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Research paper

Effect of propanol and butanol and subsequent microwave irradiation on the structure of commercial vermiculites

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ABSTRACT

As a continuation of our previous study, in this work, we investigated the effects of propanol and butanol treatments and subsequent irradiation with microwave on commercial vermiculites. No expansibility was observed after propanol or butanol treatments (k = 1.0). Samples treated with propanol or butanol and subsequently irradiated with microwaves expanded in a similar manner as they did with methanol and ethanol. The results of X-ray diffraction (XRD), thermogravimetric analysis (TG and DTA), scanning electron microscopy (SEM) and infrared spectroscopy indicated structural changes as: 1) The appearance of extra interstratified phases during the transformation from 2- to 1-WLHS (Water Layer Hydration States). 2) The improvement of the crystallinity and order of the most phases, which are the same phases of the untreated vermiculites or even some more, due to migration of potassium.

1. Introduction

Generally, the term -vermiculite- is used to describe commercially exploited deposits of micaceous minerals which can be exfoliated when heated rapidly to high temperatures (Kogel et al., 2006). However, in the mineralogical sense, vermiculite belong to the 2:1 group of phyllosilicates. The 2:1 layer is composed of one octahedral sheet between two tetrahedral sheets. The positive charge deficiency is compensated by hydrated exchangeable cations (as Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}) located in the interlayer space between the parallel 2:1 layers (Foster, 1963). Vermiculite has water layers between the silicate layers and, therefore, it can undergo processes of dehydration-hydration which depend on temperature, pressure, chemical composition, size and relative humidity (Mathieson and Walker, 1954; Walker, 1956; Vali and Hesse, 1992; Collins et al., 1992; Reichenbach and Beyer, 1994, 1995, 1997; Ruiz-Conde et al., 1996; Marcos et al., 2003; Marcos et al., 2009; Marcos and Rodríguez, 2010). The hydration state of vermiculite is defined by the number of water layers in the interlayer space, with a development corresponding to different phases, such as zero-, one- and two-water layer hydration states (0-, 1- and 2-WLHS, respectively) (Suzuki et al., 1987). As an example, for Mg-vermiculites the basal spacing are 9.02 Å for 0-WLHS, 11.50 Å for 1-WLHS and 14.40 Å for 2-WLHS (e.g.: Suzuki et al., 1987; Ruiz-Conde et al., 1996; Marcos et al., 2003; Marcos et al., 2009).

As a result of their lamellar structure, vermiculite shows the diversity of properties related to the structural characteristics, such as layer charge associated with the numerous isomorphic substitutions and mixed layered structure, and to dehydration-rehydration ability (Mathieson and Walker, 1954; Shirozu and Bailey, 1966; Grim, 1968; Brown and Brindley, 1980; de la Calle and Suquet, 1988; Marcos et al., 2004; Argüelles et al., 2009 and Argüelles et al., 2010). It is an interesting mineral as a model system in physics, chemistry and the biological sciences (Satapathy et al., 2011; Wu et al., 2011; Eom et al., 2011), but it is also an attractive material due to its numerous thermal and insulation applications (Strand and Stewart, 1983; Suzuki et al., 1989, Suzuki and Suzuki, 2001; Hindman, 1992; Bergaya et al., 2006; Klein and Dutrow, 2007; Abollino et al., 2008; Zhang et al., 2009; Marcos et al., 2012; Marcos and Rodríguez, 2014).

In addition to water, inorganic or organic substances can be adsorbed in the expandable interlayer space (Brigatti et al., 2005; Jiménez de Haro et al., 2005). Numerous studies on the intercalation of polar organic molecules by clay minerals have been carried out. The adsorption properties of alcohols is the most widely studied (Yariv and Cross, 2002; Bergaya et al., 2006).

The present paper aims at completing the investigation on commercial vermiculites treated with the most common alcohols, previously with methanol and ethanol (Marcos and Rodriguez, 2016) and now with propanol and butanol. Structural changes induced in the samples were detected by using X-ray diffraction, thermogravimetric analysis and infrared spectroscopy.

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Table 1
Expansibility coefficient k of the vermiculites treated with alcohol (propanol and butanol), and alcohol and subsequently irradiated with microwaves. The standard deviation was lower than 0.002.

Sample	Treatment time (hours)(* = 1 month)	Propanol		Butanol	
			+ microwaves		+ microwaves
Santa Olalla	1	1.0	1.3	1.0	1.0
	24	1.0	1.2	1.0	1.0
	168	1.0	1.1	1.0	1.1
China	1	1.0	3.3	1.0	3.5
	24	1.0	3.4	1.0	2.7
	168	1.0	5.1	1.0	2.8
	1		1,4		2,8
Libby	1	1.0	4.0	1.0	4.5
	24	1.0	4.1	1.0	5.2
	168	1.0	4.5	1.0	4.5
	1		4,7		3,7

2. Experimental

2.1. Materials

Vermiculite samples from Santa Olalla (Huelva, Spain), Libby (Montana, EEUU) and China (provided by Vermiculita y Derivados S.A. company of Gijón, Spain) were present in form of small packets with maximum dimensions of ca. 5 × 5 mm in diameter and 0.5–1 mm thick. Chemical and thermogravimetric analyses of the samples were previously published (Marcos and Rodríguez, 2010; Marcos and Rodríguez, 2014). Santa Olalla vermiculite with K_2O content lower than 0,033% (Velde, 1978; Justo et al., 1986) is purer than Libby and China samples with a higher K_2O (5.614 and 9.682%, respectively). They are referred as “commercial vermiculites”, which are the vermiculite mined and beneficiated particles larger than 1 mm in size.

