

Zinc phyllosilicates containing amino pendant groups

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Abstract

Two new zinc silicate hybrids were synthesized via sol–gel process from the reaction of zinc ions with trialkoxyaminesilanes in aqueous basic medium at room temperature and at 373 K. The inorganic–organic hybrids obtained, named SILZn ($x = 1$ or 2) are related to 3-aminopropyl- and *N*-propylethylenediaminetrimethoxysilane, respectively. From nitrogen content, the number of pendant moles of organic groups in the matrices SILZn $_x$ ($x = 1$ to 2) were determined as 5.14 and 3.25 mmol g⁻¹, respectively. The thermogravimetric curves showed mass losses of 50.7% and 58.0% for the same sequence of hybrids, to give the oxides as residue. X-ray diffraction patterns gave basal distances of 2065 and 2814 pm for SILZn $_x$ ($x = 1, 2$), with well-formed particles of irregular shapes and sizes, as a characteristic of such material obtained from sol–gel process. The infrared spectra confirmed the attachment of the organic moieties on siloxane groups on the inorganic framework.

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1. Introduction

A set of inorganic matrices such as oxides, silicates and glasses have been used as adsorbents for contaminants species dispersed in solution, such as heavy cations, pesticides, herbicides and surfactants [1–4]. Taking into account the possibility of chemical modification of these materials by employing silylation reactions is an alternative route of inorganic–organic hybrid synthesis, in order to improve such properties [5]. On the other hand, the new materials obtained can be used for a series of new technological applications involving immobilization of catalysts [6,7], enzymes [8,9], cation extractions [10,11] and chromatographic determinations [12,13].

From the point of view of synthetic procedure of the modified inorganic matrices via silylant agents, two distinct routes can be used: (i) immobilization of silylant agents onto inorganic surface or (ii) through sol–gel process which occurs promptly with a simultaneous formation of the inorganic substrate, by including

organic moieties covalently attached to the prepared material [14]. Although a large number of investigations involving the first method, for example, for applied on silica gel, however, sol gel method has been received large attention due to the advantage of these synthetic hybrids over the natural ones. These special properties manifested as high purity, homogeneity and controlled porosity, which are desirable when these synthesized materials addressed for new applications as observed for many catalytic systems [15].

A remarkable number of investigations have been focused on synthesis of organic modified magnesium phyllosilicates through sol–gel process, recently. In the course of such preparations, the available magnesium ions are incorporated in the inorganic framework formed by trialkoxysilane reagents in aqueous basic conditions [16–24]. This procedure permitted the attachment of organic molecules in an inorganic network with similar talc structure. This phyllosilicate is a non-expandible layered magnesium silicate characterized as a 2:1 layer structure. This arrangement can be briefly described as magnesium sandwiched structure. With the participation of the other phyllosilicate component, the silicon atom, which is tetrahedrally coordinated by

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oxygen atoms, in bridging magnesium and the resulted brucite-type layer structure is formed by octahedral magnesium atom coordinated by oxygen atoms and hydroxyl groups. In case of hybrid material formed the organic chains originating from alkylalkoxysilane precursor distributed inside the interlayer region [16–24].

A great variety of compositions can be obtained by considering not only the metallic cation employed but also the specific organosilane used as precursor agent. Thus, the existence of distinct organophilic functionalities distributed into the interlayer cavities of phyllosilicate is closely dependent on the silane precursor. Thus, the employment of desired silane, which has organic functions attached on pendant chains, is a normal procedure to dispose donor centers such as nitrogen and sulfur in the prepared structures. The chosen donor centers can display chelating properties for extracting heavy cations from aqueous and non-aqueous solutions. In this context, the new desired hybrids can be applied for special adsorption of heavy cations in contaminated waters, pre concentration of cations and catalytic processes [1–7].

Some investigations on the commonest synthetic procedures involving magnesium and nickel phyllosilicates have been elucidated recently [16–18,20–23]. However, phyllosilicates containing cations like zinc, aluminum or copper are limited [19,24]. By exploring either the property of cations in forming phyllosilicates and the ability of nitrogen in coordinating [25,26], for this purpose the synthesis starting from a source of zinc and a silylant agent, containing amino groups to design the new route for a desirable material.

