Intercalation of LDH NO₃ with short-chain intercalants

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Abstract. Intercalation behaviour of layered-double hydroxide (LDH) with short-chain intercalants $-(\text{CH}_2)_n-$, $n < 9$ is significantly difficult and less reported than with long-chain intercalants. The present study reports an efficient way to intercalate LDH with short-chain intercalants ($n = 4$ and 8) and investigates the effect of layer charge on intercalation behaviour of LDHs. Short-chain anionic surfactants were successfully intercalated with synthetic LDHs $[\text{Zn}_{1-x}\text{Al}_x(\text{OH})_2\text{NO}_3 \cdot n\text{H}_2\text{O}]$, $x = 0.2-0.33$ by an ion-exchange intercalation technique in a slightly acidic medium ($\text{pH} = 5.4$). The adverse effect of a carbonate anion was avoided by performing the ion-exchange intercalation in slightly acidic medium ($\text{pH} = 5.4$). It was found that basal spacing (d_{003}) and experimental organic loading of intercalated LDH (O-LDH) increase monotonically with increasing anion-exchange capacity of LDH and intercalant chain length. The evolution of intercalated LDH (O-LDH) structures with increasing intercalant chain length and layered charge has been deciphered by correlating basal spacing of O-LDHs (by X-ray powder diffraction), organic loading data (by thermogravimetric analysis) and molecular conformation of O-LDHs (by Fourier-transform infrared spectroscopy) within the LDH gallery. Successful intercalation of LDH with these short-chain intercalants in slightly acidic medium has not been reported previously.

Keywords. LDH; intercalation; short-chain intercalants; anion-exchange capacity; organic loading.

1. Introduction

Layered-double hydroxides (LDHs) are synthetic layered clay materials with anion-exchange properties. Its structure is related to brucite $[\text{Mg}(\text{OH})_2]$, where aliovalent lattice substitution (viz., Mg^{2+} by Al^{3+}) leads to formation of positive charge in the brucite layer. This charge is neutralized by extraneous exchangeable anions in the interlayer position. These exchangeable anions impart important characteristics called anion-exchange capacity (AEC). This anion-exchange property is exploited to intercalate organic moieties within the inorganic LDH layers i.e., to synthesis inorganic-organic hybrid composite. These hybrid composites have created significant interest in recent years in various fields viz., catalytic application [1,2] additives for polymers [3], photofunctional materials [4], adsorption of dye, heavy metals [5,6], chromates [7] etc.

The term ‘intercalation’ is used to describe the insertion of intercalant molecules inside the galleries i.e., in between the adjacent pairs of LDH layers. Intercalation affects the basal spacing and the texture of a layered structure. Interestingly, the anion-exchange process also affects [8] the order/disorder and crystallinity of the LDH. Different techniques are adopted by researchers to achieve a successful intercalation with LDH after the pioneering work by Miyata *et al* [9] in 1973.

These techniques are broadly categorized as: (i) ion-exchange method, (ii) intercalation *via* reconstruction method and (iii) *in-situ* intercalation method [10,11].

The intercalation behaviour of LDH has been mostly explored with intercalants having a long $(\text{CH}_2)_n$ group where $n = 12, 14$ and 16 with different anionic heads viz., carboxylic acid and sulphates [12], sulphonate [13] etc. Surfactants with long alkyl groups are predominantly hydrophobic, which helps in intercalation reaction through ion exchange. In the reversible exchange reaction, the intercalated product separates out of aqueous reaction medium due to high hydrophobicity and this enhances the forward reaction rate through the Le Chatelier’s principle. In contrast, surfactants with smaller hydrophobic tails could not exert a similar beneficial effect on intercalation reaction. Understandably, researchers found difficulty in intercalating short-chain intercalants within the LDH gallery ($n < 9$) [12–17] despite employing harsh conditions viz., high temperature [14], refluxing [17] and an excess amount of intercalant [12]. Apart from short-chain length intercalants, the intercalation behaviour of LDH is severely affected by the presence of carbonate anions. Being a bidentate ligand, a carbonate anion strongly holds the positively charged LDH layer (electrostatic bonding) which makes ion exchange with an intercalant difficult [11,15,18–20]. Successful intercalation of a

Table 1. Ratio of Zn^{2+} and Al^{3+} solutions for synthesis of different LDH NO_3 .

Sample code	Theoretical layer charge	1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (ml)	1 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ml)
LDH-0.20	0.20	80	20
LDH-0.25	0.25	75	25
LDH-0.30	0.30	70	30
LDH-0.33	0.33	60	30

short-chain intercalant $(-(\text{CH}_2)_n-, n < 9)$ is a real challenge with and/or without using harsh reaction conditions and an excess amount of intercalant. The effect of pH on the intercalation of LDH is also not studied for an ion-exchange process, which may reveal new insights into the unsuccessful intercalation with short-chain intercalants. The information regarding the effect of layer charge on the organic loading and the corresponding d_{003} value is essential to understand the orientation of intercalants within the interlayer position, which may reveal interesting insights about the structure of O-LDHs.

