

LAYERED DOUBLE HYDROXIDES FOR THE SYNTHESIS OF ORGANIC COMPOUNDS

Submitted in partial fulfilment of the requirements for the award of

Master of Science Degree in Chemistry

By

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SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)

Accredited with Grade "A" by NAAC

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **GAYATHRI A (41910007)** who carried out the project entitled "**LAYERED DOUBLE HYDROXIDES FOR THE SYNTHESIS OF ORGANIC COMPOUNDS**" under our supervision from November 2022 to May 2023.

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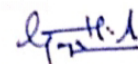
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DECLARATION

I **GAYATHRI A (41910007)**, hereby declare that the Project Report entitled "**LAYERED DOUBLE HYDROXIDES FOR THE SYNTHESIS OF ORGANIC COMPOUNDS**" done by me under the guidance of **Dr.V.KAVITHA, M.Sc.,M.Phil,Ph.D.,** Professor, Department of Chemistry at **Sathyabama Institute of Science and Technology, Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai – 600119** is submitted in partial fulfillment of the requirements for the award of Master of Science degree in Chemistry.

DATE **08-05-2023**

PLACE **CHENNAI**



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ACKNOWLEDGEMENT

I am pleased to acknowledge my sincere thanks to Board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

I convey my thanks to **Dr. Rekha Chakravarthi, Associate Professor and Dean School of Science and Humanities** and **Dr. J KARTHIKEYAN, Head, Dept. of Chemistry** for providing me necessary support and details at the right time during the progressive reviews.

I would like to express my sincere and deep sense of gratitude to my Project Guide **Dr.V.KAVITHA, Professor**, Department of Chemistry for their valuable guidance, suggestions and constant encouragement paved way for the successful completion of my project work.

I wish to express my thanks to all Teaching and Non-teaching staff members of the Department of Chemistry who were helpful in many ways for the completion of the project.

A.GAYATHRI.

ABSTRACT

Ca-Al were obtained by thermal decomposition of the corresponding layered double hydroxides (LDH) precursors and used as catalysts for Claisen-Schmidt reaction of ketones and aldehydes. The co-precipitation method, which combines aqueous solutions of CaCl_2 and AlCl_3 under regulated circumstances, is used in the synthesis process. The final LDHs are characterized using a variety of methods, such as X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). In-depth reviews of the structural traits of CaAl-LDH phases, the underlying mechanism for chloride removal, and the possible removal rate and capacity in the current work were conducted.

Keywords: LDH, XRD, FTIR, Calcined, Uncalcined

TABLE OF CONTENTS

ABSTRACT	v
LIST OF TABLES	viii
LIST OF FIGURES	viii
1. INTRODUCTION	1
1.1 LAYERED DOUBLE HYDROXIDES	1
1.2 PROPERTIES OF LDH	5
2. LITERATURE SURVEY	10
3. AIM AND SCOPE	16
3.1 AIM	16
3.2 SCOPE	16
3.3 OBJECTIVE OF STUDY	16
4. MATERIALS AND METHODOLOGY OF LDH	17
4.1 MATERIALS AND METHODS OF LAYERED DOUBLE HYDROXIDES	17
4.1.1 MATERIALS	17
4.2 SYNTHESIS OF LAYERED DOUBLE HYDROXIDES	17
4.3 STRUCTURE OF LAYERED DOUBLE HYDROXIDE	19
4.4 EXPERIMENTAL METHODOLOGY	19
4.4.1 CO-PRECIPITATION METHOD	19
4.4.2 CO-PRECIPITAION BY ADDITION	19
4.5 DOUBLE HYDROXIDE PREPARATION	20
4.5.1 CALCIUM CHLORIDE & $AlCl_3$ IN NaOH (CALCINED)	20

4.5.2 CALCIUM CHLORIDE & AlCl_3 IN NaOH / Na_2CO_3 (UNCALCINED)	21
4.5.3 CALCIUM CHLORIDE & AlCl_3 IN NaOH / Na_2CO_3 (CALCINED)	21
4.6 CHARACTERIZATION OF LAYERED DOUBLE HYDROXIDES	22
4.6.1 X-RAY DIFFRACTION	22
4.6.2 FOURIER TRANSFORMER INFRARED SPECTROSCOPY	24
5. RESULTS AND DISCUSSION	26
5.2 CHEMICAL REACTIONS	28
5.2.1 LDH REACTING WITH CINNAMALDEHYDE	28
5.2.2 LDH REACTING WITH METHYL ETHYL KETONE	29
5.2.3 LDH REACTING WITH ETHYL ACETO ACETATE	30
5.3 CLAISEN SCHMIDT REACTION WITH ALDEHYDES AND KETONES	31
6. SUMMARY AND CONCLUSION	32
REFERENCES	33

LIST OF TABLE

TABLE.NO	TITLE	PAGE.NO
5.1.1	FTIR of Ca-Al LDH in NaOH and Na ₂ CO ₃	27

LIST OF FIGURES

FIGURE.NO	TITLE	PAGE.NO
1.1.1	Structure of Pyroaurite	2
1.1.2	Structure of Hydrotalcite	2
1.1.3	Layered Double Hydroxides	4
1.2	Various applications of LDH	7
4.1	Structure of layered double hydroxide (LDHs).	17
4.4	Co-Precipitation	20
4.5	Double Hydroxide Preparation	21
4.5.3	Ca-Al LDH is kept in muffle furnace for calcination	22
4.6.1	Schematic representation of Bragg's law	23
4.6.2	Schematic representation of FTIR	24
5.1	XRD GRAPH FOR 1:1, 1:2, 1:3 RATIO	26
5.1.1	FTIR GRAPH FOR 1:1, 1:2, 1:3 RATIO	27
5.2.1	LDH Reaction with Cinnamaldehyde	28
5.2.2	LDH Reaction with Methyl Ethyl Ketone	29
5.2.3	LDH Reaction with Ethyl Aceto Acetate	30

