

# A new method of intercalation by anion exchange in layered double hydroxides

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A new anion exchange method of intercalation in layered double hydroxides (LDHs), based on the formation and organic phase extraction of a salt between dodecylsulfate anions and a cationic surfactant (CTA), is described which is shown to be a very fast and efficient way to obtain a wide variety of LDH-intercalated organic and inorganic anions, using the precursor Zn(II)–Cr(II)–dodecylsulfate LDH.

Layered double hydroxides (LDHs), or the so-called hydroxide-like compounds, can be represented by the general formula  $[M^{II}_{1-x}M^{III}_x(OH)_2](A^{m-})_{x/m} \cdot nH_2O$ . The structure of this kind of compound, based on the stacking of positively charged layers with hydrated anions in the interlamellar domain, confers relatively high mobility on these anions.<sup>1–3</sup>

Direct synthesis of LDHs can be conducted by various methods, e.g. coprecipitation,<sup>1,2</sup> the salt–oxide method,<sup>2,3</sup> hydrothermal synthesis,<sup>1</sup> as well as less studied methods.<sup>4,5</sup> However, there are some indirect methods based on the use of LDH precursors prepared by direct synthesis in order to obtain a new different compound. Indirect synthesis can traditionally be conducted using three main techniques: (i) direct anion exchange, using an LDH intercalated with chloride (sometimes nitrate or perchlorate) as the precursor;<sup>2,3,6</sup> (ii) anion exchange by elimination of the precursor interlamellar species (usually carbonate or terephthalate) susceptible to acid attack;<sup>7–9</sup> and (iii) regeneration of the material obtained by the calcination of an LDH intercalated with carbonate (eventually others), in a solution containing the anion of interest.<sup>1,10–12</sup>

In this work a new method of anion exchange in a surfactant-intercalated LDH is described. The mechanism involved is based on the formation of a salt between an anionic surfactant (sulfated or sulfonated) and a cationic one (e.g. *N*-cetyl-*N,N,N*-trimethylammonium bromide, CTAB, or benzyltrimethylammonium chloride, BAC).<sup>13</sup> The salt is then removed from the aqueous medium into an organic phase such as dichloromethane, chloroform, di- and tri-chloroethanes or hexane.

The LDH precursor used in this method should contain an anionic surfactant (in this work dodecylsulfate, DS, was used) in the interlayer domain. The precursor was synthesised by the coprecipitation method at constant pH ( $7.0 \pm 0.2$ ), with a Zn : Cr ratio of 3 : 1.<sup>2</sup> This one-step synthesis is very easy to perform. The product obtained is well-crystallised without further treatments, as can be seen from the powder X-ray diffraction (PXRD) pattern of this precursor in Fig. 1a (Siemens X-ray diffractometer D5005, Cu- $K_{\alpha}$  = 1.5406 Å). This fact can be attributed to the self organisation of DS anions in the interlamellar domain, promoted by interactions between the hydrophobic chains. The obtained basal spacing is very close to those reported in the literature.<sup>8</sup> The high crystallinity of the precursor is very important for the synthesis of LDHs by indirect methods since the crystallinity of the product is directly related to that of the precursor.<sup>1,9,12</sup>

The anion exchange was carried out by adding 20 mL of a 0.15 M CTAB solution to an aqueous mixture containing 20 g of a suspension of the precursor (approximately 1.3 g of Zn–Cr–DS–LDH), 50 mL of the solution of the anion of interest containing an excess of the amount necessary for a quantitative exchange and the organic phase (30 mL of chloroform was used). The surfactant anion was removed from the interlayer domain by the formation of the salt with the cationic surfactant,

which migrates to the organic phase favouring the concomitant intercalation of the anion of interest. The formation of this salt and its migration to the organic phase are fast and so is the anion exchange process. The surfactant salt is insoluble (or only sparingly soluble) in the aqueous phase, so its migration to the organic medium enhances the efficiency of the process by displacing the equilibrium to the surfactant salt formation. A schematic illustration of the process is shown in Fig. 2. The contact time was 30 minutes, after which the material obtained was washed three times with chloroform, once with acetone and twice with water, and separated by centrifugation. The materials obtained were dried under vacuum. No pH control was carried out, except in the case of polyoxometalate, where the pH was adjusted to 5.0 in order to obtain the decavanadate species.<sup>14</sup>

To test this method a great variety of anions, including chloride, carbonate, some carboxylates, decavanadate and a tetrasulfonated phthalocyanine, were used to displace the DS anion. The occurrence of anion exchange without the addition of the cationic surfactant was tested using the carbonate anion to substitute the DS anion. The choice of carbonate anion to test the exchange without the addition of CTAB was made due to its high stability when intercalated, compared with the other anions used. The occurrence of the exchange starting from the dried precursor was also checked.

The presence of bromide anions (CTAB counter ion) in the obtained materials was also tested using a model 9635 ionplus series bromide electrode from Orion Res. Inc.

