

Study on the effect of the interfacial structure of supported NiO nanocluster catalysts to 1-phenylethanol oxidation reaction

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Introduction

Base metal catalysts can be novel metal substituting catalysts. In particular nanocluster catalysts have been gathering much attention due to its unique property which bulk catalysts do not possess. However, research on base metal nanocluster catalysts is fewer since their preparation is not easy compared to novel metal nanocluster catalysts. We have succeeded in preparing a SiO₂ supported NiO nanocluster catalyst and found that a composite oxide, nickel silicate, between NiO nanocluster and SiO₂ had a promoting effect for thiophenol coupling reaction [1] and 1-phenylethanol oxidation reaction [2]. In this presentation, we focused on an interfacial structure property of catalysts which do not have the composite oxide phase. An activated carbon (AC) supported NiO nanocluster catalyst, not having the composite oxide phase, was found to be active to 1-phenylethanol oxidation reaction. A correlation between local structure and catalysis will be discussed.

[1] T. Sasaki, N. Ichikuni *et al.*, *J. Phys.: Conf. Ser.*, 2016. [2] T. Sasaki, N. Ichikuni *et al.*, *Catal. Today*, *in press*.

Experimental methods

Size regulated NiO catalysts were synthesized as follows: Ni colloidal solution was prepared by the reduction of Ni(acac)₂ using NaBH₄ with *t*-butoxide as a stabilizer in THF solvent at 338 K under reflux condition. The support was immersed in the Ni colloidal solution for 1 h, followed by dried in air at RT. Obtained catalysts were analyzed by XAFS (proposal no: 2016G069, KEK-IMSS, PF BL-12C) and applied to 1-phenylethanol oxidation reaction.

Results and Discussion

XAFS revealed that Ni nanocluster on the support was fully oxidized at RT and its particle size was very small. Among four types of supports, AC, SiO₂, Al₂O₃ and MgO, only AC support has a significant effect on the catalysis. A shrinkage of Ni-(O)-Ni coordination distance was found only in the AC supported NiO nanocluster catalyst. It can be said that there is an electronic interaction between NiO and AC. XPS also showed this interaction as a shift of binding energy. The modified interfacial structure seemed to have a key role for the catalysis.

Conclusion

AC supported NiO nanocluster catalyst was active to 1-phenylethanol oxidation reaction. The catalysis strongly depended on the local structure of the interface between NiO nanocluster and AC.

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