New layered inorganic–organic nanocomposites containing n-propylmercapto copper phyllosilicates

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Magnesium and copper phyllosilicates, SILMSH (M = Mg, Cu), were synthesized by a sol–gel process from the reaction of these metallic cations and mercaptotrialkoxysilane in aqueous basic solution at 298 K. The inorganic–organic hybrids formed were characterized by elemental analysis, giving 4.88 and 3.68 mmol g^{-1} of organic groups, with larger thermal stability for the magnesium compound and surface areas of 46.9 ± 1.8 and 107.0 ± 3.0 m^2 g^{-1} for magnesium and copper hybrids, respectively. X-Ray diffraction patterns gave basal peaks associated with an interlayer distance of 1300 pm for SILMgSH due to the presence of the organic radical chain in the structure. However, for the copper hybrid an interplanar distance of 695 pm was obtained. The terminal S–H groups on organic chains in the structure were confirmed by infrared data, showing a stretching band at 2556 cm^{-1} for the magnesium hybrid, while this same band was absent in copper phyllosilicate. ^{29}Si NMR showed the presence of silicon species: R–Si*–(OSi)$_3$, R–Si*–(OSi)$_2$–OH and R–Si*–(OSi)–(OH)$_2$ in the inorganic–organic backbone structure. The first species demonstrated that better polymerization occurred in the SILMgSH hybrid. The amount of copper adsorbed on the magnesium phyllosilicate was 5.93 mmol g^{-1}. The interaction of this cation in the SILMgSH matrix can be related to two processes: rearrangement of inorganic layers around copper cations and formation of interlayer complexes with S–H groups. The nanocomposite containing adsorbed copper has a similar structure to the SILCuSH hybrid, suggesting a new route for these copper compounds. A simple low-temperature procedure was employed to synthesize these reproducible SILMgSH/Cu and SILCuSH hybrids, which are 1 : 1 phyllosilicates.

Introduction

Recently, an important series of publications appeared about the use of copolymerization of organotrialkoxysilanes in the presence of metallic ions, whereby nanocomposites can be synthesized to yield layered organoclay-like structures. An interesting feature associated with these inorganic layer compounds is connected to the existence of organophilic functionalities distributed in the interlayer cavities.[1–6] These hybrid materials are members of a family of 2 : 1 organo-modified trioctahedral phyllosilicates whose resulting structure is similar to that found in natural talc, formulated as Si$_8$Mg$_6$O$_{20}$(OH)$_4$.

The major advantage of this synthesis route is the one-step direct synthesis, where all reactions involved occur at room temperature. On the other hand, a great variety of compositions can be obtained depending on the metallic ion and the characteristics of the organosilane employed. To date, mercaptosilane-derived phyllosilicates were synthesized and the reactivity of the S–H groups was investigated with the aim of oxidation of these groups to yield disulfides as final products.[6] Surfaces such as silica gel having anchored thiol groups possess a great ability to adsorb cations from aqueous and non-aqueous solutions.[7]

From a structural point of view, it was previously argued that the existence of copper-rich natural clays is unlikely,[8] because the properties of copper are incompatible with a regular clay structure. This argument was based on the unsuccessful attempt to synthesize copper smectites at lower temperatures, which resulted in copper oxide or unreacted starting materials as final products. Trioctahedral smectites of copper were obtained from reaction containing a mixture in which the ratio Cu/(Cu + Mg) was below 0.5. No other copper phyllosilicates containing attached organic moieties, which could be derived from the organosilane compound employed in the synthetic method, were described up to now.

The present investigation deals with the synthesis and characterization of an organic copper phyllosilicate and the interaction of copper with the available mercapto groups in a magnesium phyllosilicate. The product obtained from this adsorption process behaves similarly to copper phyllosilicate. A comparative study was undertaken with both copper containing compounds.

Experimental

All chemicals used were reagent grade. Bidistilled water was used throughout the experiments. The silylating agent 3-mercaptopropyltrimethoxysilane (Aldrich), (H$_3$CO)$_3$Si-(CH$_2$)$_3$SH, magnesium chloride or copper nitrate hexahydrate (Fluka), methanol and sodium hydroxide (Merck) were used in the synthesis.

Synthesis of modified phyllosilicates

Copper and magnesium phyllosilicates were synthesized by reacting 0.052 mol of the hexahydrate metallic salt with 0.033 mol of the silylating agent. This corresponds to a metal : silicon ratio of 1.33, found in talc. In the case of the copper phyllosilicate more than 0.052 mol of the cation in relation to the silylating agent was used. In any preparation the salt was initially dissolved in 300 cm^3 of bidistilled water. To this solution 1.39 mol dm^{-3} of the 3-mercaptopropyltri-methoxysilane dissolved in methanol was added dropwise. The mixture formed white or green suspensions for magnesium or copper preparations, respectively. To this mixture, 500 cm^3

of aqueous $0.10 \, \text{mol dm}^{-3}$ sodium hydroxide solution was slowly added. This suspension was aged for 24 h at room temperature, and a solid settled out which was filtered off, washed with water to a neutral pH and dried under vacuum at 323 K for 2 days. White or dark green solids were formed for mercaptopropyl magnesium or copper phyllosilicates, respectively, which were named SILMgSH and SILCuSH.

