

Structural insight into the photoinduced $E \rightarrow Z$ isomerisation of cinnamate embedded in ZnAl and MgAl layered double hydroxides

Zita Timár^{a, b}, Gábor Varga^{a, b}, Márton Szabados^{a, b}, Krisztián Csankó^c, Tünde Alapi^d, Claude Forano^e, Vanessa Prevot^e, Pál Sipos^{b, d}, István Pálínkó^{a, b, *}

^a Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720, Hungary

^b Materials and Solution Structure Research Group and Interdisciplinary Excellence Centre, Institute of Chemistry, University of Szeged, Aradi Vértanúk tere 1, Szeged, H-6720, Hungary

^c Biological Research Centre, Temesvári krt. 62, Szeged, H-6726, Hungary

^d Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720, Hungary

^e Université, Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, F-63000, Clermont-Ferrand, France

ARTICLE INFO

Article history:

Received 8 April 2020

Received in revised form

24 May 2020

Accepted 28 May 2020

Available online 4 June 2020

Keywords:

Layered double hydroxides

Cinnamate

$E \rightarrow Z$ isomerisation

Photoinduced reaction

Nanoreactors

ABSTRACT

Hybrid E-cinnamate- and Z-cinnamate-intercalated layered double hydroxides (Mg₂Al- E- or Z-Cin LDH and Zn₂Al- E- or Z-Cin LDH) were prepared by the co-precipitation method, and structurally characterised by powder X-ray diffractometry, UV–Vis, FT-IR and ¹³C CP MAS solid-state NMR spectroscopies to gain further insights on the arrangement of the organic anions in the interlamellar domain. UV light irradiation induced E–Z isomerisation reaction was subsequently attempted in the solid state and in methanolic suspension. Although reaction was observed in the solid state; however, E–Z isomerisation mainly occurred in the slurry phase. The fact that there was no isomerisation when E-Cin was solely adsorbed on the surfaces of pristine LDHs highlights that the reaction took place in the interlayer region. Similar behaviour was observed for the two LDH compositions proving that the LDH structures acted as nanoreactors confining the photoinduced isomerisation.

© 2020 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Having well-defined spaces at the nanoscale, inorganic solid-phase nanoreactors, such as (nano)materials with porous and low-dimensional structures (0-D, 1-D, 2-D), such as mesoporous materials or certain zeolites, can not only control selectivities and rates of confined chemical reactions, but the conformation, the stereochemistry and the size of the products as well [1–5]. An additional advantage if structural modifications are possible, is to tailor the nanoreactor properties to needs [1–10].

Layered double hydroxides (LDH) ([M^{II}_{1-x}M^{III}_x(OH)₂]⁺[X^{q-}_{x/q}.nH₂O]), which are well-known lamellar inorganic materials with positively charged layers ([M^{II}_{1-x}M^{III}_x(OH)₂]⁺) and negatively charged interlayer gallery ([X^{q-}_{x/q}.nH₂O]) and expanding structure under intercalation, meet the above requirements. Therefore, they have good potential of acting as nanoreactors, especially when the

reaction partner(s) is/are intercalated into the interlayer domain [8,11–17]. Indeed, the high density of hydrophilic OH groups (~12 OH/nm²) covering the surface of the interlayer gallery added to the presence of positive (intralayer metal cations) and negative (interlayer anions) sites may favour selective binding interactions for organic substrates in a well-defined environment, may act as H-bond catalyst [18]. This was shown by Yu and He [19] for the L-proline confined in LDH or by Dutta and Tummanapelli using computational investigation to describe interaction between the anionic layered host and a neutral guest molecule (Chloranil) [20]. Hybrid LDHs may also have important role in prebiotic chemistry carrying chiral information due to the intercalated/adsorbed optically active amino acids in anionic forms [21–23]. The high number of papers on hybrid LDH materials demonstrate the high capacity of these 2-D materials to intercalate a large variety of organic molecules and macromolecules offering an open field for confined catalytic reactions [24].

However, there are not many examples of LDH acting as a nanoreactor for *in situ* catalytic transformations [25–27].

Alkene E,Z isomers are involved in the synthesis of a large

* Corresponding author. Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720, Hungary.

E-mail address: palinko@chem.u-szeged.hu (I. Pálínkó).

variety of highly valuable organic molecules, therefore, there is a need to find better strategies the stereoselective synthesis of E and Z isomers. Direct pathways to the formation of Z olefins is still rare. Therefore, E→Z isomerisation appears as a green strategy to reach this challenge instead of more atom costly Z-selective catalytic olefin cross-metathesis [28]. Recently Li et al. [29] reported the efficient photocatalytic E to Z isomerisation of cinnamyl derivatives. Photoisomerization of indolinespirobenzopyran was achieved in the interlayer of MgAl LDHs [30,31]; however, the role of the LDH support was not discussed. J. Valim et al. [32] achieved the intercalation of p-chlorocinnamate in MgAl LDH ($d_{hs} = 1.98$ nm); however, under UV-irradiation dimerization competed with E to Z isomerisation. These preliminary results were not investigated much further. The recent examples reporting light-assisted cis-trans isomerisation in LDH mainly concern azobenzene molecules [33,34].

In one of our earlier works [14], the E isomers of various acrylate ions were intercalated into CaFe-LDH, and the samples were irradiated with a non-heating xenon light source working in the 220–400 nm wavelength range. Topotactic [2 + 2] cyclo-dimerization was achieved solely. To promote the cyclo-dimerization, domains were needed in the host layered structure where the intercalated anions were in close proximity and in suitable arrangement. Surprisingly, E–Z isomerisation was not observed. Acrylic acid derivatives on UV irradiation preferentially underwent cyclodimerization in solution too, E–Z isomerisation was rare, occurring only when methanol was used as the solvent [35]. The E–Z isomerisation of the E-cinnamic acid can be followed by UV–Vis spectroscopy: the conveniently detectable absorption maxima for the E and the Z compounds are at 268 nm and 258 nm, respectively [36,37]. The positions of the absorption maxima did not change even when the anionic forms of these compounds were intercalated into LDH matrices [38].