The PXRD patterns of the samples obtained by anion exchange are shown in Fig. 1. A well-organised hydroxide-

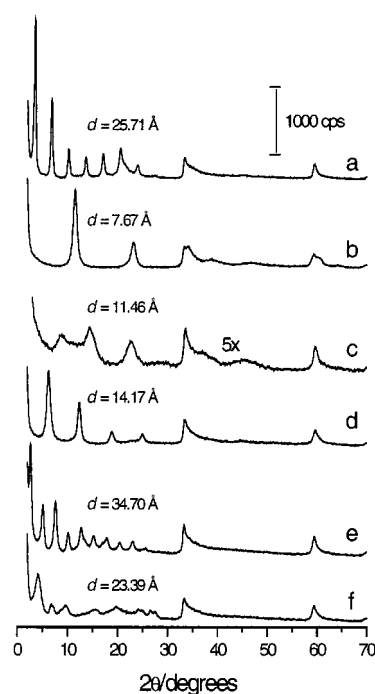


Fig. 1 PXRD patterns for the prepared samples: (a) DS-intercalated LDH precursor; and LDH anion-exchanged by (b) carbonate; (c) decavanadate; (d) terephthalate; (e) cholate; and (f) copper(II) phthalocyaninetetrasulfonate.

like compound with a basal spacing close to reported data<sup>3</sup> was obtained (see Fig. 1b) by the exchange of dodecylsulfate by carbonate anions (using the precursor suspension). Similar results were obtained when the precursor was dried and re-suspended (particles were dispersed by brief sonication, for less than 1 min). The exchange of DS with chloride ion (data not shown,  $d = 7.78 \text{ \AA}$ ) presented similar results to those obtained for carbonate anion. Without the addition of CTAB, the anion exchange of DS with carbonate did not occur. Even when the contact time was increased to 24 h, the resulting PXRD pattern was very close to that obtained from the precursor.

Based on these results, it is possible to conclude that the presence of CTAB in the medium is necessary to promote anion exchange. The extraction of the salt formed between the cationic and anionic surfactants into the organic phase should enhance the exchange process, making it faster and more efficient. The exchange process by this method is not affected if the precursor is dried before use. This is a very important observation, since the literature reports that drying the precursor can hinder the anion exchange when using both methods, the one based on chloride (or nitrate or perchlorate) containing precursors<sup>2,6</sup> and the one based on the acidification of carbonate (or terephthalate) containing precursors.<sup>7-9</sup>

The PXRD pattern for decavanadate anion exchange is shown in Fig. 1c. The low crystallinity obtained is characteristic of LDHs intercalated with decavanadate, and the basal spacing obtained is close to reported data.<sup>8,9</sup> The intercalation of carboxylate anions also presented good results, as can be seen in Fig. 1d and e for terephthalate and cholate respectively. High structural organisation is again observed, as well as phase purity. Similar results were obtained for the naphthoate anion (data not shown,  $d = 20.54 \text{ \AA}$ ). Note that, even though cholate is considered to be a surfactant, the exchange occurs successfully, emphasising the fact that the formation of the water-insoluble salt is characteristic of sulfated and sulfonated surfactants. Furthermore, the cholate anion was successfully intercalated with a basal spacing ( $34.70 \text{ \AA}$ ) greater than that obtained for the DS anion, showing that it is possible to expand the interlayer spacing by this anion exchange method. The basal

spacing obtained for the naphthoate intercalate is close to reported data,<sup>10</sup> and indicates that this anion was intercalated as a bilayer in the interlayer domain.

The intercalation of the phthalocyanine anion showed a material with crystallinity and basal spacing (see Fig. 1f) comparable with those reported for a similar compound.<sup>12</sup> In this case it is also important to note that the negative charge of this anion is derived from sulfonate groups, although no salt formation was observed between this macrocycle anion and CTA. This was demonstrated by the observation that the chloroform phase collected at the end of the preparation process did not show the characteristic blue colour of this anion.

A quantity of the anionic-cationic surfactant salt was prepared separately in order to take its PXRD pattern, which showed very intense and sharp peaks (data not shown). These peaks were not observed in the solid PXRD patterns, but were observed in the PXRD pattern of the residue from the evaporation of the organic phase used in the anion exchange. Chemical analysis showed the presence of a small amount of sulfur in some samples, which is probably due to high affinity adsorption of DS anions with LDHs.<sup>15</sup>

The analysis of bromide in the materials obtained showed a concentration in the range 0.15 to 0.22% (in mass). This amount of bromide anions can be assigned to both adsorbed and intercalated bromide. However, if we consider that all this bromide is intercalated, neutralising the layer charges, we will obtain a relation of only 1.0 to 1.5% of substitution by bromide anions.

Based on these results, we conclude that through this method it is possible to obtain a wide variety of organic or inorganic anions intercalated in LDHs in a simple manner. The synthesis of a precursor containing DS anions is required, but this can be carried out very easily. Moreover, this method presents great versatility: (i) it can be applied within a large range of pH values, depending only on the pH range supported by the substituting anion and by the LDH; (ii) the anion exchange is very fast and efficient; (iii) the maintenance of the precursor in a suspension is not necessary; and (iv) the formation of the water-insoluble salt with an ammonium quaternary surfactant is specific for sulfated and sulfonated surfactants.

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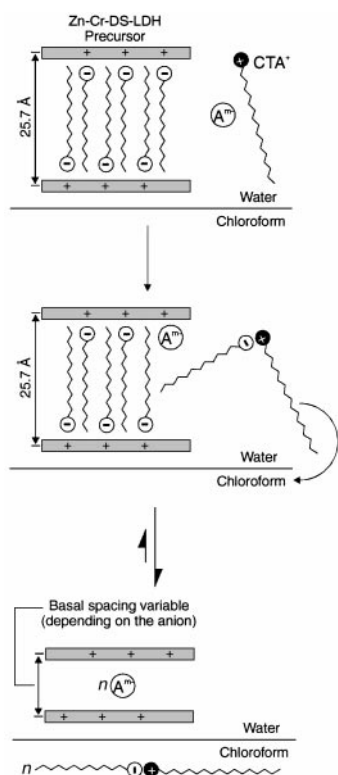


Fig. 2 Schematic representation of the proposed mechanism.

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