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Sol-gel synthesis of hydrotalcite — like compounds

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Sol-gel hydrotalcite-like compounds were prepared using two different magnesium precursors, on the one hand magnesium ethoxide and on the other magnesium acetylacetonate. The aluminum precursor was always aluminum acetylacetonate. The resulting interlayer anions were ethoxide–acetylacetonate and acetylacetonate, respectively. Instead of the conventionally accepted thermal autoclave treatment, a new gelling and crystallization method is proposed using microwave irradiation. The solids were characterized by X-ray diffraction, nitrogen physisorption, thermogravimetric analysis, infrared spectroscopy and transmission electron microscopy. It is found that the acetylacetonate precursors determine surface area and crystallinity. Microwave irradiation guarantees a high surface area for an irradiation time as low as 10 min. © *2006 Springer Science + Business Media, Inc.*

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1. Introduction

Hydrotalcite-like compounds, also referred as double layered hydroxides, are anionic clays. The layer structure is determined by divalent cations octahedrally coordinated to the surrounding hydroxide ions. Some of them may be isomorphously replaced by three-valent atoms which produce positively charged layers whose charge is neutralized by $SO_4{}^{2-}$, Cl^- or $NO_3{}^-$ anions among others [1–4]. The most common hydrotalcite-like compound, known as hydrotalcite, is constituted by magnesium and aluminum. In this material, the positive charges are compensated by $CO_3{}^{2-}$ solvated anions.

Hydrotalcite conventional synthesis method has been significantly improved substituting the conventional hydrothermal treatment step by microwave irradiation [5–7]. The autoclave high temperature treatment is, in this way, avoided and the long crystallization time is substantially reduced. However, the crystallite size of the obtained solids was found to be smaller. It seems, therefore, that the features of hydrotalcite-like compounds depend, among other factors, on the synthesis method. Furthermore, in previous works, López *et al.* [8] have correlated the aluminum precursor to the particle size and the crystallinity in the sol-gel synthesis. Comparing hydrotalcites prepared by the sol-gel and coprecipitation methods, Prinetto *et al.* [9] have emphasized the role of precursors to obtain well crystallized Mg/Al hydrotalcite-like compounds. Almost pure Ni/Al phases resulted from acetylacetonate precursors, hydrolysed with HCl, while unsuccessful trials were done with HNO_3.

To summarize, synthesis parameters determining the characteristics of this kind of materials are: the precursors, the synthesis method (sol-gel conditioned by catalysts or coprecipitation) and hydrothermal conditions. As discussed previously, the effect of precursors is already known; HCl is recommended as catalyst in sol-gel

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synthesis to obtain high surface area materials. However, the hydrothermal conditions using new environments (microwave irradiation) have not been systematically studied. In this work, the effect of two different magnesium precursors in the sol-gel synthesis, in presence of microwave irradiation, is discussed. The conditions providing the best crystallinity and surface area are determined.

2. Experimental methods

2.1. Synthesis

Two series of samples were prepared depending on the precursors, either utilizing magnesium ethoxide and aluminum acetylacetonate (samples EA) or utilizing magnesium acetylacetonate and aluminum acetylacetonate (samples AA).

2.2. Samples EA

A solution was prepared with 150 mL of ethanol and 4 mL of 35% HCl, which was constantly stirred for one minute with a nitrogen flow. Magnesium ethoxide (4.25 g) was mixed with 4.32 g of aluminum acetylacetonate and added to the solution, under constant stirring during the whole process. The pH value of the mixture was found to be 5.65. The obtained gel was irradiated in a sealed reactor (Sistemas *y* Equipos de Vidrio S.A de C.V.) operating at 120 W for 20 min; the pressure was 600 kPa under hydrothermal conditions. The final pH value of the mixture was adjusted to 11.5 with ammonium hydroxide. Deionized water (4 mL) was added. The resulting mixture was again irradiated, for 10, 20 and 30 min, under the same controlled pressure, temperature and stirring. The solid was separated by decantation and washed several times with ethanol. Ethanol was evaporated from the solution with a nitrogen flow. The material was dried at 70°C for 3 h. The three samples were referred as EA10, EA20 and EA30. Deionized water was used throughout all the preparation as well as N_2 atmosphere.

2.3. Samples AA

This group of samples was prepared as previously explained but with 16.43 g of magnesium acetylacetonate instead of magnesium ethoxide. Before adjusting the pH value to 11.5, the pH of the mixture was 6.25. The obtained materials were labeled as AA10, AA20 and AA30, depending on the hydrothermal treatment time.

