

INDOLE-2-CARBOXYLATE- AND DIHYDROINDOLE-2-CARBOXYLATE-CaFe LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES – SYNTHESIS, CHARACTERISATION AND THE EFFECT OF SYNTHESIS VARIABLES

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Abstract

Potential organocatalysts, N-containing fully or partially unsaturated heterocyclic anions, indole-2-carboxylate and dihydroindole-2-carboxylate) were immobilised in CaFe layered double hydroxide with the dehydration-rehydration method from aqueous ethanol and acetone. The structure of the resulting organic-inorganic hybrids was characterised by various instrumental methods (powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray fluorescence with elemental mapping, thermogravimetry) and molecular modelling. It was found that the solvent mixture used for the synthesis exerted tremendous difference in the interlayer spacings of the obtained inorganic-organic hybrids.

1 Introduction

The family of layered double hydroxides (LDHs) is a class of (mostly) synthetic anionic layered clays that can be represented by the general formula of $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[X^{m-}]_{x/m} \cdot nH_2O]^{x-}$ [1-3]. The partial isomorphous substitution of divalent cations for trivalent ones results in positively charged layers balanced by simple, fully or partially hydrated inorganic anions in the interlayer space. These ions can be exchanged to more complex organic anions forming organic-inorganic functional nanocomposites [4]. These materials can be of many uses like, *e.g.*, immobilised organocatalysts [5-7], protected organic moieties from unwanted transformations (like, *e.g.*, racemisation [8]), targeted delivery of medicine with lengthened effects [9], *etc.* Many varieties of LDHs are known, and most of them can be found in nature, however, for applications they are usually synthesised. The most often used preparation method is the co-precipitation of the component salt with the help of a base in solution [10]. There also numerous methods for the introduction of organic anions into the interlayer space. One obvious method is anion exchange, but there are frequently used alternative methods as well, like including the organic anion in co-precipitation or using the memory effect of LDHs [11]. The memory effect means that on heat treatment the LDH gradually dehydrates and at a certain temperature depending on the specific material, the layer structure is lost. However, if

the temperature was not too high (again, it depends on the specific LDH), the layered structure can be recovered under humid conditions or simply suspending it in water. If the organic anion is dissolved in water used for rehydrating the dehydrated LDH, intercalation takes place. This method was used in the experimental work leading to this contribution.

We have written a couple of lines earlier that the organic-inorganic LDH composite may be used as immobilised organocatalyst. Let us briefly discuss what organocatalysis and organocatalyst are. In organocatalytic reactions small organic molecules consisting of C, O, N, S and P are used as catalysts, *i.e.* in less than stoichiometric amounts. They often perform better than the organometallic compounds [12] and are not or at least less sensitive to oxygen or moisture, easily accessible and cheap, they are not or just hardly poisonous (for reviews, see, *e.g.*, refs. [13-15], for a book, see, *e.g.*, ref. [16]). One of the drawbacks with organocatalytic transformations is that the organocatalysts are in the same phase as the reactants and the products making work-up, recovery and recycling are very difficult if not impossible. However, if they are attached to a solid or quasi-solid support, all these problems are solved. There are many possibilities of immobilisation (covalent grafting, non-covalent attachment [ion exchange, hydrogen bonding interactions], biphasic catalysis [organocatalyst bonded to ionic liquids]) and the support can be of many kinds (functionalised/modified resins, silica gel or silicates, cyclodextrins, *etc.*) [17, 18]. Interestingly, LDHs were very sparingly applied as host materials [5-7]. It is surprising, because they should be ideal hosts, since the interlayer distance can be varied with relative ease, and the intercalated ions are kept within the layers with strong ionic bonds. Therefore, the resulting organic-inorganic composite has appreciable stability; it certainly will be a more robust material than the organic molecule in the homogeneous phase.

In the followings, we describe the syntheses of two organic-inorganic functional nanocomposites using CaFe LDH as host and two indole-2-carboxylates as anions. The effects of synthesis variables, mostly those of the solvents, are examined and full characterisation of the obtained substances is given. The work has been performed with the long-term aim of preparing durable composite materials that are able to act as catalyst in various organic transformations.

