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New layered double hydroxides intercalated with substituted pyrroles. 2. 3-(Pyrrol-1-yl)-propanoate and 7-(pyrrol-1-yl)-heptanoate LDHs

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Abstract

We report the synthesis and characterization of organic–inorganic hybrid materials: Zn_2-Al-LDHs (layered double hydroxides) containing 3-(1*H*-pyrrol-1-yl)-propanoate and 7-(1*H*-pyrrol-1-yl)-heptanoate as the interlayer anions. The LDHs were synthesized by the co-precipitation method at constant pH followed by hydrothermal treatment for 72 h. The materials were characterized by PXRD, ^{13}C CP-MAS NMR, TGA, and ESR. The basal spacing found by PXRD technique is coincident with the formation of bilayers of the intercalated anions. The solid state ^{13}C NMR showed that the interlayered anions remain identical after intercalation. ESR data suggest that the monomers connect each other in a limited number of guests when a thermal treatment is applied. The inorganic LDH sheets delay the temperature of degradation of the monomers.

Keywords: A. nanostructures; A. polymers; C. X-ray diffraction; D. nuclear magnetic resonance (NMR); D. electron paramagnetic resonance (EPR)

1. Introduction

Hybrid materials based on the assembly between layered double hydroxides (LDHs) and polymers have received considerable attention in the last years [1–17]. This new emerging class of materials shows potential applications such as nanofiller for polymer nanocomposite for the enhancement of the mechanical properties, gas permeability or ionic diffusion for the polymer electrolytes [1–4]. layered double hydroxides (LDHs), or the so-called anionic clays are described considering the $Mg(OH)_2$ brucite structure, with a part of the divalent cations isomorphously replaced by trivalent cations. The hydrotalcite-like structure results in positively charged layers with anions present into the lamellar gap [1,2]. The combination of M^{2+}, M^{3+}, and anion enables the preparation of a large range of these materials [18–24]. LDHs can be represented by the general formula $\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]^{x+}A^{m-}_{x/m}\cdot nH_2O$. Taking advantage of their exchange capacity different polymers and/or monomer molecules have been incorporated into LDHs host structure, as exemplified by poly(aniline) [6–8], poly(vinyl)alcohol [9], poly(styrene sulfonate) [10,11] poly(vinyl sulfonate) [12], poly(acrylic acid) [13,14], poly(ethylene glycol) dicarboxylic [15], poly(ethylene glycol) [15], biopolymers [16] and polypyrrole [17].

The synthesis of polymer-intercalated LDHs can be conducted by different methods considering three principal options: (a) intercalation of the monomer molecules and subsequent in situ polymerization, (b) direct incorporation of extended polymer chains in the host lattice via exchange reaction in the case of small molecular weight or via coprecipitation method, (c) transformation of the host material into a colloid system and its subsequent restacking in the presence of the polymer [1,2].

In this paper, we report the synthesis and characterization of two new bi-dimensional organic–inorganic hybrid materials, Zn_2-Al-LDHs containing 3-(1*H*-pyrrol-1-yl)-propanoate and 7-(1*H*-pyrrol-1-yl)-heptanoate as the interlayer anions.

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2. Experimental methods

The LDHs hybrid materials were prepared using the constant pH coprecipitation technique. A solution containing 1.92×10^{-3} mol of $Zn(NO_3)_2\cdot6H_2O$ and 9.60×10^{-4} mol of $Al(NO_3)_3\cdot9H_2O$ in 18 cm^3 of water was added into a solution containing 1.92×10^{-3} mol of 3-(1*H*-pyrrol-1-yl)-propanoic acid, noted as PyP, or 7-(1*H*-pyrrol-1-yl)-heptanoic acid, noted as PyH, in 70 cm^3 of water. During this addition, a 0.5 mol L^{-1} NaOH solution was also added into the reaction mixture, in order to keep the pH constant at 8.5 ($\pm$0.2 units). The solid product was separated by centrifugation, washed with water and ethanol. The obtained materials were suspended in the solution containing either PyP or PyH, at pH of 8.5 ($\pm$0.2 units), and then submitted to hydrothermal treatment at 70 °C during 72 h. After the hydrothermal treatment, the obtained material was separated, washed, and dried. The LDHs hybrid materials are noted as Zn_2Al/PyP and Zn_2Al/PyH.

2.1. Characterisation

The powder X-ray diffraction patterns (PXRD) for the solid materials were obtained using Siemens D5005 equipment with a graphite monochromator selecting the Cu Kα radiation. A step of 0.02° was used in the angular domain 2–70°. The Zn/Al ratio was determined by energy dispersive spectroscopy (EDS) analyses, using a Zeiss DSM 960-digital scanning microscope. Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 equipment, under air at a heating rate of 10 °C min^{-1}. Solid state NMR ^{13}C spectra in CP-MAS condition were recorded in a Varian INOVA 300 spectrometer operating at 75.42 MHz. Electron Spin Resonance spectra were recorded at room temperature using a X Band Bruker EMX spectrometer operating at 9.658 GHz. Diphenylpicrylhydrazyl (DPPH) was used to determine the resonance frequency ($g=2.0036\pm0.0002$). The sweep width was of 200 G and the receiver gain 100,000.

