Anion exchange in layered double hydroxides by surfactant salt formation

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In this paper a method of anion exchange in layered double hydroxides (LDHs) based on the formation of a salt between an anionic and a cationic surfactant, which is extracted from aqueous solution into an organic unmixed phase, is discussed. Two Zn(II)–Cr(III) LDHs, synthesised by direct coprecipitation under constant pH intercalated with dodecylsulfate (DS) and dodecylbenzenesulfonate (DBS), were used as starting materials (precursors). By this method various inorganic and organic anions can be intercalated by exchange with the surfactant anion in the interlamellar domain, resulting in new intercalated materials. The kinetics of such exchange and the possibility of controlled partial exchange are also discussed.
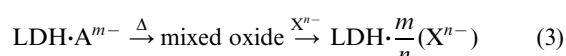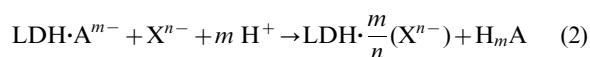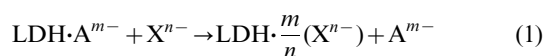
The exchanged materials obtained showed phase purity and considerable high crystallinity. Another advantage of this method is related to the conditions in which the precursor and the final products can be obtained, *i.e.* the precursors are very easy to synthesise and no further treatments for use in this exchange, such as hydrothermal treatment, are required in either case. Moreover, the kinetic study showed that the anion exchange is very quick. An advance on anion exchange process in LDHs is also demonstrated by the possibility of controlled quantitative substitution.

Introduction

Layered double hydroxides (LDHs), or the so-called anionic clays, are a class of materials that have received increased attention due to their particular properties and applications.[1,2] These properties are derived from their structure, which consists of stacking of brucite-like layers $[Mg(OH)_2]$ with a positive residual charge. This residual charge is originated by the isomorphous substitution of the M^{2+} cation by a trivalent one. In order to attain electroneutrality, an appropriate number of hydrated anions must occupy the interlamellar domain. The general formula that represents this kind of material is, $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}A^{m-}_{x/m}\cdot nH_2O$, where M^{2+} is a bivalent cation, M^{3+} is a trivalent cation and A an interlamellar anion with charge $m-$. They can be applied as catalysts,[1–6] catalyst precursors or catalyst supports;[7,8] adsorbents;[9,10] anion exchangers,[11,12] and in medicinal applications,[13,14] among other uses.

The direct synthesis of such materials can be conducted by various methods, such as coprecipitation (or salt–base method),[15,16] salt–oxide method[16–18] and hydrothermal synthesis.[15,16] Other methods of direct synthesis are found in the literature, such as electrochemical synthesis[19,20] and sol–gel synthesis,[21] but these methods are barely studied up to now.

On the other hand, indirect synthesis makes use of a directly synthesised LDH resulting in compounds containing identical brucite-like layers and different interlamellar anions. Three main methods, and some variations of these, have been applied to perform anion exchange up to now. These methods may be schematised as follows:

$$LDH\cdot A^{m-} + X^{n-} \rightarrow LDH\cdot\frac{m}{n}(X^{n-}) + A^{m-} \qquad (1)$$

$$LDH\cdot A^{m-} + X^{n-} + m\,H^+ \rightarrow LDH\cdot\frac{m}{n}(X^{n-}) + H_mA \qquad (2)$$

$$LDH\cdot A^{m-} \xrightarrow{\Delta} \text{mixed oxide} \xrightarrow{X^{n-}} LDH\cdot\frac{m}{n}(X^{n-}) \qquad (3)$$

In method 1 the precursor contains univalent anions, such as chloride, nitrate or perchlorate, which have a weak interaction by electrostatic forces with the layers.[11,16,18] By this method a great variety of anions have been intercalated, such as oxo-anions,[16,18,22,23] halides,[16,18] polyoxometalates (POMs),[24,25] and various organic anions.[2] Recently, Kaneyoshi and Jones[26] showed that the exchange of anionic species such as terephthalate, which presents strong electrostatic attraction with the layers, may be done in neutral media, using a highly concentrated solution of the substituting anion.

In method 2 the precursor should contain anions susceptible to acid attack, such as carbonate. Precursors containing carboxylates, *e.g.* terephthalate, are also utilised. This method was (first) proposed by Bish,[27] who showed the anion exchange of carbonate by chloride, nitrate, bromide and sulfate. An application of this method has received great attention in the last decade: the exchange of carbonate or terephthalate by polyoxometalates (POMs).[25,28,29] A variation of this method was demonstrated by Carlino and Hudson,[30] where the solid precursor containing carbonate anions reacts with molten carboxylic acids.