2.4. Characterization

Powder X-ray diffraction patterns (XRD) were obtained with a Bruker-axs D8 Advance diffractometer coupled to a copper anode tube. The cell parameters were determined using an internal standard (corundum) which presents a peak at $2\theta=25.57^\circ$ for copper wavelength. This method ensures interplanar distances with an accuracy of less than 0.01 Å. FTIR spectra in the region 4000–400 cm^{-1} were obtained with a Magna-IR Spectrometer 550 Nicolet. A TGA 51, Thermogravimetric Analyzer, TA Instruments, was used to determine the weight loss with temperature at a heating rate of 10°C/min up to 1000°C in a N_2 flow (50 mL/min). The BET surface areas were determined by the standard multipoint technique with a Micromeritics Gemini 2360, the samples were pretreated at 200°C for 2 h in N_2 atmosphere. A JEOL1020 transmission electron microscope coupled to an EDXS detector provided the sample micrographs and the corresponding elemental composition.

3. Results and discussion

3.1. Setting conditions

To operate in the most convenient conditions several setting experiments were performed. The dissolvent, the pH and the precipitating agent effects were studied. Water, ethanol, methanol and acetone were tested. Ethanol was retained as it provided the purest hydrotalcite-like compounds. After a screening of pH values from 9 to 12, only for pH values higher than 11, using NH_4OH instead of NaOH, pure hydrotalcite-like compounds were obtained. Note that at pH values lower than 10, only non lamellar compounds were formed. Hence, the following results correspond to ethanol as solvent, NH_4OH as precipitating agent and pH values higher than 11. Furthermore, It was found that samples should be washed with ethanol until pH values were comprised between 9 and 10.

3.2. Structure

All X- ray diffraction patterns corresponding to EA and AA samples were identified as hydrotalcite, (JCPDS 22-0700). Fig. 1 compares the EA diffractograms and shows that in the EA30 sample (with 30 min of irradiation time) the relative intensity of the 006 peak is the highest. However, an irradiation time of 10 min is enough to obtain a well ordered material. Instead, in the second series of samples, Fig. 2, after 10 min of irradiation the obtained material presents peaks attributed to a hydrotalcite-like compound and broad unresolved peaks at *ca*. 19, 26 and 30° (2θ) corresponding to some non crystalline material. However, the sample treated for 20 min (AA20) is

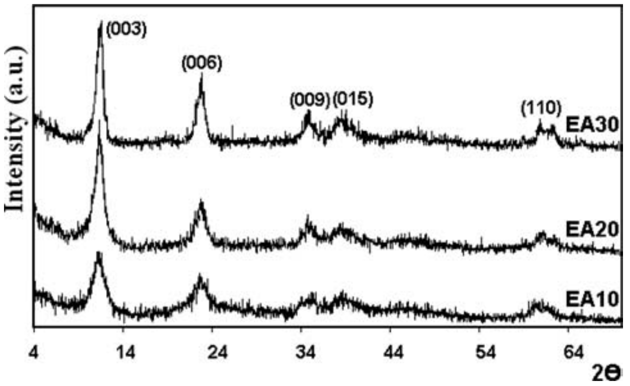


Figure 1 EA samples: comparison of the X- ray diffraction patterns as a function of irradiation time.

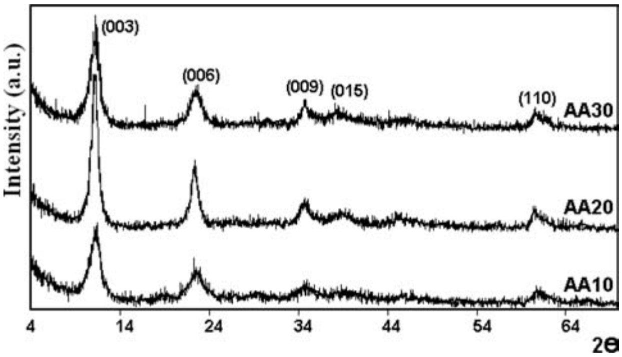


Figure 2 AA samples: comparison of the X- ray diffraction patterns as a function of irradiation time.

