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Layered double hydroxide-like materials: nanocomposites for use in concrete

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Abstract

Nitrobenzoic acid (NBA), naphthalene-2, 6-disulfonic acid (26NS), and naphthalene-2 sulfonic acid (2NS) salts were intercalated into a layered double hydroxide-like host material (LDH). The intercalation process was achieved by anion exchange of nitrates in the host material, $Ca_2Al(OH)_6NO_3$, nH_2O (CaAl LDH), which was prepared by a coprecipitation technique. The resulting organo derivatives CaAlNBA LDH, CaAl26NS LDH, and CaAl2NS LDH produced a tilted orientation of NBA and 26NS anions in the interlayer space, while 2NS anions induced a perpendicular bilayer arrangement.

Materials characterization was carried out using X-ray diffraction (XRD), IR-spectroscopy, thermal analysis, and scanning electron microscopy (SEM). These preliminary results open up a new direction towards the synthesis of nanocomposites using polymeric entities and layered materials for future applications in cement and concrete science, e.g., control of the effect of admixtures on the kinetics of cement hydration by programming their temporal release.

Keywords: Layered double hydroxides; Intercalation; Cement; Admixtures

1. Introduction

Sustainable development of concrete infrastructure continues to be of importance to the construction industry. The development of new or modified concrete is an important part of existing strategies to improve performance and minimize life-cycle costs. The use of supplementary cementitious materials in concrete is an integral component of these strategies. Environmental issues are also of concern to both the cement and construction industries. For example, efficient technologies are needed to immobilize heavy metals in incinerator ash. Furthermore, the disposal of cement kiln dust is of concern to some North American cement plants. The preceding represent challenges for cement science. One particular challenge of interest to the authors is to optimize and maximize the use of supplementary cements in high-performance concretes through the novel application of admixtures. Dispersing agents, such as superplasticizers, are commonly used in these concretes. There are, however, practical problems, such as loss of workability with time, that are controlled by interactions with cement components. It is felt that the ability to control the introduction of the admixture in real time after the initial mixing of the concrete would be useful. Therefore, the primary interest of the study is to explore the promise of layered double hydroxide-like materials as hosts suitable for intercalation of organic admixtures with a long-term view to controlling their release rate in concrete. The inorganic–organic nanocomposites would be blended (in small amounts) with the cement.

The paper reports on the synthesis of a calcium aluminate-based layered double hydroxide and experiments designed to address the viability of intercalating selected organic molecules of relevance to the concrete industry. Results of characterization methods applied to the nanocomposites are also reported.

The primary objective of this paper, then, is to provide preliminary information to assess the plausible use of LDH-like materials as models for obtaining a better understanding of the mechanism of interaction between organic admixtures and cement phases. The synthesis and characterization of a series of LDH-like materials intercalated with three different organic acid salts, including nitrobenzoic acid (NBA), 2,6-

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naphthalene sulfonic acid (26NS), and 2-naphthalene sulfonic acid (2NS), are described. These organic compounds are commonly used as admixtures in the making of concrete [31]. The development of information on the properties of concrete containing these nanocomposites is in progress.

2. Layered double hydroxide materials and their applications

Naturally occurring hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, and synthetic hydrotalcite-like compounds, also called layered double hydroxides (LDH), have been investigated for many years [1,2]. Taylor [3] described these phases as being structurally related to brucite the same way the AFm phases are to Portlandite. The formula of the LDH can be generalized to $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}.mH_2O]^{x-}$ where M^{2+} can be Ni^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+}, etc.; M^{3+}: Al^{3+}, Ga^{3+}, Fe^{3+}, Cr^{3+}, etc.; and A^{n-}: NO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}, etc. [4].

The high anion exchange capacity of LDH-like materials makes their interlayer ion exchange by organic and inorganic anions versatile and easily achieved [5–7]. LDH have been studied extensively for a wide range of applications utilizing catalysts [1,8,9], ceramic precursors [10] adsorbents [11], bio-organic nanohybrids [12,13], and scavengers of pollutant metals and anions [14]. Recent research has shown great flexibility of the LDH-like materials in tailoring the chemical and physical properties of materials to be used for specific applications, e.g., molecular recognition, optical storage, batteries, etc. [15–17]. Furthermore, by introducing various transition [1] and noble metals [18] into the sheets of the LDH structure, researchers have been able to produce catalyst precursors. More recently, there have been a tremendous number of new developments using an LDH as a matrix for storage and delivery of biomedical molecules [19,20] and as a gene carrier [21,22].