2 Materials and testing methods

2.1 Materials used

Concentrated NaOH (~20 M) stock solutions were prepared from Millipore MilliQ water and *a.r.* grade solid NaOH (VWR International) and their carbonate content was minimised as described previously [19]. The precise concentration was determined through accurate density measurement. The solution was stored in airtight, caustic resistant Pyrex bottle. This solution can be kept carbonate-free easily, therefore this was used for the making of the 3 M NaOH solution actually used in the synthesis. CaCl₂, (Molar Chemicals, puriss), iron chloride (FeCl₃.6H₂O, Molar Chemicals, puriss special) were used as received. Commercially available (Aldrich, purity > 98%) various N-heterocyclic compounds (indole-2-carboxylic acid, dihydroindole-2-carboxylic acid, Figure 1) were transformed to their sodium salts before intercalation. Acetone and ethanol were also the products of Aldrich Chemical Co.



Figure 1. The intercalated compounds; (a) indole-2-carboxylic acid and (b) dihydroindole-2-carboxylic acid.

2.2 Methods of synthesis

CaFe LDH was prepared by the co-precipitation method, *via* dropwise addition of 3 M NaOH solution to vigorously stirred and N₂-blanketed CaCl₂/FeCl₃ solution with 3:1 molar ratio [20]. The precipitates formed were rapidly filtered until air dry in a practically CO₂-free atmosphere, with the aid of a caustic resistant vacuum filter unit (Nalgene) equipped with an appropriate membrane (Versapor 129, 0.45 μm). The host materials were calcined before attempting intercalation at 773 K for 5 hours in N₂ atmosphere.

The carboxylate anions were intercalated into CaFe LDH with the dehydration-rehydration method, utilising the memory effect of the layered double hydroxides. The heterocyclic compounds were suspended in aqueous ethanol or aqueous acetone. In both solvents the LDH was stirred for a week. Upon rehydration intercalation occurred. The solid catalyst was filtered and washed with distilled water. The crystals obtained were kept at room temperature in a desiccator over P₂O₅.

2.3 Characterisation

The key method for studying the structural features of the host as well as the host-guest hybrids was powder X-ray diffraction. The diffractograms were taken in the 3-60° 2θ region with 4°/min scanning rate on a Rigaku Miniflex II instrument using the Cu_{Kα} radiation (λ= 0.15418 nm). The (003) reflection was used for calculating the basal spacings. The accurate positions of the reflections were determined after fitting Gaussian-type functions.

The morphologies of the synthesised nanocomposites were studied with a Hitachi S-4700 scanning electron microscope (18 kV acceleration voltages) at various magnifications. The elemental maps of the substances were determined with a Röntec QX2 energy dispersive X-ray fluorescence spectrometer coupled to the microscope. It was mainly concentrated on verifying the presence of the host anions in the samples *via* detecting the carbon and/or nitrogen of the organic salts and displaying its distribution.

In order to learn about the thermal behaviour of the materials, the thermogravimetric curves and their derivatives were registered with a Setaram Labsys derivatograph. TG-DTG curves were recorded in N₂ atmosphere at 4 °C/min heating rate.

The Fe³⁺-content of the LDH was determined with a Thermo's IRIS Intrepid II ICP-OES spectrometer, and the quantities of the intercalated carboxylate anions were measured by UV-Vis spectroscopy.

The sizes of the various intercalated carboxylate ions were determined after performing full geometry optimization with the PM3 [21] semiempirical quantum chemical method included in the Hyperchem 8.0 [22] molecular modelling package.

3 Results and discussion

Powder XRD measurements were performed first on the pristine LDH, the sodium salt of the carboxylic acids, and then, the intercalated samples obtained from both solvent mixtures. The obtained diffractograms are typical of LDH (of course, except that of the salts) and are seen in Figs. 2/(a) and (b).