The present investigation deals with the synthesis and characterization of a zinc phyllosilicate containing amino groups attached on different pendant length chains. The influence of some effects associated with the reaction such as temperature, precursor salts and catalytic process involved are now reported.

2. Experimental

2.1. Chemicals

The silylant agents, 3-aminopropyl- and *N*-propyl-ethylenediaminetrimethoxysilanes (Aldrich) were reagents grade. Both zinc chloride and nitrate hexahydrate compounds (Fluka), methanol, sodium hydroxide (Merck) were all reagents grade, which were used without previous purification.

2.2. Synthesis of modified silicates

Zinc chloride or nitrate compounds (0.052 mol) were individually dissolved in 300 cm³ of deionized water and

the mixture was stirred at room temperature. Then, a solution of 1.39 mol dm⁻³ of the desired silane dissolved in methanol was slowly added dropwise to form a white suspension. In this preparation Si/Zn molar ratio was maintained at 1.33, as required for natural talc compound. After 1 h, 1.0 dm³ of 0.1 mol dm⁻³ sodium hydroxide solution was slowly added under stirring. This suspension was aged for 24 h at room temperature and the gel formed was centrifuged, successively washed with water until a detection of neutral pH in the filtrated portion and the solid was dried under vacuum during 24 h. The white formed solid was ground to yield a powdered material. Other synthesis were performed by using the same procedure, but maintaining a heating at 373 K or in absence of sodium hydroxide. An experiment control was performed under same conditions, without the presence of silylant agent, resulted the zinc hydroxide preparation.

2.3. Characterization

Carbon, hydrogen, and nitrogen contents were determined on a Perkin-Elmer model 2400 analyzer. At least two determinations were performed for each sample. The percentages of zinc in the materials were determined by atomic absorption spectroscopy. For this determination, the samples were first digested with HF and the resulting solutions were analyzed.

The XRD patterns were obtained with nickel-filtered CuK α radiation on a Shimadzu model XD3A diffractometer.

Infrared spectra were recorded on a Bomem MB-Series spectrophotometer, being the solid sample in KBr pellet, with 4 cm⁻¹ of resolution.

Thermal analyses were performed using a DuPont model 1090 B thermogravimetric apparatus coupled with a thermobalance 951 heated to 1273 K with a heating rate of 0.17 K s⁻¹, in a dry nitrogen atmosphere. The samples varied in weight from 15.0 to 30.0 mg.

Solid-state ¹³C NMR spectra were performed on a Bruker AC300/P spectrometer at room temperature. The measurements were made at frequencies at 75.5 MHz for using CPMAS technique. The spectra were obtained with a pulse repetition time of 3 s and contact time of 3 ms. The spinner rate was 4 kHz and the frequency was 75.5 MHz.

The distribution of particle sizes of all hybrids was estimated and the morphology studied through the analysis of the micrographs obtained by scanning electron microscopy. 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 the microscope Jeol JSTM-300.

2.4. Adsorption of copper

The isotherms of copper adsorption were obtained using the batchwise method [2,11], which consisted in suspending a series of samples of 25.0 mg of the modified zinc phyllosilicate (SILZn1 or SILZn2) in 20.0 cm³ of aqueous solutions, containing copper cation at several different concentrations, varying from zero to 0.01 mol dm⁻³. The solutions were mechanically stirred for 2 h at 298 ± 1 K and the solid was separated by centrifugation and dried at 313 K. The metal concentrations adsorbed were determined by using absorption atomic instrument of GBC 808 AA model.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis values for the synthesized zinc-phyllosilicates with 3-aminopropyltrimethoxysilane (SILZn1) and *N*-propylethylenediaminetrimethoxysilane (SILZn2) are listed in Table 1. The empirical and ideal values are based on R₄Si₄Zn₃O₈(OH)₂, where *R* is (CH₂)₃NH₂ or (CH₂)₃NH(CH₂)₂NH₂ for SILZn1 and SILZn2, respectively. This composition is very similar to the idealized structure of talc Si₄Mg₃O₁₀(OH)₂. Both carbon and zinc percentage values are in agreement with the expected calculated percentages for each compound taking account the idealized propose structure. Based on nitrogen content in both samples 7.20 ± 0.02% and 9.12 ± 0.01%, respectively, the number of pendant moles of organic groups in the matrices SILZn1 and SILZn2 were calculated as 5.14 and 3.26 mmol g⁻¹. Identically, from carbon content analyzed the expected C/N ratio were calculated, which values are very close to the predicted values, showing an agreement for both hybrids, and also indicating that organic chain originating from silylant agents were maintained intact in the hybrid. An inspection of carbon, nitrogen and hydrogen contents listed in Table 1, it is observed an increase of these elements as the size of the organic chain attached to the inorganic-organic hybrid is formed.

