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Thermal and Spectroscopic Analysis of a Fatty Acid-Layered Double-Metal Hydroxide and Its Application as a Chromatographic Stationary Phase

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The thermal and spectroscopic properties of myristic acid-exchanged lithium aluminum layered double metal hydroxide is examined. In an anaerobic environment, the layered structure is stable up to 250 °C. Differential thermal analysis indicates that in this temperature range there is partial dehydroxylation of the metal layer. This results in a material of considerably higher surface area. The myristic acid chains after heat treatment assume a disordered state, which is retained upon cooling the sample. The high porosity and the hydrophobicity make this material a candidate for a stationary phase in gas chromatography.

Introduction

The structure and properties of hydrophobic molecules in layered clay materials have been extensively investigated and enjoy a considerable amount of technological use.[1] In the case of smectite clays, long-chain organic molecules containing cationic functionalities such as tetraalkylammonium ions can be readily ion-exchanged into the interlayers.[2] These organic clays have been used in environmental applications, as selective adsorbents, fillers, and as stationary phases in gas chromatography.[3] An example of a commercial clay stationary phase is Bentone 34, which is composed of dimethyldioctadecylammonium salt exchanged into a smectite mineral, montmorillonite.[4] Bentone 34 is one of the most popular stationary phases used in packed-column gas chromatography for the separation of aromatic isomers. Problems associated with these stationary phases are limited selectivity (they must often be combined with conventional liquid stationary phases), and thermal instability. Most clays must also be chemically treated, purified, and size fractionated before they are used. Thus, there is considerable interest in exploring the properties of new materials.

The group of compounds belonging to the class of layered double metal hydroxides, such as hydrotalcites, represent a system complementary to that of smectite clays. In these compounds the layers containing the metal are positively charged, with anions existing between the layers.[5] Various metal combinations, with structures represented by the formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]A^{n-}_{x/n}\cdot zH_2O$, where M^{II} = Mg, Zn, Fe, Co, Ni, Cu and M^{III} = Al, Cr, Fe make up the metal hydroxide layer, whereas A^{n-} are the anions occupying the interlayers. These materials are finding use as catalysts, ion-exchangers, antacids, and selective adsorbents and are beginning to show potential similar to the widely used smectite clays.[6] $LiAl_2(OH)_6{}^+A^-$ is also an example of a layered double-metal hydroxide (LDH),[7] whose properties have been extensively investigated in our group.[8] It is composed of sheets of lithium and aluminum atoms octahedrally surrounded by hydroxyl groups. The charge balancing anions between the interlayers can easily be exchanged with a wide variety of inorganic, organic, and organometallic ions.[8,9]

The lithium and aluminum atoms are ordered within the layer. A hexagonal unit cell is appropriate for indexing the diffraction pattern,[9a] though recently, a monoclinic cell has been suggested.[9j,k] The high charge density (25 Å^2/unit charge)[8a] distinguishes this material from smectite clays.[1] Previous studies have shown that a hydrophobic environment can be created in the interlayer region of LDHs by exchanging long-chain

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organic molecules into the interior.[10] Fatty acid exchanged LiAl−LDHs display interesting properties, such as formation of bilayers and the ability to swell with an increase in temperature.[11]

In this paper, we continue to explore the properties of fatty acid exchanged LiAl−LDHs, focusing mainly on the disorder created by high-temperature treatment of this material. In particular, the structure and dynamics of myristic acid ($CH_3(CH_2)_{12}COOH$) exchanged lithium aluminate (LiAl−LDH−MA) are examined. We have previously shown that as-prepared LiAl−LDH−MA can partition polycyclic aromatic hydrocarbons from solution phase,[11b] and in this study we examine gas chromatography as a way of determining accessibility of the hydrophobic interlamellar region of thermally treated LDHs to organic molecules from the vapor phase. This also establishes the potential of these materials as novel stationary phases.

Experimental Section

The preparation of LiAl−LDH−Cl has been described previously.[7,11] Sodium hydroxide (0.4 mol) was dissolved in nanopure water, followed by the slow addition of aluminum powder (0.10 mol) and then lithium chloride (0.50 mol). This mixture was heated for several days at 100 °C, filtered, and then stirred with 100 mL of 0.50 M sodium chloride for 24 h. The final product was filtered, washed with water, and stored wet. Care was taken to exclude CO_2 from all solutions. The chloride LDH was washed with ethanol, followed by the exchange of myristic acid from a 0.10 M ethanolic solution. The lithium myristate salt was synthesized by neutralizing the acid with LiOH. The aluminum myristate salt was prepared by exchanging sodium myristate (Sigma, 0.0005 mol) with a solution of 0.7 M $AlCl_3 \cdot 6H_2O$.

