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Research paper

Heteroatom framework distribution and layer charge of sodium Taeniolite

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ABSTRACT

The most advanced applications of clays depend crucially on their hydration state and swelling is probably the most important feature of expandable 2:1 layered silicate. Sodium Taeniolite, Na-TAE, a swelling trioctahedral fluormica, has been synthesized and studied using thermogravimetric analysis, X-ray diffraction, scanning electron microscopy and infrared and solid state NMR spectroscopies. The results indicated the formation of a swelling 2:1 phyllosilicate with actual layer charge lower than the nominal one. Herein, a new heteroatom distribution and more accurate composition could be deduced.

1. Introduction

Swelling silicates of the 2:1 phyllosilicate family with low negative charge are 2D host materials with multiple and diverse physicochemical applications going from the well-known catalysis (Alves et al., 2014; Breu et al., 1999; Centi and Perathoner, 2008; Cheng, 1999; Thomas, 1988; Vaccari, 1999) and adsorption/separation (Barrer, 1989; Mercier and Pinnavaia, 1998; Okada and Ogawa, 2017; Tomohiko et al., 2014) to the latest nanotechnology (Schollhorn, 1996; Schoonheydt and Umemura, 2017), sensor technology (Mallouk and Gavin, 1998) and optoelectronics.(Kunz et al., 2013; Lezhnina et al., 2007).

Chemical structure is the ultimate responsible of those interesting applications. The structure, an octahedral sheet sandwiched between two tetrahedral sheets, is extremely flexible to isomorphic substitutions. Additionally, the interlayer cation can be substituted by cation exchange reactions and large inorganic or organic molecules can be introduced in the interlayer space giving those materials a wide adaptability.

Chemical reactivity and stability in the interlayer space as a reaction media strongly depends not only of the layer charge but also from its origin (Alba et al., 2001a, 2001b; Alba et al., 2010; Alba et al., 2009; Chain et al., 2013). On the one hand, cation substitutions on tetrahedral sheet favor reconstructive reactions under subcritical conditions (Alba et al., 2001a). On the other hand, cation substitutions on octahedral sheet provides an excess of negative charge that is delocalized in the framework (Sposito and Prost, 1982), and, thus, a more homogeneous distribution of cations in the interlayer space. Moreover, the hydration properties of 2:1 phyllosilicates are also governed by those structural features because their swelling behaviour depends on the repulsive forces relating to the interactions between the 2:1 layers and the attractive forces between the interlayer cation and the negative charged siloxane surface (Pavon et al., 2014).

True and brittle natural micas constitute a major group of those 2D host materials but layer charge is high and strong Coulomb interactions with interlayer cations usually inhibit their swelling and hence, a very low cation-exchange capacity (CEC) results and limits applicability. However, as will be shown in the following, swelling high-charge micas can be easily synthesized and their CEC tuned via the degree of isomorphous substitution, broadening their wide-ranging uses.

Depending on the origin of the layer charge, two family of swelling mica can be found. First, synthetic fluorine micas have been recently synthetized (Alba et al., 2006) that are able to swell despite their high layer charge originated in the tetrahedral sheet by Si/Al replacements (Alba et al., 2006; Naranjo et al., 2015; Pavon et al., 2013). Consequently, those materials, referred as Na-*n*-Mica or Na-Mica-*n* (being *n* the layer charge and related to the ratio Si/Al) have potential used as decontaminants and storage media (Alba et al., 2006; Garcia-Jimenez et al., 2016; Gregorkiewitz and Rausell-Colom, 1987; Park et al., 2002; Paulus et al., 1992).

Second, synthetic sodium Taeniolite, an analogous of the swelling fluoromica Na-Mica-2, where substitutions in the octahedral sheet (Mg/Li) are the ultimate responsible of layer charge (Kitajima et al., 1985; Kitajima and Takusagawa, 1990; Kitajima et al., 1991). Sodium Taeniolite ($NaSi_4Mg_2LiO_{10}F_2{\cdot}xH_2O$) exhibits reversible swelling (Toraya

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et al., 1977) and Kitajima et al. (1973) explained its swelling characteristics by the high hydration energy of the interlayer sodium ions. Taeniolite derivatives are interesting microporous host materials that can be used as sensors for redox-active ambient gas (Baumgartner et al., 2008; Mariychuk et al., 2007).

