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Some features associated with organosilane groups grafted by the sol–gel process onto synthetic talc-like phyllosilicate

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Abstract

Two new lamellar inorganic–organic magnesium silicates have been successfully synthesized by using sol–gel based processes under mild temperature conditions. The talc-organosilicates derived using two silylating agents as the silicon source, (i) 3-chloropropyltrimethoxysilane, and (ii) from the attachment of 5-amino-1,3,4-thiadiazole-2-thiol molecule to this precursor agent, yielded PhMg-Cl and PhMg-Tz phyllosilicates. These organoclays were characterized through elemental analyses, infrared spectroscopy, X-ray diffractometry, surface area, thermogravimetry, and carbon and silicon solid state nuclear magnetic resonance spectroscopy. The results confirmed the presence of organic moieties covalently bonded to the inorganic silicon sheet network of the 2:1 class of phyllosilicates, with a density of organic molecules of 6.6 ± 0.1 and 2.7 ± 0.2 mmol g^{-1} anchored on the inorganic layer and with interlayer distances of 1158 and 1628 pm, respectively. The nuclear magnetic resonances results in the solid state are in agreement with the sequence of carbons distributed in the pendant chains of the original silylating agents and the silicon bonded to oxygen atoms or carbon atoms of the inorganic sheets, as expected for the organically functionalized phyllosilicates. The enhanced potential of the new compound PhMg-Tz as a multi property material was explored in adsorbing cations from aqueous solution. The basic sulfur and nitrogen centers attached to the pendant chains inside the lamellar cavity can coordinate mercury, by presenting an isotherm saturated at 0.19 mmol g^{-1} of this heavy metal. The functionality of this organoclay-like material expresses its potential for heavy cation removal from an ecosystem.

Keywords: Phyllosilicate; Organosilane; Sol–gel; Adsorption

1. Introduction

Layered inorganic–organic crystalline compounds originating from one-step syntheses at room temperature, based on sol–gel process, lead to ordered self-assembled materials, which have been extensively investigated in recent years. Such combinations have properties that are explored not only associated with chemical intercalations, providing ordered stable organic moieties inside the inorganic matrices that enable them to act in many applications, but also to couple two properties in a unique solid, such as those related to the inorganic framework and to the attached organic moiety. The new generation of nanoscaled compounds, consisting of inorganic–organic hybrids, displays a promising class of materials, in which direct covalent bonds were established between the organic and inorganic sides of the formed layer. Silicon atoms attached to the inorganic backbone proceeded from an alkoxyde to form tetrahedral SiO_4 sheet units or from a desired silylating agent, to give covalent Si–C bonds, also adjusted in tetrahedral sheets. Normally the chosen metallic divalent cation components are located in an octahedrally arrangement in the layer by forming 1:1 or 2:1 families [1–6]. The synthetic materials have some advantages over the similar natural clays, such as smectite or mica, due to the purer chemical composition or controlled quantities of defects in the final product [7]. A series of layered inorganic–organic materials is based on the common magnesium silicates, resembling the talc parent structure $Si_8Mg_6O_{20}(OH)_4$, synthesized from the sol–gel process, enabling the attachment of covalently-linked organic functionalities through a one-step direct-synthesis procedure with the advantage of using mild reaction conditions, as previously proposed [8–11].

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The design of the new hybrid largely depends on the distinct organofunctional trialkoxysilanes used in the sol–gel process. Thus, the choice should be based on the specific silylating agent that contains the organic moiety with a desired functionality, which will covalently attach onto the C–SiO_3 tetrahedra formed in the final structure. For instance, short [12] or long [13] chains can be formed in the phyllosilicates as a consequence of the agent employed in these synthetic processes.

The majority of this class of layered organosilicate compounds has magnesium as the octahedral cation, followed by nickel [8,11–20]. However, other organically modified phyllosilicates have also been synthesized, including aluminium [11,21,22], copper [18], zinc [23], and calcium [24] inside the inorganic layer. The layered orgnanosilane hybrids containing magnesium and nickel have a lamellar structure analogous to 2:1 trioctahedral phyllosilicates. When aluminium and copper metals are involved, structures similar to 2:1 dioctahedral phyllosilicate or 1:1 phyllosilicate are formed. The hectorite-like phyllosilicate derivative was synthesized under basic condition by combining magnesium and the silylating agent [25].