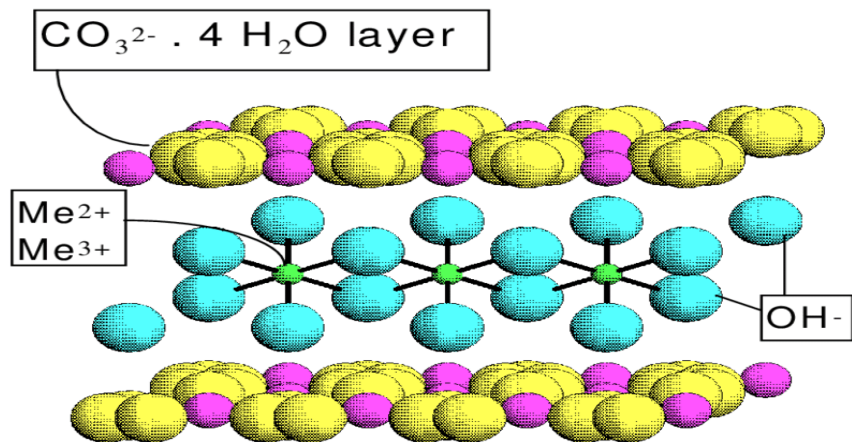
CHAPTER 1

INTRODUCTION

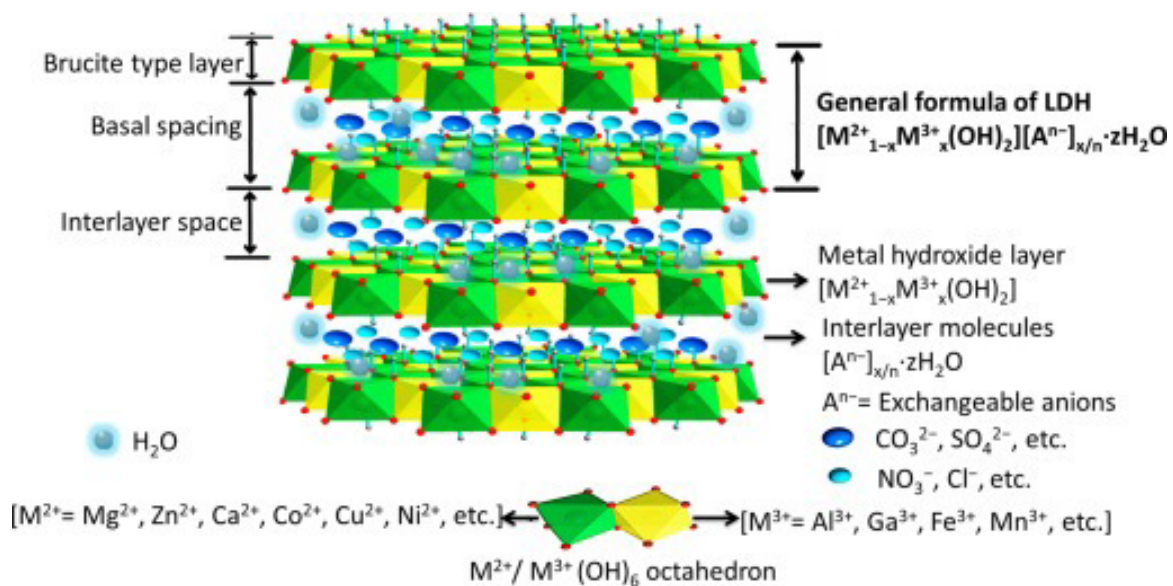
1.1 LAYERED DOUBLE HYDROXIDES

Layered double hydroxides (LDHs) have been known for a very long time. Around 1842, naturally forming LDHs minerals were discovered in Sweden. Crushing these minerals leads to a white powder similar to talc. These materials were first synthesized by a German scientist, W. Feithnecht (1942), through reaction between dilute solutions of metals with bases, which he named “doppelschichtstrukturen” or double-sheet structure. The LDHs are also known as hydrotalcite-like compounds (HTLCs). Hydrotalcite (HT) is a hydroxycarbonate of magnesium and aluminium which occurs in nature in foliated and contorted plates or fibrous masses. During the discovery of hydrotalcite another hydroxycarbonate of magnesium and iron was found, which was called pyroaurite.

Pyroaurite was later recognized to be isostructural with hydrotalcite and other minerals containing different elements, all of which were recognized as having similar features. Hydrotalcites have been studied for their use as catalysts and precursors to various other catalysts as early as 1970. Allman and Taylor studied single crystal X-ray diffraction on mineral samples which revealed the main structural entities of LDHs and disproved Feitknecht’s theory. These studies shows that the two cations were in fact located in a single layer and the interlayers were composed of water and carbonate ions.



1.1.1 Structure of Pyroaurite



1.1.2 Structure of Hydrotalcite

Although the main entities of LDHs have been elucidated, Evans and Slade have suggested that several intrinsic details still remain to be fully understood. These include the possible stoichiometric range and composition, and the position and arrangement of metals within each cationic layer. Prior to the study by Evans and Slade, Miyata and Okada described many structural features of LDHs/HTLCs which have different guest anions.

Layered double hydroxide materials appear in nature and can be readily prepared in the laboratory. In nature they are formed from the weathering of basalts or precipitation in saline water. Unlike clays, however, layered double hydroxides are not discovered in large, commercially exploitable deposits. The LDHs have been prepared using many combinations of divalent and trivalent cations including magnesium, aluminium, zinc, nickel, chromium, iron, copper, indium, gallium and calcium.

Due to their potential applications, LDHs have received considerable attention such as in catalysis, drug delivery systems and bio sensors. Besides, it has also been used in pharmaceutical preparation, organic synthesis and also in environmental protection. Ca–Al LDH, also called hydrocalumite.

Calcium aluminate-layered double hydroxides (CaAl-LDH) phases are capable of removing chlorides induced by chemisorption mechanism; thus, the phases have potential applicability as an adsorbent. The structural characteristics, chloride removal mechanism, synthesis methods, and potential chloride removal rate and capacity of CaAl-LDH phases in the present study were thoroughly reviewed [Gwangmok Kim] . The present paper provides in-depth information to adopt CaAl-LDH phases as an adsorbent for the removal of chlorides.

The layered double hydroxides (LDHs) consist of brucite-like layers, also known as anionic clays, and are broadly utilized in the field of catalysis and anion exchange processes. LDHs are composed of cationic metal-containing layers with

charge-balancing hydrated anions in the interlayer spaces, with the general formula $[M^{2+}(1 - X) M^{3+}(X) (OH)_2] X^+ (A^{n-}) X/n.mH_2O$, where M^{2+} and M^{3+} represent bivalent (Cu^{2+} , Ca^{2+} , Mg^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} .) and trivalent cations (Al^{3+} , Fe^{3+} , Ga^{3+} , Cr^{3+} .), respectively, whereas the A^{n-} is the interlayer (Cl^- , Br^- , NO_3^- , I^- , OH^- , SO_4^{2-} .) anion with coulombic charge n , and x represents the molar ratio of divalent to trivalent cations, which is generally in the order of 2.0–6.0.

A diagram of LDH represented is shown in **Figure 1.1 (c)**. A wide range of distinctive countercharge anions can be intercalated into the LDH structure, including natural and inorganic species, the most common being halides (chlorides) and oxyanions (carbonates, nitrates).

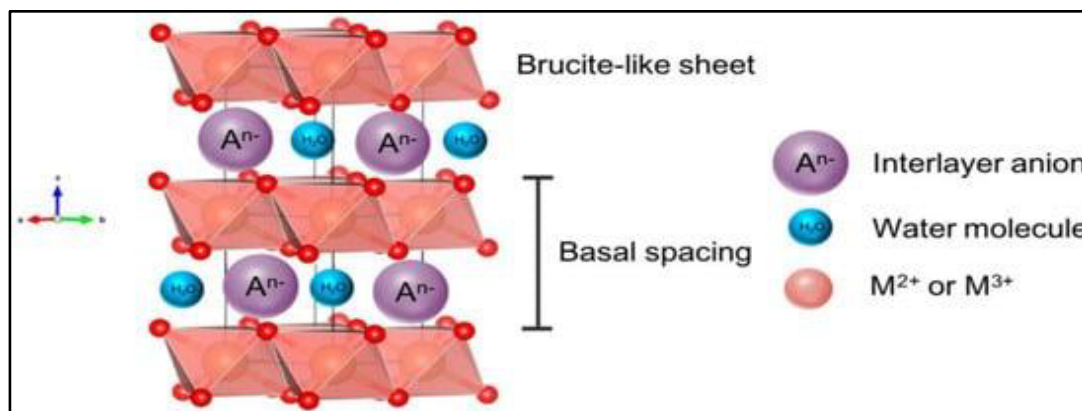


Figure 1.1.3 Layered Double Hydroxides

LDHs can be synthesized by different techniques depending on the requirements of the final product, such as phase purity, high crystallinity, and porosity. The varied combinations of metals and anions can be utilized to acquire desired properties. LDHs bring about an enormous class of isostructural materials with tunable physicochemical characteristics. Various direct synthetic techniques, such as coprecipitation, hydrothermal, urea, sol–gel, have been deployed for the preparation of

LDH and LDH-containing hybrids.

Coprecipitation and hydrothermal methods are the most widely accepted methods due to ease of synthesis as well as separation. The presence of exchangeable interlayer anions in the LDH is responsible for adsorptive removal of charged contaminants of wastewater.

Because of their tunable anion exchange capacity, LDHs are exceptionally useful for various applications, such as sorbent materials for a wide variety of pollutants covering inorganic species, such as oxyanions, metals, and phosphate, and organic pollutants, such as pesticides, herbicides, and dyes, among others.

1.2 PROPERTIES OF LDH:

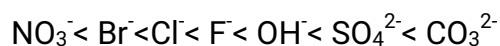
Layered double hydroxides (LDHs) display unique physical and chemical properties close to those of clay minerals. Some interesting properties of these materials summarized by Del Hoyo are:

- High specific surface area ($100 \pm 300 \text{ m}^2/\text{g}$)
- Memory effect
- Anion exchange capacities
- Synergistic effects.

The LDHs exhibit anion mobility, surface basicity and anion exchangeability due to their positively charged layered structure. The anions and water, which fill the interlayer space, are labile. Therefore a variety of inorganic and organic anions can be intercalated in the interlayer of LDHs through anion exchange reactions. The mixed metal oxides obtained on calcination of LDH usually exhibit properties such as high surface area, surface basicity and formation of homogeneous mixture with small

crystallite size when heated to higher temperature. The LDHs as well as the oxides obtained from them exhibit excellent catalytic activity. Structure reconstruction, or so called “memory effect,” is another important property of LDHs which is unique to this class of layered solids. Structure reconstruction is usually achieved by first decomposing the LDH at suitable high temperature followed by treating the resultant mixed metal oxides with a solution containing a suitable anion. These materials have a high capacity for adsorbing anions as well as cations. Magnetic properties of the LDHs depend on the space between the layers.

