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Insights on the influence of the precursors on the sol-gel synthesis of hybrid organic-inorganic saponite-like materials

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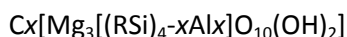
Abstract Lamellar organic-inorganic hybrid materials, especially talc and saponite-like structures, have been broadly investigated over the past decades due to the combination of the thermal and mechanical properties of the inorganic part with the possibility to finely tune hydrophilic-hydrophobic balance, ion exchange capacity and properties through the choice of the silicon source. These compounds are generally produced by co-precipitation or hydrothermal synthesis methods, allowing the formation of well-crystallized particles but time and energy consuming. More recently, hybrid organic-inorganic lamellar materials have been synthesized by using sol-gel method, which is attractive as it is a one-step method performed under mild conditions, with low energy consumption and short formation times. The originality of this research stands in the study of the influence of the reactants on the formation of saponite-like hybrids and especially on the role of the aluminium source **in the sol-gel synthesis of hybrid organic-inorganic lamellar materials**. The obtained materials have been characterized by XRD, FT-IR, solid-state NMR and TGA, and it was shown that hydrotalcite-like compounds can be obtained beside saponite-like compounds depending on the aluminum source.

Résumé De nombreuses études ont été menées récemment sur les matériaux hybrides organique-inorganiques de structure lamellaire, type talc et saponite notamment, suite à la combinaison des propriétés thermiques et mécanique de la fraction inorganique d'une part, avec la possibilité d'adapter la balance hydrophile/hydrophobe, la capacité d'échange cationique, ainsi que les propriétés associées au choix de la source de silicium. Ces composés sont généralement synthétisés par co-précipitation ou par synthèse hydrothermale qui permettent la formation de particules bien cristallisées, mais demandent beaucoup de temps et d'énergie. Plus récemment, ces matériaux ont été synthétisés par la méthode sol-gel qui permet d'obtenir des matériaux de grande pureté en des temps très courts avec une faible nécessité énergétique. L'originalité de ce travail repose sur l'étude de l'influence des réactifs sur la formation de matériaux hybrides organique-inorganiques de structure de type saponite, notamment le rôle de la source d'aluminium **dans la synthèse par voie sol-gel de matériaux hybrides organique-inorganique de structure lamellaire**. Les matériaux synthétisés ont été analysés par DRX, IR-TF, RMN solide, et ATG, ce qui a permis de découvrir que des composés similaires à des hydrotalcites peuvent être obtenus selon la source d'aluminium employée.

Keywords: Clays, Hybrids, Hydrotalcite, Materials, Saponite, Sol-gel, Synthesis.

1. Introduction

Saponite belongs to the 2:1 clay mineral family with one octahedral sheet made of magnesium sandwiched between two tetrahedral sheets containing silicon partly substituted by aluminum. These structural substitutions induce a charge deficit that is compensated by counterions in the interlayer space (generally sodium Na^+ , calcium Ca^{2+} , or potassium K^+). In the case of organic-inorganic hybrids having a saponite-like structure, an organoalcoxysilane is used as silicon source, by this way, an organic chain is covalently bounded to the silicon and thus, to the inorganic framework. The general chemical formula materials can be denoted as:



Where x represents the tetrahedral substitution rate and C the counterions used to compensate the charge deficit induced by the substitutions in the tetrahedral sheets into the structure [1-7] as shown in Fig. 1. Synthesis methods play an important role on the crystallinity, shape, and particle size of these compounds, so the preparation methods remain an important research subject in the field of layered materials [3-6]. Many methods have been developed over the last decades, but the main ones include co-precipitation, hydrothermal synthesis [3,5,8-11], and sol-gel method [12-18]. However, the morphology and crystallinity of such materials are related to the synthesis conditions.

Sol-gel method is becoming a new way to synthesize hybrid organic-inorganic lamellar materials. It consists in dissolving inorganic salts containing divalent and trivalent cations, such as magnesium and aluminium salts for example, into a solvent and increasing the pH by adding NaOH to promote the condensation that occurs preferentially in basic media [12-18]. The solution is kept under constant stirring and fixed temperature, generally room temperature, during several hours. This process allows obtaining high purity materials in short times with low energy consumption, but the products generally present lower crystallinity than those obtained using co-precipitation or hydrothermal synthesis methods [3-6].

The novelty of this study stands on the **sol-gel** synthesis conditions and mechanisms bringing to the formation of **different lamellar materials depending on the precursors, especially the use of different aluminum source**. These materials were intended as materials presenting acidic properties, and a series of analysis has been performed (X-Ray Diffraction, Fourier Transform Infrared, and solid-state Nuclear Magnetic Resonance spectroscopy) to characterize such materials.

2. Experimental

2.1. Reactants

N-Propyltriethoxysilane $\text{C}_9\text{H}_{22}\text{O}_3\text{Si}$ (ABCR, 97 wt%), Trimethoxyphenylsilane $\text{C}_9\text{H}_{14}\text{O}_3\text{Si}$ (TCI Chemicals, >98 wt%), magnesium chloride hexahydrate $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, BioXtra, $\geq 99.0\%$), magnesium nitrate hexahydrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, aluminum acetylacetonate $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ (Sigma-Aldrich, ReagentPlus[®], 99%), aluminum chloride hexahydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Fluka Analytical, $\geq 99.0\%$), ethanol $\text{CH}_3\text{CH}_2\text{OH}$ (Carlo Erba Reagents, $\geq 97\%$), sodium hydroxide NaOH (Carlo Erba Reagents, 99.9%), and distilled water were used as received during the study.

2.2. Synthesis of the lamellar materials

The synthesis of organic-inorganic saponite-like hybrid materials involve magnesium chloride or magnesium nitrate, aluminium acetylacetonate or aluminum chloride, and N-propyltriethoxysilane or trimethoxyphenylsilane as sources of the hybrid materials framework. The sol-gel synthesis process of hybrid organic-inorganic materials can be described as follow: the required amount of magnesium salt and aluminium source are respectively dissolved into ethanol, according to the desired Si/Al substitution rate in the saponite structural formula, $Cx[Mg_3[(RSi)_{4-x}Al_x]O_{10}(OH)_2]$ with $0.5 \leq x \leq 1.2$, and their molar masses. A fixed quantity of organo-alcoxysilane (2g in this work) is added under stirring, and then sodium hydroxide (NaOH) 1M is added until the pH reaches 10. The amounts of the different precursors are detailed in the Table 1. The solution is left under stirring at room temperature for 24h, before being centrifuged at 11000 rpm for 10 min, washed 3 times with 30mL of ethanol, and dried for 24h in an oven at 60°C for further analysis. Samples are labelled as DCHxSy (for saponite-like hybrid samples) and DCHT00y (for talc-like hybrid samples), with x the theoretical Si/Al substitution rate according to the structural formula, and y the number of the sample.

