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Structural insight of photoinduced *E*→*Z* isomerisation of cinnamate embedded in ZnAl- and MgAl layered double hydroxides

Zita Timára[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 Pálinkó[a,b*]

[a] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720, Hungary*
[b] *Materials and Solution Structure Research Group, 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*

ABSTRACT

Hybrid E-cinnamate- and Z-cinnamate-intercalated layered double hydroxides (Mg_2Al- E- or Z-Cin LDH and Zn_2Al- 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 ^{13}C 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.

Keywords: Layered Double Hydroxides; Cinnamate; *E–Z* isomerisation, photoinduced reaction, nanoreactors.

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 [1e5]. An additional advantage if structural modifications are possible, is to tailor the nanoreactor properties to needs [1-10]. Layered double hydroxides (LDH) ($[M^{II}_{1-x}M^{III}_x(OH)_2^{q+}][X^{q-}_{x/q}.nH2O]$), which are well-known lamellar inorganic materials with positively charged layers ($[MII1-xMIIIx(OH)_2^{q+}]$) and negatively charged interlayer gallery ($[X^{q-}_{x/q}.nH_2O]$) and expanding structure under intercalation, meet the above requirements. Therefore, they have good potential of acting as nanoreactors, especially when their action partner(s) is/are intercalated into the interlayer domain[8,11e17]. Indeed, the high density of hydrophilic OH groups (~12OH/nm2) covering the

* To whom correspondence should be addressed.
E-mail: palinko@chem.u-szeged.hu (I. Pálinkó)

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 (Chloranyl) [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 [21e23]. 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 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. Photoisomerisation of indoline spirobenzopyran 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 (dbs¼1.98 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 the220e400 nm wavelength range. Topotactic [2+2] cyclo-dimerization was achieved solely. To promote the cycle-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 photo induced E-Z isomerisation to occur in the presence of Zn_2Al or Mg_2Al LDHs were investigated. To high-light 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) andsolid-state13C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (13C 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), $Zn(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, $Mg(NO_3)_2.\ 6H_2O$, 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 acide3-phenylpropiolic acide 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 cm^3 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 over-night at room temperature under N_2 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 and254 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 sus-pended in 250 cm3of methanol) and (iii) a solution of pure E-Cin(0.1 g dissolved in 250 cm3methanol), admixed with 0.4 g of pristine MgAl LDH or ZnAl LDH. After conducting the reactions for a given time duration (from 1to 24 h), the solid components were filtered, washed with methanol several times and dried at room temperature in desiccator filled with P_2O_5.

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 CuKα radiation (k¼1.5418 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-1650spectrophotometer equipped with diffusion reflectance accessory. Solid-state NMR spectra were collected on a Bruker 17.6 T superconducting magnet operating at13C 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 CeH 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 $M(II)_2Al(OH)_6NO_3.nH_2O$ pristine LDH andt heir 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 thetypical (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#89e5434). 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 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 theMg2Al-Z-Cin LDH and the Zn_2Al-Z-Cin LDH, respectively. Since the dimensions of the Z-Cin ion are 4.98 Åx2.26 Åx7.71 Å by PM3 semi empirical 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 interlaye rdistance 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_2AleNO_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 (d-OH vibration at1643 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 β(CH)ar and ν(CH)ar vibrations often combined with other bands, the alkene or cinnamic group with typical β(CH)cin at 1244 cm^{-1} and the carboxylate function with the characteristic $\nu as(COO^-)$ at 1550±12 cm^{-1} and $\nu s(COO^{-1})$ 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 of asymmetric and symmetric carboxylate vibrations $\Delta(\nu as(COO^-)-\nu s(COO^{-1}))$ (Table S1, last column) for the free and intercalated cinnamate isomers are noticeably different being 133/143 cm^{-1} and 205/187 cm^{-1} for the E and Z