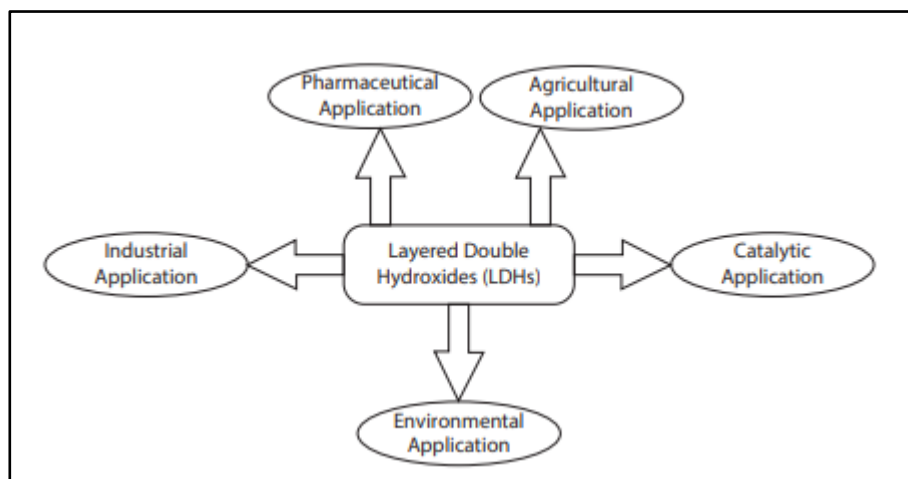
This space can be adjusted by insertion of organic anions with different chain lengths. This suggests that these hybrid materials would work as tunable magnets. The LDHs intercalated with long-chain surfactant molecules such as dodecyl sulphate have the ability to swell in organic solvents. This property of delamination is exploited in the preparation of monolayers, which are used extensively in the synthesis of nano hybrids and nano composites. The interlayer anions present in LDHs can be exchanged by other anions. The order of preference for some common inorganic anions is as follows:



NO_3^- is an anion which can be easily replaced by a more strongly held one like CO_3^{2-} . Therefore when preparing precursor for interaction, nitrate salts are preferred and CO_3^{2-} is tried to be kept away. The interaction involves a guest molecule that is introduced into the host without affecting the structure of the host. Upon interaction of the guest molecule, the existing ion is replaced. The interlayer anions weakly bonded to hydroxide layers (e.g., NO_3^- , Cl^-) can be exchanged more easily.

Layered double hydroxides (LDHs) represent one of the most technologically promising materials as a consequence of their low cost, easy preparation and the large number of composition variables that can be used. At present, a great deal of applications of LDHs in the field of heterogeneous catalysis, covering a wide range of areas, have made substantial progress, especially in the past decade. There are many possible applications of LDHs, not only as catalysts but also as scavengers of ions in water

purification. Their applications in drug delivery systems are also well known. Some possible applications of LDHs.



1.2 Various applications of LDH

CATALYTIC APPLICATIONS:

Due to their flexible composition, the interest in layered double hydroxide materials has increased over the last decade. They are a relatively easy to synthesize, inexpensive, versatile and potentially recyclable source of a variety of catalyst supports, catalyst precursors or actual catalysts. The use of LDH materials in the field of catalysis is well known and has been reported for basic catalysis (e.g., polymerization of alkene oxide, aldol condensation, transesterification reactions, etc.), reforming of hydrocarbons with H_2O , hydrogenation (production of methane, alcohols, paraffins, olefins, etc.), oxidation reactions, and support for Ziegler-Natta catalysts during polymerization of olefins etc.

AGRICULTURAL APPLICATIONS:

Layered double hydroxides possess excellent potential as green carrier for plant nutrients, pesticides and growth regulators and as active principle in animal feeds. However, not much attention has gone into exploring the full potentiality of LDHs. They are one of the idealized inorganic materials for a wide range of agricultural fields not only because their framework can be composed of plant nutrients, but also because their structure offers charming features such as accommodation and controlled release of various active anionic agro-substances, high buffering capacity, high water retention ability and acid neutralizing potential [Amita Jaiswal].

PHARMACEUTICAL APPLICATIONS:

Pharmaceutical applications of LDHs mainly depend on the acid buffering effect and anion exchange property. LDH-derived antacid and antipeptic are representative of their applications in pharmaceuticals. Powdered LDHs have been demonstrated to be one important type of green carrier or host for genes and drugs due to the excellent biocompatibility and nontoxicity or low toxicity. MgAl-LDH is used as an important component of drugs, or as nano carrier for delivery of drugs and genes into cells. Wei et al. demonstrated that LDH was able to be used as an effective nanocarrier by greatly enhancing the thermal- and photo-stabilities for L-Dopa and L-Tyrosine. Choi et al. have made significant investigations on the toxicity of LDH nanoparticles in vitro and in vivo in applications. Xu et al. recently reported an efficient LDH-based delivery for siRNA [Amita Jaiswal].

ENVIRONMENTAL APPLICATIONS:

In the field of environmental technology, much attention has been paid to the potential applications of synthetic materials as sorbents for organic and inorganic pollutants in water. Layered double hydroxides (LDHs) are used for the decontamination

of the environment and prevent the dispersion of pollutants in nature. A wide range of contaminants can be removed from industrial effluents or wastewater by anion exchange, adsorption process and catalytic remediation, using LDHs. Recently, many other molecules such as pesticides, toxic organic chemicals, greenhouse gases, heavy metals and some other undesirable inorganic substances have increasingly been targeted for remediation by using LDHs for the protection of earth, health and the environment [Ravindra Kumar Gautam].

REMOVAL OF DYE:

The discharged effluents of industries contain a large number of dyes, increasing the total COD of wastewaters. Although most of the dyes are nontoxic, many of them are highly toxic, like metals (Cr), with harmful consequences to aquatic life. Moreover, the persistence of color appearance (at concentration > 1mg/L) in treated wastewater prevents their reuse.

The LDHs have high adsorption capacities for dye molecule and can be very competitive with other sorbents. They have been demonstrated in environmental applications due to their high ability to removed color or dye by adsorption reaction [Ravindra Kumar Gautam].

REMOVAL OF SURFACTANTS:

Layered double hydroxides have strong surface and interlayer hydrophilic properties due to their high content of hydroxyl groups and water molecules. These properties limit the adsorption and the intercalation of nonionic or hydrophobic contaminants. However, anionic surfactants such as alkyl carboxylate, alkyl sulphate or alkyl sulphonate are easily adsorbed and exchanged in LDH structure. Dekany et al. compared the adsorption properties of both cationic surfactant / smectites and anionic surfactant/LDH antitype systems. The higher charge density of the anionic clays explains their higher adsorption capacities in terms of ion exchange capacity percentage. Pavan et al. studied the adsorption of dodecyl sulphate, octylsulphate,

dodecyl benzene sulphonate and octyl benzene sulphonate by Mg-Al-LDH [Mahesh Chandra Chattopadhyaya].

CHAPTER 2

LITERATURE SURVEY

Layered double hydroxides (LDHs) are a class of inorganic materials that exhibit a layered crystal structure. Also known as hydrotalcite-like compounds or anionic clays, LDHs are composed of positively charged metal hydroxide layers and interlayer anions or water molecules to balance the charge. The general formula for LDHs is $[M_{1-x}^{2+} M_x^{3+}(\text{OH})_2]^{x+} \cdot [A_{x/n}]^{n-} \cdot m\text{H}_2\text{O}$, where M^{II} and M^{III} represent divalent and trivalent metal cations, respectively, and A^{n-} denotes the interlayer anion.

CO-PRECIPITATION AT LOW SUPER SATURATION:

Co-precipitation at constant pH and at temperature between 60–80°C by the slow addition of mixed solution of M(II) and M(III) salts in the chosen ratio and the base solution. The rate of addition has to be controlled in order to obtain a more homogeneous phase. These conditions are best to obtain higher crystallinity of the material due to the fact that at constant pH the rate of crystal growth is generally lower than the rate of nucleation.

This method is most often used, as it is the most effective one. For example, Marchi et al. obtained an amorphous precipitate of Cu/Co/Al hydrotalcites catalysts by co-precipitation at high super saturation while under the conditions of low

super saturation a crystalline HT was precipitated.

CO-PRECIPITATION AT HIGH SUPER SATURATION:

In this method, a solution containing a mixture of the metal ion is quickly added to the basic solution and mixed rapidly. This results in the formation of LDHs which are generally not very crystalline, but sometimes amorphous product is obtained due to the high number of nuclei formation. The precipitates obtained by this method are washed with distilled water in order to eliminate adsorbed ions and are dried at temperatures up to 120°C.