In cement chemistry, the hydration products of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) are hexagonal-layered materials denoted C_2 (A,F)H_8, C_4 (A,F)H_{13}, and C_4 (A,F)H_{19}. These hydrates, along with the AFm phases (tetracalcium aluminate monosulfate), all belong to the LDH family.

The extensive use of cement and concrete and the frequent occurrence of kuzelite (a sulfate-bearing AFm phase) in hardened concrete [23,24] and in heavy metal-bearing phases [25,26] make LDH and LDH-like materials good models to elucidate the interaction of organic admixtures with cement phases. Indeed, the use of organic admixtures in cement-based materials influences the hydration process, the nature of the hydrated products, and consequently, the mechanical properties of the hardened concrete [27–29]. These effects can be complex and difficult to understand because of the nature and number of phases that exist in cement. LDH-like compounds can be used as host materials for a variety of organic molecules of interest to cement scientists.

$[M(II)_{1-x}\,M(III)x\,(OH)_2\,]\,[A^{n-}x/n\,,\,mH_2O\,]\ \ 2 < 1\text{-}x/x < 5$

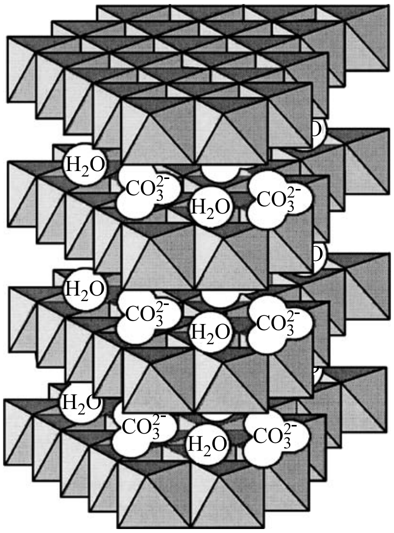

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Fig. 1. Schematic diagram of a typical LDH structure.

2.1. Structure and synthesis of layered double hydroxides

AFm phases belong to the wider family of compounds called layered double hydroxides [30–32]. The structure of an LDH is basically built up from the parent structure brucite $Mg(OH)_2$ by isomorphous substitution of divalent cations [4,33] (Fig. 1). The replacement of Mg^{2+} by M^{3+} ions generates an excess of positive charge within the inorganic layers, which has to be balanced by incorporation in the interlayer space of anions, such as NO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}, etc. In addition to anions, the interlayer space region can also contain water molecules connected to the inorganic layers via hydrogen bonding [14].

Considerable effort has been invested in the preparation of LDH and LDH-like materials [1]. Most of these synthetic materials are prepared via coprecipitation methods using M^{2+} and M^{3+} sources at constant pH and under basic conditions [1,8,17,34–37]. Their high anion exchange capacity (2.4 to 4.1 milliequivalents/g) makes the interlamellar ion exchange by organic and inorganic anions versatile and easily achieved [1,2,5–7,9].

3. Experimental

3.1. Materials

All reactions were carried out by using reagent grade chemicals (>98% purity) from Aldrich without further purification. Deionised distilled water was used for the preparation of aqueous solutions.

3.2. Synthesis

The synthetic preparation methods were adapted from previously reported studies [34,38].

3.2.1. Preparation of CaAl LDH

The CaAl LDH was prepared by a pH-controlled coprecipitation technique of the corresponding metal nitrate salts at room temperature (RT) [34,38]. Typically, a solution containing 0.28 mol of $Ca(NO_3)_2.4H_2O$ and 0.12 mol of $Al(NO_3)_3.9H_2O$ in 320 ml of distilled water was added drop wise to a solution containing 0.6 mol of NaOH and 0.4 mol of $NaNO_3$. The pH of the final mixture was 9.6. The suspension was heated for 16 h at 65 °C with vigorous stirring, after which the solid precipitate was collected by filtration and washed thoroughly with distilled water several times and then with acetone. The cake-like material was then dried for 16 h at 100 °C in vacuum.

