

RAPID AND DIRECT SYNTHESIS OF SPHERICAL ORGANOTALC

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Abstract—Organotals, in which organic moieties are covalently bonded to Si atoms belonging to the tetrahedral sheets, are usually prepared by a sol-gel process starting from ethanolic solution of Mg nitrate, organo-alcoxysilanes, and aqueous sodium hydroxide solution. In this case, gypsum-like particles are obtained. In this work, evaporation-induced self-assembly within aerosols was used for the first time in order to prepare organotalc spheres. These hybrid lamellar materials can be used as environmental barriers, as polymer fillers, and as catalytic supports. Using octyltriethoxysilane as a source of Si, spherical particles with sizes ranging from 20 nm to 1 μ m are obtained. X-ray diffraction and transmission electron microscopy images show that the d_{001} value equals 2.8 nm meaning that, in this case, organic moieties are either alternatively distributed or identically tilted in the interlayer space. Compared to the classical synthesis at room temperature or in autoclaves, and besides being a continuous process, the reaction time is reduced to several minutes instead of hours. Homogeneous forms are obtained by aerosol whereas irregular shapes are obtained in the classical synthesis.

Key Words—Aerosol, EISA procedure, Spherical Organotalc, Synthesis, TEM, X-ray Diffraction.

INTRODUCTION

Innovative strategies to produce well defined nanoparticles, and other nanostructures such as nanofibres, lamellar hybrids, or mesoporous materials, have revitalized materials science because of the potential benefit to society. Complex porous hybrid solids have been synthesized (Mann, 2000; Mann and Ozin, 1996), among which inorganic-organic materials with a lamellar structure have been developed intensively over the last decade (Sales *et al.*, 2006). These materials are usually in the classical gypsum-like particle shape (Alimi and Gadri, 2004) but the spherical form has also been reported (Patil *et al.*, 2004). For use in a wide range of applications, particle size and shape need to be controlled (Shin *et al.*, 2000), *e.g.* particles possessing nm-scale pores of well defined size and connectivity are of interest in terms of use in the controlled release of drugs and in pigments or as hosts for optically active compounds (Ozin, 1992; Imhof and Pine, 1998). Many methods are used to prepare spherical porous solids, *e.g.* using a very uniform dispersion of liquid emulsion droplets as a template around which solid material is grown (Shin *et al.*, 2000), or evaporation-induced self-assembly (EISA) within aerosols (Rao *et al.*, 2002; Lu *et al.*, 1999). The EISA method was first reported by the Brinker group working on mesostructured silicas, which originated from pioneer work by Mobil on surfactant-templated materials (Kresge *et al.*, 1992).

The premise in the current project was to use the EISA method, within aerosol, in the fabrication of organotalc spheres. Organotalc has a lamellar structure consisting of an octahedral sheet, filled with Mg, between two tetrahedral silicic sheets. The layers are bonded by Van der Waals forces. These materials have been reported in the literature and were prepared by a sol-gel process (Da Fonseca, 2000; Jaber *et al.*, 2002); they are poorly organized, can be exfoliated in non-polar solvents (Ukrainczyk *et al.*, 1997), and have no specific morphology. Shin *et al.* (2000) reported the preparation of spherical organotalc obtained using the emulsion droplet approach. These solids were prepared at temperatures ranging from room temperature to 170°C and were aged from 1 to 7 days. These hybrid lamellar materials can be used as environmental barriers, polymer fillers, and catalytic supports. Other potential applications, which have been reported, include the improvement of optical and mechanical properties (Ukrainczyk *et al.*, 1997). They are prepared from an ethanolic solution of an organo-alcoxysilane and an inorganic salt such as Mg nitrate. The formation of the solid is ensured by precipitation in alkaline medium. The organo-alcoxysilane is suggested to act as a surfactant: the silanol groups represent the hydrophilic head and the carbon chain the hydrophobic tail. This leads to auto-assembly around the organic parts of the molecule. To date, no method of synthesizing organotalc involving EISA within aerosols has been reported. This is a difference from bulk-solution methods in which all species are initially confined to droplets which undergo evaporation-driven concentration changes as they pass through the process. Solidification of the inorganic network, principally by condensation reactions, occurs during the flash stay in the oven.

