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New lamellar Si-Al inorganic-organic hybrid material

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One important way of modifying the physical and chemical properties of porous silicates is the incorporation of organic components, either on the silicate surface, as part of the silicate walls, or trapped within the channels [1, 2]. Recent works describe structures where the inorganic and organic units are bound through covalent Si—C bonds. Different ways of silylation have been employed: grafting, coating and co-condensation reactions. The studied structures were essentially mesoporous materials [3]. A well-defined mesostructure of the M41S family is the MCM-50 having an unstable lamellar structure. A way to obtain a directly functionalized lamellar structure is the sol-gel process which has been used to prepare many layered magnesium, nickel, aluminum and Mg-Al silsesquioxane hybrids [5–14]. In this process, the synthetic layered materials have been obtained by a simple low-temperature route, in a direct-synthesis procedure, involving reactions of copolymerization of metallic ions with organosubstituted trialkoxysilanes under neutral and alkaline conditions (pH between 6 and 11). The organic components provide mechanical, thermal, or structural stability, whereas the organic features introduce flexibility into the framework and change the optical properties of the solid. This paper focuses on the synthesis and characterization of a lamellar hybrid organic-inorganic aluminosilicate. The organic functionalities are directly bonded to the silicate sheets via the Si—C bond. The presence of aluminum in this material has many advantages. First it creates negative charges induced by the substitution of Si by Al, charges which are balanced by exchangeable sodium cations (Na^+) in the interlayer. The lamellar sample studied was prepared by a one step procedure. A typical synthesis included the mixture of two ethanolic solutions: 0.4 M of octyltriethoxysilane (5.76 g in 50 mL of ethanol) and 0.27 M of aluminum acetylacetonate (3.27 g in 50 mL of ethanol). After the formation of a clear solution (stirring for 15 min), an excess of sodium hydroxide (100 mL of 0.5 M NaOH) was added. The resulting gel was stirred for 24 h at room temperature, filtered off, washed with distilled water and dried at 60 °C. The molar composition of the starting gel was the following: $RSiO_{3/2}$: 0.25 Al_2O_3: 64 $(CH_3CH_2)_2O$: 1.13 Na_2O. Fig. 1 shows the XRD pattern of the hybrid aluminosilicate. Two peaks are present: one at 3° (2θ) and one at 6° (2θ). The corresponding periodicities (2.8 nm and 1.4 nm) prove the lamellar structure of the hybrid aluminosilicate.

The lamellar structure was also verified by transmission electron microscopy (TEM) (Fig. 2). The micrograph shows a (001) reflection of 2.8 nm which is in agreement with the value obtained by XRD. A disorder is observed in the stacking of the sheets. This is caused by the presence of organic moities in the interlayer space.

The chemical analysis shows that the Si to Al and Na to Al molar ratios are about 2 and 0.90 respectively, which are in agreement with the theoritical values.

The ^{27}Al MAS NMR spectrum exhibits two signals. The signal at −60 ppm corresponds to the tetracoordinated aluminum (Fig. 3). The very weak signal at −9 ppm is attributed to the hexacoordinated aluminum.

The ^{29}Si MAS-DEC NMR of the as synthesized material provides information about the nature of the attachments of pendant groups on silicate hybrids. Four signals at −68, −65, −57 and −52 ppm are associated with (T^3) and (T^2) groups (Fig. 4). They were quantified by deconvolution of the peaks to give 23% of T^3 and 77% of T^2. This suggests the presence of a high number of silanol groups, indicating that the polycondensation is not fully achieved.

To check the ion exchange properties of this material, two cations were used: Sr^{2+} and $C_{16}TMA^+$ (hexadecyltrimethylammonium). 0.5 g of the hybrid lamellar aluminosilicate were in contact with 100 mL of an aqueous solution of $SrCl_2$ (0.6 M) and another 0.5 g in contact with 33 mL of an aqueous solution of CTMACl (0.75 M). In the case of the inorganic cation, 85% of Na^+ cations were exchanged however, only 30% were exchanged in the case of the organic cation. The exchanged materials were characterized by XRD and their patterns exhibit a slight increase of the d_{001} value (3 nm) in the case of organic cations. This suggests that

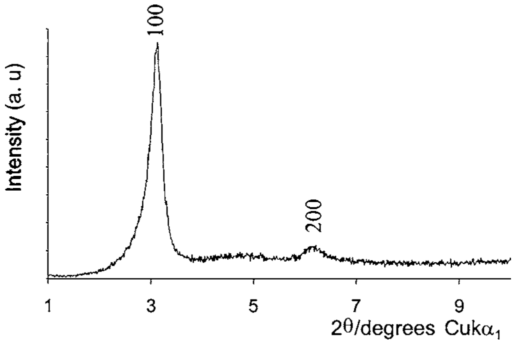

Figure 1 XRD pattern of aluminosilicate mesostructured material.

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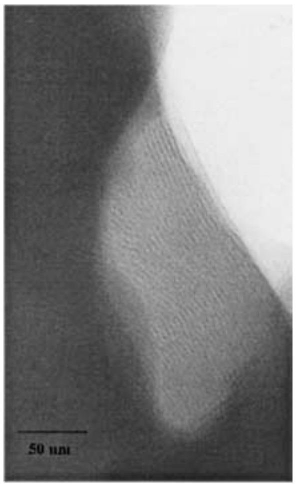

Figure 2 TEM image of aluminosilicate mesostructured material.

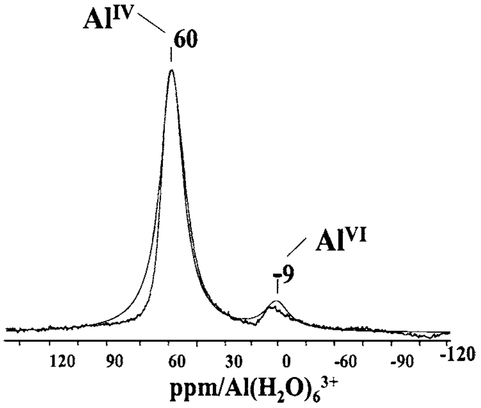

Figure 3 ^{27}Al MAS NMR spectrum of aluminosilicate mesostructured material.

cations are interpenetrated with the organic chains in the interlayer space.

The synthesis of the hybrid organic-inorganic aluminosilicate is the first example of a lamellar aluminosilicate prepared by a one step synthesis with organic functionalities directly bonded to silica sheets via Si—C bonds. The substitution of silicon by aluminum in the tetrahedral sheet induces negative charges which are compensated by sodium cations in the interlayer space. This is the origin of the ion exchange properties of this material. The determination of the structure by NMR and the use of this product in nanoreinforcement and adsorption are under progress and will be detailed later.

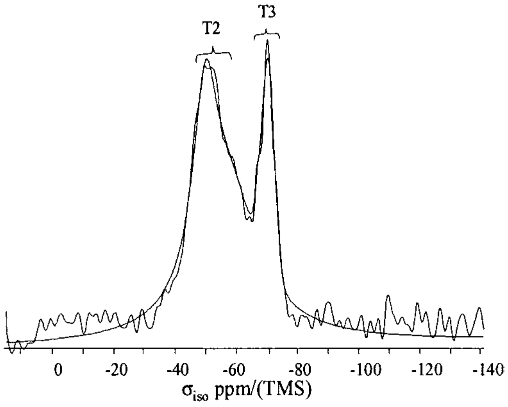

Figure 4 ^{29}Si NMR MAS spectrum of aluminosilicate mesotructured material.

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