We wanted to explore the possibility of carrying out intracrystalline reactions in an anionic clay. We studied intracrystalline reactions by intercalating a suitable organic anion within the interlayer of an anionic clay and subjecting the intercalated clay to reactions with suitable reagents leading to the formation of a product anion which is held on to the interlayer. We could extend this method to form layered composites by interlayer reaction. This chapter is divided into two sections. Section A discusses intercalation of organic anions into an anionic clay followed by an addition reaction of the intercalated organic anions. Section B deals with intercalation of oxalate ion followed by an interlayer redox reaction between intercalated oxalate anions and permanganate ion to yield anionic clay-birnessite composite.
Section A

Anionic clays as hosts for anchored synthesis: Interlayer bromination of maleate and fumarate ions in nickel-zinc layered hydroxy double salt

Anionic clay-like nickel zinc hydroxyacetate, Ni$_3$Zn$_2$(OH)$_8$(OAc)$_2$·2H$_2$O was ion exchanged with maleate and fumarate ions. While the maleate enters as monoanion, fumarate enters as dianion. Also these anions take up different orientations in the interlayer region. The intercalated organic species could be reacted with bromine water in such a way that the brominated product remains intercalated making the reaction a true intracrystalline reaction. The stereochemistry of the reaction of the intercalated fumarate was identical to that of the free fumarate ion – both yielding only anti addition product. While free maleate ion yielded only anti addition product, the intercalated maleate ion yielded both syn and anti addition products. The organic products could be quantitatively recovered by anion exchange with oxalate ions.
3.1 Introduction

Organo-inorganic hybrids based on anionic clays have been well studied in the past. From simple organic anions [1] to large surfactant anions [2] and biomolecules [3] have been intercalated in the interlayer region of anionic clays. The intercalation process has been used in selective sorption and isomer separation [4,5]. The interlayer region of anionic clay has been recently used as a molecular container to prevent racemisation of amino acids [6].

While there are many studies leading to application of anionic clays in organic chemistry, the possibility of immobilizing anionic organic substrates, which can then be subjected to further reaction in the interlayer region, has not been well explored. Reactions in the interlayer region can be carried out in such a way that the desired product is contained in the interlayer region which has the advantage that it can be recovered in the pure form easily, free from the other side products and the excess reactants used. In addition, the anchored organic substrate could be subjected to a series of reactions and the final product deintercalated from the layered solid. One could also anticipate regioselectivity and stereoselectivity as the anions take up specific geometry in the interlayer region. Reactions in the interlayer region of anionic clays have been carried out in the past but the motive has not been to contain the product in the interlayer region itself [7]. Here we demonstrate anchoring anionic organic substrates in the interlayer region of an anionic clay, carry out a reaction on these substrates in such a way that the product remains anchored to the layered solid and recover the product by a simple anion exchange reaction.

In this work, we have chosen Ni-Zn hydroxysalt as the anionic clay as anion exchange here is easier and contamination due to carbonate (which is a major problem when working with layered double hydroxides) is minimal. Ni$_3$Zn$_2$(OH)$_8$(OAc)$_2$·2H$_2$O derives its structure from the hydroxynitrate, Zn$_5$(OH)$_8$(NO$_3$)$_2$·2H$_2$O [8]. In these compounds, M$^{2+}$ ions occupy only 75% of the octahedral sites in brucite-like M(OH)$_2$ layers. A quarter of the octahedral sites are unoccupied and the tetrahedral sites adjacent to the vacant octahedral sites – one above and one below – are occupied by Zn$^{2+}$ ions, which show preference towards tetrahedral occupancy. Thus the layer gets positively charged with the composition [M$_3$$^O_{□•}$Zn$_2$$^T$(OH)$_8$]$^{2+}$, where O and T refer to octahedral and tetrahedral sites and □ refers to vacancy. Anions get incorporated in the interlayer region to compensate the
positive charge on the layers. A water molecule each coordinates to the Zn$^{2+}$ ions to complete the tetrahedral coordination.