Another important feature to mention with these synthetic materials is related to their applicability, and in some cases, requires an special sequence of reactions in order to incorporate other organic molecules, also giving conditions to enlarge the original chain from the previous, initially bonded substrate. Thus, a mixture of organosilane precursors lead to multifunctional layered magnesium organosilicates [14]. Although the organic moiety attached to the inorganic backbone restricts the use of high temperature, these phyllosilicates can be applied as sorbents, environmental barriers, polymer fillers, catalytic supports or chemical sensors [26]. The ferromagnetic properties in talc-like cobalt phyllosilicates were also determined [27]. The aminofunctionalized phyllosilicate hybrid immobilized with a porphyrin derivative has been used in alkane or alkene oxidation reactions by iodosylbenzene and hydrogen peroxide [28].

The synthesized magnesium, nickel, copper or zinc phyllosilicates containing attached amine, thiol or macrocyclic groups bonded onto the organic moieties, within the layered inorganic–organic nanocomposites, useful host matrices for the adsorption of cations from aqueous solution at the solid/liquid interface are prepared [10,12,17–19,23]. The first example involved the reaction of a glycidoxypropyl modified nickel phyllosilicate with a macrocyclic molecule to determine the binding constant for some divalent first transition cations [10] and the thermodynamic data of the cation/ligand bond formation have also been determined [12,18,19].

The reactivity of this class of layered inorganic nanocompounds are mostly explored to cation removal, mainly those that containing nitrogen [17,23] and sulfur [12,18] basic centers attached to the pendant groups directly bonded to the inorganic backbone. Those magnesium phyllosilicates that included mercapto groups demonstrated so efficient agent to heavy cation removal [29]. Thus, isolated brown-colored samples are originating from adsorption and in situ tetrachloauric acid reduction, to display nanosized gold particles within the pyllosilicate layers [11]. As a general behavior, the cation complex formation inside the lamellar cavity causes an increase in interlayer distance and in some cases an acidic treatment enabled to recover the material without changing its adsorption property [19]. The ability in extracting heavy cations from aqueous solution at the solid/liquid interface is a promising property to be explored in many applications for such class of compounds.

This investigation deals with the synthesis and characterization of covalently linked inorganic–organic lamellar hybrids based on magnesium organophyllosilicate. The resembled functionalized organoclays were synthesized under mild temperature conditions from methanolic solutions containing magnesium nitrate and organotrialkoxysilanes. Two lamellar talc-like compounds were functionalized by using (a) the precursor silylating agent 3-chloropropyltrimethoxysilane and (b) a new agent resulting from the reaction of the 5-amino-1,3,4-thiadiazole-2-thiol molecule with the precursor silane.

2. Experimental

2.1. Reagents and solvents

The reagents 3-chloropropyltrimethoxysilane (CPTS), 5-amino-1,3,4-thiadiazole-2-thiol (ATT) (Aldrich) and magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$, were used without further purification. Triethylamine (Aldrich) was previously treated with a pellet of potassium hydroxide (Nuclear) for 24 h and distilled under nitrogen. Methanol reagent grade was also previously distilled before use. Mercuric solutions were prepared from mercury chloride in doubly distilled water obtained from an ultra-pure Milli-Q Millipore 18.2 MΩ cm system.

2.2. Synthesis

Two different organophyllosilicates were synthesized from mixtures of magnesium nitrate and silylating agents:

(a) To a polyethylene flask containing 1.07 g (4.16 mmol) of magnesium nitrate hexahydrate dissolved in 100 cm^3 of doubly distilled water, a methanolic solution containing 1.0 cm^3 (5.41 mmol) of the silylating agent 3-chloropropyltrimethoxysilane was added dropwise at room temperature. The molar relation Si/Mg was calculated to be 4/3. The dense pale suspension was stirred for 1 h, 20 cm^3 of an aqueous solution of sodium hydroxide 0.10 $mol\,dm^{-3}$ was added dropwise. The suspension was aged for 24 h at room temperature, followed by filtration and washing with doubly distilled water to neutral pH [13]. The solid, named PhMg-Cl, was dried under vacuum for 48 h at 323 K.

(b) *The silylating agent* was synthesized under anhydrous conditions [30]. Thus, 5.0 cm^3 (27.1 mmol) of CPTS in 25 cm^3 of dry methanol was added to 3.61 g (27.1 mmol) of ATT, dissolved in the same volume of methanol, followed by addition of 2.0 cm^3 of triethylamine (14.3 mmol), which is used as a deprotonating agent This solution was maintained under reflux in a nitrogen atmosphere for 24 h. After this time, one third of the solvent was removal under vacuum. The freshly prepared silylating agent was added through an addition funnel to a stirred solution containing 5.22 g (20.4 mmol) of magnesium nitrate hexahydrate dissolved in 200 cm^3 of water, in order to maintain