

Mixed Mg(Al)O oxides synthesized by the combustion method and their recrystallization to hydrotalcites

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Abstract

Hydrotalcite-like compounds were successfully synthesized by using the combustion method from aluminum and magnesium nitrates and sodium carbonate. Sugar (saccharose) was used as fuel. The fuel amount, carbonate amount, and synthesis temperature were systematically varied. Furthermore, the obtained hydrotalcites were calcined until lattice destruction and recrystallized in presence of a carbonate aqueous solution. This cycle (memory effect) was sequentially reproduced three times. The resulting structural modifications were evaluated by solid-state nuclear magnetic resonance and X-ray diffraction, and compared with those observed, under similar conditions, in hydrotalcites prepared by co-precipitation and sol-gel methods.

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1. Introduction

Hydrotalcite-like compounds are anionic clays built up from brucite-like layers. The general chemical formula is $[M_{1-x}^{2+}M_x^{3+}[\text{OH}]_2]^{x+}[\text{A}_{x/z}^{z-} \cdot n\text{H}_2\text{O}]^{x-}$ where M^{2+} is a di-valent cation (Mg, Ni, Zn, Co, Fe, etc.), M^{3+} is a three-valent cation (Al, Fe, Cr, Mn). The layers are positively charged as M^{3+} cations substitute M^{2+} cations. This charge is balanced by A anions with charge $z-$, for instance CO_3^{2-} , SO_4^{2-} , Cl^- , OH^- or NO_3^- , among others. Carbonates are preferred [1–3]. Hydrotalcite-like compounds are included in the layered double hydroxides family (LDH), and they are used as catalysts, anion exchangers, hosts of electro-active and photo-active species as well as radionuclide sorbents [4–8]. Unfortunately, their structure collapses at temperatures of 200–400 °C due to dehydration, dehydroxilation

and decarbonation. The obtained mixed oxides are usually solid solutions with a periclase-like structure, which is able to recover the layered structure if in contact with an anion aqueous solution.

The recrystallization of hydrotalcites from periclase-like structure is referred in the literature as “memory effect”. During calcination the coordination of M^{3+} ions is partially lowered from octahedral to tetrahedral. Moreover, in the rehydration step, some of the tetrahedral M^{3+} do not recover the octahedral coordination [9,10]. Then, the reconstructed structure may vary and the physicochemical properties turn out to be different.

The LDHs occur naturally but they are scarcely found. They are, then, usually synthesized. Two methods are followed: co-precipitation and sol-gel [11,12]. Although many modifications can be found in the literature (decomposition–recrystallization, urea method and microwave irradiation) [13,14], these procedures are time consuming and require high amounts of water.

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A synthesis method reported in the bibliography to reduce preparation time is combustion. This method has been successful in the preparation of ceramics as it saves energy and time [15–17]. The combustion synthesis is a very rapid chemical process. The method is based on the explosive decomposition of some organic fuels as urea or glycine, among others [18]. The reaction is started with heat.

Combustion synthesis has not been used to prepare LDHs. Indeed LDHs commonly are obtained by sol–gel or co-precipitation methods, spending high amounts of solvents and heating at low temperatures for longtime (several hours or days). In this sense, the combustion method is interesting because of the heating time (some minutes), nature of fuel or temperature should be easily tuned to obtain hydrotalcite. We started this work with the aim to explore the combustion synthesis of magnesium–aluminum mixed oxides using commercial sugar as fuel, keeping in mind its highly exothermic combustion. The oxides should recrystallize as LDH after being in contact with a Na_2CO_3 solution. As a source of carbonates, aluminum and magnesium, sodium carbonate and aluminum and magnesium nitrates were used, respectively. Our purpose is to report on the conditions to synthesize Mg–Al hydrotalcite by combustion and to characterize the obtained material. The effects of calcinations and recrystallization in these new hydrotalcites are discussed.

2. Experimental

2.1. Materials

Analytical grade reagents were purchased from Merck. They were used without further purification. Fuel was sugar (saccharose).

