Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 533–535

EFFECT OF HEAT TREATMENT ON AMINO ACID INTERCALATED IN MONTMORILLONITE

T. Kollár[1]*, I. Pálinkó*[2*] *and I. Kiricsi*[1]

[1]Department of Applied and Environmental Chemistry, Rerrich B. tér 1, Szeged 6720, Hungary
[2]Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged 6720, Hungary

The protonated forms of glycine, *L*-alanine, *L*-tryptophane, *L*-histidine, *L*-methionine or *L*-lysine were ion-exchanged into montmorillonite, a cationic layered silicate. The organic-inorganic hybrid nanostructured materials underwent complex mass-loss procedures upon thermal treatment. They were the loss of physisorbed water, decarboxylation, deintercalation through the decomposition of the organic material, the loss of structural hydroxy groups until the collapse of the layered structure.

Keywords: *effects of heat treatment, glycine, intercalation, L-alanine, L-histidine, L-lysine, L-methionine, L-tryptophane, montmorillonite*

Introduction

Preparation of host-guest substances [1, 2] in general and nanostructured hybrid organic-inorganic materials [3–5] in particular is in the forefront of research efforts throughout the world. These material types are of special interest when the organic part is chiral. A relatively durable host substance containing chiral intercalated organic moieties offer numerous application possibilities. Among others it may serve as a chromatographic column for chiral separation or chiral catalyst unifying in fortunate cases the chiral environment of the guest the acidic or basic properties of the host (if it is an aluminosilicate or layered double hydroxide, respectively) and shape selectivity of the intercalated material due to nanosized pore openings [6]. The host may also serve as a durable container of chiral building blocks used for syntheses of complicated organic compounds [7].

Recently, we have been involved in studying the synthesis, characterisation and catalytic properties of pillared layer clays (PILCs) [8] as well as layered double hydroxides (LDHs) [9]. The pillars for the clays were mainly of inorganic, however, the easy way of introducing bulky inorganic anions into LDHs is through ion exchange of organic anions first (then interchanging them to inorganic anions). Obviously, organic cations can be ion-exchanged into clays too. Whether preparing pillared materials via ion exchange of inorganic or organic ions, nanostructured substances are obtained. It seemed to be interesting to do the ion exchange with chiral compounds of amphoteric character. On the basis of this property the cationic and the anionic forms of the same compound may be introduced into cationic clays and anionic LDHs, respectively. Amino acids being chiral as well as compounds of amphoteric character were the molecules of choice for intercalation [10]. Later, the variety of amino acids were increased and in their acidic forms they were intercalated into montmorillonite [11]. These materials were studied by infrared (FTIR) spectroscopy [11] and in the followings their changes are discussed upon thermal treatment.

Experimental

The host material was Na-montmorillonite (Mont), a dioctahedral layered silicate. It was a commercial product capable of cation exchange (Bentolit H, SCP Laport, ion-exchange capacity: 80 meq/100 g).

The amino acids (Fig. 1), to be intercalated, glycine (pI[the pH of the isoelectronic point]=6.0), *L*-alanine (pI=6.0), *L*-tryptophane (pI=5.9), *L*-histidine (pI=7.6), *L*-methionine (pI=5.7) and *L*-lysine (pI=9.7), were obtained from Aldrich Co. and were used as received.

Ion exchange was performed at pH=4. Na-montmorillonite was preswollen in double-distilled water for 24 h, and the pH of the slurry was set to 4 by 0.1 mol dm^{-3} HCl solution. Then, the aqueous solution of the amino acid was mixed into it with rigorous stirring at room temperature. The suspension was stirred for an additional day. Then, the intercalated material was filtered off, washed free of excess (protonated) amino acid, and dried in air. The procedure was repeated four times to make sure that the ion exchange was complete.