All thermal treatments were carried out under N_2 in a calcination chamber. Samples were also cooled under N_2 to room temperature before being exposed to air. Infrared spectra were recorded on a Mattson Cygnus FTIR spectrometer, and powder diffraction patterns were taken with a Rigaku Geigerflex D/Max 2B diffractometer using Ni filtered Cu Kα radiation, under ambient conditions. A Micromeritics Pulse Chemisorb 2700 was used to measure BET surface areas. Thermal analysis was performed using a Seiko simultaneous TG/DTA, Model 320. Experiments were conducted at a heating rate of 10 °C/min under an argon atmosphere.

The chromatographic packing materials were created by adding Chromosorb WHP (Supelco, 60/80 mesh), to myristic acid or myristate salt (lithium) dissolved in ethanol, or myristic acid exchanged LDH dispersed in ethanol or toluene. The solvent was evaporated, and the material was air dried overnight. The loadings were varied from 5 to 20% (LDH, myristic acid or salt/Chromosorb, w/w), in each case. Besides an increase in retention at higher loadings, no appreciable differences in chromatographic behavior were observed with respect to percent of sample on Chromosorb. All of the chromatographic work in this paper was performed with stationary phases at a loading of approximately 10%. Approximately 1.25 g of the stationary phase/support was packed into a 1.2 m section of 2.2 mm i.d. stainless steel tubing. The ends were plugged with glass wool, and the column conditioned for 12 h under helium flow in the gas chromatograph (Hewlett-Packard 5890). For the separations, the oven temperature and flow rate were kept constant at 70 °C and 30 mL/min, respectively. The analytes used were either a mixture of equal volumes of neat liquids or this mixture diluted in isooctane. Sample injection amounts were between 0.1 and 0.4 μL.

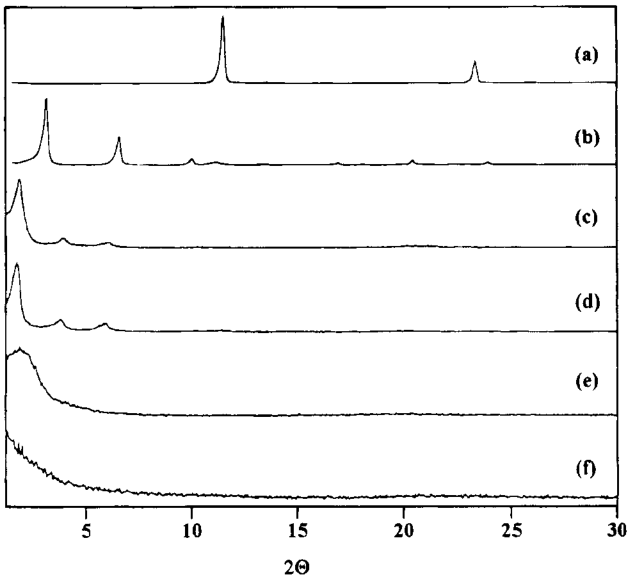

Figure 1. X-ray diffraction patterns of (a) LiAl−LDH−Cl and LiAl−LDH−MA heat treated at (b) 25, (c) 100, (d) 150, (e) 250, and (f) 300 °C. (Samples were cooled to room temperature in a N_2 atmosphere before the XRD pattern was collected.)

Results

LiAl−LDH−MA samples were heated up to 450 °C under anaerobic conditions. Structural changes brought about by this treatment were investigated by diffraction, thermal analysis, and infrared spectroscopy under ambient conditions.

