

## XAFS Study on Mo/SiO<sub>2</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> Photocatalysts for the Selective Oxidation of CO with O<sub>2</sub> in the Presence of H<sub>2</sub> at 293 K

Takashi KAMEGAWA<sup>1</sup>, Masaya MATSUOKA\*<sup>1</sup>, Masakazu ANPO<sup>1</sup>

<sup>1</sup>Department of Applied Chemistry, Graduate School of Engineering  
Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531

### Introduction

The preferential oxidation (PROX) of CO is one of the most straightforward methods to reduce the CO contamination in H<sub>2</sub>-rich gas. For now, noble metals supported catalysts generally have been tested and proposed for thermal PROX reaction. To the best of our knowledge, no attempt has been made to apply photocatalysis for the PROX reaction. Therefore, we have applied the Mo/SiO<sub>2</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> photocatalysts for PROX reaction at 293 K.

### Experimental

Mo/SiO<sub>2</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> (0.60 wt% molybdenum as metal) were prepared by an impregnation method of SiO<sub>2</sub> (aerosil 300; Degussa) or Al<sub>2</sub>O<sub>3</sub> (Aluminium Oxide C; Degussa), respectively, using an aqueous solution of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O. Photocatalytic reactions were carried out in a closed system using quartz reactor under UV irradiation at 293 K using a 100 W high-pressure mercury lamp.

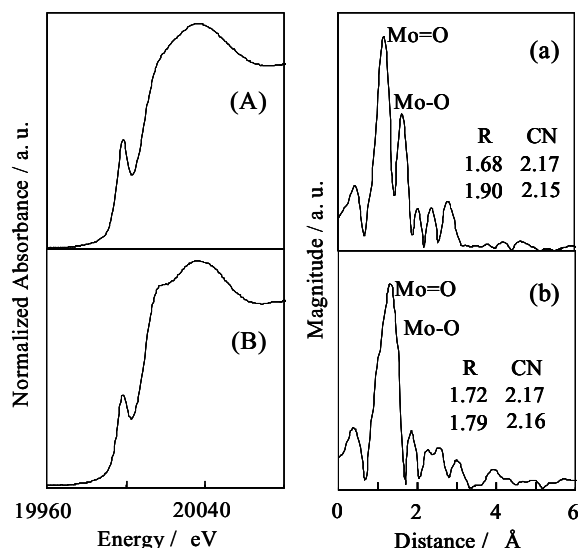
XAFS spectra at Mo K-edge were measured in a transmission mode at room temperature at the BL-10B station. Curve fitting analysis of the EXAFS spectra was conducted on  $k^3\chi(k)$  in  $k$ -space ( $k$  range = 3–12 Å<sup>-1</sup>) with a REX2000J program (Rigaku).

### Results and Discussion

The photocatalytic selective oxidation of CO into CO<sub>2</sub> with O<sub>2</sub> in the presence of H<sub>2</sub> was investigated on Mo/SiO<sub>2</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> under UV light irradiation at 293 K. After UV irradiation for 180 min, concentration of CO gas reached below the detection limit of GC analysis (less than 8 ppm), while the amount of H<sub>2</sub> remained constant [1]. The CO conversion and selectivity reached ~100% and 99%, respectively, on Mo/SiO<sub>2</sub>, while no reaction proceeded on Mo/Al<sub>2</sub>O<sub>3</sub>. Moreover, Mo/Al<sub>2</sub>O<sub>3</sub> exhibited quite weak photoluminescence as compared to that of Mo/SiO<sub>2</sub>.

The XANES spectra of Mo/SiO<sub>2</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> exhibit well-defined pre-edge peaks due to the 1s-4d transition of Mo atoms, indicating that Mo<sup>6+</sup>-oxide species exist in a tetrahedral symmetry for both samples (Fig. 1 (A), (B)). The Fourier transform of EXAFS spectra of Mo/SiO<sub>2</sub> and Mo/Al<sub>2</sub>O<sub>3</sub> showed peaks due to the existence of neighboring oxygen atoms (Mo-O) at around 0.8–2.0 Å, while the additional peak due to the Mo-O-Mo bond was not observed between 3.0–4.0 Å (Fig. 1 (a), (b)). These

results suggest that Mo<sup>6+</sup>-oxide species are highly dispersed on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.



Moreover, the results of curve fitting analysis of Mo-O bonds suggest that Mo<sup>6+</sup>-oxide species on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have two short Mo=O double bonds and two long Mo-O single bonds, while Mo<sup>6+</sup>-oxide species on Al<sub>2</sub>O<sub>3</sub> has longer M=O double bonds and shorter Mo-O single bond than that on SiO<sub>2</sub>. The short Mo-O single bond of Mo<sup>6+</sup>-oxide species on Al<sub>2</sub>O<sub>3</sub> can be ascribed to the large ionic character of framework metal-oxygen bond (Al-O) of Al<sub>2</sub>O<sub>3</sub> as compared to that (SiO) of SiO<sub>2</sub> [2]. The shorter Mo-O single bond also indicates the strong interaction between Mo<sup>6+</sup>-oxide species and Al<sub>2</sub>O<sub>3</sub>.

From the results of XAFS measurements, the weak photoluminescence intensity of Mo/Al<sub>2</sub>O<sub>3</sub> can be explained by the efficient thermal deactivation from photoexcited Mo<sup>6+</sup>-oxide species to support, which is enhanced by the strong interaction between Mo<sup>6+</sup>-oxide species and Al<sub>2</sub>O<sub>3</sub> as suggested by XAFS results. The efficient thermal deactivation process of photoexcited state of Mo<sup>6+</sup>-oxide species on Al<sub>2</sub>O<sub>3</sub> dramatically decrease catalytic reaction rate on Mo/Al<sub>2</sub>O<sub>3</sub>.

### References

- [1] T. Kamegawa, R. Takeuchi, M. Matsuoka, and M. Anpo, *Catal. Today.*, 111, 248 (2006).
- [2] Y. Iwasawa, *Adv. Catal.*, 35, 187 (1987).

\* matsumac@chem.osakafu-u.ac.jp