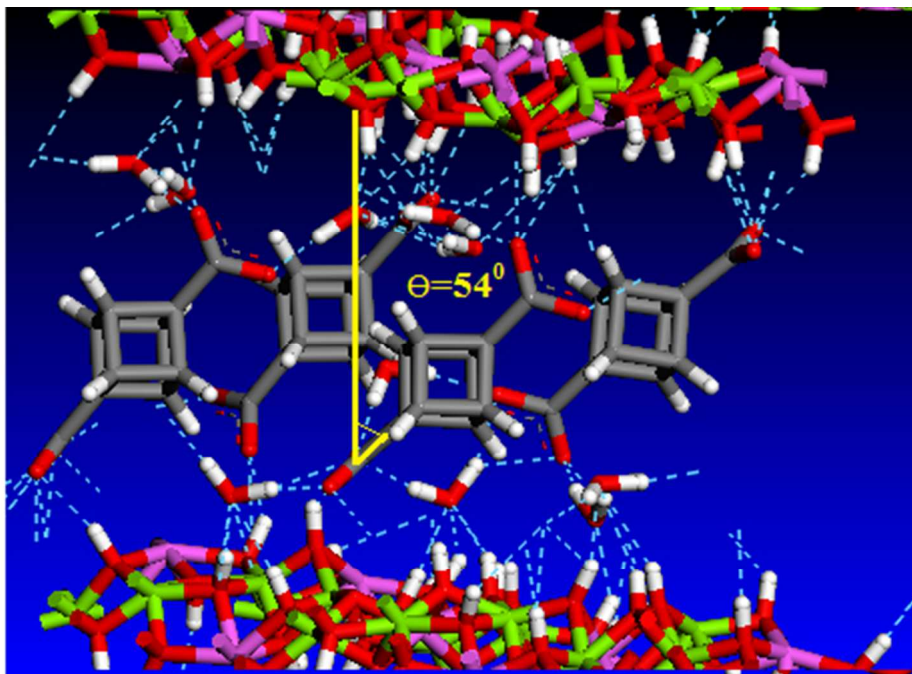




Synthesis and characterization of Mg-Al-layered double hydroxides intercalated with cubane-1,4-dicarboxylate anions

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Graphical Abstract
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Synthesis and characterization of Mg-Al-layered double hydroxides intercalated with cubane-1,4-dicarboxylate anions

Zolfaghar Rezvani*, Farzad Arjomandi Rad and Fatemeh Khodam

Abstract

In the present research work Mg_2Al layered double hydroxide (LDH) intercalated with cubane-1,4-dicarboxylate anions was prepared by coprecipitation method, when solutions of Mg(II) and Al(III) nitrate salts, react with an alkaline solution of cubane-1,4-dicarboxylic acid. The successful preparation of nanohybrid of cubane-1,4-dicarboxylate(cubane-dc) anions with LDH was confirmed by powder X-ray diffraction, FTIR spectroscopy and thermal gravimetric analysis(TGA). The increase in the basal spacing of LDHs from 8.67 Å to 13.40 Å shows that cubane-dc anions were successfully located into the interlayer space. Thermogravimetric analyses confirm that the thermal stability of the intercalated cubane-dc anions is largely enhanced compared to the pure form before intercalation because of the host-guest interaction involving the hydrogen bonds. The interlayer structure, hydrogen bonding, and subsequent distension of LDH compounds containing cubane-dc anions were shown on the molecular simulation. The RDF (radial distribution function), mean square displacement (MSD), and self-diffusion coefficient were calculated using the trajectory files on the basis of molecular dynamics (MD) simulations, and the results indicated that the cubane-dc anions was more stable when intercalated into the LDH layers. A good agreement between calculated and measured X-ray diffraction patterns and between experimental and calculated basal spacing was obtained.

Keyword: layered double hydroxide- cubane-1,4-dicarboxylic acid - molecular simulation- powder X-ray diffraction

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Introduction

Layered organic–inorganic hybrid compounds containing biological and biomedical organic anions are a new class of materials and present a appropriate advance for obtaining multifunctional materials.¹ Recently, there have been remarkable attentions to many organic anions incorporated into layered inorganic host structures in order to improve their thermal and physicochemical properties.² The interlayer spacing of these inorganic host structures are easily expandable due to easy breaking of weak van der Waals or hydrogen bondings.³ Among these layered inorganic host structures, the layered double hydroxides (LDHs) attracted more attentions. Layered double hydroxides (LDH) consist of positively charged brucite-like layers and negatively charged anions in the interlayer space. These structures can be represented by the following general formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}[(A^{n-})_{x/n} \cdot m\text{H}_2\text{O}]$, where M^{2+} and M^{3+} are di- and trivalent metal cations, respectively, A^{n-} represents an exchangeable interlayer anion with the charge of $n-$.⁴ LDH systems were widely studied for advancing their potential applications and from a molecular simulations point of view.⁵ There has been a remarkable attention to many organic anions incorporated in LDHs. These new materials show new photophysical behaviors and several useful advantages for the eco-friendly development. A homogeneous distribution of the organic anions at molecular level can be facilitated by H-bond and Van der Waals interaction and the host-guest interaction based on electrostatic forces in the LDH galleries.⁶

The anions in the interlayer gallery are generally exchangeable, and indeed anion exchange is the most widely used intercalation method. Many different kinds of anions have been successfully intercalated into LDH, including almost all of the common inorganic anions, many organic anions including carboxylates, sulfonates, benzoates, and biomolecular anions such as aminoacides, enzymes, DNA and biopolymers.⁷ Investigation of the interlayer arrangement of these compounds is in common problematic as they usually exhibit a certain degree of disorder, which can block the structure analysis based on diffraction data only. A method that successfully solves this problem is a combination of molecular modeling and experimental measurements.⁵