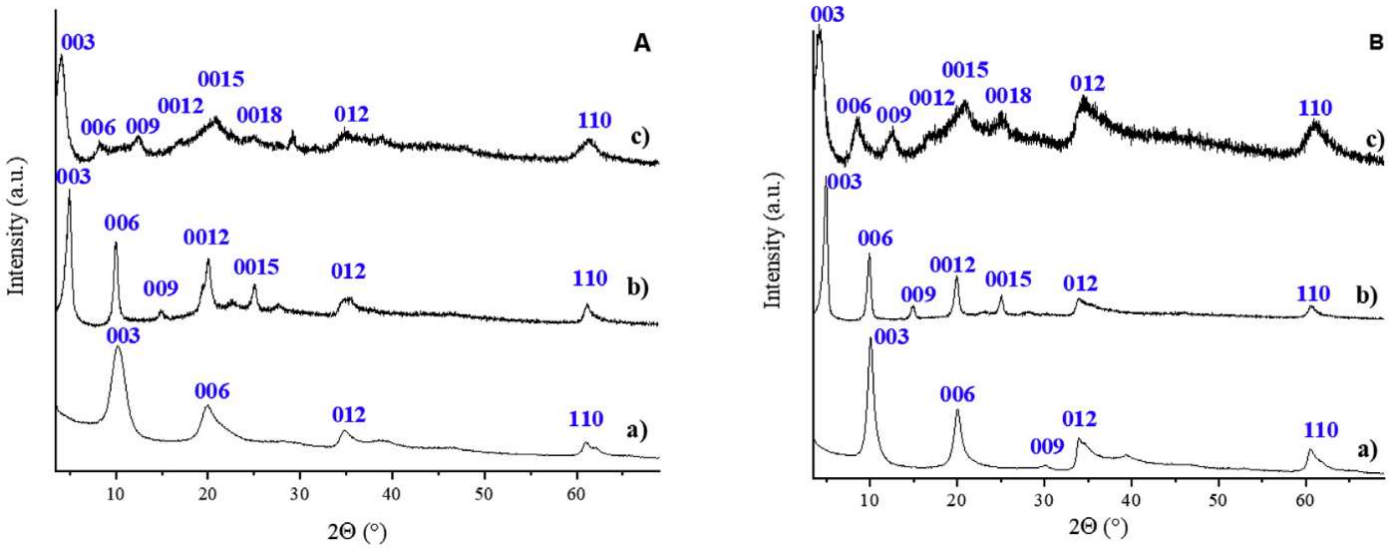

Fig. 1.X-ray diffractograms of the a) $M(II)_2Al$-NO3LDH, b) $M(II)_2Al$-E-Cin LDH, c) $M(II)_2Al$-Z-Cin LDH for A: M(II)=Mg and B: M(II)=Zn.

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.

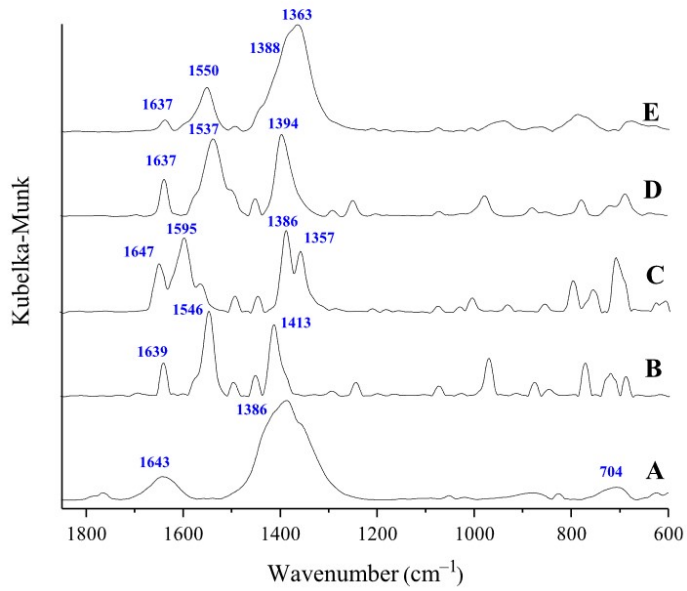

Fig. 2. IR spectra of the A: pristine Mg2AleNO3LDH, B: sodium E-Cin, C: sodium Z-Cin,D: Mg2Al-E-Cin LDH, E: Mg2Al-Z-Cin LDH.

^{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 130-150 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 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 there orientation 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.

