

Influence of carbonate intercalation in the surface-charging behavior of Zn–Cr layered double hydroxides

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ABSTRACT

The influence of interlayer composition in the surface charge and reactivity of layered double hydroxides (LDHs) has been explored. With this purpose, a chloride-intercalated Zn–Cr-LDH has been synthesized by the constant pH coprecipitation method and afterwards exchanged with carbonate to obtain solids with different $\text{Cl}^-/\text{CO}_3^{2-}$ ratios. The solids structure has been characterized by elemental chemical analysis, powder X-ray diffraction and infrared spectroscopy, while its surface-charging behavior and reactivity have been studied by acid–base potentiometric titrations and electrophoretic mobility determinations. The chloride-intercalated sample shows an increasing hydroxyl adsorption with increasing pH and decreasing support electrolyte concentration and the particles present positive electrophoretic mobility in the measured pH range. As carbonate content increases in the samples, the total OH^- uptake diminishes and the samples show an isoelectric point at pH around 10. When the gallery is totally occupied by carbonate anions, the OH uptake vs. pH curves registered at different electrolyte concentrations merge at around pH 10. A LDH–water interface model has been used to give an interpretation to the experimental data. The model indicates that as carbonate content increases, the sample behavior becomes similar to that of a metal (hydr)oxide and that surface (bi)carbonate anions undergo acid–base reactions.

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1. Introduction

Layered double hydroxides (LDHs) are anionic exchangers with important applications in catalysis, pharmacy, environmental decontamination, etc. Their structure can be described as an hexagonal close packing of hydroxyl anions where metal cations (both divalent and trivalent) occupy half of the octahedral sites, filling completely one layer and leaving the next unoccupied. Trivalent cations cause a permanent positive charge excess within the layers and, in order to maintain the electroneutrality of the solid, anions are intercalated between the layers, where also water molecules are located. Due to the relatively weak bonds between the layers, LDHs are swellable and show anion exchange properties: anions of different size and nature, either inorganic (from chloride or nitrate to polyoxometalates), organic, coordination compounds or even biomolecules can be intercalated [1–3].

Many LDH applications (pharmaceutical, environmental, etc.) are influenced by its surface reactivity and charging behavior, which determines the particles aggregation as well as the exchange and adsorptive properties of these solids [4,5]. Thus, many attempts

have been performed in order to understand and model the surface of these solids [6,7].

When LDHs are in solid phase, the electroneutrality condition forces the interlayer anions to fully compensate the positive permanent charge of the layers but, when immersed in aqueous solutions, some anions are released into the solution, producing charge excess in the solid surface and the development of an electric double layer at the solid–water interface. In addition, the presence of reactive groups at the surface of LDHs particles allows the binding of ions and molecules from the aqueous solution. For example, hydroxyl groups located at the basal surface or at the edges of the LDH layers are protonated or deprotonated depending on the pH of the aqueous solution. High pH values result in deprotonated, negatively charged groups, whereas low pH values may result in protonated, positively charged groups.

In a previous work [8] we have described and modeled the LDH particle surface taking into account the presence of positive permanent charges, which rule exchange reactions, and surface variable charges, produced by acid–base reactions of hydroxyl groups. This model was combined with the Stern–Gouy–Chapman model of the electrical double layer to explain the electrokinetic behavior and hydroxyl anions uptake of a Zn–Cr-LDH. The model indicates that most of the structural charge is screened by the intercalated anions or the negatively charged surface groups, but the remaining non-

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Table 1
Elemental chemical analysis data of Zn–Cr LDH samples with different interlayer $\text{CO}_3^{2-}/\text{Cl}^-$ ratios.