Because of the considerable increase in computational power over the past decades, molecular dynamics (MD)^{8,9} proved to be useful tools to study the phenomena of molecular self-assembly and they can yield a detailed, atomistic level insight into the three dimensional structure of the model system. The theoretical simulations give a complementary and

effective method to study and predict the properties and structures of the new kinds of the functional materials, and some attractive results can be gained.⁶

Science Eaton synthesized cubane, numerous studies have been made in terms of the syntheses and characterization of cubane derivatives.¹⁰⁻¹⁴ Cubane derivatives are widely used as novel organic anions with high-energy explosive properties, oligomeric compounds developers and pharmaceutical materials. For example, they are highly lipophilic molecules that bind avidly to the envelope of the AIDS virus. On the basis of literature data the syntheses and characterization of nanohybrids of several organic compounds with LDHs have reported in last decade, but on the basis of our best knowledge, synthesis, characterization and molecular modeling investigation of LDHs with cubane derivatives have not been reported before in the literature.

In the present work the preparation of Mg–Al hydrotalcite intercalated with Cubane-1,4 dicarboxylate anions (hereafter abbreviated as cubane-dc) is reported. The product obtained by coprecipitation method, when solutions of Mg(II) and Al(III) salts, react with an alkaline solution of cubane-1,4 dicarboxylic acid. Since the physicochemical properties of the intercalates are influenced by the structure of the interlayer space, the molecular modeling was used to describe the arrangement of cubane-dc anions in the interlayer space.

Experimental

Materials

Cubane-1, 4 dicarboxylic acid was prepared by the methods described in the literature.^{10, 14, 15} All reagents were purchased from Merck chemical company and used without further purification. NO₃-Mg-Al-LDH was prepared according to the literature.

Characterizations

Powder X-ray diffraction patterns (PXRD) of the samples were recorded with a Bruker AXS model D8 Advance diffractometer using Cu-K_α radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV, 35 mA with a Bragg angle ranging from 2 to 70° 2θ . Fourier transform infrared spectra (FT-IR) were recorded in the range of 4000–400 cm⁻¹ using the KBr pellet technique with a Perkin-Elmer spectrophotometer. TGA was carried out with a Mettler-Toledo TGA 851e apparatus at a heating 10 Kmin⁻¹ in a nitrogen atmosphere. The scanning electron microscopy (SEM) was used to study the morphology of samples using ultrahigh resolution FESEM device, model

ULTRA55, Carl Zeiss MST AG, Germany. Elemental (C, H, and N) analyses were carried out on a Perkin-Elmer automatic equipment model 240B. Mg and Al contents of the samples were determined by using inductively coupled plasma spectroscopy (Jobin Yvin JY24) after dissolving the samples in nitric acid.

Syntheses of cubane-dc-LDH

A solution containing cubane-1,4 dicarboxylic acid (0.172 g, 0.001 mol) dissolved in NaOH (20 mL, 0.1 M) was slowly added to an aqueous mixed solution (20 mL) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5128 g, 0.002 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.375 g, 0.001 mol) with vigorous stirring in a nitrogen atmosphere. The pH of collection was adjusted in 10.2 by dropwise adding of NaOH or HCl, and the system was heated to reflux at 55 °C for 72 h. The product (cubane-dc-LDH) was centrifuged at a speed of 2000 rpm for 10 min. and the solid washed thoroughly with deionized water and finally dried at room temperature under vacuum. Anal. calculated for $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}](\text{C}_{10}\text{H}_6\text{O}_4) \cdot 2.5\text{H}_2\text{O}$: C, 20.33; H, 3.90; Mg, 16.47; Al, 9.15. Found: C, 19.9; H, 3.98; Mg, 16.0; Al, 8.7.

Molecular modeling

The whole simulations were conducted by using the Discover and Forcite modules in the Materials Studio software package.¹⁶ These modules involve a range of well-validated force fields for dynamics simulations, minimization, and analysis searches for periodic solids. It can be desirably employed in studying the system of molecular and a variety of materials types. In this article, a perfect LDH layer model with hexagonal supercell was made. At first, DFT method was used to get the geometry optimization configuration for the cubane-dc. After determination of atomic charges, this information would be used in the molecular dynamic simulations. A classical force field CVFF was used for the cubane-dc-LDH system.^{17,18,19} The first step in the simulation was the preparation of the positively charged Mg-Al-LDH layers as host structure. The host structure was constructed using atomic coordinates from the formerly reported crystal structure of hydrotalcite,²⁰ $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}](\text{CO}_3) \cdot 3\text{H}_2\text{O}$, whose X-ray crystal structure had been refined in a rhombohedral unit cell with space group $R\bar{3}m$ and lattice parameters $a=b=3.054 \text{ \AA}$, $c=22.81 \text{ \AA}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$. In order to study the mutual arrangement of the guests in the interlayer space, a $P1$ superlattice with the dimensions $6a \times 4a \times 3d_{\text{exp}}$ was developed where d_{exp} is d_{003} of cubane-dc-LDH which was obtained from the X-ray diffraction data. The interlamellar carbonate ions and water mole

cules were omitted, then a supercell was developed by $6a \times 4b \times 1.76c$ with supercell parameters $6a = 18.324 \text{ \AA}$, $4b = 12.216 \text{ \AA}$, $1.76c = 45.625 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. In fact, $3d_{003}$ or $3d_{\text{exp}} (= 40.2 \text{ \AA})$ of cubane-dc-LDH is equal to the $1.76c$ of the hydrocalcite structure. The ratio of Mg and Al atoms in the framework was 2:1, and the Mg and Al atoms were scattered in every layer arbitrarily. Every hydroxide layer had 8Al^{3+} and 16Mg^{2+} ions, with the latter arranged in a way that they were not placed in the adjacent octahedra. The cubane-dc anions were randomly located in the interlamellar area of the LDH to neutralize the positive charges for the hybrid system, and then to form a tilted bilayer arrangement. The molecules of water (10 molecules) were also randomly inserted into the interlamellar area. The atomic charges can be determined from the Mulliken charge, APT charge and ESP charge. In this work Mulliken method^{20,21} was used for calculation of atomic charges. Fig. 1 shows the Mulliken charge of the cubane-dc. Dmol₃ program at the GGA-PBE/DND level optimized the cubane-dc structure. The atomic charges are very essential in explaining the cubane-dc structure and the MD properties when cubane-dc anions molecule placed into the LDH layer.

