Aminopropyl-grafted CTA-Magadiite: precursors/supports for polymerization catalysts

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Abstract
Cetyltrimethylammonium-intercalated magadiites were prepared by direct synthesis using different CTA/Na molar ratio. This procedure was followed by $\gamma$-aminopropyltrimetoxyisilane (APTS) grafting in order to study the influence of the CTA$^+$ surface density on the magadiite capacity to bind $\gamma$-aminopropyl groups. X-ray diffraction (XRD) showed a 1.46 nm increase in the interlayer space for all the samples. Elemental analyses of C, H and N were carried out in order to quantify the real CTA$^+$ concentration. The structural order of CTA-magadiites and its APTS-grafted form was probed through solid-state nuclear magnetic resonance (NMR) techniques.

Key words: Cetyltrimethylammonium-magadiite, Grafted Magadiite, Intercalation.

Introduction
Magadiite, a hydrated crystalline layered silicate (Na$_2$Si$_4$O$_{10}$$\cdot$10H$_2$O), is a good candidate for the formation of organic-inorganic nanocomposites because it is a chemically stable silanol-terminated surface. This property allows us to heterogenize homogeneous polymerization catalysts, easing the separation of the catalyst and increasing the thermal and mechanical stability of the final polymer. In order to graft these groups, the interlayer space must be large enough to allow the grafting agent to access the internal sites. A larger interlayer space can be found in intercalated magadiite. In this sense, CTA-magadiites were synthesized by one-step synthesis, using different CTA/Na molar ratio. These solids were then grafted with APTS.

Results and Discussion
CTA-magadiite was synthesized with different CTA$^+$/Na$^+$ molar ratio in the gel. To avoid the pH lowering by the CO$_2$ adsorption during the sodium metasilicate dissolution, the experiment was performed under inert atmosphere. Fig. 1 shows the XRD profiles of the obtained materials.

These solids show a relative decrease in crystallinity in the region between 23º and 30º 2θ due to the turbostratic effect caused by CTA$^+$ presence. The CHN analyses results confirm there is a maximum concentration for CTA$^+$ insertion around CTA/Na=0.5.

APTS was grafted onto CTA-magadiite as indicated by the presence of T sites on $^{29}$Si NMR spectrum (Fig. 2A). $^{13}$C NMR spectrum (Fig. 2B) shows besides the carbons assigned to the CTA$^+$ cation, three different chemical shifts assigned to the aminopropyl groups.

Conclusions
One-step synthesis of CTA-magadiites generates materials where the maximum CTA$^+$/Na$^+$ molar ratio is 0.5. Grafting organic groups was successful, as observed through NMR techniques.

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Figure 1. XRD of Na-magadiite (top curve) and CTA-magadiites and their respective CHN analyses (Table).

The CTA$^+$ intercalation on magadiite increases the interlayer distance from 1.54 nm (5.74º 2θ) to 3.0 nm (2.96º 2θ) in all CTA-magadiites (Fig. 1).