Layered Inorganic−Organic Talc-like Nanocomposites

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New layered inorganic−organic magnesium organosilicates were prepared by a single-step template sol−gel synthesis through the reaction of magnesium ions with a synthetic homologous series of urea−alkoxysilanes with the general formula $(CH_3CH_2O)_3Si(CH_2)_3$-$NHC(O)NH(CH_2)_nCH_3$, for $n = 2$, 4, and 6. The nanocomposites were characterized by elemental analysis, solid-state ^{29}Si and ^{13}C nuclear magnetic resonance, X-ray diffraction, and thermogravimetry. The results showed that the hybrid materials exhibit lamellar structures similar to those found in the natural inorganic silicate talc. The influence of the length of the organic group of the urea−alkoxysilane employed in the formation of these layered structures is clearly observed by ^{29}Si NMR spectroscopy. A high degree of condensation for the hybrid synthesized with urea−alkoxysilane containing the longest alkyl chain was obtained. These materials seem to be promising as sorbents for solid-phase extraction of organic pollutant molecules, when dispersed in water, because of their highly hydrophobic character.

Introduction

Layered magnesium, nickel, and aluminum silsesquioxane hybrids have been synthesized previously, leading to new inorganic−organic materials, obtained through the procedure of [(3-methacryloxy)propyl]trimethoxysilane copolymerization with magnesium or nickel salts in basic aqueous solutions.[1] Up to now, the syntheses of a considerable number of hybrids with different organic functionalities have been reported following this initially established synthetic route.[2−6] The hydrophobicity and other properties of the silsesquioxanes can be changed by the simple choice of trialkoxysilanes with the desired functionalities.[7]

These kind of hybrids are of enormous interest, not only because of the synthetic method used but also because only a one step sol−gel template reaction is employed, under mild conditions, to obtain the self-organized layered hybrid materials. As previously stated,[7] a probable mechanism for the formation of these self-organized structures should be similar to that involved in the formation of mesoporous silicas,[8] aluminosilicate molecular sieves,[9] and also inorganic−organic nanocomposites[10] by using different surfactants as templates.[11] This approach is based on the use of ordered arrays of surfactant molecules as templates, generally with positively charged quaternary ammonium micelles, which can attract the anionic inorganic species in solution. As a result, polymerization and condensation of the inorganic framework happens at the water/surfactant interface.[9] The hybrids obtained by this route exhibit several remarkable features, such as well-defined pore size and shape, including a fine adjustment of the pore size by the choice of the surfactant used as the template.[12]

For the synthesis of these layered magnesium silicate hybrids, a similar mechanism would be expected. During the sol−gel template synthesis, the alkoxy groups of the trialkoxysilane molecules are hydrolyzed and the remaining silanol groups can act as the headgroup of the surfactant employed in the preparation of the mesoporous silicas. Following the hydrolysis, the silanol groups can be negatively charged because of the basic medium and can thus attract other metal species from solution by forming a stable inorganic matrix with covalently attached organic functionalities.[7]

For the magnesium silsesquioxanes, the inorganic−organic nanocomposites show lamellar structures analogous to the natural silicate talc, of general composition $Si_4Mg_3O_{10}(OH)_2$, whose inorganic structure is formed by a layer of octahedrally coordinated magnesium oxide overlaid on both sides with a tetrahedrally coordinated silicate network.[2] For the hybrids, the same inorganic

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matrix is formed, where the organic groups are covalently bonded within the interlayer space, through the Si−C bonds derived from the trialkoxyorganosilane employed in the template synthesis.

The presence of these organic functionalities allows these kinds of hybrids to act in some applications such as sorbents, polymer fillers, and chemical sensors, although the thermal stability of the organic groups is limited for some other applications.[7]

Some reports have investigated the reactivity of the organic functionalities in the gallery space. A mercaptopropyl functionality was used to synthesize uniform gold particles of 2-nm diameter within the interlamellar space of a hybrid clay.[2] Another example is the use of an epoxide-containing organosilicate to yield a polymer−inorganic lamellar nanocomposite. The reaction was carried out through polymerization of the epoxy groups with *m*-phenylenediamine under heating. The reactivity of covalently linked epoxy groups was also investigated by undertaking a ring-opening reaction in the presence of methyl thioglycolate. ^{13}C NMR spectroscopy confirmed the presence of a ring-opened hydrosulfide derivative in the new hybrid clay.[3]