2.3. Samples characterization

Firstly, the structure of the as synthesized samples was investigated by X-Ray Diffraction, using a Panalytical X'Pert PRO MPD with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), and performed from 2 to 70°2 θ with a step of 0.017°2 θ , on randomly oriented powder samples.

Potassium Bromide (KBr) pellets were prepared to perform Fourier Transform Infrared (FT-IR) spectroscopy, made with 5mg of the samples mixed with 100mg of KBr. The measurements were performed in the 400-4000 cm^{-1} region using a Bruker Equinox 55 spectrometer with a DTGS detector. The number of scan was fixed at 100 scans with a resolution of 4 cm^{-1} .

Thermogravimetric analysis of the synthesized samples were performed with a Mettler-Toledo TGA/DSC1 LF1100 apparatus under argon, in alumina sample holders, with a flow rate of about 100 $\text{mL}\cdot\text{min}^{-1}$ from 25 to 600°C and a heating rate of 5°C. min^{-1} . An empty sample holder was recorded as reference to correct baseline deviation.

^{29}Si and ^1H decoupled ^{29}Si magic angle spinning (MAS and single pulse MAS, respectively) Nuclear Magnetic Resonance (NMR) spectroscopy spectra were recorded on a Bruker AVANCE II 300 MHz spectrometer at 59.6 MHz. Samples were analyzed in a 7 mm diameter cylindrical rotor, at a spinning frequency of 4 kHz, and recorded during 24h. ^1H decoupled ^{29}Si NMR experiments have been performed with a $\pi/4$ pulse duration of 2.57 μs with a recycle time of 90 s. ^{27}Al magic angle spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy spectra were recorded on a Bruker AVANCE II 400 MHz spectrometer at 104.3 MHz. Samples were analyzed in a 2.5 mm diameter cylindrical rotor at a spinning frequency of 25 kHz, and recorded during 8h. ^{27}Al spectrum were recorded with a delay time of 1 s by using 4 μs single pulse, corresponding to a pulse angle of $\pi/12$.

3. Results and discussion

3.1. Syntheses with aluminum chloride

Sample	Mg amount (g)	Al amount (g)	Si amount (g)	Si/Mg Molar ratio	Si/Al Molar ratio	Mg/Al Molar ratio	pH	Mass obtained (g)
<i>DCH0,5S014</i>	1,757	0,352	1,998	1,166	6,911	5,928	11	1,42
<i>DCH0.75S014</i>	1,893	0,560	2,003	1,084	4,355	4,014	10,5	1,38
<i>DCH1S014</i>	2,05	0,811	2,004	1,002	3,009	3,002	11	1,32
<i>DCH1,2S014</i>	2,195	1,042	1,999	0,934	2,336	2,502	10,5	1,28

Table 3. Sol-gel synthesis parameters of the samples synthesized with aluminum chloride, trimethoxyphenylsilane, and magnesium chloride hexahydrate. Theoretical molar ratios have been calculated according to the amounts of each element.

Syntheses with aluminum chloride have first been performed during this study. The compositions and molar ratios of the synthesized samples are reported in **Table 1**, with experimental Si/Al, Al/Mg and Si/Mg molar ratio calculated according to the molar masses of the different precursors.

Diffraction patterns of lamellar materials generally shows (00 l) reflections due to their 2-dimensional structure, which allows to estimate the c-cell parameter (thickness of the lamellar material) by adding the interlayer distance and the thickness of a single layer. **Fig. 2** displays the X-Ray diffraction patterns of the samples synthesized in presence of aluminum chloride. Four main reflections are observed: 5.53-6.42, 20.1, 36, and 60.6°2 θ , which correspond to distances of 16-13.5 (d₀₀₁), 4.4 (d_{110,020}), 2.5 (d_{130,200}), and 1.53 Å (d₀₆₀) respectively, according to the Bragg's law :

$$2d_{hkl} \cdot \sin(\theta) = n \cdot \lambda$$

(With d_{hkl} the distance of the plane (hkl), θ the diffraction angle, λ the K α radiation used and n the periodicity index).

The broadness of these peaks indicates a low organization of the structure (crystallinity) due to the synthesis process and the presence of an organic chain linked to the organo-alcoxyasilane, but these positions are typical from a trioctahedral 2:1 clay-like structure according to the positions of (001) and (060).

Fourier Transform Infra-Red has been performed in order to detect typical bounds between aluminum, magnesium, and silicon. The results are shown in **Fig. 3**, with a large wide band around 3500 cm⁻¹ corresponding to the presence of water in the structure. **However, the sample DCH0,5S014 (with the lower amount of aluminum in the structure) shows two vibrational bands at 3715 and 3620 cm⁻¹ corresponding to stretching Si-Al. These bands tend to disappear with increasing aluminum content into the samples, so they correspond to stretching Si-Al bounds.** The two small bands at 3072 and 3049 cm⁻¹ correspond to the C-H stretching vibrational bands, and the presence of stretching Si-C around 1151 cm⁻¹ indicates the silicon precursor has efficiently been incorporated in the structure with the organic chain. Additional small bands between 1300 and 1200 cm⁻¹ proves the presence of magnesium into the structure of the materials, but also aluminum with Al-OH vibration band at 860 cm⁻¹. Moreover, **two** intense combination bands at 1967 and 1760 cm⁻¹ are visible in these spectra and are related to the incorporation of aluminum and magnesium into the structure.

To deeply analyze the samples, solid-state Nuclear Magnetic Resonance (NMR) spectroscopy has been performed to probe the local environment of ²⁷Al and ²⁹Si into the samples. Regarding ²⁹Si NMR (CP-MAS and single pulse MAS), clay-like materials generally exhibit 3 main resonances between -40 and -80 ppm, called Tⁿ environments where T stands for trifunctional silane and n the number of oxygen bounded to the probed silicon atom, according to the formula of the silicon part RSi(OM)n(OH)3-n with M corresponding to silicon or magnesium. Thus, T³ environments correspond

to very well condensed silicon atoms without surrounding OH groups and generally located at the center of the tetrahedral sheets ($\text{RSi}(\text{OM})_3$), whereas T^2 and T^1 are related to silicon atoms at the border of these sheets, with respectively 1 and 2 surrounding OH groups [4-6,14,17]. Fig. 4 (A) shows that the samples exhibit these three main features: around -76, -67, and -60 ppm, corresponding respectively to T^3 , T^2 , and T^1 environments. It also shows an evolution of the condensation of silicon into the tetrahedral sheet: T^3 environment tends to decrease with increasing aluminum amount into the samples, which induces more defects into the structure. ^{27}Al MAS NMR has also been performed to probe the position of this element into the structure, which depends on its coordination state. According to Fig. 4 (B), two resonances can be seen: around 8.5 and 53 ppm, corresponding respectively to aluminum into octahedral (Al VI) and tetrahedral (Al IV) sheets. As the four samples exhibit those positions, aluminum is located in both sheets, which does not correspond to pure theoretical saponite. However, the area of the first peak around 53 ppm seems higher than the second one, which may indicate a more important presence of aluminum into the tetrahedral sheet.