To prepare the Mg–Al–O mixed oxides, which are the precursors of LDH, 1 g of a solid mixture was prepared from magnesium nitrate, aluminum nitrate and sodium carbonate; the amount of Al and Mg nitrates was maintained constant (Mg/Al ratio of 3) and the amount of sodium carbonate varied from 0 to 0.20 g per gram of mixture. Two hundred milligrams of fuel were added and, then, the mixture was suspended in water. Suspension was heated at 80 °C until water evaporated. The resulting paste was transferred into a 30 ml crucible which was introduced into a muffle furnace, Barnstead Thermolyne Corporation (20 × 20 × 17 cm). The heating temperatures were 450–850 °C. The combustion process was over in 5 min producing mainly a mixture of oxides, these samples were labeled (Mg–Al–O)–X–Y, where X is the synthesis temperature and Y represented the amount of carbonate/gram of precursor mixture. The mixed oxides were put in contact with 60 ml of 0.1 N Na_2CO_3 solution at room temperature. The obtained products were shaken for 5 min and the solid was separated by centrifugation. They were, then, washed with deionized water and dried at 100 °C. Once recrystallized, the solids were labeled HT–X–Y.

For comparison purposes, another two samples were synthesized, the first one was obtained by the co-precipitation method (sample referred as HT-CP) and the second one by the sol–gel route, this sample was labeled HT-SG.

The sample HT-CP was prepared at pH 9, by slowly adding a 1 N solution of magnesium and aluminum nitrates and a 1 N NaOH solution to a 0.1 N solution of Na_2CO_3 . The resulting solid was washed with distilled water and then dried at 100 °C for 8 h. The sample HT-SG was prepared when magnesium ethoxide (Aldrich, 99%), dissolved in butanol, was mixed with the hydrolysis catalyst, HNO_3 (Aldrich) to give a pH value of 5. This solution was refluxed and stirred for 3 h at 80 °C. Afterwards, aluminum ethoxide mixed with ethanol was slowly dropped into the solution. The mixture was refluxed until the gel formed, which was, then, dried at 100 °C.

Table 1 summarizes the experimental conditions for the samples under study.

2.2. Memory effect

HT samples were thermally decomposed by heating them at 450 °C for 8 h. Heat treatment caused the formation of periclase-like (Mg,Al)-oxide solutions which recovered the layered structure upon treating with carbonate aqueous solutions. This procedure was repeated three consecutive times for each sample.

2.3. Characterization

Materials were characterized by X-ray diffraction (XRD), infrared spectroscopy and solid-state nuclear magnetic resonance (NMR).

The powder XRD patterns were recorded in a Siemens D500 instrument using Cu K_α radiation.

The FTIR spectra were acquired at 2 cm^{-1} resolution at room temperature on a Perkin Elmer 1600 series-FTIR spectrometer, equipped with a DTGS detector. The samples were prepared with the KBr pellet technique.

The single pulse solid-state ^{27}Al MAS NMR spectra were obtained operating the spectrometer at a resonance frequency of 78.15 MHz. The samples were spun at

Table 1
Sample label, Mg/Al ratio, synthesis temperature and synthesis method

Sample label	Mg/Al ratio	Na_2CO_3 (mg)/g mixture reacting	Temperature synthesis (°C)	Preparation method
HT-450-0	3	0	450	Combustion
HT-450-20	3	20	450	Combustion
HT-450-200	3	200	450	Combustion
HT-650-20	3	20	650	Combustion
HT-850-20	3	20	850	Combustion
HT-SG	3	–	–	Sol–gel
HT-CP	3	–	–	Co-precipitation

10 kHz. Calibrated $\pi/2$ pulse was 2 μ s. A repetition time of 0.5 s was used. Chemical shifts were referenced to an aqueous AlCl_3 solution.

