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NOTES

CONTAMINATION OF MAGADIITE BY FLUORINE IN COMMONLY USED SYNTHETIC PROCEDURES

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INTRODUCTION

Lamellar polysilicates are an interesting class of compounds which have lately received a lot of attention (Lagaly 1979; Sprung et al. 1990; Dailey and Pinnavaia 1992a, 1992b; Wong and Cheng 1993; Wang et al. 1996). For example, recently kanemite was used as a starting material for the preparation of mesoporous materials (Inagaki et al. 1993). Several lamellar polysilicates occur naturally in lakes of high alkalinity. This is the case for magadiite (Eugster 1967; McAtee et al. 1968; Rooney et al. 1969) of approximate formula $Na_2Si_{14}O_{29}{\cdot}xH_2O$ (Lagaly et al. 1975) or $Na_2H_2SiO_{30}{\cdot}xH_2O$ (Dailey and Pinnavaia 1992a), which was discovered by Eugster in 1967. The synthesis of this mineral was reported for the first time in 1972 by Lagaly et al. The appropriate amounts of NaOH, SiO_2 and H_2O were mixed and heated in sealed glass vessels or ampullae at 100 °C for at least 4 weeks. With the interest generated by these lamellar minerals in the late eighties, other synthetic approaches have been proposed, using shorter times of reaction (Fletcher and Bibby 1987; Garces et al. 1988; Sprung et al. 1990; Dailey and Pinnavaia 1992b). Most of these syntheses were performed in a Teflon-lined autoclave at higher temperatures for shorter periods of time (Garces et al. 1988; Sprung et al. 1990; Dailey and Pinnavaia 1992b). For example, reaction mixtures heated at autogenous pressure in a Teflon-lined autoclave to 175 °C for 21.5 h produced magadiite (Sprung et al. 1990). We have also used the same approach (Sprung et al. 1990), obtaining magadiite referred to as MAG1 below. The X-ray powder diffraction (XRD) pattern of the material obtained in our laboratory was always characteristic of magadiite, identical to previously reported patterns, with a $d(001)$ of 15.5 Å and showing several higher $[00l]$ lines. (Figure 1) We have systematically observed a loss of weight of 2 to 3% occurring between 450 and 550 °C in addition to the loss of weight occurring below 200 °C attributed to the loss of water. The loss observed around 500 °C could possibly be attributed to some dehydroxylation process, as was suggested in the literature (Dailey and Pinnavaia 1992a, 1992b). However, the analysis of the material obtained in further reacting this magadiite MAG1 showed the presence of fluorine, suggesting that the starting magadiite used for the reaction was contaminated by fluorine. This was confirmed by ^{19}F magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of MAG1 (at 188.25 MHz, the sample was spun at 6 kHz; a 90° pulse of 3.5 μsec was used). A ^{19}F signal was obtained at −48 ppm, with reference to trifluoroacetic acid (the liquid was put in a zirconia rotor sealed with a zirconia cap; a single 90° pulse was given without spinning the sample). This chemical shift was in the range expected for Si-F and C–F bond. An ionic chromatography analysis of MAG1 showed the presence of 90 ppm of fluorine in the material. Since the most probable origin of the contamination was in the Teflon used in the autoclave, we prepared magadiite under identical reagent conditions, but replacing the Teflon lining with one made of stainless steel. The TGA curve of the resulting material, MAG2, is shown on Figure 2. The loss of weight around 500 °C was no longer observed, and no ^{19}F signal could be detected. The ionic chromatography analysis did not detect fluorine (the detection limit of the method is 50 ppm). The XRD pattern was identical to the one shown on Figure 1 and to those reported in the literature.

One can speculate that some oligomeric parts of Teflon are inserted in the magadiite structure during

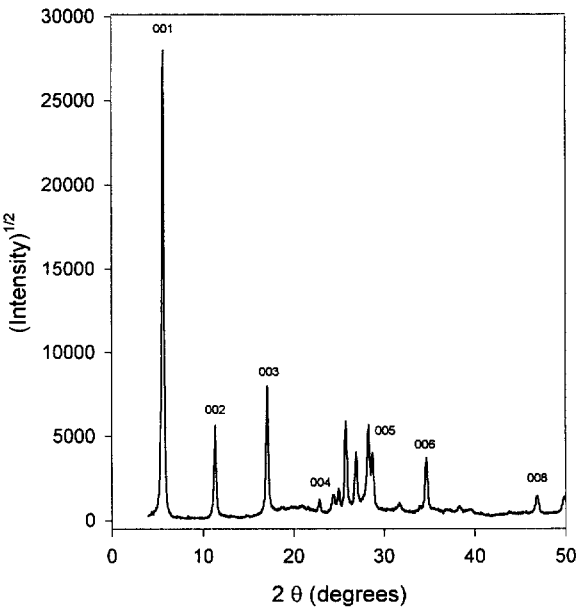

Figure 1. XRD pattern (2–50 °2θ) of a magadiite sample (MAG1). The (00*l*) peaks are indicated.

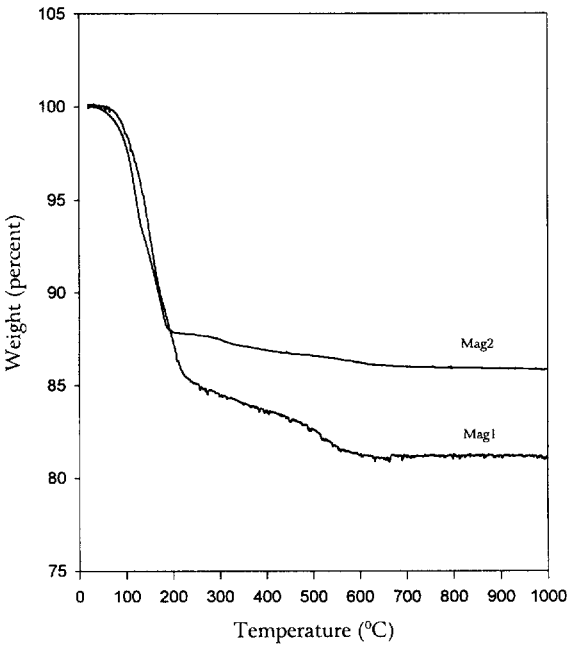

Figure 2. TGA curves (20–1000 °C) for 2 magadiite samples (MAG1 and MAG2), under nitrogen flow.

its synthesis, by abrasion of the liner. We continue to investigate the role of the presence of fluorine compounds in the synthetic procedures of magadiite.

Given the intense current interest in these layered materials, we believe that it is important to warn users of synthetic magadiite and other layered silicates against their probable contamination by fluorine when Teflon liners are used during their preparation, as has been the case in reported procedures.

EXPERIMENTAL

Synthetic sodium magadiite was prepared under hydrothermal conditions by the reaction of sodium hydroxide and silica gel following a published method with some slight modification (Sprung et al. 1990). Addition of 0.537 mol of SiO_2 was made to 80 mL of 1.25 *M* NaOH. The solution was stirred for 1 h. In a first synthesis, the reaction mixture was heated in a Teflon-lined stainless steel autoclave at 180 °C for 20 h, leading to magadiite labeled MAG1. In a second synthesis, the reaction was carried out in a stainless steel-lined autoclave, leading to MAG2.

Both samples were analyzed by ^{29}Si and ^{19}F MAS NMR, XRD (Philips PW3710 diffractometer with Cu*K*α radiation) and thermogravimetric analyses (TGA) performed under nitrogen flow (Polymer Labs STA 1500H instrument), where samples were heated to 1000 °C at a heating rate of 20 °C/min.

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