

**Influence of particle Size and Ammonia on Thermochemical  
Properties of Ca(OH)<sub>2</sub>@SiO<sub>2</sub> Nano-Composites**



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Degree of MS in Physics

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**National University of Sciences & Technology****MS THESIS WORK**

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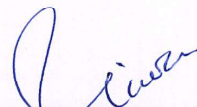
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## Dedication

*I want to dedicate all the hard work and research activity to my dearest parents. I was never able to work that much without their love, support, and unstoppable care. My passion is able to go far away from here just because I have my parents support behind me.*

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**Muhammad Rashid Farooq**



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## Abstract

Energy crises in one of the main issues for under developing countries in current era. Scientist and researchers have shifted their focus on renewable energy resources. Wind energy, Hydropower, Ocean Energy, Bio Energy and Thermal Energy etc are some of the main examples of sustainable energy resources. Thermal energy can be a promising candidate as sustainable, less expensive and environment friendly energy source. Thermo- Chemical Energy Storage is an efficient method to resolve the storing problem of the thermal energy in high density. Due to its structure and higher thermal stability, the cyclic process of  $\text{Ca(OH)}_2$  &  $\text{CaO}$  is one of the best available cycles for high density thermal energy storage. At the same time the effects of agglomeration and inhomogeneity of particles can reduce thermal efficiency as well as mass and heat transport.

This study is proposed to see a comparative effect between nano and micro level silica coated  $\text{Ca(OH)}_2$  particles. Silica coating can prevent early conversion of calcium hydroxide to calcium oxide, and it can also resist the conversion of calcium hydroxide to calcium carbonate. At high temperature, around  $410^\circ\text{C}$  to  $425^\circ\text{C}$ , when we got conversion of calcium hydroxide to calcium oxide, we get high chances of getting calcium silicate formation in normal atmosphere. We avoid the formation of calcium carbonate at this stage because of inert atmosphere provided during applicational testing. In start we have purchase sigma ducson micro sized calcium hydroxide particles. Due to low surface to volume ration, we got low reactivity of these particles with air. This was the major reason of not finding calcium carbonate in these particles. On the other side, silica coating was also done on synthesized nanoparticles in lab from sole gel method. These particles attain higher surface to volume ratio. This results higher surface to volume ration that results in higher reactivity with air. Resultantly it shows 8-10% calcium carbonate weight loss in synthesized nanoparticles in TGA-DSC.

In XRD, a clear result for larger sized particles for proper hexagonal structure got observed. But in case of nanoparticles, these same peaks were found with some extra peaks for calcium carbonate formation. This distorts the pure crystal structure of calcium hydroxide mixed with calcium carbonate. In SEM analysis, we see the morphological difference between nano and micro sized particles. The surface to volume ration describes the difference in agglomeration and shape change in pure calcium hydroxide. In case of carbonate formation, they didn't exhibit round and spherical share. The EDX analysis shows almost same ratios in elemental analysis in pure and different levels of coating. FTIR show the intensity wise presence of different functional groups in all respective samples. Similarly, RAMAN Spectroscopy used to find same analysis by scattering

of laser from different functional groups. TGA-DSC was used for applicational testing under an inert atmosphere created by nitrogen. The percentage weight loses at different stages while having different heating rates. All conversions from one to another shows weight lose according to respective presence of specific compound that gets break down at that temperature. DSC analyses were used to find heat of enthalpy calculations, which further help in finding out activation energy. Specific values of activation energy guide us about differentiating between different compounds break down at same temperature.

The effect of catalyst got studied for the formation composite ions and their effect got studied in all different characterization techniques. While applicational testing, the combine effect of ammonia and broken ethyl groups from TEOS plays a vital role in quality or sustainability of coating silica over agglomerated and or larger size single particles. By changing heating rates and comparing all the catalytic sample with the other samples without catalyst and same percentage of coating, we can separate out the effect of catalytic activity of ammonia and behaviour of silica in the presence or absence of ammonia.

In future plans, we want to enhance electrical conductivity as well. After making composite of calcium hydroxide with any conductive material, we will coat it with silica to see increment in both electrical and thermal conductivity. Secondly we want to form a set-up, where we can recycle our samples for as many cycles as many possible. This will lead us to one of the possible samples as the most suitable for larger scale energy storage.

## List of 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



## 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  $\text{Ca}(\text{OH})_2$  is discussed briefly.

### Chapter 2

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

### Chapter 3

This chapter includes the synthesis of  $\text{Ca}(\text{OH})_2$  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.

## Table of Contents

Chapter No 1 .....	1
1.1 Introduction .....	1
1.1.1 History of Nano Science & Nano Technology.....	1
1.1.2 Nanoparticles.....	1
1.1.3 Nanomaterials.....	2
1.1.4 Classification of Materials.....	2
1.1.5 High Surface to Volume Ratio .....	4
1.1.6 Properties of Nanomaterial.....	4
1.2 Introduction to Energy Resources .....	6
1.2.1 Introduction to Thermal Energy Storage.....	6
1.3 Structure of Ca(OH) <sub>2</sub> .....	11
1.4 Properties of Ca(OH) <sub>2</sub> .....	12
Chapter No 02 .....	13
2.1. Literature Review .....	13
Chapter No 03 .....	16
3.1. Synthesis Techniques of Nanomaterials .....	16
3.1.1. Top-down Approach.....	16
3.1.2. Bottom-up Approach .....	16
3.2. Synthesis Process .....	17
3.3. Material required during Synthesis. ....	17
3.4. Material preparation .....	17
3.4.1. Synthesis of Calcium Hydroxide Ca(OH) <sub>2</sub> .....	17

3.4.2. Synthesis of Ca(OH) <sub>2</sub> @SiO <sub>2</sub> Composite.....	18
3.4.3. Concentration of TEOS for Composite .....	19
3.5. Characterization Techniques: .....	19
3.6. X-Ray Diffraction .....	19
3.6.1. Introduction .....	19
3.6.2. Basic Principle.....	20
3.6.3. Bragg's Law .....	20
3.6.4. XRD Applications .....	23
3.7. Scanning Electron Microscope (SEM).....	23
3.7.1. Electron gun .....	24
3.7.2. Condenser Lens .....	24
3.7.3. Scanning System .....	24
3.7.4. Secondary Electron .....	24
3.7.5. Backscattered Electron .....	25
3.7.6. Specimen Chamber .....	25
3.7.7. Effect of Accelerating Voltage.....	25
3.8. Energy Dispersive Spectroscopy .....	25
3.9. Fourier Transform Infrared Spectroscopy .....	25
3.10. Raman Spectroscopy .....	26
3.10.1. Raman Scattering .....	27
3.10.2. Raman Effect.....	28
3.11. Laser Particle Size Analyser (LPSA).....	28
3.12. Thermo-Gravimetric Analyser (TGA) .....	29

3.12.1. Working and Construction of TGA.....	30
Chapter No 04 .....	31
4.1. X- Ray Diffraction.....	31
4.2. SEM ANALYSIS .....	36
4.3. EDX Analysis.....	37
4.4. Fourier transform Infrared Spectroscopy (FTIR):.....	38
4.5 RAMAN Spectroscopy .....	40
4.6. Laser Particle Size Analyses (LPSA).....	41
4.7. TGA- DSC.....	44
Chapter 05 .....	49
5.1 Future Recommendations.....	49
5.2 Conclusion.....	51
References .....	52

## CHAPTER NO 1

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### 1.1 INTRODUCTION

Nanotechnology is the leading and advanced technology of the current age and the developing field of the 21<sup>st</sup> 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, Nanometer is a billionth part of a meter like ( $10^{-9}$ ) which have roughly hundreds 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, despite, 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. <sup>[1]</sup>

#### 1.1.1 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. <sup>[2]</sup>

#### 1.1.2 Nanoparticles

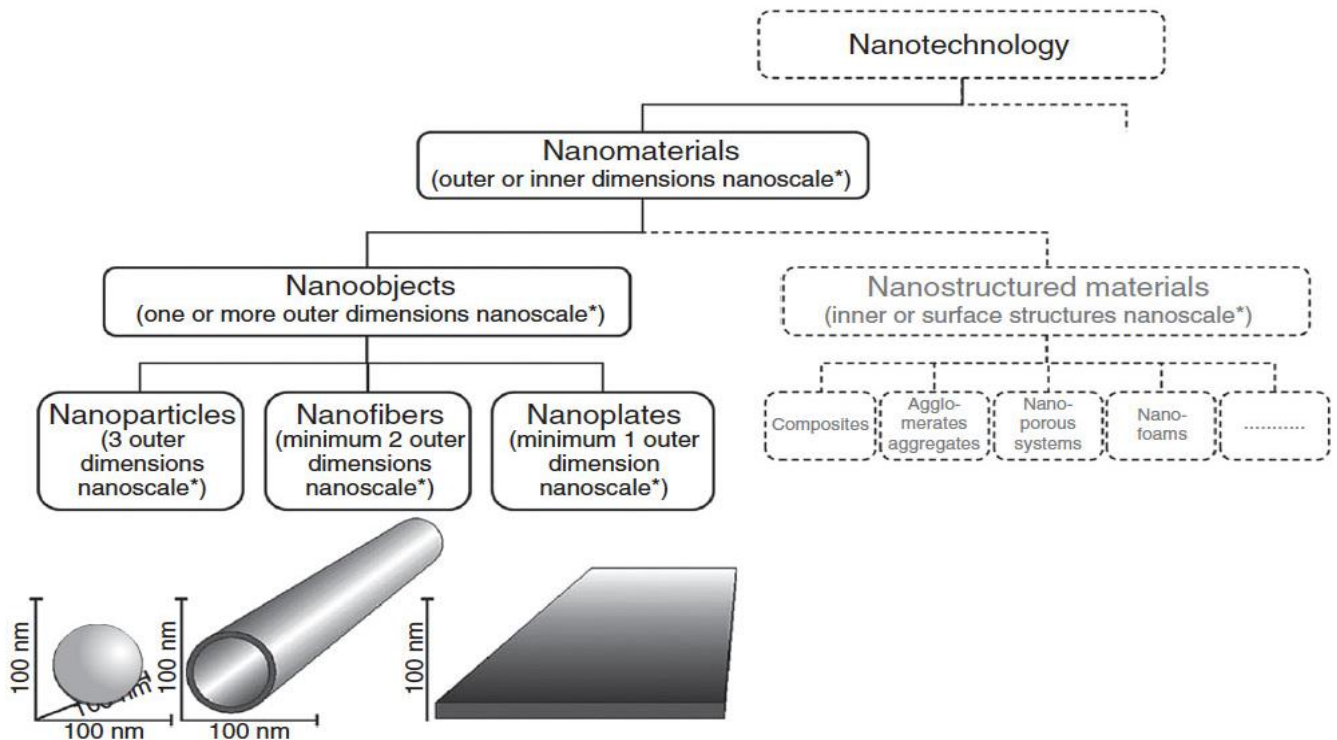
Those particles having particle size in between 1 to 100nm is called Nanoparticle. These particles exist in naturally and composed artificially. The analysis of nanoparticle shows that the nanoparticles exist naturally, and these are made by human made procedures by industry and emission of traffic.

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.

These particles are called secondary nanoparticles that formed by the oxidation of gases in atmosphere. These particles are generated by itself from low condensation volatile in the atmosphere. The surface area to volume ratio of nano material is high than bulk material, which results the greater chemical reactivity and increases their strength. <sup>[3]</sup>

### 1.1.3 Nanomaterials

Nanomaterials are the material that has structural component smaller 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 are ordinary prohibited. [4]



(Figure 1.1: Showing sub-division of Nanomaterials)

### 1.1.4 Classification of Materials

Based on dimension, we classify the Nano material in following types.

- Zero-Dimensional Material
- One-Dimensional Material
- Two-Dimensional Material
- Three-dimensional Material

#### 1.1.4.1 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.

#### 1.1.4.2 One-Dimensional Nano Material

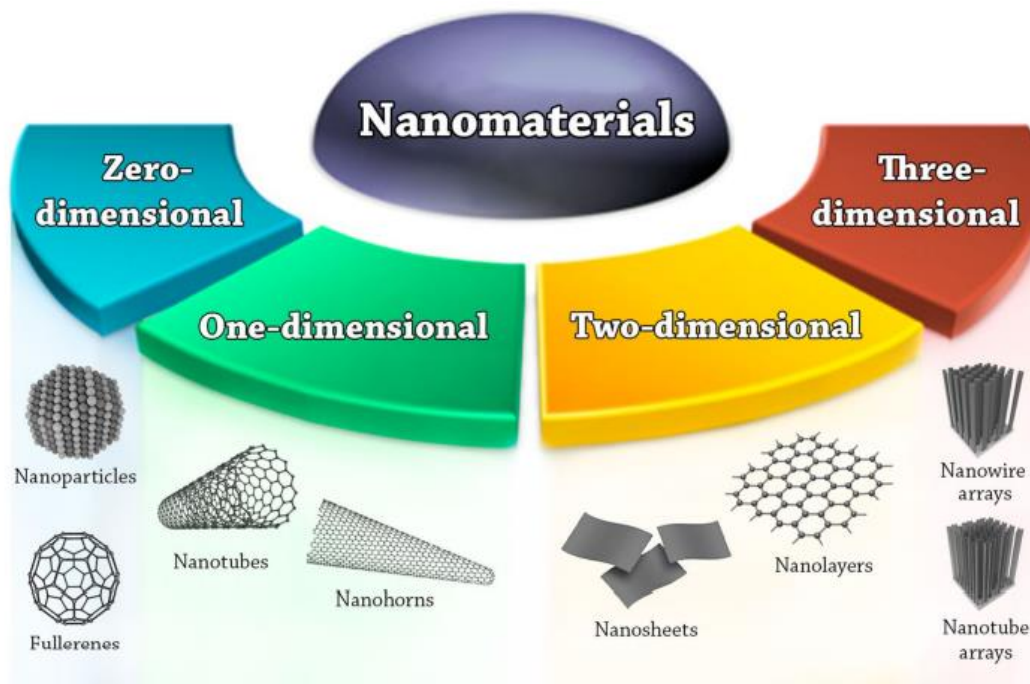
In one dimensional material (1D) which electron motion is confined in two dimensions and can move only in one direction. 1D Nano material can be crystalline or amorphous structure. Examples of 1D are nanowires and nano-rods.