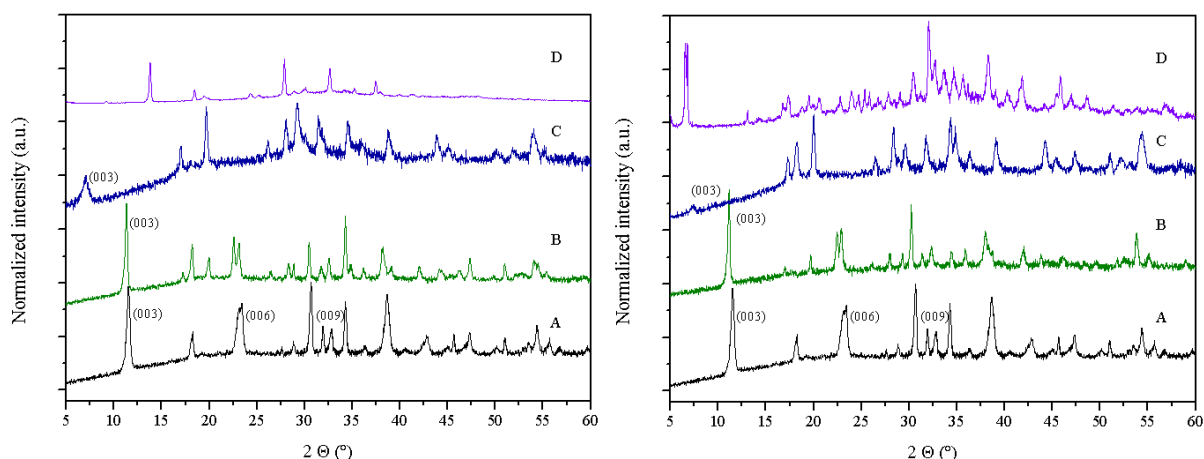


Figure 2. (a) Powder X-ray diffractograms of the host Ca_3Fe LDH (trace A), the N-heterocyclic anion- Ca_3Fe LDH prepared using aqueous ethanol (trace B), the N-heterocyclic anion- Ca_3Fe LDH prepared using aqueous acetone (trace C) and the sodium salt of the N-heterocyclic compound (trace D); the guest anions: (a) indole-2-carboxylate, (b) dihydroindole-2-carboxylate.

Basal spacings were calculated from the (003) reflection. The measured interlayer spacings contain one layer of the host material, which may be approximated as 0.48 nm. This is actually for brucite [22], since we could not find any literature data regarding Ca_3Fe LDH. However, this value is used generally for estimating the layer thickness for layered double hydroxides. Thus, the distance values between the layers are shown in Table 1 along with the dimensions of the anions, optimised by the PM3 semiempirical method.

N-containing Heterocycles	d(003) EtOH/H ₂ O (nm)	d(003) acetone/H ₂ O (nm)	dimensions of the anions (nm)*	interlayer distance EtOH/H ₂ O (nm)**	interlayer distance acetone/H ₂ O (nm)**
indole-2-carboxylate	0.79	1.25	0.50×0.00×0.53	0.31	0.77
dihydroindole-2-carboxylate	0.80	1.21	0.50×0.30×0.78 0.50×0.27×0.76	0.32	0.73

Table 1. The d(003) and interlayer distance values for the intercalated LDHs (*the edges of a cuboid in which the anion precisely fit, optimized by the PM3 semiempirical method; **calculated as the experimentally observed $d_{(003)}$ reduced by the layer thickness of brucite (0.48 nm).

Huge differences have been observed between the interlayer distances of the intercalated LDHs prepared depending on solvent mixture used during their synthesis. If the rehydration took place in aqueous acetone, the d(003) values became much larger than that of the pristine LDH. However, when the ethanol/water solvent mixture was applied the interlayer distance did not change significantly. The first observation is the sure sign of the success of the intercalation, while in the second case one may think of its failure. However, it has been found (and it is shown taking indole-2-carboxylate- CaFe LDH as an example) that both synthesised materials contained organic material (Table 2) in appreciable amounts.

In order to confirm that the organic material is not simply on the outer surface of the LDH but it resides among the layers, the samples were further studied by scanning electron microscopy (Fig. 3).

	indole-2-carboxylate-LDH EtOH/H ₂ O	indole-2-carboxylate-LDH acetone/H ₂ O
indole-2-carboxylic anion intercalated to the LDH (mol/g)	$1.88 \times 10^{-4} - 2.20 \times 10^{-4}$	$2.38 \times 10^{-4} - 2.75 \times 10^{-4}$
$(n_{\text{indole}}/n_{\text{Fe}}) \times 100$ *	27–32 %	34–40 %

Table 2. The quantities of the intercalated indole-2-carboxylate anions between the layers of the Ca₃Fe LDHs (*by ICP-OES measurements the iron-content of our LDHs is 6.859×10^{-4} mol/g).

