

THERMOGRAVIMETRIC ANALYSIS OF LAYERED DOUBLE HYDROXIDES WITH CHLORAMPHENICOL AND SALICYLATE IN THE INTERLAYER SPACE

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The thermal behavior of the new inorganic–organic nanohybrid materials obtained by intercalation of chloramphenicol and salicylate into layered double hydroxides (LDHs) by direct synthesis method, anion exchange reaction and the reconstruction method was evaluated by dynamic thermogravimetric analysis in air, at heating rates of 5°C min⁻¹. The XRD patterns of the samples are characteristic for those of well crystallized solids with layered double hydroxide structures. The FTIR spectroscopy results show the presence of the organic compound within the network structure of the synthesized LDHs. The kinetic parameters (reaction order (*n*) apparent activation energy (*E_a*) and pre-exponential factor (ln*A*) were calculated by the Coats–Redfern method. The compensation effects were determined.

Keywords: chloramphenicol, intercalation, layered double hydroxides, salicylate, thermal degradation

Introduction

The class of materials known as layered double hydroxides (LDHs) or hydrotalcite-like materials have the general formula: $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}A_{x/m}^{m-} \cdot z\text{H}_2\text{O}$, where M^{2+} =Mg, Zn, Ca, Co, Fe, Ni, Cu, etc., M^{3+} =Al, Fe, Cr, Ga, etc., A^{m-} =Cl⁻, CO₃²⁻, NO₃⁻, etc., *m* is the formal charge of anion and *x* is the stoichiometric coefficient that can vary extensively. As it is shown the formula, the formal positive charge of the layer depends on the M^{2+}/M^{3+} ratio. A variety of anions can be incorporated in the brucite-like layer. These materials have high anionic exchange capacity. Due to these properties they can be used as matrices for tailoring specific organic–clay hybrid nanostructures with new potential applications such as: designing new pharmaceuticals and biocompatible materials [1–4].

It is well known that the intercalated compounds are generally more stable than their native counterparts.

Thermal decomposition studies of intercalated compounds into lamella of layered double hydroxides were previously reported [5, 6].

We are presenting here the synthesis and characterization of a new inorganic–organic nanohybrid materials obtained by intercalation of chloramphenicol (Ch) and salicylate (Sal) into LDHs and their thermal behavior.

The following methods of intercalation were used: direct synthesis, anion exchange reaction and the reconstruction which is based on the ‘memory effect’ of the LDH-like structure [7].

Ch is a broad-spectrum antibiotic that is active against both gram-positive and gram-negative bacteria. A well known disadvantage of this antibiotic is due to its high toxicity. The incorporation of the Ch in the structure of MgAl layered double hydroxides (MgAlLDH) in principle can offer the premises for controlling the release rate of the Ch from the layered structure and reducing its toxicity [8, 9].

Sal is used in rheumatism treatment, but its adverse secondary effects, such as gastric and duodenal ulcer formation are quite common. The effect of LDHs in preventing taurcholate induced gastric injury in rat was demonstrated in the literature [10]. The intercalation of the Sal into ZnAl layered double hydroxides (ZnAlLDH) has been investigated by coprecipitation and anion exchange method.

The thermal behavior of the nanohybrid structure was evaluated by dynamic thermogravimetric analysis in air. Kinetic analysis of thermogravimetric data was established by using the Coats–Redfern integral method [11].

Experimental

Materials

All chemicals including Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NaOH were analytical grade. Ch and Sal were purchased from Aldrich and used without further purification.

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Preparation of MgAILDH

100 mL of an aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2 mol)/ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 mol) and an aqueous solution of $\text{NaOH}/\text{Na}_2\text{CO}_3$, were added drop wise to the reaction vessel, in such a way that the pH was kept at a constant value of 9.5. The resulting white precipitate was aged at 65°C for 24 h under stirring. After the aging step, the obtained precipitates were separated by centrifugation, washed extensively with warm deionized water until sodium free and dried under vacuum at 40°C .

Preparation of ChMgAILDH1 (coprecipitation method)

An aqueous solution containing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2 mol)/ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 mol) was added drop wise to Ch solutions with variable concentration. During this process the pH of the mixture was kept constant at 9.5 by addition of an aqueous solution containing $\text{NaOH}/\text{Na}_2\text{CO}_3$. The precipitate was washed with distilled water and dried in a vacuum oven at 65°C .