#### 1.1.4.3 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.

#### 1.1.4.4 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 Nanomaterials are also known as bulk Nanomaterial. These materials are characterized by having all dimensions greater than 100nm.



(Figure 1.2: Classification of materials at nanoscale<sup>[5]</sup>)

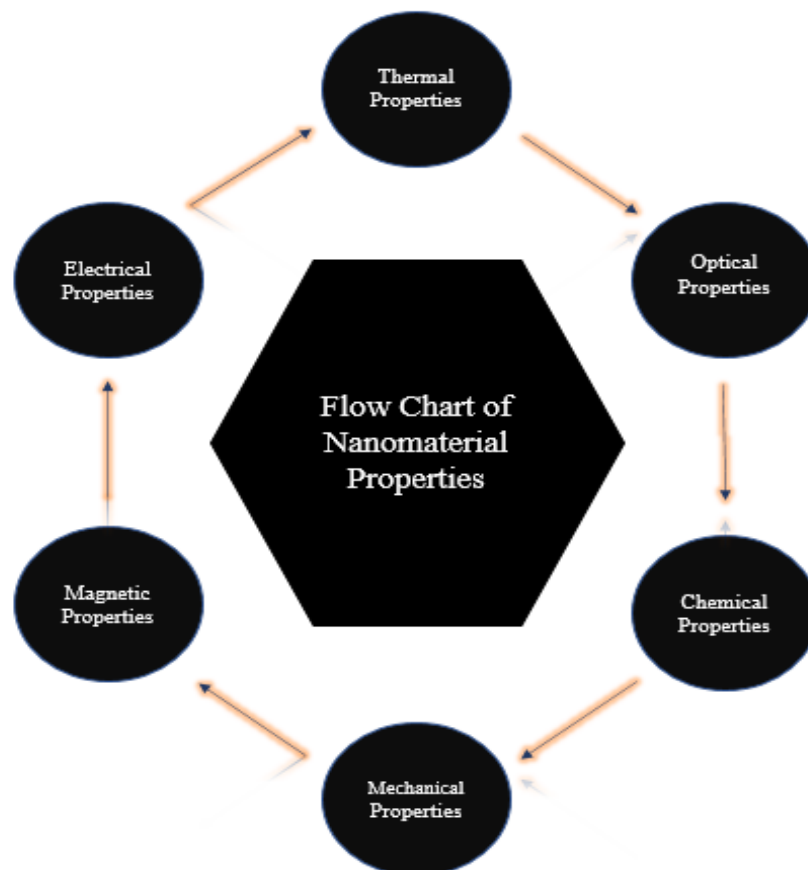
### 1.1.5 High Surface to Volume Ratio

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]

### 1.1.6 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)



### 1.1.6.1 Chemical Properties

Chemical properties of nanomaterial mainly consist of.

- 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.

### 1.1.6.2 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.

### 1.1.6.3 Magnetic Properties

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

### 1.1.6.4 Energy

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

- Graphene is used in the batteries as conventional electrode materials for significant improvement in conductivity and energy density. Uses of Graphene can make battery, durable, and suitable high-capacity energy storage.
- Nanomaterials also play a vital role in solar energy devices.

## 1.2 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<sub>2</sub> 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. Because 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. <sup>[12]</sup>

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. <sup>[13]</sup>

### 1.2.1 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 just the variance among free market activity. The benefit of thermal storage advancements is that they are modest, nature friendly, abundantly accessible material. <sup>[14]</sup>

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

There are three primary methods for (TES) given as:

- Sensible Heat Storage
- Latent Heat Storage
- Thermo-Chemical Heat Storage

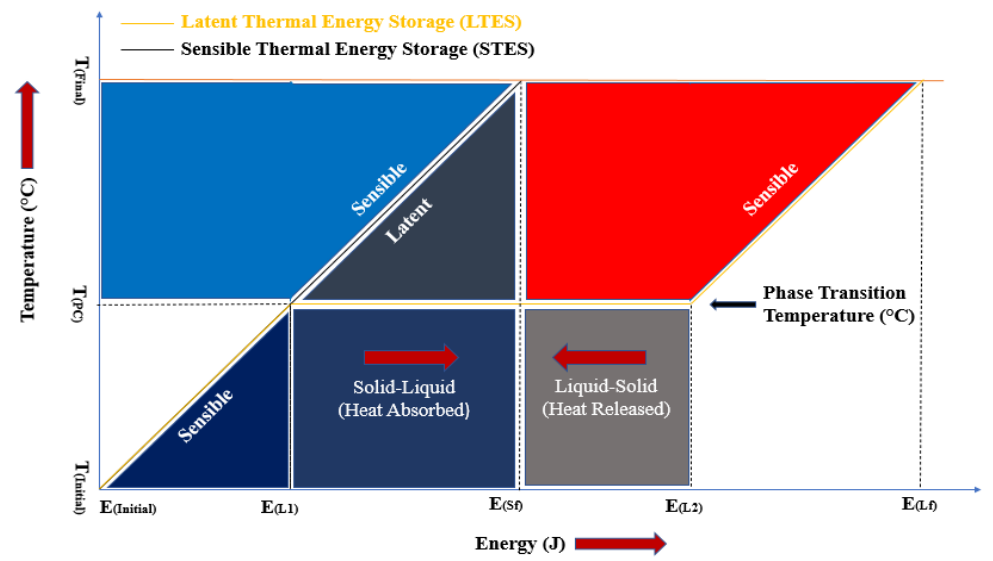
### 1.2.1.1 Sensible Heat Storage

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  $\Delta T$ , specific heat  $C_p$  and storage size in terms of mass which defined as

$$Q = m \cdot c_p \cdot \Delta T$$

### 1.2.1.2 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 ( $\Delta H_p$ ) 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 must 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.<sup>[16]</sup>)

### 1.2.1.3 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.

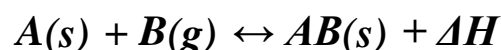


When endothermic reactions proceed, energy is absorbed and stored as a potential. This potential is used to release the energy during exothermic reaction. For higher temperature TES, a wide variety of reversible reaction occur. In addition, for suitable reaction other thermodynamic considerations are important must be considered. To determine whether a reversible reaction are suitable for thermal storage or not, equilibrium state must be evaluated. This equilibrium constant provides information about the reaction which is favored. [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. To select the suitable reaction some important criteria concerning selection must be considered.

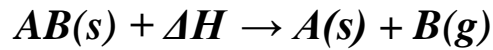
- Full reversibility of the reaction over larger number of cycles.
- No side reaction occurring.
- To ensure high charge and discharge of power, The fast kinematics of the reaction gets focused.
- High Heat Transfer properties
- Low temperature difference between charging and discharging to minimize energy loses.
- Little or no safety risk.

We have been studying science earlier, we consider some thermo-chemical reaction in which heat is incorporated or discharged. As clear from, “Therm” implied heat and chemical means chemical reaction. In the way, that synthetic response which assimilate or develop heat are known as Thermo-substance responses. For example, see a reaction equation given as

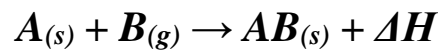


These are the reversible reactions and using these reactions, scientists came up with an idea to store heat energy. These are processes for charging and discharging. In charging, a solid is given heat to get charged or in other words that heat is provided to material to store that thermal energy. This storage of thermal energy can convert our solid material from one phase to another

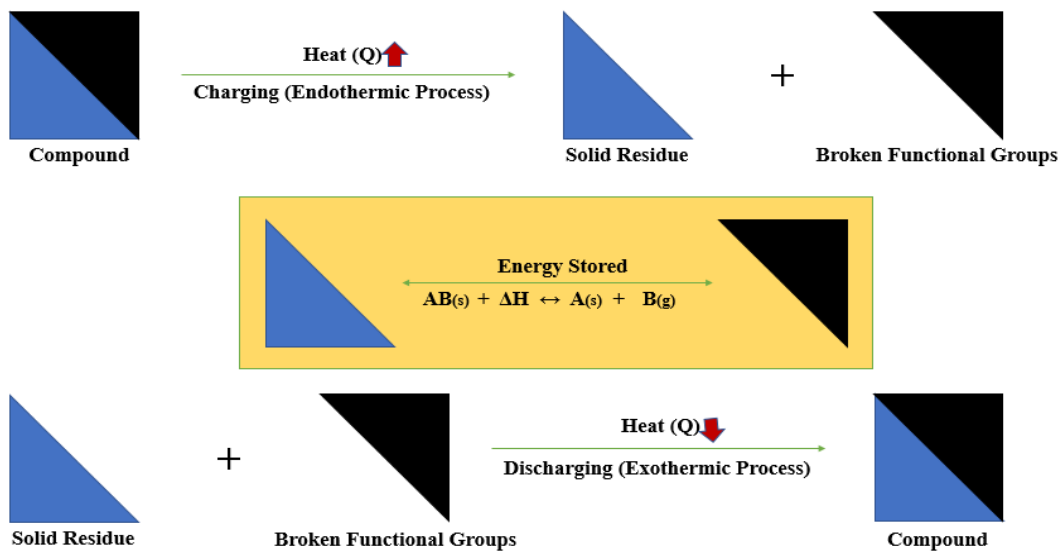
or it can turn its crystalline structure change to some of its derivative. To form new crystalline structure, some fictional group from initial structure may leave in gaseous or steam format some given high temperature of phase change.



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.



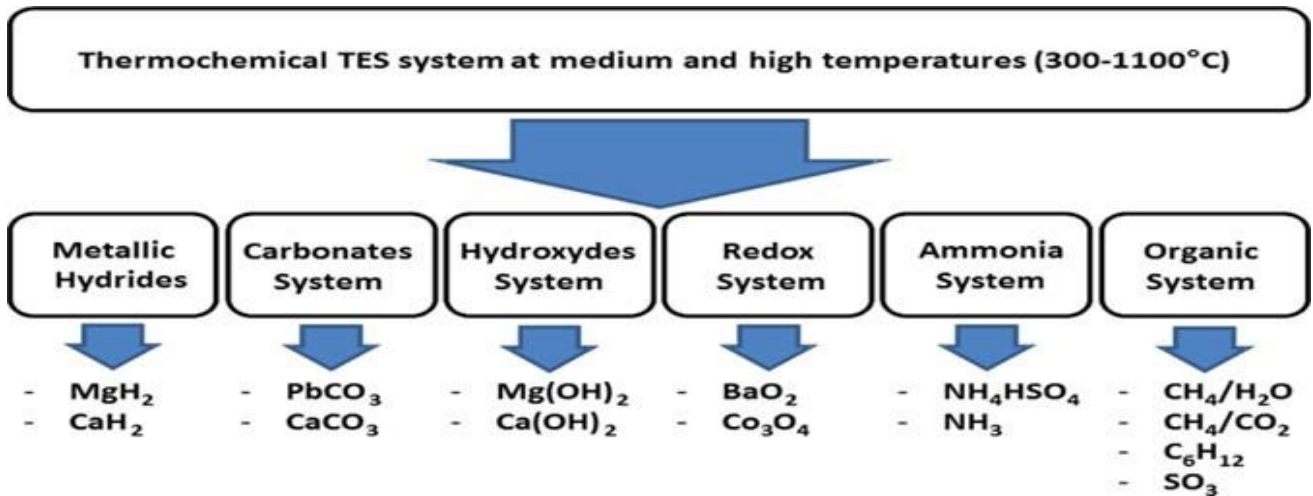
A lot of solid gas reactions like this which can assist us to store energy which incorporates carbonates, hydroxides, metal sulphate and metal oxides. Our main concern with metal hydroxide, these are very useful in TCES.



(Figure 1.5 : Processes occupied in Thermo-Chemical Energy Storage Cycle Charging, Storing, and Discharging.<sup>[17]</sup> )

Metal Hydroxides are some other valuable TCES materials, which are most investigated about and easy to manage including advantage of inviting to environment. 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 the bond, and we get steam and metal oxide. The metal oxide stores the heat energy and releases it as it get reacted again with water to get bond formation with hydroxyl group again.<sup>[18]</sup>

There are many solid gas reactions like which can help us to store energy. It 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.<sup>[19-21]</sup>



(Figure 1.6 : Different Materials, which are used in different Thermochemical procedures are Compared. )

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) <sub>2</sub> /CaO	515	104.4	1352
Mg(OH) <sub>2</sub> /MgO	265	77.7	1333
Be(OH) <sub>2</sub> /BeO	70	51.2	1191
Mn(OH) <sub>2</sub> /MnO	190	67.07	754
Ba(OH) <sub>2</sub> /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 useful for some conditions where we can negotiate large energy storage density. In metal carbonate, A CO<sub>3</sub> Is provided with the required heat to produce metal

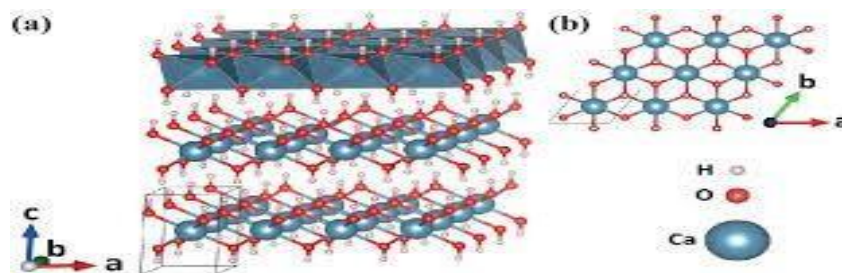
oxide in same way. But the excretion of carbon dioxide gas. This carbon dioxide gas is then again reacted with the metal oxide to gain heat stored before. Some important metal oxides are given below.