These series of analyses prove the formation of a saponite-like hybrid organic-inorganic material with different aluminum amounts into the structure, as expected in the beginning of this work. To go further in this study, the aluminum precursor has been changed in order to characterize its impact on the structure of the synthesized materials.

3.2. Syntheses with *N*-Propyltriethoxysilane

Two different magnesium salts, magnesium nitrate and magnesium chloride, have been tested as precursors during this experiment. The composition and calculated molar ratios are reported in Table 2.

X-Ray diffractograms of these samples are shown in the Fig. 5. Six main reflections are observed: 11.4, 22.8, 34.6, 38.6, 46, and 60.8-61.8°2 θ . Even if these samples are poorly crystallized according to the broadness of their peaks, their position does not correspond to hybrid organic-inorganic saponite-like materials [12-18]. According to the general indexation of hydrotalcite diffraction patterns in the literature, these peaks are assigned to (003), (006), (012), (015), (018) and (110) reflections, respectively [19-23]. As these patterns show no (001) reflection, this parameter can be estimated by multiplying the distance d_{003} by 3, which corresponds to the distance d_{001} according to the periodicity observed in the diffraction patterns. According to the Bragg's law $2d_{hkl}\sin(\theta) = n\lambda$, with d_{hkl} the distance of the plane (hkl), θ the diffraction angle, λ the $\text{K}\alpha$ radiation used and n the periodicity index, the first peak indicates a distance d_{003} of about 7.9-7.7 Å, which corresponds to a c -

Sample	Mg source	Mg amount (g)	Al amount (g)	Si amount (g)	Si/Mg molar ratio	Si/Al molar ratio	Mg/Al molar ratio	pH	Mass obtained (g)
DCHT006	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1,9	-	1,9	1,3	-	-	10,5	0,6
DCH0.5S009	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1,7	0,5	2,0	1,2	7,0	6,0	11	0,5
DCH0.5S010	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2,1	0,5	2,0	1,2	6,9	6,0	10,5	0,6
DCH0.75S009	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1,8	0,7	1,9	1,1	4,3	4,0	10,5	0,7
DCH0.75S010	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2,3	0,7	2,0	1,1	4,3	4,0	10	0,6
DCH1S009	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	1,9	1,1	2,0	1,0	3,0	3,0	11	0,6
DCH1S010	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2,5	1,1	2,0	1,0	3,0	3,0	10	0,7
DCH1.2S009	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	2,1	1,4	1,9	0,9	2,3	2,5	10,5	0,7
DCH1.2S010	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2,7	1,3	2,0	0,9	2,3	2,5	11	0,8

Table 2. Sol-gel synthesis parameters of the samples. Theoretical molar ratios have been calculated according to the amounts of each precursor. DCHT006 is a talc-like organic-inorganic hybrid to show the impact of the aluminum source.

cell parameter of about 2.57 Å. As a comparison, saponite-like materials have a basal distance of about 2 times the thickness of tetrahedral sheets plus the octahedral one and the interlayer distance, which correspond to a final d_{001} value of about 11-15 Å under a relative humidity of 80%, sometimes above depending on the size of the counterions and the structure content [7,8,17,18]. The distance observed in these diffraction patterns is much lower than the basal distance of saponite-like materials (around 10 Å plus the length of the organic chain), indicating that the structure of the synthesized materials cannot correspond to hybrid organic-inorganic saponite-like structures but to hydrotalcite-like compounds. Moreover, an interesting feature is generally observed in the low angle region: lamellar materials exhibit a peak around $60^\circ 2\theta$ corresponding to the (060;330) reflection. The position of this peak depends on the occupancy of the octahedral sheet: high angle values indicate small distances, typically dioctahedral nature (around 1.49 Å, Al^{3+} or Fe^{3+} with a vacant site for example), and the contrary indicates a trioctahedral nature (around 1.52 Å, Mg^{2+} or Fe^{2+} for example). In this case, the width of this peak indicate the presence of two different features: one for the trioctahedral character around 1.51 Å, and the second peak around 1.54 Å (quite visible in the sample DCH0.5S010) for the dioctahedral nature of the synthesized materials. This indicates the presence of both divalent and trivalent cations into the octahedral sheet, respectively Mg^{2+} and Al^{3+} considering the synthesis reactants in our case. Another interesting point is that no other phases are observed, impurities being generally represented by thin peaks in X-Ray diffractograms. Moreover, the pattern in Fig. 5 look quite similar whatever the Si/Al substitution rate (between 0.5 and 1.2 in the structural formula of hybrid organic-inorganic saponite-like materials), whereas a shift of the main peaks (001) and (060) is generally observed in diffractograms of saponite-like materials related to changes in the structure of these lamellar compounds [12-18].

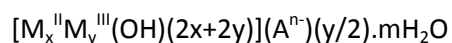
Considering these observations, Fourier Transformed Infrared (FT-IR) analysis have been performed on the synthesized samples using potassium bromide pellets. As seen from Fig. 6, the spectra obtained show several characteristic bands: the broad and strong absorption band in the range of $3700\text{-}3300\text{ cm}^{-1}$ correspond to the O-H stretching vibration of the surface and interlayer water molecules, as the O-H bending vibration centered at 1660 cm^{-1} . The three bands observed in the range of $2950\text{-}2900\text{ cm}^{-1}$ are related to the C-H stretching vibration, and the presence of the stretching Si-C vibration band around 1130 cm^{-1} proves the integrity of silicon and its organic part into the sample. Additional bands in the range of $1300\text{-}1200\text{ cm}^{-1}$ show the presence of magnesium in the materials. It is worthy to note that **the positions of the vibrational bands do not change whatever the Si/Al substitution rate into the samples, and stretching Si-Al bands are not observed in the $3500\text{-}3800\text{ cm}^{-1}$ range, similar to Mg-Al Layered Double Hydroxide samples.**