Adsorption process

Copper was adsorbed on the phyllosilicate batchwise from aqueous solution. For these adsorption measurements, samples of about 50 mg of the phyllosilicate SILMgSH were suspended in variable amounts of water containing copper in the concentration range between 5.0×10^{-3} and $0.25 \, \text{mol dm}^{-3}$. All samples were maintained in a thermostated bath under mechanical stirring for 6 h, at 298 ± 1 K. After establishing equilibrium, the solid was separated by centrifugation and aliquots of the supernatant were pipetted carefully from the suspension. The free amount of the metallic cations (N_s) was quantitatively determined by titration with sodium thiosulfate. For each experimental point, the reproducibility was checked by at least one duplicate run. The resulting solids were washed with water and dried at 353 K. These materials presented the characteristic pale or dark green color of copper, depending on the degree of metal adsorbed on the matrix. The number of moles adsorbed (N_f) per gram of solid was determined through the expression $N_f = (N_i - N_s)/m$, where N_i is the initial number of copper cation and m is the amount of magnesium phyllosilicate used. For each experimental determination, the adsorption products were analyzed by X-ray diffraction. The last experimental determination of the isotherm associated with the maximum adsorption capacity was submitted to thermal analysis and the magnesium content was analyzed.

Characterization

X-Ray diffraction powder patterns were collected on a Shimadzu model XRD6000 diffractometer using nickel-filtered Cu-Kα radiation (40 kV, 30 mA). From these data the interlayer spacing of the compounds was calculated.

Infrared spectra were recorded on a Perkin-Elmer model 1600 FTIR spectrophotometer with a resolution of $4 \, \text{cm}^{-1}$, by using samples pressed with KBr.

Thermogravimetric curves were measured on a DuPont model 1090 B apparatus coupled with a thermobalance 951 heated from room temperature to 1273 K, with a heating rate of $0.17 \, \text{K s}^{-1}$ in a dry nitrogen flux. The samples weight varied from 15.0 to 30.0 mg.

The surface area measurements were made on a Flowsorb II 2300 Micromeritics instrument, by using the BET method. The samples were previously degassed at 323 K.

Carbon, nitrogen and hydrogen contents were determined using a Perkin-Elmer PE-2400 microelemental analyzer.

Nuclear magnetic resonance spectra of the solid materials were obtained on an AC 300/P Bruker spectrometer at room temperature. The spectra were obtained at frequencies of 75.5 and 59.6 MHz for carbon and silicon, respectively. For carbon, the CP/MAS technique was used and the signals were obtained with a pulse repetition time of 3 s and contact time of 3 ms. For decoupled ^{29}Si HPDEC NMR spectra a pulse repetition time of 60 s and a pulse width of 45° were used.

Scanning electron microscopy was performed on ground samples, dispersed by sonication in isopropanol. In order to examine these non-conducting materials, the samples were coated with a conducting layer of gold and carbon by sputter coating (Plasma Science Inc). The images were obtained from the detection of the secondary electrons in a JEOL JSTM-300 microscope. The presence of silicon, copper, magnesium and sulfur in the matrices of the hybrid silicates was obtained by the EDX technique.

Results and discussion

From a structural point of view, the precursor mercaptopropyl magnesium phyllosilicate is formed by an inorganic network, having organic chains, originating from the silylating agents attached to this inorganic layer.[4] The inorganic structure of this synthetic phyllosilicate is similar to that found in natural talc, where the inorganic network is composed of tetrahedral–octahedral–tetrahedral layers and the silicon atom is located in the center of a tetrahedron. Two basal corners of the tetrahedron are occupied by oxygen atoms, the third position has carbon atoms attached from the silylating agent and the apical oxygen is bonded to the magnesium of the layer. Thus, the organic chains are covalently bonded to the inorganic backbone through Si–C bonds. The octahedral layer is composed of magnesium atoms that are coordinated to four oxygen atoms in the planes and its octahedral coordination is completed by two other oxygen atoms located out of this plane. The degree of crosslinking of the silicon sheets was estimated and found to agree with the ^{29}Si NMR data. The silicon containing species $RSi(O)_n(OH)_{3-n}$ for $n = 3$ to 1 are associated with T^1, T^2 and T^3, respectively. The three types of silicon were present in the SILMgSH hybrid. This arrangement involving the hybrids provided a layered structure, the interlayer space depends on the type and length of the organic chain of the molecule of the silylating agent incorporated into the phyllosilicate, in these self-organized systems.[9]

During the synthesis, the design of the new hybrid largely depends on the distinct organofunctional trialkoxysilanes used, which should have an organic moiety with the desired functionality to develop the proposed reaction. In the present case, the reactive thiol group is attached to the end of the organic chain. As observed before, many kinds of material containing mercapto groups, such as occur in immobilized silica gels, have been used in preconcentration of cations such as, for example, in adsorbing copper from aqueous solution.[7] Thus, when the adsorption took place, the original metallic cations located on octahedral positions of the structure are enriched by complex formation with the available S–H pendent groups in the interlayer position. For this reason, the excess of copper cation added to the solution not only caused the formation of an inorganic structure, but also is complexed in the interlayer space into the cavities.

