

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 γ -aminopropyltrimetoxysilane (APTS) grafting in order to study the influence of the CTA⁺ surface density on the magadiite capacity to bind γ -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 ($\text{Na}_2\text{Si}_{14}\text{O}_{29}\cdot 10\text{H}_2\text{O}$), 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.¹ 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 synthesis², using different CTA/Na molar ratio. These solids were then grafted with APTS.³

Results and Discussion

CTA-magadiite was synthesized with different CTA⁺/Na⁺ molar ratio in the gel. To avoid the pH lowering by the CO₂ adsorption during the sodium metasilicate dissolution, the experiment was performed under inert atmosphere. Fig. 1 shows the XRD profiles of the obtained materials.

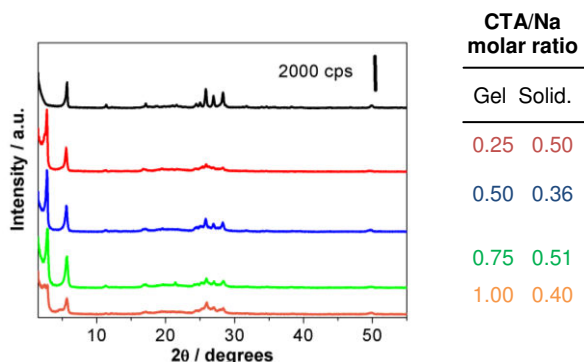


Figure 1. XRD of Na-magadiite (top curve) and CTA-magadiites and their respective CHN analyses (Table).

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

These solids show a relative decrease in crystallinity in the region between 23° and 30° 2 θ 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 ²⁹Si NMR spectrum (Fig. 2A). ¹³C NMR spectrum (Fig. 2B) shows, besides the carbons assigned to the CTA⁺ cation, three different chemical shifts assigned to the aminopropyl groups.

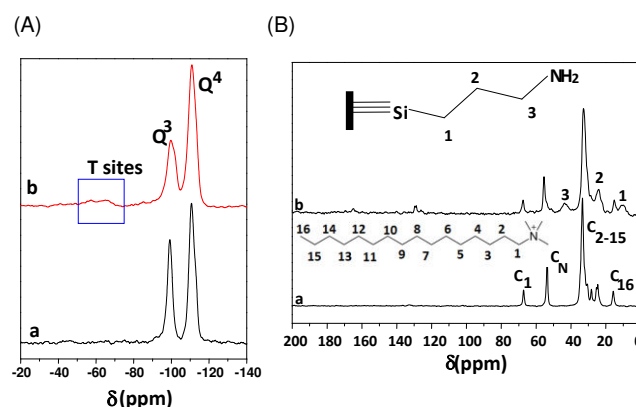


Figure 2. (A) ²⁹Si and (B) ¹³C NMR of CTA-magadiite (a) and grafted CTA-magadiite (b).

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.

Acknowledgement

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