3.2 Experimental

3.2.1 Synthesis of Ni-Zn hydroxysalt, $\text{Ni}_3\text{Zn}_2\text{(OH)}_8\text{(OAc)}_2\cdot 2\text{H}_2\text{O}$

The Ni-Zn hydroxysalt was prepared by the acetate hydrolysis route reported by Marioka et al [9]. 28.5 mmol (2.32 g) of zinc oxide was added to 200 ml aqueous solution containing 60.35 mmol (10.66 g) of nickel acetate with vigorous stirring. The slurry was heated at 65 °C in an air oven for 48 h with occasional stirring. The resultant solid was washed repeatedly by centrifugation using copious amounts of decarbonated water and dried at 65 °C in an air oven to constant weight.

3.2.2 Preparation of maleate and fumarate intercalated Ni-Zn hydroxy salts

1 g of the Ni-Zn hydroxy salt obtained from the previous step was added to 50 ml of an aqueous solution containing 10.06 mmol of maleate/fumarate, whose pH was adjusted to ~8 by the addition of required volume of 20 mM sodium hydroxide solution. The resultant mixture was stirred for 48 h with replacement of the supernatant after 24 h with the dicarboxylate solution. The product obtained was washed free of excess ions by centrifugation using decarbonated water and dried in an air oven at 65 °C to constant weight.

3.2.3 Bromination of the maleate and fumarate intercalated hydroxysalts

The maleate/fumarate intercalated samples obtained were treated with aliquots of saturated aqueous solution of bromine (bromide salt was not added to increase the solubility of bromine in water as this would lead to anion exchange of the intercalated dicarboxylate ions by bromide) until the solution remained orange yellow due to excess unreacted bromine and the amount of bromine consumed quantified by treating the unreacted bromine with potassium iodide solution and titrating the liberated iodine with sodium thiosulphate. The brominated samples (300 mg) were stirred with an aqueous solution containing excess of sodium oxalate to exchange the interlayer brominated dicarboxylate. The brominated dicarboxylicacid was recovered from the supernatant through acidification followed by ether extraction.
3.2.4 Characterisation

The metal contents in the samples were determined by atomic absorption spectrometry (Varian AA240). The carbon contents of the samples were obtained using a ThermoFinnigan FLASH EA 1112 CHNS analyzer. The samples were characterized by powder x-ray diffraction (Siemens D5005 powder diffractometer, 0-2θ Bragg-Brentano geometry, Cu-Kα radiation, 2° 2θ per min) and Infrared spectroscopy (Nicolet model impact 400D FTIR spectrometer, KBr pellets, 4 cm⁻¹ resolution). Nuclear Magnetic Resonance Spectroscopy (Bruker AMX 400 MHz, CD₃OD solvent) was used to characterize the organic products.

3.3 Results and Discussion

The metal and carbon contents of the hydroxysalt samples are given in Table 3.1. From the data we see that the approximate formula of the hydroxyacetate is Ni₃Zn₂(OH)₈(OAc)₂·2H₂O. Fumarate exchange appears to have been total from the percentage of carbon in the exchanged sample (observed: 8.1%; expected: 8.1%). The maleate exchanged sample shows a higher carbon content (observed: 13.3%; expected 13.6%) corresponding to the nominal formula Ni₃Zn₂(OH)₈(maleate)₂·2H₂O. As the pH at which intercalation was carried out was relatively low, maleic acid whose pKₐ₂ is high (6.07) might have been intercalated as a monoanion while fumaric acid whose pKₐ₂ is lower (4.44) could have formed the dianion intercalated solid. Though the pH of the medium is low, the local pH around the anionic clay should be high enough to convert maleic acid into its dianion. However, the carbon content of the sample suggests that this has not happened and the maleate has entered as monoanion in the interlayer region.

Powder XRD patterns of maleate and fumarate intercalated Ni-Zn hydroxysalts are compared with that of the parent Ni-Zn hydroxyacetate in Figure 3.1. The pattern of the hydroxyacetate (Figure 3.1a) matches with what has been reported earlier in the literature [9]. The basal spacing is 13.1 Å and the saw tooth shaped features starting at around 2θ = 33° and 60° are due to the 2D (10) and (11) reflections as the sample exhibits turbostratic disorder [10,11] While the high angle features remain the same in the anion exchanged samples (Figure 3.1b and c), the low angle reflections corresponding to the basal spacing move towards higher 2θ. The
basal spacings of the maleate and fumarate exchanged samples are 8.0 Å and 12.3 Å respectively.