To clarify above issues, in the present work, the optimum pH for ion-exchange intercalation reaction was established. Then, attempt has been made for intercalation of sodium octyl sulphate (C8) and sodium butyl sulphate (C4) with LDH NO_3 having a range of layer charge (0.20–0.33) by an ion-exchange process. Finally, the structure of O-LDH generated from different LDH NO_3 and intercalant compositions is proposed based on X-ray powder diffraction (XRD), thermogravimetric (TG) analysis and Fourier-transform infrared (FTIR) analysis.

2. Experimental

2.1 Materials

Reagents $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, hexamine (Merck India Pvt. Ltd.), sodium dodecyl sulphate ($\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$: C12, Merck, Germany), sodium octyl sulphate salt ($\text{C}_8\text{H}_{17}\text{NaO}_4\text{S}$: C8, HiMedia) and 1-butane sulphonic acid sodium salt ($\text{C}_4\text{H}_9\text{NaO}_3\text{S}$: C4, Lobachemie) were used without further purification. Ultrapure membrane filtered water (MFW) of conductivity 18.2 mS was used in all experiments.

2.2 Synthesis of ZnAlNO_3 LDH

ZnAl LDH NO_3 with different layer charges was synthesized according to Churchill *et al* [21]. For layer charge of 0.25, 1 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions were mixed in a 1:3 ratio and filtered (0.45 μm). MFW of 120 ml and ~ 16.8 g hexamine were added into 80 ml of the above mixed metal solution and kept in a stoppered conical flask (N_2 atmosphere). The resulted material was collected by the centrifugation and re-dispersion (in MFW) process until the pH of the re-dispersed solution reduced to ~ 6.5 –7.

The material was dried for 48 h in a vacuum oven at 45°C and stored under a CO_2 -free atmosphere. This synthesis process was followed for other LDHs. The batch composition is given in table 1.

2.3 Intercalation of LDH

A calculated amount of synthetic LDH was dispersed in 100 ml aqueous solution at different pH values (2.1, 5.4, 7.2, 8 and 10) at ambient temperature ($T = 34^\circ\text{C}$) for 60 min. These pH solutions were prepared by controlled addition of N/100 HCl and NaOH solution into MFW.

In a separate beaker, 100 ml solution of the calculated amount of intercalant (with respect to the AEC of corresponding LDH) was prepared and slowly added into the LDH dispersion. The reaction mixture is sonicated (250 W) in an ultrasonic bath (maintained at 34°C) for 10 min at an interval of 30 min. After several repetitions of this cycle, the reaction mixture was kept under constant stirring for 22 h. The precipitated material (O-LDH) was separated by filtration and washed with 1500 ml washing liquid. The washing liquid was prepared by the addition of 3 ml ethanol to 300 ml MFW (warmed at 60°C). The washed material was dried at 60°C under vacuum for 48 h and stored in a sealed container under a N_2 atmosphere to avoid CO_2 contamination. The equivalent amount (100% of AEC) of intercalant was added. The required weight of the intercalant is calculated using equation (2.1), where A = AEC of LDH (meq g^{-1}), B = % of AEC added, C = mass of LDH taken (g) and D = molar mass of intercalant (g mol^{-1}). For pH study, 150% AEC equivalent of intercalant was taken while for remaining studies 100% AEC equivalent was added.

$$\text{Required amount of surfactants (in g)} = A \times B \times C \times D \quad (2.1)$$

2.4 Characterization

For chemical analysis, ~ 10 mg of synthetic LDH NO_3 sample was digested in 15 ml (N/10) HCl ($\text{pH} \sim 1$) for 2 h. The concentrations of Zn^{2+} and Al^{3+} ions were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Cirus Vision, Spectro Analytical Instruments Inc.). The powder XRD patterns of LDH ($2\theta = 5$ – 75°) and O-LDH ($2\theta = 2$ – 70°) were recorded by using an X'Pert Pro diffractometer (Panalytical) with Ni-filtered

Table 2. LCD, AEC and mass loss up to 350°C of different synthetic Zn-Al NO₃ LDH.

Sample code	Experimental layer charge	d_{003} (nm)	Cation–cation distance, d_{110} (nm)	Layer charge density, LCD ($e\text{ nm}^{-2}$)	AEC (cmol kg^{-1})	Mass loss (%) up to 350°C
LDH-0.20	0.20	0.789	0.153	2.51	1.803	21.8
LDH-0.25	0.26	0.819	0.153	3.17	2.270	20.9
LDH-0.30	0.28	0.827	0.153	3.43	2.439	18.2
LDH-0.33	0.33	0.879	0.153	4.04	2.839	17.9

Cu-K α radiation. The operating condition was 40 kV/30 mA in step scan mode, with step size 0.05°. Organic loading was calculated by TG analysis. TG analysis was carried out from 25 to 1000°C with a thermal analyzer (Netzsch, STA 449F) at a heating rate of 10°C min⁻¹ under a mixed (3:1) N₂ and O₂ atmosphere. Different bonding interactions between intercalant and LDH were studied by FTIR spectra. A small amount of sample was dispersed in KBr and pelletized for FTIR spectroscopy (Nicolet-5700 FT-IR spectrometer) in the 4000–400 cm⁻¹ range in transmission mode. Before carrying out the TG and FTIR experiments, samples were heated at 60°C in a vacuum oven for 48 h to remove physisorbed water.

