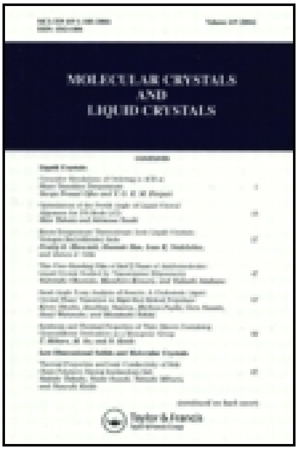

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Structure and Reduction Behavior of Platinum Chloride Intercalated in Graphite Layers

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Structure and Reduction Behavior of Platinum Chloride Intercalated in Graphite Layers

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Platinum chloride-graphite intercalation compounds ($PtCl_4$-GICs) were synthesized from platinum chloride ($PtCl_4$) and graphite under pressurized chlorine atmosphere. The analysis of XRD patterns showed that platinum chloride was inserted into graphite layers and the $PtCl_4$-GICs with a stage 3 structure were formed. The curve-fitting analysis of Pt L_{III}-edge EXAFS showed that the distance of the Pt-Cl-Pt bond of 5 wt% $PtCl_4$-GIC was 0.06 Å longer than that of the $PtCl_4$ bulk, indicating that $PtCl_4$ had a distorted structure in graphite layers. $PtCl_4$ samples were reduced in hydrogen atmosphere to produce platinum metal particles in graphite layers. EXAFS analysis showed that the coordination numbers of Pt-Pt metal bond for $PtCl_4$-GIC samples reduced at various temperatures were lower than those of the mixture of $PtCl_4$ and graphite ($PtCl_4$-Gmix) samples reduced in the same manners.

Keywords: graphite intercalation compounds; platinum chloride; platinum metal particles; EXAFS

INTRODUCTION

The size and shape of metal particles on supports are determined by the metal-support interaction and the steric effect of supports. The structure of metal particles is closely related to their catalytic properties. The synthesis [1,2] and catalytic activities [3-5] of platinum metal graphite intercalation compounds have widely been investigated. In the present work, we report the structure and reduction behavior of platinum chloride intercalated in graphite layers by XRD and EXAFS spectroscopy.

EXPERIMENTAL

Platinum (IV) chloride and graphite (KS6, Lonza) were mixed in a thick walled pyrex reactor and dried under vacuum at 423 K for 2 h. The intercalation reaction was carried out in the reactor at 723 K for 2 weeks under 3 atm of chlorine (Takachiho, 99.999 %), and then the platinum chloride intercalated compounds ($PtCl_4$-GIC) were obtained. The $PtCl_4$-GIC samples were reduced at various temperatures (423-673 K) for 1 h under 300 Torr hydrogen, and then the platinum metal intercalated compounds (Pt-GIC) were obtained.

RESULTS AND DISCUSSION

The intercalation of $PtCl_4$ in graphite layers was determined by XRD (Cu-Kα, λ = 1.5418 Å). The intensity of peak at 2θ = 26.57° ascribed to the diffraction for (002) of graphite decreased with increasing the amount of platinum chloride from 1 to 15 wt% Pt loadings, while new peaks at 2θ = 10.0°, 14.6° and 20.3° appeared and their intensities increased. No other peaks except for the three peaks and graphite peaks appeared. The diffraction peak positions calculated for (002), (003) and (004) of the repeat distance along the c axis (Ic = 17.6 Å) are 10.0°, 15.1° and 20.2°. The distance of 17.6 Å correspond to the sum of three graphite layers and one intercalated layer (7.5 Å). We have concluded that platinum chrolide is intercalated in graphite layers with a stage 3 structure from 1 to 15 wt%[6, 7].

The local structure of platinum chloride in graphite layers was investigated by in-situ EXAFS. Figure 1 shows the Fourier transforms for Pt

L_{III}-edge EXAFS spectra of 5 wt% $PtCl_4$-GIC and $PtCl_4$. Two peaks were shown in both samples. Peaks between 1 and 2 Å are assigned to the Pt-Cl bond and peaks between 3 and 4 Å to the Pt-Cl-Pt bond. The curve-fitting analysis showed that the distance of the Pt-Cl-Pt bond of 5 wt% $PtCl_4$-GIC was 0.06 Å longer than that of the $PtCl_4$ bulk, indicating that $PtCl_4$ had a distorted structure in graphite layers.

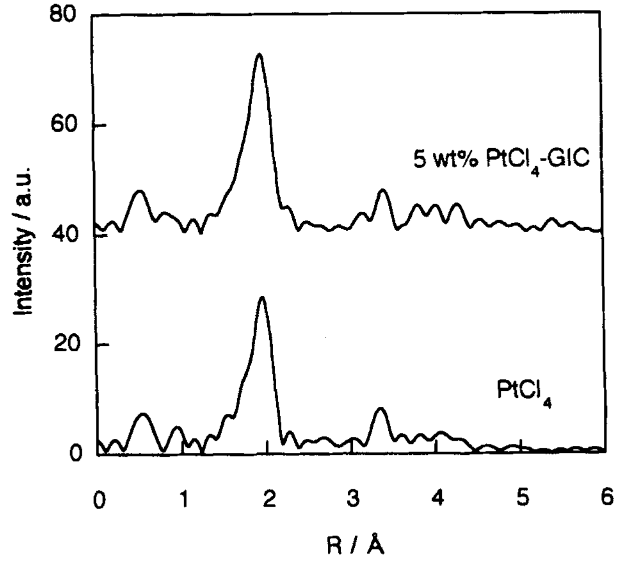

FIGURE 1 The Fourier transforms of Pt L_{III}-edge EXAFS data.

Platinum chloride in graphite layers and on graphite surface were reduced in hydrogen atmosphere to produce metal particles. EXAFS analysis showed that the coordination numbers of the Pt-Pt metal bond for $PtCl_4$-GIC samples reduced at various temperatures were lower than those of the mixture of $PtCl_4$ and graphite ($PtCl_4$-Gmix) samples reduced in the same manners (Figure 2). Small Pt metal particles were formed in graphite layers of the 5 wt% $PtCl_4$-GIC sample by reduction because $PtCl_4$ was well dispersed in graphite layers. In contrast, large Pt metal particles were formed on graphite surface of the 5 wt% $PtCl_4$-Gmix sample because $PtCl_4$ supported on graphite surface easily agglomerated to large particles during reduction.

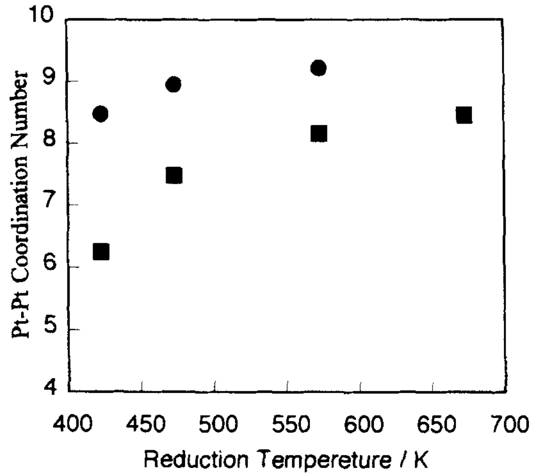

FIGURE 2 Pt-Pt coordination numbers of 5wt% Pt-GIC (■) and Pt-Gmix (●) at various reduction temperatures.

Acknowledgement

EXAFS experiments were carried out under the approval of the PF advisory committee (No. 95G211 and 98G108).

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