XAFS study on the silica supported Co oxide nanocluster catalyst

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1 Introduction
Cobalt oxide showed high catalytic activity toward oxidation reactions and are abundant, thus Co element has been thought to be one of the effective candidates for substituting the noble metal. One of the key methods to develop the active catalyst is reducing the metal particles down to nanocluster size, since nanocluster has a larger population of low-coordination sites and may have a specific property. However, conventional preparation methods for supported Co catalysts lead the particles size larger than 10 nm.

In this study, we tried to prepare the supported Co oxide nanocluster catalyst by using an metal Co colloid as a precursor. The oxidation degree from Co metal to Co oxide and the cluster size of Co oxide was estimated by XAFS analysis.

2 Experimental
Alcoholate stabilized Co colloid [1] was prepared similar manner as in the literature of Ni colloid preparation [2]; in this study, 2-butanol was applied as alcoholate precursor and pre-dehydrated Co(OAc)2 was employed. Silica (Aerosil, #200) was used for the preparation of supported nanocluster catalyst (col Co/SiO2). The Co loading was regulated as 3 wt%. Further O2 treatment of the catalyst was carried out in a closed circulating system.

Co K-edge EXAFS were collected at PF BL-9C with Si(111) double crystal monochromator in a transmission mode. The pattern-fitting analysis of XANES region and curve-fitting analysis of k2-weighted EXAFS oscillations in k-space were performed by the program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis were extracted from bulk Co3O4.

3 Results and Discussion
Co K-edge XANES spectra are shown in Fig. 1. Without O2 treatment, Co species in col Co/SiO2 is composed from Co3O4 and Co(OH)2 (Fig. 1(a)). As increasing the O2 treatment temperature, XANES profile resembles to that of Co3O4. Based on the pattern-fitting analysis, O2 treatment must be done at least 573 K to convert from Co hydroxide to Co oxide in col Co/SiO2.

Coordination number (CN) for Co-(O)-Co coordination at around 0.24 nm were calculated by curve-fitting analysis using model parameters. The CN increased with elevating the O2 treatment temperature from 2.0 (w/o treatment), 2.5 (453 K), 3.4 (573 K) and 3.5 (673 K). However, the bond length was not affected by O2 treatment and kept constant (0.286 nm). Considering the O2 treatment temperature dependence of XANES profile, it seems that the increment of CN is not due to the particle size growth of Co oxide.

Col Co/SiO2 catalysts showed the CO oxidation activity. The highest activity was obtained at 573 K O2 treatment. Although it was expected that both 573 K O2 treatment and 673 K O2 treatment catalysts show almost the same activity from XANES and EXAFS CF analysis, the 573 K treated catalyst showed the higher activity. It seems that the oxidation state of Co or surface defect as well as the valence and size may play the important role for the catalysts. Further investigation will be required.

![Fig. 1: Co K-edge XANES spectra for col Co/SiO2 catalysts oxidized at (a) w/o pretreatment, (b) 453 K, (c) 573 K, (d) 673 K and reference compounds (e) Co3O4, (f) Co(OH)2.](image)

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References

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