Synthesis and Characterization of $Ca(OH)_2$ and its Composites for Thermo-Chemical Energy Storage

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ALL OF MY WORK IS
DEDICATED
TO
MY LOVING PARENTS

"I couldn't Have Done It Without Them"

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List of Abbreviations

Words	Abbreviations
Thermal energy storage	TES
Electrical energy storage	EES
Mechanical energy storage	MES
Latent Heat storage	LHS
Sensible Heat Storage	SHS
High temperature energy storage	HTES
Thermochemical energy storage	TCES
Heat transfer fluid	HTF
Alkaline earth metal hydroxide	AEMH

Abstract

Thermo-chemical energy storage plays a promising part in the development of the concentrates solar power plants to improve the resources to store energy. Thermo-chemical energy storage is helping us to store energy with many benefits as it is a cheap source of energy storage with high storage density. During the cycling of $CaO/Ca(OH)_2$ reaction agglomeration effects arise and initiate inhomogeneity resulting the bed properties especially associated to mass and heat transport. $Ca(OH)_2$ appears to be the best candidate in the hydroxide materials due to its structure and especially for utilization of thermal properties.

This work proposed nano $Ca(OH)_2$ and its composites with SiO_2 were synthesized via sol- gel method which is easy and low cost technique. XRD was done to explore the structure of the material. The crystallite size was calculated by using Debye Scherer formula; $Ca(OH)_2$ = 30.3 nm. In composite, broad silica peak was observed in XRD which show that the addition of silica disturb crystal structure by increasing the concentration of silica. Scanning electron microscopy was used to determine the surface morphology of $Ca(OH)_2$ which showed the flakes type formation. In $Ca(OH)_2/SiO_2$ the surface morphology of the composite showed silica particles were embedded on the surface of core material. EDX pattern confirmed the presence of required material. FTIR confirmed the bonding of $Ca(OH)_2$ with the extra CO_3 bonds which can be determined by calcite peaks present in XRD. In composite, the bonding was confirmed between $Ca(OH)_2$ and silica particles by appearance of strong bond at ~ 1098 cm^{-1}. Thermo-gravimetric analysis (TGA) verified the dehydration of $Ca(OH)_2$ to CaO. While in composite the dehydration of the material was slow as compared to the pure sample. The accumulation of silica nanoparticles on the surface of $Ca(OH)_{2,}$ results in abrupt increase in mass due to the interaction of the material with atmosphere which affects decomposition. Decreased concentration of silica nanoparticles reveal better thermal behaviour and highly improved properties validating modality and stabilization of the surface structure.

Layout of Thesis

The layout of this thesis is as follows:

Chapter 1

In this chapter, the general concept of nanomaterials, classification of nanomaterials, nanoparticles, properties and application are presented. A brief introduction of thermal energy storage, types of energy storage, thermochemical energy storage and structure of $Ca(OH)_2$ is discussed briefly.

Chapter 2

In this chapter, includes the statement problem and the literature survey. Different synthesis method of $Ca(OH)_2$ and its composite including the effect of their structural , morphological and important one thermal properties is also discussed in literature.

Chapter 3

This chapter includes the synthesis of Ca(OH)2 and its nano composite by sol gel method. Different characterization techniques are used to explain the properties of the nanocomposite systems.

Chapter 4

The structural, morphological and thermal analysis of prepared samples is discussed in this chapter. Complete profile strength of each sample also discussed in following chapter.

Chapter 5

The final chapter covers the summary and conclusion of whole work and gives some potential recommendations.

Chapter No 1

1.1. Introduction

Nanotechnology is the leading and advanced technology of the current age and the developing field of the 21st century. The word ‘Nano’ is resulting from Greek word ‘Nanos’ which means ‘dwarf’. Nano science is the study of the material at Nano scale. Nanotechnology is the branch which material has only one dimension in some Nano meter to one hundred Nano meter or 1nm to 100nm. Nanotechnology deals with different branches like physics, chemistry and biology, material science etc. on a measuring scale, Nano-meter is a billionth part of a meter like (10^{-9}) which have roughly hundred of thousand thickness of human hair. When particle size decreases, the surface area to volume ratio of the material enhances. The bulk material pursue classical mechanics, in spite of, when bulk material approaches to Nano scale classical mechanics flop to amplify this phenomenon. One Nano scale quantum mechanics principles have found to be justifiable this phenomenon. Nanotechnology is the branch of Nano science and has a great impact in commercial and industrial field of life [1]

1.2. History of Nano Science & Nano technology

In 1959, a way before this was introduced by a great scientist Richard Feynman during his lecture.

He said “There is a plenty of room in the bottom” in his lecture which presented in the conference of American Physics Society.

1.3. Nanoparticles

Those particles having particle size in between 1 to 100nm is called Nanoparticle. These particles exist in naturally and composed artificially. The analysis of nanoparticle shows that the nanoparticles exist naturally and these are made by human made procedures by industry and emission of traffic.

There are two types of nanoparticles exist naturally. Those particles which are straightforwardly emitted by traffic outflow and industrial burning processes are called essential nanoparticles.

Those particles are called secondary nanoparticles that formed by the oxidation of gases in atmosphere. These particles are generated by itself from the low condensation volatile vapours in the atmosphere. The surface area to volume ratio of nanomaterial is higher than bulk material, which results the greater chemical reactivity and increases their strength [2].

1.4. Nanomaterials

Nano-materials are the material that has structural component litter than 1 micro-meter in no less than one spatial measurement. While the molecular and atomic building blocks (~ 0.2nm) of matter are considered Nano materials, illustration for example, such as bulk crystal with lattice spacing of Nano meter yet microscopic measurement generally speaking are ordinary prohibited [3].

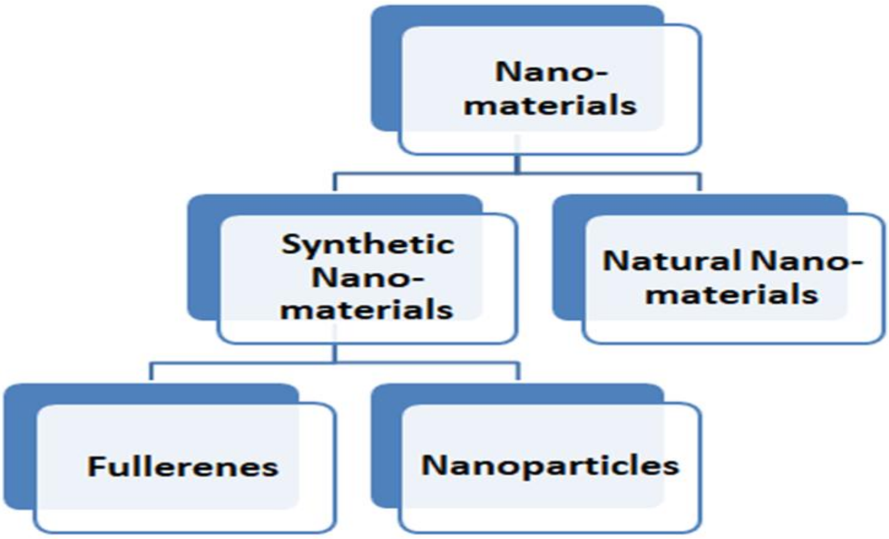


Figure 1.1: Showing sub-division of Nano-materials

1.4.1. Classification of materials

On the basis of dimension we classify the Nano material in following types.

- Zero-Dimensional Material
- One-Dimensional Material
- Two-Dimensional Material

- Three-Dimensional Material

1.4.1.1. Zero-Dimensional Nano material

In zero dimensional Nano-material (0D), which electron movement is bound in every single spatial measurement. Which implies that no measurement is more prominent than 100 nm? Quantum dots are the illustration of zero dimensional material. In zero dimensional material which relies on the properties of size ward. These materials can be amorphous or crystalline.

1.4.1.2. One-Dimensional Nano material

In one dimensional material (1D) which electron motion is confined in two dimensions and can move only in one direction. 1D Nano material can be crystalline or amorphous structure. Examples of 1D are nanowires and nano-rods.

1.4.1.3. Two-Dimensional Nano material

In two dimensional materials (2D) which electron are confined in one dimension and can move in two directions. Examples of 2D are thin films, Nano coating and quantum wells.

1.4.1.4. Three-Dimensional Nano material

In three dimensional materials (3D) which electron are not confined in all dimensions. All the dimensions of material are greater than 100 nm. These Nano-materials are also known as bulk Nano-material. These materials are characterized by having all dimensions greater than 100nm [4-5].

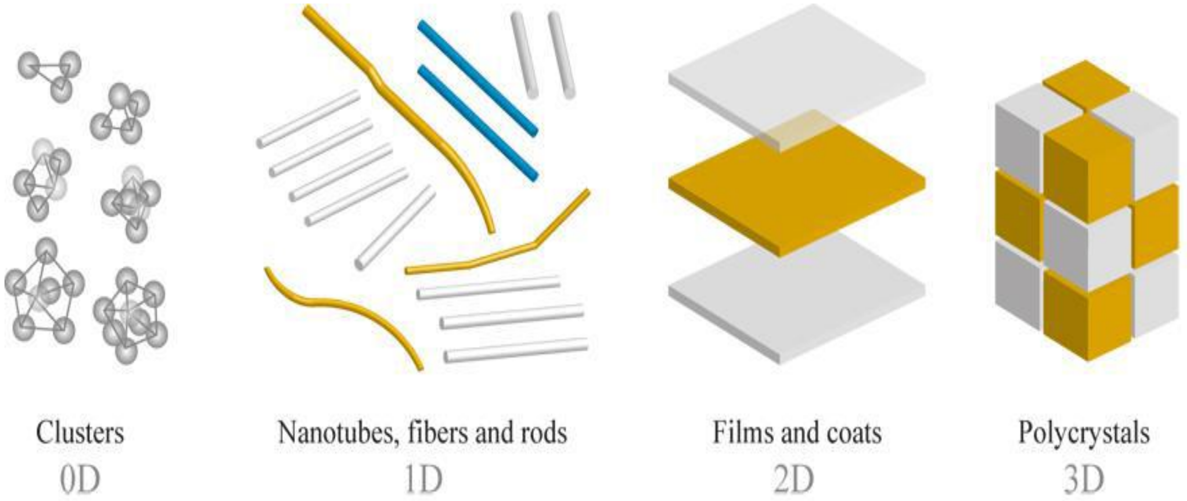


Figure 1.2: Classification of materials at nanoscale

1.4.2. High Surface to Volume Ratio:

As we go, down from bulk to nano-scale surface area large as compared to volume. In nanotechnology, surface to volume ratio is very important characteristic. More surfaces are exposed that maximize possible reactivity. This property is very effective in different chemical process and we can get various material. In conventional material most of the atoms are not at the surface. The large surface to volume ratio causes the chemical interaction more easily [6].

1.4.3. Properties of Nanomaterial:

The main property of nanomaterial depends on their shape, surface morphology, topography, size, crystallinity and solubility. All properties are changed with the degree of confinement. On the macroscopic level, material are studied they are mostly investigated for physical properties. However, at Nano scale many properties are studied at lower level such as

- Crystal Structure
- Surface Morphology
- Size Distribution

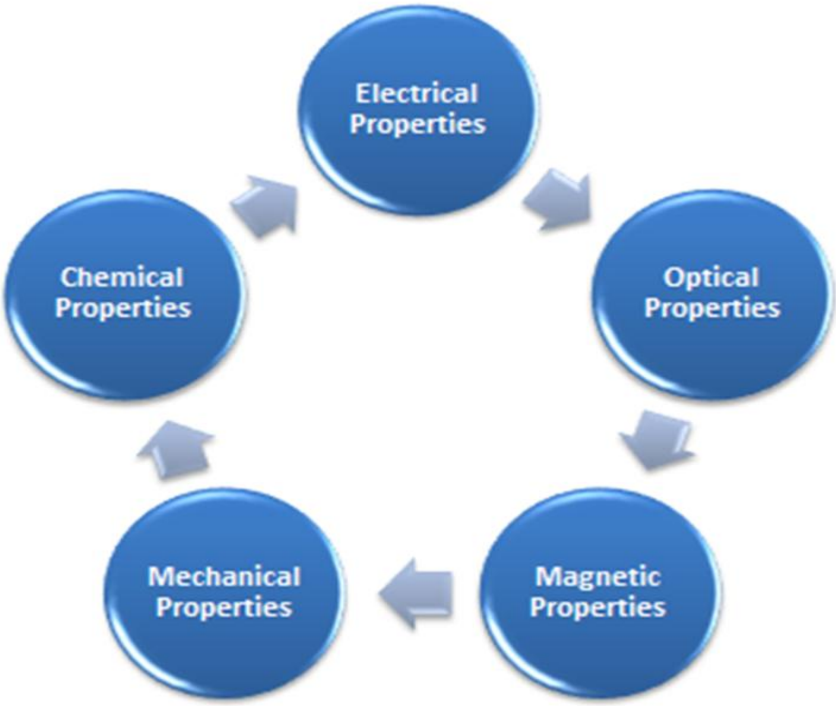


Figure 1.3: Flow Chart of Nanomaterial Properties

1.4.4. Chemical Properties

Chemical properties of nanomaterial mainly consist

- Structural formula
- Phase identification
- Degree of purity
- Composition of material
- Surface Chemistry (Physical Chemistry, Composition, Zeta Potential, Reactive sites)
- As we go on decreasing the size of material it reaches to nanoscale and atom on the surface of material become significant. The similar nanomaterial shows a change in the properties.
- Surface Energy
- Quantum Confinement
- Large fraction of surface atom which are not in the bulk material

1.4.5. Optical and Electrical Properties

Optical properties are very important in nanomaterial. As we go on decreasing the size of material, more surface exposed optically properties become completely change from bulk material [7]. Nanomaterial have distinctive and exciting properties which have great importance in solar cells, optical sensors, biomedicine, laser, to wrap things up in catalytic application such as electrochemical, photo catalysis and thermochemical[8-11] . The optical properties of nanomaterial synthesize by different method depend on nature, surface, shape and size.

1.4.6. Magnetic Properties

Magnetic properties are explored on the basis of dimensionality of the material. We can impute the different properties of the nanomaterial on the basis of dimension of that material such as medical engineering, sensor etc.

1.4.7. Energy

Nanomaterial plays an important part in the way of energy which includes storage, conversion and manufacturing process.

- Graphene are used in the batteries as conventional battery electrode materials are significantly improved conductivity and energy density. Uses of graphene can make battery lighter, durable and suitable high capacity energy storage.
- Nanomaterial has played an important role in solar energy devices.

1.5. Introduction to Energy Resources

A few measurements that show the present circumstance of powers, energy utilization and generation have been accounted for by the International Energy Agency (IEA). For instance, 81% of energy generation in 2009 was from petroleum; the price of petroleum is higher than 25 years ago, the measures of CO_2 discharges and in addition the rate of energy utilization have increased since the 70's. Consistently, it is more apparent that forms with higher energy productivity are required and that research in new technology to deliver energy is critical. The two most utilized kinds of energy are thermal and electrical. On account of electric energy, the power plants are around 30 to 40% effective relying upon the thermodynamic cycles utilized. In some energy frameworks where one can discover low efficiencies; in a burning engine, just 20% of the fuel's energy is utilized to create work, while the rest is squandered in the type of heat. Thermal Energy Storage Devices (TESD) can improve some portion of this heat making the thermal cycles more proficient [12].

In the wake up of knowing all the upcoming difficulties, the principle of researchers goes towards the sustainable power resources. They conceived several approaches to store energy as electric energy, thermal energy and mechanical energy. So they isolated sorts of energy storage and began taking a shot at each kind. Many kinds of energy storage incorporates electrical energy storage, thermal energy storage and mechanical energy storage out of which thermal energy storage is of our concern. It's additionally divided into three classes known as latent heat storage, thermo-chemical heat storage and sensible heat storage [13].

1.6. Introduction to Thermal Energy Storage

More than 190 nations worldwide consented to arrangement of climate assurance from 2015 in Paris, to decrease the gas outflow by the mid of this Century. This objective can be accomplished by control of sustainable energy sources on the planet. To increase the protection in renewable energy requires the large scale installation storage capacities in the meantime. Along these lines thermal energy storage are considered as one key innovation to adjust the variance among free market activity. The benefit of thermal storage advancements is that they are modest, natural friendly and abundantly accessible material [14].

