

XAFS Characterization of Ru-MO_x Nanoparticles Transformed from a Grafted Ru₁₂M Porphyrin Complex on SiO₂

Satoshi MURATSUGU*¹, Atsuki YAMAGUCHI¹, Gen-ichi YOKOTA¹, Tomoaki MAENO,¹
Mizuki TADA^{1,2}

¹ Department of Chemistry, Nagoya University, Furo, Chikusa, Aichi 464-8602, Japan.

² RCMS & IRCCS, Nagoya University, Furo, Chikusa, Aichi 464-8602, Japan.

1 Introduction

Ru-MO_x nanoparticles were prepared by the grafting of a Ru₁₂M porphyrin complex [**1-M**, {Ru₃O(CH₃COO)₆(Py)₂}₄ {M(C₄₀H₂₄N₈)}] (M = Cu, Ni, Zn) on a pyridine-functionalized SiO₂ surface, the stacking of SiO₂ matrix overlayers, and hydrogenation at 873 K.^[1] The local coordination structures of the prepared Ru-MO_x nanoparticles were investigated by Ru and M K-edge XAFS. The 3d metal atoms at the central position of the Ru₁₂M porphyrin complex showed great influence on the structures and catalytic performance of the Ru nanoparticles.^[1]

2 Experiment

Ru and M (M = Cu, Ni, Zn) K-edge XAFS of **1-M**, SiO₂-supported Ru₁₂M complex (**2-M**), SiO₂-matrix overlayers-stacked Ru₁₂M complex (**3-M**), and SiO₂-supported Ru-MO_x nanocluster (**4-M**, only Ru K-edge) were measured in a transmission mode at 20 K at the NW10A station with a Si(311) double-crystal monochromator, and at the BL-12C station with a Si(111) double-crystal monochromator, respectively. M K-edge XAFS of **4-M** 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 analyzed 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 coordination number (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.

3 Results and Discussion

The local coordination structures of **1-M**, **2-M**, and **3-M** were examined by Ru and M (M = Cu, Ni, Zn) K-edge EXAFS analysis, whose *k*³-weighted EXAFS Fourier transforms are shown in Figure 1(A) and 1(B). The local coordination structures of the supported Ru₁₂M porphyrin complex on **2-M** and **3-M** were similar to **1-M**, indicating that the structure of **1-M** did not decompose during the attachment. The Ru K-edge EXAFS of **4-M** (Figure 1(A)) exhibited a new peak attributed and curve-fitted to Ru-Ru bond. The small CN value indicated that the size of Ru nanocluster was very small (ca. 0.8–1.5 nm from STEM analyses), and the bond length suggested that the most Ru species were reduced on **4-M**. However, the degree of reduction was dependent on M: **4-Cu** was the most oxidized compared with **4-Ni** and **4-Zn** from Ru K-edge

XANES. The M K-edge EXAFS of **4-M** exhibited the existence of Cu–O, Ni–O, and Zn–O coordination (Figure 1(B)), suggesting the formation of MO_x species, respectively.

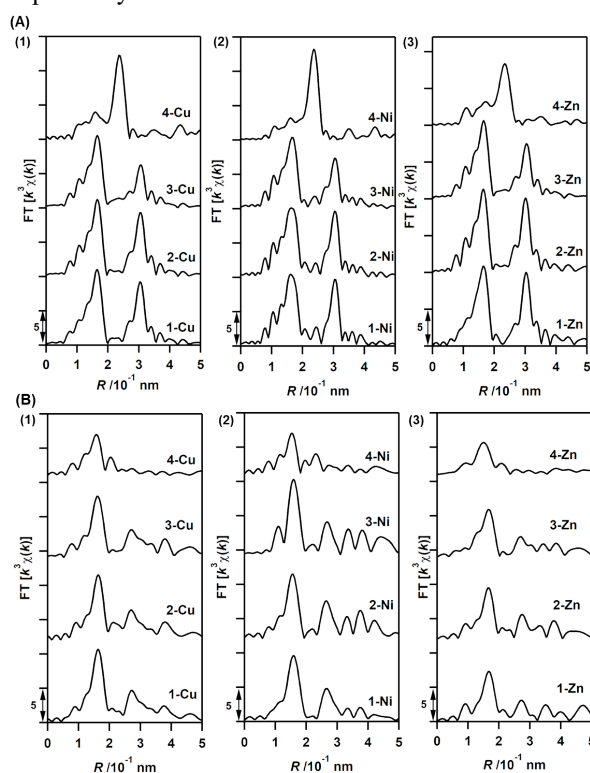


Figure 1: (A) *k*³-Weighted Ru K-edge EXAFS Fourier transforms of **1-M**, **2-M**, **3-M**, and **4-M**. (B) *k*³-Weighted (1) Cu, (2) Ni, (3) Zn K-edge EXAFS Fourier transforms of **1-M**, **2-M**, **3-M**, and **4-M**.

4-Cu exhibited considerable activity in acetophenone hydrogenation (93% conv. (6 h)) compared with **4-Ni** (13%) and **4-Zn** (40%). The major product was cyclohexyl methyl ketone, indicating that the aromatic ring was reduced more selectively than C=O. The order of catalytic activity would have a positive correlation to that of the oxidation degree of Ru nanoparticles.

References

[1] S. Muratsugu, A. Yamaguchi, G. Yokota, T. Maeno, M. Tada, *Chem. Commun.* **2018**, 54, 4842–4845.

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