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Microwave power effect on hydrotalcite synthesis

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Abstract

Hydrotalcite-like compounds, also referred as double layered hydroxides, are anionic clay-like compounds. They are microporous minerals with a layered structure. As they are scarcely found in nature they are usually synthesized through co-precipitation methods. A remarkable improvement in time and solution concentrations has been attained by microwaving the synthesis solutions. The obtained materials are original and different from those provided by the co-precipitation method. In this work, we correlate the features of the obtained hydrotalcite-like compounds, Mg/Al and Zn,Mg/Al, with the microwave intensity, the anion and cation nature, among others. When magnesium is incorporated at 200 W it remains in the outer layers of the hydrotalcite inhibiting the Zn diffusion which, then, forms zinc oxide. The irradiation power determines the homogeneity of the obtained materials as at 600 W the obtained hydrotalcite is more homogeneous than the one synthesized at 200 W.

Keywords: Hydrotalcite; Microwave irradiation; Microporous materials; Ion diffusion; Zinc; Aluminum; Magnesium

1. Introduction

Hydrotalcite-like compounds, also referred as double layered hydroxides, are anionic clays. They are microporous minerals with a lamellar structure whose symmetry is rhombohedral. As they are scarcely found in nature they are usually synthesized. The accepted chemical formula is:

$$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{m-})_{x/m} \cdot nH_2O$$

where M^{2+} may be replaced by three-valent atoms, M^{3+}, which produce positively charged layers. This charge is neutralized by A, a compensating anion with charge m^- as CO_3^{2-}, SO_4^{2-}, Cl^- or NO_3^-, among others [1–3]. The properties of hydrotalcite-like compounds are mainly determined by the metal ratio M^{2+}/M^{3+}, the concentration of the reactants in the synthesis solution and the synthesis procedure (hydrothermal, microwaves, ultrasound, pH value among others) [4,5]. The hydrotalcites may be expanded by intercalating the layers between various pillaring agents. The most frequently used are the polyoximetallate ions [2].

The hydrotalcite synthesis method has been significantly improved substituting the conventional hydrothermal treatment step by microwave irradiation [4,6]. The autoclave high temperature treatment is, in this way, avoided and the long crystallization time is substantially reduced. However, to control this synthesis procedure, the effect of the various parameters, which determine the synthesis, have to be studied. In the microwaved irradiated synthesis, correlations between the features of the obtained hydrotalcite-like compound and the microwave intensity, the anion and cation nature, the concentration of the solutions, among others, have not been established or carefully studied. The understanding of those parameters should provide a control on the structural and morphological characteristics of these materials.

In this work, the influence of microwave power on two different hydrotalcite-like compounds is presented, on the

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one hand the usual composition Mg/Al and on the other hand the Zn–Mg/Al, where Mg and Zn ions compete to form the brucite-like layer of the hydrotalcite.

2. Experimental

2.1. Hydrotalcite samples

2.1.1. Mg/Al hydrotalcite synthesis

Mg/Al hydrotalcite-like samples were synthesized from hydrous Mg- and Al-nitrate solutions, 3.2 M and NaOH, 1.86 M. The flow of each solution was adjusted to maintain a constant pH of 13. The amounts correspond to molar ratios Mg/Al of 2, 3 and 4. The resulting gels were treated in a microwave autoclave (MIC-I, Sistemas y Equipos de Vidrio S.A. de C.V.) for 10 min operating at 2.45 GHz. The power was 200 W and the temperature was fixed at 80 °C. The solids were recovered by decantation and washed with distilled water resulting in a pH of 10 for the wash solution and dried in an oven at 70 °C for 14 h. The sample Mg/Al = 3 was microwave treated at powers of 200, 400 and 600 W.

2.1.2. Zn–Mg/Al hydrotalcite synthesis

The Zn–Mg/Al hydrotalcite-like samples were prepared in the same way from Zn-, Mg- and Al-nitrates using amounts corresponding to the molar ratios (Zn + Mg)/Al of 2, 3 and 4, where the proportion Zn:Mg was 1:1. Again the samples with a ratio of 3 were microwave treated at 200, 400 and 600 W.

Both groups of samples were calcined in air at 450 °C for 4 h.

2.2. Characterization

2.2.1. X-ray diffraction

A Bruker-axs D8-advance diffractometer coupled to a copper anode X-ray tube was used to identify the compounds. A diffracted beam monochromator selected the Kα radiation.

2.2.2. FTIR spectroscopy

FTIR spectra in the region 4000–400 cm^{-1} were obtained with a Magna-IR Spectrometer 550 Nicolet. The powders were mixed with KBr to form a pellet.

2.2.3. Nitrogen adsorption

The BET surface areas were determined by the one point technique with a Micromeritics TPR/TPD 2900 after a thermal treatment of 200 °C for 2 h in N_2 atmosphere.

