

***In-Situ* XAFS Analysis for Reduction of NiO Existed at the Surface of Supported Nickel Particle**

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1. Introduction

Supported Ni particle is widely used as a catalyst for various reactions such as dry reforming of methane. In the actual catalysis reaction, the chemical state of Ni species is changed because of the contact with the reactant and product gases. The chemical conversion of surface Ni species is especially an important parameter for the catalytic activity. It has been reported that the SiO₂-supported metallic Ni particle is partially oxidized by the exposure to O₂ at room temperature [1]. The relationship between the particle size and the mole fraction of oxidized species clearly demonstrates that the partial oxidation proceeds at the particle surface. The purpose of this study is the clarification for the reduction property of the supported Ni particle with the oxidized surface layer.

2. Experimental

The SiO₂-supported Ni catalysts were prepared by the impregnation method under the existence of an organic additive. The stoichiometric amount of citric acid was added into the nickel(II) nitrate solution to control the Ni particle size. The Ni loading was set to be 5 wt.%.

The *in-situ* XAFS experiments were performed at BL-3 of the SR center (Ritsumeikan Univ.) and at BL-9C of the Photon Factory (KEK). The XAFS measurements were carried out at the Ni K edge during the temperature-programmed reduction (TPR) process under the dilute H₂ environment up to 700 °C. The surface oxidation treatment was conducted by an exposure of the diluted O₂ gas at room temperature after the pre-reduction process.

3. Results and Discussion

The XANES spectrum before and after the gas switching from H₂ to O₂ at room temperature is shown in Fig. 1(A). The XAFS spectrum of reduced Ni(0) particle was quickly

changed after the gas change. The difference spectrum is consisted with that between the bulk Ni metal and NiO, clearly indicating the partial oxidation of the supported Ni(0) particle. According to our previous research [1], the fraction of the oxidized species is almost proportional to the surface area of the supported Ni(0) particle. It is thus considered that the partial oxidation proceeds at the particle surface.

The composition change as a function of temperature is given in Fig. 1(B) during the TPR process of the supported Ni(0) particle with the oxidized surface layer. The reduction of the supported NiO particle was taken place at the temperature above 350 °C (see black lines in Fig. 1(B)), whereas the present study clearly demonstrated that the NiO species existed at the Ni(0) particle was almost completed at around 200 °C. The reduction temperature difference is ascribed by the lattice mismatch. The NiO species on the Ni(0) core is considered to have the instability as the reduction reaction. The lower reduction temperature obviously suggests that the NiO species on the metallic Ni core has an excellent ability to release the oxide ion.

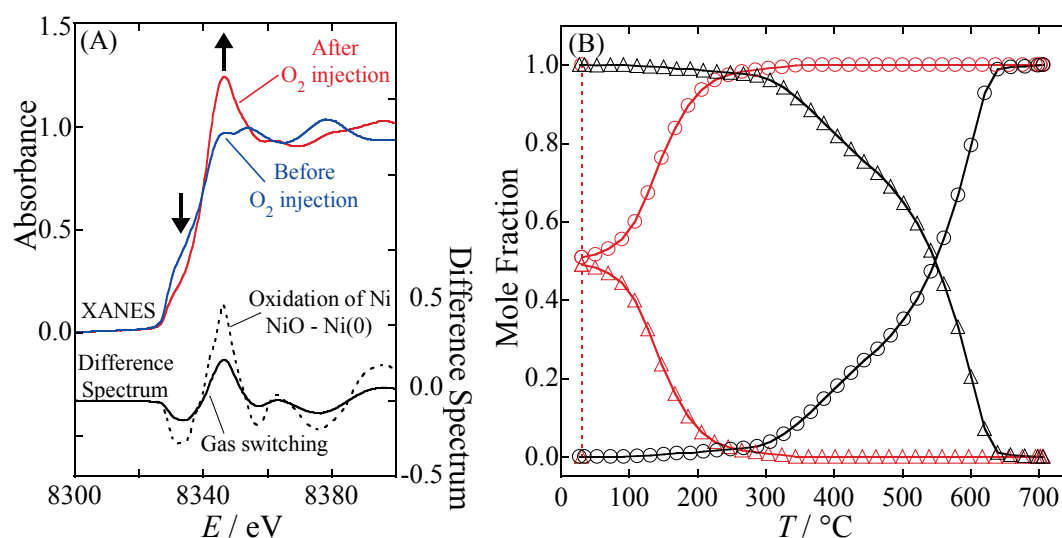


Fig. 1. The XANES spectrum change (A) at the O₂ gas exposure and the composition change of the Ni species (B) during the reduction process. In B, the red and black line shows the surface reduction and the bulk reduction, respectively. The dotted line indicates the surface oxidation process.

Reference

- [1] Y. Yamamoto, S. Yamashita, N. Afiza, M. Katayama, and Y. Inada, *J. Phys. Conf. Ser.*, **712**, 012075 (2016).