Table 1

Carbon (C), Hydrogen (H), Nitrogen (N), and Zinc (Zn) observed and (expected) percentages and the carbon to nitrogen (C/N) ratio for the hybrids synthesized using zinc nitrate as salt precursor and NaOH as catalyst at 373 K

Hybrid	C (%)	H (%)	N (%)	Zn (%)	C/N
SILZn1	18.4 (19.61)	5.76	7.20 (7.63)	25.50 (26.68)	2.98 (3.00)
ILZn2	19.54 (26.47)	4.88	9.12 (12.35)	20.90 (21.61)	2.50 (2.50)

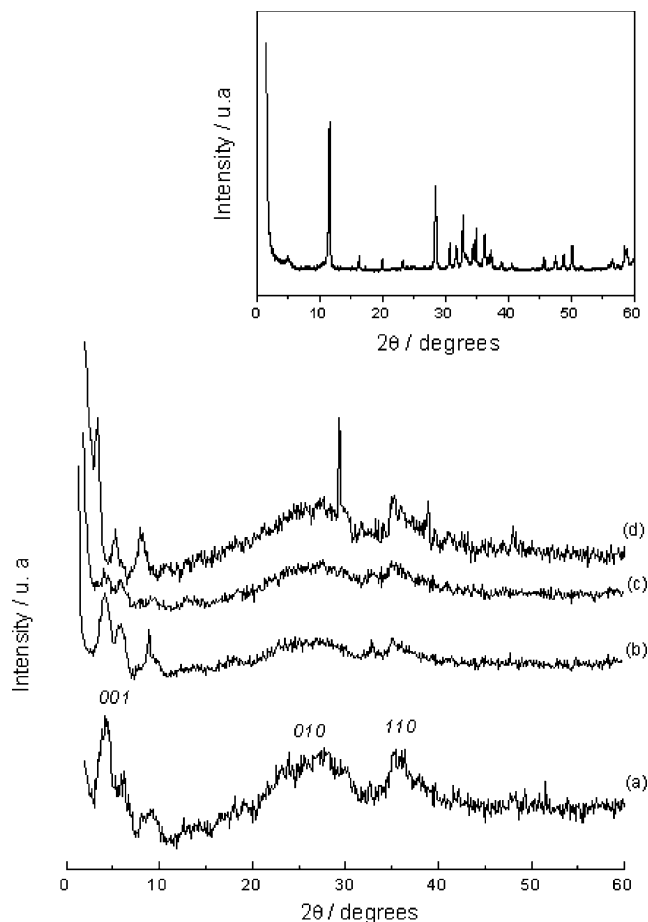


Fig. 1. X-ray diffraction of SILZn1 synthesized in different conditions: from zinc nitrate as precursor at 373 K (a), without catalyst and heating at 373 K (b), from zinc chloride and NaOH as catalyst at 338 K (c), and SILZn2 synthesized from zinc nitrate at 373 K and NaOH as catalysts (d). The inserted top figure is related to XRD data of zinc hydroxide compound.

3.2. X-ray diffraction

X-ray diffraction results for both hybrids, prepared in distinct conditions are shown in Fig. 1. The first diffraction peak for SILZn1 sample is related for the basal distances (*d*), which complete sequence is: 2065; 2082 and 2082 pm, whereas for SILZn2 *d* value was found at 2814 pm. As observed, different basal distances were obtained, dependent on the type of precursor salts used, which could be important factor to be considered in such kind of preparations.