2.2.4. Scanning electron microscopy

A scanning electron microscope LEICA, Stereoscan 440 was used. An energy dispersive detector coupled to the microscope provided the elemental local composition for a surface of approximately 2 μm depth.

3. Results

3.1. Power effect

To study the microwave power effect the samples with a ratio of Mg/Al = 3 were chosen. Diffraction patterns presented in Fig. 1 show that well crystallized hydrotalcite-like compounds are obtained, no other compounds are identified. As the interplanar distance 003 is ca. 7.76 Å,

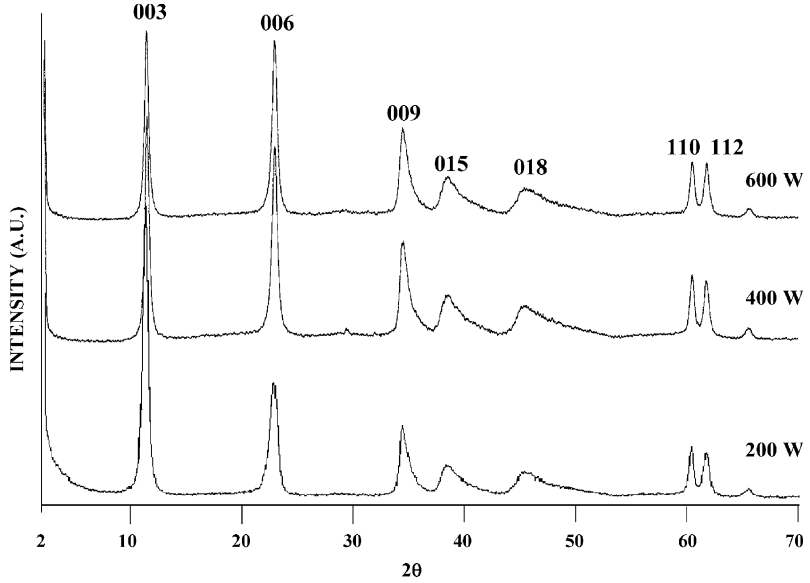


Fig. 1. X-ray diffractograms of the samples with a molar ratio Mg/Al = 3 treated at 200, 400 and 600 W. Miller indices refer to hydrotalcite-like compound.

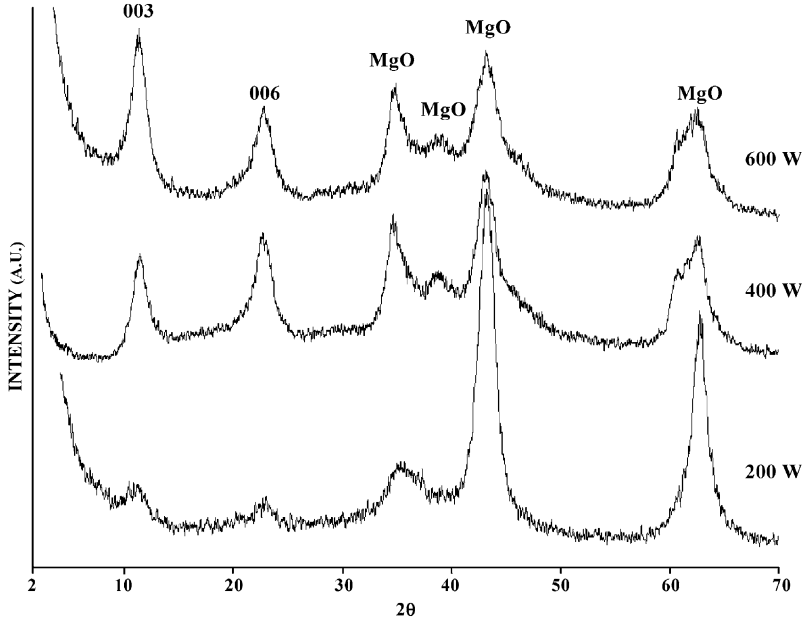


Fig. 2. X-ray diffractograms of the calcined samples with a molar ratio Mg/Al = 3 treated at 200, 400 and 600 W. Miller indices refer to hydrotalcite-like compound.

the interlayered anions are expected to be nitrates [1,3]. With calcination (450 °C/4 h) the diffraction patterns turned out to be different, Fig. 2, as the two samples treated at 400 and 600 W contain a small amount of MgO in addition to the hydrotalcite-like compound. Instead, the sample treated at 200 W is mainly MgO with a minor content of a hydrotalcite-like compound. In the 400 and 600 W treated samples, the MgO peaks are fairly broad showing that the crystallites are smaller than in the 200 W.