Concentrated solar power plant (CSP) is the main candidate for the generation of power with the expanding demand for use of renewable energy. The main feature of CSP is continuous supply power by daily and seasonal solar radiation [15].

There are three primary methods for TES are

i. Sensible Heat Storage
ii. Latent Heat Storage
iii. Thermochemical Heat Storage

1.6.1. Sensible Heat Storage

In sensible heat storage, when the temperature of storage medium changes then energy is stored in both ways. When we increase the temperature of the medium, thermal energy will absorb which can be release by changing the temperature from higher to lower level. The amount of stored energy in this way only depends on the change in temperature ΔT, specific heat C_p and storage size in terms of mass which defined as

$$\mathbf{Q = m.\ Cp.\ \Delta T}$$

1.6.2. Latent Heat Storage

In latent heat storage, energy is stored by altering the phase of the material, in which we charge & discharge by solidifying or liquidizing in storage material. Each transition of phase leads to change the enthalpy (ΔHp) of the respective substance. During transition, enthalpy change is very large comparatively temperature of the substance remains constant. In contrast to sensible heat, the selection of material is not easy for latent heat storage system, as the temperature of material has to match the temperature of associated system. So selection of material based on material temperature, specific cost, thermal conductivity and thermochemical storage capacities. The heat storage in both ways is shown in figure 1.4.

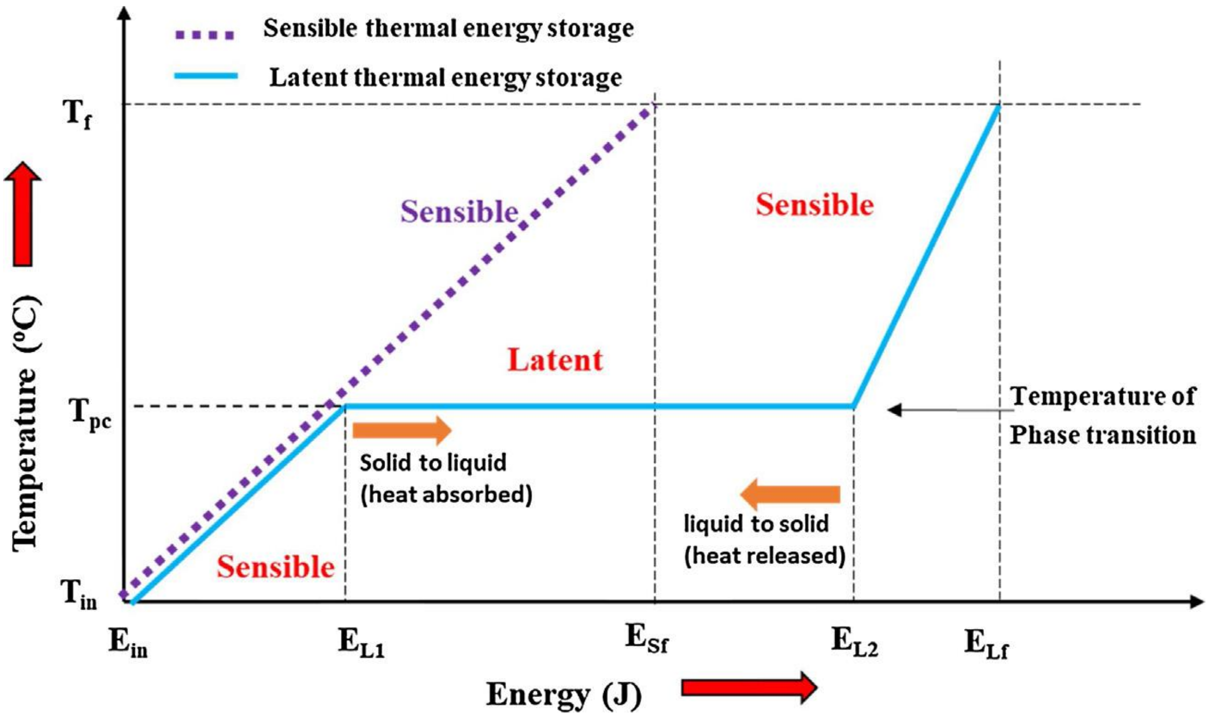


Figure 1.4: Comparison between energy storage of SES and LES [59]

1.6.3. Thermochemical Energy Storage

In last two types which we previously discussed for TES have a principle disadvantages. Enthalpy change of each system for heating or melting per mole is low. To avoid these drawbacks, by using reversible chemical reaction we can store energy in the form of reaction enthalpy.

$$\mathbf{AB}_{(s)} + \Delta \mathbf{H} \leftrightarrow \mathbf{A}_{(s)} + \mathbf{B}_{(g)}$$

When endothermic reactions proceed, energy is absorbed and stored as a potential. This potential is used to release the energy during exothermic reaction. For higher temperature TES, a wide variety of reversible reaction occur. In addition for a suitable reaction other thermodynamic considerations are important must be taken into account. To determine whether a reversible reaction are suitable for thermal storage or not, equilibrium state has to be evaluated. This equilibrium constant provides information about the reaction which is favoured [16]. This constant is to be defined as the proportion of forward reaction to reverse reaction. If $K > 1$, forward reaction is prevailing and when $K < 1$ reverse reaction is predominant. In order to select the suitable reaction some important criteria concerning selection must be taken into account.

- Full reversibility of the reaction over large number of cycles.
- No side reaction occurring.
- In order to ensure a high charge/ discharging power, due to fast kinetics of the reaction.
- High heat transfer properties.
- Low temperature difference between charging and discharging to minimize energy losses.
- Little or no safety risk.

We had been studying science earlier, we considered some thermo-chemical reaction in which heat is incorporated or discharged. As clear from, "Therm" implies heat and chemical means to the chemical reaction. In this way, the synthetic responses which assimilate or develop heat are known as thermo-substance responses. For example:

$$\mathbf{A_{(s)} + B_{(g)} \leftrightarrow AB_{(s)} + \Delta H}$$

These are the reversible reactions and using these reactions, scientists came up with an idea to store heat energy. There are two processes, charging and discharging [10].

In charging, a solid is given heat so the heat which we gives, it changes the material from one form to another and release some gas or in the form of steam.

$$\mathbf{AB(s) + \Delta H \rightarrow A(s) + B(g)}$$

Then this A(s) is stored or conserved heat which can be used later to gain that heat again by discharging process while the emitted gas can be used with further beneficial ideas.

In discharging of the system is nothing else but the other side of the reaction. When the gas passes through the solid and again reacted together, they release heat which we call as the discharging of the reaction.

$$\mathbf{A_{(s)} + B_{(g)} \rightarrow AB_{(s)} + \Delta H}$$

A lot of solid gas reactions like this which can assist us to store energy which incorporates carbonates, hydroxides, metal sulphate and metal oxides. Our main concern with metal hydroxide, these are very useful in TCES.

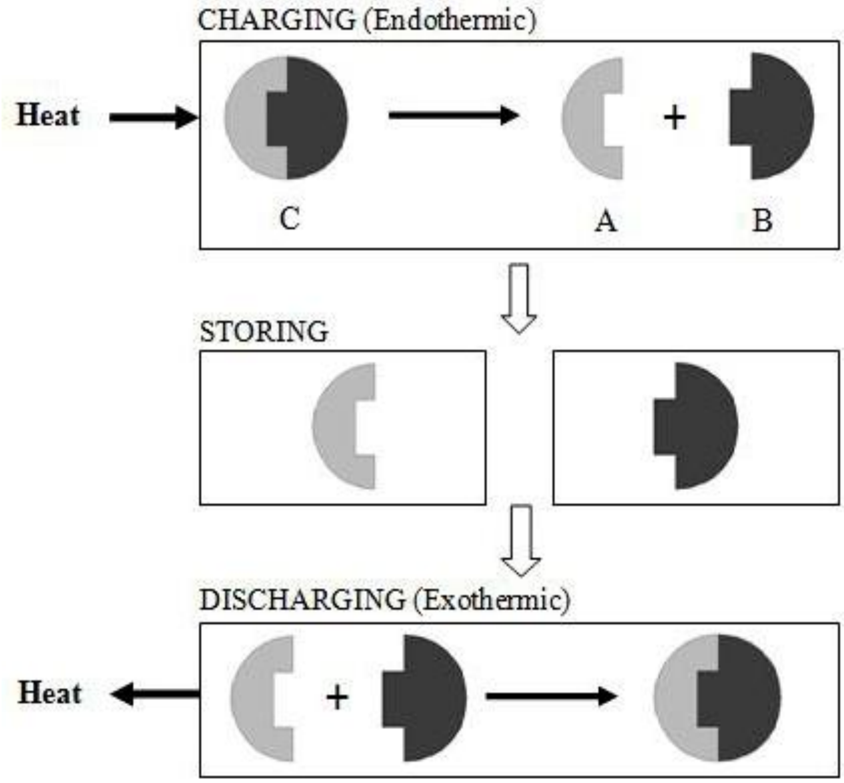


Figure 1.5: Processes occupied in a Thermochemical energy storage cycle: Charging, Storing and Discharging [60].

Metal Hydroxides are other valuable TCES materials which are most investigated about and simple to manage with the advantage of inviting to environment. The majority of these are effortlessly accessible. The structure of metal hydroxide in which hydroxyl group is attaches with the metal. While on heating, hydroxyl group breaks this bond and in product we get steam and metal oxide. This metal oxide stored the heat in the form of enthalpy and again reacted with to release the heat [17].

There are many solid gas reactions like this which can help us to store energy which includes metal sulphates, metal hydroxides, metal carbonates and pure metal oxides etc. List of many of these compounds is given below in tables one by one, which can help us to store energy [18-20].

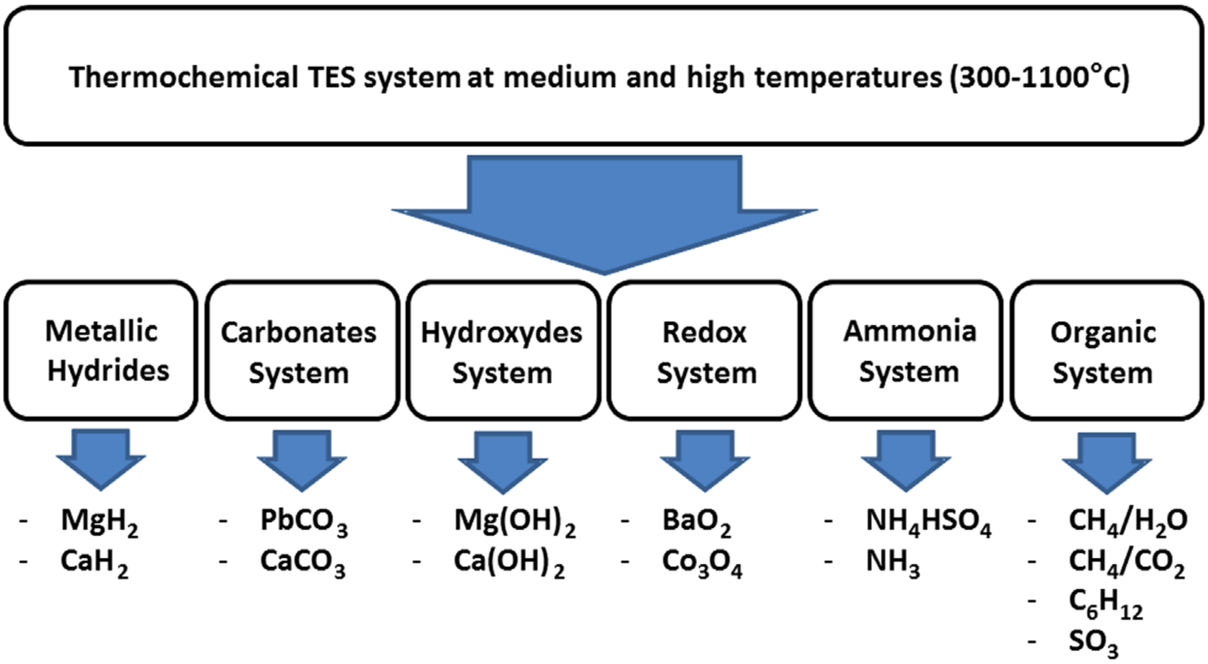


Figure 1.6: Different material are used in different systems for TES [61]

Metal Hydroxides are useful TCES materials which are most researched and easy to manage with the benefit of friendly to the environment. Most of these are easily available. In metal hydroxides a hydroxyl group is attaches with the metal which on heating, breaks the bond and gives water (steam) with metal oxide. This metal oxide is then stored and again reacted with steam to get heat back. Following are the metal hydroxides given below in the table.

Chemical Materials	**Temperature (°C)**	**Reaction Enthalpies (kJ/mol)**	**Gravimetric Energy Density (kJ/kg)**
$Ca(OH)_2/CaO$	515	104.4	1352
$Mg(OH)_2/MgO$	265	77.7	1333
$Be(OH)_2/BeO$	70	51.2	1191
$Mn(OH)_2/MnO$	190	67.07	754
$Ba(OH)_2/BaO$	1005	93.4	545.4

Table 1.1.Some important metal hydroxides

Metal Carbonates are also important candidates to TCES. Their reaction enthalpies are smaller than sulphates but they are really useful for some conditions where we can negotiate large energy storage density. In metal carbonates, $ACO_3$is provided with the required heat to produce metal oxide similarly but with the excretion of carbon dioxide gas. This carbon dioxide gas is then again reacted with metal oxide to gain heat stored before. Some important metal oxides are given below.

Chemical Materials	Temperature (°C)	Reaction Enthalpies (kJ/mol)	Gravimetric Energy Density (kJ/kg)
$CaCO_3$/CaO	885	165.83	1656.8
$SrCO_3$/SrO	1220	1370.6	1370.6
$MgCO_3$/MgO	300	1174	1174
$BaCO_3$/BaO	1555	836.6	836.6
$CdCO_3$/CdO	290	560.1	560.1

Table 1.2. Some important metal carbonates

1.7. Structure of $Ca(OH)_2$

The brucite type structure of Calcium hydroxide $Ca(OH)_2$ is important inorganic material which belongs to hydroxide group. The structure of $Ca(OH)_2$ is formed by layers of Ca sites which linked together by strong hydrogen bond in (001) plane. Synthesis of graphene not just gave scientists, access to (2D) material, however it likewise drew noteworthy consideration to comparable single-nuclear layer structures, for example, silicone, germanene, and TMDCs. Following advances in delimitation, methods of mass materials opened the likelihood of combination of the novel monolayer structures having new functionalities and their utilization in different fields of nanotechnology. Calcium hydroxide is AEMH, well known as portlandite [21].

Bulk layer of $Ca(OH)_2$ structure belongs to P-3m-1 space group and crystal structure of AEMHs comprises stacked sheets of MO_6 (M-alkaline earth metal) edge sharing octahedral. At each octahedron corner, each 'O' atom bind with 'H' atom and later interrelates with three adjacent hydroxyl group of nearby layer. By changing the temperature and pressure of $Ca(OH)_2$ may come intensely change in their crystal structure and electronic properties [22].

