



Physico-chemical of organo-functionalized magnesium phyllosilicate prepared by microwave heating



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ABSTRACT

In this work, organo-functionalized magnesium phyllosilicates were prepared via hydrothermal synthesis with four sources of silicon: 3-aminopropyltriethoxysilane (AMPTS), N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TMSPEDA), N-[3-(trimethoxysilyl)propyl]-diethylenetriamine (TMSPETA) and tetraethoxyorthosilane (TEOS). Microwave radiation (MW) was employed as heating source and the results were compared with the analogous materials synthesized by conventional heating in an oven (CE). The materials obtained were characterized using X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), solid state ^{29}Si and ^{13}C nuclear magnetic resonance (NMR), thermogravimetry (TG) and elemental analysis of carbon, nitrogen and hydrogen (CHN). The 2:1 type of trioctahedral phyllosilicate was confirmed by the presence of the 060/330 reflection, at $59.5^\circ 2\theta$. The presence of the organic modifier was proven by the bands at 2930 , 2850 , and 1490 cm^{-1} and the typical features of the phyllosilicate were found at 3700 cm^{-1} (Mg–OH) and 1014 cm^{-1} (Si–O–Si). ^{13}C -NMR showed that the organic chains were intact in the interlayer space (5–64 ppm). Thermogravimetry indicated that these pending groups were stable in this support until 200°C when they begin to decompose. Silicon-29 NMR confirmed that the pending groups were bound directly to the silicon atoms by the resonance of Si–C bond at 48 and 55 ppm. The results showed the success of the procedure for all the proportions of the silicon sources used, with a reduction of reaction time in the range from 91% to 96% using microwave radiation in relation to the conventional heating oven.

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1. Introduction

Layered silicates have found ingenious applications recently due to their ion-exchange capacity and the possibility of intercalation of organic species [1]. In general, phyllosilicates are important industrial minerals, the most important being the talc. It is a valuable material in the paper, rubbers, ceramics, polymers, paint, lubricants, cosmetics and pharmaceutical industries [2,3], because of its inertness, whiteness, low thermal and electrical conductivity and adsorption capacity of organic substances [3].

Talc, $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$, is a non-ionic member of 2:1 trioctahedral magnesium phyllosilicate series, constructed from a central layer of octahedrally coordinated oxide/hydroxide magnesium chain – the brucite layer – engaged, on both sides, to a tetrahedrally coordinated silicate structure [4], Fig. 1 [5]. Each of these three-layer-packs interacts with the next one by van der Waals forces. The layers are capable of sliding easily over one another, which results in the soft character of the mineral [2].

Generally, most of the syntheses are carried out via conventional electrical heating. In this procedure, the synthesis is performed by conductive heating with an external heat source, such as an oil bath, a heating mantle or a laboratory furnace, as in the case of hydro/solvothermal reactions [6]. Heat transfer occurs from the source to the surface of the material and is then conducted to the core of the material [7]. Although a large number of works focused on the conventional heating method it is acknowledged that it has certain limitations, such as slow and rather inefficient heating, because of its dependence on convection current and on the thermal conductivity of the several materials and substances that have to be penetrated by the heat. As a result, the temperature of the reaction vessel is generally higher than temperature of the reaction mixture [6].

In view of the considerations above and in an attempt to overcome such limitations, microwave energy has been recently employed in the syntheses of solids. Interaction of materials with microwave is generally described as dielectric heating. Several mechanisms can be responsible for this, including electronic, ionic, molecular and interfacial polarization [7], and occurs by converting electromagnetic energy into heat.

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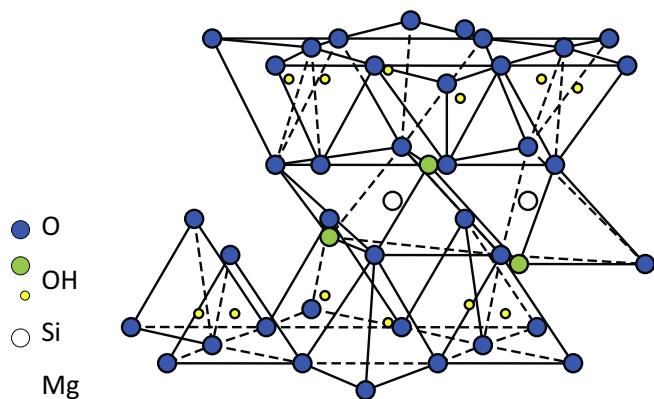


Fig. 1. Schematic representation of the talc structure (2:1 clay mineral), adapted from [5].

The microwave heating of a dielectric material have the advantages over conventional heating; some of them are fast and non-contact heating, energy transfer instead of heat transfer, selective material heating, possibility of attaining a more uniform product in crystal dimensions and composition, reduction in the synthesis time, and many more [8–10], being the reduction in time the most general and important advantage of microwave heating.

