

In-situ Energy-Dispersive XAFS Observation of the Transformation of Active Re_{10} Cluster to Inert Re Monomer in the Direct Phenol Synthesis Process

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Introduction

We have developed a new Re_{10} cluster catalyst supported on HZSM-5, which is active for the selective oxidation of benzene directly to phenol with molecular O_2 . The Re_{10} /HZSM-5 catalyst has firstly achieved a breakthrough of both 5 % conversion and 50 % selectivity with O_2 as a sole oxidant. This catalyst may be a promising catalyst for an alternative phenol process to the present cumene process.

Previously, we found that the Re_{10} cluster decomposed to Re monomers under the phenol synthesis conditions. The Re monomer was completely inert for the phenol synthesis. It is important to understand how the active multinuclear species changes to the inert mononuclear species under the working conditions because the transformation should affect high catalytic performances. In this study we performed in-situ energy-dispersive XAFS observations for structural changes in the Re_{10} /HZSM-5 catalyst under the selective oxidation reaction conditions.

Experimental

The HZSM-5-supported Re_{10} cluster catalyst was prepared according to our previous report [1, 2].

All energy-dispersive XAFS experiments at Re L_3 -edge were performed at PF-AR NW2A station. A Si(111) bent crystal (curvature radius is 2500 mm) was used as a polychromator and PDA was used as position sensitive detector in the DXAFS measurements. The acquisition time resolution was 100 ms. The active Re_{10} cluster catalyst was exposed to O_2 or benzene or a O_2 -benzene mixture gas at 538–583 K at a few seconds after the DXAFS measurements started.

Results and Discussion

The successive in-situ XANES spectra showed isosbestic points, and there were no other species observed during the course of the transformation from the Re_{10} clusters to the ReO_4 monomers under both the O_2 atmosphere and the benzene- O_2 mixture. This fact means that the successive Re-XANES spectra can be reproduced by a linear combination of the spectra for the active Re_{10} cluster and the spectra for the inert ReO_4 . Each spectrum in the successive DXAFS measurements was fitted by a linear combination of Re_{10} cluster XANES and ReO_4

XANES, and coefficients of the Re_{10} cluster portion was plotted vs. reaction time. It decreased linearly against the reaction time, which indicates the rate-limiting step of the transformation of Re_{10} clusters is the first oxidation step of Re_{10} clusters.

The rate constants at 538–583 K were estimated 49 kJ mol^{-1} and 74 kJ mol^{-1} , respectively under the both O_2 atmosphere and the gas mixture conditions. Fig. 1 shows Arrhenius plots for structural transformation of the Re_{10} clusters to the inert ReO_4 monomers. The increase of the activation energy under the gas mixture condition implies that benzene prevents the Re_{10} clusters from decomposing. This effect of benzene should contribute to an increase in the concentration of active Re_{10} species under the oxidation condition and to maintain the catalytic activity.

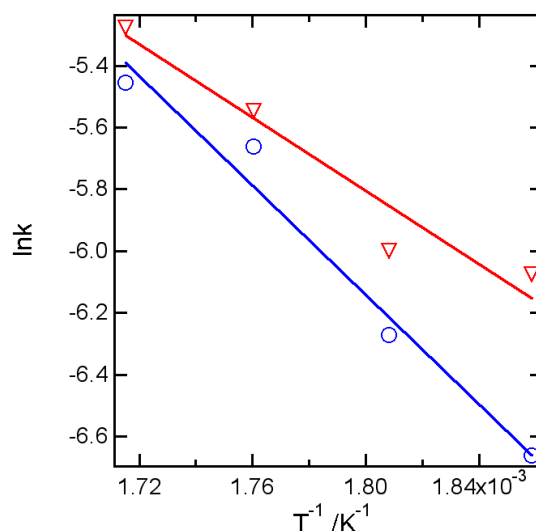


Fig. 1 Arrhenius plots for the structural transformation of active Re_{10} clusters to ReO_4 monomers; triangle : under O_2 gas; circle : under the benzene and O_2 mixture

Reference

- [1] R. Bal, M. Tada et al., *Angew. Chem. Int. Ed.* **45**, 448 (2006).
- [2] M. Tada, R. Bal, T. Sasaki, Y. Uemura, Y. Inada, S. Tanaka, M. Nomura, and Y. Iwasawa, *J. Phys. Chem. C* **111**, 10095 (2007).

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