CHAPTER-1

Introduction
Chapter-1
1. Introduction of Layered double Hydroxides
1.1. Historical background

The first mineral with features distinct to Layered Double Hydroxides (LDH) found in nature was Hydrotalcite. This was discovered in 1842 at Sweden [1-3]. This hydrotalcite was white in colour and could be easily crushed into powder. Naturally occurring hydrotalcites are foliated, at times a fibrous mass or even contorted plates. Chemically these natural hydrotalcites are hydroxycarbonates of Magnesium and Aluminium. Another LDH mineral isostructural to hydrotalcite was also discovered around this time. This mineral was a hydroxycarbonate of Magnesium and Iron and had a likeness to gold when heated. Hence this mineral was named PYROAURITE [4].

The differing valencies of the metal ions and the positive charge developed in the two dimensional layers necessitates the presence of anions in the interlayer space to maintain charge neutrality. Thus these materials are called “Anionic Clays” and “Layered Double Hydroxides”.

In 1915 E. Manasse, Professor of Mineralogy at the University of Florence, Italy was the first to publish the exact formula of hydrotalcite as $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3.4\text{H}_2\text{O}]$. He also published a list of other isomorphous materials and by doing this he was also the first to recognise that carbonate ions were essential for this type of structure. At this time it was thought these materials are mixed hydroxides and this view persisted until much later when X-Ray investigations disproved this.

In 1930 Aminoff and Broome with their extensive X-Ray investigations established that hydrotalcite crystallises in two polytypes. One having the Rhombohedral Symmetry and the other having Hexagonal Symmetry. The polytype of Hydrotalcite having hexagonal symmetry was named “MANASSEITE” in honour of Prof. Manasse [5].

The complex and unusual composition of these minerals and the lack of adequate crystallographic data led to lots of confusion and uncertainties regarding their real constitution. In 1941, the publication of “Constitution and Polymorphism of the
Pyroaurite and Sjogrenite groups” by Frondel established the real constitutions and the interrelations of these minerals. Subsequently in 1942, Feitnecht came out with the first study on synthesis, stability, solubility and structure determinations of hydrotalcite. He synthesised a large number of compounds with a hydrotalcite type structure. He named these compound as “DOPPELSCHICHTSTrukturen” meaning double sheet structures. His idea was that these compounds are basically made up of a layer of hydroxide of one cation and intercalated with a layer of the second cation. The X-Ray investigations on monocrystals of Sjogrenite and Pyroaurite in late 1960’s by Allmann and Taylor showed that both the cations are located in the same layer and only water and carbonate ions located in the interlayer [6]. The initial work on using these materials started as early as 1924 when Zelinski and Kommarewsky recognised that co-precipitated Ni, Al catalysts presented good activity in hydrogenation reactions. Molstad and Dodge in 1935 recognised the role of Zn, Cr mixed oxides in the synthesis of methanol. Still later Merlin et al in 1954, Milligan and Richardson in 1955 and Langenbeck in 1956 while working on catalysts prepared by precipitation found that a compound forms during the co-precipitation stage. The composition of thus formed compound was later found to be optimal one for the formation of hydrotalcite like compounds [7-10].

These observations implying the commercial importance of these materials resulted in the first patent on Layered Double Hydroxides (LDH) being obtained by F.J.Brocker and L.Kainer in 1970. In 1971 [11] Miyata et al while writing on basic catalysts referred to the hydrotalcite like compounds and the same author later in 1977 noted that a Manasseite like compound could be made use of in hydrogenation catalysis even though this mineral occurs only naturally.

As the importance of LDH’s in catalysis got recognised, sustained interest and research started growing from the 1970’s and there is a vast volume of literature from the 70’s to till date. Excellent reviews and the references given therein give the latest trends and the status of these materials. Some references are shown in table.1.1.1.
Table 1.1.1 Composition of Layered Double Hydroxides

<table>
<thead>
<tr>
<th>M²⁺</th>
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<th>Chemical composition</th>
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<td>OH</td>
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<td>Cr</td>
<td>n-C₆H₄₋₂SO₄</td>
<td>[Zn₆₆₆₆Cr₃₃₃₃(OH)₂][n-C₆H₄₋₂SO₄]₀.₆₆₆₆H₂O</td>
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</table>
1.1.1. Nomenclature

A LDH phase is mainly described by its chemical formula, the basal spacing of the layers and the symmetry of the stacking sequences [12], e.g. \([\text{M}^{\text{II}}_{1-x} \text{M}^{\text{III}}_x (\text{OH}_2)]^{m-} A^{m-x/3} n\text{H}_2\text{O}\).

- The qualitative chemical data between brackets, with divalent-trivalent anion symbols, in this order and separated by hyphens.
- On the left side, quantitative chemical data: trivalent metal ratio X and hydration state n based on a M(OH)$_2$ formula.
- On the right side, structural data: basal spacing ‘d’ of the layers in Å and their stacking sequence ss(3R, 2H, …...)

1.2 Formation of Layered Double Hydroxides

For many applications many methods allow the preparation of materials with tailored physical and chemical properties [5-7]. For a catalytic system, whose activity results from a cooperative effect between the active phase and mixed oxides support, a precursor containing all the components homogeneously distributed in the same phase may be a suitable choice. LDH are such types of precursors. The metal cations are homogeneously distributed inside the brucite sheets; calcination and reduction yield well-dispersed, small and stable metal particles on mixed oxides support [8]. As an example, the reduction of Pd-containing Mg–Al LDH leads to Pd/MgAl oxide bifunctional catalysts. Another way to introduce Pd in the LDH structure is anion exchange with the \([\text{PdCl}_2(\text{OH})_2]\) complex [9]. These two methods appear quite different in terms of Pd loading or structural changes in the reduction step. Table 1.2 shows the large number of elements that can be incorporated into the LDH structure. The preparation, properties, and applications of LDH were well documented [10-19]. Here we give a general overview of typical methods of synthesis.
1.2.1. Co precipitation

By the addition of a base to solutions containing a mixture of M(II) and M(III) LDH are readily prepared. In this variable-pH coprecipitation method, M(III) hydroxides or hydrous oxides are initially formed, and further addition of base results in coprecipitation or conversion into LDH. [20] reported a well-defined transition step between constant-pH precipitation of the M(III) hydroxides (M = Al, Fe) and the mixed [M(II)–M(III)] precipitates where M(II) = Mg2+, Zn2+, Co2+, Ni2+, Mn2+. The conversion of M(OH)3 (or MO(OH)) to LDH proceeds by a dissolution/precipitation mechanism. In [M(II)–Cr3+] systems (M(II) = Zn2+, Co2+, and Ni2+), the absence of pH transition is indicative of the preferential precipitation of LDH over Cr(OH)3 [21]. To obtain LDH with high chemical homogeneity, coprecipitation at constant pH is recommended. It allows the preparation of a great number of LDH with CO32−, Cl−, or NO3− anions as precursors for subsequent reactions (anion-exchange reactions, thermal decomposition, noble metal impregnations, etc.). The pH is kept constant during the reaction by the simultaneous addition of a base solution (NaOH, KOH, and NH4OH) and a mixed metal salt solution:

### Table 1.2 Chemical compositions of LDH and optimal pH of coprecipitations

<table>
<thead>
<tr>
<th>MII–MIII–X</th>
<th>pHform</th>
<th>MII/MIII (R) range</th>
<th>MII–MIII–X</th>
<th>pH</th>
<th>MII/MIII (R) range</th>
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<td>[Zn-Al-Cl]</td>
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<td>1.0≤R≤5.0</td>
<td>[Zn-Cr-Cl]</td>
<td>4.5</td>
<td>R≈2.0</td>
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<tr>
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<td>10.0</td>
<td>1.0≤R≤3.0</td>
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<td>10.0</td>
<td>2.0≤R≤3.0</td>
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<td>[Ni-Cr-Cl]</td>
<td>11.5</td>
<td>1.0≤R≤3.0</td>
<td>[Mg-Fe-CO3]</td>
<td>—</td>
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(1-x)M^{II}X_{2/q}^{q-}+xM^{III}X_{3/q}^{q-}+2\text{NaOH}+\text{nH}_2\text{O} \rightarrow M_{1-x}^{II}M_x^{III}(\text{OH})_2X_{x/q}^{q-}\cdot\text{nH}_2\text{O}+2\text{NaX}_{1/q}^{q-}

[22] demonstrated that materials prepared by this method show interesting properties for technological applications, including high crystallinity, small particle size, high specific surface area, and high average pore diameter. The pH of coprecipitation has a crucial effect on the chemical, structural, and textural properties of the phases.

1.2.1.1 Mechanism of co-precipitation

The mechanism of co-precipitation is ideally based on the condensation of hexa-aquo complexes in solution in order to build the brucite-like layers with a distribution of both metallic cations and with solvated interlamellar anions. Observation of the precipitates and X-ray diffraction characterization show that the co-formation of the main layers and interlamellar domains takes place at a very early stage of the process without clear delaminated state of the layers.

1.2.1.2 Origin of Interlamellar anions

From the metallic salts solutions the metal cations in the obtained LDH phase are obviously issued but the origin of interlamellar anions has to be discussed. If these anions are the counter anions of the metallic salts they come from the same solution. If the preparation is performed at very high pH values, the interlamellar anion can be the hydroxyl anion coming from the alkaline solution. When the alkaline solution is a sodium or potassium carbonate solution, the intercalated anion is the carbonate because of its high selectivity for LDHs interlamellar domains. Moreover, when the preparation is performed at relatively high pHs, one have to work under CO$_2$-free conditions in order to avoid carbonate contamination. Another way to intercalate a given anion is to prepare a solution of this anion in the reactor prior to the beginning of the co-precipitation.

1.2.2 The Urea method

Supersaturation of the precipitating agent (OH$^-$) is reached rapidly and maintained during the standard coprecipitation. This leads to the continuous nucleation of mixed hydroxides simultaneous with the growing and Oswald ageing (aggregation) of the particles, resulting in a wide particle size distribution. By using a base retardant as
precipitating agent, the nucleation step can be separated from particle growth, and ageing is prevented from the beginning. Coprecipitation using urea as the base was developed to prepare monodisperse particles. Urea is a very weak Bronsted base (pKb = 13.8), is highly soluble in water. According to [23], hydrolysis of urea proceeds in two steps: (i) formation of ammonium cyanate (NH$_4$CNO) as the rate-determining step; and (ii) fast hydrolysis of the cyanate into ammonium carbonate:

$$\text{CO(NH}_2\text{)}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{CO}_3^{2-}$$

The hydrolysis rate of urea can be controlled by temperature. The rate constant increases about 200 times when the temperature is increased from 60°C to 100 °C. Large platelets of well-crystallized hydrotalcite with hexagonal shape are obtained by this method [24-26]. The reaction temperature and the concentration of reactants control the particle size. Monodisperse particles between 1 and 5 mm, and up to 20 mm are obtained. M$_3^{2+}$Al(OH)$_8$(CO$_3$)$_{0.5}$·nH$_2$O (M$^{2+}$ = Mg$^{2+}$, Ni$^{2+}$, Zn$^{2+}$) LDH were synthesized by [27].

### 1.2.3 Induced Hydrolysis

When oxides such as ZnO, NiO, and CuO are contacted dropwise with acidic solutions of trivalent metal salts such as AlCl$_3$ or CrCl$_3$, the oxides are progressively dissolved, and LDH are precipitated provided the pH is buffered by the oxide and/or hydroxide suspension [12]:

$$\text{M}^{II}\text{O} + x\text{M}^{III}\text{X}_{3/q}^{q-} + (n+1)\text{H}_2\text{O} \rightarrow M_{1-x}^{II}M_{x}^{III}(\text{OH})_2X_{x/q}^{q-} \cdot n\text{H}_2\text{O} + x\text{M}^{II}X_{2/q}^{q-}$$

This synthesis was first used to prepare [Zn–Cr–Cl] LDH but was then extended to other systems, in particular [Zn–Cr–Cl], [Zn–Cr–NO$_3$], [Zn–Al–Cl], and [Zn–Al–NO$_3$] [28]. More recently, a new [Zn–Cr] LDH, [Zn$_7$Cr$_4$(OH)$_{22}$(CO$_3$)$_2$ .5H$_2$O, was prepared by reaction of a perchlorate solution of the hydrolytic dimer [(H$_2$O)$_4$Cr(μ- OH)$_2$Cr(H$_2$O)$_4$]$^{4+}$ with ZnO and subsequent anion exchange with Na$_2$CO$_3$ [29]. Induced hydrolysis is not limited to reactions between di- and trivalent cations but can involve divalent–divalent, divalent–tetravalent and trivalent–trivalent species [30].
1.2.4 Reconstruction

The reconstruction of the original LDH structure by hydration of the calcined LDH was described in [31]. In the first step the LDH containing a volatile anion is calcined into a mixture of oxides and then to rehydrated in an aqueous solution containing the anion to be intercalated. The method was used for the preparation of several LDH [32] and the intercalation of several oxoanions (CrO$_4^{2-}$, HPO$_4^{2-}$, HVO$_4^{2-}$, SiO$_3^{2-}$, HGaO$_3^{2-}$ and SO$_4^{2-}$) into [Mg–Al]. The hydrotalcite structure is reconstructed at controlled water vapour pressure by 24 h rehydration, provided that the thermal treatment of the precursors does not exceed 600°C [33]. Samples calcined at 750°C recover their original structure if they are equilibrated for 3 days. Tetrahedral Al generated by the decomposition of the parent mineral is converted again into octahedral Al in the brucite layer. Kinetic data [34], using the Avrami–Erofe’ev nucleation-growth model, are consistent with dissolution of the mixed oxide and crystallization of the LDH from solution. Using SEM and XRD techniques [35] confirmed the dissolution/reconstruction process. Repeated calcination/hydration cycles with hydrotalcite decrease the content of interlayer carbonate anions and increasing extraction of Al$^{3+}$ from the brucite layers. There is also progressive segregation of the MgAl$_2$O$_4$ spinel phase the formation of which is unusual at these soft conditions of calcination [36]. Nor can the reconstruction method be used for all MII–MIII combinations. Reconstruction of Fe$^{3+}$ containing hydrotalcites is limited by the formation of MgFe$_2$O$_4$ spinel, which appears even at low content of Fe$^{3+}$. In the case of [Mg–Al–Y], reconstruction leads to segregation of Y$^{3+}$ containing oxides and [Mg–Al] LDH [37]. In the case of [Zn–Al] LDH, restoration of the hydrotalcite-like structure is independent of the Zn/Al ratios for samples calcined between 300 and 400°C; however, a second phase, Al hydroxide or Zn oxide, is detected. At temperatures above 600°C, the formation of the spinel ZnAl$_2$O$_4$ prevents any reconstruction. The rehydrated phases have Zn/Al ratios close to 2, irrespective of the composition of the starting material [38]. This method is suitable for the preparation of hybrid LDH with large organic anions such as dyes. For instance, phenolphthalein was intercalated into Zn–Al LDH [39].
1.2.5 Sol gel technique

