Zn-Al LAYERED DOUBLE HYDROXIDE PILLARED BY DIFFERENT DICARBOXYLATE ANIONS

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Zn-Al layered double hydroxides (LDHs) intercalated by terephthalate (TPH) and biphenyl-4,4'-dicarboxylate (BPH) anions have been synthesized by direct co-precipitation from aqueous solution. The Zn/Al ratio in the final materials was 1.8. The products were characterized by powder X-ray diffraction, thermogravimetric analysis, FTIR and FT Raman spectroscopy, and MAS NMR spectroscopy. The basal spacing for the TPH-LDH intercalate was 14.62 Å, indicating that the guest anions stack to form a monolayer with the aromatic rings perpendicular to the host layers. For the LDH intercalate containing BPH anions, a basal spacing of at least 19.2 Å would be expected if the anions adopted an arrangement similar to that for the TPH anions. The observed spacing was 18.24 Å, suggesting that the anions are tilted slightly with respect to the host layers.

INTRODUCTION

Layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like compounds, are an important class of ionic lamellar solids [1]. The structure of LDHs consists of positively charged mixed metal hydroxide layers separated by charge-balancing anions and water molecules. A broad range of compositions of the type $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{m-})_{x/m}\cdot nH_2O$ (M^{2+} = = Mg^{2+}, Zn^{2+}, Ni^{2+} etc, M^{3+} = Al^{3+}, Cr^{3+}, Ga^{3+} etc) are possible, wherein the M^{2+} and M^{3+} metal ions occupy octahedral positions in the hydroxide layers. The interlayer anions A^{m-} are exchangeable, giving rise to a rich intercalation chemistry [2]. The guest species may be organic or inorganic, simple or complex [3,4]. Intercalation of a desired anionic guest is achieved by direct synthesis, ion-exchange, or by reconstruction of the layered structure when contacting the material calcined at 300-500°C with solutions of anions. LDHs find use as catalysts and catalyst supports [5], adsorbents, anion scavengers, anion exchangers, polymer stabilizers, and antacids [1].

LDHs intercalated with carboxylate anions have been studied in recent years because these materials have interesting properties and potential applications [6]. The intercalation of terephthalate and benzoate has attracted particular attention because these anions can be arranged in different orientations in the interlayer domain under different conditions [2]. Jones and coworkers [7] have demonstrated by experimental measurements and computer simulations that the orientation of terephthalate is strongly dependent upon the charge density on the layers and the interlayer water content of the LDH. Zn-Al LDHs containing terephthalate, 1,2-benzenedicarboxylate, 1,3-benzenedicarboxylate and benzoate were reported recently [8] and the results showed that terephthalate was preferentially intercalated from mixed pairs of organic acids. Thus it may be possible to use LDHs for the chemical separation of these anions from solution.

In the present work, Zn-Al LDHs intercalated by terephthalate (TPH) and biphenyl-4,4'-dicarboxylate (BPH) have been synthesized directly by co-precipitation from aqueous solution. The materials were characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), FTIR and FT Raman spectroscopy, and MAS NMR spectroscopy.

EXPERIMENTAL

Reagents

The starting materials $Zn(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot$ $\cdot 9H_2O$, 50 % aqueous NaOH, $NaNO_3$, terephthalic acid and biphenyl-4,4'-dicarboxylic acid were obtained from commercial sources and used as received.

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Characterization methods

Zn and Al were determined by ICP-OES at the Central Laboratory for Analysis, University of Aveiro (by E. Soares). Powder XRD data were collected at room temperature on a Philips X'pert diffractometer with a curved graphite monochromator (Cu-K_α radiation), in a Bragg-Brentano para-focusing optics configuration. Samples were step-scanned in 0.02°2θ steps with a counting time of 1 s per step. Thermogravimetric analysis was performed using a Shimadzu TGA-50 system at a heating rate of 5°C min^{-1} under air.

IR spectra were obtained with KBr pellets using a FTIR Mattson-7000 infrared spectrophotometer. Raman spectra were recorded on a Bruker RFS100/S FT instrument (Nd:YAG laser, 1064 nm excitation, InGaAs detector, 160 mW power, ca. 12000 scans, resolution 4 cm^{-1}). It was verified that the samples were not degraded under these conditions. ^{27}Al solid-state NMR spectra were measured at 104.26 MHz with a (9.4 T) wide bore Bruker Avance 400 spectrometer. Single-quantum ('conventional') ^{27}Al MAS NMR spectra were acquired using short and powerful radiofrequency pulses (0.6 μs, corresponding to π/12 pulses), a spinning rate of 14 kHz and a recycle delay of 1 s. Chemical shifts are quoted in ppm from $Al(H_2O)_6^{3+}$.