If zinc is incorporated into the synthesis composition the resulting compounds turn out to be hydrotalcites, similar to those previously described, Fig. 3. The composition of the samples seems to be independent of the irradiation power. When the samples are calcined all the X-ray diffraction patterns turn out to be similar: a small amount of hydrotalcite remains and narrow and well defined ZnO peaks are present. Still, a very small content of MgO can be appreciated, the peaks of this compound correspond

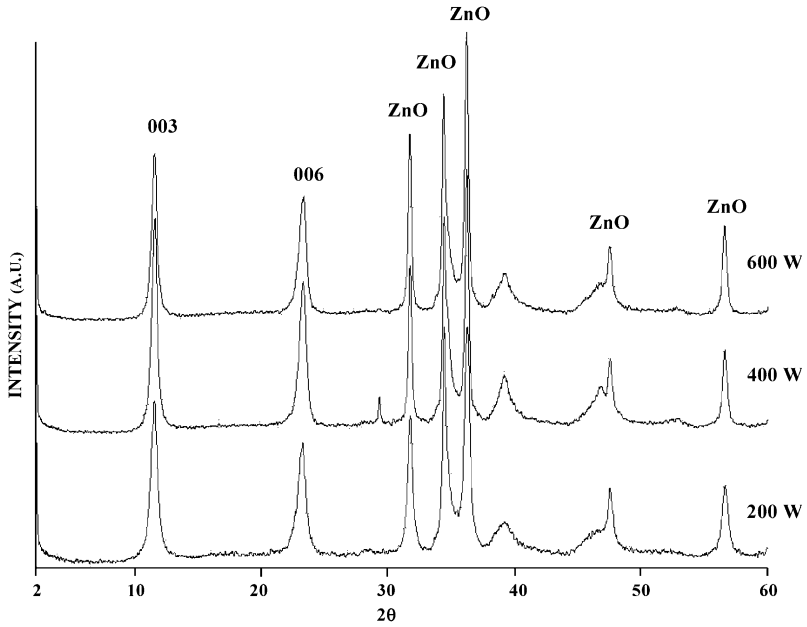


Fig. 3. X-ray diffractograms of the samples with a molar ratio Zn,Mg/Al = 3 treated at 200, 400 and 600 W. Miller indices refer to hydrotalcite-like compound.

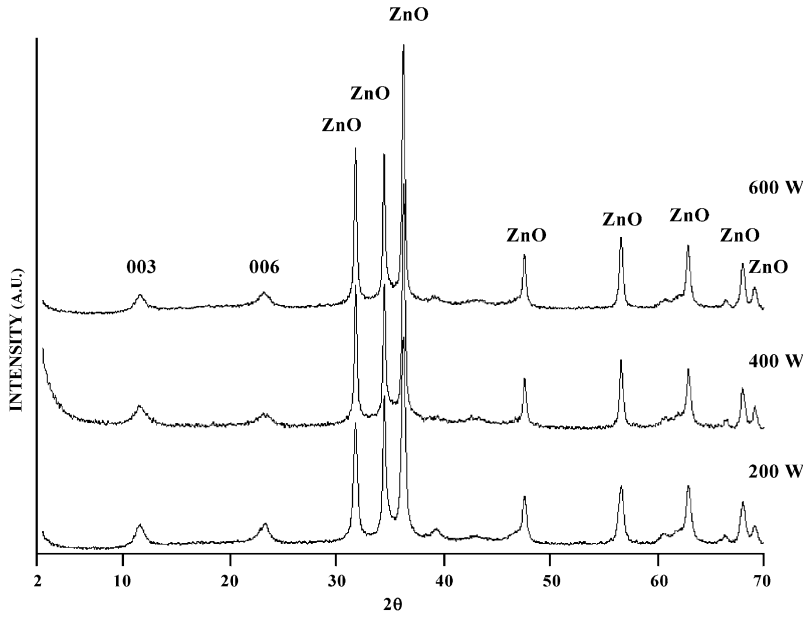


Fig. 4. X-ray diffractograms of the calcined samples with a molar ratio Zn,Mg/Al = 3 treated at 200, 400 and 600 W. Miller indices refer to hydrotalcite-like compound.

