

Intracrystalline Oxidation of Thiosulfate-Intercalated Layered Double Hydroxides

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Thiosulfate-intercalated zinc–aluminum LDH was prepared by anion exchange reaction. The interlayer thiosulfate ions of this LDH could be quantitatively oxidized to tetrathionate ions using iodine and sulfate ions using H_2O_2 . Both of these intracrystalline reactions are topotactic in nature. The reaction of the LDH with molecular iodine makes it a potential material for the removal of radioactive iodine from effluents.

Introduction

Layered double hydroxides (LDHs), also known as hydroxide-like compounds (HTLCs) or anionic clays, are layered compounds that consist of positively charged metal hydroxide sheets with intercalated anions and water molecules in the interlayer region.^{1,2} The general formula of LDHs is $[\text{M}^{\text{II}}_{(1-x)}\text{M}^{\text{III}}_x(\text{OH})_2]\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}$, where M^{II} is a divalent metal such as Mg, Co, Ni, Cu, Zn or Ca; M^{III} is a trivalent metal such as Al, Cr, Fe or Ga; A^{n-} is an anion with a valency n ; and x , defined as $[\text{M}^{\text{III}}]/([\text{M}^{\text{III}}] + [\text{M}^{\text{II}}])$, is usually between 0.25 and 0.33. These compounds derive their structure from that of brucite, $\text{Mg}(\text{OH})_2$. In brucite-like hydroxides, OH^- ions are hexagonally close packed and the M^{2+} ions occupy alternate layers of octahedral sites. Thus, the structure can be described as a stacking of charge-neutral $\text{M}(\text{OH})_2$ layers. In LDHs a part, x , of the M^{2+} ions are isomorphously substituted by M^{3+} ions, leading to positively charged layers having the composition $[\text{M}^{2+}_{(1-x)}\text{M}^{3+}_x(\text{OH})_2]^{x+}$. To compensate for the positive charge on the layers, anions, A^{n-} are intercalated in the interlayer region. LDHs show interesting properties such as anion mobility, anion exchange, surface basicity, and reconstruction behavior. Due to these properties, LDHs find applications in varied fields such as sorption, catalysis, flame-retardation, polymer stabilization, electrochemistry, photochemistry, and medicine to cite a few.^{3–12}

The anions and water, which fill the interlayer space, are labile. Therefore, a variety of inorganic and organic anions can be intercalated in the interlayer of LDHs through anion exchange reactions. Intercalation reactions of layered solids are important, as these can change the chemical, electronic, and magnetic properties of the host lattice.¹³ The intercalation chemistry of LDH hosts is extensive. There is no significant restriction to the

nature of anion that can occupy the interlayer of a LDH. A large variety of anions have been incorporated into the interlayer region of the LDHs. Simple inorganic ions, such as Cl^- , Br^- , SO_4^{2-} , and CO_3^{2-} ; larger ions, such as oxometalates; and anionic transition metal complexes have also been incorporated into LDHs.^{14,15} Large biomolecules such as peptides, vitamins, polysaccharides, and DNA have been successfully incorporated in the interlayer of LDHs.¹⁶ Most of the intercalation reactions take place at room temperature, making this method a soft chemical route to new materials with modified physical and chemical properties compared to the host lattice. Intercalation can be achieved by direct synthesis via coprecipitation, anion exchange of a precursor, and rehydration of the calcined precursor.¹³

There are many factors such as the geometry, size, charge, and the functional groups of the guest species that govern the intercalation process. The interlayer orientation of the intercalated anions depends on the charge on the hydroxide layer and the shape, hydrophilic or hydrophobic nature, and packing density of the anion.

In recent times there have been reports on the interlayer reaction of intercalated anions in anionic clays. Our group has shown that anionic clays could be used as an anchor for an organic substrate in a reaction.¹⁷ Anionic claylike nickel–zinc hydroxy acetate was exchanged with maleate and fumarate ions. The intercalated anions were reacted with bromine water in such a way that the brominated product remained intercalated, making the reaction a true intracrystalline reaction. Duan's group reported the intercalation of two kinds of amino acids, L-cysteine and L-cystine, into MgAl LDH and the oxidation of the intercalated amino acids by hydrogen peroxide and bromine.¹⁸ The oxidation products under the confined region were found to be different from those obtained from the corresponding free amino acids.