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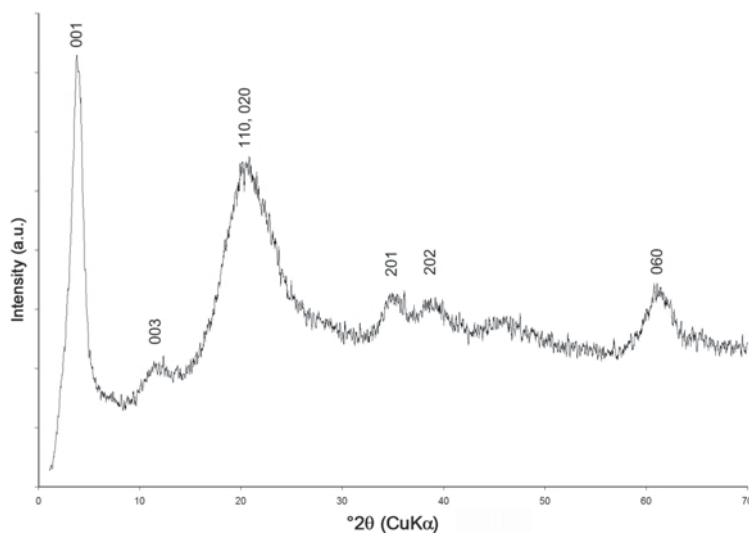


Figure 1. XRD pattern of the organotalc prepared by means of the EISA procedure ($d_{001} = 2.8$ nm).

EXPERIMENTAL

In a typical experiment, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved under stirring in ethanol (0.2 mol L^{-1}), and subsequently mixed with an ethanolic solution of octyltriethoxysilane (0.4 mol L^{-1}); 20 mL of an aqueous NaOH solution was added to give a final pH of 9. The resulting solution was transferred into the aerosol bottle. The spray-drying apparatus consists of a constant-output atomizer (TSI model 3076), nominally providing droplet particles ranging in size from 20 to 1000 nm. The solution was pumped out and sprayed out of the atomizer, by N_2 gas, in the form of fine particles and then had a flash stay in the oven at 400°C . This high-temperature environment promoted condensation reactions which led to the formation of sheets before complete evaporation of the solvent. Finally, particles were collected on a porous filter with the help of a vacuum pump, necessary to keep the flux constant. X-ray diffraction (XRD) patterns were recorded with $\text{CuK}\alpha$ radiation using an X-Pert Pro PAN analytical diffractometer ($\lambda = 0.15406 \text{ nm}$; scanning range: $1\text{--}70^\circ 2\theta$; step size: $0.02^\circ 2\theta$ per 2 s). Scanning electron microscopy (SEM) images were captured using a Philips XL30 FEG instrument. Samples were dispersed on a carbon tape and were sputter coated with gold before analysis.

Transmission electron microscopy (TEM) investigations were carried using a Philips CM200 device. One droplet of the powder dispersed in chloroform (CHCl_3) was deposited onto a carbon-coated copper grid and left to dry in air. Thermogravimetric analyses (TG-TDA) of the as-synthesized samples were performed using a TG-DTA apparatus (Setaram Labsys) under air, with a flow rate of $\sim 1.5 \text{ dm}^3 \text{ h}^{-1}$ from 25 to 800°C at a heating rate of 5°C min^{-1} . Elemental analyses were performed by X-ray fluorescence (XRF) using a Magix Philips (2.4 KW)

instrument. The as-synthesized materials were calcined at 800°C and mixed with lithium tetraborate before being fused to form beads.

^{29}Si and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on a Bruker MSL-300 spectrometer ($B_0 = 7.04 \text{ T}$) at 59.6 and 75.5 MHz, respectively, with magic angle spinning (MAS). The sample was packed in a 7 mm diameter cylindrical zirconia rotor and spun at a frequency of 4 kHz. For ^{29}Si and ^{13}C MAS decoupling NMR experiments, a $\Pi/4$ pulse duration of $1.8 \mu\text{s}$ and a $\Pi/2$ pulse duration of $1.5 \mu\text{s}$ were used, respectively, with a recycle time of 90 s.

