Chapter I

LDH

Catalyst

Support

Adsorbent

Electrodes

Composite

Medical
Introduction

1. Layered double hydroxide (LDH)
   1.1 Historical background
   1.2 Structural features
   1.3 General formula
   1.4 Catalysis
     1.4.1 Base catalysis
     1.4.2 Redox catalysis

2. Synthesis of LDH
   2.1 Co-precipitation method
   2.2 Urea & hexamine hydrolysis methods
   2.3 Sol-gel method
   2.4 Miscellaneous methods

3. LDH derived materials
   3.1 Mixed metal oxides
   3.2 Rehydrated LDH
   3.3 LDH composite materials

4. Physico-chemical characterization
   4.1 Powder X-ray diffraction (PXRD) studies
   4.2 Fourier transformed infrared (FT-IR) spectroscopy
   4.3 Thermogravimetric analysis (TGA)
   4.4 Elemental analysis
   4.5 Adsorption measurements (surface area and pore size distribution)
   4.6 Scanning electron microscopy (SEM)
   4.7 Transmission electron microscopy (TEM)
   4.8 X-ray photoelectron spectroscopy (XPS)
   4.9 Temperature programmed reduction (TPR)
   4.10 Nuclear magnetic resonance (NMR) & Mass spectrometry (MS)

5. Scope and objectives of the work

6. References
1. Layered double hydroxide (LDH)

1.1 Historical background

Clays are naturally occurring materials composed primarily of fine-grained minerals. Clay has been defined as an earthy material that forms a coherent, sticky mass when mixed with water and when wet this mass can be readily moldable. The two main features that evoke the interest on clays are their common availability and their extraordinary properties [1]. Clays find their potential application in ceramics, building materials, adsorbents, ion–exchangers, sensors, decolorizing agents and catalysis [2]. The adsorptive power and high water retention capacity of clays are responsible for their wide applications. The first and most widely known application of clay on catalysis is French Houdry cracking process developed in 1930 [3]. Clays, forms a subset of large discipline of catalysts in particular as heterogeneous catalysts. This shows the importance of working on clays and clay based compounds.

Clays are classified into two categories:

1. Cationic or smectite type of clays having layered lattice structure in which two dimensional oxy-anions are separated by layers of hydrated cations.

2. Anionic or brucite type of clays in which the charge on the layer and the gallery anion is reversed, complementary to smectic-type clays [4].

Anionic clay, synthetic and natural layered mixed hydroxides containing exchangeable anions are less well known and diffuse in nature than cationic clays. Hydrotalcite (HT) belongs to the large class of anionic clays, and will be taken as a reference name for many other isomorphous and polytype compounds. It is also evidenced from the literature that the layered perovskites (LP), pillared clays (PILC) materials are still mainly at the lab-scale development stage, while HT and especially clays find a broad range of application [5].

Hydrotalcites (HTs) or Hydrotalcite-like (HT-like) materials also called as layered double hydroxides (LDHs) are naturally available anionic clays, discovered in Sweden at 1842. It can be easily crushed into a white powder similar to talc [6]. LDH belongs to a large class of minerals with closely related structures is usually known to mineralogists as the sjogrenite-hydrotalcite group [7]. The stoichiometry of
Introduction

Chapter-I

Hydrotalcite, \([\text{Mg}_6\text{Al}_2(\text{OH})_2]\text{CO}_3\cdot4\text{H}_2\text{O}\), was first correctly determined by Manasse [8] in 1915. Aminoff and Broome [9] first recognized the existence of two polytypes of hydrotalcites with rhombohedral and hexagonal symmetry from X-ray investigation. Pioneering single crystal X-ray diffraction (XRD) studies on the mineral samples were carried out by Allmann [10] and Taylor [11, 12] in the 1960s and main structural features of LDHs were understood. However for many years the fine details of the structure such as the range of possible compositions and stoichiometry, the extent of ordering of metal cations within the layers, the stacking arrangements of the layers and the arrangement of the anions and water molecules in the interlayer galleries are not fully understood. ISI Web of knowledge [v. 4.10] database search on these materials with the topic search keyword of “Hydrotalcite* OR Layered double hydroxide*” showed 8448 records over these materials on Feb-2011 (Fig. 1.1).

![Number of articles and patents published in LDHs](image)

**Fig. 1.1** Number of articles and patents published in LDHs

Number of articles published in 2001 on LDHs is 310 and it increased to 883 in 2010; this shows the importance of working on these materials [13].

1.2 Structural features

The basic layer structure of LDH is based on that of brucite \([\text{Mg(OH)}_2]\) structure and it consists of magnesium ions surrounded approximately octahedrally by hydroxide ions. These octahedral units form infinite layers by edge-sharing, with the hydroxide ions sitting perpendicular to the plane. The layers then stack on top of one another to form the three dimensional structure. The metal cations occupy the octahedral holes between
alternative pairs of OH planes and thus occupy a triangular lattice identical to that occupied by the OH⁻ ions.

![Fig. 1.2 Structure of LDH](image)

If some Mg²⁺ ions are replaced by a higher valent ion having similar radius (such as Fe³⁺ in pyroaurite, Cr³⁺ in stichtite and Al³⁺ in hydrotalcite) [14], the brucite-type layer becomes positively charged. To maintain electrostatic neutrality, this excess positive charge is balanced by anions located in the interlayer region between brucite-layers. The schematic representation of the hydrotalcite structure is shown in Fig. 1.2. X-ray unit cell determination, based on early crystallographic work, confirmed that brucite-like sheets can stack one on the other with two different symmetries, differing only in their interlayer stacking sequences viz., rhombohedral and hexagonal [9]. The brucite-like layers in LDHs may be stacked in different ways, which gives raise to variety of possible polytype structures. LDHs usually crystallize in two different polytypes, one with two-layer hexagonal stacking sequence (polytype 2H) and another with a three-layer rhombohedral sequence (polytype 3R). All sites in the (110) plane of the close packed hydroxide layers may be represented as A, B or C related by lattice translations of (1/3, 2/3, 0) or (2/3, 1/3, 0) and the locations of octahedral holes occupied by metal cations can be described analogously as a, b or c. Thus single brucite layer can be represented as AbC (since, if close packed hydroxyl groups occupy A and C sites, the cations must, of necessity, occupy b sites). AbC layers may be stacked in various ways giving rise to a large number of possible polytypes. These polytypes may be classified in terms of the number of sheets
stacked along the \( c \) axis of the unit cell. If the opposing OH groups of adjacent layers lie vertically above one another (say both in C sites), a trigonal prismatic arrangement (denoted by =) results; if the hydroxyls are offset (say one layer in C sites and those of an adjacent layer in either A or B sites) then six OH groups form an octahedral arrangement (denoted by \( \sim \)). Thus brucite itself can be denoted as \( \ldots \text{AbC}\sim\text{AbC}\sim\ldots \) or \( 1\text{H} \), where “1” denotes a one layer polytype and the “H” denotes a stacking sequence with hexagonal symmetry. Bookin and Dirts [15, 16] have systematically derived all of the possible polytypes for other stacking sequences. There are three possible two layer polytypes, each of which has hexagonal stacking of layers, which can be denoted as,