By virtue of the pronounced anion exchange capacity, LDHs have great potential to scavenge anionic contaminants from polluted water. Removal of radioactive iodine is a potential problem that exists in the environmental chemistry. It is known

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that radioactive iodine exists in the form of elementary (molecular) iodine, iodide, iodates, and various organic compounds, especially methyl iodide.¹⁹ The radioactive molecular iodine is separated from the solution mainly using sorption filters.²⁰

In this work, we report the preparation of thiosulfate-intercalated Zn–Al LDH and the interlayer oxidation of thiosulfate using oxidizing agents such as iodine and H₂O₂. When iodine was used as the oxidizing agent, the interlayer thiosulfate was quantitatively oxidized to tetrathionate and the iodide ion formed gets intercalated. When H₂O₂ was used as the oxidizing agent, a carbonate-free sulfate-intercalated LDH was obtained.

Experimental Section

Preparation of Zn₂Al(OH)₆Cl·mH₂O. Zn₂Al(OH)₆Cl·mH₂O was prepared by the procedure of Bonnet et al.²¹ An aqueous solution (100 mL) containing ZnCl₂ and AlCl₃ in the molar ratio 2:1 was added together with a 2 M NaOH solution to a flask containing 100 mL of deionized water. The rate of addition was such that the pH was kept at 7.0 using a pH-Stat. Rapid stirring and nitrogen atmosphere was maintained throughout the addition. After the addition was complete, the resultant slurry was aged at 65 °C overnight. The solid product obtained was washed free of ions with decarbonated water followed by acetone and dried at 65 °C in an air oven to constant mass. This sample is hereafter referred to as ZnAl-Cl.

Preparation of Zn₂Al(OH)₆(S₂O₃)_{0.5}·mH₂O. The thiosulfate-intercalated LDH was obtained through anion exchange reaction. About 1 g of the ZnAl-Cl LDH was stirred with an aqueous solution of sodium thiosulfate (2 g in 50 mL) in an airtight container for 2 days. The resultant solid was filtered, washed with decarbonated water followed by acetone, and dried at 65 °C to constant mass. This sample is hereafter referred to as ZnAl-S₂O₃.

Oxidation of ZnAl-S₂O₃ by H₂O₂. To a suspension of ZnAl-S₂O₃ LDH (0.1 g in 10 mL decarbonated water) was added 3 mL of 30% H₂O₂ solution. The mixture was stirred under nitrogen atmosphere for 1 h. The product was isolated by centrifugation and dried at (i) room temperature for 2 days and (ii) 65 °C overnight. The centrifugate was collected and analyzed for SO₄²⁻ and S₂O₃²⁻ ions.

Oxidation of ZnAl-S₂O₃ by Iodine. To a suspension of ZnAl-S₂O₃ LDH (0.1 g in 10 mL of decarbonated water) was added 45 mL of iodine solution (0.033 g in 100 mL water). The mixture was stirred under nitrogen atmosphere for 1 h. The product was isolated by centrifugation and dried at 65 °C overnight. The centrifugate was collected quantitatively and analyzed for anions such as I⁻, S₂O₃²⁻, and S₄O₆²⁻. This experiment was repeated with different volumes of iodine solutions (22.5 and 11.3 mL) keeping the mass of LDH constant and the I⁻ content in the solid products estimated.