Synthesis of TPH-LDH and BPH-LDH

These LDHs were prepared by a co-precipitation method similar to that described by Drezdon [9]. Reactions were carried out under nitrogen, using distilled deionized water which was freshly decarbonated prior to use by vigorously boiling for 15 minutes. As an example, a solution of $Zn(NO_3)_2\cdot 6H_2O$ (5.95 g, 20 mmol) and $Al(NO_3)_3\cdot 9H_2O$ (3.75 g, 10 mmol) in decarbonated deionized (DD) water (40 mL) was added dropwise to a solution of terephthalic acid (1.66 g, 10 mmol) and 50 % NaOH (6.5 g, 81 mmol) in DD water (70 mL) with good mixing. The resulting white gel-like slurry was aged at 75°C for 48 h, then cooled to ambient temperature, filtered and washed several times with DD water, and dried at room temperature under reduced pressure in a vacuum desiccator. The same general method was used for the synthesis of BPH-LDH. In both cases, the pH at the end of the reaction was in the range 7-9.

- *TPH-LDH* - Anal. Calcd for $Zn_{3.6}Al_2(OH)_{11.2}[O_2CC_6H_4CO_2]\cdot 5.5H_2O$: Zn, 31.68; Al, 7.26. Found: Zn, 31.6; Al, 7.23. TGA up to 150°C revealed a sample weight loss of 13.3% (calcd: for loss of $5.5H_2O$, 13.3%). IR (KBr, cm^{-1}): 3360 (br), 2121 (w), 1954 (sh), 1566 (vs), 1504 (w), 1393 (vs), 1312 (w), 1151 (w), 1112 (sh), 1015 (w), 968 (sh), 878 (sh), 825 (w), 743 (w), 620 (w), 564 (w), 513 (w), 426 (m), 334 (w). Raman (cm^{-1}): 3081, 1596, 1494, 1406, 1386, 1316, 1288, 1263, 1239, 1145, 860, 809, 649, 553, 310, 107.
- *BPH-LDH* - Anal. Calcd for $Zn_{3.6}Al_2(OH)_{11.2}[O_2CC_6H_4C_6H_4CO_2]\cdot 5H_2O$: Zn, 29.06; Al, 6.66. Found: Zn, 28.9; Al, 6.62. TGA up to 150°C revealed a sample weight loss of 10.7% (calcd: for loss of $5H_2O$, 11.1%). IR (KBr, cm^{-1}): 3380 (br), 2068 (w), 1922 (w), 1611 (w), 1580 (vs), 1528 (vs), 1398 (vs), 1311 (w), 1269 (w), 1182 (m), 1141 (w), 1105 (w), 1005 (m), 872 (w), 854 (w), 836 (w), 800 (w), 767 (m), 700 (w), 668 (w), 627 (w), 571 (w), 526 (sh), 426 (m). Raman (cm^{-1}): 3071, 1609, 1522, 1423, 1287, 1198, 1142, 1017, 850, 797, 757, 629, 408, 329, 101.

RESULTS AND DISCUSSION

Zn-Al LDHs intercalated by terephthalate (TPH) and biphenyl-4,4'-dicarboxylate (BPH) anions were synthesized directly by co-precipitation from aqueous solution. Elemental analysis indicated an incomplete precipitation of the divalent cation since the Zn/Al ratio in the final materials was 1.8, slightly lower than the value of 2.0 used in the starting solutions.

In the IR spectrum of TPH-LDH, strong bands were observed at 1566 and 1393 cm^{-1}, assigned to $\nu_{as}(OCO)$ and $\nu_s(OCO)$ of carboxylate groups, respectively. The corresponding bands for LDH-BPH appeared at 1580 and 1398 cm^{-1}. Below 750 cm^{-1}, the spectra contained some bands due to the guest species in addition to peaks arising from the host lattice. The IR and Raman spectra confirmed that the samples did not contain measurable amounts of nitrate or carbonate anions. The LDH intercalates were also studied by ^{27}Al MAS NMR spectroscopy (spectra not shown). Each material presented a sharp peak at about 15.5 ppm with a broad low-frequency shoulder, assigned to octahedral aluminium.

