A new Al,Mg-organoclay

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A new inorganic–organic solid, with a 2:1 phyllosilicate layer structure and octyl chains directly bound to the inorganic sheets *via* Si–C covalent bonds, was prepared at room temperature from an ethanolic gel with the molar composition $RSiO_{3/2}$: 0.255 Al_2O_3 : 0.5 MgO : 130 CH_3CH_2OH : 0.62 Na_2O. Octyltriethoxysilane was used as the silica source. The introduction of octyl chains in the interlayer space was confirmed by the high d_{001} spacing values (2.5 nm). Thermogravimetric analyses show a major weight loss between 230 °C and 500 °C corresponding to the release of organic matter. The mass spectrometry analyses of the evolved gas are in agreement with the presence of octyl chains. Infrared and ^{13}C MAS NMR spectra indicate that the Si–C bonds are intact and that the siloxane functions are fully hydrolyzed giving Si–O–Al and Si–O–Mg bonds in the inorganic layers. The substitution of Si and Mg by Al was confirmed by ^{29}Si and ^{27}Al MAS NMR.

1. Introduction

Smectites belong to the 2:1 phyllosilicates family where an octahedral sheet containing either Al or Mg cations is sandwiched between two tetrahedral sheets consisting of corner-sharing SiO_4 tetrahedra. Isomorphous substitution in either the tetrahedral or octahedral sheet results in a negative layer charge balanced by exchangeable cations in the interlayer spacing. This leads to many applications in the fields of adsorption, ion exchangers, and catalysis.[1] The range of their use was substantially increased by the formation of pillared clays.[2,3] In this process, the intercalation of large cationic species followed by calcination leads to tailor-made porous materials having high specific surface area.[4] Organic cations can also be intercalated. In this case, exchanged clays can be used as polymer fillers, environmental barriers, sorbents, and catalytic supports.[5] Another way to obtain organoclays consists of the direct incorporation of organic functionalities in the interlayers by a sol–gel process.

Recent publications have mentioned the use of organofunctional trialkoxysilanes, $RSi(OEt/Me)_3$, to produce lamellar organically functionalized magnesium, nickel or aluminium silicate clays with structures analogous to the inorganic 2:1 phyllosilicates. The sol–gel based synthetic method involved the precipitation of the inorganic smectite-like framework under non-hydrothermal conditions by biomimetic template synthesis using self-organized assemblies of organic molecules.[5–10]

The present paper reports the synthesis and characterization of a covalently linked organic–inorganic lamellar composite containing both silicon, aluminium and magnesium. The aim was to prepare compounds having a saponite like structure with the general formula $Na_{4x}[(RSi)_{4(1-x)}Al_{4x}Mg_3O_{8+2x}(OH)_2]$ (where $x = 0.33$).

2. Experimental

Reactants

Octyltriethoxysilane $CH_3(CH_2)_7Si(OC_2H_5)_3$ (Aldrich, wt% 96), aluminium acetylacetonate $[CH_3COCHCOCH_3]_3Al$ (Aldrich, wt% 99), hexahydrated magnesium nitrate $Mg(NO_3)_2{\cdot}6H_2O$ (Carlo Erba, wt% 98), ethanol CH_3CH_2OH (Prolabo, wt%, 99.8), sodium hydroxide NaOH (Fluka, wt% 97) and distilled water.

Synthesis

The new organoclay was synthesized according to the procedure adapted from a protocol mentioned by Ukrainczyck *et al.*[5] The difference lies in the simultaneous presence of aluminium and magnesium in the reaction mixture. The oxide molar composition of the starting mixture was: $RSiO_{3/2}$: 0.255 Al_2O_3 : 0.5 MgO : 130 CH_3CH_2OH : 0.62 Na_2O. Typically, magnesium nitrate hexahydrate, $MgCl_2{\cdot}6H_2O$ (0.01 mol, 2.56 g) was dissolved under stirring in 50 cm^3 of ethanol and then mixed with a solution of aluminium acetylacetonate (0.01 mol, 3.24 g in 50 cm^3 of ethanol). Compared to Al nitrate or chloride as the Al source, this reactant favours the incorporation of Al in the octahedral sheet. Immediately after the addition of an octyltriethoxysilane solution (0.02 mol, 5.52 g in 50 cm^3 of ethanol), 50 cm^3 of a sodium hydroxide solution was added to precipitate a gel. The latter was kept under stirring for 24 h at room temperature. The resulting solid was recovered by filtration, washed 4 times with distilled water (100 cm^3) and dried for 48 hours at room temperature.

