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Platinum nanoclusters immobilized on polymer–clay nanocomposite films☆

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Abstract

A 40-μm-thick, self-supporting, transparent film was obtained upon slowly evaporating an aqueous mixture of synthetic hectorite, $Pt(NH_3)_2Cl_2$, and polyethylene oxide (PEO). The resulting film containing 2.4 wt.% platinum was then reduced under H_2 at 150 °C for 2–4 h, turning black upon reduction. XRD shows development of Pt(0) by the appearance of crystalline peaks upon reduction. A lineshape analysis using the Scherrer equation of the (220) peak shows Pt(0) particles from 3.8 nm to 7.5 nm depending upon processing conditions. These values are confirmed by TEM, and a high dispersion of the metal throughout the matrix is evident. XRD and TGA confirm that PEO is stable to the processing conditions. In situ small-angle X-ray scattering measurements of the reduction process were also performed. Under an inert, non-reducing atmosphere, the shape of the scattering curve does not change as the temperature is raised from 30 °C to 150 °C. Analysis of the scattering curves using the general unified fit (GUF) equation yields one Rg value of 80 Å from 30 to 150 °C under He, which is assumed to arise from the overall film morphology. Under H_2, however, the shape of the scattering curves visually changes between 100 and 120 °C. Two structural levels are needed to fit these curves at moderate temperatures in the GUF equation, with two subsequent Rg values. One of these Rg values corresponds to the film morphology (Rg=80–90 Å), while the other has an Rg=18–19 Å with a corresponding diameter of 4.8–5.1 nm. This latter Rg is assumed to arise from the reduced Pt(0) nanoparticles that form in situ during reduction.

Keywords: Hectorite; Platinum; Polymer–clay nanocomposite; Metal immobilization; Small-angle X-ray scattering

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1. Introduction

Polymer–clay nanocomposites (PCNs) are a class of materials that have been of exponentially growing interest due to their potential for mechanical reinforcement enhancement as lightweight materials, as flame retardant and ablative materials, and for gas barriers in the food packaging industry (Beall and Pinnavaia, 2000; Carrado, 2003). Possibilities for their use in specialty applications such as conductive composites (Liu and Tsai, 2003; Chang et al., 2003; Kim et al., 2002), imaging (Majumdar et al., 2003), and as light-emitting devices (Park et al., 2004) are also being explored. We have recently reported on the preparation and conductivity of polyethylene oxide (PEO)–clay nanocomposites with respect to their use as polyelectrolyte films in lithium ion rechargeable batteries (Smith et al., 2003; Sandí et al., 2003a). The efficacy of supporting small metal nanoclusters on such a support, which is self-supporting, strong, and flexible, is now under investigation. Applications of such a material lie, for example, in catalysis of reactions that occur at temperatures where the polymer of choice is thermally stable.

This report involves the formation and stability of Pt(0) nanoparticles on a PEO–PCN film. Representative previous reports of immobilized platinum nanoparticles on clay supports, without polymer, include but are not limited to the following. Dihydrocinchonidine-modified montmorillonite and hectorite clays were impregnated with H_2PtCl_6 and reduced with $NaBH_4$, yielding Pt(0) sizes of 0.8 and 1.2 nm, respectively; both clays were demonstrated as mildly enantioselective catalysts (Mastalir et al., 2002). A pillared clay loaded with $Pt(NH_3)_4^{2+}$ and reduced in H_2 at 500 °C gave nanoparticles of 4–20 nm in size depending upon the pillaring species (Vicente and Lambert, 2001; Vicente et al., 2002). A similar experiment done on an unpillared clay, with the reduction performed at only 140 °C, gave nanoclusters of 5–10 nm depending upon the loading (Harrison et al., 1988). Finally, platinum was successfully deposited on a carbon–clay composite using both chemical and electrochemical methods (Montilla et al., 2002). In this study, synthetic hectorite clays are impregnated with a platinum salt, PEO is added to the solution, and the resulting dried PCN film is reduced under H_2 at 150 °C. Metal formation is monitored via XRD, TEM, and in situ small-angle X-ray scattering (SAXS). The stability of the film is measured by XRD and thermal gravimetric analysis (TGA).

2. Experimental

2.1. Sample preparation

The Pt–PEO–clay nanocomposites were made using synthetic hectorites, the preparation of which has been described previously in detail (Carrado, 2000; Smith et al., 2003; Sandí et al., 2003a). A synthetic Li(I)–hectorite was crystallized with Li(I) as the exchangeable, gallery cations. Loading of Pt(II) salt was accomplished via a wet impregnation method by adding 0.5 g clay to a 2.5 mM aqueous *cis*-$Pt(NH_3)_2Cl_2$ solution and stirring for 24 h (24 h was used to ensure complete dissolution of the salt followed by adequate ion-exchange). This yields a material that has 4.65 wt.% Pt. The impregnation method was followed rather than an ion-exchange method in order to ensure that all of the metal used was associated with the clay. The desired amount of poly(ethylene oxide) (PEO, Aldrich, MW approximately 100,000) was then added and the solution stirred for another 24 h, with a final loading of, for example, 2.4 wt.% Pt in a 1:1 PEO–clay nanocomposite. The stirring time of 24 h was employed to ensure intercalation of PEO within the clay galleries (Smith et al., 2003; Sandí et al., 2003a). Films of 40-μm thickness were prepared by puddle-casting the slurries onto Teflon-coated glass plates and drying at 120 °C under an inert atmosphere for 24 h. The transparent, yellowish Pt–salt–PCN films were then reduced in a dilute H_2 in N_2 atmosphere at 150 °C for 2–4 h, whereupon they turned black. The films were held vertically in a quartz tube in a tube furnace for the reduction process.

2.2. Characterization

XRD patterns were recorded on a Rigaku Miniflex+ with Cu K_α radiation, a 0.05° 2θ step size, and 0.5° 2θ scan rate; the films were held in a horizontally mounted sample stage. Lateral crystallite size of the Pt(0) nanoclusters was estimated from the line broadening of the (220) reflection using the Scherrer equation (Brindley and Brown, 1980; Radmilovic et al., 1995); $L = 0.91\lambda/B\cos\theta_{max}$ where L = crystallite size in Å, $\lambda = CuK_\alpha = 1.5405$ Å, $B = \mathrm{sqrt}(B_{obs}^2 - b^2)$; B_{obs} = FWHM (220) reflection in radians observed, b = FWHM instrumental correction (in this case Si(220) reflection (Zhou et al., 2001)). The requirement that $B_{obs}/b > 2$ is met ((Brindley and Brown, 1980; Radmilovic et al., 1995).