Based on carbon, hydrogen and nitrogen analysis results from SILMgSH and SILCuSH matrices, a close agreement was obtained for the C/S ratio calculated for both hybrids, as listed in Table 1. These results showed that the organic moieties did not decompose under the experimental synthetic process. The small difference in the C/S values for SILCuSH (0.19) can be explained as being due to the high number of unhydrolyzable methoxy groups attached to the organic chain. The numbers of moles of organic chains in these nanocompounds are calculated as 4.88 and 3.68 mmol g^{-1}, for SILMgSH and SILCuSH, respectively. The degree of organofunctionalization of the hybrid influenced the surface area, determined by BET, for the inorganic–organic hybrid. The former hybrid presented an area $46.9 \pm 1.8 \, \text{m}^2 \, \text{g}^{-1}$, which is considerably lower than that of the copper hybrid with $107.0 \pm 3.0 \, \text{m}^2 \, \text{g}^{-1}$ as illustrated in Table 1.

Table 1 Percentages of hydrogen, carbon and nitrogen, C/S ratio observed (and calculated), the number of organic groups (n) and the surface area (s) of the hybrids

Hybrid	H (%)	C (%)	S (%)	C/S	n/mmol g^{-1}	s/m^2 g^{-1}
SILMgSH	4.50	17.80	15.66	3.05 (3.00)	4.88	46.9 ± 1.8
SILCuSH	2.81	13.87	11.55	3.19 (3.00)	3.68	107.0 ± 3.0

The lower value can be attributed the high number of organic groups which block the access of the gaseous nitrogen to the surface.[7] However, the decrease in the number of moles inserted did not correspond to an equivalent variation in the area of the SILCuSH hybrid. These values suggested that the variation in area seems to be also dependent on the particle size of the involved hybrid.

The large number of S–H groups disposed within the interlayer space in these hybrids are potentially coordinating centers due to the large ability of the donor sulfur atom to interact with cations in aqueous solution, in spite of some hydrophobic properties that can be associated to these modified phyllosilicates with the insertion of the organic chains.

The magnesium modified phyllosilicate demonstrated a large capacity to adsorb copper from aqueous solution as illustrated in Fig. 1, with a maximum value of N_f of 5.93 mmol g^{-1}, resulting in the new solid named SILMgSH/Cu, obtained via this process. The content of magnesium in this material was 0.53%, corresponding to 0.218 mmol g^{-1} and the initial amount of magnesium in SILMgSH was 4.04 mmol g^{-1}. As observed before, metal cations on octahedral positions in such compounds are not exchangeable.[10] Thus, a reasonable proposition is that the SILMgSH inorganic layers can be firstly dissolved and then reformed around Cu^{2+} cation. Taking into account the complete interaction caused by copper with SILMgSH, two stages are proposed: i) the magnesium occupying the octahedral position in the inorganic structure is partially replaced by the cation in solution and the phyllosilicate is reformed around the copper; and ii) the copper cations interact with the interlayer S–H groups to form interlayer complexes. This process suggests that if the same magnesium cations were replaced by the same amount of copper cations, the total number of moles of copper in the inorganic network should be 3.82 mmol g^{-1} and the remaining 2.11 mmol g^{-1} should be coordinated to S–H groups.

The ion exchange involving magnesium and divalent cations such as copper is expected due to the fact that these cations have similar ionic radii, 0.72 and 0.73 pm, respectively, when they are octahedrally coordinated.[11,12] The proximity in size of these cations favours this kind of substitution in clay structures. This behaviour has been proved just in hydrothermic synthesis of talc and in anionic clays containing magnesium, such as $[Mg_6Al_2(OH)_{16}]^{2+}[CO_3\cdot4H_2O]^{2-}$ and $[Mg_2Al(OH)_6]^{-}[2NO_3\cdot2H_2O]^{-}$.[13]

