Synthesis temperature effect on Na-Mica-4 crystallinity and heteroatom distribution

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ABSTRACT

The discovery of swelling brittle mica, Na-Mica-4, has been one of the most significant advances in the pursuit for a material with high ion-exchange capacity. For technical applications, the control of the phase evolution during the synthesis is crucial. The main aim of this study was to investigate the effect of Na-Mica-4 synthesis temperature on the crystalline phase evolution, Si–Al distribution in the tetrahedral sheet, the Al occupancy between tetrahedral and octahedral sites and their effects on the interlayer space composition. The synthesis temperature range between 600 °C and 900 °C was explored. At low temperature (600 °C), the precursors were transformed in a low-charged swelling 2:1 phyllosilicate, saponite type, which was progressively aluminum enriched with temperature. The high-charged swelling mica was completely formed at 700 °C, although a minor anhydrous contribution remained up to 850 °C. Up to 800 °C, silicates and fluorides secondary phases were detected as a minor contribution.

1. Introduction

In recent years, synthetic clays with ion-exchange capacities in the order of 2000–4680 meq kg^{-1} have been prepared and have been the subject of considerable interest, particularly with respect to their catalytic and adsorption properties [1–4]. The discovery of swelling brittle mica, Na-Mica-4, has been one of the most significant advances in the pursuit of materials with high ion-exchange capacity (IEC). Unlike true mica, which is a non-expanding silicate with a negative layer charge of one, the Na-Mica-4 readily expands and allows the exchange of interlayer sodium cation [5].

In many cases, solid state synthesis procedures have been used to prepare these materials and fluoride ions have been employed to aid mineralization [6–8]. Procedures for synthesizing fine Na-Mica-4 have been refined over a period of time and many starting materials have been tested to achieve the same final product [2,3,9–12]. Cost effectiveness is one of the main driving forces behind all those attempts.

An important aspect to be considered is the sheet composition and the framework cation ordering, as Si-Al distribution strongly affects the reactivity of layer silicates [13,14]. In this sense, the appropriate characterization techniques are the ^{29}Si and ^{27}Al MAS NMR which are sensible to the local ordering and, therefore, to the Si-Al distribution in the tetrahedral sheet and Al distribution in the framework [15,16]. For some synthetic materials produced at low temperatures, it has been established that the charge density is rather inhomogeneous, hence the intracrystalline reactivity is expected to be non-uniform [17,18]. Moreover, the various compositions and the presence of different phases or impurities may limit the potential uses without pre-treatment [19]. For technical applications, an economically prized and feasible scalable synthesis method is desirable with an accepted compromise in materials properties. A good way to overcome these problems is to control the phase evolution during the synthesis which could allow optimizing all the synthesis parameters [20,21] (the choice of starting materials [2,3,9–12], reaction time [22] and temperature settings). For the synthesis of swelling 2:1-layered silicate with a perfectly uniform distribution of isomorphous substitution, the temperature is a key parameter [23] because it needs to be high enough to ensure a true solid solution, melting of one of the component and liquid–liquid miscibility but also preventing the evaporation of fluorine [24–26].

The main aim of this study is to investigate the effect of Na-Mica-4 synthesis temperature on the crystalline phase evolution, Si-Al distribution in the tetrahedral sheet, the Al occupancy

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between tetrahedral and octahedral sites and its effect on the interlayer space composition. The Na-Mica-4 has been synthesized thorough the NaCl-melt method [11] where the nature of starting material, its stoichiometric proportion and the time reaction were fixed and the temperature was a variable factor. As melting point of NaCl is 801 °C, the range temperature explored was between 600 °C and 900 °C with the purposed of testing the influence of temperature and the presence or absence of NaCl-melt fluid. The obtained products were characterized by X-ray diffraction (XRD), thermogravimetric/differential analysis (TG/DTA) and ^{29}Si, ^{27}Al and ^{23}Na solid-state magic-angle-spinning nuclear magnetic resonance (MAS NMR).

2. Experimental

2.1. Materials

The starting materials were SiO_2 from Sigma (CAS No. 112945-52-5, 99.8% purity), $Al(OH)_3$ from Rieldel-de Haën (CAS No. 21645-51-2, 99% purity), MgF_2 from Aldrich (CAS No. 20831-0, 98% purity), and NaCl from Panreac (CAS No. 131659, 99.5% purity).

2.2. Synthesis of Na-Mica-4

A single-step procedure described elsewhere [4], similar to the NaCl-melt method [11] was employed in the synthesis of Na-Mica-4. A stoichiometric powder mixture with the molar composition $4SiO_2$:$2Al_2O_3$:$6MgF_2$:$8NaCl$ was used.

The reactants mixtures were ground in an agate mortar, weighted, and subsequently heated in a Pt crucible at the temperature range between 600 °C and 900 °C for 15 h.

After free cooling, the solids were washed in deionized water and dried at room temperature. The solids were weighted before and after washing. The weight changes relative to the initial mass are expected to shed a light on the synthesis and degradation process of the synthetic mica.