Preparation of ChMgAILDH2 (reconstruction method)

An aliquot of 0.7 g of freshly calcinated LDH material was placed in a closed flask containing 500 mL aqueous solution of 6 g Ch, under N_2 blanket, and aged under stirring for 36 h at 40°C . The obtained precipitate was filtered, washed with deionized water and dried at 37°C .

Preparation of ZnAILDH

100 mL of an aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2 mol)/ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 mol) and an aqueous solution of NaOH 1 M were mixed in the reaction flask by drop wise addition. During the whole process the alkaline flow was controlled in such a way that the pH was kept at a constant value of 8. The resulting white precipitate was aged at 65°C for 24 h under stirring. After the ageing step the precipitate was separated by centrifugation, washed extensively with warm deionized water until sodium free and dried under vacuum at 40°C .

Preparation of SalZnAILDH1 (coprecipitation method)

An aqueous solution containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2 mol)/ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1 mol) was added drop wise to Sal solutions with variable concentration. During this process the pH of the mixture was kept constant at 7.5 by addition of an aqueous solution containing NaOH . The precipitate was washed with distilled water and dried in a vacuum oven at 65°C .

Preparation of SalZnAILDH2 (ion exchange method)

150 mL of 0.1 M Sal aqueous solution were added into 250 mL aqueous dispersion containing 1 g ZnAILDH under nitrogen atmosphere and vigorous magnetic stirring. The pH of the mixture was held constant at 7.5 by simultaneous addition of 1 M NaOH solution. The exchange reaction was allowed to proceed at room temperature for 24 h. The precipitate was washed with distilled water and dried in a vacuum oven at 65°C .

Methods

X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D8 diffractometer using monochromatic CuK_α radiation ($\lambda=0.154$ nm), operating at 40 kV and 50 mA over a 2θ range from 4 to 70° .

FTIR spectra were recorded on a FTIR BOMEM MB 104 spectrometer under the following experimental conditions: 200 scans in the mid-IR range ($400\text{--}4000$ cm^{-1}) using KBr (ratio 5/95 mass%) pellets, and a resolution of 4.0 cm^{-1} . Thermal analyses (TG and DTG) were carried out in air on a Netzsch TG 209C thermal analyzer, from 25 to 900°C , at a heating rate of 5°C min^{-1} . The accurate sample temperature was detected by a thermocouple in direct contact with the sample crucible. This derivatograph allows simultaneous recording of thermogravimetric and derivative thermogravimetric analysis. Aluminum oxide (calcinated at 1000°C) as reference material, platinum melter and a sample mass of 20 ± 5 mg have been used.

Results and discussion

The powder XRD patterns for LDHs and their organic-mineral nanohybrids, ChMgAILDH and SalZnAILDH are shown in Figs 1 and 2. The basal spacing