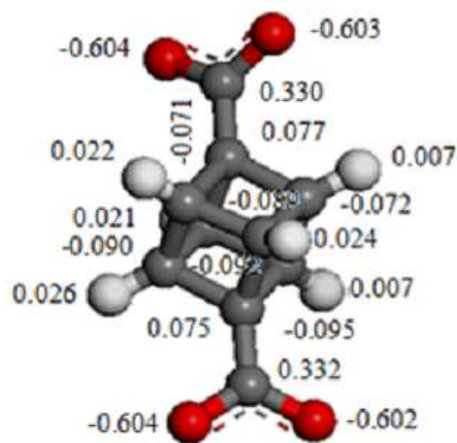


Fig. 1 Mulliken atomic charges of cubane-dc

Layer charges were calculated using the charge equilibration (QEq) method. Since the CVFF force field is more correct for LDH materials²², therefore the LDH part charges were improved with regard to CVFF force field, and the partial charge for Al was set to 1.231e or 1.278e, for Mg was set to 0.615e or 0.638e, for O was set to -0.617e or -0.628e or -0.558e and for H to 0.212e or 0.233e.

The minimization was performed in CVFF force field. The electrostatic energy was found by the Ewald summation method²³ and the van der Waals energy was shown by Lennard–Jones potential.²⁴ The total crystal energy minimization was conducted by a modified Newton method with consider to the following approach: All the layers of the host were kept as firm units in energy minimization period, and the cell parameters c , a , and β were variable. It enabled the optimization of the mutual arrangement of the host layers. All the atomic positions in the interlayer region were variable too.⁶

In this research, we concentrated on the aggregation structure about the anions of cubane-dc intercalated into LDH. The simulation was started from the structures with minimized energy, and the smart minimizer procedure was employed for the minimization. The minimized structures were employed to set the equilibrium bond lengths and angles. The molecular dynamics simulation was carried out in NPT statistical ensemble at room temperature (298 K). Time step was 0.5 fs and total time of simulation was 800 ps. **Fig. 2** shows the potential energy profile reaches a stable equilibrium after 200 ps of simulation time and last 400 ps was used for further analysis.

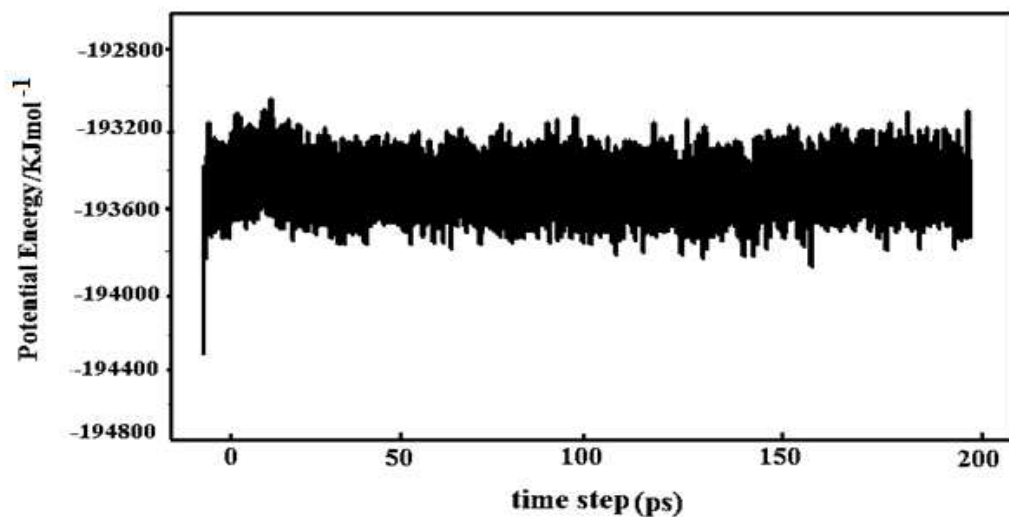


Fig. 2 Time profiles of the total energy (the last 200 ps)

Results and Discussion

XRD analyses

The XRD patterns for the Mg–Al–NO₃ LDH and the cuban-dc-LDH showed characteristic reflections related to a crystalline layered phase (Fig. 3).^{25,26} In the range of 2–70 ° for the

Mg–Al–NO₃ LDHs, the sharp and strong diffraction peaks at low 2θ values, shown in **Fig. 3(a)**, demonstrate good crystallinity of LDH nanoparticles.

