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Journal of the European Ceramic Society xxx (2006) xxx–xxx
www.elsevier.com/locate/jeurceramsoc

Synthesis and characterization of inorganic, lamellar nanofillers with high aspect ratio

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Abstract

Mesostructured silica phases with lamellar structure were prepared by the liquid crystal templating (LCT) technique, from double chain alkylammonium surfactant and sodium silicate or tetraethylorthosilicate (TEOS) silica precursors. The structural characterization of these phases is presented and compared. Surface modification of the silica layers, together with elimination of the organic template, is considered. Finally, a representative model of the microstructural organization is proposed.

Keywords: Sol–gel processes; Nanocomposites; Platelets; Silicate

1. Introduction

The precipitation of controlled-shaped particles is of great interest in the context of the manufacture of ceramics. When inorganic powders are used as precursors for oxide synthesis, their particle size, shape and agglomeration level constitute key parameters in the sintering step and the processing of the final ceramics. Among other possible shapes to be obtained, the lamellar morphology has received increasing attention: existing or potential applications of lamellar inorganic compounds generally rely on their very large specific surface area. These lamellar powders are also widely studied as nanofillers, to produce polymer-based lamellar nanocomposites. Indeed, it is now well established that the dispersion of lamellar inorganic sheets improves several properties of the composites, such as gas impermeability, Young modulus as well as fire retardancy.

Several inorganic compounds exhibiting lamellar structure were studied in this research: tabular crystals precipitated in aqueous solution, organo-modified layered clays and lamellar mesostructured silica. Only the last family of compounds is presented in this paper.

Structural and microstructural characterization of the powders were obtained by means of X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and solid state nuclear magnetic resonance (MAS-NMR).

2. Experimental part

Mesoporous materials are synthesized by the liquid crystal templating (LCT) method, which is based on the use of ordered arrays of surfactant molecules as a "template" for the polymerization of silicates.[1,2] The obtaining of lamellar phases is favoured in the biphasic systems formed by water and surfactants bearing two long alkyl chains.[3,4] The dimethyldioctadecylammonium chloride ($2 \times C_{18}Cl$) surfactant appeared to be the most efficient organic template for the oriented polymerization of a silica network with lamellar organization. The stability and reproducibility of the resulting samples allowed us to study several combinations of silica precursors and pH conditions: sodium silicate in acidic and basic medium, and TEOS in acidic or basic medium. Best results were obtained for the Na silicate/basic and TEOS/acidic systems.

2.1. Synthesis of the lamellar mesostructured silica

Dimethyldioctadecylammonium chloride ($2 \times C_{18}Cl$, KaO Corp.) is dispersed in hot water (50 °C) at a concentration of 3 wt.% with axial stirring, until a homogeneous medium is obtained. Concentrated HCl or tetramethylammonium hydroxide (TMAOH, Merck) is then added dropwise to the mixture to

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doi:10.1016/j.jeurceramsoc.2006.04.080

adjust the pH to the desired value: 0 for acidic synthesis and 12 for basic synthesis. This results in an increase of the suspension turbidity. The silica precursor is then added to the template under stirring in a molar ratio surfactant:Si = 1:0.22. Two silica precursors were used: sodium silicate solution with 25.5–28.5 wt.% SiO_2 (Silicate Na, Merck) and tetraethylorthosilicate (TEOS, Hüls). The reacting mixture is kept under stirring at 50 °C for 21 h then filtered off, washed several times with room temperature deionized water, until neutrality. The recovered solid is dried in air at moderate temperature (<50 °C) and grinded for analysis.

The lamellar mesostructured silica obtained in basic condition (hereafter named "basic substrate") is made of negative silica layers intercalated with the alkylammonium template ions. The template is anchored by ionic bonding in the interlayer space.

The lamellar mesostructured silica obtained in acidic condition (hereafter named "acidic substrate") is made of neutral silica layers intercalated with the alkylammonium chloride template molecules. The template is anchored as ions pairs by hydrogen-type bonding to the polar surface of the silica layers.

