

XAFS analysis of NiO species formed on calcium silicide

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1 Introduction

Recently, effective utilization of resources is strongly desired from the perspective of economy and resource conservation. Reducing the size of catalytic metal or oxide particles on catalyst support materials not only improves their efficiency but also promises the expression of catalytic performances specific to fine particles. Nickel is also a more abundant element compared to precious metal element as a resource for catalysts.

On the other hand, various techniques enable to use for preparation of catalysts. Metal oxides are mainly adopted as catalysts support materials. In our previous work, we report on the successful synthesis of a flower like structured calcium silicide (CaSi_2) through a simple chemical treatment of bulk CaSi_2 powder [1]. We also focus on the utilization of CaSi_2 in catalysts preparation, which is composed of abundant elements and has unique functions. In the present study, nickel oxide (NiO) was prepared by utilizing the characteristics of CaSi_2 . XAFS investigations were carried out to confirm the chemical state of NiO species formed on CaSi_2 .

2 Experiment

CaSi_2 was purchased from Kojundo chemical lab. co. ltd., and was finely crushed by a planetary ball mill. The treatment of CaSi_2 in an aqueous $\text{Ni}(\text{NO}_3)_2$ solution was carried out by following process. After CaSi_2 was suspended in an aqueous $\text{Ni}(\text{NO}_3)_2$ solution in a flask and shook at 298 K for 1 h, sample was recovered by centrifugation, dried under vacuum at 298 K after washing by deionized water. NiO-loaded SiO_2 (NiO/SiO_2) was also prepared by an impregnation method. After impregnation, sample was calcined at 773 K in air. XAFS spectra at Ni K-edge were measured in the transmission mode for reference samples and fluorescence mode for target samples at 298 K. Samples were sealed within polyethylene film under an argon atmosphere. Obtained data were examined using the analysis program (Rigaku REX2000).

3 Results and Discussion

The disappearance of the color of the solution was observed during the mixing of CaSi_2 and an aqueous $\text{Ni}(\text{NO}_3)_2$ solution. It was also confirmed that the amount of Ni species charged (1.0 wt % as metal) were completely fixed on CaSi_2 even after washing by deionized water. The local structure as well as the valence state of Ni species on CaSi_2 were also investigated by Ni K-edge XAFS measurements. As shown in Fig. 1, the shape and the edge position of the XANES spectra of sample (Fig. 1 (D)) were

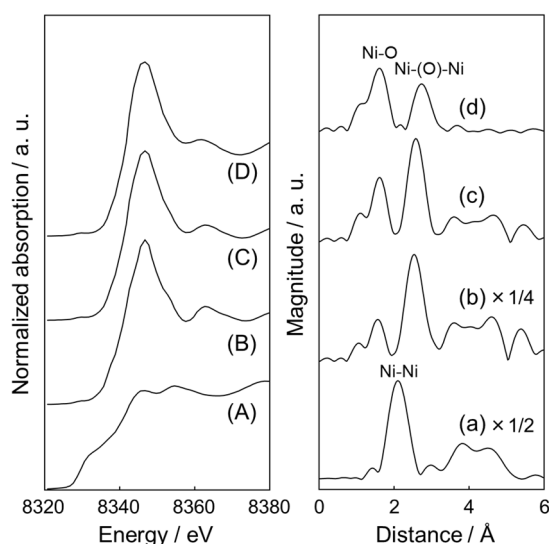


Fig. 1: (A-D) XANES and (a-d) Fourier transforms of the EXAFS spectra of (A,a) Ni foil, (B,b) NiO, (C,c) NiO/SiO₂, and (D,d) CaSi₂ after treatment in an aqueous Ni(NO₃)₂ solution, respectively.

very similar to that of bulk NiO as a reference compound (Fig. 1 (B)), showing that the divalent NiO species were supported on CaSi_2 by only mixing in an aqueous $\text{Ni}(\text{NO}_3)_2$ solution without the formation of metallic Ni. In Fourier transforms of the EXAFS spectrum (Fig. 1 (b-d)), two peaks due to the presence of the neighboring oxygen atoms (Ni-O) and nickel atoms (Ni-(O)-Ni) were observed at 1-2 and 2-3 Å, respectively (without phase-shift correction). The relative peak intensity of the neighboring nickel atoms (Ni-(O)-Ni) against the neighboring oxygen atoms (Ni-O) is smaller for NiO on CaSi_2 than NiO/SiO₂ and bulk NiO. Curve-fitting analysis also revealed that the coordination number (CN) of NiO on CaSi_2 was small as compared to those of other samples. These results clearly suggest that the particle size of NiO species is significantly reduced on CaSi_2 . This sample was also worked as a heterogeneous catalyst with a high catalytic activity in the oxidation of benzyl alcohol and oxidative coupling of benzenethiol. A good correlation was observed between CN of NiO and the catalytic activity of samples.

References

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