The powder XRD patterns obtained for the two materials TPH-LDH and BPH-LDH were typical of hydrotalcite-like materials, exhibiting sharp and symmetric (00*l*) reflections (figure 1). Indexing is based on rhombohedral symmetry (polytype $3R_1$). The (00*l*) basal reflections are easily identified as a series of equi-spaced symmetric peaks at angles below 32°2θ. Six 00*l* peaks are present for BPH-LDH and the *d*-spacing for the 003 reflection is 18.24 Å. A similar spacing was reported for a Zn-Al layered double hydroxide intercalated by 2,2'-bipyridine-5,5'-dicarboxylate anions (prepared by ion-exchange of an LDH precursor in nitrate-form) [10]. The longest dimension of the BPH anion is calculated to be about 14.4 Å (including van der Waals radii for the oxygen atoms), using the crystal structure data reported for a cadmium-organic framework material containing this anion [11]. Given that the thickness of a brucite-like layer can be taken as 4.8 Å, a basal spacing of at least 19.2 Å would be expected if the anions were lying perpendicular to the host layers. The observed spacing is shorter by about 1 Å, suggesting that the anions are tilted slightly (as depicted in figure 2).

In the case of TPH-LDH, five (00*l*) reflections were observed below 32°2θ and the value of d_{003} was 14.62 Å, corresponding to a gallery height of 9.85 Å (figure 1). The space occupied by a terephthalate anion when intercalated with its long axis perpendicular to the host layers is predicted to be 9.8-10.1 Å [12], which is consistent with the value of the gallery height obtained for TPH-LDH (figure 2).

Figure 3 shows the TGA curves for the materials synthesized. The traces for the organic-anion-pillared LDHs reveal three general regions of mass loss, the first two of which overlap to some extent. The first mass loss

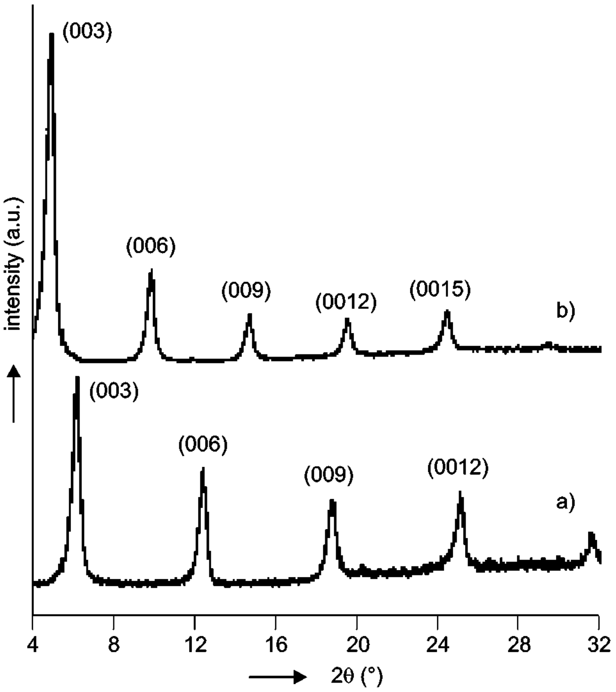

Figure 1. Powder XRD patterns at room temperature of (a) TPH-LDH and (b) BPH-LDH.

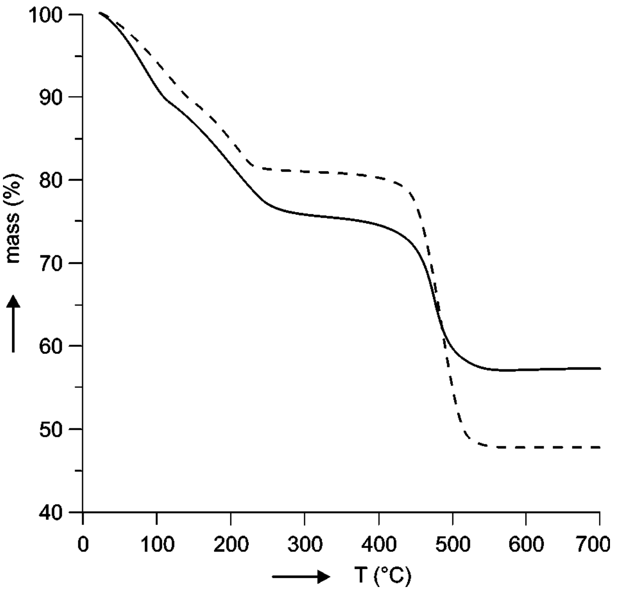

Figure 3. TGA curves for TPH-LDH (—) and BPH-LDH (---).