2.2. Surface modification

A direct template displacement method was developed to graft silane ligands onto the surface of uncalcined mesoporous silica prepared from acidic condition.[5,6] The organic surfactant can easily be recovered and re-used as the template of the mesoporous silicas. The high density of surface silanol group in acid-synthesized silica leads to high loading of silanes. The mild reaction condition and short reaction time lead to the preservation of morphology.

Hexamethyldisiloxane solvent or HMDS ($(CH_3)_3Si–O–Si(CH_3)_3$) is used, in combination with the modifying agent trimethylsilyl chloride or TMSCl ($(CH_3)_3Si–Cl$). The procedure consists in dispersing 0.5 g of the as-synthesized mesostructured lamellar silica (hereafter named the substrate) in 15 g of HMDS mixed with 10 g of TMSCl. The reacting medium is refluxed overnight (18–20 h) then cooled down to room temperature and filtered on a Büchner vase. The resulting powder is washed several times with acetone to eliminate solvent traces, then dried at moderate temperature in air.

2.3. Structural characterization

X-ray diffraction patterns were collected in a Siemens D5000 powder diffractometer using Ni-filtered Cu Kα radiation. Thermal analysis data were recorded on a Netzsch STA 449C analyzer under air, with a heating ramp of 10 °C/min and a gas flux of 50 ml/min. Transmission electron micrographs were obtained on a Philips CM100 microscope working at an acceleration voltage of 100 kV. The powders were simply deposited on a copper grid covered with a formvar thin film. The ^{29}Si MAS-NMR data were recorded in a Bruker Advance DSX400 (9.4 T) spectrometer operating at 79.5 MHz. Quantitative spectra were obtained by performing one-pulse experiments with a 90° pulse width of 5.5 μs. Quantitativity was checked by varying the delay time and an optimal value was found at 480 s.

3. Results and discussion

Silica phases precipitated from TEOS precursor are characterized by a stacking periodicity of 39 Å (Fig. 1), versus 42–52 Å for silica obtained from sodium silicate in basic and acidic conditions, respectively. However, materials obtained from TEOS have shown a more ordered lattice, richer in silica (Fig. 2).

Several parameters were studied in order to increase the thickness of the inorganic layers in the TEOS/acidic system: the acid concentration, the molar ratio between silica precursor and template, the hydrolysis or polymerization of the precursor previously to the interaction with the template. However, it is very uneasy to influence the polymerization of the growing silica layer in the direction normal to the inorganic–organic interface: the self-organization of the system occurs by charge–density matching across the interface and there is no driving force towards the incorporation of additional inorganic precursor species when the cationic charges of the surfactant are counterbalanced by a specified quantity of charged silica precursors.[7,8]

After the adjusting of the optimum synthesis conditions, the modification of the lamellar silica was envisaged by the silylating of the constitutive inorganic sheets. The silylating reaction is driven in a solvent allowing the extraction of the template at the same time as the grafting reaction of the silylating agent (trimethylsilyl chloride or TMSCl). Acidic and basic silica were