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Characterization

The X-ray diffraction (XRD) pattern was recorded with a Philips PW1800 diffractometer (CuKα radiation: $\lambda = 1.5406$ nm, scanning range: 1–70 (2θ), step size: 0.02°).

The elemental analyses of Si, C, Al, Mg, and Na were carried out by the CNRS Service Central d'Analyses, Vernaison (France).

Infrared measurements were performed with a DTGS detector and analysed with the software OPUS. The number of scans was fixed to 100 with a resolution of 4 cm^{-1}.

The thermogram of the as-synthesized sample was performed with a TG-DSC apparatus (Setaram TG-DSC 111) under nitrogen or a mixture of 50% O_2 and 50% N_2, with a flow rate of 8.3×10^{-3} dm s^{-1} from 20 °C to 850 °C and a heating rate of 8.3×10^{-2} °C s^{-1}.

The sample was heated (heating rate: 8.3×10^{-2} °C s^{-1} under nitrogen) in a mass spectrometer (quadrupolar analyzer—TRANSPECTOR of INFICON type—with masses set between 1 and 200). The released gas was condensed and trapped with liquid nitrogen and then identified with the mass spectrometer.

^{29}Si and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on a Bruker MSL-300 spectrometer ($B_0 = 7.04$ 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 spinning frequency of 4 kHz. For ^{29}Si and ^{13}C MAS decoupling NMR experiments, a $\pi/4$ pulse duration of 1.8 µs and a $\pi/2$ pulse duration of 1.5 µs were used respectively, with a recycle time of 90 s.

^{27}Al and ^{1}H NMR experiments were performed on a Bruker DSX-400 spectrometer at 104.2 and 400.1 MHz respectively, with spinning frequencies ranging from 8 to 25 kHz. The ^{27}Al spectrum was recorded with a short recycle delay of 1 s and by using a 0.7 µs single pulse, corresponding to a flip angle of $\pi/12$ in order to ensure selective excitation. The ^{1}H–^{27}Al cross-polarization magic angle spinning (CPMAS) spectrum was recorded with a 5.5 µs ^{1}H pulse-length, a contact time ranging from 100 µs to 6 ms and a recycle time of 3 s. To identify the different ^{27}Al crystallographic sites, a two-dimensional method, the multiple quantum MAS (MQMAS) technique was used.[11]

3. Results and discussion

The layered structure of the material was confirmed by X-ray powder diffraction (Fig. 1). The pattern exhibits d spacings corresponding to those of smectites[11] ($d_{(020,\ 110)} = 0.445$–0.455 nm, $d_{(130,\ 200)} = 0.252$–0.258 nm, $d_{(210)} = 0.167$–0.170 nm) and organoclays[5] ($d_{(001)} = 2.510$ nm, $d_{(003)} = 0.780$ nm, $d_{(020,\ 110)} = 0.453$ nm, $d_{(130,\ 200)} = 0.255$ nm, $d_{(060,\ 330)} = 0.151$ nm) (Fig. 1). The position of the (001) peak gives information about the basal spacing which is equal to the sum of the inter-layer space and the thickness of the silicate layer (about 0.96 nm for a 2:1 phyllosilicate). Typical $d_{(001)}$ values for talc and saponite are respectively about 1.00 nm and 1.40 nm under a relative humidity of 80%. The higher value of the latter comes from the presence of hydrated cations in the interlayer space. For the new organoclay, the rather low $d_{(001)}$ value (2.500 nm) can be explained by the inter-penetration or tilt of the alkyl chains in the inter-layer space (since the length of the two octyl chains is about 2.27 nm, a theoretical $d_{(001)}$ value of 3.4 nm is expected if they are perpendicular to the layers).[5] In pure tri- and di-octahedral organoclays, the $d_{(060)}$ values are respectively 0.157 nm and 0.151 nm. The result of the interpolation of the $d_{(060)}$ value (0.151 nm) indicates a structure close to a di-octahedral with some tri-octahedral character (estimated between 10 and 20%).

