

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 $\text{Co}(\text{OAc})_2$ was employed. Silica (Aerosil, #200) was used for the preparation of supported nanocluster catalyst (*col* Co/SiO_2). The Co loading was regulated as 3 wt%. Further O_2 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 k^3 -weighted EXAFS oscillations in *k*-space were performed by the program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis were extracted from bulk Co_3O_4 .

3 Results and Discussion

Co *K*-edge XANES spectra are shown in Fig. 1. Without O_2 treatment, Co species in *col* Co/SiO_2 is composed from Co_3O_4 and $\text{Co}(\text{OH})_2$ (Fig. 1(a)). As increasing the O_2 treatment temperature, XANES profile resembles to that of Co_3O_4 . Based on the pattern-fitting analysis, O_2 treatment must be done at least 573 K to convert from Co hydroxide to Co oxide in *col* Co/SiO_2 .

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 O_2 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 O_2 treatment and kept constant (0.286 nm). Considering the O_2 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/SiO_2 catalysts showed the CO oxidation activity. The highest activity was obtained at 573 K O_2 treatment. Although it was expected that both 573 K O_2 treatment and 673 K O_2 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 catalysis. Further investigation will be required.

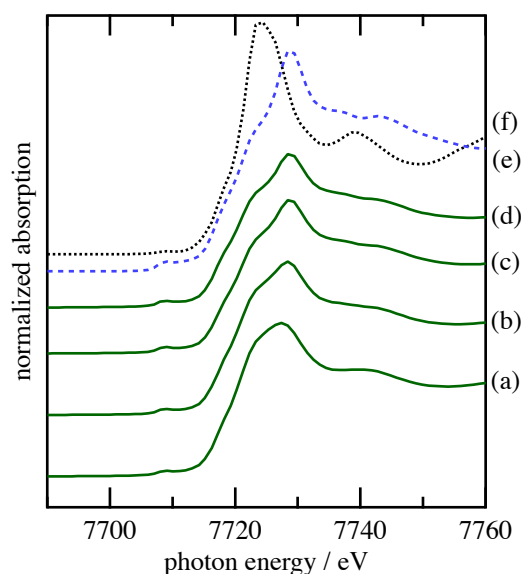


Fig. 1: Co *K*-edge XANES spectra for *col* Co/SiO_2 catalysts oxidized at (a) w/o pretreatment, (b) 453 K, (c) 573 K, (d) 673 K and reference compounds (e) Co_3O_4 , (f) $\text{Co}(\text{OH})_2$.

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References

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