Preparation and Characterization of Hybrid Organic−Inorganic Composite Materials Using the Amphoteric Property of Amino Acids: Amino Acid Intercalated Layered Double Hydroxide and Montmorillonite

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Received October 5, 1998

Deprotonated and protonated forms of L-tyrosine or L-phenylalanine were intercalated by Zn−Al hydrotalcite (HT) and Na-montmorillonite (Na-mont), respectively. The intercalated materials were characterized by powder X-ray diffraction, BET measurements, and FT-IR spectroscopy. Intercalation was successful as the increased basal spacings attested. For hydrotalcite this increase was always significantly larger than for montmorillonite. This fact indicated that the spatial arrangement of the amino acid moieties was very different. A model for this arrangement has been suggested. A variety of methods showed that L-Tyr(Phe)-HT was thermally less stable than HT, while the heat resistance of L-Tyr(Phe)-mont did not change.

Introduction

Pillared layer materials find application in separation science as well as in the 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.

Inorganic polyhydroxy cations are used for preparing pillared layer materials, most frequently pillared layer clays (PILCs).[2] Ion exchange is straightforward here; however, direct pillaring of layered double hydroxides (LDHs) with bulky inorganic anions is rarely possible.[3] Generally, bulky organic anions are used first for propping the layers open; then follows the exchange with inorganic anions.[4] Of course, this second step need not be done; LDHs pillared with organic anions may be of interest just as PILCs when the organic cation is the intercalated agent. It is especially so, if the pillars are chiral, since not only are these quasi two-dimensional channel systems well-defined structures with huge pore openings, but the optically active pillars create a chiral environment. In view of fundamental research it is an added bonus if the same compound can be used for cationic as well as anionic intercalation.

Amino acids can be the compounds of choice since, depending on the pH of preparation, they can be cations or anions. Hence, they may serve as pillars in cation as well as anion exchanger layered compounds. Moreover, their L enantiomers are easily accessible. Curiously, while many organic molecules were built into lamellar solids,[5] among them many were mono- or dicarboxylic acids;[6] amino acids were rarely targeted. Even when they were the intercalated species their anionic forms were used (the host material was a layered double hydroxide).[7] Their amphoteric character was utilized only in one instance, when glycine *zwitterion* was intercalated by vanadyl and niobyl phosphate.[8]

When pillaring is attempted by amino acids, very interesting intercalated materials may emerge. 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.

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

Experimental Section

The guest materials, L-phenylalanine ($pI = 5.5$) and L-tyrosine ($pI = 5.7$) were 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 mequiv/100 g). The other, Zn−Al hydrotalcite (HT), was prepared on the basis of Taylor's method.[9] The pH of 250 cm^3 0.1 mol/dm^3 $Al(NO_3)_3$ solution was adjusted to 7.0 with the addition of the appropriate amount of a solution containing 0.8 mol of Na_2CO_3 and 1.6 mol of NaOH in 1 dm^3 water. After stirring for 1 h, 250 cm^3 0.3 mol/dm^3 $Zn(NO_3)_2$ solution was added dropwise. The pH of the slurry was kept at 6.0−6.5 by addition of the appropriate amount of the alkaline solution described above. After the complete delivery of Zn^{2+}

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(1) Szostak, R.; Ingram, C. *Stud. Surf. Sci. Catal.* **1995**, *94*, 13.

(2) (a) Burch, R. *Catal. Today* **1987**, *2*, 185. (b) Figueras, F. *Catal. Rev. Sci. Eng.* **1988**, *30*, 457.

(3) de Roy, A.; Forano, C.; El Malki, K.; Besse, J.-P. In *Synthesis of Microporous Materials Vol II: Expanded Clays and Other Microporous Solids*; van Nostrand Reinhold: New York, 1992; p 108.

(4) Jones, W.; Chibwe, M. In *Pillared Layer Structures: Current Trends and Applications*; Mitchell, I. V., Ed.; Elsevier Applied Science: London and New York, 1991; p 67.

(5) Ogawa, M.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2593.

(6) Carlino, S. *Solid State Ionics* **1997**, *98*, 73.

(7) Whilton, N. T.; Vickers, P. J.; Mann, S. *J. Mater. Chem.* **1997**, *7*, 1623.

