

## XAFS Analysis on Reduction Process of Nickel Species with Different Particle Size

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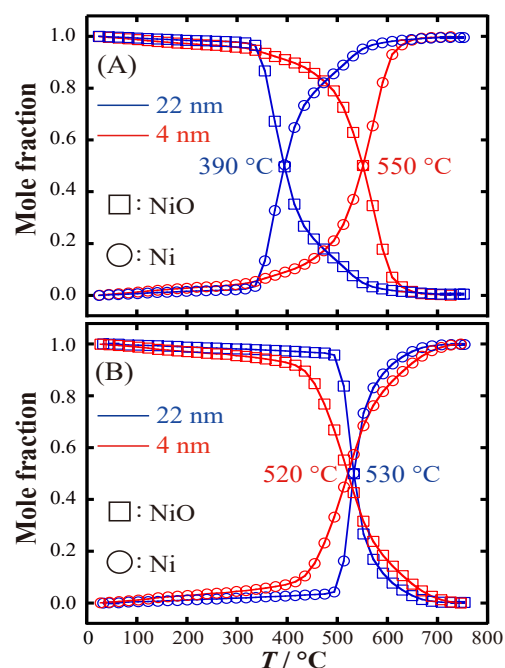
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The Ni catalysts supported on SiO<sub>2</sub> are used for various catalytic reactions, and the knowledge of the chemical state of the supported Ni species under the reaction gas environment is the most basic to improve the catalytic performance. The Ni species is known to easily change the chemical state between NiO and metallic Ni, and the existing H<sub>2</sub> and CO gases promote the reduction of NiO at elevated temperatures. In this study, the chemical state conversion from NiO to Ni has been systematically investigated using the *in-situ* XAFS technique for two NiO catalysts with the different particle size during the temperature-programmed reduction (TPR) processes.

The NiO catalysts supported on SiO<sub>2</sub> were prepared by the impregnation method using an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>. The small NiO particle was prepared by adding citric acid in the precursor solution. The impregnated samples were subject to the calcination at 600 °C in air. The crystallite size of NiO was estimated to be 4 and 22 nm for the NiO catalyst prepared with and without citric acid, respectively, by the XRD measurement.

The *in-situ* XAFS measurements were carried out at the Ni K edge at BL-3 of the SR Center (Ritsumeikan) and BL-9C of the Photon Factory (KEK) during the TPR process of the NiO particle supported on SiO<sub>2</sub>. The NiO catalyst was set in a flow-type *in-situ* XAFS cell and the temperature was elevated from 25 °C to 750 °C with the heating rate of 10 °C/min under the gas flow of H<sub>2</sub> or CO diluted by He (10 vol%) with the total flow rate of 200 cm<sup>3</sup>/min. The CO gas was started to flow during the heating process at above 150 °C to prevent the formation of toxic Ni(CO)<sub>4</sub>.

The observed spectral change clearly demonstrated the quantitative reduction from NiO to Ni during the TPR treatment for both catalysts under both gases. The linear combination fitting was applied to the observed XANES spectra to determine the composition of NiO and Ni. Figure 1 shows the composition change as a function of temperature. In the case of the reduction by H<sub>2</sub>, it was apparently observed that the reduction temperature of the smaller NiO particle was shifted to the higher temperature. It has been pointed out that the NiO species located at the interface between the NiO and SiO<sub>2</sub> particles resist the reduction due to the thermal stabilization. Because the larger amount of such NiO species is expected



**Fig. 1** The composition change of the supported Ni species as a function of temperature during the TPR process under H<sub>2</sub> (A) and CO (B) for NiO catalysts with the particle size of 4 nm (red) and 22 nm (blue).

for smaller NiO particles, the apparent higher shift of the reduction temperature is reasonably explained. Many part of the larger NiO particle is not stabilized by SiO<sub>2</sub>, and it is considered that such NiO species is reduced at *ca.* 400 °C.

On the contrary, the reduction temperature of the NiO particle was independent on the particle size for the TPR process under CO. Both NiO catalysts were reduced at *ca.* 530 °C. The comparison of four reduction temperatures implies that the reduction of the NiO species without the stabilization by SiO<sub>2</sub> is thermodynamically difficult. Figure 1(B) demonstrates that such reduction is proceeded at *ca.* 530 °C by CO, and at that temperature the stabilized NiO species is potentially reduced as clarified for the TPR process under H<sub>2</sub>. This seems to be the reason why the reduction temperature by CO is independent on the particle size of the supported NiO species.