Sample	Weight (%)				Atomic ratios		Chemical formula
	Zn	Cr	C	H ₂ O	Zn/Cr	C/Cr	
ZnCr0	36.8	14.7	0.26	9.7	1.99	0.08	$\text{Zn}_2\text{Cr}(\text{OH})_6\text{Cl}_{0.85}(\text{CO}_3)_{0.08} \cdot 1.8\text{H}_2\text{O}$
ZnCr30	37.1	14.9	0.86	9.3	1.98	0.25	$\text{Zn}_2\text{Cr}(\text{OH})_6\text{Cl}_{0.5}(\text{CO}_3)_{0.25} \cdot 1.8\text{H}_2\text{O}$
ZnCr60	37.5	15.0	1.35	8.8	1.99	0.39	$\text{Zn}_2\text{Cr}(\text{OH})_6\text{Cl}_{0.22}(\text{CO}_3)_{0.39} \cdot 1.7\text{H}_2\text{O}$
ZnCr100	37.6	15.0	1.82	8.8	1.99	0.53	$\text{Zn}_2\text{Cr}(\text{OH})_6(\text{CO}_3)_{0.53} \cdot 1.7\text{H}_2\text{O}$

screened structural charges promote a net positive charge at the particle surface. Nevertheless, variable charges in LDHs are numerous and reactive enough to reverse LDHs particle charge at high pH values. The model was also used explain the changes in proton adsorption and electrokinetic behavior of chloride-intercalated Zn–Al-LDHs with different Zn/Al ratios, and it was exposed that both permanent and variable charges are affected by the layers composition [9].

The interlayer composition also affects the LDH reactivity and charging behavior, being the main contribution due to the interlayer anion. Most related works have been performed in LDHs intercalated with chloride, which can be easily exchanged by other ions. On the contrary, it is well known that carbonate is a divalent anion that exhibits a high affinity for LDHs and can seldom be exchanged by other anions [10]. This strongly anchored anion may block permanent charges of LDHs and consequently change the charging properties of LDHs.

The aim of this work is to investigate the effects of interlayer carbonate on the surface reactivity and electrokinetic behavior of LDHs. Thus, Zn–Cr-LDHs intercalated with different chloride/carbonate ratios have been prepared and their surface properties have been studied by acid–base potentiometric titrations and electrophoretic mobilities. A model of the LDH–water interface is used to explain the behavior of the samples.

2. Materials and methods

2.1. Synthesis

The chloride-intercalated Zn–Cr-LDH sample (ZnCr0) has been prepared by the coprecipitation method at constant pH, previously used for Zn–Cr-LDHs [11]. A 100 ml solution containing 0.1 mol of ZnCl_2 and 0.05 mol of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was added dropwise to a three necked flask containing 100 ml of a 1 M NaCl solution under vigorous stirring at pH 5, fixed by the addition of a 0.1 M NaOH solution. Once the reactants addition was finished, the mixture was maintained under stirring and fixed pH (pH 5) for 2 h at room temperature. The obtained solid was then separated from solution by centrifugation, washed several times with water and finally dried at 60 °C.

Carbonate intercalation was performed by anionic exchange: 2 g portions of ZnCr0 sample were added to solutions containing 0.07, 0.14 and 0.47 g of sodium bicarbonate, respectively. The resulting slurries were equilibrated for 3 h under continuous stirring and constant pH (pH 7). As carbonate anions present high affinity for LDHs, all the carbonate anions will be intercalated and the resulting samples (ZnCr30, ZnCr60 and ZnCr100) are expected to present a carbonate content to compensate 30%, 60% and 100% of the layer charge, respectively.

The obtained solids were separated by centrifugation, washed several times with water and dried at 60 °C. All solutions were prepared with purified water (Milli-Q system), boiled and purged with N_2 .

2.2. Structural characterization

In order to perform the elemental chemical analyses of the samples, 0.1 g portions of the corresponding solid were dissolved with 35% HCl and diluted to 100 ml with water. Zn^{2+} content was determined by a complexometric titration method; using EDTA as complexing agent and eriochrome black T as indicator. Cr^{3+} was directly quantified by UV–vis spectrophotometry with a Shimadzu UV-spectrophotometer, using a $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ calibration curve. Carbon content was determined using a EuroVector Elemental Analyzer, with 2,5-Bis(5-tert-butylbenzoxazol-2-yl)thiophene (BBOT) as calibration reference. The water content of the solid was determined from the weight loss of the solid after heating at 150 °C, as at this temperature the samples are dehydrated but not dehydroxylated [1].

Powder X Ray diffraction (PXRD) patterns were recorded in a Rigaku Miniflex instrument using a CuK α lamp ($\lambda = 1.5408 \text{ \AA}$) at 40 kV and 40 mA between 5° and 90° (2 θ) in step mode (0.05°, 1.2 s).