The Sol-Gel process was first described [40] in the preparation of Mg–Al type samples. The sol-gel hydrotalcites show thermal stability up to 550°C [41]. However, LDH samples prepared by coprecipitation are more crystalline than those prepared by the sol-gel method. The marked increase in specific surface area is ascribed to the increase in mesopore volume. The textural properties of the calcined samples are not appreciably influenced by the method of synthesis [42]. As an example, Mg/M(III) (M = Al, Ga, In) LDH were prepared from magnesium ethoxide and the acetylaceonates of the trivalent metals. However, the method usually described is not exactly a sol-gel approach, since the alkoxide is first dissolved in an alcohol/acid mixed solution (EtOH/HCl, 35% in aqueous solution). A solution containing acetone and the acetylacetonate of M(III) is then added, and the pH is adjusted to 10 with aqueous ammonia [43]. Similar conditions were used for the preparation of Mg/Al (hydrotalcite) and Ni/Al (takovite). The nature of the acid used during the first step, either HNO₃ or HCl, is of great importance [44]. With the sol-gel method samples with larger Mg²⁺/Al³⁺ ratios (2.47–4.29) and up to 10–25% higher specific surface areas are obtained as compared with samples prepared by classical coprecipitation [42]. Sol-gel materials are also more basic due to different textural and morphological features [44]. For NiAl using Ni acetylacetonate and aluminium isopropylate, the oxidic forms (NiO–Al₂O₃) with a high reducibility were obtained [45]. The sol-gel approach was extended to the preparation of Mg/Cr and Ni/Cr LDH. In the latter case, some organic groups are retained on the surface [46].

1.2.6 Hydrothermal, Microwave and Ultrasound treatments

In order to control structural and textural properties different in situ or post-synthesis treatments were applied to the ‘as-prepared’ samples. Microwaves were used during synthesis in order to accelerate both the growing and ageing steps. Short microwave irradiation results in a well-crystallized material compared to conventional coprecipitation [47, 48]. The extent of enhancement in crystallinity depends on the nature of the trivalent metal ion [47]. An increase of the specific surface area from 40 up to 240m²/g is observed for synthetic hydrotalcite coprecipitated under 360W
microwave irradiation [49]. In general, the surface area and porosity of the synthetic materials are increased with the duration of microwave exposure. For Co\textsuperscript{6+}Co\textsuperscript{3+}(OH)\textsubscript{16}(NO\textsubscript{3})\textsubscript{2}. nH\textsubscript{2}O microwave-treated samples exhibit higher thermal stability, and formation of the spinel Co\textsubscript{3}O\textsubscript{4} is delayed up to 200°C [50]. Charge distribution, nature of the hydrotalcite network, and the presence of water molecules in the interlayer space lead to effective absorption of microwaves, favouring long-range ordering. Crystallinity of the phases can also be improved by ultrasound irradiation. Larger LDH crystallites are observed while adsorption capacities are enhanced [51]. Hydrothermal treatment is also used to improve the crystallinity of the compounds or to increase the anion-exchange rate of low-affinity anions such as alkyl carboxylates. Hydrothermal treatment has a strong effect on the chemical composition (Mg\textsuperscript{2+}/Al\textsuperscript{3+}) of synthetic hydrotalcite [52].

1.3 Structure of Layered Double Hydroxides

1.3.1 Properties

Anionic clays, natural and synthetic layered mixed hydroxides containing exchangeable anions, are less well known and diffuse in nature than cationic clays. Hydrotalcite belongs to the large class of anionic clays, and will be taken as a reference name for many other isomorphous and polytype compounds. The anionic clays based on hydrotalcite-like compounds have found many practical applications. The hydrotalcite have been used as such or (mainly) after calcinations. The most interesting properties of the oxides obtained by calcinations are the following:

1. Basic Surface area
2. Basic properties
3. Formation of homogeneous mixtures of oxides with very small crystal size, stable to thermal treatments, which by reduction form small and thermally stable metal crystallites.
4. “Memory effect”, which allows the reconstruction, under mild conditions, of the original hydrotalcite structure when contacting the product of the thermal treatment with water solutions containing various anions.
Properties 1, 2, 3 have found application in the field of heterogeneous catalysis (hydrogenation, reforming, basic catalyst and as support). Properties 1, 2, 4 are utilized in applications such as scavenging of chlorine ions and the purification of water containing waste anions (organic and inorganic).

### 1.3.2 Trivalent metal ratio

Most of LDH system accommodate a relatively wide range of trivalent ratios but it is not reported that it could vary from 0 to 1 without main structural changes, while larger ranges are sometimes given, the most reliable limits, are based for example on a clear evolution of lattice parameters and correspond approximately to $0.2 \leq x \leq 0.4$. Some authors describe systematically LDHs by the divalent versus trivalent ratio $R = M^{II}/M^{III}$ generally with an integer value (for eg $R=2$, $R=3$), corresponding to the relative proportions of metallic cations in the reactions during the preparations. (Fig. 1.3.2.)

![Schematic diagram of Layered Double Hydroxides](image)

Figure 1.3.2 Schematic diagram of Layered Double Hydroxides

The upper limit of trivalent ratio is generally attributed to electrostatic repulsion between neighbouring trivalent metals in the layers, which is unavoidable if $x>1/3$, and also to the repulsion between the charge balancing anionic interlamellar species. The
lower limit could correspond to a too high main distance between these interlamellar anions leading to a collapse of the interlamellar domains. The structure of the $\alpha$-variety of divalent metals hydroxides with neutral $\text{M(OH)}_2$ sheets and interlamellar domains containing salts or basic salts and water molecules seems to be close to a LDH structure with $X=0$, but, as far as we know, compared to regular LDH structure there is a solution of continuity in the values of $X$.

The metallic cations are arranged in the layers on an hexagonal framework of parameter $a_0$. For particular values of $X$, superstructures can be expected by ordering of divalent and trivalent cations. In hexagonal symmetry, the solutions are given by the relation $1/X = (a/a_0)^2$, where ‘$a$’ is any metal-metal distance in the hexagonal framework. The solutions are $X=1/3$, $1/4$, $1/7$, $1/9$, $1/12$, $1/13$,......... The survey of experimental data show that the existence of such superstructures seems clearly evidenced only a few cases. In other cases, the use of stoichiometric formula is only a simplified formalization and in fact, the studied compounds are essentially non stoichiometric, with a random distribution of metallic cations in the layers. On the contrary, a particular value can be symmetrically observed in some systems, for example, $X=1/3$ in [Zn-Cr] based LDHs. Such particular values are also often reported in minerals mainly with $X=1/3$ and $X=1/4$.