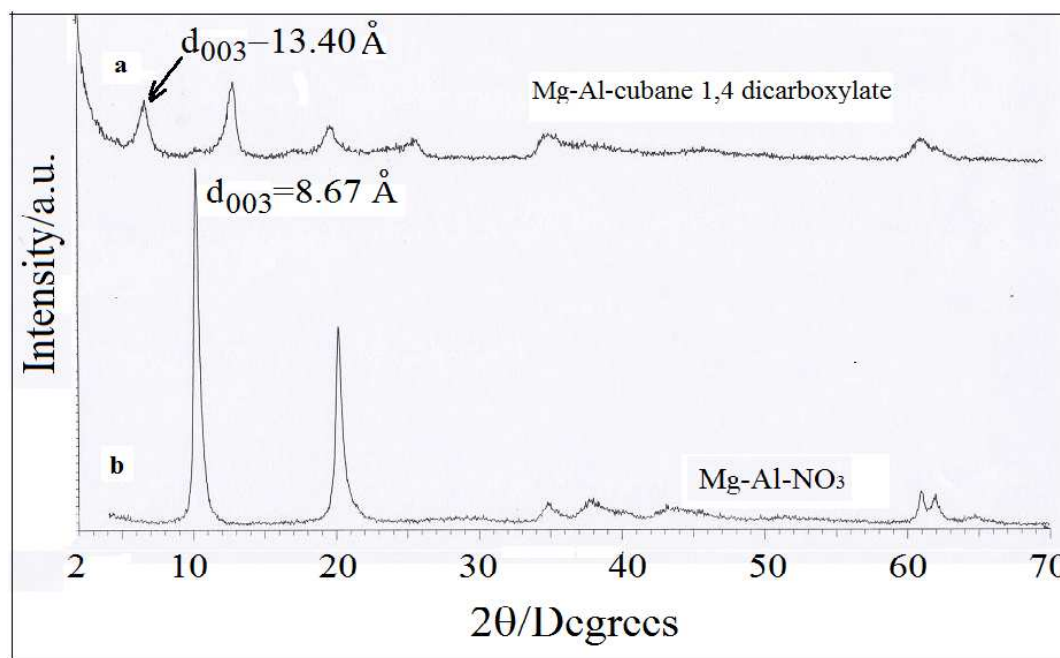


Fig. 3 PXR D patterns of the Mg-Al-NO₃-LDH and Mg-Al-LDH intercalated with cubane-dc

Mg–Al–NO₃ LDH has d_{003} basal spacing of 8.67 Å. The basal spacing value of d_{003} , representing the summation of thickness of the brucite-like layer (0.48 nm),²⁷ and the gallery height, is a function of the number, size and orientation of intercalated anions.²⁸

The XRD pattern of the sample with the intercalated cubane-dc anion is shown in **Fig. 3(b)**. During the intercalation of cubane-dc anions the layers of LDH swell to host the anions and this expansion is reflected by the value of d_{003} . The value of d_{003} is 13.40 Å. This swelling of the layers is due to the intercalation of the cubane-dc anions and the basal spacing corresponding to diffraction by planes (003) was much larger than for the LDH. Taking into account that the thickness of LDH layer is 4.8 Å and the longitudinal Van der Waals' radius of the cubane-dc anion is 7.20 Å (determined by the software ChemSketch), it was confirmed that cubane-dc anions were successfully intercalated in their anionic form, and that they were arranged as a monolayer within the interlayer.

FTIR Spectra

The structure of cubane-dc-LDH was also confirmed by FT-IR spectroscopy. The FT-IR spectra of the cubane-1, 4 dicarboxylic acid and the cubane-dc-LDH are shown in **Fig. 4(b and c)**. The FT-IR spectrum of the Mg-Al-NO₃-LDH is shown in Fig. 4a for comparison.

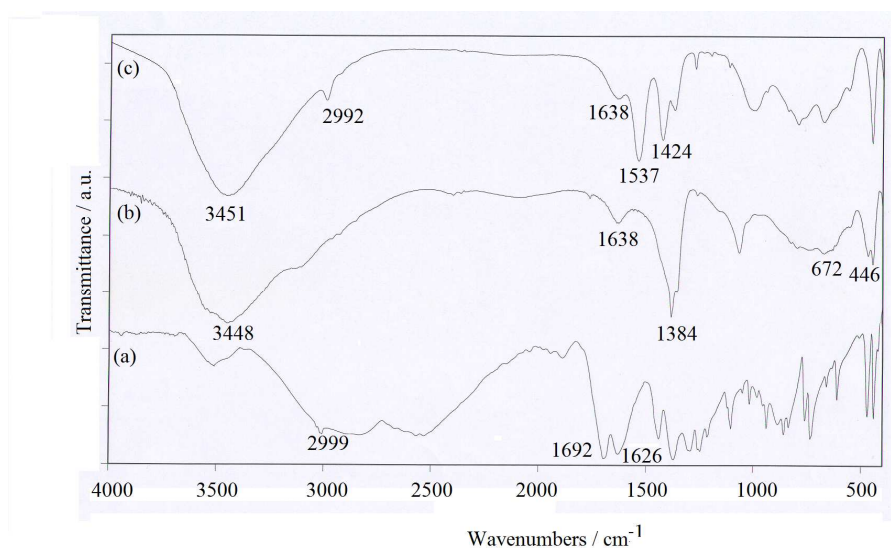


Fig. 4 FT-IR spectra of (a) Cubane-1, 4 dicarboxylic acid, (b) NO₃-LDH, and (c) Cuban-dc-Mg-Al-LDH

The spectrum for NO₃-LDH is similar to that reported in the literature.^{29, 30} Absorption at 1384 cm⁻¹ can be assigned to the ν_3 vibration of NO₃. A broad, strong absorption band centered at 3451 cm⁻¹ is ascribed to the stretching vibrations of hydroxyl groups and surface and interlayer water molecules,^{31, 32} which are found at a lower frequency in LDHs compared with the O-H stretching in free water at 3600 cm⁻¹.³³ This is attributed to the formation of hydrogen bonds between the interlayer water and the different guest anions as well as with the hydroxide groups of the layers. A weaker band at 1638 cm⁻¹ was due to the bending mode of water molecules. The bands centered at 446 and 672 cm⁻¹ are attributed to Al-O and Mg-O lattice vibrations.²⁹