FT-IR spectra were registered from KBr-pellets with 1% sample content in a FT-IR Bruker IFS28 instrument. The spectra were recorded between 400 and 4000 cm^{-1} , averaging 4 scans with a 2 cm^{-1} resolution.

2.3. Surface studies

Acid–base potentiometric titrations at different salt concentrations were performed in order to study the OH^- uptake by the synthesized LDHs. This method has been largely used to determine proton adsorption in metal oxides and clay minerals [12,13]. 0.5 g of the corresponding solid were dispersed in 60 ml NaCl solution (0.01, 0.1 and 1 M), allowed to equilibrate for 1 h under continuous stirring and N_2 bubbling and then titrated with a standardized NaOH solution. In every step, the titrant volumes were regulated to achieve a pH variation of less than 0.2 units and the dispersion was left to equilibrate until the drift of the electrode was less than 0.2 mV min^{-1} . The OH^- uptake was calculated as the difference between the OH^- consumed by the slurry and those required to bring a solution of the same volume and electrolyte concentration to the same pH. The titration was stopped at pH around 11.5 due to the high buffer capacity of water at pH >11.5, which results in unreliable blank corrections. The measurements were performed at constant temperature and N_2 bubbling.

Electrophoretic mobilities (μ) were measured with a Rank Brothers Mark II instrument equipped with 2 mm cylindrical cell. A small portion of the corresponding sample was ultrasonically dispersed in a 200 ml, 0.1 M NaCl solution. The suspension was equilibrated for half an hour and then μ determinations were performed in the 6–11 pH range in 0.5–1 pH unit steps. In every step the sample was stirred until the drift of the electrode was less than 0.2 mV min^{-1} . All dispersions were maintained in nitrogen atmosphere and constant temperature (25 °C). μ values were converted to zeta potential (ζ) using the Smoluchowski equation.

3. Results

3.1. Structural characterization

The chemical composition and formulae of the studied samples are shown in Table 1. For the formulae determination, it was assumed that only chloride and carbonate anions neutralize the positive charges of the layers. Each carbonate anion compensates two positive charges of the layers and thus the C/Cr atomic ratio is 0.5 for a fully carbonate-intercalated LDH. The Zn/Cr ratio is near 2 in all cases, in agreement with the Zn/Cr ratio of the starting solution. The carbonate content is quite small for ZnCr0 sample and increases in the following samples, being the intercalation of this anion slightly higher than expected, possibly due to some CO_2 incorporation during the synthesis.

The PXRD patterns of ZnCr0 and ZnCr100 samples are shown in Fig. 1. A single phase with a hydrotalcite-like structure, characterized by high and symmetric (001) peaks along with low and asymmetric (101) and (111) peaks [14], is detected in both cases. The cell parameter a , which represents the distance between neighboring metal cations of the layers, is the same in all samples (3.12 Å), as the layer composition is very similar.

The interlayer distance decreases from 7.8 to 7.6 Å as carbonate content of the samples increases. Although carbonate anion is larger than chloride, the former adopt a parallel arrangement to the layers and occupies the height of an oxygen atoms layer [1]. The cell parameter a and the chemical composition were used to calculate the total layer specific area, S , which represents the total area of the layers basal surfaces. S was calculated as: $S = 3^{1/2} a^2 N / M$ [6], where a is the cell parameter, N is the Avogadro's constant and M is the unit cell weight, taking into consideration that there is one metal

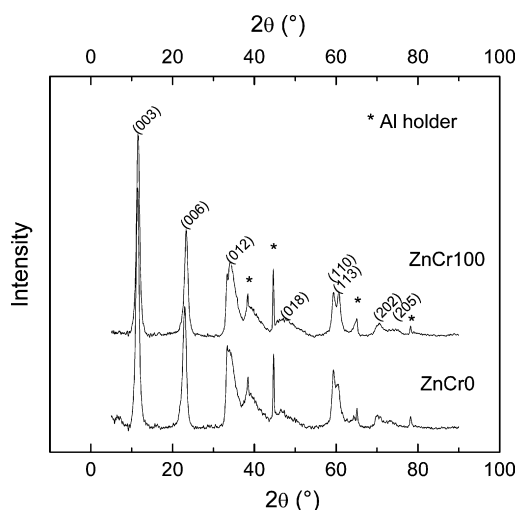


Fig. 1. PXRD patterns of ZnCr0 and ZnCr100 samples.

cation per unit cell. Since neither a nor M changed significantly in the samples, S was very similar ($800 \text{ m}^2 \text{ g}^{-1}$).