In attempting to give the index data for the diffraction planes, the following series of zinc-phyllosilicates with the known *d* values, were considered: Zn₄(OH)₂Si₂O₇ (*d* = 305 pm), Zn₄(OH)₂Si₂O₇ · H₂O (*d* = 660 pm), Zn₂SiO₄, presenting five forms with *d* = 564, 678, 407, 285 and 226 pm [27–29]. As observed, all those zinc phyllosilicates showed lower *d* values in comparison with those obtained in the present study. Then, the X-ray diffraction data did not confirm the formation of

these zinc silicate phases in the hybrid preparations. Another aspect considered is the Zn/Si ratios in these natural zinc silicates which are different from those ratio used here for synthesizing Zn1 and Zn2.

Again, by comparing the obtained basal d values, which are high in value to the phyllosilicates presented in the literature, for example talc, $\text{Si}_4\text{Mg}_3\text{O}_{10}(\text{OH})_2$, with d value of 934 pm, presented a Mg/Si ratio very close to those used here. This fact suggests that organic chains were incorporated into the interlamellar space. This conclusion was based on data related to the length of the organic chains whose were estimated by employing a bond distance model, assuming a zigzag conformation of these chains. Thus, the pendant organic group lengths (D) were calculated as 543 and 939 pm, for the organic moieties: $-(\text{CH}_2)_3\text{NH}_2$ and $-(\text{CH}_2)_3\text{NH}(\text{CH}_2)_3\text{NH}_2$ attached to the inorganic backbone. By comparing the basal distances d , it was observed they adjusted to the values $d = 934 + 2D$. Thus, the highest values of d can be related to organic moieties in interlayer region. The indexing of some planes was based in XRD patterns of talc.

An interesting feature to improve the understanding of such proposition came from the experimental control, in which the zinc nitrate was hydrolyzed in presence of sodium hydroxide without silylant agent. The product of such reaction was identified by X-ray patterns as zinc hydroxide, as it is shown in the inserted part in Fig. 1. As observed, hydroxide zinc was not formed together with SILZn1 and SILZn2. These results and the elemental analysis confirmed that the obtained materials are isolated without the interference of the other phases, such as zinc hydroxide or other zinc silicates.

3.3. Thermogravimetry

The thermogravimetric curves for both synthesized zinc phyllosilicates are shown in Fig. 2. Similar trend in thermal curves related to mass loss for the hybrids from room to 673 K was observed. Total mass losses of 55% and 39% for SILZn2 and SILZn1, respectively. As clearly observed, the mass loss is proportional to organic content in each hybrid.

In the beginning a slight mass loss of 3.8% and 3.3% was detected, that corresponding to the physical water released for SILZn1 e SILZn2, respectively. The next mass loss for SILZn1 corresponded to amount of 26.3% between up to 400 to 700 K, attributed probably due to the simultaneous pyrolysis of organic content and condensation of OH structural. Another fraction of 9.0% from 700 to 1138 K range can be due to the collapse of the inorganic structure resulting in oxides such as ZnO and SiO_2 and silicon carbides. Identically, SILZn2 hybrid presented three decomposition steps of 19.2% between 559 and 673 K due degrade organic group and dehydrate of sheets, another one of 27.5% in

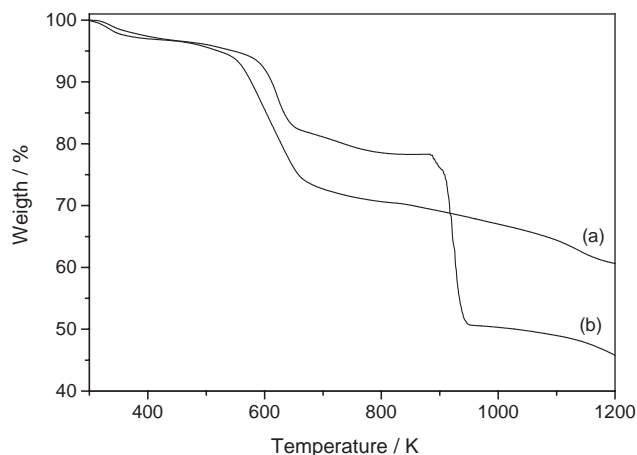


Fig. 2. Thermogravimetric curves for SILZn1 (a) and SILZn2 (b), both phyllosilicates were synthesized by using zinc nitrate as precursor and NaOH as catalyst at 373 K.