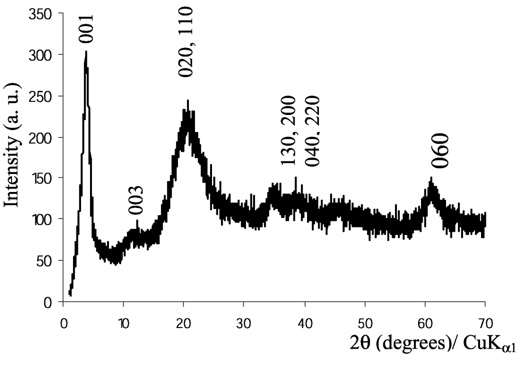

Fig. 1 XRD pattern of the new Al,Mg-organoclay.

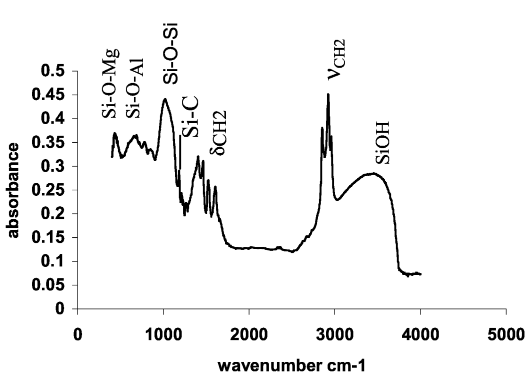

Fig. 2 DRIFT spectra of the new Al,Mg-organoclay.

Characteristic framework vibration modes corresponding to the Si–C bonds (1170 cm^{-1}) are observed in the infra-red spectrum (Fig. 2). The vibration modes in the ranges of 2850–2950 cm^{-1} (νCH_2), 1400–1600 cm^{-1} (δCH_2) and 688–721 cm^{-1} (ρCH_2), characteristic for octyl groups, reveal that these chains are intact. The presence of Si–O–Si (1019–1130 cm^{-1}), Si–O–Al (550 cm^{-1}) and Si–O–Mg (400 cm^{-1}) confirms the formation of the clay structure.

The presence of organic matter was confirmed by thermogravimetric analysis. The thermogram exhibits three weight losses: the first one (5%) in the temperature range 50–150 °C corresponds to the departure of water. The second weight loss (45%) between 230 and 500 °C can be assigned to the release of organic matter. The last one (1.5%, 550–700 °C) is due to the dehydroxylation of OH groups.

In order to identify the species resulting from decomposition of organic matter, the sample was heated in a mass spectrometer up to 350 °C under dynamic vacuum. At this temperature a mass spectrum was recorded, which exhibitts peaks at 18 and 44 (attributable to the presence of H_2O and CO_2 respectively) and peaks at 56 and 70 (first departure of organic matter). Then the temperature was raised to 500 °C and the released gases were condensed. During the subsequent evaporation of these gas, different mass spectra were taken. The spectra can be attributed to the heptene (Fig. 3). The non-condensed phase analyzed during the heating contains light gases, mainly methane and ethene. The complementary data of thermal analysis and mass spectrometry show that the octyl chain is decomposed into heptene and methane, the ethene being probably the result of a dehydration of the ethanol present in the interlayer space.

High-resolution solid-state NMR of ^{13}C, ^{29}Si and ^{27}Al has recently been applied extensively to studies of the structure and solid-state reactions of inorganic–organic aluminosilicates.[12]

^{13}C MAS NMR was used for the characterization of the organic groups (Fig. 4). The decomposition of the spectrum shows 8 isotropic resonances ranging from 14.6 to 34.6 ppm. The assigned chemical shifts are reported in Table 1 and

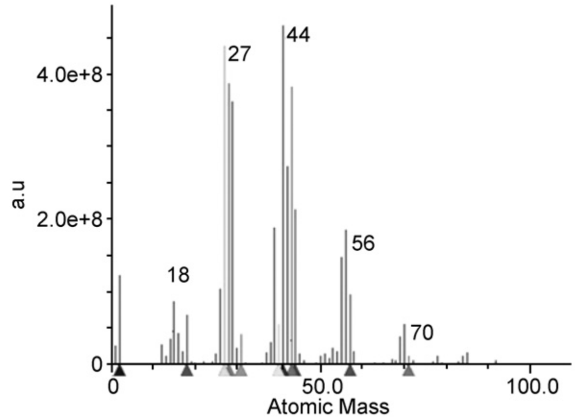

Fig. 3 Mass spectrum of the gas condensed during the heating of the new Al,Mg-organoclay between 250 °C and 350 °C.

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 C like C8 exhibits the narrowest peak.