Chemical Materials	Temperature (°C)	Reaction Enthalpies (kJ/mol)	Gravimetric Energy Density (kJ/kg)
CaCO <sub>3</sub> /CaO	885	165.83	1656.8
SrCO <sub>3</sub> /SrO	1220	1370.6	1370.6
MgCO <sub>3</sub> /MgO	300	1174	1174
BaCO <sub>3</sub> /BaO	1555	836.6	836.6
CdCO <sub>3</sub> /CdO	290	560.1	560.1

(Table 1.2. Some important metal carbonates)

### 1.3 STRUCTURE OF Ca(OH)<sub>2</sub>

The brucite type structure of Calcium hydroxide Ca(OH)<sub>2</sub> is important inorganic material which belongs to hydroxide group. The structure of Ca(OH)<sub>2</sub> 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)<sub>2</sub> structure belongs to P-3m-1 space group and crystal structure of AEMHs comprises stacked sheets of MO<sub>6</sub> (M-alkaline earth metal) edge sharing octahedral. At each octahedron corner, each 'O' atom binds with 'H' atom and later interrelates with three adjacent hydroxyl groups of nearby layers. By changing the temperature and pressure of Ca(OH)<sub>2</sub> may come intensity change in crystal structure and electronic properties. [22]



(Figure 1.7 : Structure of Ca(OH)<sub>2</sub> (a) 3D view (b) top view of one layer)

## 1.4 PROPERTIES OF $\text{Ca(OH)}_2$

$\text{Ca(OH)}_2$  is an inorganic compound and generally known as slaked or hydrated lime.  $\text{Ca(OH)}_2$  has a polymeric structure like magnesium hydroxide known as brucite type structure.  $\text{Ca(OH)}_2$  is a white powder and its solution give a milky color because it is not very soluble in water. The density of  $\text{Ca(OH)}_2$  is  $2.211\text{g/cm}^3$  with the molecular mass  $74.093\text{g/mol}$ . 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.

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

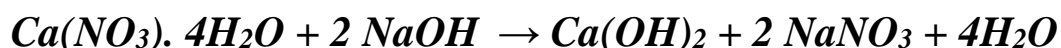
$\text{Ca(OH)}_2$  is very important for thermal energy storage properties. In hydroxide materials, calcium hydroxide has maximum reaction enthalpy of  $104\text{kJ/mol}$ . So, it is very exciting material for storing the thermal energy from any source like sun, or heat wastage from industries.



### 2.1. LITERATURE REVIEW

Synthesis of various inorganic materials have increased importance especially hydroxide due to their electrical, optical, and thermal properties. Calcium hydroxide  $\text{Ca(OH)}_2$  is a significant & cheapest inorganic material which is used to store the thermal energy.  $\text{Ca(OH)}_2$  is odorless, and it is a white color crystalline solid. It has many applications and uses in cement to preserve the building materials etc.  $\text{Ca(OH)}_2$  also transformed into calcium oxide ( $\text{CaO}$ ) 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  $\text{Ca(OH)}_2$  in which sol-gel method is one of them. Different materials are also used to get calcium hydroxide.  $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$  reacts with sodium hydroxide ( $\text{Na-OH}$ ) and formed  $\text{Ca(OH)}_2$  and  $\text{NaNO}_3$  as a product, obtained gel are washed with water and dried. Reaction mechanism is given by.



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  $\text{Ca(OH)}_2$  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  $\text{Ca(OH)}_2$  converted into  $\text{CaO}$  which was confirmed by using XRD. <sup>[23]</sup>

Zahra Mirghiasi et al. synthesized the nanoparticles of  $\text{Ca(OH)}_2$  by using thermal decomposition method.  $\text{Ca(OH)}_2$  converted into  $\text{CaO}$  by calcination at  $650^\circ\text{C}$  in furnace under  $\text{N}_2$  atmosphere. XRD analysis confirmed the crystal structure convert from hexagonal to cubic structure after heating. <sup>[24]</sup>

The effect of calcium carbonate formation in normal atmospheric conditions is also not getting excluded. All three Polymorphic structures of calcium carbonate (calcite, aragonite, and vaterite) are tried to get differentiated based on XRD analysis and TGA-DSC. XRD represent the different in the form of crystalline structure. Where as in TGA-DSC, we can see the difference based on the conversion of calcium carbonate to calcium oxide above  $650^\circ\text{C}$ . The effect of silica coating in the presence of these different types of carbonate structures is also verified by getting difference in the conversion towards oxide.

Moria Ambrosi et al. synthesized the colloidal nanoparticles of  $\text{Ca}(\text{OH})_2$  and spread in propanol. . The dynamic strength of dissemination of  $\text{Ca}(\text{OH})_2$  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  $\text{Ca}(\text{OH})_2$  under suitable condition for thermal energy. They used  $\text{Ca}(\text{OH})_2$  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  $400^\circ\text{C}$  to  $560^\circ\text{C}$  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.

C. Roßkopf et al. studied the nano coated  $\text{Ca}(\text{OH})_2$  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  $\text{Ca}(\text{OH})_2$  with Aerosol resulting the better material for thermochemical storage. The hydration / de-hydration process in which new phase of calcium silicate hydrate introduced.

In 2011 Qing Lin investigated the reactivity of silica nanoparticles with Calcium hydroxide.  $\text{Ca}(\text{OH})_2$  initiated  $\text{SiO}_2$  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  $\text{SiO}_2$  and  $\text{Ca}(\text{OH})_2$  fundamentally relies on the percentage of the mixture. Higher the percentage of  $\text{SiO}_2$  results increase in the reaction rate of  $\text{SiO}_2$  with Calcium hydroxide. [26]

Schicheng Zhang et al. synthesized the core shell nanoparticles of  $\text{CaCO}_3@ \text{SiO}_2$ . The thermal stability of the particles decreased as silica was coated on the surface of  $\text{CaCO}_3$ . The size and shape of the particle were same as the core of  $\text{CaCO}_3$ . After preparation of core shell nanoparticles, thermal stability of the core shell particles decreased as the temperature of the materials increased. [27]

C. Roßkopf studied the bed properties of the material by adding silica nanoparticles in  $\text{Ca}(\text{OH})_2$ . It showed that after addition of silica (5% wt.) the thermal and bulk properties was stabilized for some cycles and consequently cycling stability gets ensured. Addition of nanoparticles in it can prevent the material from agglomeration during the process of cycling. The bed properties of powder can get 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.

J. Yan et al. studied the process of dehydration of  $\text{Ca(OH)}_2/\text{CaO}$  by Li-doping. The study confirmed that the storage of heat capacity after doping does not affect, but kinetic study of  $\text{Ca(OH)}_2$  with Li-doping the storage of heat divided into two parts. De-hydration process for  $\text{Ca(OH)}_2$  with Li-doping was improved as well as the kinetic study parameter of  $\text{Ca(OH)}_2$  and with Li-doping are obtained. Theoretical results of  $\text{Ca(OH)}_2$  matched with experimental results for de hydration process.  $\text{Ca(OH)}_2$  with Li-doping calculation agree with the data experimentally on the similar growth but some exact calculation describe a little delay. <sup>[28]</sup>

Jose A. F. Gamelas et al. synthesized  $\text{CaCO}_3$  particle with silica by sol-gel method. A controlled synthesis was done which gave a highly branched like silica formation at the surface of  $\text{CaCO}_3$ . The addition of silica did not affect the structure of  $\text{CaCO}_3$  which was confirmed by using different techniques. The modified particles may contribute to the paper industry to improve the paper strength.

C. T. Yamashita et al. synthesized core shell nanoparticles of  $\text{CaCO}_3/\text{SiO}_2$  via sol gel method. Nanoparticles were heated at  $700^\circ\text{C}$  after successful synthesis of core shell particles and convert to  $\text{CaO}/\text{SiO}_2$  by de- carbonization of  $\text{CaCO}_3$ .  $\text{Ca(OH)}_2/\text{SiO}_2$  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  $\text{CaCO}_3$  because it didn't completely decompose to  $\text{CaO}$  due to  $\text{SiO}_2$  shell. <sup>[29]</sup>

## CHAPTER NO 03

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### Synthesis and Characterization Techniques

#### 3.1. SYNTHESIS TECHNIQUES OF NANOMATERIALS

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 favorable circumstances and detriments. Both approaches assume a precarious part in the creation and synthesis of nanostructures, yet the detriment of the top-down methodology is the weakness of the surface structure.<sup>[30]</sup>

##### 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.<sup>[31]</sup>

#### 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 PH meter
- Filtration

### 3.2. SYNTHESIS PROCESS

For the synthesis, sol-gel method was used for Calcium Hydroxide  $\text{Ca(OH)}_2$  and its composite with silica  $\text{Ca(OH)}_2@ \text{SiO}_2$  particles. Different concentrations of silica are used to synthesize the composite.

### 3.3. MATERIAL REQUIRED DURING SYNTHESIS.

The following materials are used during synthesis process.

- Calcium nitrate ( $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ )
- Sodium hydroxide (Na-OH)
- Ethylene glycol
- Distilled water.
- Deionized water
- Tetra ethyl Ortho-silicate (TEOS)
- Ethanol
- 2- Propanol (Isopropyl)

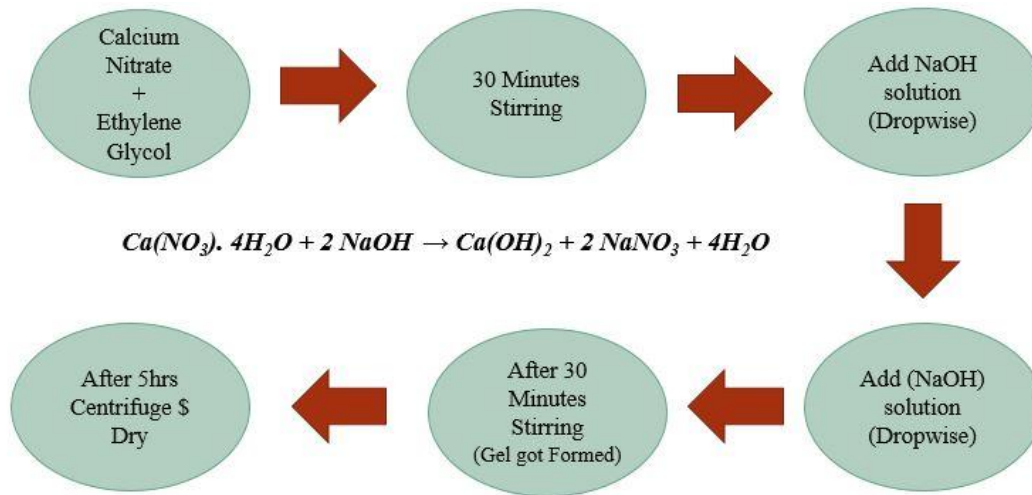
### 3.4. MATERIAL PREPARATION

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

#### 3.4.1. Synthesis of Calcium Hydroxide $\text{Ca(OH)}_2$

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

1.  $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$  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 mins 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. The remaining solution was collected by using centrifuge.
5. Then solution was dried under  $50\text{-}60^\circ\text{C}$  in oven.

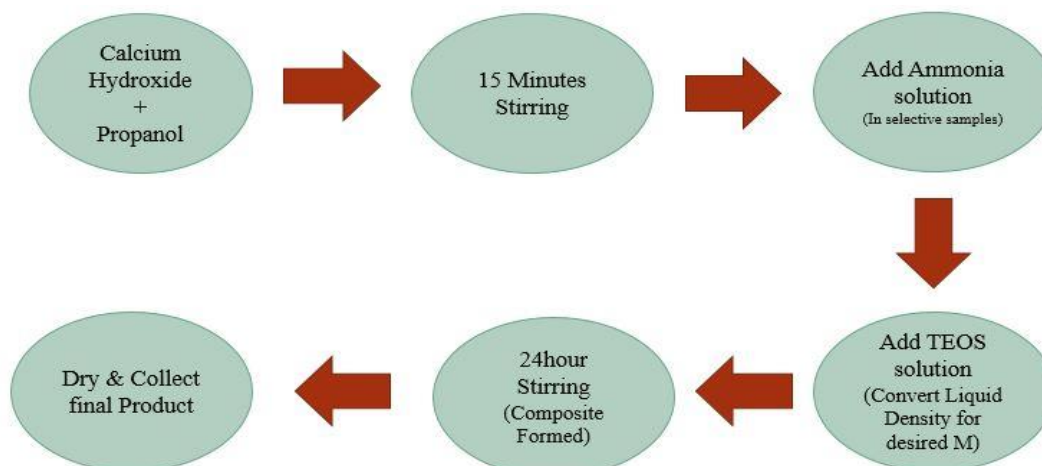


(Figure 3.1: Synthesis of Calcium Hydroxide  $Ca(OH)_2$ )

### 3.4.2. 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.

- 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.
- After 30 minutes, the required amount of TEOS was added for different concentration of composite.
- Then solution was prepared at room temperature under constant stirring for 24 hours.
- After stirring the product was dried at  $100^\circ C$  and final powder form was collected.



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

### 3.4.3. Concentration of TEOS for Composite

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

- Ca(OH)<sub>2</sub>/SiO<sub>2</sub> (**5uMM**)
- Ca(OH)<sub>2</sub>/SiO<sub>2</sub> (**10uM**)
- Ca(OH)<sub>2</sub>/SiO<sub>2</sub> (**50uMM**)

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

- **For 5uM:** 0.0002216ml TEOS added in the solution.
- **For 10uM:** 0.0004432ml TEOS added in the solution.
- **For 50uM:** 0.002216ml TEOS added in the solution.