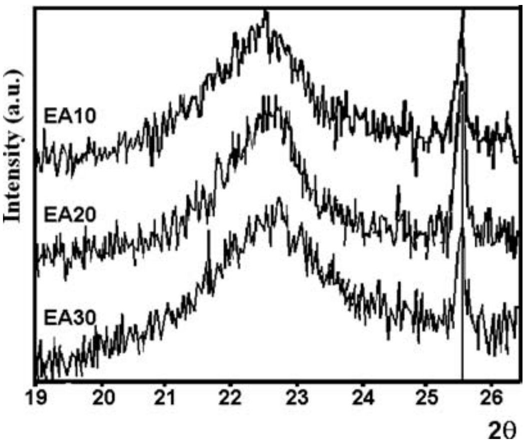
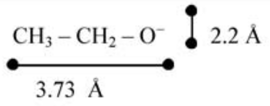
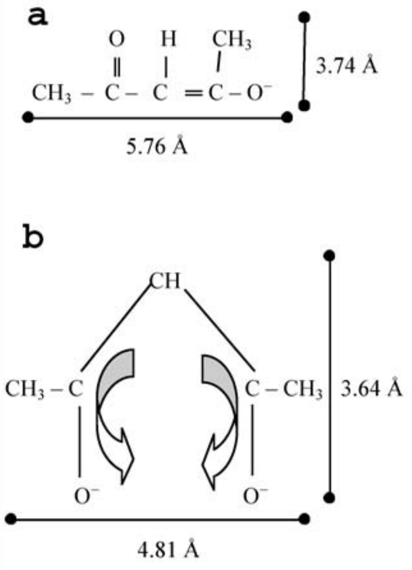


Figure 3 Shift of the EA (006) peaks as a function of the irradiation time referred to the corundum standard.

comparable with the EA30 showing that the crystallization mechanism is different and depends on the precursors. The hydrotalcite-like peaks present in the last diffractogram (AA30) are similar to those of the AA10 pattern; the non-crystalline compound is not observed. It seems that the fully crystalline hydrotalcite-like compound is obtained with an irradiation time of 20 min (sample AA20). The noncrystalline compound observed in the AA10 material is already transformed to hydrotalcite-like compound. If the irradiation time is longer (AA30) the hydrotalcite-like compound remains but the X-ray diffraction peaks are broader showing that either the acetylacetonate diffuses between the layers promoting delamination or that the acetylacetonate configuration is modified. In both cases, hydrotalcite-like compound with different interlayer distances is formed causing the peak broadening.

Fig. 3 shows the shift of the EA (006) peaks depending on the irradiation time compared to the corundum standard. As irradiation time is increased the (006) peak of the EA samples shifts towards smaller angles showing that the organic interlayered species differ. Acetylacetonate ions (4.81 × 3.64 Å as estimated from bond lengths) are, indeed, larger than ethoxide ions (3.73 × 2.20 Å) and may originate different species, Schema 1. In the AA samples the cell parameters indicate that there is an optimum irradiation time (20 min) to obtain the largest *c* cell parameter of 23.83 Å which corresponds to a 3.1 Å in-

Anion	Anion formula	Anion structural formula and dimensions
Ethoxide	$(C_2H_5O)^{1-}$	
Acetylacetonate	$(C_5H_7O_2)^{1-}$	

Schema 1 Anion structural formula and dimensions.