The samples DCH0,5S009 and DCH1,2S009 have been analyzed using ^{27}Al and ^{29}Si solid-state NMR, as shown by Fig. 7. **A third sample has been analyzed by ^{29}Si CPMAS NMR, DCHT005, a talc-like hybrid sample synthesized without aluminum in order to compare the T-type environments in these materials.** Fig. 7 (A) shows three separated peaks: -67.9, -56.9 and -48.3 ppm, whose correspond respectively to T^3 , T^2 , and T^1 environments, but in a very low amount according to the single pulse MAS analyses. This means that only a very few amount of silicon atoms are located into the structure of the synthesized materials. However, T^3 environments seem to be more important than T^2 and T^1 ones, indicating a high condensation of silicon species into the tetrahedral sheets except in the sample DCH1,2S009 which is supposed to have the higher substitution rate and a lower Si/Al molar ratio. For ^{27}Al NMR spectra, shown in the Fig. 7 (B), a sample has been prepared without silicon precursor (DCH AlMg01), corresponding to the chemistry of a pure hydrotalcite phase. All the samples exhibit one strong peak around 9.1 ppm, and a very small one at 61.3 ppm is observed in the sample DCH1,2S009. The position of the first peak indicates the presence of aluminum in octahedral positions (Al VI), as proved by the sample without silicon source, whereas the second shows the

same element in tetrahedral environment (Al IV), which is not possible in pure hydrotalcite phases. According to the results obtained by ^{27}Al and ^{29}Si NMR, it can be assumed that the synthesized materials are made of two different compounds: the first is constituted of traces of saponite-like structure, with silicon and aluminum in tetrahedral sheets, and the second part is essentially made of aluminum in an octahedral environment.

The thermal stability of the samples has been tested using Thermogravimetric Analysis (TGA) from 25 to 600°C with a slope of 5°C.min⁻¹, and is shown in Fig. 8. In all cases, the curves can be divided into 2 main regions: the first one, ranging from 25 to 250°C, is related to the dehydration (loss of the surface water) of the samples. It corresponds to a mass loss of approximately 16-18% in the samples. The second region is located between 250 and 600°C and related to the dehydroxylation and decomposition of the organic part, with a final mass loss of almost half of the starting mass (around 43-47%). Moreover, the sample DCHT006, a talc-like hybrid material synthesized the same way without aluminum, presents higher thermal stability than other materials, which can be explained by the insertion of aluminum into the structure of these lamellar materials inducing structural defects and cavities.

By using this synthesis method in our study, Mg-Al Layered Double Hydroxide (LDH) has however been surprisingly formed during the synthesis of hybrid organic-inorganic saponite-like materials. Hydrotalcite belongs to the Layered Double Hydroxide (LDH) family with a structure based on brucite (Mg(OH)₂)-like layers (similar to octahedral sheets in natural clays), in which a part of the divalent cations are substituted by trivalent ones, for example a part of Mg²⁺ ions are replaced by Al³⁺ ions [19-31]. These structural substitutions generate positive charges within the stacked layers, which are kept electronically neutral by the intercalation of anions and water among the interlayer spaces, as seen in Fig. 9. The general structural formula of layered double hydroxides can be denoted as:



Where the divalent and trivalent cations (M^{II} and M^{III}, respectively), the stoichiometric coefficient values (x and y, 2 ≤ x/y < 4), the interlayer anions (Aⁿ⁻ = (CO₃)²⁻, (SO₄)²⁻, OH⁻, Cl⁻ for example) and the water content (m) can be varied over a wide range, leading to the Layered Double Hydroxides (LDHs) family; also called anionic clays (contrary to regular clays which present negatively-charged layer, the deficit being compensated by interlayer cations [19,23-25]). A great focus is made on hydrotalcite thanks to the complex layered structure, wide range of chemical compositions, high ion exchange capacity linked to its interlayer space, and reactive surface [19,22,28,29].

To go further in the formation of this material, a different organoalcoxysilane has been tested in the same conditions.

3.2. Syntheses with trimethoxyphenylsilane

Table 3. Sol-gel synthesis parameters of the samples synthesized with trimethoxyphenylsilane. Theoretical molar ratios have been calculated according to the amounts of each element.

Synthesis carried out with trimethoxyphenylsilane were performed using magnesium chloride hexahydrate salt as magnesium source. The composition and calculated molar ratios are reported in [Table 3](#).

X-Ray diffraction patterns of the samples synthesized with trimethoxyphenylsilane are shown in [Fig. 10](#). Even if some impurities are visible, six main reflections are observed: 5.7-7, 11.4, 22.8, 34.8, 38.5, and 60.7°2 θ , which are quite similar to the ones observed in the previous samples. Moreover, this first diffraction peak at small angle tends to shift to lower angle values when the substitution rate of silicon by aluminum increases. According to the Bragg's Law and the general indexation of hybrid lamellar materials in literature, this first reflection corresponds to basal reflection values (001) between 13 (sample DCH0,5S013) and 15.5 Å. Even if the samples exhibit hydrotalcite-like features, the presence of this basal distance (001) plus the (060) diffraction peak at 1.52 Å also indicates the formation of a saponite-like material, with octahedral sheets containing divalent cations (magnesium according to our precursors).

Solid-state NMR experiments have also been performed on these samples to probe the local environment of silicon and to study the position of aluminum (whether aluminum is present in tetrahedral sheets (Al IV) and/or in octahedral sheets (Al VI) in the structure). [Fig. 11 \(A\)](#) corresponds to the ²⁹Si CPMAS analyses of the samples DCH0,5S013 and DCH1.2S013, the two extreme samples of the series according to the Si/Al substitution rates. These two samples exhibit three main local environments: -75.5, -68, and -60.7 ppm for T³, T², and T¹ environments, respectively. These values are slightly above the ones observed in the previous samples but are still in the range of T-types environments. However, T³ environments seem to be of greater importance in the sample DCH0.5S013 with the lowest Si/Al substitution rate whereas T² and T¹ environments are dominant in the sample DCH1.2S013, indicating a lower condensation of silicon in the structure, and more structural defects than the first sample. Regarding the ²⁷Al MAS NMR on the four samples, as shown in [Fig. 11 \(B\)](#), the four spectra display two resonances: a first one around 9 ppm, and a smaller one at 54 ppm, which indicates the presence of aluminum in both octahedral (Al VI) and tetrahedral (Al IV) positions respectively.

The results obtained with these materials synthesized using trimethoxyphenylsilane confirm our previous observations with the N-propyltriethoxysilane: X-Ray diffraction data proves the formation of two different lamellar materials, and ²⁷Al Nuclear Magnetic Resonance analyses show the presence of aluminum in both octahedral and tetrahedral sheets, which is respectively observed in hydrotalcite and saponite-like materials. Moreover, it seems that the increase of the aluminum content in the samples induce more defects in the structures, and a greater ratio of Layered-Double Hydroxide formed during the sol-gel synthesis.