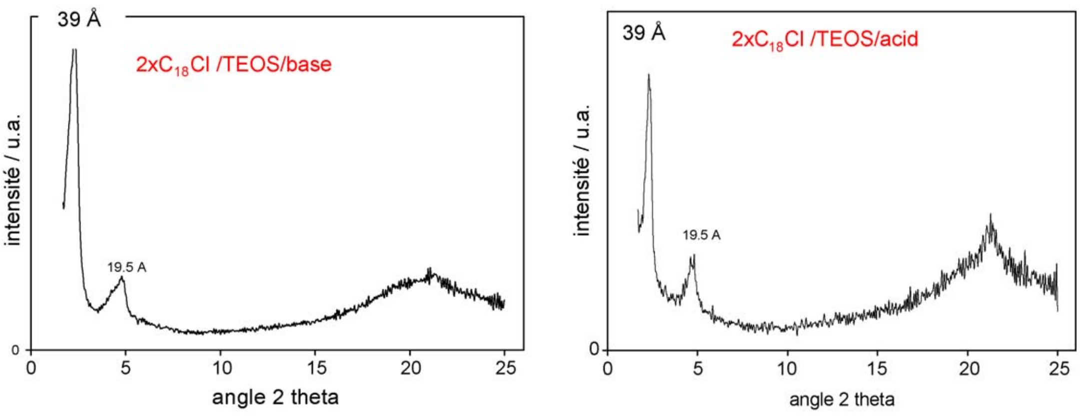

Fig. 1. XRD patterns of lamellar silica obtained from TEOS in basic medium (left) and acidic medium (right).

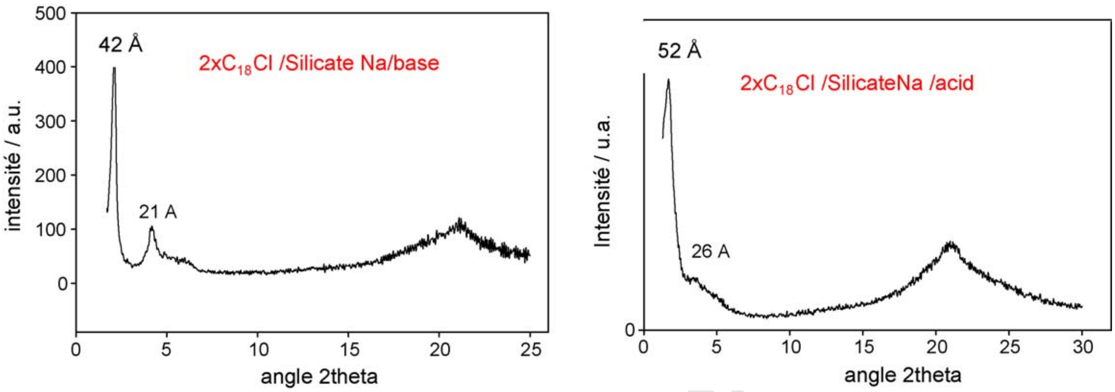

Fig. 2. XRD patterns of lamellar silica obtained from sodium silicate in basic medium (left) and acidic medium (right).

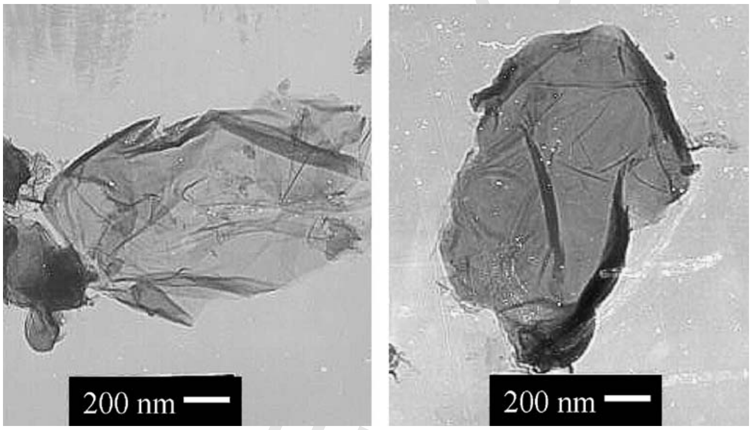

Fig. 3. Transmission electron micrographs of lamellar silica after silylting by TMSCl in HMDS.

successfully silylated. The extraction of the template, in the case of ionic binding, is possible thanks to the chloride ion released from the trimethylsilyl chloride. All characterization techniques agree to certify that the lamellar organization is preserved upon silylating, as shown for example by transmission electron microscopy (Fig. 3). Single silica layers can be observed with poor rigidity and extremely high aspect ratio.