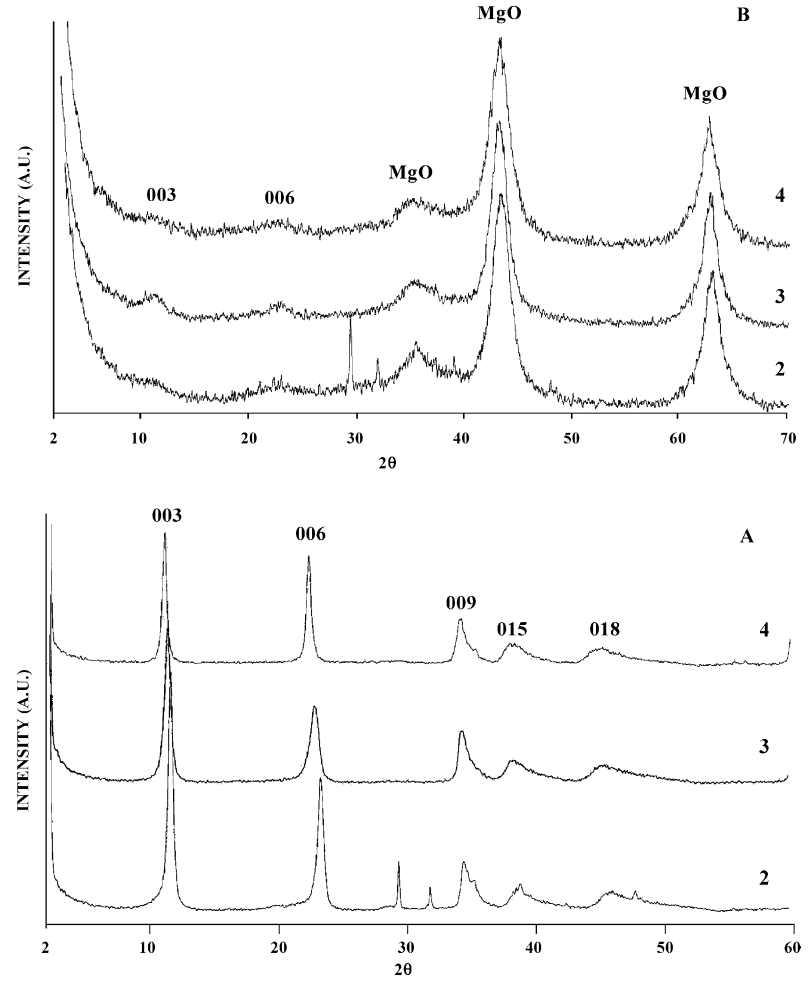


Fig. 5. X-ray diffraction patterns of the Mg/Al samples whose molar ratios are: 2, 3 and 4, all irradiated at 200 W (A) and the corresponding calcined materials (B). Miller indices refer to hydrotalcite-like compound. The two small and sharp peaks at $2\theta = 29.5°$ and 32.0° are due to $NaNO_3$.

to small crystallites as they are very broad, Fig. 4. Note that the incorporation of zinc provides samples apparently insensitive to the microwave irradiation, such is not the case for the above described Mg/Al samples.

3.2. Cation nature effect

Samples with various compositions were studied at a constant microwave irradiation power. We chose 200 W since at this power the Mg/Al = 3 sample was partially decomposed with temperature, while the other samples (400 and 600 W) with this composition remained partially stable with calcination. Fig. 5 shows the X-ray diffraction patterns of the Mg/Al samples whose nominal molar ratios are: 2, 3 and 4, all irradiated at 200 W and the corresponding calcined materials. Only when the molar ratio is 2, a small amount of nitratine, $NaNO_3$, ($d = 3.038$ and 2.805 Å) appears with the hydrotalcite (uncalcined samples). With calcinations the $NaNO_3$ remains in the Mg/Al = 2 sample. In the two other materials, only MgO is observed, the peaks are broad showing that the crystallite size is small. In the sample with Mg/Al = 3, the small and broad peaks at $d = 7.76$ and 3.95 Å show that a small fraction of the hydrotalcite-like compound is still present.

The incorporation of zinc, independently of the molar ratio, provides similar materials composed by hydrotalcite and some ZnO whose presence is not reported by Kloprogge et al. [7,8] in the corresponding co-precipitation synthesis. With calcination, the sample treated at 200 W, whose molar ratio is 2, is constituted only by ZnO and MgO. The ZnO is well crystallized (intense narrow and well defined X-ray diffraction peaks), whereas the MgO is constituted by small crystallites, Fig. 6. In the other samples, the X-ray diffraction peaks of hydrotalcite are present although the sample is mostly constituted by ZnO and some small crystallites of MgO.

3.3. Nitrates and carbonates

By infrared spectroscopy, Fig. 7, in the non-calcined samples, the obtained spectra reproduce the general features often reported for hydrotalcite-like compounds