The proposed similarity in structure of the phases was confirmed by X-ray analysis of the solids, as observed in Fig. 2. SILMgSH phyllosilicate (Fig. 2b) showed broad reflections, suggesting the existence of significant intralayer disorder as
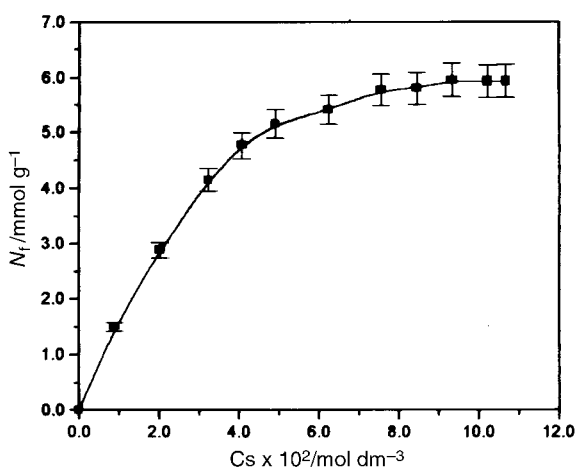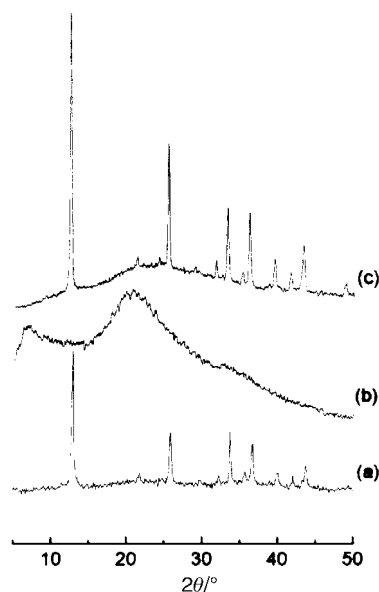

Fig. 2 X-Ray diffractograms of modified phases: a) SILCuSH, b) SILMgSH and c) SILMgSH/Cu.

already observed.[6] The broad in-plane peaks and lack of (hkl) reflections, common in layered materials, is indicative of either the disordered inorganic framework and/or the turbostratic arrangement of the plates.[10,14] However, the diffractograms of SILMgSH/Cu (Fig. 2c) and SILCuSH (Fig. 2a) indicated quite ordered materials. These results suggest that the disorder in these hybrids can really be related to the formation of the linked Si–O–Mg–O–Si groups present in the framework and not due to the presence of the interlayer organic moieties as proposed.[6] The interlayer distances, calculated from the reflections of the 001 plane, were estimated as 1300, 695 and 694 pm for SILMgSH, SILCuSH and SILMgSH/Cu, respectively. The markedly different interlayer distance of SILMgSH was not consistent with the thickness of the tetrahedral–octahedral–tetrahedral structure similar to that of talc. The similarity of the SILMgSH/Cu and SILCuSH diffractograms suggests that these phases are isostructural in nature.

The length R of the organic radicals –(CH$_2$)$_3$SH was estimated as 543 pm, which implied that the inorganic thickness value (D) can be calculated from $D = 695 - R$. This gives a value of near 152 pm, indicating a lower value for D. In this case, it is expected that R chains are oriented in inclined and alternating positions between the two successive layers into the gallery space. On the other hand, the presence of copper complexed with S–H groups may contribute to the proposed conformation of organic chains. Thus, the observed basal spacing for phases containing copper species suggests the formation of 1 : 1 phyllosilicate.[10,15]

Infrared spectroscopy was used as an important tool to identify all the organic moieties within the phyllosilicate layers and to investigate the suggested cation substitutions on the original structure. The infrared spectrum of a mineral depends not only on the chemical constitution, but also on the arrangement of the atoms in the crystal structure.[16–19] The infrared spectra of the SILCuSH and SILMgSH/Cu hybrids, illustrated in Fig. 3, are very similar. The characteristic stretching band vibration mode of the S–H group in the spectrum of SILMgSH is located at 2556 cm^{-1}. However, after the interaction of this chelating group attached to the matrix with copper, this band vanished completely. This fact suggests that when S–H groups coordinate to copper with the disappearance of the S–H stretching frequency, then a metal–sulfur bond is expected to form, as is detected in amino acids.[20] Further evidence for the occurrence of this substitution is the absorption in the OH stretching vibration

Fig. 1 Plot of adsorption of copper from aqueous solution on mercaptopropyl magnesium phyllosilicate.
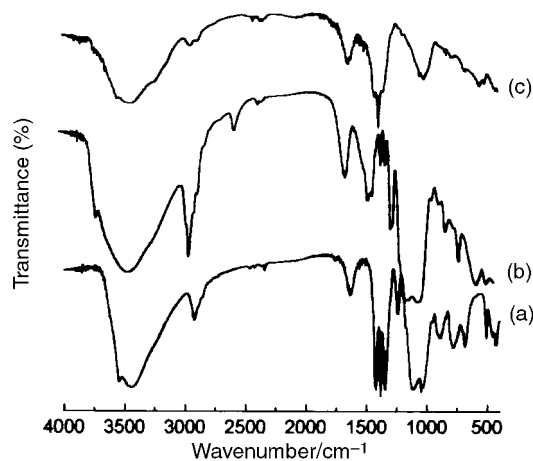
Fig. 3 Infrared spectra of samples: a) SILCuSH, b) SILMgSH and c) SILMgSH/Cu hybrids.

region. This argument is supported by the spectrum of talc, in which magnesium is partially replaced by another divalent cation.[12,21] In such cases, splitting of the fundamental hydroxyl stretching vibration mode can give at least four distinct peaks, depending on the degree of substitution. However, it was also observed that the resulting spectra show broader bands at lower frequencies.