Quantitative ^{29}Si solid state NMR has been performed on the acidic substrate before and after silylating (Fig. 4). Before surface modification, the intercalated lamellar silica is mainly constituted by Q_3 and Q_4 silicon atoms in equivalent quantity. The initial silica network can be considered as thin lamellae with 50% of “inner Si” atoms (Q_4) and 50% of “surface Si” (Q_3) atoms bearing an OH group. This reveals the very thinness of the layers, which have a very high surface/volume ratio. After the grafting of TMS, an intense peak appears in the spectrum, corresponding to the TMS signal. This new peak counts for 25% of the total spectrum area, while the Q_3 peak decreases down to 9.5% and the Q_4 increases up to 65.3%. In the modified substrate, there is thus 6.8 times more Q_4 atoms than Q_3. It can be calculated that 3/4 of the surface SiOH groups have fixed a TMS molecule, which is a large proportion regarding the size of the TMS group.[9]

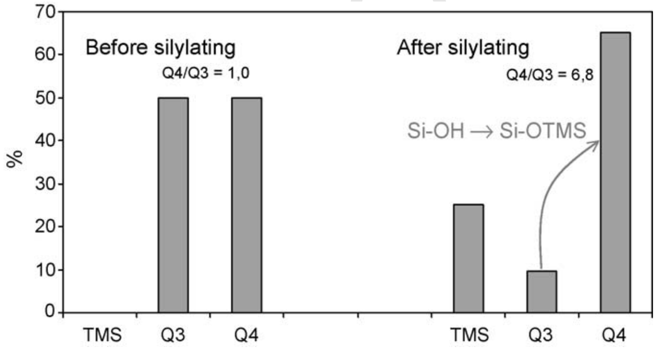

Fig. 4. Repartition of Si atoms types before and after silylating, calculated from MAS-NMR spectra.

In order to propose a comprehensive description of the inner structure of the lamellar silica’s, poorly described in the literature, we built a representative model of the inorganic–organic stacking, which consists in thin silica sheets intercalated by double layers of quaternary alkylammonium molecules (Fig. 5). The complete model describes the molecular configuration of the surfactant in the interlayer space, its anchoring mechanism at the silica surface, the molecular organization of the silica network, the lamella thickness, the surface silanol packing density and an estimation of the electrical residual charge. This will be partly described hereafter. Surfactant bearing two long alkyl chains are known to adopt a tilted bilayer configuration, close to the crystal structure of the pure surfactant salt, when intercalated in the interlayer space of lamellar silicates. Recent studies favour

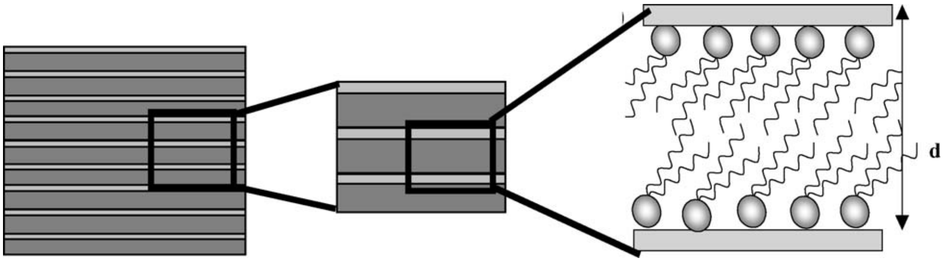

Fig. 5. Schematic representation of the lamellar organization of the as-sysnthesized mesostructured lamellar silica phases. Surfactant counter-ions, if present, are not explicitly shown for clarity.