In addition to such applications being pointed out, it can be mentioned here that the new hybrids can be promising materials for the adsorption process in liquid chromatography using aqueous solutions at highly alkaline pH values because these new materials exhibit better stability in such aqueous solution when compared with the conventional chemically modified silicas usually used as stationary phases for liquid chromatography. Another important feature is that the presence of embedded polar urea groups can reduce the hydrophobicity near the surface, allowing these composites to be dispersed in polar solvents, such as water and methanol due to hydrogen bonding with polar molecules of the solvent. However, some previous studies in our laboratory have shown that, under acidic aqueous solutions, the magnesium layer can be leached out from the hybrid matrix.

This investigation reports the synthesis of three new inorganic−organic nanocomposites obtained from the reaction of magnesium ions with a homologous series of urea−alkoxysilanes synthesized in our laboratory.[13] The main goal in this study is physicochemical characterization and a study of the influence of the length of the organic chain in the formation of the layered structures.

Experimental Section

Chemicals. The three homologous urea−alkoxysilanes, [(3-propyl)-, (3-pentyl)-, and (3-heptyl)propyl]ureatriethoxysilane, have recently been synthesized and characterized in our laboratory, according to a newly developed organic synthesis route.[13] All other reagents, such as magnesium chloride hexahydrate (Fluka), ethanol, and sodium hydroxide (Merck) were reagent-grade and used as received. Deionized water was purified using a Milli-Q water system (Millipore).

Synthesis. Three different hybrids were prepared using the homologous series of the urea−trialkoxysilanes of the general formula $(CH_3CH_2O)_3Si(CH_2)_3NHC(O)NH{-}R$ where R = propyl, pentyl, and heptyl for [(3-propyl)-, (3-pentyl)-, and (3-heptyl)]propyl]ureatriethoxysilanes, respectively. The inorganic−organic materials obtained were named as sil-Mg-prop, sil-Mg-pent, and sil-Mg-hept, respectively. These materials with the new urea functionality were prepared following the synthetic procedure initially established.[7] In all preparations the Si/Mg molar ratio was maintained at 1.33, which is the observed molar ratio found in the natural silicate talc. First, 0.024 mol of $MgCl_2{\cdot}6H_2O$ was dissolved in 200 cm^3 of ethanol and was added to the urea−alkoxysilane solution freshly prepared from 0.032 mol of each urea−trialkoxysilane in 200 cm^3 of ethanol. Approximately 96 cm^3 of a 0.50 mol dm^{-3} NaOH solution was slowly added to the resulting alcohol mixture, under stirring while the temperature was maintained at 323 K. The addition of the aqueous NaOH solution resulted in the formation of a white suspension, which was aged for 48 h at 323 K. The pH was measured at above 11. A white solid was obtained in all preparations, which was filtered, extensively washed with deionized water and ethanol, and dried under vacuum for 6 h prior to characterization.

Table 1. Carbon (C), Hydrogen (H), Nitrogen (N), and Magnesium (Mg) Percentages (%) and the Carbon to Nitrogen (C/N) Ratio, Obtained from the Elemental Analyses for the Synthesized Hybrids[a]

hybrid	C/%	H/%	N/%	C/N	Mg/%
sil-Mg-prop	30.7 (36.6)	6.61	9.79 (12.2)	3.65 (3.50)	8.7 (7.9)
sil-Mg-pent	37.4 (41.9)	7.41	9.63 (10.9)	4.53 (4.50)	6.7 (7.1)
sil-Mg-hept	45.7 (46.2)	8.36	9.65 (9.80)	5.52 (5.50)	5.6 (6.4)

[a] The empirical and (ideal) values are based on $R_4Si_4Mg_3O_8(OH)_2$, with R being equal to $-(CH_2)_3NHC(O)NH(CH_2)_nCH_3$ for $n = 2$, 4, and 6, for sil-Mg-prop, for sil-Mg-pent, and for sil-Mg-hept hybrids, respectively.