Characterization. Powder X-ray diffraction (PXRD) measurements were performed on a PANalytical Xpert Pro X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm) at 40 kV, at a scanning rate of 2° min⁻¹. The infrared (IR) spectra of samples were collected using a Nicolet IR200 FT-IR spectrometer using KBr pellets, in the range 4000–400 cm⁻¹ with 4 cm⁻¹ resolution. The interlayer anion (chloride/thiosulfate) contents were obtained by ion chromatography (IC) using a Metrohm 861 Advanced Compact ion chromatograph with Metrosep A Supp5 250 anion column and conductivity detector. The samples were dissolved in 1 N sulfuric acid or hydrochloric acid and diluted suitably for this purpose. Thiosulfate reacts slowly with dilute hydrochloric acid to give SO₂ and sulfur. To minimize the error due to this reaction, in the case of thiosulfate estimation the standard thiosulfate solutions were also treated with hydrochloric acid before injection into the chromatograph. The metal contents of

Table 1. Chemical Composition of the LDHs Used in This Study

sample	mass percentage			approximate formula
	Zn	Al	A ⁻	
ZnAl-Cl	40.1	7.9	10.7	Zn ₂ Al(OH) ₆ Cl·2H ₂ O
ZnAl-S ₂ O ₃	37.4	7.7	13.1	Zn ₂ Al(OH) ₆ (S ₂ O ₃) _{0.4} (CO ₃) _{0.2} ·2H ₂ O

the samples were estimated by atomic absorption spectroscopy (Varian AA240). The approximate formulas of the compounds were calculated by setting [OH] = 2([Zn] + [Al]), [carbonate] = [Al] – [chloride or thiosulfate], and the unaccounted mass to water.

Thermogravimetric analyses of the sulfate-intercalated LDHs obtained by oxidation of thiosulfate-intercalated LDH were carried out using a Mettler Toledo STAR^c SW 7.01 system under continuous flow of nitrogen with a heating rate of 5 °C/min.

Results and Discussion

The composition analysis data of the as-prepared LDH and the thiosulfate-exchanged product are given in Table 1. The nominal chemical formulas obtained indicate that the LDHs were formed with the expected Zn/Al ratio of 2. While the as prepared chloride-LDH is completely free of carbonate, slight carbonate contamination was observed in the thiosulfate-LDH. Though care has been taken to run the reactions under N₂ atmosphere, atmospheric CO₂ could have contaminated the samples, possibly during washing.

The PXRD patterns of ZnAl-Cl and ZnAl-S₂O₃ LDHs are shown in Figure 1. ZnAl-Cl LDH (Figure 1a) has a basal spacing of 7.7 Å (calculated from the 00l reflections), as expected for a chloride-intercalated LDH. The pattern can be indexed to a 3R₁ polytype. ZnAl-S₂O₃ (Figure 1b) obtained on anion exchange shows a basal spacing of 8.9 Å. This interlayer spacing matches with what has been reported for thiosulfate-intercalated Mg–Fe LDH.²² In comparison to ZnAl-Cl, the 101, 104, and 107 reflections increase in intensity in the PXRD pattern of ZnAl-S₂O₃, and the 105 and 108 reflections are not observed, suggesting a change to 3R₂ polytype. However, the 012 reflection continues

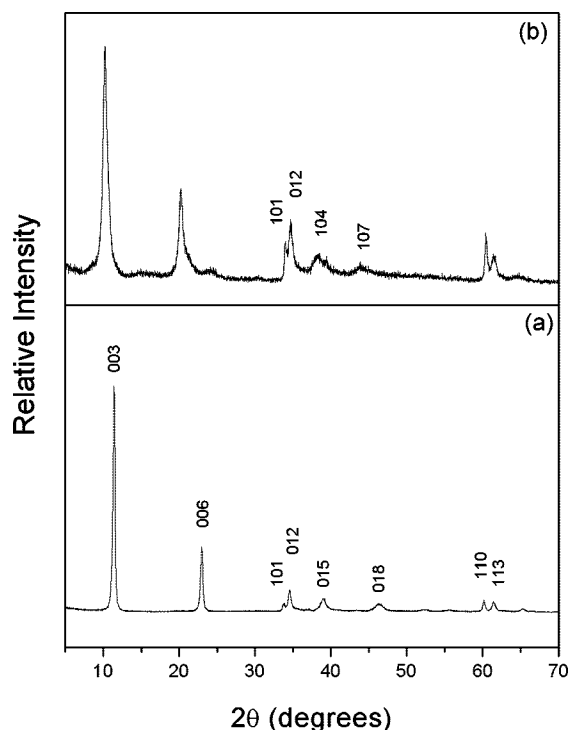


Figure 1. PXRD patterns of ZnAl-Cl (a) and ZnAl-S₂O₃ (b).