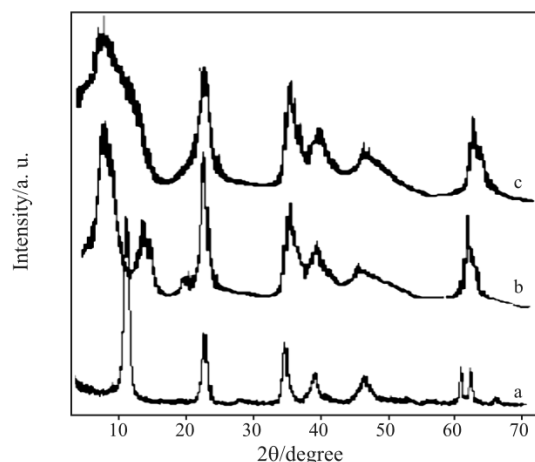


Fig. 1 XRD patterns a – MgAILDH, b – ChMgAILDH1 and c – ChMgAILDH2

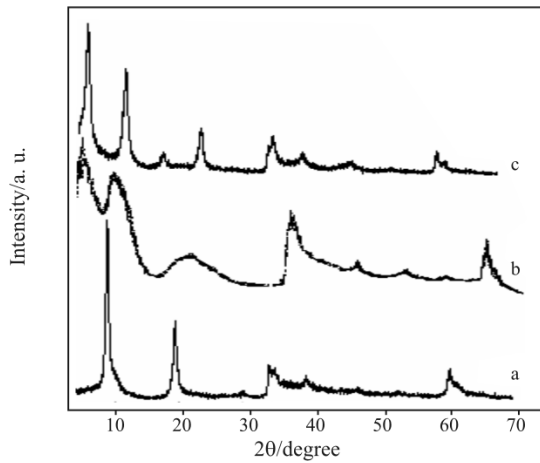


Fig. 2 XRD spectra a – ZnAILDH, b – SalZnAILDH1 and c – SalZnAILDH2

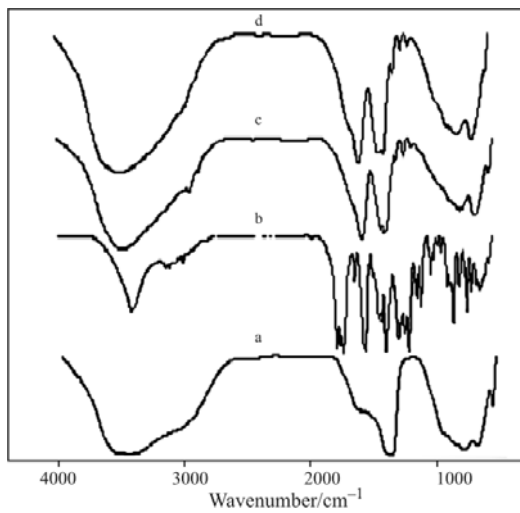


Fig. 3 FTIR spectra a – MgAILDH, b – Ch, c – ChMgAILDH1 and d – ChMgAILDH2

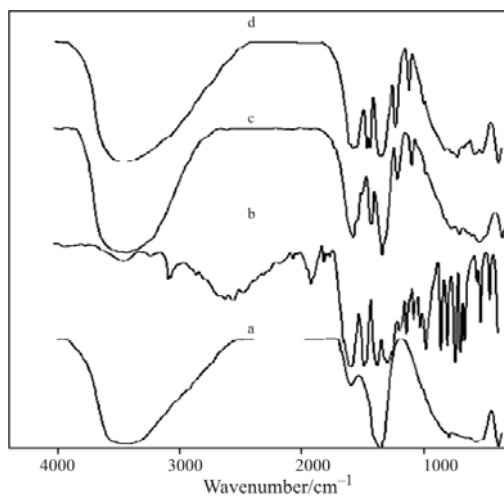


Fig. 4 FTIR spectra a – ZnAILDH, b – Sal, c – SalZnAILDH1 and d – SalZnAILDH2

width of the first peak is bigger for ChMgAILDH sample compared to the MgAILDH precursor (Fig. 1), indicating an enlargement of the interlayer space when Ch was intercalated.

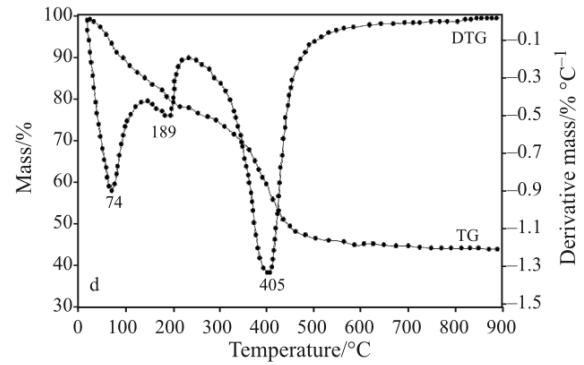
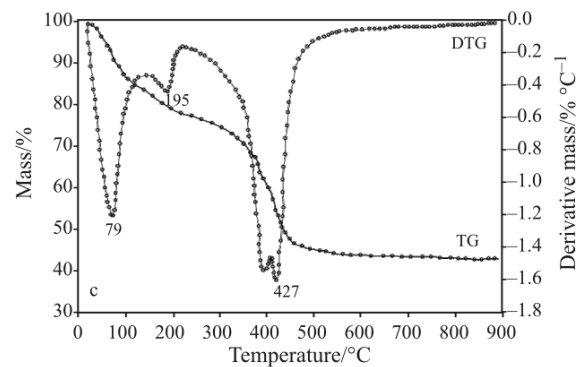
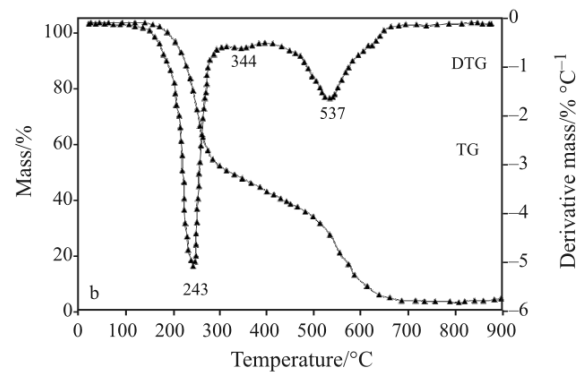
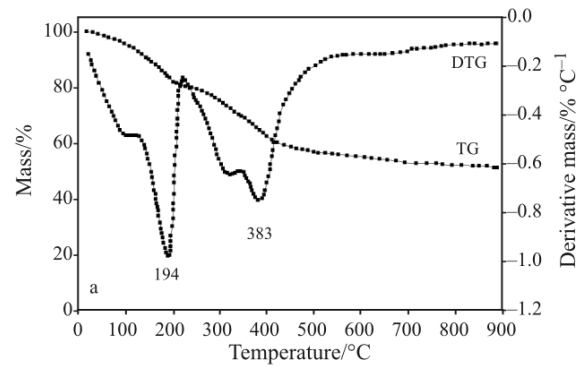


