

## *In-situ* XAFS characterization of Mo/SiO<sub>2</sub> catalyst during propene photometathesis reaction

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### Introduction

Photocatalytic activities of supported molybdenum oxide catalysts are strongly affected by their local structures. Characterization of active sites under reaction state is important to understand the photocatalysis. Since, the structure under reaction condition was often differed from under static state [1].

The Mo/SiO<sub>2</sub> catalysts, prepared by photochemical anchoring (PCA) method, are expected to have the designable Mo surroundings. In other words, the distance between dimeric Mo atoms can be finely designed by control of the irradiation energy. In this study, the changes of local structure on PCA Mo/SiO<sub>2</sub> catalysts under propene photometathesis reaction and the effect of local structure to photocatalysis were investigated by *in-situ* XAFS technique.

### Experimental

5wt% Mo/SiO<sub>2</sub> catalysts were prepared by dry-mixing of the Mo<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub> and the pre-evacuated silica (CARiACT P-10) under UV irradiation through UV35 filter ( $\lambda > 350$  nm) or without filter ( $\lambda > 250$  nm) at room temperature for 1 h *in vacuo*. The catalysts were treated with H<sub>2</sub>, followed by O<sub>2</sub> at 473 K. The catalyst was designated with UV cut-off filter's wavelength as PCA35 or PCA25.

Mo K-edge EXAFS measurements were carried out at BL-10B (PF) with a Si(311) channel cut monochrometer. *In-situ* EXAFS spectra under propene photometathesis reaction were collected using specially designed SUS cell as depicted in Fig. 1. The cell has a quartz glass window in order to penetrate the UV light to the sample disks. The catalysts were pressed into self-supporting disks and settled in the cell. The reaction was carried out at room temperature with 40 cm<sup>3</sup>·min<sup>-1</sup> flow of propene under irradiation by using a 75 W high-pressure Hg lamp.

### Results and discussion

Figure 2 shows the EXAFS Fourier transforms for the pretreated catalysts and those under the reaction condition. The curve-fitting analyses in the *k*-space were performed by using K<sub>2</sub>MoO<sub>4</sub> and MoO<sub>3</sub> as references. On PCA25, there are no differences between *ex-situ* and *in-situ* condition. It suggests that Mo=(CH<sub>2</sub>) bond (intermediate) resembled to Mo=O bond (initial state) on PCA25, and hence EXAFS could not distinguish the differences between *ex-situ* and *in-situ* conditions.

The Mo-(O)-Mo bond distances of PCA35 and PCA25 were 0.31 and 0.33 nm, respectively. CN and bond distance of Mo-O and Mo-(O)-Mo on PCA35 decreased under the reaction condition, indicated that Mo=(CH<sub>2</sub>) led to the unequalness of active sites. Since the Mo-(O)-Mo bond distance of PCA35 was short, an activated Mo=O site might be stabilized by the connected neighbouring Mo=O bond. On the other hand, Mo=O site of PCA25 acted independently from the neighbouring Mo. The structural changes of Mo/SiO<sub>2</sub> depending on Mo-(O)-Mo bond distance were observed by this technique.

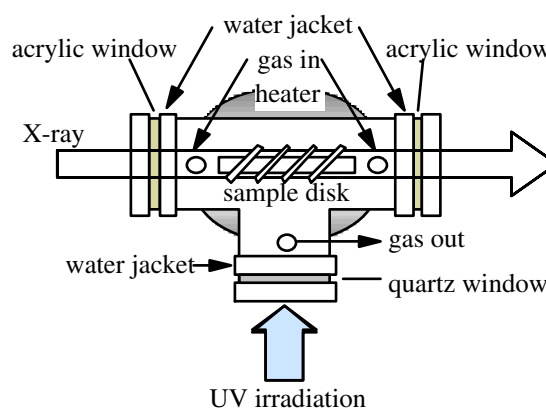


Fig. 1. Schematic of *in-situ* XAFS cell.

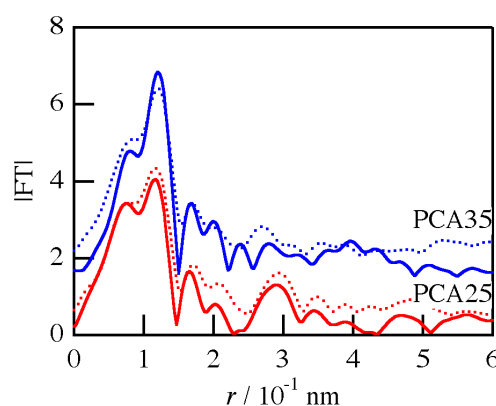


Fig. 2. FT spectra for Mo/SiO<sub>2</sub> catalysts; (solid line) pretreated, (dotted line) under propene photometathesis reaction.

### Reference

[1] N. Ichikuni, H. Murayama, K. K. Bando, S. Shimazu and T. Uematsu, *Anal. Sci.*, **17s**, i1193 (2001).

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