3. Results and discussion

3.1 Characterization of synthetic LDH NO₃

Experimental layer charge and AEC were determined from chemical analysis data and are reported in table 2. The XRD data reveal that the synthesized NO₃ LDHs are pure hydrotalcite-like compounds with the $R\bar{3}m$ space group and the unit cell parameters $a = b = 0.3068$ nm and $c = 2.637$ nm (for LDH NO₃-0.33). For other synthetic LDHs, these values are reported in the supplementary material. The TG analyses of different synthetic LDH NO₃ show mass loss of 33.2–35.5% depending on the layer charge. A three-stage mass loss irrespective of layer charge is evident from the differential TG curves. Above 700°C, no significant change in mass loss was observed. The mass loss up to 350°C was calculated from the TG curve and is reported in table 2. In FTIR spectrogram, a sharp adsorption peak appears at 1384 cm⁻¹ which is due to the asymmetric stretching of the NO₃⁻ anion. The broad and asymmetric hump at ~3000 cm⁻¹ actually consists of different types of hydroxyl stretching modes ($\nu_{\text{O-H}}$) viz. Zn–OH, Al–OH, H–OH, O–H stretchings etc. Here, the synthetic LDHs are free from carbonate impurity which was confirmed by both XRD and FTIR analysis (absence of carbonate peak at 631, 1428 and 1064 cm⁻¹). Detailed characterization of synthetic LDH NO₃ (XRD, FTIR and TG) materials is provided in the supplementary material.

The absence of other phases (XRD study) ascertains the purity of the synthetic LDH samples and further supports the close agreement of experimental and theoretical layer charge (table 2). Basal spacing of pristine LDH

Figure 1. Powder XRD patterns of intercalated LDH-0.33 with C12 (150% AEC addition) at different pH values ($T = 34^\circ\text{C}$).

increases monotonically with increasing layer charge. The cation–cation distance in the LDH layer remains constant irrespective of layer charge. A monotonic increase in Layer charge density and AEC is observed with increasing layer charge, which is quite expected. The mass loss up to 350°C decreases with increasing layer charge. Nitrate decomposition starts after 350°C and with increasing layer charge, the loss due to nitrate increases monotonically [22]. These data were used to calculate experimental organic loading in O-LDHs.

3.2 Effect of pH on intercalation

The XRD pattern of intercalated LDH-0.33 with the sodium dodecyl sulphate (C12) intercalant (150% of AEC) at five different pH values (2.1, 5.4, 7.2, 8 and 10) and at $T = 34^\circ\text{C}$ is shown in figure 1. The figure also shows the XRD pattern of pristine LDH-0.33 as a reference.

The appearance of a new series of 00 l reflections as narrow, strong peaks at low 2θ along with the characteristics XRD reflection of LDH layered structure confirms successful intercalation [4,23]. Figure 1 reveals that pH greatly affects the intercalation during the ion-exchange reaction process and successful intercalation is only achieved at pH = 5.4.

Conventionally, intercalation *via* ion-exchange reaction is performed in neutral medium [4,23–27], but here, the intercalation reaction at neutral medium (pH = 7.2) generated O-LDH with very weak 00 l reflections at lower 2θ , indicative of poor intercalation. This is attributed to the interference of soluble CO₂ in MFW. The soluble CO₂ forms carbonic acid (H₂CO₃) in MFW and remains in the ionic form in aqueous medium as follows:

This bivalent carbonate anion replaces the monovalent nitrate anion (during the dispersion of LDH NO₃) from LDH NO₃ before it could take part in the ion-exchange reaction with the intercalant. Carbonate being a bivalent anion strongly holds (electrostatic and hydrogen bonding interaction) the layers so ion-exchange reaction becomes very difficult and most of the cases lead to unsuccessful intercalation [11,15,18,20]. To overcome this problem, ion-exchange reaction is performed in slightly acidic medium. Chakraborty *et al* [4] successfully exchanged the carbonate anion (Zn-Al LDH CO₃) with a monovalent anion (perchlorate) by ion-exchange reaction in acidic medium. Here, the interference of the soluble CO₂ was minimized by making the aqueous solution slightly acidic (pH = 5.4). The addition of a dilute acid increases the [H⁺] in aqueous medium and it shifts the equilibrium of the H₂CO₃ ionization reaction to the left-hand side according to the Le Chatelier's principle (equation (3.1)). Intercalation of any intercalant by an ion-exchange process in strong acidic medium (pH < 3) is never performed as LDHs are unstable at low pH [28,29]. Therefore, an unsuccessful intercalation is quite obvious (figure 1) at low pH and it is performed in this study only for reference. Intercalation *via* an ion-exchange process in alkaline medium is uncommon but has been reported in the literature [30,31]. This is also tested for reference. The XRD data at pH 8 and 10 show similar patterns where a new set of 00 l reflections at lower 2θ was absent. The probable reason behind the unsuccessful intercalation at alkaline medium is due to the formation of carbonate ions by reaction of atmospheric CO₂ with alkaline solution. The interference of carbonate ions is evident from the shift of the 003 reflection (for pH = 8 and 10) towards the higher 2θ compared with the pristine LDH-0.33 (figure 1). For a fixed layer charge, the basal spacing for LDH CO₃ is smaller than that of LDH NO₃.

Therefore, the pH study reveals an unsuccessful and/or poor intercalation of LDH in highly acidic medium (pH = 2.1, due to destruction of LDH layer), neutral medium (pH = 7.2, due to interference of dissolved CO₂) and alkaline medium (pH = 8 and 10, due to dissociation of carbonate). Effective intercalation of LDH by ion-exchange reaction can be achieved at slightly acidic medium (pH = 5.4) where the interference of dissolved CO₂ is minimized by making the aqueous solution slightly acidic prior to the dispersion of LDHs. Thus, the most favourable pH for intercalation is fixed

at pH = 5.4. Surprisingly, intercalation of C12 with LDH in acidic medium has not been previously reported.

3.3 Intercalation with short-chain intercalants

As mentioned earlier, intercalation of LDH with short-chain intercalants is challenging. We report the intercalation of LDH with two intercalants [*viz.*, octyl sulphate (C8) and butyl sulphonic (C4) acid salts] into LDH NO₃. The structure of intercalated LDH generated from different LDH NO₃ and intercalant compositions can be ascertained by XRD, TG and FTIR analysis. XRD data precisely prove the success of intercalation by deciphering the expanded interlayer spacing along the *c*-axis. The thermogravimetric data quantify the amount of intercalant incorporated into the O-LDH. The bonding interaction between the intercalant molecules and LDH is clearly reflected in the FTIR spectra.

3.3a XRD analysis: The XRD patterns of different O-LDHs with C8 and C4 intercalants (figure 2) reveal the emergence of new 00 l reflections at lower 2θ for LDH-0.33. Before intercalation, the d_{003} value ($2\theta = 9.8^\circ$) for LDH-0.33 was 0.879 (figure 4a) and after intercalation with C8 and C4 the value increases to 2.195 ($2\theta = 4.12^\circ$) and 1.559 nm ($2\theta = 5.59^\circ$), respectively. The analysis and assignment of these new reflections form the basis of structure of intercalated LDH along with TG data to quantify the organic material incorporation into LDH.

Assignment of basal reflections to O-LDH here is complicated. Unless the trend of emergence of these 003 n reflections is analysed for every layer charge, there is possibility of misinterpretation. For the highest layer charge, it is possible to discern several 003 n basal reflections ($n = 1, 2, 3, 4, 6$ and 7) irrespective of intercalants. With decreasing layer charge (from 0.33 to 0.2, figure 2), the appearance and the intensity of the first two reflections are reduced. The most intense reflection for C8 O-LDH at $2\theta \sim 12^\circ$ for layer charge 0.25 and 0.20 assigned as 009—corresponds to 009 reflection of O-LDH-0.33. Similarly, for C4 O-LDHs the most intense reflection at $2\theta \sim 11.3^\circ$ assigned as 006 reflection. For C4 O-LDHs (except for LDH-0.33), the corresponding *d*-spacing (if assumed to be $d_{003} \sim 0.755$ nm) is smaller compared with pristine LDH-0.20 (0.789 nm, supplementary material), which apparently contradicts with general perception of increase of basal spacing during intercalation. But this apparent anomaly can be explained by studying the set of 003 n reflections of C4 and C8 O-LDH-0.33. For higher layer charge, well defined basal reflections (003 and 006) are present along with 009, but for lower layer charge only 009 reflection is prominent. Such assignment of basal reflections has been validated by TG and FTIR analyses to confirm degree of intercalation (sections 3.3b and 3.3c). After assigning the basal reflections, it is seen that 006 and 009 reflections are the most prominent reflections for C4 and C8 intercalants, respectively. The initial position of 003 (LDH NO₃) shifts to very low angle for both cases (C4 and C8). The smallest

Figure 2. Powder XRD patterns of: (a) C8 and (b) C4 O-LDH NO₃ having different layer charges.

intercalant (C4) shifts the 003 reflection to near Bragg angle of 5° while C8 pushes it further to >5°. These shifts in basal reflections translate into larger gallery height between the brucite layers, where the intercalants reside after intercalation. The gallery heights calculated from these reflections are reported later (section 3.3d) and correlated with the length of the intercalant.