Figure 3.1 PXRD patterns of Ni-Zn hydroxyacetate (a), Ni-Zn hydroxymaleate (b) and Ni-Zn hydroxyfumarate (c).

The observed d-spacings of the maleate and fumarate intercalated samples can be accounted by assuming that these ions are differently oriented in the interlayer region. The fumarate ion stands vertically in the gallery space with the C-C double bond parallel to the c-axis with its two carboxylate groups H-bonded to two different layers. The maleate anion must be lying perpendicular to the c-axis with both the carboxylate groups H-bonded to the same layer. The interlayer geometries of the two samples are shown schematically in Scheme 3.1. It should be noted that the orientation of maleate ion observed here is different from what has been observed for this ion in Li-Al LDH by Fogg et al [12]. These authors observed that both fumarate and maleate ions stand vertically in the interlayer region with the C-C double bond parallel to the c-axis.
**Scheme 3.1** Schematic representation of interlayer geometry of Ni-Zn hydroxymaleate (a) and Ni-Zn hydroxyfumarate (b)

**Figure 3.2** IR spectra of Ni-Zn hydroxyacetate (a), Ni-Zn hydroxymaleate (b) and Ni-Zn hydroxyfumarate (c)

Infrared spectra further confirm intercalation of the organic anions. While the IR spectrum of the parent hydroxyacetate (Figure 3.2a) shows a strong absorption at 1400 and 1550 cm\(^{-1}\) due to the carboxylate stretching and absorptions at 2830 and 2910 cm\(^{-1}\) due to the methyl C-H stretching, the maleate (Figure 3.2b) and fumarate
(Figure 3.2c) intercalated samples show absorptions due to carboxylate at 1561 and 1428 cm\(^{-1}\) for maleate, 1578 and 1397 cm\(^{-1}\) for fumarate. Both the samples show vinyl C-H absorptions at 2925 and 2854 cm\(^{-1}\).

Both maleate and fumarate intercalated solids react readily with bromine water. However, maleate intercalated sample consumes approximately twice the amount of bromine compared to the fumarate analogue (Table 3.1).

**Table 3.1** Composition analysis data of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight percentage</th>
<th>Nominal Formula</th>
<th>Number of moles of Br(_2) consumed per mole of hydroxy salt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Zn</td>
<td>C</td>
</tr>
<tr>
<td>hydroxyacetate</td>
<td>29.4</td>
<td>21.9</td>
<td>8.0</td>
</tr>
<tr>
<td>hydroxyfumarate</td>
<td>29.8</td>
<td>22.1</td>
<td>8.1</td>
</tr>
<tr>
<td>hydroxymaleate</td>
<td>24.9</td>
<td>18.6</td>
<td>13.3</td>
</tr>
</tbody>
</table>

This further confirms that the maleate ions and fumarate ions are present as mono and dianions respectively in the interlayer region. The powder XRD patterns of the brominated intercalated solids are shown in Figure 3.3. The basal spacing changes from 8.0 Å to 11.8 Å for brominated maleate and from 12.3 Å to 12.0 Å for brominated fumarate sample suggesting the conversion of hybridization of carbon atoms from sp\(^2\) to sp\(^3\) and incorporation of the large Br atoms. It is also interesting to note that the interlayer arrangement in both the cases is now similar – the brominated carboxylate ions standing upright with their carboxyl ends forming H-bonds with adjacent layers. The monoanionic maleate species should have been converted into a dianion during the bromination reaction. This is confirmed by the fact that the
supernatant after the bromination of the maleate-intercalated sample contains dibromosuccinate species while that of the fumarate-intercalated sample does not.

![Figure 3.3](image.png)

**Figure 3.3** Powder XRD patterns of brominated samples of Ni-Zn hydroxymaleate (a) and Ni-Zn hydroxyfumarate (b). The peaks marked * are due to impurity.

