XAFS Characterization of Pt-containing Bimetallic Nanowires in Mesoporous Materials

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Introduction

Nanostructured metal particles and wires are expected to show unique physical and chemical properties different from those of bulk metals. In particular, metal nanowires have attracted much attention in terms of nanotechnology due to their potential magnetic, optical, electrical, and catalytic properties based on their low-dimensionality. We reported that rod-like Pt nanowires were formed by the photoreduction of H_2PtCl_6 in FSM-16 [1]. Recently we have reported the template synthesis of Pt-containing bimetallic nanowires in hybrid mesoporous HMM-1 [2]. In this work, the XAFS characterization of the nanowires in HMM-1 is studied.

Results and discussion

In a typical synthesis, HMM-1 (2D hexagonal, pore diameter 3.1 nm, BET surface area 812 m^2g^{-1}) was impregnated with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ and $RhCl_3 \cdot 3H_2O$ (Pt/Rh = 1.0, total metal 2.5 wt%). After drying under vacuum, the sample was exposed to the vapors of water (20 Torr) and methanol (100 Torr). Then the sample was exposed to UV-VIS light with a high-pressure Hg lamp (100 W, 250-600 nm) for 24 h to give Pt-Rh nanowires in HMM-1 (Fig. 1). XAFS data were acquired at BL 10B of KEK-PF at 300 K. The data were analyzed with a program of TECHNOS.

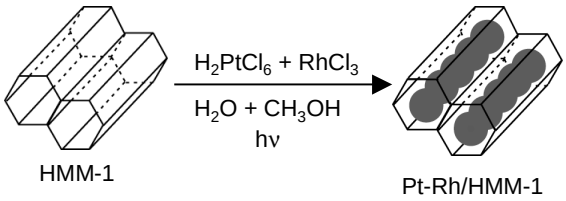

Fig. 1: Template synthesis of Pt-Rh nanowires in HMM-1.

Fig. 2 shows the Fourier transforms of Pt L_{III}- and Rh *K*-edge EXAFS $k^3\chi(k)$ of Pt-Rh wire/HMM-1. Table 1 summarizes the results of curve-fitting analysis of the major peaks at ca. 1.5-3.0 Å in Fig. 2. The results indicate the formation of Pt-Rh bonding for Pt-Rh/HMM-1. The contributions of Pt-Cl and Rh-Cl were also observed in the curve-fitting analyses, suggesting that the photoreduction of H_2PtCl_6 and $RhCl_3$ is not completed.

In the TEM study of Pt-Rh/HMM-1, the Pt-Rh nanowires (3 nm diameter, 10-50 nm length) are observed in the mesopores of HMM-1. The EDX analyses show that the observed Pt/Rh ratios (1.2-1.3) are similar to the ratio of charged precursors (Pt/Rh = 1.0). Furthermore, lattice fringes (*d* spacing 0.23 nm) are observed in the HRTEM of the Pt-Rh wires. From these results, we conclude that the nanowires in Pt-Rh/HMM-1 consist of Pt-Rh alloy phase. The XRD patterns for the Pt-Rh/HMM-1 indicate that the pore structure of HMM-1 was maintained in the formation of nanowires.

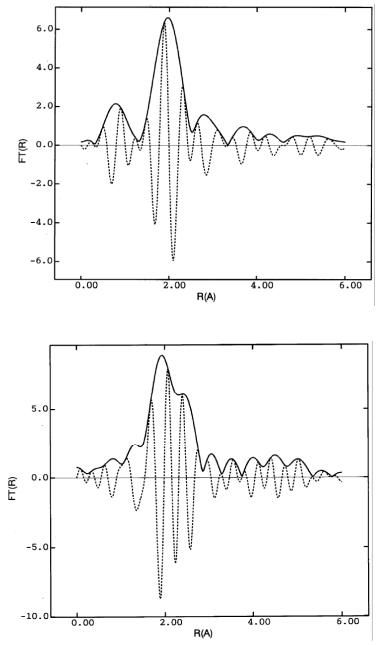

Fig. 2: Fourier transforms of Pt L_{III}- (upper) and Rh *K*-edge (lower) EXAFS $k^3\chi(k)$ of Pt-Rh wire/HMM-1.

We are optimizing the synthetic methods of Pt-Rh, Pt-Pd and Pt-Ru nanowires in HMM-1, and detailed EXAFS characterization of the nanowires is now in progress.

Table 1: Results of curve-fitting analyses.

Bond	N	R/Å	σ/Å	ΔE_0/eV	R/%
Pt-Pt	5.9	2.75	0.040	11.3	
Pt-Rh	3.0	2.68	0.041	11.1	3.4
Pt-Cl	1.2	2.27	0.062	1.0	
Rh-Rh	4.1	2.70	0.060	-8.3	
Rh-Pt	3.3	2.73	0.080	-11.9	1.7
Rh-Cl	2.5	2.47	0.076	-2.2	

References

[1] M. Ichikawa, A. Fukuoka et al., Micro. Mesoporous Mater., 21, 597 (1998); J. Mol. Catal. A, 141, 223 (1999).
[2] A. Fukuoka, Y. Sakamoto, M. Ichikawa et al., J. Am. Chem. Soc., 123, 3373 (2001).