

METAL-ORGANIC LAYERED SILICATE INTERCALATION NANOCOMPOSITES: A ROUTE FOR THE PREPARATION OF CERAMIC NANOPARTICLES

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Kaolinite is a 1:1 dioctahedral clay mineral composed of structurally asymmetric layers: a gibbsite-like layer, with aluminum atoms in octahedral coordination with apical oxygens and hydroxyls, and a silicate layer structure, with silicon in tetrahedral coordination with oxygen [1]. In the intercalation complexes of kaolinite, the reactive guest molecules are located in the interlayer spaces, expanding the silicate layers [2]. The inserting molecule breaks the hydrogen bonds between the kaolinite hydroxyl groups and the oxygens of the next adjacent siloxane layer. Then, the inserting molecule forms hydrogen bonds with the siloxane layer or with the hydroxyl surfaces of the gibbsite-like layer [3]. Intercalation of kaolinite is a promising area of research since different and unique properties can be obtained as a combination of the ones of the silicate and the the organic-inorganic compound. New fabrication routes of ceramic nanoparticles can be obtained by intercalating organ-metallic compounds. In this work, Aluminum isopropoxide was intercalated in kaolinite resulting in a composite with an increased ability of expanding its interlaminar distance with temperature. This improved expansion ability is of interest for catalysis applications. The interlaminar distance at 25 °C was 11.24 Å, while at 200 °C that distance increased to 15.12 Å and at 410 °C the distance was 20.56 Å. Temperatures above 1000 °C lead to mullite formation and high purity mullite was obtained above 1200 °C. The intercalation was performed by the displacement of dimethyl sulphoxide (DMSO) and other compounds previously intercalated [4-6]. The intercalated nano-composite was characterized by DRX, TDRX, FTIR, TG-DSC, SEM and TEM.

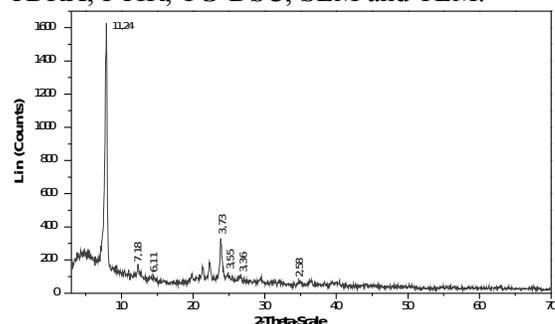


Fig. 1. XRD spectrum of the aluminium isopropoxide-kaolinite nanocomposite.

Fig 1 shows diffractions at 11.24 and 3.73 Å, which are typical of the intercalated compound. Basal diffractions of kaolinite (d001 7.18Å, d002 3.55Å and d003 2.58Å) appear at low intensity, which indicates a high degree of transformation of kaolinite. Presence of pseudohematite, resulting from Aluminum isopropoxide hydrolysis at room

temperature [7] is also observed (d020p 6.11). Analysis of the relative intensities of the main reflections gives a 96.7% of intercalated compound.

Thermal Behavior. The following endothermic peaks, observed in Figure 2, can be assigned as follows:

118°C Dehydration process (mass loss: 11.44%).

150°C De-adsorption process (8.53%).

204°C Reactive melting (9.11%).

292°C Reactive decomposition (9.70%).

318°C Combustion of products from reactive decomposition (11.68%).

497°C Dehydroxylation of the kaolinite matrix (1.64%).

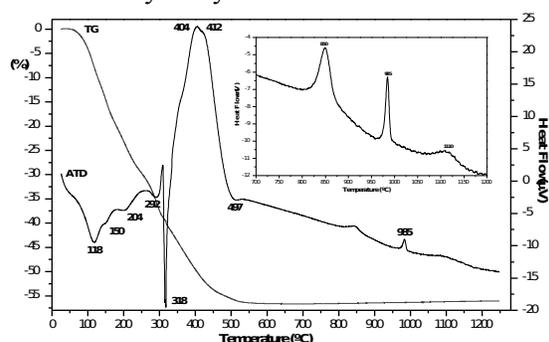


Fig 2. TG and DSC plots obtained in a Setaram Labsys TG-DTA, using air at 1.5 bar and a 5K/min heating rate.

Heating between 100 and 500°C caused the removal of the guest molecules, which occurs over several stages. The following exotherms can be observed:

404°C Combustion of products from the reactive decomposition.

412°C γ -alumina formation.

850°C θ -alumina formation

985°C Crystallinity reorganization of the kaolinite matrix.

1100°C α -alumina formation

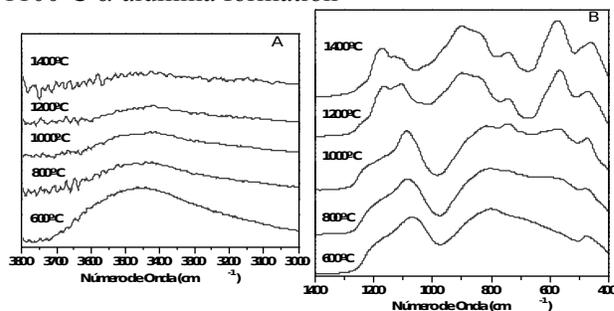


Fig 3. FTIR spectra obtained after isothermal treatments at different temperatures.

