

XAFS Study on Re/Zeolite Catalysts for Direct Phenol Synthesis from Benzene with Molecular Oxygen

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Introduction

Phenol is an important chemical in industry but has been produced from benzene by the three-steps of cumene process. Direct phenol synthesis from benzene is one of the important subjects. However, no selective catalyst with good performance in an economically and environmentally favourable benzene-O₂ system has been discovered to date. We have found Re/HZSM-5 promoted the direct phenol synthesis from benzene with 88% (steady-state) and 94% (pulse) selectivity using molecular oxygen as an oxidant under co-existing NH₃.

Experimental

HZSM-5 supported Re catalysts were prepared by a conventional impregnation method using NH₄ReO₄ and a CVD method with CH₃ReO₃ at 333 K. The both catalysts were pretreated in a He flow at 673 K for 1 h. The selective catalytic reactions were conducted in a fixed bed down flow reactor with the reaction gases of He: O₂: NH₃: benzene = 46.4: 12.0: 35.0: 6.6 (mol%), analyzed by on-line GC.

XAFS spectra at Re LIII-edge were measured in a transmission mode at 15 K at the BL-10B and 12C stations. The samples were measured without exposing to air. Background subtraction was conducted by the AUTOBK program, and Fourier-transformed spectra were fitted in R space by FEFFIT program.

Results and Discussion

It was found that Re/HZSM-5 catalysts are active for the selective oxidation of benzene with molecular oxygen when ammonia was coexisted. The CVD catalyst was almost 18 times more active than the impregnated catalyst. The selectivity was much higher on the CVD catalyst (88%) than on the impregnated catalyst (28%). The catalytic performances depended on the kind of zeolites.

Figure 1 shows Re LIII-edge EXAFS Fourier transforms and curve fitting spectra for the CVD Re/ZSM-5 sample after NH₃ treatment and the steady-state oxidative reaction. It is obvious that the structure of the Re species changes remarkably by NH₃. The NH₃ treatment caused a drastic transformation to Re cluster with Re-Re bonds at 0.276±0.001 nm (CN=5.1±0.3). There were two types of Re-O bonding attributed to Re=O at 0.173±0.001 nm (CN=0.5±0.2) and longer Re-Obridge and/or Re-Olattice at 0.202±0.001 nm (CN=2.4±0.3). The structure of the Re cluster was modelled by DFT as a N-interstitial Re₉ cluster

composed of two octahedral Re₆ frameworks with plane share to each other. The treatment with NH₃ at 553 K reduces Re oxidation state to the lower valence proved by ReL₁ XANES and XPS.

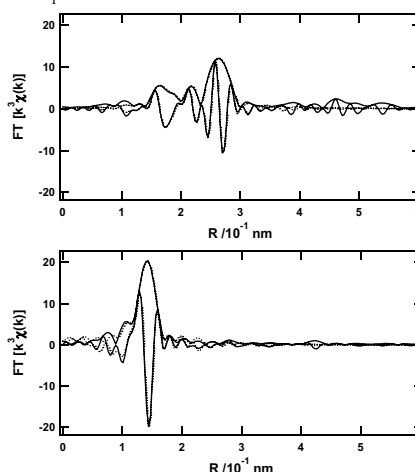


Figure 1. Fourier-transformed Re LIII-edge EXAFS spectra of Re cluster after the NH₃ treatment (top) and Re monomer after the reaction (bottom).

The NH₃ pretreated catalyst did not produce phenol when only benzene was pulsed. This indicates that the lattice oxygen of the Re cluster is not involved for the selective oxidation. The pulse of benzene + O₂ on the NH₃ pretreated catalyst produced phenol with 94% selectivity, which demonstrates that the Re cluster is active species.

In the pulse experiment the phenol formation rate became zero after 4 pulses. Thus the coexistence of NH₃ is indispensable for the phenol formation, and the Re cluster is not stable under O₂ in the absence of NH₃. The active Re cluster was transformed to inactive Re monomers with Re=O bonds at 0.173±0.001 nm (CN=3.7±0.2) and Re-O bond at 0.213±0.003 nm (CN=1.3±0.7) as proved by EXAFS.

In presence of ammonia about 3 - 4 % of the [ReO₄] monomers are estimated to be transformed to Re₉ clusters, which are responsible for the formation of phenol. A mechanism for the phenol formation may involve oxygen free radical formation on Re₉ cluster. Alternatively, molecular oxygen associatively adsorbed on the partially reduced Re₉ cluster may be the active oxygen species for the formation of phenol from benzene. On the latter case the maximum selectivity would be 93.9%.

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