\[
\ldots \text{AbC}=\text{CbA}=\text{AbC} \ldots \quad 2\text{H}_1
\]
\[
\ldots \text{AbC}\sim\text{AcB}\sim\text{AbC} \ldots \quad 2\text{H}_2
\]
\[
\ldots \text{AbC}\sim\text{BcA}=\text{AbC} \ldots \quad 2\text{H}_3
\]

The interlayers in the \( 2\text{H}_1 \) polytype are all prismatic and those in the \( 2\text{H}_2 \) polytype are all octahedral, whilst in the \( 2\text{H}_3 \) polytype both types of interlayers are present. There are nine possible three-layer polytypes. Two of these have rhombohedral symmetry (3R):

\[
\ldots \text{AbC}=\text{CaB}=\text{BcA}=\text{AbC} \ldots \quad 3\text{R}_1
\]
\[
\ldots \text{AbC}\sim\text{BcA}\sim\text{CaB}\sim\text{AbC} \ldots \quad 3\text{R}_2
\]

the remaining seven have hexagonal symmetry:

\[
\ldots \text{AbC}\sim\text{AcB}\sim\text{AcB}\sim\text{AbC} \ldots \quad 3\text{H}_1
\]
\[
\ldots \text{AbC}\sim\text{AcB}\sim\text{CaB}\sim\text{AbC} \ldots \quad 3\text{H}_2
\]
\[
\ldots \text{AbC}\sim\text{AcB}=\text{BcA}=\text{AbC} \ldots \quad 3\text{H}_3
\]
\[
\ldots \text{AbC}\sim\text{AcB}=\text{CbA}=\text{AbC} \ldots \quad 3\text{H}_4
\]
\[
\ldots \text{AbC}\sim\text{AcB}=\text{BaC}=\text{AbC} \ldots \quad 3\text{H}_5
\]
\[
\ldots \text{AbC}\sim\text{AcB}\sim\text{BcA}=\text{AbC} \ldots \quad 3\text{H}_6
\]
\[
\ldots \text{AbC}\sim\text{AbA}\sim\text{BcA}=\text{AbC} \ldots \quad 3\text{H}_7
\]
For the $3R_1$ polytype, the interlayers are all prismatic and in the case of $3R_2$, $3H_1$ and $3H_2$ they are all octahedral; other polytypes involve both types of interlayers. Bookin and Drits have also described the large number of possible six-layer polytypes, some of which have rhombohedral symmetry ($6R$) and the remaining hexagonal symmetry ($6H$).

1.3 General formula

The chemical composition of LDH phase is generally described by:

$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+n}[A^{n-x/n}]^{x^-}\cdot mH_2O$$

where $M(II)$ and $M(III)$, represent divalent and trivalent metal ion respectively, $A$ is the interlayer anion with charge $n$, $x\{M(II)/M(III)\}$ is the fraction of the trivalent cations and $m$ is the water of crystallization. The value of $x$ can be in the range 0.2 - 0.35. For values outside this range pure hydroxides or other compounds with different structure are obtained (with some exceptions) [17, 18]. The main criteria for elements to crystallize in this network are their ionic radius. $M(II)$ and $M(III)$ having an ionic radius not too different from that of $Mg^{2+}$ may be accommodated in the octahedral sites of the close-packed configuration of the $OH^-$ ions in the brucite-like layers to form HT-like compounds. The ionic radii of $M(II)$ cation between 0.65 to 0.80 Å and $M(III)$ cation of 0.62 to 0.69 Å (with the main exception of Al 0.5 Å) can form LDHs [19].

Higher ionic radii (Cd and Sc) seem to be incompatible with the formation of true brucite-like layers. LDHs can also be obtained with a Li-Al monovalent-trivalent and Co-Ti divalent-tetravalent associations. The single phase formation of hydrotalcite occurs, after proper selection of $M(II)$ and $M(III)$ ions. A wide variety of anions like inorganic anions ($CO_3^{2-}$, $SO_4^{2-}$, $NO_3^-$, $OH^-$, $CrO_4^{2-}$, $WO_4^{2-}$, $S_2O_3^{2-}$ etc.), isopoly anions ($V_{10}O_{28}^{2-}$, $Mo_7O_{24}^{2-}$ etc.), heteropoly anions ($PMo_{12}O_{40}^{3-}$, $PW_{12}O_{40}^{3-}$ etc.), complex anions ($Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $IrCl_6^{2-}$ etc.) and organic anions (carboxylates, porphyrins, pharmaceutically active functional anions and alkyl sulfates etc.) can be intercalated in the LDH layers.
1.4 Catalysis