Diffraction. The X-ray diffraction pattern (XRD) for thermally treated myristic acid exchanged LDH is displayed in Figure 1. The regularly spaced reflections are assigned as (00*l*) reflections. The powder pattern has been indexed with both a double- and triple-layer stacking to form the unit cell.[9a,k] The interlayer spacing can be calculated from the basal spacing by subtracting the thickness of the framework, 4.8 Å.[7,8a] After exchange of the LDH with myristic acid, the interlayer spacing increases from 2.8 to 21.5 Å (Figures 1a,b) which corresponds to a distinct monolayer of myristic acid molecules oriented perpendicular to the hydroxyl layers. Figures 1c−e shows that heat treatment results in a steady increase in interlayer spacing, which reaches a maximum of approximately 43 Å at 250 °C. The diffraction patterns are recorded at room temperature after heat treatment. At temperatures higher than 250 °C, the material appears to have lost long range order. Upon heat treatment beyond 100 °C, there appears a weak, broad, diffuse reflection at 2θ between 20 and 25°, whose relative intensity remains unaltered in samples heated to 300 °C. This amorphous material is probably arising from decomposition of the small amounts of unexchanged LiAl−LDH−Cl (note reflection at $2\theta = 12°$ in Figure 1b).

Thermal Analysis. The thermal gravimetric (TGA) and differential thermal analysis (DTA) of the LiAl−LDH−MA is displayed in Figure 2. The DTA trace displays four separate endothermic peaks at 75, 219, 317, and 404 °C, accompanied by weight losses in the TGA curve corresponding to 10, 16, 7, and 32% respectively.

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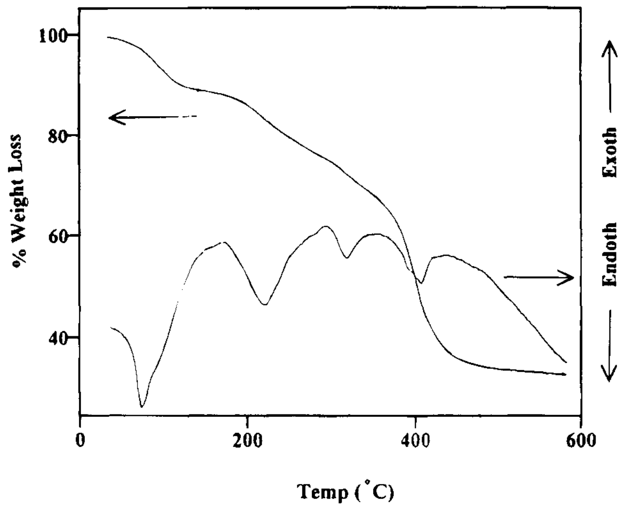

Figure 2. Thermal gravimetric and differential thermal analysis of LiAl−LDH−MA.

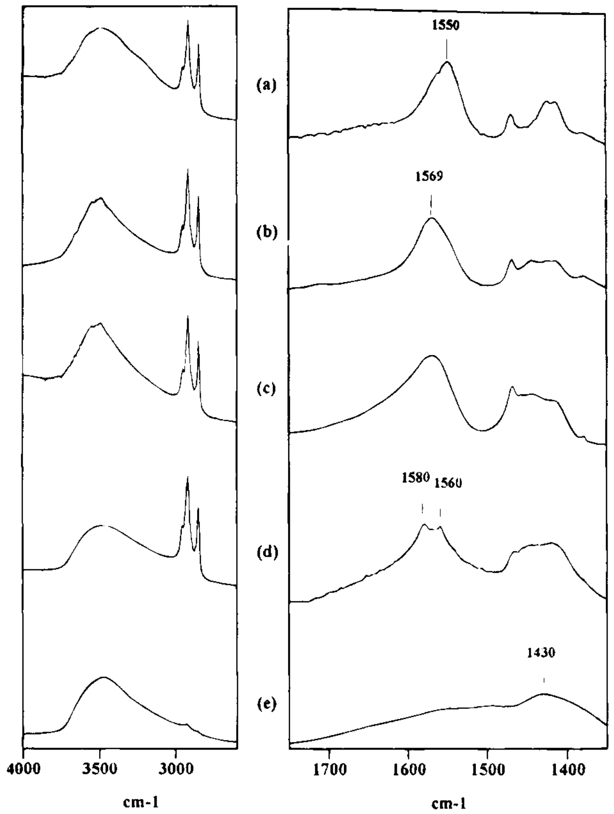

Figure 3. Infrared spectra of LiAl−LDH−MA as a function of conditioning temperature; (a) 25, (b) 100, (c) 150, (d) 250, and (e) 300 °C. The spectra were collected at room temperature.