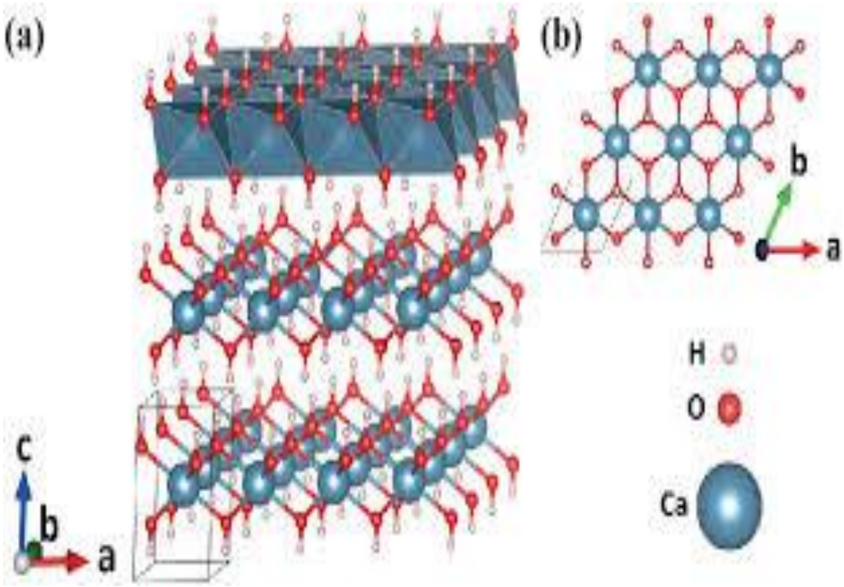


Figure 1.7: Structure of $Ca(OH)_2$ (a) titled view (b) top view of one layer

1.8. Properties of $Ca(OH)_2$:

Ca $(OH)_2$ is a inorganic compound and generally known as slaked or hydrated lime. $Ca(OH)_2$ has a polymeric structure like magnesium hydroxide known as brucite type structure. $Ca(OH)_2$ is a white powder and its solution give a milky colour because it is not very soluble in water. The density of $Ca(OH)_2$ is 2.211g/cm^3 with the molecular mass 74.093g/mol. It is soluble in acid and glycerol and insoluble in alcohol. Unsaturated solutions are typically clear or dreary, with a slight natural smell and an intense basic taste of calcium hydroxide.

$Ca(OH)_2$ or $Mg(OH)_2$ is the rising material for solar cell applications. It has been utilized for a surface adjustment of TiO_2 nanoparticles, which is one of the promising procedures in enhancing conversion efficiency in the cell. For example, covering the TiO_2 nanoparticles with a metal oxide has improved the change proficiency of the phone. $Ca(OH)_2$ are also used in cements and commonly used for dental work.

$Ca(OH)_2$ is very important for thermal energy storage properties. In hydroxide materials, calcium hydroxide has maximum reaction enthalpy of 104kJ/mol. So it is very exciting material for storing the thermal energy from any source like sun, or heat wastage from industries.

Chapter No 02

Literature review

Review of the problem

Synthesis of various inorganic materials have increased importance especially hydroxide due to their electrical, optical and thermal properties. Calcium hydroxide $Ca(OH)_2$ is an significant& cheapest inorganic material which is used to store the thermal energy. $Ca(OH)_2$ is odourless and it is a white colour crystalline solid. It has many application and also used in cement to preserve the building materials etc. $Ca(OH)_2$ also transformed into calcium oxide (CaO) at a fixed temperature range. So it is very helpful for scientist to use this material for thermal energy.

There are many methods to synthesize $Ca(OH)_2$ in which sol-gel method is one of them. Different materials are also used to get calcium hydroxide. $Ca(NO_3).4H_2O$ reacts with sodium hydroxide (Na-OH) and formed $Ca(OH)_2$ and $NaNO_3$ as a product, obtained gel are washed with water and dried. Reaction mechanism is given by.

$$\mathbf{Ca(NO_3).\ 4H_2O + 2\ NaOH \rightarrow Ca(OH)_2 + 2\ NaNO_3 + 4H_2O}$$

Other methods which includes sono-chemical method, precipitation and micro emulsion method in which different organic solvent are used to get the desire material.

Mohammad Amin Aalvi et al. described the synthesis of $Ca(OH)_2$ nanoparticles by using sono-chemical method. By changing the concentrations of the material, aging time show the change of size, growth and the morphology of the particles. By giving heat treatment Ca(OH)2 converted into CaO which was confirmed by using XRD [23].

Zahra Mirghiasi et al. synthesized the nanoparticles of Ca(OH)2 by using thermal decomposition method. $Ca(OH)_2$ converted into CaO by calcination at 650^oC in furnace under N_2 atmosphere. XRD analysis confirmed the crystal structure convert from hexagonal to cubic structure after heating [24].

Moria Ambrosi et al. synthesized the colloidal nanoparticles of $Ca(OH)_2$ and spread in propanol. . The dynamic strength of dissemination of $Ca(OH)_2$ particles in water and propanol has likewise been considered in perspective of their conceivable application in wall painting preservation[25].

Yolanda A. Cariado et al. studied the reaction kinetics of the pure $Ca(OH)_2$ under suitable condition for thermal energy. They used $Ca(OH)_2$ particles which are in large size, hydration and de hydration process have been completed satisfactory. The focus of this study is on the effect of pressure, temperature and particles size of the material. Temperature ranges for de-hydration/hydration process between 400^oC to 560^oC and steam partial pressure in between 0 to 100kPa. On the account of substantial particle size of the material, particle grinding down has been recognized and need to synthesize a suitable material for storing thermochemical energy [26].

C. Roβkopf et al. studied the nano coated $Ca(OH)_2$ for thermochemical energy storage. On approach is to stabilize the material by coat them the responding material with nanoparticle to limit the attracting forces prompting less agglomeration. In case of high temperature surface configuration, change of volume, reaction of the gas and mechanically stress inside the storage represent the challenges for nanoparticles. By mixing $Ca(OH)_2$ with Aerosil resulting the better material for thermochemical storage. The hydration / de-hydration process in which new phase of calcium silicate hydrate introduced [27].

In 2011 Qing Lin investigated the reactivity of silica nanoparticles with Calcium hydroxide. $Ca(OH)_2$ initiated SiO_2 through an exothermic process, which is for the most part credited to break down into Si-OH and Si-O bonds which offering come up to calcium silicate hydrate. The reactivity of SiO_2 and $Ca(OH)_2$ fundamentally relies on the percentage of the mixture. Higher the percentage of SiO_2 results increase in the reaction rate of SiO_2 with Calcium hydroxide [28].

Schicheng Zhang et al. synthesized the core shell nanoparticles of $CaCO_3@SiO_2$. The thermal stability of the particles decreased as silica was coated on the surface of $CaCO_3$. The size and shape of the particle were same as the core of $CaCO_3$. After preparation of core shell nanoparticles, thermal stability of the core shell particles decreased as the temperature of the materials increased [29].

C. Roβkopf studied the bed properties of the material by adding silica nanoparticles in $Ca(OH)_2$. It showed that after addition of silica (5% wt) the thermal and bulk properties was stabilized for some cycles and consequently cycling stability ensured. Addition of nanoparticles it prevents material for agglomeration during the process of cycling. The powder bed properties improved the mass and heat transfer. The possibility to improve the bed properties and cycling stability during the thermochemical reaction could be transfer application to deal with fine powder material [30].

J. Yan et al. studied the process of dehydration of $Ca(OH)_2/CaO$ by Li-doping. The study confirmed that the storage of heat capacity after doping does not affected, but kinetic study of $Ca(OH)_2$ with Li-doping the storage of heat divided into two parts. De-hydration process for $Ca(OH)_2$with Li-doping was improved as well as the kinetic study parameter of $Ca(OH)_2$ and with Li-doping are obtained. Theoretical results of $Ca(OH)_2$ matched with experimental results for de hydration process. $Ca(OH)_2$ with Li-doping calculation agree with the data experimentally on the similar growth but some exact calculation describe a little delay [31].

Jose A. F. Gamelas et al. synthesized $CaCO_3$ particle with silica by sol-gel method. A controlled synthesis was done which gave a highly branched like silica formation at the surface of $CaCO_3$. The addition of silica did not affect the structure of CaCO3 which was confirmed by using different techniques. The modified particles may contribute in the paper industry to improve the paper strength [32].

C. T. Yamashita et al. synthesized core shell nanoparticles of $CaCO_3/SiO_2$ via sol gel method. Nanoparticles were heated at 700^oC after successful synthesis of core shell particles and convert to CaO/SiO_2 by de- carbonization of $CaCO_3$. $Ca(OH)_2/SiO_2$ particles were achieved by using water vapors and thermal storage was confirmed by TGA. Efficiency of core shell particles did not achieve theoretical value of $CaCO_3$ because it didn’t completely decompose to CaO due to SiO_2 shell [33].

Chapter No 03

Synthesis and Characterization Techniques

3.1. Synthesis techniques of Nano-materials

There are two major techniques that we use for the synthesis of nanomaterial

- Top down approach
- Bottom up approach

3.1.1. Top down approach

A top down approach is effectively breaking down arrangement to pick up knowledge into its compositional sub system. In top down approach, nanoparticle can be arranged by mechanically granulating e.g. Ball processing. These nanoparticles have a few favourable circumstances and detriments. Both approaches assume a precarious part in the creation and synthesis of nanostructures, yet the detriments of the top down methodology is the weakness of the surface structure [34].

3.1.2. Bottom up approach

In bottom up approach which small component of atomic or molecular components are self-assemble and form large and organized particle. Bottom up synthesis approach an ionic precursor is used to prepare nanoparticles e.g. by co precipitation method, sol gel method, electrochemical deposition and molecular beam epistaxis etc. [35-36]

3.2. Apparatus description

For synthesis of different materials the following apparatus are required

- Hot plate
- Digital balance
- Water bath sonicator
- Centrifuge
- Vacuum oven

- PH paper or meter
- Filtration

3.3. Synthesis process

For the synthesis, sol-gel method was used for Calcium Hydroxide $Ca(OH)_2$and it's composite with silica $Ca(OH)_2@SiO_2$ particles. Different concentrations of silica are used to synthesize the composite.

3.4. Material required during Synthesis

The following materials are used during synthesis process.

- Calcium nitrate $(Ca(NO_3)_2.4H_2O$
- Sodium hydroxide (Na-OH)
- Ethylene glycol
- Distilled water
- Deionized water
- Tetra ethyl Ortho-silicate (TEOS)
- Ethanol
- 2- propanol (Isopropyl)

3.5. Material preparation

All material synthesis is composed of total 2 steps as shown below.

3.5.1. Synthesis of Calcium hydroxide $Ca(OH)_2$

Calcium hydroxide is an inorganic material and known as portlandite or white lime. Calcium hydroxide were prepared by sol gel method as shown in Fig. no. The stepwise synthesis process is given below.

1. $Ca(NO_3)_2 . 4H_2O$ was mixed in ethylene glycol in a typical run by stirring. After the calcium salt was dissolved, the solution of Sodium Hydroxide (NaOH) in distilled water was added drop wise at the rate of 1ml/sec in the above solution.
2. The solution was vigorously stirred at the room temperature for 30 mints to achieve a uniform size particle.
3. After stirring, the gel was kept for 5 hours in static state.

4. After 5 hours, the supernatant solution was discarded and the remaining solution was collected by centrifugation.
5. Then the solution was dried under vacuum oven at 50-60°C for 24 hours.

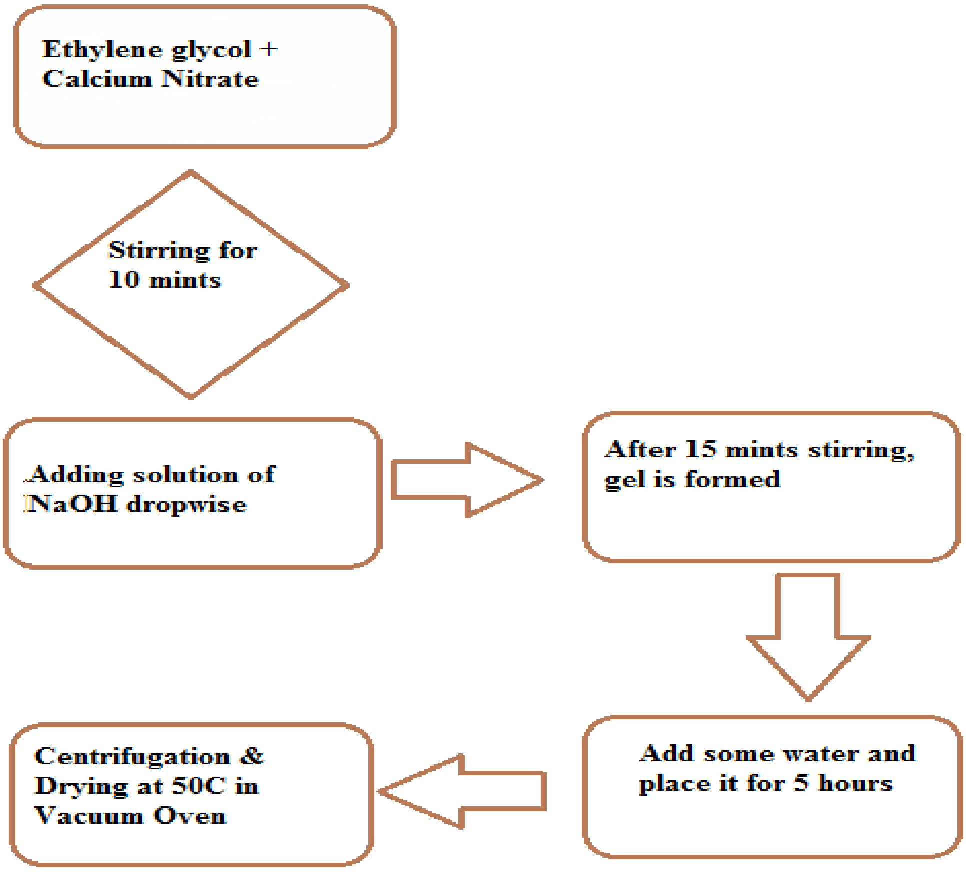


Figure 3.1: Synthesis of Calcium Hydroxide $Ca(OH)_2$

3.5.2. Synthesis of $Ca(OH)_2@SiO_2$ Composite

For synthesis of $Ca(OH)_2$ with silica ($Ca(OH)_2@ SiO_2$), typically sol-gel method was used for polymerization of TEOS in the presence of $Ca(OH)_2$ as shown in fig. The following steps are involved in the process of synthesis.

1. 0.03 M solution of $Ca(OH)_2$ particles were dispersed in 2-propanol (Iso-propyl) by using magnetic stirring. 0.5 ml anhydrous ammonia added in solution and stirred for 30 minutes.

2. After 30 minutes, the required amount of TEOS was added for different concentration of composite.
3. Then solution was prepared at room temperature under constant stirring for 24 hours.
4. After stirring the product was washed and centrifuged with DI water three times.
5. The final product was dried in vacuum oven at 50-60°C.

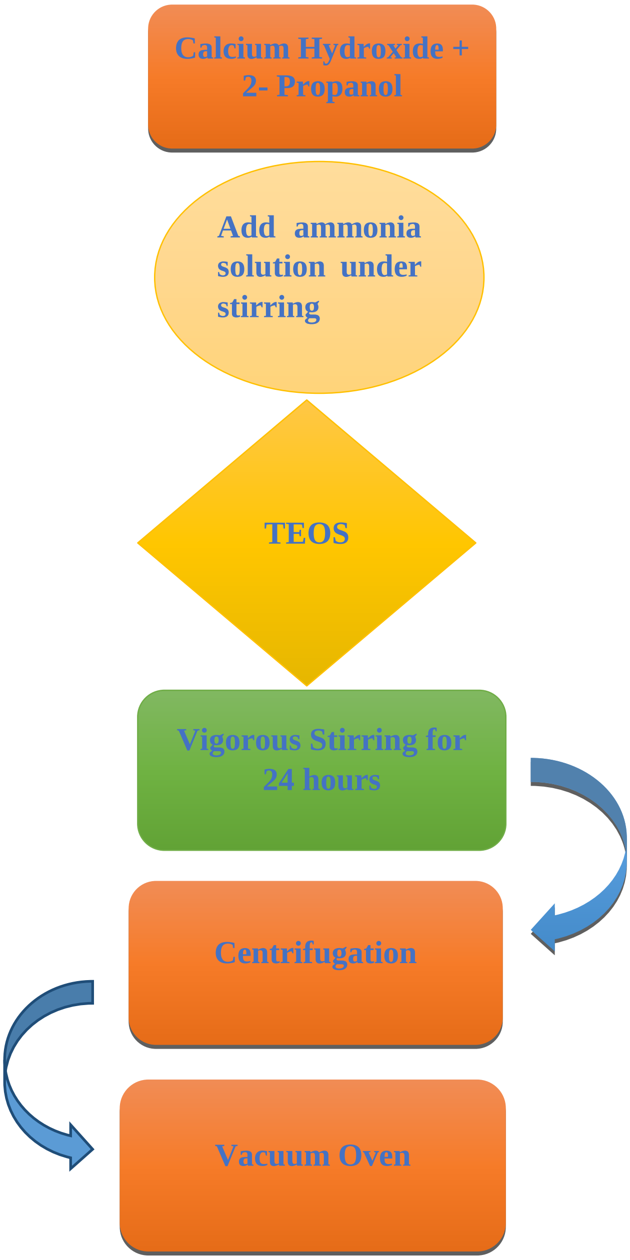


Figure 3.2: Synthesis of $Ca(OH)_2@SiO_2$ composites

3.5.3. Concentration of TEOS for Composite

In order to synthesize different composite, different amount of TEOS are used. The following synthesis of composites has different concentration of TEOS.