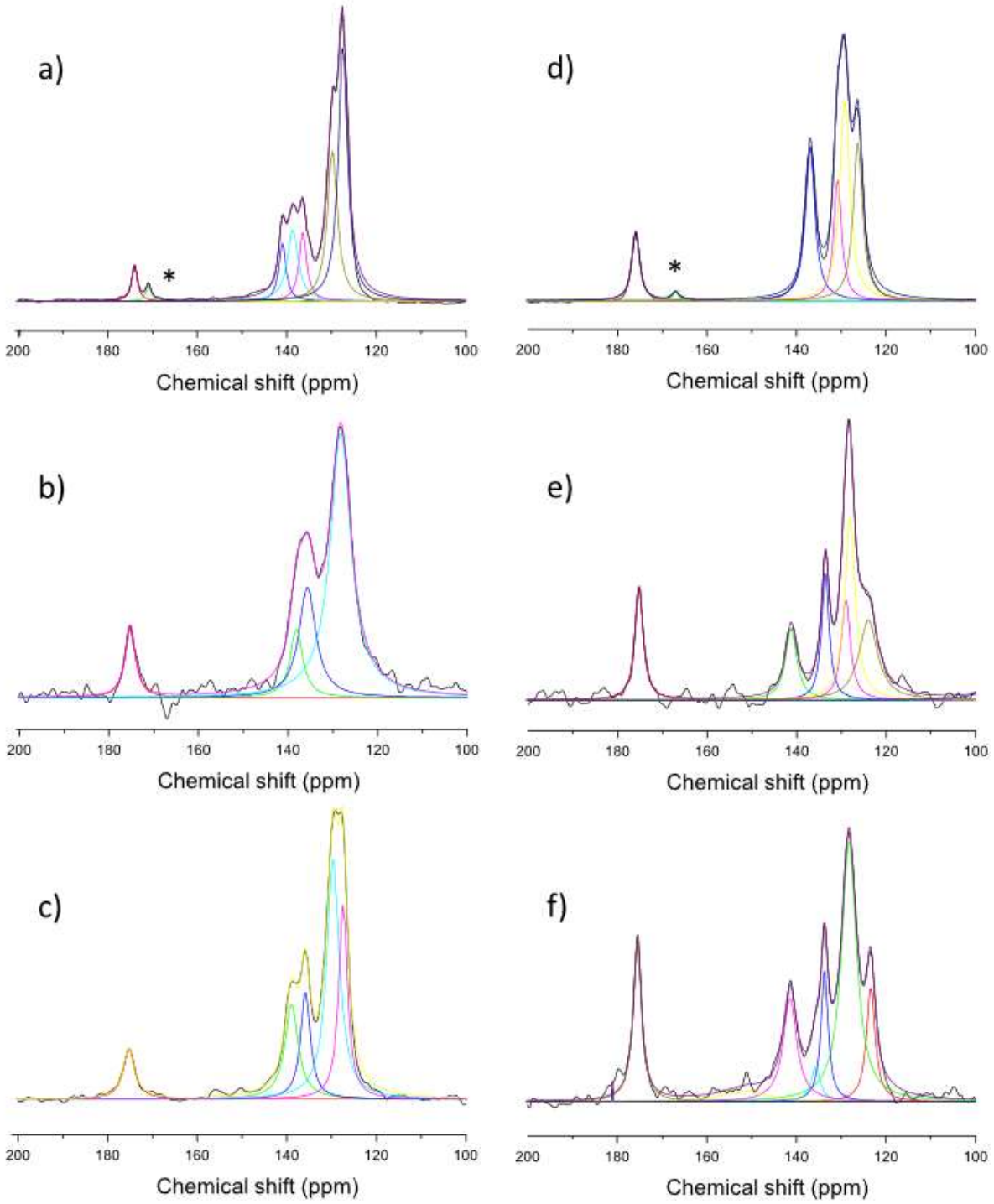

Fig. 3. Experimental and deconvoluted ^{13}C SS-CP MAS NMR spectra of a) E-Cin, b) Zn_2Al-E-Cin, c) Mg_2Al-E-Cin, d) Z-Cin, e) Zn_2Al-Z-Cin, f) Mg_2Al-Z-Cin. (*) traces of cinnamic acid.

3.2. Photoinduced interlayer isomerisation of E-Cin

To detect and possibly to follow the EeZ 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}CP NMR spectra are different for the two isomers. Irradiation was first performed directly on E-Cin intercalated inMg_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

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	Zn_2Al-E-Cin	Mg_2Al-E-Cin	Na-Z-Cin	Zn_2Al-Z-Cin	Mg_2Al-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

identical to those of the precursors (Fig. 4Ac and S3Ac). Although the ν($\nu_{as}(COO^-)$- $\nu_s(COO^{-1})$) 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 1450-1300 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 pat-terns 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 $\Delta(\nu_{as}(COO^-)$-$\nu s(COO^-))$ became 160 cm^{-1} (Table S1, last column), which is a strong indi-cation 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). How-ever, the characteristic absorption maximum gradually shifted to-wards 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 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.

