Preparation of Cd/Al layered double hydroxides and their intercalation reactions with phosphonic acids

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Layered double hydroxides (LDHs) containing cadmium as the divalent metal and aluminium as the trivalent metal have been prepared by coprecipitation from a mixed metal nitrate solution, and were obtained with nitrate and carbonate as the counter anions, and as single crystalline phases. XRD patterns show that these LDHs are isostructural with synthetic hydrotalcite, with interlayer spacings of 8.24 and 7.54 A for $Cd/Al/NO_3$ and $Cd/Al/CO_3$ LDHs, respectively. These compounds were intercalated with phenylphosphonic acid (PPA) and 2-carboxyethylphosphonic acid (CEPA). Intercalation is confirmed by XRD, where increased interlayer spacings were observed for the intercalation compounds. Interlayer distances of 14.59 A were observed for the PPA intercalation compounds, independent of the original counter anion. CEPA intercalated LDHs present interlayer spacings of 11.74 A for Cd/Al/CEPA obtained from $Cd/Al/NO_3$ LDH and a double interlayer distance of 11.35 and 12.21 A for Cd/Al/CEPA obtained from $Cd/Al/CO_3$ LDH. IR and NMR measurements suggest that this double interlayer spacing is due to the interaction of CEPA to the layers through both of its extremities, *i.e.* a phosphonate and a carboxylate interaction.

Hydrotalcite like compounds, also known as layered double hydroxides (LDHs), have the general formula $M^{II}{}_xM^{III}{}_y(OH)_{2x+3y-nz}(A_z{}^{n-})\cdot tH_2O$, where M^{II} and M^{III} are di- and tri-valent metals, respectively, and A is an anion. LDHs have been prepared with various different metals, such as, for example, Li^I, Mg^{II}, Ni^{II}, Zn^{II}, Fe^{II}, Co^{II}, Al^{III}, Fe^{III}, V^{III}, Cr^{III}, among others. These compounds are known as excellent precursors, upon calcination, for heterogeneous catalysts in which the acid–base character is determined by M^{II}, M^{III} and their ratio.[1–3] The calcination of LDHs leads to the formation of homogeneous mixtures of oxides with very small crystal sizes.[4] Non-calcined LDHs tend to behave as Lewis bases, with small or no Lewis acidic character.[5] The structure of an LDH derives from that of brucite, $Mg(OH)_2$, where the metal atoms are octahedrically surrounded by hydroxy groups. These octahedra share edges to form infinite sheets. In LDHs, a fraction of the divalent metal is substituted by a trivalent metal, thus generating a net positive charge in the brucite-like sheets. This charge is compensated by the formation of a layered structure in which the positive ordered sheets are separated from each other by a disordered layer of counter anions and water molecules, forming a lamellar structure with alternating positive and negative layers. For this reason, these compounds are also known as mixed layered hydroxides. Usually, the most stable anion in the interlayer region is carbonate, but LDHs with other anions can be prepared by various methods, although contamination with CO_2 is difficult to prevent.[6–8]

Calcined LDHs present catalytic properties with possible applications in many organic conversions, such as dehydration and disproportionation,[9] alkylation,[10] and photoisomerization,[11] among others, and the mechanism for the thermal conversion of LDHs to catalytic mixed oxides has been the subject of detailed studies.[12]

LDHs also present anion exchange properties, which makes intercalation with a wide range of anionic organic and inorganic substances possible. Compounds as distinct as fatty acids,[13–16] alkyl sulfates and dicarboxylates[16] sulfonates,[17] and inorganic polyvanadates[18] have been intercalated into LDHs. Polymerisation reactions have also been performed inside the interlayer region, yelding a new range of composites and organoceramic compounds.[19,20] A novel phenylphosphonic acid intercalation procedure achieved by reacting the molten acid with an Mg/Al LDH or its calcined derivative has recently been described by Carlino *et al.*[21]

More recently, LDHs have found an ecological application, as sorbents for organic substances from water.[22–24]

Here we describe the preparation of LDHs containing Cd as divalent metal, and Al as the trivalent metal. These LDHs were prepared with nitrate and carbonate as counter anions, and were submitted to intercalation with two different phosphonic acids. This is, to our knowledge, the first time that LDHs having Cd as the divalent metal have been successfully prepared. The preparation of an LDH containing Cd as the divalent metal has been described by Miyata and Kumura,[25] but they seem to have obtained a mixture of the desired product and $CdCO_3$. We have obtained LDHs with Cd as the divalent metal and nitrate and carbonate as the counter anions in the form of crystalline single phases.