Bromination of a double bond is a stereoselective reaction. In aqueous solution synthesis, the addition is anti with fumarate giving meso dibromosuccinate and maleate giving the racemic dibromosuccinate [13]. Also in aqueous solution reaction halohydrin is formed as an additional product. Proton NMR spectrum of the product obtained in case of fumarate-intercalated sample exactly matches with that of the product obtained in the control reaction in which an aqueous solution of fumarate ions was treated with bromine solution. Both the samples show a peak at 4.56 ppm as expected for meso 2,3-dibromosuccinic acid. However, the proton NMR spectrum of the product of bromination of the maleate-intercalated sample differs slightly from that of the product in the control reaction. While the control reaction product shows only a peak at 4.80 ppm corresponding to d/l dibromosuccinic acid, the product from maleate-intercalated anionic clay shows a strong peak at 4.80 ppm and a weak peak at 4.56 ppm indicating the presence of a small percentage of meso 2,3-dibromosuccinic acid. This may be explained as follows. As the maleate ion lies
perpendicular to the c-axis of the layered solid, it can undergo only \textit{syn} addition leading to the \textit{meso} product. However, after initial stages of the reaction the interlayer distance is increased and the usual \textit{anti} addition takes over leading to the formation of \textit{d/l} mixture.

\subsection*{3.4 Conclusion}

In conclusion we have shown that maleate and fumarate ions intercalated in an anionic clay could be subjected to an intracrystalline reaction and the product formed could be recovered through anion exchange. Thus anionic clays could be used as an anchor for an organic substrate in a reaction. The two isomeric ions take up different geometries in the interlayer region leading to a minor change in the stereoselectivity of the reaction.

\section*{References}


Section B

Preparation of anionic clay-birnessite manganese oxide composites by interlayer oxidation of oxalate ions by permanganate

Oxalate intercalated anionic clay-like nickel zinc hydroxysalt was obtained starting from nickel zinc hydroxyacetate, Ni$_3$Zn$_2$(OH)$_8$(OAc)$_2$·2H$_2$O, by anion exchange. The intercalated oxalate species was reacted with potassium permanganate in such a way that the layered manganese oxide formed was within the interlayer region of the anionic clay resulting in a layered composite in which the negative charges on the birnessite type manganese oxide layers compensate the positive charges on the anionic clay layers. Birnessite to anionic clay ratio could be varied by varying the reaction time or the amount of potassium permanganate used.
3.5 Introduction

Composites of layered solids have been synthesized so that the hybrid material formed would have varying degrees of properties of the starting materials or could give rise to new properties. A number of anionic clay based composites have been studied in the past. For example, oleate–layered double hydroxide (LDH) composites prepared by reconstruction method were found to be much more acid resistant than the parent LDH, making the composite a good candidate for oral drug delivery [1]. A composite of SnO$_2$ and MgAl-LDH showed enhanced photocatalytic activity towards photolysis of methylene blue dye, than either SnO$_2$ or the MgAl-LDH individually [2]. Composites of anionic clay and metal complexes have been made to obtain materials that can be active in heterogeneous catalysis [3-5]. Composites of anionic clay and nanoparticles have been made to modify the optical properties of the nanoparticles [6]. Composites of two anionic clays have been made by various methods to enhance the thermal stability [7,8] of the anionic clay and to increase the stability of the anionic clays in alkaline media so that they can be used in alkaline battery application [9].

Hydroxy double salts (HDSs), which can be represented by the general formula $[M_3^{O\square\cdot O}Zn^T_{2}(OH)_{8}]^{2+}(A^{n-})_{2/n}\times H_2O$, where M is a divalent metal ion, $A^{n-}$ is an anion with valency ‘n’, O and T refer to octahedral and tetrahedral sites and $\square$ refers to octahedral vacancies, belong to a class of anionic clays [10]. The structure of HDSs can be regarded as a variation of the hypothetical C6 or CdI$_2$-type M(OH)$_2$ structure [11]. In HDS one quarter of the divalent metal atoms (M) are removed from the octahedral sheet of the M(OH)$_2$ type structure, so that each filled metal octahedron has common edges with two unoccupied and four other occupied octahedra. Tetrahedrally coordinated zinc atoms are located above and below the unoccupied octahedra. Three corners of the tetrahedron are occupied by hydroxide ions belonging to the sheet described above and the fourth corner by a water molecule. The resulting complex sheet is positively charged and has the composition $[M_3^{O\square\cdot O}(OH)_6Zn^T(H_2O)_2]^{2+}$. Anions get incorporated in the interlayer region to compensate the positive charge on the layers.