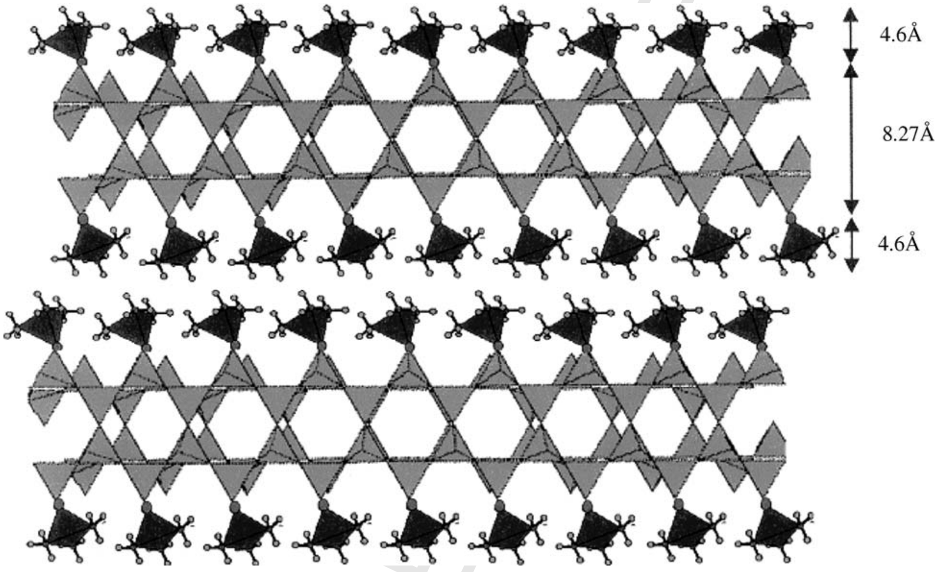

Fig. 6. Proposed structure of the lamellar silica phase after silylating. Light grey tetrahedra constitute SiO_2 layers with tridymite crystal structure, dark grey tetrahedra represent the grafted TMS groups.

Table 1
Comparison of the structural characteristics of lamellar silica's obtained in acidic and basic conditions

Silica precursor	Synthesis pH of the substrate (before silylating)	d_{max} of as-synthesized substrate (Å)	d_{max} of substrate modified by TMSCl (Å)	TMS fixed amount (wt.%)	SiO_2 content (dry residue at 1000 °C) (wt.%)	Estimated layer thickness (Å)
TEOS	0	37.6	20.5	3.5	88.3	11.3
Na silicate	12	41.5	17.0	4.0	71.4	7.8

Behavior under silylating treatment by TMSCl and estimated silica layer thickness.

a more disordered configuration, closer to the liquid state, but with a similar thickness of the organic bilayer.[10]

The proposed structure, based on experimental observations, is represented in Fig. 6. The silica layers are very thin and the constitutive Si–O tetrahedra are arranged in a tridymite-like structure,[11] with pointing-out silanols groups on both sides of the sheet. However, this structure must be disordered since the silica appears amorphous in the XRD patterns. Both sides are covered with a molecular layer of trimethylsilyl (TMS) groups, represented as dark grey tetrahedra, with a tilt angle of 149°, calculated from hexamethyldisiloxane Si–O–Si angle.[12] Crystal structure models allow to measure the thickness of such a TMS layer, which is estimated to be 4.6 Å.

Combining thermogravimetric determination of the TMS content, which appears similar for both acidic and basic substrates, and stacking periodicity obtained from XRD patterns, it is possible to give an estimation of the silica sheet layer thickness (Table 1). The thickness is evaluated by subtracting two TMS layers thickness from the d_{max} of the silylated material. This confirms the extremely small value of the silica layer thickness, and shows that TEOS-based materials are actually made of thicker silica sheets than sodium silicate-based materials, with a difference on the order of 3.5 Å.[13]

4. Conclusions

We have studied a wide variety of inorganic phases with lamellar structure, from the synthesis to their complete microstructural characterization.

The liquid crystal templating method is a suitable way to produce silica phases with lamellar organization exhibiting good structural properties. The surface modification and elimination of the organic template is a very promising way to develop silica layers with a huge aspect ratio, combined with customized surface functionality.

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