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XAFS Characterization of High-Loaded, Size-Regulated Pt Nanoparticles Prepared from Pt_4 Complex and Polymer on Carbon Support

Satoshi MURATSUGU*[1], Kentaro ICHIHASHI[1], Mizuki TADA[1,2]

[1] Department of Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602, Japan.
[2] Research Center for Materials Science (RCMS) & Integrated Research Consortium on Chemical Science (IRCCS), Nagoya University, Furo, Chikusa, Aichi 464-8602, Japan.

1 Introduction

We succeeded in preparing size-regulated Pt nanoparticles from carbon-attached Pt tetranuclear (Pt_4) complex precursors (Pt loading: maximum 4 wt%) and organic polymer matrix overlayers and demonstrating the durability of Pt nanoparticle catalyst on organic reactions (e.g. N-alkylation reaction).[1] We next investigated a method to prepare size-regulated Pt nanoparticle catalyst to increase Pt loading for electrocatalyst. A newly prepared Pt_4 complex was polymerized together with polymer precursor under the presence of multi-walled carbon nanotubes (MWCNTs), and successive reduction yielded size-regulated Pt nanoparticles with high Pt loading. The oxidation states and the local coordination structures of the Pt_4 complex and MWCNT-supported Pt nanoparticle were investigated by Pt L_{III}-edge XAFS.

2 Experimental

A newly prepared Pt_4 complex (**1**) and a Pt nanoparticle rsample after reduction (**A**) were prepared, respectively.

Pt L_{III}-edge XAFS was measured in a transmission mode at 20 K at the BL-12C station with a Si(111) double-crystal monochromator. Ionization chambers filled with pure N_2 and pure Ar were used to monitor incident and transmitted X-rays, respectively. 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 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 the Pt_4 complex and Pt nanoparticles were analyzed by Pt L_{III}-edge EXAFS (Figure 1). **1** had Pt-Pt bond at 0.250 ± 0.001 nm (Coordination number (CN): 2.3 ± 0.3) and two Pt-O bonds at 0.200 ± 0.002 nm (CN: 2.3 ± 0.6) and 0.219 ± 0.002 nm (CN: 1.6 ± 0.6), which were very similar to the $Pt_4(CH_3COO)_8$ complex.

The bond distances of the Pt-Pt coordination in **A** after the reduction were fitted as 0.275 ± 0.001 (CN = 4.0 ± 1.0), whose value was identical to Pt^0 foil (R = 0.277 ± 0.001). This result indicates that the Pt species was reduced to ca. zero. The white line peak of Pt L_{III}-edge XANES of **A** was decreased, indicated that the Pt oxidation stare of was reduced to ca. zero, supporting the EXAFS data. Two contributions from Pt-C/O (CN = 0.6 ± 0.5, R = 0.205 ± 0.003 nm) and Pt-O/N (CN = 0.5 ± 0.4, R = 0.219 ± 0.003 nm) were observed. TEM image analyses of **A** exhibited small Pt nanoparticles of 1.1–1.6 nm with the narrow size distribution (0.3~0.5 nm). The Pt loading of **A** was increased to ca. 12 wt. These results indicate that we succeeded in increasing Pt loading while keeping the small size of Pt nanoparticles.

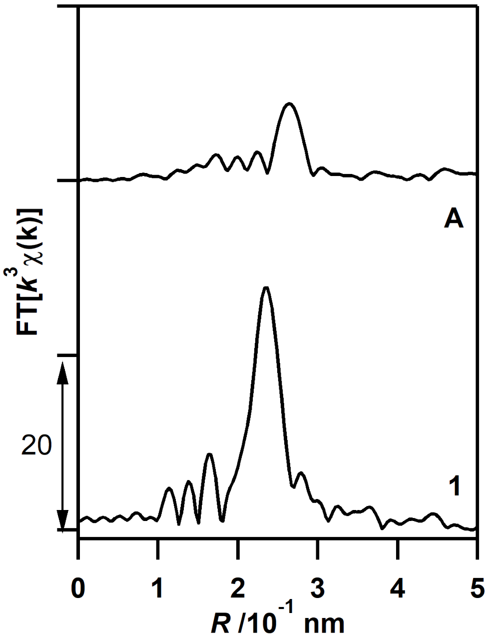

Figure. 1: k^3-Weighted Pt L_{III}-edge EXAFS Fourier transforms of **1** and **A**.

[1] S. Muratsugu, S. Miyamoto, K. Sakamoto, K. Ichihashi, C.-K. Kim, N. Ishiguro, M. Tada, **2017**, *33,* 10271–10282.

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