The capability of the 2:1 structure to vary the framework chemical composition and heteroatom distribution is crucial to design new materials with desired properties; however, it leaves one worrying about the homogeneity of the synthesized material. In many cases, the charge densities vary not only from one silicate layer to other in a crystallite (Lagaly, 1994) but also from domain to domain within a single silicate layer (Muller et al., 1997) and this heterogeneous distribution of negative charge influences the distribution cations in the interlayer space (Breu et al., 1999).

The charge density of the silicate layers is of utmost importance for the properties of the material. Na-Mica-n have been extensively analysed (Alba et al., 2006) but, to our knowledge, the only available information of Na-Taeniolite is related to their crystalline order and swelling capacity (Kitajima et al., 1985; Kitajima et al., 1973; Miyake et al., 1993; Moore et al., 1997; Toraya et al., 1977). Thus, the goal of this research was to shed some light on the uniformity of their composition, charge density, and interlayer composition by the combination of characterization techniques that provide structural information at long and short range.

2. Experimental section

2.1. Synthesis method

The reagents of SiO_2 (Sigma, 99.8% CAS N° 112,945–52-5), LiF (Aldrich, 99.99%, CAS N° 1309–48-4), MgO (Aldrich, 99.9%, CAS N° 1309–48-4) and NaF (Aldrich, 99.0%, CAS N° 7681–49-4) were dried at 100 °C for 24 h and carefully weighed out according to the formulae $[Na_2][Si_8][Mg_{24}Li_2]O_{20}F_4$.

All reagents were mixed and vigorously ground before heating at 1100 °C in a Pt crucible for 2 h. After cooling up to 950 °C, the solid was quenched to room temperature (RT) and equilibrated at RT ambient humidity. The as-synthesized sample was named as Na-TAE.

2.2. Characterization

TG/DTA experiment was carried out using a TA (model STD-Q600) instrument, in Characterization Service (CITIUS, University of Seville, Spain), with alumina as reference. The sample was placed into a Pt crucible and maintained at air throughout the heating period. The temperature was increased at a constant rate of 10 °C/min.

Powder X-ray diffraction (XRD) was performed at the X-ray laboratory (CITIUS, University of Seville, Spain) on a Bruker D8 Advance Bragg-Brentano instrument equipped with a Cu K_α radiation source operating at 40 kV and 40 mA. The diffractogram was obtained in the 2θ range of 3–70° with a step size of 0.015° and a step time of 0.1 s.

FTIR spectrum was recorded in the range 4000–300 cm^{-1} by the Spectroscopy Service of the ICMS (CSIC-US, Seville, Spain), as KBr pellets, using a Nicolet spectrometer (model 510P) with a nominal resolution of 4 cm^{-1}.

The morphology of the sample was analysed by Scanning Electron Microscopy, SEM, (JEOL, Model JSM 5400) at 20 kV in the Microscopy Service of ICMS (CSIC-US). An EDX system (Oxford Link ISIS) was fitted to the SEM equipment to perform chemical analyses of the sample using a Si/Li detector with Be window.

Single-pulse (SP) MAS NMR spectra were recorded in the Nuclear Magnetic Resonance Unit at the University of Cordoba (Spain) on a Bruker AVANCE WB400 spectrometer equipped with a multinuclear probe. Powdered sample was packed in 3.2 mm zirconia rotors and spun at 10 kHz. ^{29}Si MAS NMR spectrum was acquired at a frequency of 79.49 MHz, using a pulse width of 2.7 μs (π/2 pulse length = 7.1 μs) and delay times of 3 s. ^{6}Li MAS NMR spectrum was recorded at 58.86 MHz with a pulse width of 0.9 μs (π/2 pulse length = 1.8 μs) and a delay time of 30 s, in this case the rotor was spun at 14 kHz to improve the spectral resolution. ^{23}Na MAS NMR spectrum was recorded at 105.84 MHz with a pulse width of 0.75 μs (π/2 pulse length = 4.5 μs) and a delay time of 0.1 s. The ^{19}F MAS spectrum was obtained using typical π/2 pulse widths of 2.9 μs and a pulse space of 2 s. The chemical shift values were reported in ppm from tetramethylsilane for ^{29}Si, from NaF for ^{19}F and from a 0.1 M LiCl and NaCl solution for ^{6}Li and ^{23}Na, respectively. Spectra were simulated using the DMFIT software (Massiot et al., 2002). A Gaussian-Lorentzian model was used for all peaks, and linewidth, position and amplitude were the fitted parameters.