(8) Zima, V.; Beneš, L.; Melánová, K. *Solid State Ionics* **1998**, *106*, 285.

(9) Taylor, R. M. *Clay Miner.* **1984**, *19*, 591.

10.1021/ic981176t CCC: $18.00

Table 1. Characteristic Data on the Host Materials and the Intercalated Structures

samples	basal spacing[a]/nm	BET area/m^2 g^{-1}
Na-montmorillonite	1.20	58.6 (393 K)[b]
L-Tyr-montmorillonite	1.46	71.1 (393 K)
L-Phe-montmorillonite	1.49	93.5 (393 K)
		40.6 (473 K)
		42.1 (573 K)
		29.8 (673 K)
hydrotalcite	0.89	83.0 (393 K)
L-Tyr-hydrotalcite	1.75	101.2 (393 K)
L-Phe-hydrotalcite	1.80	96.4 (393 K)

[a] Calculated from the d(001) reflection for the montmorillonite and the d(003) reflection for the hydrotalcite derivatives. [b] Temperature of evacuation for 3 h.

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 an 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^3 HCl solution. Then, the aqueous solution of the amino acid was mixed into it with vigorous 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. An HT aqueous suspension was prepared, and its pH was set to 8 by 0.1 mol/dm^3 NH_4OH solution. The aqueous solution of the amino acid was mixed into it with 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, washed free of excess (deprotonated) amino acid and dried in air.

XRD measurements were performed on a DRON 2 powder X-ray diffractometer using Cu Kα radiation. Diffractograms of the air-dried samples were registered. The reflections of the host materials were indexed,[10,11] and their shifts after intercalation were followed. Basal spacings were determined from the position of the d(001) reflection (Na-mont, L-Phe-mont, and L-Tyr-mont) or the d(003) reflection (HT, L-Phe-HT, and L-Tyr-HT). Data are in the second column of Table 1.

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. For L-Phe-montmorillonite various other temperatures were also applied (473, 573, and 673 K). Data are listed in the third column of Table 1.

The KBr pellet technique (1 mg of sample in 200 mg of KBr) was applied for monitoring changes in the IR spectra of the samples (Figures 3 and 4). The FT-IR spectra of the host and guest materials and the host−guest complexes were taken and compared. The 4000−500 cm^{-1} range was investigated. Spectra were recorded by a Mattson Genesis I spectrophotometer with 2 cm^{-1} resolution.

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 an inert gas flow (Ar) from 293 to 1300 K with a 10 deg/min temperature ramp. The DTG curves are depicted in a way to allow comparisons among the host, guest, and intercalated materials (Figures 5 and 6). The evolving substances were qualitatively analyzed by a Hewlett-Packard 5890 gas chromatograph equipped with a quadrupole mass-selective detector. There was a heated empty column in the GC.

Thermal behavior of the intercalated materials was monitored by FT-IR spectroscopy as well, on the same spectrophotometer in the 4000−800 cm^{-1} range with 2 cm^{-1} resolution. Self-supported wafers were pressed from the intercalated materials, and they were subjected to 3 h pretreatments in a vacuum at various temperatures, in the 293−773 K range with 100 deg increments. Spectra corresponding to L-Tyr-HT and L-Phe-HT are depicted in Figure 7, while spectra concerning L-Tyr-mont and L-Phe-mont are in Figure 8.

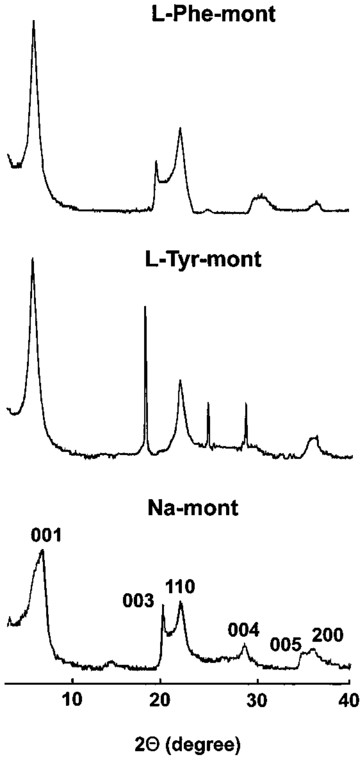

Figure 1. Powder XRD spectra of Na-montmorillonite (Na-mont), L-tyrosine-montmorillonite (L-Tyr-mont) and L-phenylalanine-montmorillonite (L-Phe-mont).