3.2.2. Preparation of the organic derivatives

The intercalation reactions of organic molecules were performed using anion exchange reactions described elsewhere [34,38]. The reactions were carried out under nitrogen to avoid contamination with carbonates from the atmosphere. CaAlNBA LDH, CaAl26NS LDH, and CaAl2NS LDH were obtained by anion exchange of nitrates with nitro benzoic acid (NBA), naphthalene-2, 6-disulfonic acid (26NS), and naphthalene-2 sulfonic acid (2NS) salts, respectively. Typically, 2.5 g of the CaAl LDH compound was dispersed in 250 ml 0.1 M aqueous solutions of organic salts. The mixtures were allowed to react for 16 h, under nitrogen and vigorous stirring at 65–70 °C. The organic derivatives were isolated by filtration and washed thoroughly with distilled water and acetone several times. They were then dried under vacuum for 4 h at 100 °C.

3.3. Characterization

Powder X-ray diffraction (XRD) was performed on a Scintag XDS 2000 X-Ray diffractometer using Cu-Kα radiation at 45 kV and 35 mA between 4° and 65° (2θ) with a graphite secondary monochromator. FTIR spectra were recorded on a Bohmem MB 100 instrument. Thermal analyses on powder samples (10–20 mg) were carried out using a Seiko simultaneous thermal analyzer (STA) TG/DTA320 in flowing Ultra zero air (150 ml/min) at 20 °C/min from RT to 1000 °C. Scanning electron microscopy and chemical analyses (SEM/EDS) were conducted using a Cambridge Systems Stereoscan 250 instrument equipped with an Oxford Instruments Inca 200 EDS.

4. Results and discussion

4.1. X-ray diffraction analysis

The Ca/Al (molar) ratio found for the host material, CaAl LDH, by EDS was equal to 2, suggesting the following formula: $Ca_2Al(OH)_6\ NO_3.mH_2O$. The diffraction pattern for the synthetic material CaAl LDH (Fig. 2) shows a typical layered structure with high crystallinity, similar to those previously reported in the literature for LDH-like materials [34,35]. For the frequently occurring carbonate form of LDH, the basal spacing represented by the reflection at approximately 10° (2θ) in the XRD profile is usually equal to 0.78 nm [35], whereas the nitrate form has a basal spacing of 0.88 nm [35]. The value of the basal spacing (0.86 nm) corresponds to the sum of the thickness of the $[Ca_2Al(OH)_6]^{2+}$ layer (0.48 nm) and of the interlayer space

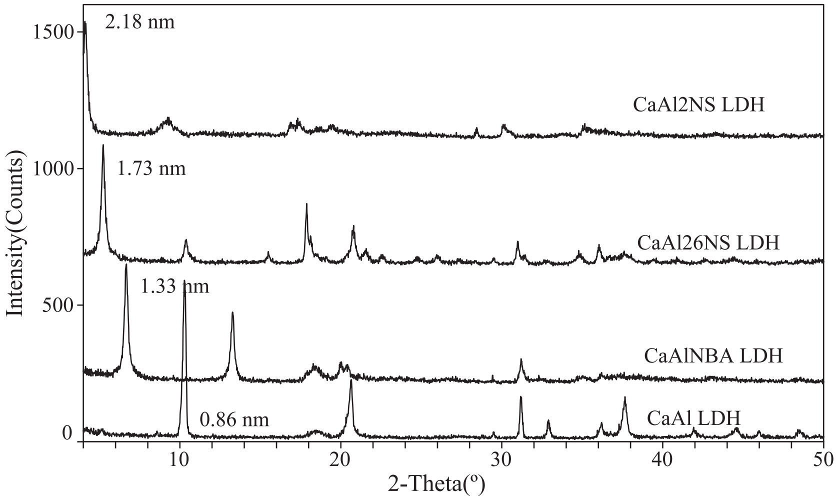

Fig. 2. Powder XRD patterns of CaAl LDH, CaAlNBA LDH, CaAl26NS LDH, and CaAl2NS LDH.

