A comprehensive and in-depth analysis of the synthesis of advanced adsorbent materials

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ABSTRACT

Na-Mica-4, a synthetic fluorophlogopite, is an attractive adsorbent. However, the synthesis at large scale demands an economically prized, feasible scalable and sustainable synthesis method, which requires a deep knowledge of the influence of each synthesis step. A set of Na-Mica-4 were synthesized by methods that had one synthesis parameter as variable. The purity, crystallinity and heteroatoms distribution were analysed thorough X-ray diffraction and nuclear magnetic resonance. The results shed a light on the main factors for the design of the final product and indicated that an environmental friendship synthesis could be possible.

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1. Introduction

Clay minerals are appropriate adsorbent materials that are used in applications such as catalysis, ion exchange and decontaminant. However, natural clays contain other minerals that are not adequate for those applications. For many important applications, pure synthetic clays are preferred.

Na-Mica-4, a synthetic fluorophlogopite is an attractive adsorbent for its unique combination of high charge and swelling and cation exchange properties (Alba et al., 2006; Gregorkiewitz and Rausellcolom, 1987; Morikawa et al., 1982; Paulus et al., 1992). They have also shown preferential selectivity for harmful divalent and heavy metal cations, (Pavon et al., 2017) (Pavon et al., 2014a) hence they have been proposed as efficient adsorbents for removal of pollutants (Pazos et al., 2017) and immobilization of radioactive waste from water (Osuna et al., 2017). Moreover, their chemical and physical properties can easily be tuned by an appropriated synthesis design.

For the technical applications of those synthetic micas, feasible and economical scalable synthesis methods should be investigated. Moreover, an effective control of each synthesis step is crucial for an optimization of the synthesis parameters (Kloprogge et al., 1999; Zhang et al., 2010) such as chemical precursors (Gregorkiewitz and Rausellcolom, 1987; Kodama and Komarneni, 1999; Paulus et al., 1992), time (Alba et al., 2011) and temperature of reaction (Naranjo et al., 2015).

Synthesis procedure of clays has been refined and different starting materials were tested to achieve a cost efficient production (Gregorkiewitz and Rausellcolom, 1987; Kodama and Komarneni, 1999; Naranjo et al., 2014; Park et al., 2002a; Paulus et al., 1992). In fact, several studies have been conducted to find more cost-efficient aluminosilicate sources, such as fly ashes (Park et al., 2002a) or kaolinite (Kodama and Komarneni, 1999) for future large-scale applications. To elucidate the role of each synthesis step and parameters on the purity and structure of the Na-Mica-4, a strategy of synthesis has to be designed. A large-scale synthesis is possible as soon as all the synthesis steps are tuned.

Therefore, the goal of this research was to explore the effect of each synthesis parameter and steps on phase evolution and framework heteroatoms distribution to shed a light on an economical and sustainable method of synthesis that could be transferred to industrial sector.

2. Materials and methods

2.1. Synthesis

For the synthesis of Na-Mica-4, the NaCl melt method was followed (Park et al., 2002a). The general procedure consists in the use

of a powdered mixture with the following stoichiometry: Si: Al: 1.5 Mg: 2Na. The starting materials were commercial oxides and salts (SiO_2, $Al(OH)_3$, MgF_2, NaCl) and a set of natural clay minerals, series C and D, (Table S1). Kaolinites, KGa-1b and KGa-2, were used as commercially provided and after miller.

The starting mixtures were grounded in an agate mortar, except sample B2, which was grounded in a planetary mill. The heating time and temperature was 900 °C and 15 h, except in the samples E2, E4, and E5, where the effect of time in the synthesis was evaluated and 30, 7.5 and 3.0 h were used. The reaction was held in Pt crucible for all the samples, except E1 and E2-E5, where SiC and Al_2O_3 crucible were used, respectively. The heated solids were cooled up to room temperature and washed with distiller water, except sample G2, which was washed with tap water. Finally, they were dried at room temperature. The changes on the synthesis steps, the details of the synthesis and the name of the samples are summarized in Table 1 and Table S2.

2.2. Characterization

The mechanical grinding was performed using a Restch PM 200 planet miller with three tungsten carbide balls at 250 rpm during 5 min for B2 sample and during 15 min for the kaolinites used as precursor of the synthesis of D1 and D2 samples.