Fig. 5 TG and DTG curves for a new inorganic–organic nanohybrid structure obtained by intercalation of chloramphenicol into LDHs; a – MgAILDH, b – Ch, c – ChMgAILDH1 and d – ChMgAILDH2

The ZnAILDH precursor has an XRD pattern similar to those previously reported [12], with a basal spacing (d_{003}) of 8.7 Å (Fig. 2a). After reacting with Sal, the powder XRD pattern of the product maintains the characteristic features of ZnAILDH (Fig. 2b). The main diffraction peaks of SalZnAILDH structure

appear at 5.07, 11.7 and 17.5°, with an expanded basal spacing (d_{003}) of 15.4 Å.

The insertion of Ch and Sal into the lamella of MgAILDH and ZnAl LDH were also confirmed by the FTIR technique (Figs 3 and 4). All the vibration bands of the organic anions are observed together with the absorption bands of the LDHs. The absorption band at around 3431 cm^{-1} is attributed to the OH stretching due to the presence of hydroxyl group of LDHs and/or physically adsorbed water molecules. The appearance of a strong band at 1381 cm^{-1} can be assigned to the ν_3 of nitrate group, the counter anion in the LDHs. Two other bands at 611 and 426 cm^{-1} can be attributed to the Al–OH and MgAl–OH or ZnAl–OH bending vibration [13, 14], respectively. For the samples containing Ch (Figs 3c and d), the characteristic peaks of aliphatic C–H stretch can be identified at 2858 and 2927 cm^{-1} although the broad adsorption band of the hydroxyl stretching mode partially overlaps the ν_{CH_3} vibrations. The spectrum recorded after incorporation of the Sal is presented in Figs 4c and d. Due to the ionization of the acid group, the band previously detected for free Sal at 1651 cm^{-1} disappears, while a new band is recorded at 1570 cm^{-1} . The appearance of this band is caused by the asymmetric vibration $\nu_{\text{as}(\text{COO}^-)}$ mode. Another band recorded at 1364 cm^{-1} is due to the symmetric vibration $\nu_{\text{s}(\text{COO}^-)}$. The band originated from the $\delta_{(\text{CH}_3)}$ mode is recorded at 1386 cm^{-1} . The band assigned to the nitrate group (1381 cm^{-1}) had lower intensity after the ion-exchange reaction, thus supporting the assumption that NO_3^- anion was replaced by organic anions.

The thermal behavior of the new inorganic–organic nano hybrid material obtained by intercalation of Ch and Sal within the layers of LDHs was evaluated by dynamic thermogravimetric analysis in air. Figures 5