RESULTS AND DISCUSSION

The powder XRD pattern of the as-synthesized particles displays reflections characteristic of an organophyllosilicate structure: 001, 003, 110, 020, 201, 202,

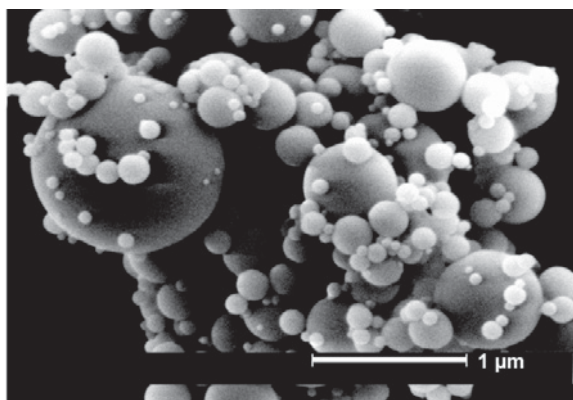


Figure 2. SEM image of organotalc prepared by means of the EISA procedure.

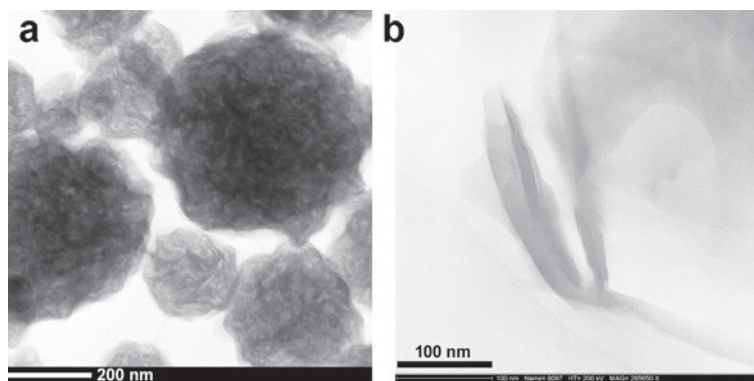


Figure 3. TEM image of the organotalc prepared by means of the EISA procedure (a) and by the sol-gel process (b).

and 060 (Figure 1, $d_{001} = 2.8$ nm). However, these reflections are broader than those observed for the parent phyllosilicates as previously mentioned in the literature ($d_{001} = 0.936$ nm) (Brindley, 1966). This behavior is explained by the presence of organic chains in the interlamellar space. Assuming that the silicate layer thickness is equal to 0.96 nm (Templin *et al.*, 1997) and that the length of the octyl group (R) is 1.10 nm, the d_{001} value should be equal to 3.16 nm ($2R + 0.96$) considering that the organic chains are perpendicular to the sheets. The experimental value obtained, $d_{001} = 2.80$ nm, suggests that the organic chains are bonded to adjacent lamella and the chains are either alternatively distributed or identically tilted in the interlayer space. The 060 reflection present at $60^\circ 2\theta$, associated with an interplanar distance of 0.156 nm, is characteristic of a trioctahedral character (all octahedral cavities are filled with Mg). Scanning electron microscopy (SEM) images show spherical particles of disparate sizes possessing a smooth surface morphology (Figure 2). The particle size ranges from 20 nm to 1 μm . Indeed, as the solvent is evaporated from the solution reservoir by the atomizer, the remaining solution becomes more concentrated, thus causing the aerosol particle size to increase.

If this is compared with the synthesis of organotalc prepared by the sol-gel process (from the same reagents), the XRD patterns are similar but the SEM images show no particular morphology in contrast to the case of the organotalc obtained by the aerosol process (Jaber *et al.*, 2005).