Oxides of manganese have been synthesized and used as catalysts [12], battery materials [13], supercapacitors [14] and sensors [15]. Composites of MnO$_2$ have been
made, with nickel oxyhydroxide and used as electrode materials for alkaline secondary cells [16], manganese containing LDH and manganese species intercalated LDH have been used as catalysts for total combustion of toluene [17]. Layered composite comprising of negatively charged MnO$_2$ layers and positively charged Mg–Al LDH layers has been made by the layer-by-layer (LBL) technique, to prepare functional thin films which have potential applications in optical and electrochemical devices [18].

Various intracrystalline reactions of anionic clays have been studied in the past. Recently we reported the oxidation of thiosulfate ions by iodine to tetrathionate ions within the ZnAl-LDH [19] and nitrite to nitrate using hydrogen peroxide within the interlayers of MgAl-LDH [20]. L-cysteine could be converted to L-cystine using bromine or hydrogen peroxide within the interlayers of MgAl-LDH [21]. It has also been shown that the interlayer region could be used for organic synthesis [21-23]. One could also use interlayer reactions for composite preparation. Preparation of metal oxides in the interlayer region by redox reactions was studied by Josanlet et al [24]. They subjected permanganate intercalated Mg-Al LDH to reduction using glucose, ethanol or ascorbic acid. The reduction products had a reduced concentration of Mn species and had a mixture of manganese oxides which the authors suggest are intercalated in the LDH.

In this work, we revisit the interlayer reaction of permanganate with a reducing agent in an anionic clay with the aim of forming negatively charged birnessite type manganese oxide layers in the interlayer region of the anionic clay. Reversing the protocol of Josanlet et al [24] we treated oxalate ion intercalated anionic clay with potassium permanganate solution at room temperature and at 90 ºC. The resulting redox reaction between intercalated oxalate ions and permanganate ion seems to occur within the interlayer region, resulting in a composite of anionic clay and birnessite-type manganese oxide.

3.6 Experimental

3.6.1 Synthesis of Ni-Zn hydroxyacetate, Ni$_3$Zn$_2$(OH)$_8$(OAc)$_2$·2H$_2$O

Ni-Zn hydroxyacetate was prepared by the acetate hydrolysis route reported by Marioka et.al [25]. To 200 ml of an aqueous solution containing 60.35 mmol (10.664 g) of nickel acetate tetrahydrate 28.5 mmol (2.32 g) of zinc oxide was added
with vigorous stirring. The resultant slurry was heated at 65 °C in an air oven for 48 h with occasional stirring. The green solid obtained was washed repeatedly by centrifugation using copious amounts of decarbonated water and dried at 65 °C in an air oven to constant weight.

3.6.2 Preparation of oxalate intercalated Ni-Zn hydroxysalt

About 1 g of the Ni-Zn hydroxyacetate obtained in the previous step was added to 50 ml of an aqueous solution containing 10.06 mmol (1.3465 g) of sodium oxalate. The resultant mixture was stirred for 3 days at room temperature. The product obtained was separated by centrifugation, washed free of excess ions using decarbonated water and dried in an air oven at 65 °C to constant weight.

3.6.3 Reaction of the oxalate intercalated Ni-Zn hydroxysalt with permanganate

The oxalate intercalated Ni-Zn hydroxysalt obtained in the previous step was treated with 3, 4, 5 and 7 times the stoichiometric excess of potassium permanganate and the solution stirred for 3 days at room temperature. Reaction was also carried out at 90 °C for two days with oxalate intercalated Ni-Zn hydroxysalt and 7 times stoichiometric excess of potassium permanganate; aliquots of the reaction mixture were withdrawn periodically to monitor the consumption of permanganate ions.

A control reaction was carried out between di-sodium oxalate and potassium permanganate in basic conditions at 90 °C for two days by reacting 25 ml of an aqueous solution containing 420 mg of di-sodium oxalate with 25 ml of an aqueous solution containing 660 mg of potassium permanganate and 150 mg of sodium hydroxide.

The product obtained on treating the hydroxysalt with 7 times excess of potassium permanganate was soaked in 1M acetic acid for 4 days to leach out the anionic clay component and the undissolved material was separated by centrifugation, washed with water and dried at 65 °C overnight.

