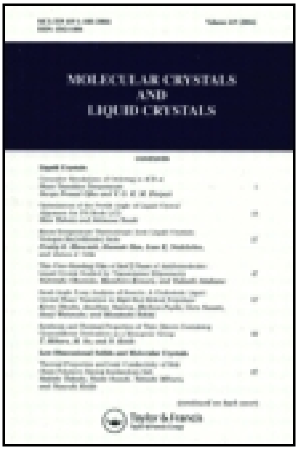

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Liquid Sorption and Nanoparticle Intercalation in Layer-Structured Materials

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Liquid Sorption and Nanoparticle Intercalation in Layer-Structured Materials

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Alkylammonium intercalated graphite oxides (R-GO), palladium intercalated alumina-pillared montmorillonites (Pd/Al_2O_3-PILC) and titania-pillared montmorillonites (TiO_2-PILC) have been prepared and the intercalation materials have been characterized by BET surface area analysis, UV/VIS spectroscopy, ICP-AES, DTG-DTA, XRD and TEM measurements. R-GO particles were prepared by oxidation of natural graphite followed by organophilization with cationic surfactants. For TiO_2-PILC and Pd/Al_2O_3-PILC the synthesis included the interlamellar adsorption of precursor species (polyaluminium-hydroxide, Pd-acetate and tetraethyl orthotitanate) from dilute solutions and subsequent chemical reactions at the montmorillonite/solution interface.

Keywords: graphite oxide; palladium particles; titanium dioxide; pillared clays; nanoparticles; intercalation

INTRODUCTION

The intercalation of ions, molecules and nanoparticles into layer-structured materials have received considerable attention in the past few years [1-7]. The physicochemical properties of the host materials may be advantageously modified by the guest materials and *vice versa*: the guest species may benefit from the interfacial interactions with the solid host as well as from the geometric constrain imposed on the guest species upon the intercalation process. Several intercalation methods have been developed so far [1-7]. A novel preparation procedure is applied in the present work taking advantage of the adsorption layer in the interlamellar space which may be used as a versatile nanophase reactor suitable for the preparation of intercalated species.

EXPERIMENTAL

Preparation of alkylammonium intercalated graphite oxides (R-GO)

10 g of natural graphite (Kropfmühl, Germany) was treated with $NaClO_3/HNO_3$ = 85 g:60 cm^3 at 333 K for 24 h. The oxidized graphite (GO) was purified first with concentrated HCl solution, then with distilled water. The cation exchange capacity, attributed to acidic groups of GO [5], was found to be 5.5 $mmol.g^{-1}$. Intercalations of alkylammonium chlorides (R = C_{14}, C_{16} and C_{18}) were achieved by using an excess of surfactant solutions at 323 K for 1 week. The products were purified by Soxhlet-extraction.

Preparation of titania-pillared montmorillonite (TiO_2-PILC).

1 g of montmorillonite (Wyoming, USA) samples were dispersed in 50 cm^3 of dry 2-propanol. Then, 20 cm^3 of $Ti(OEt)_4$ solutions (1, 7.5 and 15 w/v % in 2-propanol) were added to the suspensions. The preadsorbed $Ti(OEt)_4$ underwent hydrolysis upon the addition of aqueous 2-propanol solution (0.9, 6.1 and 12.2 cm^3 water, respectively, each dissolved in 20 cm^3 of 2-propanol). The intercalated $Ti(OH)_4$ was transformed to TiO_2 by calcination at 593 K for 4 h.

Preparation of Pd intercalated alumina-pillared montmorillonite (Pd/Al_2O_3-PILC).

1 g of sodium montmorillonite (Süd-Chemie AG, Germany) was pillared in

aqueous aluminium-hydroxide solution in the usual way [6]. The wet solid was transferred to 100 cm^3 of ethanol:toluene=6:94 (v/v) by several centrifugation/redispersion cycles. Then, 30 cm^3 of 1% Pd(II)-acetate in toluene was introduced into the system. The progress of $Pd^{2+} \rightarrow Pd^0$ reduction in the interlayer space was monitored spectrophotometrically [7]. After 90 min the product was purified by centrifugation in toluene, dried and samples were taken for calcination at 383, 573 and 723 K.

Equipments.

The basal spacings (d_L) of the layer-structured materials were determined with a Philips PW 1830 X-ray diffractometer. N_2 adsorption measurements at 77 K (BET surface area and pore size analyses) were performed by using a Micromeritics Gemini 2735 sorptometer. DTA-DTG measurements on the TiO_2-PILC samples were carried out with a MOM Q-1500 D derivatograph. Band-gap values for TiO_2 were obtained by using an UVIKON 930 UV/VIS spectrophotometer. The Pd content of the Pd/Al_2O_3-PILC's was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jobin Yvon 24). Transmission electron micrographs of the Pd particles were taken with a Philips CM-10 electron microscope.

RESULTS AND DISCUSSION

R-GO's. The basal spacing d_L of the R-GO derivatives increases with increasing the length of R and a further increase in d_L can be observed upon the addition of various organic solvents which penetrate into the GO layers (Table 1). The interlamellar swelling increases with decreasing polarity of the organic solvent which may be related to the solvation efficiency of the surface-bound alkyl chains by the organic liquids.

