

## Oxidation property of SiO<sub>2</sub>-supported small nickel particle prepared by the sol-gel method

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**Abstract.** The oxidation property of SiO<sub>2</sub>-supported small Ni particle has been studied by means of the *in-situ* XAFS method. The Ni particle with the average diameter of 4 nm supported on SiO<sub>2</sub> was prepared by the sol-gel method. The XANES spectrum of the small metallic Ni particle was clearly different from that of bulk Ni. The exposure of diluted O<sub>2</sub> gas at room temperature promoted the surface oxidation of Ni(0) particle. During the temperature programmed oxidation process, the supported Ni(0) particle was quantitatively oxidized to NiO, and the oxidation temperature was lower by *ca.* 200 °C than that of the SiO<sub>2</sub>-supported Ni particle with the larger particle radius of 17 nm prepared by the impregnation method.

### 1. Introduction

The supported Ni catalyst shows the high activity for CO<sub>2</sub> reforming reaction of methane, and its improvements are continued to achieve the high selectivity and the long lifetime. The reduction of the particle size of active Ni species is one of the important approaches to control the catalytic performance. The fine particle of the active Ni species is expected to have high catalytic activity because of the large surface area. Under the actual reaction conditions, the Ni particles are exposed to the reactant and product gases, and thus the environmental atmosphere must affect to the chemical state of the Ni species. Furthermore, the possible aggregation and dispersion of the supported Ni particle modify the catalytic activity. The knowledge about the chemical state of the supported active Ni species in relation to the particle size is thus necessary to understand the catalysis performance and to construct the guiding design for the high performance Ni catalyst. In the present study, the clarification of the chemical state changeover of the SiO<sub>2</sub>-supported Ni catalyst have been performed for the small Ni particles prepared by the sol-gel (SG) method during its oxidation process at elevated temperatures. The results will be compared with those for the corresponding Ni catalysts prepared by the conventional impregnation (IMP) method [1].

### 2. Experimental

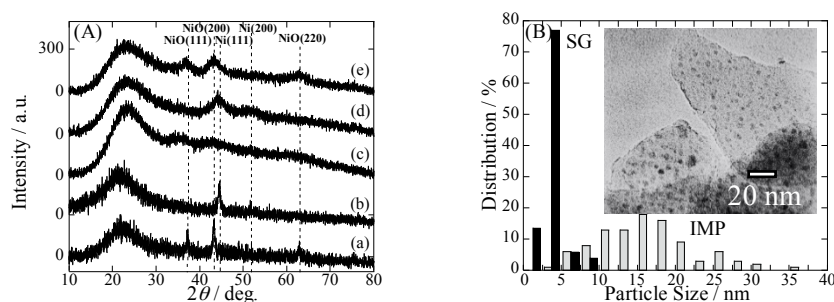
The supported Ni catalyst was prepared by the SG method according to the reported procedure [2]. The Ni loading was set to be 5 wt%. Nickel(II) nitrate hexahydrate, citric acid, tetraethyl orthosilicate, and deionized water were dissolved in ethanol. The vaporization of the solution at 80 °C formed the solid gel, and it was calcined at 600 °C in air. The obtained Ni catalyst was reduced at 700 °C under H<sub>2</sub> gas flow diluted by Ar. The corresponding sample was also prepared by the IMP method [1]. The XRD patterns were recorded using Ultima IV (Rigaku) with the Cu K $\alpha$  radiation. The transmission electron microscopy (TEM) observation was performed with JEOL2010 microscope (JEOL).



*In-situ* XAFS measurements during the temperature-programmed oxidation (TPO) process were carried out at the BL-12C station of Photon Factory (KEK, Japan) in transmission mode. The higher-order harmonics were removed by detuning the Si(111) double-crystal monochromator. Before the TPO measurements, the Ni catalyst was reduced at 700 °C under dilute H<sub>2</sub> gas flow (10 vol.%, 200 cm<sup>3</sup>/min) in the observation cell to ensure the quantitative reduction. After that, the gas flow was switched to O<sub>2</sub> diluted by He (10 vol.%) with the total flow rate of 200 cm<sup>3</sup>/min at room temperature. The sample was heated up to 700 °C with the increasing rate of 10 °C/min. The measurement time of one XAFS spectrum was 1 min, and the XAFS spectra were recorded with the interval time of 2 min. The EXAFS analysis was conducted by using the FEFFIT program. Fourier transformation was applied to  $k^3$ -weighted EXAFS data in the  $k$  range from 2 to 12 Å<sup>-1</sup>, and the curve fitting analysis was performed in the  $R$  range from 1.0 to 3.2 Å. The amplitude reduction factor  $S_0^2$  was set to 0.84 and 1.05 for metallic Ni and NiO, respectively. The edge shift energy  $\Delta E_0$  was estimated to be 0.8 eV (Ni metal) and -0.2 eV (NiO). The statistical error ( $R$  factor) for all fittings was less than 1 %.