Fig. 2 shows the FT-IR spectra of the fully chloride- and the fully carbonate-intercalated samples. Both spectra exhibit a broad absorption band between 2200 and 4000 cm^{-1} (stretching vibration modes of the layer hydroxyl groups and interlayer water molecules), a band in the 1600 – 1700 cm^{-1} range (OH bending mode of water molecules) and several bands at wave numbers lower than 1000 cm^{-1} that correspond to vibrational modes of the hydroxylated layers [15,16]. The main carbonate IR modes are situated in the 1600 – 1000 cm^{-1} range. ZnCr0 presents weak bands in this region, indicating low carbonate content. As carbonate content increases, carbonate anion bands appear and become more intense. Thus, ZnCr100 sample spectra show a band at 1348 cm^{-1} with a shoulder at 1486 cm^{-1} , which can be both assigned to the antisymmetrical stretching mode ν_3 (E') of the free carbonate anion, which loses symmetry between the layers due to interactions with interlayer water and the hydroxyl groups of the layers. Nevertheless, the split of the ν_3 band has also been assigned by other authors

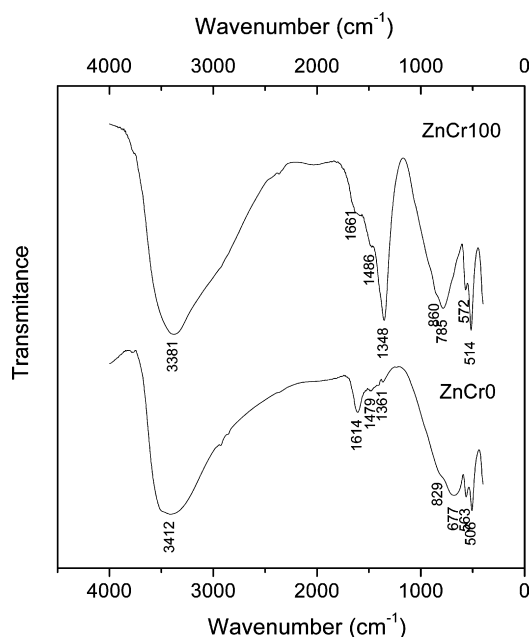


Fig. 2. FT-IR spectra of ZnCr0 and ZnCr100 samples.

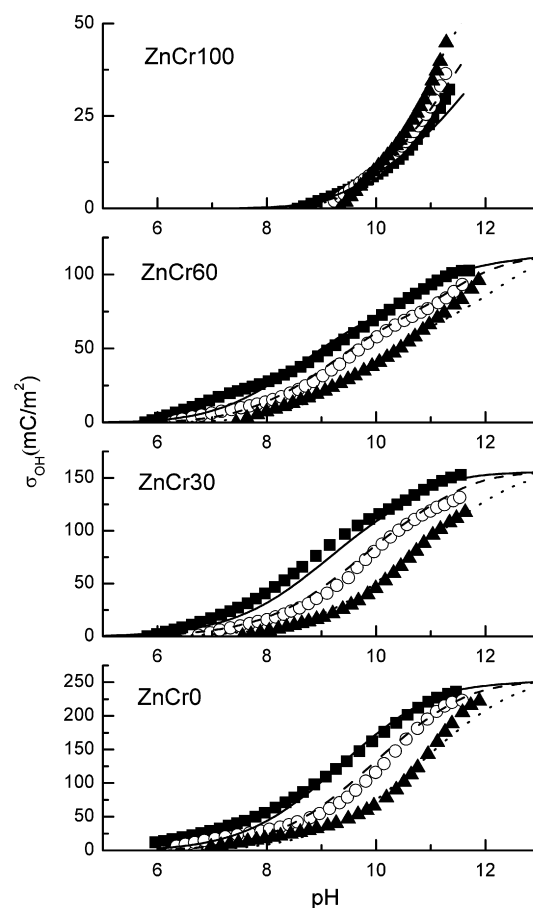


Fig. 3. Experimental (symbols) and calculated (lines) σ_{OH} vs. pH curves. Squares and solid lines: 0.01 M NaCl ; circles and dashed lines: 0.1 M NaCl ; triangles and dotted lines: 1 M NaCl . The ionic strength value in the calculations was obtained from NaCl concentrations using the Davies equation.