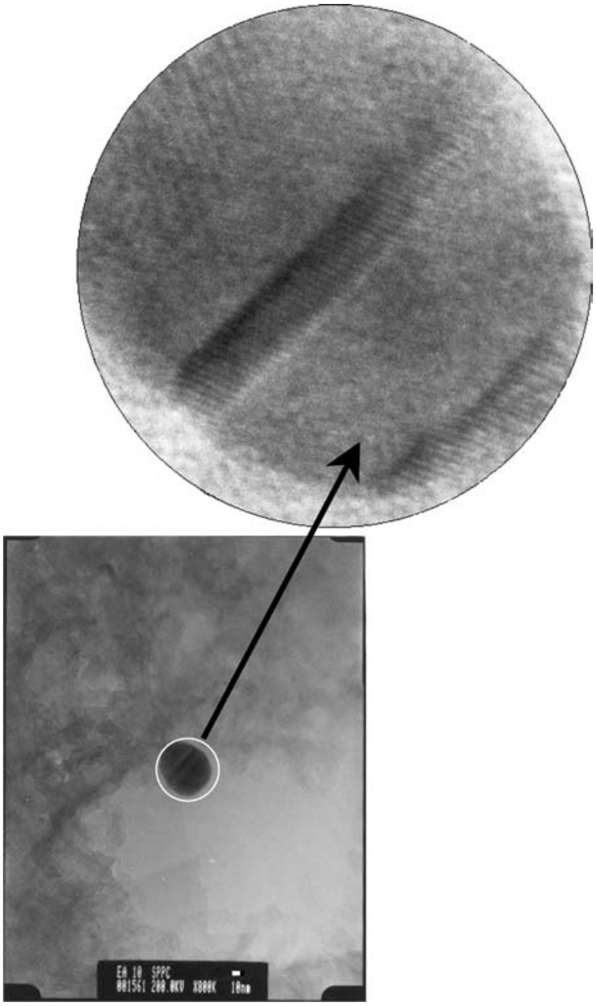


Figure 4 Transmission electron microscope image of the EA10 sample, showing the local ordering of the hydrotalcite sheets.

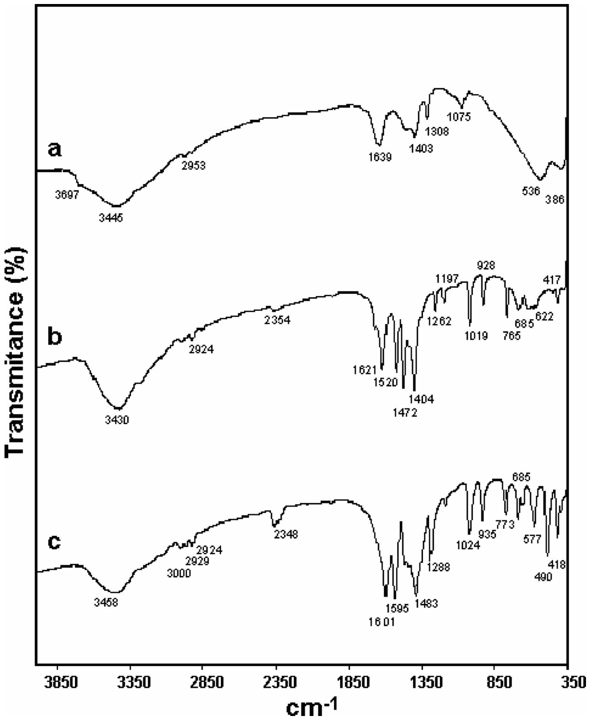


Figure 5 FTIR spectra of the a) magnesium ethoxide, b) magnesium acetylacetonate and c) aluminum acetylacetonate precursors.

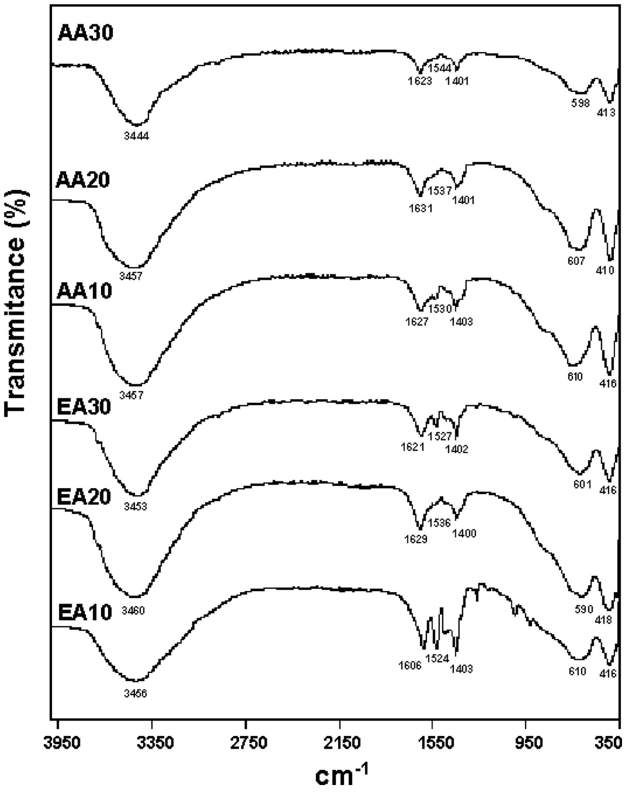


Figure 6 FTIR spectra of the EA and the AA samples.

