TG-FTIR study of the thermal stability of smectites exchanged with different chain-length organocations.

R. Solano, V. Ferrer, J. Sánchez, E. Choren, A. Moronta
Centro de Superficies y Catálisis, Facultad de Ingeniería, La Universidad del Zulia, PO. Box 15251, Maracaibo 4003A VENEZUELA. amoronta@luz.ve; rjsolano@luz.ve

Introduction

The exchangeable cations on natural clays can be replaced with different organocations by simple ion exchange. A variety of alkylammonium ions may be used in this regard to form organoclays that are effective adsorbents for removing organic contaminants from water [1]. It has been found that when freshly dried organoclays (prepared from a natural clay) are heated at a regular temperature program, the organocation start to decompose at 523-553 K [2]. However, to date, the thermal stability of organoclays prepared from Na- and autotransformed-clays using the alkylammonium method is unknown. Autotransformation means that H-smectite is converted spontaneously to (H,Al,Fe,Mg)-form upon ageing [3]. Therefore, the aim of this work is to study the exchange of primary ammonium (n-alkylammonium chlorides), with a variable carbon chain length (ranging from C₆ to C₁₆), into Na-form clays (Na-clays) and autotransformed H-clays (An-clays) derived from SAz-1, SWa-1, ST and JP, and to determinate whether autotransformation produces an improved thermal stability and to evaluate the decomposition process of the organoclays using thermogravimetry coupled with infrared spectroscopy.

Results and Discussions

Figure 1 shows the total infrared chromatogram evolution of aliphatic species, carbon dioxide, ammonia and water as a function of time for (a) ST-Na-C₆NH₃⁺ and (b) ST-An-C₆NH₃⁺ samples, the total weight loss curve and the reconstructed chromatogram are also included. In Figure 1a there is a broad band in the reconstructed chromatogram from 25 to 45 min. In this time range, it is clearly seen that this band contains contributions from the breakdown of the alkylammonium ions to give mainly aliphatic hydrocarbons, ammonia, water and a small amount of carbon dioxide [4]. The aliphatic species present two maxima at 31 and 39 min (583 and 745 K), the desorption of ammonia also has two maxima, but not well resolved, the highest maximum is centered at 36 min (701 K). The maximum of water occurs at 35 min (657 K). After 45 min, only the evolution of CO₂ is observed in the chromatogram, which reaches the maximum absorbance at 63 min (1223 K).

The decomposition of alkylammonium ions in autotransformed samples occurs at a lower temperature than in those derived from the Na-form (not shown). Indeed, the maxima for the evolution of aliphatic species in ST-An-C₆NH₃⁺ sample (Figure 1b) appeared at 27 and 33 min (523 and 626 K). Ammonia is found in a very broad band centered at 32 min (603 K), as well as water, the maximum for CO₂ occurs at 64 min (1250 K).
In general, the decomposition of the organocations occur between 31 – 39 min (587-743 K), in this range, the species present are water (for SWa-1 and ST), ammonia, aliphatic hydrocarbons and a small amount of CO$_2$. The evolution of CO$_2$ at this stage indicates that the alkylammonium ions undergo thermal degradation. As the temperature increases the absorbance of the bands associated with CH (2868, 2937 and 2972 cm$^{-1}$), NH$_3$ (931 and 960 cm$^{-1}$) and H$_2$O (3500-4000 cm$^{-1}$) gradually decrease and the bands of CO$_2$ (2328 and 2368 cm$^{-1}$) and CO (2183 and 2108 cm$^{-1}$) start to increase. Bands for unsaturated hydrocarbons were very weak.

Some samples did not present maxima for the evolution of water (SAz-1 and JP clays). Indeed, in the FTIR chromatogram, the desorption of water was not detected throughout the heat treatment of all these samples. It could be possible, perhaps, to infer that water in these particular samples is used to form carbon dioxide due to the earlier appearance of CO$_2$, especially in SA-An-C$_6$NH$_3^+$ sample. Additionally, SAz-1 and JP clays presented a low water content.

![Figure 1. FTIR chromatograms for the decomposition of alkylammonium ions from (a) ST-Na-C$_6$NH$_3^+$ and (b) ST-An-C$_6$NH$_3^+$ samples](image)

In this study, the thermal stability of alkylammonium samples derived from the Na-clays was higher than those resulting from autotransformation. The results are explained in terms of the ability of the organocations to displace Na cations on exchange sites in Na-clays. The weight loss in autotransformed samples was higher than for Na-counterparts. This trend is ascribed to the generation of more hydrophobic surface during the autotransformation process.

References