

# XAFS study on structure of Bi species supported on amorphous silica

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## Introduction

The direct gas phase epoxidation of propene by molecular oxygen has been desired, and has been attempted by many researchers. As a new approach, we have investigated 'photoepoxidation' of propene using only O<sub>2</sub> over several systems, and have reported that Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> showed high activity for propene photoepoxidation [1]. In the present study, we prepared a series of Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples, and investigated the structure of Bi species on silica and their propene photoepoxidation activity.

## Experimental

Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> was prepared by the conventional impregnation method from amorphous silica prepared by sol-gel method with a nitric acid aqueous solution of Bi(NO<sub>3</sub>)<sub>3</sub>, followed by calcination at 773 K for 5 h in flowing dried air. The photooxidation of propene was performed in a similar manner as previously reported. [1]

Bi L<sub>III</sub>-edge XAFS spectra were measured at the BL-10B station [2] at KEK-PF with a Si(311) channel cut monochromator in transmission mode at room temperature. Prior to measurement, the samples were treated with 100 Torr oxygen (1 Torr = 133.3 N m<sup>-2</sup>) at 773 K for 1 h, followed by evacuation at 673 K for 1 h. The pretreated sample was sealed in a polyethylene bag under a dried N<sub>2</sub> atmosphere without exposing to air.

## Results and Discussion

The photooxidation of propene by molecular oxygen was investigated over Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples containing different amount of Bi (0.7 – 30 mol%). With increasing Bi content, the conversion of propene increased up to 1.5 mol% of Bi, and then decreased. The selectivity to PO was high such as 23 % on the samples containing below 1.5 mol% of Bi, and decreased with increasing Bi content. These results mean that the highly dispersed Bi species would be active sites for this reaction.

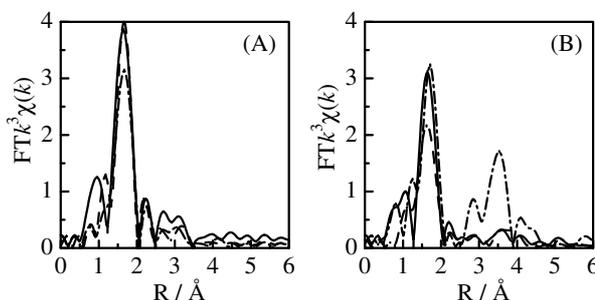
From XRD patterns, it was shown that α-Bi<sub>2</sub>O<sub>3</sub>, β-Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>SiO<sub>5</sub> were formed over the Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples containing more than 10 mol% of Bi.

Fig. 1 shows the Fourier Transforms of Bi L<sub>III</sub>-edge EXAFS spectra of Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> and Bi<sub>2</sub>O<sub>3</sub> samples. All of Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples showed a clear maximum at 1.65 Å owing to Bi-O bonds. Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> 0.7 mol% and 1.5 mol% samples showed the peak with high intensity. With increasing Bi content, the peak became lower. This would be attributed to the formation of α-Bi<sub>2</sub>O<sub>3</sub>, β-Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>SiO<sub>5</sub> that have a variety of Bi-O distances. The peaks

due to Bi-Bi bonds were not clearly observed over all the spectra of Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples.

Table 1 shows structural parameters of the first Bi-O shell determined by the curve-fitting analysis on Fourier-filtered EXAFS of Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> 0.7 mol% and 1.5 mol % samples using empirical parameters of Pb-O shell extracted from EXAFS spectrum of PbO. Δ(σ<sup>2</sup>) corresponds to the relative Debye-Waller factor deviated from those of PbO (Pb-O shell). The coordination number and the distance of the nearest Bi-O bond were 4.0 ± 0.1 and 2.31 Å, respectively. This coordination number is quite different from those of α-Bi<sub>2</sub>O<sub>3</sub>, β-Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>SiO<sub>5</sub>. Bi species would be highly dispersed and 4-fold coordinated in the silica matrix below 1.5 mol% of Bi content.

From these results, it is suggested that the highly dispersed tetrahedral Bi species are active for photoepoxidation of propene, while the Bi clusters, α-Bi<sub>2</sub>O<sub>3</sub>, β-Bi<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>SiO<sub>5</sub>, are less active for photooxidation of propene.



**Fig. 1** Fourier Transforms of Bi L<sub>III</sub>-edge EXAFS spectra of (A) Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> 0.7 mol % (—), 1.5 mol % (---), and 3.0 mol % (-·-·). (B) Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> 10 mol % (—), 30 mol % (---), and Bi<sub>2</sub>O<sub>3</sub> (-·-·). The *k*-range for the Fourier transformation: 4-12 Å<sup>-1</sup>.

**Table 1** Curve-fitting results on Fourier-filtered EXAFS of Bi<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples.

Bi content / mol %	CN	r / Å	Δ(σ <sup>2</sup> ) / 10 <sup>-3</sup> Å <sup>2</sup>	R <sub>f</sub> / %
0.7	4.1	2.31	-3.41	10.5
1.5	3.9	2.31	-3.31	9.65

The *R*-range for back Fourier transformation: 1.1-2.3 Å, the curve fitting *k*-range : 4-11 Å<sup>-1</sup>.

## References

- [1] H. Yoshida, et al., J. Catal., **194**, 364 (2000).
- [2] M. Nomura et al., KEK Report 89-16, (1989).

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