### 3. Results and discussion

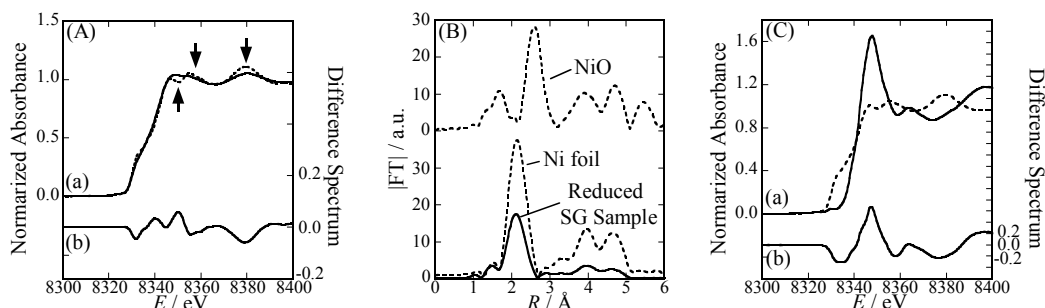
The observed XRD patterns are given in figure 1(A). The reduced samples show diffraction lines assigned to Ni(111) at 44.5° and Ni(200) at 51.9°, and it is confirmed that the reduction treatment at 700 °C generates the metallic Ni(0) particle. The diffraction lines corresponding to NiO(111) at 37.3°, NiO(200) at 43.2°, and NiO(220) at 62.9° were observed for the oxidized samples after the TPO process, and they clearly demonstrate the existence of NiO. It is noted that the diffraction lines of the SG sample are broader than those for samples prepared by the IMP method. The crystallite size of the supported Ni species for the SG sample is found to be smaller than the IMP sample. Figure 1(B) shows the size distribution of the supported Ni particles estimated by TEM after the reduction treatment. The average diameter of the Ni(0) particle for the SG and IMP sample was 4 nm and 17 nm with the size distribution range of 2–10 nm and 3–40 nm, respectively. It is clarified that the small and uniform Ni particles are generated in the SG sample.



**Figure 1.** XRD patterns (A) of the calcined IMP sample (a), the reduced IMP sample (b), the calcined SG sample (c), the reduced SG sample (d), and the oxidized SG sample (e), and the particle size distribution of the reduced sample (B) estimated by the TEM images. A typical TEM image of the SG sample is inserted.

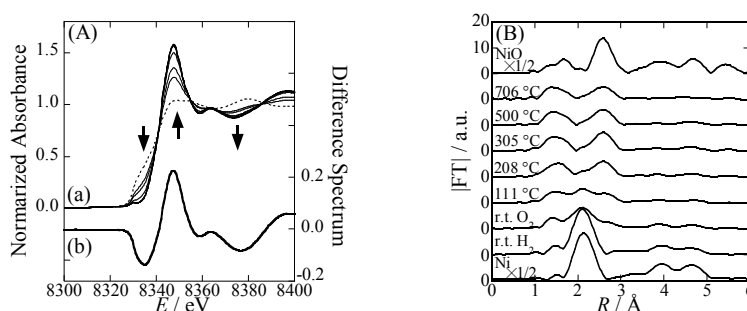
Figure 2 shows the XANES spectrum and the Fourier transform function of the reduced SG sample measured at room temperature under the H<sub>2</sub> atmosphere. The absorption edge energy of the reduced SG sample is in agreement with that of Ni foil. Furthermore, the Fourier transform function indicates that the Ni species with other valence states do not exist. These results indicate that the supported Ni species after the reduction treatment quantitatively reduced to Ni(0). However, the XANES spectrum of the supported Ni(0) particle is clearly different from that of bulk Ni(0). The difference spectrum given in figure 2(A) obviously indicates that the origin of the spectral difference is not the partial oxidation of the Ni(0) particle, because the spectral difference is not consistent with the difference spectrum between Ni(0) and NiO (figure 2(C)). It is evident from these results that the supported small

Ni(0) particles show the specific XANES spectrum as shown in figure 2(A). The 4p band structure can be affected by the particle size.



**Figure 2.** XANES spectrum (A) and Fourier transform function (B) of the reduced SG sample measured at room temperature. In A, the XANES spectra of the SG sample (solid line) and bulk Ni foil (broken line) are compared in (a), and the difference spectrum is given in (b). In C, the XANES spectrum of bulk NiO (solid line) and Ni foil (broken line) are compared in (a), and the difference spectrum is given in (b).

The XANES spectral change and the Fourier transform functions are shown in figure 3 for the TPO process. A rapid spectral change was observed just after the switch of the atmosphere gas from  $H_2$  to  $O_2$  at room temperature. The structure parameters determined by the curve-fitting procedure of the EXAFS data are summarized in table 1. The spectral change observed at room temperature resembles to the difference between Ni(0) and NiO given in figure 2(C). In addition, a weak interaction peak was generated at *ca.* 1.6 Å (see figure 3(B)) after the gas switch, and the average coordination number for the Ni–Ni interaction was decreased from 8.8 to 6.5. The composition analysis based on the linear combination of XANES spectra revealed that *ca.* 40 percent of the Ni species was oxidized to NiO. The similar spectral change was also observed at the beginning of the TPO process for the IMP sample, whereas the fraction of the partial oxidation (*ca.* 10 %) was small because of the larger particle size. The composition difference is quantitatively ascribed to the difference in the surface area of the supported Ni(0) particle. These results indicate that the surface oxidation of the Ni(0) particle proceeded at room temperature by the exposure to  $O_2$ .