The assignments of some vibrations of infrared spectra are illustrated in Table 2. The phyllosilicate SILMgSH presented a band related to νMg–OH at 3702 cm^{-1}, which was shifted to 3548 cm^{-1} in the SILMgSH/Cu matrix. For SILCuSH, the same band appeared at 3541 cm^{-1} and could be associated to the Cu–OH vibration mode. Other bands in these hybrids were attributed as follows: 3422–3446 cm^{-1} [νSi–OH and adsorbed water], 2925–2930 [νC–H], 1112–1127 cm^{-1} [νSi–C]; and the triplet at 1420, 1384 and 1340 cm^{-1} is associated to nitrate anion.[22–24] A vibration associated to Si–O–Si was observed at 1029 cm^{-1} for the SILMgSH hybrid and at 1046 cm^{-1} for both SILMgSH/Cu and SILCuSH hybrids. The band at 700 cm^{-1} in the SILMgSH spectrum is classically assigned to the overlap of Si–O and δ3Mg(OH) vibration mode in trioctahedral magnesium clays. For SILMgSH/Cu and SILCuSH matrices the bands at 771 and 784 cm^{-1} can be associated to δCuMg(OH) bending vibrations, which are more evident in the richest copper phyllosilicate as already mentioned in the literature.[21] For SILMgSH and other samples including SILMgSH/Cu and SILCuSH, the bands at 550, 511 and 510 cm^{-1} were attributed to Si–O groups. The band at 460 cm^{-1} is related to Mg–O for the SILMgSH hybrid and the band at 431 or 430 cm^{-1} was attributed to Cu–O in the SILMgSH/Cu and SILCuSH matrices, respectively.

The thermogravimetric curves of the phyllosilicates gave weight losses of 49.0; 41.4 and 47.0% for SILMgSH,

Table 2 Assignment of frequencies of vibration (cm^{-1}) of infrared spectra of mercaptopropyl hybrids

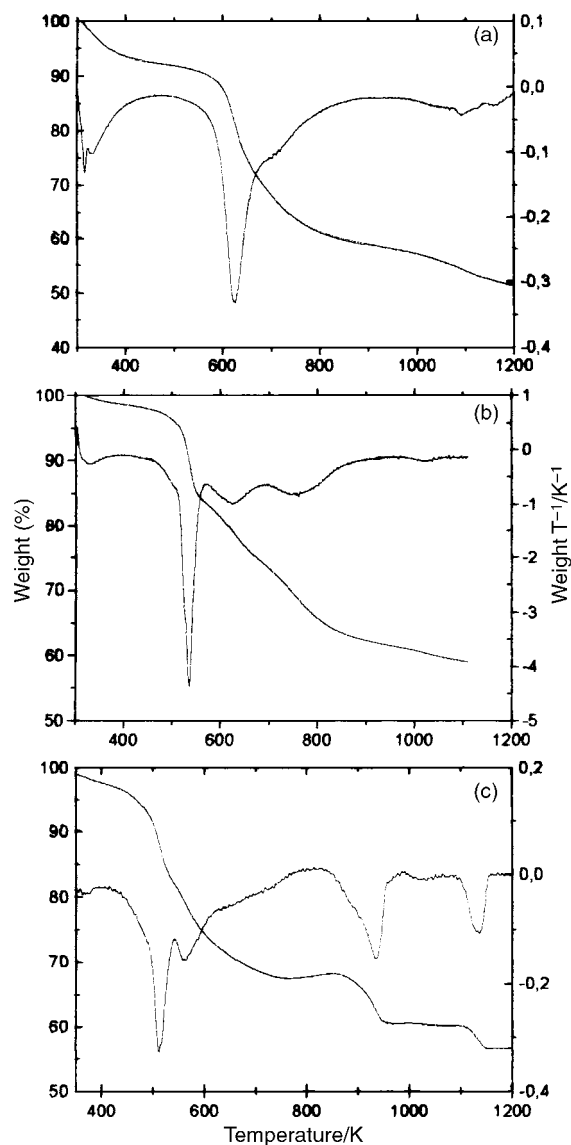| Vibrations	SILMgSH	SILCuSH	SILMgSH/Cu
νMg–OH	3702	—	—
νCu–OH	—	3541	3548
νSi–OH or νH$_2$O	3426	3446	3422
νC–H	2930	2925	2927
νS–H	2550	—	—
νSi–C	1123	1112	1127
νSi–O	1029	1046	1046
δCuMg(OH)	—	784	771
δ3Mg(OH)	700	—	—
δSi–O	550	510	511
δMg–O	460	—	—
δCu–O	—	430	431

Fig. 4 Thermogravimetric data for a) SILMgSH, b) SILMgSH/Cu and c) SILCuSH.