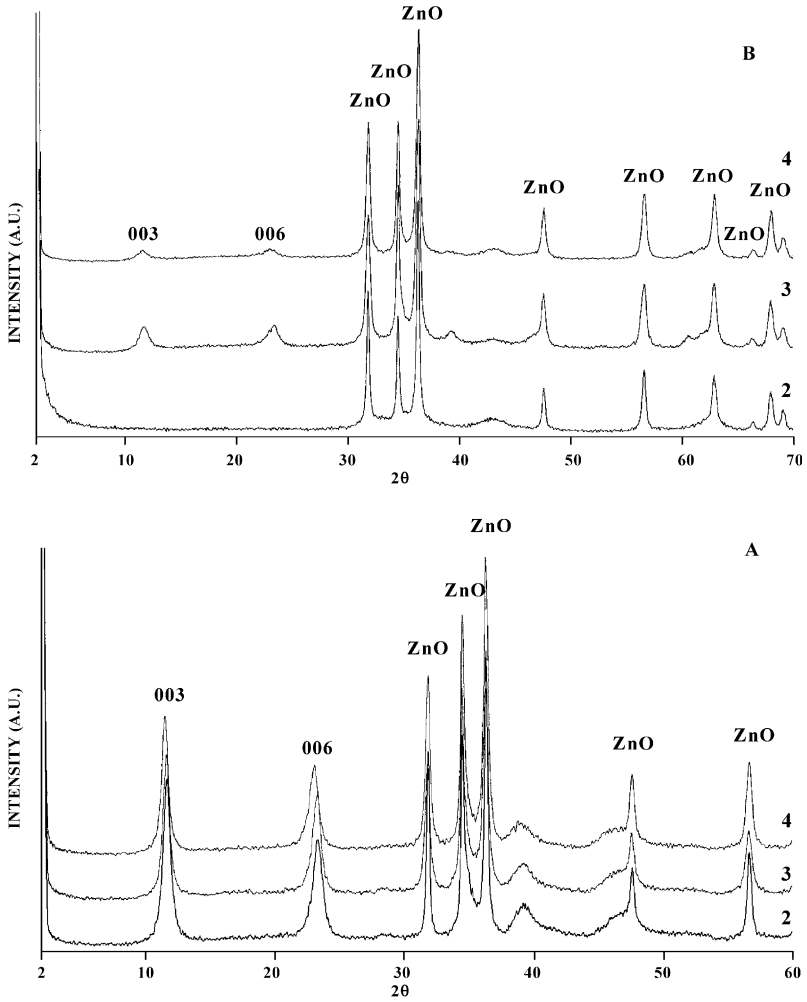


Fig. 6. X-ray diffraction patterns of the Zn–Mg/Al samples whose molar ratios are: 2, 3 and 4, all irradiated at 200 W (A) and the corresponding calcined materials (B). Miller indices refer to hydrotalcite-like compound.

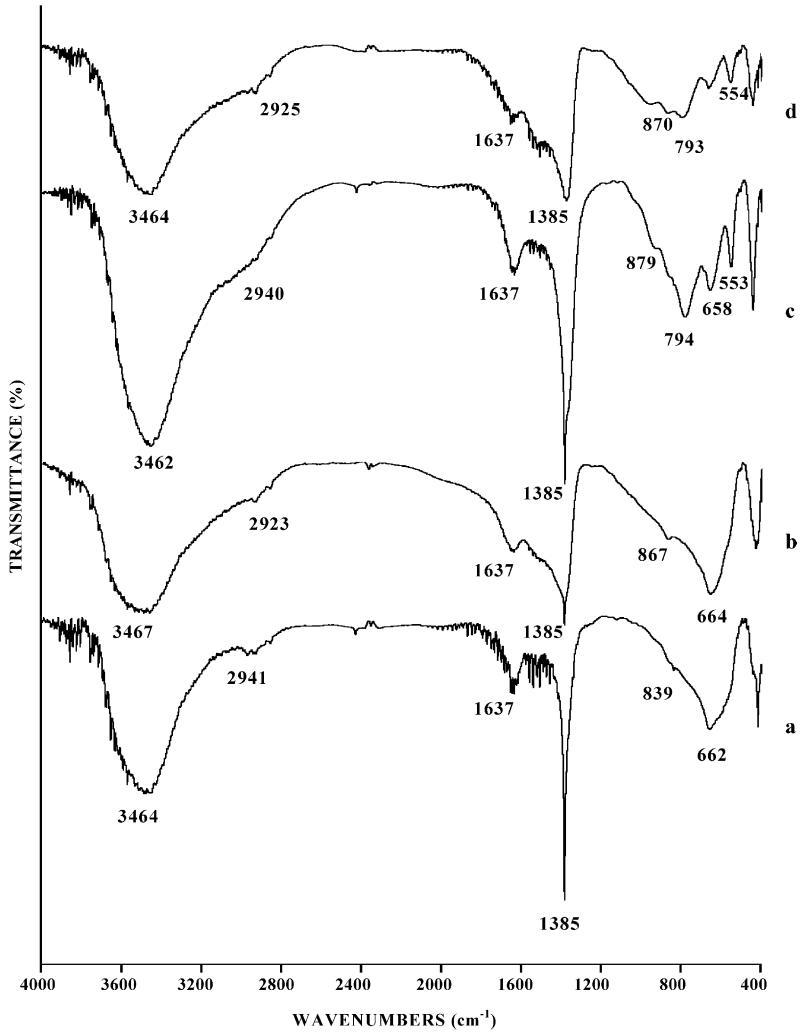


Fig. 7. Infrared spectra of the samples: (a) Mg/Al = 3, (b) calcined Mg/Al = 3, (c) Zn,Mg/Al = 3 and (d) calcined Zn,Mg/Al = 3. The bands are attributed in the text.

[1,7]. The presence of both, nitrates and carbonates (unresolved band at ca. 1383 cm^{-1}), is shown. With calcinations this absorption band diminishes as hydrotalcite decomposes but, under our conditions, it is always present showing that hydrotalcite is not fully destroyed.