In the case of pure cubane -1, 4 dicarboxylic acid, strong absorption bands centered at 3416 and 3500 cm⁻¹ are attributed to the stretching vibrations of OH groups. Furthermore, absorption bands at 1692, 1626 cm⁻¹ are related to the C=O of carboxylate groups. In cubane-dc-LDH, the absence of the NO₃ bands at 1384 cm⁻¹ indicates that the preparation process was complete. The band at 1692 and 1626 cm⁻¹ due to the COOH group disappears, while the

two bands at ca 1537 and 1422 cm^{-1} due to the anti-symmetric and symmetric stretching vibrations of -COO^- appear and shift to lower wavenumbers, compared to free -COOH in cubane -1,4 dicarboxylic acid, indicating that the intercalation in the interlayer space involves hydrogen bonding, besides the obvious electrostatic attraction between the electropositive cations in layer and organic anions in interlayer.^{28, 34, 35}

Thermal analyses

The suitable tools for the determination of thermal stability of material are thermogravimetric analyses (TGA). The thermal stability of the cubane - and the cubane-dc-LDH are investigated by using TGA analysis. The TGA curves are shown in **Fig. 5(a, b)**. In the case of cubane -1, 4 dicarboxylic acid (**Fig. 5a**) there are two steps in the temperature range of 220–300 °C and 300–500 °C that is attributed to decomposition of cubane-1, 4 dicarboxylic acid. The mass losses value at 850 °C of the cubane -1, 4 dicarboxylic acid is 87.5%.

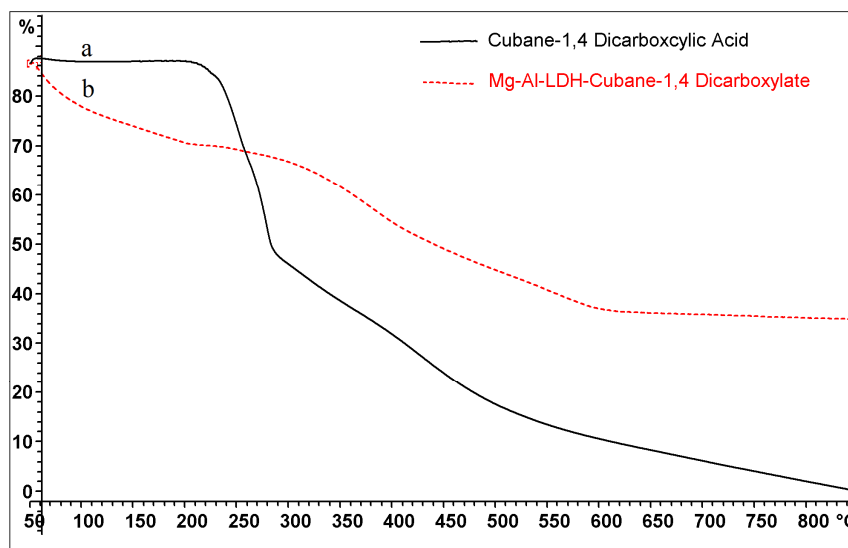


Fig. 5 TGA thermograms of (a) Cubane-1,4 dicarboxylic acid ,
And (b) Mg-Al-LDH-cubane-dc

Cubane-dc-LDH shows major mass losses in three steps. The first mass loss observed in the 50–200 °C corresponds to the loss of both adsorbed and interlayer water molecules. A following rapid mass loss in the region 300–400 °C is attributable to the cubane-dc decomposition and dehydroxylation of the LDH layer. This temperature is higher than the decomposition temperature of pure Cubane-1,4 dicarboxylic acid, which occurs at 220 °C. It is confirmed that the thermal stability of intercalated cubane-DC molecule was improved by the value of 80

°C. The third mass losses in the temperature range of 400–600 °C is attributed to further dehydroxylation of LDH layers. The mass losses value at 850 °C of the cubane-dc-LDH is 52.17%. Decomposition of cubane-dc-LDH leads to the formation of MgO and Al₂O₃ with Mg/Al ratio 2. On the bases of the formula of the cubane-dc-LDH [Mg₄Al₂(OH)₁₂](C₁₀H₆O₄).2.5H₂O, the calculated mass mass loss is 55.61% . This difference(3.44%) between calculated and observed mass loss may be related to the fact that the oxidation of a rest carbon is not fully completed .

For further confirmation of the thermal stability improvement of cubane-DC anions intercalated into LDH layers, the virgin crystals of this sample stored at 300 °C for 2 hours, and then X-ray diffraction pattern and IR spectrum (**Fig. 6**) were recorded .As seen in **Fig. 6(a)**, the layered structure of sample is preserved in annealed sample, but the basal spacing (d_{003}) slightly decreased from 13.40 Å to 12.90 Å which confirms the loss of water molecules from the interlayer spacing. The FTIR spectrum of annealed sample (**Fig. 6b**) shows all vibrations of cubane-dc-LDH, but as can be seen from spectrum the intensity of water molecule bending mode (1638 cm⁻¹) decreased in comparison with virgin sample(**Fig. 5c**) which confirms the loss of water molecules from the interlayer spacing.

