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XAFS Characterization of Re-Pt Bimetallic Catalyst in ZSM-5 Zeolite for Selective Benzene Oxidation

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Introduction

Oxide-supported metal complexes are expected to show unique and tremendous catalysis and to possess the great advantages of both homogeneous and heterogeneous catalysts. We have found that ZSM-5-supported Re-Pt bimetallic catalysts are active for selective benzene oxidation to phenol with NH_3.[1] The oxidation states and local coordination structures of the supported Re-Pt bimetallic catalysts pretreated under different conditions were investigated by Re L_{III}-edge XANES and EXAFS, and the determined structural parameters were compared to catalytic performances for the phenol synthesis by benzene hydroxylation.

Experimental

ZSM-5-supported Re-Pt bimetallic catalysts were prepared by ion exchange with $[NH_3]_4Pt(NO_3)_2$ in water, followed by filtering and drying, and the subsequent impregnation of methyltrioxorhenium in ethanol solution. After calcination at 773 K, the samples were treated with a flow of NH_3 or a flow of an NH_3-O_2-bezene mixture to activate the catalyst for the selective oxidation of benzene.

Re L_{III}-edge XAFS spectra were measured at 20 K in a transmission mode with a Si(111) channel-cut double-crystal monochrometer at the BL-9C and BL-12C stations, using ion chambers with N_2(85%)/Ar(15%) and Ar(100%) for I_o and I_t, respectively. XAFS spectra were also measured in a fluorescence mode using a Lytle detector with Ar(100%) for I_f. Phase shifts and backscattering amplitudes were calculated by the FEFF8.0 code. EXAFS data were fitted with IFEFFIT in *R*-space.

Results and Discussion

Figure 1 (left) shows XANES spectra at Re L_{III}-edge for Re(2.5 wt%)-Pt(2.1 wt%)/ZSM-5 samples pretreated with O_2 at 773 K for 0.5 h, NH_3 at 553 K for 2 h, NH_3-O_2-benzene at 493 K for 1 h, and NH_3-O_2-benzene at 493 K for 1 h & H_2O-benzene at 493 K for 18 min. The catalysts pretreated with O_2 at 773 K for 0.5 h, with NH_3-O_2-benzene at 493 K for 1 h, and with NH_3-O_2-benzene at 493 K for 1 h & H_2O-benzene at 493 K for 18 min were similar to each other, which indicate an oxidized Re state.

Figure 1 (right) shows the Fourier transform of EXAFS data for the Re(2.5 wt%)-Pt(2.1 wt%)/ZSM-5 catalyst pretreated with O_2 at 773 K. The EXAFS Fourier transform was fitted by Re=O at 0.176 nm (CN: 3.3) and Re-O at 0.209 nm (CN: 0.6), which indicates a monomeric $[ReO_4]$ structure bonded to ZSM-5 pore wall.

Figure 2 shows the EXAFS Fourier transform and fitting result for the catalyst after NH_3 pretreatment at 553 K for 2 h, where a cluster formation was suggested by the presence of Re-Re (partially Pt) bonds at 0.270 nm (CN: 2.4) and 0.300 nm (CN: 0.7) besides Re=O at 0.174 nm and Re-O at 0.199 nm. It is suggested that the catalyst after NH_3 pretreatment possesses a cluster structure, but the catalyst in the steady state reaction for the phenol synthesis decomposes to distorted $[ReO_x]$ monomers.

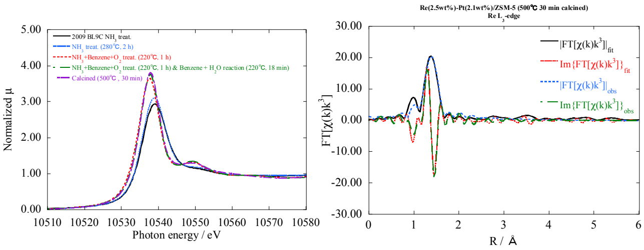

Fig.1 (left) Re L_{III}-edge XANES spectra and (right) EXAFS Fourier transforms for Re(2.5 wt%)-Pt(2.1 wt%)/ZSM-5.

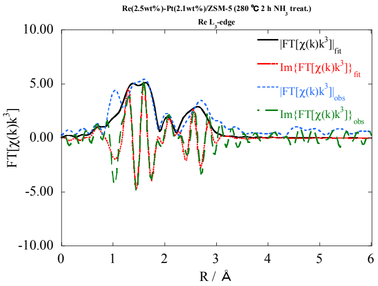

Fig.2
Re L_{III}-edge EXAFS Fourier Transforms for the NH_3-pretreated Re (2.5 wt%)-Pt(2.1 wt%) /ZSM-5 catalyst.

Reference

[1] 王林勝, 唯美津木, 永松伸一, 佐々木岳彦, 岩澤康裕, *触媒* **54**, 147-149, 2012.

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