

Microwave-Assisted Synthesis of Fe³⁺ Saponites. Characterization by X-Ray Diffraction and FT-IR Spectroscopy

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INTRODUCTION.

Natural clay materials have been used for many different applications. However, they show some drawbacks against synthetic materials: a) It is not easy to find solids with the desired concentration of catalytically active elements. b) The chemical and mineralogical composition of these solids is not homogeneous nor their catalytic properties and structures. Consequently, controlling the parameters for preparation of tailored catalysts from natural clays is difficult or even impossible. On the contrary, synthetic materials show advantages such as: (1) They have the desired concentration of catalytically active elements, well dispersed in their structure. (2) The chemical composition of these solids is homogeneous and so their catalytic properties and structures. (3) The protocol for preparing these solids can be adjusted for pre-established properties.

Usually, the synthesis has been carried out through hydrothermal methods (Prihod'ko, et al. 2002; Kloprogge, 1998, Kawi and Yao, 1999, Bisio et al., 2008) non-hydrothermal methods are scarce (Prihod'ko, et al. 2002). High temperatures and long treatment times are needed when using hydrothermal methods. To diminish the time requirements and the temperature of the synthesis, microwave heating has been used in recent years. The microwave assisted processing is fast, clean, simple and often energetically more efficient than conventional heating. Microwave energy can reach the bulk of the dielectric materials, where it is absorbed and transformed into heat by different absorption mechanisms such as dipolar relaxations or ionic conduction. Zemanová et al. (2006) have modified the layer charge

of smectites by means of microwave radiation treatment.

In this work we have synthesized solids with the saponite structure with Mg²⁺ or Ni²⁺ as octahedral cations and Fe³⁺ in the tetrahedral sheet by using microwave radiation. The solids obtained have been characterized by element chemical analysis, Powder X-Ray Diffraction, FT-IR spectroscopy, and specific surface area measurements.

MATERIALS AND METHODS.

Samples were prepared following the method described by Kawi and Yao but the hydrothermal treatment was carried out in a microwave oven. A buffer solution was prepared by dissolving 3.6 g of NaOH and 6.56 g of NaHCO₃ in 50 ml of distilled water. Solution A was prepared by adding a sodium silicate solution (SiO₂.NaOH, SiO₂ 27%, density 1.39, Aldrich) to the buffer solution and the mixture was stirred; solution A had a pH close to 13. Solution B was prepared by dissolving stoichiometric amounts of FeCl₃·6H₂O and MgCl₂·6H₂O in 5.0 ml of

distilled water. In order to maintain a homogeneous high pH value during mixing, solution B was slowly added to solution A under vigorous stirring until a uniform gel was obtained. The gel was sealed into a 100 ml Teflon reactor and was hydrothermally treated in a microwave furnace MILESTONE ETHOS PLUS at 180 °C with a power of 600 W during 8 hours, thus obtaining sample SMgFe. Sample SNiFe was obtained by the same way but changing MgCl₂·6H₂O by NiCl₂·6H₂O. The powder X-ray diffraction patterns were recorded in a Siemens D-500 diffractometer with Diffract-AT software and a DACO-MP microprocessor, a copper ($\lambda=1.5405 \text{ \AA}$) anode and a graphite filter. The FT-IR spectra were recorded following the KBr pellet technique in a Perkin-Elmer FTIR-1600 spectrometer, with a nominal resolution of 4 cm⁻¹ and averaging 20 scans to improve the signal-to-noise ratio.

RESULTS

Formulae of the solids synthesized calculated from the element chemical

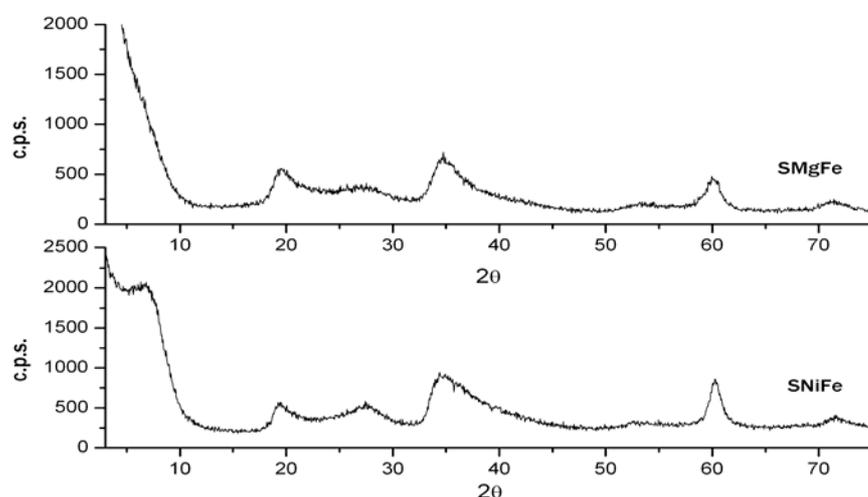


Fig. 1. PXRD patterns of the NiFe and MgFe saponites.