In method 3 the precursor contains carbonate as the interlamellar anion, and is based on the "memory effect". This method is conducted by the calcination of the precursor until the elimination of the interlamellar anion. Then, the calcined product is put in contact with a solution of the desired anion. The lamellar structure is then reconstituted, with the concomitant intercalation of the selected anion. Although this method is applicable to various anions,[2,15,29] it is limited to LDHs that exhibit this "memory effect". Mg–Al-LDHs and Zn–Al-LDHs[31] have this property. Calcined LDHs have also been applied as sorbents, removing anions such as dodecylsulfate and dodecylbenzenesulfonate,[32] and picrate[33] from the solution by both intercalation and adsorption processes.

Some works reported in the literature show systematic comparisons between these indirect methods of synthesis with direct ones. Ulibarri and coworkers[29] and Yun and Pinnavaia[25]

showed comparisons between some of the cited methods in the synthesis of Mg–Al-LDH intercalated with polyoxometalates. Jones and coworkers[34] reported a systematic comparison between the direct synthesis by coprecipitation and the indirect synthesis by reconstitution of calcined precursors on the preparation of organic-intercalated LDHs. Recently, the synthesis of organic-intercalated LDHs was revised by Newman and Jones.[2]

The efficiency of anion exchange in LDHs can be considerably high. Values up to 98% were reported for the exchange of chloride by carbonate.[18] However, the efficiency may be very low if the substituting anions present weak interaction with the layers.[35] For method 2, Bish[27] reported efficiencies very close to 100% for the exchange of carbonate in acid medium. However, to achieve such efficiency low pH values must be used, which can lead to a partial decomposition of the layers. The necessary time for an efficient exchange can vary depending not only on the method used, but also on the anionic species involved. Actually, contact times ranging from 2 hours to some days have been used to perform the exchange; however, the time usually used ranges from 6 to 12 hours.[16,18,28,34]

Recently, we described a new method of anion exchange.[36] This method is based on the use of an LDH precursor intercalated with an anionic surfactant (sulfated or sulfonated), e.g., dodecylsulfate (DS). The anion exchange can be promoted by the addition of a cationic surfactant (e.g., N-cetyl-N,N,N-trimethylammonium bromide, CTAB) in a mixture containing the precursor suspended in a solution of the anion of interest in contact with an unmixed organic phase (e.g., chloroform). The exchange is achieved by the formation of a water insoluble salt between the precursor's anionic surfactant and the cationic one added. The surfactant salt is instantaneously removed from the aqueous suspension to the organic phase. Such an exchange mechanism makes this method easy and fast to carry out. It was shown that the exchange of dodecylsulfate by a set of different anions (chloride, carbonate, terephthalate, cholate and a sulfonated Cu-phthalocyanine) was achieved within 30 minutes with efficiency higher than 98.5%. It was also shown that the formation of the surfactants' salt is specific between the surfactants used, i.e., SDS and CTAB. Moreover, it was concluded that the absence of the cationic surfactant in the medium completely hinders the anion exchange. This method may be schematised as follows:

$$LDH \cdot DS_{(s)} + CTA_{(aq)}{}^{+} + X_{(aq)}{}^{n-} \rightarrow$$
$$LDH \cdot \frac{1}{n}(X^{n-})_{(s)} + CTA-DS_{(org)} \qquad (4)$$
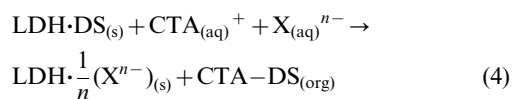
In the present work, a detailed approach about this method, including the use of a different anionic surfactant in the precursor, i.e., dodecylbenzenesulfonate, is presented. Moreover, we show results about the exchange kinetics and the controlled partial substitution.

Materials and methods

Chemicals

Sodium dodecylsulfate (min. 99.0%) was purchased from Merck. Copper(II) phthalocyaninetetrasulfonic acid tetrasodium salt and sodium dodecylbenzenesulfonate (80% min.) were purchased from Aldrich. Terephthalic acid (99.9%) was kindly donated by Rhodiaco Indústrias Químicas Ltda. All other reagents were of analytical grade and were purchased from Merck. Distilled water was further purified by passing through a Millipore Milli-Q system.