The 110 reflection corresponds to bi- and trivalent metal cation distances in the brucite layer of LDH. Here the position of the 110 ($2\theta \sim 60^\circ$) reflection in O-LDHs remains unaltered compared with the pristine LDH NO₃ (table 2). Thus, the intercalation process does not affect the individual brucite layers [32].

It is important to compare the basal spacing values of the present work with previous reports (table 3) to verify the success of this study. A comparative analysis shows that even without using excess intercalant and harsh conditions

(high temperature and reflux), a comparable basal spacing is achieved with C8 (~ 2.2 nm) and higher basal spacing with C4 (~ 1.5 nm). Williams *et al* [33] reported a successful intercalation with the C8 intercalant by an ion-exchange reaction using fivefold excess of intercalant and high temperature (60°C) with a layer charge as low as 0.16. Other studies could achieve successful intercalation only with LDH with a high-layer charge (0.33) by an ion-exchange process. In the case of C4 intercalant, apart from employing the *in-situ* technique, researchers mostly used dicarboxylic acid salts for intercalation. It is quite expected that bidentate ligands viz., dicarboxylic acids have higher propensity to attach to the positively charged LDH layer compared with C4 used here (monodentate ligand). There is no earlier report of successful intercalation with C4 i.e., 1-butane sulphonic acid sodium salt intercalant and the intercalation behaviour with low AEC of LDH is also not verified. Another interesting fact is that, without using excess intercalant and harsh conditions we are able to achieve higher basal spacing than the previously reported values. Only Miyata *et al* [9] reported a higher basal spacing (1.2 nm for d_{006}) with succinic acid compared with this study; unfortunately the detailed information regarding the intercalation technique is not available in the text. With C8 and C4 intercalants, a monotonic increment in basal spacing (d_{003}) is not observed with increasing AEC (or layer charge), which again is consistent with the literature (table 3).

Thus, this study showed that the ion-exchange method in acidic medium is effective for intercalation of LDH NO₃ (having low AEC) even with an intercalant with short alkyl chains. Most importantly intercalation *via* an ion-exchange process in acidic medium is not reported previously for intercalants mentioned in this study.

The intercalation of LDHs depends on the AEC value of LDH and the alkyl chain length of the intercalant. All these factors are in proportional relationship with successful intercalation. Interference of carbonate anions is a common deterrent for different intercalation techniques. Researchers adopted different modifications to minimize the adverse effect of carbonate anions during the intercalation. Here, the adverse effect of carbonate anions is avoided by slight acidification of the aqueous medium, which results in successful intercalation even with a short-chain intercalant and LDH of low AEC. Higher AEC value of LDHs increases the extent of intercalation.

3.3b TG analysis: Although XRD studies indicate increase in basal spacing as a proof of successful intercalation reaction, it cannot quantify the amount of intercalant present in the interlayer gallery. During intercalation reaction, the anionic intercalants progressively replace the counter anion of LDH (here nitrate) and anchor to the brucite layer. The extent of such replacement depends on several factors. It is also possible for the intercalants to attach to LDH by physical adsorption only. The types of anchorage and quantification of the amount of intercalant associated with LDH

Table 3. Effect of the intercalation method and di and trivalent metal ratios on the basal spacing for C8 and C4 intercalants.

Intercalant	Layer charge	Technique	d spacing (d_{003}) (nm)	Reaction conditions	Reference
C8	0.16	Ion exchange	2.120	Fivefold excess intercalant, 60°C, 24 h	[30]
	0.20	Ion exchange	2.203	22 h, 34°C, stoichiometric amount intercalant	<i>This study</i>
	0.25	Ion exchange	2.245	22 h, 34°C, stoichiometric amount intercalant	<i>This study</i>
	0.30	Ion exchange	2.238	22 h, 32°C, stoichiometric amount intercalant	<i>This study</i>
	0.33	Ion exchange	Failed	20 times molar excess intercalant	[10]
		<i>In situ</i>	2.17	Constant pH of 7.0, 100°C, 18 h	[14]
		Ion exchange	2.195	22 h, 32°C, stoichiometric amount intercalant	<i>This study</i>
		Ion exchange	Failed	pH = 7	[13]
		Reconstruction	2.0	Calcined at 300°C for 3 h, stoichiometric amount intercalant	[11]
		Ion exchange	Failed	50 times molar excess intercalant, pH = 7	[10]
C4	0.20	Ion exchange	Failed	22 h, 34°C, stoichiometric amount of intercalant	<i>This study</i>
	0.25	Ion exchange	1.555	22 h, 34°C, stoichiometric amount of intercalant	<i>This study</i>
		<i>In situ</i>	1.230	10 times molar excess tartaric acid	[31]
	0.30	Ion exchange	1.580	22 h, 32°C, stoichiometric amount of intercalant	<i>This study</i>
	0.321	Ion exchange followed by refluxing	1.2 nm	pH > 9, 2 h reflux, more than twice molar excess tartaric acid	[15]
	0.33	Ion exchange	1.559	22 h, 32°C, stoichiometric amount of intercalant	<i>This study</i>
		—	1.2 for d_{006}	Succinic acid	[7]
		<i>In situ</i>	1.234	10 times molar excess intercalant	[31]

Figure 3. TG plots of: (a) C8 and (b) C4 O-LDHs having different layer charges.

are determined by analysis of multistage mass loss at elevated temperatures.