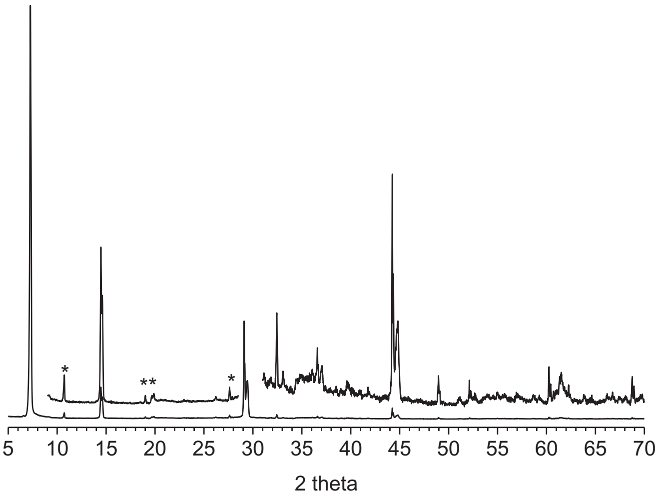

Fig. 1. XRD of Na-TAE. * = protoamphibole = 00–013-0409.

3. Results and discussion

The XRD pattern (Fig. 1) is similar to the previously reported for the one-layer hydrated 2:1 structure of Na-Taeniolite (Miyake et al., 1993; Suzuki et al., 2008; Yamaguchi et al., 2012) and showed a sharp *001* diffraction peak at 7.2° 2θ (d_{001} = 12.2 Å) and high order *00l* reflections corresponding to the single-layer hydrate state of the interlayer cations (Kitajima et al., 1985). Kalo et al. (2010) also observed that $Na_{0.6}$-fluorohectorite spontaneously absorbs air moisture to form a monolayer hydrate (ca. 2 H_2O per unit cell) at ambient conditions. Additionally, some reflections due to protoamphibole (PDF 00–013-0409), an orthorhombic fluoroamphibole,(Gibbs et al., 1960) are detected in the XRD patterns, as previously reported for Na-fluorohectorite (Kitajima et al., 1985). Also, Yamaguchi et al. (2012) observed some impurities in Taeniolite obtained from Na-rich raw batches (≥3 mol NaCl) that they could not identify and nor remove after rigorous washing.

Fig. S1 showed the c-axis projection of the K-Taeniolite structure (Toraya et al., 1977) and the a-axis projection of protoamphibole structure (Gibbs, 1969), the similarity of building blocks of both, protoamphibole being slightly denser, may favor that protoamphibole acts as a natural competitor for the 2:1 layer structure (Breu et al., 2001).

The hydration state of the Na-TAE was tested by thermogravimetric analysis (Fig. S2). In the region between 25 °C and 150 °C, where water molecules are desorbed, a unique weight lost was observed with the maximum in the DTG curve at 66 °C, associated to a 4.92% of weight loss. If the ideal formula, $Na_2Si_8Mg_4Li_2O_{20}F_4{\cdot}xH_2O$, is taken into account this weight loss corresponds to 2.23 H_2O per unit cell. This value is low as previously reported for Na-Taeniolite (Miyake et al., 1993), $Na_{0.6}$-fluorohectorite (Kalo et al., 2010) and for Na-Mica-2, a fluoromica with layer charge originated in the tetrahedral sheet instead of in