XAFS study on the active species in ZnO/SiO_2 for photo-epoxidation of propene by molecular oxygen at room temperature

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Introduction

Propene oxide (PO) is an important chemical intermediate for industry. Although the direct oxidation of propene to PO by molecular oxygen should be the most desirable way, any heterogeneous catalytic system has not been established still now. We found that ZnO/SiO_2 promoted this reaction in high PO selectivity [1,2]. In the present study, we investigated the structure of zinc oxide species on several ZnO/SiO_2 samples by using XAFS.

Experimentals

Silica-supported zinc oxide sample, ZnO/SiO_2, was prepared by impregnation method [1,2]. ZnO was commercially obtained. The photooxidation test on the sample evacuated at 673 K was carried out as described in our previous paper [1,2]. The reaction time was 2 h.

Zn K-edge XAFS spectra were measured on BL-7C or 9A [3,4] of the Photon Factory (2.5 GeV, 300-430 mA) in a transmission/fluorescence mode at room temperature with a Si(111) double-crystal monochromator detuned to 60% maximum intensity. The sample was evacuated at 673 K, then transferred into polyethylene pack in dry atmosphere. Curve-fitting analysis of Fourier-filtered EXAFS were carried out as described elsewhere [5] by using empirical parameters extracted from ZnO.

Results and discussion

Table 1 shows the results on photooxidation over SiO_2, ZnO/SiO_2 and ZnO samples. The ZnO/SiO_2 samples of lower ZnO content less than 0.1 mol% exhibited higher PO selectivity than others. The selectivity was not influenced by the conversion so much. XANES spectra of ZnO/SiO_2 (Fig. 1) were different from that of ZnO bulk and the line shape varied gradually with Zn loading, implying that the dispersion of zinc oxide species varied gradually. Curve-fitting analysis on Zn-O shell (Table 2) revealed that oxygen coordination number to Zn on ZnO/SiO_2 sample was almost constantly below four. The zinc species on 0.1 mol% ZnO/SiO_2 sample had slightly shorter Zn-O shell and exhibited lower Debye-Waller factor than others. This suggests that the each short Zn-O bonds are well stabilized. These results propose that the zinc oxide species on low content ZnO/SiO_2 are highly dispersed, atomically isolated and low coordinated surface species; for example, such as $Zn(OSi)_2$. In conclusion, the zinc oxide species showing the high PO selectivity in ZnO/SiO_2 sample are proposed to be such zinc oxide species on the silica surface.

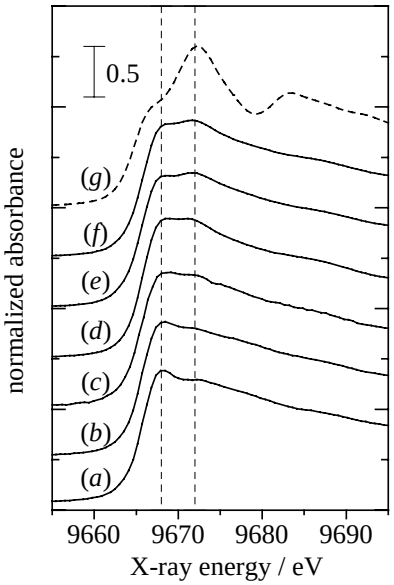

Fig. 1 Zn K-edge XANES spectra of the Zn/SiO_2 samples whose Zn content were 0.01 (a), 0.05 (b), 0.1 (c), 1.0 (d), 5.0 (e) and 30 mol% (f), and that of ZnO (g).

Table 1 Results on photooxidation of propene

Sample	Conv.(%)	PO selec. (%)
SiO_2	0.76	18.7
0.01 mol% ZnO/SiO_2	0.47	48.7
0.1 mol% ZnO/SiO_2	1.91	45.3
1 mol% ZnO/SiO_2	4.78	27.1
5 mol% ZnO/SiO_2	6.70	16.7
ZnO	1.25	1.9

Table 2 Curve-fitting results on Fourier-filtered EXAFS

sample	CN	r / Å	$\Delta\sigma^2$ / 10^{-3} Å^2
0.1 mol% ZnO/SiO_2	2.6	1.95	-2.3
1.0 mol% ZnO/SiO_2	2.4	1.98	-0.19
5.0 mol% ZnO/SiO_2	3.3	1.97	1.03
ZnO	4	1.98	0

References

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