Infrared Spectroscopy. The FTIR spectra of the thermally treated LiAl−LDH−MA recorded at room temperature are presented in Figures 3 and 4 and contains five major regions of interest:[12,13]

(1) 4000−3000 cm^{-1}: OH stretching region due to the hydroxyl groups associated with the framework of the LDH, and any solvent ethanol associated within the interlayers.

(2) 3000−2800 cm^{-1}: CH stretching region of the myristic acid exchanged in the interlayer.

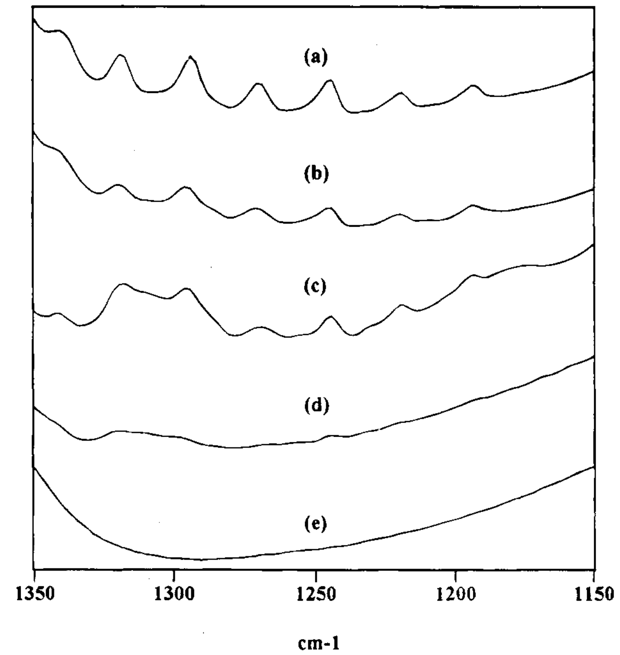

Figure 4. Infrared spectra of LiAl−LDH−MA as a function of conditioning temperature in the CH_2 wagging region; (a) 25, (b) 100, (c) 150, (d) 250, and (e) 300 °C. The spectra were collected at room temperature.

(3) 1750−1350 cm^{-1}: COO^- asymmetric and symmetric stretches of the head group of the exchanged acid occur at 1550 and 1425 cm^{-1}, respectively. In addition, CH_2 rocking modes are present at 1468 and 1414 cm^{-1}.

(4) 1350−1150 cm^{-1}: CH_2 wagging region. These bands arise due to the primarily trans configuration of the alkyl chains, and are intensified due to coupling with the CO stretch (Figure 4).

(5) 1150−350 cm^{-1}: region is composed of framework structure bands[8a,9a] due the Al-O (stretching) at 753 cm^{-1} and Al−O (bending) at 535 cm^{-1} and a band due to the framework hydroxyl group OH bending motion at 950 cm^{-1}. This region of the spectrum is not shown.

LiAl−LDH−MA as a Partitioning Media for Gas Chromatography. The interaction of organic molecules from the gas phase with the thermally treated LiAl−LDH−MA was examined. The analyte test mixture was an equal volume mixture of isooctane, benzene, toluene, ethylbenzene, and *p*-, *m*-, and *o*-xylene (boiling points of 99, 80, 111, 136, 137, 139, and 144 °C, respectively).[14] The columns were prepared by coating the LDH on Chromosorb (a diatomaceous earth support) as described in the Experimental Section and then conditioned at different temperatures prior to separating the analytes at an oven temperature of 70 °C. Several stationary phases were used as blanks to verify that the interaction of the analytes with the LDH was mainly determined by the interlayer exchanged myristic acid. Figure 5 shows the separation of the analytes achieved with the various stationary phases.

A column consisting of just Chromosorb, conditioned at temperatures between 150 and 250 °C showed absolutely no retention for the analytes, with all of the components eluting with air. Figures 5a,b shows the results with a column consisting of 10 wt % LiAl−LDH−Cl coated on Chromosorb W conditioned at 70 and 250

