

## In-Situ XAFS Study on Re/Zelite Catalysts for Direct Phenol Synthesis from Benzene with Molecular Oxygen

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### Introduction

Phenol is one of the most important chemicals and prepared by cumene processes with three-steps acid-base reactions in industry. The direct phenol synthesis from benzene with molecular oxygen is one of the most attractive subjects, but the selective oxidation is still difficult. There were no reports on selective oxidation catalysts for the direct phenol synthesis with high phenol selectivity. We found that a H-ZSM-5-supported Re catalyst exhibited high selectivity (88% for steady-state reaction and 94% for pulse reaction) for the direct phenol synthesis from benzene and O<sub>2</sub> [1]. The structure of active species in zeolite and the structural changes in the catalytic reaction were investigated by in-situ step-scan XAFS and time-resolved energy-dispersive XAFS (DXAFS).

### Experimental

HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 19) supported Re catalyst was prepared by a CVD method of CH<sub>3</sub>ReO<sub>3</sub> at 333 K. The obtained catalyst was pretreated in a He flow at 673 K for 1 h and oxidized in an O<sub>2</sub>/He gas flow. The reduction of the Re catalyst was carried out in a NH<sub>3</sub> flow at 553 K for 2 h. In-situ XAFS measurements were performed with the gas O<sub>2</sub> at 553 K after the treatment with NH<sub>3</sub> (selective oxidation), while the in-situ formation of active Re cluster was performed under NH<sub>3</sub> (the flow rate of NH<sub>3</sub> is around 20 ml/min) at 553 K after the reaction of O<sub>2</sub>.

Re L<sub>III</sub>-edge step-scan XAFS was measured in a transmission mode with a Si(111) double-crystal monochromator at a BL-12C station. Time-resolved energy-dispersive XAFS was measured at a NW2A station of PF-AR and Si(111) bent crystal was used as a polychromator. A self-scanning photodiode array was used as a position sensitive detector. X-rays were detected by position-sensitive PDA recording every 50 ms or 100 ms. The time-resolved measurements started by the injection of the reaction gases (O<sub>2</sub>, O<sub>2</sub> and benzene, and NH<sub>3</sub>) to the evacuated system. Background of these XAFS spectra were subtracted by AUTOBK program and the obtained EXAFS oscillations were Fourier-transformed and fitted in *R*-range by FEFFIT program.

### Results and Discussion

The active structure of the Re/HZSM-5 catalyst for the selective benzene oxidation was found to be Re<sub>10</sub> cluster with Re-Re bonds at 0.276 nm by Re L<sub>III</sub>-edge EXAFS. Figure 1 shows time-resolved energy-dispersive

XANES spectra of true active Re catalyst at Re L<sub>III</sub>-edge measured at 553 K by the exposure to O<sub>2</sub> (reaction feed). The peak top of the XANES region increased when the selective oxidation proceeded, indicating that the active Re cluster converted to Re<sup>7+</sup> monomers during the selective oxidation reaction in the presence of O<sub>2</sub>.

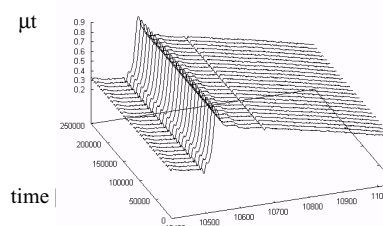


Figure 1. The series of in-situ energy-dispersive XANES spectra at 553 K in the presence of molecular oxygen (13.9 kPa). These spectra were recorded every 150 ms with the exposure time of 50 ms.

Figure 2 shows that changes in the intensity of

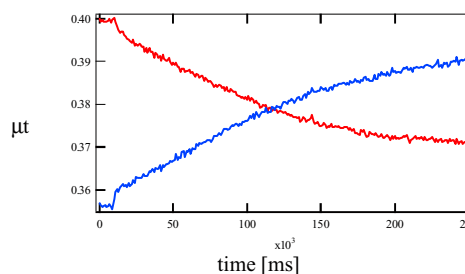


Figure 2. Changes in the intensity of Re L<sub>III</sub>-edge XANES at 553 K in the presence of molecular oxygen (16.0 kPa). These spectra were recorded every 1000 ms with the exposure time of 100 ms. (blue:10612 eV, red:10595 eV)

XANES during the selective oxidation process. The structural changes by benzene and molecular oxygen were completed within 100 ms as shown in Figure 2. On the other hand, the reduction to the active Re cluster much slowly proceeded and the existence of intermediate structures was suggested.

[1] R. Bal, M. Tada, T. Sasaki, and Y. Iwasawa, *Angew. Chem. Int. Ed.* 45, 448-452 (2006) (Selected as Hot Paper of *Angew. Chem. Int. Ed.*).

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