The external surface was analysed by nitrogen adsorption isotherm at 77 K using a Micromeritics model ASAP 2010 and all samples were dried at 100 °C overnight under vacuum before the nitrogen sorption measurement. Those measurements allowed analysing the reactive surface of the starting materials.

The feature of the framework atoms bonds was studied by infrared (FTIR) spectroscopy. FTIR spectra were recorded in the range 4000–300 cm^{-1} by the Spectroscopy Service of the ICMS (CSIC-US, Seville, Spain), as KBr pellets, using a JASCO FT/IR-6200 IRT-5000 instrument.

In order to get information of the long-range structural transformations and the generation of the new crystalline phases, x-ray diffraction (XRD) patterns were obtained at the X-ray laboratory (CITIUS, University of Seville, Spain) on a Bruker D8 Advance instrument equipped with a Cu K$_\alpha$ radiation source operating at 40 kV and 30 mA. Diffractograms were measured in the range 3–70° 2θ with step time of 0.1 s and step size of 0.015°.

The changes of local environments of the framework heteroatoms during the synthesis process were analysed thorough nuclear magnetic resonance under magic angle spinning spectroscopy (MAS NMR). Single-pulse MAS NMR experiments were recorded on a Bruker AVANCE WB400 spectrometer equipped with a multinuclear probe. Powdered samples were packed in 3.2 mm zirconia rotors and spun at 10 kHz. The ^{1}H MAS NMR spectra were obtained using pulse widths of 2.25 μs (π/2) and a delay time of 5 s ^{29}Si MAS NMR spectra were acquired at a frequency of 79.49 MHz, pulse width of 2.7 μs (π/6) each 3 s ^{27}Al MAS NMR spectra were recorded at 104.26 MHz with a pulse of 0.38 μs (π/20) and a delay time of 0.5 s ^{23}Na MAS NMR spectra were recorded at 105.84 MHz with a pulse of 0.75 μs (π/12) and a delay time of 0.1 s. The ^{19}F MAS NMR spectra were obtained using typical a π/2 pulse of 2.9 μs and a pulse space of 2 s. The chemical shift values were reported in ppm from tetramethylsilane for ^{29}Si and ^{1}H, from NaF for ^{19}F and from a 0.1 M $AlCl_3$ and NaCl solution for ^{27}Al and ^{23}Na, respectively. Spectra were simulated using the DMFIT software (Massiot et al., 2002) and Gaussian-Lorenztian ratio, position, linewidth and amplitude were the fitted parameters.

3. Results and discussion

3.1. Effect of the precursor mixing

3.1.1. Effect of stoichiometry

In order to identify the stoichiometry tolerance of the components for large-scale synthesis, two series of samples were

Table 1
Synthesis conditions.

Samples	Precursor mixing			heating		washing
	Chemical source	Stoichiometry	Mixing	Crucible material	Crucible cap	Water volume (ml)
A1	Commercial oxides and salts	Si:0.98Al:1.39 Mg:2.02Na	agate	Pt	No	100
A2	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
B1	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
B2	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	ball[a]	Pt	No	100
C1	KGa-1b	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
C2	KGa-2	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
C3	Kaolinite Fluka	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
C4	Talc	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
C5	Bentonite FEBEX	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
C6	Bentonite MX80	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
D1	KGa-1b[b]	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
D2	KGa-2[b]	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
E1	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	SiC	No	100
E2	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Al_2O_3[c]	No	100
E3	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Al_2O_3	No	100
E4	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Al_2O_3[d]	No	100
E5	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Al_2O_3[e]	No	100
F1	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Pt	No	100
F2	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Pt	Yes	100
G1	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Pt	No	20
G2	Commercial oxides and salts	Si:Al:1.5 Mg:2Na	agate	Pt	No	100[f]

Heating time:
[a] The mixed amount milled was double in B2 than in B1. In this serie, the hated amount of sample was double than in the rest of the series.
[b] Before mixing the kaolinites were grinding in a ball grinder.
[c] 30 h.
[d] 7.5 h and.
[e] 3.0 h.
[f] Washed with tap water.