In the current experimental work leading to this contribution, the possibilities for the photoinduced E–Z isomerisation to occur in the presence of Zn_2Al or Mg_2Al LDHs were investigated. To highlight the role of the organic anion confinement into the layered domain, the E-cinnamate (Cin) was either admixed to a suspension of LDH (Zn_2Al or Mg_2Al) or intercalated into the LDH structure. The aim was to explore if any of the LDH forms can be identified as efficient nanoreactor(s) and promote the formation of the Z-Cin. Techniques such as powder X-ray diffractometry (PXRD), Fourier-transformed infrared (FTIR), ultraviolet–visible (UV–Vis) and solid-state ^{13}C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C CP MAS NMR) spectroscopies were used to comprehensively characterise the materials and to follow *in situ* the isomerisation reaction.

2. Experimental

E-Cinnamic acid (E-Cin), $Zn(NO_3)_2 \times 6H_2O$, $Al(NO_3)_3 \times 9H_2O$, $Mg(NO_3)_2 \times 6H_2O$, methanol, ethanol and NaOH were purchased from Sigma Aldrich and used as received. Z-cinnamic acid (Z-Cin) was prepared in our laboratory starting from the E isomer through the sequence of (2R,3S)-dibromo-3-phenylpropanoic acid–3-phenylpropionic acid–Z-cinnamic acid. The last step was a Z-selective partial hydrogenation over Lindlar's palladium catalyst. Details are to be found in Ref. [39].

2.1. Preparation of cinnamate-intercalated Zn_2Al LDH and Mg_2Al LDH

E-Cin-intercalated Zn_2Al LDH (Zn_2Al -E-Cin LDH) and Mg_2Al LDH (Mg_2Al -E-Cin LDH) were prepared by the co-precipitation method using (deionised) water-ethanol (1:1) solvent mixture. A mixture

containing 0.30 M M(II)-nitrate and 0.15 M Al(III)-nitrate (M(II)/Al(III) molar ratio = 2.0) in 25 cm³ solvent mixture was added simultaneously with an appropriate amount of sodium hydroxide solution (0.3 M) to maintain the pH constant (pH = 8.0 for $ZnAl$ LDH and pH = 10.5 for $MgAl$ LDH). 0.065 mol of E-cinnamic acid (0.065 mol) (E-Cin/Al(III) molar ratio = 17.33) was initially placed into the reactor. After addition, the suspension was stirred overnight at room temperature under N₂ atmosphere. The obtained slurry was filtered, washed with deionised water and ethanol several times, and dried at 60 °C overnight. Z-Cin-intercalated substances (M(II)₂Al-Z-Cin LDH) were synthesized in the same way.

2.2. Interlayer photoinduced isomerisation of E-Cin

The reaction was attempted by irradiating the samples with a mercury or monochromatic UV lamps, working at 365 nm and 254 nm, respectively, at 298 K.

Photoreactions were performed on (i) 0.4 g E-Cin-intercalated LDH solid samples, (ii) a slurry (0.4 g of the composite was suspended in 250 cm³ of methanol) and (iii) a solution of pure E-Cin (0.1 g dissolved in 250 cm³ methanol), admixed with 0.4 g of pristine $MgAl$ LDH or $ZnAl$ LDH.

After conducting the reactions for a given time duration (from 1 to 24 h), the solid components were filtered, washed with methanol several times and dried at room temperature in desiccator filled with P₂O₅.

2.3. Instrumental methods of sample characterisation and detecting E-Z isomerisation

The X-ray diffractograms (XRD) of the solid samples were recorded on a Rigaku Miniflex II (Japan) X-ray diffractometer using CuK α radiation ($k = 1.5418$ Å), with 40 kV accelerating voltage at 30 mA.

The FT infrared spectra were registered in diffuse reflection mode (DRS) on a BIO-RAD Digilab Division FTS-65A/896 FT-IR spectrophotometer with 4 cm^{−1} resolution. The 1850–600 cm^{−1} wavenumber range was investigated.

The isomerisation reaction was followed in the liquid as well as the solid phase by UV–Vis spectroscopy using a Shimadzu UV-1650 spectrophotometer equipped with diffusion reflectance accessory.

Solid-state NMR spectra were collected on a Bruker 17.6 T superconducting magnet operating at ^{13}C Larmor frequencies of 188.6 MHz. The experiments were performed at a spinning frequency of 12 kHz with a Bruker double-resonance 4 mm probe head. Cross-polarization (CP) contact times were set to 0.25 ms to favour short C–H distances, with 1024 scans for signal accumulation.

3. Results and discussion

3.1. Synthesis of cinnamate-intercalated $ZnAl$ LDH or $MgAl$ LDH

The XRD patterns of M(II)₂Al(OH)₆NO₃·nH₂O pristine LDH and their E-Cin- and Z-Cin-intercalated derivatives with M(II) = Mg (A) and Zn (B) are given in Fig. 1. They orderly displayed the (00l) diffraction line series characteristic of layered structure beside the typical (012) and (110) reflections that account for the structure of the layer. They are all consistent with a rhombohedral unit cell, analogous to that of nitrate-containing hydrotalcite (JCPDS #89–5434). Unit cell parameters and basal spacings are reported in Table S1.

