

Re- L_{I} and L_{III} edge XAFS study on ReOx/ γ -Fe $_2$ O $_3$ catalysts

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Introduction

We have found that rhenium oxide supported on Fe $_2$ O $_3$ has a unique property in the methanol selective oxidation reaction to produce methylal [1]. To elucidate the local structure of active Re species, we measured Re L_{I} and L_{III} XAFS spectra for ReOx/ γ -Fe $_2$ O $_3$.

Experimental

Catalyst Preparation

ReOx/ γ -Fe $_2$ O $_3$ catalysts were prepared by an incipient wetness impregnation method using an aqueous solution of ammonium perrhenate (NH $_4$ ReO $_4$), followed by drying at 383 K for 12 h. The sample was put into a glass-made fixed-bed reactor in a flow system and heated at 673 K for 6 h in a He flow and held.

XAFS measurements

XAFS spectra were measured at room temperature in a transmission mode at BL 9A and 12C. A Si(111) double crystal was used as a monochromator and the X-ray intensities before and after the sample were monitored by ionization chambers filled with pure N $_2$ and Ar, respectively. Re L_{III} EXAFS spectra were analyzed by the UWXAFS package. The k - and R -ranges for the Fourier transformation and curve fitting range were 30–140 nm $^{-1}$ and 0.1–0.2 nm, respectively. The phase shift and backscattering amplitude were calculated by the FEFF 8 code and the coefficient of multiphoton effects were calculated from the EXAFS of reference compounds.

Results

Figure 1 shows the Re L_{I} -edge XANES spectra of ReO $_2$, ReO $_3$, Re $_2$ O $_7$, NH $_4$ ReO $_4$ and ReOx/ γ -Fe $_2$ O $_3$ catalysts with various loadings. An intense pre-edge peak was observed at 12534 eV on the XANES spectra of NH $_4$ ReO $_4$, Re $_2$ O $_7$, and ReOx/ γ -Fe $_2$ O $_3$ samples. The pre-edge peak is characteristic of tetrahedral Re species. The XANES result indicates that Re species in ReOx/ γ -Fe $_2$ O $_3$ has a tetrahedral structure. This also reveals that the majority of Re species of ReOx/ γ -Fe $_2$ O $_3$ exist as tetrahedral species at all loadings.

Re L_{III} -edge EXAFS also supports the idea. Figure 2 shows the Fourier transforms of the k^3 -weighted Re L_{III} -edge EXAFS oscillation of ReOx/ γ -Fe $_2$ O $_3$ catalyst (9.2wt%). The Re-O distance was 0.175 ± 0.001 nm and the coordination number was 4.0 ± 0.5 , which suggests that the rhenium cations were coordinated by four

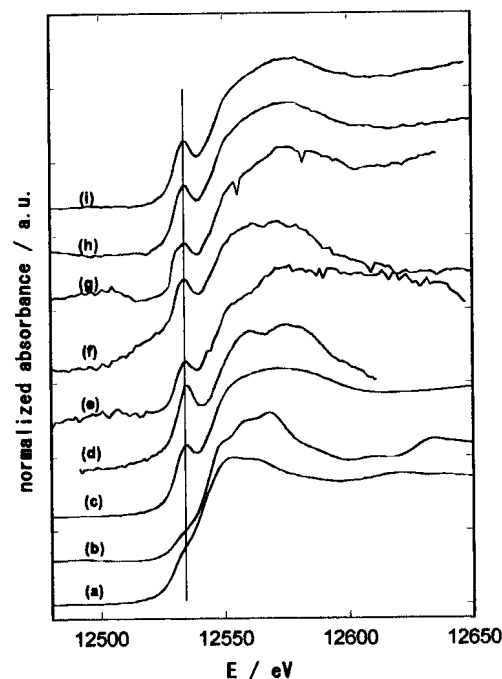


Figure 1. Re L_{I} -edge XANES spectra of (a)ReO $_2$, (b)ReO $_3$, (c)Re $_2$ O $_7$, (d)NH $_4$ ReO $_4$ and (e)-(i)ReOx/ γ -Fe $_2$ O $_3$ with the following loadings;(e)2.5 wt%, (f)3.4 wt%, (g)4.9wt% and (h)6.4 wt%

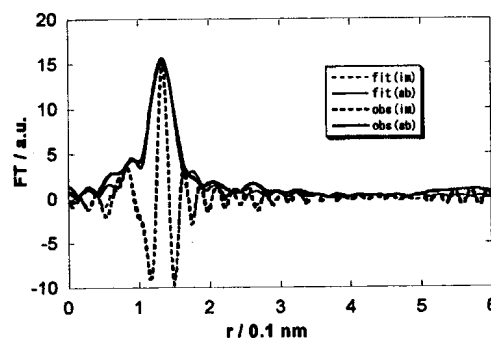


Figure 2. Fourier transforms of the k^3 -weighted EXAFS oscillation of Re/ γ -Fe $_2$ O $_3$ (9.2 wt%).

oxygen anions with a shorter Re-O distance, which were similar to the parameters of NH $_4$ ReO $_4$. The EXAFS result also indicates that the Re species in ReOx/ γ -Fe $_2$ O $_3$ has a tetrahedral structure.

In this study, we have found that the rhenium species supported on γ -Fe $_2$ O $_3$ exists as tetrahedral structure, independent of the loading weight. This rhenium species may contribute as an active species to the methanol selective oxidation reaction.

References

[1] Y. Yuan et al., Chem. Commun. 15, 1421 (2000).