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Stability of layered aluminum and magnesium organosilicates

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Abstract

New nanostructered layered inorganic–organic aluminum (Sil–Al) and magnesium (Sil–Mg) organosilicates – were prepared by a single step template sol–gel route under mild conditions, using a new alkoxysilane [(3-urea-dodecyl)propyl]triethoxysilane, containing embedded polar urea groups. The hybrids were characterized by elemental analysis, infrared spectroscopy, solid-state ^{29}Si, ^{13}C and ^{27}Al nuclear magnetic resonance and X-ray diffraction. The XRD data showed that the magnesium hybrid material exhibits a lamellar structure similar to talc, a natural inorganic silicate. In order to employ these alternative sorbent materials for solid phase extraction applications, the chemical stability of the hybrids were investigated over a wide pH range varying from 2 to 12.

Keywords: Organosilicates; Phyllosilicate; Silsesquioxanes; Hybrids; Sol–gel; Urea-alkoxysilanes

1. Introduction

Organoclay materials can be prepared through many different synthetic routes. Nowadays, there is a renewed interest in the synthesis of nanostructured inorganic–organic clays [1] using one-pot sol gel template reactions under mild conditions [2–5]. The pioneer research in this field was the preparation of layered magnesium and nickel organosilicates, in which 3-(methacryloxy)propyl chains were covalently bonded to a 2:1 phyllosilicate-like framework, by forming stable Si–C bond [6]. From the structural viewpoint, the organoclays obtained exhibited well-ordered octahedral and slightly disordered R–SiO_3 tetrahedral sheets [7].

The principal synthetic procedure, based on the reaction of organotrialkoxysilane with magnesium salts in a basic medium, under mild conditions, was explored for a great variety of silanes containing different organic functionalities [8–17]. Similar synthetic routes were also employed to produce transition metal organophyllosilicates by co-polymerization of the alkoxysilane with other inorganic salts such as nickel [6,18], aluminum [7,10,16], copper [19], zinc [20] and calcium [21]. Syntheses under hydrothermal processes were also investigated for preparation of these layered organoclays, using the same reagents: a trialkoxysilane as silicon source and an inorganic salt in an aqueous basic medium [22–27].

Structural studies demonstrated that the resulting materials exhibit phyllosilicate structures analogous to those found for natural minerals, in which the organic functionalities are allocated into the interlayer space [22]. For the magnesium silsesquioxanes, the hybrids showed lamellar structures with a composition that can be approximated to $Si_8R_8Mg_6O_{16}(OH)_4$, taking into account the parent structure of talc, $Si_8Mg_6O_{20}(OH)_4$ [8]. Normally, the phyllosilicate structure is formed by two single R–SiO_3 tetrahedral layers overlaid by a brucite layer, in which magnesium is sited in an octahedral environment, bonded to four oxygen atoms and two OH groups.

For the aluminum organosilicates, the layered structure is similar to natural pyrophyllite whose chemical formula is $Si_4Al_2O_{10}(OH)_2$. Here, the two single layers in pyrophyllite are bonded by Al^{3+} instead of Mg^{2+}. All octahedral

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centers in talc are occupied by magnesium, while in pyrophyllite, only two thirds are loaded by aluminum ions. Consequently, talc shows a trioctahedral cation occupation unit and for pyrophyllite a dioctahedral structure is found.

The mechanism of phyllosilicate structure formation was first proposed taking into account a prior mesoporous silica model [10]. This model suggests an initial micelle organization of the silylating agent, induced by its hydrophobic chains, while the external sphere is composed of negatively charged silanols, which are derived from the hydrolyzed alkoxy groups. From our point of view, this model does not explain the layered structures observed for organophyllosilicates. Later on, another proposition considered the formation of the brucite layer in basic medium templates to establish the lamellar structure, in which the $RSiO_3$ units are linked to the inorganic magnesium framework by Si–O–Mg bonds [28]. Nowadays this latter model is more acceptable.

A new generation of these hybrids displays a promising class of materials, especially for anchoring nanoparticles through interacting with the mercaptopropyl groups attached to the inorganic backbone [8]. Another advantage is the exfoliation of these hybrids in polar or non-polar solvents [29] in order to increase their surface area, as well as for the fabrication by spin coating of thin films over different substrates.