1.3.3 Metal cations in the layers

The divalent and trivalent metal cations found in LDHs belong mainly to the third and fourth periods of the periodic classification of the elements

- Divalent Cations: Mg, Mn, Fe, Co, Ni, Cu, Zn.
- Trivalent Cations: Al, Mn, Fe, Co, Ni, Cr, Ga.

The ionic radii are in the range 0.65-0.80Å for divalent cations and 0.62-0.69Å for trivalent cations (with the main exception, Al : 0.50Å).

Higher ionic radii (Ca, Cd and Sc, La) seem to be incompatible with the formation of true brucite like layers. LDHs can also be obtained with a LiAl monovalent-trivalent
1.3.4 Structure of the layers

The structure of LDH’s consists the following main major factors:- (a) stoichiometry and the possible compositions, (b) stacking arrangement of the layers, (c) extent of ordering of metal cations with the layers, (d) arrangement of anions and water molecules in the interlayer while X-Ray diffraction continues to be the major tool for determination of LDH structures, Extended X-Ray Absorption Fine Structure (EXAFS), Vibrational Spectroscopy, Nuclear Magnetic Resonance (NMR), Mossbauer Spectroscopy as also Ultra Violet Spectroscopy have also been used in studying the structure of LDH’s. Brucite [Mg(OH)$_2$] with small polarisable cations and polarisable anions has the typical structure the family of LDH’s shown in fig 1.3.4. Brucite has a layer structure consisting of magnesium ions surrounded octahedrally by hydroxide ions. These octahedral units form infinite layers by edge-sharing with the hydroxide ions sitting perpendicular to the plane of the layers. The layers stack up on top of each other resulting in a three dimensional structure. The structure is composed of close packed planes of hydroxyl anions that lie on a Triangular lattice. The metal cations occupy the space between alternate pairs of OH planes in the octahedral holes, thus making a triangular lattice identical to that formed by the OH ions. This is an ideal closed packed arrangement. The local geometry of the cations as well as the close packing of the hydroxyl anions are distorted from these ideal arrangements with the octahedral compressed along the stacking axis. This compression results in increasing the O-O and Mg-Mg parallel to the plane from the ideal 0.2973nm of O$_H$ geometry to the experimentally observed 0.3142nm. The thickness of the layers decrease from 0.2427 to 0.2112nm. Thus it can be seen this geometry is much closer to D$_{3d}$. The O-M-O bond angles become 96.7° to 83.3° rather than the regular 90°. This distortion of the brucite layer does not change the hexagonal symmetry (a$_o$=b$_o$=0.3142nm and c$_o$=0.4766nm, $\gamma$=120°) and the space group is P3$_m$1.
The general observation with regard to the stoichiometry of LDH’s is that these phases can be formed only in the range 0.2<x<0.33, i.e., $\text{M}^{\text{II}}/\text{M}^{\text{III}}$ ratios in the range 2-4. The argument being for x>0.33, $\text{M}^{\text{III}}$-O-$\text{M}^{\text{III}}$ linkages may occur which from the Cation Avoidance rule (charge repulsion) are unfavourable.

The stoichiometry of x=0.25 found in the naturally occurring Hydrotalcite seems to be the best fit when theoretical calculations are made based on first principles molecular dynamics for Mg$_n$Al LDHs. These calculations showed that the most stable LDH’s are those for n=3 (x=0.25).

However there are values as low as 0.07 for Mg/Ga -CO$_3$ LDH’s [45] and as high as 0.41-0.48 for $\text{M}^{\text{II}}/\text{M}^{\text{III}}$ –CO$_3$ LDHs [46-50] and 0.5 for Fe$^{\text{II}}$/Fe$^{\text{III}}$ LDHs [51] reported in literature.

The difficulties in determining the exact value of x in LDHs mainly because LDHs tend to have impurity & amorphous phases, preferred orientation of LDHs and preferential leeching of n$^{\text{II}}$ ions from the layers during ion-exchange processes more so at low pH.

While these values of x cannot be taken for absolutely certainty, it has been clearly established that MIII - O- MIII linkages can occur in LDH’s at least in the case of M-Cr. The observed broadening of the d-d transitions of CrIII ions in LDH’s is associated with the distortion of Oh to D3d ideal arrangement of LDH’s. Also unlike conventional LDH’s where all the octahedral sites are occupied, in a novel variant of LDH’s having the formula [$\text{M}^{\text{II}} \text{Al}_4$(OH)$_{12}$](NO$_3$)$_2$, only half the cations are filled even though the MII/Al ratio is 1:4 ( where MII=Co,Ni,Cu,Zn). These LDH’s have been prepared by reacting activated Gibbsite with the corresponding $\text{M}^{\text{II}}$(NO$_3$)$_2$ solutions. It is also worth noting here that in Gibbsite [$\gamma$ – Al(OH)$_3$] lattice only two thirds of the octahedral sites are occupied by cations.

Thus it can be safely said that the range of stoichiometry for LDH’s is 0.2 < x < 0.33 is well established for LDH’s, the possibility for extending this narrow range for small
increments is possible even though the unusually high or low values reported in literature at present may not be pure single phases.

The LDH structure is based on $\text{M(OH)}_6$ octahedral units sharing edges in order to build $\text{M(OH)}_2$ brucite like layers. The layers contain both divalent and trivalent metallic cations; the main layers are therefore positively charged and the charge density is proportional to the trivalent metal ratio $X = \frac{\text{M}^{\text{II}}}{\text{M}^{\text{II}} + \text{M}^{\text{III}}}$. The whole structure is constituted by the stacking of such layers, intercalating charge balancing anionic species and water molecules as shown in fig.1.3.4

![Figure 1.3.4 Structure of Layered Double Hydroxides](image)
1.3.5 Interlamellar anions
The most remarkable features are-

- The band gap between brucite and smallest basal spacings in LDHs, corresponding to the intercalation of an interlamellar monolayer.
- The small distance range for a series of small anions- hydroxyl, fluoride, carbonate, chloride, attributed to a “leveling” effect of water molecules.
- The clear separation between inorganic anions intercalated LDHs with basal spacings lower than 15Å, even for species such as decavanadate and hybrid LDHs intercalating organic anions and displaying distances larger than 15Å.

1.3.6 Interlamellar structure
The structure of interlamellar domains is more difficult to characterize than the main layers [52]. With small anionic species, such as halides and carbonates and up to sulphate containing LDHs with a basal spacing of 11Å, a regular stacking of the layers is observed in the X-ray diffractograms. With bulky anions, the stacking of the layers displays, in most cases no more long-range ordering (turbostatic effect) and the diffractograms show only lines relative to the basal spacing and to the structure of the main layers.