Sample	Mg amount (g)	Al amount (g)	Si amount (g)	Si/Mg Molar ratio	Si/Al Molar ratio	Mg/Al Molar ratio	pH	Mass obtained (g)
<i>DCH0,5S013</i>	1.8	0.5	2.0	1.2	7.0	6.0	11	1.4
<i>DCH0,5S013b</i>	1.8	0.5	2.0	1.2	7.0	6.0	10.5	0.9
<i>DCH0,75S013</i>	1.9	0.8	2.0	1.1	4.3	4.0	11	1.2
<i>DCH0,75S013b</i>	1.9	0.8	2.0	1.1	4.3	4.0	11	0.9
<i>DCH1S013</i>	2.1	1.1	2.0	1.0	3.0	3.0	10	0.9
<i>DCH1S013b</i>	2.1	1.1	2.0	1.0	3.0	3.0	10.5	1.4
<i>DCH1,2S013</i>	2.2	1.4	2.0	0.9	2.3	2.5	10.5	1.1
<i>DCH1,2S013b</i>	2.2	1.4	2.0	0.9	2.3	2.5	11	2.2

The most plausible hypothesis to the formation of such material instead of the expected hybrid organic-inorganic saponite-like product is the non-formation of tetrahedral Si-Al sheets, which may be related to the precursors. According to the results mentioned above, NMR data shows the synthesized materials are mainly made of aluminum in octahedral positions, even if some traces of tetrahedral silicon is detected. The XRD patterns of the synthesized materials are similar to Mg-Al LDHs called hydrotalcite, and the remaining silicon into the samples can be related to the presence of some layers of lamellar hybrid organic-inorganic, as expected at the beginning of this study.

4. Conclusion

As hybrid organic-inorganic saponite-like materials were expected by the use of the sol-gel synthesis process, the experiments have been performed according to M. Jaber et al. [6]. Depending on the precursors, X-Ray diffraction and solid-state NMR results shows the formation of another type of lamellar material made of magnesium and aluminum, even if silicon has been used during the synthesis process. The presence of small amounts of silicon into the samples showed by ^{29}Si solid-state NMR proves the formation of some saponite-like layers with silicon and aluminum in tetrahedral positions, but the samples are mainly made of a stacking of brucite layers with magnesium partly substituted by aluminum, also called Mg-Al hydrotalcite or layered double hydroxide. Aluminum is present in octahedral sheets (Al VI), and the basal distance between the layers is estimated at 7.7\AA according to X-Ray Diffraction analyses, which is much lower than the values expected with saponite-like materials plus the length of the organic chain. Aluminum acetylacetonate is known in the synthesis of lamellar materials, but is not always the best choice depending on the type of material expected.

By changing the different precursors, especially the aluminum source, the analyses showed the formation of (1) almost pure Mg-Al Layered Double Hydroxides, also called hydrotalcites, or (2) a mixed phase between hydrotalcite and saponite-like structure, or finally (3) pure saponite-like materials by changing the aluminum salt, as outlined in Fig. 12. The changes in the formation of these lamellar materials may be related to the affinity of the aluminum precursors over the organo-alcoxysilane: aluminum acetylacetonate might have a lower affinity to *N*-propyltriethoxysilane and trimethoxyphenylsilane than aluminum chloride, and this interaction reduces hydrolysis and condensation rates during the addition of sodium chloride, as shown by A. E. Danks et al. [32]. This is the reason why the choice of the appropriate precursors for the sol-gel synthesis of lamellar materials is an important parameter to take into account. Further studies concerning the formation mechanisms of these materials instead of saponite-like hybrids are under progress.

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No conflicts of interests to declare.

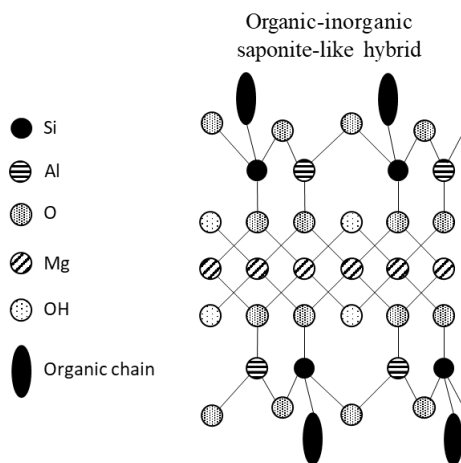


Fig. 1. Schematic representation of organic-inorganic saponite-like hybrid.

Schéma de la structure d'un hybride organique-inorganique de structure de type saponite.

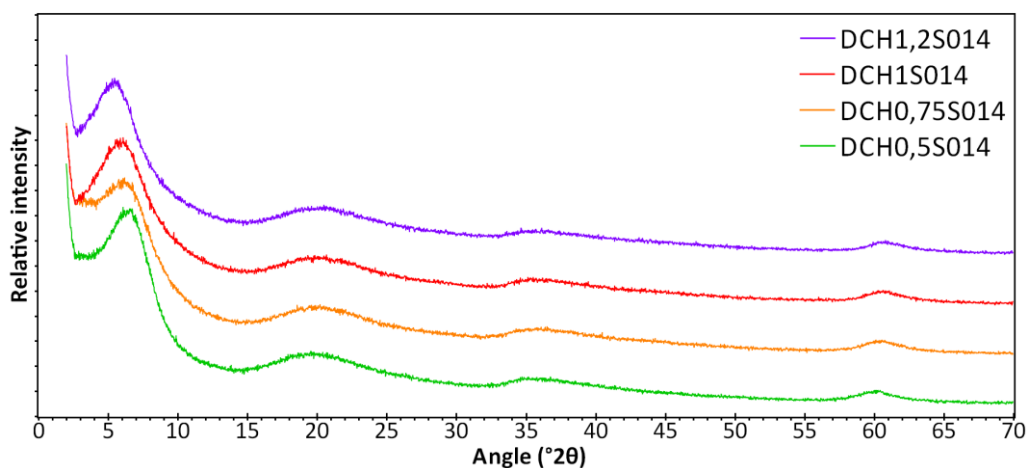


Fig. 2. XRD patterns of the samples S014 synthesized with aluminum chloride by sol-gel method, washed 3 times with ethanol.

Diffractogrammes de Rayons X des échantillons S014 synthétisés avec du chlorure d'aluminium hexahydraté par voie sol-gel, lavés trois fois à l'éthanol.