Characterization. Carbon, hydrogen, and nitrogen percentages for the new hybrids were determined on a Perkin-Elmer model 2400 analyzer. At least two determinations were performed for each material. The percentages of magnesium in the samples were determined by atomic absorption spectroscopy. For this determination, the samples were first digested with HF and the resulting solutions were analyzed. Infrared spectra were recorded on a Bomem MB-Series spectrometer, using KBr pressed samples at 4 cm^{-1} of resolution. Solid-state ^{13}C and ^{29}Si NMR spectra were performed on a Bruker AC300/P spectrometer. For the ^{13}C nucleus, cross polarization and magic-angle spinning were employed with a contact time of 3 ms and a repetition time of 4 s. The spinner rate was 4 kHz and the frequency was 75.5 MHz. For the ^{29}Si nucleus, the HPDEC technique (high-power decoupling) was employed with a relaxation time of 60 s at a frequency of 59 MHz. Liquid tetramethylsilane was used as an external reference for all NMR spectra. X-ray diffraction patterns were collected on a Shimadzu model XRD 6000 diffractometer using Cu Kα radiation at 45 kV and 30 mA. The thermogravimetric curves were obtained in a DuPont model 1090 apparatus coupled to a thermobalance. The samples were heated at the rate of 0.17 K s^{-1} in a nitrogen atmosphere.

Results and Discussion

In the synthetic procedure, under basic solution, the ethoxy groups of the organosilane are quickly hydrolyzed to form new silanol groups, which may be negatively charged due to the pH of approximately 11. The negatively charged species can aggregate into ordered molecular arrays similar to anionic surfactants, which are commonly used to synthesize mesoporous silicas.[8] The negatively charged micelles may function as templates and can attract the magnesium cations from solution to yield a layered hybrid structure, whose inorganic phase is formed by Si−O−Mg bonds.

The elemental analysis results presented in Table 1 conform to hybrid compositions of the general formula $R_4Si_4Mg_3O_8(OH)_2$, in agreement with the proposed

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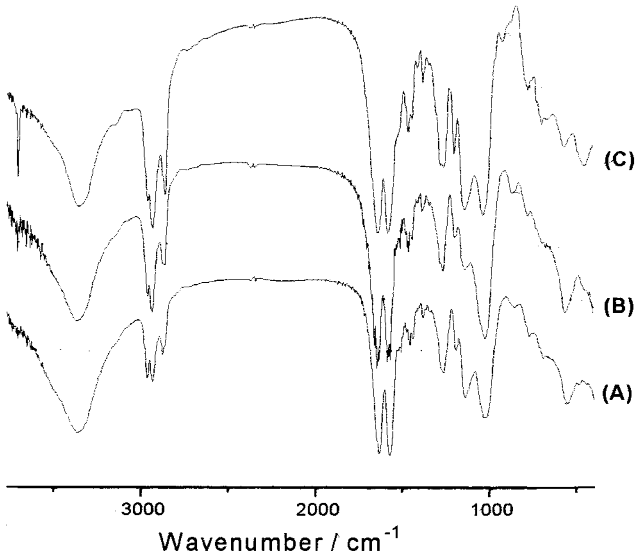

Figure 1. Infrared spectra of (A) sil-Mg-prop, (B) sil-Mg-pent, and (C) sil-Mg-hept hybrids.

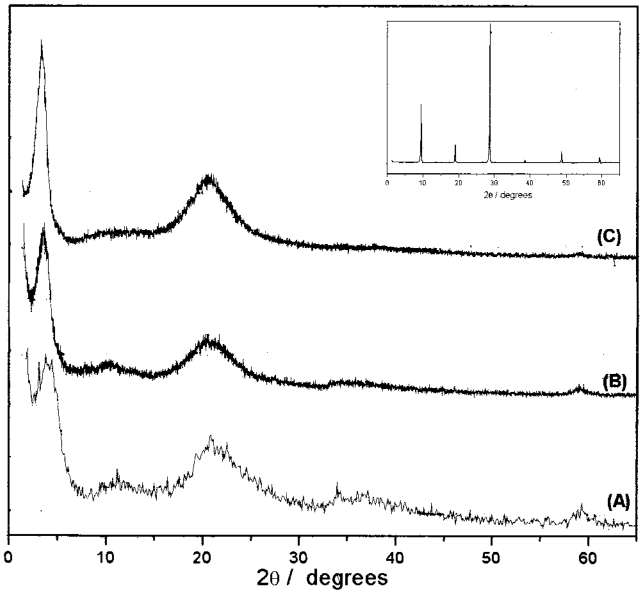

Figure 2. Powder XRD patterns of (A) sil-Mg-prop, (B) sil-Mg-pent, and (C) sil-Mg-hept hybrids. The insert shows the XRD patterns of natural silicate talc, $Si_4Mg_3O_{10}(OH)_2$.