Catalysis is one of the most important fields in chemistry, which has very good application in industrial research [20]. Catalyst can be defined as “a substance that alters the rate of attainment of chemical equilibrium without itself undergoing chemical change” and catalyst did not influence the position of equilibrium. If the rate of a forward reaction is speeded up in presence of a particular catalyst, the reverse reaction will likewise be facilitated to the same degree. A catalyst can also be defined as an entity that makes it possible for the reaction to proceed at rates high enough to permit their commercial exploitation on a large scale, resulting in economic benefits. In 1814, Kirchhoff noticed that acid catalyzed hydrolysis occurring in starch – a classic example of homogeneous catalysis. The first application of catalysis was done in 1820s by Dobereiner, who introduced “tinderbox” which was commercially used for the purpose of lightning fires and smoking pipes. A jet of hydrogen produced by zinc and sulphuric acid was directed on to the supported platinum where it catalytically combined with oxygen to yield gentle flame (Million tinder boxes sold in 1820). In 1836, Berzelius first introduced the term catalysis (comes from Greek word katalysis; meaning breaking down or loosening) endowed catalysts with mysterious quality. Followed by them several important industrial applications on catalysis found such as

- Industrial oxidation of HCl to Cl₂ using clay brick impregnated with cupric salt as catalyst (Deacon process 1871).
- Karlsruhe Fritz Haber prepared copious quantities of ammonia from nitrogen and hydrogen in presence of a reduced magnetite (Fe₃O₄) catalyst using high pressure apparatus (1909).
- Industrial synthetic production of methanol using zinc oxide – chromium oxide catalyst at 400 °C and 200 bar pressure (1923).
- Synthetic zeolites were first reported for the selective isomerization of hydrocarbons in 1960.
- Over a billion (10⁹) kilograms of fructose were produced in USA for soft drink from corn syrup using immobilized glucose isomerase as catalyst (1980).
Now more than 90% of chemical manufacturing processes in use throughout the world utilize catalysts in one form or another. Much of the food we eat and medicines we take, many of the fabrics and building materials that keep us warm and almost all the fuels that transport us by road, sea or air are being produced by heterogeneously catalyzed reactions.

A literature survey of layered materials, over the period of 2000–2006 (limiting to English as language), revealed that nearly 20,000 papers have been published on clays which includes layered perovskites (LP), pillared clays (PILC) and LDH materials, of which about 85% were dealing on catalysis. Among the publications dealing on catalysis, the percentage of patents was about 2% for LP, 26% for LDH and 6% for PILC. This evidences that the LP and PILC materials are still mainly at the lab-scale development stage, while LDH and especially clays find a broad range of application [4]. The presence of both Lewis and Bornsted type basic sites in LDHs and ability to host different metal ions extended its applications in both base catalyzed reactions and oxidation reactions [21].

1.4.1 Base catalysis

Base catalysts play a decisive role in a number of reactions essential for fine-chemical synthesis as compared to acid catalyst which finds applications in petroleum refining. Heterogeneous base catalysts are widely used in industrial research, due to easy recovery, recycling, atom utility and enhanced stability. Solid-base catalysts find application in reactions including isomerization, aldol condensation, Knoevenagel condensation, Michael condensation, oxidation and Si–C bond formation [22]. Base catalyzed condensation is one of the well known methods for C-C bond formation. Busca recently reviewed the basic properties of different solids which found application in industrial catalysis [23] and one among them is LDHs. Compared to other basic materials like sepiolite, zeolites and organic resins, LDH derived materials show improved thermal stability and diffusion resistance [24]. These materials on calcination (weight loss of up to 40 %) leads to formation of highly dispersed, large surface area and porous nano dimensional mixed metal oxides, which can be potentially used for many base catalyzed reactions [25].
The basic property of these materials was initially envisaged by Nakatsuka et al. [26], Reichle [27] and Laylock et al. [28], for catalytic polymerization and aldol condensation reactions. The basicity of LDH is affected by the calcination procedure, typically at 673–773 K and by structural and compositional parameters [28, 29]. Cations like Zn or Ni give less basicity than Mg; less basic catalysts are also obtained from Cl⁻ or SO₄²⁻ precursors than from CO₃²⁻ or OH⁻ containing materials [27] and the basicity also depends on the Mg/Al ratio [30, 31].

Corma et al. studied the basic property of the materials by carrying out the condensation of benzaldehyde with activated methylenic groups with different pKa values, in the presence of a Mg-Al LDH catalyst. They found that this material shows basic sites with pKa values up to 16.5, which normally uncommon among the other commercial basic zeolite material. In the use of zeolites as catalyst, the only reaction observed was Knoevenagel condensation, while on calcined LDHs showed other reactions like Michael-type addition and Claisen condensation, which requires stronger basic sites. The total amount of basic sites and their strength distribution in the material were determined by carrying out the Knoevenagel condensation reaction with methylenic groups of different pKa values in presence of increasing amount of benzoic acid. By increasing the Mg/Al ratio in the LDH, the number of basic sites with 9.0 ≤ pKa ≤ 13.3 increases, whereas the amount of basic sites within 13.3 ≤ pKa ≤ 16.5 decreases [32]. The correlation of the LDH basic properties with the Mg/Al ratio, however, is not always straightforward [27].

Yamaguchi et al. used MgAl mixed oxides derived from LDHs as catalyst for the synthesis of cyclic carbonates from epoxide and carbon dioxide (Fig 1.3). Mg-Al mixed oxides obtained by the calcination of hydrotalcites acted as efficient catalysts for the addition of CO₂ with various epoxides under mild reaction conditions [33] and mixed oxide with the Mg/Al ratio of 5 calcined at 400 °C showed the highest catalytic activity. Cooperative action of acid-base sites derived from the formation of Mg-O-Al bonds leads to higher activity.
CO₂ and NH₃ TPD experiments and FT-IR spectroscopy, using CO₂ and NH₃ as probe molecules on calcined LDHs showed the presence of strong O²⁻ Lewis basic sites, M²⁺ Lewis acid sites, M²⁺-O²⁻ pairs and OH⁻ Bronsted sites [34]. Sol-gel derived materials showed higher basic character than the co-precipitated materials. Different other synthetic procedures like microwave and sonication leads to materials with different basic characters. Homogenous particles of ~80nm average particle size and with higher defects was produced using sonication showed high basicity [35].