Experimental

All reagents were used as received, without further purification.

Layered double hydroxides

The method of preparation of the LDHs was based on that described by Reichle.[1] A solution containing 0.1 mol dm^{-3} of $Cd(NO_3)_2\cdot 6H_2O$ (reagent grade, Ecibra) and 0.05 mol dm^{-3} of $Al(NO_3)_3\cdot 9H_2O$ (reagent grade, Ecibra) in 70 ml of deionized water, was added to a solution containing 28 g of a 50% m/m NaOH solution in 100 ml of deionized water. The addition was performed slowly and with vigorous stirring. For the preparation of the carbonate LDH, 10 g (0.09 mol) of anhydrous Na_2CO_3 (reagent grade, Merck) were added to the NaOH solution prior to mixing with the metal nitrates solution. After the addition was complete, a thick slurry was obtained. This was heated for 18 h at 75 °C in a round-bottomed flask with an adapted condenser to prevent loss of water. The resulting mass was then filtered at reduced pressure and washed thoroughly with deionized water until a neutral pH was observed for the washing waters. The compounds were dried at room temperature (*ca.* 30 °C) for 48 h, or until a

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Table 1 Interlayer distances for the LDHs and temperature and time conditions for the intercalation reactions

LDH	temperature/°C	time/h	interlayer spacing/Å
Cd/Al/NO_3	—	—	8.24
Cd/Al/CO_3	—	—	7.54
Cd/Al/NO_3/PPA	25	24	14.59
Cd/Al/CO_3/PPA	70	24	14.59
Cd/Al/NO_3/CEPA	70	48+48	11.74
Cd/Al/CO_3/CEPA	70	48+48	11.35, 12.21

constant mass was observed, and were stored in a dissecator over silica gel.

Intercalation compounds

Intercalation of PPA, $PhPO_3H_2$ and CEPA, $H_2PO_3(CH_2)_2COOH$, (both reagent grade, Aldrich) into the prepared LDHs was performed in a Schlenk flask, using an LDH/phosphonic acid molar ratio of 1:1.3. The LDH and acid were mixed together to form a homogeneous powder. A portion of deionized water was then added to the powder mixture, so that the mass of water was ten times that of solid (LDH+acid) in the flask. The reactions were performed under constant stirring, using different times and temperatures. A list of the reaction conditions used in this work is given in Table 1. The resulting products were then separated by centrifugation, washed with deionized water until a constant pH of 6 was observed, and air dried at room temperature for 48 h. For the intercalation of CEPA, it was noted that the addition of a second portion of acid after 48 h is necessary to complete the reaction. This two-step intercalation process has been previously observed by Yamanaka and Hattori[26] for intercalation reactions of γ-zirconium phosphate.

Powder X-ray diffraction (XRD) patterns were obtained in a Shimadzu XD3-A diffractometer using Cu-Kα radiation. Fourier-transform IR (FTIR) spectra were obtained in Nujol (1500–400 cm^{-1}) and Fluorolube (4000–1300 cm^{-1}) mulls between halide windows in a Perkin-Elmer 1600 FTIR Series 40 spectrometer, with 16 scans for each sample. Density measurements were performed on a Micromeritics 1305 multipicnometer, using helium as the displacement gas. The samples were dried in an oven at 120 °C for 1 h and purged with helium before recording the density data. Magic angle spinning nuclear magnetic resonance for aluminium (^{27}Al MAS NMR) spectra were obtained in a Bruker AC 300 CXP spectrometer, operating at 78.21 MHz (corresponding to proton resonance frequency of 300 MHz). The r.f. pulse width was 5 μs, and a sample rotating frequency of 4–4.5 kHz. Chemical shifts were measured in relation to $[Al(H_2O)_6]^{3+}$. Sixty thousand scans were performed on each sample, with a delay of 0.1 s between successive scans. Chemical analysis was performed using atomic absorption techniques, by Puriquima Ltd., Sao Paulo.

For clarity, we will refer to the prepared compounds through a simple naming system. For instance, the LDH containing Cd as the divalent metal, Al as the trivalent metal, and nitrate as the counter anion, will be written as Cd/Al/NO_3. For the intercalation compounds, the name of the acid will be added, as in Cd/Al/NO_3/PPA, meaning the intercalation compound obtained through the reaction of Cd/Al/NO_3 with PPA.