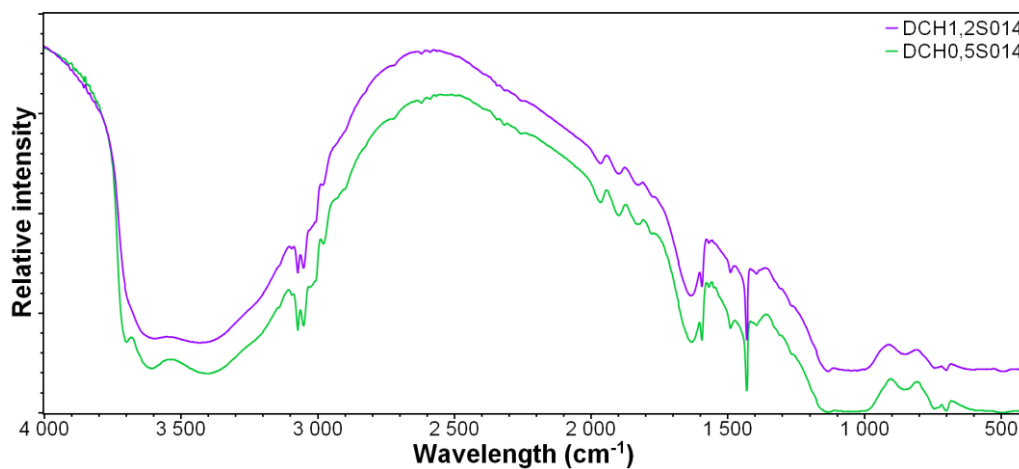


Fig. 3. FTIR spectra of the samples S014 recorded from 400 to 4000 cm^{-1} .

Spectres Infrarouges des échantillons S014 enregistrés de 400 à 4000 cm^{-1} .

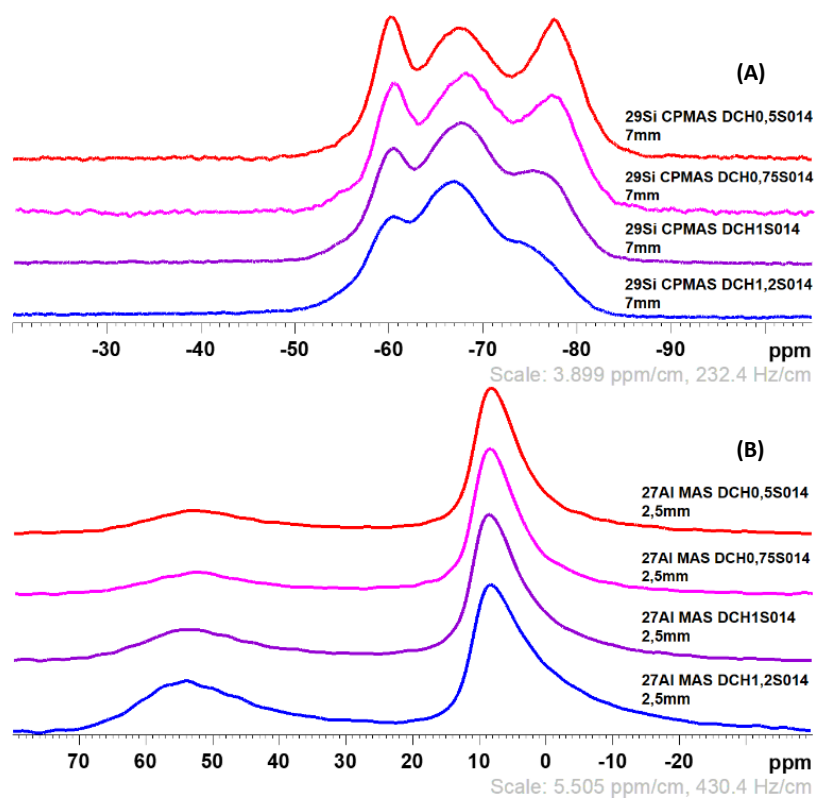


Fig. 4. ^{29}Si CPMAS NMR (A) and ^{27}Al MAS NMR (B) spectra of the samples S014.
 Spectres RMN du ^{29}Si en CPMAS (A) et du ^{27}Al en MAS (B) des échantillons S014.

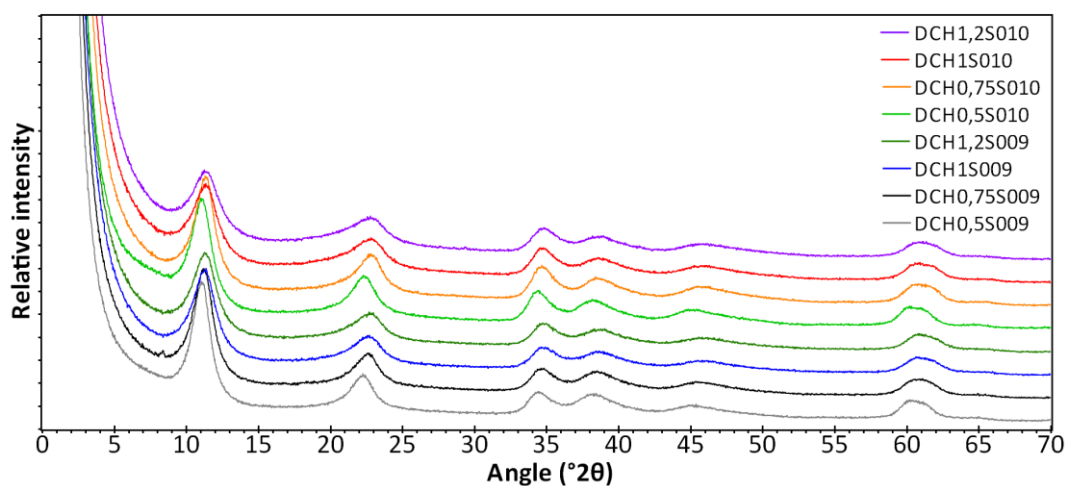


Fig. 5. XRD patterns of the samples S009 (down) and S010 (up) synthesized by sol-gel method with rising Si/Al substitution rates from 0.5 to 1.2 for each series, washed 3 times with ethanol.

Diffractogrammes de Rayons X des échantillons S009 (en bas) et S010 (en haut) synthétisés par voie sol-gel, avec des taux de substitution Si/Al croissants de 0,5 à 1,2 pour chaque série, lavés trois fois à l'éthanol.

