and the other peaks were assigned to be Mo-O(s) and Mo-O(l) bonds with the length of 0.198 nm and 0.242 nm, respectively. Coordination numbers (CN) of Mo-O bonds were changed during the photoreaction as shown in Fig. 2. During the first 150 min of photo-oxidation reaction, decrease of CN for Mo-O(l) corresponded to the increase of CN for Mo-

O(s). It suggests that the Mo-O(l) was changed to Mo-O(s) species during photo-oxidation reaction, and the diminishment of Mo=O bond accompanied with the length of Mo-O bond.

From 150 to 300 min, although CN for Mo-O(s) did not change, CN for Mo-O(l) gradually reduced. The diminishment of Mo-O(l) means that the Mo-O(l) bond reacted with CO under UV irradiation. The CO photo-oxidation reaction might measure not only Mo=O bond but also Mo-O bond.

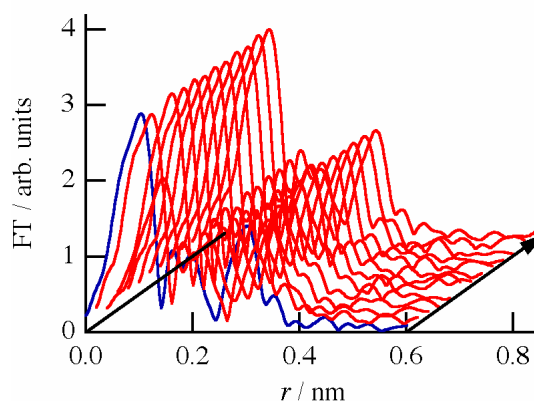


Fig. 1. FT of *k*³-weighted Mo K-edge EXAFS for Mo/MCM-41 during CO photo-oxidation.

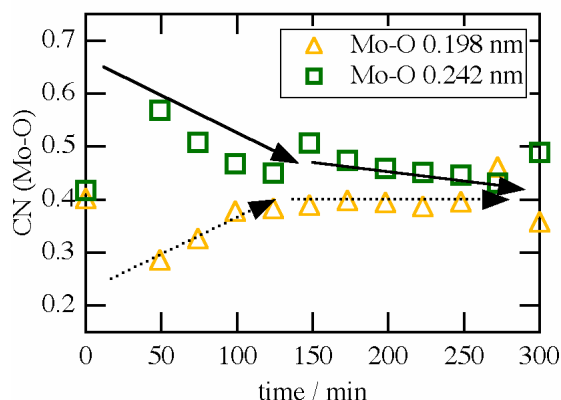


Fig. 2. Change of coordination number during CO photo-oxidation.

Reference

- [1] M. Anpo *et al.*, *J. Chem. Soc., Faraday Trans. 1*, **84**, 2771 (1988).
- [2] J. M. Aigler *et al.*, *J. Phys. Chem.*, **99**, 11489 (1995).

* ichikuni@faculty.chiba-u.jp