3. Results

3.1. Samples as synthesized

Samples, as emerged from the combustion process (before treating with carbonate solution), exhibit the XRD patterns typical of $\text{Mg}(\text{Al})\text{O}$ mixed oxides with a periclase-like structure, Fig. 1a. Previous works [19,20] have shown that these mixed oxides have a chemical composition close to $\text{Mg}_6\text{Al}_2\text{O}_9-(x+y)(\text{OH})_{2x}(\text{CO}_3)_y$ and they can be turned out to recrystallize as hydrotalcite-like compounds after being in contact with a CO_3^{2-} containing aqueous solution, Fig. 1b–f. All the samples prepared by combustion behave in the same way, independently of the combustion temperature or the amount of sodium carbonate present in the burned reacting mixture, even the sample synthesized without sodium carbonate leads to a layered structure. The XRD patterns of HT-650-20 and HT-850-20 samples, Fig. 1c and d, show a diffraction peak around $2\theta = 19^\circ$ which is due to nitrates of magnesium and aluminium.

The sample synthesized at the highest temperature, HT-850-20, contains a small amount of magnesium oxide shown by the X-ray diffraction peaks at 42 and 63 degrees (2θ).

As expected, the sol-gel and co-precipitation samples turn out to be hydrotalcite-like compounds, Fig. 1B. However, the diffractogram of the sample prepared by sol-gel shows very broad and asymmetric peaks revealing that crystals, in this sample, are smaller or present a higher

degree of strain than those in samples synthesized by combustion or co-precipitation methods.

Fig. 2 compares the FTIR spectra of samples synthesized by each one of the synthesis methods. No significant differences are observed. The characteristic absorption bands for HT-like compounds are present: The band at 1650 cm^{-1} is ascribed to the bending mode of interlayer molecular water; the strong bands between 1600 and 1450 cm^{-1} are due to stretching vibrations of carbonate anions [7,21]; lastly, the absorption bands due to vibrations of Al–O are found around 630 cm^{-1} .

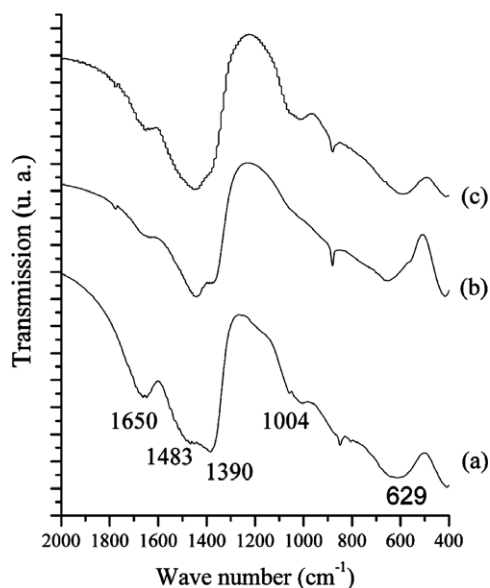


Fig. 2. FTIR spectra of hydrotalcite-like compounds synthesized by combustion (sample HT-650-20), co-precipitation and sol-gel methods, (a)–(c) respectively.