Syntheses of the precursors

Two precursors were synthesised with a 3:1 Zn(II):Cr(III) ratio, one containing dodecylsulfate (DS) and the other

containing dodecylbenzenesulfonate (DBS) as the interlamellar anion. The syntheses were carried out by the coprecipitation method under constant pH. A solution containing 0.250 mol of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.083 mol of $Cr(NO_3)_3 \cdot 9H_2O$ in 175 cm^3 of water was added to an anion solution containing 0.166 mol of the anionic surfactant in 700 cm^3 of water, under vigorous mechanical stirring, at a rate of 2 cm^3 min^{-1}. A 2 mol dm^{-3} NaOH solution was added in order to maintain the pH at 7.0 ± 0.2. The obtained material was washed and separated by centrifugation. One portion was vacuum dried to proceed with the characterisation. The major washed portion was kept in water, resulting in 1.3 g of the solid precursor per 20 g of suspension. The chemical analysis gave Zn 26.21%, Cr 7.32%, C 22.64%, O 33.02%, H 5.76% and S 5.04% for DS-containing LDH, and Zn 25.20%, Cr 6.70%, C 30.53%, O 27.35%, H 5.64% and S 4.52% for DBS-containing LDH.

By this same method, LDHs containing terephthalate or copper(II) phthalocyaninetetrasulfonate were also synthesised. These preparations were carried out in order to compare the properties of the obtained materials with those of similar intercalated materials obtained by anion exchange. The synthesis followed exactly the procedure described above, but using anion solutions containing 0.0830 or 0.0415 mol of terephthalate or copper(II) phthalocyaninetetrasulfonate respectively.

Anion exchange

The anion exchange process followed the steps described in our previous communication.[36] A portion of 25 cm^3 of a 0.15 mol dm^{-3} CTAB solution was added into a mixture containing 20 g of the precursor's suspension, 50 cm^3 of a substituting anion solution containing an excess of 100% in relation to the stoichometric amount, and an organic phase (30 cm^3 of chloroform). This system was kept for 30 minutes, after which the solid material was washed (three times with chloroform, once with acetone and twice with water) and separated by centrifugation. The obtained materials were vacuum dried. The exchange was tested by the same method using carbonate, terephthalate and copper(II) phthalocyaninetetrasulfonate as the substituting anions.

It is important to note that the preparation of the 0.15 mol dm^{-3} CTAB solution must be done at a temperature around 313 K. The solution is kinetically stable, but if stored recrystallization may occur, and heating of the solution is necessary again before use. It is also important to emphasise that the solid separation could sometimes be difficult, due to the formation of a stable suspension containing the solid material. In this case, centrifugation leads to the formation of three phases, where the suspension containing the solid material is between the aqueous and the organic phase. In this sense, the separation may be done by the addition of a portion of approximately 20 cm^3 of acetone, which makes the suspension unstable.

Exchange kinetics

The kinetics of the anion exchange were studied for the exchange of the DS-containing precursor with terephthalate. The procedure followed the same steps described for the conventional exchange, and its rate was determined by measuring the terephthalate concentration in the supernatant of aliquots collected after 2, 6, 10, 20, 30, 60 and 110 minutes of contact time, keeping the mixture under vigorous stirring to allow the exchange. The terephthalate concentration was determined spectrophotometrically ($\lambda = 239$ nm) by an appropriate dilution of the supernatant, and compared with a calibration curve for this anion.

Controlled partial exchange

The controlled partial exchange was also investigated for the exchange of precursor's DS anions by terephthalate. The exchange control was done by varying the CTAB solution concentration while all of the other variables were kept constant. Therefore, 25 cm³ of CTAB solutions with the concentrations zero, 0.030, 0.045, 0.060, 0.090, 0.120, and 0.150 mol dm⁻³, were added into separate beakers containing the other reactants. The contact time was also 30 minutes.

Characterisation

Powder X-ray diffraction (PXRD) data were collected with a Siemens D5005 X-ray diffractometer using Cu-Kα radiation ($\lambda = 1.5406$ Å) and a graphite crystal as monochromator, with a 2θ step of $0.02°$ s⁻¹. Zinc and chromium were quantified by atomic absorption spectrophotometry, using a Varian AA-175 instrument. The presence of bromide (CTAB counter ion), a potential contaminant, was tested using a model 9635 Ionplus series bromide electrode from Orion Res. Inc. The presence of DS (or DBS) anions as well as CTAB in the obtained materials was tested by elemental analysis of sulfur and nitrogen, respectively. The analysis of C, H, N and S was performed using a Perkin-Elmer Elemental Analyser 2400 CHN.