As expected, the intercalation of the E-cinnamate led to an increase of the interlayer distance for the cinnamate-containing derivatives with a similar d_{inter} of 17.7 Å for both Mg_2Al -E-Cin and

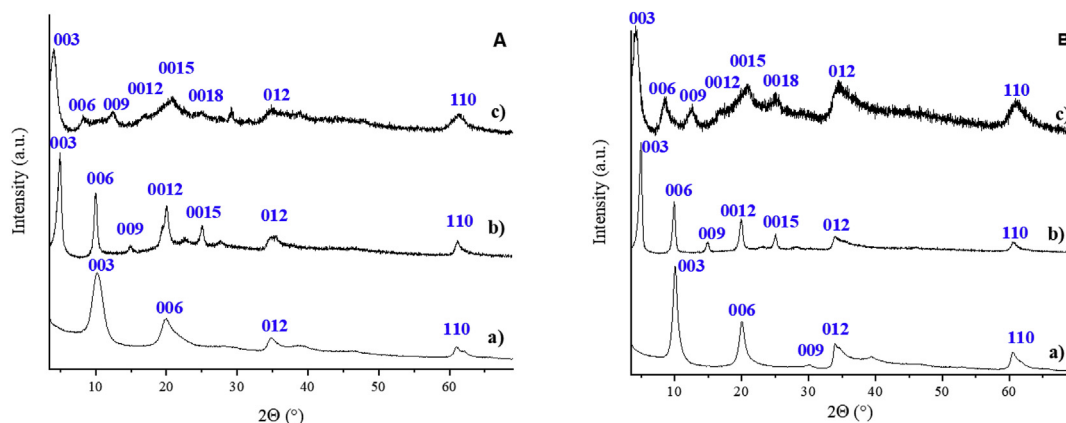


Fig. 1. X-ray diffractograms of the a) $M(II)_2Al-NO_3$ LDH, b) $M(II)_2Al-E-Cin$ LDH, c) $M(II)_2Al-Z-Cin$ LDH for A: $M(II) = Mg$ and B: $M(II) = Zn$.

$Zn_2Al-E-Cin$, in good agreement with the literature [40,41]. Performing the intercalation with the home-made Z-Cin resulted in materials with larger basal spacings of 21.8 Å and 20.8 Å for the $Mg_2Al-Z-Cin$ LDH and the $Zn_2Al-Z-Cin$ LDH, respectively. Since the dimensions of the Z-Cin ion are $4.98 \text{ Å} \times 2.26 \text{ Å} \times 7.71 \text{ Å}$ by PM3 semiempirical calculations (Fig. S1) and the layer thickness for both LDHs is 4.8 Å, a bilayer arrangement of Z-Cin among the layers seems quite feasible. Similar conclusion can be drawn for E-Cin intercalated in both LDH, with a lower expansion of the interlayer distance due to the structural difference between the two isomers (Fig. S1). It is to be noted that the Z-Cin intercalated LDH structures are novel, since the Z isomer is not accessible easily. To the best of our knowledge, Z isomer has not been intercalated into LDH of any kind as yet.

The FT-IR spectra of Mg_2Al-E , Z-Cin LDH samples and that of the pristine Mg_2Al-NO_3 LDH are displayed in Fig. 2. Based on the assignments reported by Kalinowska et al. for cinnamate alkali salts [42] all vibration bands were clearly identified (Table S2). The usual characteristic bands of LDH structures ($\delta-OH$ vibration at 1643 cm^{-1} or $Al-O-Al$ skeletal stretching vibrations at 704 cm^{-1} [43]) were present. Free and intercalated E- and Z-cinnamate ions

displayed a series of vibration bands characteristic of the different groups, i.e. the aryl group with $\beta(CH)_{ar}$ and $\nu(CH)_{ar}$ vibrations often combined with other bands, the alkene or cinnamic group with typical $\beta(CH)_{cin}$ at 1244 cm^{-1} and the carboxylate function with the characteristic $\nu_{as}(COO^-)$ at $1550 \pm 12 \text{ cm}^{-1}$ and $\nu_s(COO^-)$ occurring at 1413 cm^{-1} and 1394 cm^{-1} for E-Cin and $Mg_2Al-E-Cin$, respectively, and 1357 cm^{-1} and 1363 cm^{-1} for Z-Cin and $Mg_2Al-Z-Cin$, respectively. Note that the differences between asymmetric and symmetric carboxylate vibrations $\Delta(\nu_{as}(COO^-) - \nu_s(COO^-))$ (Table S1, last column) for the free and intercalated cinnamate isomers are noticeably different being $133/143 \text{ cm}^{-1}$ and $205/187 \text{ cm}^{-1}$ for the E and Z isomers, respectively, due to the different structures of the isomers and thus different interactions with the LDH hydroxylated layers. Therefore, these specific data can be used as probe values for the stereoisomers. These values are characteristic of a symmetric interaction between two adjacent OH layers and the carboxylate groups. The IR spectra of Zn-LDH and its intercalated derivatives displayed very similar vibrations (Fig. S2) due to analogous structures.

^{13}C CP MAS solid-state NMR spectroscopy is an efficient tool to learn about the structure of the cinnamate salts in the solid state and those intercalated in the LDHs.

The experimental ^{13}C CP-MAS NMR spectra of sodium salts and LDH-intercalated E,Z-cinnamate are displayed in Fig. 3 with spectral deconvolutions. NMR results confirmed the presence of E-Cin and Z-Cin isomers embedded in both Zn_2Al and Mg_2Al LDH structures as already shown by XRD and FTIR characterizations. Moreover, NMR analysis allowed a clear differentiation of E and Z isomers, particularly in the $130\text{--}150 \text{ ppm}$ chemical shift range, the ^{13}C spectra being better resolved for the E isomer in this region. Attempts to resolve the spectra were performed using Lorentzian deconvolutions. Chemical shifts of the different carbon atoms are given in Table 1 and structurally assigned according to Januar et al. [44] and Hanai et al. [45]. From Table 1, main differences between chemical shifts of intercalated and free E- and Z-cinnamates appeared for the carbon atoms of the aromatic cycle. Intercalation of cinnamate anions in the LDH galleries probably forced the reorientation of the aryl groups in order to minimize the repulsion energies and optimise the cinnamate packing. This is enhanced particularly for the Z-Cin isomer; when intercalated in LDH, a new peak appeared at 104.1 ppm . One must also notice that the Zn_2Al-E , Z-Cin samples displayed much broader NMR bands than Mg_2Al-E , Z-Cin.