TABLE 1 Basal spacings (d_l/nm) of R-GO samples

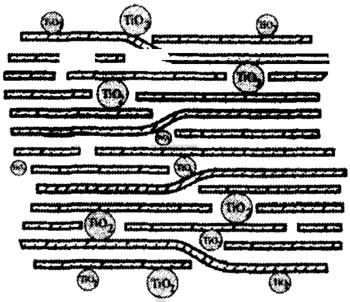
GO-derivative	air-dried	in ethanol	in toluene	in cyclohexane	in n-heptane
GO	0.68	0.94	0.76	0.75	0.79
C_{14}-GO	1.45	2.35	3.68	4.10	3.57
C_{16}-GO	1.56	2.49	4.10	4.80	4.20
C_{18}-GO	1.59	2.55	4.27	4.77	4.47

TiO_2-PILC's. Table 2 shows that the basal spacing, the particle size of the pillaring agent (proportional to the band-gap λ_g)), the specific surface area a^S_{BET} and the micropore area a^S_{mp} of the pillared clay can be controlled by the concentration the precursor compound $Ti(OEt)_4$ which adsorbs from 2-propanol preferentially. The trend in Table 2 strongly supports the assumption that the formation of TiO_2 particles takes place *in situ* in the interlamellar space and not in the bulk liquid phase followed by particle deposition onto the clay lamellae. XRD and DTA-DTG measurements indicated that the $Ti(OH)_4 \rightarrow$ anatase transition takes place between 593 and 643 K. The micropore surface structure appears at intermediate concentration of $Ti(OEt)_4$. The proposed structure of TiO_2-PILC is sketched in Figure 1.

TABLE 2 Characterization of TiO_2-PILC samples calcinated at 593 K

$Ti(OEt)_4$ (w/v%)	d_L (nm) 298K	$\frac{I\ (d_L=4.0nm)}{I\ (dL=0.96nm)}$ 593K	λ_g (nm) in susp.	a^S_{BET} (m^2/g) 298K	a^S_{mp} (m^2/g) 298K
0.00	1.18	0.81	-	6.9	0.0
1.00	1.39	0.73	322	50.7	12.0
7.50	1.43	2.84	344	100.6	4.1
15.00	2.99	3.29	346	198.0	0.0

FIGURE 1 The structure of TiO_2-PILC (schematic).

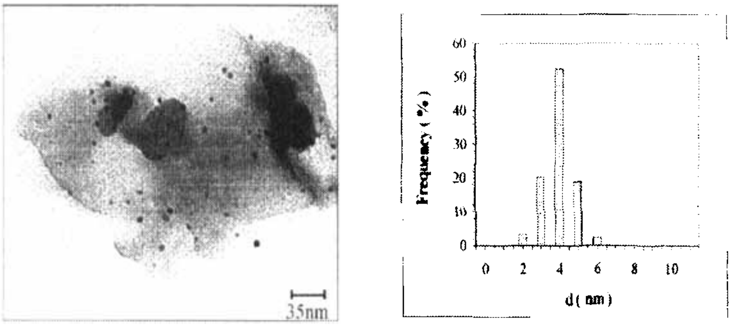


Pd/Al_2O_3-PILC's. The preferential adsorption of Pd(II)-acetate between the neighbouring silicate sheets, rich in ethanol, ensures that Pd particle formation takes place predominantely in the interlamellar space of the clay which is related to the high values of a^S_{mp} (Table 3). The effect of calcination temperature on the properties of the Pd/Al_2O_3-PILC samples are given in Table 3. Although no systematic variations can be observed in the BET surface area and the micro pore area, the Pd particle size d_{TEM} insreases and the basal spacing d_L decreases with increasing thermal treatment. These observations may be attributed to sintering of the finely divided metal particles accompanied by migration of the particles from internal to external surface sites. The TEM image of the 573 K sample is given in Figure 2 indicating quasi-spherical morphology and fairly monodisperse particle size distribution.

TABLE 3 Characterization of Pd/Al_2O_3-PILC samples (1.24 w/w % Pd)

calcination T (K)	d_L (nm)	d_{TEM} (nm)	a^S_{BET} (m^2/g)	a^S_{mp} (m^2/g)
383	6.12	3.7	177.2	106.5
573	5.73	4.4	159.5	69.2
723	4.99	5.8	194.4	102.1

FIGURE 2 The TEM image of Pd/Al_2O_3-PILC sample, calcinated at 573K



CONCLUSIONS

R-GO particles have been prepared by oxidation of natural graphite followed by organophilization with cationic surfactants. The extent of interlamellar swelling can be controlled by the polarity of the dispersion medium. TiO_2-PILC and Pd/Al_2O_3-PILC intercalation materials have been prepared *via* interlamellar chemical reactions taking advantage of the preferential adsorption of precursor species in the interlamellar space of montmorillonite dispersion. The properties of the intercalation materials produced can be readily controlled by the experimental conditions.

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