3.6.4 Characterization

Powder X-ray diffraction (PXRD) measurements and infrared (IR) spectroscopy of samples were done as described in section 2.2.4. A 300 kV high-resolution field-emission transmission electron microscope (TEM, JEOL, JEM-3000F) equipped with an energy-dispersive X-ray analyzer (EDX), and a high-angle
annular dark-field scanning transmission electron microscopy detector (HAADF-STEM) (JEOL JEM-2100FEF) was used for recording the TEM images. Ni, Zn and Mn contents of the composites were obtained by ion chromatography (IC) using a Metrohm 861 Advanced Compact Ion Chromatograph with Metrosep C2 250 cation column and a conductivity detector. The solids were dissolved in acetic acid and the solutions diluted suitably for IC analysis. The average oxidation states of Mn in the samples were estimated by treating the samples with KI and H₂SO₄ and titrating the liberated iodine with sodium thiosulphate.

### 3.7 Results and Discussion

PXRD pattern of oxalate intercalated Ni-Zn hydroxysalt is compared with that of the parent Ni-Zn hydroxyacetate in Figure 3.4. The pattern of the hydroxyacetate (Figure 3.4a) matches with what has been reported earlier in the literature [25]. The basal spacing is 12.9 Å and the saw tooth shaped features starting at around \(2\theta = 33^\circ\) and 60° are due to the 2D (10) and (11) reflections indicating that the sample has turbostratic disorder [26]. The basal spacing of the oxalate exchanged sample was found to be 10.4 Å, which was higher than 9.9 Å, that has been reported for oxalate intercalated LDHs [27,28]. Here the interlayer oxalate ions can be assumed to be oriented perpendicular to the layer [29].

![Figure 3.4 PXRD patterns of Ni-Zn hydroxyacetate (a) and oxalate intercalated Ni-Zn hydroxysalt (b).](image-url)

Figure 3.4 PXRD patterns of Ni-Zn hydroxyacetate (a) and oxalate intercalated Ni-Zn hydroxysalt (b).
In Figure 3.5 the IR spectra of the parent Ni-Zn hydroxyacetate is compared with that of oxalate intercalated hydroxysalt. The carboxylate absorptions at 1338, 1408 and 1575 cm\(^{-1}\) of the intercalated acetate of the parent solid change to 1323, 1435, 1633 and 780 cm\(^{-1}\) for the oxalate intercalated Ni-Zn hydroxysalt confirming intercalation of oxalate ions [30].

![Figure 3.5 IR spectra of Ni-Zn hydroxyacetate (a) and oxalate intercalated Ni-Zn hydroxysalt (b).](image)

In Figure 3.6 the PXRD patterns of the oxalate intercalated hydroxysalt and the products obtained on reacting this solid with various amounts of KMnO\(_4\) are shown. The patterns of the products (Figure 3.6 b-d) are similar to that of the precursor (Figure 3.6a) except that there is a steady decrease in the observed basal spacing as the amount of KMnO\(_4\) reacted is increased, from the starting material (10.4 Å) to the product obtained on treatment with the highest amount of KMnO\(_4\) (9.4 Å). In the patterns of the products reflections due to manganese oxides are not seen. This is possibly due to the fact that individual birnessite-type layers are present in the interlayer of the anionic clay. The PXRD pattern of the manganese oxide obtained by leaching out the anionic clay component of the composite obtained by the reaction of 7 times excess of permanganate with the anionic clay at room temperature (Figure
3.6g) shows the high angle reflections corresponding to the control birnessite (Figure 3.6f) but the basal reflection is absent. Possibly the slow dissolution of the anionic clay component from the composite does not allow stacking of the birnessite-type layers.

**Figure 3.6** PXRD patterns of oxalate intercalated Ni-Zn hydroxysalt (a); the products obtained on reacting oxalate intercalated Ni-Zn hydroxysalt with three (b), five (c) and seven (d) times excess of KMnO$_4$ at RT; product obtained by reacting oxalate intercalated Ni-Zn hydroxysalt with seven times excess of KMnO$_4$ at 90 °C (e) and the product of reaction of disodium oxalate with seven times excess of KMnO$_4$ in basic conditions at 90 °C (f). The PXRD pattern of the manganese oxide component obtained by acid leaching of the composite formed in the reaction between oxalate intercalated Ni-Zn hydroxysalt with seven times excess of KMnO$_4$ at RT is given in (g).
In Figure 3.7 the IR spectra of the oxalate intercalated sample and the products obtained on reacting this solid with various amounts of KMnO₄ are shown. There is a decrease in the intensities of the absorptions due to oxalate in the spectra of the products (Figure 3.7 b-d). This can be seen clearly from the trend in the intensity of the peak appearing at 780 cm⁻¹ which is distinctly due to the oxalate ion. It can also be seen that even in the case of the product obtained on reaction with 7 times excess of potassium permanganate at room temperature a small amount of oxalate is still present.