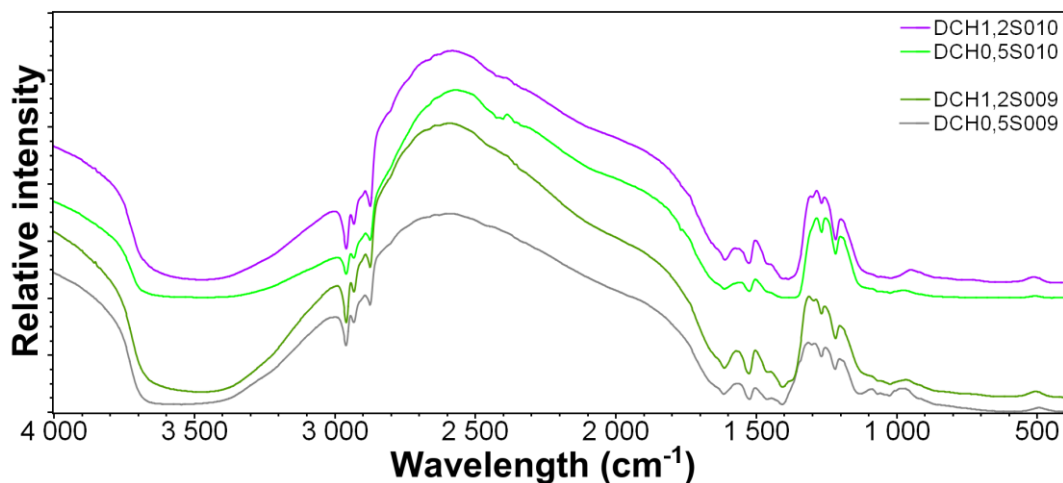


Fig. 6. FTIR spectra of the series of samples S009 and S010 recorded from 400 to 4000 cm^{-1} .
Spectres infrarouges des séries d'échantillons S009 et S010 enregistrés de 400 à 4000 cm^{-1} .

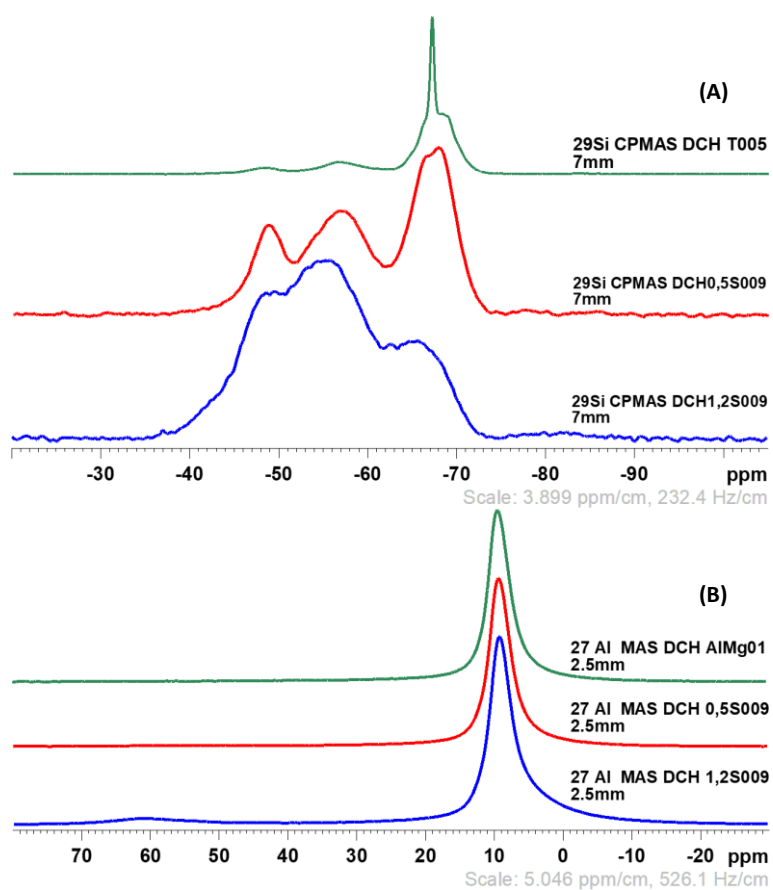


Fig. 7. ^{29}Si CPMAS NMR spectra (A) of the samples DCH0,5S009 (red) and DCH1,2S009 (blue) compared to a synthesized talc-like hybrid (green), and ^{27}Al MAS NMR spectra (B) of the samples S009 compared to a sample synthesized only with aluminum and magnesium (green).

Spectres RMN du ^{29}Si en CPMAS (A) des échantillons DCH0,5S009 (en rouge) et DCH1,2S009 (en bleu) en comparaison avec un hybride de structure de type talc (en vert), et spectres RMN du ^{27}Al en MAS (B) des échantillons S009 en comparaison avec un échantillon synthétisé en absence d'organo-alcoxysilane (en vert).

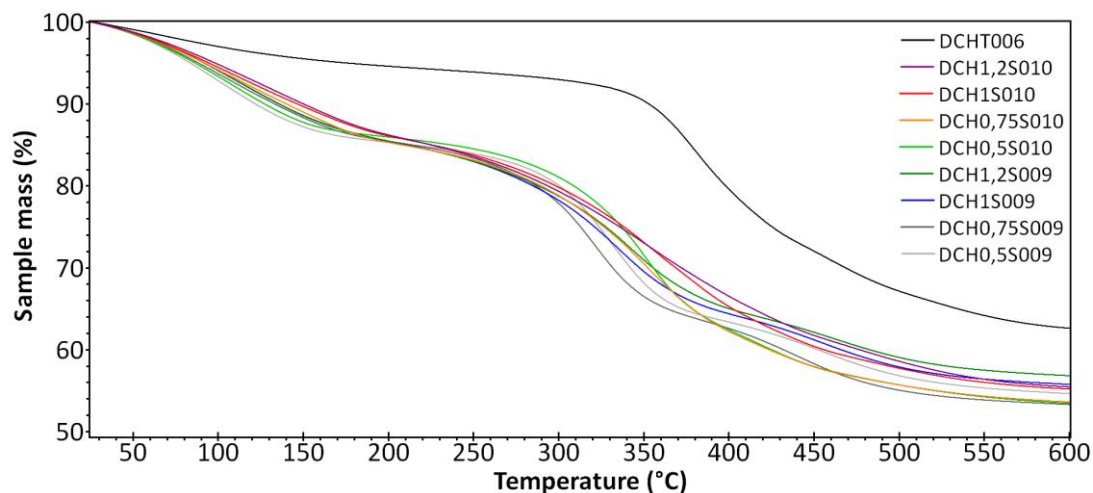


Fig. 8. Thermogravimetric Analyses of the samples S009 and S010, from 25 to 600°C. DCHT006 is a talc-like hybrid synthesized the same way, without aluminum.

Analyses thermogravimétriques des échantillons S009 et S010, de 25 à 600°C. DCHT006 est un hybride de structure de type talc synthétisé par la même méthode, en absence d'aluminium.

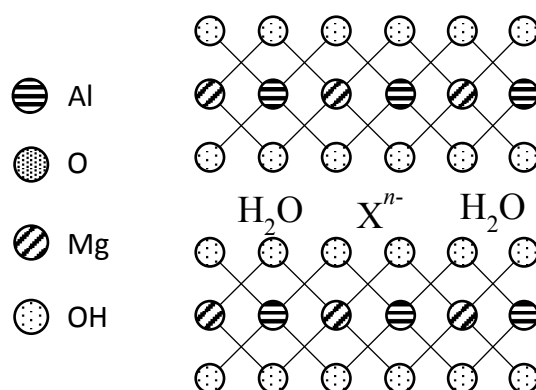


Fig. 9. Schematic representation of an Al-Mg Layered Double Hydroxide (LDH, also called hydroxycalcite).