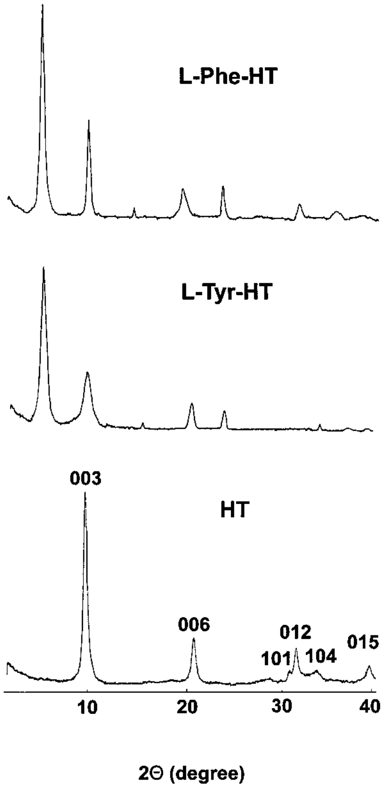

Figure 2. Powder XRD spectra of Zn−Al hydrotalcite (HT), L-tyrosine-Zn−Al hydrotalcite (L-Tyr-HT), and L-phenylalanine-Zn−Al hydrotalcite (L-Phe-HT).

A schematic model (Scheme 1) for visualizing the possible spatial arrangement of the amino acid (protonated or deprotonated) was built

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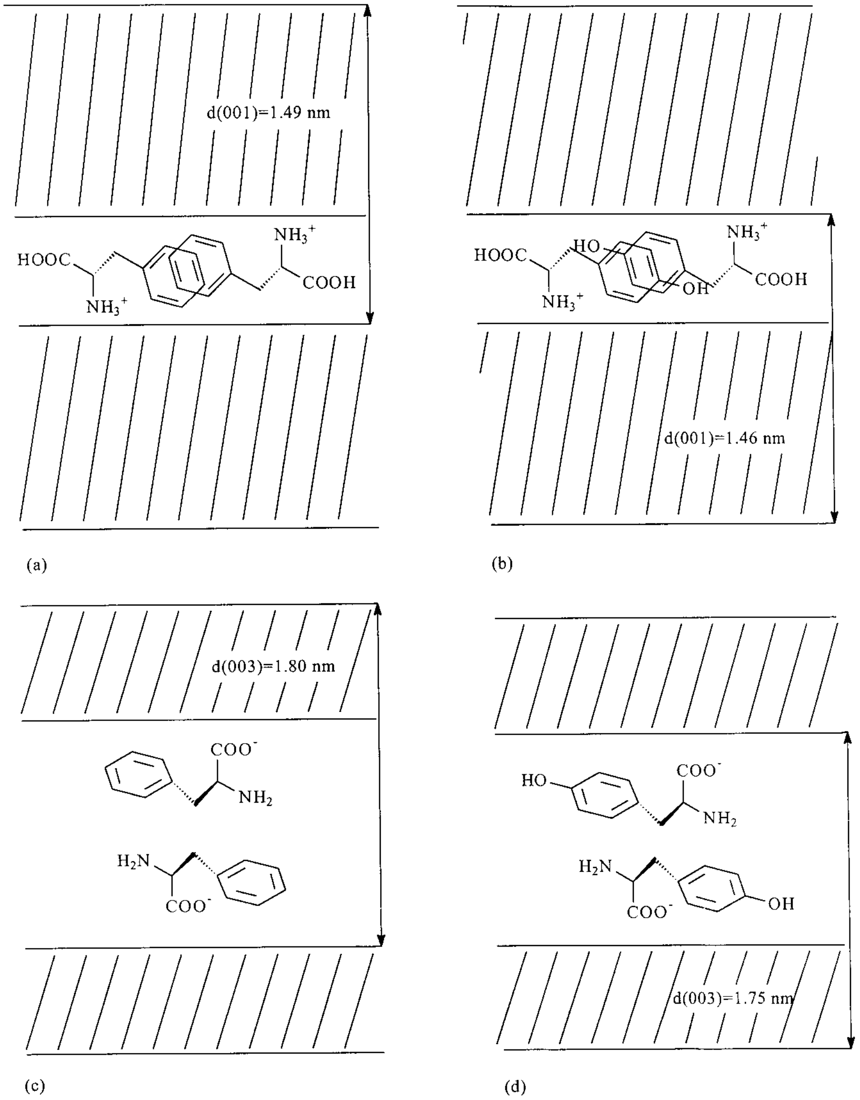
(10) Nemecz, E. *Clay Minerals*; Akadémiai Kiadó: Budapest, 1981; p 170.