SILMgSH/Cu and SILCuSH, respectively, in a wide temperature range between 298 and 1123 K as illustrated in Fig. 4. The DTG curves showed a maximum peak at 623 K for SILMgSH and at 536 and 513 K for both matrices SILMgSH/Cu and SILCuSH, indicating that the thermal stability is lower for phyllosilicates containing copper. These mass losses occurred continuously with increasing temperature for the mineral with magnesium, while for SILCuSH plateaux are defined. The initial loss of mass can be associated to the release of water, giving 5.72% for SILMgSH, however, the release of water and organic material was observed for SILCuSH between 298 and 743 K. For SILMgSH, the organic group was released between 443 and 873 K, representing 35.3%, and another 8% between 873 and 1223 K is associated to crystalline transformations of inorganic layers.

The infrared spectra and DTG data showed sensible differences between the SILMgSH/Cu and SILCuSH hybrids. This fact indicates that these two samples can show identical crystalline structures, but the presence of the remaining magnesium in SILMgSH/Cu has a great influence on the properties of this nanocompound.

Solid state ^{13}C NMR spectroscopy is an important auxiliary tool to elucidate the structures of the silylating agent attached to the hybrids of these silicates. ^{13}C CP/MAS spectra for the solid SILMgSH and SILCuSH hybrids are shown in Fig. 5.
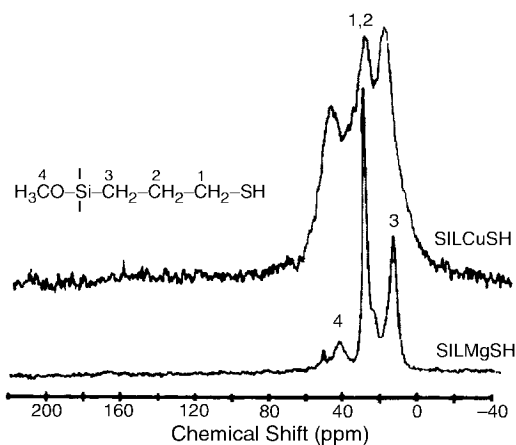
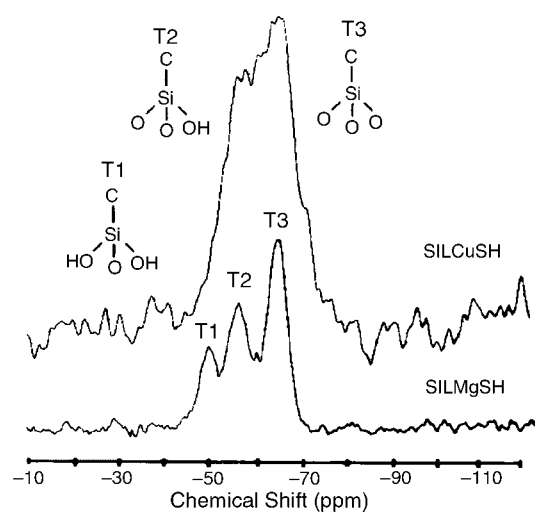**Fig. 5** ^{13}C CP/MAS NMR spectra of SILMgSH and SILCuSH hybrids.

Fig. 6 ^{29}Si HPDEC NMR spectra of mercaptopropyl magnesium and copper phyllosilicates.

The signals are in good agreement with the previous reported data on corresponding silica hybrids.[25–27] The spectra show a peak at 43.1 ppm associated to the C_4 atom of the methoxy groups of the organosilane. This result indicates that the hydrolysis of the silylating agent was incomplete. The peak at 28.7 ppm was assigned to both methylene groups, corresponding to carbons C_1 and C_2, and that at 13.3 ppm is due to the methylene group of carbon C_3. These data confirmed the presence of the complete organic chain bonded to the inorganic layer. The presence of broad and unresolved peaks associated to methylene groups in SILCuSH shows that the organic chains may be in a rigid solid-like environment.[28] The presence of copper species coordinated to SH groups may contribute to this behaviour. However, the same features are not observed for the SILMgSH matrix, because magnesium cations do not coordinated to SH moieties in the interlayer space.