TG (figure 3) and differential TG (figure 4) analyses of C8 and C4 O-LDH reveal a multistage thermal decomposition pattern of these O-LDHs. The total mass loss increases with increasing layer charge irrespective of the intercalant. Only notable difference is that the comparable thermal stability of C4 O-LDH with pristine LDH $\text{NO}_3\text{-0.20}$ (supplementary material), indicating unsuccessful intercalation but needs detailed analysis before reaching any conclusion.

The multistage decomposition involved removal of physio-adsorbed water [34] (stage I, up to 150°C), simultaneous organic (stage II) and hydroxyl loss (stage III) [23,35] (up to 350°C) and unexchanged nitrate and different inorganic sulphate (MSO_4) at much higher temperature [36,37]. Therefore, the organic loss region is 150–350°C.

The main objective of the TG analysis is to quantify the organic material which incorporated within the LDH

Figure 4. dTG plots of: (a) C8 and (b) C4 O-LDHs with different layer charges.

gallery after intercalation. This quantification is utilized to differentiate between a successful and a failed intercalation as well as support XRD analysis. The organic only loss (150–350°C) for different O-LDHs is calculated using the following formula:

$$\text{Organic only loss} = [\text{Mass loss of O-LDHs (150–350°C)} - \text{Mass loss of pristine LDH (up to 350°C)}].$$

The quantification of the organic loss with respect to the AEC of different LDHs was done using equation (3.2), after Ganguly *et al* [35]:

$$\begin{aligned} &\text{Experimental organic loading } (L_{\text{exp}}) \\ &= \left[\frac{(n \times 10^7)}{(\text{MW of intercalant} \times \text{AEC of LDH} \times (100-n))} \right]. \end{aligned} \quad (3.2)$$

Table 4. Effect of layer charge and intercalant on L_{exp} (for $L_{\text{theo}} = 100$).

LDH	Intercalant	Mass loss (%)			L_{exp}
		O-LDHs 150–350°C	Pristine LDH up to 350°C	Organic only	
LDH-0.33	C8	29.3	17.9	11.4	37.1
	C4	26.3		8.4	23.8
LDH-0.30	C8	28.6	18.2	10.4	35.3
	C4	24.8		6.6	21.3
LDH-0.25	C8	28.2	20.9	7.3	26.5
	C4	22.6		1.7	12.8
LDH-0.20	C8	27.1	21.8	5.3	23.9
	C4	22.4		0.6	2.5

The mass loss of pristine LDH NO_3 up to 350°C was calculated by TG analyses (supplementary material) and subtracted from the total loss up to 350°C for O-LDH. Accordingly, the MW of the intercalants considered for the organic part only leaving the inorganic anion and cation (113 g mol^{-1} for $\text{C}_8\text{H}_{17}\text{NaO}_4\text{S}$ and 57 g mol^{-1} for $\text{C}_4\text{H}_9\text{NaO}_3\text{S}$).

All the intercalation reactions were performed with 100% AEC equivalent of anionic intercalant, so the theoretical loading (L_{theo}), $L_{\text{theo}} = 100$. But TG data show that only a fraction of the intercalant present in the reaction medium can replace the anion of LDH and form O-LDH. For a fixed $L_{\text{theo}} = 100$, with decreasing layer charge (of LDH) and intercalant chain length L_{exp} decreases monotonically. Here, L_{exp} is lower than L_{theo} in each and every case, which reduces the possibility of surface adsorbed intercalants.

Intercalation with C8: For intercalation of C8 with LDH-0.25 and LDH-0.20, the absence of 003 and 006 reflections was difficult to explain along with the success of intercalation from XRD data. But organic quantification from TG analyses revealed L_{exp} of 26.5 and 23.9% for LDH-0.25 and LDH-0.20, respectively. This clearly established the successful intercalation of C8 with LDH of low layer charges, which was uncertain from XRD analysis. The absence of first two basal reflections is attributed to the considerable decrease in L_{exp} on going from LDH-0.30 ($L_{\text{exp}} = 35.3$) to LDH-0.25 ($L_{\text{exp}} = 26.5$). This low experimental organic loading was unable to produce reflections at lower 2θ angle in XRD. For the lowest layer charge, the poor experimental organic loading ($L_{\text{exp}} = 23.9$) indicates the moderate contribution of the hydroxyl loss in the region of 150–350°C, which is evident from the appearance of a prominent second peak ($\sim 237^\circ\text{C}$) which is absent for higher layer charge LDHs.