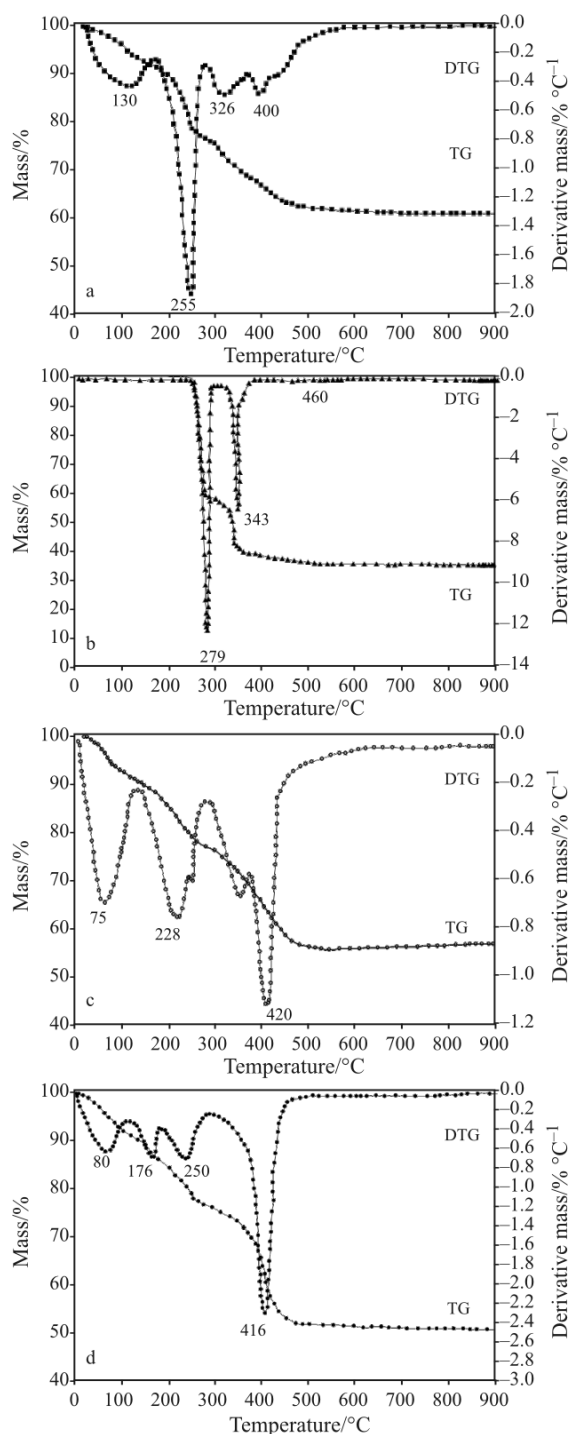


Fig. 6 TG and DTG curves for a new inorganic – organic nano hybrid structure obtained by intercalation of salicylate into LDHs; a – ZnAILDH, b – Sal, c – SalZnAILDH1 and d – SalZnAILDH2

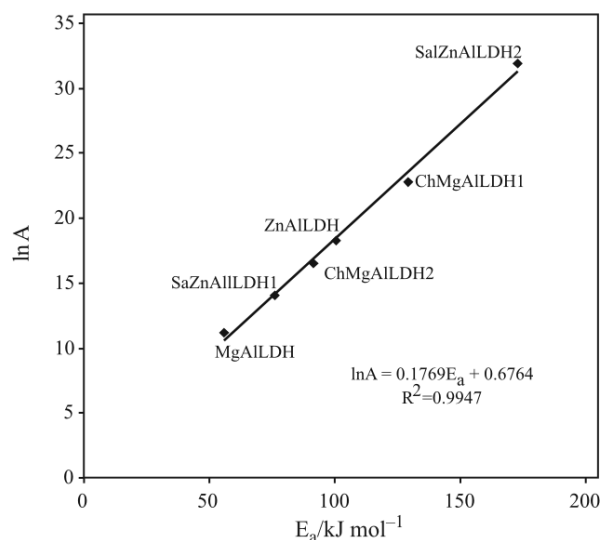


Fig. 7 The pre-exponential factor dependence as function of the activation energy

Table 1 The kinetic characteristics for a new inorganic–organic nanohybrid structure obtained by intercalation of chloramphenicol and salicylate into layered double hydroxides (LDHs)

Sample code	Stage 1 ^a			Stage 2 ^b			Stage 3 ^c			Stage 4 ^d						
	E_a^e /kJ mol ⁻¹	n^f	$\ln A^g$	$(r^2)^h$	E_a^e /kJ mol ⁻¹	n^f	$\ln A^g$	$(r^2)^h$	E_a^e /kJ mol ⁻¹	n^f	$\ln A^g$	$(r^2)^h$	E_a^e /kJ mol ⁻¹	n^f	$\ln A^g$	$(r^2)^h$
MgAILDH	35	1	11.26	0.987	56	1	11.17	0.998	–	–	–	–	–	–	–	–
Ch	84	1	20.30	0.995	42	1	8.15	0.992	136	1	20.89	0.989	–	–	–	–
ChMgAILDH1	56	1	20.03	0.998	25	1	6.56	0.993	129	1	22.78	0.991	–	–	–	–
ChMgAILDH2	43	1	15.53	0.949	28	1	7.17	0.988	92	1	16.53	0.994	–	–	–	–
ZnAILDH	28	1	8.36	0.998	133	1	31.3	0.999	97	1	19.4	0.999	100	1	18.30	0.98
Sal	370	1	83.41	0.999	154	0	33.63	0.988	44	1	7.12	0.997	–	–	–	–
SalZnAILDH1	46	1	16.77	0.999	38	1	9.60	0.999	76	1	14.08	0.999	–	–	–	–
SalZnAILDH2	64	1	22.4	0.977	40	1	11.2	0.998	85	1	20.97	0.998	172	1	31.88	0.97

^aFirst; ^bsecond; ^cthird process of the compounds decomposition; ^dthe last process of the compounds decomposition; ^eapparent activation energy; ^freaction order; ^gpre-exponential factor; ^hcorrelation coefficients.

and 6 present the TG and the differential mass loss (DTG) curves of the samples.

Analyzing the recorded curves, we notice that the degradation occurs in two or three stages with various mass rate losses for the compounds MgAILDH, Ch, ChMgAILDH1 and ChMgAILDH2. As it can be seen from DTG curves of these compounds, the degradation process exhibited two or three maxima of decomposition.

The first stage for sample MgAILDH starts as soon as heating commences and it is completed by 220°C, showing a 20% of the samples mass loss. This stage is associated with the dehydration of surface water molecules and the loss of crystallization water located in the interlayer region. The next stage in the TG pattern of sample MgAILDH occurs up to a temperature 570°C, accounting for 28.85% of the sample mass loss. The broad DTG peaks reveal that the decomposition process is complex. The end products from this decomposition process were assumed to be a mixture of metal oxides and mixed metal oxides.

The thermal degradation of Ch takes place in three stages with various percentages of mass loss. The biggest percentage of mass loss is recorded in the first stage and it is about ≈50%. The maximum decomposition rates in the three stages correspond to temperatures of 243, 344 and 537°C respectively (Fig. 5b).

The data presented in Figs 5c and d shows that the modification of the synthesis method leads to a change of mechanism in the thermal decomposition of samples ChMgAILDH1 and ChMgAILDH2, at least in the first two stages. The DTG curves exhibit maximum decomposition rates at 75 and 190°C, respectively. Bigger differences are observed in the third stage. A possible explanation is given by the presence of CO₃²⁻ as an impurity in ChMgAILDH1. This assumption is supported by the XRD analysis as well.

In the samples containing intercalated salicylate, the modification of the synthesis method has a bigger influence upon the mechanism of thermal decomposition. The decomposition of SalZnAILDH1 takes place in three stages, while the decomposition of SalZnAILDH2 takes place in four stages.

The percentage of leftover residue is the same in both cases, about 50%. Significant differences between the decomposition mechanisms of these samples appear in the 150 and 350°C region, respectively (Figs 6c and d).

The thermal decomposition of salicylate also takes place in three stages, like the chloramphenicol, but we found out that the former is more stable than the latter. The decomposition process starts around 250°C and the residue is larger (about 33%).

The degradation mechanism for all the samples was analyzed using the Coats–Redfern integral method [9]. The results, including reaction order (n),

activation energy (E_a) and pre-exponential factor ($\ln A$) are presented in Table 1. The reaction order values reflect the influence of transport phenomena such as diffusion.

From the kinetical data we can conclude that Sal is more thermostable than Ch. The activation energy for the first decomposition stage was found to be 370 kJ mol⁻¹ for Sal and 84 kJ mol⁻¹ for Ch.

The stability and thermal behavior of Ch were investigated also by Macedo *et al.* [15]. The thermal decomposition of the Ch obeys first-order kinetics. For getting more proof regarding the degradation mechanism of the new inorganic–organic nanohybrids the compensation effect has been evaluated. By plotting $\ln A$ as function of E_a as shown in Fig. 7, the mathematical equation describing the compensation effect was obtained: $\ln A = 0.1769E_a + 0.6764$.

The linear dependence confirms a similar degradation mechanism for the analyzed compounds in the temperature range of 240 to 680°C, with a slope of the lines of around 0.18.

Conclusions

The intercalation of the Ch and Sal into layered double hydroxides was confirmed by DRX and FTIR spectroscopy. The XRD patterns of the samples are typical to those of well crystallized solids with layered double hydroxide structures. All the vibration bands of the organic anion are observed together with the absorption bands of LDHs.

The thermal stability and degradation kinetics of the new inorganic – organic nanohybrid compounds is strongly influenced by the synthesis method.

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