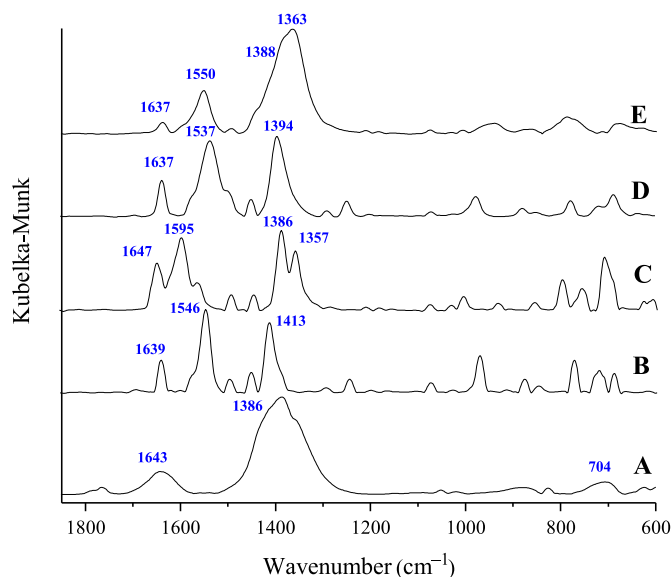


Fig. 2. IR spectra of the A: pristine Mg_2Al-NO_3 LDH, B: sodium E-Cin, C: sodium Z-Cin, D: $Mg_2Al-E-Cin$ LDH, E: $Mg_2Al-Z-Cin$ LDH.

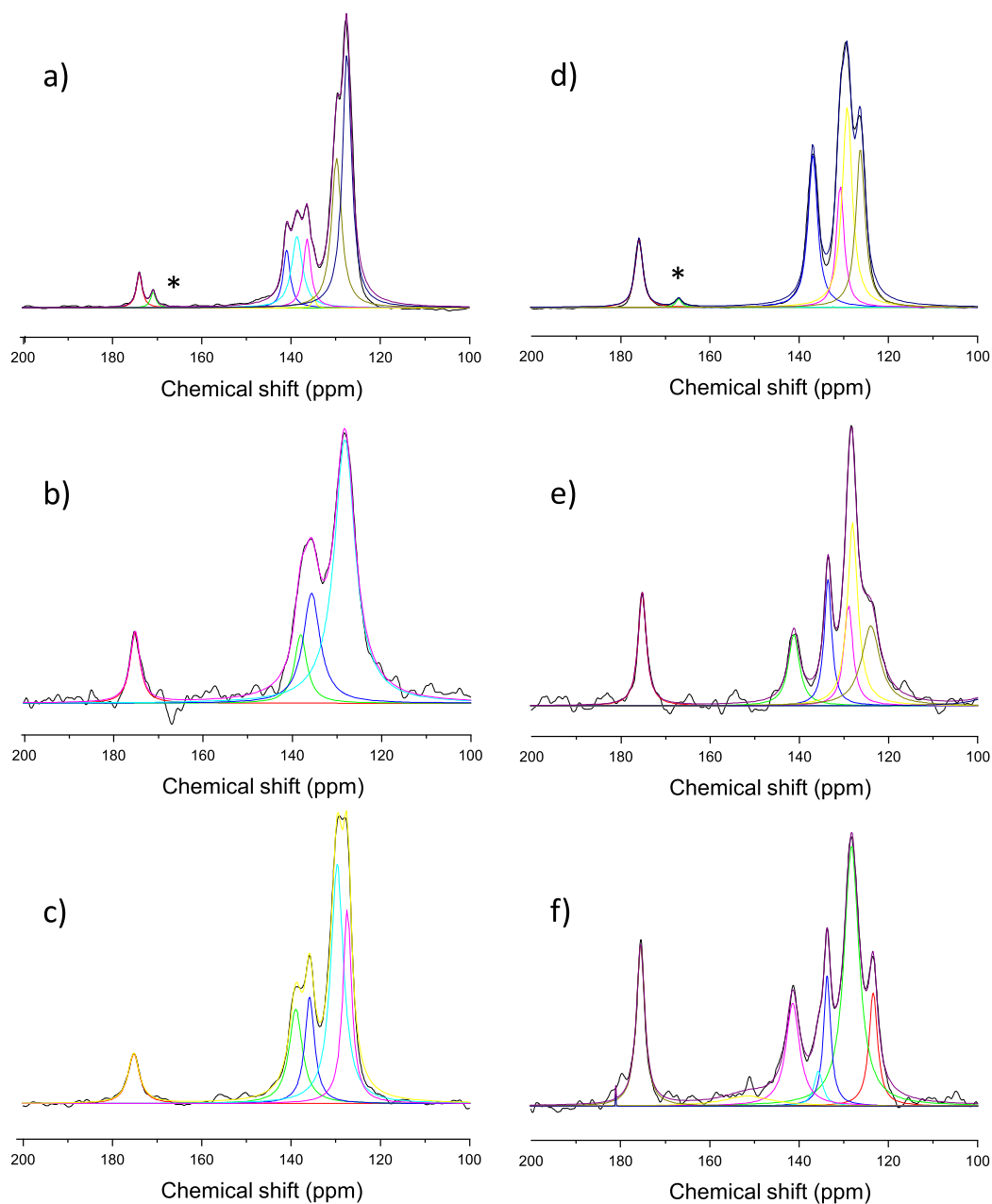


Fig. 3. Experimental and deconvoluted ^{13}C SS-CP MAS NMR spectra of a) E-Cin, b) $\text{Zn}_2\text{Al-E-Cin}$, c) $\text{Mg}_2\text{Al-E-Cin}$, d) Z-Cin, e) $\text{Zn}_2\text{Al-Z-Cin}$, f) $\text{Mg}_2\text{Al-Z-Cin}$. (*) traces of cinnamic acid.

Table 1

^{13}C δ chemical shift extracted from Lorentzian deconvolution of NMR spectra for sodium salts and intercalated E or Z-cinnamate.