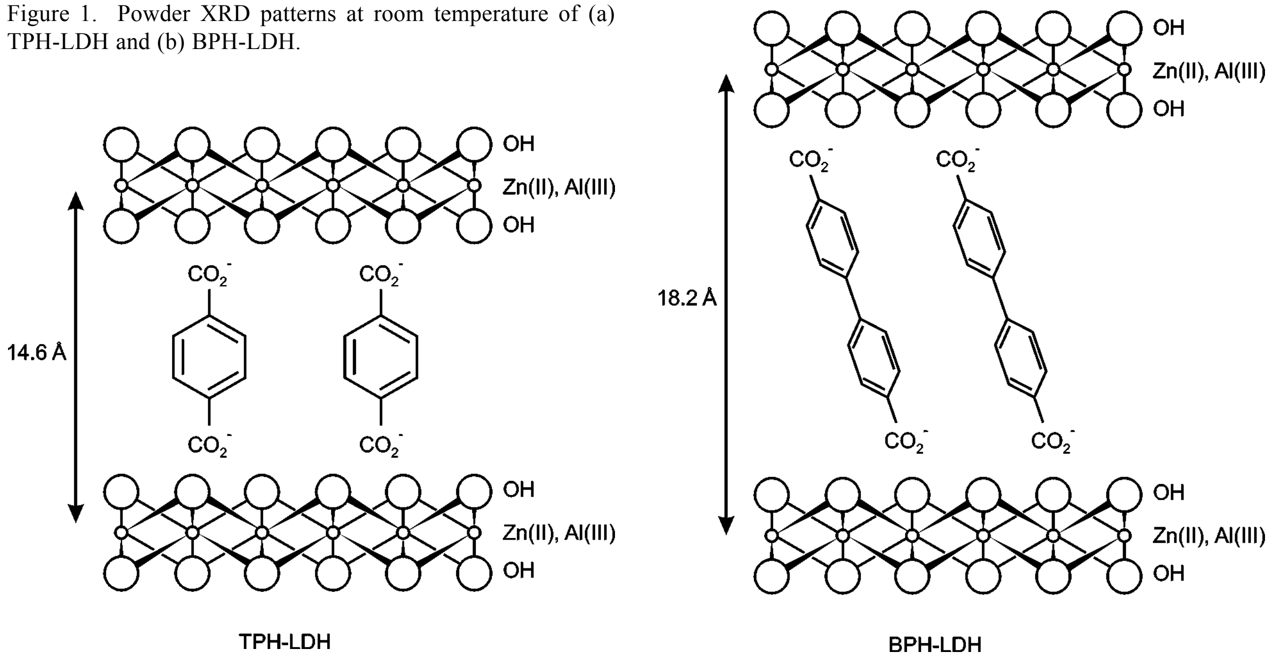

Figure 2. Models for the orientation of terephthalate (TPH) and biphenyl-4,4'-dicarboxylate (BPH) in the LDH intercalates prepared by direct co-precipitation.

(11-14 %), corresponding to removal of interlayer water, occurs from room temperature to approximately 160°C. The second step, which takes place up to about 270°C, is assigned to partial dehydroxylation of the double hydroxide layers [13]. Complete dehydroxylation and partial elimination/decomposition of the organic anions take place abruptly above 400°C. As expected, the mass loss for this step is higher for BPH-LDH (32 %) than for TPH-LDH (18 %).

CONCLUSIONS

Organic-anion-pillared layered double hydroxides have successfully been prepared by direct synthesis. The interlayer arrangement of biphenyl-4,4'-dicarboxylate anions is similar to that found previously for a Zn-Al layered double hydroxide pillared by 2,2'-bipyridine-5,5'-dicarboxylate anions, despite the fact that the materials were prepared by different routes.

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PODVOJNÉ VRSTEVNATÉ HYDROXIDY Zn-Al S RŮZNÝMI DIKARBOXYLÁTOVÝMI ANIONTY V MEZIVRSTVĚ

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Podvojné vrstevnaté hydroxidy Zn-Al (LDH) interkalované tereftalátem (TPH) a bifenyl-4,4'-dikarboxylátem (BPH) byly připraveny přímým spolusrážením z vodného roztoku. Poměr Zn/Al ve výsledném materiálu byl 1.8. Produkt byl charakterizován práškovou rtg difrakcí, termogravimetrickou analýzou, FT IČ a FT Ramanovou spektroskopií a MAS NMR spektroskopií. Bazální mezirovinná vzdálenost TPH-LDH interkalátu byla 14.62 Å, což ukazuje, že hostující anion je uložen do monovrstvy s aromatickými kruhy orientovanými kolmo na vrstvy hostitele. Podobný LDH interkalát s BPH aniontem by měl mít bazální mezirovinnou vzdálenost nejméně 19.2 Å, pokud by byl anion orientován stejně jako anion TPH. Skutečně pozorovaná vzdálenost 18.24 Å ale ukazuje, že anion je mírně nakloněn vzhledem k hostitelovým vrstvám.