2.1 Synthesis of Calcium-Aluminium Layered Double Hydroxide Nanohybrid Material : A Review

NuramirahAinaa Jamil et al. [1]has explained the intercalation of nanohybrid materials which is Calcium-Aluminium Layered Double Hydroxide (Ca-Al LDH). The nanocomposites are well built multiphase-materials of one or more dissimilar phases of dimensional between less to 100 nm range repetitively. LDH has a significant and unique shape due to its structure is quite robust with a wide range of possible composites by positively charged brucitelike sheets of hydroxides intercalated by negatively charged anion in the hydrated interlayer regions mainly found in mineral materials.

2.2 Adsorption of Cr VI in layered double hydroxides

RajibLochanGoswamee et al. [2] has discussed about Adsorption of Cl through ion exchange in uncalcined LDH is slower in rate and smaller in amount than in calcined one where the adsorption occurs via rehydration. Adsorption is higher in the Ca-Al LDH than in Ca(NO₃), Zn-Cl LDH. A two-step first-order rate kinetics was observed for the adsorption process which follows the Freundlich-type adsorption isotherm. The explanation of adsorption phenomenon has been supported by X-ray diffraction patterns.

2.3. Layered Double Hydroxides and the Environment: An Overview

AmitaJaiswal et al [3]. has examined that There are two broad classes of clays: Cationic clays (or clay minerals), widespread in nature, and Anionic clays (or layered double hydroxides), more rare in nature but relatively simple and inexpensive to synthesize on a laboratory or industrial scale. Cationic clays have negatively charged alumina-silicate layers with small cations in the interlayer space to balance the charge, while anionic clays have positively charged brucite type metal hydroxide layers with balancing anions and water molecules located interstitially. The layered double hydroxides (LDHs) belonging to the general class of anionic clay minerals can be of both synthetic and natural origin. Also known as hydrotalcite - like compounds (HTLCs), these materials are interesting because their layer cations can be changed among a wide selection, and the interlayer anion can also be freely chosen. Like cationic clays, they can be pillared and can exchange interlayer species, thus increasing applications and making new routes to synthesize the derivatives. This chapter deals with the brief history of layered double hydroxides, their structure, properties, synthesis by different methods and characterization, along with their applications mainly in the environmental field [3].

2.4 Chloride Removal of Calcium Aluminate-Layered Double Hydroxide Phases: A Review

Gwangmok Kim and Sangwon Park [4] are discussed that Chlorine is a critical element with respect to the use of fossil fuel, recycling of industrial wastes, and water purification. Chlorine could form toxic chemical compounds, corrode pipe systems and boilers, and contaminate surface and ground waters. Calcium aluminate-layered double hydroxides are one of the most promising materials to remove chlorides due to the chemisorption mechanism, since the phases have positively charged interlayers. Many studies on the synthesis and the characterization of calcium aluminate-layered double hydroxides have been extensively conducted, whereas few studies have been conducted on the chloride removal characteristics of the phases.

2.5 Synthesis and applications of calcium-aluminum layered double hydroxides – an overview

Ira WahadahMdGhazali et al. [5] has explained that The synthesis and application of layered calcium-aluminum double hydroxides (Ca-Al LDHs) for the encapsulation of organic anions is discussed. The mechanism of the encapsulation process was explained. These types of compounds have great potential and can be used in targeted therapies, including in drug dosing systems.

2.6 Synthesis and optical properties of Mg-Al layered double hydroxides precursor powders

Chia-Hsuan Lin et al.[6] has examined that The Mg-Al LDH precursors were synthesized by a coprecipitation route with various processes.

2.7 Layered Double Hydroxide Materials: A Review on Their Preparation, Characterization, and Applications

JitendraKameliya et al. [7] has explained about the LDHs can capture and exchange both organic and inorganic anions as well as cations. Such properties make these materials unique, as they show increased selectivity for the carbonate ions because of their flat location in the interlayer space and position parallel to the layers of the matrix. Carbonate salts are reported to be the most common salt form of LDH.

2.8 Recent Advances on the Application of Layered Double Hydroxides in Concrete—A Review

ZahidM.Mir et al. [8] explained that in LDH method aqueous solution of desired divalent and trivalent metallic salts are slowly added into a mixer containing water and allowed to simultaneously co-precipitate in an alkaline environment. The pH is held constant by adding an alkaline solution of desired pH.Usually co-precipitation is done in the pH range of 8–10. It is important to note that the ion-exchange method is

strictly influenced by the affinity of LDH towards the guest anion, the type of the exchange medium, temperature, pH value of the medium as well as the chemical composition of the LDH itself. Both the co-precipitation method and the ion-exchange method can be used to synthesize LDH with corrosion inhibiting ions, e.g., NO_2^- .

2.9 Applications of Layered Double Hydroxide Materials: Recent Advances and Perspective

Rui Tian et al. [9] explained that 2Firstly, how the confinement effect and host–guest interaction of LDHs functions remains a key scientific issue. Secondly, the connections between the microscopic structure and macroscopic performance need to be better understood. With persistent efforts and deepened understanding, we firmly believe that the large-scale preparation of novel multifunctional LDH materials can be realized, which may lead to many exciting industrial applications.

2.10 Layered Double Hydroxides: Structure–Property Relationships

Shan He et al. [10] have synthesized DOX@MSPs/Ni-LDH-folate nanohybrids, and the loaded doxorubicin (DOX) could only be released in tumor cells, which enabled the diagnosis and imaging of cancer cells. In addition, separation and purification of recombinant proteins can be realized. Shao and coworkers have designed a core–shell structure of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{NiAl-LDH}$, where the NiAl-LDH shell provides abundant docking sites for the His-tagged protein via the binding between Ni^{2+} and the His-tag, and thus allowed the efficient magnetic separation of His-tagged proteins.

2.11 Layered double hydroxides – multifunctional nanomaterials

Birgul Zumreoglu-Karan and Ahmet Nedim Ay [11] have found that The

LDH family is quite promising in various branches of materials chemistry. Important progress has been achieved in the development of new types of LDHs for current and novel applications; however, additional studies to develop more feasible synthetic procedures for mass-production particularly in full-scale anion exchange applications and to improve selective absorption properties of multi-anionic systems are still required.

2.12 Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials

Geetanjali Mishra et al. [12] have discussed that Layered double hydroxide is a functional material having all types of applications in almost every field starting from ceramics, cosmetics, biotechnology, drug delivery, sensors to environmental remediation. In each field this anionic clay could be proved as the best suited materials. The greatest use of it is because of its interlamellar spacing which is its exclusive characteristics. of applications in almost every field starting from ceramics, cosmetics, biotechnology, drug delivery, sensors to environmental remediation. In each field this anionic clay could be proved as the best suited materials. The greatest use of it is because of its interlamellar spacing which is its exclusive characteristics

2.13 Layered Double Hydroxides

Giuseppe Prestopino and Giuseppe Arrabito[13] discussed that this work provides a possible link between the role of LDHs in the origin of life and the formation of pre-biotic molecules, to inspire the fabrication of artificial LDH-based compartments that mimic prebiotic assemblies. The design of LDH-based systems for life-like and life-inspired devices.

2.14 Synthesis of layered double hydroxides through continuous flow processes: A review

Didier Tichit et al. [14] have reviewed the results concerning the different preparation processes of LDHs and LDH-based hybrids and composites since the pioneering work which uses a continuous coprecipitation method under steady-state conditions in a laboratory cylindrical tank reactor. They emphasize the versatility of the approaches implemented and the characteristics of the materials obtained.

CHAPTER 3

AIM AND SCOPE

3.1 AIM:

Synthesis of the double layered hydroxides from the compounds Calcium Chloride, Aluminium Chloride, Magnesium Chloride using Cinnamaldehyde, Ethyl Aceto Acetate, Methyl Ethyl Ketone.

3.2 SCOPE:

Our scope of the project is to find Double Layered Hydroxides in the compounds which can be used as the starting material in pharmaceutical industry. LDHs have high adsorption ability, high cation exchange capacity, high internal surface area, reactions between the interlayers, and less toxic properties that make them valuable in the biological and pharmaceutical fields.

3.3 OBJECTIVE OF THE STUDY:

1. Layered Double Hydroxides compounds are prepared using Co-precipitation method.
2. The prepared hydroxides LDH are characterized by FTIR and XRD methods.
3. It is applied for Claisen-Schmidt reaction where the formed compounds are used as a starting material in various pharmaceutical industries.