C atom	Na-E-Cin	$\text{Zn}_2\text{Al-E-Cin}$	$\text{Mg}_2\text{Al-E-Cin}$	Na-Z-Cin	$\text{Zn}_2\text{Al-Z-Cin}$	$\text{Mg}_2\text{Al-Z-Cin}$
1	174.0	175.2	175.2	175.9	175.2	175.5
2	127.3	—	127.4	126.3	124.0	123.4
3	140.9	—	—	—	141.2	141.4
1'	138.6	138.1	139.0	136.9	133.6	135.7
2'/6'	134.8	—	—	129.2	129.0	128.2
3'/5'	129.7	128.2	129.7	130.7	128.0	128.2
4'	136.3	135.7	135.9	132.3	130.4	133.7

3.2. Photoinduced interlayer isomerisation of E-Cin

To detect and possibly to follow the E–Z isomerisation reaction, there are four markers in our hands: (i) changes in the basal spacing

detected by XRD, (ii) the distances between the asymmetric and symmetric infrared vibrations of the carboxylate ions, (iii) the positions of the UV absorbance maxima and (iv) the MAS ^{13}C NMR spectra are different for the two isomers.

Irradiation was first performed directly on E-Cin intercalated in Mg_2Al and Zn_2Al LDH in the solid state in order to evaluate the ability of the LDH interlayer confined spaces to absorb light and favour an *in situ* reactivity toward isomerisation. No structural change was by powder XRD nor using FT-IR for the intercalated ZnAl LDH sample. XRD patterns for the irradiated solid samples were identical to those of the precursors (Fig. 4Ac and S3Ac). Although the $\nu(\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-))$ infrared probe remained unchanged for both the free and the intercalated cinnamate (Figs. 4B and S3B), the FT-IR spectrum of the intercalated MgAl LDH sample irradiated in the solid state (Fig. 4Bc) indicates that isomerisation proceeded to some extent (see, the similar profiles for the set of bands in the $1450\text{--}1300\text{ cm}^{-1}$ range for spectra c and d; in spectrum d a band at 1363 cm^{-1} is the sure sign of the appearance of the Z isomer in the irradiated slurry). Combining the results of these two measurement types, it is safe to state that no double bond isomerisation took place in the solid state for the intercalated ZnAl LDH sample; however, it proceeded in the intercalated MgAl LDH sample.

The photoreaction was attempted on cinnamate-intercalated samples suspended in methanol and characterization measurements were performed on solid samples extracted from the slurry. As far as the host structure is concerned, no change could be detected in the basal spacing by PXRD, and the powder patterns remained very similar before and after irradiation (compare patterns a) and d) in Fig. 4 and Fig. S3), which is not in favour of a structural modification of the intercalated species. However, in the FTIR spectrum recorded after irradiating the E-Cin-intercalated samples in the slurry, the difference $\Delta(\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-))$ became 160 cm^{-1} (Table S1, last column), which is a strong indication that E–Z isomerisation did proceed in the slurry of both composites.

This indication is further strengthened by the results of UV–Vis measurements of the supernatants. As a reference, UV–Visible spectra of E-Cin and Z-Cin sodium salts in water are used (Fig. 1 in Ref. [36]). The UV–Vis spectra of the supernatants of the mixtures of E-cinnamate and Mg_2Al LDH or Zn_2Al LDH confirmed that they only contained one isomer even after lengthy irradiation of the mixtures indicated by the absorption maximum at 269 nm , typical of the E-Cin ion. There was no observable band at 258 nm , which would reveal the presence of the Z isomer (Figs. S4 and S5). However, the characteristic absorption maximum gradually shifted towards lower wavelength on increasing the irradiation time of the slurries containing the intercalated substances (Fig. S6). As is seen in Fig. 5 (and Fig. S6 for Zn_2Al), the 2 h irradiation treatment was

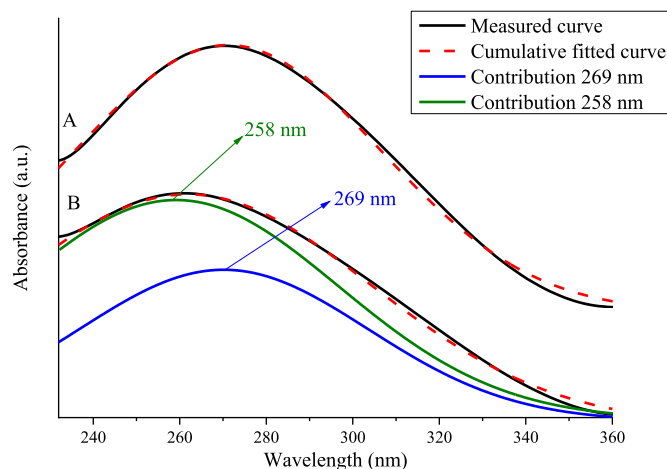


Fig. 5. The deconvoluted UV–Vis absorbance spectra of the supernatant of the Mg_2Al -E-Cin LDH slurry, A: before the irradiation (there is one component only), B: after irradiation for 2 h (could be decomposed to two components).

sufficient to achieve appreciable extent of isomerisation indicated by the intense band at 258 nm . The above-described results mean that the observed isomerisation in the slurry of the hybrid Mg_2Al -E-Cin LDH was not due to Cin adsorbed on the outer surface of the LDH, but it took place in the interlayer region.

^{13}C CP MAS solid-state NMR can also be used as local probe for detecting and, at least semi-quantitatively, following the E–Z isomerisation reaction. ^{13}C CP MAS solid-state NMR measurements clearly attested the E–Z isomerisation did partially occur in the slurry (Fig. 6), since after the irradiation, the peaks characteristic of Z-Cin appeared for the irradiated sample at 128.1 , 133.5 and 140.0 ppm .

