Size Dependent Redox Property of Supported Ni Catalyst

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1. Introduction

The particle size of active species for supported metal catalysts is an important factor to improve the catalytic activity. In the case of supported Ni catalysts, its particle size affects to the selectivity for the hydrogenation reactions [1]. Understanding of the reaction property for such small Ni particles will provide the useful information to design new catalysts with improved performance. The purpose of this study is the clarification of the redox property for the small Ni particles supported on SiO_2 prepared by the impregnation method with citric acid (ImpCA). The results will be compared with those for the corresponding Ni catalysts prepared by the standard impregnation method (Imp) [2].

2. Experimental

The SiO_2-supported Ni catalyst was prepared by the Imp method. The stoichiometric amount of citric acid was added into the nickel nitrate solution to control the Ni particle size for the ImpCA method. The Ni loading was set to be 5 wt% for both preparation methods.

The XAFS measurements were carried out at BL-3 of the SR center (Ritsumeikan University) and BL-9C of the PF (KEK). The *in-situ* XAFS experiments were performed at the Ni K edge during the temperature-programmed oxidation (TPO) and reduction (TPR) process under the dilute O_2 and H_2 environment up to 700 °C, respectively.

3. Results and Discussion

The particle size of the Ni species was estimated by the TEM measurements. The small nickel particles with the radius of *ca.* 4 nm were formed by the ImpCA method. The particle size was very homogeneous and was smaller than that (17 nm) prepared by the Imp method. It is found that the complexation of the Ni(II) ion in the aqueous solution can contribute to enhance the dispersion of the supported Ni species.

Figure 1 shows the temperature change of the average coordination number during the TPO (A) and TPR (B) process. A partial oxidation was observed at the beginning of the TPO process at room temperature, and the proportion of oxidized species (40 %) for the sample prepared by ImpCA was larger than that (10 %) for the Imp sample. The oxidized portion is almost ascribed by the surface oxidation of the metallic Ni(0) particle in considering their particle size. In addition, it was revealed that the bulk oxidation temperature of the ImpCA sample was by *ca.* 200 °C lower than that of Imp sample. On the other hand, the TPR process shows the opposite difference. The reduction temperature of the small ImpCA sample is shifted to higher temperature, indicating the flatten shape of the small NiO particle because of the interaction with the supporting SiO_2 surface. The present results suggest that the redox property of small Ni particle is significantly different from that of the supported Ni species prepared by the conventional impregnation method.

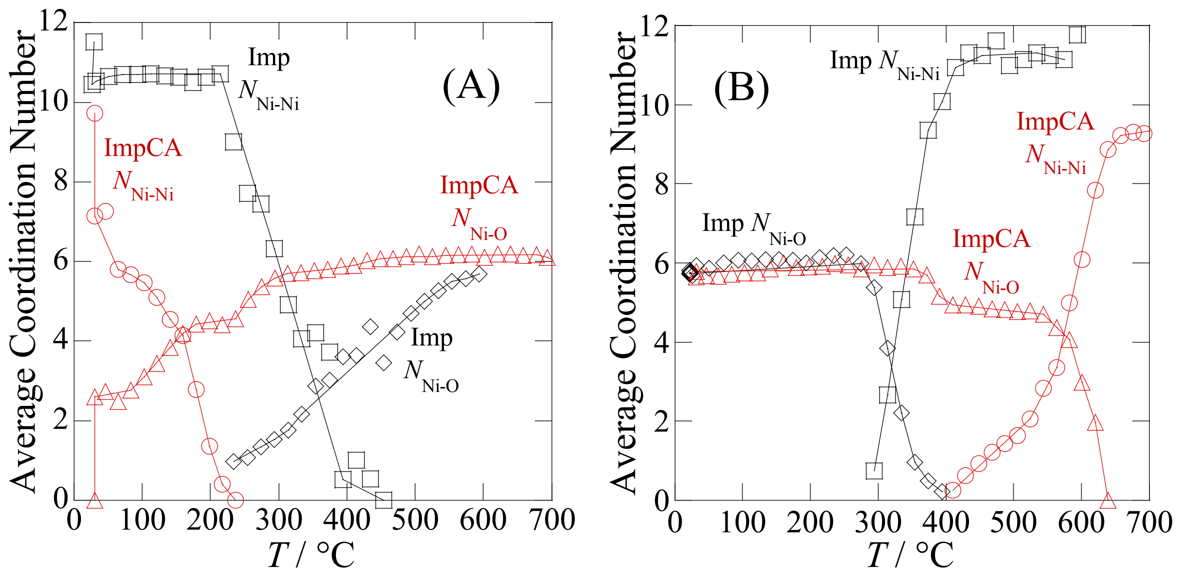

Fig. 1 Temperature change of average coordination number of the nearest Ni–O interaction in NiO ($N_{\text{Ni-O}}$) and the nearest Ni–Ni interaction in Ni(0) ($N_{\text{Ni-Ni}}$) during the oxidation (A) and reduction (B) process. The black and red line represent the Ni catalyst prepared by the Imp and ImpCA method, respectively.

References

[1] A. Ueno, H. Suzuki, and Y. Kotera, *J. Chem. Soc. Faraday Trans. I*, **79**, 127 (1982).
[2] S. Yamashita, M. Katayama, and Y. Inada, *J. Phys. Conf. Ser.*, **430**, 012051 (2013).