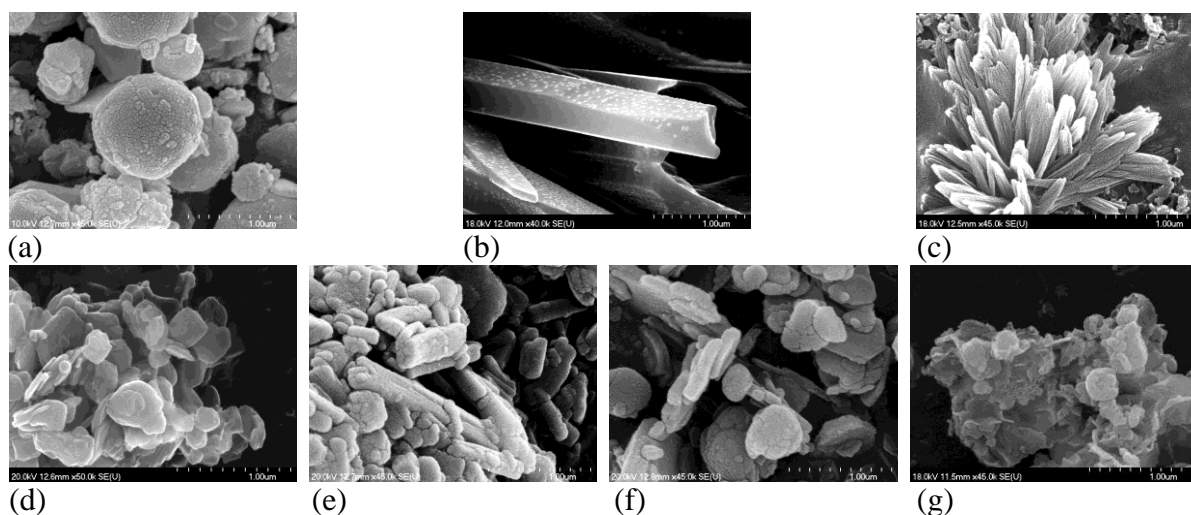
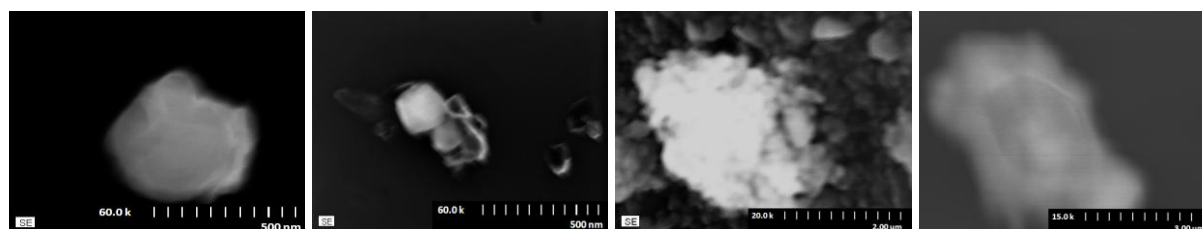


Figure 3. SEM images of the pristine Ca₃Fe LDH (a), the sodium salts of the indole-2-carboxylic acid (b) and the dihydroindole-2-carboxylic acid (c), the indole-2-carboxylate–Ca₃Fe LDH prepared using aqueous ethanol (d), aqueous acetone (e) and the dihydroindole-2-carboxylate–Ca₃Fe LDH prepared using aqueous ethanol (f), aqueous acetone (g).

The lamellar morphologies of the LDHs are reflected in the images both for the pristine LDH and those containing the organic anion, hopefully in-between the layers. There are, however, phenomenological differences depending on the solvent mix used for the syntheses. Note, that on the SEM images of the carboxylate salts needle-like structures are observed: this type of structure is not seen at all in the images of the organic material treated LDH samples. This finding and the results of the organic content analysis prove that intercalation also occurred when aqueous ethanol was used for the syntheses.

Further verification could be obtained when the elemental maps made on the basis on SEM–EDX measurements are examined. The close to even distribution of the ions on the Ca–Fe elemental map indicated that double hydroxides are formed, indeed. The N elemental maps revealed that the organic material were present and again in close to even distribution (Figure 4).