CHAPTER 4

MATERIALS AND METHODOLOGY OF LDH

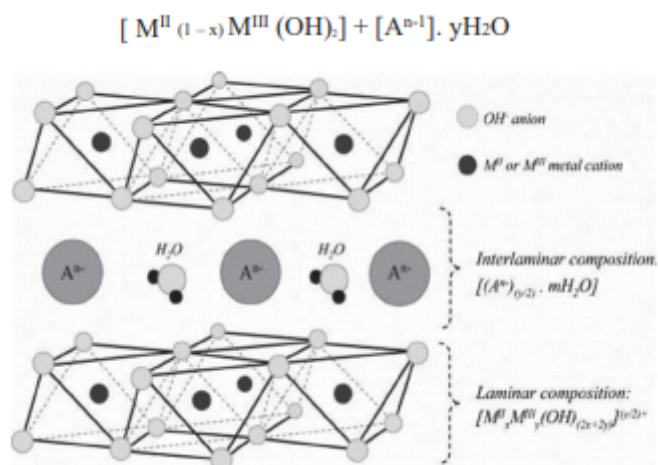
4.1 MATERIALS AND METHODS OF LAYERED DOUBLE HYDROXIDES:

4.1.1 MATERIALS:

Materials used are Calcium Chloride, Calcium Chloride, Cinnamaldehyde, Ethyl Aceto Acetate, Methyl Ethyl Ketone, Acetone, Ethanol

4.2 STRUCTURE OF LAYERED DOUBLE HYDROXIDE:

LDHs, or Layered Double Hydroxides, have a chemical formula of $[M_{1-x}^{2+} M_x^{3+}(\text{OH})_2]^{x+} \cdot [A_{x/n}]^{n-} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are the divalent and trivalent metal ions, respectively, A^{n-} are inorganic or organic anions, m is the number of interlayer water, and $x = M^{3+}/(M^{2+} + M^{3+})$ is the layer charge density, or molar ratio. They consist of positively charged octahedral layers formed by M^{2+} and M^{3+} cations and negatively charged interlayers that can accommodate anions and water molecules.



4.1 Structure of layered double hydroxide (LDHs)

PROCEDURE:

From the above calcination process, the amount of LDH yield is high in calcium chloride & $AlCl_3$ in NaOH / Na_2CO_3 (CALCINED) and then it is made with 1:1, 1:2 and 1:3 ratio

1:1 Ratio:

With 25ml of 0.1M NaOH and 0.3M Na_2CO_3 filled in a burette, 0.785g of $CaCl_2$ and $AlCl_3$ are titrated, filtered, dried and calcined in muffle furnace at $500^\circ C$. It is then calcined. The dry salt is then stirred with 5ml of cinnamaldehyde for 1 hour, heated at $35^\circ C$ to $45^\circ C$, added to acetone for 30 minutes in a reflux condensor, transferred to a sintered crucible, suctioned dried, and weighed to equal 0.078g. It is then heated with ethanol, crystals are created, and it is weighed to equal 1.083g. X-ray diffraction and

FTIR studies are also performed on the catalyst.

1:2 Ratio:

1.57g of CaCl_2 and 0.44g of AlCl_3 are titrated with 25ml of 0.1M NaOH and 0.3M Na_2CO_3 in a burette, and then the solution is titrated, filtered and dried, before being calcined. The dry salt is then stirred with 5ml of cinnamaldehyde for 1 hour, heated at 35°C to 45°C, added to acetone for 30 minutes in a reflux condensor, transferred to a sintered crucible, suctioned dried, and is weighed to equal 0.078g. It is then heated with ethanol, crystals are created, and it is weighed to equal 1.083g. X-ray diffraction and FTIR studies are also performed on the catalyst.

1:3 Ratio:

2.355g of CaCl_2 and 0.44g of AlCl_3 are titrated with 25ml of 0.1M NaOH and 0.3M Na_2CO_3 in a burette, and then the solution is titrated, filtered, before being calcium carbonate-calcined. The dry salt is then stirred with cinnamaldehyde for 1 hour at a temperature between 35°C and 45°C, heated for 30 minutes, transferred to a sintered crucible, and suctioned dried before being weighed at 0.078g. Additionally, it is heated with ethanol, crystals are created, and it weighs 1.083g. Also performed on the catalyst are X-Ray diffraction and FTIR analyses.

4.3 SYNTHESIS OF LAYERED DOUBLE HYDROXIDES:

Layered double hydroxides (LDHs) can be synthesized with a wide range of compositions and a variety of M(II)/M(III) cation combinations containing different anions in the interlayer spaces. A number of synthetic techniques have been successfully employed in the preparation of LDHs.

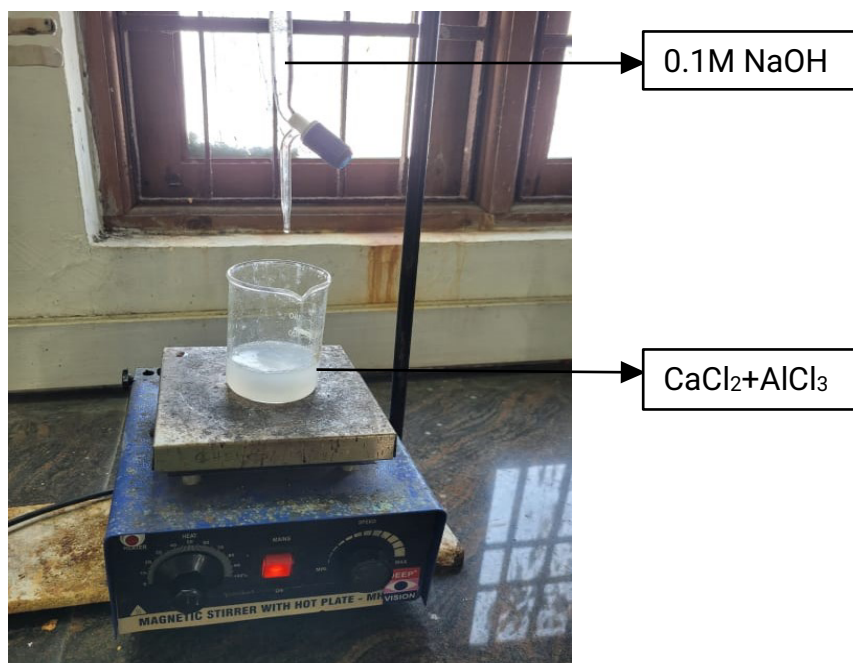
4.4 EXPERIMENTAL METHODOLOGY:

4.4.1 CO-PRECIPITATION METHOD:

Co-precipitation remains the most commonly used technique for the synthesis of LDHs. This technique involves the addition of aqueous solutions of M(II), M(III) and the anion that will be incorporated into the LDH structure. This method allows the direct preparation of LDHs for a variety of anions and cations. Therefore, this method is commonly used for the formulation of organic-anion LDHs, which are difficult to obtain by other methods. Following are the three methods of co-precipitation which can be used for the synthesis of LDHs.

4.4.2 CO-PRECIPITATION BY ADDITION:

In this method, a metal salt solution is titrated against a basic solution during which not only solids of LDHs structure occur, but also other solid phases are formed, due to the precipitation of less soluble metal hydroxides prior to the precipitation of the LDHs.



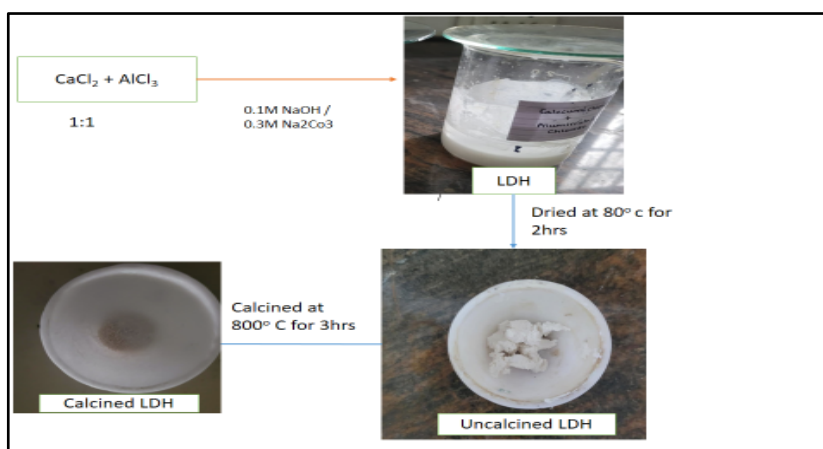
4.4 Co-precipitation

4.5 DOUBLE HYDROXIDE PREPARATION:

CaCl_2 and AlCl_3 were titrated with 0.1 M NaOH , stopped at 25 ml on a stirrer, and then transferred to a beaker where they were left overnight to settle. After that, it is dried after being rinsed with ethanol, filtered on Whatmann filter paper, and suctioned with water. It is then heated for 1 hour at 35° to 45°C with the addition of 5ml of cinnamonaldehyde, stirred for 30 minutes, and then kept for suction in a crucible, dried, and weighed to equal 1.083g. And after being heated with ethanol, it crystallised. It was then weighed, coming in at 0.143 g, and was given for characterization.

