Materials Science

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XAFS analysis of the alkoxide stabilized Ni nanocluster catalysts

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Introduction

Recently, great attention has been paid to the metal nanoparticle due to their potential applications in both industrial and academic fields. Supported Ni catalysts are one of the most useful catalysts used for various catalytic reactions. However, conventional preparation methods of supported Ni catalysts give metal particle size usually lager than 10 nm, and hence, the development of the Ni nanocluster preparation method is required.

In this study, we demonstrate a synthesis of supported Ni nanocluster catalyst by using alkoxide stabilized Ni colloid as a Ni precursor. SiO_2 as well as Al_2O_3 were used as the support. The effect of hydrogen treatment temperature on the Ni cluster size was presented by XAFS analysis.

Experimental

Ni colloid was synthesized by reduction of $Ni(OAc)_2$ using NaH with *t*-BuOH in refluxing THF at 338 K [1]. Supported Ni catalysts were prepared by impregnating Al_2O_3 (Aerosil, Alumina C) or SiO_2 (Aerosil, #200) with the colloidal Ni solution, followed by solvent removal *in vacuo*. Catalysts were treated with hydrogen at 673 K or 773 K to reduce the chemical state of Ni down to zero. Catalysts were designated with reduction temperature in the parentheses, as Ni/Al_2O_3(673R). The Ni loadings were regulated to 3 wt%.

Ni *K*-edge EXAFS were collected at PF BL-7C with Si(111) double crystal monochromator in a transmission mode. 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 Ni metal.

Results and discussion

FT of Ni *K*-edge EXAFS spectra for H_2 treated catalysts and the reference compounds were shown in Fig. 1. The hydrogen treated catalysts were sealed in an aluminum cell with Kapton windows without contacting air. FT profile of catalysts is similar to that of Ni foil, and the main peak at around 0.21 nm can be well reproduced by using Ni-Ni coordination extracted from Ni foil. The curve-fitting results of this main peak (Ni-Ni) are listed in Table with model parameters for Ni foil.

The coordination numbers (CN) of Ni-Ni for 673 K reduced catalysts were 8.1 and 8.8 for the Al_2O_3 support and SiO_2 support, respectively. As elevating the reducing temperature up to 773 K, the CN for Ni/Al_2O_3(773R) was unchanged, whereas that for Ni/SiO_2(773R) increased a little (8.8 to 9.1). The effectiveness to sustain the smaller Ni particles can be demonstrated by using Al_2O_3 than SiO_2 as the support. Although small aggregation of Ni cluster was observed for Ni/SiO_2(773R), Ni particles still remained its size on the support. It can be said that the thermally stable Ni nanocluster catalyst is synthesized on oxide support by using *t*-BuONa stabilized colloidal Ni as the precursor.

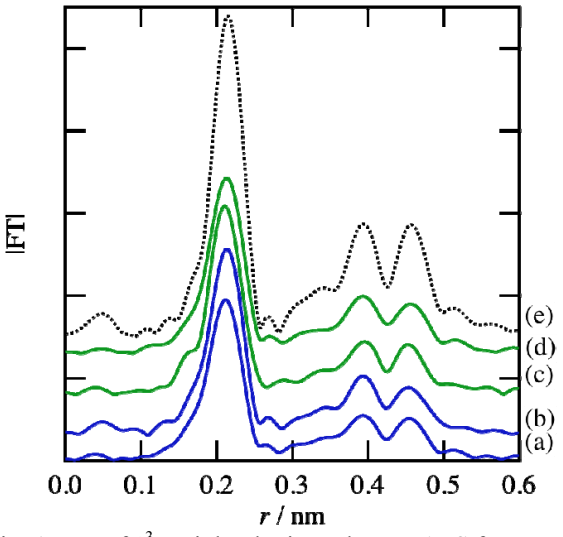

Fig. 1. FT of k^3-weighted Ni *K*-edge EXAFS for supported Ni catalysts after H_2 treatment and reference compounds; (a) Ni/Al_2O_3(673R), (b) Ni/Al_2O_3(773R), (c) Ni/SiO_2(673R), (d) Ni/SiO_2(773R), (e) Ni foil.

Table: Curve fitting results for Ni-Ni coordination

sample	*N*	*r* / nm	d*E* / eV	*DW* / nm
Ni/Al_2O_3(673R)	8.1±0.3	0.248	-2.3	0.007
Ni/Al_2O_3(773R)	8.0±0.3	0.248	-1.7	0.007
Ni/SiO_2(673R)	8.8±0.3	0.247	-2.6	0.007
Ni/SiO_2(773R)	9.1±0.3	0.248	-1.5	0.007
Ni foil (model)	12	0.249	0.0	0.006

FT *k*-range: 30-150 nm^{-1}.

Reference

[1] P. Gallezot, C. Leclercq, Y. Fort, P. Caubère, *J. Mol. Catal.*, **93**, 79 (1994).

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