1.4 Modification of Layered Double Hydroxides
1.4.1 Modification of LDH by intercalation of metal complexes
Intercalation of metal-containing anions in the interlayer space of hydrotalcites provides several advantages for an improved use: in the case of catalysts, it permits incorporation of, at least, a third metal component in the mixed oxide obtained upon thermal decomposition. In other materials, the interlayer space provides unique reaction conditions, thus permitting some reactions to take place under softer experimental conditions than in its absence. The preparation and characterization of these materials changes induced in their properties (as compared with those displayed by the same anions in the bulk form), and their applications, are also considered.
1.4.1.1. Layered double hydroxides intercalated with halocomplexes.

LDHs intercalated with halo-complexes have been investigated as catalysts for chloride exchange reactions, and also as modified electrodes. The reactivity of some halo-complexes in the interlayer space has been also investigated. López-Salinas and Ono [53] have prepared Mg,Al–LDH with [NiCl$_4^{2-}$] or [CoCl$_4^{2-}$] in the interlayer by anion exchange (from a nitrate-containing precursor) in non-aqueous media. However, exchange is not complete (IR spectra of the LDH halo-complexes show a band at 1376 cm$^{-1}$, ascribed to mode $\nu_1$ of NO$_3^-$ anions), and the complexes partially decompose during the exchange process or the washing: drying steps. In addition, the IR spectra evidence the formation of a small amount of nickel nitrato-complexes, where the nitrato anions coordinate to nickel as bidentate ligands, as concluded from the positions of the $\nu_5$ and $\nu_1$ nitrate bands [54]. The nature of the non-aqueous solvent (ethanol or nitromethane) used during synthesis seems to play no major role on the nature of the interlayer species (for the Ni-compound).

1.4.1.2. Layered double hydroxides intercalated with cyanocomplexes

Layered double hydroxides intercalated with cyano complexes of iron, cobalt, molybdenum and some other metals have been synthesized and are used for hydrocarbon adsorption and electrochemical behavior. In addition to X-ray diffraction, so useful to characterize these layered materials, IR and Mossbauer (in the case of iron and cobalt-containing cyanides) spectroscopies have been also widely used. The methods of synthesis used have been coprecipitation and anionic exchange in most of the cases, although reconstruction of the layered structure from a carbonate LDH precursor calcined at 500°C has been also used [55].

The change in the capacity for carbon dioxide adsorption on a Mg,Al, [Fe(CN)$_6$]$_4^+$ LDH with the Mg:Al ratio (between 1 and 7) has been studied by Mao et al. [56]. Maximum adsorption was observed for Mg:Al=1.7, i.e. it depends not only on the width of the interlayer space (ranging, although not steadily, from 10.64 to 10.96 Å), but also on the layer charge. The isosteric heat of adsorption was calculated to be 43.3 kJ mol$^{-1}$, a value
similar to that reported by Miyata and Hirose [57], who found the adsorption capacity for CO2 of a Mg,Al–[Fe(CN)$_6$]$^{4-}$ LDH to be 60% of that of zeolite 5A.

1.4.1.3. Layered double hydroxides intercalated with oxocomplexes.

Corma et al. have reported the preparation of Zn,Al–LDHs containing Mo oxo-complexes in the interlayer, and their role as heterogeneous catalysts for the oxidation of thiols [60-61]. [Mo$^{VI}$O$_2$(O$_2$CC(S)Ph)$_2$]$_2^-$ ([O$_2$CC(S)Ph]$_2^-$ being the sterically hindered 2,2-diphenyl-2-mercaptoethanoate ligand) is able to oxidize aliphatic thiols under homogeneous conditions [58,59,60], it being reduced to a monomeric complex [Mo$^{V}$O(O$_2$CC(S)Ph)$_2$]. However, this is clearly a disadvantage, as this second complex does not undergo oxidation with Me$_2$SO, so cancelling the possibility to design catalytic cycles.

The LDH–Mo$^{VI}$ intercalation compound was prepared by anionic exchange of the LDH in its nitrate form. The d-spacing of (00l) reflection increases from 13 Å to 17.6Å due to expansion of interlayer space [62].

1.4.1.4. Layered double hydroxides intercalated with macrocyclic ligand containing complexes

Modification of LDH by intercalation of macrocyclic ligand by anion exchange process. One of systems most widely studied in recent years concerning LDHs, corresponds to those where the interlayer anion is a coordination compound with macrocyclic ligands; also, where the interlayer anion is the anionic ligand itself. The role of modified LDH as biomimetic catalysts, heterogeneous catalysts, LDH modified electrodes or as gas or optical sensors [63-65].

1.4.2 Modification of LDH by intercalation of azo dyes

Intercalation of organic host into the layers of double hydroxides has created its own domain by achieving its potential applications, in catalysis and photovoltaics [66-68]. The interest stems from the peculiar molecular arrangement imposed by the host structure, the thermal stability supplied by the inorganic constituent and the stability
against the dissolution process, the whole contributing to maintain the optical properties of the intercalated dye.
Azo dyes are known for their potential efficiency in non linear optics (second harmonic generation) and for their ability to photoisomerization [69-71].

1.4.3. Modification of LDH by intercalation of heteropolyacids

1.4.3.1. Layered double hydroxides intercalated with low-nuclearity oxometalates
Intercalation of polyoxometalates are carried out by ion exchange process. Polyoxometalates with several nuclearities have been incorporated into the interlayer space of different LDHs. The polyoxometalates containing chromium and vanadium are widely used. General reports on the preparation of polyoxometalates intercalated LDHs and their applications have been published [72-74].
The reactivity of simple oxometalates, such as chromate and dichromate, inside interlamellar domains of Zn,Al or Zn,Cr, or Cu,Cr–LDHs after ageing under moderate thermal treatment, has been studied. Pillaring and grafting processes have been put into evidence from structural and spectroscopic data for these compounds and their application in several catalytic processes has been also tested.

1.4.3.2. Layered double hydroxides intercalated with medium-nuclearity oxometalates (such as vanadates and molybdates)
Among all metal-containing anions incorporated into the interlayer space of hydrotalcites and other LDHs, oxovanadates represent the widest studied group. Although mostly as decavanadate, some studies have been also devoted to intercalation of lower oligovanadates. Oxometalate pillared LDHs are in many cases prepared by a two-step anion exchange method, through intermediate intercalation of a large organic anion, to swell the brucite-like layers [75].
Evolution of intercalated decavanadate to other species by thermal treatment has been widely studied, as interest in these polyoxometalate hydrotalcite materials also stems from their potential use as catalytic materials, as prepared or after thermal decomposition [76]. Kagunya and Jones [77] have reported aldol condensation of acetaldehyde on a Mg,Al-vanadate LDH calcined at 450°C, although the activity is lower than in solids prepared, at the same temperature, from a carbonate precursor,
probably because of a decrease in surface basicity, required for self-condensation of acetaldehyde.