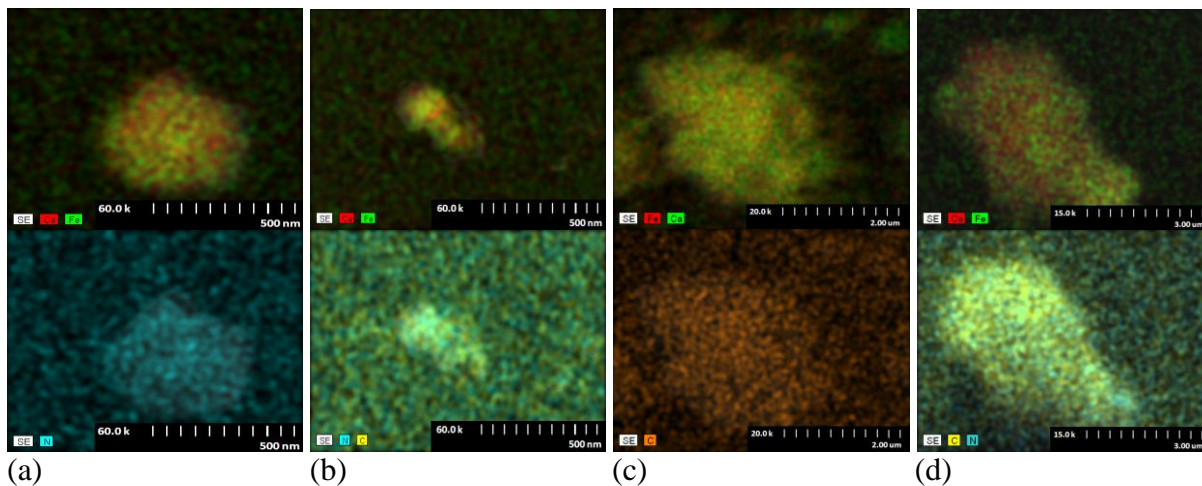


Figure 4. The SEM–EDX elemental maps of the indole-2-carboxylate–Ca₃Fe LDH prepared using (a) aqueous ethanol, (b) aqueous acetone and the dihydroindole-2-carboxylate–Ca₃Fe LDH prepared using (c) aqueous ethanol, (d) aqueous acetone.

The thermal behaviour of the samples (of course, except that of the sodium salt of the organic anion) was also that of an LDH (Fig. 5).