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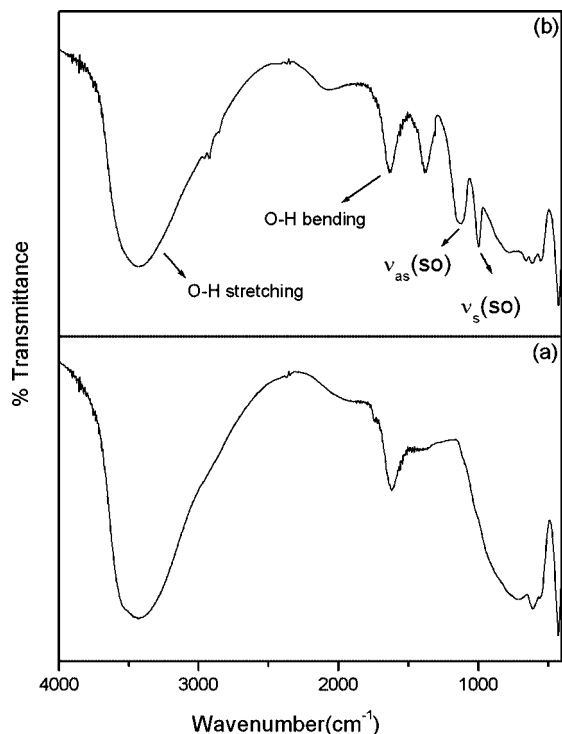
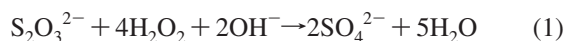


Figure 2. IR spectra of ZnAl-Cl (a) and ZnAl-S₂O₃ (b).

to be present, and the 104 and 107 reflections are quite broad, suggesting that the sample has considerable stacking disorder.

The IR spectra of ZnAl-Cl and ZnAl-S₂O₃ LDHs are shown in Figure 2. The broad absorption at 3500 cm⁻¹ in both the samples is due to O–H stretching vibration of the hydroxyl groups of the brucite-like sheets and water in the interlayer space. The O–H bending vibration of the interlayer water is observed at 1630 cm⁻¹. The IR spectrum of ZnAl-Cl LDH (Figure 2a) has no absorption in the range of 900–1500 cm⁻¹, as expected of a chloride-intercalated LDH. There is no absorption at 1356 cm⁻¹, confirming the complete absence of carbonate ions in the LDH. S_nO_m²⁻ compounds (*n* = 2, 3, 4,...) exhibit two typical vibrations between 900 and 1300 cm⁻¹, which are due to the antisymmetric and symmetric S–O stretching vibrations.²³ In ZnAl-S₂O₃ LDH (Figure 2b) the symmetric and antisymmetric stretching vibrations of thiosulfate are observed at 995 and 1137 cm⁻¹. These values match well with what has been reported for thiosulfate-intercalated Mg–Fe-LDH.²²

The interlayer thiosulfate ions could be topotactically oxidized using H₂O₂. Many products are possible when thiosulfate ion reacts with H₂O₂.²⁴ However as the interlayer region is very alkaline, we expect the thiosulfate ions to give sulfate ions according to the equation:



Ion chromatographic (IC) analysis of the oxidation product confirms the formation of sulfate ions. The net charge on the product ions is twice that of the starting thiosulfate ions. This leads to (i) the complete removal of the carbonate contaminant from the interlayer of the LDH and (ii) the excess sulfate ions to come to the solution. IC analysis of the H₂O₂-oxidized LDH shows that only sulfate ions are present in the interlayer with no trace of carbonate ions and the sum of the number of moles of