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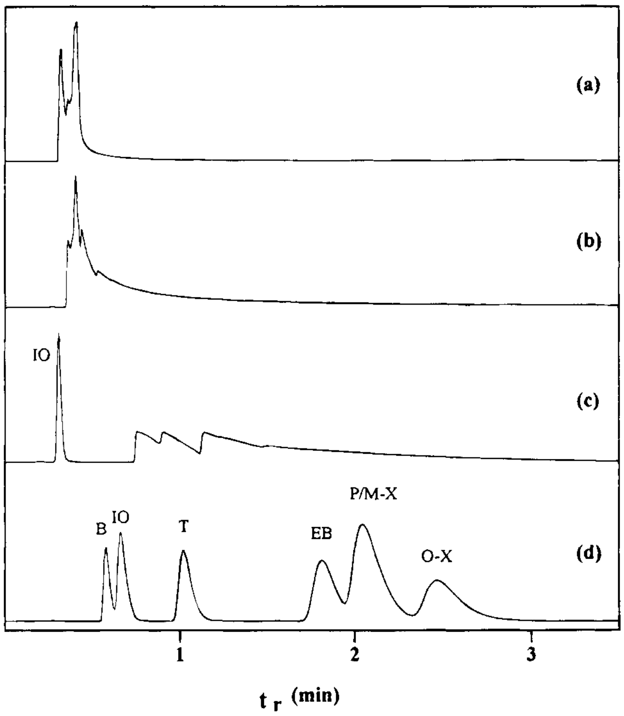

Figure 5. Separation of isooctane (IO),benzene (B), toluene (T), ethylbenzene (EB), *p*-xylene (P-X), *m*-xylene (M-X), and *o*-xylene (O-X) using the following stationary phases: (a) LiAl−LDH−Cl, (b) LiAl−LDH−Cl conditioned at 250 °C, (c) LiAl−LDH−MA conditioned at 150 °C, and (d) LiAl−LDH−MA conditioned at 250 °C. The temperature of the GC oven was 70 °C in all cases.

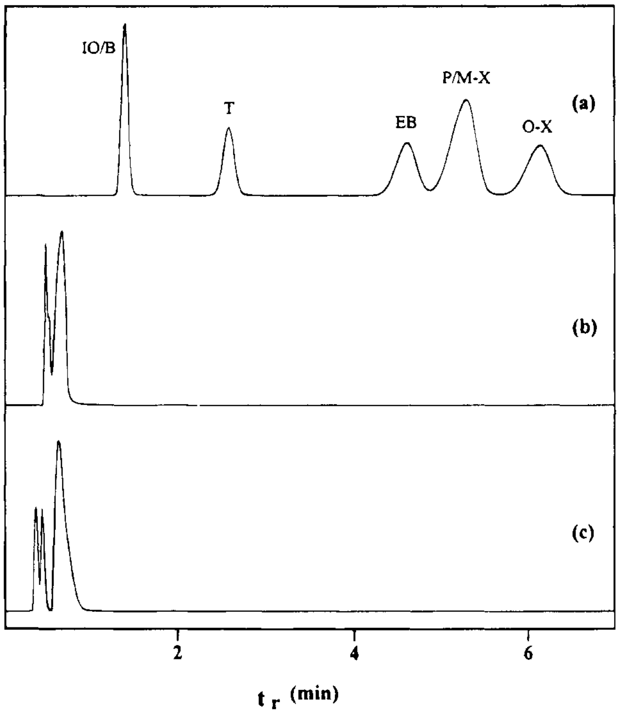

Figure 6. Separation of isooctane (IO), benzene (B), toluene (T), ethylbenzene (EB), *p*-xylene (P-X), *m*-xylene (M-X), and *o*-xylene (O-X) using the following stationary phases: (a) myristic acid, (b) myristic acid conditioned at 150 °C, and (c) lithium myristate as stationary phases. The temperature of the GC oven was 70 °C in all cases.

°C. At 70 °C, the LDH is intact with an interlayer spacing of 2.8 Å. This is barely large enough to accept the analyte molecules even in parallel orientation with the LDH framework. Thus, it is not surprising that very little retention is displayed, and the molecules essentially elute together. At 250 °C, the LiAl−LDH−Cl is an amorphous material, as evidenced by diffraction and infrared data, and the chromatogram is similar to that at 70 °C.