1.4.3.3. Layered double hydroxides intercalated with high-nuclearity oxometalates: iso and hetero-polyoxometalates

High nuclearity oxometalates and hetero polyoxometalates such as the Keggin-type, or related, larger structures, Dawson and Finke [78] or Preyssler types [79] were intercalated in pure LDH by anion exchange process. One of the aims of these studies was to expand the layers further than the values obtained with decavanadate; it has been also observed improved catalytic properties of these systems. In a Keggin-type structure, twelve metaloxygen octahedra form a shell surrounding a tetrahedrally coordinated heteroatom (P, Si, B, etc.); the shape is close to spherical, with a diameter of ca. 10 Å.

1.4.4. Modification of LDH by intercalation with nanoparticles

In order to prepare mesoporous materials or multifunctional catalysts, intercalation of oxide nanoparticles was performed in different ways. Manganese oxide nanoparticles were intercalated into Mg–Al LDH by ion exchange of interlayer nitrate with permanganate anion, followed by reduction with organic reagents (D(+)-glucose, ethanol, L(+)-ascorbic acid) or by photodecomposition [80]. The requirement by industry for materials with a high surface area stimulated research into developing of nano-sized LDH. Nano-size CoIIAl-hydrotalcite-like particles (5–7nm) on g-Al2O3 as support were synthesized by [81] and [82]. g-Al2O3 also acts as the source of Al3+ ions. [83] synthesized LDH [Mg1-xAlx(OH)2](CO3)0.5x2yH2O (x = 1.7-3.3) by separating the nucleation and ageing steps. The key features of this method are a very rapid mixing and nucleation process in a colloid mill followed by separated ageing. Uniform crystals with a narrow range of diameters are obtained.

1.4.4.1 Grafting reaction

After grafting, the interlayer anions are not exchanged with other anions, and are then stabilized in the interlayer space [85]. Grafting also occurs in other combinations of LDH and guest anions, such as Cu–Cr LDH/CrO42- and Cr2O72-, Zn–Al LDH/ethylene glycol, and Zn–Al and Cu–Cr LDH/organic anion [84, 86-89].
Reaction Mechanisms
Anion-Exchange Reactions

The anion-exchange capacity (AEC) is dependent on $x$. For the ideal composition of $M^{II}_{1-x}M^{III}_x(OH)_2X$, 0.66$H_2O$, it can be calculated as $AEC=x.10^5/FW$ (cmol/kg) where the formula weight $FW = (M_{MII}+46)+x(M_{MIII}+M_X-M_{MII})$. and 0.66$H_2O$ accounts for the total occupancy of interlayer vacant sites by water. $FW$ relates to full occupancy (2/3) of the interlayer crystallographic sites by water molecules (0.66$H_2O$/metal). Since AEC is dependent on $x$, it is constant for some LDH materials such as LiAl$_2$, Zn$_2$Cr, and Cu$_2$Cr, and highly tunable for some others like ZnxAl ($1<x<4$) or GaxAl ($1<x<7.5$)[90]. The layer charge densities ($c.d.=(a^2\sqrt{3}/2x)^{-1}$) and the free cross sectional area ($S_{free} = 1/c.d.$ (nm$^2$/charge)) per layer for a series of LDH. The usual values range from 200 to 400 cmol/kg (= meq/100 g) and show the higher AEC of LDH in comparison to clay minerals [91]. For Mg–Al LDH with Mg/Al=3 and containing simple anions, the AEC value is 320–360 cmol/kg. However, measured AEC values for LDHs are often less than the values calculated from the structural formula, due to contamination by carbonate anions, which have a strong affinity for LDHs. The charge densities for LDHs range from 0.25 to 0.40nm$^2$/charge [92]. From a thermodynamic point of view, exchange in LDH depends mainly on the electrostatic interactions between positively charged hydroxylated sheets and the exchanging anions, and to a small extent on the free energy involved in the changes of hydration [93]. Another important feature is that the equilibrium constant increases when the radius of the bare anion decreases. Exchange is therefore favoured for ingoing anions with a high charge density. By calculating the equilibrium constant of various exchange reactions, [94] were able to list the order of affinity of LDH for monovalent anions $OH^->F^->Cl^->Br^->NO_3^->I^-$ and divalent anions $CO_3^{2-}>C_{10}H_4N_2O_8S^2->SO_4^{2-}$. These results confirm the strong affinity for carbonate anions and underline the strong need to prepare these compounds under a $CO_2^-$ free atmosphere. For [Cu–Al–X/Y] systems, determined a similar selectivity sequence for monovalent anions, while for divalent oxoanions the following order was proposed: $HPO_4^{2-}>HAO_4^{2-}>CrO_4^{2-}>SO_4^{2-}>MoO_4^{2-}$. The selectivity for divalent anions is higher than for monovalent anions. According to these results, nitrate- and
chloride-containing LDHs appear to be among the best precursors for exchange reactions.

For Ni$_{1-x}$M$_x$(OH)$_2$(CO$_3$)$_{1/2}$. n(H$_2$O) (M = Co, Fe), a strong dependence of basal spacings on the size and charge of the intercalated ions is observed. The spacing increases in the following order:

CO$_3^{2-}$ < NO$_3^-$ < SO$_4^{2-}$ < ClO$_4^-$ < OAc$^-$

These hydroxides exhibit a selectivity for the anions in the sequence

CO$_3^{2-}$ ≥ SO$_4^{2-}$ > Cl$^-$ > ClO$_4^-$ > NO$_3^-$ > OAc$^-$

1.5 Applications of Layered Double Hydroxides

Figure 1.5 Applications of Layered Double Hydroxides
1.5.1 Catalytic application

The hydrotalcires have high surface area with very regular pore size dimensions. Due to these properties it becomes carriers on which catalytically active phases such as transition metals, heteropolyacids can be intercalated. Due to intercalation, it generates Bronsted acid. On generating Bronsted acidity, one can think of the possibility of increasing the basicity of the conjugate base by exchanging protons by alkaline ions. This introduces mild basicity which is useful for less demanding base catalysed reactions. Finally, the intercalation of transition metals will give catalytic redox properties which are used in selective oxidation as well as for air pollution abatement.

Mixed oxides obtained by calcinations of LDH can serve as solid-base catalyst for (i) polymerization of alkene oxides; (ii) aldol condensation of aldehydes and ketones; (iii) methane or hydrocarbon steam reforming; (iv) methanation; (v) synthesis of methanol and higher alcohols; (vi) hydrocarbon (Fischer-Tropsch) synthesis; and (vii) hydrolysis of nitriles [10, 95]. The thermal decomposition of LDH, containing transition metal ions, was intensively studied because the products are potentially useful as catalyst precursors. The transition metals including Ni [96-101], Co [102-105], Fe [106,107] and Cu [108-111]. The reactivity of LDH itself (as a solid-base catalyst) was investigated using 2-methyl-3-butyn-2-ol as a probe [112].

Friedel-Crafts Alkylation and Acylation reactions:-

The formation of a bond between a carbon atom of an aromatic ring and an aliphatic carbon atom is an important reaction in organic synthesis. The first example of such alkylation was reported by Friedel and Crafts in 1877. The two types of Catalyst used in Friedel Crafts reaction are

i. Lewis Acids: Usually the more reactive the substrate, the weaker need be the Lewis Acid used. AlCl$_3$>BF$_3$>SbCl$_5$>FeCl$_3$>SnCl$_4$>ZnCl$_2$


There appears to be at least two possible mechanism that can operate with alkylhalide Lewis Acid complex (bimolecular mechanism) and the other involving an alkyl carbonium ion (unimolecular mechanism).
The main limitation of alkylation reaction is due to the activating affects that alkyl group have on the aromatic ring so that after first alkylation, reactivity towards second alkylation increases and ultimately leads to polyalkylation. The second problem is isomerisation.