Results and discussion

Synthesis of Zn–Cr–DS-LDH and Zn–Cr–DBS-LDH precursors

PXRD patterns obtained for the precursors are shown in Fig. 1. As can be seen, the precursors showed good crystallinity in their inter- and intra-lamellar organization. From (00l) peaks [$1/3c$ (unit cell parameter) $= 1/7(1d_{003} + 2d_{006} + 3d_{009} + 4d_{0012} + 5d_{0015} + 6d_{0018} + 7d_{0021})$] using the Bragg equation, we found a basal spacing of $d = 25.7 \pm 0.2$ Å for the DS-intercalated LDH and 29.5 ± 0.1 Å for the DBS-intercalated LDH. These values are in agreement with literature data.[37] The good crystallinity and phase purity were obtained without any other further treatment, such as the hydrothermal one. In other words a precursor with these characteristics can be easily obtained.

The high crystallinity obtained for these LDHs may be attributed to the self-organization of the DS anions in the interlamellar domain. The self-organization may be attributed to the interactions between the hydrophobic chains of the surfactant anions. We think that these interactions occur in a similar manner to that observed in micelles. In micellar systems the surfactant shows a tendency to aggregate through the interactions between the hydrophobic chains, while the polar
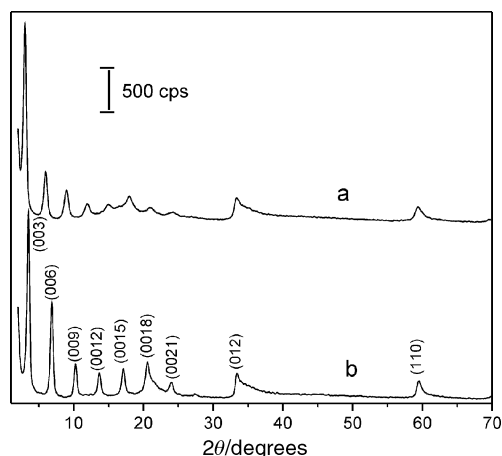
heads are kept in contact with the aqueous medium. In this case, the LDH interlayer domain constitutes a medium with very adequate features to stabilise the surfactant. The average area available per monovalent anion in the Zn–Cr-LDHs used in this work, obtained by calculation based on the *a* parameter of the hexagonal unit cell following a method described in the literature,[38] is about 30 Å². This area is in the same order of magnitude as the cross section area reported in the literature for the linear, long alkylic chains of alcohols and carboxylic acids, which is around 23 Å².[39] So, it is possible to infer that the disposition of the surfactants in the interlamellar domain of the LDH should maximise the interactions between the hydrophobic chains of the surfactant anion, while the polar head (a sulfate or benzenesulfonate group) gets the negative charge balanced by the positive charges of the planar layers. All of these interactions together can contribute to the stabilisation of the system, so the high crystallinity obtained is not surprising. Therefore, it is possible to conclude that the weak interactions between the hydrophobic chains of the surfactant molecule play a very important role on the organization of the structure of the obtained materials.

From the chemical analysis the following molecular formulae were obtained: $Zn_{0.74}Cr_{0.26}(OH)_2(DS)_{0.29}\cdot0.65H_2O$ for DS intercalated LDH and $Zn_{0.75}Cr_{0.25}(OH)_2(DBS)_{0.28}\cdot0.51H_2O$ for DBS intercalated LDH. The obtained Zn:Cr ratio was around 2.9 for both LDHs, lower than the starting ratio of 3. This difference may be attributed to the preferential solubilisation of the bivalent metal hydroxide, a phenomenon widely reported in the literature for LDH systems.[15] In both LDHs a surfactant:Cr ratio higher than expected (1:1) was observed. This fact may be attributed to the adsorption of the surfactant on the LDH surface, since this kind of anion shows a high tendency to be adsorbed on LDH.[9,10]

The anion exchange process

The exchange process is induced by the formation of a salt between the interlamellar DS anions and the cationic surfactant CTAB. The formation of this salt is a reaction usually employed to quantify anionic surfactants (sulfated and sulfonated) from aqueous solutions.[40] The formation of such salt displaces the DS present in the precursor. The displacement of the interlamellar DS is favoured by the migration of the salt to an already present organic phase (in which it is soluble). To occupy the sites left by the DS anions, an appropriate amount of the other anion present in the aqueous solution is intercalated, keeping therefore the LDH electroneutrality. A schematic illustration of this process can be seen in Fig. 2.

The surfactant salt formed during the exchange process has a characteristic PXRD pattern, and, together with the precursors' PXRD patterns, they contain important information, since a correlation with the PXRD patterns showed for the obtained materials can demonstrate their absence as a contaminant phase. Fig. 3 shows the PXRD patterns for both the CTA⁺–DS⁻ and CTA⁺–DBS⁻ salts. As one can see, the CTA⁺–DS⁻ salt presents a PXRD pattern with intense and sharp peaks, and may be easily recognisable if present as a contaminant phase in the obtained materials. Even though it is less crystalline, the CTA⁺–DBS⁻ salt also has a recognisable sharp peak.