analysis data resulting:

SNiFe: $[\text{Si}_{7.136}\text{Fe}_{0.864}] [\text{Ni}_{5.813}] [\text{Na}_{0.810}] \text{O}_{20}(\text{OH})_4 \cdot 13\text{H}_2\text{O}$

SMgFe: $[\text{Si}_{7.200}\text{Fe}_{0.800}] [\text{Mg}_{5.820}] [\text{Na}_{0.7020}] \text{O}_{20}(\text{OH})_4 \cdot 9\text{H}_2\text{O}$

The PXRD patterns corresponding to the two saponites synthesised are recorded in Figure 1. In the 15-75 2 theta degree interval, both patterns show similar peaks, with d spacings close to 4.56, 3.28, 2.59 and 1.54 Å, corresponding to the (003), (113), (200) and (06,33) reflections of the saponite structure. These spacing values are considered the standards ones for saponites (Brindley and Brown, 1980). The main difference among the PXRD patterns of the samples is due to the (001) reflection that corresponds to the separation between layers. It can be concluded that for sample containing Mg^{2+} layers are not well stacked, the solid obtained in this case being a delaminated material. On the contrary the X-Ray diffraction pattern of sample SNiFe shows a well defined peak centred at 13.15 Å due to the 001 planes diffraction thus confirming that stacking of the layers along the c axis exists.

FT-IR spectra of both synthetic saponites in the 400 to 4000 cm^{-1} region are included in Figure 2. The characteristic IR absorption bands for natural saponites are observed for both samples. In these spectra the lattice vibration bands are recorded at about 1010, 660-695, and 456 cm^{-1} and they can be assigned to Si-O-Si, M^{2+} -OH stretching and Si-O- M^{2+} bending modes, respectively.

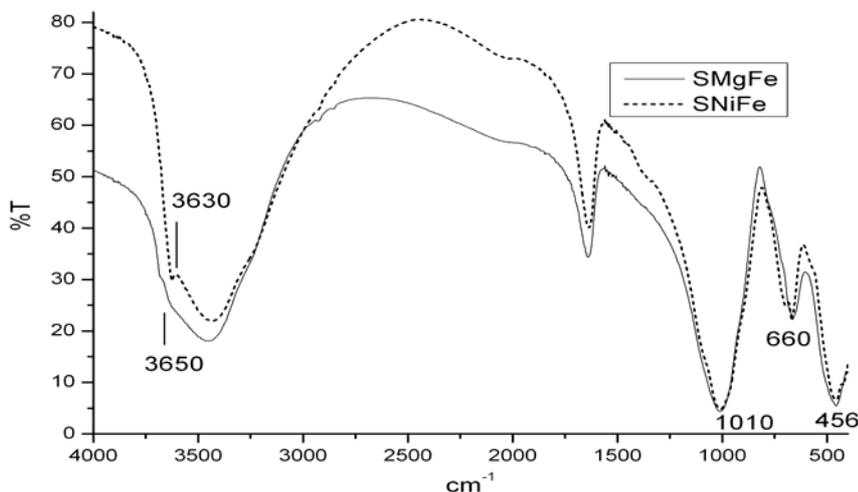


Fig. 2. FT-IR Spectra of samples SMgFe and NiFe.

Shoulders around 3650 and 3630 cm^{-1} belonging to the stretching vibrational modes of Fe-OH and Mg-OH, respectively are recorded in high wavenumbers range. These features confirm the trioctahedral character of the synthesized saponites (Madejová, 2006).

The band around 3440 cm^{-1} is due to the stretching modes H-O-H of adsorbed H_2O molecules, which bending mode is registered at 1635 cm^{-1} . The shoulder around 3220 cm^{-1} can be due to the O-H stretching mode of H-bridged OH groups (Alzamora et al., 1981).

Specific surface area of the samples have been determined from the adsorption-desorption isotherms of N_2 at -196 °C. Both samples have micropores and the obtained values of the specific surface area and the external one are included in Table 1 together with the area due to micropores. The specific surface area of sample SMgFe is more than twice that of sample SNiFe as it could be expected because of the larger crystallinity observed for the latter one in the PXRD diffractogram.

	SMgFe	SNiFe
S_{BET}	467	217
S_{Ext}	376	166
$S_{\text{micropore}}$	91	51

Table 1. Values of BET specific surface area, external surface and micropore surface all in m^2/g .

CONCLUSIONS

New materials with the saponite

structure have been synthesised by using microwave radiation. Both have Fe^{3+} cation in the tetrahedral sheet.

The data obtained from PXRD and FT-IR spectra confirm the saponite structure of both samples.

Differences between them arise from the different cation existing in the octahedral sheet.

ACKNOWLEDGEMENTS.

Authors acknowledge the financial support from AECl (grant C/016234/08) and from Junta de Castilla y León (grant SA101A07).

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