Intercalation of acrylate anions into the galleries of Zn–Al layered double hydroxide

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Abstract

Acrylate and methacrylate anions containing double bond and carboxylic groups, were intercalated in the interlayer region of a layered double hydroxide of formula: \([\text{Zn}_{0.66}\text{Al}_{0.34}(\text{OH})_2](\text{NO}_3)_{0.34} \cdot 0.62\text{H}_2\text{O}\). The intercalation compounds obtained have been characterized for their chemical composition and with different instrumental techniques (X-ray powder diffraction, thermal analysis, FT-IR absorption spectroscopy, electron scanning microscopy). Furthermore, they have been used to carry out a preliminary study concerning the in situ polymerization of the intercalated acrylate and methacrylate ions to obtain new interstratified inorgano-organic hybrid materials.

1. Introduction

In organo-organic hybrids based on layered inorganic solids, capable of intercalation, have recently received much attention as additives of organic polymers. The composites or nanocomposites obtained show substantial enhancement in mechanical, thermal and barrier properties when compared with those of the neat polymers [1]. The dispersion of the hybrid material in the polymer to obtain the composites is generally achieved with different compounding techniques (melt extrusion, casting, moulding) [2], while little attention has been given to the intercalation of monomers in the interlayer region of the layered host, followed by in situ polymerization and dispersion of the interstratified material in the polymer. The present paper reports a study on the preparation of intercalation compounds of layered double hydroxide (LDH) with acrylate and methacrylate anions and subsequent in situ polymerization. The preparation of nanocomposite LDH/ acrylic polymers has been published by some authors [3–8].

The structure of LDH consists of brucite-like sheets, in which divalent cations are partially replaced by trivalent cations. Consequently, the layers are positively charged and interlayered anions, \(A^{n-}\), neutralize these charges and can be replaced by other anions [9] with anion exchange procedure. The LDH general formula is thus: \((\text{M}^{2+})_{x-y} \cdot \text{M}^{3+} \cdot (\text{OH})_2\)\(_2\) \(\cdot \text{A}^{n-}\) \(\cdot x\) \(\cdot \text{H}_2\text{O}\), where \(\text{M}^{2+} = \text{Mg, Zn, Ni, Cu, Mn}; \text{and} \text{M}^{3+} = \text{Al, Cr, Fe}; x = 0.2–0.4\).

Generally, the intercalation of anion can be made by [10]: (a) anion exchange in which the LDH is contacted with a solution of anion, (b) co-precipitation by addition of a \(\text{M}^{2+}\) and \(\text{M}^{3+}\) solution to a basic solution of the anion, (c) rehydration of a calcined MgAl-LDH with a solution containing the anion and (d) thermal reaction.

In this paper an LDH having \(\text{M}^{2+} = \text{Zn}^{2+}, \text{M}^{3+} = \text{Al}^{3+}, \text{A}^{n-} = \text{NO}_3\) and \(x = 0.34\) was taken into account as precursor and the replacement of the nitrate ions with organic anions containing a \(\text{C} = \text{C}\) double bond in their molecular structure with anion exchange procedure was made.

The \(\text{C} = \text{C}\) functional group, inserted in the interlayer region of LDH, can be used to prepare interstratified

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inorgano-organic hybrid materials by in situ polymerization. Preliminary tests of in situ polymerization over some of the obtained intercalation compounds have been performed.

2. Experimental

2.1. Materials

Hydrotalcite-like compound with the chemical formula \([Zn_{0.66}Al_{0.34}(OH)_{2}](CO_3)_{0.17}0.5H_2O]\) was prepared by the urea method [11]. The nitrate form, LDH-NO3, was obtained by titration, at room temperature, of the carbonate form dispersed in a 1 M NaNO3 aqueous solution (mass/volume \(\approx 2 g/100 mL\)) with a 0.1 M HNO3 solution, by means of a Radiometer TITRALAB VIT 90 automatic titrator operating in the pHstat mode at pH 5.

2.2. Intercalation of the acrylate \([H_2C=C(H)COO^-]\) and methacrylate anions

Aqueous solution of sodium acrylate 0.1 M was prepared by dissolution of a convenient weighted amount of salt in CO2-free deionized water. A sample of LDH-NO3 (300 mg) was contacted with 30 mL of an aqueous solution of sodium acrylate obtained by dilution of the 0.1 M solution. A parameter \(r\) defined by the ratio between the mmol of acrylate ions added and calculated anion exchange capacity based on the chemical formulae of the LDH-NO3 has been used in ion exchange procedure. In the case of sodium acrylate, the concentration of the solution was varied to give a molar ratio, \(r\), in the range 0.5 \(\leq r \leq 3.0\). In the case of methacrylate 300 mg of LDH-NO3 was contacted with 30 mL of the solution of sodium methacrylate prepared by dilution of those 0.1 M to give a molar ratio, \(r\), of 2.0. The obtained dispersions were stirred, at room temperature, for 24 h. The solids were separated from the solutions by centrifugation, washed by water and dried in a dessicator over NaCl saturated solution (75% relative humidity).

