In-Situ XAFS Study on Re/Zeolite 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 O₂ [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 (SiO₂/Al₂O₃ = 19) supported Re catalyst was prepared by a CVD method of CH₃ReO³ at 333 K. The obtained catalyst was pretreated in a He flow at 673 K for 1 h and oxidized in an O₂/He gas flow. The reduction of the Re catalyst was carried out in a NH₃ flow at 553 K for 2 h. In-situ XAFS measurements were performed with the gas O₂ at 553 K after the treatment with NH₃ (selective oxidation), while the in-situ formation of active Re cluster was performed under NH₃ (the flow rate of NH₃ is around 20 ml/min) at 553 K after the reaction of O₂.

Re L₃-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 (O₂, O₂ and benzene, and NH₃) 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 Re₉₀ cluster with Re-Re bonds at 0.276 nm by Re L₃-edge EXAFS. Figure 1 shows time-resolved energy-dispersive XANES spectra of true active Re catalyst at Re L₃-edge measured at 553 K by the exposure to O₂ (reaction feed). The peak top of the XANES region increased when the selective oxidation proceeded, indicating that the active Re cluster converted to Re⁷⁺ monomers during the selective oxidation reaction in the presence of O₂.

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 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.

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