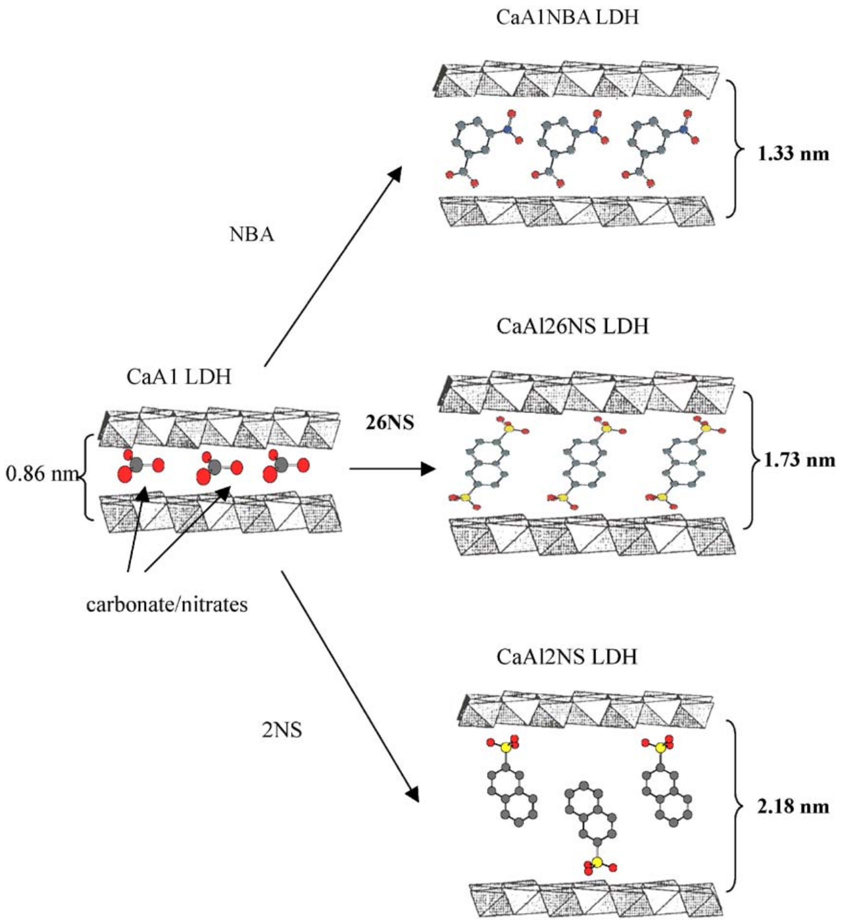

Fig. 3. Interlamellar arrangement for CaAl LDH with NBA, 26NS, and 2NS.

occupied by the anion, whose ionic diameter, in the case of nitrates, is about 0.38 nm. This is in agreement with the predicted value for the basal spacing, considering a planar orientation of anions, mainly nitrates, and water molecules within the interlayer space of LDH-like materials (Fig. 3).

The reaction of CaAl LDH with NBA, 26NS, and 2NS salts produces materials whose diffraction patterns are given in Fig. 2. The intercalation between the layers of CaAl LDH samples is confirmed by an increase in the basal spacing, the value of which represents the sum of the thickness of the inorganic layer (0.48 nm) and interlayer space (Table 1). The results for CaAlNBA LDH and CaAl26NS LDH show that the interlayer space available cannot accommodate NBA and 26NS molecules based on their respective anionic size measured on a CPK model (see Table 1). Therefore, the values obtained for the interlayer spacing could be explained by either a grafting of the anions on the hydroxylated inorganic layers or by tilted orientations of the molecules with respect to the double hydroxide layers. The first hypothesis is unlikely to be true because the thermal analysis (Table 1) does not show any high thermal stability of the organic derivatives compared with the starting material, CaAl LDH. For both CaAlNBA LDH and CaAl26NS, the organic molecules can only orient themselves slightly tilted with respect to the oxide layers (Fig. 3). Conversely, the CaAl26NS LDH shows an interlayer space concurring with the 26NS molecules lying in a perpendicular head-to-tail bilayer arrangement towards the oxides layers (Fig. 3). Previous intercalation results in LDH-like materials have shown the propensity of this class of

Table 1
Summary of XRD and TGA data for CaAl LDH, CaAlNBA LDH, CaAl26NS LDH, and CaAl2NS LDH