(11) Barriga, C.; Jones, W.; Malet, P.; Rives, V.; Ulibarri, M. A. *Inorg. Chem.* **1998**, *37*, 1812.

Scheme 1. Spatial Arrangement of the Intercalated Ions of (a) L-Phenylalanine in Montmorillonite, (b) L-Tyrosine in Montmorillonite, (c) L-Phenylalanine in Hydrotalcite, and (d) L-Tyrosine in Hydrotalcite



with the help of the AM1 semiempirical method[11] included in the Hyperchem 4.5 package.[12] The protonated and deprotonated derivatives of L-Phe and L-Tyr were optimized with the routine, and the sizes of the ions were measured and used in constructing the model.

Results and Discussion

Comparison of the XRD spectra of hosts and the modified substances made clear that the structures of the hosts were altered only in one direction on treatment with the appropriate forms of the amino acids (Figures 1 and 2). Only the positions of the 00*x* (*x* is a positive integer) reflections for the modified montmorillonite and those of the 00(3*x*) reflections of the modified hydrotalcite were changed. The 110 and 200 reflections for montmorillonite and the 101 and 104 reflections for hydrotalcite remained unaltered upon treatment with the amino acids.

This means that the basic structures of the hosts are kept, the layers only propped open, and the basal distances increased significantly (Table 1, column 2), providing evidence that intercalation has occurred. For hydrotalcite this increase was always substantially larger than for montmorillonite. Even though the intercalated material (the protonated or unprotonated amino acids) did not form a separate phase seen by XRD, the varying but always substantial increase in the basal spacings is an obvious indication that the spatial arrangement of the amino acid moieties is very different in the clay-based or the hydrotalcite-based intercalated materials.

There was a significant increase in the BET surface when montmorillonite was used as host; however, in the case of hydrotalcite, although there was an increase, it was considerably smaller (Table 1, column 3). Let us note that the temperature of pretreatment may not be sufficient to fully remove chemisorbed water (Table 1, column 3). Elevating the temperature of pretreatment would seem beneficial in this respect; however, the intercalated substances, especially those based on hydrotalcite, are very temperature sensitive, and deintercalation easily occurs.

The FT-IR spectra of the guest materials, the parent amino acids from which the guest ions are derived, and the intercalated substances are collected in Figures 3 and 4 (the KBr pellet technique was used).

When the spectra of L-Phe, L-Phe-mont, and Na-mont are compared, certain differences can be observed. In the region above 3000 cm^{-1}, the second band at 3410 cm^{-1} became more

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(12) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

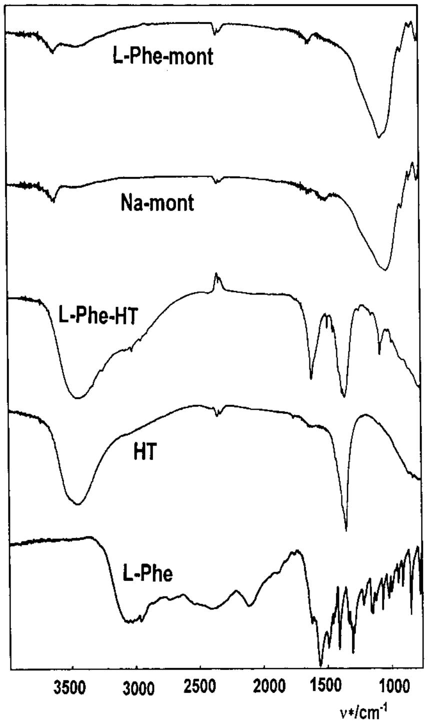

Figure 3. FT-IR spectra of the air-dried montmorillonite and hydrotalcite intercalated L-phenylalanine, protonated and deprotonated, respectively, the guest substances and the pure amino acid (KBr technique).