---

[*] Author for correspondence: palinko@chem.u-szeged.hu

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

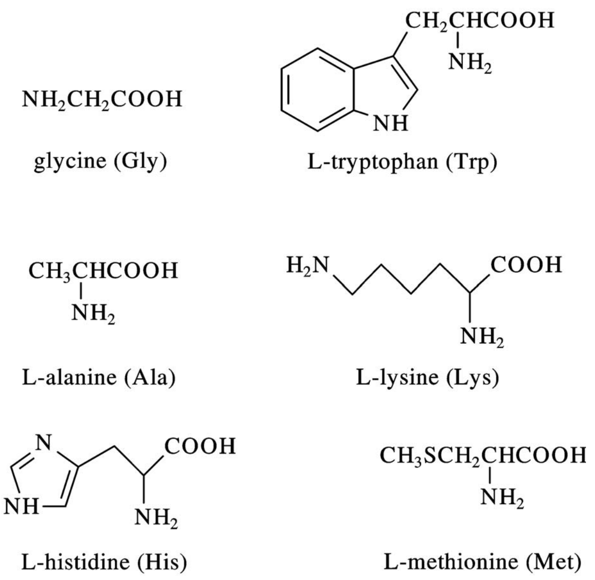

Fig. 1 The amino acids used for intercalation

The host material and the intercalated air-dried samples were characterized by X-ray diffractometry (XRD), Fourier-transform FTIR spectroscopy and surface area (BET) measurements [11]. Possible arrangements of the protonated amino acid cations (both the monomers and the dimers) were suggested on the basis of molecular modeling [11]. The effects of heat treatment were also touched upon, however, they will be described in more detail in the followings.

For studying the thermal behavior of the host and guest materials as well as the intercalated substances a computerized 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 K to 1300 K with 10° min^{-1} temperature ramp. TG and DTG curves were recorded. The temperature of various events were read from the DTG curves. The events occurring were well-resolved as the exemplary spectra attest and were reproducible (within generally ±5 K) on repeated runs.

Results and discussion

X-ray diffractometry and BET surface area measurements revealed that intercalation was successful with each protonated amino acid. The layers were propped open upon swelling and the basal distances remained higher after the ion exchange of the protonated amino acid than it was in the as-received sample even after removing the solvent and washing off excess amino acid from the outer surface of the clay (Table 1, column 2). There was 20 to 50 percent increase in the BET surface areas as well depending on the protonated amino acid intercalated (Table 1, column 3). The relatively moderate increase in surface area may be due to stuffing the interlayer space with the guest protonated amino acids.

Generally, heat treatment resulted in similar events in all the intercalated materials. First, desorption of the physisorbed water occurred (event I). This procedure is often hardly seen in the thermogravimetric curves, since the materials were calcined at 393 K for 3 h. Then, decarboxylation took place (event II). Carbon dioxide could be detected in the gas phase and the process was found to be endothermic. Upon further increase in temperature deintercalation took place through the destruction of the organic material (event III). At still higher temperature the loss

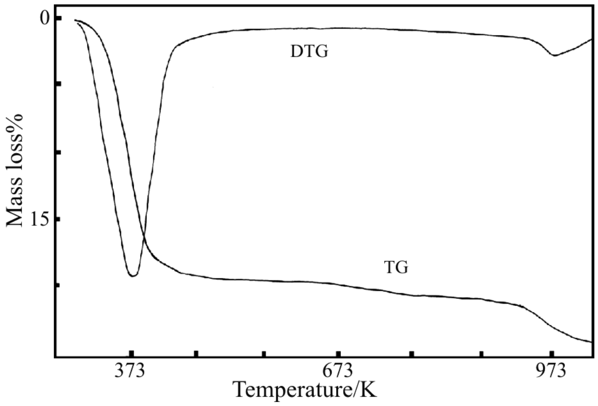

Fig. 2 TG and DTG curves for the parent montmorillonite

Table 1 Characteristic data on the host material and the intercalated substances

Substances	$d(001)$/nm	BET surface area/m^2 g^{-1} [b]
Na-montmorillonite (Mont)	1.20(0.24)[a]	58.6
Gly-Mont	1.32(0.36)	70.4
Trp-Mont	1.59(0.63)	92.6
Ala-Mont	1.35(0.39)	84.4
Lys-Mont	1.36(0.40)	76.5
His-Mont	1.42(0.46)	74.9
Met-Mont	1.68(0.72)	90.1

[a] interlayer distance (gallery height) in nm; [b] pretreatment: 393 K, 3 h

Table 2 Temperatures of various events taking place on heat treatment on the basis of DTG minima

Substances	Temperature of events on thermal treatment/K				
	I	II	III	IV	V
Mont	378	–	–	–	968
Gly-Mont	377	499	609	772	925
Trp-Mont	369	485	556	751	950
Ala-Mont	375	510	616	740	920
Lys-Mont	368	460	550	746	921
His-Mont	381	479	575	749	920
Met-Mont	371	503	597	734	930

