Reduction by CO of NiO Supported on SiO$_2$

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1. Introduction

The Ni catalysts supported on SiO$_2$ show a high activity for generation of syngas by CO$_2$ reforming reaction. The produced syngas composed of CO and H$_2$ have been widely used for the Fischer-Tropsch reaction to synthesize hydrocarbons. It is known that not only the sintering of the active Ni particles but also the carbon deposition cause the catalytic deactivation. Therefore, the speciation of the supported Ni species under reaction gas atmosphere is very important to prevent the deactivation. In this study, the chemical states of the Ni species have been analyzed by means of the X-ray absorption fine structure (XAFS) spectroscopy for Ni catalysts supported on 4 kinds of SiO$_2$ with different structure under CO gas atmosphere at elevated temperature, and will be compared with those reduced by H$_2$ published previously [1].

2. Experimental

The Ni catalysts supported on SiO$_2$ was prepared by the impregnation method. The used SiO$_2$ were SIO-10 distributed by Catalysis Society of Japan, commercially available SIO-39 and MCM-41, and originally prepared SBA-15. The surface area measured by the N$_2$ adsorption isotherm is 190 (SIO-10), 390 (SIO-39), 720 (SBA-15), and 900 m$^2$/g (MCM-41). Both SBA-15 and MCM-41 have meso-structure with the pore radius of 2.1 and 3.6 nm, respectively. The Ni loading was set to be 10 wt%.

The *in-situ* XAFS measurements were carried out at BL-3 of SR Center in Ritsumeikan University at the Ni-K edge in the transmission mode. A Si(220) double-crystal monochromator was used at the maximum parallerism. A flow-type sample cell was first heated up to 423 K under pure He flow (200 cm$^3$/min) to avoid the generation of Ni(CO)$_4$ with high toxicity, and was followed by heating to 1023 K under the diluted CO flow (10 vol% balanced by He, 200 cm$^3$/min). The XAFS measurements were carried out with the interval of 2 min.

3. Results and discussion
The observed XANES spectral change is shown in Figure 1 for the reduction process on SIO-10. The initial spectrum is perfectly consistent with that of NiO, and the final spectrum is in accordance with that of Ni foil. This observation indicates that the Ni species is quantitatively reduced from NiO formed by the calcination to the metallic Ni(0). The similar spectral changes were observed on the other silica support. The clearly observed isosbestic points indicate that the transition from NiO to Ni(0) proceeds without any other metastable states.

The mole fraction of NiO was evaluated by a linear combination fitting of an XANES spectrum using the spectra of NiO and Ni(0). The obtained values are plotted versus temperature in Figure 2. The reduction of NiO is completed at ca. 800 K on SiO₂ without meso pore structure. At that temperature, about 30% of NiO is remained on SBA-15 and MCM-41. The partial delay of reduction can be assigned to the support of NiO in the meso pore of SiO₂. The CO gas diffusion is necessary to contact with such NiO species, and thus the internally supported NiO in the meso pore is concluded to be more stable against the redox reactions with gas molecules.

The reduction by H₂ of supported NiO on SiO₂ proceeds at ca. 600 K [1]. The reduction by CO under higher temperature is ascribed by the weak reducing alibility of CO molecule. In addition, the oxidation of supported Ni(0) on SiO₂ proceeds at around 600–700 K suggests that the CO combustion is catalyzed at higher than 700 K using the Ni catalysts supported on SiO₂ by the reversible conversion between NiO and Ni(0).

Reference