In-situ Time-Resolved DXAFS of a Re-Cluster Catalyst for Direct Phenol Synthesis from Benzene and O_2

We have succeeded in preparing a novel Re_{10} cluster catalyst which shows high activity and selectivity for the direct synthesis of phenol from benzene and O_2. The dynamic structural changes in the active cluster during synthesis have been investigated using in-situ time-resolved energy-dispersive XAFS (DXAFS) for the first time. We found that the reactant benzene inhibited the unfavorable decomposition of the active Re_{10} cluster, and we proposed the concept of the structural kinetics of the active species during the catalytic reaction.

Phenol is the major source of Bakelite and phenol resins, and is produced using the cumene process in industry all over the world. The three-step cumene process however has many disadvantages, such as high energy consumption, the production of many by-products, the use of sulphuric acid, and the explosive cumene hydroperoxide intermediate, resulting in low phenol yield. Direct synthesis of phenol from benzene and O_2 in one step is the most desirable reaction, but no catalysts with high phenol yield have been discovered to date since it is difficult to activate molecular oxygen to selectively promote the oxidation of benzene to phenol. In 2006, we succeeded in preparing a novel N-interstitial Re_{10} cluster in HZSM-5 pores by the chemical vapour deposition of CH_3ReO_3. As a catalyst for the direct synthesis of phenol from benzene using O_2 as an oxidant, a phenol selectivity of 94% was achieved [1], the highest to date. The benzene conversion was 9.9%. The role of NH_3 and the dynamic structural transformations of catalytically active Re clusters were investigated using in-situ time-resolve DXAFS [2].

The energy-dispersive XAFS of the active Re_{10}-cluster catalyst was recorded at AR-NW2A. White X-rays from the tapered undulators were vertically focused by a Rh-coated bent mirror (polychromator). A self-scanning photodiode array coupled by a CsI(Tl)-embrocated fiber optical plate was used as a linear detector. A disk of the supported Re catalyst on HZSM-5 was enclosed in a batch reactor with X-ray windows. The reactant gas (pure O_2 or a mixture of benzene and O_2) was admitted to the XAFS cell, and DXAFS spectra at the Re L_{III}-edge were recorded every 50 ms in real time.

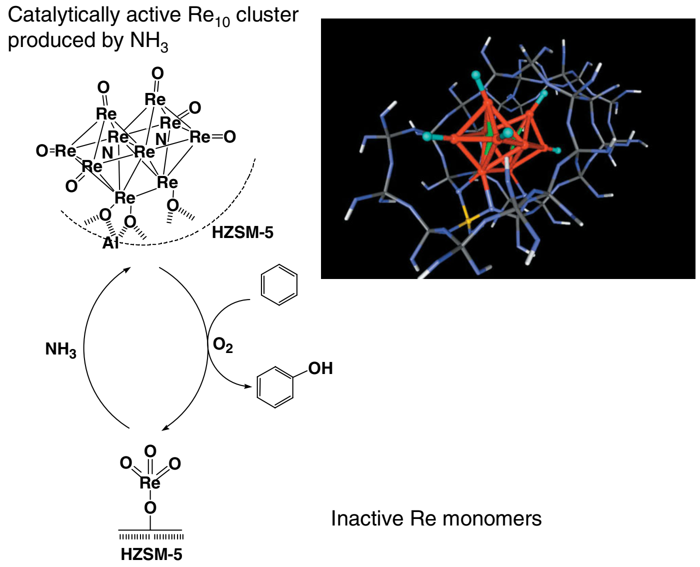

Figure 1
Dynamic structural changes in the supported Re species on HZSM-5 under the conditions for phenol synthesis.

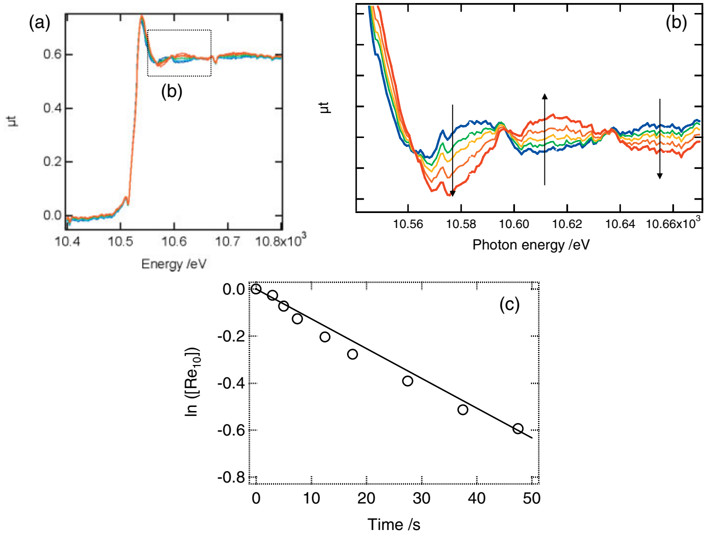

Figure 2
(a) Series of in-situ time-resolved Re L_{III}-edge DXANES spectra recorded at 553 K at 500 ms intervals during the selective oxidation with benzene and O_2. p_{O2} = 9.7 kPa and $p_{benzene}$ = 4.8 kPa. (b) Expanded spectra of (a). (c) Time dependence of Re_{10}-cluster concentration estimated from fits to the Re L_{III}-edge XANES spectra. 553 K, p_{O2} = 9.7 kPa and $p_{benzene}$ = 4.8 kPa.

The supported Re catalyst showed dynamic structural changes during the catalytic oxidation process. NH_3, which was used to keep steady-state activity, led to the production of N-interstitial Re_{10} clusters, which became the catalytically active species for selective benzene oxidation. The Re_{10} clusters smoothly produced phenol from benzene and O_2, subsequently converting to inactive Re monomers, as shown in Fig. 1. Figure 2 (a) shows the series of in-situ time-resolved Re L_{III}-edge DXANES spectra recorded during the direct phenol synthesis (active Re_{10} cluster → inactive Re monomers). At least three isosbestic points were observed (at 10562, 10597, and 10636 eV), as shown in Fig. 2 (b), indicating that definite intermediates did not exist during the active Re_{10}-clutser decomposition. The spectra could be successfully fitted with linear combinations of the DXANES spectra of the initial state (Re_{10} cluster) and the final state (Re monomers), and the time dependence of the Re_{10} cluster concentration, shown in Fig. 2 (c), indicates a first-order reaction. These results indicate that the decomposition of the active Re_{10} clusters to inactive Re monomers proceeded without metastable intermediates under the oxidation conditions. If intermediate structures with low phenol selectivity were present, the total phenol selectivity would decrease no matter how high the phenol selectivity of the initial cluster. The immediate decomposition of the active species to a completely inactive species is suggested as an explanation for the high phenol selectivity of the prepared Re catalyst.

The activation energy of the structural change from Re_{10} cluster to Re monomers was estimated to be 74 kJ mol^{-1} in the presence of benzene, and 49 kJ mol^{-1} in the absence of benzene. We have succeeded in determining the structural kinetics of the catalytically active Re_{10} clusters during phenol synthesis for the first time. The difference in the activation energies indicates that the reactant benzene inhibits unfavorable decomposition of the catalytically active Re_{10} clusters under the catalytic oxidation conditions.

REFERENCES

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BEAMLINE

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