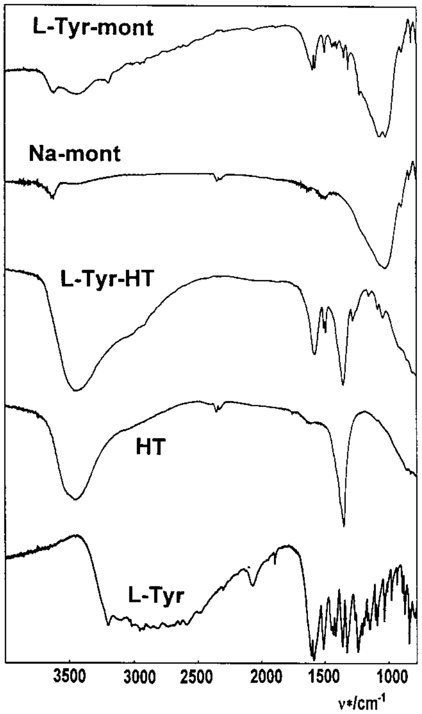

Figure 4. FT-IR spectra of the air-dried montmorillonite and hydrotalcite intercalated L-tyrosine, protonated and deprotonated, respectively, the guest substances and the pure amino acid (KBr technique).

pronounced in the intercalated material than it was in the host Na-mont, just as the band at 1643 cm^{-1}. This latter one coincides with an intense band of L-Phe-HT and the pure L-Phe, and it does not appear in the amino acid free HT spectrum. The appearance of this band may be taken as the sign of successful intercalation. There are no significant differences in the OH region of the spectrum for L-Phe-HT and HT indicating that the deprotonated form takes part in the intercalation process. However, another sharp band at 1007 cm^{-1} is seen in the spectra of L-Phe-HT, and it is not in that of HT. This band again coincides with a band in the spectrum of pure Phe.

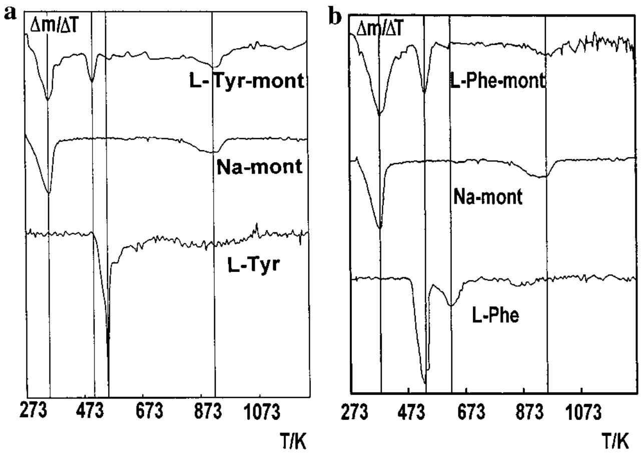

Figure 5. DTG curves (100 mg of sample, 10 deg/min temperature ramp) of (a) L-tyrosine (L-Tyr), Na-montmorillonite (Na-mont), and L-tyrosine-montmorillonite (L-Tyr-mont) and (b) L-phenylalanine (L-Phe), Na-montmorillonite (Na-mont), and L-phenylalanine-montmorillonite (L-Phe-mont).

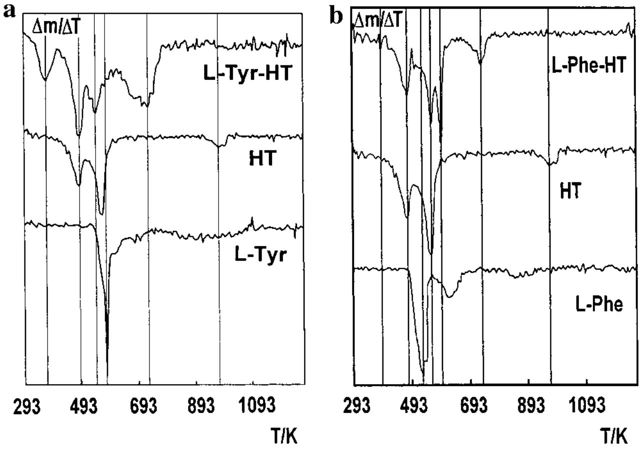

Figure 6. DTG curves (100 mg of sample, 10 deg/min temperature ramp) of (a) L-tyrosine (L-Tyr), Zn−Al hydrotalcite (HT), and L-tyrosine-Zn−Al hydrotalcite (L-Tyr-HT) and (b) L-phenylalanine (L-Phe), Zn−Al hydrotalcite (HT), and L-phenylalanine-Zn−Al hydrotalcite (L-Phe-HT).