![IR spectra](image)

**Figure 3.7** IR spectra of oxalate intercalated Ni-Zn hydroxysalt (a); the products obtained on reacting oxalate intercalated Ni-Zn hydroxysalt with three (b), five (c) and seven (d) times excess of KMnO₄ at RT; product obtained by reacting oxalate intercalated Ni-Zn hydroxysalt with seven times excess of KMnO₄ at 90 °C (e) and the product of reaction of disodium oxalate with seven times excess of KMnO₄ in basic conditions at 90 °C (f).

In order to see if complete removal of oxalate and hence better yield of birnessite is possible when the reaction is carried out at higher temperature the oxalate
intercalated hydroxysalt was reacted with 7 times excess of permanganate at 90 °C. A control manganese oxide sample was prepared by reacting disodium oxalate with permanganate at 90 °C under alkaline condition. The PXRD pattern of the control sample (Figure 3.6f) matches with that of K-birnessite with a basal spacing of 7.2 Å [31, 32]. The product obtained in high temperature reaction does not have the basal reflections of the anionic clay as well as birnessite but have all the high angle reflections due to anionic clay and birnessite layers (Figure 3.6e). Possibly both the layered solids are extensively exfoliated in the composite.

When the reaction was carried out at 90 °C the oxalate ions were completely consumed as indicated by the IR spectrum of the product (Figure 3.7e) in which the oxalate absorptions are totally absent. A broad peak at 1033 cm\(^{-1}\) with a shoulder at ~1150 cm\(^{-1}\) that can be attributed to Mn\(^{3+}\)-OH vibrations is seen in the control birnessite (Figure 3.7f). While the peak at 1150 cm\(^{-1}\) matches exactly with what has been observed for birnessite [32] the broad peak has been red-shifted by ~40 cm\(^{-1}\) possibly due to disorder. These two peaks are observed in the case of all the composites (Figure 3.7b-d) with intensities increasing with the amount of permanganate used. There are peaks characteristic of birnessite at 520 and 470 cm\(^{-1}\) [32] in both the control (Figure 3.7f) and the product obtained on reacting the anionic clay with permanganate ions at 90 °C (Figure 3.7e).

PXRD and IR studies do not clearly indicate the nature of the manganese oxide component in the composites. In order to ascertain that the oxide is birnessite type we estimated the average oxidation states of Mn in some selected composites. These values are presented in Table 3.2. In all the cases the average oxidation state of Mn was above 3.6 indicating that the manganese oxide component in the composites is birnessite phase.

In order to understand how the interlayer reaction proceeded, aliquots of the reaction mixture at various time intervals were withdrawn and analyzed by PXRD and IR. Figure 3.8 shows the PXRD patterns of the products obtained when Ni-Zn hydroxoyxalate was reacted with seven times excess of KMnO\(_4\) at 90 °C for different durations. It can be seen from the PXRD patterns that there is a steady decrease in intensity of the first peak at \(2\theta = 8.9^\circ\) which corresponds to the oxalate intercalated Ni-Zn hydroxysalt with reaction time as the interlayer reaction between intercalated oxalate and permanganate ion proceeds. Carbon dioxide formed during the reaction
escapes from the interlayer rather than getting intercalated within the interlayer of Ni-Zn hydroxysalt as seen from the absence of carbonate peaks in the IR spectra of the products (Figure 3.7). This leads us to assume that in the resulting disordered composite the positive charge on the anionic clay layers is compensated by the negatively charged manganese oxide layers formed within the interlayer of the anionic clay. With the reaction time the amount of birnessite deposited in the interlayer of the anionic clay increases.

