

## XAFS Analysis of Ni Particles Supported on Carbon Prepared from Ni(II) hydroxide

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The size of metal particles is one of the significant factors for improving the performance of the functional materials. Understanding the relationship between the particle size and the performance is valuable for the materials design. The purpose of this research is to synthesize small Ni clusters supported on carbon. The use of polyamidoamine (PAMAM) dendrimers and the liquid-phase reduction by  $\text{NaBH}_4$  have been tried to achieve the purpose. The chemical state of the Ni species was analyzed by the XAFS technique.

An aqueous solution of PAMAM (3  $\mu\text{M}$ ) was added into an aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (3 mM). The amount of Ni(II) was adjusted to be 30 times of PAMAM. The powders of  $\text{NaBH}_4$  and carbon were added into the solution and the suspension was stirred for 2 h. The Ni loading was set to 1 wt% relative to carbon. The obtained powder was separated by the suction filtration and was dried overnight in vacuo.

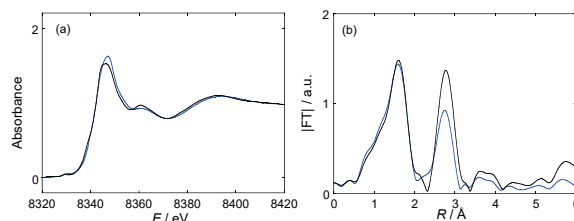
The XAFS measurements of the prepared sample were performed in the transmission mode at BL-3 of the SR center (Ritsumeikan Univ.) and at BL-9C of the Photon Factory (KEK). The sample powder was set in a flow-type *in-situ* XAFS cell and was heated up to 600 °C under 10 vol%  $\text{H}_2/\text{He}$  gas flow (100  $\text{cm}^3/\text{min}$ ).

The XAFS data of the prepared sample are shown in Fig. 1. The XANES spectrum was similar to that of  $\text{Ni}(\text{OH})_2$ , clearly indicating that the Ni(II) ion was not reduced by  $\text{NaBH}_4$  in water and the hydrolyzed product was supported on carbon because of the basicity of  $\text{NaBH}_4$ . The higher energy shift of the white line peak and the shorter distance between the Ni(II) ions than those of  $\text{Ni}(\text{OH})_2$  were observed in Fig. 1. The similar characteristics have been reported for a single-layered  $\text{Ni}(\text{OH})_2$  supported on  $\text{SiO}_2$  [1]. The large surface area of carbon could contribute to form the thin layer of  $\text{Ni}(\text{OH})_2$  when the hydrolysis reaction occurred in the precursor solution.

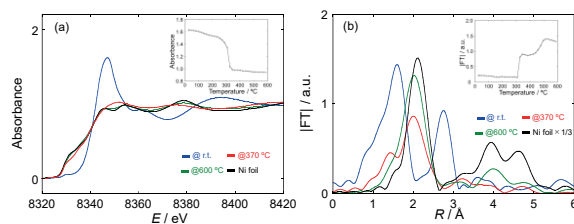
The prepared sample was thus reduced under  $\text{H}_2$  at elevated temperatures to carry out the gas-phase reduction. The XANES spectral change is given in Fig. 2(a) for the reduction process. The white line peak was disappeared at around 320 °C, and the absorption edge was shifted to the lower energy side. The absorbance change given in an inset of Fig. 2(a) suggested that the reduction was completed at *ca.* 350 °C. A drastic change was also observed at the same temperature in the Fourier transform (FT)

function as shown in an inset of Fig. 2(b). Both data showed a further small modification at above 450 °C. The formed Ni(0) nanoparticles could aggregate to enlarge the particle size by the high temperature treatment. This consideration is supported by the increase in the interatomic peak between the Ni(0) atoms (see Fig. 2(b)). At 370 °C, the XANES spectrum showed the flattened fine structure and the Ni–Ni interaction peak of Ni(0) was very small, suggesting that the Ni(0) nanoparticle was formed by the gas-phase reduction under the mild heating condition. The characteristics of XANES are consistent with those for the small Ni(0) cluster reported previously [2].

### References



**Fig. 1** XANES spectra (a) and Fourier transform functions (b) of the prepared sample (blue) and  $\text{Ni}(\text{OH})_2$  (black).



**Fig. 2** (a) XANES spectra and (b) Fourier transform (FT) functions during the reduction process. The absorbance at 8.347 keV and the FT intensity at 2.0 Å are plotted as a function of temperature in the inset of (a) and (b), respectively.

- [1] Y. Ichiyanagi, H. Kondoh, T. Yokoyama, K. Okamoto, K. Nagai, and T. Ohta, *Chem. Phys. Lett.*, **2003**, 379, 345.  
[2] N. Afiza, Y. Yamamoto, K. Maruyama, K. Nakamura, S. Yamashita, M. Katayama, and Y. Inada, *Adv. X-ray Chem. Anal.*, **2016**, 47, 301.