Very similar but more spectacular observations may be made when the spectra of L-Tyr-mont, Na-mont, L-Tyr-HT, HT, and L-Tyr are compared (Figure 4). Here, again, the band at 3410 cm^{-1} becomes intense in L-Tyr-mont. Moreover, the fine structure of the band in the 1650−1100 cm^{-1} range closely resembles that portion in the spectrum of L-Tyr. In the 3700−3000 cm^{-1} region the spectra of L-Tyr-HT and HT are also very similar: obviously the carboxylate form was intercalated. The intense peaks in the spectrum of L-Tyr-HT at higher wavenumbers than 1400 cm^{-1} are signs of successful intercalation as well. They are not observed in the spectrum of HT.

Physisorbed water could largely be removed by the 3h evacuation at 393 K, as the low-temperature peak (378 K) in the DTG curves of the intercalated structures attest (Figures 5 and 6).

DTG profiles of L-Tyr-mont or L-Phe-mont (Figure 5a,b, topmost curves) are similar to each other and are significantly simpler than those of L-Tyr-HT or L-Phe-HT (Figure 6a,b, topmost curves). They are roughly the superposition of the host

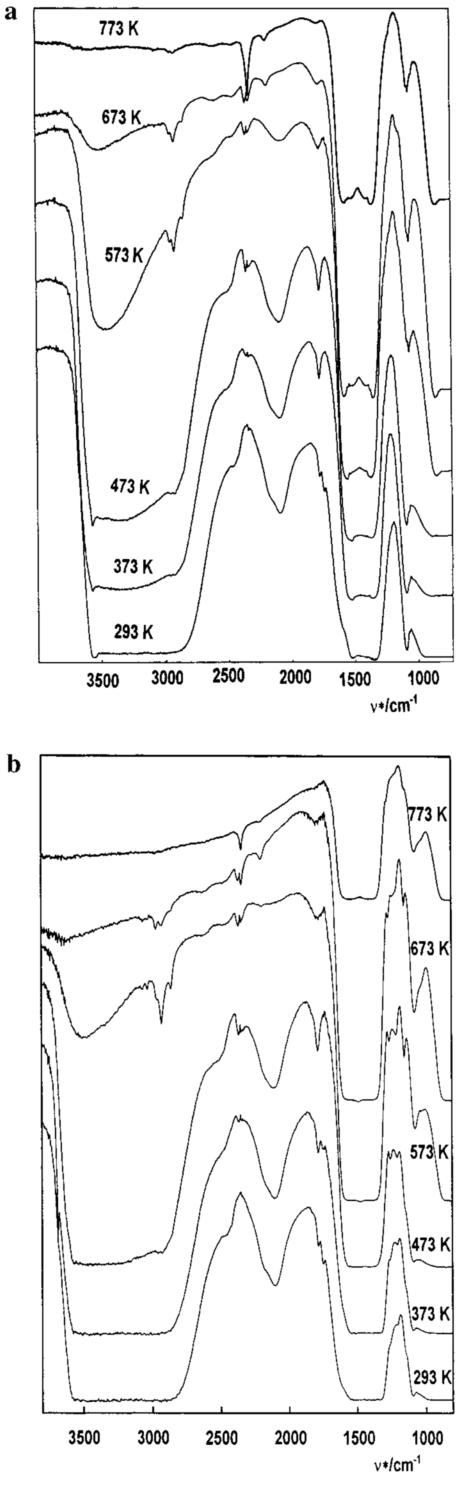

Figure 7. FT-IR spectra of (a) L-tyrosine-Zn–Al hydrotalcite (L-Tyr-HT) and (b) L-phenylalanine-Zn–Al hydrotalcite (L-Phe-HT) treated in a vacuum at various temperatures for 3 h (in transmittance, self-supported wafers).