Figure 5c,d shows the chromatograms with LiAl−LDH−MA conditioned at temperatures of 150 and 250 °C. At a conditioning temperature of 150 °C, there is a separation of the analytes, but with significant amount of tailing in the chromatogram. For this material, the peak shapes are also dependent upon the concentration of the analytes. As the concentration of the aromatic analytes is reduced, by diluting the mixture of neat compounds to a 2.5% solution in isooctane (v/v), the capacity factors of all analytes increase, and the amount of tailing decreases significantly (data not shown). This is indicative of a nonlinear isotherm, thus implying a type of adsorption interaction with the LDH. Since the retention increases at these lower concentrations, there are probably a limited number of adsorption sites, which could be the myristic acid groups exchanged on the surface of the LDH.

At a conditioning temperature of 250 °C, several changes occur. The peak shapes become Gaussian in nature, the capacity factors increase, and the retention order closely follows the boiling points of the components, with the *m*- and *p*-xylene isomers coeluting before *o*-xylene. Also, there is no longer a change in the capacity factors or peak shapes at lower concentrations, as compared to the 150 °C treated material. Assuming partitioning, the plate height is calculated to be approximately 9.0×10^{-4} m.[15]

Two other stationary phases, consisting of free myristic acid and the lithium salt of myristic acid coated on Chromosorb, were also investigated. As seen in Figure 6a, the chromatogram using the free myristic acid column conditioned at 70 °C displays peaks with a Gaussian profile, with a selectivity that is very similar to that of the 250 °C heat treated LiAl−MA−LDH. As the conditioning temperature was increased to 150 °C, the capacity factors of the analytes gradually decreased over a period of 12 h until the column displayed very little retention for all components (Figure 6b). Infrared spectra of the stationary phase before and after conditioning (not shown) reveal that most of the free acid is desorbed from the Chromosorb support at temperatures above 140 °C. In the case of Li−myristate salt as the stationary phase (Figure 6c), no appreciable retention occurred for any of the analytes studied. The conditioning temperature was varied from 70 to 300 °C, with little effect on the chromatogram. These experiments were repeated using fatty acids of different lengths, from decanoic (10 carbons) to palmitic acids (16 carbons), in addition to using sodium salts. The selectivity was the same for all of the acids, and none of the salts displayed any appreciable retention.

Discussion

Structural Changes as a Function of Temperature. A detailed discussion of some of the lower temperature dynamics of LiAl−LDH−MA in an aerobic

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environment (<100 °C) can be found in our preceding papers.[11] Essentially, the fatty acid is exchanged primarily as the anion. Thorough washing prevents the adsorption of any free acid on the exterior of the clay, which would show up as the C=O stretch of the free acid at 1720 cm^{-1} in the infrared. The chains are tightly packed and retain a primarily trans configuration, as indicated by the intensity in the CH_2 wagging region and the structure in the CH stretching region. The aliphatic chains are oriented perpendicular to the framework, forming a strict monolayer. This is in agreement with other studies of organic–LDHs, which have used double carboxylic acids and long chain sulfonates.[10] All studies have indicated a highly ordered perpendicular orientation of the anions in the interior.

75–200 °C. The first peak in the DTA curve at 75 °C (Figure 2) arises due to loss of solvent (ethanol). This includes both ethanol adsorbed on the surface of the platelets and that which is intercalated in the hydrophobic interior of the LDH. The weight loss from the TGA corresponds to approximately 10%, which agrees well with measured weight losses after heating at 100 °C for several hours. The loss of ethanol initiates an increase in the interlayer spacing from 21 to 42 Å (Figure 1c) and a decrease in intensity in the OH stretching region near 3200 cm^{-1}. In addition, the frequency of the COO^- asymmetric stretch shifts from 1550 to 1569 cm^{-1} (Figure 3b). The ethanol is hydrogen bonded to the COO^- head group of the acid and the framework hydroxyl groups. Upon loss of the ethanol, the CO stretching frequencies increase due to the decrease in the hydrogen bonding.[11c] A partial loss of intensity in the CH_2 wagging region (Figure 4b) indicates that disordering occurs in the all-trans packing of the alkyl chains.

This type of behavior is distinct from that of smectites[16] or other organic LDH's.[11a] Upon increasing temperature, irreversible disorder develops in the chain packing through the formation of kink blocks and gauche blocks, which causes a decrease in the interlayer spacing. In contrast, the interlayer distance of LiAl–LDH–MA increases with respect to temperature while retaining a significant amount of order.