- $Ca(OH)_2/SiO_2$ (10mM)
- $Ca(OH)_2/SiO_2$ (5mM)
- $Ca(OH)_2/SiO_2$ (2mM)

Other materials like Ca(OH)2, 2- propanol, ammonia solution are in same amount in all experiments. TEOS concentration

- **For 10mM:** 2.216ml TEOS added in the solution.
- **For 5mM:** 1.1074ml TEOS added in the solution.
- **For 2mM:** 0.44ml TEOS added in the solution.

3.6. Characterization Techniques:

To investigate the arrangement of the crystal, morphology and its different properties, different techniques are used. To check the crystal structure and phase of the material X-Ray diffraction can be used. To study and confirm the morphology of the material SEM are available. To check the elemental analysis and the thermal properties of the required material EDS and TGA can be used.

These characterization techniques are used in this research work,

- ➢ X-Ray Diffraction (XRD)
- ➢ Scanning Electron Microscopy (SEM)
- ➢ TGA
- ➢ EDS
- ➢ FTIR

3.6.1. X-Ray Diffraction

3.6.1.1. Introduction

X-Ray diffraction is used to determine the crystalline structure and lattice parameters of the material. It is also called non-destructive technique. In X-ray diffraction, X-ray beams are scattered when they interact with the material. These scattered beams enhance their effect in many directions. Due to constructive interference these beams reinforce each other. This process is known as X-ray diffraction. Illustration of XRD is shown in figure 3.3 [37].

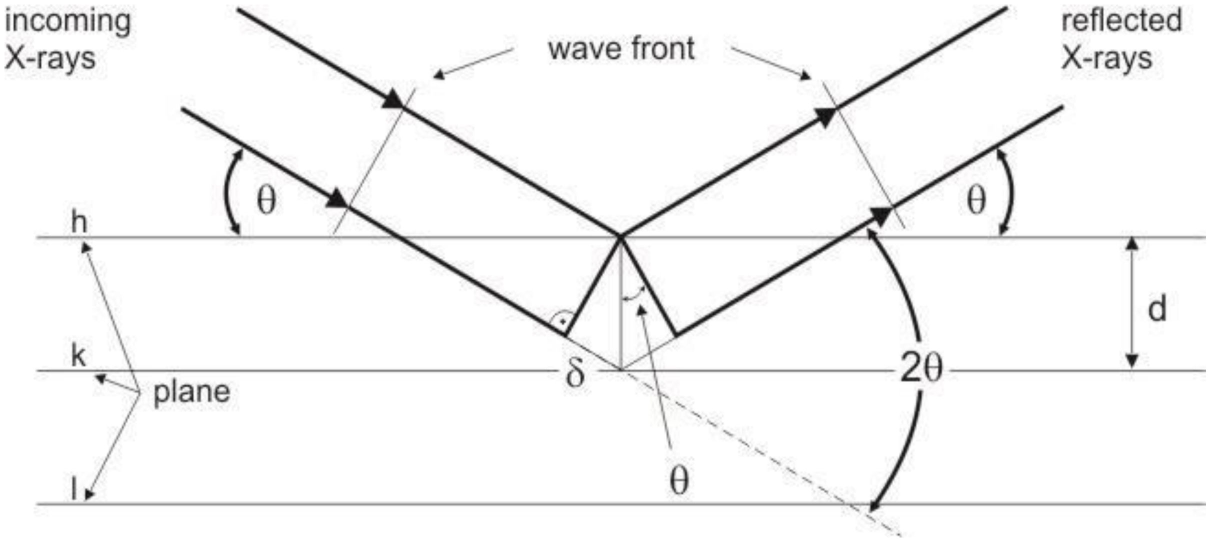


Figure 3.3: X-rays interaction with the Crystal planes (hkl)

The crystals of material consist of the atomic planes and these atomic planes tell us about the structure. When X-rays falls on the atomic planes, they interact with each other. X-ray diffraction defines the structure pattern of the crystal and tells us much about the internal arrangement of atoms in crystal.

3.6.1.2. Basic Principle

The electrons oscillates, when the X-ray beam incident on the crystal and strike with the atom as shown in figure 3.3. The frequency of the incident beam and the frequency of oscillating electrons are identical. In some direction, the combining rays are showed out of phase when there is destructive interference. Contrary due to the periodic and regular arrangement of atom in few directions, there is constructive interference. This is due to the rays which have significant impact and are in phase on the sample. By using Bragg's Law, the occurrence of constructive interference can be explained.

3.6.1.3. Bragg's Law

In the crystal, due to scattering of the beam, Bragg's law demonstrates the X-ray interference and in 1913 this law was given by W.H. Bragg and hid son W.L. Bragg.

$$\mathbf{n\,\lambda = 2d\,\sin\Theta}$$

Where,

d = inter planar distance of atoms, ions or molecules

ϴ = angle of scattering

λ = wavelength of X-rays

n = number of planes of crystal

The illustration of Bragg’s law is shown in figure. This shows that there are two layers of atoms separated by distance d. When two beams of X-rays are incident at these two layers, they scattered by an angle ϴ and reflected by undergoing an additional distance shown in Fig (3.4).The necessary condition for Bragg’s law is that two reflected beam are in phase, additional distance must be integral multiple of the wavelength, reflective angle and angle of incident must be equal.

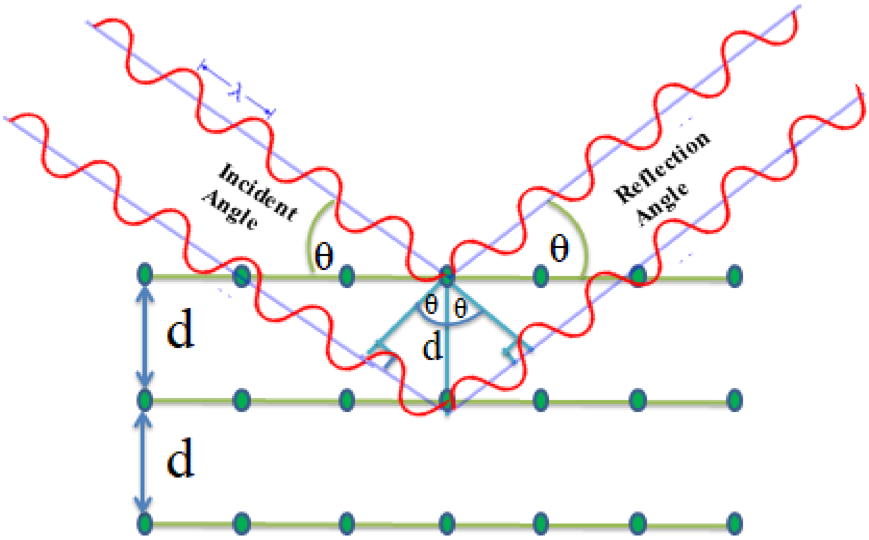


Figure 3.4: The mechanism of X-Ray diffraction

When these conditions will be satisfied then diffraction will occur which is mathematically described by Bragg’s equation

$$\mathbf{n\,\lambda = 2d\,sin\Theta}$$

From XRD analysis we can find the crystal structure, phase of the material and average particle size by using Scherer's formula.

$$\mathbf{D} = k\lambda / \beta cos\theta$$

$\mathbf{k} =$ shape factor for specific crystal

$\boldsymbol{\lambda}$ = wavelength of X-ray

$\boldsymbol{\beta} =$ FWHM

The production of X-beams pursues the phenomenon of excitation and de excitation of electrons by incident electron of beam. The electrons with high speed are turning out from an electron gun and hit the target of Cu. The electrons in the orbit are hit by the incoming beam of electron and they scattered the electron out of the shell. The higher energy electron will fall into lower energy orbit and release some energy which corresponds to X-rays. Particular energy of waves are released relying on whether electron is dislodged from the higher or lower enrgy state. The K lines are most important as are easily take part in the specimen. So to get the beams from the K level, the excitation incident beam must of the near energy to dislodge the K shell electrons. The generation of X-beams depends upon the energy levels K, L, M and N of the dislodged electrons.

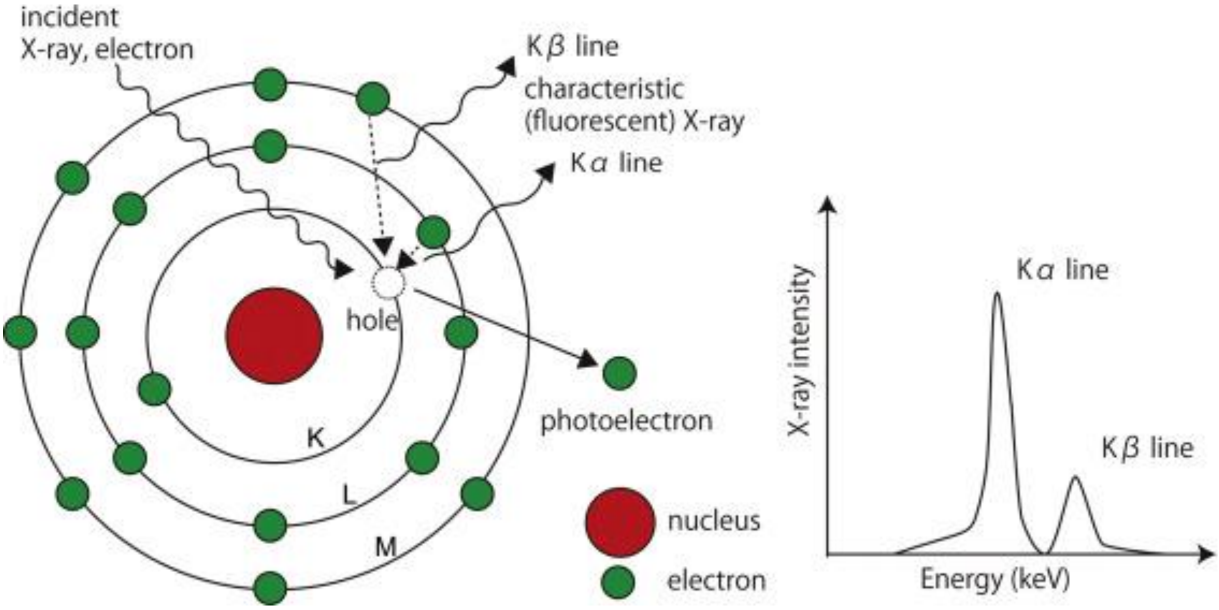


Figure 3.5: Mechanism of production of X- Ray for different energies

By changing the metal target, energies can be changed, a few target are stated in the fig. (3.5)

Target Element	K α (A^0)
Cu	**1.541**
Fe	**1.937**
Co	**1.790**
Cr	**2.291**

Table No 3.1. Different Target material used in XRD

3.6.1.4. XRD Applications

XRD has many applications in material science. The most important application are

1) XRD can be used to determined atomic arrangement
2) XRD can measure the average spacing between two spaces
3) XRD can determine the crystalline phases
4) XRD can obtain the Integrated intensities
5) XRD can also measure the crystal structure of unknown material

3.6.2. Scanning Electron Microscope (SEM)

The Scanning electron microscope is an uncommon kind of electron microscope which operates the exceedingly focused electron beam for any sample’s surface morphology. With the electrons of the sample, the occurrence beam communicated and makes some signals which hold data about its surface morphology.

SEM requires an electron optical structure to yield an electron probe, a simple stage to place a sample, a secondary electron indicator, a picture show unit and an operation outline to perform many operations. The electron optical system comprise of electron gun, condenser lens, target lens to deliver electron probe, an inspection coil to inspect the electron probe and different parts [37].

3.6.2.1. Electron gun

Positioned at the highest point of the segment where free electron are formed by thermionic discharge of tungsten filament at ~2700 K and electron hastened at 200 V to 30kV.

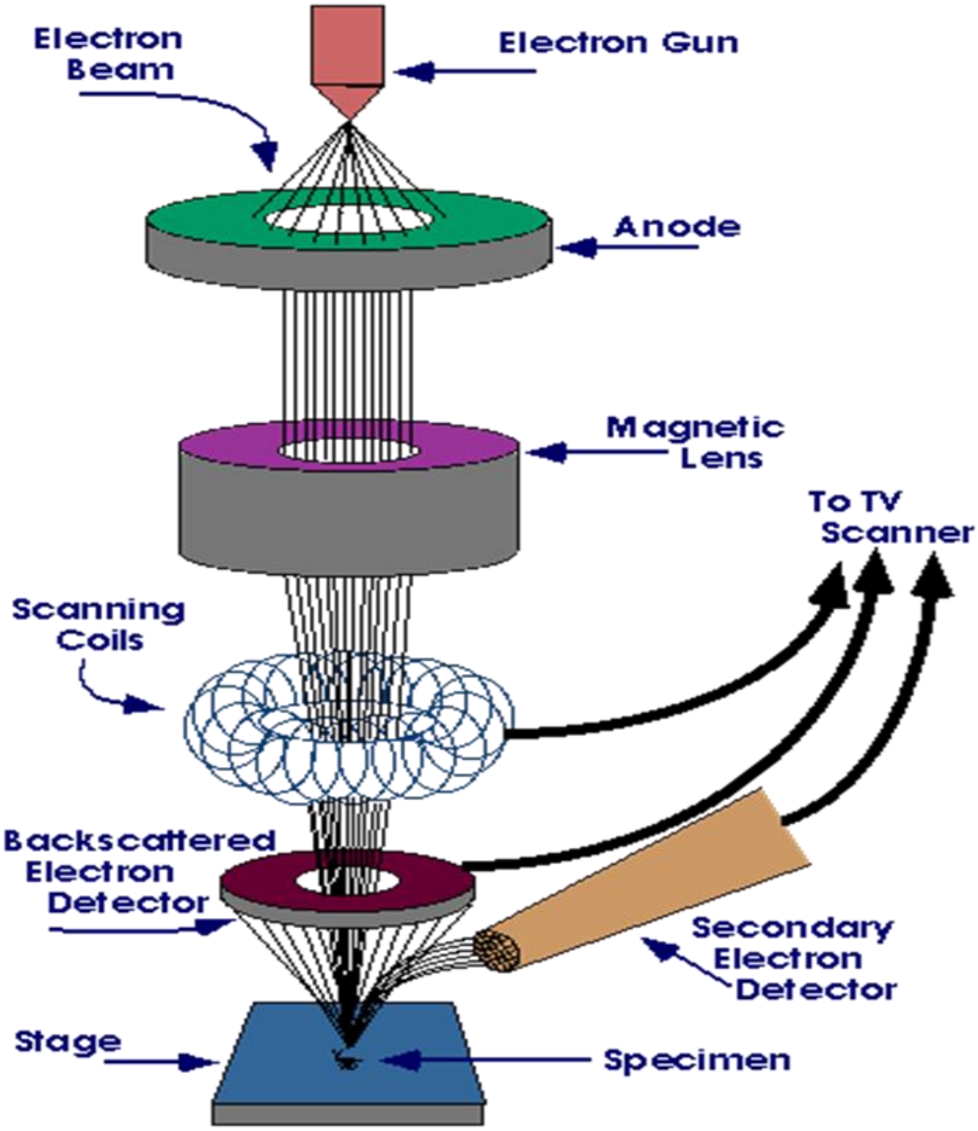


Figure 3.6: The detailed schematic of SEM

3.6.2.2. Condenser Lens

After the beam spirits from anode it is exaggerated by two lenses of condenser which helps beam to converge and go over and done with a point of convergence and electron beam is involved 1000 times to its unique size. By selected acceleration up we can likewise focus intensity of electron beam when strike sample [38].

3.6.2.3. Scanning System

Images are melded by roistering the electron beam crosswire over sample utilizing redirection coils inside objective lens. The magnetic field is utilized to diminish the distortion of electron beam.