structure for the hybrids. This composition is very similar to the idealized parent structure of natural talc, $Si_4Mg_3O_{10}(OH)_2$. In the sol−gel process, the incorporation of a silicon atom in the inorganic matrix leads also to the attachment of an organic chain through the Si−C bond, which is contained in the original structure of the urea−trialkoxysilane employed. For this reason, the proposed Si/R molar ratio is 1:1, where R represents an organic chain with a polar urea functionality. Both the carbon and magnesium percentage values are in agreement with the expected calculated percentages for each compound, taking into account the idealized proposed structure. For the sil-Mg-hept hybrid, not only is the carbon percentage very similar but also the magnesium content. The observed and the calculated C/N ratios are in close agreement with the structure of the urea groups throughout the synthetic process, as represented by the close agreement of the respective ratios, and also show a complete hydrolysis of the ethoxy groups.

The infrared spectra for the inorganic−organic hybrids in Figure 1 show the presence of the organic groups covalently attached to the inorganic matrix. The band at 3350 cm^{-1} is due to the N−H stretching vibration of the urea groups. The methyl and methylene units presented bands at 2960, 2930, and 2870 cm^{-1}. The bands at 1640 and 1570 cm^{-1} are attributed to C═O stretching and to N−H bending, which appear because of the urea functionality attached to a pendant chain. The band at 1030 cm^{-1} is attributed to Si−O stretching,[14] which is present in the inorganic structure of the hybrids and it is also observed for natural talc silicate. Another prominent band is also observed at ≈1100 cm^{-1}, which is attributed to Si−C stretching.[4] The band at 3700 cm^{-1}, which is also observed for talc, is an indication of the Mg−OH stretching vibration, whose intensity decreases in the sil-Mg-pent and sil-Mg-prop samples. For Mg−O stretching, the bands are observed at 550 and 470 cm^{-1}, as occurs in natural talc. Undoubtedly, the presence of the bands around 2960, 1640, and 1570 cm^{-1} in the spectra for all hybrids shows the integrity of the organic urea functionalities bonded to the inorganic matrix because of the success of the synthetic route.

XRD powder patterns of the three hybrids are shown in Figure 2. The presence of peaks at $2\theta = 3.9°$, 3.4°, and 3.3° for sil-Mg-prop, sil-Mg-pent, and sil-Mg-hept is a clear indication that lamellar structures were formed, corresponding to interlayer distances of 2300, 2500, and 2700 pm, respectively. In a comparison of the XRD patterns of the three hybrids with the natural silicate, also inserted in Figure 2, much broader basal peaks are observed. This behavior implies that these structures are quite similar to those of talc; however, these structures are less well-organized because of the presence of the organic chains included in the interlamellar space. A small peak at $2\theta = 59°$ can be observed in all XRD patterns. This reflection is presumably the same 060 spacing reflection, as observed for talc XRD patterns, inserted in Figure 2. This intralayer reflection ($d = 156$ pm) is characteristic not only for the 2:1 trioctahedral structure of talc but also for the synthesized inorganic−organic hybrids.[15]

The pendant organic group lengths attached to the hybrids were calculated assuming a fully extended conformation and the values obtained were compared with the interlamellar distance calculated from the XRD data for all materials. The R group length versus the interlayer space plot is shown in Figure 3. It can be observed that increasing the organic chain length of the urea−alkoxysilane covalently attached to the inorganic matrix leads to a proportional increase in the interlayer spacing. By a comparison of the interlamellar spacings, which were calculated from the experimental XRD data, with the expected distances (d), this behavior can be adjusted to the expression $d = R + 960$ pm. The value 960 pm represents the basal spacing for the natural silicate and R is the calculated extended length of the