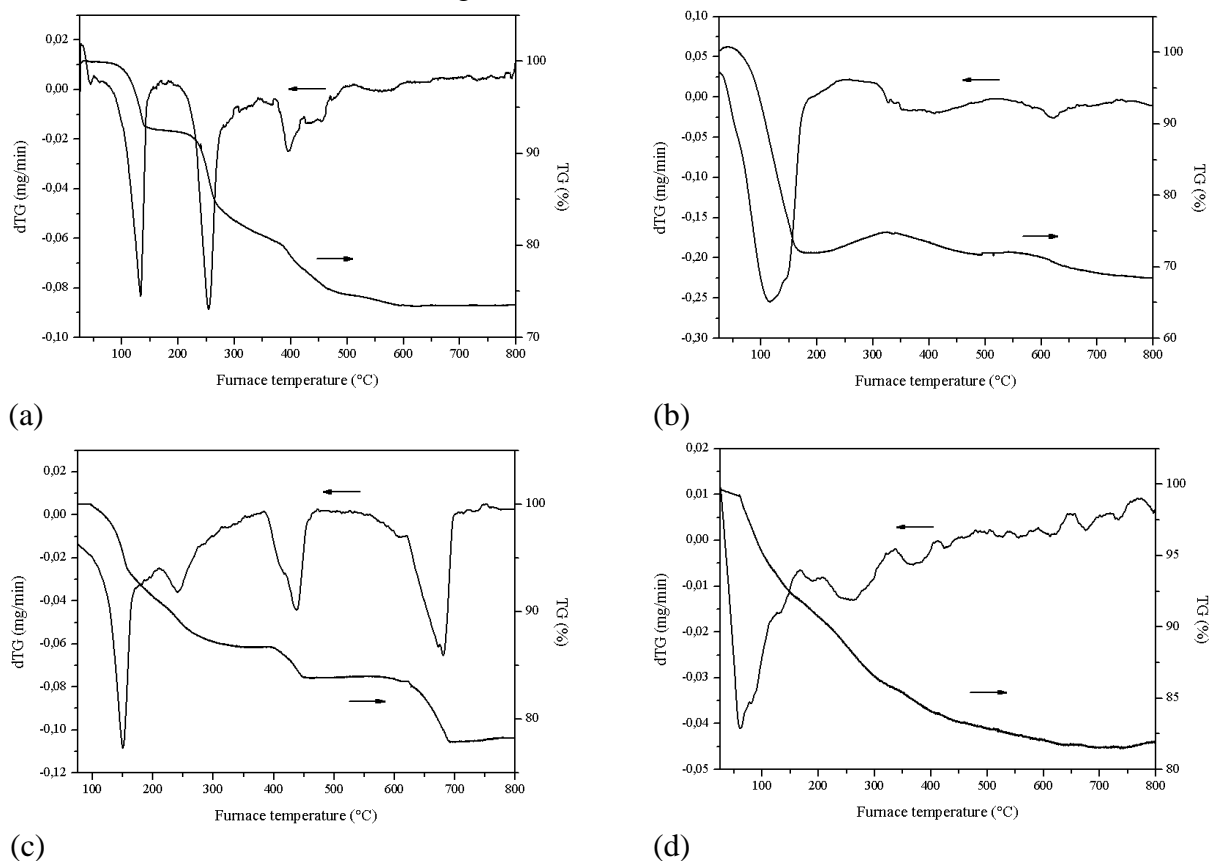


Figure 5. Thermogravimetric analysis (TG, DTG) of (a) the pristine Ca₃Fe LDH, (b) the sodium indole-2-carboxylate, (c) the indole-2-carboxylate–Ca₃Fe LDH EtOH/H₂O and (d) the indole-2-carboxylate–Ca₃Fe LDH acetone/H₂O.

From the pristine CaFe LDH sample, first, the physisorbed water was desorbed in a relatively narrow temperature range (383–423 K), then, the interlayer water was gradually removed in a wider temperature range (423–613 K), then the structural water left, again in a relatively narrow temperature range (643–723 K) and finally, the layered structure collapsed. The intercalated structure behaved differently in the sense that now we did not see the slowly

disappearing interlayer water. Instead, within 100 degrees (623–723 K) the organic material and possibly the structural water left together and the layered structure collapsed. Note that for the organic-inorganic hybrids the weight losses occurred at somewhat lower temperatures when aqueous acetone was the solvent mix used.

After verifying that the organic anions were intercalated indeed, whichever solvent mix was used, we can take the interlayer distance values and size data of the organic anions from Table 1 and attempt to give a picture about the possible arrangement of the anions between the layers. It can be envisaged that when aqueous ethanol was used during preparation both the indole-2-carboxylate and the dihydroindole-2-carboxylate fit between the layers if they are located horizontally. On using aqueous acetone the anions can be accommodated in perpendicular orientation to the layers (Fig. 6).

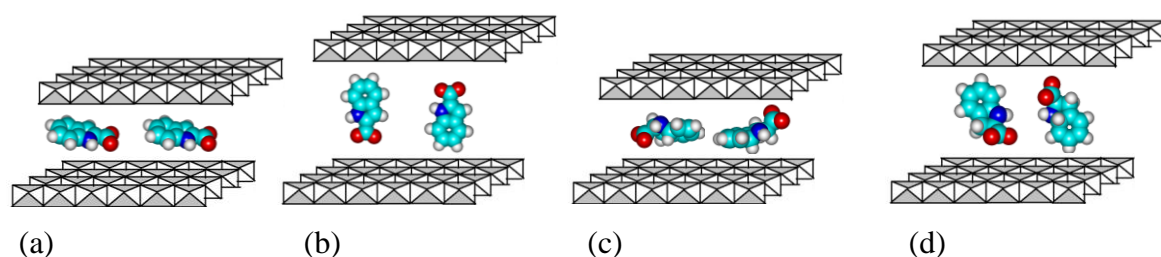


Figure 6. The possible arrangement of indole-2-carboxylate between the layers depending on the solvent mixture used during the synthesis, (a) ethanol/water, (b) acetone/water; and the possible arrangement of dihydroindole-2-carboxylate between the layers when either (c) ethanol/water or (d) acetone/water was used.

4 Conclusions

N-containing heterocyclic anions could be introduced among the layers of Ca_3Fe LDH with relative ease. The success of intercalation was verified with a range of instrumental methods. The interlayer distance values from XRD measurements and size data of the anions from molecular modelling calculations allowed giving an approximate picture on the arrangement of the anions among the layers. Most importantly it was shown that the choice of solvent mixture used during the intercalation dramatically influenced the interlayer distance in the hybrids, thus significantly influencing the geometry of the intercalation.

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