Friedel Crafts acylation reaction involve attack by an acyllium ion, which is generated by interaction of an acyl chloride (or acid anhydride) with a Lewis Acid.

An emerging trend is the application of LDH-derived catalyst in green chemistry. Solid-base catalysts are environment friendly, as compared with their liquid counter-parts, because their waste products are easier to dispose than the huge volumes of liquid alkali waste [113]. Solid bases from LDH were used in mercaptan oxidation for sweetening [114], formation of C-C bonds [115, 116], and condensation of citral and ketones [116]. Environment friendly technologies using LDH were also developed for the production of hydrogen from vegetable oils [117], simultaneous production of hydrogen and nanocarbon by decomposition of methane [118] and high-rate synthesis of amine N-oxides [119-121] investigated Cu-Zn-Al-Zr-LDH as precursors of catalysts for steam reforming of methanol to produce CO-free hydrogen for fuel cells.

1.5.2 Sorbent for pollutant

Due to the property of higher anion exchange capacity of LDH, it makes them promising materials for the elimination of ecologically undesirable inorganic and organic anions. The removal of chromate [122, 123] nitrate, phosphate, arsenate or vanadate anions [124, 125] as well as humic substances [126, 127] and radioactive elements [128, 129] from contaminated water or waste streams by LDH have been demonstrated. Also numerous papers have reported the use of LDH or their calcined derivatives as organic contaminate adsorbents such as the adsorption of phenolic compounds [130, 131] and pesticides [132-135].

1.5.3 Vector/Drug release

$\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot4\text{H}_2\text{O}$ LDH is known to be an effective antacids, [136] but other bio-applications were recently reported. Many common nonsteroidal anti-inflammatory drugs [137-139] such as Diclofenac, Ibuprofen, Gemfibrozil and Naproxen have been
intercalated in the interlayer space of LDH compounds by anion-exchange reaction as well as bio-related polymers and large bio-macromolecules such as polyaspartate [141], alginate [141] and DNA [142]. Apart from a chemical curiosity, the drug intercalated LDH hybrids as a controlled drug-release system could control the point of release and pharmokinetic profile by tuning the desired composition in the host layers. Besides, the host layers improve the long-term stability and storage since these drug molecules are isolated from the environment by the hydroxide layers. Another application largely described by Choy et al. in the literature is the use of LDH as DNA delivery system. Indeed, these authors have shown that LDH can protect DNA from degradation and the charge neutralization enhances the transfer of DNA-LDH hybrid into mammalian cells through endocytosis [144].

1.5.4 Filler in polymer
LDH can enhance the mechanical properties, gas permeability and be of interest in polymer electrolyte. The incorporation of polymer between LDH galleries proceeds via different pathways such as coprecipitation, exchange [144], in situ polymerization [145]. The latter method presents the advantage to tune the tactility and the molecular weight of the generated polymer by varying the layer charge density and the particle size of the host structure, respectively [146-148]. A large variety of LDH/polymer systems can thus be obtained, thermally more stable than the pristine inorganic compound leading to potential applications in fire-retardant composites [149] LDH/polymer nanocomposites can also be served as LDH inorganic fillers dispersed into a polymer (161) For example, nanoparticles of Zn₃Al-dodecyl sulfate dispersed in the linear low density polyethylene (LLDPE) were found to enhance the thermal and mechanical properties of pure LLDPE [150].

1.5.5 Nanoreactor
LDH can also provide a confinement for the organic moiety suitable after a charring process to the formation of high surface area (2300 m²/g) carbonaceous materials, using the interleaved monomers and polymers between the hydroxide layers of LDH as
Furthermore, a variety of nanoparticles such as Co, Ni, Pt, PbS, etc. have been prepared using LDH materials (Li$_2$Al, MgRAl, Ni0.7Al and Co0.7Al etc.) as a nanoreactor intercalated with complex anions containing the desired metal: [M(EDTA)]$^{2-}$ (M = Co$^{2+}$, Ni$^{2+}$), [Pt(OH)$_6$]$^{2-}$ and [Pb(S$_2$O$_3$)$_2$]$^{2-}$ [152-154]. With this method, it is possible to avoid the aggregation and the formation of well dispersed nanoparticle was indeed observed.

### 1.6 Physicochemical characterization

A number of experimental techniques were used to characterize the layered double hydroxides and intercalated LDH. This techniques give the idea about purity, crystallinity, surface area, structure, adsorption capacity, catalytic property etc of the layered double hydroxides.

#### 1.6.1 PXRD

The powdered XRD study is the first step for characterization of solid particles. This technique can identify a particular frameworks structure and give the following information.

- The nature of materials such as amorphous or crystalline.
- Types of structure and phase.
- Degree of crystallinity and thermal stability.
- Whether metal atom has been incorporated into the framework by measuring a unit cell volume.

The powdered diffraction pattern of layered double hydroxides are generally recorded between 2θ values of 5°-80°. The PXRD, d spacing’s of pure LDH and intercalated LDH can be indexed (fig.1.6.1).
1.6. 2 FTIR

The Diffuse Reflectance Fourier-Transform Infrared (DRFT-IR) spectroscopy helps to identify characteristics bands of the layered double hydroxides. Besides that, information about the type of bonds formed by the anions and about their orientations can also be obtained. Fig.1.6.2(a) and fig.1.6.2(b) display the IR spectra of M(II)AlCO3 HTIcs with different cations [155], and of NiAlA-HTIcs (with x= 0.25 and 0.33), with A=(CO\textsubscript{3})\textsuperscript{2−} and (NO\textsubscript{3})\textsuperscript{−} [156]. The absorption at 3500-3600 cm\textsuperscript{-1}, present in all HTIcs. is attributed to the H-bonding stretching vibrations of the OH group in the brucite-like layer. The maximum of this band is shifted depending on x; for Mg(OH)\textsubscript{2}(x= 0) the maximum of this absorption band is at the higher frequency of 3700 cm\textsuperscript{-1}. 