### 3.5. 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.

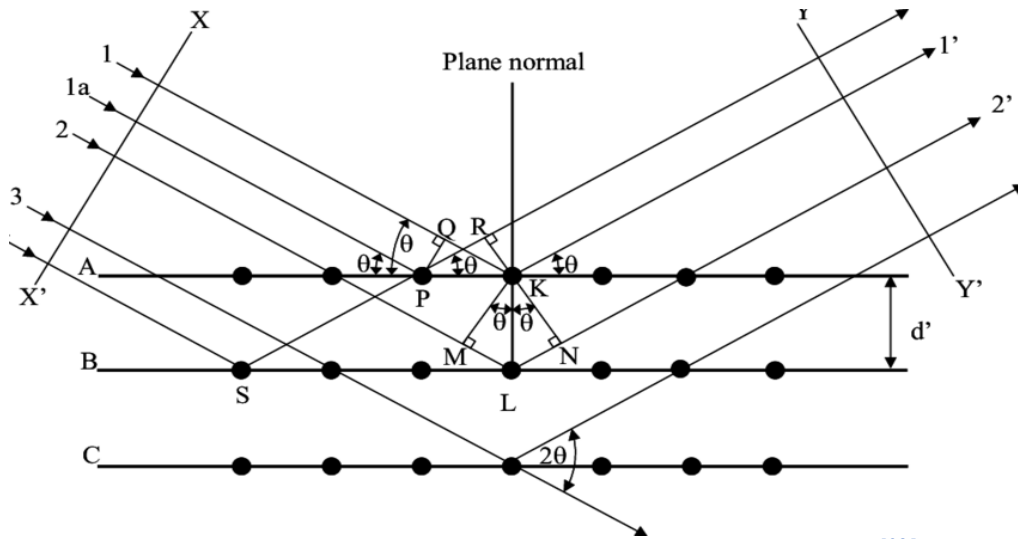
These characterization techniques are used in this research work,

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

### 3.6. X-RAY DIFFRACTION

#### 3.6.1. 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 interreact with the material, these scattered beams enhance their effect in many directions. Due to constructive interference, these beams reinforce each other. This illustration is known as R-Ray Diffraction. The phenomenon of X-Ray Diffraction analysis is clearly shown in figure 3.3.



(Figure 3.3: X-rays interaction with the Crystal planes (hkl)<sup>[32]</sup>)

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.

### 3.6.2. 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.

### 3.6.3. 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.

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

Where,

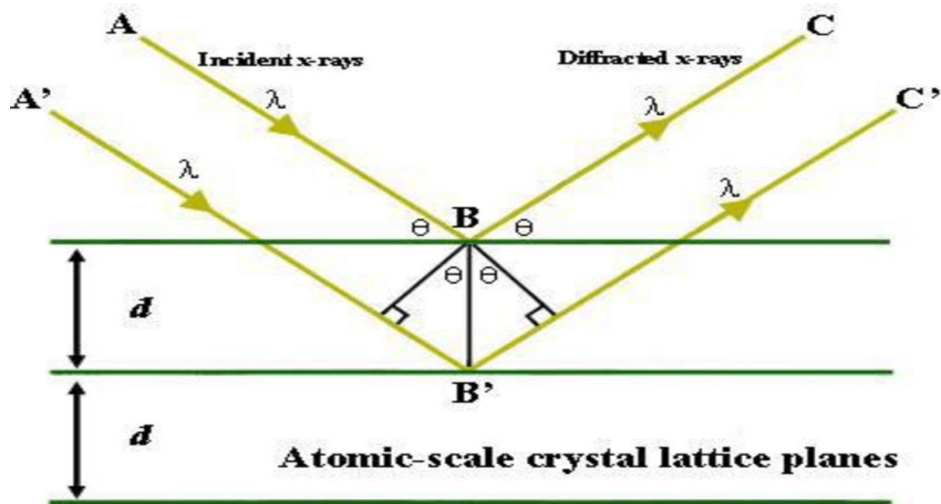
$d$  = inter planar distance of atoms, ions, or molecules  $\theta$  = angle of scattering

$\lambda$  = 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  $\theta$  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<sup>[33]</sup>)

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

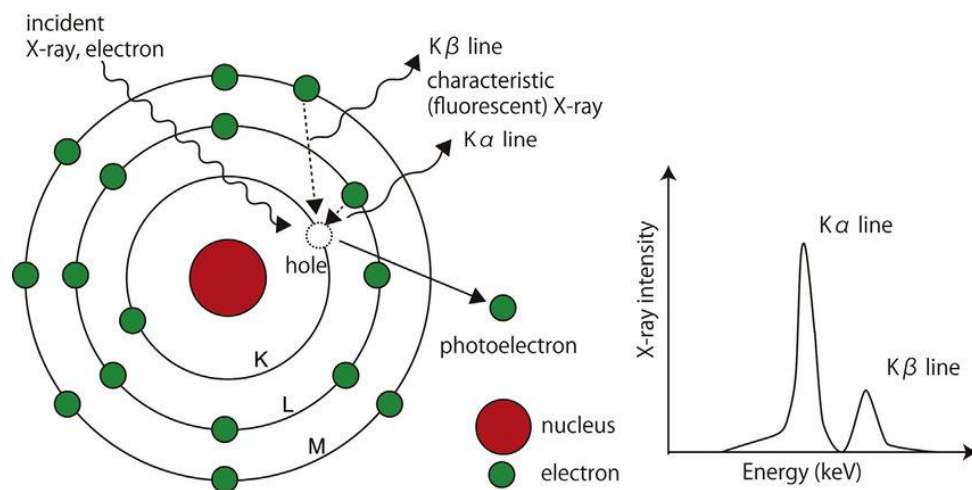
$$n\lambda = 2d \sin \theta$$

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

$$D = \frac{k\lambda}{\cos \theta}$$

$k$  = shape factor for specific crystal  
 $\lambda$  = wavelength of X-ray  
 $\beta$  = 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. Energy of waves are released relying on whether electron is dislodged from the higher or lower energy 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<sup>[34]</sup>)

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

Target Element	K $\alpha$ ( $\text{\AA}$ )
Cu	1.541
Fe	1.937
Co	1.790
Cr	2.291

(Table No 3.1. Different Target material used in XRD.)

### 3.6.4. XRD Applications

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

- XRD can be used to determined atomic arrangement.
- XRD can measure the average spacing between two spaces.
- XRD can determine the crystalline phases.
- XRD can obtain the Integrated intensities.
- XRD can also measure the crystal structure of unknown material.

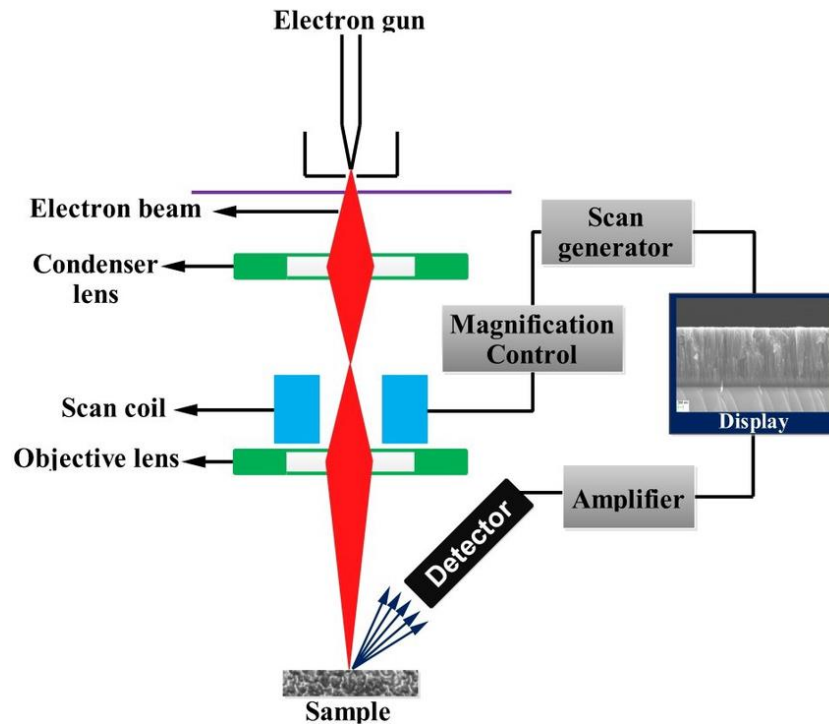
### 3.7. SCANNING ELECTRON MICROSCOPE (SEM)

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.

### 3.7.1. Electron gun

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



(Figure 3.6: The detailed schematic of SEM<sup>[35]</sup>)

### 3.7.2. Condenser Lens

After the beam spirals 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. <sup>[36]</sup>

### 3.7.3. 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.

### 3.7.4. 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.

### **3.7.5. 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.

### **3.7.6. 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.

### **3.7.7. 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.

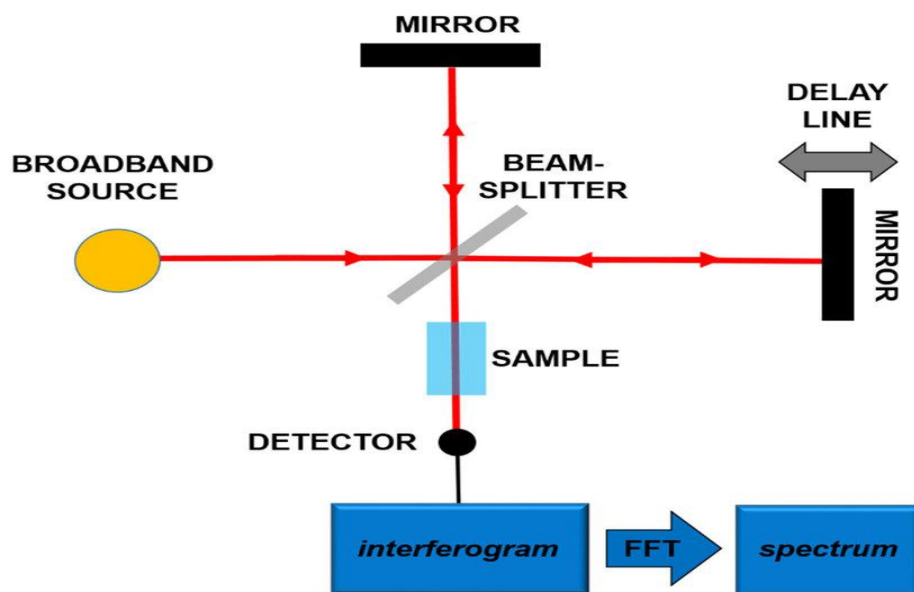
## **3.8. ENERGY DISPERSIVE SPECTROSCOPY**

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 and fill the vacancy. When high energy electron falls 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.

## **3.9. FOURIER TRANSFORM INFRARED SPECTROSCOPY**

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. <sup>[37]</sup>



(Figure 3.7: Schematic diagram of Fourier-Transforms Infrared Spectrometer<sup>[38]</sup>)

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 spark 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.

### 3.10. RAMAN SPECTROSCOPY

Raman spectroscopy is based on an effect known as Raman scattering presented by C.V Raman and K.S. Krishnan in 1982. This spectroscopy is based upon inelastic scattering of incident monochromatic light from the sample. In this spectroscopy, the sample is irradiated by strong laser source in UV-visible region and scattered light is observed at perpendicular direction to the incident beam. Main parts of the Raman spectroscopy are laser excitation source, excitation delivery optics, collection optics, wavelength separation apparatus, detector , recording device and sample material.

There are some specific advantages get specified given as:

- Raman is a non-destructive technique, so it didn't produce any chemical or structural change in sample.
- Raman can be used to obtain info about molecules, which can give help in understanding chemical structure, phase changes, and vibrational modes etc.
- Use of high-power laser (Monochromatic light)
- Suitable for all three phases including solids, liquids, and gases.
- No sample preparation is required.

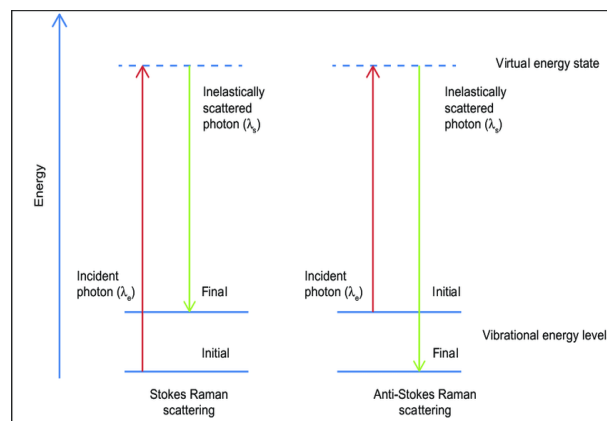
Raman analysis include two types of phenomena known as “Raman scattering” and “Raman effect”. Most of the incident light on the object gets scattered without having any change in the wavelength. That is known as Rayleigh or elastic scattering. A very small fraction about (0.0001%) of the total amount of incident light gets experience of change in wavelength.

### 3.10.1. Raman Scattering

Raman scattering analysis gets related with the interaction of incident light photons with vibrating molecules is set in wavelength and frequency change. This change gets visible with change in the color of outgoing light. The fraction of “RAMAN Scattered” light is the figure print that helps to study the change in the chemical and structural composition of given samples. The shift occurred due to change in wavelength and frequency can get classified as

If the emitted photon has less frequency (or less energy) then it's known as Stokes shift.

If the emitted photon has greater frequency (or greater energy) then it's known as Anti-Stokes Shift.



(Figure 3.8 : Stokes and Anti-Stokes Difference<sup>[39]</sup>)

### 3.10.2. Raman Effect

Raman effect is too weak to get observed visually. A spectrometer with high sensitivity can be used to analyze the emitted light. Spectrometer filters and wavelength selectors are used to separate and block all the Rayleigh scattering to get high resolution Raman Spectrum.