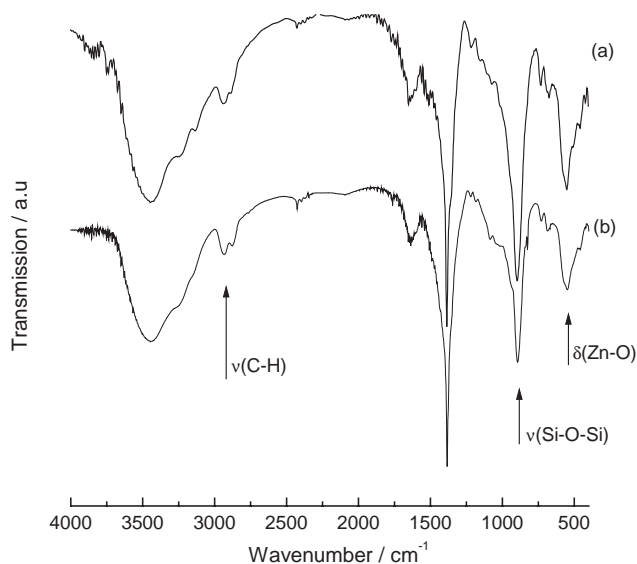


Fig. 3. Infrared spectra of SILZn1 (a) and SILZn2 (b) samples.

the 873 to 954 K interval and more one of 5.0% in 997 to 1209 K interval of temperature are also detected. Last decomposition reactions are related to the formations of oxide.

3.4. Infrared spectroscopy

The infrared spectra for inorganic–organic hybrid showing the presence of the organic groups covalently attached to inorganic matrix are illustrated in Fig. 3. These inorganic–organic hybrids presented identical bands for these new materials, which bands at 2986 and 2858 cm^{-1} can be attributed to asymmetric and symmetric C–H stretching and a band at 1506 cm^{-1} is due to the bending vibration of the protonated amino group. Another set of absorption bands were assigned

for $[\nu(\text{NO}_3^-)]$, $[\nu(\text{Si}-\text{C})]$, $[\nu(\text{Si}-\text{O}-\text{Si})]$, $[\delta(\text{Si}-\text{O})]$ and $[\delta(\text{Zn}-\text{O})]$ at 1384, 1112, 895, 550 and 463 cm^{-1} , respectively [30–35].

The presence of protonated amino groups in such structures can be due the interaction of hydroxyl of silanol groups or eventually due to the presence of OH linked to zinc. In both spectra were observed stretching bands at 3245 and 3145 cm^{-1} related to N–H vibration of the primary amines [30–32].

3.5. ^{13}C nuclear magnetic resonance

Solid state ^{13}C NMR spectroscopy is a useful tool to characterize the structures of the silylant agent attached in many inorganic structures [36–39], which procedure can be also applied to the presented hybrids. Thus, ^{13}C CP/MAS spectra for hybrids are shown in Fig. 4. The signals assigned as numbered in the established formula, are in a good agreement with the previous reports on corresponding silica hybrids, which were also synthesized by using a sol–gel process [36–39]. For SILZn1, three distinct signals were observed at 14.6; 23.8 and 43.4 ppm related to carbons C_1 , C_2 and C_3 , respectively.