The propanol (99.5%) used was from Panreac. The nonvolatile matter = 0.004%, the trace impurities (Cu, Pb, Ni) of propanol were = 0.00002% and Fe = 0.00005%. The butanol (99.8%) used was from Analar NORMAPUR, with Al, Ca < 0.5 ppm; Ba, Cu, Fe, Pb, Sn, Zn < 0.1 ppm; B, Co, Cr, Cu, Mg, Mn < 0.02 ppm; Cd < 0.05 ppm.

2.2. Methodology

The methodology used in this work was the same as with methanol and ethanol (Marcos and Rodriguez, 2016). The samples were used in the experiments after elimination of other minerals by hand-picking and no treatment previous was performed on the vermiculites, in order to respect their natural characteristics as much as possible and to evaluate their retention behaviour and their efficiency as adsorbents without applying others costly or time-consuming pretreatments. Two experiments were made: 1) Immersion of each vermiculite sample into propanol and butanol, respectively, at room temperature for different periods of time. 2) Microwaves irradiation for 20 or 40 s of vermiculite samples treated with alcohol for 168 h and 1 month.

The expansibility, k (k = density of the raw sample/density of the

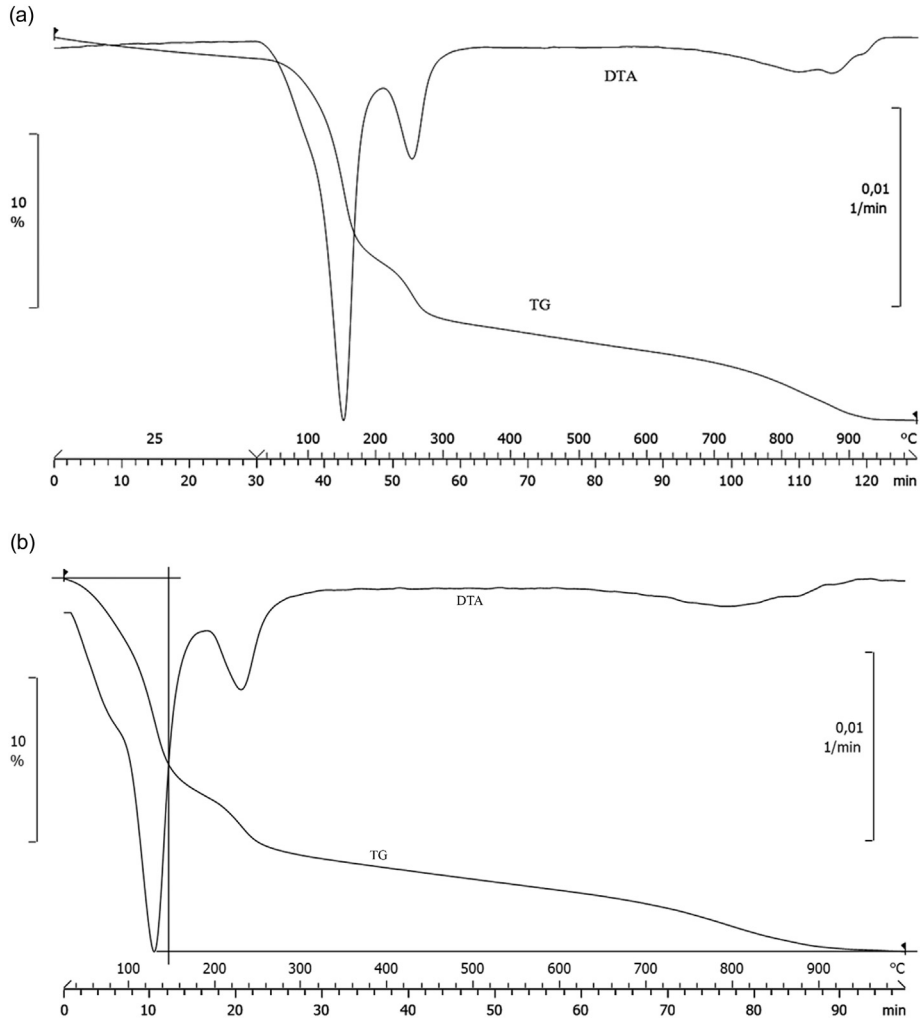

Fig. 1. TG and DTA of treated samples from Santa Olalla: (a) propanol, (b) butanol.