Kustrowski et al. studied the acidic and basic properties of the MgAl mixed oxides derived from LDHs with different interlayer anions using both NH₃ and CO₂ TPD [36]. These results showed that concentration of basic sites are in the order of CO₃²⁻ > Cl⁻ > HPO₄²⁻ > Terephthalate > SO₄²⁻ and the acidic sites are in the order of CO₃²⁻ > Terephthalate > Cl⁻ > HPO₄²⁻ > SO₄²⁻. Both CO₃²⁻ and Cl⁻ showed higher basic sites whereas HPO₄²⁻, SO₄²⁻ and terephthalate showed weak basic sites.

Kustrowski et al. also studied the variation of Mg/Al ratio over the acidic and basic property of the LDH using NH₃ and CO₂ TPD [37]. Materials calcined at different temperatures showed different acid base behaviours. For materials calcined at 550 °C the concentration of acidic sites are in the order of 3.5:1 > 3:1 > 4:1 > 2:1 Mg:Al ratios, whereas concentration of basic sites are in the order of 2:1 > 3:1 > 3.5:1 > 4:1.
Ebitani *et al.* showed that reconstructed LDH found to be active for the aldol reactions to produce α-hydroxy carbonyl derivatives in the presence of water and also can promote the aqueous Knoevenagel and Michael reactions using nitriles. The mechanism of the above unique catalysis of the reconstructed HT is discussed on the basis of the nature, strength, and amount of surface acid-base sites [38] given in Fig 1.4.

![Fig. 1.4 Mechanism on LDH surface (reproduced from ref. 38)](image)

Followed by them Chimenta *et al.* studied the effect of using mechanical stirring or ultrasound during reconstruction of the mixed oxides and showed that this leads to an enhancement in the catalytic activity. Modifications in the structure and basicity of the resulting materials, together with an increased surface area and improved accessibility to the active sites lead to high activity. Increasing the rehydration time during stirring or sonication also strongly affects the final catalyst and the performance of these materials has been disclosed for the epoxidation of styrene [39].

Onda *et al.* used activated hydrotalcites for the lactic acid production from D-glucose in flow reactors at 323 K under water media. The number of accessible Brønsted-base sites determined by the ion-exchange method with sodium salts, based on the OH/Al
ratio. The catalytic activity for the lactic acid production showed a linear increase with the number of the Bronsted-basic sites [40].

Zeng et al. showed that calcined LDH with Mg/Al molar ratio of 4.0 exhibited the highest catalytic activity in the synthesis of propylene glycol methyl ether from etherification of propylene oxide with methanol. The catalytic activity of the material was correlated with the amount of the basic sites determined by Hammett indicators [41].

Recently LDHs have been exploited for various base catalyzed transformations such as condensation [27, 42], double bond isomerization of allylic substrates such as eugenol and safrole [43-45] and dehydrogenation of 2-propanol [46].

1.4.2 Redox catalysis

The ability of different transition metal ions (Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Fe$^{3+}$ and Cr$^{3+}$ etc.) to be crystallized in LDH and potential surface for adsorption of different metals extended its application in redox catalysis. Functionalized anions can be intercalated into the interlayers which are otherwise difficult to incorporate in the two-dimensional sheets thereby creating new active centers for redox catalysis is another approach in this direction.

Ruthenium incorporated LDHs showed excellent activity for oxidation of allylic alcohol to aldehydes and ketones using molecular oxygen [47]. Alcohol reacts with Ru hydroxide of LDH to form alkoxide species and which undergoes β elimination to form a aldol product. Molecular oxygen reacts with remaining Ru-hydride species to generate the Ru-hydroxyl species on the hydrotalcite. In another application ruthenium grafted LDHs showed multifunctional catalytic activity in the one-pot synthesis of quinolines from 2-aminobenzyl alcohol and various carbonyl compounds via aerobic oxidation and aldol reaction [48] and also in the α-alkylation of nitriles with primary alcohols [49]. Kishore et al. reported the catalytic oxidation of isophorone to ketoisophorone over ruthenium supported MgAl-LDH [50].

Velu et al. synthesized the manganese incorporated LDH using co-precipitaion method and tested the liquid phase oxidation of toluene using tert-butyl hydroperoxide as oxidant [51]. Maximum conversion of 14.3% with 75% benzoic acid selectivity was
obtained. Choudhary et al. synthesized MnO$_4^-$ exchanged LDH through reconstruction method and studied the molecular oxygen catalyzed oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone [52].

Fe containing LDHs showed excellent catalytic activity for the reduction of 4-nitrotoluene to 4-aminotoluene using phenyl hydrazine or hydrazine as reducing agent [53]. Coq et al. showed catalytic reduction of nitriles over Co/Ni/Mg/Al LDH derived mixed oxides [54]. High activity of this catalyst is due to the bifunctional mechanism over the metal sites. Mg-Fe LDH showed excellent activity for the catalytic reduction of aromatic nitro compounds with hydrazine hydrate [55]. Recently iron (III) porphyrins immobilized on Mg–Al LDH modified with triethanolamine showed cyclohexane oxidation using iodosylbenzene as oxidant [56] and Fe (III)-Schiff base complex in a Zn-Al LDH was found to be an effective catalyst for the catalytic oxidation of cyclohexane using H$_2$O$_2$ as oxidant [57].

In LDH catalyzed oxidation, the basic property of the material activate either the substrate or oxidant giving rise to electrophilic attack on carbanions or nucleophilic attack with peroxyanions [58, 59]. Multi-metallic LDHs have been found to show high catalytic activity for the heterogeneous Baeyer–Villiger oxidation of various carbonyl compounds using a combination system of molecular oxygen and benzaldehyde [60]. LDHs with high basic character showed high activity for Baeyer–Villiger oxidation. Sn exchanged LDHs showed selective Baeyer–Villiger oxidation of ketones using hydrogen peroxide as oxidant [61].