^{29}Si NMR spectra can also provide information about the nature of the attachment of organic chains to the silicate hybrids; the peak assignments are based on previous results for analogous systems, which involved modified silicas and other phyllosilicates.[29–35] The ^{29}Si HPDEC NMR spectrum for SILMgSH is shown in Fig. 6. Three signals at −66.5, −56.0 and −48.4 ppm are associated to R–Si*–(OSi)$_3$, R–Si*–(OSi)$_2$–OH and R–Si*–(OSi)–(OH)$_2$ groups, respectively, which were quantified by deconvolution of the main peak as 39.8, 26.4 and 17.5% of these groups in the synthesized hybrids. This fact suggested the presence of a high degree of silanol groups within the phyllosilicate inorganic framework. This behavior was more pronounced for the SILCuSH hybrid where the broad signal between −45.0 and −69.0 ppm, with a maximum at −64.9 ppm, confirmed the proposed fact. Finally, these results suggested that in these materials, mainly in the SILCuSH hybrid, the condensation of silicon atoms to form the brucite framework structure was incomplete.

Based on the XRD results, infrared and NMR spectroscopic data the possible structure of the copper hybrid is represented in Fig. 7, where the presence of copper complexed with SH basic centres of the organic moieties in the interlayer space is shown.

The scanning electron micrographs (Fig. 8) in all cases show one agglomeration of small particles, and their sizes could not
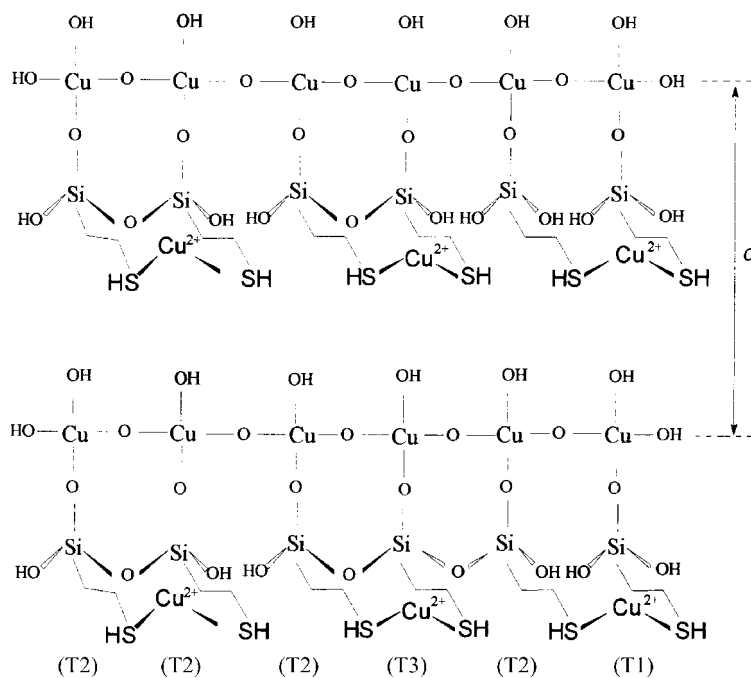

Fig. 7 Suggested structure of copper modified phyllosilicates, showing the formation of interlayer complexes involving two adjacent S–H groups. The network consists of a tetrahedral–octahedral arrangement with a basal spacing d. T1, T2 and T3 species are associated to silicon species in the backbone $RSi(O)_n(OH)_{3-n}$ for $n = 3$ to 1, respectively.
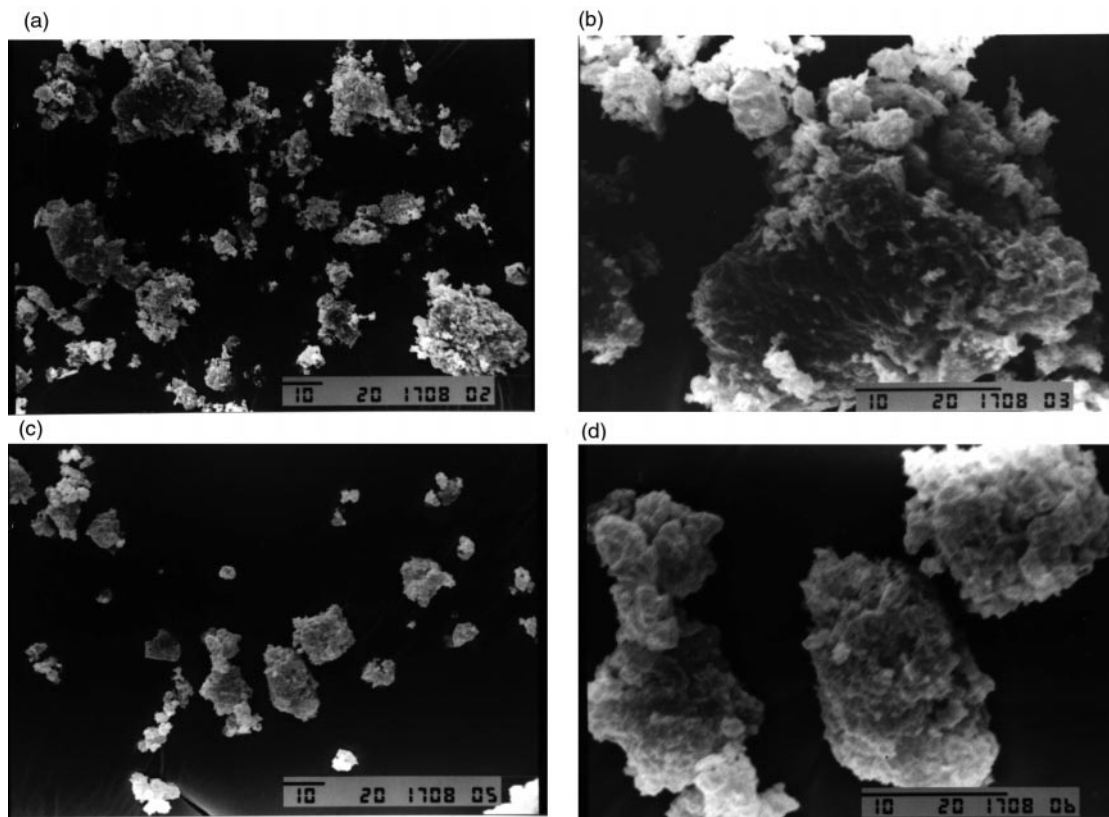
Fig. 8 Scanning electron micrographs for a) SILMgSH/Cu, b) SILMgSH/Cu (close-up view), c) SILCuSH and d) SILCuSH (close-up view). The scale bar represents 10 μm in each case.

