

XAFS study on structure of Ag species in MFI for HC-SCR in the presence of H₂

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Introduction

Selective catalytic reduction of NO by hydrocarbon (HC-SCR) has received much attention because of its potential application to removal of NO_x from exhaust containing excess oxygen. Ag-containing zeolites show less activity for HC-SCR below 723 K [1]. Recently, we have reported that the low temperature activity of Ag/Al₂O₃ catalyst for the SCR by C₃H₈ is significantly improved by the addition of H₂ [2]. In the present study, we carried out the SCR by C₃H₈ in the presence of H₂ over Ag-MFI and investigated the structure of Ag species in MFI-type zeolite during the SCR by using XAFS.

Experimentals

Ag-MFI was prepared by a conventional ion-exchange of H-MFI (Tosoh, Si/Al = 22) with an aqueous AgNO₃ solution [1], followed by calcination at 773 K for 6 h in flowing dried air. The catalytic activity was measured with a fixed-bed flow reactor by passing a mixture of 1000 ppm NO, 1000 ppm C₃H₈, 10% O₂ and 0 or 0.5% H₂ in He at a rate of 100 cm³ min⁻¹ over 0.20 g of catalyst.

Ag K-edge XAFS spectra of Ag-MFI were measured at the BL-10B station [3] at KEK-PF with a Si(311) channel cut monochromator in transmission mode at room temperature. Before measurements, the samples were treated with exposing various gas mixtures at 573 K for 30 min and were sealed in cells made of borosilicate.

Results and Discussion

The SCR by C₃H₈ in the absence and presence of H₂ over Ag-MFI was investigated. By the addition of H₂, NO conversion increased from 12 % to 50 % at 573 K. In the NO+H₂+O₂ reaction, however, reduction of NO by H₂ was not observed. This result indicates that H₂ is not a reducing agent but a promoter for the HC-SCR as well as Ag/Al₂O₃ [2].

Fig. 1 shows the Ag K-edge XANES spectra of Ag-MFI after the various treatments. XANES spectra of Ag-MFI after the treatment of NO + C₃H₈ + O₂ and of NO + C₃H₈ + O₂ + H₂ were different from those of Ag-MFI after O₂ treatment, Ag foil, Ag₂O and Ag₂SO₄.

Table 1 shows curve-fitting analysis on Fourier-filtered EXAFS of Ag-MFI. After O₂ treatment, only Ag-O shell at 2.06 Å was observed, which indicated that Ag was anchored within the micropores of the MFI zeolite in an isolated state [4]. After exposing the SCR atmosphere, particularly in the presence of H₂, Ag-Ag shell was observed. Coordination number and distance of Ag shell after exposing NO+C₃H₈+O₂+H₂ were 1.9 and 2.73 Å, respectively. This coordination number, lower than that of

Ag foil, indicates formation of Ag cluster. From the previous literature [5], it is strongly suggested that Ag cluster are composed of Ag atoms from two to five.

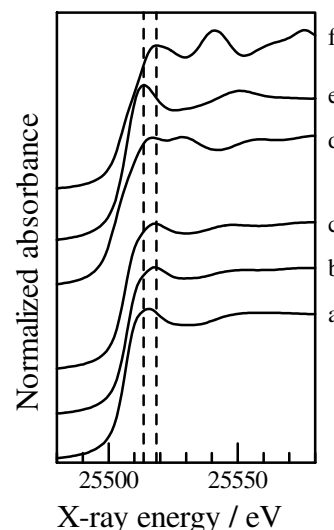


Fig. 1 Ag K-edge XANES spectra of Ag-MFI after treatment of (a) O₂, (b) NO+C₃H₈+O₂ and (c) NO+C₃H₈+O₂+H₂ at 573 K for 1 h, and those of (d) Ag₂O, (e) Ag₂SO₄ and (f) Ag foil.

Table 1 Curve-fitting results on Fourier-filtered EXAFS

sample	treatment	scatter atom	CN	r / Å	$\Delta\sigma^2 / 10^{-3} \text{Å}^2$
Ag-MFI	O ₂	O	0.9	2.06	0.74
		Ag	0.5	2.07	2.25
	NO+C ₃ H ₈ +O ₂	Ag	0.9	2.74	4.86
Ag-MFI	NO+C ₃ H ₈ +O ₂ +H ₂	Ag	1.9	2.73	3.34
Ag foil ¹⁾	—	Ag	12	2.89	—
Ag ₂ O ¹⁾	—	O	2	2.04	—

1) data from crystallography

References

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