Ni/Mg/Al LDH with high dispersion of nickel found to be the active catalyst for the partial oxidation of propane [62]. Choudhary et al. claimed that molecular oxygen was activated over NiAl-LDH and gave excellent catalytic activity for alcohol oxidation [63]. Followed by them Kawabata et al. showed that alcohol oxidation was accelerated by the presence both Mg and Ni sites together and proposed that the Ni(II) sites work as the active sites by activating molecular oxygen assisted by the Mg(II) sites as a base and simultaneously alcohol was activated by the Al(III) sites as an acid, resulting in an enhancement of the activity of the Mg2.5(Ni0.5)–Al LDH heterogeneous catalyst for alcohol oxidation [64]. NiAl-LDH also showed excellent activity for the solvent-free liquid-phase selective oxidation of ethylbenzene to acetophenone with 1 atm of molecular
Li et al. recently showed the Ni/Mg/Al catalyzed hydrogen production from ethanol steam reforming, the NiMgO solid solution phase exhibited high activity and stability for ethanol steam reforming [66]. Supported Ni nanoparticles via self-reduction of hybrid NiAl-LDH/C composites, exhibited excellent activity for catalytic growth of CNTs, which could be delicately tuned by varying the compositions of hybrid composites [67]. In another investigation CuMgAl-LDH showed high activity for the total oxidation of phenol [68].

Mastalir et al. synthesized the hydrophobic Pd nano particles incorporated LDH using ion exchange of nitrate containing LDH with Pd hydrosol stabilized by the anionic surfactant sodium dodecyl sulfate [69]. These materials showed excellent activity for selective semihydrogenation of alkynes. Albertazzi et al. used Pd/Pt supported on MgAl mixed oxides derived from LDH as catalyst for the hydrogenation and hydrogenolysis of naphthalene [70].

Hydrogen peroxide in presence of LDH leads to the formation of active hydrogen peroxide ion (HOO\(^{-}\)), which gives nucleophilic epoxidation of electron deficient olefins [71]. Synergism between the interaction of Co and Ru cations gave high activity of CoAlRu-LDH over molecular oxygen catalyzed oxidation of various alcohol (aromatic allylic, benzylic, secondary saturated alcohols) to the corresponding carbonyl compounds in high yields [72]. Several works are being published on hydroxylation of phenol using various transition metals containing multi-metallic hydrotalcites [73-76].

Zavoianu et al. synthesized molybdenum containing LDHs through ion exchange method and studied cyclohexene oxidation using H\(_2\)O\(_2\) [77]. The catalysts containing Mo\(_7\)O\(_{24}\)\(^{5-}\) species was more active for epoxidation and low Mo content (about 2.5–2.8\%) in the form of MoO\(_4^{2-}\) was more active for hydroperoxidation.

Recently Kaneda et al. used silver and copper nano particles supported on LDH for oxidant free alcohol dehydrogenation [78, 79]. It was also observed that Ag/LDH showed the highest chemoselectivity for the dehydrogenation of cinnamyl alcohol to cinnamaldehyde without hydrogen transfer or isomerization. Silver nanoparticles supported on LDH efficiently catalyzed the deoxygenation of styrene oxide derivatives into the corresponding alkenes using CO/H\(_2\)O as a reductant [80]. LDH supported gold nanoparticles acted as a reusable catalyst for synthesis of lactones from diols using
molecular oxygen as an oxidant under mild conditions [81] and lactonization of 1,4-butanediol gave $\gamma$-butyrolactone with an excellent turnover number of 1400. Au nanoparticles supported on Mg-Al-layered double hydroxide (Au/LDH) synthesized by ion-exchange and reduction showed excellent catalytic activity for alcohol oxidation [82]. Vasile et al. synthesized W containing LDHs through ion exchange method and studied the catalytic oxidation of thiophenes and thioethers using H$_2$O$_2$ as oxidant [83]. The catalytic activity depends on the nature of the W-containing anions present.

This shows the importance of working with LDH and LDH derived materials and superior properties of the materials can be obtained through deeper understanding of the synthesis methodology and post synthetic treatments.

2. Synthesis of LDH

2.1 Co-precipitation method

Mg–Al hydrotalcites are conventionally synthesized by co-precipitation of aqueous alkaline solutions of Mg and Al salts (nitrates or chlorides) at fixed pH under stirring and inert atmosphere (Fig. 1.5). Classically, an aqueous NaOH or KOH solution is used to adjust the pH and an aqueous Na$_2$CO$_3$ or K$_2$CO$_3$ solution is added as the carbonate source [84]. After ageing of the slurry, the resulting material is filtered and washed with deionised water and dried ($\sim$373 K). The ageing step may itself be used as a tool to change the properties of the final material. For example, microwave irradiations may be used during aging in order to provoke a reduction of the size of the particles, an increase in the specific surface areas and an increase in the basicity [85]. Hydrotalcites based on other metals (Co, Ni, Cu, etc.) can be synthesized in the same way by introducing the proper nitrate salt, [86, 87] however it is necessary to precipitate at a pH higher than that of pH of precipitation of metal hydroxides. Materials synthesized by this method has several advantages like high surface area, multiple metal ions containing LDHs can be synthesized simply by taking different metal nitrate precursors, highly dispersed metal
ions containing LDHs and crystallinity of the material can be tuned by varying the ageing time and temperature. Several tetravalent metal cations containing LDHs were also synthesized successfully using this method [88, 89].

### 2.2 Urea & hexamine hydrolysis methods

Urea on hydrolysis at high temperature releases ammonia which precipitates the metal cations in the synthesis of LDH.

![Fig. 1.6 SEM and particle size distribution of hydrotalcites synthesized at (a)100 °C, (b) 120 °C (c) 150 °C (reproduced from ref. 93)
The urea method was developed by Costantino and co-workers [90] has become very popular and has undergone several modifications. A typical synthetic procedure is as follows: An aqueous stock solution of urea (1.0 M), magnesium chloride (0.1 M) and aluminium chloride (0.1 M) are mixed together at the molar Mg/Al/urea ratio of 4:1:10 with magnetic stirring at room temperature. The concentrations of the components in the starting solutions are $4 \times 10^{-3}$, $1 \times 10^{-3}$, and $1 \times 10^{-2}$ M for MgCl$_2$, AlCl$_3$ and urea respectively.

Then the homogeneous solution is transferred into a Teflon-lined autoclave and heated ranging from 100 to 180 °C for different time intervals. After cooling to room temperature, the solid precipitate is collected by centrifugation and washed with deionized water subsequently.