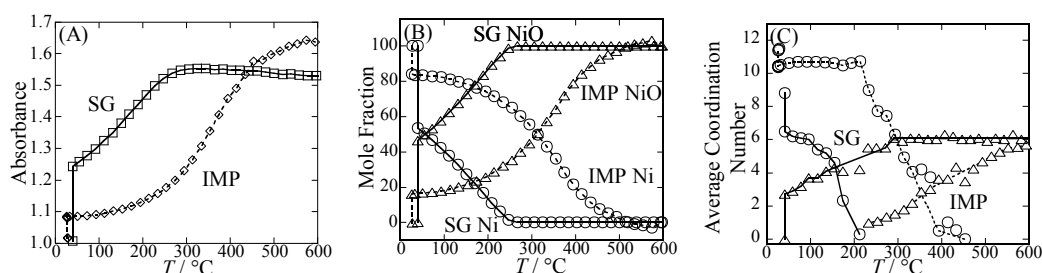
**Figure 3.** The XANES spectral change (A) and the Fourier transform functions (B) for the TPO process. In A, a broken line means the XANES spectrum before the gas switch to  $O_2$ , and the spectral difference at the gas change is shown in (b).

Figure 4 shows the temperature change of the X-ray absorbance, the composition change estimated by the linear combination fitting of XANES spectrum, and the average coordination number determined by the EXAFS analysis. The oxidation of small Ni(0) particles prepared by the SG method

completed at 300 °C. It is lower by *ca.* 200 °C than the corresponding temperature for the larger Ni particles in the IMP sample. The temperature change of the average coordination number supports the lower shift of the oxidation temperature for the SG sample. The temperature difference indicates the relative stability of the smaller NiO particles under the O<sub>2</sub> atmosphere and is interpreted by the easy oxygen migration in the small Ni(0) particle. In addition, the lower shift of oxidation temperature suggests the increased surface active sites for the smaller Ni(0) particles.

**Table 1.** Structure parameters of the Ni species during the TPO process.

Sample	$T / ^\circ\text{C}$	Gas	Interaction	$N$	$R / \text{pm}$	$\sigma^2 / 10 \text{ pm}^2$
Ni foil	rt	Air	Ni–Ni	12 (fixed)	$250 \pm 1$	$6.3 \pm 0.2$
NiO	rt	Air	Ni–O	6 (fixed)	$206 \pm 3$	$6.5 \pm 1.5$
SG	rt	H <sub>2</sub>	Ni–Ni	$8.8 \pm 0.4$	$250 \pm 1$	$9.5 \pm 0.4$
			Ni–Ni	$6.5 \pm 0.6$	$253 \pm 4$	$13.7 \pm 0.8$
			Ni–O	$2.7 \pm 0.3$	$202 \pm 6$	$14.1 \pm 1.9$
	111	O <sub>2</sub>	Ni–Ni	$5.4 \pm 0.9$	$257 \pm 8$	$16.8 \pm 1.5$
			Ni–O	$3.7 \pm 0.3$	$203 \pm 5$	$17.8 \pm 1.9$
	208	O <sub>2</sub>	Ni–Ni	$0.3 \pm 0.5$	$264 \pm 15$	$4.2 \pm 11.0$
			Ni–O	$4.2 \pm 0.9$	$203 \pm 6$	$12.0 \pm 4.0$
	305	O <sub>2</sub>	Ni–O	$5.9 \pm 0.9$	$204 \pm 4$	$15.8 \pm 2.6$
	706	O <sub>2</sub>	Ni–O	$6.1 \pm 0.7$	$205 \pm 4$	$23.8 \pm 2.6$



**Figure 4.** The temperature change of the X-ray absorbance (A) at the white line peak of NiO (8347 eV), the composition change (B), and the average coordination number (C) for the Ni–O interaction (triangles) in NiO and the Ni–Ni interaction (circles) in metallic Ni(0) during the TPO process. The solid and broken line means the change of the SG and IMP sample, respectively.

#### 4. Conclusions

The solid-phase oxidation of the SiO<sub>2</sub>-supported small Ni(0) particle prepared by the SG method has been clarified by means of the *in-situ* XAFS method. The small Ni(0) particles show the specific XANES spectrum, and the *in-situ* XAFS measurements demonstrated the surface oxidation at room temperature by the exposure to O<sub>2</sub>. The temperature of the bulk oxidation becomes lower in comparison to that of the larger Ni(0) particle prepared by the conventional IMP method.

#### Acknowledgement

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#### References

- [1] Yamashita S, Katayama M and Inada Y 2013 *J. Phys. Conf. Ser.* **430** 012051
- [2] Wu C and Williams P T 2012 *Environ. Technol.* **33** 631