XAFS studies on local structure of Ti supported on Cu/HZSM-5 catalysts for the synthesis of phenol

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Introduction
The partial oxidation of hydrocarbons into various derivatives such as alcohols, aldehydes, ketones, carboxylic acids and epoxides has been extensively investigated, because such products are industrially significant. However, the industrial oxidation process usually demands high selectivities, high yields, energy efficiency or economical efficiency. Phenol production, which is an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics, is mainly carried out through the Cumene process. However, this process consists of three steps and produces acetones as byproduct. The direct oxidation of benzene is more desirable for the phenol production, because of more economical and without byproducts.

We have reported that supported Cu/HZSM-5 catalysts effectively oxidize the benzene to phenol with molecular oxygen.[1] In this study, we have investigated the direct gas-phase oxidation of benzene to phenol over Cu/HZSM-5 added with Ti. The XAFS study has clarified the relation between the structure of titanium species and the selectivity of products.

Experimental Section
Ti/HZSM-5 was prepared by impregnation with an aqueous solution of titanium ammonium oxalate. The solvent was removed by evacuation at ca. 330 K. The resulting wet solid was freeze-dried, then calcined in air for 5 h at 773 K. The sample will be designated as Ti/HZSM-5. Copper oxide supported on Ti/HZSM-5 was prepared by impregnation with an aqueous solution of copper acetate. The solvent was removed by evacuation at ca. 330 K. The resulting wet solid was freeze-dried, then calcined in air for 5 h at 773 K. The sample will be designated as Ti/HZSM-5.

Profiles of X-ray absorption near-edge structure (XANES) for the samples were taken at room temperature in Transmission mode for K-edges of Ti at beam-line BL-7C of Photon Factory. After the calcination of samples at 773 K for 1 h, the samples also were sealed with polyethylene films in nitrogen atmosphere.

Results and Discussion
In the presence of oxygen, Cu/Ti/HZSM-5 catalyst oxidizes the benzene to phenol and COx (CO₂, CO). Ti addition to Cu/HZSM-5 also led to the increase of phenol yield and selectivity. Although, the increase of Ti/Cu ration from 0.2 to 1.0 adversely caused the decrease of phenol selectivity. The situation of Ti species on the Cu/Ti/HZSM-5 catalysts seems to influence on the activity of phenol formation.

Figure shows the XANES spectra of Cu/Ti/HZSM-5 catalyst having different Ti/Cu ratio. The intensity of the preedge peak of catalyst of which Ti/Cu ratio is 0.2 was higher than Ti/Cu=1.0. It has been reported that XANES spectrum of the tetrahedral coordination state of titanium oxide species has a strong intense peak and the spectrum of the octahedral coordination state has the weak three peaks. Hence, it is indicated that the catalysts having the lower Ti/Cu ratio mainly consist of the tetrahedral titanium species, and the higher Ti/Cu ratio leads to the increase of the octahedral Ti species. The presence of the octahedral Ti species may cause the formation of COx in this reaction.

Figures. XANES spectra of Cu/Ti/HZSM-5 catalysts calcined at 773 K. (Cu=0.7wt%, Ti/Cu=0.2, 1.0)

References

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