3.4. Morphology

The particle morphology obtained by SEM is compared in Fig. 8(a)–(c). As the irradiation power increases the particle size diminishes. In the 200 W irradiated sample large irregular and compact chunks (70 μm) are present, instead, if power is 600 W, the size distribution and the shape become more homogeneous (10–20 μm). The surface area of the Mg/Al sample irradiated at 200 W turned out to be 69 m^2/g, which is a common value for large hydrotalcite particles [3].

Fig. 8(d)–(f) compares the materials (Zn,Mg/Al = 3) obtained varying the irradiation power. All micrographs can be described in terms of large agglomerates (100 μm) and a large number of smaller ones (10 μm). The size distribution is very broad although in the 200 W irradiated sample the number of large particles is higher than in the other two materials. Thus, Zn has a determinant effect on the agglomerate and particle size.

3.5. Elemental composition

To determine whether the various irradiations promoted a faster diffusion to the surface of some elements, the surface elemental composition was determined by EDX, Fig. 9. In the Zn–Mg/Al samples, the ratio of the Mg peak area to the Al peak area diminished linearly from 5.5 to 3.6, whereas the Zn/Al proportion seems to reach a plateau for the sample irradiated at 400 W, Table 1.

4. Discussion

With an increasing irradiation power several effects were observed: the sample treated at 600 W is thermally (450 °C)

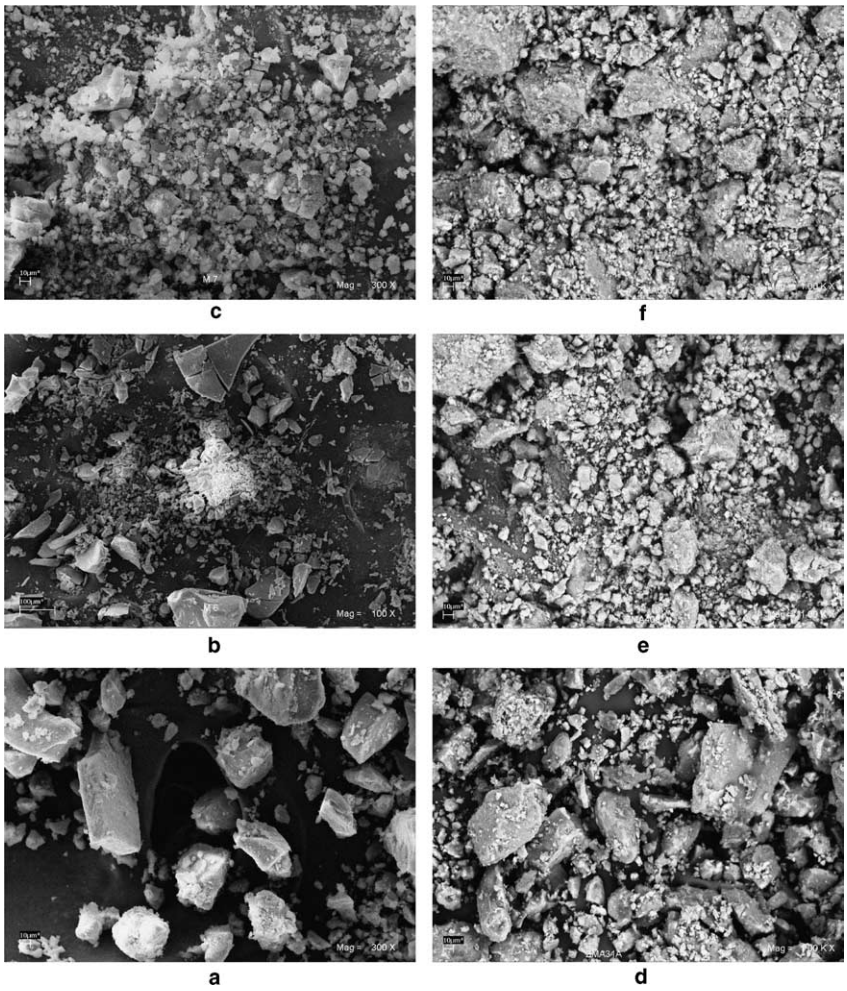


Fig. 8. SEM images of the Mg/Al = 3 samples treated at 200 W (a), 400 W (b), and 600 W (c), and Zn,Mg/Al = 3 samples treated at 200 W (d), 400 W (e), and 600 W (f).

more stable as a fairly high amount of hydrotalcite (HT) remains after calcination concerning the Mg/Al samples. The introduction of Zn in the preparation mixture generates similar structures which are not influenced by irradiation power although ZnO is segregated. A very low amount of HT is present after thermal treatment, as shown by infrared spectra.