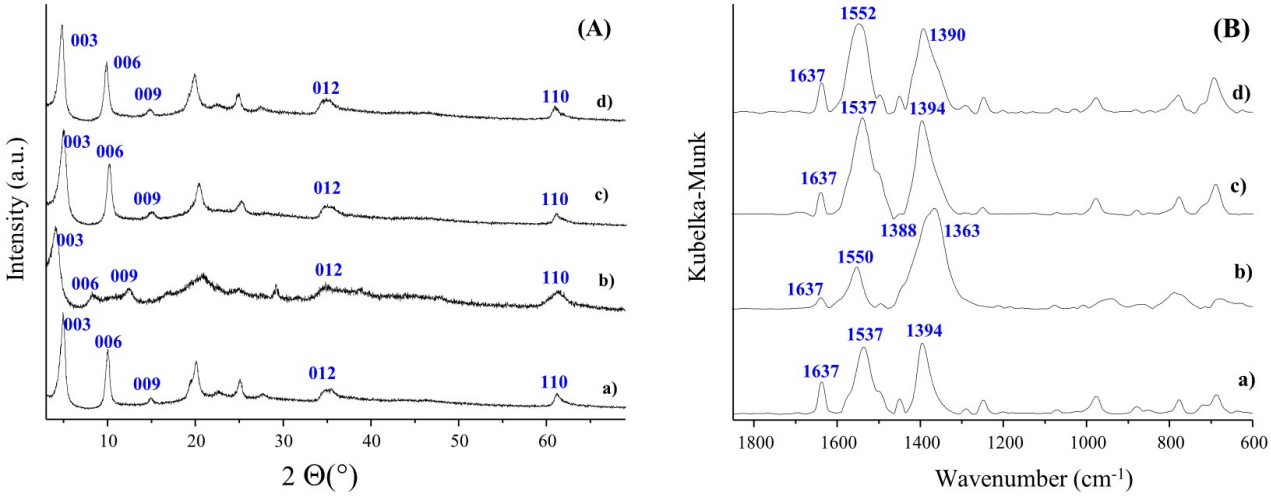

Fig. 4.(A) X-ray diffractograms and (B) FTIR spectra of a) Mg2Al-E-Cin, b) Mg2Al-Z-Cin, c) Mg2Al-E-Cin (solid state) irradiated at 254 nm for 2 h, d) Mg2Al-E-Cin (slurrye suspendedin methanol) irradiated at 254 nm for 2

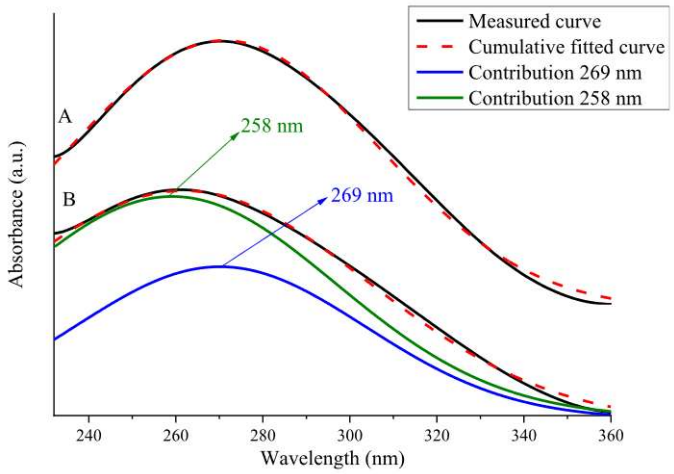

Fig. 5. The deconvoluted UV-Vis absorbance spectra of the supernatant of the Mg_2Al-E-Cin LDH slurry, A : before the irradiation (there is one component only), B: after irradiation for 2 h (could be decomposed to two components).

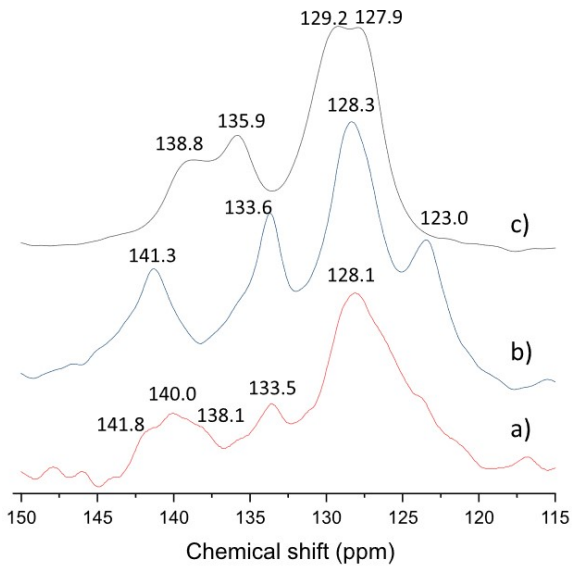

Fig. 6. ^{13}C CP MAS NMR spectra of the a) Mg_2Al-E-Cin (in slurry -suspended in methanol) irradiated on 254 nm for 2 h, b) Mg_2Al-Z-Cin and c) Mg_2Al-E-Cin.

^{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 M^{II}_2Al-E-Cin into M^{II}_2Al-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 M^{II}_2Al-Z-Cin. Similar behaviour toward Cin photoisomerisation was observed for both 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 Zn2Al 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 Mg2Al or Zn2Al 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. There action 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.

Appendix A. Supplementary data

Supplementary data to this article can be found online athttps://doi.org/10.1016/j.molstruc.2020.128561.

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