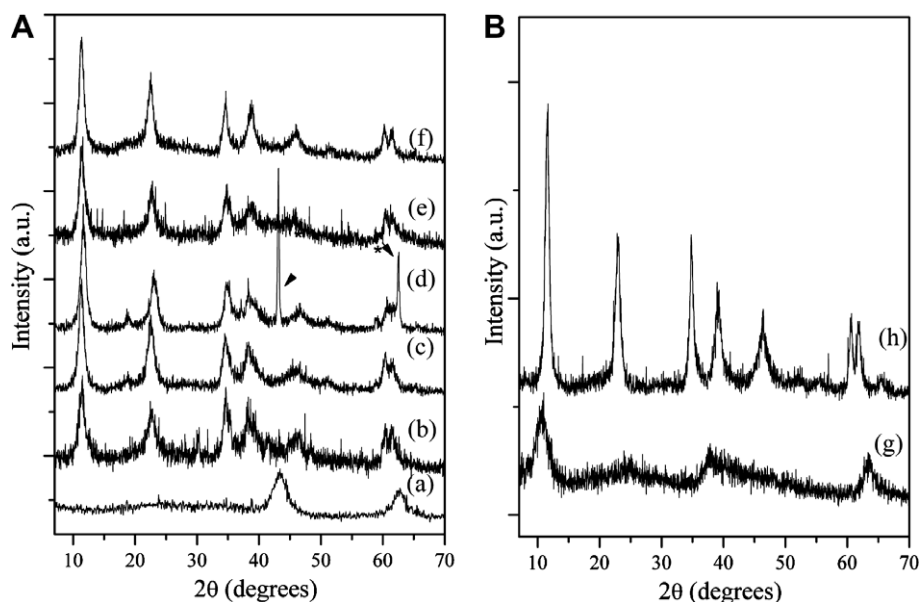


Fig. 1. XRD pattern of a mixed oxide synthesized by the combustion method at 450°C , (a) and the XRD patterns of hydrotalcite-like compounds prepared from recrystallization of mixed oxides (A) and conventional methods (B). (b) HT-450-20, (c) HT-650-20, (d) HT-850-20, (e) HT-450-0, (f) HT-450-200, (g) HT-SG, (h) HT-CP. Peaks labeled * correspond to magnesium oxide, all other peaks correspond to hydrotalcite JCPDS file (220700).

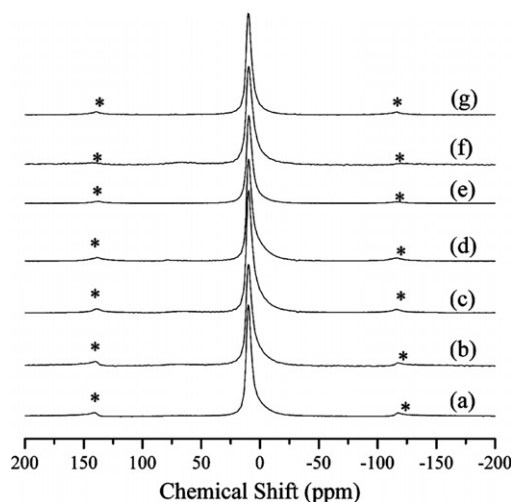


Fig. 3. ^{27}Al MAS NMR spectra of hydrotalcite-like compounds prepared from combustion, sol-gel and co-precipitation: (a) HT-450-20, (b) HT-650-20, (c) HT-850-20, (d) HT-450-0, (e) HT-450-200, (f) HT-SG, (g) HT-CP. Peaks labeled * indicate spinning side bands (10 kHz).

Fig. 3 displays the ^{27}Al MAS NMR spectra for HT samples. They are all composed by a single resonance peak close to 0 ppm. This result confirms the octahedral coordination of aluminum into the brucite-like layers. The absence of signals in the range 50–10 ppm indicates that no extra framework aluminum is present.

3.2. Sequential recrystallization

The X-ray diffraction patterns of the resulting materials after one, two or three cycles of thermal treatment and recrystallization are compared in Fig. 4. The behavior of the combustion prepared hydrotalcite is presented in parallel to the co-precipitated hydrotalcite. The diffractograms of hydrated samples present the HT-like structure, and

the calcined samples the periclase-like structure. The HT-SG sample reproduces this behavior. The X-ray diffraction results do not reveal the formation of other crystalline compounds as a consequence of the three memory cycles performed in the three starting hydrotalcites (combustion, co-precipitation and sol-gel).

Instead, the ^{27}Al MAS NMR spectra of the calcined-rehydrated samples show significant changes in the aluminum coordination depending on calcination–rehydration, Fig. 5. In the fresh HT samples, aluminums are selectively sixfold coordinated (Al^{VI}), as shown by the single signal close to 0 ppm, but, if samples are calcined, a fraction of those octahedral aluminums turn out to be tetrahedral (peak close to 60 ppm) [22,23]. If these calcined samples are rehydrated, almost all tetrahedral aluminum cations, generated in the calcination steps, recover the octahedral coordination and the layered structure reappears as shown by XRD. However, a minor percentage of aluminum remains as Al^{IV} , even after rehydration. The amount of Al^{IV} increases in all samples as the number of calcination–rehydration cycles increases.