	Anion size (nm) [CPK model]	Interlayer spacing (nm)	RT–200 °C weight loss %	200–450 °C weight loss %	450–1000 °C weight loss %
CaAl LDH	0.38	0.86	9.8	17.5	16.8
CaAlNBA LDH	0.61	1.33	7.7	21.6	8.9
CaAl26NS LDH	1.26	1.73	12.2	18.0	25.1
CaAl2NS LDH	0.86	2.18	9.9	14.1	28.9

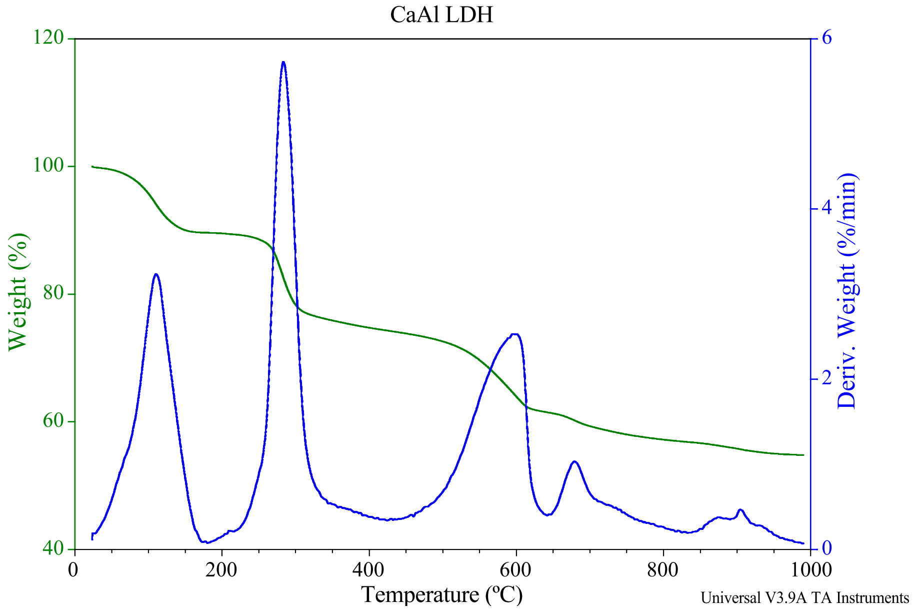

Fig. 4. Typical TGA curve for CaAl LDH.

layered materials to incorporate organic anions in a perpendicular arrangement [34]. Based on the anionic size of 26NS (Table 1), it can be assumed that there are voids between the organic molecules themselves and between the anions and the hydroxide layers. These voids can connect to each other and can be partially occupied by water molecules. The presence of this intercalated water was indeed confirmed by DTG data (not shown), which indicates the presence of two distinct desorption processes (physisorbed and intercalated water) from RT to 200 °C. These observations are comparable with previously reported results for LDH [36,37,39–43].