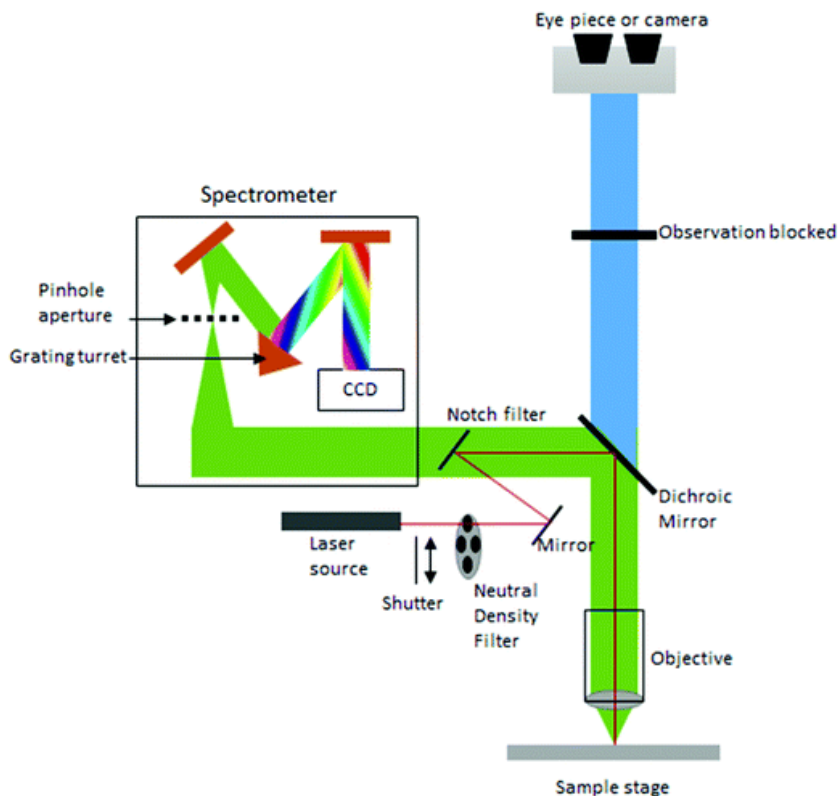
The major parts of Raman set-up can be listed as follows.

Excitation Source (Laser)

Lenses to focus and collect the incident and emitted light.

Filters to filter out effects of Rayleigh scattering.

High quality Diffraction grating to find out clear difference in different Raman spectrums.



(Figure 3.9 : Raman Spectroscopy Set-up<sup>[40]</sup>)

### 3.11. Laser Particle Size Analyser (LPSA)

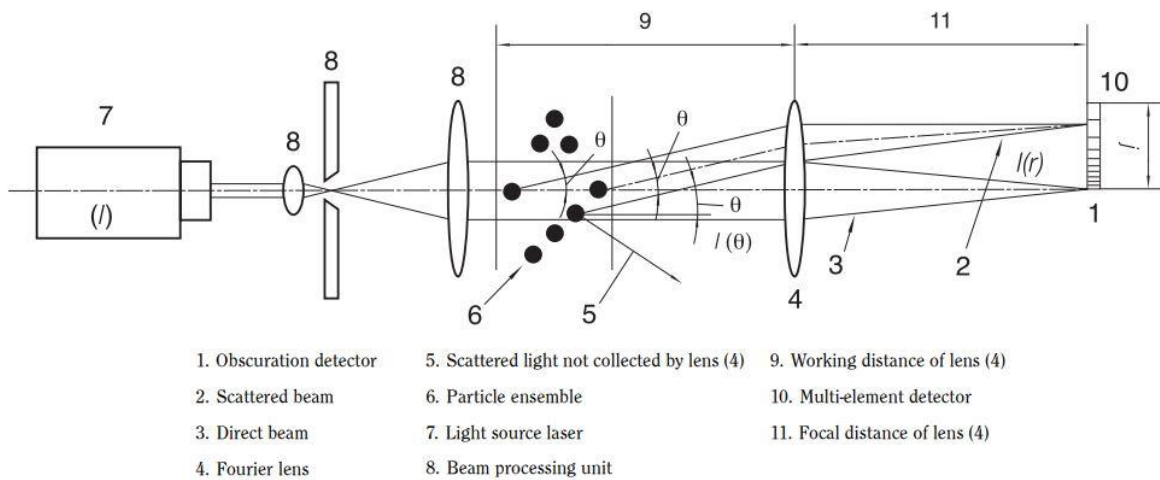
Laser particle size analyser (LPSA) is a modern laser diffraction technique, which is used to measure particle size distribution over a very wide dynamic range between 10nm-4mm. This range is further divided into 4,00,000<sup>th</sup> factor among smallest to largest particles. A typical way out to find particle size by having diffraction of laser light around the particles (which are got dispersed in some suitable liquid). The dispersion also reduces the effect of agglomeration and reduce error in overall distribution result.



### 3.11.1. Laser Particle Size Analyser (LPSA) Working

Laser particle size analyser contains a light source that gets pass through optics mechanism to get directed. Later on, for measurement purpose, a set of Fourier lens can get used to detect multi-scattered color light. A data analysis set-up required in separate side lines to receive data and get distributed form of results from volumetric calculations on the basis of received data. The particles can enter from second position, which is parallel to the light beam, but that spot is before collecting lens and maintain a specific distance. It may cause a so-called reverse Fourier optics and that can converge the light beam. It provides a specific advantage in conventional set-up to have a reasonable path length inside working range of lens. The other type of set-ups allows shorter lengths, but they can put scattered at larger angles, which results an extra-advantage to go in submicron levels.

The interaction between incident light beam and ensemble of dispersed particles results in scattering pattern with different light intensities at different angles. The total angular intensity distribution has both incident (direct) and scattered light results incorporated. This gets send to a series of lens for multi-element detection. These lenses form a scattering pattern within the limits, but it doesn't depend upon the position of the specific element inside incident light beam. Resultantly, the continuous angular intensity distribution is converted into a discrete special intensity distribution on a set of detector elements. We assume that collective pattern of assemble is sum of all individual particles single patterns present at different relative places in assemble.



(Figure 3.10 : Laser Particle Size Analyser (LPSA)<sup>[41]</sup>)

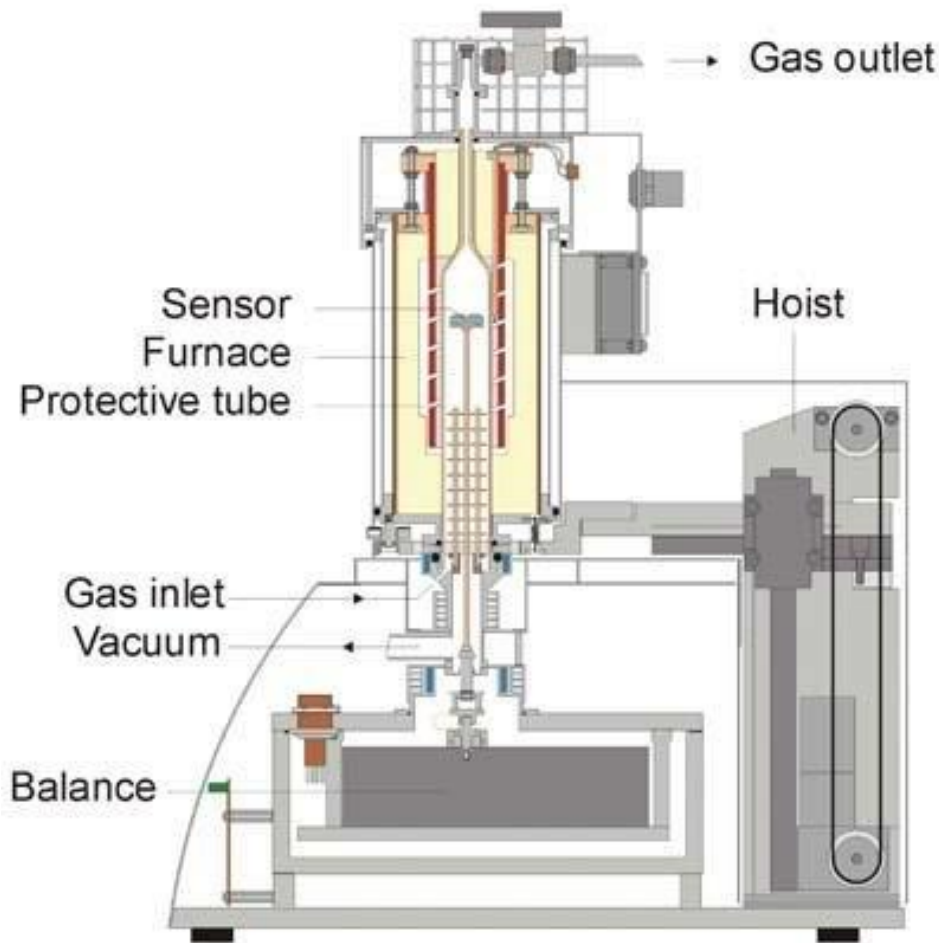
### 3.12. Thermo-Gravimetric Analyser (TGA)

Thermo-Gravimetric Analyses is a technique which is used to study the thermal behaviour of material. The change in mass gets observed as a function temperature and time in this set up. A small amount of given material is required to check the decomposition into different levels before getting highly stable at any desired heating rate gives a huge advantage to study any kind of phase change or side reaction occurrence at any required temperature can get easily studied.

Besides the study of any phase change in normal atmosphere, we can attach our desired atmosphere also. In most of the cases for inert atmosphere, we can attach nitrogen or argon connection.

### 3.12.1. 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, N<sub>2</sub>, He) atmosphere depending on reaction conditions. [42]



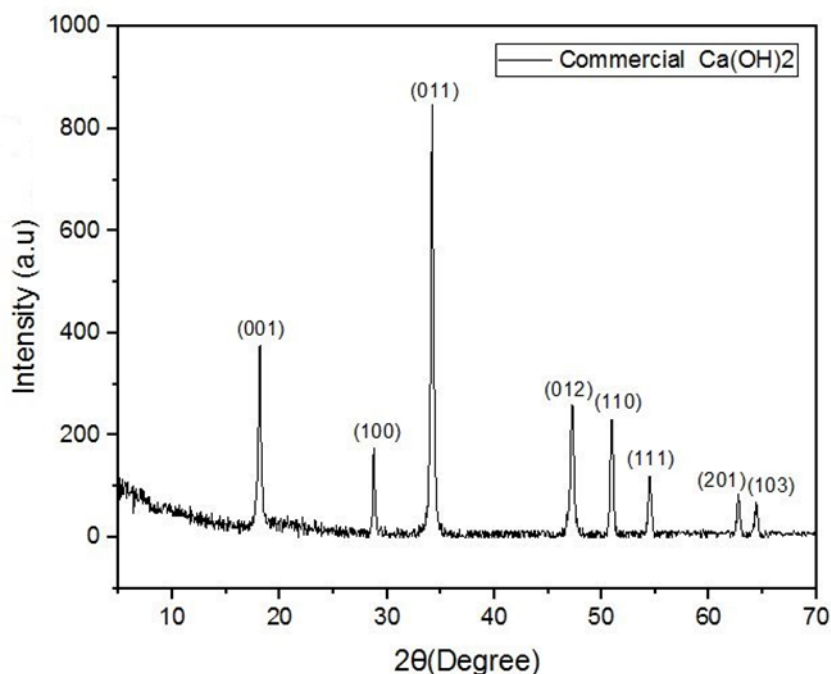
(Figure 3.11: Instrumental set-up of Simple TGA analysis<sup>[43]</sup>)

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.

### Results and Discussion

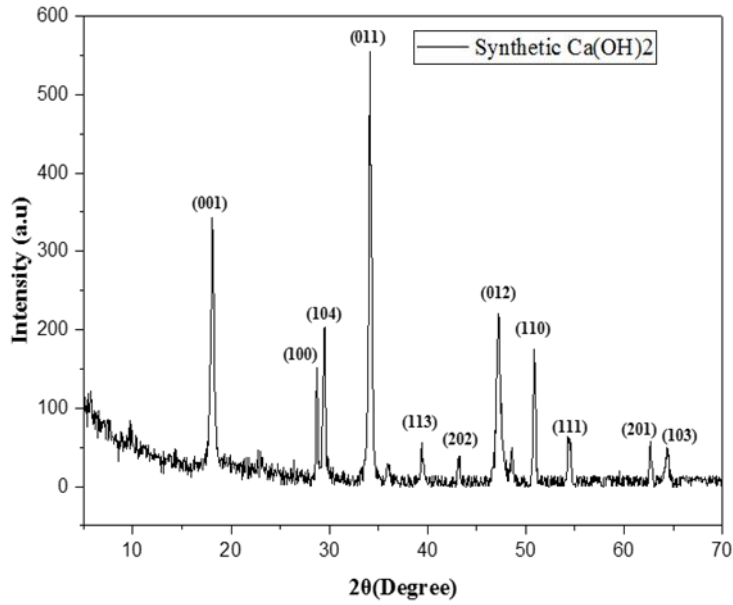
#### 4.1. X- RAY DIFFRACTION

XRD has been done to analyze the data of the powder sample. The XRD of the purchased sample match with the pattern of  $\text{Ca(OH)}_2$ . The crystalline structure of  $\text{Ca(OH)}_2$  is hexagonal with lattice parameter  $a = 3.5899 \text{ \AA}$ ,  $c = 4.916 \text{ \AA}$ ,  $z = 1$  confirmed by (ICSD card No. 44- 1481). The diffraction peaks of the sample indicates that the crystalline structure of  $\text{Ca(OH)}_2$  can be easily attained under synthetic circumstance. The sharpness of peaks also indicates great size of particles.<sup>[44]</sup>



(Figure 4.1: XRD pattern of  $\text{Ca(OH)}_2$ )

While preparing nano sized particles, we have found some extra peaks in above graph at  $2\theta = 29.35^\circ$ ,  $38.95^\circ$  and  $42.5^\circ$ . These peaks shows formation of  $\text{CaCO}_3$  by reaction of  $\text{Ca(OH)}_2$  with  $\text{CO}_2$  from atmosphere. The broadening in other peaks in comparison of previous sample shows reduction in particle size. <sup>[44]</sup>



(Figure 4.2 : XRD of carbonated  $\text{Ca}(\text{OH})_2$ )

Before moving on towards silica coating experiments, we have checked dehydration of above-mentioned samples. The greater sized particles shown stability and get converted into CaO. The crystalline structure of CaO is cubic with lattice parameter  $a=b=c= 4.805 \text{ \AA}$  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.<sup>[45]</sup>

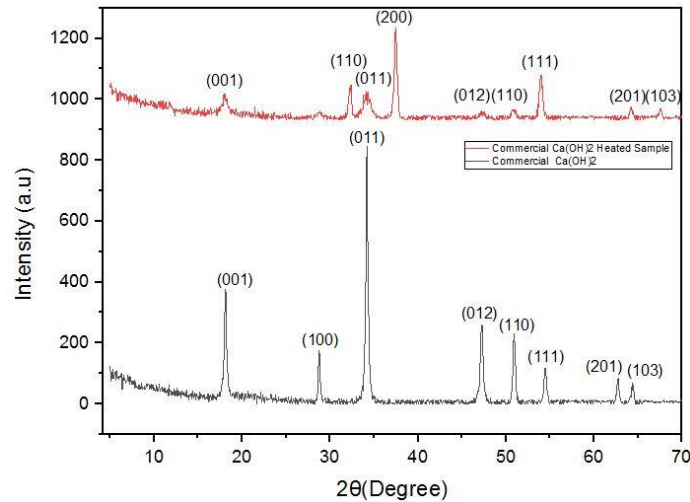
The lattice strain and crystallite size can be acquired from peak broadening analysis of the sample. The peak broadening identifies that the material is in nanoscale. The crystallite size can be resolute by utilizing Debye-Scherer's formula.<sup>[46]</sup>

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where “D” is the crystallize size of the particle, “ $\lambda$ ” is the wavelength of the X-rays, “k” is the shape factor (0.94) and “ $\beta$ ” is the FWHM (full width half maximum of the diffraction peaks). The average crystallize size was measured by using Scherer formula of  $\text{Ca}(\text{OH})_2$  that was 30.3 nm.

