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NANOSTRUCTURED MATERIALS

Growth of nearly monodisperse palladium nanoparticles on disaggregated kaolinite lamellae

Abstract Palladium nanoparticles were prepared by in situ growth between kaolinite layers. Expansion of the interlayer space kaolinite was effected by intercalation of dimethyl sulfoxide (DMSO) at 65 °C. The basal spacing increased from 0.72 to 1.12 nm during this process. After washing with methanol (partial displacement of DMSO), nonionic poly(vinylpyrrolidone)/kaolinite, cationic poly(diallyldimethylammonium)/kaolinite and octylammonium/kaolinite complexes were generated by adsorbing the polymer or the surfactant from solution.

Kaolinite samples containing palladium nanoparticles were prepared by hydrazine and NaBH₄ reduction of palladium ions adsorbed from a solution of H₂PdCl₄ (pH 4). The size of the palladium particles formed was determined by transmission electron microscopy measurements which showed that nearly spherical, nearly monodisperse particles of size of about 1 nm were generated.

Key words Palladium nanoparticles · Kaolinite · Intercalation · Polymer stabilization

Introduction

Several procedures were devised for the preparation of nanoparticles in the 1–50-nm size range [1]. In these procedures an important role is assigned to stabilizing agents which protect the nanoparticles formed against aggregation, making possible the preparation of nanoparticles with diameters of a few nanometers [2, 3]. Polymers and surfactants are most often used as stabilizing agents for sols of subcolloidal size. Particles of controlled size can also be prepared within the internal space of micelles and microemulsions [4, 5]. Silicate minerals and layer double hydroxides are excellent supports for the preparation of semiconductor and transition-metal particles with diameters of a few nanometers on the surface of these layered compounds but also in the interlamellar space. Clay minerals (montmorillonite, hectorite, etc.) are especially suitable for this purpose because they swell readily in aqueous media and, therefore, provide a large (500–800 m² g⁻¹) internal surface area [6, 7].

Pd, Pt and Au nanosols stabilized by poly(vinylpyrrolidone) (PVP) in aqueous media have been synthesized using alcohol and H₂ for reduction [8–10]. Chen and Akashi [11] obtained Pt sols from H₂PtCl₆ in water–ethanol mixtures of a volume fraction of 0.6 with respect to ethanol and showed the formation of particles in the polymer-stabilized system.

Transition-metal particles are most conveniently grown within the interlamellar space of clay minerals by displacing the exchangeable by precursor transition-metal cations and by subsequent reduction. Au and Ag clusters were obtained in laponite by Aihara et al. [12], with hydrazine hydrate, sodium borohydride and UV irradiation as reducing agents.

In our earlier studies the adsorption layer at the solid/liquid interface was employed as a “nanophase reactor” for the generation of nanocrystalline semiconductor particles (CdS, ZnS, TiO₂) and for their stabilization [6, 7]. To summarize briefly, the procedure consists of adsorbing the precursor ions of the nanocrystalline material in the interfacial adsorption layer of
solid particles (i.e. about 1-nm thick lamellae) dispersed in a liquid phase. The synthesis is carried out in the adsorption layer by introducing the appropriate reagent. [6, 7]. The nanoparticles are formed attached to the surface in a well-controllable number and size between the silicate layers. Király et al. [13, 14] reported the synthesis of Pd nanoparticles in organic suspensions on hydrophobized montmorillonite by alcohol reduction of Pd acetate. We now present new procedures for the preparation of nanocrystalline palladium in the interlamellar space of kaolinite, a clay mineral that does not swell in water. The large specific surface area necessary for nanoparticle growth is created by breaking the hydrogen bonds between the kaolinite lamellae, i.e. by delamination of the mineral particles. According to Weiss et al. [15], silicate lamellae develop strong dipole-dipole interactions with, for example, dimethyl sulfoxide (DMSO), and hydrogen bonds with formamide, acetamide and hydrazine. The study of the intercalation of kaolinite with similar molecules is well known [15–20]. Gábor et al. [18] obtained the intercalation complex of kaolinite with hydrazine and potassium acetate. The basal spacing of kaolinite is 0.72 nm, that of the kaoline–hydrazine complex is 1.05 nm and that of the kaoline–potassium acetate complex is 1.41 nm. The maximum degree of intercalation was shown to increase with the time of reaction and the concentration of the guest compound but was found to be unaffected by changes in temperature. In the case of hydrazine, the reaction was 94% complete within 1 h, whereas with potassium acetate the reaction never exceeded 86% completion, even after prolonged reaction times.