2.3. Sample characterization

Thermal analysis (TG/DTA) experiments were carried out using a NETZSCH STA 409 PC/PG system, with alumina as the reference. The samples were placed in Pt crucibles and maintained under air throughout the heating period. The temperature was increased at a constant rate of 10 °C min^{-1}.

X-ray diffraction (XRD) patterns were obtained with a Bruker D8 instrument, at the Centro de Investigación, Tecnología e Innovación (CITIUS), Universidad de Sevilla, Sevilla, Spain, using Cu Kα radiation at 40 kV and 40 mA. Diffractograms were obtained from 3° to 70° (2θ) at a scanning speed of 1° min^{-1} and a scan step of 0.05°.
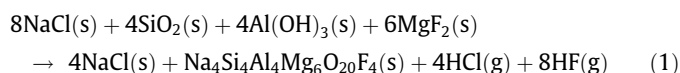
Solid state nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker DRX400 spectrometer equipped with a multinuclear probe, at the Instituto Ciencia de los Materiales de Sevilla (CSIC-US). Powdered samples were packed in 4 mm zirconia rotors and spun at 10 kHz. ^{29}Si MAS NMR spectra were acquired at a frequency of 79.49 MHz, using a pulse width of 2.7 μs ($\pi/2$ pulse length = 7.1 μs) and a delay time of 3 s. ^{27}Al MAS NMR spectra were recorded at 104.26 MHz with a pulse widths of 0.92 μs ($\pi/2$ pulse length = 9.25 μs) and a delay time of 0.5 s. ^{23}Na MAS NMR spectra were recorded at 105.84 MHz with pulse widths of 2.0 μs ($\pi/2$ pulse length = 12.0 μs) and a delay time of 0.1 s. The chemical shift values are reported in parts per million (ppm) from tetramethylsilane for ^{29}Si, from a 0.1 M $AlCl_3$ solution for ^{27}Al, and from a 0.5 M NaCl solution for ^{23}Na. A modified version of the WinFit program, which handles the finite spinning speed in MAS

experiments, was used for the modeling of the spectra [27]. The fit parameters were the chemical shift and full-width at half-height values (fwhh), as well as the area under the curve of the different contributions.

3. Results and discussion

3.1. Gravimetric results

Fig. 1 shows the weight changes of the products produced in the calcination and washing step as a function of the synthesis temperature. In the calcination step, represented by open square symbols in the Fig. 1a, a progressive increasing of the weight loss was observed. The chemical reaction involved in the calcination step, Eq. (1) implied a calculated weight loss of ca. 22% (dash line, Fig. 1a):

$$8NaCl(s) + 4SiO_2(s) + 4Al(OH)_3(s) + 6MgF_2(s)$$
$$\rightarrow 4NaCl(s) + Na_4Si_4Al_4Mg_6O_{20}F_4(s) + 4HCl(g) + 8HF(g) \quad (1)$$

At $T \leqslant 750$ °C, the weight loss was lower than the calculated value from the reaction drawn on Eq. (1). The formation of the intermediate species and/or the partial conversion of the starting materials could be the responsible. At 750 °C $< T \leqslant$ 800 °C, the weight loss was similar to the calculated value. However, at
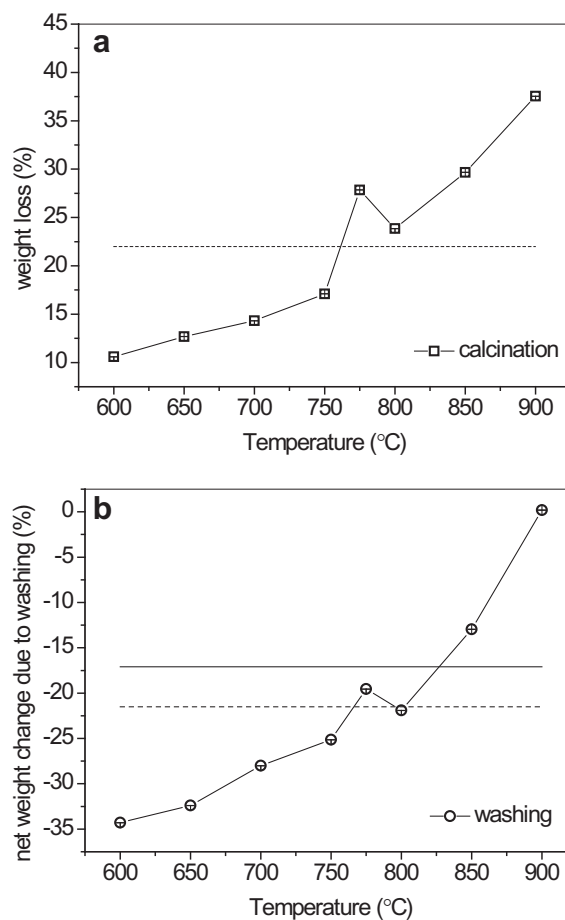

Fig. 1. (a) Total weight loss after calcination and (b) net weight change after washing process, as a function of the calcination temperature. Dash line = theoretical weight loss due to calcination (Eq. (1)), dotted line = theoretical net weight change due to the NaCl excess (Eq. (2)), and, solid line = theoretical net weight change due to the NaCl removal and hydration (Eq. (3)).