^{27}Al and ^{29}Si MAS NMR provide information about the inorganic framework. The signals of ^{29}Si are observed between −50 and −70 ppm (Fig. 5) and they correspond to silicon in a $RSiO_3$ environment. The resonances between −60 and −66 ppm are assigned to T3 silicon sites and those ranging from −54 to −57 ppm are T2 silicon sites.[14,15] No resonance in the −90 to −102 ppm range[12] was observed which proves the absence of silicon not bound to C.

Further information about the structure of the inorganic framework can be gained from ^{27}Al MAS NMR. The spectrum (Fig. 6) exhibits two broad resonances (second order quadrupolar interactions) between 40–90 ppm and 20–0 ppm, which correspond to tetra- and hexacoordinated aluminium respectively (intensity ratio tetra/octa: ~55/45).

CPMAS was performed with a short contact time (200 μs). The enhancement of the hexacoordinated aluminium resonance confirms the presence of Al–OH bonds (Fig. 6).

A 5QMAS experiment (Fig. 7) allows the identification of three distincts tetracoordinated (S1, S2 and S3, Table 2) and one hexacoordinated aluminium (S4, Table 2) sites. The contour plots are parallel to isotropic axis (F1 dimension of the sheared 5QMAS spectrum) which means a distribution of chemical shifts for each crystallographic aluminium site (this suggest an interlayer disorder due to the organic moieties).[16,17]

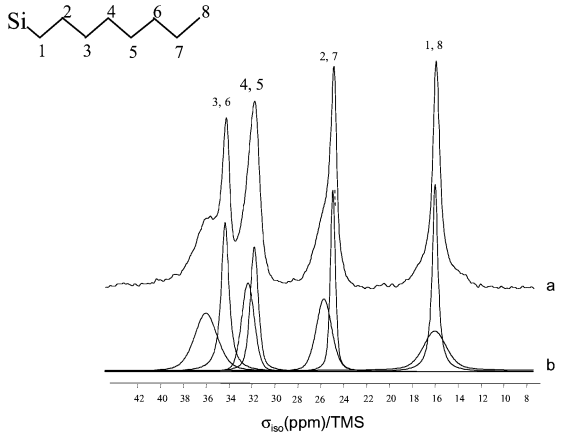

Fig. 4 Decoupled ^{13}C NMR MAS spectrum of as-synthesized new Al,Mg-organoclay (a), the deconvolution of the peaks is also shown (b).

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

Site	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

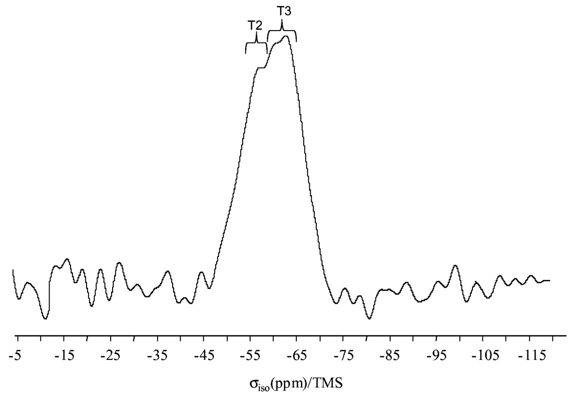

Fig. 5 ^{29}Si NMR MAS spectrum of as-synthesized new Al,Mg-organoclay (ν_r = 4 kHz).

Numerical simulations of F2 slices yield the quadrupolar coupling constant (CQ) and asymmetric parameter (nQ) reported in Table 2. As can be seen, S2 and S3 tetrahedral sites have similar chemical environments (their quadrupolar constants are very similar).

The different analysis and characterization results can be summarized:

$Mg_{0.5}Na_{0.5}[(octyl\text{-}Si)_{3.4}(Al^{IV})_{0.6}(Al^{VI}{}_{0.9}Mg_{0.9})_{dioct}(Mg_{0.3})_{trioct}\text{-}O_{8.3}(OH)_2]$.

- the ratio between octahedral and tetrahedral coordinated aluminium determined by ^{27}Al MAS NMR is close to 55/45.

- the ratio between di-octahedral and tri-octahedral filling of the octahedral sheet estimated from the position of the $d_{(060)}$ value measured on the XRD pattern is between 9/1 and 8/2.