200–300 °C. The second DTA transition occurs at approximately 225 °C (Figure 2). This transition is accompanied by a 16% weight loss. For samples heated just beyond this transition, the most obvious change in the infrared spectrum of LiAl–LDH–MA is the splitting of the COO^- asymmetric stretch into two bands at 1580 and 1560 cm^{-1} (Figure 3d). The frequencies of the COO^- stretching bands in fatty acid salts shift when replaced with different cations as a result of dissimilar electrostatic interactions.[12,17] The infrared spectra of the lithium and aluminum salts of myristic acid reveal information about the interaction with the COO^- head group and is shown in Figure 7. The asymmetric COO^- stretching band for the aluminum salt of myristate occurs at 1588 cm^{-1}, while that of the lithium salt of myristate is split into two bands at 1580 and 1557 cm^{-1} similar to that of the LiAl–LDH–MA sample heated at 250 °C. This splitting is assigned to the anisotropic interaction of the head group with the lithium cation. Thus, for the 250 °C treated LiAl–MA–LDH, the myristic anion is directly interacting with the lithium cations, indicating that dehydroxylation has occurred. However, since there is still intensity in the OH stretching region, it indicates that residual hydroxyl groups (~3500 cm^{-1}) are still present. The diffraction pattern reveals a pseudolayered structure, though the higher order (00*l*) reflections are not observed. Intensity and structure in the wagging region in the infrared spectrum have been eliminated (Figure 4d), indicating that a significant amount of disorder is present, and that the packing arrangement of the alkyl chains is no longer predominantly trans. Surface areas (BET analysis) of the 150 and 250 °C conditioned LiAl–LDH–MA samples are 13.5 and 140 m^2/g, respectively. The SEM micrographs show that the morphology of the particles remain unaltered up to thermal treatment of 250 °C. This indicates that exfoliation of the layers is not occurring and is similar to the observations of Reichle and co-workers on thermally decomposed MgAl–LDH.[5f] The venting of water leads to the development of fine pores in the framework, which leads to increased surface area. Thus, the loss of hydroxyl groups associated with the lithium ions in the framework is generating porosity along with a permanently disordered arrangement of the myristic acid chains.

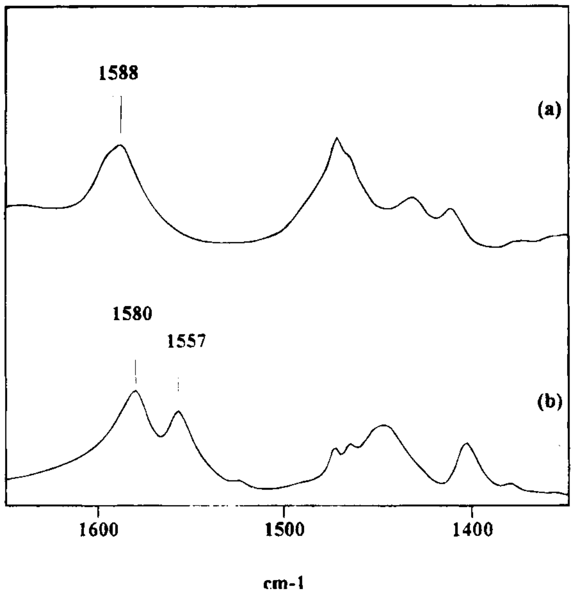

Figure 7. Infrared spectra of (a) aluminum and (b) lithium salts of myristic acid.

>300 °C. The third and fourth peaks in the DTA occur at 317 and 404 °C, and are accompanied by a final weight loss of 7 and 32%. At 300 °C, there is very little intensity left in the CH stretching region (Figure 3e), in addition to loss of bands in the COO^- stretching region. The broad bands at 1490 and 1430 cm^{-1} are characteristic of lithium carbonate. For samples heated at 450 °C only the carbonate bands remain, and there is no intensity in the OH stretching region. From the diffraction data, it is also evident that the material is amorphous. Therefore the third and fourth peaks can be assigned to the loss of organic molecules and final loss of hydroxyl groups from the framework.

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Thermal analysis of other LDHs also show the loss of hydroxyl groups in two stages. Examples are MgAl−LDH and ZnCr−LDH, with losses at 350, 440 °C[18] and 190, 470 °C,[19] respectively. Clearfield et al. have examined the properties of long chain sulfonates in various LDHs with TGA and mass spectrometry, and have observed three weight losses.[10c] For a NiAl−LDH, these included water loss (25−180 °C), organic loss (180−380 °C), and final hydroxyl loss (380−500 °C).[10c] These observations are consistent with the present study on the LiAl−LDH−MA system. The key observations from a material point of view are that the upper temperature limit of the layer structure for myristic acid exchanged LDH is approximately 250 °C and that considerable porosity is introduced through the partial loss of OH groups associated with framework lithium cations.