be estimated. Energy dispersive scanning spectra showed the presence of strong silicon and magnesium peaks for the SILMgSH matrix and silicon and copper peaks for SILCuSH phyllosilicate as shown in Fig. 9. For SILMgSH/Cu, the spectrum showed a new peak associated to copper and no peak related to magnesium species. These results are also in agreement with elemental analytical data.
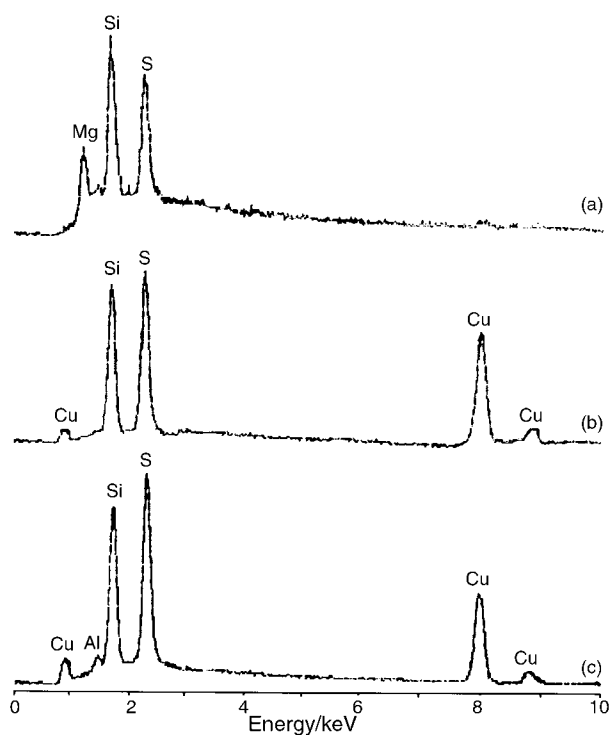

Fig. 9 EDX spectra showing the presence of copper, silicon, magnesium and sulfur species in (a) SILMgSH, (b) SILMgSH/Cu and (c) SILCuSH hybrids.

Conclusion

A series of layered organosilicates containing organic chains with distinct functional groups, covalently attached to inorganic layers, can be synthesized *via* the sol–gel method, in a simple low-temperature route. The magnesium phyllosilicate has significant intralamellar disorder, in contrast with the copper hybrid. This fact shows that the synthesis of the phyllosilicate structure *via* the sol–gel process, involving metallic cations in solution in the presence of trialkoxysilanes, depends on the nature of the cation and also on the hydrophobicity of the organic chain of the silane used. These hybrids are found to favour interactions with metallic cations from aqueous solution. For magnesium hybrids, the adsorption processes occurred through ion-exchange and are completed by complex formation, involving the organic groups within the cavity. These results suggest that the presence of organic moieties in the interlayer space change the properties of the inorganic–organic hybrids. The product containing adsorbed cations has been shown to be very similar to the organic copper phyllosilicate. The synthetic process has therefore been shown to be an alternative route to obtain the copper phyllosilicates, which was previously proposed as incompatible with such structures; this route has the great advantage that the synthesis is reliable at room temperature. These hybrids form a group of interesting compounds to investigate from the points of view of structural, chemical and catalytic properties, among another features.

Acknowledgements

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