Transmission electron microscopy (TEM) images, captured using the Philips CM200 apparatus, were taken along a longitudinal direction, *i.e.* with the electron beam perpendicular to the sheets. Spherical particles were observed in which the packing of the sheets can be distinguished (Figure 3). The measured $d_{001} = 2.8$ nm fits well with the XRD results. The size of the particles varied from 20 to 1000 nm.

The presence of organic matter was confirmed by thermogravimetric analysis (Figure 4). The thermogram exhibits three weight losses: the first (5%) in the temperature range 50–150°C corresponds to the departure of water. The second (45%), between 230 and 500°C, can be assigned to the release of a portion of the organic matter (the product recovered is black, indicating that some of the organic matter is still attached to the inorganic lattice). The third (1.5%, between 550 and 700°C) is due to the dehydroxylation of OH groups.

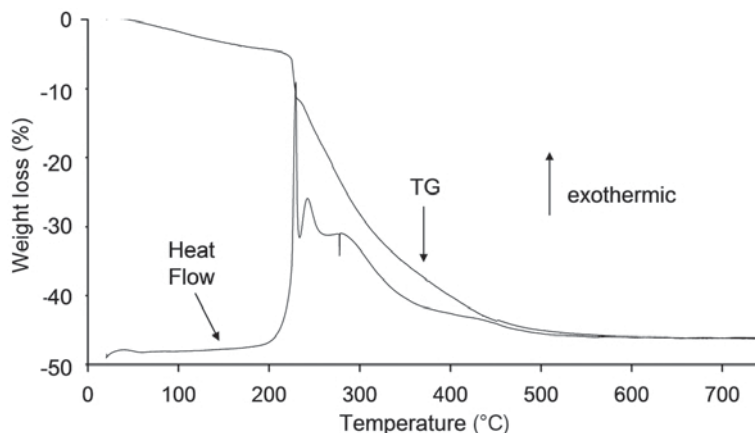


Figure 4. Thermogravimetric analysis of the organotalc prepared by means of the EISA procedure.

The elemental analyses allow the determination of the chemical formula, which corresponds approximately to an ideal formula: $Mg_3(RSi)_4O_8(OH)_2$.

$^{29}Si\{^1H\}$ NMR was used to characterize the inorganic framework, and to obtain information about the degree of structural polycondensation. The spectrum (Figure 5) shows three regions: the range from -63 to -72 corresponds to the T3 groups, that at -58 ppm to the T2 groups, and that at -48 ppm to the T1 group (Yokoi *et al.*, 2004). T_n represents a silicon atom bonded to one organic (R) and a varying number of O–M (M = Si or Mg) and O–H groups, *i.e.* $Si(R)(OM)_n(OH)_{3-n}$. Three kinds of T3 signals could be distinguished: (R)Si[(OSi)₂] Δ [(Mg)] \square (Δ represents the tetrahedral sheet; and \square , the octahedral sheet). The differences are due to the silicon neighborhood which can be either in a T1 or T2 environment.

The ^{13}C MAS NMR was used to characterize the organic groups (Figure 6). The decomposition of the spectrum shows eight isotropic resonances ranging from 14.6 to 34.6 ppm. The chemical shift assignments (Table 1) confirm that the alkyl chain is intact [5,13]. The relative intensity of each ^{13}C resonance is close to 1:1:1:1:1:1:1:1.

The width of the different peaks is related to the mobility of the corresponding carbons; the most mobile, C8, exhibits the narrowest peak.

Alkaline media favor the hydrolysis of ethoxy groups from organo-alkoxysilane to form silanol groups. The latter might be negatively charged due to the pH being 9. These negatively charged species probably aggregate into ordered molecular arrays similar to anionic surfactants, commonly used to synthesize mesoporous silicas (Jaber *et al.*, 2005). The negatively charged micelles may function as templates and attract Mg cations from solution to yield a layered hybrid structure, with an inorganic lattice consisting of Si–O–Mg and Si–O–Si bonds. Usually, organoclays are prepared at room temperature following this mechanism (Brindley, 1966). Using the EISA procedure, the species condensation probably occurs first during the spray process but carries on in the oven, where even a short stay is sufficient to continue the silica polymerization. According to Ukrainczyk *et al.* (1997),

Table 1. Chemical shifts and half height widths of the resonances for each carbon site of the octyl chain.