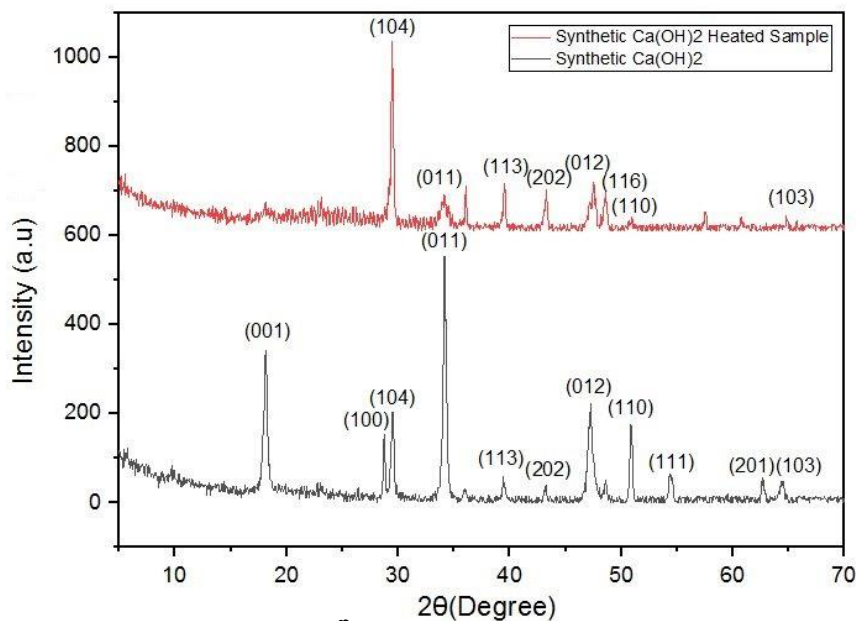
$\text{Ca}(\text{OH})_2$  was converted into CaO by annealing the sample by giving the temperature at 300°C. The structure of Calcium Oxide (CaO) was confirmed by using XRD analysis. XRD pattern confirmed the structure decomposed easily from  $\text{Ca}(\text{OH})_2$  to CaO. The crystalline structure of CaO is cubic with lattice parameter  $a=b=c= 4.805 \text{ \AA}$  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. [47]



(Figure 4.3 : Comparison between  $\text{Ca(OH)}_2$  and Dehydrated sample)

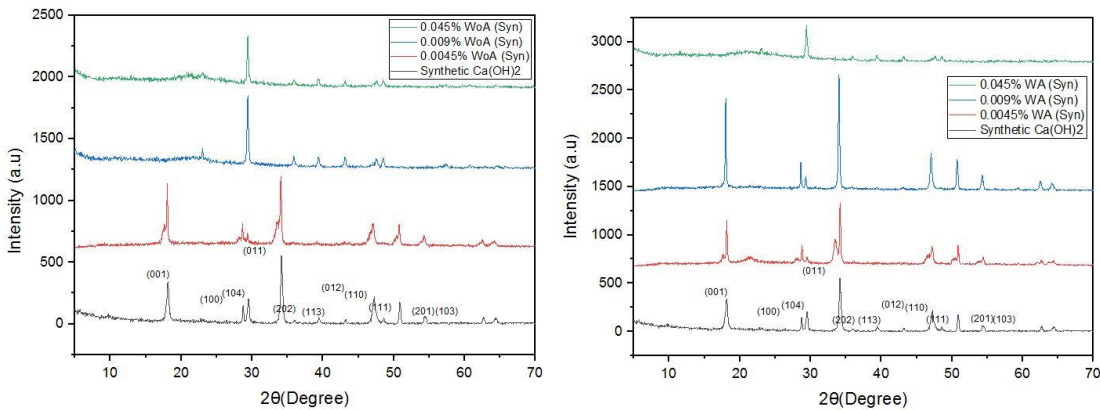
But in case of nano-particles, we have seen  $\text{CaCO}_3$  formation due to low temperature and high surface to volume ratio.  $\text{CaCO}_3$  can get converted into CaO above  $650^\circ\text{C}$ . [48]



(Figure 4.4 : Synthetic  $\text{Ca(OH)}_2$  and its dehydrated sample)

Figure 4.4 shows the conversion of  $\text{Ca(OH)}_2$  nano-particles to CaO. Afterwards, due to normal atmosphere conditions and high temperature, these nano-particles didn't show stability. The reaction with  $\text{CO}_2$  from atmosphere converts CaO into  $\text{CaCO}_3$ . The peaks at  $29.33^\circ$ ,  $38.95^\circ$  and  $42.5^\circ$  clearly gets enlarged. On the other side, the major peaks of  $\text{Ca(OH)}_2$  got reduced after dehydration. Now let's observe the impact of silica coating over these synthetic nano-particles as well as on the purchased micro-sized particles. In next step, a clear difference of the effect of

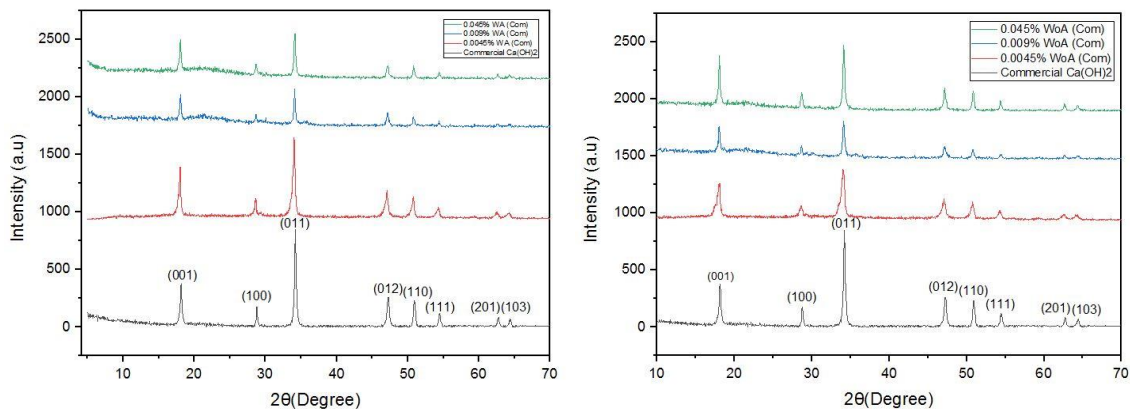
presence and absence of catalyst (Ammonia) was also studied. Let's start with nano-sized synthetic particles.



(Figure 4.5 : XRD of silica coated synthetic  $Ca(OH)_2$  (Left) In the absence of Ammonia (Right) In the absence of Ammonia)

Now in the presence of ammonia, at the weightage of 0.009% weightage coating, we observe that crystallite size (calculated from Debye Scherer's equation ) is in range of 42.6nm to 46.8nm. After increasing the amount of silica from this point, we observe formation of calcite. A clear peak at  $29.33^\circ$  shown the presence of carbonate in case of higher coating with the presence of ammonia. On the other hand, we found carbonate presence even in case of 0.009% weightage in presence of ammonia. This shows that presence off ammonia plays a vital role in improvement of coating quality in case of synthesized nano-particles. It also tried to avoid formation of carbonate as compared to its absence side. On PH scale, it forms basic nature by its presence in sample and it can get observed at any stage of formation easily.

In case of larger sized particles, there is a strong chance of great stability because of low surface to volume ration. Let's see the effect of coating same amounts of silica in the presence or absence of ammonia over these larger sized particles. The comparison will indicate actual suitability of particle size and effect of catalyst for enhancement of Thermochemical energy storage.



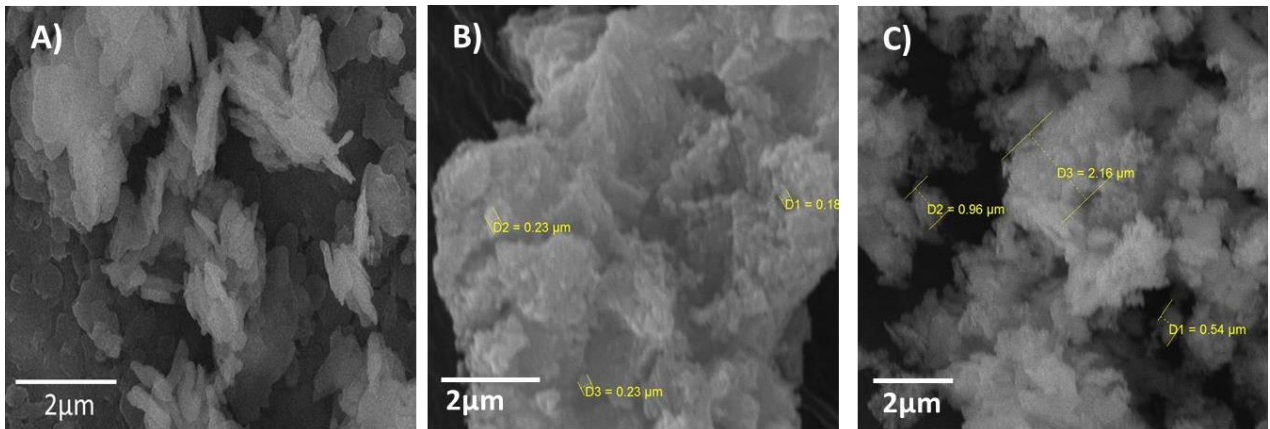
*(Figure 4.6 : Commercial Ca(OH)<sub>2</sub> Coated with Silica (Left) In the presence of Ammonia (Right) In the absence of Ammonia)*

Here in both cases, we didn't find any calcite formation as we didn't find (104) plane at 29.33°. The other two peaks of carbonate at 39° and 43° are also absent in these results. This shows the higher stability even after completing coating reaction. A clear improvement in coating was observed in the presence of ammonia, which is completely avoiding calcium carbonate formation. In the absence of ammonia, a clear reduction in intensity of peaks was observed, which clearly indicates less stability of less quality of coating, and it is unable to stop phase changing of calcium hydroxide to calcium oxide or calcium silicate.

A separate effect of agglomeration was seen in case of nano-sized synthetic particles. With high surface to volume ratio, they can react easily with CO<sub>2</sub> to form calcium carbonate or with SiO<sub>2</sub> to form Calcium silicate. The effect of changing amount of silica availability also shows difference due to agglomeration in case of synthetic samples. There was no agglomeration seen in case of larger sized particles. This nonuniform agglomeration can represent irregular coating results after completing 24hrs coating reaction. Secondly the change in size after getting agglomeration also produce difference in carbonate formation. That is why we can find different crystalline polymorphic structures in carbonate formation (e.g., Calcite, aragonite or vaterite formation).

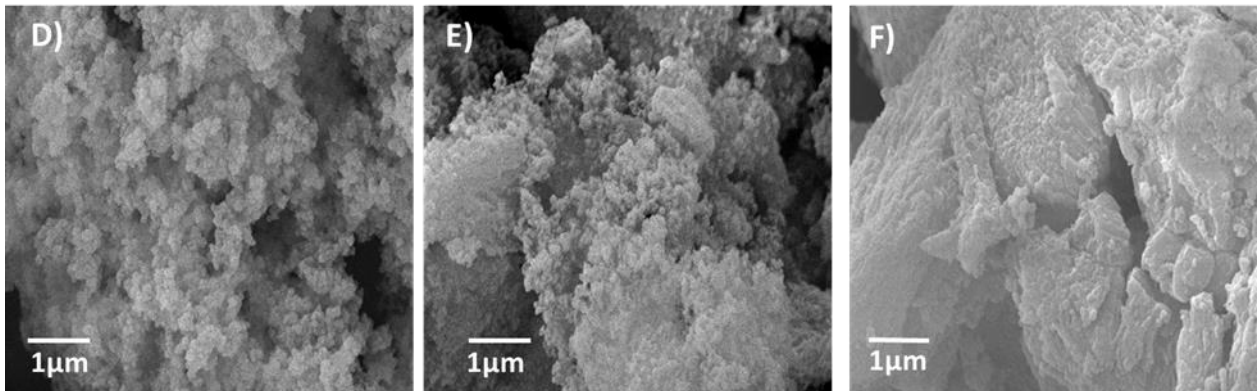
## 4.2. SEM ANALYSIS

Surface morphological analysis were done by scanning electron microscope. In case of nano particles as we have clearly noticed carbonation of pure hydroxide before it gets coating reaction with silica. In SEM analysis, we have seen clear agglomeration of nano-particles. We observe flakes and hexagonal arrangement in pure sample in (a). In (b) and (c) we have seen a comparison between 5uM and its 10 times 50uM coating reaction.