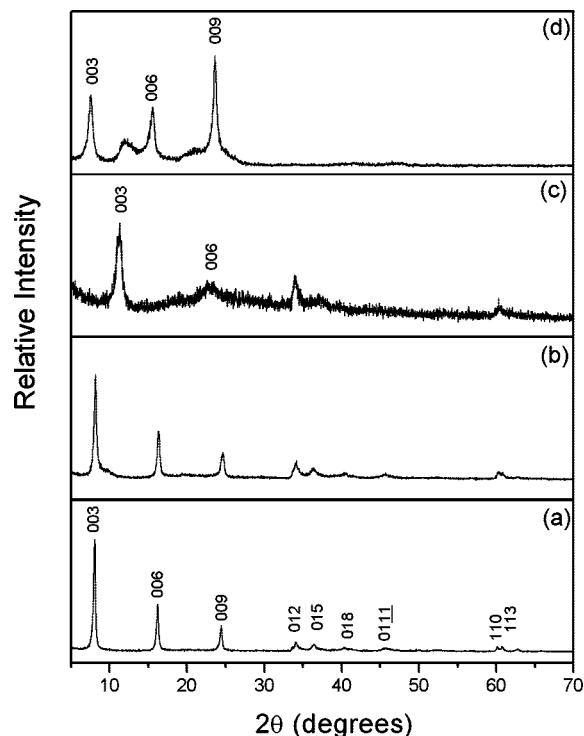


Figure 3. PXRD patterns of ZnAl-S₂O₃ subjected to oxidation by H₂O₂ and dried at different temperatures: room temperature (a), 100 °C (b), and 150 °C (c). PXRD pattern of ZnAl-S₂O₃ subjected to oxidation by iodine (d).

sulfate ions in the oxidized LDH and the supernatant is twice the number of moles of thiosulfate ions in the starting LDH.

When the H₂O₂-oxidation product was dried at room temperature, a crystalline LDH with a basal spacing of 10.9 Å (Figure 3a) was obtained. Two phases of sulfate-intercalated LDHs—the usual phase with a basal spacing of 8.9 Å and an uncommon phase with a higher basal spacing—have been encountered in the past.^{25,26} In the uncommon phase, usually obtained under high humidity, an additional layer of water is present between the sulfate layer and the metal hydroxide layer, leading to a basal spacing of ~11 Å.²⁵ The observed basal spacing in our oxidized product suggests that there is an additional layer of water in the interlayer of this sulfate-LDH. When the H₂O₂-oxidized sample was subjected to drying at up to 100 °C for 2 days, there is no change in the PXRD pattern (Figure 3b) and the LDH retains the structure. While this behavior is different from what was observed for Zn–Cr sulfate LDH,²³ it matches with what was observed by Radha et al.²⁶ for Zn–Al sulfate LDH. However, the LDH obtained here differs from the one prepared by these authors in polytypism. Our sample is the 3R₁ polytype, as we observe (Figure 3a) the 012, 015, 018, and 0111 reflections, but the LDH reported by Radha et al.²⁴ was 1H polytype with turbostratic disorder. When the H₂O₂-oxidized sample was dried at a higher temperature (150 °C) we obtained a layered phase (Figure 3d) with a lower basal spacing of 7.7 Å due to the complete removal of interlayer water. This sample could not be completely rehydrated to the parent 11 Å phase. When stirred in water for two days, this sample yielded a mixture of the LDH phases having basal spacings 7.7 and 11 Å along with Al(OH)₃.