terlamellar space. This value is smaller than any of the dimensions of the molecule. If the linear configuration is considered (Schema 1a), as it presents only one charged oxygen, two layers of acetylacetonate should be intercalated, the expected interlayer space would be 7.48 Å. Thus, this hypothesis has to be discarded. If the resonant configuration is accepted (Schema 1b) only one layer of acetylacetonate can balance the charge of two exchange sites, each one located in opposed lamellae. The acetylacetonate, indeed, presents two charged oxygen atoms which will tend to anchor it. As the interlayer space is so small only one acetylacetonate molecule can occupy it, bridged from one brucite-like layer to the other. Furthermore, this configuration must be positioned diagonally. As expected, the 23.83 Å value reproduces the cell parameter obtained for the EA30 sample. Note that if irradiation time is 30 min the structure of the AA samples is modified. The transmission electron microscope image of the EA10 sample, Fig. 4, presents the local ordering of the hydrotalcite sheets. In this micrograph two interlamellar distances are clearly appreciated. The arrow points to the largest distance and the other may be observed in the dark zones. Although each distance could be attributed to acetylacetonate or to ethoxide, micrographs are only qualitative as they are not statistically representative. The EDXS measurements indicate that the corresponding molar Mg/Al ratios are 2.7 for EA samples and 2.8 for AA samples. The carbon determinations were 29.3 and 28.4% for the EA10 and the AA10 samples, showing that a high

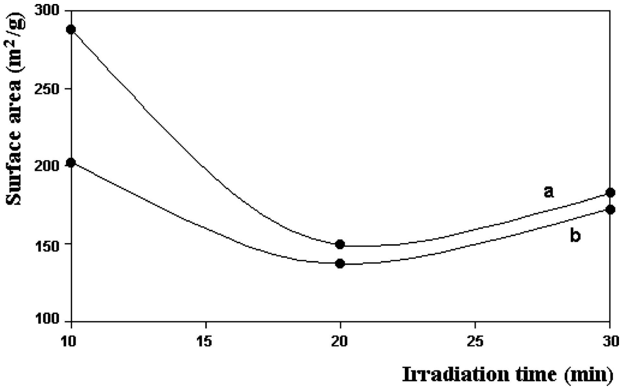


Figure 7 Surface areas of the a) EA and the b) AA samples.

amount of carbon containing species is interlayered: the higher the aluminum amount, the highest the carboncontent, as the number of aluminum atoms is proportional to the exchange sites.

Fig. 5 compares the FTIR spectra of the precursors used in this study. The FTIR spectrum of EA10 sample, Fig. 6, reproduces the main bands of the acetylacetonate spectrum. Therefore, most acetylacetonate is in the external surface area, and it vibrates as if it was in solution. With irradiation time, samples EA20 and EA30, the organic compound diffuses into the layers being anchored and, therefore, the IR spectrum varies. Furthermore, in this ethoxide containing samples, it is conceivable that acetylacetonate occupies exchange positions.

This spectrum is reproduced by all the AA samples, i.e., even for an irradiation time as low as 10 min the acetylacetonate is interlayered. Thus, the acetylacetonate structure is preserved and the hypothesis of configuration modification of the precursor may be discarded. These propositions are confirmed by the surface area values.