Although the partial photoinduced isomerisation of $\text{M}^{\text{II}}_2\text{Al}$ -E-Cin into $\text{M}^{\text{II}}_2\text{Al}$ -Z-Cin was accompanied by basal spacing expansions; however, they did not reach the basal spacings of the Z-Cin intercalated materials. We suggest that in the slurry, the interlayer water content is gradually replaced by methanol, *i.e.* the interlayer environment is changing. Because of this and the partial and gradual formation of the intercalated Z isomer in presence of the unreacted intercalated E isomer, a different arrangement was adopted compared to that of the pure $\text{M}^{\text{II}}_2\text{Al}$ -Z-Cin. Similar behaviour toward Cin photoisomerization was observed for both

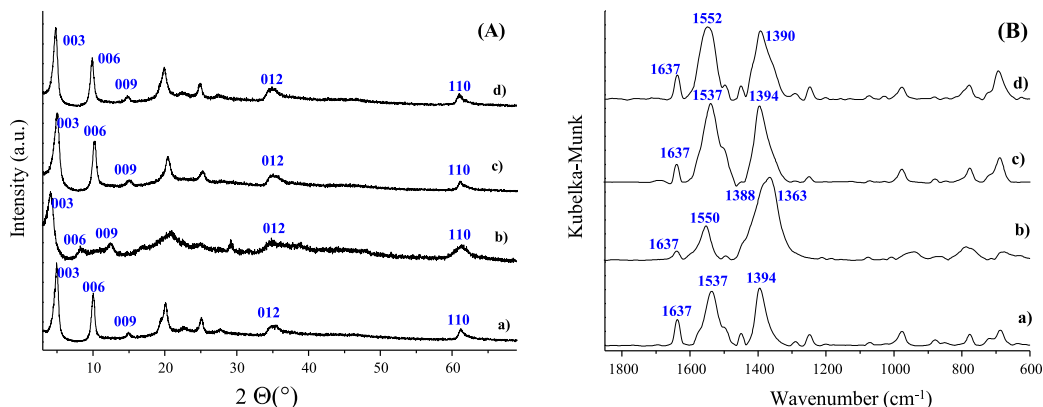


Fig. 4. (A) X-ray diffractograms and (B) FTIR spectra of a) Mg_2Al -E-Cin, b) Mg_2Al -Z-Cin, c) Mg_2Al -E-Cin (solid state) irradiated at 254 nm for 2 h, d) Mg_2Al -E-Cin (slurry – suspended in methanol) irradiated at 254 nm for 2 h.

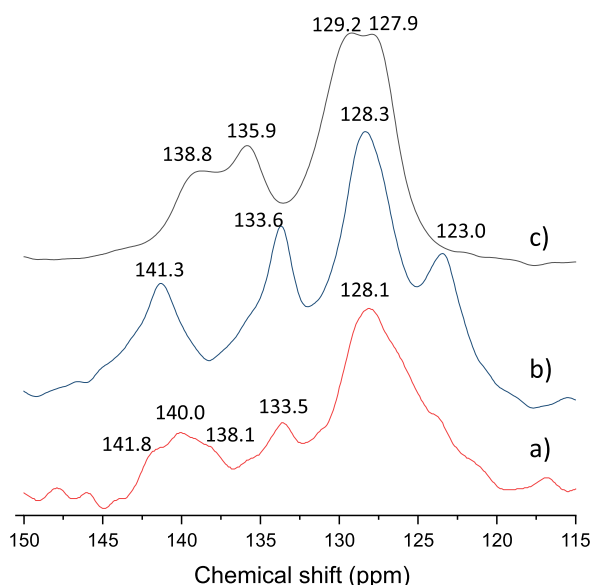


Fig. 6. ^{13}C CP MAS NMR spectra of the a) $\text{Mg}_2\text{Al-E-Cin}$ (in slurry – suspended in methanol) irradiated on 254 nm for 2 h, b) $\text{Mg}_2\text{Al-Z-Cin}$ and c) $\text{Mg}_2\text{Al-E-Cin}$.

LDH hybrid matrices, which seems to indicate that the chemical composition of the LDH layer did not play key role in the photo-induced process.

4. Conclusions

Hybrid Mg_2Al and Zn_2Al intercalated by E and Z cinnamate (Cin) were obtained by direct co-precipitation. Besides the already described LDH samples intercalated by E-Cin, two novel pure Z-Cin-intercalated LDH derivatives were prepared, and structurally characterized by a range of techniques by various spectroscopic methods and powder X-ray diffractometry. Two distinct interlayer distances were obtained in this work by modifying the nature of the Cin isomer (E or Z) involved in the process. LDH intercalated by Z-Cin led to a larger interlamellar distance compared to intercalated E-Cin in good agreement with a bilayer arrangement of the organic anions in between the Mg_2Al or Zn_2Al layers. The characterization of the hybrid phases by FTIR, UV–Vis and solid-state NMR spectroscopies allowed to highlight the main differences between the two intercalated isomers, while the nature of the LDH layer did not influence the orientation of the intercalated Cin anions. Starting from LDH intercalated with the E-Cin isomer, partial isomerisation of the organic species by UV light irradiation was evidenced. The reaction took place in the interlayer region, but mainly when a slurry phase was used, in which there was possibility of interlayer solvent exchange in favour of molecular rearrangement.

Credit Author Statement

All authors significantly contributed to the manuscript. Their contributions are as follows. Zita Timár, Tünde Alapi, Krisztián Csankó, Gábor Varga: experimental work (synthesis of the model compounds and the intercalated materials, performing the isomerisation reactions). Zita Timár, Márton Szabados, Gábor Varga, Pál Sipos, Claude Forano, Vanessa Prevot (instrumental characterization, interpreting the diffractograms and spectra). Zita Timár, Gábor Varga: writing the first draft. Claude Forano, Vanessa Prevot: rewriting and complementing the first draft. István Pálkó: conceptualisation, supervising the project, taking part in each step

interpreting and writing, finalising the manuscript, doing the revision

Declaration of competing interest

The authors have no conflicting interests of any kind.

Acknowledgements

This work was supported by the Hungarian Government and the European Union through grant GINOP-2.3.2-15-2016-00013. The financial helps are highly appreciated. One of us, G. Varga thanks for the postdoctoral fellowship under the grant PD 128189.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2020.128561>.