When comparing the spectra obtained after treatment at 600 and 800 °C, a new band can be observed at 570 cm⁻¹. It is due to Aluminum in octahedral coordination (AlO₆), indicating pre-mullite formation [8]. Treatment at 1000 °C produces a new band at 740 cm⁻¹, which corresponds to Al-

O bond in tetrahedral coordination (AlO_4) [8]. The band at 1170 cm^{-1} , which appears after the $1200\text{ }^\circ\text{C}$ treatment, corresponds to the Si-O bond in tetrahedral coordination (SiO_4). The band intensities at 1170 , 570 and 740 cm^{-1} increase with the treatment temperature. Stoichiometry of the sample can be obtained from the relation of the band intensities at 1100 and 1170 cm^{-1} [9]. Accordingly, it can be deduced that the treatment at $1400\text{ }^\circ\text{C}$ produces the transformation of an Al_2O_3 rich mullite into a 3:2 mullite. The intensity variation through the treatment temperature reflects the changes of chemical composition produced along the mullite formation. This fact is confirmed by the changes observed in the Aluminum coordination, which passes from tetrahedral to octahedral as can be inferred from the FTIR spectra: the increase of the 570 cm^{-1} band intensity with respect to the 800 cm^{-1} one is typical of a 3:2 mullite formation [8], and the new band at 1170 cm^{-1} is due to disappearance of tetrahedral Aluminum [10]. It can be observed in Figure 4a how kaolinite lamellae join to form small packets. The small packets group together to form bigger structures. Figure 4b shows a $8 \times 2\text{ }\mu\text{m}$ group composed of smaller lamina packets.

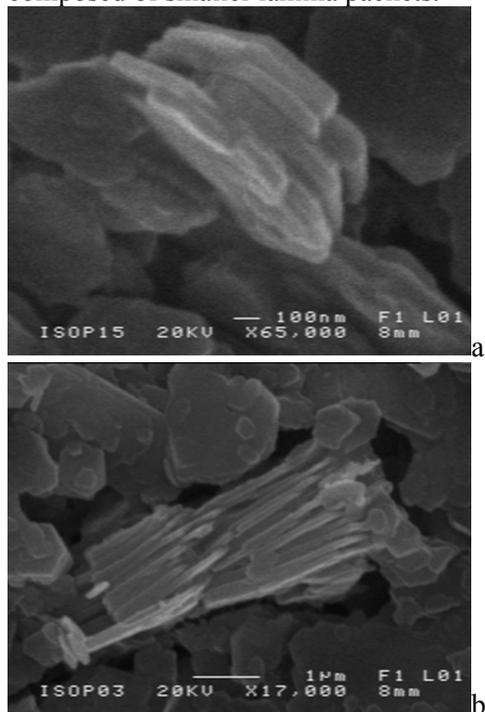


Figure 4. SEM micrographs of the kaolinite-Aluminium isopropoxide complex.

Figure 5 shows that the packet structures produced by intercalation are still present after the $800\text{ }^\circ\text{C}$ treatment. The morphology of the metakaolinite laminae composing the packet structures remains still unaltered. Nevertheless, small $\gamma\text{-Al}_2\text{O}_3$ crystals can be observed on the packets and on the single lamina. These structures, still small, are typical of mullite formation and are produced by the reaction of metakaolinite from the laminae with the previously formed $\gamma\text{-Al}_2\text{O}_3$. The treatment at $1400\text{ }^\circ\text{C}$ produced a 3:2 type mullite, which can be observed in Figure 6. Rhombohedral particles of size ranging from 400 nm to more than $1\text{ }\mu\text{m}$

can be observed. Some of the bigger particles seem to be formed by sintering of small particles.

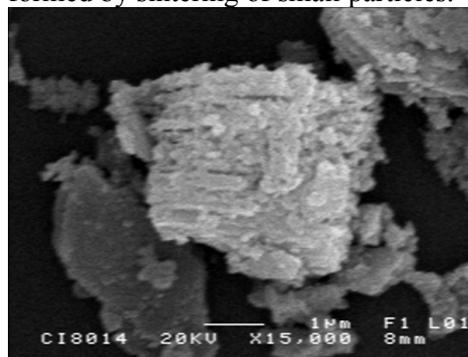


Fig 5. SEM micrograph of the kaolinite-Aluminium isopropoxide complex after the $800\text{ }^\circ\text{C}$ treatment.

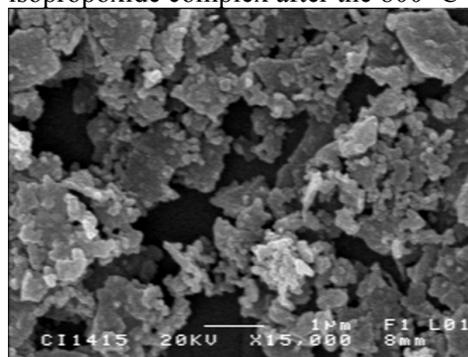


Fig 6. SEM micrograph of the kaolinite-Aluminium isopropoxide complex after the $1400\text{ }^\circ\text{C}$ treatment.

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