"MEMORY" EFFECTS OF HYDROTALCITES

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The "memory" effects of synthetic hydrotalcite $Zn_6Al_2CO_3(OH)_{16}.4H_2O$ have been studied using hot stage Raman spectroscopy through both heating and cooling in a flow of moist air. Thermal analysis coupled with mass spectrometry was used to complement the spectroscopic results. Hydrotalcites are layered anionic clays which are based on the brucite structure, $Mg(OH)_2$ (Costantino et al., 1998; Frost et al., 2003; Lopez et al., 1996), where a trivalent cation substitutes for some of the divalent cations. The consequent positive layer charge is balanced by the incorporation of anions and water into the interlayer. The resulting mineral has octahedrally coordinated metals, which form sheets. As there is no overall charge, hydrotalcites are quite stable. The general formula for hydrotalcites is: $[M^{II}_{1-x} M^{III}_x. (OH)_2]A^{n-}_{x/n}. mH_2O$; where $0.2 < x < 0.33$ and M = metal, A = anion (Costantino et al., 1998). The interesting properties of hydrotalcites arise when they are calcined; this process removes the interlayer water, interlayer anions, and the hydroxyls. The calcined hydrotalcite is able to reform the original structure when it is exposed to water and anions (Palomares et al., 2004). This is known as the "memory" effect. Thermal analysis (TG) coupled with mass spectrometry (MS) has been used to study a synthetic hydrotalcite ($Zn_6Al_2CO_3(OH)_{16}.4H_2O$). It was found that there are four mass losses which occur up to 300°C. The first three can be assigned to loss of absorbed water, interlayer water and hydroxyls. The fourth mass loss is assigned to loss of carbonate as carbon dioxide. There is a fifth mass loss which occurs at 550°C, which is most likely a loss of oxygen.

A Raman microprobe spectrometer coupled with a thermal stage was used to follow a calcination of ZnAl hydrotalcite (Frost et al., 2004; Frost and Weier, 2004a; Frost and Weier, 2004b). There are three types of OH stretching vibrations which can be seen which are MOH, HOH and HOH---OCO_2. There is an increase in the intensity of the hydrogen bonded water bands as the temperature is increased, while a decrease in intensity of the water bands occurs simultaneously. Only MOH bands remain after 150°C. There are bands of carbonate anions hydrogen bonded to interlayer water at 1077 cm^{-1} and surface OH units at 1060 cm^{-1}. As the temperature is increased, the intensity of the bands of the anion hydrogen bonded to interlayer water decreases in proportion to those hydrogen bonded to the surface OH units. It is proposed that as the interlayer water is removed, the more carbonate anions are forced to bond with the surface OH units. Another band appears at 150°C due to the anion bonded to two OH units, which is caused by the anion being brought into closer contact with the surface.

This paper will present a thermoanalytical and spectroscopic study of the memory effects of hydrotalcites.

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