Results and Discussion

Chemical analysis

Chemical analysis was performed on the LDHs to determine the Cd/Al ratio. In all the prepared LDHs this ratio was found to be very close to 2, which gives the formulae $Cd_2Al(OH)_5(NO_3)_2 \cdot 1.5H_2O$ and $Cd_2Al(OH)_5CO_3 \cdot 1.5H_2O$. The water content was determined by thermogravimetric analysis, which gave values close to 1.5 for t.

X-Ray diffraction

XRD patterns of the obtained LDHs correspond to that of synthetic hydrotalcite,[27,28] as can be seen in Fig. 1. The carbonate LDH is more crystalline in relation to its nitrate equivalent, resulting in a diffractogram with narrower and more intense peaks. It also presents a slightly lower interlayer distance. This can be explained if we consider that the carbonate ion is better accommodated in the interlayer region than the nitrate ion, due to its net negative charge of 2. It is known that the carbonate ion maintains its symmetry inside the layers, so that the plane containing the anions remains parallel to them. This leads to a minimum energy configuration and, consequently, better ordering.[27,29] The nitrate ion is also planar, but has a net negative charge of 1, so that twice the number of ions, in relation to carbonate, are necessary to neutralise the layer charge, resulting in greater repulsion between adjacent anions. We believe that this may be the cause for the higher disorder observed for the nitrate compounds. Also, the presence of twice as many anions in the interlayer region would account for the slightly larger value observed for the interlayer spacing in the nitrate LDHs.

Intercalation is confirmed by the increase in the interlayer spacing, as shown in Fig. 1.

The interlayer spacings for the LDHs and their intercalation compounds are presented in Table 1.

For the Cd/Al/CO_3/CEPA compound, two different interlayer spacings are observed. We attribute this to the fact that CEPA can interact with the hydroxide layers through either of its extremities, thus leading to different spacings within the same structure. The regions where the interactions occur through both CEPA ends should have a lower spacing than those where the interactions occur through only one end.

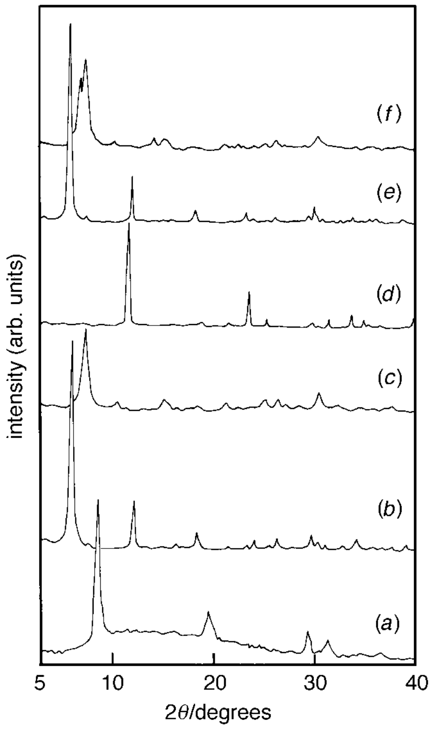

Fig. 1 X-Ray diffractograms of the cadmium LDHs and their intercalation compounds: (*a*) Cd/Al/NO_3, (*b*) Cd/Al/NO_3/PPA, (*c*) Cd/Al/NO_3/CEPA, (*d*) Cd/Al/CO_3, (*e*) Cd/Al/CO_3/PPA, (*f*) Cd/Al/CO_3/CEPA

Density measurements

Another way to confirm the occurrence of intercalation is to measure the density of the compounds before and after the intercalation reaction. A decrease in the value of density is a strong indication that intercalation has taken place. This happens because an increase in one of the crystallographic parameters leads to an increase in the unit cell volume, which causes the value of density to decrease.

The results presented in Table 2 show that intercalation causes a decrease in the observed density. The larger the interlayer spacing, the lower is the density. However, a higher value of density is observed for the PPA intercalation compound. This is probably due to its higher ordering in relation to the CEPA compound, as can be seen from its narrower and more intense diffraction peaks (Fig. 1). This higher ordering would be the result of a more densely packed structure. Nevertheless, it can be seen that in all cases intercalation leads to a decrease in density, as expected.

IR spectroscopy

LDHs. The IR spectra of the LDHs and intercalation compounds are presented in Fig. 2. The spectra of Cd/Al/NO_3 and Cd/Al/CO_3 [Fig. 2(*a*) and (*b*)] are alike. The broad bands around 3400 cm^{-1}, corresponding to the (O—H) stretching, are narrower than those normally observed for LDHs with an M^{II}/M^{III} ratio of 3:1. This, according to Hernandez-Moreno *et al.*,[27] represents a better ordering of the cations in the interlayer region.