Carbonate anions were easily intercalated in the Zn–Cr–DS-LDH and Zn–Cr–DBS-LDH precursors by this method of anion exchange. As can be seen in Fig. 4a and 4b, phase purity and high crystallinity (comparable to those shown by the precursor) were obtained, even though the exchange conducted with the Zn–Cr–DBS precursor resulted in a material less crystalline than the one obtained from the DS-containing precursor.

The PXRD pattern for the material obtained by the

Fig. 1 PXRD pattern of the precursors (a) Zn–Cr–DBS-LDH, and (b) Zn–Cr–DS-LDH.
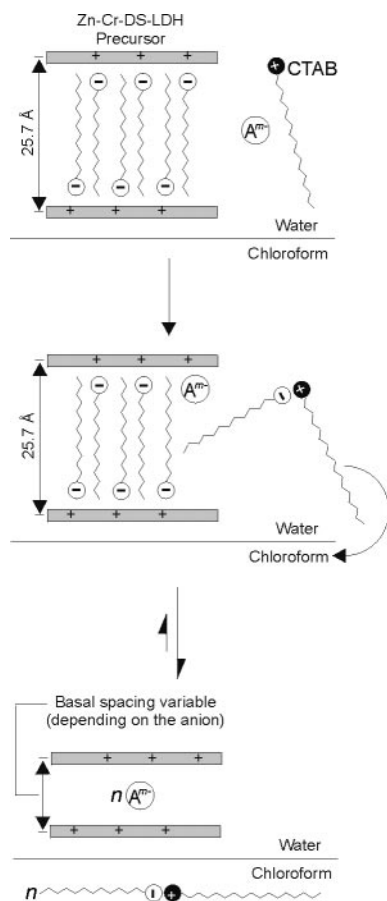
Fig. 2 Scheme of anion exchange by the formation of a salt between an anionic and a cationic surfactant in LDHs.

Fig. 3 PXRD patterns of the surfactant salts formed during the anion exchange: (a) CTA^+–DS^- and (b) CTA^+–DBS^- salt.
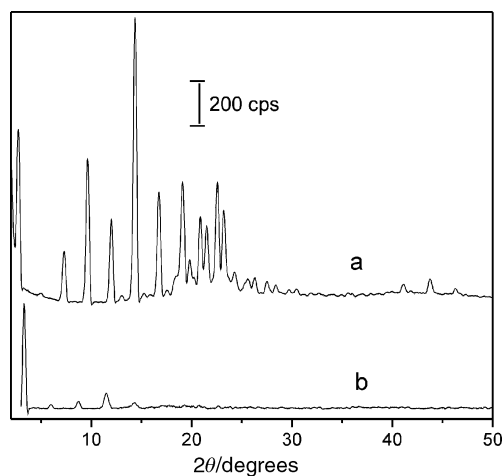
exchange of carbonate from the dried precursor is shown in Fig. 4c. The phase purity, crystallinity and basal spacing of the obtained material are comparable to those showed by the exchange when the fresh suspension was used. This result suggests that the maintenance of the precursor in suspension is not strictly necessary.

Fig. 4d shows that the presence of CTAB in the medium is essential for the exchange. Even though carbonate anions can be easily intercalated, they cannot displace DS from the interlamellar domain without the formation of the surfactant salt, so the PXRD pattern obtained presents the same characteristics as those obtained for the precursor. Therefore the presence of CTAB in the medium is an indispensable factor for anion exchange.

The intercalation of terephthalate by this method was tested using both precursors. As can be seen from Fig. 5a, the materials obtained showed high crystallinity and phase purity, but the one obtained by using the Zn–Cr–DBS precursor was less crystalline. The basal spacing obtained for the intercalation of terephthalate, which was the same when using both precursors, is in good agreement with reported data.[28]

Fig. 5b shows the PXRD pattern of the copper(II) phthalocyaninetetrasulfonate containing LDH obtained by this exchange method using both precursors. The intercalation of the phthalocyanine anion showed a material with crystallinity and basal spacing (23.4 Å) comparable with reported data for a similar compound.[41] In this case, it is also important to note that the negative charges of this compound are derived from sulfonate groups. However, no salt formation was observed between this anion and CTAB. This fact was evidenced by the chloroform phase collected at the end of preparation, which was free of the characteristic blue colour shown by this anion.