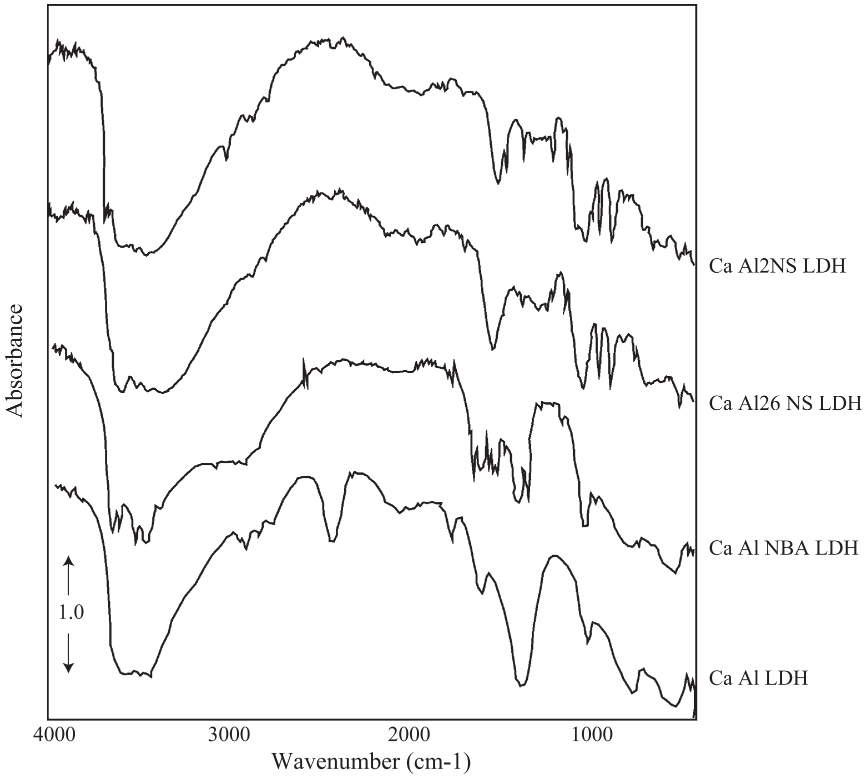

Fig. 5. FTIR spectra of CaAl LDH, CaAlNBA LDH, CaAl26NS LDH, and CaAl2NS LDH.

4.2. Thermal analysis

The thermogravimetric analysis (TGA) curve of CaAl LDH is comparable with previous data of LDH-like materials [44]. A typical TGA/DTG curve is shown in Fig. 4. The results show an initial reduction in weight between RT and 200 °C arising from physisorbed and interlayer water. A second weight loss between 200 and 450 °C results from a concomitant dehydroxylation of the inorganic layers and a reduction of nitrates to nitrites [45,46]. Beyond 450 °C, a further condensation of hydroxyls and decomposition of nitrites have been observed as reported elsewhere [46]. The corresponding DTG trace shows three main effects associated with these weight losses. Based on previous analysis [46] and the suggested formula from the EDS analysis, $Ca_2Al(OH)_6\ NO_3.mH_2O$, the first weight loss corresponds to two water molecules ($m = 2$ in the formula). The second (17.5%) and third (16.8%) weight losses, caused by a combination of structural water loss (dehydroxylation) and of nitrates decomposition, may be described by a combination of the evaporation of two water molecules and the decomposition of one nitrate ion [46], as follows:

$$Ca_2Al(OH)_6NO_3 \rightarrow Ca_2AlO(OH)_2 + 2H_2O + NO$$

Table 1 summarizes the weight loss data obtained from the thermogravimetric analyses of CaAl LDH, CaAlNBA LDH, CaAl26NS LDH, and CaAl2NS LDH. In the case of the organic derivatives, the weight loss between 450 and 1000 °C is attributed to a combination of two events: dehydroxylation of the Ca–Al hydroxide layers and decomposition of organic molecules. A temperature treatment beyond 600 °C caused a collapse of the layered structure (XRD results not shown) for all compounds and gave rise to new crystalline phases (mixed oxides, e.g., spinel forms) [47–49].

4.3. Infrared analysis

FTIR spectroscopy showed characteristic frequencies associated with the presence of intercalated anions. Fig. 4 shows the FT-IR spectra of CaAl LDH, CaAlNBA LDH, CaAl26NS LDH, and CaAl2NS LDH. In all samples, a broad band between 3600 and 3400 cm^{-1} represents the stretching vibrations of the O–H groups of the inorganic layers and the interlayer water. Another common frequency for LDH-like materials is the presence of the bending vibrations of water molecules at 1600 cm^{-1} [50]. In the case of CaAl LDH, the absorption centered at 1380 cm^{-1} is assigned to the presence of nitrate anions within the structure. However, due to the broadness of this band, it may also correspond to the presence of carbonate ions, which usually occurs at 1360–1370 cm^{-1} [50]. For organic derivative materials, this region is dominated by absorption bands caused by C–H stretching vibrations in an aromatic ring. For CaAlNBA LDH, characteristic peaks of NBA were present in the spectrum, including antisymmetric and symmetric stretchings of CO_2^- in carboxylic acid salts (1610–1650 and 1400–1300 cm^{-1}, respectively), NO_2 symmetric stretching in aromatic nitro compounds (1360–1320 cm^{-1}), C–N stretching mode (920–830 cm^{-1}), and NO_2 bending vibration in aromatic compounds (580–520 cm^{-1}). In the case of both CaAl2NS LDH and CaAl26NS LDH, the main characteristic peaks are quite similar and comparable with previously published data [51]. The intercalation of the naphthalene molecules is shown qualitatively by in- and out-of-plane ring bending absorptions (640–615 and 490–465 cm^{-1}, respectively), the aromatic ring C–C single and double bonds (690 and 1640–1490 cm^{-1}, respectively), and the S–O bondings of the sulfonate groups at 1170 and 1125 cm^{-1}. The presence of all these organic bands, combined with XRD results, confirms a successful intercalation reaction of NBA, 2NS, and 26NS within the interlayer space of CaAl LDH-like materials.

