

Redox Property of the Supported Ni Catalyst Prepared by Sol-Gel Method

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1 Introduction

The particle size of active species for the supported metal catalyst is an important factor to improve the 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 the small Ni particle will provide the useful principle to design new catalysts. One of the standard preparation methods of small active species is the sol-gel (SG) method, because it is expected that the active species is homogeneously dispersed in the supporting material. The purpose of this study is the clarification of the redox property for the supported small Ni particles prepared by the SG method and to compare the characteristics with the corresponding Ni catalysts prepared by the impregnation (Imp) method [2].

2 Experiment

The SiO₂-supported Ni catalysts were prepared by the SG method. The hexahydrate of nickel nitrate and citric acid were dissolved into ethanol. Tetraethyl orthosilicate and deionized water were added into the solution, and the mixed solution was changed to a gel by the vaporization for 8 h at 80 °C. The obtained powder was subjected by the calcination in air for 3 h. After that the sample was reduced and oxidized for 3 h at 700 °C under H₂ and O₂ atmosphere, respectively.

The X-ray absorption fine structure (XAFS) measurements were carried out at BL-12C of the Photon Factory (KEK). The *in-situ* XAFS measurements were performed during the temperature programmed reduction by H₂ and oxidation by O₂ from room temperature to 700 °C. The gas atmosphere was switched at room temperature.

3 Results and Discussion

The X-ray diffraction patterns shown in Fig. 1 indicate that the reduced sample shows diffraction lines assigned to Ni(111) at 44.5° and Ni(200) at 51.9°. Therefore, the metallic Ni(0) particle was formed in the reduction process. On the other hand, the diffraction lines of NiO(111) at 37.3°, NiO(200) at 43.2°, and NiO(220) at 62.9° observed for the oxidized samples clearly demonstrated that the Ni species exists as NiO. These diffraction lines are broader than those observed for the samples prepared by the Imp method, indicating that the crystallite size of the supported Ni species for the SG sample is smaller than that of the Imp sample. The crystallite diameter of the reduced Ni(0) particle

estimated by the Scherrer equation is 5 nm (SG) and 29 nm (Imp).

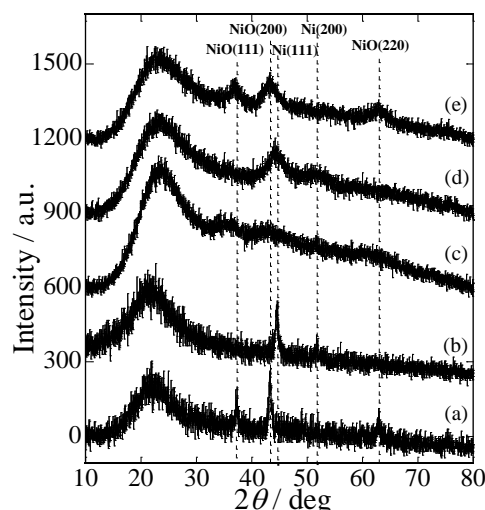


Fig. 1: XRD patterns of the supported Ni catalysts prepared by the Imp (a and b) and SG (c, d, and e) method. The patterns of a and c are the calcined catalysts, and those of b and d are the reduced samples. The pattern e corresponds to that after the oxidation.

Figure 2 shows the TEM image and the particle size distribution of the reduced Ni catalysts prepared by the SG and Imp method. The distribution range of the particle size was 2–10 nm (SG) and 3–40 nm (Imp). The sharp distribution was observed for the SG sample, and the SG method produced the small and uniform Ni particles.

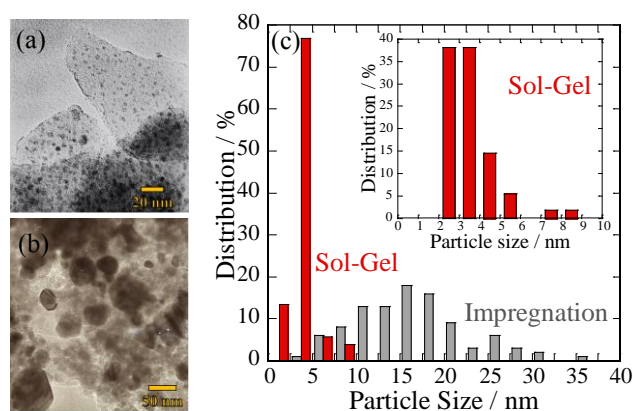


Fig. 2: TEM images of the reduced Ni catalysts prepared by the SG (a) and Imp (b) method. Histograms of the particle size are shown in (c).