Intercalation with C4: Table 4 reveals, with decreasing layer charge L_{exp} for C4 O-LDHs decreases drastically and the mass loss predominantly due to brucite hydroxyl loss (up to 350°C). It is well evident from the appearance of a prominent decomposition peak around $\sim 248^\circ\text{C}$ (hydroxyl decomposition). Further, the appearance of an unexchanged

nitrate anion decomposition peak ($\sim 396^\circ\text{C}$) supports the conclusion of poor intercalation with C4 and NO_3 LDHs (figure 4). Chakraborty *et al* [4] concluded L_{exp} of $<4\%$ along with no change in basal spacing, which indicates unsuccessful intercalation. Here, TG analyses revealed that for C4 and LDH-0.20, intercalation was unsuccessful ($L_{\text{exp}} = 2.5$) and further supported by FTIR analysis which reveals the absence of an organic material within the LDH gallery (section 3.3c).

Therefore, our approach to complement the XRD data by TG analyses successfully decipher the complex XRD pattern for C4-intercalated O-LDHs and it is finally concluded that LDHs having low AEC were successfully intercalated with short-chain intercalants. The degree of intercalation deteriorated with decreasing both AEC and alkyl chain length of the intercalants progressively and finally an unsuccessful intercalation was observed with LDHs having lowest AEC (1.80 meq g^{-1} , layer charge 0.20) and shorter intercalant (C4).

3.3c FTIR analysis: FTIR is an important tool which not only supports the presence of the intercalants within the LDH gallery but also provides better insight into the conformations of the intercalants. FTIR spectrograms of O-LDHs show (figure 5) the appearance of new frequencies (due to organic loading) which were initially absent in the pristine LDH (supplementary material). Two singlet frequencies ($\delta_{\text{C-H, rocking}}$ and $\delta_{\text{C-H, scissoring}}$ [38]) appeared around 722 and 1469 cm^{-1} in each case (except for C4 O-LDH-0.20), which supports the formation of an organic–inorganic hybrid (O-LDH). Therefore, the FTIR analyses also indicate that LDHs are successfully intercalated with short-chain intercalants. The absence of these frequencies for C4 LDH-0.20 indicates the absence of organic material within the gallery of LDH i.e., an unsuccessful intercalation and further complements the same inference drawn from XRD and TG analyses.

The peak around 1367 cm^{-1} ($\nu_{\text{N-O}}$) appeared due to the presence of nitrate anions which are not exchanged with the intercalants during the ion-exchange reaction. The analysis of the spectrograms reveals that the intensity of this band decreases with increasing AEC for any particular intercalant.

Figure 5. FTIR spectrograms ($400\text{--}4000\text{ cm}^{-1}$) and CH_2 stretching (symmetric and anti-symmetric, $2800\text{--}3000\text{ cm}^{-1}$) of intercalated LDHs with intercalants ($a = \text{C8}$; $b = \text{C4}$).

This clearly indicates that with increasing AEC of LDHs better intercalation is achieved (less intense $\nu_{\text{N-O}}$ band). These findings from FTIR analysis are also supported by both XRD and TG analyses.

The appearance of methylene symmetric ($\nu_{\text{sym}}(\text{CH}_2)$) ($2851\text{--}2856\text{ cm}^{-1}$) and anti-symmetric ($\nu_{\text{asym}}(\text{CH}_2)$) ($2920\text{--}2927\text{ cm}^{-1}$) stretching frequencies is also associated with the formation of organic–inorganic hybrids [38,39] like C–H frequencies. As expected, these two frequencies are also absent only for LDH-0.20 and C4 combination (an unsuccessful intercalation).

Therefore with the help of XRD, TG and FTIR analyses, the successful and unsuccessful formation of organic–inorganic hybrids with LDH and short-chain intercalant is confirmed, which is not reported previously. After understanding the successful intercalation, attempt has been made to evaluate the orientation of intercalants within the LDH gallery and find if there is any effect of layer charge on the orientation.

3.3d Evolution of structure of intercalated LDH: The structure of intercalated LDHs can be explained with (i) gallery height of O-LDH, (ii) orientation of intercalant, (iii) layer charge of LDH and (iv) degree of intercalation (%AEC). In the following discussion, correlation between these parameters is presented.

Basal spacing and chain length of intercalant: The shift in basal reflections towards lower Bragg angle in XRD translates into larger gallery height between the brucite layers. The gallery height—which is calculated by subtracting thickness of brucite layer from d_{003} —varies marginally with layer charge of LDH, but predominantly with the chain length of intercalant. The smallest intercalant C4 with the length of 0.84 nm could reach the gallery height of $1.075\text{--}1.119\text{ nm}$. Longer intercalant C8 expands the gallery to $1.723\text{--}1.758\text{ nm}$. Although, the gallery height marginally increases with layer charge, the dominance of intercalant chain length is clearly

Table 5. Orientation of intercalants within the LDH interlayer.