The synthesis of materials such as mesoporous molecular sieves [11], hydrotalcites [12], layered phyllosilicates [13,14], organoclays [15], zeolites [16,17] and organo-functionalized solids or hybrids through direct synthesis [18,19] were reported. Although syntheses using microwave radiation as heating source are methods in the way to be successfully established, to the best of our knowledge, it has not been applied for the preparation of functionalized magnesium phyllosilicate samples. In this work, organo-functionalized magnesium phyllosilicate are synthesized using microwave heating and conventional heating for comparison in order to determine possible reductions in the syntheses durations and variations in the nature or quality of the final materials.

2. Materials and methods

2.1. Materials

In this work, sodium hydroxide (NaOH, Merck), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Ecibra), tetraethoxyorthosilane (TEOS, Acros), 3-aminopropyltriethoxysilane (AMPTS, Sigma Aldrich), N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TMSPEDA, Sigma Aldrich) and N-[3-(trimethoxysilyl)propyl]-diethylenetriamine (TMSPETA, Sigma Aldrich) were used.

2.2. Synthesis of organo-functionalized magnesium phyllosilicate

The organo-functionalized magnesium phyllosilicates were prepared following the method reported by Ferreira et al. [1]. In a typical synthesis, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (12 mmol) was dissolved in distilled water (100 mL). Silicon sources (TEOS, AMPTS, TMSPEDA or TMSPETA) were added in volumes displayed in [Support Information Table S1](#) and resulting in N:total silicon molar ratios of 25%, 50%, 75% and 100%. Then, NaOH (48 mL, 0.5 mol L^{-1}) was added dropwise under magnetic stirring. The resultant suspension was aged for 4 h, at 50°C , and hydrothermally treated using a microwave oven (DTG 100 Plus model, Provecto Analítica) under the conditions reported in [Support Information Table S2](#). The total reaction time was 2 or 4 h. Samples were prepared also by conventional heating (CE) for comparison. The same gel used in microwave

heating was treated during 48 h, at 100°C . The product mixture was dispersed in distilled water, left overnight, and centrifuged, washed with distilled water, dried at room temperature and size sieved at 0.074 mm.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

The X-ray diffraction patterns of the organo-functionalized magnesium phyllosilicates were obtained using a Shimadzu model XRD 7000 diffractometer, operating in continuous scan mode with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The scan speed, voltage and current were $2^\circ 2\theta \text{ min}^{-1}$ (from 1.4° to $70^\circ 2\theta$), 40 kV and 30 mA, respectively, with graphite monochromator, at room temperature using 0.5° , 0.5° and 0.3 mm slits for entrance, scattering and exit.

2.3.2. Fourier transformed infrared spectra (FTIR)

The infrared spectra were obtained using a Nicolet model 6700 FT-IR spectrophotometer, with 128 scans at 4 cm^{-1} resolution of 0.05 wt.% KBr pressed pellets. All the data were normalized with the intensity of the Si–O–Si peak.

2.3.3. Magic angle spinning nuclear magnetic resonance spectra (MAS NMR)

The nuclear magnetic resonance spectra of the organo-functionalized magnesium phyllosilicates were obtained using Bruker Avance II + 400, at room temperature. The measurements were made at a resonance frequency of 79.5 MHz for ^{29}Si and 100.6 MHz for ^{13}C . For the ^{29}Si spectra, decoupling of the proton was employed, with a pulse repetition time of 60 s and pulse angle of 90° . For ^{13}C spectra, the CPMAS technique was employed, with a pulse repetition time of 3 s and a contact time of 0.003 s.

2.3.4. Elemental analysis

Elemental analysis of carbon, hydrogen and nitrogen was performed using a CHNS/O Analyzer 2400, Series II, from Perkin Elmer.

2.3.5. Thermal analyses

Approximately 10 mg of the organo-functionalized magnesium phyllosilicates were measured in alumina crucible and the thermal analyses were obtained using a TGA/DTA Setaram Instrumentation Setsys 16/18 model, coupled with a mass spectrometer, ThermoStar model, from Pfeiffer. The samples were analyzed using N_2 flow (16 mL min^{-1}), from 20 to 1000°C , at a heating rate of $10^\circ\text{C min}^{-1}$.

3. Results and discussion

3.1. Synthesis of organo-functionalized magnesium phyllosilicate

The organo-functionalized magnesium phyllosilicate synthesis using MW as the heating source was successfully performed with significant reduction in the synthesis time: from 48 h in the CE to 2 or 4 h under MW conditions. Several results to be discussed here show that the resulting materials are of similar or better quality.

The amine:TEOS molar ratios used in this study, indicated in the Experimental Part, were chosen in order to study the development of materials with a variable quantity of organic groups linked to surface silicon atoms while keeping the N:Si molar ratios constant. In that sense, monoamine modified phyllosilicates at 25% AMPTS/total Si molar ratios have the same N/Si molar ratio as the 12.5% TMSPEDA/total Si and as the 8.33% TMSPETA/total Si molar ratios.

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