2.3. In situ polymerization of the intercalated ions

The LDH intercalation compounds were dispersed, under stirring, in aqueous solution \(7.4 \times 10^{-5} M\) of 
K2S2O8 and maintained at 60°C for 24 h. The solids were recovered by centrifugation, washed by water and dried.

2.4. Methods

An ion chromatograph Dionex DX500 was used for chemical determination of Zn2+, Al3+ and nitrate ions. For the Zn and Al determination, a weighed amount of the sample (\(\approx 100 mg\)) was dissolved in few drops of concentrated HCl and diluted with water to 50 mL.

Column Dionex CS5a; eluent pyridine-2,6-dicarboxylic acid (flow rate 1.0 mL min\(^{-1}\)), 4-(2-pyridylazo)-resorcinol as reagent for post column reaction and spectrophotometric detector were used in Zn determination.

Column Dionex CS5a; eluent HCl 0.75 M (flow rate: 1.0 mL min\(^{-1}\)), tiron for post column reaction and spectrophotometric detector were used in Al determination.

The Zn and Al contents were also confirmed by titration with EDTA.

The nitrate content was determined suspending the sample (\(\approx 50 mg\)) in 50 mL of 1.0 M Na2CO3 for 24 h at 80°C. Column Dionex AS11; eluent KOH (concentration gradient, flow rate: 2.0 mL min\(^{-1}\)) and a suppressed conductivity detector were used.

2.5. Characterizations and measurements

The X-ray powder diffraction patterns (XRPD) were obtained with a Philips PW 1710 X-ray diffractometer, using CuKα radiation (\(\lambda = 1.54050 Å\)). The generator voltage was 40 kV and the generator current was 30 mA. The step scanning was 0.1/min.

Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out in air with a Netzsch STA 490 C thermobalance from room temperature to 800°C with a heating rate of 5°C/min.

FT-IR spectra were recorded in KBr dispersion on a Jasco model FT/IR-410, 420 Herschel series (Jasco Corporation Tokyo, Japan).

Differential scanning calorimetry (DSC) analyses were performed using an automatic thermal analyser (Mettler Toledo DSC8211°). Temperature calibrations were performed using indium as a standard. Holed aluminium pans were employed in the experiments for all samples and an empty pan, prepared in the same way, was used as a reference. Samples of 3–6 mg were weighted directly into the aluminium pans and the thermal analyses were conducted at a heating rate of 10°C/min from 25 to 500°C.

Scanning electron microscopy was made using a Philips XL30 with LaB6 source and EDAX/DX4 rivelator.

3. Results and discussion

3.1. Preparation and characterization of LDH-acrylate

Intercalation of acrylate into interlayer region of LDH was performed by acrylate/nitrate ion exchange: the precursor \([Zn_{0.66}Al_{0.34}(OH)_{2}](NO_3)_{0.34}0.62H_2O]\) was dispersed in 30 mL of the aqueous solutions containing different amounts of sodium acrylate to give a molar ratio \(r\) in the range 0.5–3.0 (see experimental). The XRPD patterns of the precursor LDH-NO3 and of the obtained intercalation compounds (LDH-acrylate) are shown in Fig. 1.
The presence of the peak at $2\theta = 10^\circ$ (corresponding to 0.88 nm) is a proof that the initial LDH-NO$_3$ phase is present in the sample. From the sequence of the XRPD patterns it is possible to see that, when the molar ratio $r$ increases to 1.0, the intensity of the peak at 0.88 nm decreases while, for $r \geq 1.0$, it completely disappears. At the same time, the intensity of the peak at $2\theta = 6.5^\circ$ (1.35 nm) increases. This corresponds to first diffraction maxima of the intercalate LDH-acrylate which is the only phase present in the samples when $r \geq 1.0$. In the compounds prepared with $r$ molar ratios less than 1.0 two phases, corresponding to the initial and final phases, are simultaneously present in the sample and, thus, the ion exchange acrylate/nitrate occurs in a single step and no intermediate compounds are formed.

It was also found that if the concentration of external solution is less than 0.01 M no intercalation of the acrylate ions is observed.

The interlayer distance of LDH-acrylate of 1.35 nm is similar to that reported for the acrylate intercalation in other LDH precursors, like NiFe-LDH [3] or MgAl-LDH [8].

TG and DTA analysis of the LDH-acrylate prepared using $r = 2.0$ are shown in Fig. 2. A gradual and endothermic weight loss occurs from 100 to 400 °C. This weight loss is due to the combination of more processes, like the hydration water loss and the partial degradation of the sample. An exothermic weight loss occurs around 400 °C, attributable to oxidative decomposition of the organic residue [8].

TG and chemical analyses of the solid obtained with $r \geq 1.0$ confirm that the nitrate ions have been completely substituted by acrylate ions, to afford a solid of composition $[\text{Zn}_{0.66}\text{Al}_{0.34}(\text{OH})_2]\text{C}_3\text{H}_3\text{O}_2\text{H}_{0.34}\cdot 0.90\text{H}_2\text{O}$. The 43.9% weight loss at 800 °C is consistent with the proposed chemical formula.