References

- [1] K. Renggli, P. Baumann, K. Langowska, O. Onaca, N. Bruns, W. Meier, Selective and responsive nanoreactors, *Adv. Funct. Mater.* 21 (2011) 1241–1259.
- [2] J. Liu, S.Z. Qiao, J.S. Chen, X.W. Lou, X.R. Xing, G.Q. Lu, Yolk/shell nanoparticles: new platforms for nanoreactors, drug delivery and lithium-ion batteries, *Chem. Commun.* 47 (2011) 12578–12591.
- [3] A.N. Khlobystov, Carbon nanotubes: from nano test tube to nano-reactor, *ACS Nano* 5 (2011) 9306–9312.
- [4] T.H. Tran-Thi, R. Dagnelie, S. Crunaire, L. Nicole, Optical chemical sensors based on hybrid organic–inorganic sol–gel nanoreactors, *Chem. Soc. Rev.* 40 (2011) 621–639.
- [5] I. Pálkó, Z. Kónya, Kukovecz Á, I. Kiricsi, Zeolites, in: R. Vajtai (Ed.), *Springer Handbook of Nanomaterials*, Springer-Verlag, Berlin, Heidelberg, 2013, pp. 819–857. Ch. 22.
- [6] L. Song, W. Shi, C. Lu, Confinement effect in layered double hydroxide nano-reactor: improved optical sensing selectivity, *Anal. Chem.* 88 (2016) 8188–8193.
- [7] M.Q. Zhao, Q. Zhang, J.Q. Huang, F. Wei, Hierarchical nanocomposites derived from nanocarbons and layered double hydroxides – properties, synthesis, and applications, *Adv. Funct. Mater.* 22 (2012) 675–694.
- [8] M. Wei, Z.Y. Shi, D.G. Evans, X. Duan, Study on the intercalation and interlayer oxidation transformation of L-cysteine in a confined region of layered double hydroxides, *J. Mater. Chem.* 16 (2006) 2102–2109.
- [9] W.Y. Shi, M. Wei, D.G. Evans, X. Duan, Tunable photoluminescence properties of fluorescein in a layered double hydroxide matrix and its application in sensors, *J. Mater. Chem.* 20 (2010) 3901–3909.
- [10] Y.B. Song, S.J. Zhu, S.Y. Xiang, X.H. Zhao, J.H. Zhang, H. Zhang, Y. Fu, B. Yang, Tunable photoluminescence properties of fluorescein in a layered double hydroxide matrix and its application in sensors, *Nanoscale* 6 (2014) 4676–4682.
- [11] J. Sun, H. Liu, X. Chen, D.G. Evans, W. Yang, X. Duan, Synthesis of graphene nanosheets with good control over the number of layers within the two-dimensional galleries of layered double hydroxides, *Chem. Commun.* 48 (2012) 8126–8128.
- [12] A.L. García-Ponce, V. Prévot, B. Casal, E. Ruiz-Hitzky, Intracrystalline reactivity of layered double hydroxides: carboxylate alkylations in dry media, *New J. Chem.* 24 (2000) 119–121.
- [13] V. Prévot, B. Casal, E. Ruiz-Hitzky, Intracrystalline alkylation of benzoate ions into layered double hydroxides, *J. Mater. Chem.* 11 (2001) 554–560.
- [14] D.F. Srankó, S. Canton, A. Enghdahl, Sz. Muráth, Á. Kukovecz, Z. Kónya, M. Sipiczki, P. Sipos, I. Pálkó, Radiation induced topotactic [2+2] dimerisation of acrylate derivatives among the layers of a CaFe layered double hydroxide followed by IR spectroscopy, *J. Mol. Struct.* 1044 (2013) 279–285.
- [15] M. Wei, J. Guo, Z. Shi, Q. Yuan, M. Pu, G. Rao, X. Duan, Preparation and characterization of L-cysteine and L-cysteine intercalated layered double hydroxides, *J. Mater. Sci.* 42 (2007) 2684–2689.
- [16] M. Wei, X. Tian, J. He, M. Pu, G. Rao, H. Yang, L. Yang, T. Liu, E.G. Evans, X. Duan, Study of the in situ postintercalative polymerization of metanilic anions intercalated in NiAl-layered double hydroxides under a nitrogen atmosphere, *Eur. J. Inorg. Chem.* (2006) 3442–3450.
- [17] F. Leroux, C. Taviot-Gueho, Fine tuning between organic and inorganic host structure: new trends in layered double hydroxide hybrid assemblies, *J. Mater. Chem.* 15 (2005) 3628–3642.
- [18] G. Hincapié, D. López, A. Moreno, Infrared analysis of methanol adsorption on mixed oxides derived from Mg/Al hydrotalcite catalysts for transesterification reactions, *Catal. Today* 302 (2018) 277–285.
- [19] C. Yu, J. He, Synergic catalytic effects in confined spaces, *Chem. Commun.* 48 (2012) 4933–4940.