Fig. 6 shows that $\text{Al}^{\text{VI}}/(\text{Al}^{\text{IV}} + \text{Al}^{\text{VI}})$ ratio is sensitive to the synthesis method. After three memory cycles, the co-precipitation prepared sample produced only 8% of tetrahedral aluminum and 92% of octahedral aluminum. In contrast, the combustion prepared sample (HT-450-20) contains a large fraction (up to 22%) of tetrahedral aluminum. In the combustion prepared samples the Al^{IV} fraction increases and Al^{VI} diminishes as the synthesis temperature increases.

4. Discussion

4.1. Synthesis of HT by the combustion method

The heat released per mol of burned sugar (saccharose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is 5635 kJ/mol. This energy is available to

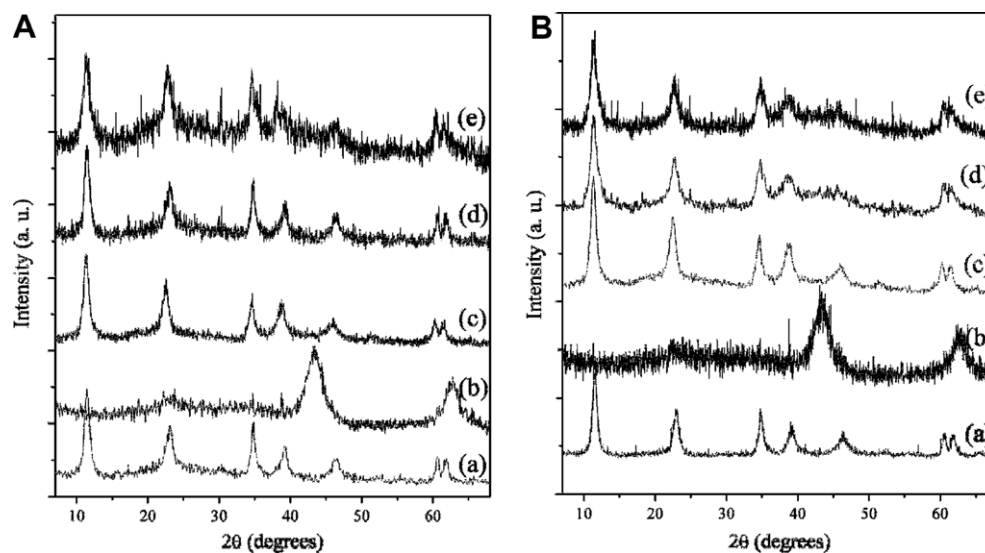


Fig. 4. Evolution of XRD patterns as the samples HT-650-20 (A) and HT-CP (B) are calcined and rehydrated: (a) sample as synthesized, (b) sample calcined, (c) sample calcined-rehydrated (one time), (d) sample calcined-rehydrated (two times), (e) sample calcined-rehydrated (three times).