Figure 1.6.2(a) FTIR of MgAl LDH
Sema et al. [155] reported that both the hydrogen stretching and bending frequencies in HTlcs increase as the M(II)/M(III) ratio increases from 2 to 3 (thus decreasing x). This shift has been correlated with the modification in the layer spacing; moreover, it was observed that the half-width was smaller in the Mg/Al= 2/1 (x= 0.33) hydrotalcite, thus suggesting a more ordered cation distribution inside the brucite-like layer. A shoulder may be present around 3000 cm$^{-1}$; this has been attributed to hydrogen bonding between H$_2$O and the anion in the interlayer [6, 158]; an H$_2$O bending vibration also occurs at 1600 cm$^{-1}$. The intensity of these latter two bands depends on the type of anion and the amount of water. In the 200-1000 cm$^{-1}$ region there are some bands related to vibrations of the anions, and some related to cation-oxygen vibration. This region has been thoroughly studied only by Sema et al. [155, 159]; the authors made a complete assignment of the observed infrared lattice vibrations for the ion [Al$_2$LiO$_6$] with the ideal D$_{3d}$ symmetry for motions within one octahedral sheet; an ordering of octahedral cations in the bmcite-like sheet was also found. The main absorption bands of the anions are observed between 1000 and 1800 cm$^{-1}$. The carbonate anion in a symmetric environment is characterized by a D$_{3h}$ planar symmetry, with three IR active absorption bands, as well as in the case of the free carbonate anion. In most HTlcs the three bands are observed at 1350-1380 cm$^{-1}$ ($\nu_3$), 850-880 cm$^{-1}$ ($\nu_2$) and 670-690 cm$^{-1}$ ($\nu_4$).
However, in some cases the presence of a shoulder around 1400 cm$^{-1}$, or of a double band in the region 1350-1400 cm$^{-1}$ [158], has been attributed to a lowering of the symmetry of the carbonate (site of symmetry C$_{2v}$), and to the disordered nature of the interlayer [156, 158], which causes the removal of the degeneracy of the $\nu_3$ and $\nu_4$ modes. The lowering of the symmetry also causes the activation of the $\nu_1$ mode around 1050 cm$^{-1}$; this mode is Raman active when the anion retains D$_{3h}$ symmetry. Miyata [155] has explained the observed lowering of symmetry by hypothesizing two different kinds of anion coordination: the carbonate anion can exist in the interlayer region as a monodentate or a bidentate complex. The same explanation has been reported by the author in order to justify the band splitting in some HTlcs containing different anions ((NO$_3^-$), (SO$_4^{2-}$), (ClO$_4^-$) in [155, 160].

1.6. 3 TGA

Thermogravimetry (TG) is a technique that measures the variation in mass of the sample when it undergoes temperature scanning in a controlled atmosphere. This variation in mass may be either loss of mass (vapour emission) or a gain of mass (gas fixation). Differential thermal analysis (DTA) is a technique that measures the difference in temperature between a sample and a reference while subjecting both of them to the same linear temperature rise. The DTA provides the information on exothermic and endothermic reactions taking place in the sample.

1.6.4 Surface Area

Adsorption of molecules has been widely used to evaluate the pore size distribution of solid catalysts. The most common method of measuring surface area of catalytic materials is based on the theory developed by Brunauer, Emmett and Teller assuming multilayer adsorption. The isotherm points are transformed with the linear form of BET equation. Nitrogen adsorption-desorption isotherms of the hydrotalcite at a Mg/Al molar ratio of 3.5 with respect to time measured at liquid nitrogen temperature(77K) [161]. The shapes of all of the isotherms are type IV according to the IUPAC classification and represent a mesoporous adsorbent with strong adsorbent-adsorbate interaction. The desorption started immediately after completion of adsorption. The
hysteresis is associated with capillary condensation in the meso structures [162]. The slight changes in the hysteresis loops was observed due to synthesis methodology and hydrothermal treatment conditions related to the shape and homogeneity of the pore size. At 3hr aging time, the loop closes at around 0.5 relative pressure with a small plateau at high relative pressure which attributed to the mesoporous nature of these samples. As the aging time increases, the relative pressure for the loop closing also increases toward the higher value [163]. The hysteresis loops are almost vertical and parallel over an appreciable range of relative pressure and such shape of the loops suggests aggregates of plate like particles leading to slit-shaped pores of the hydrotalcite. Average pore-size distribution and surface areas for the hydrotalcite samples having a Mg/Al molar ratio of 3.5 synthesised at 70°C with 3-7 hr aging time are taken [164]. The pore diameter was observed to increase on increasing time. For example, pore diameter was observed to increase from 9.3-11.5nm on increasing the aging time from 3-7 hr. The increase in pore diameter could be attributed to the difference in the nature of aggregation of primary particles (constituent crystallites) during the crystallization process. As the crystallization time increased, the primary particles of hydrotalcite grew, resulting in larger pore diameters [165] However, significant changes were not observed in the pore volume of hydrotalcite samples at a Mg/Al molar ratio of 3.5 with respect to time at 70°C. Surface area (BET) of the hydrotalcite samples was observed to decrease with an increase in aging time and hydrothermal treatment temperature (which is determined) [166]. The increase in the surface area on increasing Mg/Al molar ratio is attributed to the observed decrease in the calculated crystallinity and crystallite size of hydrotalcite from PXRD pattern. Generally, smaller crystallite sizes of hydrotalcites yield larger surface areas [166]. The hydrothermal treatment conditions have influenced the surface area of hydrotalcite significantly, since these textural properties are directly related to the agglomeration of the particles and particle size. The decrease in the surface area of the hydrotalcite on increasing the aging time and temperature could be correlated to the simultaneous nucleation, which enhanced the crystallinity of material and larger crystallite size, which is in good agreement with observed PXRD data. The other reason for the lower
surface area is face-to-face or card-house type aggregation of crystallites, which is responsible for the lower specific surface area of hydrotalcite at higher hydrothermal treatment temperature and crystallization time. It is assumed that the rapid enhancement in the crystallinity leads to lower probability for face-to-face aggregates formation, which results in the increasing specific surface area of hydrotalcite during short aging time and low hydrothermal treatment temperature [39].

1.6.5 Scanning Electron Microscopy (SEM) study
This technique is used to study the overall topography. SEM scans over a sample surface with a probe of electrons (5-50 kV) and detects the yield of either secondary or back-scattered electrons as a function of the position of the primary beam. Morphology, Crystallite shape, size and size distributions are easily obtained by this technique. The estimated particle size approximately 0.3-o.5 µm. After silylation, the particle sizes were 0.5-0.7 µm, a bit bigger.

1.6.6 HRTEM
This technique helps to determine the degree of cubic order and the type of unit cell or projection. The diameters of the particles were found to range from 0.15pm to 0.6pm. The ordered pore structure at the (110), (100), (111) etc can be determined.

1.6.7 NMR
It is a powerful technique for the characterization catalytic reaction catalysed by layered double hydroxides used as catalyst. This technique arises due to different behavior of nuclear spin interaction. The fixed orientation of the local environments of NMR active isotopes causes line broadening. In principle, the three line broadening mechanisms are dipolar interactions, chemical shift anisotropy and quadropolar interaction.

Nuclear magnetic resonance (NMR) spectroscopy is an effective technique in studying the structural environments and dynamical behavior due to its unique ability to simultaneously probe element-specific local structure with high resolution and to investigate atomic and molecular motion.

Solid state NMR technique has been used to characterize the Al- species in MgAlCO$_3$-HT during decomposition of the HT. The Al species has been characterized by observing the $^{27}$Al-NMR signals [167]. In order to characterize the Cu$^{2+}$ species in Cu-
based HTLcs we can used ESR technique. The intensities of ESR signals decreases progressively with increasing temperature during calcinations. At low temperature a very large band is observed. At 623K two overlapping signals were observed. One an anisotropic shape with hyperfine structure and a broad symmetric line at g=2.15 with ∆H= 500G [168].

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