XAFS Characterization of Size-regulated Ru/Ni Nanoclusters Transformed from a Grafted Ru$_{12}$Ni Complex on SiO$_2$ and SiO$_2$ Matrix Overlayers

Satoshi MURATSUGU*[1], Atsuki YAMAGUCHI[1], Genichi YOKOTA[1], Mizuki TADA[1,2]

[1] Department of Chemistry, Graduate School of Science, Nagoya University, Furo, Chikusa, Aichi 464-8602, Japan.

[2] Research Center for Materials Science, Nagoya University, Furo, Chikusa, Aichi 464-8602, Japan.

1 Introduction

Small and size-regulated Ru/Ni nanoclusters (coordination number (CN) =) were prepared by the grafting of a Ru$_{12}$Ni complex [**1**, {Ru$_3$O(CH$_3$COO)$_6$(Py)$_2$}$_4${Ni(C$_{40}$H$_{24}$N$_8$)}] on a pyridine-functionalized SiO$_2$ surface, the stacking of SiO$_2$ matrix overlayers, and hydrogenation at 873 K. The local coordination structures of the prepared Ru/Ni nanoclusters were investigated by Ru and Ni K-edge XAFS.

2 Experiment

A SiO$_2$-supported Ru$_{12}$Ni complex (**2**) was prepared by the attachment of **1** on a SiO$_2$ surface functionalized with pyridine ligands. SiO$_2$-matrix overlayers were stacked on **2** to prepare supported complex (**3**). Then **3** was heated at 873 K under the vacuum, following H$_2$ (40 kPa) reduction (873 K) to prepare SiO$_2$-supported Ru/Ni nanocluster (**4**).

Ru K-edge XAFS was measured in a transmission mode at 20 K at the NW10A station with a Si(311) double-crystal monochromator. Ni K-edge XAFS was measured in a fluorescence mode at 20 K at the BL-12C station with a Si(111) double-crystal monochromator and MSSD. EXAFS spectra were analysed using ATHENA and ARTEMIS programs. k^3-Weighted EXAFS oscillations were Fourier transformed into R-space, and curve-fitting analysis was performed in R-space with CN, interatomic distance (R), Debye-Waller factor (σ^2), and correction-of-edge energy (ΔE_0). Phase shifts and backscattering amplitudes were calculated by the FEFF8 code using the crystal structures of Ru metal, RuO$_2$, Ru$_3$O(CH$_3$COO)$_6$(Py)$_3$, Ni metal, NiO, and Ni porphyrin complex.

3 Results and Discussion

The local coordination structures of the the SiO$_2$-supported Ru$_{12}$Ni complex and Ru/Ni nanocluster were examined by Ru and Ni K-edge EXAFS analysis, whose k^3-weighted EXAFS Fourier transforms are shown in Figure 1(A) and 1(B). From Ru K-edge EXAFS, the local coordination structures of the supported Ru$_{12}$Ni complex on **2** and **3** were similar to **1**, indicating the dispersed grafting of **1** on SiO$_2$ surface and stacking of SiO$_2$-matrix overlayers without decomposition of Ru$_3$O(CH$_3$COO)$_6$(Py)$_3$ cores. The Ru K-edge EXAFS of **4** showed exhibited a new peak at 0.2-0.3 nm, which was different from those of **1**, **2**, and **3**. They were curve-fitted to be a Ru-Ru bond at 0.266 ± 0.001 nm (CN = 4.1 ± 0.7). The small CN value indicated that the size of Ru nanocluster is very small (ca. 1 nm), and the bond length suggested that the most Ru species were reduced on **4**. From Ni K-edge EXAFS, the local coordination structures of the supported Ru$_{12}$Ni complex on **2** and **3** were also similar to **1**, indicating the dispersed grafting of **1** on SiO$_2$ surface and stacking of SiO$_2$-matrix overlayers without decomposition of Ni porphyrin core. The Ni K-edge EXAFS of **4** showed exhibited a new peak at 0.1-0.2 nm, which was different from those of **1**, **2**, and **3**. Although the curve-fitting analyses have not completed, this result might suggest the formation of Ru/Ni species or oxidised Ni species, since the Ni K-edge XANES of **4** suggest that the valence state of Ni was not zero.
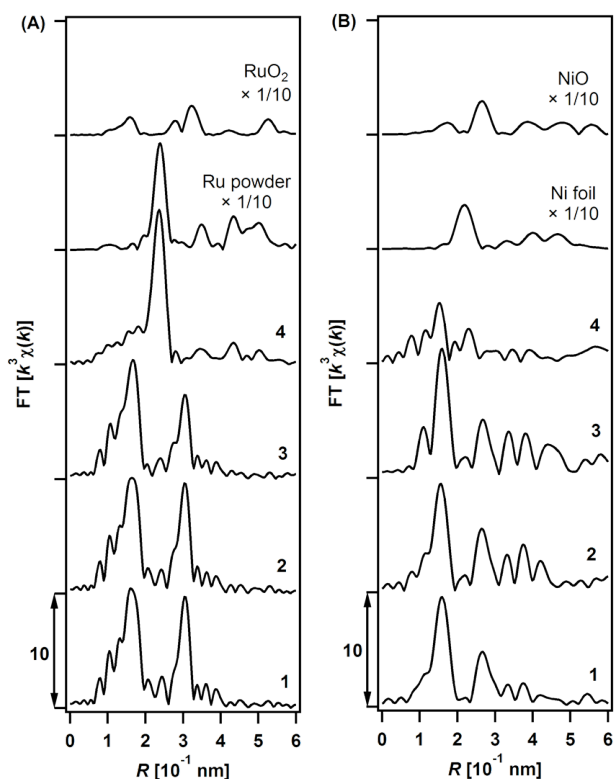

Figure 1 (A) k^3-Weighted Ru K-edge EXAFS Fourier transforms of **1**, **2**, **3**, **4**, Ru powder, and RuO$_2$ (3 < k < 18). (B) k^3-Weighted Ni K-edge EXAFS Fourier transforms of **1**, **2**, **3**, **4**, Ni foil, and NiO (3 < k < 13).

* smuratsugu@chem.nagoya-u.ac.jp