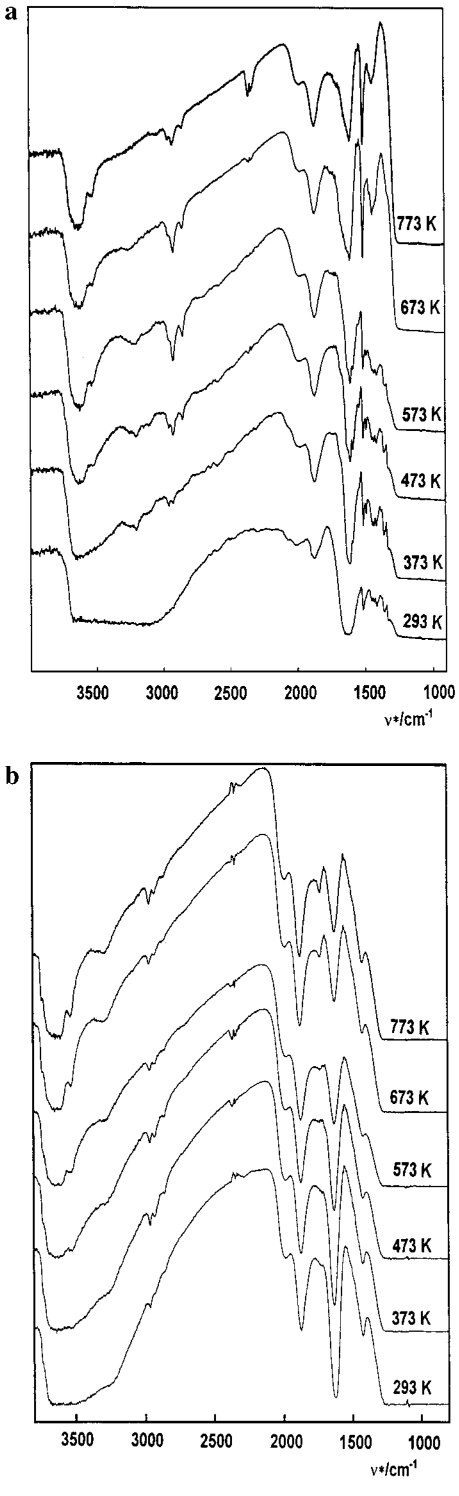

Figure 8. FT-IR spectra of (a) L-tyrosine-montmorillonite (L-Tyr-mont) and (b) L-phenylalanine-montmorillonite (L-Phe-mont) treated in a vacuum at various temperatures for 3 h (in transmittance, self-supported wafers).

material and the (parent) guest compounds. Obviously, protonated tyrosine and phenylalanine are the intercalated agents; therefore, it may be expected that the weight loss peak (the loss of the carboxylic group) is not exactly at the same temperature for the pure acids as in the intercalated structures. L-tyrosine loses CO_2 around 528 K; with L-Tyr-mont it occurs around 578 K. Decarboxylation of L-Phe takes place in (at least) two steps. The first one is around 540 K (the curve may be resolved to two components), and the second, smaller one is around 623 K. L-Phe-mont also decarboxylates in one major step, which involves dehydroxylation as well (CO_2 as well as H_2O could be detected.) The layered structure collapses by 1000 K.

The basic features in the DTG curve of L-Tyr-HT, L-Phe-HT, and HT, at least in the low-temperature region, may be rationalized 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 intercalated substances) further dehydroxylation takes place. Deintercalation and the collapse of the layered structure of L-Tyr-HT or L-Phe-HT take place, however, at lower temperature than that of HT (around 900 K). These transformations peak around 710 K for both materials, and they are final before 800 K. The process is over at lower temperature in the case of L-Phe-HT. By inspecting the shape of the curve it seems to be less complicated than that of L-Tyr-HT, but analysis of the evolving products reveals that structural dehydroxylation (leading to the collapse of the layered structure) and decarboxylation (leading to deintercalation) are overlapping processes for both materials. All in all, the intercalated substances are thermally less stable than the host material.

The FT-IR spectra of the heat-treated samples (self-supported wafers were used) demonstrate clearly visible changes for L-Tyr-HT (Figure 7a) and L-Phe-HT (Figure 7b). The indicative absorption is at 2066 cm^{-1}. This band is intense at low temperatures and disappears above 573 K. At the same time gradual dehydroxylation takes place. Deintercalation seems to be complete by 673 K, while even the layered structure seems to be collapsed by 773 K. Comparison of the intensities of these peaks after the pretreatment at 573 K indicates that deintercalation is easier for L-Phe-HT than for L-Tyr-HT. On heat treatment, changes in the region above 3000 cm^{-1} are also observed. The band sharpens as dehydroxylation proceeds. By 773 K it disappears completely. Dehydroxylation is easier for L-Phe-HT once again; here the band is hardly seen even after treatment at 673 K.