Schéma de la structure d'un Hydroxyde Double Lamellaire Al-Mg (HDL, également appelé hydroxycalcite).

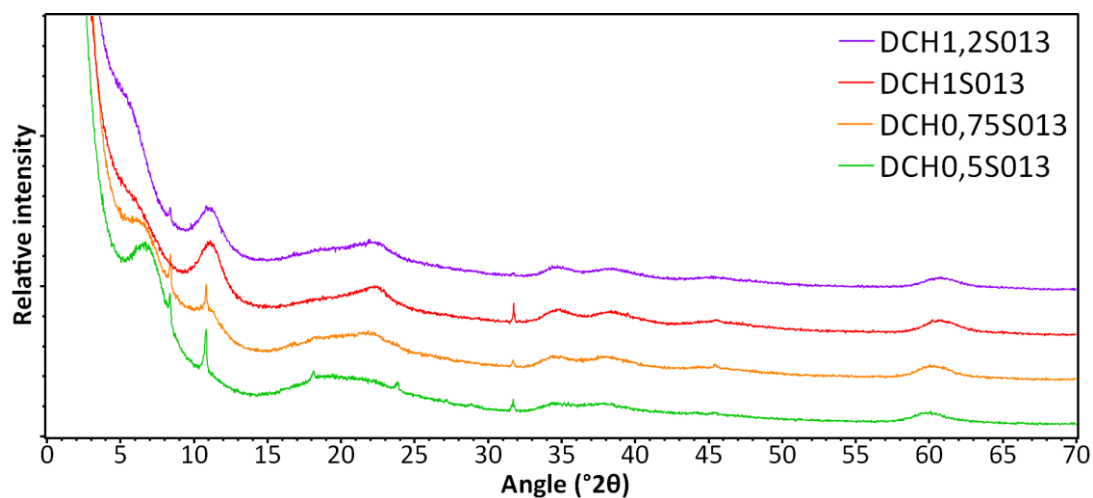


Fig. 10. XRD patterns of the samples synthesized with trimethoxyphenylsilane by sol-gel method, washed 3 times with distilled water.

Diffractionogrammes de Rayons X des échantillons synthétisés avec du phényltriméthoxysilane par voie sol-gel, lavés trois fois à l'eau distillée.

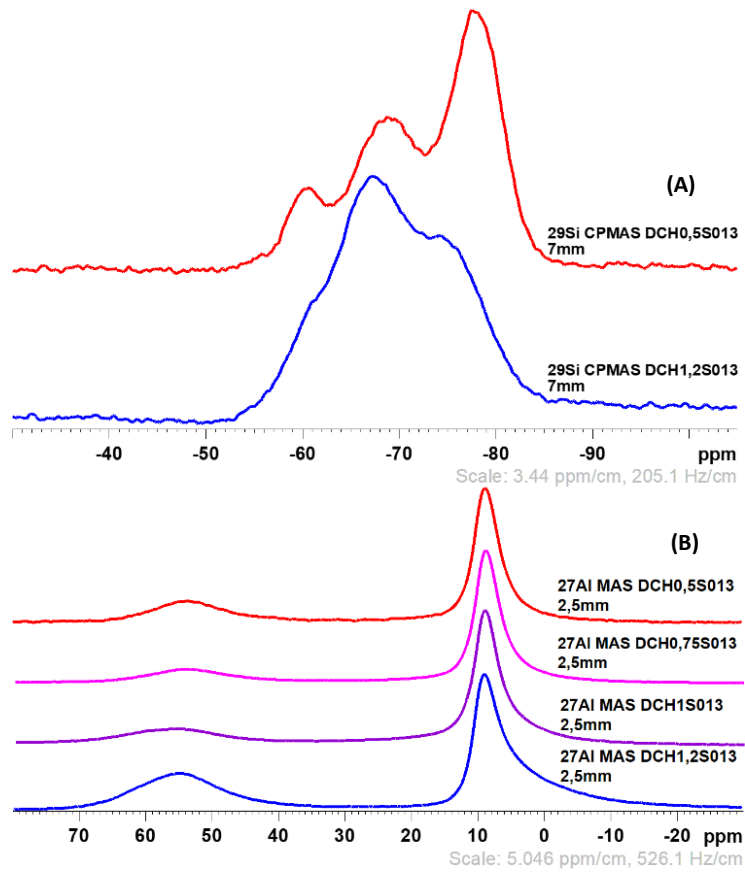


Fig. 11. ^{29}Si CPMAS NMR spectra (A) of the samples DCH0,5S013 (red) and DCH1,2S013 (blue), and ^{27}Al MAS NMR spectra (B) of the samples S013.

Spectres RMN du ^{29}Si en CPMAS (A) des échantillons DCH0,5S013 (en rouge) et DCH1,2S013 (en bleu), et spectres RMN du ^{27}Al en MAS (B) de la série d'échantillons S013.

Aluminum acetylacetonate + <i>N</i> -propyltriethoxysilane + Magnesium chloride	Aluminum acetylacetonate + Trimethoxyphenylsilane + Magnesium chloride	Aluminum chloride + Trimethoxyphenylsilane + Magnesium chloride
<p>Hydrotalcite (Mg-Al Layered Double Hydroxide)</p> <p>H₂O Xⁿ⁻ H₂O</p>	<p>Organic-inorganic saponite-like hybrid</p> <p>Hydrotalcite (Mg-Al Layered Double Hydroxide)</p> <p>H₂O Xⁿ⁻ H₂O</p>	<p>Organic-inorganic saponite-like hybrid</p>

Fig. 12. Summary of the sol-gel synthesis conditions and impact of the different precursors.

Résumé des différentes conditions de synthèses et de leur impact.

Sample	Mg amount (g)	Al amount (g)	Si amount (g)	Si/Mg Molar ratio	Si/Al Molar ratio	Mg/Al Molar ratio	pH	Mass obtained (g)
<i>DCH0,5S014</i>	1,757	0,352	1,998	1,166	6,911	5,928	11	1,42
<i>DCH0.75S014</i>	1,893	0,560	2,003	1,084	4,355	4,014	10,5	1,38
<i>DCH1S014</i>	2,05	0,811	2,004	1,002	3,009	3,002	11	1,32
<i>DCH1,2S014</i>	2,195	1,042	1,999	0,934	2,336	2,502	10,5	1,28

Table 1. Sol-gel synthesis parameters of the samples synthesized with aluminum chloride, trimethoxyphenylsilane, and magnesium chloride hexahydrate. Theoretical molar ratios have been calculated according to the amounts of each element.