The XANES spectral changes of 5 wt% Ni/SiO₂ prepared by the SG method are given in Fig. 3 for the reduction and oxidation processes at elevated temperature. During the reduction process, the X-ray absorbance at the white line of NiO decreased and the lower energy shift was observed for the absorption edge, shown in Fig. 3(a). The absorption edge of the final spectrum was in agreement with that of Ni foil, suggesting that the valence state of the supported Ni species was changed from +2 to 0. The opposite changes of the absorption edge and the NiO white line were observed during the oxidation process. The metallic Ni(0) species were quantitatively oxidized during the present oxidation process. The existence of some isosbestic points suggests that the redox reactions between two components, Ni(0) and NiO, proceed without any other stable species with different valence states.

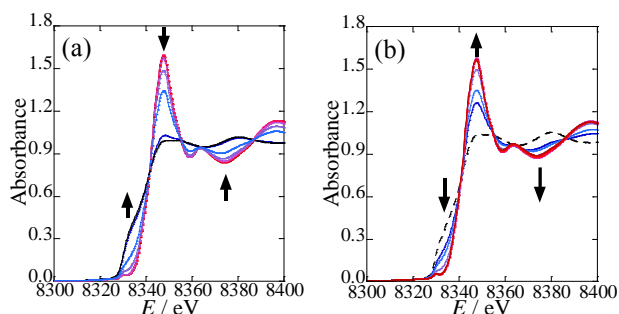


Fig. 3: XANES spectral change during the reduction (a) and the oxidation (b) process for the Ni catalyst prepared by the SG method. The dashed line shows the XANES spectrum before the switch of the atmosphere gas.

As clearly seen in Fig. 3(b), the XANES spectrum of metallic Ni(0) was quickly changed by the switch of the atmosphere gas from dilute H₂ to O₂ at room temperature. This change is perfectly consistent with that from Ni(0) to NiO, and thus the partial oxidation of the Ni(0) particles proceeded at room temperature. The composition analysis based on the linear combination fitting of the XANES spectrum revealed that the 40 percent of the Ni(0) species was oxidized to NiO. The similar change was observed for the Ni catalyst prepared by the Imp method, whereas the fraction of the formed NiO (10 %) species was diminished. The difference is quantitatively ascribed to the size difference of the supported Ni(0) particles. This relationship suggests that the partial oxidation proceeded at room temperature corresponds to the surface oxidation of the Ni(0) particles.

Figure 4 shows the temperature change of the average coordination number determined by the EXAFS analysis. The oxidation of small Ni(0) particles prepared by the SG method completed at 200 °C. It is lower than the corresponding temperature of the larger particles formed by the Imp method, as seen in Fig. 4(a). The difference indicates the relative stability of smaller NiO particles

under the O₂ atmosphere and may be interpreted by the easy oxygen migration in the smaller Ni(0) particle.

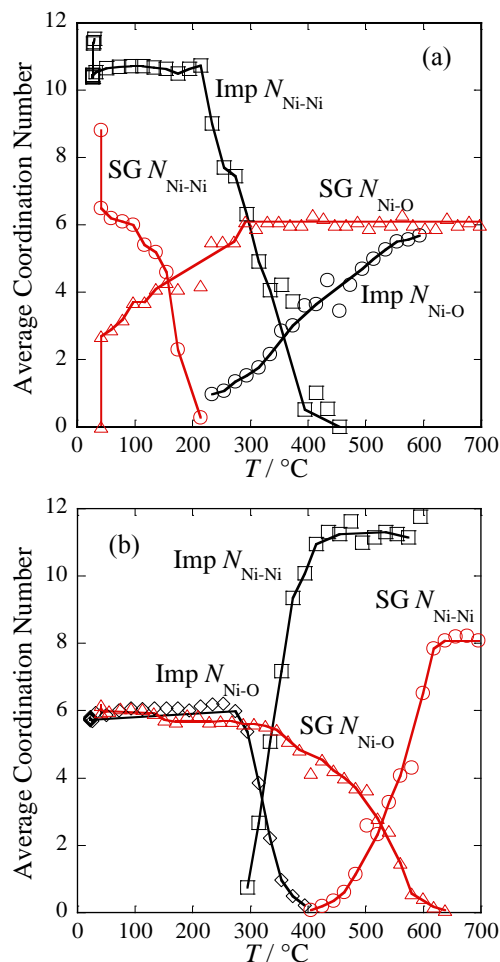


Fig. 4: Temperature change of average coordination number of the nearest Ni–O interaction in NiO ($N_{\text{Ni-O}}$) and the nearest Ni–Ni interaction in Ni(0) ($N_{\text{Ni-Ni}}$) during the oxidation (a) and reduction (b) process. The black and red line represent the Ni catalyst prepared by the Imp and SG method, respectively.

In contrast, Fig. 4(b) shows that the reduction of the smaller NiO particles in the SG sample proceeds at higher temperature than the larger particles. The final $N_{\text{Ni-Ni}}$ values after the reduction support that the size difference has been kept after the redox cycle. The peculiar high temperature of the reduction for small NiO particles also indicates the stability of the NiO species even under the H₂ atmosphere.

References

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- [2] S. Yamashita *et al.*, *J. Phys. Conf. Ser.*, **430**, 012051 (2013).