Intercalation was successful in the case of L-Tyr-mont and L-Phe-mont as well. It is attested by the broad complex band in the 3600−3200 cm^{-1} region (stretching vibrations of variously associated carboxylic OH) and the doublet in the 2020 and 1880 cm^{-1} region (Figure 8). Changes occurred in the OH region of both intercalated materials on heat treatment. The peaks are sharpened, indicating water desorption, dehydroxylation, and partial decarboxylation. However, complete deintercalation did not occur even after a 3 h curing at 773 K. Neither did the layered structure collapse. The intercalated structure remained largely intact even after this relatively high temperature treatment, as the virtually unchanged doublet also attests.

These findings for the four intercalated substances are in good agreement with those based on the DTG curves.

Differences in basal distances and the significant alterations in the spectra of cation or anion intercalated structures clearly show that protonated and deprotonated forms are arranged differently between the layers of the guest materials. Semiempirical quantum chemical (AM1) calculations gave numerical data as far as ionic dimensions of the amino acid ions are concerned. Data in nanometers for the minimum structures of protonated and deprotonated L-Phe are 0.53 × 0.40 × 1.11 and 0.59 × 0.38 × 0.88, respectively. Interlayer spacings for L-Phe-mont and L-Phe-HT are 0.53 and 1.32 nm, respectively. They were calculated from the measured basal distances, taking into account the thickness of the layer (for montmorillonite, 0.96 nm;[14] for the Zn−Al LDH, 0.48 nm[15]). Similar data for L-Tyr are 0.51 × 0.41 × 1.07 (protonated), 0.59 × 0.39 × 0.96 (deprotonated) and 0.50 nm (L-Tyr-mont), 1.27 nm (L-Tyr-HT). Although the calculated data can only be taken as approximations, since the conformation of the intercalated species may be different from the isolated ones, still dimensions probably would not be influenced dramatically. Thus, knowing that the directions of the charged functional groups are perfect for the protonated species and good for the anions (actually they are directed toward the body diagonal of the imaginary parallelepiped containing the anions), models for the spatial arrangement of the anionic or cationic pillars may be given. It is depicted schematically in Scheme 1.

Even keeping in mind the above-described limitation, it seems to be clear that one layer of protonated amino acid fits into the interlayer space of montmorillonite. This layer is possibly structured. A driving force is the negative charge of the layers. C−H···π interaction may be the other one. It may arise between two aromatic rings. This means that the rings of the two protonated amino acids are not face to face (as misleadingly the schematic representation suggests), but somewhat shifted relative to each other.

Two layers of deprotonated amino acids fit into the interlayer space of HT. They are also structured. Electrostatic repulsion makes the arrangement depicted in the scheme highly probable.

Conclusions

L-tyrosine and L-phenylalanine in their protonated and deprotonated forms can be intercalated between the layers of montmorillonite and hydrotalcite, respectively. The thermal behavior of the intercalated materials shows the features of the host as well as the guest materials. The thermal stability of (L-amino acid)-mont remained the same as that of Na-mont; however, (L-amino acid)-HT became significantly less stable than hydrotalcite. On the basis of XRD data, IR spectra, and common chemical sense (supported by calculations), a model can be given for the spatial arrangement of the pillars. If the intercalated materials can be made more sturdy and the pillar density is optimized, there is a good chance to use them as chiral catalysts in a wide variety of acid−base reactions.

Acknowledgment. This work was supported by the National Science Foundation of Hungary via Grant T016941. The financial help is highly appreciated.

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(13) *Hyperchem 4.5*; Hypercube Inc.: Gainesville, FL, 1994.

(14) Izumi, Y.; Urabe, K.; Onaka, M. *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*; Kodansha, VC: Tokyo, Weinheim, New York, Cambridge, Basel, 1992; p 53.

(15) Kuk, W.-K.; Huh, Y.-D. *J. Mater. Chem.* **1997**, *7*, 1933.