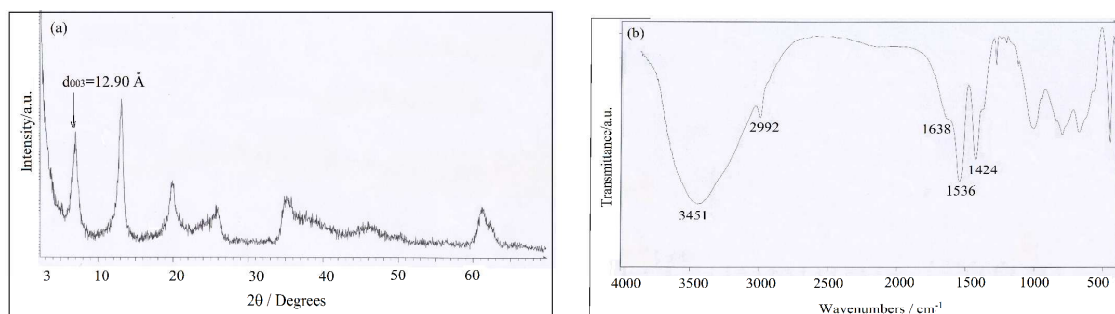


Fig. 6 XRD patterns of cubane-DC-LDH (a), and FTIR spectrum of Cubane-dc-LDH (b), annealed at 300 °C for 2 hours.

Results of the molecular modeling

Aggregation structure at the microscopic level is a very important factor for determining the macroscopic behavior of the cubane-dc anions intercalated into the layers of LDH. The simulation of MD can show the orientation of the intercalated molecules at the molecular level and lead to the conclusion about the mutual arrangement of the guest cubane-dc anions in the interlayer region. **Fig. 7(a,b)** shows the snapshot of equilibrium structures of the cubane-dc-LDH system before and after MD simulation. It is

worthy to note that the cubane-dc anions and water molecules are placed randomly in the interlayer space of the LDH. Through analyzing the trajectories, the equilibration of the simulation systems reveals the arrangement of cubane-dc anions. Molecular dynamic calculations reveal that the long axis of the cubane-dc anions in the interlayer space display a tilting approximately 54° from perpendicular orientation to the LDH layer. Molecular dynamics showed that guest anions are not freely distributed in the interlayer space but they have a tendency to assemble in rows with a certain disorder.

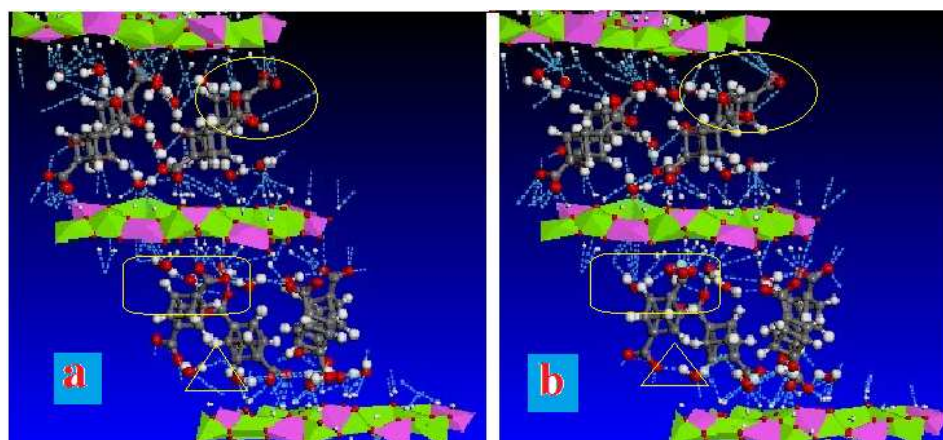


Fig. 7 Snapshot of the equilibrium structures for cubane-dc-LDH,
(a) Before, and (b) after MD simulation

The endgroup–water interaction can be achieved from the partial *radial distribution functions* (RDFs) which explain how many atoms of type A are on average at a distance r of an atom of type B.⁶ Relevant RDF of water molecules with cubane-dc anions endgroups are calculate over the last 800 ps (**Fig. 8**). As can be seen from **Fig. 8**, the water molecules are dispersed in the interlayers of LDH around the endgroups, and can be divided into two main shells which are placed around 0.97 \AA and 1.57 \AA to the cubane-dc anions endgroup respectively. Most of the water molecules form close contacts with OH^- of LDH layer and the $-\text{COO}^-$ group of guest anions. **Fig. 9** indicates the scheme of H-bond structure between the endgroup and the water molecules which shows that most of hydrogen bonds in the hybrid systems are developed by O atom of endgroups with OH^- in the layers of LDH, and then with the water molecules.

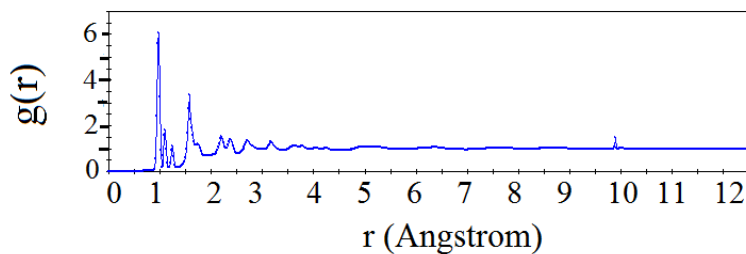


Fig. 8 RDFs between endgroup and water

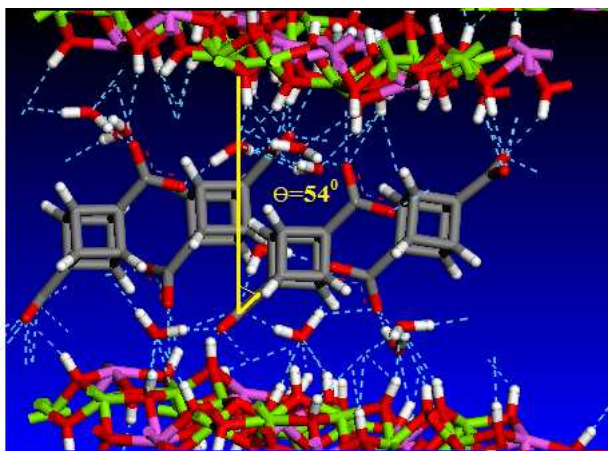


Fig. 9 Hydrogen bonds in the hybrid system.