Sites	δ_{iso} (ppm)	Width (ppm)
C1	14.6	2.4
C2	24.3	1.6
C3	34.6	2.4
C4	30.9	1.3
C5	30.4	0.8
C6	32.9	0.8
C7	23.5	0.5
C8	14.6	0.6

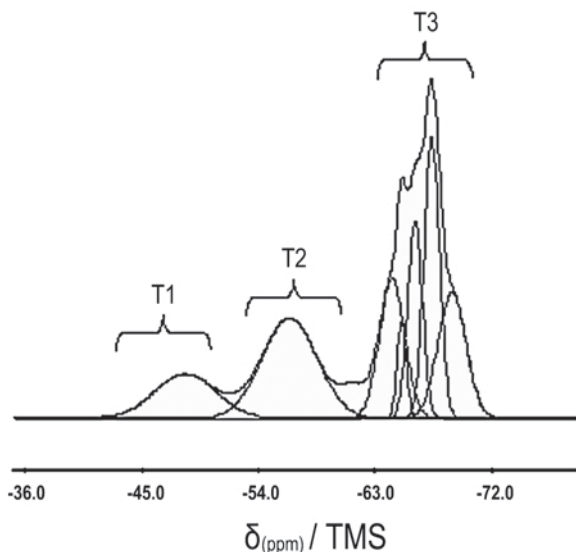


Figure 5. $^{29}Si\{^1H\}$ NMR spectrum of the organotalc prepared by means of the EISA procedure.

the most plausible hypothesis for the formation of the lamellar hybrid material is the formation of a brucite-type structure and the grafting of the silicic species into interlamellar spaces. Layers of short surface side are observed in the TEM image. This is in agreement with the description of stacking plates, which appear in the first step of the formation of these materials with some silicic species possibly grafted between these layers. The weak extension sides (lateral length) of these stacked layers allow the progressive insertion of the silicic species in order to complete the formation of the tetrahedral sheets. A very important point to mention is the greater organization of the layers, even with short sides, comparing organoclays obtained by the sol-gel synthesis. Indeed, great stacking of layers has never been reported for such materials before.

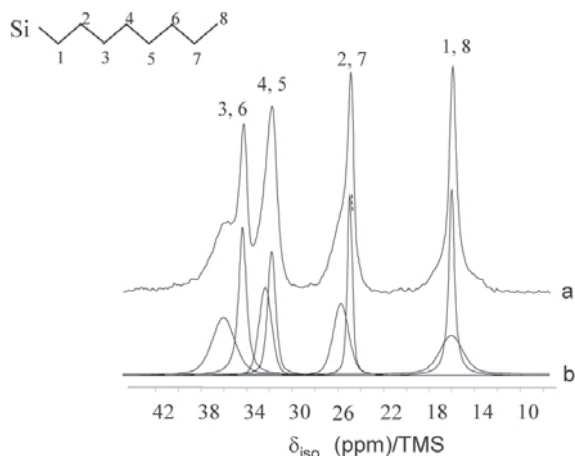


Figure 6. ^{13}C CP-MAS NMR spectrum of the organotalc prepared by means of the EISA procedure.

Compared to the classical synthesis at room temperature or in autoclaves, and besides being a continuous process, the reaction time is reduced to several minutes instead of hours. In terms of morphology, an homogeneous form is obtained by the aerosol method whereas irregular shapes are obtained in the classical synthesis.

CONCLUSIONS

Layered Mg organosilicates with covalently linked octyl chains (via Si–C bonds) protruding into the interlayer space were prepared at room temperature from ethanolic gels containing Mg nitrate and octyl triethoxysilane. For the first time, using the aerosol approach, synthesis of spherical organotalc particles by atomizing a precursor suspension of organotalc was achieved successfully. In addition to the spherical morphology, a better organization of the lattice is observed. This quick, continuous, and reproducible process could be used in a wide range of applications such as catalysis, chromatography, and in nanocomposites.

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