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EXAFS studies on the Ni/SiO_2 catalysts prepared from *t*-BuONa-Ni colloid

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Introduction

Colloidal metal particles have been expected as a superior catalyst precursor because of their small particle size and the narrow size distribution. But the stabilizer, which is needed to synthesize metal colloid, remained on the metal surfaces and lead to lower the metal surface area as well as the catalytic activity. Thus, the effective removal of the stabilizer from the colloidal metal particles on the catalysts is expected.

Ni catalysts are very useful for several catalytic reactions. But the size of Ni particles on catalyst is typically 20 - 100 nm. It is difficult to prepare small Ni particle on the support because of magnetic attractions of Ni metal. The study on the nano-sized Ni catalysts is very few.

In this study, we prepared Ni/SiO_2 catalysts from *t*-BuONa stabilized Ni colloid by impregnation method. Size of Ni particle and chemical state of Ni/SiO_2 catalyst was characterized by EXAFS analysis.

Experimental

The overall preparation process of Ni colloid was carried out under N_2 atmosphere. Ni colloid was synthesized by reduction of $Ni(OAc)_2$ using NaH-*t*-BuONa in refluxing THF [1]. 3 wt% Ni/SiO_2 catalyst was prepared by impregnation of SiO_2 (Aerosil#200) with Ni colloid solution. In order to remove the residual stabilizer, hydrogen treatment was carried out at 573 K. Catalysts were denoted as Ni/SiO_2 (as synt) and Ni/SiO_2 (H_2) for before and after the hydrogen treatment, respectively.

Ni K-edge EXAFS spectra were measured at BL-12C of the Photon Factory with Si(111) double crystal monochromator. The powder samples were transferred into 3 mm length of Al cells with Kapton windows. Curve-fitting analyses of k^3-weighted EXAFS oscillations in the *k*-space were performed by the EXAFS analysis program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis (back scattering amplitude and phase shift) were extracted from an EXAFS oscillation collected for bulk Ni (N =12, *r* =0.2492 nm).

Results and discussion

FT of Ni K-edge EXAFS spectra for Ni/SiO_2 catalyst was shown in Fig. The FT profile of Ni/SiO_2 (as synt) was similar to that of bulk NiO. Thus, Ni species on Ni/SiO_2 catalyst was in oxidized form. It is suggested that the colloidal Ni particle was easily oxidized in air atmosphere during the impregnation method due to its smallness.

To remove the stabilizer, Ni/SiO_2 catalyst was treated in hydrogen at 573 K. The main peak of Ni/SiO_2 (H_2) could be attributed Ni-Ni coordination in the Ni metal. NiO on Ni/SiO_2 catalysts was reduced into Ni metal by H_2 treatment at 573 K.

Coordination number of Ni-Ni in Ni/SiO_2 (H_2) catalyst was 8.0 as shown in Table 1. If Ni particle on the catalyst was in the cuboctahedron structure, the size of Ni particles can be estimated at less than 2 nm.

It can be said that impregnation method by using *t*-BuONa-Ni colloid can provide the small Ni particles. Since Ni species on Ni/SiO_2 catalysts is in oxidized form, hydrogen treatment over 573 K is needed to apply it to the catalytic reaction. Although the hydrogen treatment temperature is high, such as 573 K, Ni particle still remained small.

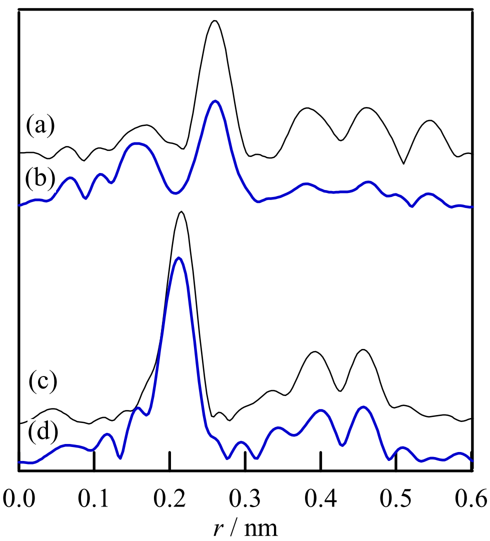

Figure FT of k^3-weighted Ni K-edge EXAFS; (a) NiO (x0.5), (b) Ni/SiO_2 (as synt), (c) Ni foil (x0.5), (d) Ni/SiO_2 (H_2).

Table 1: Curve fitting result for Ni-Ni coordination

sample	N	*r* / nm	d*E* / eV	DW / nm
Ni/SiO_2 (H_2)	8.0	0.247	-7.522	0.008
bulk Ni	12	0.2492	0.0	0.006

Reference

[1] Pierre Gallezot, Christiane Leclercq, Yves Fort and Paul Caubere, *J. Mol. Catal.*, **93**, 79-83 (1994)

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