

## XAFS studies on the oxide supported Ni nanocluster catalysts

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### Introduction

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

Colloidal metal particles have been expected as a superior catalyst precursor for supported solid catalyst because of their small particle size and the narrow size distribution. In this study, we demonstrate a synthesis of supported Ni nanocluster catalyst by using Ni colloid as a Ni precursor. SiO<sub>2</sub> as well as Al<sub>2</sub>O<sub>3</sub> were used as the support. The supported Ni catalysts were reduced by hydrogen and were characterized by XAFS analysis.

### Experimental

Ni colloid was synthesized by reduction of Ni(OAc)<sub>2</sub> using NaH-*t*-BuONa in refluxing THF at 338 K [1]. Supported Ni catalysts were prepared by impregnating Al<sub>2</sub>O<sub>3</sub> (Aerosil, Alumina C) or SiO<sub>2</sub> (Aerosil, #200) with the colloidal Ni solution, followed by solvent removal *in vacuo*. Catalysts were designated as col-Ni/Al<sub>2</sub>O<sub>3</sub> or col-Ni/SiO<sub>2</sub>. Conventional impregnation catalysts were also prepared by using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as Ni precursor (imp-). The Ni loading was regulated to 3 wt%.

Ni *K*-edge EXAFS were collected at PF BL-7C and 9C with Si(111) double crystal monochromator in a transmission mode. Curve-fitting analysis of *k*<sup>3</sup>-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

It is likely that fine Ni particles are thought to be easily oxidized as exposing to air even at room temperature. Thus, the catalyst has to be treated with hydrogen at 673 K to reduce the chemical state of Ni down to zero before applying the catalytic reaction.

Figure 1 shows the FT of Ni *K*-edge EXAFS spectra for H<sub>2</sub> 673 K treated catalysts and the reference compounds. The hydrogen treated catalysts were sealed in an aluminum cell with Kapton windows without contacting an air. FT profile of catalysts is similar to that of Ni foil, except for imp-Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. Alumina is well known as having the strong interaction with the metal, and hence, easily forms the composite oxides.

Once nickel aluminate formed, the Ni<sup>0</sup> cannot be provided by such a low temperature reduction. The main peak at around 0.2 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.

The coordination number (CN) of Ni-Ni for imp-Ni/SiO<sub>2</sub> was large as 11.2, close to the bulk (12), whereas that for col-catalyst was less than 9. The effectiveness to produce the smaller Ni particles can be demonstrated by using Ni colloid as the Ni precursor. The CNs of Ni-Ni were 8.1 and 9.0 for col-Ni/Al<sub>2</sub>O<sub>3</sub> catalyst and for col-Ni/SiO<sub>2</sub> catalyst, respectively. It is suggested that the Ni nanocluster can be synthesized on Al<sub>2</sub>O<sub>3</sub> support by using colloidal Ni as the precursor.

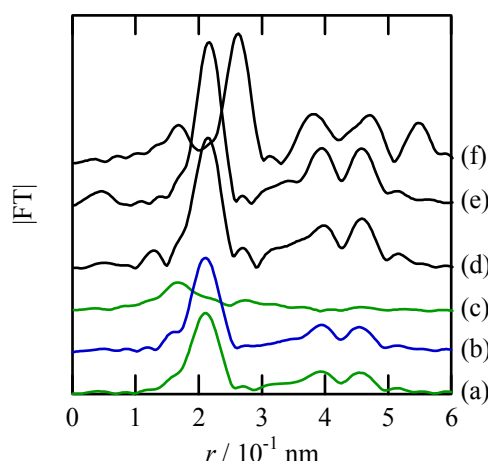


Fig. 1. FT of *k*<sup>3</sup>-weighted Ni *K*-edge EXAFS for supported Ni catalysts H<sub>2</sub> treated at 673 K and reference compounds; (a) col-Ni/Al<sub>2</sub>O<sub>3</sub>, (b) col-Ni/SiO<sub>2</sub>, (c) imp-Ni/Al<sub>2</sub>O<sub>3</sub>, (d) imp-Ni/SiO<sub>2</sub>, (e) Ni foil and (f) NiO.

Table: Curve fitting results for Ni-Ni coordination

sample	<i>N</i>	<i>r</i> / nm	d <i>E</i> / eV	D <i>W</i> / nm
col-Ni/Al <sub>2</sub> O <sub>3</sub>	8.1±0.3	0.248	-2.3	0.007
col-Ni/SiO <sub>2</sub>	9.0±0.3	0.248	-2.2	0.007
imp-Ni/Al <sub>2</sub> O <sub>3</sub>	2.0±0.4	0.249	-2.9	0.009
imp-Ni/SiO <sub>2</sub>	11.2±0.2	0.248	-2.1	0.007
Ni foil	(12)	(0.249)	(0.0)	(0.006)

### Reference

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

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