The intercalation conducted with the DBS-containing precursor resulted in a material with lower crystallinity when compared to the one obtained by using the DS-containing precursor. Even though the exchanges conducted with the Zn–Cr–DBS-LDH precursor resulted in the desired material, their crystallinities were always lower than those obtained with the Zn–Cr–DS precursor. This difference may derive from the high organization in the interlamellar domain promoted by the intercalation of DS anions. As discussed here, these anions are able to self-organise, contributing to the well-organised structure obtained. These characteristics are not so pronounced with the DBS anions, probably due to the polar head (benzenesulfonate is more voluminous than the sulfate of the DS anion) and the angular disposition between the polar head and the tail (the disposition of DS anion chain is almost linear with its head). This feature can be seen in the PXRD patterns of both precursors in Fig. 1. Therefore, based on the results it is possible to note that the higher the organization of the precursor in the interlamellar domain, the higher the crystallinity presented by the material resulting from the anion exchange by this method.

Fig. 5 also shows the PXRD patterns for terephthalate and copper(II) phthalocyaninetetrasulfonate containing LDHs synthesised by the coprecipitation method. For terephthalate containing LDH, it is possible to note that the overall crystallinity is comparable with the one of materials obtained by anion exchange. However, it is possible to see that the non-basal diffraction peaks (012 and 110) are a little more intense for anion exchanged materials. This feature may be related again with the high structural organization of the precursors, as discussed above. For the copper(II) phthalocyaninetetrasulfonate containing LDH obtained by the direct coprecipitation method, the PXRD pattern showed that the material is much less organised than the ones obtained by anion exchange, and that this material contains a non identified impurity. Therefore, it is possible to conclude that, in this case, the anion exchange method is much more efficient than the coprecipitation method.

The chemical analysis of the obtained materials showed that these materials kept the Zn : Cr ratio of their respective precursors. This same analysis also showed that sulfur was completely absent in the obtained materials, indicating the stoichometric elimination of the DS anions. The analysis of bromide (counter-ion of CTAB, a potential contaminant) gave amounts between zero and 0.2% of the sample. Considering that all bromide is intercalated the higher amount of bromide obtained corresponds to about 1.5% of the intercalated anion, *i.e.*, the efficiency ranges from 98.5 to 100%. The high efficiency shown by this method may be attributed to the displacement of the equilibrium promoted by the formation of the surfactant salt and the migration of this species to a second, organic phase.
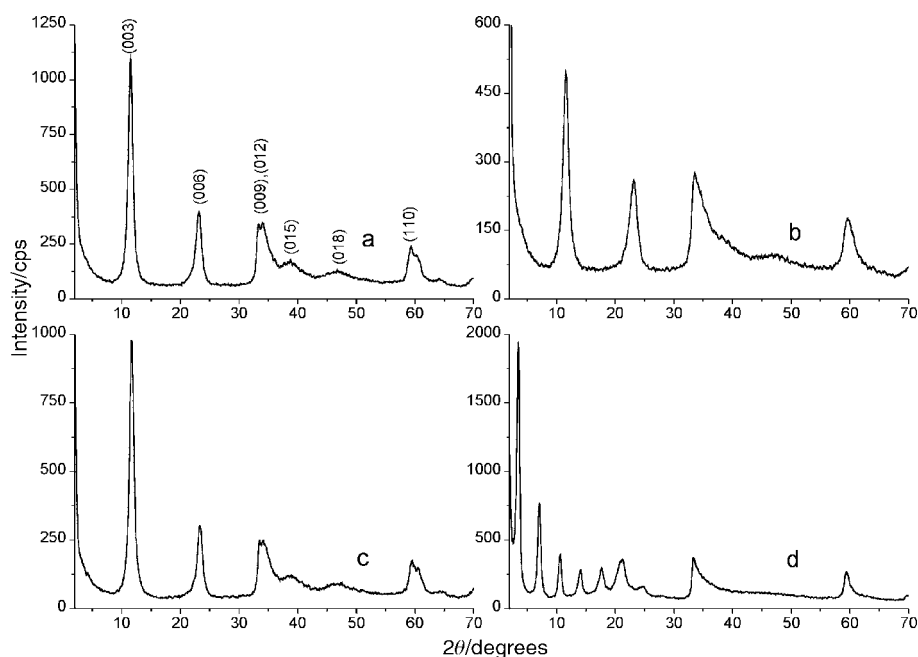
Fig. 4 PXRD patterns showed by the carbonate–LDH exchange experiments when (a) suspension of the Zn–Cr–DS-LDH precursor was used; (b) suspension of the Zn–Cr–DBS-LDH precursor was used; (c) dried Zn–Cr–DS-LDH precursor was used; and (d) suspension of the Zn–Cr–DS-LDH precursor was used but no CTAB was added.

Exchange kinetics

In the study of the exchange kinetics, the first analysed time, 2 minutes, is just the time necessary to separate the supernatant from the solid material, *i.e.*, the first aliquot was collected immediately after the addition of CTAB solution. It was possible to observe, by the obtained results, that after just 2 minutes of contact the terephthalate concentration is approximately the same as that observed after 110 minutes. This result showed that the process is practically instantaneous.

In order to compare the properties of the materials obtained with different contact times, a PXRD analysis was conducted on such materials (Fig. 6). It is possible to observe that the PXRD patterns obtained with the first and last contact times studied are very similar. Therefore, the results showed that the exchange process occurs almost instantaneously. The final product is already obtained immediately after the addition of the CTAB solution. This rate for obtaining a crystalline LDH without any further treatment by an indirect (or even a direct)

method has never been reported before. The anion exchange in LDHs by the indirect methods usually needs several hours to reach equilibrium. This time is quite long if compared with the instantaneous process that occurs with this new exchange method. Regarding the efficiency of this method, here it is also possible to attribute the high speed observed to the displacement of the equilibrium promoted by the surfactant salt formation and their migration into the organic phase.

Controlled partial exchange

The results obtained from the analysis of the supernatant of the exchanges conducted with terephthalate and the Zn–Cr–DS-LDH precursor are shown in Fig. 7. These results are plotted against the amount (in mmol) of CTAB added.

From Fig. 7 one can see that the exchange process is directly related to the amount of CTAB added. The exact amount at which the exchange occurs lies around 2.52 mmol as expected, and the total amount added in all of the exchanges, *i.e.* 3.75 mmol, represents an excess (taken to guarantee the total DS removal). In other words, Fig. 7 shows that this anion
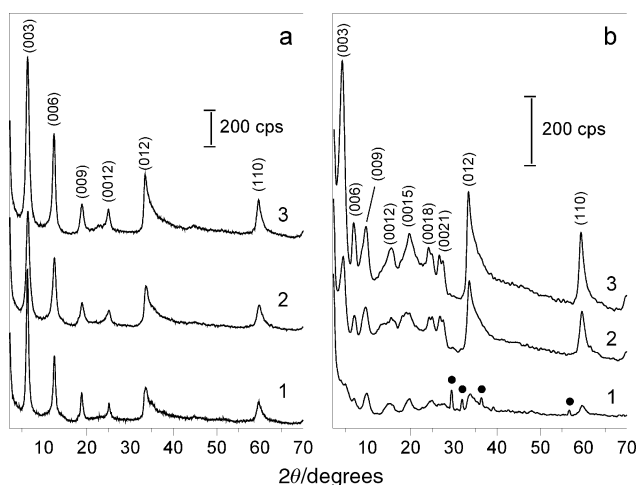
Fig. 5 PXRD patterns of (a) terephthalate containing LDHs and (b) copper(II) phthalocyaninetetrasulfonate obtained by: (1) direct synthesis by the coprecipitation method; (2) anion exchange using the Zn–Cr–DBS-LDH precursor; and (3) anion exchange using the Zn–Cr–DS-LDH precursor. (●) impurity (unidentified phase).
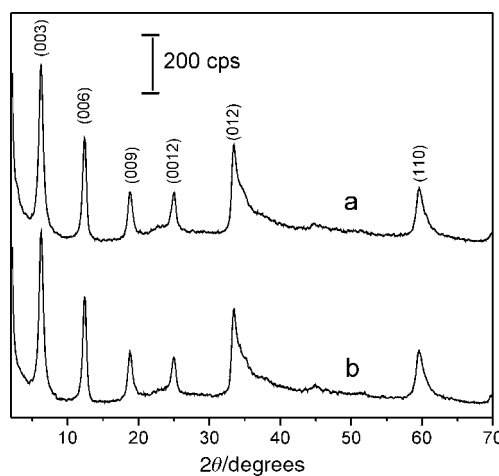
Fig. 6 PXRD patterns of terephthalate containing LDHs obtained by anion exchange of Zn–Cr–DS-LDH precursor after (a) 2 minutes and (b) 110 minutes of contact time.
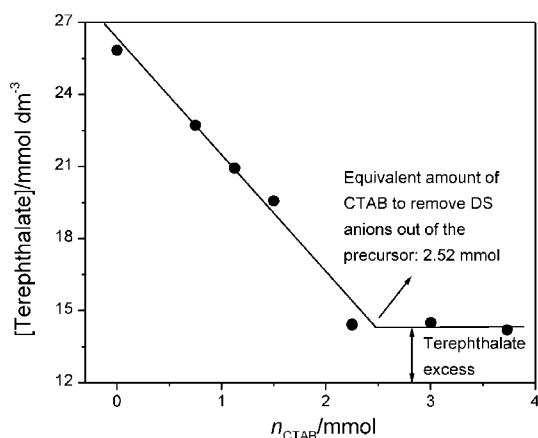
Fig. 7 Decay of terephthalate concentration relative to the amount of CTAB added.

exchange process can be controlled by the amount of the cationic surfactant added, and also that the exchange occurs quantitatively, as can be seen by the residual amount of terephthalate in solution, which represents the excess of this anion added. These results demonstrate again that the exchange process is completely dependent on the addition of CTAB.