Table 2 Densities of the nitrate LDHs and their intercalation compounds

compound	density/g cm^{-3}
Cd/Al/NO_3	2.662
Cd/Al/NO_3/PPA	1.565
Cd/Al/NO_3/CEPA	1.237

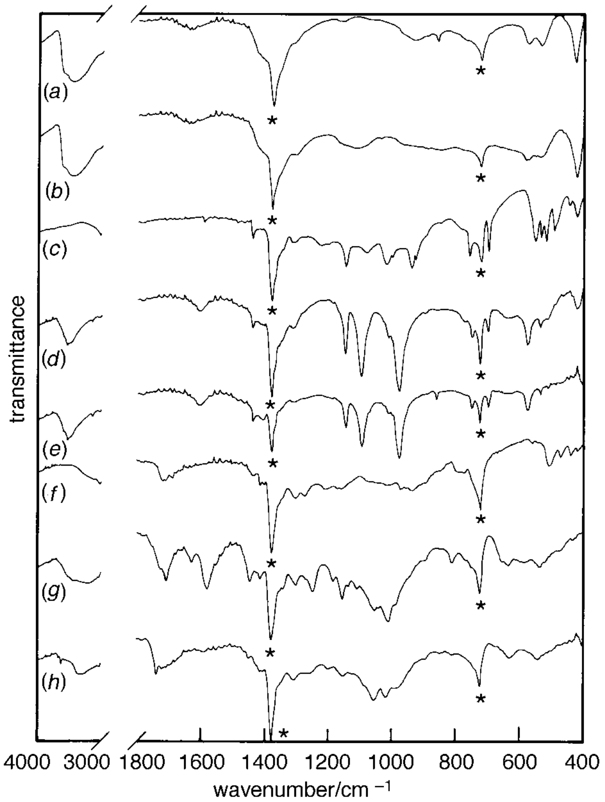

Fig. 2 FTIR spectra of the LDHs: (*a*) Cd/Al/NO_3, (*b*) Cd/Al/CO_3, (*c*) PPA, (*d*) Cd/Al/NO_3/PPA, (*e*) Cd/Al/CO_3/PPA, (*f*) CEPA, (*g*) Cd/Al/NO_3/CEPA, (*h*) Cd/Al/CO_3/CEPA (* = Nujol)

PPA intercalation compounds. Several modifications due to intercalation are observed when one compares the spectra of PPA [Fig. 2(*c*)] with those of its intercalation compounds [Fig. 2(*d*) and (*e*)]. (*i*) The ν(P=O) stretching broad weak band at 1220 cm^{-1} can only be seen in the pure acid, and disappears in the intercalation compounds. This band is broadened in the pure acid due to the formation of rotational isomers having slightly different energies.[30] (*ii*) The ν(P—O) stretching bands between 900 and 1180 cm^{-1} appear stronger and somewhat narrower in the intercalation compounds. There are also some changes in the $\delta(PO_3)$ bands that appear between 500 and 600 cm^{-1}. (*iii*) The bands assigned to out-of-plane ν(C—H) stretching modes at 695 and 757 cm^{-1} show changes in their relative intensities.

From these observations, some interesting conclusions can be drawn, regarding the short-range interactions that cause change in the spectra of the intercalation compounds. (*a*) The absence of the band assigned to the ν(P=O) stretching in the intercalation compounds shows us that there is the formation of PO_3^{2-} groups that present ionic interactions with the positive layers.[31] (*b*) The modifications that occur in the 900–1180 cm^{-1} [ν(P—O)] and 500–600 cm^{-1} [$\delta(PO_3)$] regions could be caused by two factors. First, the absence of the P=O bond affects the P—O vibrations, due to a change in the symmetry of the PO_3^{2-} groups. Secondly, the free acid has intramolecular hydrogen bonds, which are responsible for the broadening of its P—O bands.[32] In the intercalated phosphonate, these hydrogen bonds are no longer present, and the only possibility of hydrogen bonding is with the hydroxy groups from the positive layer and/or with the interlayer water molecules. In either case, these bonds are weaker, leading to smaller bandwidths. (*c*) Changes in position and intensity of the out-of-plane ν(C—H) bands are an indication that the aromatic ring suffers perturbations upon intercalation.