To study the delivery effective of cubane-dc anions which use LDH as carriers, we have obtained the *mean square displacements* (MSDs) of the cubane-dc and water molecules from the last 200 ps (time step = 0.5 fs and total time of simulation =400 ps) MD trajectory. The analysis of the MSD yields important information about the stability of the cubane-dc- LDH system. As the slope of the MSD versus time curve is consistent with the system achieving equilibrium, the MSD of the two different molecules in the 200 ps of trajectory has been shown in **Fig. 10**. The MSD was obtained from Eq. (1),⁶

$$\text{MSD}(t) = \left\langle \frac{1}{N} \left[\sum_{i=1}^N [r_i(t) - r_i(0)]^2 \right] \right\rangle \quad (1)$$

where N is the number of target molecules and $r_i(t)$ is the location of molecule i at time t. Then diffusion coefficient (D) can be obtained by using the famous Einstein relation (Eq. (2))

$$D = \frac{1}{2dN\alpha} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle [r_i(t) - r_i(0)]^2 \right\rangle \quad (2)$$

where d is the system dimensionality, $r_i(t)$ and $r_i(0)$ are the center of mass coordinates of the i th cubane-dc and water molecules at the times t and $t=0$, respectively. Once the MSD as function of time are calculated, you are ready to calculate self-diffusion coefficient. Eq.1 implies that MSD exhibits linear dependence on time, and *self-diffusion coefficient* is just the slope of the line. For short times, the MSD dependence on time is clearly not linear, and it becomes linear for longer times. Thus, diffusion coefficient should be determined only using data in the region, where MSD depends linearly on time. Linear regression should be used to determine diffusion coefficient.³⁷ **Fig.10** indicates the obtained MSD for the dispersed water molecules in comparison with the obtained MSD for the anions of cubane-dc. According to the MSD curves the self-diffusion coefficients of water and cubane-dc were calculated $(1.647 \pm 0.05) \times 10^{-7} \text{ cm}^2/\text{s}$ and $(6.543 \pm 0.05) \times 10^{-8} \text{ cm}^2/\text{s}$ respectively. Based on this result the self-diffusion coefficient of cubane-dc is lower than the water molecule significantly. From the above mentioned analysis we can conclude that, the cubane-dc anions are restricted in the layers of LDH and the cubane-dc anions are more stable when intercalated into the layers of LDH. The stability is highly important since it can overcome the thermal instability when cubane-1,4-dicarboxylic acid is alone used.²⁷

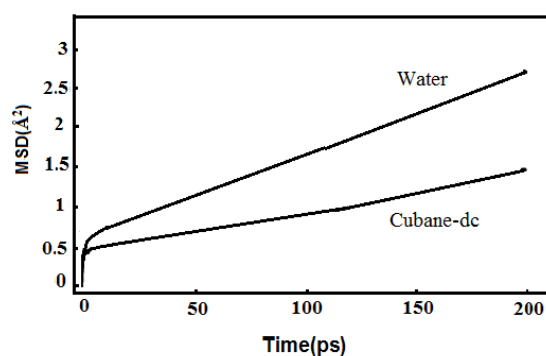


Fig.10 Comparison of the calculated MSD for cubane-dc and water molecules.

Comparison of experimental and calculated XRD

The orientation of cubane-dc anions within the interlayer space depend on the space available to the guest anions in the interlayer region. On the bases of the d_{003} value of cubane-dc-LDH (measured by x-ray diffraction) the space available to the cubane-dc anions in the interlayer space is 8.6 Å which can be calculated approximately by subtracting the layer thickness of 4.8 Å from the interlayer spacing (13.4 Å). According to the longitudinal van der Waals' radius of the cubane-dc anion (7.20 Å), the enough vacant space is available for guest anions.

On the other hand the orientation of guest anions depends on the interactions of guest anions with LDH layers, interlayer water molecules, and also interaction of guest-guest anions.

Experimental XRD results combined with molecular simulations can determine the potential orientations of the cubane-dc guest anions in the interlayer space. Water content of interlayer space and position of the interlayer water, and also orientation of guest anions (cubane-dc) are strongly influenced on the x-ray diffraction patterns. By using molecular modeling and molecular dynamic calculations, the water molecules and guest anions arranged within the interlayer so that the calculated XRD pattern agrees with measured one. **Fig. 11** shows the calculated and experimental XRD pattern of cubane-dc-LDH.

Experimental XRD pattern shows that the peaks maxima of d_{003} , d_{006} and d_{009} were observed in 13.40, 6.92 and 4.52 Å respectively. According to the calculated XRD pattern, calculated d_{003} , d_{006} and d_{009} were observed in 13.39, 6.69 and 4.46 Å respectively. Calculated d_{003} (13.39 Å) is in good agreement with the experimental basal spacing ($d_{003} = 13.40$ Å), but the calculated $d_{006} = 6.69$ Å is slightly lower than experimental $d_{006} = 6.92$ Å. This fact may be related to the crystal size broadening effect and high disorientation of guests in the structure model which is not taken into account in the calculating software.⁵

As can be seen from Fig. 11, the experimental intensities of (003) and (006) peaks are inverted compared to the calculated XRD pattern. This observation is due to the roughness of the surface of the experimental sample which is not considered in the calculating software.⁵ This effect is common when the electron density of the interlayer space is comparable or higher than that of the brucite sheet.