3.6.2.4. Secondary Electron

When incident beam of electron falls on the sample, it knocks out the electron from the sample layers. The energy of those electrons is between (0-30 eV) which help for making image.

3.6.2.5. Backscattered Electron

When incident beam interact with the specimen some electron will bounce back due to elastic collision. The energy of these electrons lies (15-30keV) which helps to making the image.

3.6.2.6. Specimen Chamber

At lower part of the section, the sample stage and controls are found. The optional electrons from sample are pulled into the detector by positive charge.

3.6.2.7. Effect of Accelerating Voltage

We get high resolution, more damage and unclear surface structure from the high accelerating voltage. And we get low resolution, clear surface structure and low damage from the low accelerating voltage.

3.6.3. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FT-IR) technique is used to get an infrared range of emission, absorption and photo-conductivity of liquid, gas and solid. This technique is also used to collect the data of high resolution over wide range, which permits the advantage over a dispersive spectrometer which measures the intensity over a thin wavelength at a time. This term of FTIR originate from mathematical term Fourier Transform which converts crude information into actual spectrum [39].

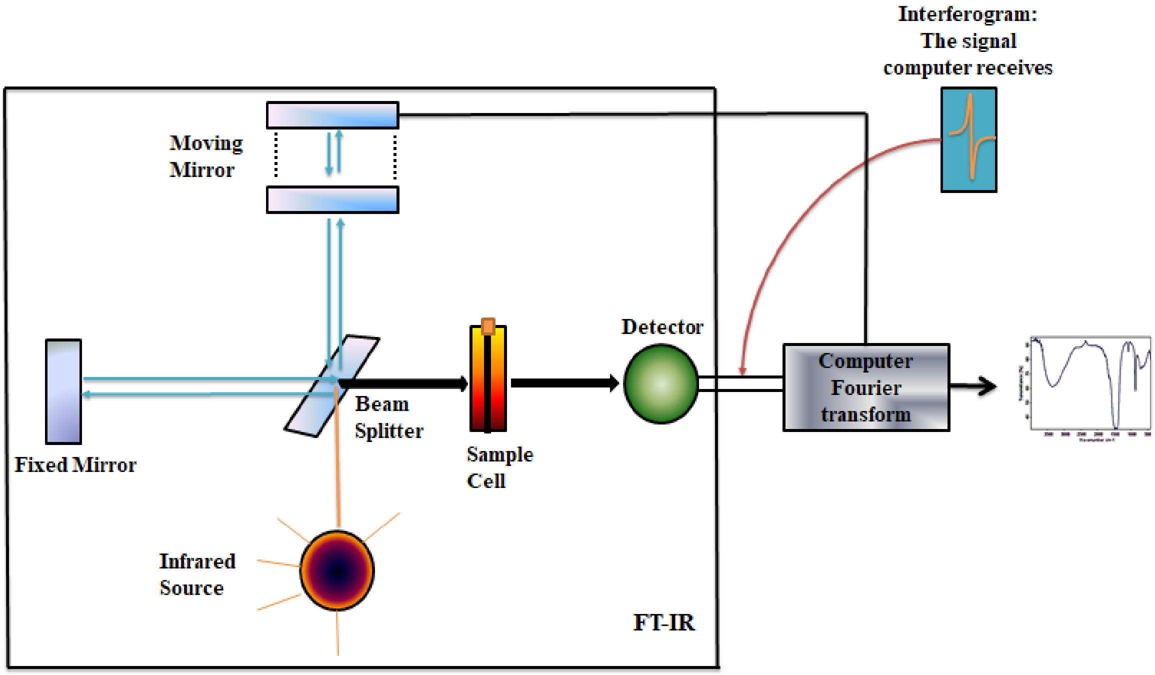


Figure 3.7: Schematic diagram of Fourier-Transforms Infrared Spectrometer.

The objective of any absorption spectroscopy is to quantify how fine a sample absorbs light at every wavelength. The most straight forward approach to do this is by shining a monochromatic light bar at the specimen, measure how a great part of light is retained, and repeat for each diverse wavelength. Fourier transform spectroscopy is less understanding than monochromatic light emission on the sample. This method sparkle a beam containing of number of frequencies of light on the double and measure the amount of light emission assimilated.

As we can observe that a monochromatic beam of light having full spectrum of wavelength is obtained from Michelson interferometer. Distinctive wavelength is squeezed at various rates so that every beam coming out has distinctive spectrum. As shown in given fig. raw data obtained is called "interferogram" and then this data is processed through a computer to get desired results.

3.6.4. Energy Dispersive Spectroscopy

EDS or EDX is a technique, which is used for elemental analysis with the combination of SEM. It recognizes the X-ray emitted from the sample to characterize the elemental analysis of the sample when exposed. When electron beam falls on the sample, it gets bombarded and the electron from the sample eject out from the sample. When these electrons eject out from the sample, high energy electron falls down and fill the vacancy. When high energy electron falls down to low energy level it emits radiation to balance the difference of energy of two states in the X-rays form. This energy belongs to characterize X-rays of the element they get discharged from. The EDS is utilized to measure the relative plenitude of these x-beams versus their vitality.

At the point when transmitted x-ray hit with the detector it offers ascend to a pulse of charge which be determined by the energy of the x-rays, this pulse of charge at that point changes over into voltage beat by a charge sensitive amplifier. The signal at that point sent to multi-channel to category the pulse by the voltage. The energy decided from the voltage versus counts at that point showed on screen of a PC.

3.6.5. Thermo-gravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) is a technique which is used to study the thermal behaviour of any material. In TGA, change in mass of the sample can be measured as a function of temperature & time. To check the thermal behaviour, a small amount of sample is required which gave the result in the form of TG curve with depression or hills with the steps as temperature increases [40].

3.6.5.1. Working and Construction of TGA

In TGA, a high temperature crucible is used with supporting precision balance, temperature with linear change programmed furnace and inlet of the gas. Usually platinum crucible or alumina pans are used but in TGA it depends on temperature conditions. For TG analysis a very small amount of material is used which is placed in the crucible and put it in thermo-balance in the furnace. The sample can be heated at constant rate of change of temperature which is carried out in an inert gas (Ar, N2, He) atmosphere depending on reaction conditions [41].

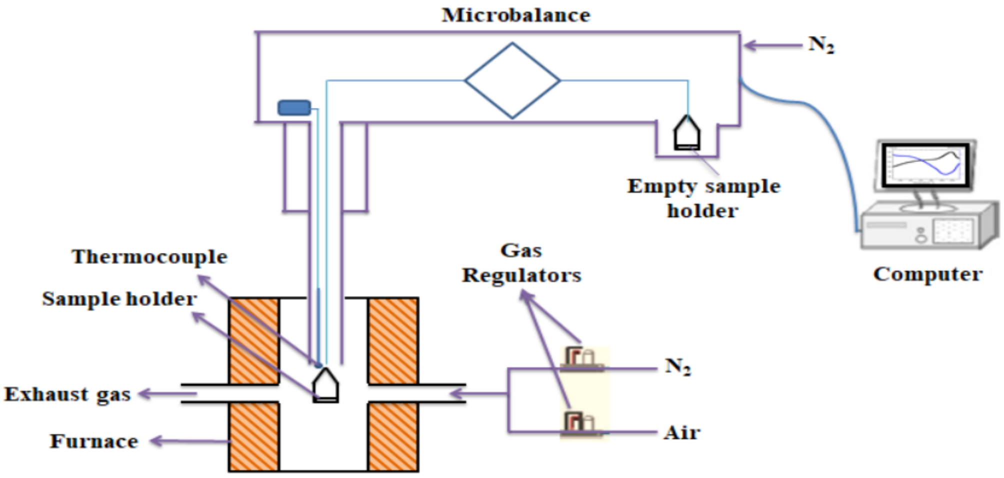


Figure 3.8: Instrumentation of Simple TGA analysis

Firstly, some amount of gas inserted and exit through exhaust. The sample mass is continuously monitored during analysis. The mass loss indicates the mixture in the sample or degradation of the sample which shows in a step of the TG curve. If the mass is increased as the temperature rises, it is accredited the reaction or oxidation of the sample with the surrounding. Following fig.3.8 explain the instrumentation of the sample.

Chapter No 04

Results and Discussion

4.1. X- Ray Diffraction

XRD has been done to analyze the data of the powder sample. The XRPD of the prepared sample match with the pattern of $Ca(OH)_2$. The crystalline structure of $Ca(OH)_2$ is hexagonal with lattice parameter a= 3.5899 A^o , c = 4.916 A^o, z = 1 confirmed by (ICSD card No. 44-1481). The diffraction peaks of the sample indicates that the crystalline structure of $Ca(OH)_2$ can be easily attained under synthetic circumstance. The peaks at 2Θ = 29.35°, 38.95° and 42.5° corresponds to $CaCO_3$. Because CO_2 present in atmosphere reacts with $Ca(OH)_2$ and the resultant it make small amount of $CaCO_3$[42].

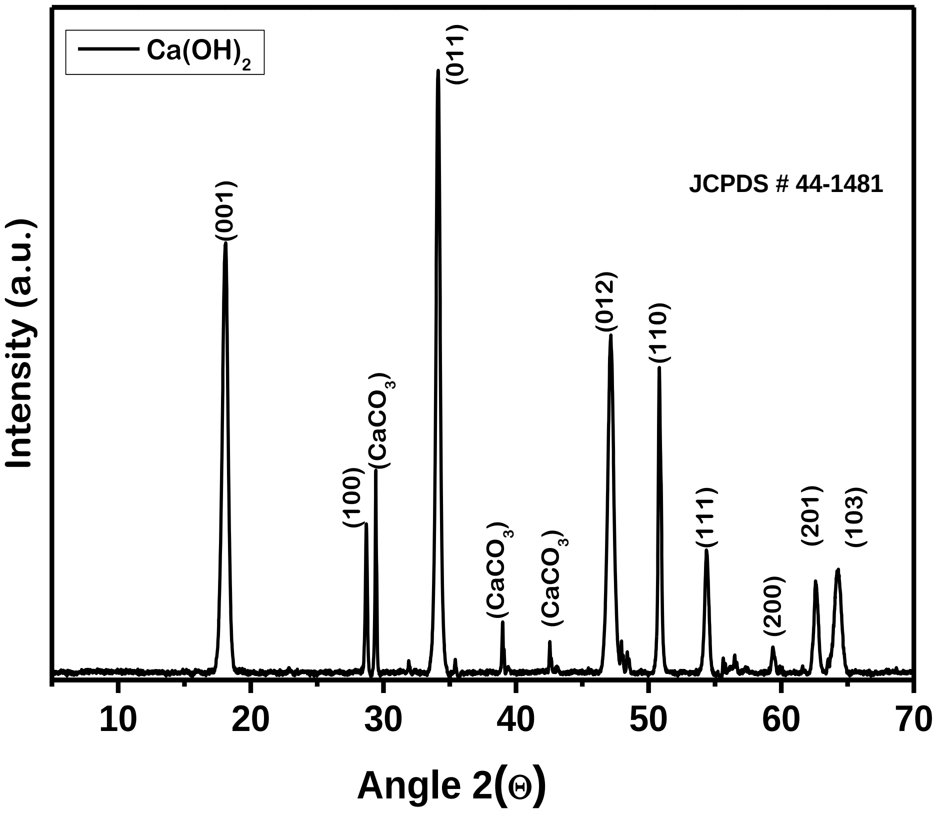


Figure 4.1: XRD pattern of $Ca(OH)_2$

The lattice strain and crystallite size can be acquired from peak broadening analysis of the sample. The peak broadening identifies that the material is in nanoscale. The crystallite size can be resolute by utilizing Debye-Scherer's formula [43].

$$\mathbf{D} = k\lambda / \beta cos\theta$$

Where "D" is the crystallize size of the particle, "λ" is the wavelength of the X-rays, "k" is the shape factor (0.94) and "β" is the FWHM (full width half maximum of the diffraction peaks). The average crystallize size was measured by using Scherer formula of $Ca(OH)_2$that was 30.3 nm.

$Ca(OH)_2$ was converted into CaO by annealing the sample by giving the temperature at 600^oC. The structure of Calcium Oxide (CaO) was confirmed by using XRD analysis. XRD pattern confirmed the structure decomposed easily from $Ca(OH)_2$ to CaO. The crystalline structure of CaO is cubic with lattice parameter a=b=c= 4.805 A^o confirmed by (JCPDS Card No. 78-0649) with space group Fm-3m. The diffraction peaks of the sample indicate the crystalline structure with no impurity peak has been detected. Average crystallize size of CaO was measured by Scherer formula that was 77 nm [44].

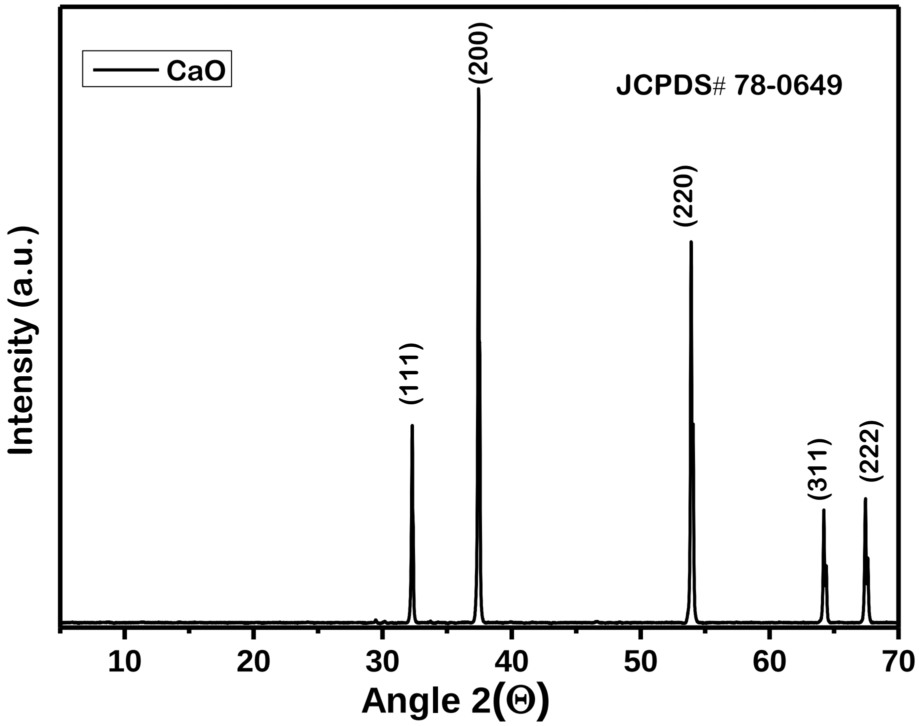
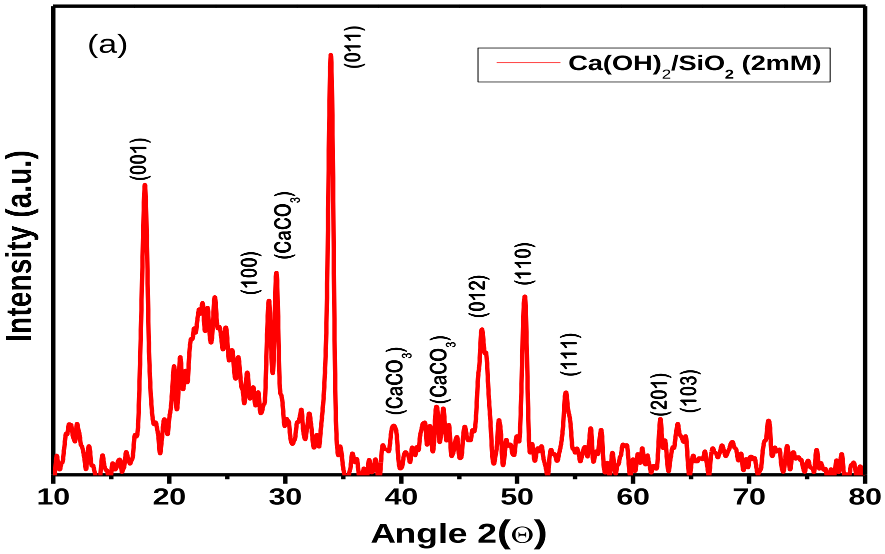
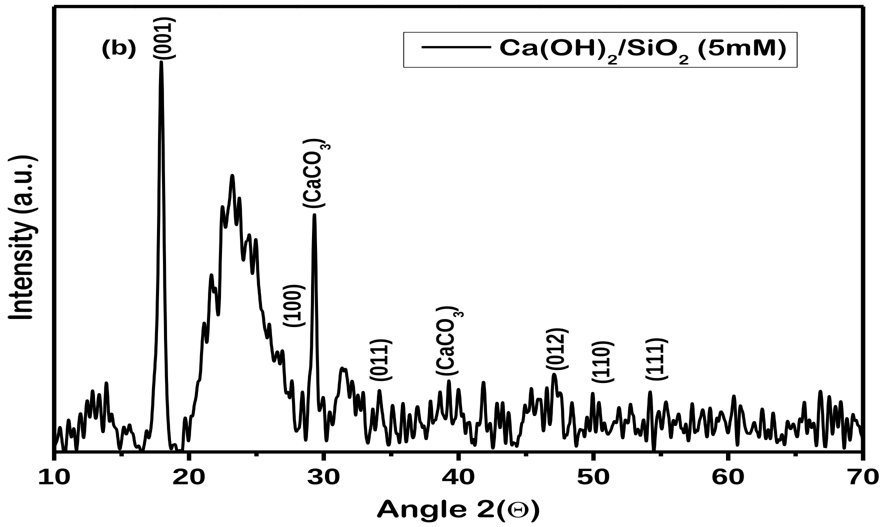