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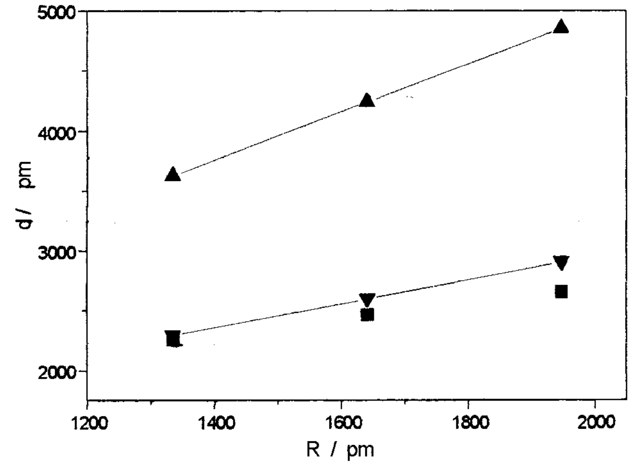

Figure 3. The observed interlamellar distance (*d*) versus the fully extended R group length (*R*) (■). The lines represent the $2R + 960$ pm (−▲−) and $R + 960$ pm (−▼−) theoretical distances.

organic groups $-(CH_2)_3NHC(O)NH(CH_2)_nCH_3$ attached in the case of the inorganic−organic materials, where $n = 2$, 4, and 6 for the sil-Mg-prop, sil-Mg-pent, and sil-Mg-hept hybrids, respectively. The exact conformation of the R groups in the gallery space cannot be determined from the results obtained from the XRD data. However, these results show that the R groups are disposed into the lamellar spacing organized into interpenetrating bilayers between two opposite monolayers, within the Si/Mg inorganic framework.

As stated before,[7] the arrangement of the organic chains in the gallery space is due to the micelle structures formed, when trialkoxysilanes are hydrolyzed in a basic medium. The reactions of hydrolysis of the alkoxy (methoxy or ethoxy) groups form new silanols, favored by the basic medium, which can form negatively charged ($\equiv Si-O^-$) groups. The molecular structures formed should exhibit a negatively charged headgroup and a hydrophobic tail, originating from the organic chain of the trialkoxysilane employed, which can be aggregated in micelles. These micelles are known to be responsible for the ordering and the growth of the structures. In this arrangement, the negatively charged groups of the organosilane can form the inorganic framework through their condensation with other, positively charged, inorganic species in solution because of the presence of the magnesium cations.

Valuable information about the chemical structure of the organic groups attached to an inorganic matrix can be obtained from ^{13}C CP/MAS solid-state NMR spectroscopy.[16] The ^{13}C CP/MAS NMR spectra of all three hybrids obtained are shown in Figure 4. To clarify, in each spectrum the proposed ligand structure is presented with all carbon atoms numbered, as illustrated in the insertion in each spectrum. The signal assignments were based on a previous report on the ^{13}C CP/MAS NMR spectroscopy of modified silicas with the same homologous series of urea−alkoxysilanes, evaluated as stationary phases for liquid chromatography.[17]