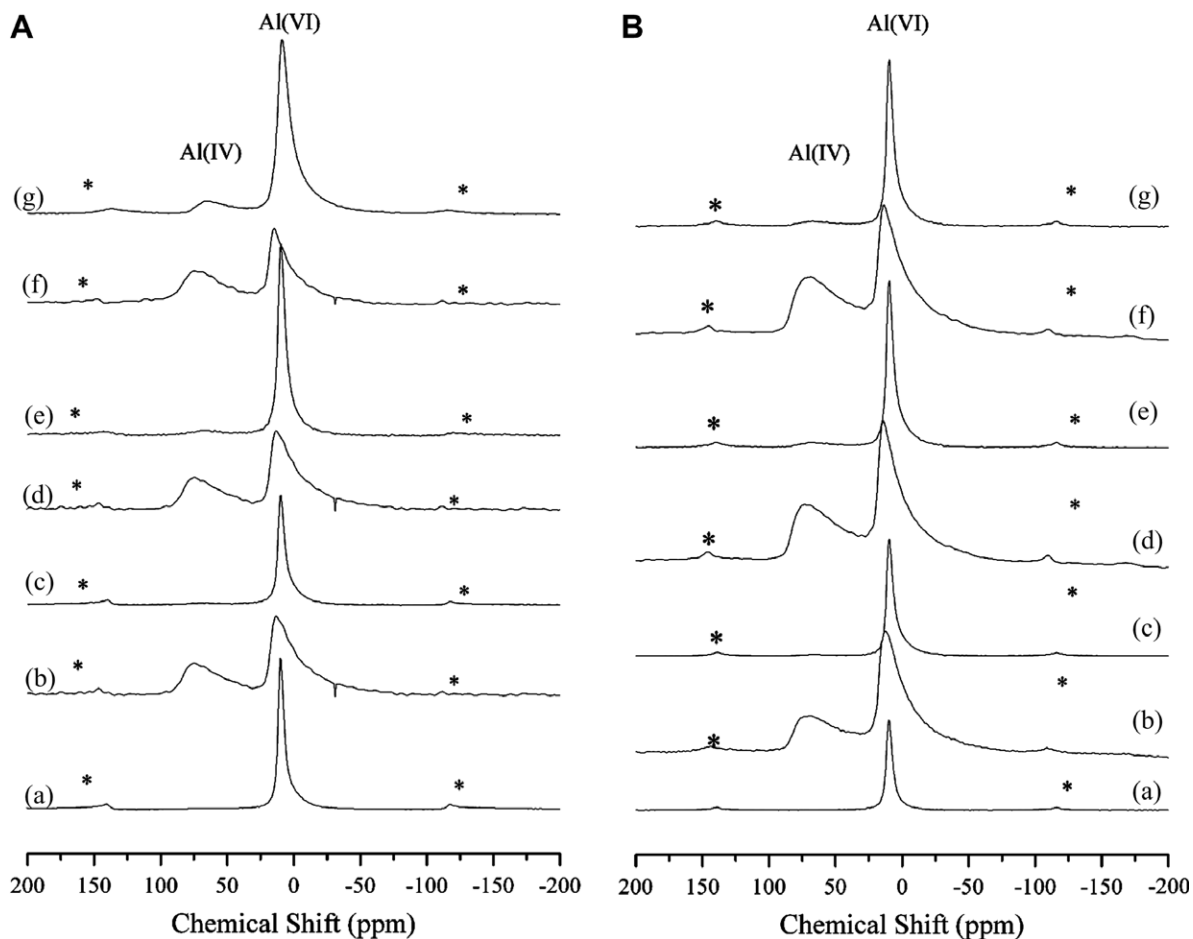


Fig. 5. Evolution of ^{27}Al MAS NMR spectra as the samples HT-650-20 (A) and HT-CP (B) are calcined rehydrated: (a) sample as synthesized, (b) sample calcined, (c) sample calcined-rehydrated (one time), (d) sample (c) after another calcination, (e) sample calcined-rehydrated (two times), (f) sample calcined another time, (g) sample calcined-rehydrated (three times).

