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Silica–clay nanocomposites†

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A new class of porous nanocomposite materials have been prepared by reaction of alkoxysilanes with alkylammonium-exchanged phyllosilicates (clay minerals), using a sol–gel procedure which produces the complete delamination of these layered solids.

Nanostructured solids based on layered silicates of the smectite family are materials of increasing interest based on both, structural characteristics and functional applications. Among these compounds, polymer–clay nanocomposites involving different polymers and inorganic substrates (smectites) have been widely studied.[1] Delaminated organic–inorganic systems derived from these compounds are receiving much attention in view of their behaviour as reinforcing agents[2] or as electroactive materials.[3]

Similar structural arrangements have been achieved here by the generation of a silica network in place of an organic polymer, to separate the elemental layers of the silicate. These kinds of materials can be of great interest because they combine textural properties (high specific surface area, mesoporosity) with ion-exchange capacity inherent to the clay substrate. In addition, they can be easily functionalised by grafting of organosilane reagents on the silica network.

Attempts to combine at the molecular scale silica and different layered silicates have been reported using different procedures and starting materials. Certain processes involve reactions of smectite clay minerals exchanged with cetyltrimethylammonium (CTMA) species with a source of silica, such as TEOS in the presence of a co-surfactant (decylamine). In this way, adducts in which the silica is intercalated as a pillar separating the layers by some few Ångströms and forming mesoporous clay heterostructures after calcination have been reported.[4] Silica pillared clays showing high surface area and good thermal stability have also been prepared using TEOS in the presence of Fe^{3+} ions.[5] In this case, the silica sol particles are inserted between the silicate layers giving a regular and permanent expansion of about 6 nm.

To prepare the silica–clay nanocomposites consisting in elemental silicate layers dispersed into a silica matrix, we have developed a new procedure based on the formation of an intermediate gel resulting from the reaction of an organoclay with an alkoxysilane in a well controlled water–solvent media.

Fig. 1 shows the different steps from the starting silicate to the silica–clay nanocomposite. Na-smectites (montmorillonites from Wyoming, USA and Gafsa, Tunisia) treated with cetyltrimethylammonium bromide (CTAB) give alkylammonium exchanged clays (CTMA-SWy & CTMA-Gafsa, respectively). The crucial novel step in our procedure consists in the treatment of organoclay/*n*-butanol dispersions (10% in weight) with alkoxysilanes (tetramethoxysilane TMOS, tetraethoxysilane TEOS or ethyltrimethoxysilane ETEOS) using 1/1,1/2 and 1/5 w/w ratio. The slow addition of water (molar ratio of 4 : 1 or 3 : 1 H_2O : tetra or tri-alkoxysilane, respectively) containing traces of HCl, to the former dispersion maintained at 50 °C under continuous stirring, gives spontaneous gelation of the system. The time required for the formation of the gel depends on the nature of both, the starting organoclay and the involved alkoxysilane (Table 1). In the case of TMOS the gel is rapidly formed whereas the system prepared from ETEOS does not form gel even after 15 days of treatment.

Air-drying at 50 °C of the silica–organoclay gel phase gives mesophases that are the precursors of the silica–clay nanocomposites, which are obtained after removing the alkylammonium species by calcination.

Different techniques of characterisation such as chemical and thermal analysis, N_2 adsorption isotherms, XRD, FTIR and solid-state NMR spectroscopies, have been used to follow the structural arrangements during the formation of the silica–clay nanocomposites.

The clear evidence of the delamination of the smectites in the formation of the silica–organoclay mesophases is deduced from the XRD patterns (Fig. 2) that show the lose of crystallinity of these materials (absence of the 00l rational orders characteristic of the starting silicates). The amorphization of the product is particularly appreciable in the case of samples prepared from the Gafsa clay which are completely delaminated even when a small clay/silica ratio (*e.g.* 1/1 clay/TMOS; w/w) was used. For Wyoming smectite derivatives a shoulder corresponding to the 001 reflection is observed in the XRD diagram suggesting that a small fraction of clay (< 15%) remains as the unaltered organoclay precursor.

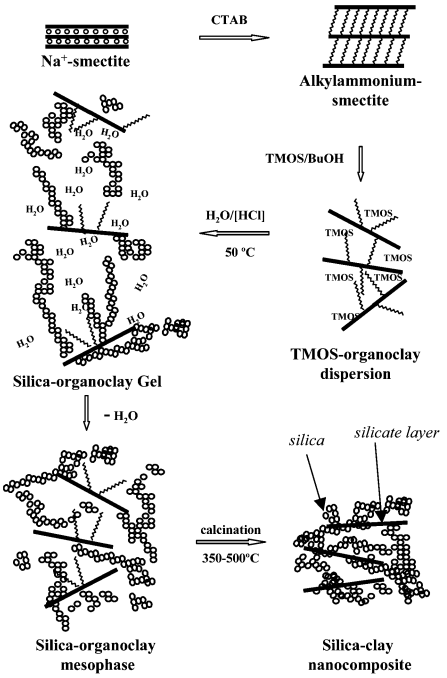

Fig. 1 Scheme showing the steps in the procedure of synthesis of the silica–clay nanocomposites.

