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Effects of Diameter and Dimension of Ordered Mesoporous Metal Oxides as Templates on Formed Pt Nanoparticles and Pt–C Nanocomposites

Kazuki Oka,[1] Teruaki Koizumi,[2] Takashi Kawase,[2] Hideaki Yoshitake,[2] and Yasuo Izumi[1,*]

[1] *Department of Chemistry, Graduate School of Science, Chiba University, Inage-ku, Chiba 263–8522*

[2] *Division of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, Hodogaya-ku, Yokohama 240–8501*

1. Introduction

Significant part of catalysts to make fossil fuel and to convert chemical energy to electricity depends on platinum [1]. It is essential to study the minimum size of Pt particles to perform the decomposition of hydrocarbons and electro-redox reactions of H_2 and O_2 and to maximize available surface Pt atoms in the catalytic reaction space.

In this proposal, effects of diameter and dimension of ordered mesoporous aluminum–silicon oxides on formed Pt nanoparticles and Pt–carbon nanocomposites were investigated using Pt L_3-edge XANES and EXAFS.

2. Methods

One-dimensional mesoporous ordered Al–SiO_2 Al–MCM-41 (1.1 wt% Al) was purchased from Aldrich. Three-dimensional mesoporous order Al–SiO_2 Al–MCM-48 (1.1 wt% Al) and Al–KIT-6 (1.1 wt% Al) were synthesized. The uniform pore size of Al–MCM-41, Al–MCM-48, and Al–KIT-6 was 3, 3, and 8 nm, respectively. $Pt^{II}(NH_3)_4(OH)_2{\cdot}mH_2O$ was ion-exchanged with Al–MCM-41, Al–MCM-48, or Al–KIT-6 from aqueous solution [1]. The Pt–exchanged samples were heated in hydrogen at 573 K. The samples were further reacted with acetylene diluted with nitrogen at 973 K. Then, the Al–SiO_2 part was removed by washing with hydrofluoric acid solution. Obtained replica samples were denoted as Pt–C-M41, Pt–C-M48, and Pt–C-K6, respectively.

Pt L_3-edge XAFS spectra were measured on a beamline 9C. H_2–treated samples were measured in H_2 atmosphere, but acetylene- or HF–treated samples were measured as exposed to air. The data were analyzed using the package XDAP, XAFS Services International.

3. Results and Discussion

The best-fit results of Pt L_3-edge EXAFS data are listed in Table 1. For Pt–Al–MCM-41, only a Pt–Pt peak appeared. In contrast, coordination numbers (*N*) of Pt–O bond for Pt–Al–MCM-48 and Pt–Al–KIT-6 were 2.5–2.6, suggesting that three-dimensional ordered mesoporous Al–MCM-48 and Al–KIT-6 were susceptible to interact strongly with Pt nanoparticles.

The *N* values of Pt–Pt bonds for Pt–C–M41 and Pt–C-M48 decreased to 2.5–1.2 compared to that for samples before acetylene and/or HF treatments. In contrast, the *N* values of Pt–Pt bonds for Pt–C–K6 did not decrease (3.1–4.2). It was suggested that ordered three-dimensional pores of 8 nm were most suitable to synthesize stable Pt–C nanocomposite for polymer electrolyte fuel cells and other related electro/photocatalysis.

Table 1. Best-fit Results of Pt L_3-edge EXAFS for Pt–Ordered Mesoporous Metal Oxides (Al–MCM-41, Al–MCM-48, and Al–KIT-6), Acetylene-treated Samples, and HF-treated Samples

Sample	Pt–O (or Pt–C)		Pt–Pt	
	N	*R* (nm)	*N*	*R* (nm)
Pt–Al–MCM-41	—	—	4.2	2.74
Pt–C–Al–MCM-41	1.9	2.16	4.3	2.67
Pt–C-M41	3.6	1.96	2.5	2.81
Pt–Al–MCM-48	2.5	2.15	4.4	2.72
Pt–C-M48	3.6	1.99	1.2	2.80
Pt–Al–KIT-6	2.6	2.15	3.3	2.93
Pt–C–Al–KIT-6	2.2	2.06	3.1	2.59
Pt–C-K6	2.6	2.02	4.2	2.78

Reference

[1] K. Oka, Y. Shibata, T. Itoi, Y. Izumi, *J. Phys. Chem. C,* **114**, 1260–1267 (2010).

*yizumi@faculty.chiba-u.jp