Another difference in the spectra of the intercalation compounds is the narrowing of the ν(O—H) stretching band around 3400 cm^{-1}, revealing that the hydrogen bonds in the intercalated compounds are weaker when compared to the pure LDHs. This fact may be due to a greater distance between the layers, caused by the presence of the organic molecules in the interlayer region.

CEPA intercalation compounds. The spectra for CEPA and its intercalation compounds are presented in Fig. 2(*f*), (*g*) and (*h*). In these compounds, we have observed some differences between the spectra of the free acid and the intercalated phosphonate. These are very similar to those observed for the LDH/PPA compounds, specially in the 900–1180 and 500–600 cm^{-1} regions. These differences can be attributed to modifications in the intramolecular hydrogen bond system.

However, the most striking feature of these spectra is the band that appears at *ca.* 1580 cm^{-1} in Cd/Al/NO_3/CEPA [Fig. 2(*g*)]. This band is associated with the deprotonated form of carboxylic acids, the carboxylate ion.[33] This result suggests that the interaction of CEPA with the layers occurs through both of its ends. This would explain the formation of carboxylate. In this case, the interaction would occur through a COO^- group at one end, and/or a PO_3H^- group on the other.

Nuclear magnetic resonance

In order to obtain further information about the interaction of the acids with the layers, ^{27}Al MAS NMR spectra were obtained for Cd/Al/NO_3 LDH and its intercalation compounds. These spectra are presented in Fig. 3. For the non-intercalated LDH, a chemical shift of δ 14.5 is observed. In a

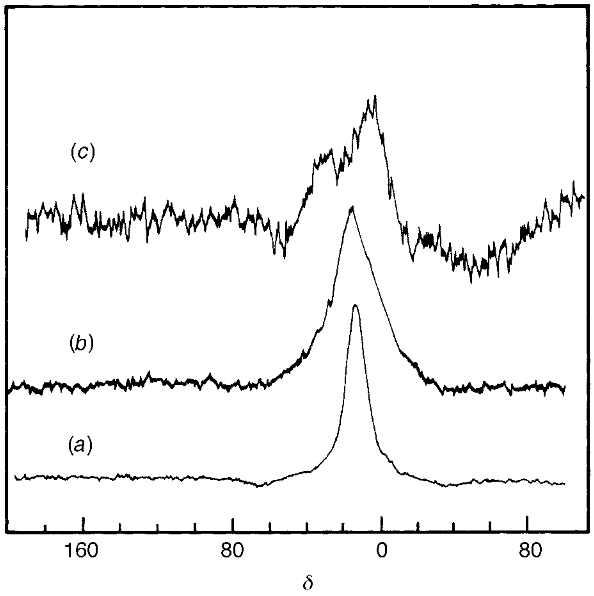

Fig. 3 ^{27}Al MAS NMR spectra of Cd/Al/NO_3 and its intercalation compounds: (*a*) Cd/Al/NO_3, (*b*) Cd/Al/NO_3/PPA, (*c*) Cd/Al/NO_3/CEPA

perfectly octahedral environment, the resonance line is expected at δ 0, and according to Hudson *et al.*,[12] the departure from that value observed in the spectrum is probably due to changes in the mean Al—O bond lengths, as well as from minor variations in the electric field gradient at the Al nuclei caused by distortions of the octahedral arrangements of the coordinating atoms. For the PPA intercalated LDH, no major changes are observed in the spectrum, and the resonance is observed at δ *ca.* 17.5. However, a slight increase in the linewidth is observed. This could be caused either by an increase in the Al relaxation time, due to interactions with the phosphonic acid, or by the presence of quadrupolar interactions between the phosphorus and aluminium nuclei.

For the CEPA intercalated compound, however, more drastic changes take place. Two distinct peaks, with δ -0.8 and 30.1, are observed. This suggests the interaction of CEPA through both of its ends with the positive layers, leading to different chemical environments around the Al nuclei, and consequently to different chemical shifts.

Conclusion

Layered double hydroxides containing cadmium as the divalent metal, aluminium as the trivalent metal, and nitrate and carbonate as the counter anions were obtained as single crystalline phases by a coprecipitation method. These compounds were intercalated with two different phosphonic acids by anion exchange. Intercalation is confirmed by X-ray diffraction and density measurements.

Modifications in the local symmetry of the phosphonate groups upon intercalation are detected by infrared spectroscopy. The presence of a band assigned to the carboxylate group suggests that CEPA interacts with the positive layers through either or both of its ends. This result is corroborated by NMR measurements that show two different chemical environments for the Al atoms in the Cd/Al/NO_3/CEPA intercalation compound.

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