This behavior may be understood if the micrographs and the EDX analyses are considered. The morphology of the samples depends on the irradiation power as a 600 W irradiation generates small particles in the samples without zinc. Hence, with this power much more crystallization nuclei are simultaneously formed. Furthermore, the surface composition of these particles (600 W treated) reproduces the expected Mg/Al molar ratio of 3, within error range, Table 1, and these particles are therefore homogeneous. In the large chunks observed in 200 W irradiated sample the surface Mg/Al molar ratio was higher by a factor of 1.5. Therefore, irradiation power in this samples promotes the diffusion of Mg into the Al matrix.

To understand the preference of the hydrotalcite to incorporate Mg ions in the Zn–Mg/Al samples, some considerations on the respective atoms have to be advanced. The ion mobility in aqueous solution of Mg^{2+} and Zn^{2+} is comparable at room temperature, but this is not the case in the presence of microwave irradiation. The observed differences in the Zn containing samples have to be attributed to differences in weight, charge and size as these features are most relevant in the presence of microwaves. With irradiation the Mg mobility is more increased than the mobility of Zn ions, which are heavier and larger. Table 1 presents the ratios of the atomic contents determined by EDX. As in the zinc-free materials, the atomic ratio Mg/Al decreases from 1.80 (200 W) to 1.69 (600 W) which is very close to the nominal 1.50. In the 200 W treated sample the ratio Zn/Al is 3.19, which is much higher that the nominal 1.5 value or the 1.8 obtained for Mg/Al sample. Therefore, firstly, hydrotalcite (HT) nuclei are preferentially formed with a high amount of Al. Irradiation then drives Mg into the incipient hydrotalcite lattice. Hence, the particles present an onion-like structure, where the core is Al enriched, the following zones are Mg enriched and the particle surface is constituted by a zinc hydrotalcite enriched zone or ZnO, Scheme 1.

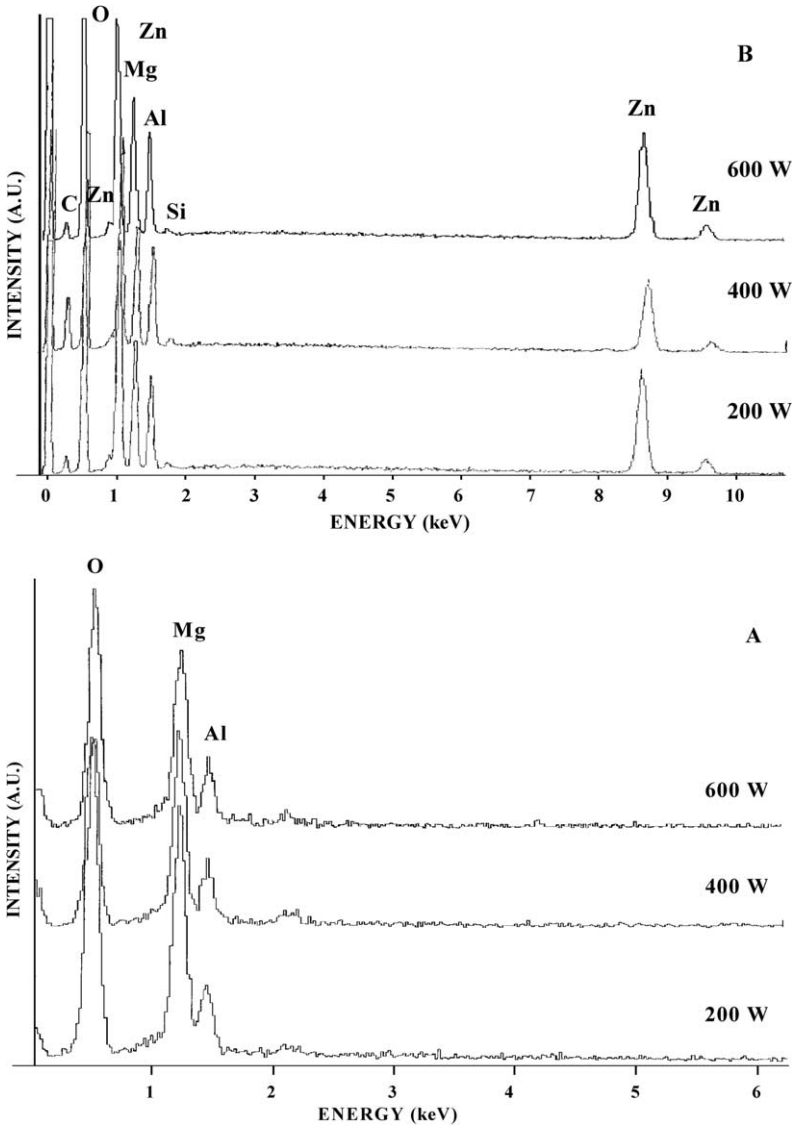


Fig. 9. EDX spectra as a function of the irradiation power. (A) Mg/Al = 3 samples treated at 200, 400 and 600 W; (B) Zn,Mg/Al = 3 samples treated at 200, 400 and 600 W.