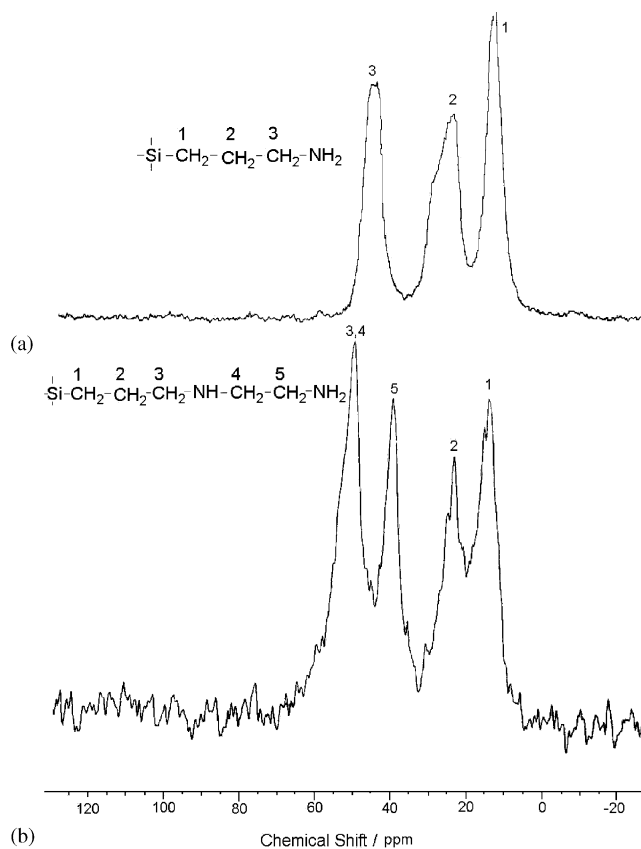


Fig. 4. ^{13}C NMR spectra of hybrids SILZn1 (a) and SILZn2 (b) synthesized by using zinc nitrate as precursor and NaOH as catalyst at 373 K.

For SILZn2 15.9; 23.8; 41.2; 52.3 ppm attributed to carbons C_x ($x = 1$ to 5), as shown in Fig. 4.

The presence of a possible unhydrolyzed methoxy group, originating from the silylant agent was not detected, because the free $\text{O}-\text{C}^*\text{H}_3$ group should be appeared with a single signal, as expected around 50 ppm, corroborating with the complete hydrolysis of this groups in basic medium. This result suggested that the structure of the organic chain of the silylant agent bonded to the backbone of the phyllosilicates did not change during the synthetic route employed. This conclusion is a support for previous elemental analyses.

3.6. Scanning electronic microscopy

The photomicrographs obtained by scanning electron microscopy shown in Figs. 5a and b for both

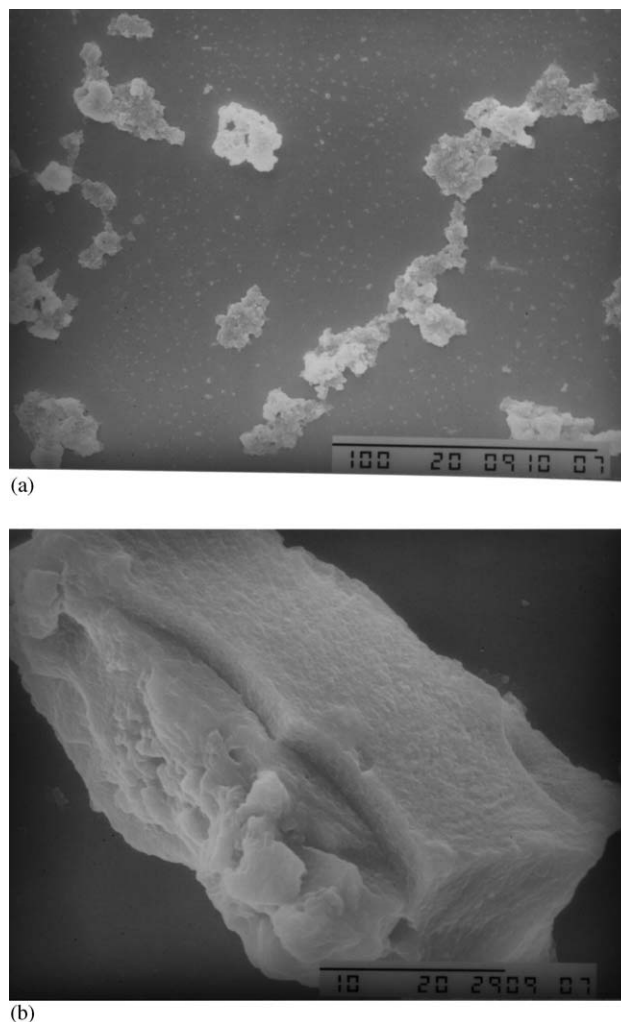


Fig. 5. Scanning electronic micrographs for SILZn1 (a) and SILZn2 (b) both silicates were obtained by using zinc nitrate as precursor and NaOH as catalyst at 373 K. The scale bar represents 10 μm in each case.

phyllosilicates, demonstrated a presence of well-formed particles of irregular shapes and sizes, which were characteristic for materials obtained from sol–gel process. This same behavior has been previously observed for other hybrids [22–24].