4.5.1 CALCIUM CHLORIDE & AlCl_3 IN NaOH (CALCINED):

0.785g of CaCl_2 and 0.44g of AlCl_3 were titrated with 25ml of 0.1M NaOH and 0.3M Na_2CO_3 of 25ml filled in burette and titrated and filtered with Whatmann filter paper, Suctioned, dried, and it is kept in Suctioned. Suctioned washed with water and ethanol and dried in Oven. 1.085g of calcined calcium chloride and aluminiumchloride in NaOH and 0.853 of uncalcined calcium chloride and aluminium chloride in NaOH then it kept for Reflux with stirrer and heated at 35°C to 45°C along with Cinnamaldehyde (5ml) to stabilize the carbocation for 1 hour and Acetone(5ml) is added and stirred for 30 minutes and then it is transferred to Sintered crucible Suctioned dried & weighed. And it is heated with ethanol and it forms crystal and weighed = 0.048g and it is given for characterization.



4.5 Double Hydroxide Preparation

4.5.2 CALCIUM CHLORIDE & AlCl_3 IN NaOH / Na_2CO_3 (UNCALCINED):

0.785g of CaCl_2 & 0.44g of AlCl_3 titrated with 0.1M NaOH and stopped at 25 ml and it is transferred to beaker and filtered with Whatmann filter paper and suctioned & dried and it is kept in muffle furnace at 500°C for 3 hours. It is kept in muffle furnace at 500°C for 3 hours after it is taken out and calcined. Then dried salt is kept in Reflux in Stirrer at 35°C to 45°C heated with Cinnamaldehyde (5ml) for 1 hour and acetone is added kept for 30min and then it is transferred to sintered Crucible suction dried and weighed = 0.078g. And it is heated with ethanol and it formed crystals and it is weighed = 0.163g and it is given for characterization.

4.5.3 CALCIUM CHLORIDE & AlCl_3 IN NaOH / Na_2CO_3 (CALCINED):

0.785g of CaCl_2 and 0.44g of AlCl_3 are titrated with 25ml of 0.1M NaOH and 0.3M Na_2CO_3 in a burette, and they are titrated, filtered, and dried. The dried it is kept in muffle furnace at 500°C before being calcined. After 1 hour of refluxing at 35°C – 45°C with 5ml of cinnamonaldehyde, 5ml of acetone is added, the mixture is agitated for 30 minutes, transferred to a sintered crucible, vacuum dried, and weighed 0.078g. The substance is then heated with ethanol, causing crystals to form, weigh 1.083g, and be made in a variety of ratios for characterisation.



4.5.3 Ca-Al LDH is kept in muffle furnace for calcination

4.6 CHARACTERIZATION OF LAYERED DOUBLE HYDROXIDES:

Characterization have been used to characterize LDHs. Some of the most commonly used techniques are XRD, FTIR and TG/ DTA. Some other techniques are more specific for some LDHs such as SEM, DSC, NMR and Raman spectroscopy.

4.6.1 X-RAY DIFFRACTION:

XRD is one the characterisation technique that reveals the structural properties of nanoparticles. It provides information on the phase, chemical composition, symmetry of unit cells, crystallinity, lattice constant and properties of the nanoparticles. This technique is employed for the identification of both single and multiphase nanoparticles.

XRD is considered as one of the oldest non-destructive methods for the analysis of nanoparticles. The XRD pattern is influenced by the size and shape of the unit cell of the crystal. Consequently, properties of a material are dependent on their structure. Of about 90% solid materials are crystalline in nature and each crystalline has a significant X-ray diffraction pattern which can be used as fingerprint to detect the material.

Diffraction pattern is obtained only when the X-rays are interacted with the crystal. Information like symmetry of the unit cell, stress, strain, size of crystallite and growth orientation etc. are obtained from the diffraction patterns.

BRAGG'S LAW

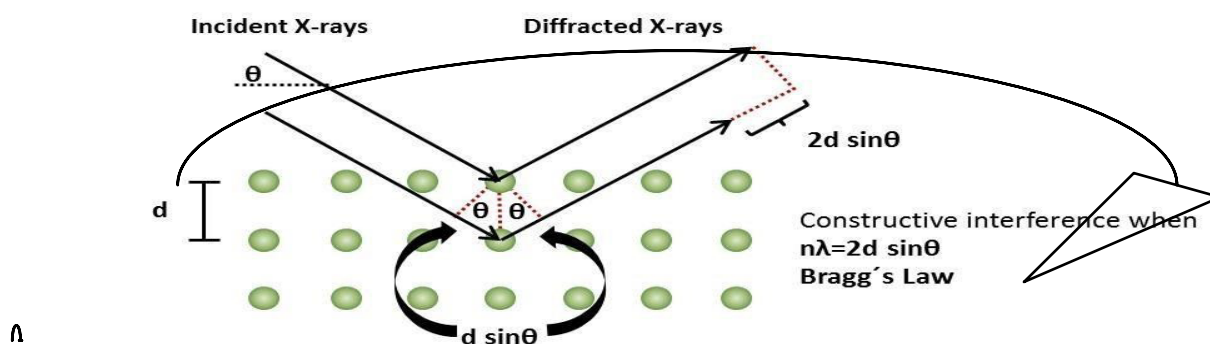
When a material is irradiated with a monochromatic light of wavelength around the inter atomic distance of the material, light gets dispersed by the atoms and

interfere to give rise to diffracted light with a higher intensity. The arrangement of atoms in the material is related to the intensity of the scattered light. If wavelength of light is λ and the incident angle is θ and the constructive interference is obtained at an angle 2θ from the incident beam of light if Bragg's equation is satisfied. Bragg's equation is given by,

$$n\lambda = 2d \sin \theta$$

where,

n is the diffraction order, d is the distance between the diffracting planes and θ is the Bragg's angle.



4.6.1 Schematic representation of Bragg's law

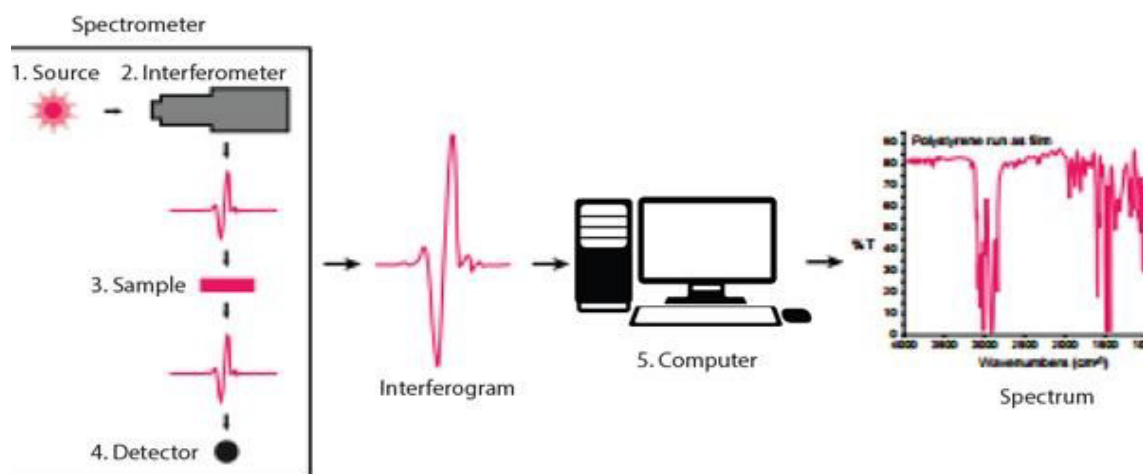
4.6.2 FOURIER TRANSFORMER INFRARED SPECTROSCOPY:

Fourier transform infrared (FTIR) spectroscopy is a very efficient nondestructive characterization technique for surface characterization of nanoparticles' surfaces, providing a specific setup is connected to the spectrometer. It is used to determine the functional groups. The chemical structure of the nanoparticles' surface and the surface reactive sites responsible for surface reactivity can be determined under particular conditions.