In aqueous solutions, urea decomposes on heating to give ammonia and HNCO:

$$\text{CO(NH}_2\text{)}_2 \rightarrow \text{NH}_3 + \text{HNCO}$$

In acidic or neutral media, HNCO is converted into CO$_2$, and ammonia takes up a proton to give NH$_4^+$

$$\text{HNCO} + \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{CO}$$

$$\text{NH}_4 + \text{H}^+ \rightarrow \text{NH}_4^+$$

Both reactions lead to consumption of H$^+$ and hence increase the pH of the medium [91, 92] Urea hydrolysis is found to be one of the best method to produce the highly crystalline LDHs [93]. Size and morphology controlled LDHs (Fig. 1.6) obtained through this method [94] prompted us to synthesize various materials using this synthesis methodology.

Hexamethylenetetramine (HMT) also called as hexamine, found to hydrolyze at higher temperature in aqueous solution releasing ammonia, which makes the solution alkaline. In a typical procedure metal nitrates or chlorides with hexamine in molar ratio of $(\text{M}^{2+} + \text{M}^{3+}) : \text{HMT}$ with 0.15 M : 0.45 M were taken in a Teflon inner vessel with a stainless steel outer vessel and allowed to react at 140 °C for 24 h. Pioneer synthesis of LDH using hexamine was done by Iyi et al. [95] and they have achieved hexagonal crystalline MgAl-LDH. Hexamine on hydrolysis gives ammonia and formaldehyde, this
formaldehyde on reductive amination with ammonia (Leuckart reaction) gives formic acid and which leads to carbonate containing LDH. It was also proposed that slow release of ammonia leads to highly crystalline hexagonal shape LDH. Followed by Iyi several works were reported on the synthesis of LDH as well as brucite-like mixed hydroxides using HMT hydrolysis [96-98].

2.3 Sol-gel method

The sol–gel synthesis of materials based on the hydrolysis and condensation of molecular precursors is used to prepare a wide range of inorganic materials. This procedure gives sols and these sol colloidal particles suspended in a liquid, progress through a gelation process to form two interpenetrating networks between the solid phase and the solvent phase. Although the roots of sol–gel chemistry can be traced to the 19th century, only during the past 30 years this field witnessed remarkable growth in its sophistication and applications.

Fig. 1.7 TEM images of sol-gel LDHs: (a) MgAl, (b) NiAl-A, (c) NiCoAl, (d) NiAl-N (reproduced from ref. 104)

This technique limits the amount of alkaline required and thus sometimes preferred for industrial synthesis processes [99, 100]. The synthesis procedure is as
follows: Magnesium ethoxide was dissolved by acid hydrolysis with HCl (35% in water) or with HNO₃ (65%) into 120 ml of ethanol; the dissolution was refluxed at 353 K, under constant stirring. A second solution, containing a suitable amount of aluminium acetylacetonate in 80 ml of a mixture acetone/ethanol 1:1 was added, in order to obtain Mg²⁺/Al³⁺ ratios in the range 3±6, was then slowly added, and the pH was adjusted to about 10 with NH₄OH. The solution was refluxed at 353 K up to 17 h, until the gel was formed.

Gel was then repeatedly washed with ethanol and dried overnight at 353 K and gel can also be exchanged with Na₂CO₃ aqueous solution to get carbonate in the interlayers of LDH [101]. Sol-gel synthesis of ZnAl-LDH without impurity phase was prepared [102] which was not possible previously. Recently, Valente et al. synthesized the novel multi-metallic LDHs with nanocapsular morphology (Fig. 1.7) using sol-gel method [103, 104] and one of the advantage here is that these material shows high surface area than both co-precipitation and urea/hexamine hydrolysis materials.

2.4 Miscellaneous methods

Apart from these three important largely attempted methods, several other methods are also available. Duan et al. synthesized LDH nanomaterials with uniform crystallite size using separate nucleation and aging steps [105] and explored these materials for various applications. NiAl-LDH was synthesized by Mizuhata et al. using liquid phased deposition (LPD) using aluminium metal [106], highly stable LDH obtained through this method can be applied in nickel–metal hydride batteries. Davila et al. synthesized MgAl-mixed oxides using combustion method using sugar as fuel [107] and which was further converted to LDH using memory effect. Recently O’Hare synthesized LDHs with unique morphologies using reverse microemulsion method [108], the surfactant/water ratio enables them obtain nanometer sized LDH platelets typically with a 40-50 nm diameter and 10 nm thickness. MgAl and ZnAl-LDH were synthesized using lazer ablation in water [109] and they can also be synthesized through electrochemical methods [110].
3. LDH derived materials

3.1 Mixed metal oxides

Thermal calcinations of LDHs materials results in 30-45% weight loss leads to the formation of non-stoichiometric mixed metal oxides with characteristic properties, which are exploited as active catalysts for many important catalytic transformations. Thermogravimetric analyses (TGA) of LDHs reveal successive steps of weight loss during temperature rise. In the range of 343–553 K first step is attributed to the loss of adsorbed and interlayer water. The second step in the 553–1073 K range accounts for the loss of hydroxyl groups from the brucite-like structure. Multi weight-loss steps can be detected for hydrotalcites that contain carbonate and nitrate counter ions attributed to the evolution of the corresponding CO$_2$ and NO$_x$ molecules [111]. Fresh HTs exhibit poor basic properties, because adsorbed water hinders the access to basic sites on the surface [112]. The nature of the surface basic sites varies with severity of pre-treatment conditions. Besides removal of water and carbon dioxide, rearrangement of surface and bulk atoms occurs during pre-treatment, which changes the number and nature of the basic sites with increasing pre-treatment temperature. Therefore, the optimum pre-treatment temperature varies with the type of reaction [113]. Highly dispersed mixed metal oxides obtained through LDHs showed superior properties as compared to other processes. Cu/ZnAlO obtained through LDH showed excellent catalytic property towards oxidative methanol reforming [114]. CuMgAlO obtained through CuMgAl-LDH showed high activity for aqueous phase ozonation of phenol and oxalic acid [68]. Recently Duan et al. showed that ZnO based mixed metal oxides obtained through the calcinations of ZnAl-LDH showed superior UV-blocking properties to both commercial ZnO and a physical mixture of ZnO and ZnAl$_2$O$_4$ [115].

3.2 Rehydrated LDH

Calcined LDHs can be reconstructed back to a layered structure if put in contact with water and appropriate anions [21]. This property is called retro-topotactical transformation and is also known as the “memory effect” [116-118]. Reconstruction process of the LDH (Fig. 1.8) can also be followed by XRD (Fig. 1.9): by the appearance of diffraction lines characteristic of the hydrotalcite.
The memory effect depends on the calcination temperature of the parent LDH; high calcination temperature leads to reduced memory effect \[119\] and the calcination temperature has to be lower than that which leads to phase segregation (spinel). Rehydration results in an decrease of the specific surface area with respect to the corresponding calcined LDH \[120\].

Nature of divalent cation also has considerable influence on the reconstruction of LDH \[121\]. Reconstruction of decomposed hydrotalcites is reported to enhance the catalytic activity in several base-catalyzed reactions, for which OH\textsuperscript{−} acts as active Brønsted basic site. Reconstructed MgAl-LDH showed higher catalytic activity for aldol condensation between benzaldehyde and acetone compared to as-synthesized and calcined LDHs \[122\]. Recently Gunawan and Xu synthesized spherical hollow nano spheres of LDH using reconstruction behavior \[123\] and Duan et al. have done erasable nanoporous antireflection coatings based on the reconstruction effect of layered double hydroxides \[124\].
3.3 LDH composite materials

Recently, polymer/layered double hydroxide (LDH) nanocomposites have attracted great interest in the field of materials chemistry because of their novel mechanical, optical, fire retardant and thermal properties. Generally, the performance of these unique properties mainly depends on the dispersion degree of LDH layers in the polymer matrix [125, 126]. Thus, it is required that the LDH layers should have hydrophobic surfaces and completely exfoliated structures to reach a stable homogeneous dispersion in the polymer matrix. However, because of their strong interlayer electrostatic interactions and significantly hydrophilicity, LDHs have very tight layer stacking and it is very difficult to exfoliate these layers. There are three principal options to obtain a polymer intercalated LDHs,

- Direct intercalation of extended polymer chains in the LDH lattice.
- Transformation of the host material into a colloidal system and precipitation in the presence of polymer.
- Intercalation of the monomer molecules and subsequent in situ polymerization.

Recently, several efforts have been made to synthesize polymer intercalated LDH, in which the most common strategy is the pre-intercalation of pristine LDHs by organic materials, such as sodium dodecyl sulfate (SDS) [127, 128]. Through this method, the organo-modified LDHs are endowed with hydrophobic characteristics ready to be intercalated into polymer chains. However, the introduction of these organic materials with small molecules will deteriorate some properties of the nanocomposites especially when the LDH content is high. Thermal properties of the polymer/LDH nanocomposites were sharply decreased when the LDH loadings were increased from 2–5 wt% to 10–20 wt%. This is because that the charged layers are no longer stable enough during the thermal degradation when a relatively large content of polymer is introduced along with the LDH layers [129-131]. On the other hand, most recently, living radical polymerization (LRP) has been proved an efficient strategy for preparing well-dispersed and high quality polymer/layered inorganic nanocomposites, such as atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT) polymerization [132, 133]. Qu et al. synthesized polystyrene (PS)/layered double
hydroxide (LDH) nanocomposites by in situ reversible addition–fragmentation chain transfer (RAFT) polymerization using the multifunctional RAFT agent SBC, sodium 4-(benzodithioyl)-4-cyanopentanoic salt with enhanced thermal properties [134].

4. Physico-chemical characterization

4.1 Powder X-ray diffraction (PXRD) studies

The powder X-ray diffraction (PXRD) is a diagnostic tool for the phase identification of these compounds. The PXRD patterns of all clay minerals possess layered structure generally with sharp, symmetric peaks at lower angels (2θ) and broad, asymmetric peaks at higher diffraction angles. The thickness of the brucite-like layers (4.8 Å) [135], and the interlayer space varied depending on the size and orientation of anion (2.8 Å shows presence of carbonate anion with its molecular plane parallel to the brucite-like layers). Lattice parameter ‘a’ is the distance between the neighboring cations in the brucite-like layers, which can be estimated from the ionic radii of the cations in the brucite-like lattice [86] and their molar fractions in the samples while the parameter ‘c’ is three times the distance between the adjacent brucite-type layer, controlled mostly by the size (and orientation) of the interlayer anion and the electrostatic forces operating between the interlayer anion and the layers. PXRD was carried out in a Philips X’Pert MPD system using Cu Kα radiation (λ = 1.5406 Å). The operating voltage and current were 40 kV and 30 mA, respectively. A step size of 0.04° with a step time of 2 seconds was used for data collection. The data were processed using the Philips X’Pert (version 2.2e) software. Identification of the crystalline phases was made by comparison with the JCPDS files [136].

4.2 Fourier transformed infrared (FT-IR) spectroscopy

Although infrared (IR) analysis is not a primary tool for the characterization of LDHs, yet it has been routinely used especially for the identification of the foreign anions in the interlayer space and its interaction with the brucite-like sheets. Besides that, information about the type of bonds formed by the anions and about their orientation can also be discerned.
FT-IR absorption spectra of the samples were recorded in a Perkin-Elmer FT-IR spectrometer (Model-FT-1730). The powdered samples were ground with KBr in 1:20 ratio and pressed into pellets for recording the spectra. 64 spectra (recorded with a nominal resolution of 4 cm\(^{-1}\)) were accumulated and averaged to improve the signal-to-noise ratio.

4.3 Thermogravimetric analysis (TGA)

The thermal behavior of LDHs is generally characterized by two transitions: The first one being reversible, endothermic, at low temperature corresponds to the loss of interlayer water, without collapsing the structure and the second one endothermic, at higher temperature is due to the loss of hydroxyl group from the brucite-like layer as well as of the anions. The nature of these two transitions depends on many factors such as: M(II)/M(III) ratio, type of anions, low temperature treatment (hydration, drying etc.) heat treatment (in case of oxidizable element such as Cr(III)).