(Figure 4.7 : SEM results of synthetic  $\text{Ca(OH)}_2$  and coated samples (a) Synthetic  $\text{Ca(OH)}_2$  (b) 5uM Coated Sample (c) 50uM coated Sample)

Now in the figure 4.8, we can observe a comparative analysis between above sample and larger particles and coating over those greater size samples. In larger size particles, we can observe less agglomeration as compared to nano-particle samples. Due to larger size particles, we observe less amount of coating in 5uM coating as compared to nano-particles because in that case we have seen coating on bunch of particles. In case of 50uM samples we feel that silica is enough to coat both sized particles.

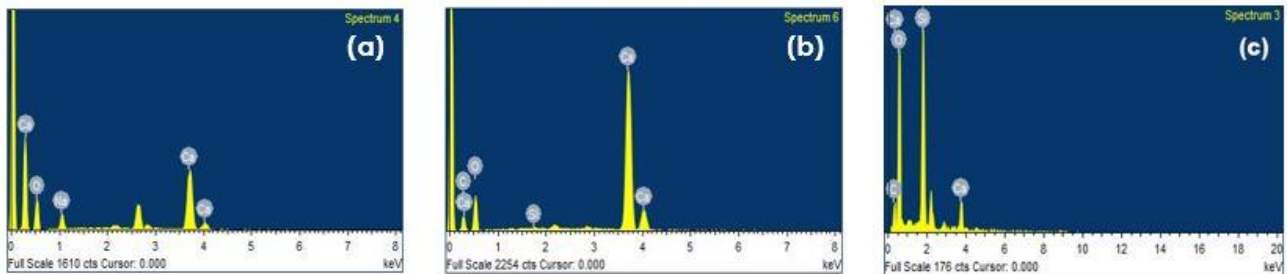


(Figure 4.8 : Commercial  $\text{Ca(OH)}_2$  and coated samples SEM results (d) Commercial  $\text{Ca(OH)}_2$  (e) 5uM coated sample (f) 50uM coated sample)



### 4.3. EDX ANALYSIS

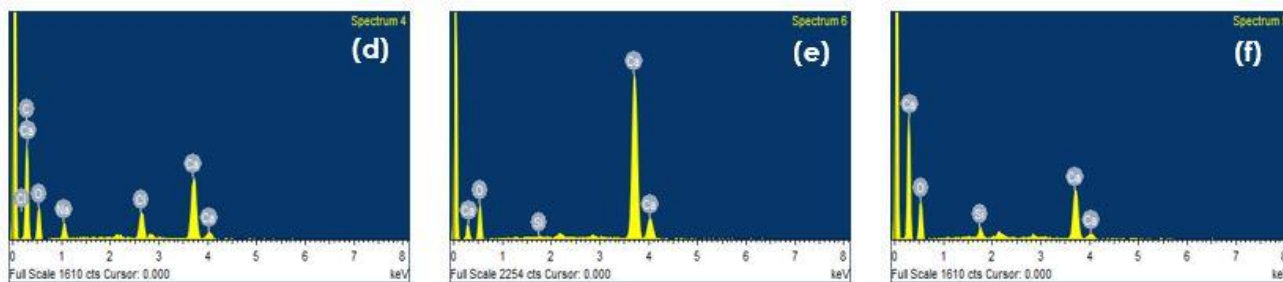
The elemental analyses were completed with the help of EDX attached with SEM set-up. SEM results were taken for both pure samples (Commercial and Synthetic). In commercial sample we get only Ca and O. But in case of pure synthetic sample, we find carbon C also. An extra amount of carbon got observed as we have used carbon tape to stick our sample on substrate. This represents the formation of carbonate. A very small amount of Na indicates the remaining amount of (NaNO<sub>3</sub>) or non-reactive (NaOH).



(Figure 4.9 : EDX of Synthetic Samples and Coating Composites (a) Synthetic Ca(OH)<sub>2</sub>, (b) 5uM Synthetic WA (c) 50uM Synthetic WA)

A comparative result taken without carbon to find out the concentration of pure Ca, O, and Si presence in respective ratios. The pure sample doesn't contain Si. 5uM sample contain 2.67% of Si. And 50uM shows 26.9% Si. This shows exactly around 10 times of 5uM. But if we consider carbon as an extra factor then these exact ratio gets disturbed. The presence of ammonia also incorporates nitrogen presence, but we didn't consider it here as giving good time for drying can remove it completely.

In case of commercial samples, we didn't find much carbonate in pure sample. That is why the exact ratio didn't shift much as compared to nano-sized particles case. Secondly these particles show more stability as their initial ratio of Ca and O remains almost same at each point as it was before reaction.



(Figure 4.10 : EDX of Commercial  $\text{Ca(OH)}_2$  and its coated composites (d) Commercial  $\text{Ca(OH)}_2$ (e) 5uM Commercial WA(f) 50uM Commercial WA)

The results in which we took carbon ratios differ due to initial difference of presence of carbonate in pure samples case. Secondly commercial samples show less reactivity due less surface to volume ratio. so, they lack in the carbonate formation. But in case of nanoparticles, we already have calcium carbonate formation. In coating samples, for less amount of silica, they again get a chance to form calcium carbonate. Agglomeration is another reason for the difference in the ratio present in incorporation of carbon. The inert nature of micro-sized calcium hydroxide with silica helped these samples to stay in added ratios at initial steps.

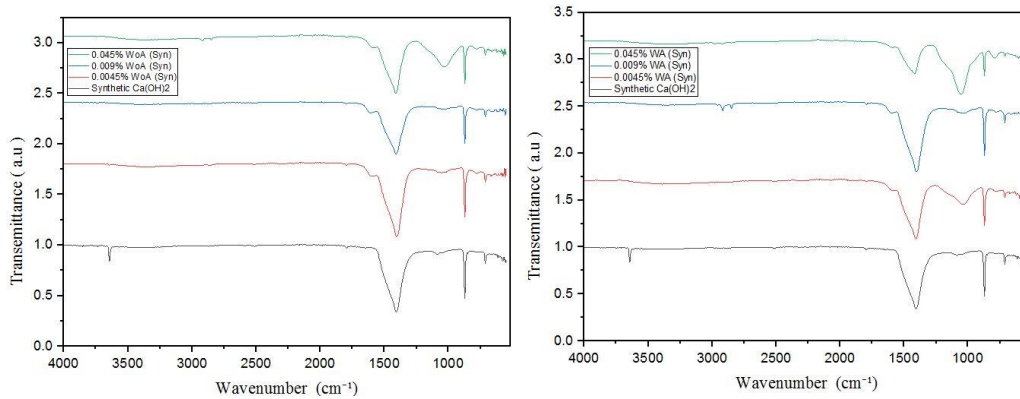
#### 4.4. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR):

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 sections, the infrared range can be scattered as

- The far infrared range exist at ( $< 400 \text{ cm}^{-1}$ ).
- The midinfrared range lies in between ( $4000\text{-}400 \text{ cm}^{-1}$ ).
- The near infrared range exist between ( $13000\text{-}4000 \text{ cm}^{-1}$ ).
- To investigate our material, mid infrared range ( $4000\text{-}400\text{cm}^{-1}$ ) spectrum was used. The peaks in this area give us the data about the components which are available in material. The mid-infrared region can get further divided into four more regions on basis of frequency. These regions are enlisted as follows.
- The region ( $4000\text{-}2500 \text{ cm}^{-1}$ ) is study and corresponds to X-H stretching in the mid infrared region.
- The region ( $2500\text{-}2000 \text{ cm}^{-1}$ ) is a triple bond region of atom in a mid-infrared region.
- The region ( $2000\text{-}1500 \text{ cm}^{-1}$ ) is study as a double bond in the mid infrared region.
- The region ( $1500\text{-}400 \text{ cm}^{-1}$ ) corresponds to single bond region of the atoms and called as a fingerprint region.

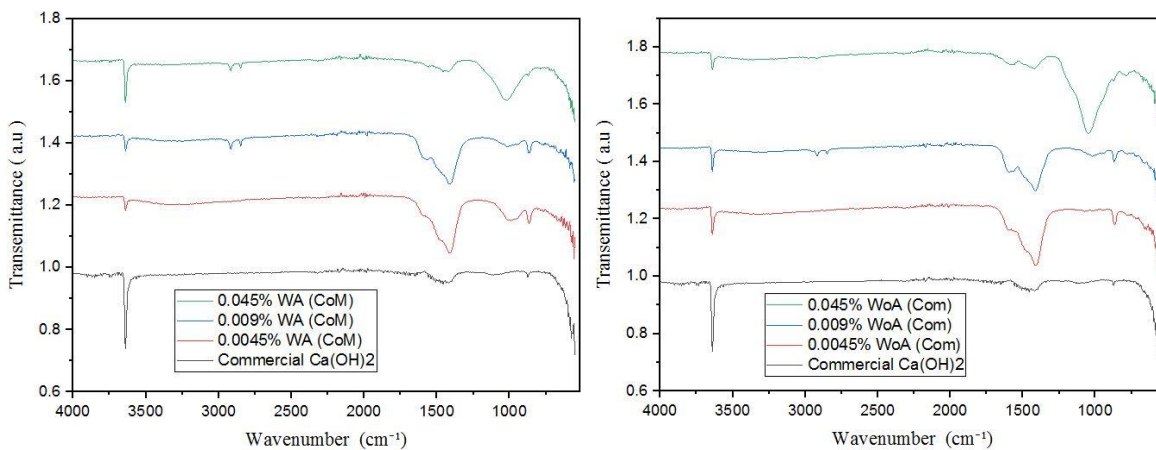
The FTIR range (Fig. 4.10) of the synthesized powder showed the band characteristics of both hydroxide and carbonate gatherings of calcium. The decently solid ingestion bond at  $\sim 3642 \text{ cm}^{-1}$

identified with the sharp - OH stretching bond, The OH expanding absorption bond was not too sharp.



(Figure 4.10 : Synthetic  $Ca(OH)_2$  and its coated samples (Left) Without Ammonia  
(Right) With Ammonia)

Functional groups study was conducted through FTIR. In above diagram, we observe presence of hydroxide group around  $3642\text{ cm}^{-1}$ . But it gets disappeared in both case of coating w.r.t presence of ammonia. At  $871\text{ cm}^{-1}$ , we observe carbonate presence. This group is indication for the formation of calcium carbonate. At  $798\text{ cm}^{-1}$ , we have Si-O-Si stretching. This refers to the presence of silica in composite. With its increment we got high chances for the formation of calcium silicate on the expense of both calcium hydroxide and calcium carbonate break down in coating reaction.



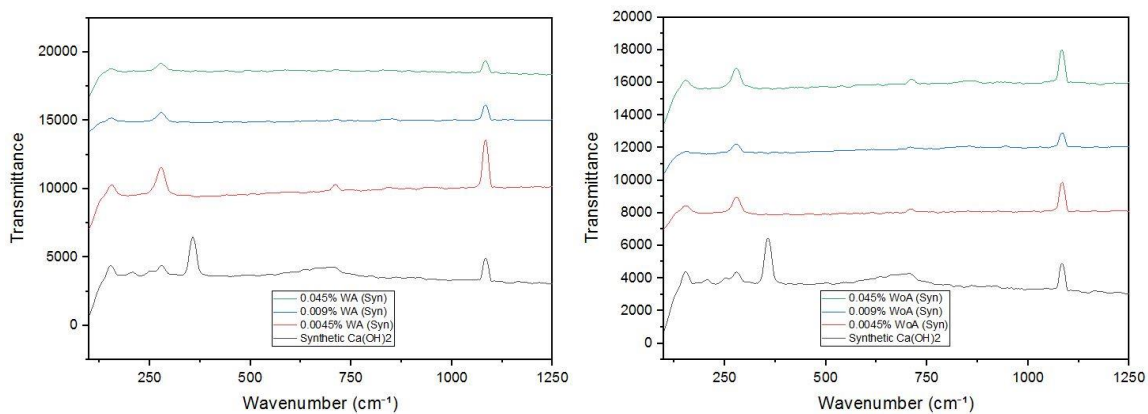
(Figure 4.11 Commercial  $Ca(OH)_2$  and coating on it (Left) In the Absence of ammonia  
(Right) In the presence of Ammonia)

Now let's see the initial difference of presence of (OH) Even after coating reaction of silica. This represents the stability of larger sized particles to avoid formation of calcium carbonate. It got observed that other two peaks at same spots as well but there is only one more difference other

than hydroxide groups difference. That shows the effect of size of particles (connected with reactivity) and required amount of silica for a proper coating. A clear difference got observed from shift of  $798\text{cm}^{-1}$  ( Which represents Si-O-Si) is now got emerged and the joint peak of hydroxide group is also got reduced. Due to less reactivity of larger  $\text{Ca(OH)}_2$ , we already know that they are harder to get converted in calcium carbonate. But here in presence of ammonia, they can get reacted to form calcium silicate. In comparison with nano-particles, we observe that formation of calcium silicate from calcium hydroxide larger sized particles is easier because of less carbonate formation.