- [20] D. Dutta, A.K. Tummanapelli, Spectroscopic and computational investigations on the origin of charge transfer between included neutral guest molecules and a functionalized anionic layered host, *Phys. Chem. Chem. Phys.* 18 (2016) 22379–22389.
- [21] H.C. Greenwell, P.V. Coveney, Layered double hydroxide minerals as possible prebiotic information storage and transfer compounds Orig. Life Evol. Biosph. 36 (2006) 13–37.
- [22] V. Erastova, M.T. Degiacomi, D.G. Fraser, H.C. Greenwell, Mineral surface chemistry control for origin of prebiotic peptides, *Nat. Commun.* 8 (2017) 1–9, 2033.
- [23] P.V. Coveney, J.B. Swadling, J.A.D. Wattis, H.C. Greenwell, Theory, modelling and simulation in origins of life studies, *Chem. Soc. Rev.* 41 (2012) 5430–5446.
- [24] C. Taviot-Guého, C. Forano, C. Mousty, V. Prevot, G. Renaudin, F. Leroux, Tailoring materials properties of hybrid LDH for the development of innovative applications, *Adv. Funct. Mater.* 28 (2018) 1–33, 1703868.
- [25] M. Wei, X. Zhang, D.G. Evans, X. Duan, X. Li, H. Chen, Rh-TPPTS intercalated layered double hydroxides as hydroformylation catalyst, *AIChE J.* 53 (2007) 2916–2924.
- [26] S. Nakagaki, K.A.D.F. Castro, G.M.U. Halma, V. Prevot, C. Forano, F. Wypych, Anionic iron(III) porphyrin immobilized on/into exfoliated macroporous layered double hydroxides as catalyst for oxidation reactions, *J. Braz. Chem. Soc.* 25 (2014) 2329–2338.
- [27] G. Varga, V. Kozma, V.J. Kolcsár, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálkó, Gy Szöllősi, β -Isocupreidine-CaAl-layered double hydroxide composites – heterogenized catalysts for asymmetric Michael addition, *Mol. Catal.* 482 (2020) 1–7, 110675.
- [28] S.J. Meek, R.V. O'Brien, J. Llaveria, R.R. Schrock, A.H. Hoveyda, Catalytic Z-selective olefin cross-metathesis for natural product synthesis, *Nature* 471 (2011) 461–466.
- [29] H. Li, H. Chen, Y. Zhou, J. Huang, J. Yi, H. Zhao, W. Wang, L. Jing, Selective synthesis of Z-cinnamyl ethers and cinnamyl alcohols via visible light promoted photocatalytic E to Z isomerization, *Chem. – An Asian J.* 15 (2020) 555–559.
- [30] H. Tagaya, T. Kuwahara, S. Sato, J. Kadokawa, M. Karasu, K. Chiba, Photoisomerization of indolinespirobenzopyran in layered double hydroxides, *J. Mater. Chem.* 3 (1993) 317–318.
- [31] H. Tagaya, S. Sato, T. Kuwahara, J. Kadokawa, K. Masa, K. Chiba, Photoisomerization of indolinespirobenzopyran in anionic clay matrixes of layered double hydroxides, *J. Mater. Chem.* 4 (1994) 1907–1912.
- [32] J. Valim, B.M. Kariuki, J. King, W. Jones, Photoactivity of cinnamate-intercalates of layered double hydroxides, *Mol. Cryst. Liq. Cryst. Sci. Tech. A* 211 (1992) 271–281.
- [33] G. Abellan, E. Coronado, C. Marti-Gastaldo, A. Ribera, J.L. Jorda, H. Garcia, Photo-switching in a hybrid material made of magnetic layered double hydroxides intercalated with azobenzene molecules, *Adv. Mater.* 26 (2014) 4156–4162.
- [34] J. Han, D. Yan, W. Shi, J. Ma, H. Yan, M. Wei, D.G. Evans, X. Duan, Layer-by-layer ultrathin films of azobenzene-containing polymer/layered double hydroxides with reversible photoresponsive behavior, *J. Phys. Chem. B* 114 (2010) 5678–5685.
- [35] M. D'Auria, G. Piancatelli, A. Vantaggi, Photochemical dimerization of methyl 2-furyl- and 2-thienylacrylate and related compounds in solution, *J. Chem. Soc. Perkin 1* (1990) 2999–3002.
- [36] J. Li, M. Zhao, H. Zhou, H. Gao, L. Zheng, Photo-induced transformation of wormlike micelles to spherical micelles in aqueous solution, *Soft Matter* 8 (2012) 7858–7864.
- [37] M.L. Salum, P.A. Mañez, F.J. Luque, R. Erra-Balsells, Combined experimental and computational investigation of the absorption spectra of E- and Z-cinnamic acids in solution: the peculiarity of Z-cinnamics, *J. Photochem. Photobiol., B* 148 (2015) 128–135.
- [38] Y. Li, L. Tang, X. Ma, X. Wang, W. Zhou, D. Bai, Synthesis and characterization of Zn-Ti layered double hydroxide intercalated with cinnamic acid for cosmetic application, *J. Phys. Chem. Solid.* 107 (2017) 62–67.
- [39] K. Csankó, PhD Dissertation University of Szeged, Ch. 4.5 General Methods for the Stereoselective Synthesis of Z-Cinnamic Acids, 2015, pp. 36–38 (downloadable from, http://doktori.bibl.u-szeged.hu/2538/1/Csanko_Krisztian_PhD_Dissertation.pdf).
- [40] Y. Kameshima, A. Nakada, T. Isobe, A. Nakajima, K. Okada, The effect of UV radiation on cinnamate/layered double hydroxide (LDH) composites, *J. Ceram. Soc. Jpn.* 121 (2013) 303–307.
- [41] W. Sun, Q. He, L. Lu, H. Liu, Synthesis and properties of layered double hydroxides intercalated with cinnamic acid series organic UV ray absorbents, *Mater. Chem. Phys.* 107 (2008) 261–265.
- [42] M. Kalinowska, R. Świsłocka, W. Lewandowski, The spectroscopic (FT-IR, FT-Raman and ^1H , ^{13}C NMR) and theoretical studies of cinnamic acid and alkali metal cinnamates, *J. Mol. Struct.* 834 (2007) 572–580.
- [43] V. Rives, S. Kannan, Layered double hydroxides with the hydrotalcite-type structure containing Cu^{2+} , Ni^{2+} and Al^{3+} , *J. Mater. Chem.* 10 (2000) 489–495.
- [44] S.E. Januar, P. Sugita, B. Arifin, Identification of trans-cinnamic acid in *Sinjo Nakal* (*Duranta repens*) fruits' methanol extract, *Int. Res. J. Pure Appl. Chem.* 8 (2015) 73–80.
- [45] K. Hanai, A. Kuwae, T. Takai, H. Senda, K.-K. Kunimoto, A comparative vibrational and NMR study of cis-cinnamic acid polymorphs and trans-cinnamic acid, *Spectrochim. Acta, A* 57 (2001) 513–519.