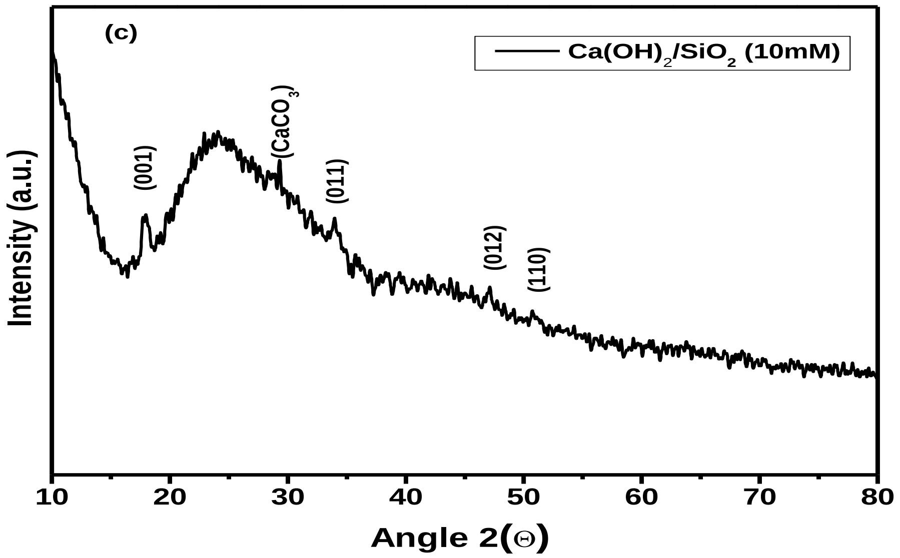
Figure 4.2: XRD Pattern of CaO

Figure 4.3 shows the composite of $Ca(OH)_2$@$SiO_2$by adding different concentration of TEOS (2mM, 5mM, 10mM). XRD pattern of pure $Ca(OH)_2$ shows the crystalline structure with higher peak intensity. In $Ca(OH)_2$@SiO_2 (2mM TEOS) shows that all peaks of $Ca(OH)_2$ are present with the addition of broad peak of amorphous silica nanoparticle is present at angle $2\Theta = 22.5^o$. This means that addition of SiO_2 nanoparticle do not affect the structure of the material at this concentration of silica. Moreover the addition of more $SiO_{2,}$ the intensity of $Ca(OH)_2$ peaks decreases as well as SiO_2 disturb the crystal structure of $Ca(OH)_2$ because particles are coated on the surface of $Ca(OH)_2$. The intensity of diffraction peaks of $Ca(OH)_2$ decreases as we increase the amount of silica [45].





As we increase the concentration of TEOS (i.e 5mM, 10mM) the peak intensity of crystal structure is decrease which confirm by SEM analysis.



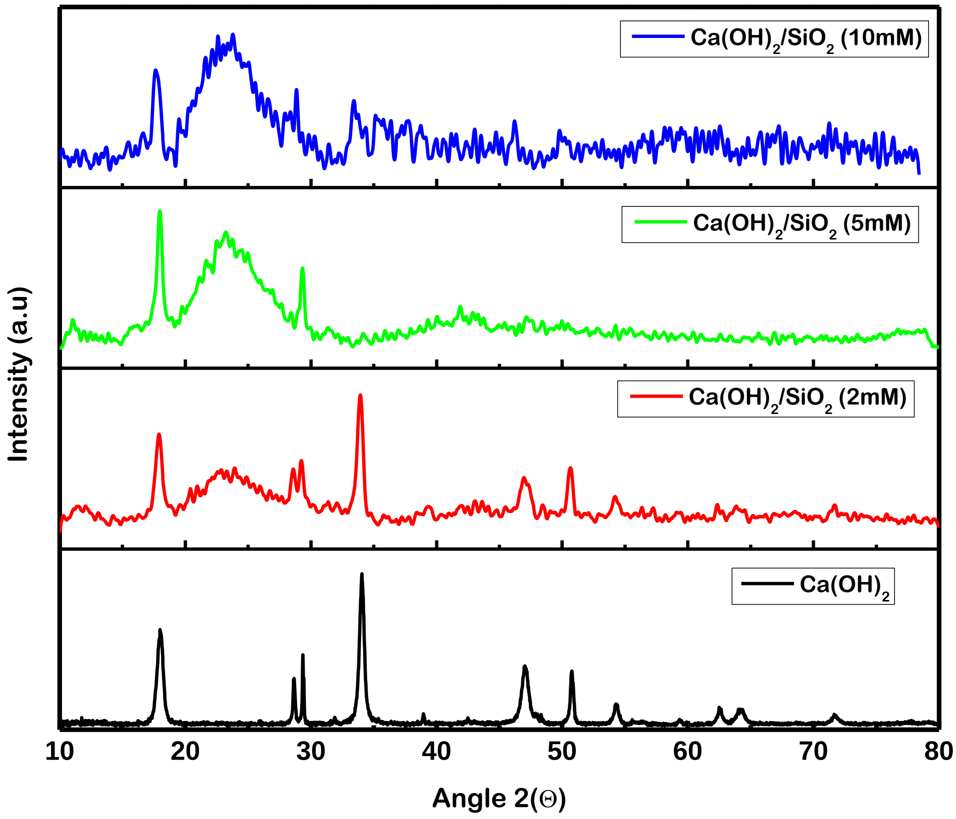


Figure No 4.3 : (a) XRD pattern of $Ca(OH)_2/SiO_2$ (2mM) (b) XRD pattern of $Ca(OH)_2/SiO_2$ (5mM) (c) XRD pattern of $Ca(OH)_2/SiO_2$ (10mM) (d) Combine XRD pattern

4.2. SEM Analysis

In figure 4.4, the surface morphology of nano $Ca(OH)_2$ and its composites with SiO_2 were studied by using Scanning Electron Microscope (SEM). The structure of $Ca(OH)_2$ are like platelets or flakes type structure. In figure 4.4(a), the SEM demonstrates that the particles were not scattered properly and the morphology of those particles were hexagonal [46].

In $Ca(OH)_2/SiO_2$ (2mM) composite, the morphology of SiO_2 nanoparticles are spherical and they seem to cover the surface of $Ca(OH)_2$ completely. Which indicates that a good composite formation under given condition. The electron dispersive spectrum shows the elemental analysis.

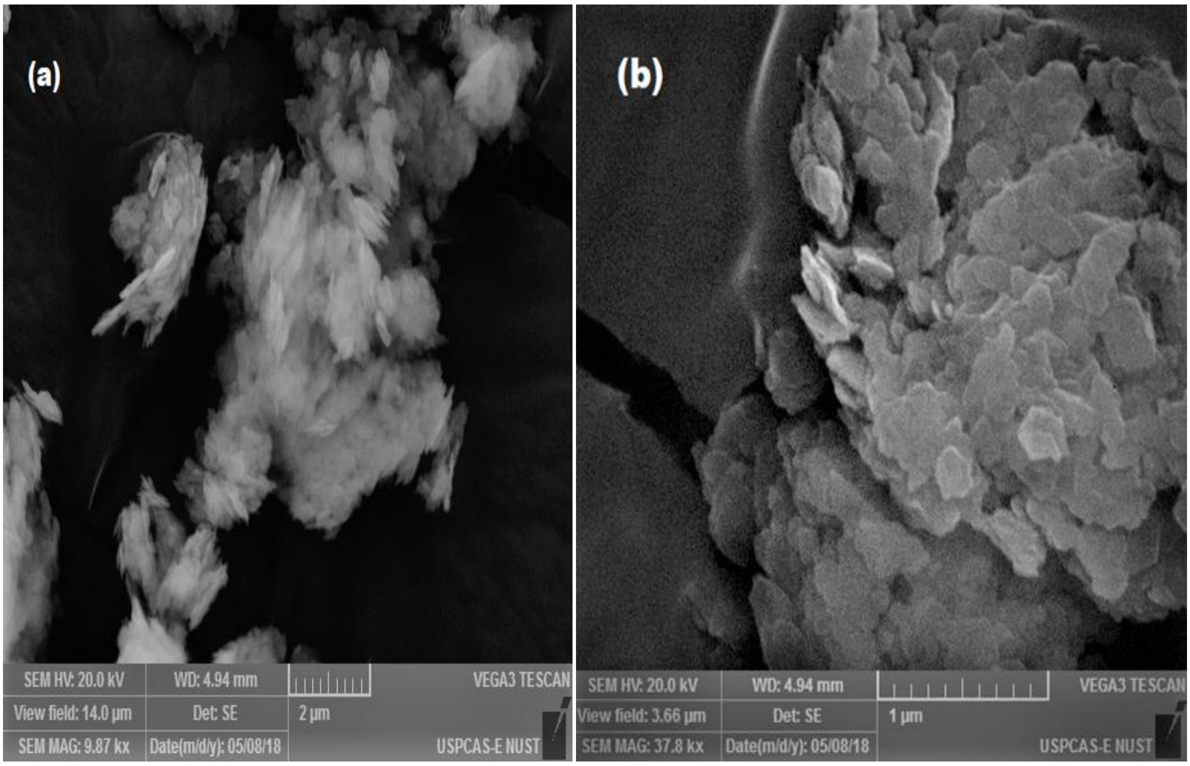


Figure 4.4 (a-b) SEM images of $Ca(OH)_2$

As we increase the concentration of TEOS, more SiO_2 particles form which covers the surface of $Ca(OH)_2$ as compare with 2mM composite. In case of 5mM Composite, more silica particles cover the surface of $Ca(OH)_2$ which seems that good composite formation. The formation of silica particles is due to condensation of tetra- alkoxysilanes as a precursor.

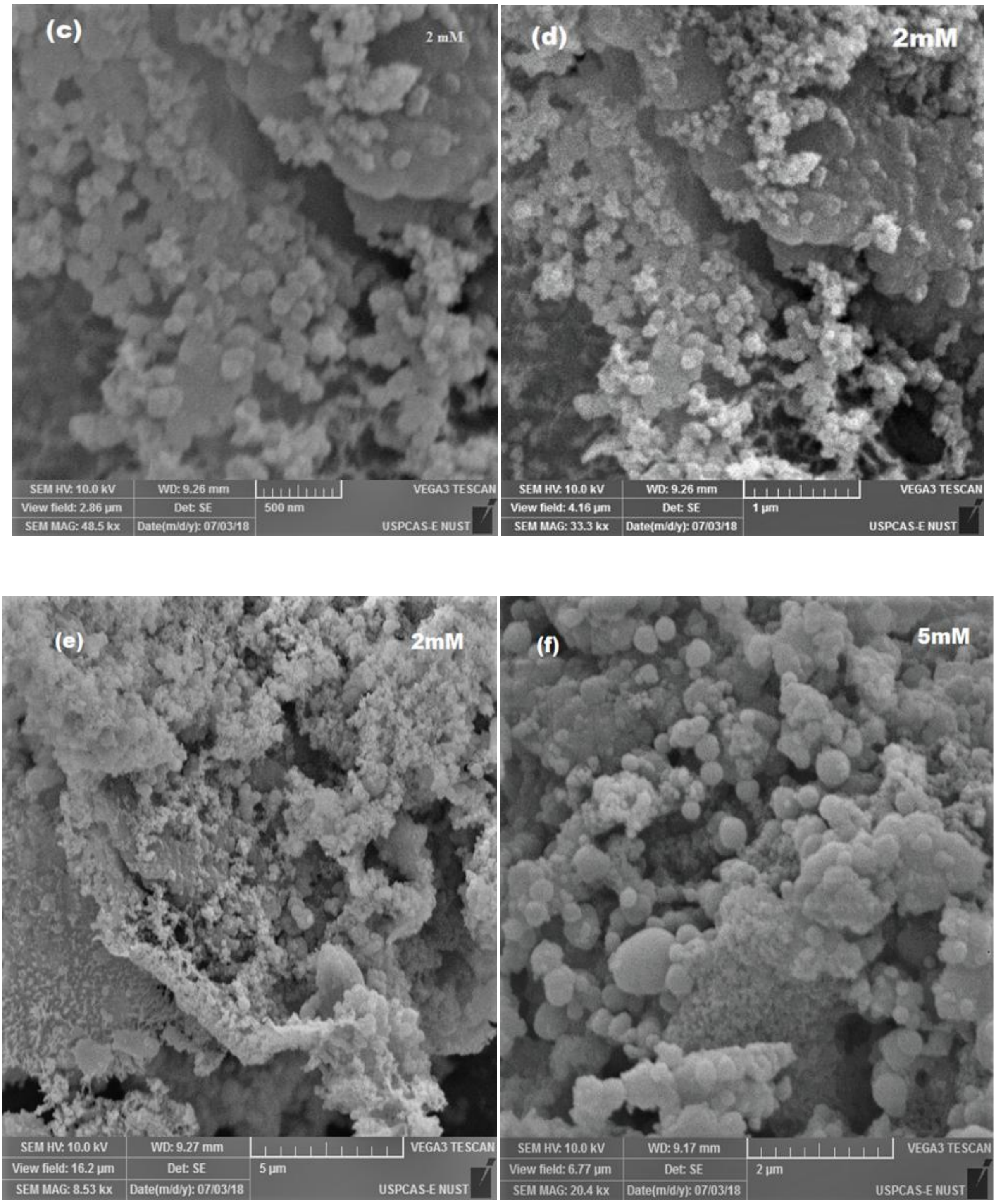


Figure 4.5 (c-e) SEM images of $Ca(OH)_2/SiO_2$(2mM) (f) SEM image of $Ca(OH)_2/SiO_2$ (5mM)

The reaction can be done in aqueous medium or more times in the mixture of propanol and ammonia solution and are exceptionally delicate to the Si molar proportion, pH, co-solvent impact, temperature and time of response, among different variables [47].

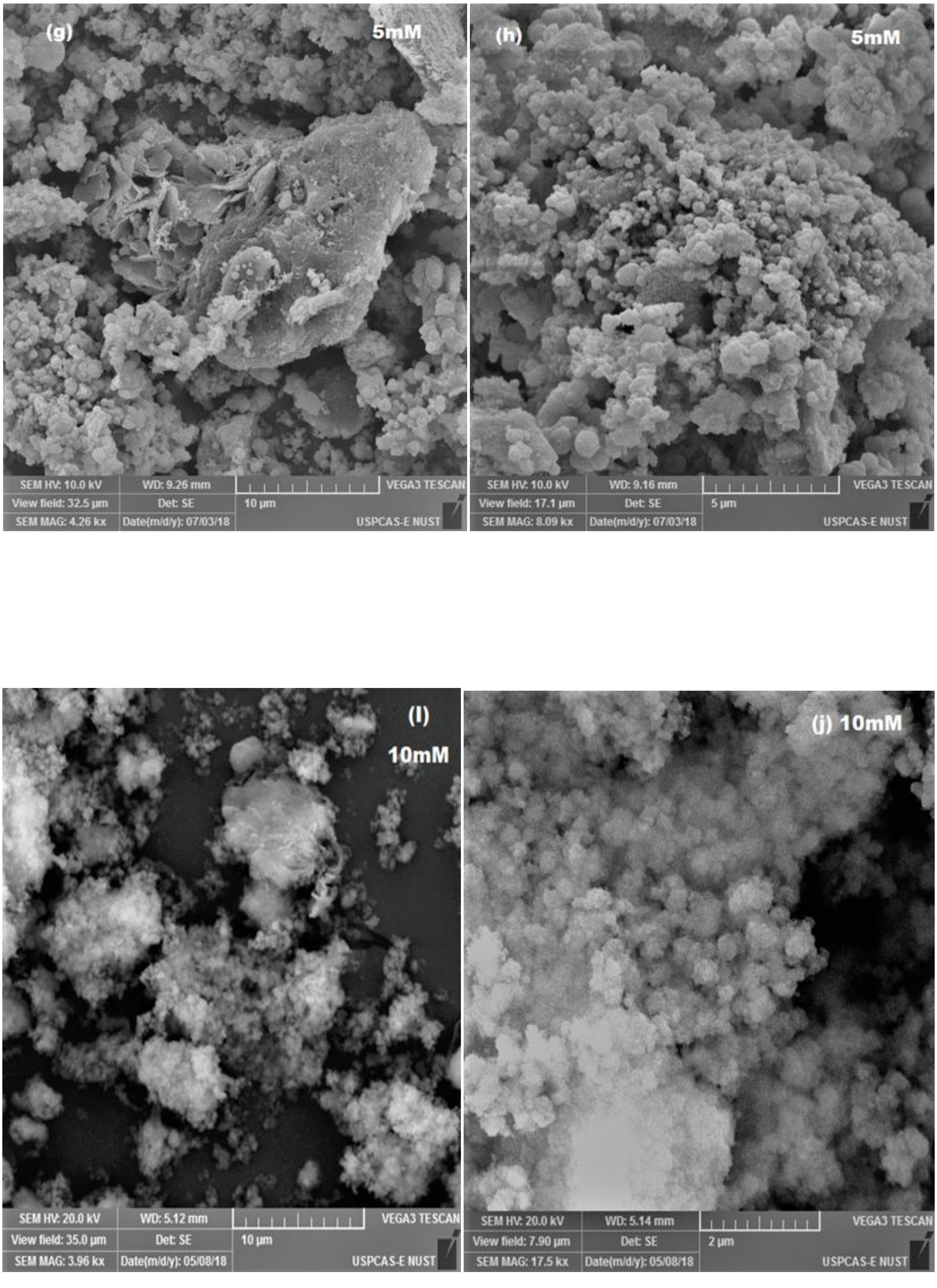
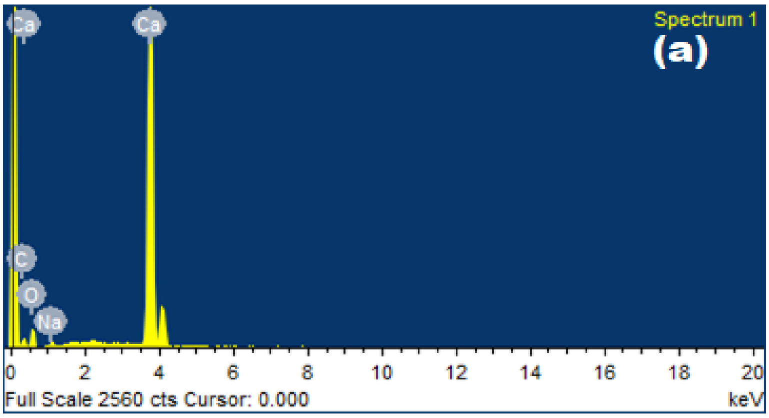


Figure 4.6 (g-h) SEM images of $Ca(OH)_2/SiO_2$ (5mM) (i-j) SEM images of $Ca(OH)_2/SiO_2$ (10mM)

In 10mM Composite, nanoparticles embedded on the surface of $Ca(OH)_2$ completely as well as they grow separately. As we increase the amount of TEOS, a certain amount of silica nanoparticles cover the surface of Ca(OH)2 and the remaining particles grow separately. To prepare the $Ca(OH)_2/SiO_2$ composite, the reaction should not be done under acidic surroundings because the suspension of $Ca(OH)_2$. The reaction done in aqueous solution in just two step method in which propanol was used as a catalyst for hydrolysis and then ammonia to speed up the condensation of silica particles[48]. Ammonia solution plays an important role for the formation of silica nanoparticles. If we increase the amount of ammonia in the solution, more silica nanoparticles will covers the surface of the material.

4.3. EDX Analysis

The elemental analysis was done by EDX furnished with SEM. Figure 4.5(a) shows EDX spectra of $Ca(OH)_2$ demonstrating that the sample contains Ca, C and O. While in figure 4.5(b) shows EDX spectra of $Ca(OH)_2/SiO_2$ (2mM), confirming the occurrence of the components i.e. Ca, C, O, Si. The acquired results additionally verified the purity of the material. In fig. 4.5(c), the EDX pattern of the sample $Ca(OH)_2/SiO_2$ (5mM) shows all the elements was present and the quantity of Si and O also increased. As we increase the concentration of TEOS, the concentration of Si and O always increased. In fig. 4.5 (d), the EDX pattern of $Ca(OH)_2/SiO_2$ (10mM) confirmed the presence of all elements with increased the concentration of Si and O.



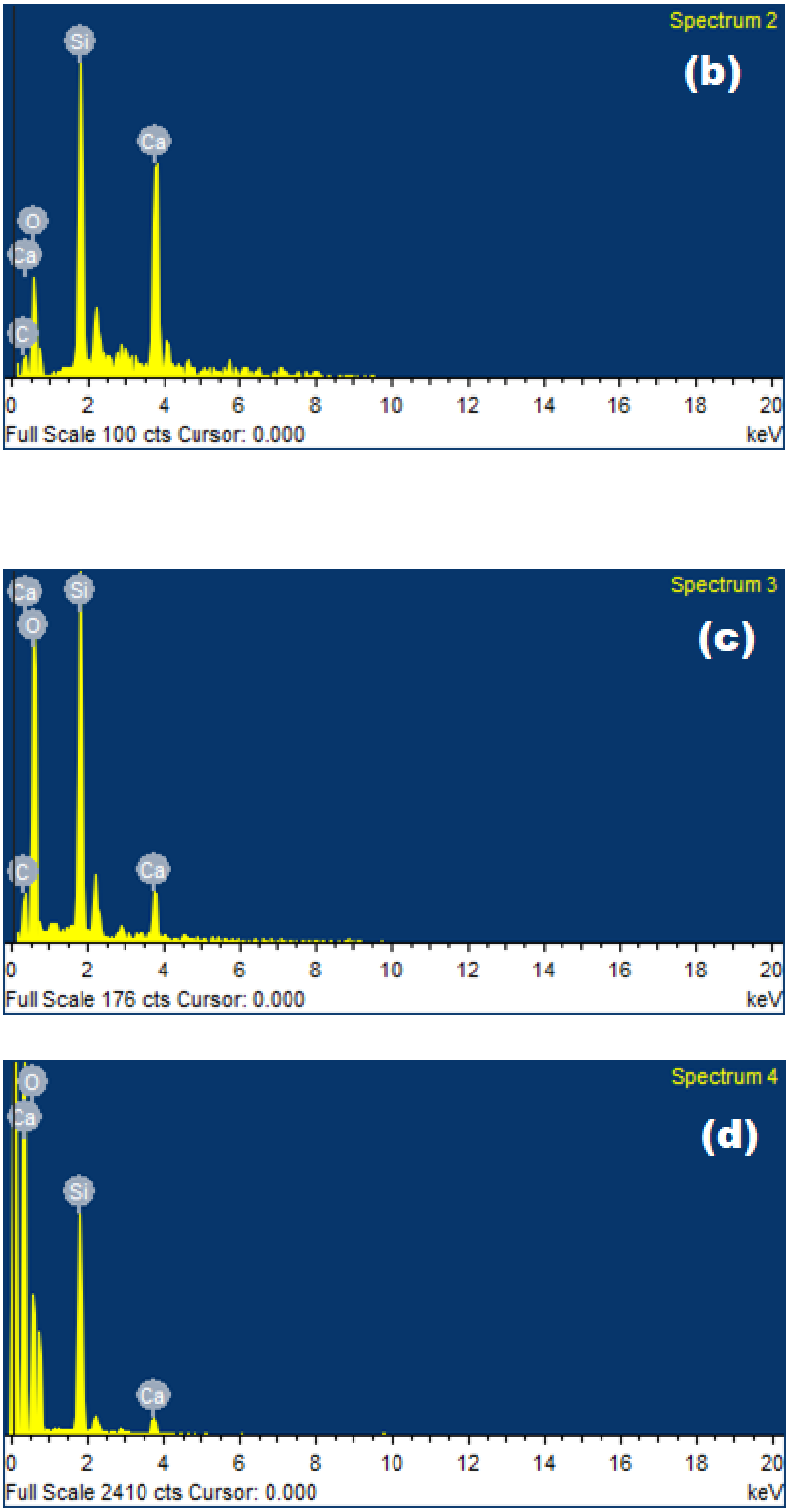


Figure. 4.7: (a) EDX pattern of $Ca(OH)_2$ (b) EDX pattern of $Ca(OH)_2/SiO_2$ (2mM) (c) EDX pattern of $Ca(OH)_2/SiO_2$ (5mM) (d) EDX pattern of $Ca(OH)_2/SiO_2$ (10mM)

4.4. Fourier transform Infrared Spectroscopy (FTIR):

FTIR analysis is extensively used method to define the functional group of a material. It can likewise be utilized to decide the bond in the required material or the recognition of attached group or it very well may be steady in deciding the scope of oxidation/reduction of materials. In three primary section, the infrared range can be scattered as

The (< 400 cm^{-1}) is a far infrared range.

- The (4000-400 cm^{-1}) is a mid- infrared range.
- The (13000-4000 cm^{-1}) is a near infrared range.

To investigate our material, mid infrared range (4000-400cm^{-1}) spectrum was used. The peaks in this area give us the data about the components which are available in material. The frequency of the mid infrared region can be divided into four more regions. These region can be insulated as follows [49].

- The region (4000-2500 cm^{-1}) is study and corresponds to X-H stretching in the mid infrared region.
- The region (2500-2000 cm^{-1}) is a triple bond region of atom in a mid-infrared region.
- The region (2000-1500 cm^{-1}) is study as a double bond in the mid infrared region.
- The region (1500-400 cm^{-1}) corresponds to single bond region of the atoms and called as a finger print region.

The FTIR range (Fig. 4.8) of the synthesized powder showed the band characteristics of both hydroxide and carbonate gatherings of calcium. The decently solid ingestion bond at ~3642 cm^{-1} identified with the sharp - OH stretching bond [52-53]. The OH expanding absorption bond was not too sharp. This relatively showed that rather than pure phase of hexagonal calcium hydroxide, some mixed. In like manner, the broad band from ~3580 to 3250 cm^{-1} in likewise contrasted with the -OH stretching modes. This band was engaged at around 3360 cm-1.The minor fluctuation in range 2160-2020 cm^{-1} was because of CO2 adsorption from environment [50]. The small peaks in range 3000-2800 were due to fully saturated C-C-H bonds. The sharp peaks at 1420 cm^{-1} and 872 cm^{-1} were corresponded due to asymmetric and symmetric stretching of CO_3^{-2} group respectively. The sharp peak was present at 1598 cm^{-1} due to symmetric C=O stretching bond [51]. So CO_3 group suggesting the formation of $CaCO_3$

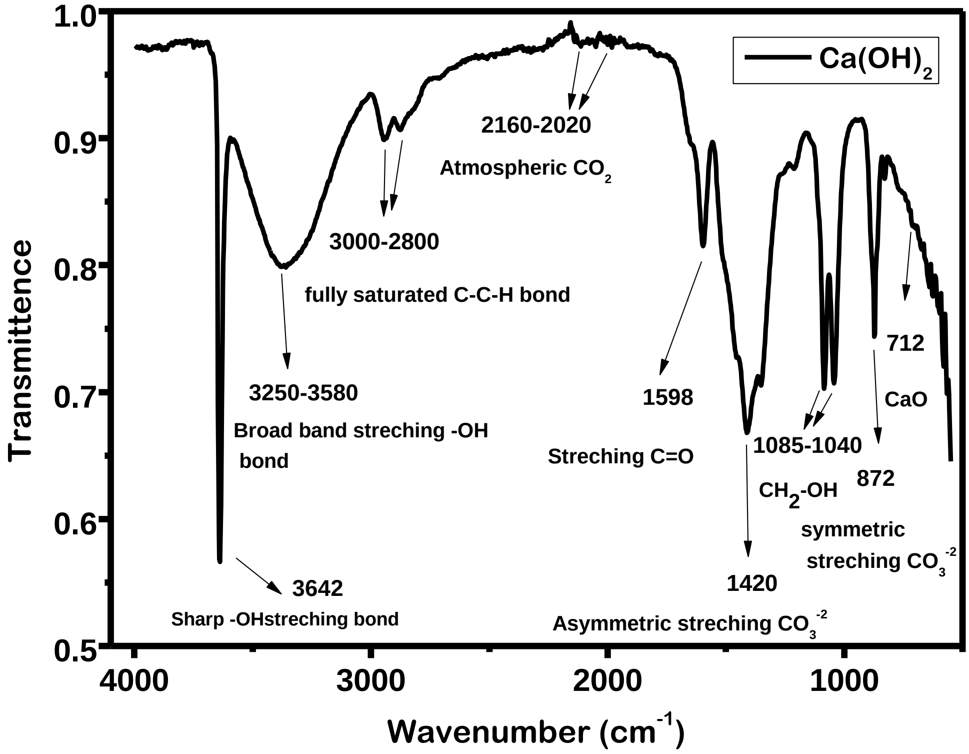


Figure 4.8: FTIR spectra of $Ca(OH)_2$

The FTIR spectra of the synthesized $Ca(OH)_2/SiO_2$ composite powder material demonstrated the bond characteristic. In composite, a broad band from 3580-3250 cm^{-1} correspond the –OH stretching bond [54]. The sharp peak at ~ 1060 cm^{-1} corresponded to the asymmetric stretching of Si-O-Si bond which confirm the presence of SiO_2 in the material. The peak at ~ 792 cm^{-1} was due to the behaviour of symmetric vibration of Si-O. The peaks at 1420 cm^{-1} and 872 cm^{-1} was due to the asymmetric stretching and symmetric stretching of CO_3^{-2} group suggesting the calcite formation in the material [55]. The minor fluctuation at ~ 2160-2020 cm^{-1} was due to adsorption of CO_2 from atmosphere. The sharpness of the peaks varied in the composite. At 1060 cm^{-1}, transmittance shows the behaviour of Si-O-Si bond in the formation of composite. The stretching vibration at 1060 cm^{-1} varied in all composite which give us the information of Si-O bond and clearly tells us that silica is produced on the surface of $Ca(OH)_2$ [56]. A small bending at 712 cm^{-1} was observed due to vibration of Ca-O bond.