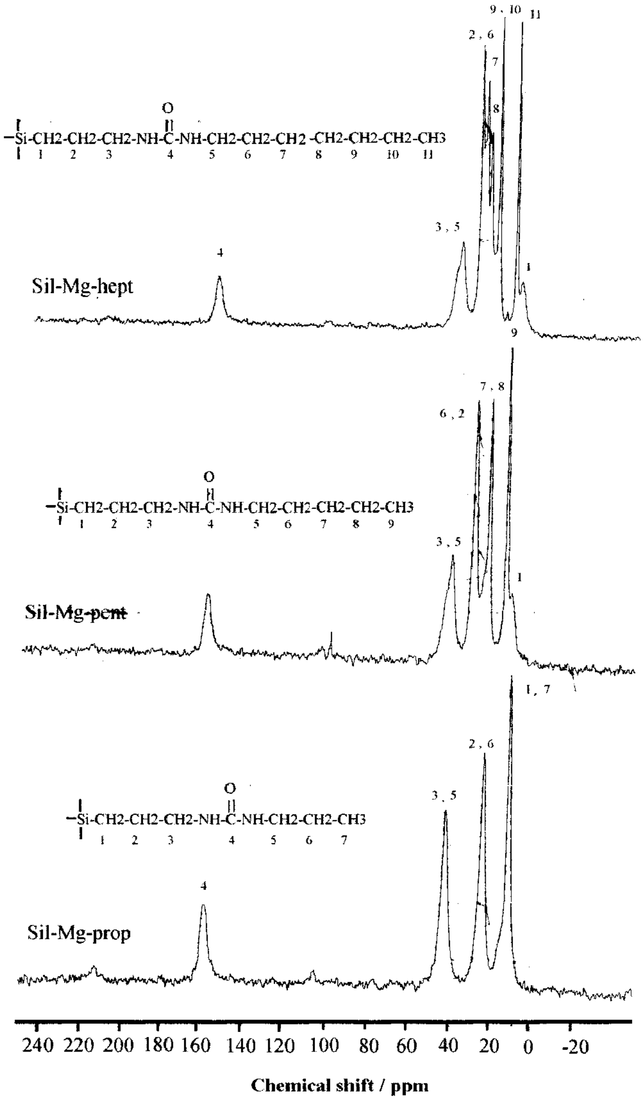

Figure 4. ^{13}C CP/MAS NMR spectra for the synthesized hybrids.

All peaks in the spectra were attributed as represented by the respective numbers, as shown in Figure 4. An interesting feature to mention is related to the identical sequence and position of the peaks found in the modified silicas. This behavior indicates that no chemical change occurred with the urea silyl groups during the synthetic procedures. Small bands at 105 and 220 ppm can be observed; however, these signals are spinning sidebands.

The hybrids were also characterized by ^{29}Si NMR spectroscopy, as illustrated by the ^{29}Si HPDEC spectra of all materials in Figure 5. The species found in all hybrids are described here as T^n species, which are related to the number of oxygens bound to the silyl groups $[RSi(OMg)(OSi)_{n-1}(OH)_{3-n}]$. The signals observed at −49, −55, and −67 ppm are related to the T^1, T^2, and T^3 species, respectively.[4,18−20] The degree of hydrolysis of the precursor alkoxy groups and the degree of condensation between the silicate sheets, in principle, can be studied by ^{29}Si NMR spectroscopy. For this

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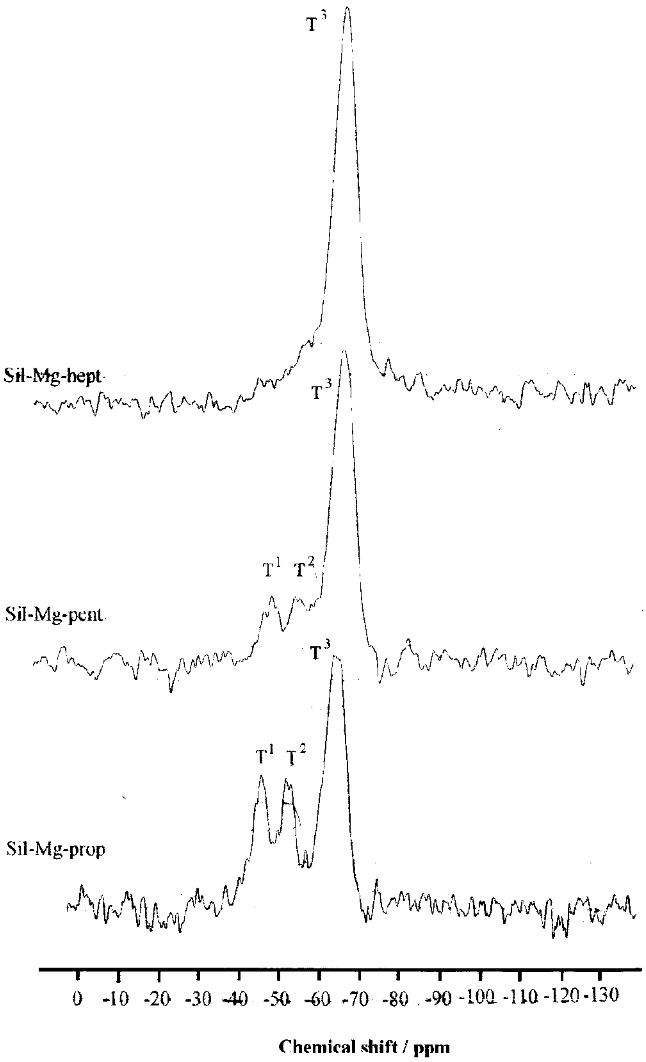

Figure 5. ^{29}Si HPEDC NMR spectra for the inorganic–organic hybrids.