The structure and bands of the synthesised nanoparticles, FTIR may be used to test a variety of components, including bulk or thin films, liquids, solids, pastes, powders, fibres, and other materials. FTIR analysis may be used for quantitative

(amount) analysis as well as qualitative (identification) analysis of materials where appropriate criteria are used. FTIR can test samples up to 11 mm in diameter and weigh in bulk or the top 1 mm of the sample.

The difficulty in FTIR characterization is mainly because of high degree of overlapping of the IR absorption bands which makes difficult for the attribution of certain functional groups, despite the fact that up to date computer searchable databases are available.



4.6.2 Schematic representation of FTIR

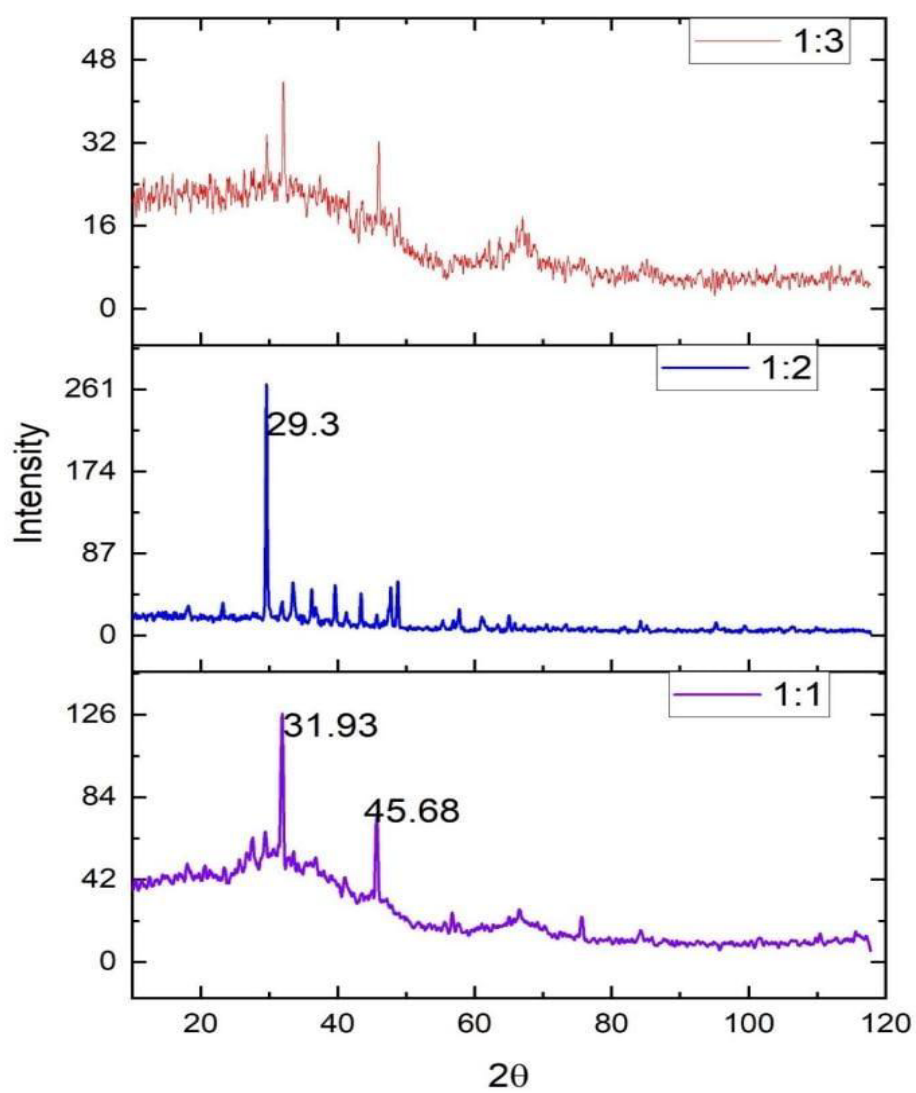
Claisen Schmidt Reaction:

The hydroxide is used as an alternate catalyst for the corrosive NaOH for the Claisen Schmidt reaction. The reaction is carried out in the absence of the organic solvent. The efficiency of the catalyst is tested with 5 ml of Cinnamaldehyde and acetone by refluxing at 50-60°C for 30 minutes. The yellow precipitate is filtered using suction and crystals are obtained using hot ethanol.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 XRD GRAPH FOR 1:1, 1:2, 1:3 RATIO:



The peak at 29.3° represents the d003 plane which indicates the formation of LDH

5.1.1 FTIR GRAPH FOR 1:1, 1:2, 1:3 RATIO:

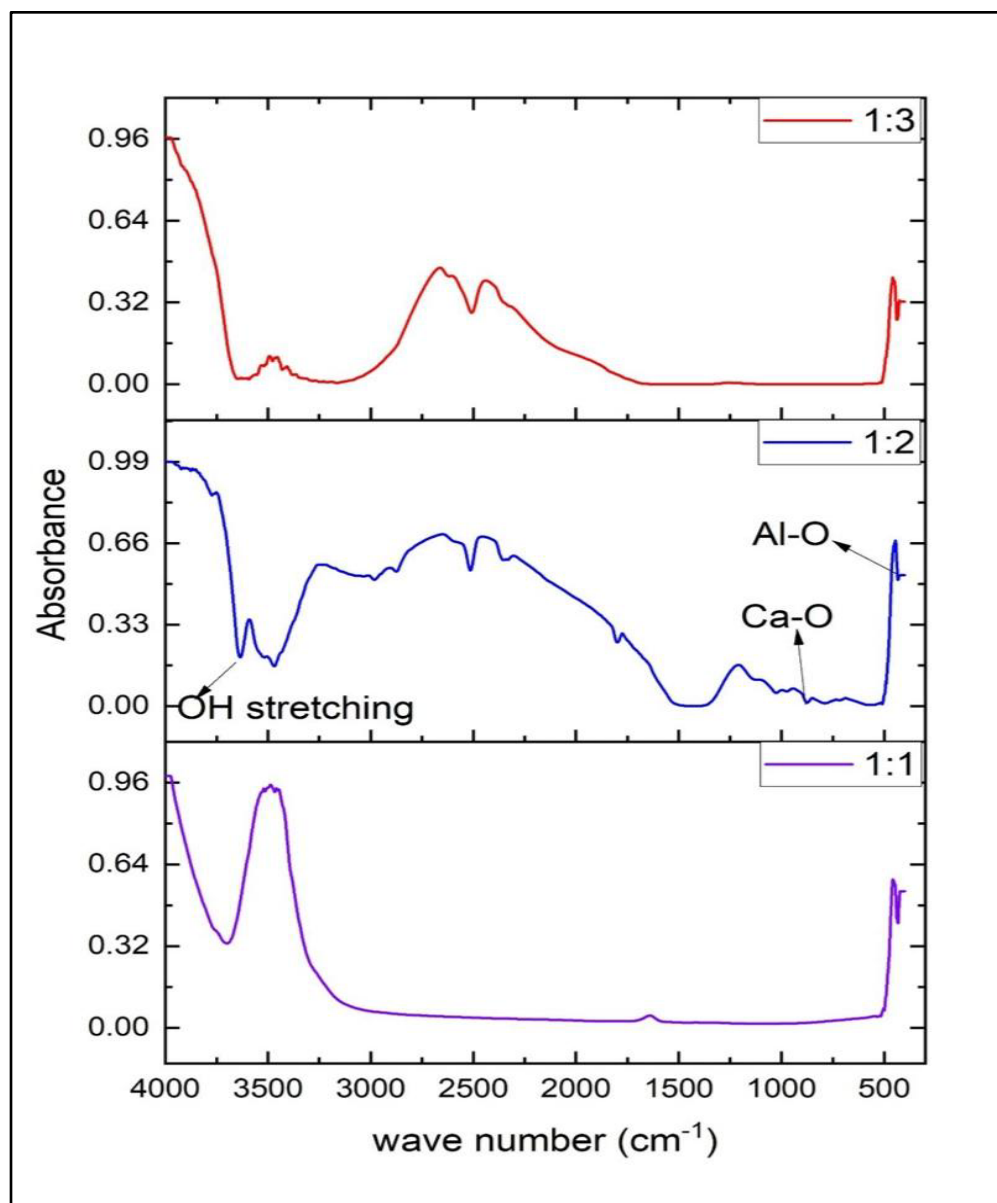


Table 5.1.1 FTIR
NaOH and
5.2

REACTIONS:

S.NO	FUNCTIONAL GROUP	WAVENUMBER
01.	Calcium Oxide(CaO)	780 cm^{-1}
02.	Aluminium Oxide (AlO)	430 cm^{-1}
03.	OH (stretching)	3300 cm^{-1}

of Ca-Al LDH in
 Na_2CO_3
CHEMICAL

The above 1:1 ratio Calcium Chloride and Aluminium Chloride in NaOH& Na_2CO_3 (uncalcined) is treated with cinnamaldehyde, ethyl methyl ketone, ethyl aceto acetate.