The information given from this study opens a new field of study in LDHs, controlled partial exchange. With this property one can obtain LDHs with two (or more) phases by adding the appropriate amounts of the cationic surfactant solution and the desired amount of the anions of interest. Fig. 8 exemplifies this property with the PXRD patterns of some of the materials obtained from this study.

As one can see, two sets of basal diffraction peaks were observed, one set showing a basal spacing in agreement with DS containing LDH and the other in agreement with TA (terephthalate) containing LDH. To explain the presence of these two sets of basal diffraction peaks we considered three different possibilities of interlayer arrangement: (i) the coexistence of both anions inside two successive layers; (ii) an ordered interstratification of DS containing and TA containing layers; and (iii) the formation of two different phases, each one containing one anion.

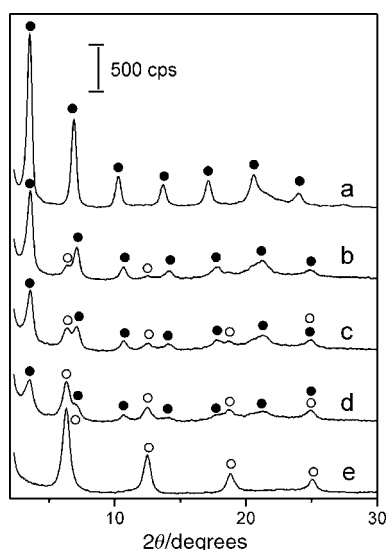The first hypothesis implies that the observed PXRD pattern

Fig. 8 PXRD patterns of the materials obtained in the intercalation of terephthalate with the Zn–Cr–DS-LDH precursor by varying the amount of the cationic surfactant added. a) 0; b) 0.75; c) 1.13; d) 1.50; and e) 3.00 mmol of CTAB added. The symbols indicate (●) Zn–Cr–DS-LDH and (○) Zn–Cr–TA-LDH.

might show only one set of basal diffraction peaks, with the basal spacing of the largest one, *i.e.*, the DS anion. The presence of such an arrangement cannot be investigated by the used analysis methods (PXRD, FT-IR and elemental analysis). However, Schöllhorn and Otto[35] showed that the formation of an LDH with two different anions in the interlayer space is energetically unfavourable. So, it is difficult to believe in the existence of such an arrangement.

The second hypothesis might show two sets of peaks as observed. However, such an arrangement implies the presence of a third set of basal diffraction peaks, with a basal spacing close to the sum of the basal spacings of the DS containing LDH and the TA containing LDH, as shown by Kooli and coworkers.[42] As this third hypothetical set of basal peaks was not observed, this hypothesis may be ruled out.

We considered the last hypothesis as the most probable. The presence of two different phases can easily explain the presence of two sets of basal diffraction peaks. The high level of heterogeneity existent in the LDH structure, evidenced by many features such as broad diffraction peaks, disorder in the interlamellar domain, different levels of hydration state and even the anion exchange properties,[16] might imply the presence of sites (or portions of the material) that react with different anion exchange rates. This heterogeneity could lead to the formation of different phases during the exchange process.

Conclusions

By the results obtained it is possible to conclude that the presented method is advantageous when compared with the previously reported ones because high efficiency is reached in a very short time. In fact, it is the fastest method reported for anion-exchange in LDHs up to now. As discussed in this work, these characteristics of the method may be attributed to the displacement of the equilibrium promoted by the formation of the surfactant salt and their migration into the organic phase. This method also showed high specificity, since the cationic surfactant did not form salts with anions different from the anionic surfactant. Moreover, as shown by the results, this method is very versatile, since it may be conducted in a very wide pH range: from 4.5 for exchange by decavanadate (applied in our previous report[36]) to 11.5 for exchange by carbonate.

A singular characteristic of this method is the possibility of a partial, controlled exchange, which is not possible to be done with any other method reported before. It is very important because it allows control between two different anions in the structure of the material, as can be controlled by the M^{II}/M^{III} ratio during the direct synthesis. So, it may be considered an advance in the design of LDHs, allowing not only the control of the metal cations ratio, but also the anions ratio.

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