to the presence of bicarbonate anions [17], which present a lower symmetry than carbonate.

3.2. Surface studies

Hydroxyl uptake (σ_{OH}) vs. pH curves at different NaCl concentrations are shown in Fig. 3. Symbols represent experimental data while lines correspond to model predictions (see Section 4). For ZnCr0 sample, the hydroxyl uptake decreases as the electrolyte concentration increases at fixed pH value. The curves separation is maximum between pH 9 and 10 and, at higher pHs, the curves approach. The curves extrapolation suggests that they would merge or cross at a pH around 12 or higher, where a plateau is reached. The total hydroxyl uptake is quite high when compared to those of metal (hydr)oxides [11] which is due to exchange reactions with chloride anions in the LDHs interlayer. The curve profile is similar to that obtained for other chloride-intercalated LDHs [8].

For ZnCr30 and ZnCr60 samples, the curves profile is similar to that of ZnCr0, but the total hydroxyl uptake is strongly dependent on the carbonate content of the samples, being around 250 , 150 and 100 mC m^{-2} for ZnCr0, ZnCr30, ZnCr60, respectively.

On the other hand, the curve profile for ZnCr100 sample is quite different. It shows an intersection point at around pH 10: hydroxyl uptake decreases as electrolyte concentration increases below this intersection point, and the opposite trend is obtained above it. Finally, the total hydroxyl uptake is the lowest of all the samples (50 mC m^{-2}), which indicates that exchange reactions are diminished drastically.

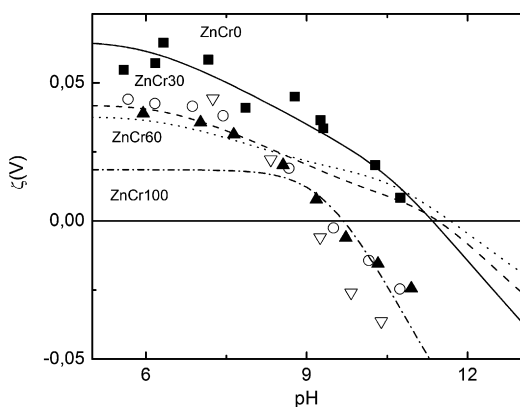


Fig. 4. Experimental (symbols) and calculated (lines) ζ vs. pH curves in 0.01 M NaCl: filled squares and solid lines, ZnCr0 sample; empty circles and dashed lines, ZnCr30 sample; filled triangles and dotted lines, ZnCr60 sample; and empty triangles and dot-dash lines, ZnCr100 sample.

Zeta potential (ζ) vs. pH curves are shown in Fig. 4. For ZnCr0 sample ζ is positive in the whole pH range studied, but it slowly decreases as pH increases. The curve extrapolation suggests that this sample would present an isoelectric point (i.e.p.) at a pH around 11.5. A somewhat different behavior is shown for all the carbonate containing samples: the zeta potential diminution is produced at lower pH values and an i.e.p. is obtained at around 9.5.

4. Discussion

The LDHs structure produces positively charged layers, which generate anions intercalation in the galleries. The general formula of these compounds can be written as $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]A_x^{n-} \cdot n\text{H}_2\text{O}$, where M^{II} , M^{III} , and A^{n-} represents the divalent cation, the trivalent cation and the interlayer anion, respectively. Although LDHs can be generally prepared with different M^{II}/M^{III} ratios, Zn–Cr-LDHs can only be prepared with a Zn/Cr ratio = 2 [18], which has been attributed to a regular distribution of both layers constituting cations. In this structure, all hydroxyl groups are coordinated to two Zn^{2+} cations and one Cr^{3+} cations and therefore equivalent [9,11].