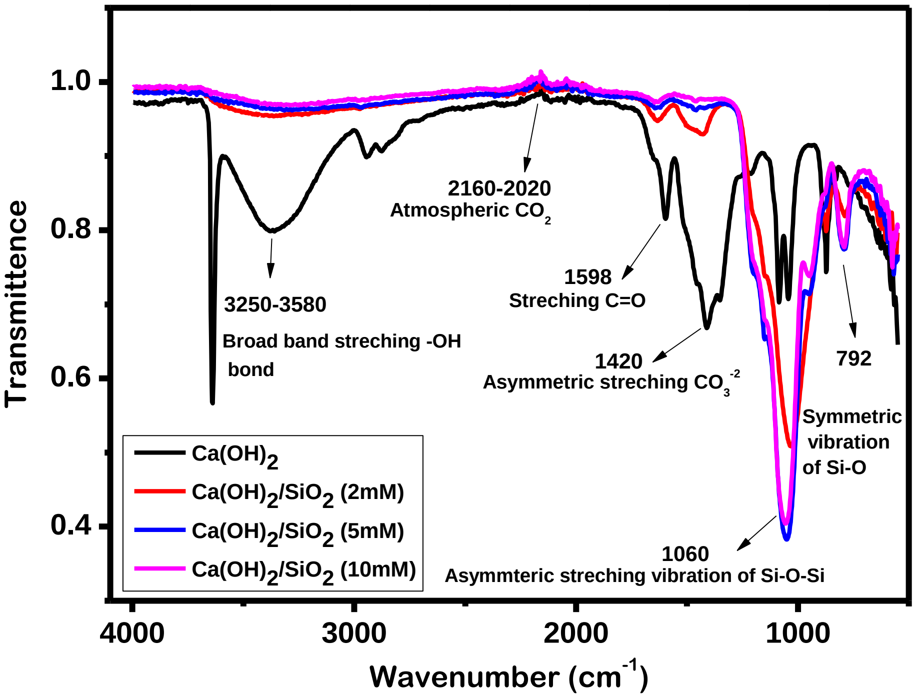


Figure 4.9. FTIR analysis of combine $Ca(OH)_2/SiO_2$ Composites

4.5. Thermo-gravimetric Analysis (TGA):

In Fig 4.10 thermo-gravimetric analysis (TGA) of Ca(OH)2 was carried, the sample was heated up to 1000°C with temperature range of 5°C/min under N_2 atmosphere . Three main weight losses were observed; 50°C to 360°C, 360°C to 527°C and 527°C to 700°C. The result was consistent as before investigated by olga et al [57]. The first weight loss was corresponds to the vaporization of adsorbed water. The weight loss from 360°C to 527°C was due to decomposition of $Ca(OH)_2$ into CaO. The peak from 527°C to 700°C was corresponds to decomposition of $CaCO_3$ to CaO. Zhu et al. revealed the comparative study in which starting and ending temperature were 594.4 to 721°C respectively. CaO nanoparticles could be acquired through calcination at 500°C [58]. The principle weight reduction of 12% identified with change of $Ca(OH)_2$ to CaO and 17% related with the change of $CaCO_3$ to CaO stage were very much related with the figured weight reduction.

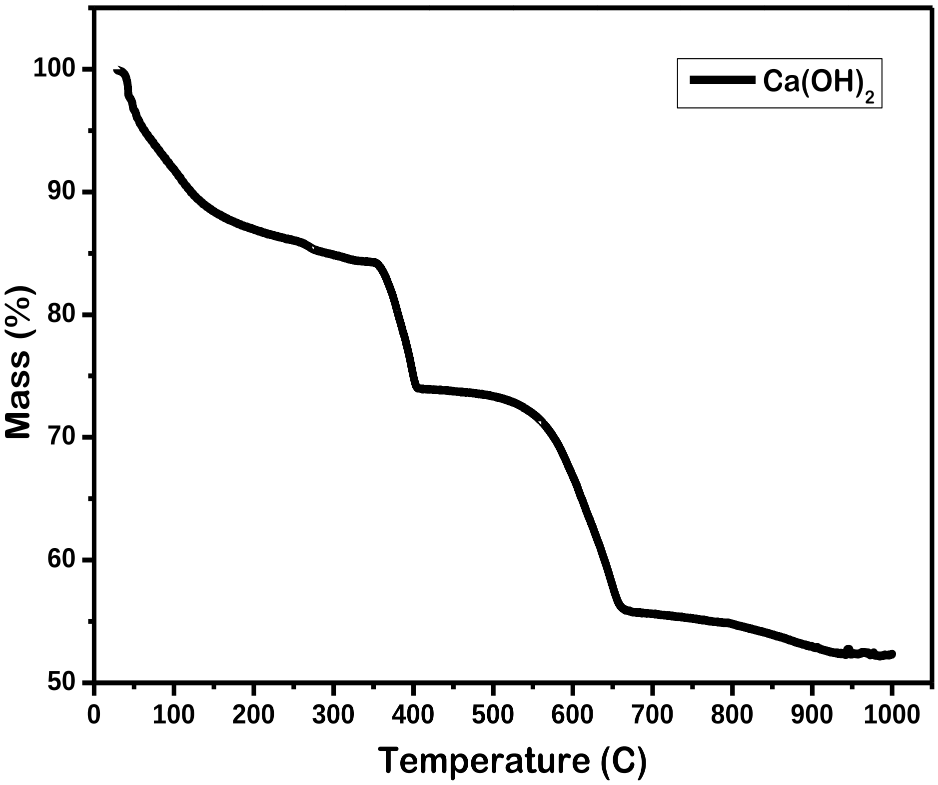


Figure 4.10: TGA curve of Ca(OH)$_2$

In Ca(OH)$_2$/SiO$_2$ (10mM) composite, the TGA analysis was carried out by heating the sample from room temperature to 1000^{o}C at the heating rate of 5^{o}C/min under N$_2$ atmosphere. First weight loss was observed due to evaporation of absorbed water on the surface of Ca(OH)$_2$/SiO$_2$ composite. At 372^{o}C, the abrupt change in the mass was due to the interaction of the sample with the atmosphere or due to absorption from the atmosphere. Firstly, 1% mass loss was observed and then abruptly 6% mass gain which give the information about the absorption of the composite from atmosphere or which illustrates the formation of another transitional compound. The temperature was increased at constant heating rate and another mass loss observed. It was observed that during dehydration cycle the composite did not loss the weight as compare to the pure sample. Because silica nanoparticles covers the surface of core material, which did not allow the decomposition of the material completely.

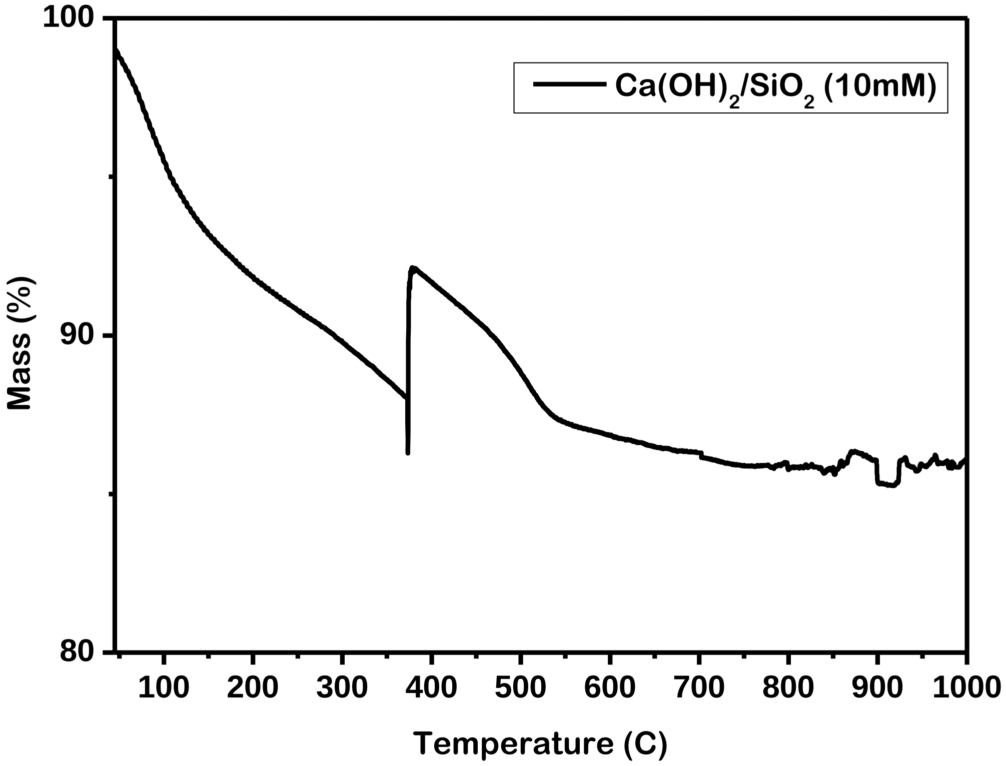


Figure 4.11: TGA curve of $Ca(OH)_2/SiO_2$ (10mM)

In $Ca(OH)_2/SiO_2$ (5mM), the TGA curve shows the thermal behaviour of the sample. The analysis was done under N_2 atmosphere. TGA analysis was carried out by heating the sample from room temperature to 1000^oC at the rate of 5^oC/min under ambient atmosphere. In Fig. 4.10, the first weight loss was observed due to vaporization of adsorbed water on the surface of the material and the mass decreased from 100 to 85 percent. At 418^oC, the mass of the sample abruptly increases 1% due to the interaction of the sample with the atmosphere or due to absorption from the atmosphere. The temperature of the sample increased at constant rate, and observed another mass loss at the temperature range of 450^oC-550^oC. It was observed that the mass loss of $Ca(OH)_2/SiO_2$ (5mM) is less as compare to $Ca(OH)_2$ because the attachment of silica nanoparticles on the surface of $Ca(OH)_2$ .This mass loss corresponds to the phase change from hexagonal to cubic structure. A small fluctuation of mass loss is observed above 600^oC which shows that CO_2 is removed from the material.

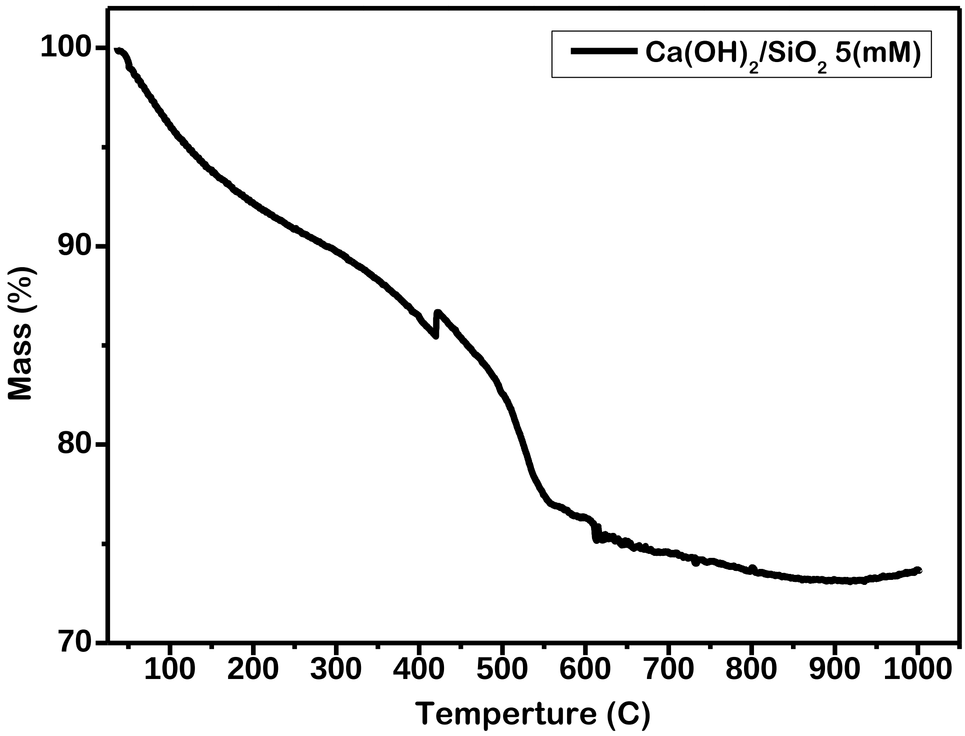


Figure 4.12: TGA curve of Ca(OH)2/SiO2 (5mM)

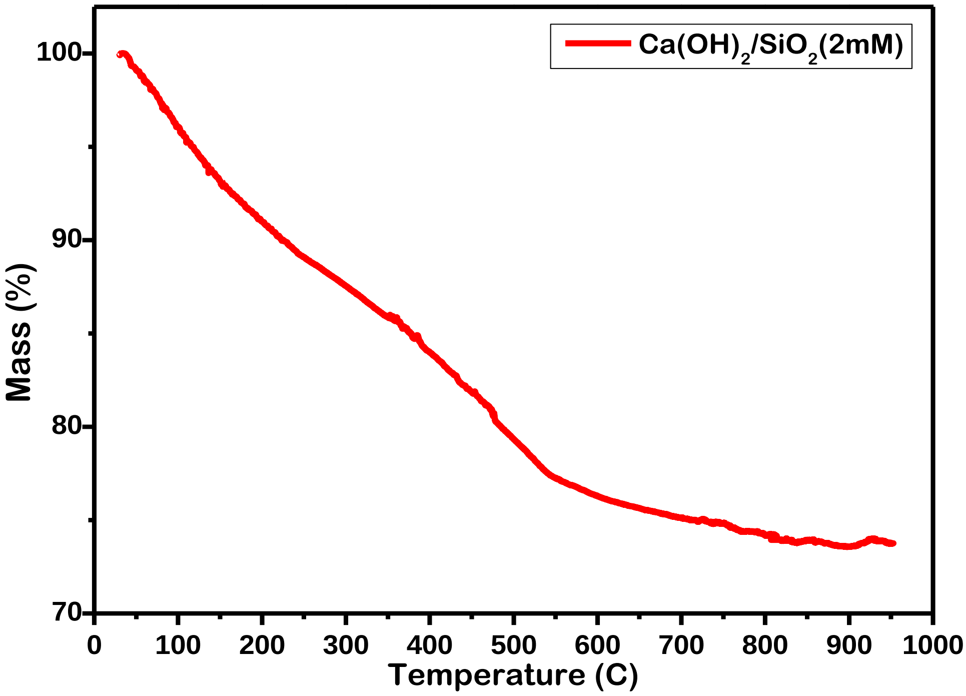


Figure 4.13: TGA curve of $Ca(OH)_2/SiO_2$ (2mM)

In case of $Ca(OH)_2/SiO_2$ (2mM) composite, TGA analysis was done at room temperature to 1000^oC under N_2 atmosphere, the curve shows as temperature increases the mass gradually decreases up to the temperature reaches at around 370^oC. Form 370^oC to 520^oC, 6% mass decreases due to the decoration of silica particles on the surface of $Ca(OH)_2$ which is less than $Ca(OH)_2$. As temperature increases the mass of the sample continuously decreases with no abrupt change in the mass. Due to the attachment of silica nanoparticles on the surface of $Ca(OH)_2$, the weight loss of composite was lower and tended to be a constant at 200^oC. A small fluctuation above 700^oC is observed shows the CO_2 is not remove completely.

Chapter 05

Conclusion and Future Recommendation

Thermochemical frameworks propose high storage densities and long term capacity conceivable outcomes because of the synthetically stored thermal energy. Be that as it may, because of the for the most part fine powdered material and its conceivably cohesive character, an application is obstructed due to a simple arrangement of bulk inhomogeneity like e.g. agglomeration. So, to avoid this agglomeration behaviour $Ca(OH)_2$ and $Ca(OH)_2/SiO_2$ composite have been synthesized successfully via sol gel method. The structural analysis was confirmed by using XRD and morphological analysis indicated the attachment of silica nanoparticles on the surface of $Ca(OH)_2$. $Ca(OH)_2/SiO_2$ composites were synthesized via sol gel method by using different concentration of TEOS. FTIR was engaged to analyze the vibrational and stretching band of composite. FTIR of $Ca(OH)_2$ confirmed the bonding with extra CO_3 bond. The band in range of 1060 cm^{-1} confirmed the presence of Si-O-Si in composite sample while EDX analysis was used to determine the composition of the samples. Thermogravimetric analysis were used to determine the thermal behaviour of pure $Ca(OH)_2$ and $Ca(OH)_2/SiO_2$ to confirm the decomposition. TGA analysis showed decomposition of Ca(OH)2 into CaO. In composite, TGA observed abrupt change in mass which probably due to surface interaction with atmosphere which affect the decomposition. As we decrease the concentration of silica nanoparticles, change in mass decreases and which effect the decomposition of the material. The addition of silica nanoparticles reveals better thermal decomposition and improve surface properties. Also, the conditions for thermochemical cycling of reinhardbraunsite and its thermophysical properties are of premium and will be explored in future works.

In future it would be better to work on the following aspects

- To decrease concentration of silica and improve decomposition.
- As these material have exciting thermal properties. So the investigation of these properties would likewise be an exceptionally encouraging work in future.
- To improve thermal conductivity of material and it would be better to use those material whose thermal conductivity is higher.
- The kinetics study of de – & rehydration of composite for thermochemical energy storage.

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