The TG curves of ZnAl-S₂O₃ subjected to oxidation by H₂O₂ and dried at 100 °C and at 150 °C are shown in Figure 5. The

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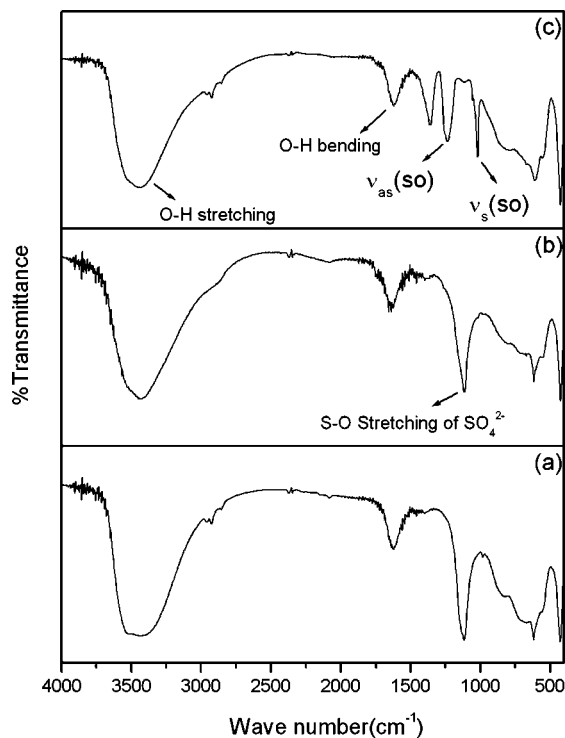


Figure 4. IR spectra of ZnAl-S₂O₃ subjected to oxidation by H₂O₂ and dried at different temperatures: room temperature (a) and 100 °C (b). IR spectrum of ZnAl-S₂O₃ subjected to oxidation by and iodine (c).

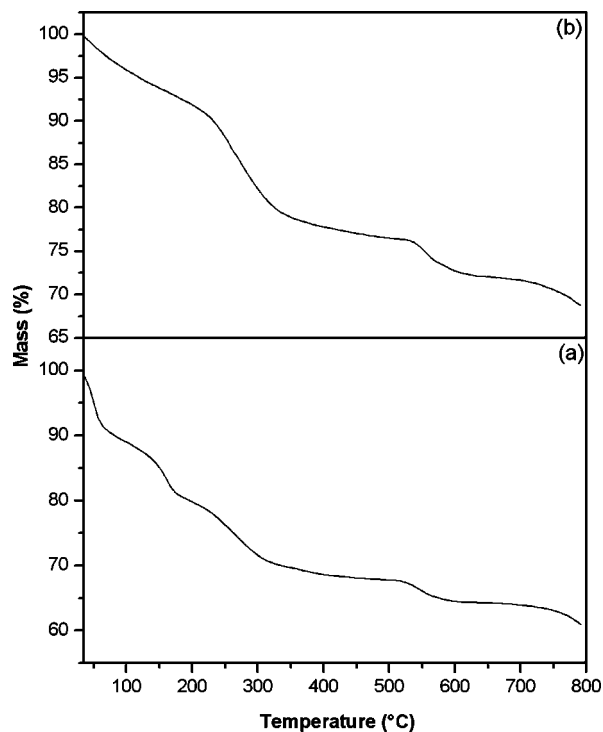


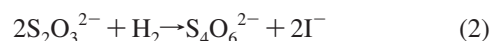
Figure 5. TG curves of ZnAl-S₂O₃ subjected to oxidation by H₂O₂ and dried at 100 °C (a) and 150 °C (b).

sample dried at 100 °C (Figure 5a) shows a total mass loss of ~20% in two steps from room temperature to 175 °C, while the sample dried at 150 °C (Figure 5b) shows only a single step mass loss of ~8% in this range. The TG data indicate that the LDH phase with the higher basal spacing contains more interlayer water than the phase with the lower basal spacing, and the two-step loss shown by the former suggests that there are two different

kinds of interlayer water molecules in this phase. These results further confirm that the LDH phase with the higher basal spacing has an additional layer of water in the interlayer.

