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XAFS Characterization of Molecularly-Imprinted Ru Porphyrin Complex Catalysts for Cholesterol Epoxidation

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1 Introduction

A molecularly imprinted Ru porphyrin complex catalysts was prepared on a SiO_2 surface from a SiO_2-supported Ru porphyrin complex with SiO_2-matrix overlayers.[1] The local coordination structures of the prepared molecularly imprinted Ru porphyrin complex catalysts were investigated by Ru K-edge XAFS. The chemoselective epoxidation of cholesterol derivatives was achieved on the molecularly imprinted Ru complex catalyst.[1]

2 Experiment

The molecularly imprinted Ru catalyst was prepared in a step-by-step manner: (A) The attachment of a Ru porphyrin complex (**1**) on a SiO_2 surface to produce (**2**), (B) the removal of CO ligand to produce (**3**), (C) the coordination of a template to produce (**4**), (D) the stacking of SiO_2-matrix overlayers to produce (**5**), and (E) the removal of the template to produce the molecularly imprinted Ru catalyst (**6**).

Ru K-edge XAFS of **1**, **2**, **3**, and **4** were measured in a transmission mode, and that of **5** and **6** were measured in a fluorescence mode at 20 K at the NW10A station with a Si(311) 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.

3 Results and Discussion

The local coordination structures of the molecularly imprinted Ru porphyrin complexes were analyzed by Ru K-edge XANES and EXAFS (Figure 1). The shape of Ru K-edge XANES of **1**, **2**, **3**, **4**, **5**, and **6** were almost similar, indicating that the oxidation state of Ru in Ru porphyrin was almost identical. The Ru K-edge XANES of The curve-fitted CN and *R* for Ru-N (porphyrin) bond of **1**, **2**, **3**, **4**, **5**, and **6** were 0.205 ± 0.001 nm (CN = 4.3 ± 0.9), 0.205 ± 0.001 nm (CN = 3.7 ± 1.1), 0.206 ± 0.001 nm (CN = 3.2 ± 0.6), 0.204 ± 0.001 nm (CN = 4.2 ± 0.8), 0.206 ± 0.001 nm (CN = 3.8 ± 1.0), and 0.207 ± 0.001 nm (CN = 3.2 ± 0.4), respectively, indicating the maintenance of Ru porphyrin structure. This was also supported with the results of ^{13}C SS NMR and UV/vis spectra. The existence of Ru-N (template) bond was also observed on **4** and **5**, whose CN and *R* were 0.184 ± 0.003 nm (CN = 0.9 ± 0.7), 0.186 ± 0.006 nm (CN = 0.4 ± 0.6), respectively.

High chemoselectivity for the C_5=C_6 epoxidation of cholesterol derivatives without protecting 3-position OH group was achieved on the molecularly imprinted Ru porphyrin complex catalyst (**6**). The yield of C_5=C_6 epoxide for cholesterol epoxidation was increased to be 95% on **6** compared to that on **1** (30%) and on **2** (23%).

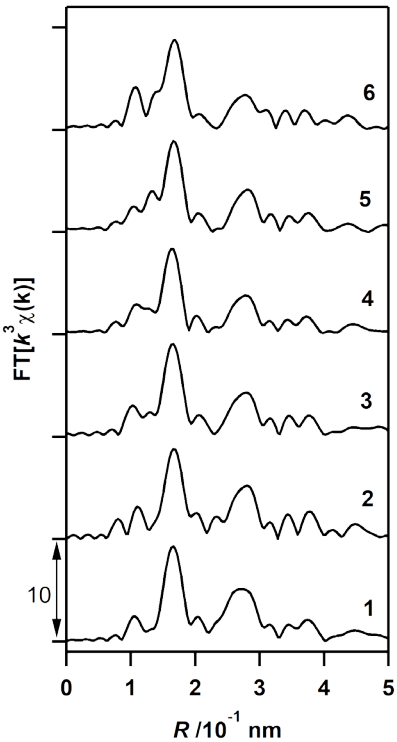

Figure. 1: k^3-Weighted Ru K-edge EXAFS Fourier transforms of **1**, **2**, **3**, **4**, **5**, and **6** (k = 30–160 nm^{-1}).

References

[1] S. Muratsugu, H. Baba, T. Tanimoto, K. Sawaguchi, S. Ikemoto, M. Tasaki, Y. Terao, M. Tada, *Chem. Commun.* **2018**, *54*, 5114 - 5117.

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