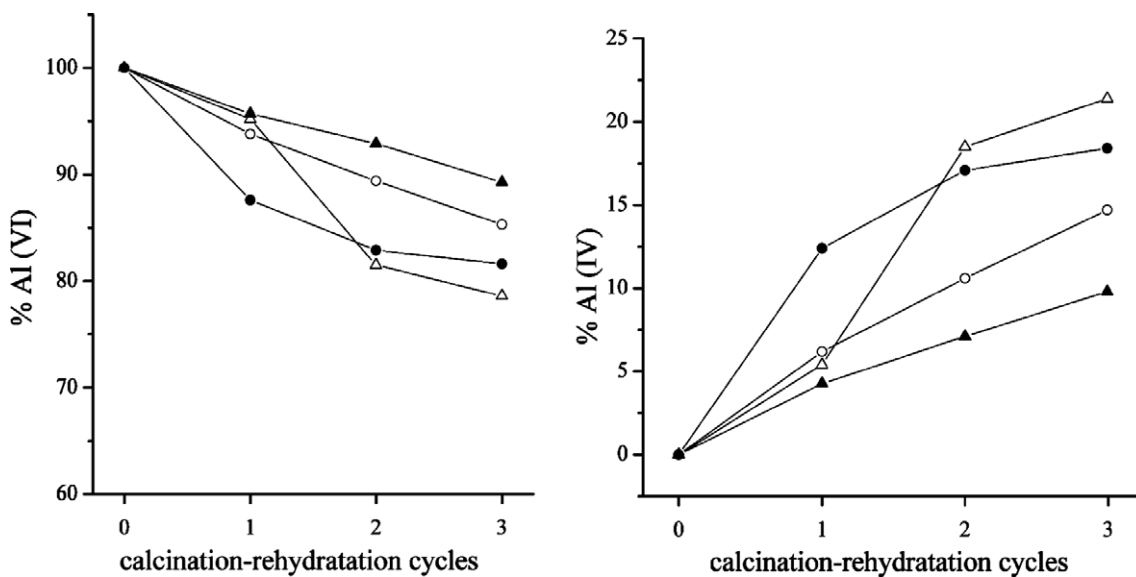


Fig. 6. Percentage of octahedral and tetrahedral aluminum, as determined by deconvolution of ^{27}Al MAS NMR spectra after the memory effect. (▲) HT-CP, (△) HT-450-20, (●) HT-650-20, (○) HT-850-20.

decompose the magnesium and nitrate salts and produce an oxide network. Indeed, the enthalpy required to form Mg–O and Al–O bonds is 363.2 and 511 kJ/mol, respectively, *i.e.* the enthalpy to form Mg–O is lower than Al–O bonds. Thus, a network of $\text{Mg}^{2+}\text{--O}^{2-}$ is initially formed and the aluminum is progressively incorporated to constitute a mixed oxide with a periclase-like structure. As the heat capacity of the MgO is relatively low ($47\text{--}53 \text{ J mol}^{-1} \text{ K}^{-1}$), this material needs a small amount of energy to increase its temperature. Thus, the network vibration is easily increased, and this is suitable to incorporate aluminum atoms. A mixed oxide, then, results, which is the precursor of the hydrotalcite-like compounds with the typical layered structure. The conversion of periclase to a layered structure occurs in presence of carbonates. The sodium carbonate used in this work decomposes thermally producing CO_2 which adsorbs on the mixed oxide surfaces. Those mixed oxide–carbonate complexes are easily layered when in contact with anion solutions.

However this mechanism is not unique. This behavior has been observed when the combustion mixture is carbonate free. In the synthesis proposed, CO_2 and H_2O are the compounds produced by the combustion reaction of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. Both products, CO_2 and H_2O , can be adsorbed on (Mg,Al)-oxide periclase-like structure. Indeed CO_2 is usually taken as a probe molecule of oxide surfaces because various adsorption forms can take place (monodentate, bidentate, bridged), sometimes, in the presence of water, leading to formation of carbonates on the surface [24]. This explains the formation of the layered structure in this sample and points out that sodium carbonate is not required in the combustion mixture. In absence of carbonate and fuel, no sources of CO_2 and heat-energy are available and only a mixture of nitrates is obtained.

It is worth mentioning that, in the synthesis of the mixed oxides which are the precursors of hydrotalcite-like compounds, the sample synthesized at the highest temperature exhibited a small amount of magnesium oxide which did not recover the hydrotalcite structure. In this sample, as the temperature is increased, the MgO particles could sinter and then segregate as an additional phase.

4.2. Memory effect

Although the X-ray diffraction and FTIR results show the viability of synthesis of hydrotalcites by the combustion method, the NMR and memory effect results support that these new hydrotalcites have very different structural stability if compared to the hydrotalcites synthesized by the co-precipitation and the sol–gel methods.