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Table 1 Ability of silica–organoclay systems to form intermediate gel phases

CTMA-SWy/ Alkoxide (w/w)	TMOS	TEOS	ETEOS
1/1	Gel (*f*)	Gel (*s*)	No Gel*
1/2	Gel (*f*)	Gel (*s*)	No Gel*
1/5	Gel (*f*)	Gel (*s*)	No Gel*
CTMA-Gafsa/ Alkoxide (w/w)	TMOS	TEOS	ETEOS
1/1	Gel (*vf*)	No Gel*	No Gel*
1/2	Gel (*vf*)	No Gel*	No Gel*
1/5	Gel (*vf*)	No Gel*	No Gel*

(*f*): fast gel formation (< 2h); (*vf*): very fast gel formation (< 0.5 h); (*s*): slowly gel formation (> 1 day); (*) No gel is formed after 2 weeks.

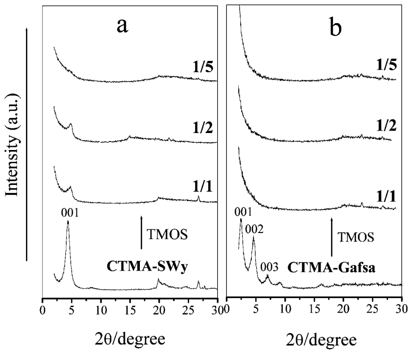

Fig. 2 XRD patterns of silica–organoclay mesophases prepared from TMOS and CTMA-SWy (a) and CTMA-Gafsa (b) organoclays, for different organoclay/TMOS w/w ratios (1/1, 1/2 and 1/5).

The ability to form homogeneous gels incorporating both, silica and clay is mainly related to the nature of the smectites, in particular regarding the location of electrical charges which is the only significant difference between the two clays.[6] In fact, the montmorillonite from Wyoming is essentially non-beidellitic material whereas the Gafsa sample shows significant isomorphous substitutions in the tetrahedral layers.[6] However, more work is necessary on the role of the alkoxysilane to postulate a convincing mechanism of delamination.

No appreciable changes in the diffractograms are observed after calcinations of the mesophases derived from the Gafsa smectite, whereas the residual XRD peaks in the case of Wyoming montmorillonite, disappear after thermal treatment in air (> 350 °C). Treatment of calcinated samples with ethyleneglycol produces in the Wyoming samples the development of new diffraction peaks of low intensity at around 1.7 nm, which corresponds to the residual non-delaminated montmorillonite fraction. No change was observed for the Gafsa derivatives, supporting the existence of a complete delamination and an irreversible loss in the stacking order.

The specific surface areas of the silica–clay nanocomposites are strongly enhanced with respect to the starting clays, *i.e.* from *ca.* 80 $m^2 g^{-1}$ to. *ca.* 550 $m^2 g^{-1}$ for 1/1 w/w TMOS/clay ratio. The adsorption isotherm indicates the simultaneous presence of micro and mesopores, with a pore volume of 0.28 cm^3 in the range of 0–2 nm pore diameter. Gafsa clay gives solids with higher surface area than the corresponding Wyoming derivatives, a fact that could be related to their ability to give complete delaminated materials.

One of the main features of these new porous materials is their ability to act as a bipolar ion-exchange heterostructure. In this way the nanocomposites can be functionalised by reaction with 3-aminopropyltrimethoxysilane in the presence of HCl, allowing the grafting of positively charged centres which act as the anion-exchanger sites. The clay platelets preserve its cation exchange capacity (CEC), providing the ability to the uptake of cations. The CEC value (*e.g.* 40 meq per 100 g in the TMOS–clay 1/1 (w/w) nanocomposite) is almost that corresponding to the starting clay (*i.e. ca.* 100 meq per 100 g) taking in consideration the dilution in the silica matrix at about 50% in weight. Treatment of these derivatives with salt solutions results in the retention of both cationic and anionic species, as shown by the treatment under mild conditions of the protonated 3-aminopropylsilyl-silica Gafsa-clay 1/1 nanocomposite with an excess of NH_4SCN used as a molecular probe (immobilization of 55 and 60 meq per 100 g of NH_4^+ and SCN^-, respectively, deduced from the elemental chemical analyses). The IR bands at 2064 and 1409 cm^{-1} attributed to the stretching and deformation vibrations of the thiocyanate and the ammonium species, respectively, are in agreement with the entrapment of the ammonium thiocyanate salt, which is not desorbed after water washing. The non-functionalised nanocomposite (*blank*), produces the uptake of ammonium species but not the retention of the thiocyanate anions. By increasing the content in aminopropyl grafted species, the uptake of SCN^- increases almost in the same proportion. This behaviour is of great importance because it could be the basis for the preparation of inorganic bipolar membranes of interest in many industrial and environmental applications,[7] including fuel cell technology, membrane electrolysis, electrocatalysis and electrodialysis (desalination). Also of note is the ability of the intermediate gel phase to develop continuous films required for membrane preparations.

In conclusion, the method reported in this communication, consisting of the gel development of organoclays in a polar medium, is a novel procedure which affords new kinds of nanocomposites based on silica–clay systems and characterized by a complete delamination of the silicate layer. This procedure opens ways to the preparation of novel heterostructures based on different metal oxides and layered solids derived from metal alkoxides, clays and possibly other inorganic lamellar substrates.

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