Komori et al. [19] cleaved interlamellar hydrogen bonds in kaolinite by N-methylformamide (d_l = 1.08 nm) and in methanol (d_l = 1.11 nm) and their PVP was incorporated (d_l = 1.24 nm). Intercalation of alkylamines (C = 6–18) and water was also accomplished by the same authors [20]. The layers were expanded by N-methylformamide, washed with methanol and the methanol-wet product was treated with alkylamine; alternatively, methanol was displaced by treatment with water. The basal spacing increased with the alkyl chain length in a linear way in the range 2.69–5.75 nm with a slope of 0.225 nm per carbon atom.

We chose direct intercalation of DMSO for expanding the kaolinite structure. The excess DMSO was displaced from the kaolinite by washing with methanol before the polymer and surfactant were adsorbed. When palladium ions were added to the suspension, they were also adsorbed on the external and internal surfaces and the Pd^{2+} ions were reduced by addition of a reducing agent. Thus, the previously adsorbed polymer or surfactant promotes the adhesion of newly formed nanoparticles on the surface of the lamellae.

### Experimental

#### Materials

**Supports**

Kaolinite from Zettlitz (Germany, particle diameter: 10–20 μm) was used as a support for the preparation of nanoparticles. The basal spacing was 0.72 nm. The specific surface area as determined by N₂ adsorption measurement was 14 m²/g.

**Reagents**

The reagents were used as received without further purification. The metal precursor PdCl₂ (purity 99%) was obtained from Aldrich. PVP (K-30, average molecular weight 40,000, Fluka), a 20% aqueous solution of poly(diallyldimethylammonium chloride) (PDGA, average molecular weight 40,000–50,000, Aldrich), and octylamine (purity 99%, Fluka) were used as protective agents for the Pd nanoparticles. Methanol (Reanal, Hungary) was of analytical purity. DMSO (analytical purity, Reanal, Hungary) was used for delamination of the kaolinite particles. The hydrazine hydrate reducing agent was a 55% aqueous solution (Carlo Erba).

**Methods**

**Preparation of Pd nanoparticles**

The kaolinite was expanded by the intercalation of DMSO at 65 °C. The excess DMSO was removed from the sample by several washings with methanol over 5 days. Pd/kaolinite complexes were prepared directly by reduction of Pd^{2+} ions (0.7 mM aqueous solution) previously adsorbed in the methanol/DMSO/kaolinite system and by applying a polymer and surfactant to ensure binding to the lamellae and steric stabilization. Macromolecules were adsorbed on the support from a methanol or aqueous solution and this was followed by adsorption and reduction of Pd^{2+} ions. Intercalation complexes of nonionic PVP/kaolinite and cationic PDGA/kaolinite (0.02–0.4 g polymer/g kaolinite) were prepared by this method in systems containing various (0.1–2.0%) concentrations of methanol/PVP, PDGA or water/PVP, PDGA by polymer adsorption. Intercalation complexes of octylammonium/kaolinite (0.12–1.2 g/g kaolinite) were prepared at pH 4.0 in systems containing various (0.5–0.05 M) concentrations of water/octylamine. Methanol/DMSO/kaolinite intercalation compound (1 g) was dispersed in 20 ml polymer or surfactant solution, and the mixtures were stirred at room temperature for 24 h. Kaolinite samples containing different amounts of palladium were obtained by (0.9–3.6 ml, 0.1 M) hydrazine or (1.8 ml, 0.1 M) NaBH₄ reduction of the palladium ions. The metal content of the products was 0.45–1.4% (Table 1). The schematic diagram of the synthesis is presented in Fig. 1.

**X-ray diffraction experiments**

X-ray diffraction measurements were made using a Philips PW 1820 diffractometer (Cu Kα radiation, 40 kV, 35 mA). The basal spacing was calculated from the (001) Bragg reflections using the PW 1877 automated powder diffraction software.

**Electron microscopy**

Transmission electron microscopy (TEM) images were made using a Philips CM-10 transmission electron microscope with an