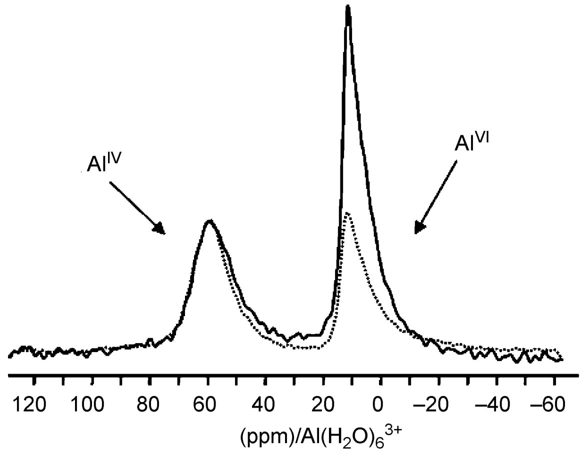

Fig. 6 ^{27}Al NMR spectrum of the new Al,Mg-organoclay (ν_r = 8 kHz), (a) MAS - - -, (b)^1H–^{27}Al CP/MAS —.

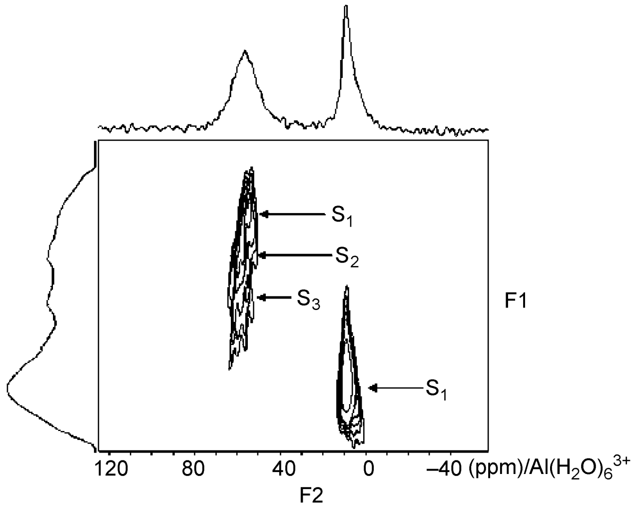

Fig. 7 Sheared ^{27}Al 5QMAS contour plot of the new Al,Mg-organoclay (arrows indicate the different aluminium sites).

Table 2 ^{27}Al quadrupolar interaction parameters of each aluminium site for the new Al,Mg-organoclay

	S1	S2	S3	S4
δ_{iso} (ppm)	58.60	62.80	65.50	13.01
CQ ± 0.1/MHz	3.3	3.8	3.7	2.6
nQ ± 0.02	0.27	0.32	0.33	0.80

- the TGA weight loss between 230 and 500 °C, which corresponds mainly to the mass of the removed octyl chains minus the mass of the OH groups replacing the octyl chains on the silicon atoms, allows one to calculate a Si/Al ratio of 5.7 in the tetrahedral sheet.

- chemical analysis results: Na%: 1.55; Mg%: 4.28; Al%: 4.65; Si%: 11.34.

Aluminium substitutes silicon in the tetrahedral sheet, with a decrease of the number of octyl chains, and magnesium in the octahedral sheet, with a change into a di-octahedral structure type. Unfortunately it is not possible to calculate a complete structural formula for the material. There is a contradiction between the di-octahedral character estimated from the value of the $d_{(060)}$ peak and the value of the Mg/Al ratio, estimated as about 2 from the chemical analyses, after the removal of the tetrahedral aluminium. Even if some Mg is probably located in the interlayer with the sodium cations to compensate the negative charges, the amount of Mg which remains is too high. Further investigation is necessary to determine the repartition of Al and Mg on the octahedral sheet.

4. Conclusion

A new layered magnesium–aluminium organosilicate with covalently linked octyl chains (*via* Si–C bonds) protruding into the inter-layer space was prepared at room temperature from ethanolic gels containing magnesium nitrate, aluminium acetylacetone and octyltriethoxysilane. The formation mechanism can be related to the one already described for organotalcs:[5] formation of a layer structure induced by lamellar micelles with hydrophilic silanol heads which allow and control the condensation of the magnesium and aluminium species. In this new material, which belongs to the 2:1 phyllosilicate family, Al substitutes Si in the tetrahedral layer like in a saponite-type structure and Mg substitutes Al in the octahedral layer like in a montmorillonite-type structure. However, the exact composition and the Al,Mg distribution of the octahedral layer remain unclear.

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