Table 3.2 Manganese oxide content in the composites formed under different reaction conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction temperature (°C)</th>
<th>[KMnO₄]/[oxalate]</th>
<th>Reaction time (h)</th>
<th>[anionic clay]/[birnessite]</th>
<th>Average oxidation state of Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>2.0</td>
<td>48</td>
<td>6.1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>2.7</td>
<td>48</td>
<td>5.0</td>
<td>3.65±0.01</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>3.3</td>
<td>48</td>
<td>4.5</td>
<td>3.60±0.05</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>4.7</td>
<td>48</td>
<td>4.3</td>
<td>3.70±0.02</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td>4.7</td>
<td>2</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>4.7</td>
<td>3</td>
<td>2.1</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>90</td>
<td>4.7</td>
<td>48</td>
<td>1.5</td>
<td>3.63±0.01</td>
</tr>
</tbody>
</table>

*The anionic clay component of the composite is formulated as [Ni₀.₇₅Zn₀.₃(OH)₂]₀.₂₅⁺ and the birnessite component is formulated as [MnO₂]⁻.₃. Thus [anionic clay]/[birnessite] = 0.75[Ni]/[Mn].*
From the PXRD and IR data it is clear that the anionic clay to birnessite ratio in the composites is controlled by the amount of KMnO₄ used, reaction temperature and time. These ratios obtained by estimating Ni and Mn contents by IC in the composites prepared under different reaction conditions are listed in Table 3.2. For the purpose of normalizing layer charges to charge per octahedron the anionic clay layer is formulated as [Ni₀.75Zn₀.5(OH)₂]₀.₂₅⁺ and the birnessite type MnO₂ layer is formulated as [MnO₂]⁻₀.₃ [29]. Thus the [anionic clay]/[birnessite] ratio listed in Table 3.2 is 0.75[Ni]/[Mn]. As the charge per Ni(OH)₆ octahedron of the anionic clay layer is ~0.25+ and the charge per MnO₆ octahedron of the birnessite layer is ~0.3—the best scenario where the layers of the two layered solids neutralize the charges on each other the [anionic clay]/[birnessite] ratio should be ~1.2.

From Table 3.2 it is clear that the birnessite load in the composite increases with increase in the amount of KMnO₄ used, reaction temperature and duration of the reaction with the maximum load, matching with what is expected when the two types of layers compensate for each other’s charges, achieved in the reaction in which the anionic clay was treated with 7 times excess of KMnO₄ at 90 °C for 48 h.

Figure 3.8 PXRD patterns of oxalate intercalated Ni-Zn hydroxysalt reacted with seven time’s excess of KMnO₄ at various reaction times (a) 2 h, (b) 3 h and (c) 48 h.
Figure 3.9 Bright field TEM images of oxalate intercalated Ni-Zn hydroxysalt reacted with seven time’s excess of KMnO₄ at 90 °C for 48 h: low (a) and high (b) magnification images. The HAADF STEM image of the sample (c) along with the spatially resolved Mn (d), Ni (e) and Zn (f) elemental maps.

The bright field TEM images of oxalate intercalated Ni-Zn hydroxysalt reacted with seven times excess of KMnO₄ at 90 °C for 48 h (Figure 3.9 a and b) show the presence of thin transparent wrinkled layers. The absence of particles
suggests the presence of layers of birnessite in the sample along with the anionic clay layers. In order to investigate the distribution of birnessite layers in Ni-Zn hydroxide matrix EDS elemental mapping was done. The HAADF STEM image (Figure 3.9c) of oxalate intercalated Ni-Zn hydroxysalt reacted with seven times excess of KMnO₄ at room temperature and the corresponding elemental mapping of Mn, Ni and Zn (Figure 3.9 d, e and f) confirms a uniform distribution of elements further corroborating the formation of layer by layer composite.

3.8 Conclusions

Composites made of alternating negatively charged manganese oxide and positively charged Ni-Zn hydroxide layers have been synthesized via an interlayer reaction in the gallery of Ni-Zn hydroxyoxalate. The advantage of this reaction is that the birnessite layers formed coexist with the anionic clay layers for charge neutralization leading to good mixing of the two components of the composite. Another feature of this method is that the birnessite to anionic clay ratio can be controlled by altering either the amount of KMnO₄ used or the reaction time.

References:


