

## **AMINO ACID-PILLARED LAYERED DOUBLE HYDROXIDE AND MONTMORILLONITE**

### **Thermal characteristics**

*Á. Fudala<sup>1</sup>, I. Pálinkó<sup>2\*</sup>, B. Hrivnák<sup>1</sup> and I. Kiricsi<sup>1</sup>*

<sup>1</sup>Applied Chemistry Department, József Attila University, Rerich B. tér 1, Szeged

<sup>2</sup>Department of Organic Chemistry, József Attila University, Dóm tér 8, Szeged, H-6720 Hungary

### **Abstract**

Zn-Al hydrotalcite (HT) and Na-montmorillonite (Na-mont) were pillared by the deprotonated and the protonated forms of *L*-tyrosine, respectively. Pillaring was successful as the increased basal spacings due to intercalation attest. *L*-Tyr-HT proved to be thermally less stable than HT, while that of *L*-Tyr-mont did not change compared to Na-mont. DTG curves showed more mass loss steps for the hosts than for the intercalated compounds. The extra steps belonged to the decomposition of the amino acid derivatives. FT-IR spectra of the samples pretreated in vacuum in the 293–773 K temperature range also showed that intercalation was successful and *L*-Tyr-HT is more temperature sensitive than *L*-Tyr-mont.

**Keywords:** anionic and cationic intercalation of *L*-tyrosine, DTG, FT-IR, Na-montmorillonite, thermal behaviour, Zn-Al hydrotalcite

### **Introduction**

Pillared layer materials find application in separation science as well as in fine chemical industry [1]. They are of two main types depending on the method of intercalation. Certain bulky organic or inorganic cations [2] and anions [3] may be used as pillaring agents via cation and anion exchange, respectively.

When pillaring is attempted by amino acids very interesting intercalated materials may emerge. First, the pillars are chiral, consequently, the whole material may be chiral offering the perspective of immediate applications in separation science as well as in enantioselective catalysis. Second, amino acids are amphoteric in character, that is, depending on the pH they can be cations or anions. Hence, they may serve as pillars in cation as well as anion exchanger layered compounds.

In this work we report on the thermal properties of *L*-tyrosine intercalated montmorillonite and Zn-Al layered double hydroxide (or Zn-Al hydrotalcite). Thermogravimetry as well as FT-IR spectroscopy were used as tools facilitating the comparison of the thermal behaviour of the various materials and studying the heat stabilities of the intercalated substances.

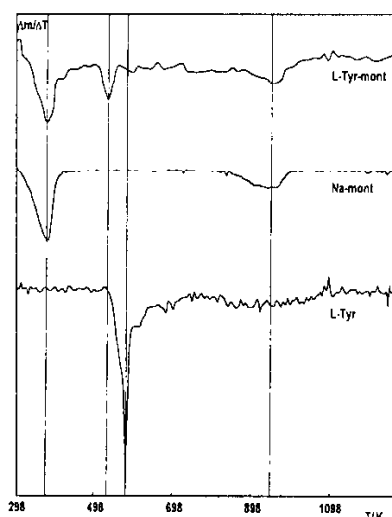
\* Author for correspondence: fax: +36 62 321 523; e-mail: palinko@chem.u-szeged.hu

## Experimental

The guest material *L*-tyrosine (pH=5.7), was obtained from Aldrich and used as received.

One of the host substances, Na-montmorillonite (Na-mont), was a commercial product: (Bentolit H, SCP Laport, ion-exchange capacity: 80 meq/100 g). The other, Zn-Al hydrotalcite (HT), was prepared on the basis of Taylor's method [4]. The pH of 250 cm<sup>3</sup> 0.1 mol dm<sup>-3</sup> Al(NO<sub>3</sub>)<sub>3</sub> solution was adjusted to 7.0 with the addition of the appropriate amount of a solution containing 0.8 mol Na<sub>2</sub>CO<sub>3</sub> and 1.6 mol NaOH in 1 dm<sup>3</sup> water. After stirring for 1 h, 250 cm<sup>3</sup> 0.3 mol dm<sup>-3</sup> Zn(NO<sub>3</sub>)<sub>2</sub> solution was added dropwise. The pH of the slurry was kept at 6.0–6.5 with adding appropriate amount of the alkaline solution described above. After the complete delivery of Zn<sup>2+</sup> solution, the slurry was boiled for 1 week under reflux. The gel formed was autoclaved at 458 K for 18 h in a teflon-coated container. Double-distilled, chloride-free water and inert atmosphere (Ar) were used throughout the synthesis.

Cationic pillaring was done at pH=4, while for anionic intercalation the pH was set to 8. Na-mont was preswollen in double-distilled water for 24 h and the pH of the slurry was set to 4 by 0.1 mol dm<sup>-3</sup> HCl solution. Then, the aqueous solution of the amino acid was mixed to it under vigorous stirring at room temperature. The suspension was stirred for an additional day. Then, the intercalated material was filtered off and dried in air. A HT aqueous suspension was prepared and its pH was set to 8 by 0.1 mol dm<sup>-3</sup> NH<sub>4</sub>OH solution. The aqueous solution of the amino acid was mixed to it under vigorous stirring at room temperature. The temperature was raised to 333 K and the suspension was stirred for an additional day. Finally, the intercalated material was filtered off and dried in air.



**Fig. 1** DTG curves of *L*-tyrosine (*L*-Tyr), Na-montmorillonite (Na-mont) and *L*-tyrosine-montmorillonite (*L*-Tyr-mont) (100 mg of sample, 10°C min<sup>-1</sup> temperature ramp)

XRD measurements were performed on a DRON 2 powder X-ray diffractometer using the  $\text{CuK}\alpha$  radiation. Diffractograms of the air-dried samples were registered. Basal spacings were determined from the position of the  $d(001)$  reflection (Na-mont and *L*-Tyr-mont) or the  $d(003)$  reflection (HT and the *L*-Tyr-HT). Data are in the second column of Table 1.

**Table 1** Characteristic data on the host materials and the intercalated structures

Samples	Basal spacing <sup>a</sup> /nm	BET area /m <sup>2</sup> g <sup>-1</sup> (393 K) <sup>b</sup>
Na-montmorillonite	1.20	58.6
<i>L</i> -Tyr-montmorillonite	1.46	71.1
Hydroalcite	0.89	83.0
<i>L</i> -Tyr-hydroalcite	1.75	101.2

<sup>a</sup>calculated from the  $d(001)$  reflection for the montmorillonite and the  $d(003)$  reflection for the hydroalcite derivatives

<sup>b</sup>temperature of evacuation for three hours

BET measurements were performed in a conventional volumetric adsorption apparatus at the temperature of liquid nitrogen (77 K). Before measurements the samples were evacuated for 3 h at 393 K. Data are listed in the third column of Table 1.

For studying the thermal behaviour of the host and guest materials as well as the intercalated substances a computerised Derivatograph Q instrument was used. The powdered material (100 mg) was placed on a platinum sample holder and was heated under inert gas flow (Ar) from 293 to 1300 K with 10°C min<sup>-1</sup> temperature ramp. The DTG curves were determined and depicted in a way to allow comparisons among the host, guest and intercalated materials (Figs 2 and 3).

The FT-IR spectra of the intercalated materials were taken on a Mattson Genesis I spectrophotometer with 1 cm<sup>-1</sup> resolution. The 4000–800 (500) cm<sup>-1</sup> range was investigated. Self-supported wafers were pressed from the intercalated materials and they were subjected to 3 h pretreatments in vacuum at various temperatures, in the 293–773 K range with 100-degree increments (Figs 3 and 4).

## Results and discussion

XRD measurements made clear that pillaring was successful. The layers propped open and the basal distances increased substantially (Table 1, column 2). For hydroalcite this increase was always significantly larger than for montmorillonite. This fact is an obvious indication that the spatial arrangement of the amino acid moieties is very different.

BET surface areas are not high because the temperature of pretreatment is not sufficient to fully remove chemisorbed water (Table 1, column 3). Physisorbed water could be largely removed by the 3 h evacuation at 393 K as the low-temperature peak (378 K) in the DTG curves of the intercalated structures attests.

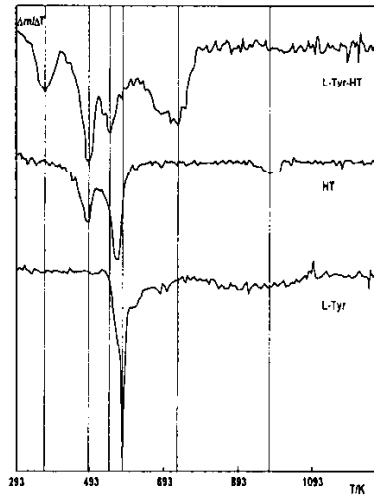


Fig. 2 DTG curves of *L*-tyrosine (*L*-Tyr), Zn-Al hydrotalcite (HT) and *L*-tyrosine-Zn-Al hydrotalcite (*L*-Tyr-HT) (100 mg of sample,  $10^{\circ}\text{C min}^{-1}$  temperature ramp)

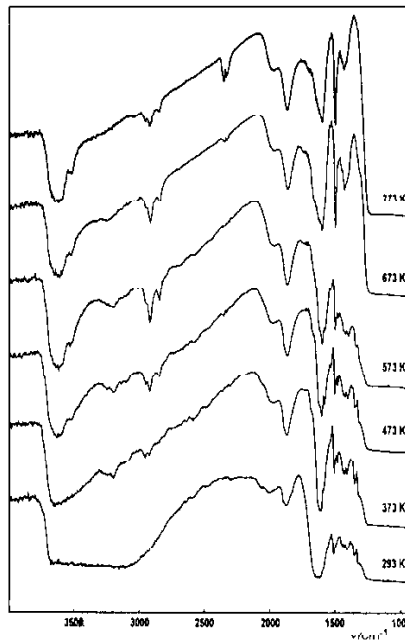


Fig. 3 FT-IR spectra of *L*-tyrosine-montmorillonite (*L*-Tyr-mont) treated in vacuum at various temperatures for 3 h (in transmittance, self-supported wafers)

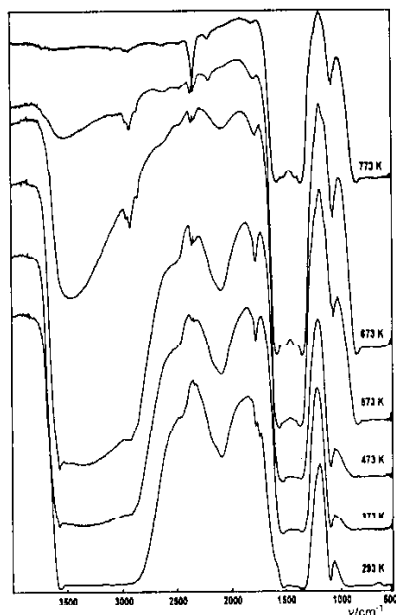


Fig. 4 FT-IR spectra of *L*-tyrosine-Zn-Al hydrotalcite (*L*-Tyr-HT) treated in vacuum at various temperatures for 3 h (in transmittance, self-supported wafers)

DTG profile of *L*-Tyr-mont (Fig. 2, topmost curve) is significantly simpler than that of *L*-Tyr-HT (Fig. 3, topmost curve). It is roughly the superposition of the host material and the (parent) guest compound. Obviously, amino protonated tyrosine is the pillaring agent, therefore it may be expected that the mass loss peak (the loss of the carboxylic group) is not exactly at the same temperature in *L*-Tyr-mont (around 528 K) than in *L*-Tyr (around 578 K). However, the layered structure collapses at about the same temperature like Na-mont. It is final by 1000 K.

The basic features in the DTG curve of *L*-Tyr-HT and HT, at least in the low-temperature region, may be rationalised similarly to those of *L*-Tyr-mont and Na-mont. First, desorption of physisorbed water occurs (around 373 K), then, the substance loses chemisorbed (crystal) water (in the vicinity of 483 K for the host as well as the intercalated materials) and at still higher temperature (around 573 K for the host HT and in the vicinity of 543 K for the pillared substances) structural dehydroxylation takes place. The layered structure of *L*-Tyr-HT, however, collapses at lower temperature (it peaks near 690 and is final by about 800 K) than that of HT, which is over by about 900 K. The event is mainly decarboxylation and some further dehydroxylation. Of course decarboxylation is more spectacular in *L*-Tyr-HT. All in all, the intercalated structure is thermally less stable than the host material.

Inspection of the FT-IR spectra of the heat-treated samples allows similar conclusions to be drawn. Intercalation was successful. The indicative peaks for *L*-Tyr-mont

are at  $3560\text{ cm}^{-1}$  (carboxylic OH) and the doublet at  $2000$  and  $1882\text{ cm}^{-1}$  (Fig. 3). For *L*-Tyr-HT it is at  $2066\text{ cm}^{-1}$  (Fig. 4). Although changes in the OH region of *L*-Tyr-mont and *L*-Tyr-HT occurred on temperature treatment (the peaks are sharpened indicating water desorption and some dehydroxylation), the indicative absorptions weakened (treatment at  $573\text{ K}$ ) and, finally, disappeared (treatment at  $673\text{ K}$ ) only for *L*-Tyr-HT.

## Conclusions

*L*-tyrosine in its protonated and deprotonated forms can be intercalated between the layers of montmorillonite and hydrotalcite, respectively. The thermal behaviour of the intercalated materials shows the features of the host as well as the guest materials. The thermal stability of *L*-Tyr-mont remained the same as that of Na-mont, however, *L*-Tyr-HT became significantly less stable than hydrotalcite. If the intercalated materials can be made more sturdy there is a good chance to use them as catalysts in a wide variety of acid-base reactions.

## References

- 1 R. Szostak and C. Ingram, *Stud. Surf. Sci. Catal.*, 94 (1995) 13.
- 2 R. Burch, *Catal. Today*, 2 (1987) 185; F. Figueras, *Catal. Rev. Sci. Eng.*, 30 (1988) 457.
- 3 A. de Roy, C. Forano, K. El Malki and J.-P. Besse in *Synthesis of Microporous Materials*, Vol. II: Expanded Clays and Other Microporous Solids, van Nostrand Reinhold, New York 1992, p. 108.
- 4 R. M. Taylor, *Clay Miner.*, 19 (1984) 591.