3. Results and discussion

The PXRD patterns for the obtained materials are represented in Fig. 1. The PXRD data and the M(II):M(III) ratios are presented in Table 1. The materials exhibit several orders of basal reflections (00*l*) indicating well-crystallized LDH materials. The widths of the harmonic diffraction lines are not similar between each other. Moreover, some shoulders are also observed, therefore the presence of an additional phase coming from the contamination by carbonate cannot be discarded. The values of basal spacing were calculated by the Bragg equation from (00 *l*) peaks using the average $1/6(d_{003}+2d_{006}+3d_{009}+4d_{012}+5d_{015}+6d_{018})$. A basal spacing of 1.72 nm for Zn_2-Al-PyP-LDH and 2.48 nm for Zn_2-Al-PyH-LDH are consistent with those expected for the incorporation of two layers of PyP and PyH anions between LDH sheets, as previously observed for 4-(1*H*-pyrrol-1yl)benzoate anions [17]. Schematic representations of the possible arrangement for the intercalated anions are shown in Fig. 2.

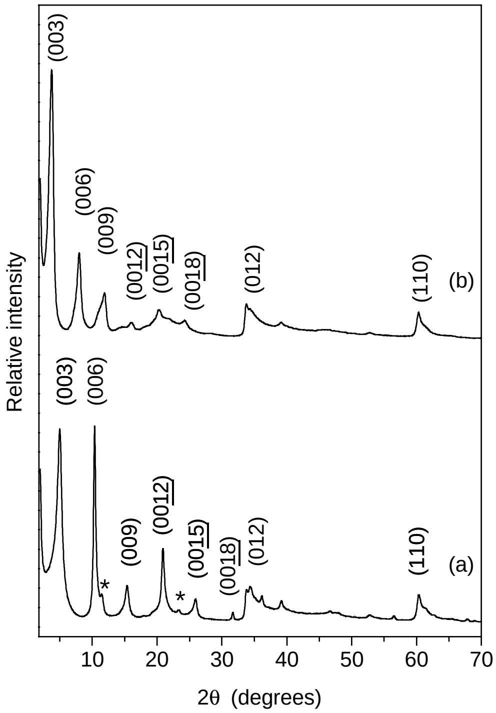

Fig. 1. PXRD of (a) Zn_2Al/PyP and (b) Zn_2Al/PyH. *Carbonate LDH phase.

To investigate the chemical nature of the intercalated anions, ^{13}C CP-MAS NMR was applied. The numbering scheme and the assignments of the ^{13}C chemical shifts for the organic monomers are displayed in Table 2. ^{13}C CP-MAS spectrum of 3-(1*H*-pyrrol-1-yl)-propanoic acid exhibits resonances lines characteristic of aliphatic carbons at 46 ppm (C4) and 40 ppm (C5), and for carbon of the carbonate function at 180 ppm (C1). The carbon nuclei of the pyrrole ring, C2 and C3, present the resonance lines at 121 and 108 ppm, respectively. For 7-(1*H*-pyrrol-1-yl)-heptanoic acid, the aliphatic carbons are located at 51 ppm (C4), 35 ppm (C5), 34 ppm (C6), 30 ppm (C7), 29 ppm (C8), and 26 ppm (C9). The resonance peak for the carbon of the acid group C1 is located at 182 ppm. The carbon nuclei of the pyrrole ring are located at 121 ppm (C2) and 108 ppm (C3). The solid state NMR ^{13}C spectra in CP-MAS condition for the hybrid materials are shown in Fig. 3. The resonances peaks of the hybrid materials do not present notable variation in comparison to the respective monomers. The similarity of the spectra before and after incorporation of PyP and PyH into LDHs host structure seems to indicate that the monomers do not connect each others spontaneously during the synthesis.

Thermogravimetric curves of PyP, PyH, Zn_2-Al/PyP, and Zn_2-Al/PyH are shown in Fig. 4. As usually observed in the

Table 1
X-ray powder diffraction data for LDHs and M(II):M(III) ratio

Sample	Basal spacing (nm)	Domain size[a] (nm)	M(II):M(III)
Zn_2Al/PyP	1.72	21.5	2.31
Zn_2Al/PyH	2.48	12.7	2.48

[a] The size of the scattering domain along the *c*-axis was determined from the width of the second and third 00*l* X-ray harmonics of oriented samples.