The IR spectra of the H₂O₂-oxidized products—dried at RT and at 100 °C—are shown in Figure 4, parts a and b. In both the cases, we observe a strong absorption at 1117 cm⁻¹ due to the sulfate ions. The two spectra are identical, indicating that the geometry and orientation of the sulfate ions in the LDH is not affected by the heat treatment. There is no peak at 1356 cm⁻¹, confirming the absence of carbonate ions in these samples. This is in agreement with the IC analysis data. The fact that carbonate-free LDH could be obtained by the oxidation of thiosulfate-intercalated LDH makes this reaction a useful method to prepare sulfate LDHs.

The ZnAl-S₂O₃ LDH reacts quantitatively with iodine. The PXRD pattern of the product obtained on oxidation of ZnAl-S₂O₃ LDH by iodine (Figure 3d) shows a basal spacing of 11.6 Å. This higher basal spacing is due to the tetrathionate ion formed during the intracrystalline oxidation according to the equation:



As the charge on thiosulfate ion is equal to the net charge on the anions produced by the oxidation, one would expect the iodide ions to be intercalated in the interlayer of the LDH. The IC analysis of the solid product and the supernatant after the reaction reveals that only ~60% of the iodide ions formed during the reaction get intercalated in the interlayer of the LDH. Possibly the iodide ions formed due to the reaction between iodine and the thiosulfate ions in the layer edges do not get incorporated in the interlayer region. The relative intensities of the 00l lines in Figure 3c indicate the presence of heavy I⁻ ions in the interlayer.

In the IR spectrum of iodine-oxidized sample (Figure 4c), there are two peaks corresponding to S—O stretching vibrations at 1017 and 1230 cm⁻¹. This suggests that the interlayer anion in this sample is the tetrathionate ion. The sulfate absorption at 1117 cm⁻¹ is almost absent, suggesting that the tetrathionate ion has not been further oxidized to sulfate ion. However, there is a prominent peak at 1356 cm⁻¹, indicating the presence of carbonate ions in the interlayer.

As the thiosulfate-intercalated LDH reacts quantitatively with molecular iodine, it is a potential material for scavenging radioactive molecular iodine. Removal of radioactive iodine from aqueous and gaseous sources is an important problem.^{27–29} Most of the methods involve sorption and filter techniques.³⁰ Intercalation could be a better method compared to sorption due to the permanent fixing of anions in the layer. Though the results of this study suggest the possibility of the thiosulfate-intercalated LDH to be a suitable material for scavenging radioactive iodine, this can be confirmed only after carrying out studies with ¹³¹I₂, since the equilibrium constant of a chemical reaction can change when the reaction is carried out with the radioactive analogue.

Theoretically, I⁻ produced during the oxidation should remain in the interlayer to balance the charge. However, when the oxidation of the thiosulfate LDH was carried out with a stoichiometric amount of iodine, ~40% of the iodide was detected in solution and the remaining was intercalated in the LDH. The

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Table 2. Effect of Starting Amount of Iodine on the Extent of I⁻ Incorporation in the LDH

volume of iodine solution added (mL)	amount of iodine (mmol)	amount of iodide in LDH solid (mmol)	amount of iodide in supernatant (mmol)	percentage of iodide in LDH solid
45.0	0.059	0.076	0.051	64
22.5	0.029	0.032		55
11.3	0.015	0.013		43

percentage of iodide intercalated in the solid decreases with a decrease in the amount of iodine that reacts with the LDH (Table 2). When we decrease the amount of iodine, as less and less iodine molecules are available, the fraction of reaction with the edge thiosulfate ions increases, leading to a reduction in the intercalated iodide content. This method is quite fast, as it takes only a few seconds for the reaction to go to completion. It is an added advantage compared to the sorption techniques, which take much longer time.

Conclusions

Thiosulfate-intercalated ZnAl LDH could be prepared by anion exchange reaction. This on oxidation with H₂O₂ yields a very

crystalline carbonate-free sulfate LDH and with iodine yields tetrathionate as well as iodide-intercalated LDH. Intracrystalline reactions of the kind described here could open up means to prepare carbonate-free LDHs and to scavenge contaminants like radioactive molecular iodine.

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