3.7. Isotherms of cooper adsorption

The ability of modified zinc phyllosilicates in extracting copper cations was evaluated measuring the sorption capacities. The initial white solids SILZn1 and SILZn2 changed their original color for cyan and blue, respectively, after copper adsorption. These colored solids were washed exhaustively with water and their structure was maintained indicating the occurrence of chemical adsorption and not a simple physical interaction.

The amount of copper adsorbed on solid was calculated by using the expression $N_f = N_i - N_s/m$, where N_f is the number of moles cooper adsorbed on solid, N_i and N_s are the initial and equilibrium numbers moles of cations on solution, respectively, and m is the mass of the modified zinc phyllosilicates. The comparative adsorption isotherms involving the two phyllosilicates for copper (II) from aqueous solution are shown in Fig. 6, where absence of a plateau in every case indicated that the basic centers of organic moieties are not saturated by this cations. The largest value of adsorption capacity was observed for SILZn2 associated the larger content of nitrogen in this solid.

Two possible forms of these interactions are shown in Fig. 7 illustrating the formation of different types of copper complexes on hybrids. The increment in adsorption suggested an effectiveness of the bidentate chelating moiety on the pendant groups in coordinating copper cations.

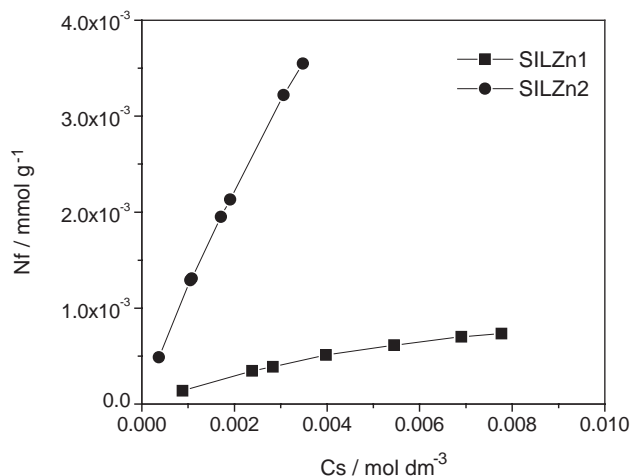


Fig. 6. Isotherms of cooper adsorption on zinc phyllosilicates.

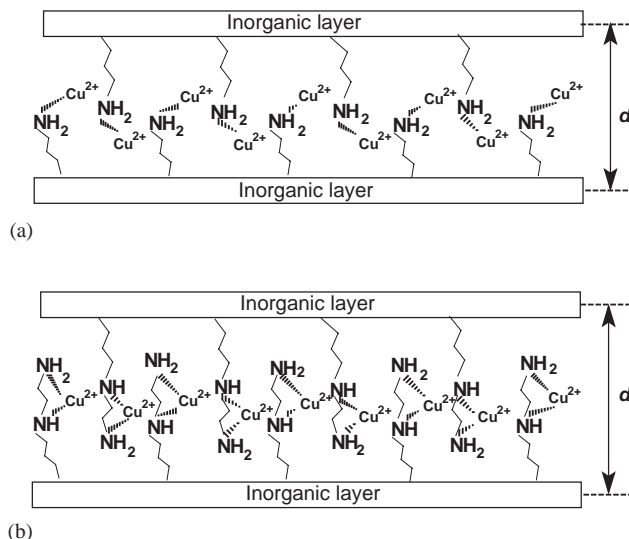


Fig. 7. Proposal structures of complexes formed on hybrids SILZn1 (a), and SILZn2 (b).

4. Conclusions

Two well-formed zinc hybrids corresponding to the phyllosilicate structures, containing amino groups covalently attached to inorganic network. Both compounds were synthesized via the condensation reaction involving zinc cations and the desired alkoxy silane in a single step route, which process is very convenient from the synthetic inorganic product point of view. These results indicated that the new synthetic hybrids presented a layered structure, whose interlamellar space depends on the type and length of the organic chain molecule incorporated into the phyllosilicates in these self-organized systems.

A relevant feature to be considered in the hybrid formed is related to the condition established for the reaction, which could be influenced by temperature and the specific catalyst, to give the expected crystallinity of final hybrid. Thus, the use of nitrate salts and appropriated temperature can derive the especial synthetic hybrid containing large amount of organic moieties covalently bonded to the formed inorganic framework.

Acknowledgments

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