As already mentioned in Section 1, the interlayer anion affects both the reactivity and the charging behavior of the resulting solid. Chloride anion charge, size and spherical symmetry produce weak anion–layer interaction that allows its replacement by higher charged, smaller or less symmetrical anions [1]. Carbonate, on the other hand, is a planar, divalent anion that arranges parallel between the LDH layers. Consequently, strong electrostatic interactions with the host layers are produced [16,19] and carbonate anions can seldom be exchanged by other anions, even trivalent ones. Only at pHs lower than 5, carbonate affinity diminishes and this anion can be removed from the interlayer [20].

The inclusion of carbonate anions in the chloride-intercalated Zn–Cr-LDH precursor is expected to reduce the exchange capabilities of the solid, but it may also produce changes in the particles charging behavior and its acid–base reactivity. Carbonate anions, which present a weak base character, are not expected to undergo acid–base reactions in the solid bulk, as they are stabilized by their strong interactions with the layers. But those located at the external surface are not so tightly bonded and may be active.

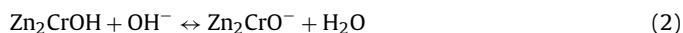
Acid–base potentiometric titrations shown in Fig. 3 indicate that an increasing hydroxyl uptake with increasing pH is produced in all samples. As stated in previous works [8,9], hydroxyl uptake is due to two main processes. One of them is anion exchange between chloride in the interlayer and hydroxyl ions in solution, which can

be written as follows:



where X represents an exchange site capable of attaching Cl^- or OH^- anions, and XCl^- and XOH^- represent Cl^- and OH^- attached to X sites, respectively. These sites are also capable of attaching CO_3^{2-} anions, but it must be considered that each carbonate anion occupies two X sites, neutralizing two positive charges that become permanently blocked. Eq. (1) indicates that increasing pH or decreasing Cl^- concentration produces increasing OH^- uptake, which agrees with the σ_{OH} vs. pH curves showed in Fig. 3 except for ZnCr100 sample.

OH^- uptake by LDHs is also produced by protonation–deprotonation reactions of surface hydroxyl groups, similar to those of metal (hydr)oxides [8,9]. In our samples, which present a Zn/Cr ratio = 2, each hydroxyl group is bonded to two Zn^{2+} and one Cr^{3+} cations and thus they can be written as Zn_2CrOH groups, which are all equivalent and may have the same reactivity. The acid–base reactions of these groups can then be written as follows:



In order to describe the overall OH^- consumption of the studied LDH samples, the two above mentioned processes have to be taken into account. In addition, since hydroxyls and chloride are charged species, the electrical potential decay through the LDH–water interface must be considered. In previous works, a mathematical model that considers both reactions and interface electrostatics has been proposed [8,9]. Only a brief description is given here, as details of the mathematical tools can be found in those articles. The model can be divided in two parts: one represents the LDH particle surface and the other describes the charge distribution and potential decay in the aqueous side of the interface.

The model of the particle surface assumes that structural charges are internal and located in an internal plane, parallel to the interface. These structural charges express in the particle surface as discrete, neutral exchange sites (X sites) that bind and exchange anions that compensate the structural charge, while unoccupied X sites represent unscreened structural charges that will give an overall positive charge to the particles. The surface density of these sites is designated as N_{str} (mol m^{-2}) while the anions affinity for X sites is expressed as intrinsic binding constants ($K_{\text{Cl}}^{\text{int}}$, $K_{\text{OH}}^{\text{int}}$).

The particle surface also presents Zn_2CrOH groups that consume hydroxyl anions according to Eq. (2), which may produce two effects: (1) structural charge compensation, diminishing the solid exchange capacity and (2) surface charge diminution, which may even cause particle charge reversal at high pH values. The intrinsic deprotonation constant of these variable charge Zn_2CrOH groups (K_a^{int}) expresses the equilibrium between protonated and deprotonated groups, while the surface density of Zn_2CrOH groups is symbolized by N_v .