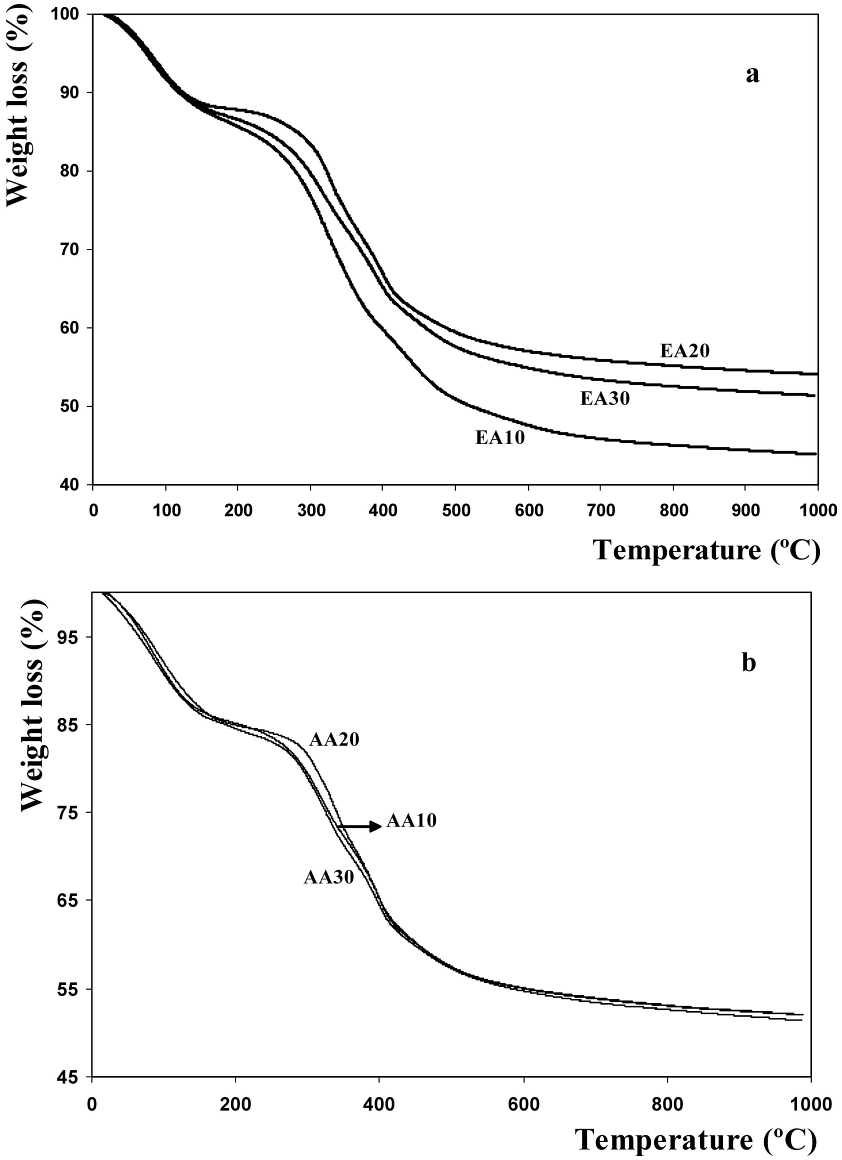


Figure 8 Weight loss of the a) EA and the b) AA samples.

3.3. Surface areas

On the one hand, a general behavior is that the samples irradiated for 10 min present higher surface areas than those treated for 20 or 30 min. On the other, depending on the series, this difference is enhanced, Fig. 7. The acetylacetonate is expected to adhere to the upper and lower hydrotalcite layer blocking a large volume of the free space. In fact, the highest surface area (288 m^2/g) was obtained for the EA10, which may be compared with the values reported in the literature for other preparation methods and other anions [10, 11]. The expected correlation between crystallinity and surface area in the EA samples is not observed. Indeed, depending on the amount of the interlayered (or exchanged) acetylacetonate a variable fraction of the internal area is reached by the adsorbed gas. Therefore, the ratio of internal to external area can be controlled playing on the irradiation time and the anion features as already determined by X-ray diffraction and IR spectroscopy.

3.4. Thermal stability

The weight losses for EA and AA samples are compared in Fig. 8. Up to 200°C, adsorbed water is lost; from 200 to 650°C the dehydroxylation as well as the decomposition of interlayered species occur [12]. All AA profiles (Fig. 8b) are similar showing that the irradiation time does not alter the thermal behavior. Even if the samples AA10 and AA30 are not as crystalline as the AA20 they retain the same amount of acetylacetonate. The differences observed in X-ray diffraction, then, have to be attributed to stacking differences promoted by the diffusion of acetylacetonate. The total weight loss is 47% which is similar to EA samples (Fig. 8a) irradiated 20 and 30 min, 45 and 49% respectively, these values are slightly higher than those reported by Prinetto *et al.* [8] for similar non-irradiated preparations. Only the EA10 reaches a significantly different value (54%) which could be attributed to a higher content of ethoxide.

4. Conclusion

Hydrotalcite surface area and crystallinity are due to the acetylacetonate precursor, whereas the microwave irradiation time during synthesis determines the location, in terms of diffusion, of the acetylacetonate compensating anion. With both precursors, even for an irradiation time as low as 10 minutes, well crystallized samples are obtained. The AA10 sample with acetylacetonate interlayered radicals presents a surface area of 204 m^2/g but it is not fully crystallized. Although, the EA10 reaches 288 m^2/g, it retains a high amount of ethoxide, as shown by infrared spectroscopy and TGA analysis. Two interlamellar distances are observed in this sample by transmission electron microscopy.

Therefore, the combination of a derived sol-gel method with the use of microwave irradiation during the gelling and crystallization steps is an adequate route to prepare controlled high surface area hydrotalcite-like compounds. These materials present high purity and they are obtained in short preparation times.

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