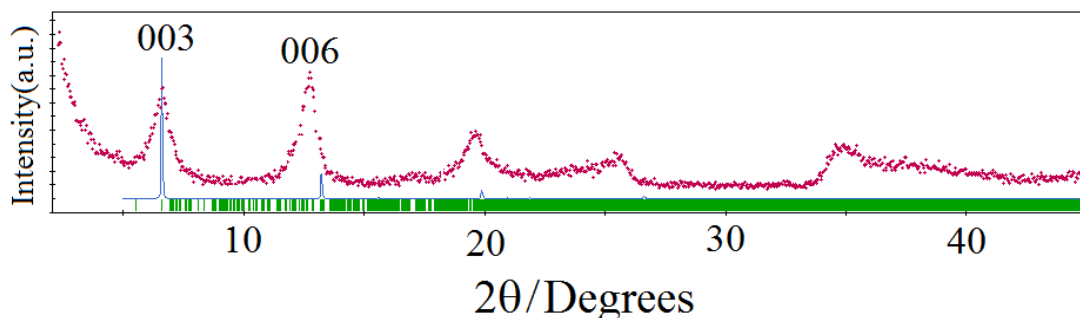


Fig. 11 The calculated (solid) and experimental (dotted) x-ray diffraction patterns.

Comparison with terephthalate-intercalated Mg-Al-LDH

G. Lagaly et al have been reported the syntheses, characterization and basal spacings of several dicarboxylate-intercalated-Mg-Al layered double hydroxides.³⁸ Among the reported cases, the

size of the terephthalate dianions is very close to the cubane-dc anions. Distance between carboxylate endgroups in the terephthalate and cubane-dc is 7.1 Å and 7.2 Å respectively. The basal spacing (d_{003}) of terephthalate-Mg-Al-LDH hybrid is 14.3 Å. This value is significantly higher (0.9 Å) than cubane-dc-Mg-Al-LDH nanohybrid basal spacing (13.40 Å). This difference may be related to the tilted arrangement of cubane-dc dianions in the interlayer region.

SEM

Scanning electron microscopy (SEM) image of cubane-dc-LDH nanohybrid is depicted in **Fig. 12**. The irregular sheet-like character of cubane-dc-LDH nanohybrid can be seen obviously in **Fig. 12**. In fact cubane-dc-LDH is composed of aggregates of irregular sheet-like nanoparticles with sheet thickness in the range of 40–60 nm. The broadening of XRD pattern of cubane-dc-LDH (Fig. 11) is due to the non-sized particles.

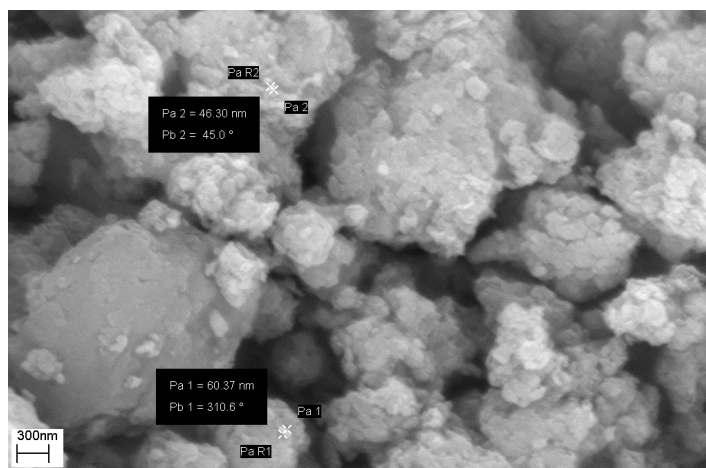


Fig. 12 SEM image of cubane-dc-LDH

Conclusions

The synthesis and characterization of Mg–Al hydrotalcite intercalated with cubane-dc anions is reported. The successful intercalation of cubane-1,4-dicarboxylate anions into the interlayer space of LDH was confirmed by powder X-ray diffraction, FTIR spectroscopy and thermal gravimetric analysis (TGA). During the intercalation of cubane-dc anions, the layers of LDH swell to host the anions and this expansion is reflected by the value of d_{003} . A molecular dynamic simulation has been used to investigate the arrangement the guest anions

within the interlayer space of LDH. The results showed that the long axis of cubane-dc anions present a tilting approximately 54° from perpendicular orientation to the LDH layer. Based on RDF results the water molecules are dispersed in the interlayers as two main shells which are positioned around 0.97 \AA and 1.57 \AA to the cubane-dc anions endgroup. The dynamical properties such as the mean-square displacement (MSD) and thus the self-diffusion coefficients (D) were also analyzed for intercalated cubane-dc anions and water molecules. The results of the MD showed that the Cubane-dc anions were more stable when intercalated into layers of LDH.

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Legend of figures

Fig. 1 Mulliken atomic charges of cubane-dc.

Fig. 2 Time profiles of the total energy (the last 200 ps).

Fig. 3 PXRD patterns of the Mg-Al-NO₃-LDH and Mg-Al-LDH intercalated with cubane-dc.

Fig. 4 FT-IR spectra of (a) Cubane-1, 4 dicarboxylic acid,(b) NO₃-LDH, and (c) Mg-Al-cubane-dc.

Fig. 5 TGA thermograms of (a) Cubane-1,4 dicarboxylic acid ,and (b) Mg-Al-LDH-cubane-dc.

Fig. 6 XRD patterns of cubane-DC -LDH (a), and FTIR spectrum of Cubane -dc-LDH (b), annealed at 300 °C for 2 hours.

Fig. 7 Snapshot of the equilibrium structures for cubane-dc-LDH,(a) Before, and (b) after MD simulation.

Fig. 8 RDFs between endgroup and water.

Fig. 9 Hydrogen bonds in the hybrid system.

Fig.10 Comparison of the calculated MSD for cubane-dc and water molecules.

Fig. 11The calculated (solid) and experimental (dotted) x-ray diffraction patterns.

Fig. 12 SEM image of cubane-dc-LDH.