

Structural characterization of noble metal clusters supported on ordered mesoporous carbons by XAFS

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Introduction

Platinum nanoclusters and Pt based bimetallic clusters, supported on porous carbons, have attracted much interest due to applicability as fuel cell electrode catalysts [1]. Recently, we have reported the synthesis of highly ordered mesoporous carbon materials, referred to as CMK-*n*, using mesoporous silicas as templates [2,3]. In the porous carbons, mesopores are regularly arranged with uniform diameters in the range of 2 - 6 nm. The ordered mesoporous feature seems to play a key role for the preparation of supported metal clusters with uniform diameter that are useful for catalytic and electrocatalytic applications. In our preliminary experimental results, the nanoporous carbons showed high metal dispersion of Pt and Ru clusters, compared with conventional porous carbons such as carbon blacks and activated carbons, which was confirmed by transmission electron microscopy (TEM) and gas (hydrogen and oxygen) chemisorption. This report presents structural characterization of Pt and Ru clusters supported on the ordered mesoporous carbons by extended x-ray absorption fine structure (EXAFS).

Experimental

In this study, a pipe-type mesoporous carbon, referred to as CMK-5 was used as support for Pt and Ru clusters. The CMK-5 nanoporous carbon was synthesized via the reported method, using SBA-15 mesoporous silica as a template [6]. Pt and Ru clusters were supported on the CMK-5 mesoporous carbon via incipient wetness impregnation of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, and subsequent reduction at 300 – 400 °C in H_2 flow.

Pt L_{III} and Ru K edge EXAFS spectra were measured at room temperature under H_2 atmosphere, using BL 10B at the Photon Factory in Tsukuba. Analysis of the EXAFS data was carried out by standard methods using the XFIT and FEFF 6.01, an ab initio XAFS program.

Results and Discussion

Figure 1 shows Pt L_{III} edge EXAFS Fourier transform of Pt/CMK-5 samples with various Pt loadings. The Fourier transform was performed from a k range of 30 – 140 nm^{-1} . The radial distribution thus obtained was inverse-Fourier transformed from R range of 0.14 – 0.30 nm. The coordination numbers (n) of nearest Pt-Pt pairs and bond distances obtained from curve fittings are listed in Table 1. The coordination number of the 16.7% Pt/CMK-5 sample is 6.3, which is comparable to highly

dispersed 1 nm Pt cluster engaged in the supercage of NaY zeolite [4]. Even when the Pt loading is increased up to 50%, the coordination number still remains at 8.8, corresponding to the particle size around 2.5 nm [5]. The CMK-5 mesoporous carbon is also effective for the preparation of very small, uniform Ru clusters. The curve fitting results of Ru/CMK-5 samples (Table 1) indicate that the coordination numbers of Ru-Ru pairs range from 5.4 to 8.8.

The EXAFS data, together with gas adsorption and TEM results indicate that the highly dispersed, uniform metal nanoparticles can be prepared on mesoporous carbons even with high metal loading, which is highly desirable for the application to fuel cell catalysts.

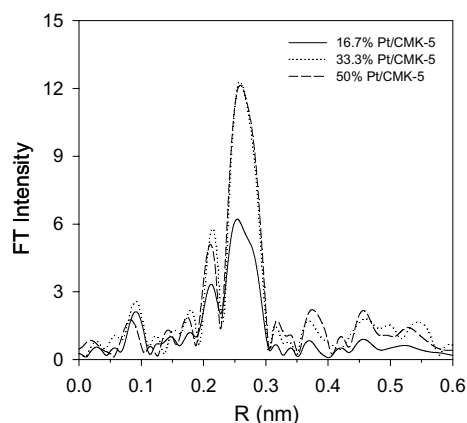


Figure 1. Fourier transforms of k^3 -weighted Pt L_{III} edge EXAFS oscillation for Pt/CMK-5 samples

Table 1: Curve-fitting results for Pt and Ru clusters

Sample	pair	R / nm	n	σ^2 / pm^2
16.7% Pt/CMK-5	Pt-Pt	0.274	6.3	82
33.3% Pt/CMK-5	Pt-Pt	0.275	7.8	63
50% Pt/CMK-5	Pt-Pt	0.275	8.8	67
5% Ru/CMK-5	Ru-Ru	0.262	5.4	82
10% Ru/CMK-5	Ru-Ru	0.262	7.4	77
30% Ru/CMK-5	Ru-Ru	0.264	8.8	65

References

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