The interlayer distance of the LDH-acrylate is 0.47 nm higher than that of the precursor LDH-NO$_3$, which, if compared with the estimated length of acrylate ion of about 0.6 nm [3], is consistent with the formation of a bilayer of acrylate ions partially interpenetrated in the interlayer region of LDH.

SEM micrography of LDH-acrylate (Fig. 3) shows that the most part of obtained solid is formed from platelets of dimensions of about 5 µm.

Intercalation compound with methacrylate was carried out by ion exchange of nitrate ions: the precursor LDH-NO$_3$ was contacted with a sodium methacrylate solution. Molar ratio $r$ equal to 2.0 was used. The XRPD patterns of the obtained compound is shown in Fig. 4.

Chemical analysis of this compound indicates the absence of nitrate ions in the final solid and fully
methacrylate exchanged LDH \([\text{Zn}_{0.64}\text{Al}_{0.36}(\text{OH})_2}\]
\((\text{C}_4\text{H}_5\text{O}_2)_{0.36}0.70\text{H}_2\text{O}\), was obtained. The water content of the LDH-methacrylate conditioned at 75% r.h. (0.70 mol/mol) is less than those of the LDH-acrylate (0.90 mol/mol) probably caused from the steric hindrance of additional methyl group in the methacrylate ion. This could also explain the little difference between the interlayer distance of LDH-acrylate and LDH-methacrylate conditioned at 75% r.h. The interlayer distances of both the compounds do not change consequently drying over \(\text{P}_4\text{O}_{10}\) indicating that in the interlayer region are present free cavities of dimensions sufficient to place in it water molecules.

TG and DTA curves of LDH-methacrylate sample are shown in Fig. 5. The behaviour is similar to that of the LDH-acrylate: the weight loss is completed before 450 \(^\circ\)C and it is composed from more steps not well separated each one.

### 3.2. Polymerization of the intercalated ions

The \(\text{C}==\text{C}\) double bond of anions inserted in the interlayer region of the intercalation compounds can react, in the presence of a convenient activator, to give in situ addition polymerization. Preliminary experiments on the polymerization of the acrylate ions intercalated in the interlayer region of LDH-acrylate have been performed using potassium persulfate and hydrogen peroxide. In the latter case no modification in the XRPD spectra of the recovered solid was found.

The reaction of polymerization was performed starting from the LDH-acrylate or LDH-methacrylate and the obtained products will be indicated LDH-PAA and LDH-PMA, respectively. The intercalated compound was dispersed in an aqueous solution of \(\text{K}_2\text{S}_2\text{O}_8\) at 60 \(^\circ\)C for 24 h and compounds with an interlayer distance of 1.26 nm for LDH-PAA and 1.24 nm for LDH-PMA were obtained (see Fig. 4). The reduced interlayer distance agrees with the polymerization of acrylate and methacrylate groups in the interlayer region [3] and the presence of these peaks in the XRPD patterns suggests that the inorganic layers of the LDH and organic polymer are regularly alternated to form an interstratified compound.

The FTIR spectra (data not reported) of the intercalate LDH-acrylate show a broad absorption peak between 3200 and 3600 cm\(^{-1}\) relative to the \(\nu\text{O-H}\), and absorption peaks at 1559.2, at 1404.3 and at 1637.8 cm\(^{-1}\) attributable to the \(\nu\text{asCOO}^-\), \(\nu\text{scCOO}^-\) and \(\nu\text{C}==\text{C}\), respectively. In the FTIR spectra of the LDH-PAA the absorption peak at 1637.8 cm\(^{-1}\) almost disappeared. This agrees with \(\text{C}==\text{C}\) addition reaction.

Fig. 6 reports the DSC curves of LDH-PAA and of the LDH-acrylate precursor. The decomposition of the LDH-
acrylate occurs at about 400 °C. The DSC curve of the polymerization product, LDH-PAA, shows that its decomposition occurs at about 440 °C and a distinct shoulder around 400 °C is present. This shoulder may be attributed to LDH-acrylate monomer decomposition. As expected, LDH-PAA decomposition occurs at a temperature higher than that of decomposition of the LDH-acrylate precursor.

Experiences performed by induced photopolymerization in acetonitrile solutions bring to compounds with the same characteristics and properties of the LDH-PAA.

4. Conclusions

Some organic anions containing double bond and carboxylic groups were intercalated in the interlayer region of a hydrotalcite-like material. Fully exchanged layered solids were obtained and characterized by powder X-ray diffraction, FTIR, thermogravimetric and DSC analysis. A preliminary study concerning in situ polymerization of the intercalated acrylate and methacrylate ions were performed and interstratified inorgano-organic hybrid materials were obtained. The results of XRD, FTIR and DSC analysis are consistent with in situ polymerization of intercalated monomers.

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