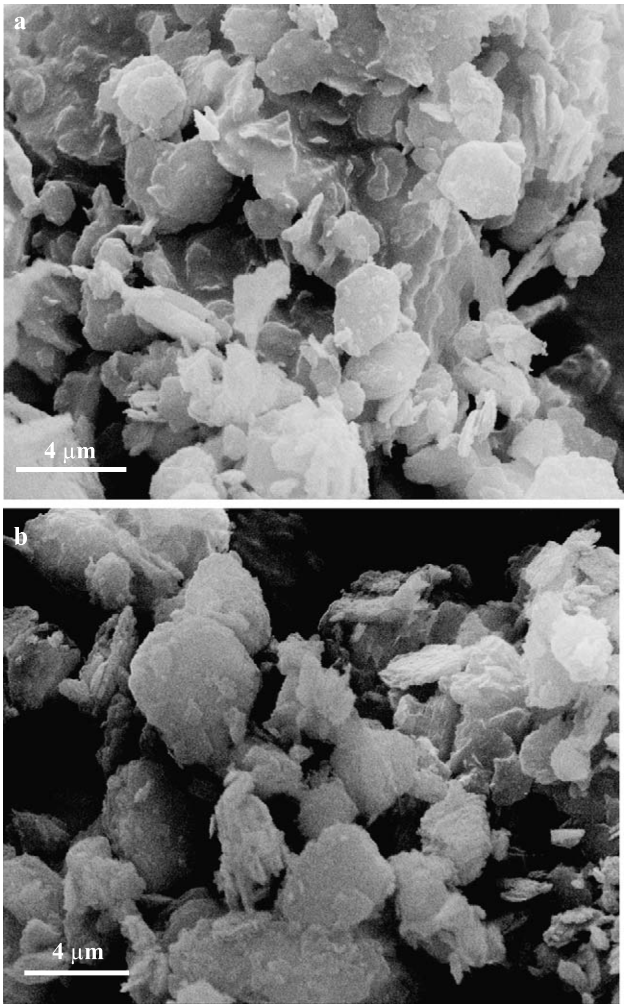

Fig. 6. SEM micrographs of (a) CaAl LDH and (b) CaAlNBA LDH.

4.4. SEM/EDX

The comparison between the scanning electron micrographs of CaAl LDH and CaAlNBA LDH (Figs. 5 and 6) shows that the former has well-formed and regular hexagonal-shaped particles stacked on top of each other, a characteristic of other lamellar phases in the groups of AFm phases and LDH-like compounds [52,53]. In the case of CaAlNBA LDH composite, the material appears to be constituted of nonuniform, round-edged, hexagonal plate-like particles. The other two composites, CaAl26NS LDH and CaAl2NS LDH, showed similar features. Very likely, the presence of organic molecules in the interlamellar space has produced a change of the superficial interaction between particles that influences the aggregation between particles. It is known that if slowly precipitated, hydrotalcite-like structures give hexagonal plates that display some edge rounding upon intercalation [53].

5. Conclusions

New layered double hydroxide derivatives have been synthesized and characterized. Their investigation by means of XRD, TGA, and IR has shown that different structures of the composite materials are observed, depending on the nature of the anion. Indeed, NBA and 26NS were intercalated within the interlayer space, tilted with respect to the hydroxide layers, while 2NS was perpendicularly oriented. Such results open up a new route for the synthesis of nanocomposites using polymeric entities and layered materials. Some potential future applications for these composite materials could be to control the effect of admixtures on the kinetics of cement hydration by programming their temporal release. A study to probe the effects of the intercalated organic molecules on the stability and on the bonding to CaAl LDH by means of MAS NMR will be reported in a future paper.

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