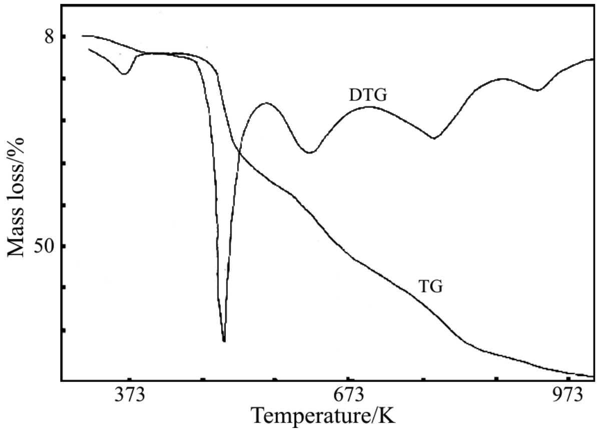

Fig. 3 TG and DTG curves for the Gly- Mont sample

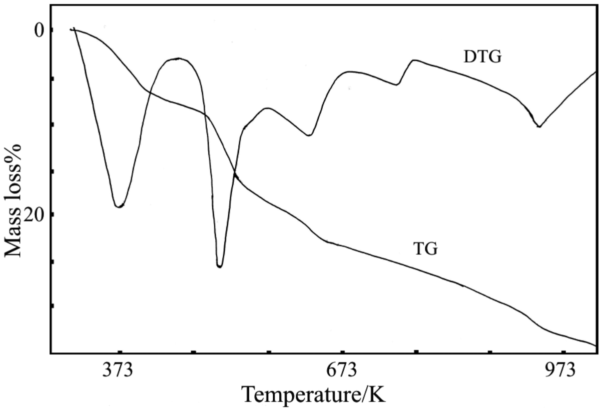

Fig. 4 TG and DTG curves for the Ala-Mont sample

of structural OH groups starts (event IV) until the collapse of the layered structure (event V). The temperatures of these events from DTG measurements are collected in Table 2.

Exemplary thermoanalytical curves are depicted in Figs 2–4.

Conclusions

The protonated forms of six amino acids were intercalated in montmorillonite. The intercalation was successful. The hybrid organic-inorganic substances underwent mass losses on heat treatment. The procedure could be decomposed to various events. They are as follows in the order increasing temperature: water desorption, decarboxylation of the intercalated protonated amino acid, deintercalation of the guest ion, loss of structural OH groups, collapse of the layered structure. The temperatures or temperature ranges of these events varied depending on the intercalated amino acids.

Acknowledgements

This work was supported by the National Science Fund of Hungary through grants OTKA T034793 and T034184. The financial help is highly appreciated.

References

1 M. Kubranová, E. Jóna, E. Rudinská, K. Nemčeková, D. Ondrušová and M. Pajtášová, J. Therm. Anal. Cal., 74 (2003) 251.
2 F. Taneri, T. Güneri, Z. Aigner, O. Berkesi and M. Kata, J. Therm. Anal. Cal., 74 (2003) 769.
3 K. Kuramato, H. Izu, M. Matsumoto, K. Yamano, H. Hirano and Y. Nakagawa, US Pat. Appl. Publ. (2003) USXXCO US 20030228120 A1 20031211.
4 N. Shiga, K. Obi, A. Goto, T. Takeyama and M. Shirai, US Pat. Appl. Publ. (2003) USXXCO US 2003231403 A1 20031218.
5 Z. Y. Cheng, B. X. Gao, M. L. Pang, S. Y. Wang, Y. C. Han and J. Liu, Chem. Mater., 15 (2003) 4705.
6 L. P. Szabo, E. H. Lippai, P. Hadik, E. Nagy, F. Mizukami, J. Shimizu and I. Kiricsi, Hung. J. Ind. Chem., 26 (1998) 147.
7 Q. Yuan, M. Wei, Z. Wang, G. Wang and X. Duan, Clays Clay Miner., 52 (2004) 40.
8 I. Pálinkó, Á. Molnár, J. B. Nagy, K. Lázár, J. Valyon and I. Kiricsi, J. Chem. Soc., Faraday Trans., 93 (1997) 1591.
9 A. Béres, I. Pálinkó, I. Kiricsi, J. B. Nagy, Y. Kiyozumi and F. Mizukami, Appl. Catal., A 182 (1999) 237.
10 Á. Fudala, I. Pálinkó and I. Kiricsi, Inorg. Chem., 38 (1999) 4653.
11 T. Kollár, I. Pálinkó, Z. Kónya and I. Kiricsi, J. Mol. Struct. 651 (2003) 335.