Size Effect of Supported Ni Particle for XANES Spectrum

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1. Introduction

The particle size of active species for the supported metal catalyst is an important factor to increase catalytic activity. In fact, the supported Ni catalyst with the particle size of a few nm can promote the oxidative coupling of thiophenol [1]. The investigations about such unique reaction property of small Ni particle will provide useful principle for new catalyst design. The X-ray absorption spectroscopy is the most powerful technique for research about supported metal species, because the chemical state is evaluated by the analysis of XANES spectrum. However, the feature of XANES spectrum is not fully elucidated for such small and supported Ni particle. Therefore, in this study, the XANES spectrum of small Ni particles and its particle size effect will be evaluated.

2. Experimental

The supported Ni catalysts (5 wt%) were prepared by the sol-gel (SG) method and the liquid phase reduction (LPR) method. $Ni(NO_3)_2 \cdot 6H_2O$ and citric acid were dissolved into ethanol. TEOS and deionized water were added into the solution, and the solution was turned into a gel by vaporization for 8 h at 80 °C. The powder was subjected by calcination in air for 3 h. LPR method was conducted under an inert gas atmosphere. Nickel acetate was reduced to metallic Ni colloid at 66 °C in THF, in which NaH and *t*-BuOH were dissolved. After that, SiO_2 was added and stirred for 3 h. A catalyst powder obtained by filtration was dried *in vacuo* for 12 h. The particle size (4 nm for SG and 3 nm for LPR) of supported Ni species was estimated from TEM images.

XAFS measurements were carried out at BL-3 of SR center (Ritsumeikan University) and BL-12C of Photon Factory (KEK). The *in-situ* measurements were performed at room temperature after the reduction or oxidation process by H_2 or O_2 at 700 °C under the reaction

gas conditions.

3. Results and Discussion

The average coordination number of reduced sample was 8.8 (SG) and 9.8 (LPR). The values are in accordance with the estimation using the particle size estimated by TEM. The observed XANES spectra are given in Figs. 1 and 2 for the reduced and oxidized Ni species, respectively, in which the difference spectra between the supported catalyst and bulk are included. For both conditions, the absorption edge is in agreement with that of bulk sample. In addition, the EXAFS analysis revealed that there is no contribution from the Ni species with the other valence state. A clear difference of the XANES spectrum is observed at *ca*. 8345 eV for the Ni(0) species. It is indicated that the 4p band structure is affected by the particle size of metallic Ni(0). The spectral difference is not due to the partial oxidation of Ni(0) particle, because the difference spectrum is obviously distinct from that between bulk Ni and NiO. Similarly, the XANES spectrum of NiO nanoparticle is slightly different from that of bulk NiO. The white line is broadened when the particle size becomes small. These specific XANES spectra of supported nanoparticles have been evaluated by the *in-situ* measurement.

Reference

[1] N. Ichikuni, O. Tsuchida, J. Naganuma, T. Hara, H. Tsunoyama, T. Tsukuda, and S. Shimazu, *Trans. Matter. Res. Soc. Jpn.*, **37**, 177-180 (2012).

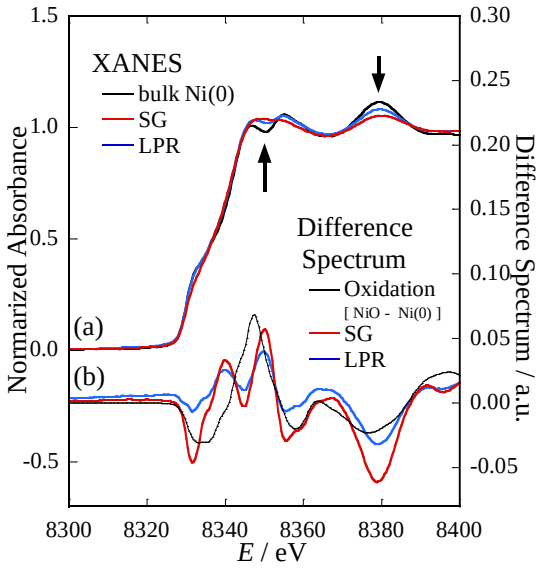

Fig. 1. XANES spectra (a) and difference spectra (b) of Ni(0) nanoparticle.

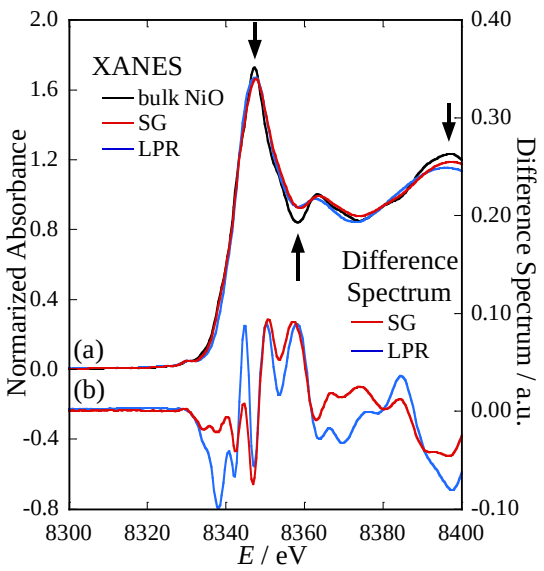

Fig. 2. XANES spectra (a) and difference spectra (b) of NiO nanoparticle.