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XAFS study on the oxidation of Ni(0) nanocluster into Ni(II) nanocluster catalyst

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Introduction

Metal nanoclusters are currently attracting much attention because of their unique characteristics. Supported NiO are used for various catalysis, such as oxidative dehydrogenation of hydrocarbons. However, conventional preparation methods of supported NiO catalysts give metal particle size usually lager than 10 nm, and hence, the development of the NiO nanocluster preparation method is expected.

In this study, we demonstrate a synthesis of SiO_2 supported Ni(II) nanocluster catalyst by oxidizing polyvinylpyrrolidone (PVP) stabilized Ni(0) colloid on SiO_2. Ni(0) colloid is sensitive toward oxygen and is easily oxidized by exposing to air. The effect of oxidation time and method on the Ni(II) nanocluster was investigated by XAFS analysis.

Experimental

Ni(0) colloid was synthesized by reduction of $NiCl_2$ using $NaBH_4$ in refluxing MeOH at 338 K in the presence of PVP [1]. PVP/Ni molar ratio was varied from 1 to 5.

Supported Ni(0) catalysts were prepared by impregnating SiO_2 (Aerosil, #200) with the colloidal Ni(0) solution, followed by solvent removal *in vacuo*. Then, catalysts were exposed to air and were washed with distilled water. Catalysts are designated with PVP/Ni ratio in the parentheses as Ni/SiO_2 (*PVP1*). The catalyst exposed to air at room temperature for 12 h before washing was denoted as Ni/SiO_2 (*PVP1*)-ox. 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. Samples were pressed into self-supporting disc and sealed in polyethylene bag. Curve-fitting analysis of k^3-weighted EXAFS oscillations in k-space were performed by REX2000 (Rigaku Co.). Model parameters for curvefitting analysis were extracted from bulk NiO.

Results and Discussion

It was expected that Ni(0) catalysts were changed into NiO by exposing to air. However, Ni(0) catalysts may react with water as well as oxygen. Thus, $Ni(OH)_2$ generation will be also expected by washing treatment.

FT of Ni K-edge EXAFS for catalysts were shown in Fig.1. The peak at around 0.27 nm can be well reproduced by using Ni-(O)-Ni. It is revealed that these supported Ni(0) catalysts were oxidized by exposing to air or washing treatment, and is suggested that the catalyst is composed of both NiO and $Ni(OH)_2$.

The curve-fitting results are listed in Table. The coordination numbers (CN) of Ni-(O)-Ni for Ni/SiO_2 (*PVP1*), Ni/SiO_2 (*PVP3*) and Ni/SiO_2 (*PVP5*) catalysts were almost the same as 6.7. PVP amount did not affect the Ni nanocluster size in these molar ratios. On the other hand, CN for catalysts exposed to air for 12 h became larger as 7.5 to 8.0. Cluster size growth is not expected by exposing to air for long time. This increment of CN can be explained by changing the ratio of NiO to $Ni(OH)_2$ because CN for $Ni(OH)_2$ is small as 6. It can be said that to increase purity of NiO, it is necessary to expose catalysts to air for a long time before washing treatment.

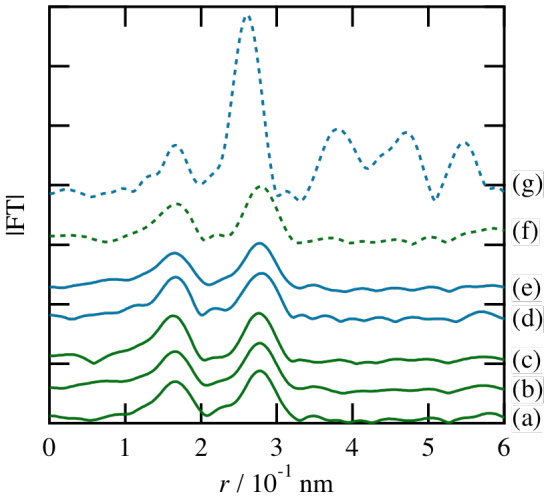

Fig.1: FT of k^3-weighted Ni K-edge EXAFS oscillations for Ni catalysts and reference compounds; (a) Ni/SiO_2 (*PVP1*), (b) Ni/SiO_2 (*PVP3*), (c) Ni/SiO_2 (*PVP5*), (d) Ni/SiO_2 (*PVP1*)-ox, (e) Ni/SiO_2 (*PVP5*)-ox, (f) $Ni(OH)_2$ and (g) NiO.

Table: Curve fitting results for Ni-(O)-Ni coordination

catalyst	CN	r / nm	dE / eV	DW / nm
Ni/SiO_2 (*PVP1*)	6.7	0.308	0.7	0.008
Ni/SiO_2 (*PVP3*)	6.8	0.308	2.3	0.008
Ni/SiO_2 (*PVP5*)	6.7	0.309	2.3	0.009
Ni/SiO_2 (*PVP1*)-ox	7.5	0.310	-0.9	0.009
Ni/SiO_2 (*PVP5*)-ox	8.0	0.309	3.8	0.009
NiO (model)	12	0.295	0.0	0.006

FT k-range: 35-150 nm^{-1}.

Reference

[1] Ö. Metin and S. Özkar, *J. Mol. Catal. A.* **295**, 39 (2008).

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