Chromatography. The partitioning of volatile organic molecules into the thermally treated LiAl−LDH−MA has parallels in the chemistry of organic−smectite materials, such as Bentone 34, which have been extensively studied and are in commercial use.[4] Retention mechanisms for these layered materials have been explained in terms of a combination of partitioning, adsorption, and steric sieving.[3c,20] Attempts have been made at altering the selectivity, decreasing peak asymmetry, and increasing the thermal stability and efficiency by using different clay minerals as supports and changing the identity of the interlayer cation.[20] Various clay minerals such as montmorillonite, hectorite, and vermiculite have been used, and there is evidence that beidellite type clays are possibly superior because of their greater charge density at the basal surface. In the beidellite clays, the charge mainly resides in the tetrahedral sheet, as opposed to the octahedral sheet for the montmorillonite clay.[20a] The presence of the charge closer to the interlayer region is believed to give rise to a more ordered external surface. The selectivity of the clay is also influenced by the structure of the exchanged cation. The alkyl chains in many organic−clay materials lie parallel to the clay surface.[21] Besides the interlayer height, the lateral distance between the chains and the surface area of the clay are also important in determining the separation ability of the clay.[20f]

LiAl−LDH is more crystalline than naturally occurring clays, and the charge is dispersed at the surface of the octahedral sheets, directly adjacent to the interlayer region. In addition, because the charge density is 4 times greater than that of clays such as montmorillonite, the packing of the alkyl chains is much tighter, and they are oriented perpendicular to the LDH framework. Thus, the LDH system displays many desirable qualities when compared to clay systems.

These studies show for the first time that organic−LDHs can also act as a partitioning medium. The role of the LDH framework alone is minor, since the chloride-exchanged LDH displays little or no retention of any analytes. The myristic acid exchanged LDH which was conditioned at 150 °C shows increased retention, but a significant degree of tailing. At 150 °C, the framework of the organo−LDH is intact, with an interlayer spacing of 43 Å. It is still a relatively well-crystalline material as is evidenced from the sharpness of the diffraction peaks. This material still has a high packing density which prevents the penetration of analyte molecules into the interlamellar region. To penetrate this region, the analyte molecules must disrupt the van der Waals forces between the adjacent chains. Any retention is probably due to interaction with the relatively small percentage of exchanged myristic anions located on the surface of the LDH. This would explain the increase in retention of the aromatic molecules when the concentration is reduced.

The chromatogram using the 250 °C treated LDH as a stationary phase looks similar to that of the free acid on Chromosorb. However, the possibility of free acid on the exterior of the LDH can be ruled out because of vigorous washing, along with the fact that any free acid present would be observed in the infrared, and would desorb from the LDH at a conditioning temperature of 150 °C or greater. Also, the possibility of dispersed lithium myristate salt on the surface of the LDH can be eliminated, since most of the organic material is exchanged between the layers, and the free salt was shown to be ineffective as a partitioning media. The similarity of the separation profile using the free liquidlike myristic acid and LiAl−LDH−MA is a reflection of the fact that the level of disordering of the alkyl chains are similar in both cases.

The loss of some of the hydroxyl groups after conditioning at 250 °C creates porosity in the interior of organic−LDH. This is reflected in the surface area, which increases by an order of magnitude. At the same time, permanent disorder is created in the chain packing. Both factors contribute to better accessibility of the analyte molecules to the interlayer region. In addition, because the alkyl chains are in a disordered state, the analyte molecules can partition into the hydrophobic region.

Conclusion

Fatty acid exchanged LiAl-LDH exhibits a variety of structural forms between ambient and 400 °C. After thermal treatment at 250 °C, the material has a porous pseudolayered structure, with alkyl chains significantly disordered, and the carboxylate head group intimately associated with the lithium cations in the framework. This system has several intrinsic qualities which make it an interesting material as a stationary phase in gas chromatography. Parallels between this system and the commercially popular Bentone stationary phase indicate the potential of these LDH materials.

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