5.2.1 LDH REACTING WITH CINNAMALDEHYDE:

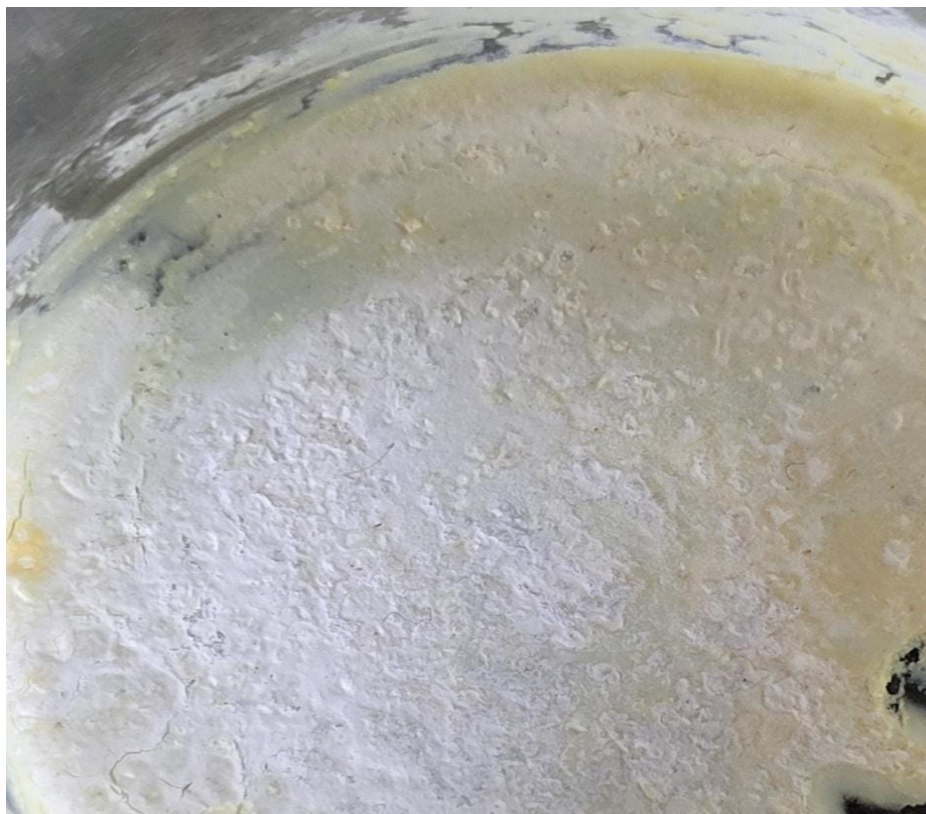
1.083g of LDH catalyst obtained from 1:1 ratio calcium chloride and aluminium chloride in NaOH and Na_2CO_3 (Calcined) is added to round bottom flask with 5ml of cinnamaldehyde along with glass beads and kept in reflux condenser for stirring and it is heated for 1 hour at 60-80°C. Then 5ml of acetone is added to it and heated for 30 minutes in magnetic stirrer. Then the solution is suctioned in sintered crucible dried and weighed 0.853g. The precipitate is weighed and it is heated with 5ml of ethanol and it is kept for some time and there will be a formation of pale yellow crystals and white precipitates left behind and then it is weighed 1.453g.



5.2.1 LDH Reaction with Cinnamaldehyde

5.2.2 LDH REACTING WITH METHYL ETHYL KETONE:

1.083g of LDH catalyst obtained from 1:1 ratio calcium chloride and aluminium chloride in NaOH and Na_2CO_3 (Calcined) is added to round bottom flask with 5ml of methyl ethyl ketone along with glass beads and kept in reflux condenser for stirring and it is heated for 1 hour at 30-35°C. Then 5ml of acetone is added to it and heated for 30 minutes in magnetic stirrer. Then the solution is suctioned with sintered crucible and it is kept in oven for drying. The precipitate is weighed and it is heated with 5ml of ethanol and it is kept for some time and there will be a formation of pale yellow crystals and white precipitates left behind and then it is weighed 1.253g.



5.2.2 LDH REACTING WITH METHYL ETHYL KETONE

5.2.3 LDH REACTING WITH ETHYL ACETO ACETATE:

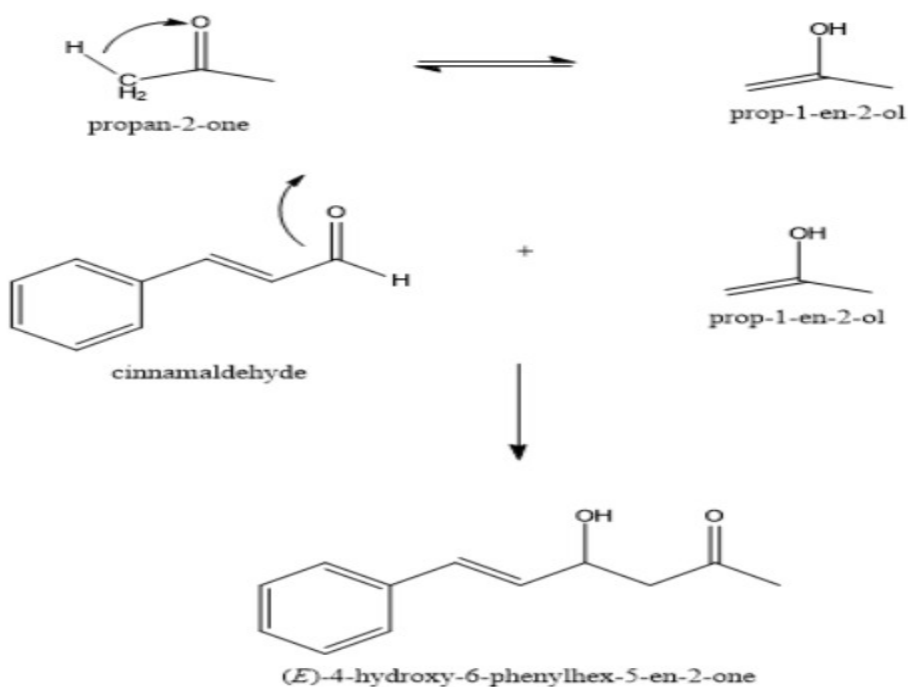
1.083g of LDH catalyst obtained from 1:1 ratio calcium chloride and aluminium chloride in NaOH and Na_2CO_3 (Calcined) is added to round bottom flask with 5ml of ethyl aceto acetate along with glass beads and kept in reflux condenser for stirring and it is heated for 1 hour at 30-35°C. Then 5ml of acetone is added to it and heated for 30 minutes in magnetic stirrer. Then the solution is suctioned with sintered crucible and it is kept in oven for drying. The precipitate is weighed and it is heated with 5ml of ethanol and it is kept for some time and there will be a formation of pale yellow crystals and white precipitates left behind and then it is weighed 0.983g.



5.2.3 LDH REACTING WITH ETHYL ACETO ACETATE

5.3 CLAISEN SCHMIDT REACTION WITH ALDEHYDES AND KETONES

The Claisen-Schmidt reaction of acetone (5ml) with cinnamaldehyde (5ml) in the presence of an equimolar amount of solid Ca-Al LDH without any solvent after grinding with a mortar and pestle for 5 min.



CHAPTER 6

SUMMARY AND CONCLUSION

- (1) The CaAl-LDH phases have unique structural characteristics induced by the interlayers similar to lamellar portlandite-like structures. The interlayers consist of cations being divalent and trivalent, which is responsible for the

positive charge between the interlayers. The positively charged interlayers can include the anions and water molecules. The understanding of the structural characteristics is helpful for the application of CaAl-LDH phases as an adsorbent.

- (2) Various synthesis techniques such as coprecipitation, ultra-high lime with the aluminate process, and green synthesis methods have been adopted to synthesize CaAl-LDH phases. Factors including temperature, anions provided by starting materials, pH values, and so on significantly affected the formation of CaAl-LDH phases. Proper conditions for the synthesis of CaAl-LDH phases in the present study were summarized.
- (3) In the summary to produce LDH phases Ca-Al in NaNO_3 and in NaOH is calcined upto 500°C can only partially restored the LDH phase through rehydration. The Calcination temperature appears to be an important factor for a efficient rehydration

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