LDH NO ₃ and intercalant		<i>d</i> ₀₀₃ (nm)	Brucite layer thickness (nm)	Gallery height (nm)	Intercalant chain length (nm)	Orientation
LDH	Intercalant					
LDH-0.33	C8	2.195	0.48	1.715	1.460	Perpendicular interpenetrating monolayer
	C4	1.599		1.119	0.840	Perpendicular interpenetrating monolayer
LDH-0.30	C8	2.238		1.758	1.460	Perpendicular interpenetrating monolayer
	C4	1.580		1.100	0.840	Perpendicular interpenetrating monolayer
LDH-0.25	C8	2.245		1.765	1.460	Perpendicular interpenetrating monolayer
	C4	1.555		1.075	0.840	Perpendicular interpenetrating monolayer
LDH-0.20	C8	2.203		1.723	1.460	Perpendicular interpenetrating monolayer
	C4	No intercalation		—	—	—

Figure 6. The variation of basal spacing and experimental organic loading (L_{exp}) with intercalant chain length for each LDH.

evident from the data of table 5. The relationship between the length of intercalant and gallery height allows prediction of orientation of the intercalant molecule.

Orientation of intercalants within the LDH gallery: Depending on the gallery height (basal spacing–thickness of LDH layer (0.48 nm [4,40])) of O-LDHs and length of the intercalant molecules, different orientations viz., perpendicular monolayer, perpendicular interpenetrated monolayer, perpendicular bilayer, paraffinic or in a slanted angle with LDH layers may be achieved. If gallery height > intercalant chain length, then the most probable orientation of intercalant is a perpendicular interpenetrating monolayer. For gallery height $\sim$ intercalant chain length, the most probable orientation of intercalant is a perpendicular monolayer [41–43].

The length of the intercalants is calculated using software ChemDraw 3D Pro 7.0 after energy minimization and it was 1.46 and 0.84 nm for C8 and C4, respectively. Orientation of intercalants within the gallery of O-LDHs is reported in table 5.

With C8 O-LDHs, a perpendicular interpenetrating monolayer orientation was achieved, which is consistent with the previous studies (table 3). Although intercalation in acidic medium effectively intercalates C8 with low layer charge LDH the orientation of C8 does not affect. But higher basal spacing (in this study) compared with the previous studies for C8 O-LDHs indicates a better organic loading (table 3). The better organic loading is attributed to the minimization of adverse effects of carbonate anions by intercalation in slightly acidic medium (pH $\sim$ 5.4). A similar comparison is difficult for C4 O-LDHs as previous studies reported intercalation with different dicarboxylic acids (different chain lengths). But a

Figure 7. Proposed arrangement of intercalants within the interlayer space of O-LDHs based on XRD, TG and IR study.

higher basal spacing compared with those of previous studies also indicates the better loading with C4.

Layer charge of LDH and experimental organic loading: The variation of basal spacing (d_{003}) and L_{exp} with the intercalant chain length for each O-LDH is shown in figure 6. Higher layer charge of LDH always favoured greater experimental organic loading of any intercalant, irrespective of the chain length. This may be attributed to facile anion-exchange reaction due to enhancement of the forward reaction rate through the Le Chatelier's principle, where O-LDH is favourably removed from the aqueous reaction medium due to greater hydrophobicity.

From the above discussion, the correlation of basal spacing of O-LDHs, organic loading data from TG analysis and molecular conformation of intercalant molecules within the LDH gallery by FTIR spectroscopy are derived and the proposed arrangement of intercalants within the interlayer space of O-LDHs is shown in figure 7. This represents the complete scenario of intercalation of LDHs with different layer charges using different short-chain intercalants. For both short-chain intercalants, the gallery spacing remains slightly larger than the length of the intercalant, indicating perpendicular alignment of the alkyl chain with the brucite layer. With greater layer charge, the gallery spacing increases due to increased steric crowding between the alkyl chains.

4. Conclusion

1. Successful intercalation of short-chain (four carbon atoms) intercalants with LDHs having AEC as low as

227 meq per 100 g is established. In this study, intercalation behaviour of LDHs with short-chain intercalants is explored in detail, which is not reported earlier.

2. Conventional intercalation reaction in neutral medium is affected by the interference of dissolved carbonate anions. This adverse effect was minimized by intercalating in slightly acidic medium ($\text{pH} \sim 5.4$). This successful approach is first reported here for octyl sulphate (C8) and 1-butane sulphononic acid (C4), and even for most commonly used intercalant dodecylsulphate (C12).
3. The basal spacing (d_{003}) and experimental organic loading (L_{exp}) increases monotonically with increasing AEC of LDHs (layer charge) and intercalant chain lengths.

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