Other potential applications include use as sorbents for heavy metal removal [30] by formation of complex species with the pendant organic groups available in the lamellar space. Polymer composites were also investigated using a methacryloxypropyl-functionalized magnesium phyllosilicate [31]. This a very interesting application since organoclays act as nanosized filler/reinforcement particles and due to their hydrophobic nature, they are better dispersed and show better interfacial bonding to the bulk polymer matrix, when compared to conventional microsized inorganic fillers.

Recently, biomolecules were successfully immobilized into the gallery space of aminopropyl-functionalized magnesium phyllosilicates [11]. The enzyme–organoclay nanocomposites showed higher catalytic activity mainly when compared with the native enzyme in solution, under aggressive conditions, such as pH 9–10 and a temperature of 65 °C. However, applications of these layered organoclays in catalysis are somewhat limited due to the quite low stability of these organic moieties at higher temperatures.

The aim of this paper is to report the synthesis of new inorganic–organic nanocomposite obtained from the reaction of magnesium or aluminum ions with the silylating agent [(3-urea-dodecyl)propyl]triethoxysilane, having embedded polar urea groups [32]. The main goal in this study is the physicochemical characterization and the chemical stability evaluation over a wide pH range, in order to employ these materials as an alternative sorbent for solid phase extraction applications.

2. Experimental

2.1. Chemicals

The silylating agent [(3-urea-dodecyl)propyl]triethoxysilane, $(CH_3CH_2O)_3Si–(CH_2)_3–NH–C(O)–NH–(CH_2)_{11}–CH_3$, was synthesized and characterized in our laboratory, according to a previous described synthetic route [32]. All other reagents, such as magnesium and aluminum nitrates (Carlo Erba), ethanol and NaOH (Merck) were reagent grade and used as received. The phosphate buffers in the acid range were prepared using H_3PO_4, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ (Aldrich), while other ammonium buffers were prepared with NH_4OH and NH_4Cl (Carlo Erba). The amount of each reagent to prepare all buffer solutions was determined using the equation: $pH = pK_a + \log[A^-]/[HA]$, to reach the desired pH value. Metallic magnesium and aluminum (99.9%) were used for the preparation of the standard solutions and were also purchased from Aldrich. Deionized water was purified using a Milli-Q water system (Millipore).

2.2. Synthesis

The inorganic–organic hybrid material, containing a C_{12} urea functionality was prepared following a previous described synthetic procedure [15]. For the magnesium organosilicate synthesis, the Si/Mg molar ratio was maintained at 1.33, which is found in the stoichiometric natural talc silicate. Firstly, 10.00 g (23.0 mmol) of the alkoxysilane dissolved in 100 cm^3 of ethanol was added to a freshly prepared solution containing 4.46 g (17.4 mmol) of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 cm^3 of ethanol. Approximately, 70 cm^3 of a 0.50 mol dm^{-3} NaOH solution was slowly added to the resulting alcohol mixture with an addition funnel, under magnetic stirring, while the temperature was maintained at 323 K. The pH was checked by using a freshly calibrated pHmeter (Micronal B474) and a value of 11.5 was obtained. The addition of the aqueous NaOH solution caused the formation of a white suspension, which was aged for 24 h at 323 K. After that, the white solid was filtered, extensively washed with deionized water and ethanol and dried under vacuum for 6 h.

A similar procedure for synthesizing the pyrophylite-like hybrid containing aluminum was based on a Si/Al molar ratio of 2. Briefly, a 100.0 cm^3 of ethanol containing 4.33 g (11.6 mmol) of $Al(NO_3)_3 \cdot 9H_2O$ was added to 10.00 g (23.0 mmol) of the C_{12} urea alkoxysilane dissolved in the same volume of ethanol at 323 K. Under magnetic stirring, 70 cm^3 of 0.50 mol dm^{-3} NaOH solution was slowly added and a white suspension was obtained, which was aged, filtered, washed and dried as described for the Sil–Mg organophyllosilicate.

2.3. Characterizations

Carbon, hydrogen and nitrogen percentages for the new hybrids were determined on a Perkin Elmer model 2400