XAFS Characterization of Size-Regulated Carbon-Supported Pt Nanoclusters with Polymer Matrix Overlayers

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1 Introduction

We prepared size-regulated Pt nanoclusters from carbon-attached Pt tetranuclear (Pt_4) complex precursors and organic polymer matrix overlayers. A newly prepared Pt_4 complex was attached to the multi-wall carbon nanotube (MWCNT) and polypyrrole (PPy) matrix overlayers were successively stacked on the Pt_4 complex attached MWCNT. This composite was transformed to Pt nanoclusters for catalytic N-alkylation reaction. The oxidation states and the local coordination structures of the Pt_4 complex and Pt nanocluster supported on MWCNT were investigated by Pt L_{III}-edge XAFS.

2 Experimental

A Pt_4 complex (**1**) with anchoring ligand was attached on MWCNT (**A**). Then PPy matrix overlayers were stacked on the surface of **A** (**B**). Finally **B** was reduced to form Pt nanocluster catalyst (**C**). To see the effect of PPy matrix overlayres, **A** was reduced in a similar way of **B** to prepare Pt catalyst (**D**). 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 MWCNT supported Pt complex and Pt nanocluster were analyzed by Pt L_{III}-edge EXAFS analysis (Table 1). **1** had Pt-Pt bond at 0.250 ± 0.001 nm (Coordination number (CN): 3.9 ± 0.8) and two Pd-O bonds at 0.200 ± 0.001 nm (CN: 2.0 ± 0.6) and 0.215 ± 0.003 nm (CN: 1.6 ± 0.6), which were similar to the $Pt_4(CH_3COO)_8$ complex precursor. The bond distances of the Pt-Pt coordination in **A** and **B** were both fitted as 0.250 ± 0.001 (CN: 1.9 ± 0.2 for **A**, 1.5 ± 0.2 for **B**), those of Pt-O coordination were both fitted as 0.200 ± 0.002 nm (CN: 2.7 ± 0.7 for **A**, 2.7 ± 0.4 for **B**) and 0.216 ± 0.004 nm (CN: 1.5 ± 0.6 for **A**, 1.3 ± 0.4 for **B**), respectively, indicating that the local coordination structure of **1** was maintained after it was

attached to the MWCNT surface and successive stacking of PPy matrix overlayers.

The bond distances of the Pt-Pt coordination in **C** and **D** after the reduction were fitted as 0.273 ± 0.001 and 0.277 ± 0.001, respectively, which were larger than those of **A** and **B**, and were close to Pt^0 species. The Pt L_{III}-edge XANES of **C** and **D** indicated that the Pt oxidation stare of was reduced to ca. zero, supporting the EXAFS data. The CN (Pt-Pt) of **C** was 3.5 ± 1.1, which was smaller than that of **D** (4.8 ± 0.7), indicating that the size of Pt nanocluster in **C** was much smaller. In fact, TEM image analyses of **C** exhibited small Pt nanoclusters of 1.0–1.3 nm with the narrow size distribution (0.3~0.5 nm), while broad size distributions with Pt particles with diameters of 3–4 nm were observed on **D**, suggesting that the PPy matrix overlayers had a positive effect to control size-regulation.

Table 1 Structural Parameters Determined by Curve-Fitting Analysis of Pt L_{III}-edge EXAFS Measured at 20 K

Shell	CN	R /nm	ΔE_0 /eV	σ^2 /$\times 10^5$ nm^2
1 [a]				
Pt–Pt	2.2 ± 0.3	0.250 ± 0.001	7 ± 3	2 ± 1
Pt–O	2.0 ± 0.6	0.200 ± 0.001	5 ± 2	2 ± 2
Pt–O	1.6 ± 0.6	0.215 ± 0.003	5 ± 2	2 ± 2
A (Pt: 2.0 wt%) [b]				
Pt–Pt	1.9 ± 0.2	0.250 ± 0.001	7 ± 2	2 ± 1
Pt–O	2.7 ± 0.7	0.200 ± 0.002	3 ± 3	4 ± 2
Pt–O	1.5 ± 0.6	0.216 ± 0.004	3 ± 3	4 ± 2
B (Pt: 1.5 wt%) [c]				
Pt–Pt	1.5 ± 0.2	0.250 ± 0.001	7 ± 2	2 ± 1
Pt–O	2.3 ± 0.4	0.200 ± 0.002	4 ± 2	3 ± 1
Pt–O	1.3 ± 0.4	0.216 ± 0.004	4 ± 2	3 ± 1
C (Pt: 1.8 wt%) [d]				
Pt–Pt	3.5 ± 1.1	0.273 ± 0.001	11 ± 3	7 ± 1
Pt–O	0.7 ± 0.3	0.202 ± 0.001	21 ± 3	3 ± 2
Pt–C	1.3 ± 0.6	0.221 ± 0.003	21 ± 3	3 ± 2
D (Pt: 2.0 wt%) [e]				
Pt–Pt	4.8 ± 0.7	0.277 ± 0.001	14 ± 2	4 ± 1

[a] $k = 30 – 180$ nm^{-1}, $R = 0.12 – 0.30$ nm, $R_f = 0.3\%$.
[b] $k = 30 – 180$ nm^{-1}, $R = 0.12 – 0.30$ nm, $R_f = 0.3\%$.
[c] $k = 30 – 180$ nm^{-1}, $R = 0.12 – 0.30$ nm, $R_f = 0.4\%$.
[d] $k = 30 – 180$ nm^{-1}, $R = 0.12 – 0.32$ nm, $R_f = 3.1\%$.
[e] $k = 30 – 180$ nm^{-1}, $R = 0.18 – 0.32$ nm, $R_f = 1.8\%$.

Reference

[1] S. Muratsugu, S. Miyamoto, K. Sakamoto, K. Ichihashi, C.-K. Kim, N. Ishiguro, M. Tada, *Submitted*.

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