Table 2. Relative Percentages (%) for T^n Species Denoted as $[R-Si-(OMg)(OSi)_{n-1}(OH)_{3-n}]$ for the Hybrids by ^{29}Si RMN Spectroscopy

	relative amount/%		
hybrid	T^1	T^2	T^3
sil-Mg-prop	25	25	50
sil-Mg-pent	14	15	71
sil-Mg-hept	1	3	96

reason all spectra were obtained under the same experimental conditions and peak deconvolution was performed, assuming that peaks exhibit Gaussian shapes and the area for each T^n species was calculated for each hybrid. The results are summarized in Table 2, and as can be seen, a relative increase in the percentages of the fully condensed species T^3 was observed in sequence from sil-Mg-prop to sil-Mg-pent to sil-Mg-hept. The results suggest that, with the increase of the organic group length of the urea–alkoxysilane employed and also a relative increase in the hydrophobic characteristics, a higher degree of condensation was obtained for the hybrid formed. The influence of the organic chain length is clearly observed because all materials were obtained under identical experimental conditions, using the homologous series of urea–alkoxysilanes. The highest degree of condensation for sil-Mg-hept suggests that the structure formed is very close to the proposed structure of $R_4Si_4Mg_3O_8(OH)_2$, which was previously confirmed by elemental analysis.

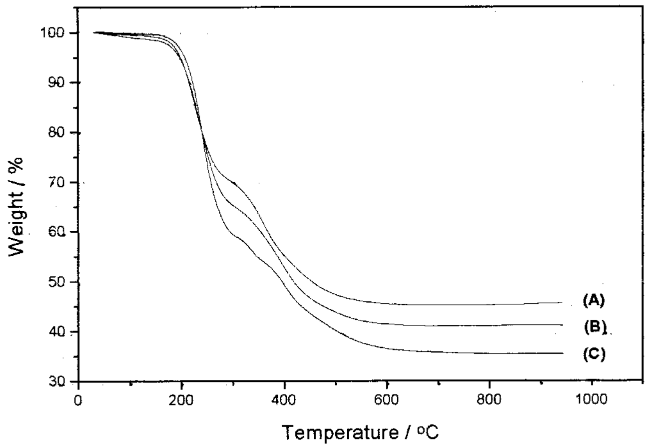

Figure 6. Thermogravimetric curves for (A) sil-Mg-prop, (B) sil-Mg-pent, and (C) sil-Mg-hept.

The thermal stability of the hybrids was investigated by thermogravimetric analyses for all hybrids, as shown in Figure 6. Mass losses of 54.4, 58.9, and 64.7% for sil-Mg-prop, sil-Mg-pent, and sil-Mg-hept, respectively, were determined. The mass loss is proportional to the mass of the organic group attached in each hybrid. Above the temperature of 200 °C, the observed mass loss is probably due to the pyrolysis of the organic groups followed by condensation and collapse of the inorganic structure, resulting in oxides such as MgO and SiO_2 and also silicon carbides.[7]

Conclusion

New hybrid inorganic–organic layered nanocomposites, containing urea–alkyl groups embedded into the gallery space of a talc-like structure were prepared in a single step involving sol–gel template synthesis. The physicochemical characterizations lead to the conclusion that the hybrids have a similar composition to the natural inorganic silicate talc. The influence of the organic group length of the urea–alkoxysilane employed in the formation of the layered structure is clearly observed by ^{29}Si NMR spectroscopy, which showed that the highest degree of condensation was obtained for sil-Mg-hept because of the absence of the silyl groups, as represented by resonances for T^1 and T^2 species. Such behavior leads to the conclusion that the formation of the layered structures is driven by lamellar micelles formed by the hydrolysis of the alkoxysilanes during the synthetic procedure. These hybrids may be promising alternative sorbents for solid-phase extraction of organic pollutant molecules.

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