Memory effect is understood as the hydrotalcite recrystallization from the periclase-like solid solution. Two mechanisms have been proposed, either such conversion may occur topotactically without the dissolution of the sample or the memory effect proceeds through the dissolution of the mixed oxide and subsequent hydrotalcite crystallization [10,20,25,26]. Hibino and Tsunashima [9] have

shown that the regeneration of the layered structure is not fully reversible as the carbonate content diminishes with the number of repetitive calcination–rehydration cycles. Aluminum is, then, extracted from the brucite-like layers and constitutes an aluminum enriched spinel. Extracted aluminum should be present on the external layers, thus, around the edges of calcined HT crystallites. Rebours et al. [27] reported that Al-rich phases, likely alumina or magnesium aluminates, are found in the surface region of the calcined Mg–Al hydrotalcites. Of course, this Al on the edges of crystallites should be found in unsaturated coordination, *i.e.* as Al^{IV} or Al^{V} .

Our study shows that the fresh HT samples prepared by combustion do not contain Al^{IV} , neither Al^{V} . However, first calcinations produced Al^{IV} , the higher the synthesis temperature, the higher $\text{Al}^{\text{IV}}/(\text{Al}^{\text{VI}} + \text{Al}^{\text{IV}})$ ratio. This is easily explained by the model proposed above: aluminum is progressively incorporated into the MgO network, as temperature is increased more aluminum is included. In contrast, at low synthesis temperature, aluminum diffuses slowly and does not reach the crystallite core. Therefore, high Al-content regions are generated between the crystallites promoting the formation of spinel nuclei. The unsaturated coordinated aluminum cations, generated in the calcination steps, are susceptible to recover the octahedral coordination in the rehydration step. Note that, after rehydration, in the combustion sample series, the $\text{Al}^{\text{IV}}/(\text{Al}^{\text{VI}} + \text{Al}^{\text{IV}})$ ratio evolves in the opposite sense than calcined samples, the higher the synthesis temperature the lower $\text{Al}^{\text{IV}}/(\text{Al}^{\text{VI}} + \text{Al}^{\text{IV}})$ ratio. Then, a higher amount of Al^{IV} recovers the octahedral coordination with synthesis temperature. If the crystallites are isolated or separated (although complete isolation and separation of crystallites is virtually impossible), extracted Al might easily reenter the structure when reconstructed or the Al^{IV} can be “cured”. Thus, it has to be concluded that contact among the crystallite platelets is needed to form spinel nuclei.

The $\text{Al}^{\text{IV}}/(\text{Al}^{\text{VI}} + \text{Al}^{\text{IV}})$ ratio in the combustion samples was always lower than the corresponding value found in the samples prepared by co-precipitation and sol–gel, *i.e.* these two methods promote a deeper inclusion of aluminum in the brucite-like layers than the combustion method. Co-precipitation method includes a step of crystal growth, where the concentration of Al^{IV} surely diminishes. Instead, the sol–gel method includes cross-linking reactions where the creation of Al^{IV} centers can be inhibited. Note that combustion synthesis proceeds through a very different mechanism if compared with sol–gel and precipitation. Indeed, the two conventional methods include steps where the homogeneous distribution of metal ions in the solid lattice is favoured by water or organic solvents [28,29]. Instead, in combustion method, temperature, due to lack of solvent, is the determining factor in the distribution of metal ions into the LDH network. These different distributions of Mg^{2+} and Al^{3+} ions affect strongly the behavior of LDHs in the recrystallization, memory effect. Of course, it is worth mentioning that this synthesis method is also suit-

able because of eco-friendly conditions, *i.e.* no production of wash water as occur in sol–gel and co-precipitation methods.

5. Conclusion

Magnesium aluminum hydrotalcite-like compounds can be synthesized by the combustion method using saccharose. If the heating temperature is varied from 450 to 850 °C, the obtained materials are similar as determined by FTIR and XRD.

However, ²⁷Al MAS NMR results show that synthesis temperature determines the coordination of aluminum into the network. Hence, the hydrotalcites synthesized by combustion behave differently in the recrystallization process from the mixed oxides.

The differences between the samples prepared by the combustion, the co-precipitation or the sol–gel methods can be understood through the differences in aluminum diffusion degree into the oxide network.

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