Structural analysis of iron oxide nanocluster catalyst and its application to benzyl alcohol oxidation reaction

Nobuyuki ICHIKUNI, Hiroyuki OIDE, Takayoshi HARA, Shogo SHIMAZU
(Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, JAPAN)
ichikuni@faculty.chiba-u.jp

Keywords: iron oxide nanocluster, catalyst, XAFS, benzyl alcohol oxidation

Introduction

Much research about nano-sized metal catalysis has been carried out and reported. Almost all the research was focused on precious metal catalysis. However, precious metals have the limitation of resources and the development of the precious metal substituting materials is strongly desired. For this point of view, developing active catalysts using base metals is highly required. Fe is abundant and a less expense element, and expected to be the candidate for this objective. Since nano-sized materials have unique characteristics, preparation of nano-sized base metal catalyst seems to be an effective way for developing precious metal substituting catalysts. In this report, we prepared supported iron oxide nanocluster catalysts and characterized them by XAFS. Obtained iron oxide nanocluster catalysts showed the activity toward liquid phase benzyl alcohol oxidation reaction.

Experimental methods

Supported iron oxide nanocluster catalysts (PVP-Fe/AC) were prepared as follows: Polyvinylpyrrolidone (PVP) stabilized Fe colloid was synthesized and supported on activated carbon (AC), followed by thermal treatment under various conditions. Fe K-edge XAFS data were obtained at BL-12C of PF, KEK-IMSS in a transmission mode at room temperature (proposal no: 2016G069). X-ray was monochromatized by Si(111) double crystal. Obtained XAFS data were analyzed by programs Athena and REX2000. To evaluate the catalysis, the oxidation of benzyl alcohol by molecular oxygen at 353 K was carried out.

Results and discussion

By analyzing edge energies of Fe K-edge, the formal valence of Fe species in the catalyst was determined to be Fe(III). To clarify the coordination geometry about Fe atoms, the pre-edge region analysis was applied. The pre-edge peak intensity for spinel structure (gamma-Fe_2O_3) and that for corundum structure (alpha-Fe_2O_3) were strong and weak, respectively. The intensity of pre-edge peak was getting stronger as increasing the thermal treatment temperature. This result indicated that Fe species in the catalyst was transformed from a corundum into spinel structure as elevating the temperature. Moreover, the benzaldehyde yield was correspond to the content of the spinel structure.

Conclusion

AC supported iron oxide nanocluster catalyst showed the activity of benzyl alcohol oxidation reaction into benzaldehyde. XAFS analysis revealed that the tetrahedrally coordinated Fe in spinel structure had a key role for the benzyl alcohol oxidation reaction.

Acknowledgement

This study was supported by JSPS KAKENHI Grants 26420784 and 17K06912.