Thermogravimetric analysis (TGA) was carried out in Mettler TGA/SDTA 851\(^e\) and the data were processed using Star\(^e\) software, in flowing nitrogen in a flow rate of 60 ml/min and at a heating rate of 10 °C/min.

4.4 Elemental analysis

Elemental chemical analyses of the samples were determined using inductively coupled plasma emission spectrometry (ICPES; Perkin Elmer, OES, Optical 2000 DV). The samples were digested in minimum amount of concentrated HNO\(_3\) and diluted using milli Q water <10 ppm and analyzed.

4.5 Adsorption measurements (surface area and pore volume)

Specific surface area and pore size analysis of the samples were measured by nitrogen adsorption at -196 °C using a sorptometer (ASAP-2010, Micromeritics). The samples were degassed under vacuum at 120 °C for 4 h prior to measurements in order to expel the interlayer water molecules. The BET specific surface area (SA) was calculated by using the standard Brunauer, Emmett and Teller method [137] on the basis of adsorption data. Pore volume (PV), micropore area and mesopore area were determined.
by using the t-plot method of De Boer [138]. Average pore size distributions (APD) were calculated from the desorption branch of the isotherms using the Barret, Joyner and Halenda (BJH) method [139].

4.6 Scanning electron microscopy (SEM)

The electron microscopic study has been done with scanning electron microscope (Leo series VP1430) equipped with Oxford instruments EDX facility, having silicon detector. The samples were coated with gold using sputter coating before analysis to avoid charging effects during recording. Analyses were carried out with an accelerating voltage of 20 kV and a working distance of 17 mm, with magnification values up to 100,000x.

4.7 Transmission electron microscopy (TEM)

Transmission electron microscope (TEM) images were obtained with a JEOL JEM-2100 microscope with acceleration voltage of 200 kV using carbon coated 200 mesh copper/gold grids. The samples were ultrasonically dispensed in ethanol for 5 min and deposited onto carbon film using capillary and dried in air for 30 min. Elemental mapping and analysis were done using STEM mode of HRTEM using an energy dispersive X-ray (EDX) detector (Oxford EDX detector: Model INCAx-Sight).

4.8 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were acquired on a VG Microtech Multilab ESCA 3000 spectrometer using a non-monochromatized Mg Kα, X-ray source (1253.6 eV) on in situ scraped fresh catalyst pellets and powder samples of spent catalysts. Base pressure in the analysis chamber was maintained in the range of 3–6×10⁻¹⁰ Torr. The error in the reported BE values is ±0.1 eV [140].

4.9 Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) measurements were done using Autochem-2920 series. Prior to TPR analysis, the samples were heated at 200 °C under nitrogen flow and cooled to room temperature. TPR studies were carried out by passing
10% H₂ in argon. Flow rate of the gas and amount of the catalyst were calculated as reported by fixing the characteristic number $K = 100$ [141]. The temperature of the catalyst was increased at a heating rate of 10 °C/min from 50 to 800 °C.

4.10 Nuclear magnetic resonance (NMR) & Mass spectrometry (MS)

FT-NMR data were recorded using a BRUKER DPX-200 NMR spectrometer at 200 MHz using TMS as standard and CDCl₃ as solvent. High-resolution mass spectrometry (HRMS) analyses were performed using electrospray ionization (ESI+) technique on a Waters Q-TOF micromass spectrometer.
5. Scope and objectives of the work

The potential application of LDHs and their derived materials for functional nanocomposites or nano structures, sensors, fire retardants, films and materials having electrochemical response attracted our research on LDHs. High surface area, acid-base property, ability to accommodate different metal cations homogeneously in the layer and improved basic property through memory effect promises these materials for catalysis. Synthesis methodology has profound influence on the final properties of LDHs; hence there is great scope to synthesize LDHs using different/novel synthetic procedures and study their properties. In this thesis, chapters II & III discuss about the synthesize of cobalt containing LDHs, owing to their good electrochemical behavior and application in catalysis, using different ammonia releasing agents like urea and hexamine at different hydrolysis temperature and hydrothermal conditions. It also covers the synthesis of delaminated LDH and morphologically different cobalt carbonate materials using novel synthetic route. Recently copper containing LDHs showed potential application in oxidation reaction; however interaction of copper with other divalent metal ion and mechanism of the oxidation was not studied in detail. Chapters IV & V discuss the oxidation behavior of copper containing LDHs. Homogeneously dispersed copper containing LDHs with different co-bivalent ions are synthesized by co-precipitation method and their hydroxylation behavior is studied for benzene and phenol to delineate the interaction of different co-bivalent ions on the catalytic activity. Sequential or concomitant reactions find application in the greener production of industrially important chemicals. Due to the tunable basic and redox properties, LDHs can potentially be applied for green catalytic processes. Chapters VI & VII discuss the multifunctional property of LDHs. LDHs are explored for the multi-component synthesis of precursors for liquid alkanes and Hantzsch pyridines. Further, wherever possible structure property relationship is deduced.

The objectives of the present thesis contain the following:

- Synthesis of delaminated LDH: A facile two step approach.
- Synthesis of CoCO₃ and Co₃O₄: Soft chemical approach using LDH as precursor.
- Hydroxylation of benzene to phenol over copper containing LDHs.

- Hydroxylation of phenol to catechol and hydroquinone over copper containing LDHs.

- Liquid fuels from renewable using LDHs derived materials as multifunctional catalyst in water.

- Hantzsch pyridine synthesis of dihydropyridines using LDHs as solid base.
6. References


L. Perioli, M. Nocchetti, V. Ambrogi, L. Latterini, C. Rossi, U. Costantino,
F. Prinetto, G. Ghiotti, P. Graffin, D. Tichit, Microporous Mesoporous Mater., 39
D. Tichit, O. Lorret, B. Coq, F. Prinetto, G. Ghiotti, Microporous Mesoporous Mater.,
80 (2005) 213.
J. S. Valente, M. S. Cantu, J. G. H. Cortez, R. Montiel, X. Bokhimi, E. Lopez-
V. Davila, E. Lima, S. Bulbulian, P. Bosch, Microporous Mesoporous Mater., 107
133  N. Salem, D. A. Shipp, Polymer, 46 (2005) 8573.