

## In-Situ Time-Resolved Energy-Dispersive XAFS Study on A $\text{Re}_{10}$ -Cluster/HZSM-5 Catalyst for Direct Phenol Synthesis from Benzene and $\text{O}_2$

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### Introduction

Direct phenol synthesis from benzene and  $\text{O}_2$  in one step reaction with high benzene conversion and high phenol selectivity is one of the most important reactions in chemical synthesis. We have succeeded in the preparation of a novel  $\text{Re}_{10}$ -cluster/HZSM-5 catalyst, which exhibited the highest phenol selectivity (94%) with 10% benzene conversion<sup>[1]</sup>. In this study, we report the mechanism of structural transformation between the catalytically active  $\text{Re}_{10}$  cluster and its oxidized Re monomers for the selective benzene oxidation by in-situ time-resolved DXAFS<sup>[2,3]</sup>.

### Experimental

Supported  $\text{Re}_{10}$  cluster catalyst on HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 19$ ) was prepared by chemical vapor deposition of  $\text{CH}_3\text{ReO}_3$  at 333 K.  $\text{NH}_3$  was reacted with the HZSM-5-supported catalyst at 553 K for 2 h for the clusterization of the supported Re species.

Energy-dispersive XAFS at Re  $L_3$ -edge was measured at PF-AR NW2A station. Si(111) bent crystal of a Bragg reflectron type and PDA were used as polychromator and position sensitive detector, respectively, for the DXAFS measurements. Time resolution was 100 ms.  $\text{O}_2$  or the mixture of  $\text{O}_2$  and benzene was admitted to the  $\text{Re}_{10}$ -cluster catalyst at 538 - 583 K and the changes in Re  $L_3$ -edge XANES were monitored by DXAFS.

### Results and Discussion

Oxygen not only oxidizes benzene to phenol but also oxidizes the active  $\text{Re}_{10}$  clusters to inactive  $\text{ReO}_4$  monomers competitively under catalytic reaction conditions. We measured structural changes from the  $\text{Re}_{10}$  cluster to the Re monomers by DXANES. Figure 1 shows a series of time-resolved DXANES at Re  $L_3$ -edge measured at 553 K during the selective oxidation with benzene and  $\text{O}_2$  on the  $\text{Re}_{10}$  cluster. At least three isosbestic points were observed for the oxidation reaction, indicating that direct transformation of the  $\text{Re}_{10}$  cluster to the Re monomers occurred without the existence of definite intermediates in this time scale. Thus the series of DXANES spectra can be given by the linear combination of the DXANES spectra for the initial  $\text{Re}_{10}$  cluster and the final Re monomers. Fitting was performed well with the linear combination and the sum of coefficients ( $P(t)$ :  $\text{Re}_{10}$  cluster and  $Q(t)$ : Re monomer) were always  $1.0 \pm 0.005$  at the whole stage of the selective

oxidation process with benzene and  $\text{O}_2$  in the temperature range of 538-583 K.

The plots of  $\ln(P(t))$  vs. reaction time reveal that the  $\text{Re}_{10}$  cluster disintegration shows the first-order reaction kinetics. Together with the existence of the isosbestic points in the DXANES spectra, these result indicate that the first step for the oxidation reaction is the reaction between the  $\text{Re}_{10}$  cluster and  $\text{O}_2$  followed by faster decomposition steps to the Re monomers in the presence of extra  $\text{O}_2$  molecules. No existence of intermediate structures with lower phenol selectivity is suggested to be one of the main reasons for the high phenol selectivity on the prepared  $\text{Re}_{10}$ -cluster catalyst.

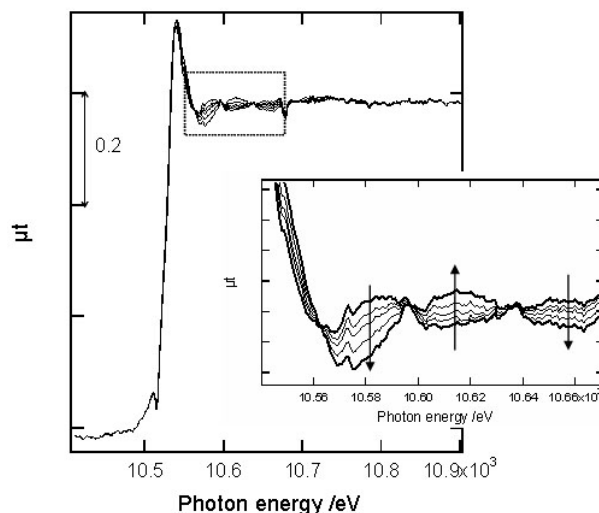


Fig. 1 A series of time-resolved DXANES at Re  $L_3$ -edge measured at 553 K during the selective oxidation with benzene (4.8 kPa) and  $\text{O}_2$  (9.7 kPa).

### References

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