A positive charge excess exists near to the Zn_2CrOH groups due to the presence of a Cr^{3+} cation, which is not explicitly written in the group because it is already considered as part of the structural charge responsible of the exchange reactions. Nevertheless, the presence of structural charges in the vicinity of a reacting group will affect its reactivity. The application of the MUSIC (MULTiSite Complexation) model, developed by Hiemstra et al. [21,22], to LDHs indicates that Zn_2CrOH groups should have a $\text{p}K_a^{\text{int}}$ value between 8.6 and 12.5. Indeed, a value of $\text{p}K_a^{\text{int}} = 10.85$ has been previously determined by modeling the OH^- uptake by a chloride-intercalated Zn–Cr-LDH [8].

In order to complete the model it is necessary to define the charge distribution and the potential decay in the aqueous side of the interface. The Stern–Gouy–Chapman model connects the surface charge with the potential distribution in the electrical double layer formed in the aqueous side of the interface. This model

Table 2
Refined parameters of the proposed model for Zn–Cr-LDH samples with different $\text{CO}_3^{2-}/\text{Cl}^-$ ratios.

Sample	$\text{p}K_a^{\text{int}}$	$\text{p}K_{\text{Cl}}^{\text{int}}$	$\text{p}K_{\text{OH}}^{\text{int}}$	N_{v} (C m^{-2})	N_{str} (C m^{-2})	C (F m^{-2})
ZnCr0	10.44	−0.47	−1.97	0.22	0.25 (0.29)	0.068
ZnCr30	10.28	−0.47	−1.97	0.13	0.15 (0.17)	0.013
ZnCr60	9.94	−0.47	−1.97	0.07	0.11 (0.08)	0.077
ZnCr100	10.69	−0.47	−1.97	0.07	0.01 (0)	>3

K_a^{int} , intrinsic protonation constant of Zn_2CrO^- groups. Initial parameter $\text{p}K_a^{\text{int}} = 10.5$.

$K_{\text{Cl}}^{\text{int}}$, intrinsic binding constant of Cl^- to X groups. Not adjusted.

$K_{\text{OH}}^{\text{int}}$, intrinsic constant of OH^- to X groups. Not adjusted.

N_{v} , surface density of $\text{ZnCrOH}/\text{ZnCrO}^-$ groups. Estimation from the structure, $N_{\text{v}} = 1.93 \text{ C m}^{-2}$.

N_{str} , structural charge density = surface density of X sites. In parenthesis, calculated values, obtained from the solid structure and chemical formula.

C , capacitance in the Stern layer. Initial estimate $C = 0.1 \text{ F m}^{-2}$.

assumes that the surface plane and the diffuse layer are separated by a region of constant capacitance (C) called the Stern layer and that the potential decay in the diffuse layer is described by the Gouy–Chapman equation. The equations describing potential decay along the electrical double layer can be found also in previous works [8].

The Stern layer capacitance (C) is the main adjustable parameter describing the second part of the model and, together with the five parameters that describes the particle surface (N_{str} , N_{v} , K_a^{int} , $K_{\text{Cl}}^{\text{int}}$, and $K_{\text{OH}}^{\text{int}}$) completes the description of the surface charging and reactivity of LDH particles. $K_{\text{Cl}}^{\text{int}}$ and $K_{\text{OH}}^{\text{int}}$ parameters for Zn–Cr-LDHs have been calculated in previous works [8], and here all the solids are considered to present the same values (see Table 2). The rest of the parameters are obtained by fitting σ_{OH} vs. pH and ζ vs. pH curves using the Simplex method [23]. Some of them can be estimated from the structural data or the MUSIC model and used as initial parameters in the fitting procedure. Thus, N_{str} can be estimated from the total layer specific area and the Cr^{3+} content of the solid. Here we will consider that carbonate anions do not experiment exchange reactions. Although surface (bi)carbonate anions are less tightly attached to the solid and they are expected to be more easily exchangeable, they are only a small portion of the total carbonate content. N_{str} can then be expressed as: $N_{\text{str}} = N_{\text{Cr}^{3+}} - 2N_{\text{CO}_3^{2-}}$, where $N_{\text{Cr}^{3+}}$ and $N_{\text{CO}_3^{2-}}$ represent the density of Cr^{3+} cations and CO_3^{2-} anions, respectively (Table 2). The N_{v} value can be estimated from the number of OH^- groups per gram and the total layer specific area (S) if all the hydroxyl groups of the layers are considered reactive. Nevertheless, the obtained value (around $2 \times 10^{-5} \text{ mol m}^{-2}$) overestimates the actual variable charge sites density, as most of the OH^- groups are inactive because they are not accessible to OH^- ions from solution. Finally, the initial $\text{p}K_a$ parameter was 10.5, an intermediate value of the range calculated with the MUSIC model.