Table 1
Atomic ratios determined by EDX of the Mg/Al and Zn–Mg/Al samples

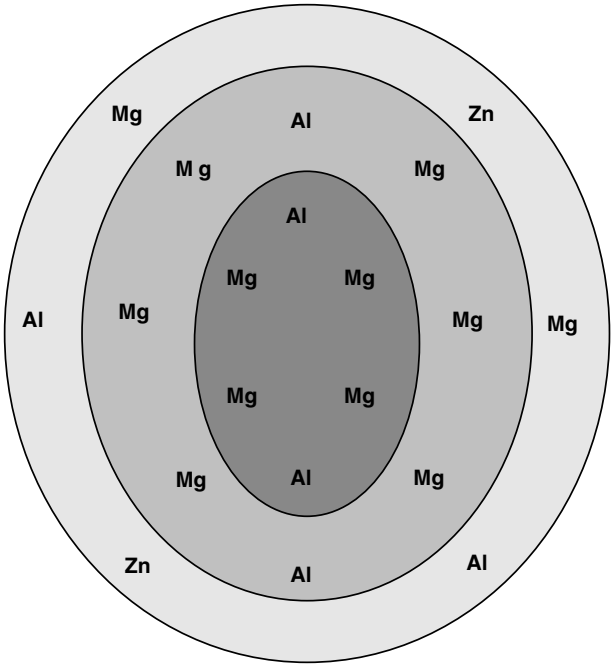
Microwave irradiation power (W)	Mg/Al sample	Zn–Mg/Al sample	
	Mg/Al[a]	Mg/Al[b]	Zn/Al[c]
200	5.53	1.80	3.19
400	4.54	1.48	2.24
600	3.62	1.69	2.96

[a] Nominal composition Mg/Al = 3.
[b] Nominal composition Mg/Al = 1.5.
[c] Nominal composition Zn/Al = 1.5.

Some reactions are selectively accelerated by microwave irradiation [9,10]. Furthermore, these reactions occur at the contact surface without involving the bulk, thus avoiding many of the possible side-effects [11]. Our results show that with an adequate irradiation power the compositional gradient in the prepared samples may be modified. The highest the power, the more homogeneous is the sample. Then, at high power the thermal effects dominate, instead at low power the reaction occurs conventionally, providing compositionally layered hydrotalcite-like compounds.

5. Conclusion

Microwave irradiation can be used not only to reduce the preparation time as a fast heating method, but also to prepare original materials. In Mg/Al hydrotalcite synthesis the irradiated materials present a concentration gradient, where the core is aluminum enriched. This result may be interpreted in terms of the competitive diffusion determined by charge, weight and ion size. The reaction occurs at the contact surface between the solid and the solution without involving the crystallized bulk. We have found that in Zn–Mg/Al hydrotalcites an aluminum enriched core is first formed and, then, magnesium is driven



Schema 1. Illustration of the metallic distribution in Zn–Mg/Al hydrotalcite-like samples.

into the structure. Finally, zinc remains on the hydrotalcite surface in agreement with the weight and size of the considered elements. When magnesium is incorporated at 200 W it remains in the outer layers of the hydrotalcite inhibiting the Zn diffusion which, subsequently, forms zinc oxide. The irradiation power determines the homogeneity of the obtained materials as at 600 W the obtained hydrotalcite is more homogeneous than the 200 W synthesis.

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References

[1] F. Cavani, F. Trifirò, A. Vaccari, Catal. Today 11 (1991) 173.
[2] F. Trifirò, A. Vaccari, in: G. Alberti, T. Bein (Eds.), Supramolecular Chemistry: Two- and Three-Dimensional Inorganic Networks, vol. 7, Pergamon, Oxford, 1996, p. 251 (Chapter 8).
[3] V. Rives, M.A. Ulibarri, Coord. Chem. Rev. 181 (1999) 61.
[4] G. Fetter, F. Hernández, M. Maubert, V.H. Lara, P. Bosch, J. Porous Mater. 4 (1997) 27.
[5] D. Tichit, A. Rolland, F. Prinetto, G. Fetter, M.J. Martínez-Ortiz, M.A. Valenzuela, P. Bosch, J. Mater. Chem. 12 (2002) 3832.
[6] B. Zapata, P. Bosch, G. Fetter, M.A. Valenzuela, J. Navarrete, V.H. Lara, J. Inorg. Mater. 3 (2001) 23.
[7] J.T. Kloprogge, L. Hickey, R.L. Frost, J. Raman Spectrosc. 35 (2004) 967.
[8] J.T. Kloprogge, L. Hickey, R.L. Frost, J. Solid State Chem. 177 (2004) 4047.
[9] P. Lidström, J. Tierney, B. Wathey, J. Westman, Tetrahedron 57 (2001) 9225.
[10] L. Perreux, A. Loupy, Tetrahedron 57 (2001) 9199.
[11] A. Fini, A. Breccia, Pure Appl. Chem. 71 (1999) 573.