

XAFS studies on the supported Ni catalysts prepared from Ni colloids

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Introduction

It is well known that Ni catalysts are very useful for many catalytic reactions. But the size of Ni particles on catalyst is typically 20-100 nm and the preparing the smaller Ni particles on the support is desired. 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 prepared Ni metal colloid by using *t*-BuONa as a stabilizer and used for the Ni catalyst precursor. Non-porous SiO₂ as well as meso-porous SiO₂ (HMS) 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)₂ using NaH-*t*-BuONa in refluxing THF at 336 K [1]. HMS support was prepared as in the literature [2]. Supported Ni catalysts were prepared by impregnating HMS or SiO₂ (Aerosil, #200) with the colloidal Ni solution, followed by solvent removal *in vacuo*. Catalysts were designated as col-Ni/HMS or col-Ni/SiO₂. Conventional impregnation catalysts were also prepared by using Ni(NO₃)₂·6H₂O as Ni precursor (imp-).

Ni *K*-edge EXAFS were collected at PF BL-9C with Si(111) double crystal monochromator in a transmission mode. Curve-fitting analysis of *k*³-weighted EXAFS oscillations in the *k*-space were performed by the program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis were extracted from bulk Ni.

Results and discussion

Figure 1 shows the Ni *K*-edge XANES for supported Ni catalysts and reference compounds.

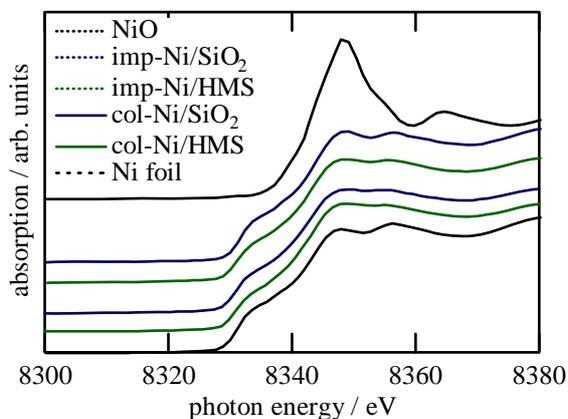


Fig. 1. Ni *K*-edge XANES for supported Ni catalysts and reference compounds.

The catalyst has to be treated with hydrogen at 673 K before applying the catalytic reaction. It is demonstrated from XANES (Fig. 1), Ni species on the support were reduced to Ni⁰ state after the hydrogen treatment.

Figure 2 shows the FT of Ni *K*-edge EXAFS spectra. Coordination numbers (CNs) for Ni-Ni were listed in Table. The effectiveness to produce the smaller Ni particles can be demonstrated by using Ni colloid as the Ni precursor. Moreover, CN of Ni-Ni for col-Ni/HMS is smaller than that for col-Ni/SiO₂. The smaller Ni particles can be obtained by using Ni colloid and HMS for Ni precursor and the support, respectively.

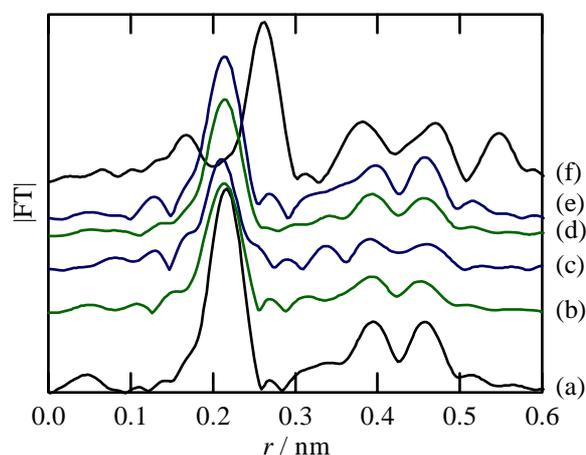


Fig. 2. FT of *k*³-weighted Ni *K*-edge EXAFS for supported Ni catalysts and reference compounds; (a) Ni foil, (b) col-Ni/HMS, (c) col-Ni/SiO₂, (d) imp-Ni/HMS, (e) imp-Ni/SiO₂ and (f) NiO.

Table: Curve fitting results for Ni-Ni coordination

| sample | N | <i>r</i> / nm | d <i>E</i> / eV | DW / nm |
|-------------------------|------|---------------|-----------------|---------|
| imp-Ni/SiO ₂ | 11.6 | 0.248 | -2.0 | 0.0065 |
| imp-Ni/HMS | 9.7 | 0.248 | -1.7 | 0.0069 |
| col-Ni/SiO ₂ | 9.1 | 0.247 | -3.4 | 0.0077 |
| col-Ni/HMS | 8.5 | 0.248 | -1.4 | 0.0065 |
| Ni foil | 12 | 0.249 | 0.0 | 0.006 |

References

- [1] P. Gallezot, C. Leclercq, Y. Fort, P. Caubère, *J. Mol. Catal.*, **93**, 79 (1994)
- [2] P. T. Tanev, T. J. Pinnavaia, *Science*, **267**, 865 (1995).

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