The calculated σ_{OH} vs. pH and ζ vs. pH curves are compared to experimental data in Figs. 3 and 4, respectively. The model fits reasonably well the shape of σ_{OH} vs. pH curves, the electrolyte concentration effect and the total hydroxyl uptake diminution as the samples carbonate content increases. It also predicts the curves profile change when the solid is fully intercalated with carbonate anions. On the other hand, the ζ vs. pH curve for ZnCr0 sample is correctly fitted but the fit is not so good for the carbonate containing samples, as the model can not predict the i.e.p. displacement towards lower pH values. As previously mentioned, (bi)carbonate anions located at the particles surface are reactive and may undergo protonation/deprotonation reactions [4]. This reaction produces a negligible effect in the OH uptake behavior but will affect significantly the surface charge of the particle, as it introduces negative charges in the particle surface. (Bi)carbonate

protonation/deprotonation reactions are not included in the model for the sake of simplicity and may explain the bad performance of the model in describing the ζ vs. pH curves of these samples.

Table 2 shows the best fit parameters of each modeled sample, which present good agreement with the initial estimates: $\text{p}K_a^{\text{int}}$ parameter values are within the range calculated by the MUSIC model and N_{str} values are quite similar to that calculated by structural data. N_{v} values are lower than the initial estimate, indicating that less than 10% of the Zn_2CrOH groups are capable of protonation–deprotonation reactions.

Nevertheless, differences are found between the samples. As expected, increasing carbonate content produces decreasing N_{str} values due to the X sites blocked by carbonate anions. On the other hand, N_{v} values also decreases with the sample carbonate content, which can be related with a better stacking of the LDH layers that reduce the exposed surface of the LDH particles and the Zn_2CrOH groups capable of undergoing deprotonation reactions.

For ZnCr100 sample, the N_{str} value is almost zero, indicating that the solid has lost its anion exchange capacity and the main contribution to OH uptake is due to acid–base reactions. Indeed, this solid is mostly behaving as a normal metal oxide, with a zero point charge at around 9. At pHs lower than 9 the particle surface charge is positive, due to the permanent charge that although small is not compensated by the variable charge groups, while at pHs higher than 9 the negative charge developed by deprotonation of Zn_2CrOH groups overcomes the positive structural charge. For this type of solids the surface charge behavior is especially important as anionic exchange reactions are absent and the adsorption at the surface is the only way LDHs can uptake anions.

This model is also capable to explain the behavior of other LDHs in aqueous solution dispersions. For example, this model reproduces the σ_{OH} vs. pH curves obtained by How et al. for LDHs containing mainly hydroxyl anions in the interlayer [6,7], which are similar to that of ZnCr100 sample. For OH^- containing LDHs no exchange reactions are produced and, consequently, the solid behaves as a metal (hydr)oxide and a crossing point is also obtained in their σ_{OH} vs. pH curves.

5. Conclusions

The acid–base reactivity and the surface-charging behavior of Zn–Cr-LDH particles with different interlayer composition (different carbonate/chloride ratios) have been studied as a function of pH and NaCl concentration. Increasing carbonate content produces a diminution of the OH^- uptake by the solid and the displacement of the particles isoelectric point towards lower pH values.

A model for LDH reactivity has been proposed where contributions of anion exchange and surface hydroxyl acid–base reactions are considered. As carbonate content increases the calculated structural charge diminishes due to the exchange capacity reduction caused by the strong electrostatic bonds between carbonate anions and the layers, resulting in permanently screened structural charges. Consequently, the fully carbonate-intercalated samples possess no exchange capacity and the particles charging behavior and reactivity are similar to those of metal (hydr)oxides. It also predicts that carbonate anions placed at the particle surface may undergo acid–base reactions, modifying the surface charge of LDH particles.

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