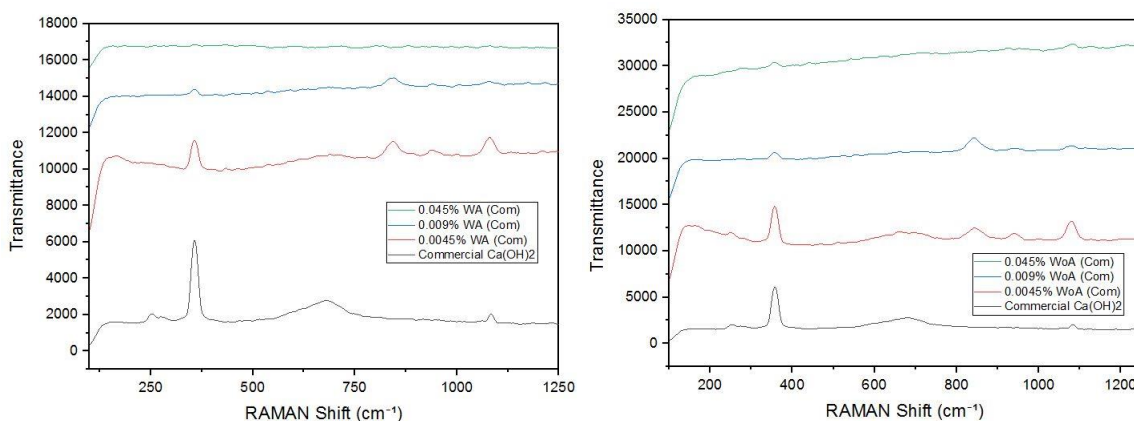
## 4.5 RAMAN SPECTROSCOPY

RAMAN Spectroscopy can clearly differentiate between functional groups by vibrational (Both translational and rotational) modes. In case of synthetic nano-particles, we have a clear observation at  $252\text{ cm}^{-1}$ ,  $357\text{ cm}^{-1}$  and  $680\text{ cm}^{-1}$  clearly correspond to (-OH) presence with two  $A_{1g}$  and one rotational  $E_g$  against  $\text{Ca}^{+2}$  cations. [49] In case of nanoparticles, a clear observation is studied that calcium hydroxide is got converted in calcium carbonate. [50] Figure 4.12 shows the difference of presence of catalyst in case of synthetic samples.



(Figure 4.12 : RAMAN results of synthetic samples coating (Left) In the presence of Ammonia (Right) In the absence of Ammonia)

Now in case of larger sized particles, we have seen calcium carbonate formation in initial cases. But as we increase the amount of TEOS, that carbonate formation decreases to subsequent level. But we observe a new band at  $710\text{ cm}^{-1}$  in case of nano particles, which indicates the presence of aragonite (A polymorph of calcium carbonate with orthorhombic crystal structure). [51]



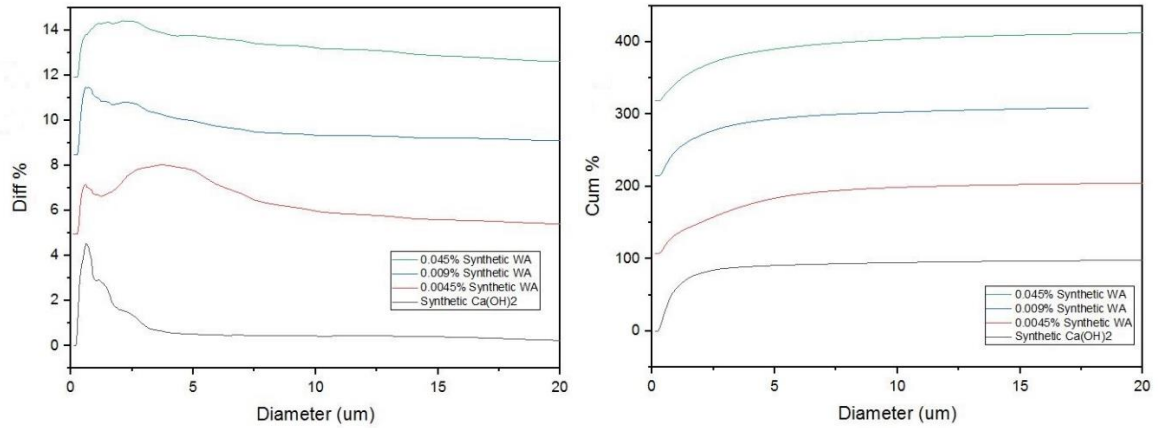
(Figure 4.13 : RAMAN Results of Commercial  $\text{Ca}(\text{OH})_2$  Coated samples (Left) In the presence of Ammonia (Right) In the absence of Ammonia)

The presence of different polymorph structures in different samples having different concentration of calcium carbonate can affect the cyclic conversion of calcium hydroxide to oxide and can result in the conversion into a range rather than a sharp conversion from one to other crystal structure. We can observe the fact in TGA-DSC results, and it can only be resolved by applying slow heating rate or having ramping in different interval at different temperatures corresponding to different crystal structure changes in a normal heating rate.

#### 4.6. LASER PARTICLE SIZE ANALYSES (LPSA)

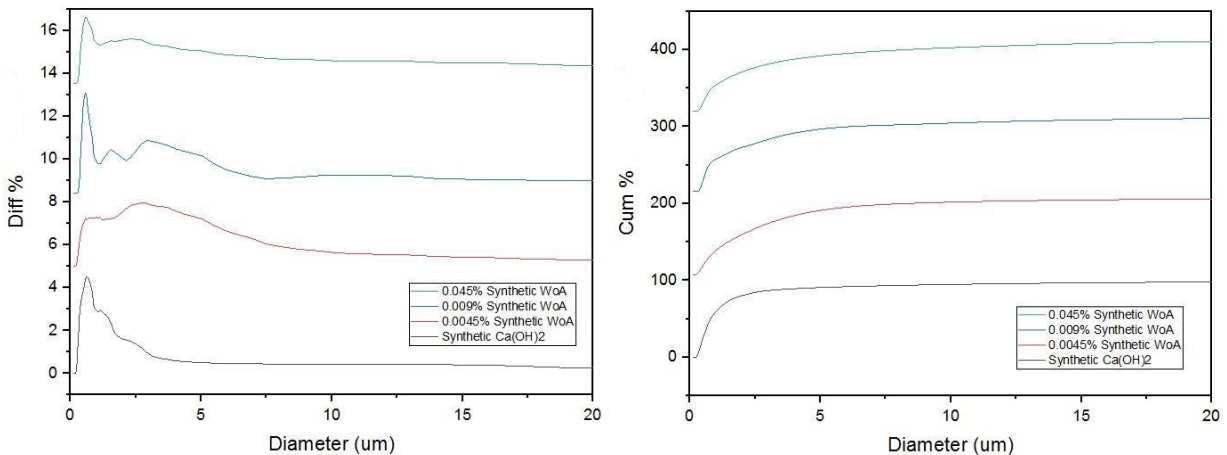
To estimate the difference between the size of particles in both cases, the size got determined on the bases of laser scattering and combined effect of laser-particle interaction. Secondly, it also provides info about different types of particles present inside mixer of different compounds. The phenomena help us to differentiate between different phase change and reactions. As we were concern about particle's size from day one, because it is directly connected to reactivity of particles. The percentage tendency of shifting gives us idea about type of coating on individual or on agglomerated group. They change in particle due to formation of calcium carbonate or calcium silicate can also get picked by comparing with pure samples in both cases.

In case of nano-particles, the size extends with the coating silica. But the formation of calcium carbonate or silicate also get changed. In the presence of ammonia, we can clearly observe the difference between different coating and size changes. The greater amount of silica coatings shows more stability as compared to less one. At central point we can also observe difference between both samples of 10uM values for the presence and absence of catalytic ammonia.



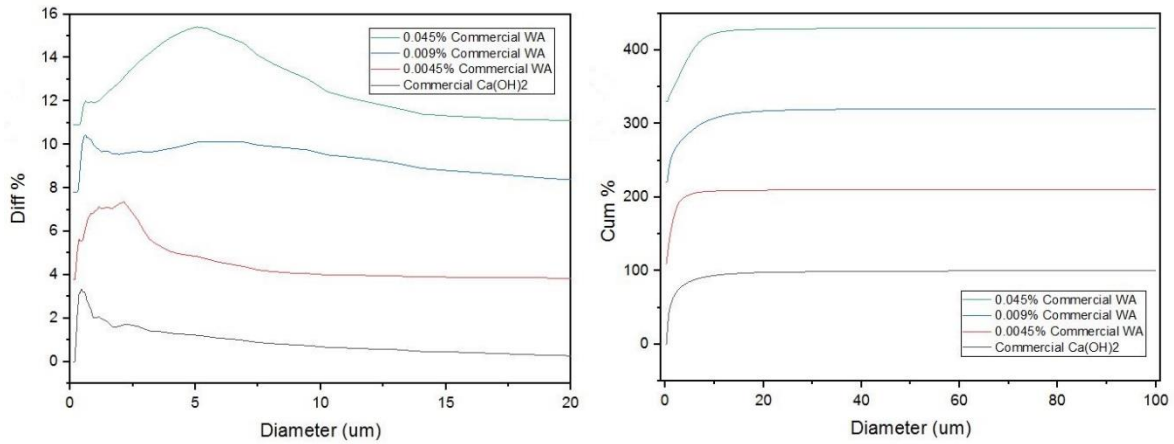
(Figure 4.14 : Laser Particle Size Analyses for synthetic coating in the presence of ammonia )

In the absence of ammonia, the stability decreases as the quality of coating reduced in the absence of catalyst. That is why, calcium carbonate got observed even in 10uM samples. A small peat of Calcium silicate can also be found in same sample. But in both cases, we got more stability in higher coatings. More amount of silica availability can give better covering to this agglomerated bunches.



(Figure 4.15 : Laser Particle Analysis of Synthetic coating Samples in the absence of ammonia)

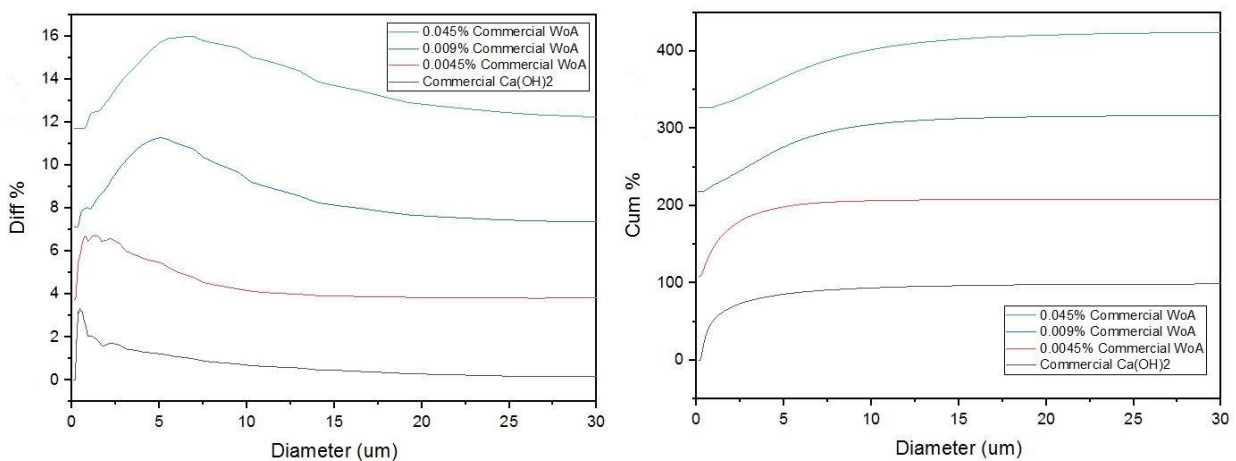
In case of commercial calcium hydroxide samples, the stability in normal atmosphere was already observed. In case LPSA results, the only info about increasing amount of coated silica gets cleared as minimum side reactions occurred. The only difference that got visible is due effect of catalyst. This factor can change the quality of coating, which gets prominent in case of catalytic presence.



(Figure 4.16 : Laser Particle size Analyses for Commercial Samples in the presence of Ammonia)

In case of ammonia presence, we can see clear coating in 5uM case. In other two samples a big hump shows remaining amount of silica presence. This extra silica forms its own particles on separate bases. In largest amount presence, the difference between both types gets hidden because silica is more than enough to get coated on individual and non-agglomerated particles.

In the absence of ammonia case, the quality of coating gets reduced, and we can find more stretched graph instead of a little sharp one that was observed in case of ammonia presence. Here in the same amount silica, we can see size increase in case of 5uM sample as previous one. But due to low level of coating, we get more stretched graph for 10uM and 50uM samples. The non-coated silica arranged itself independently at different sized particles.

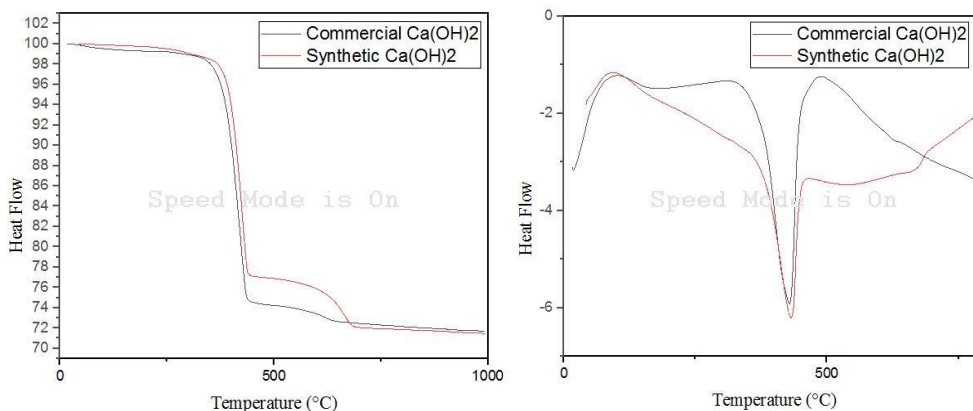


(Figure 4.17 : Laser Particle size analyses of commercial calcium hydroxide samples coated in the absence of ammonia)

## 4.7. TGA- DSC

Thermal decomposition of mixture of different compounds (calcium hydroxide, calcium carbonate or calcium silicate) can get differentiated by Thermal Gravimetric Analyzer. On basis of temperature increment at some specific rate and ramping conditions, we can obtain specific breakdown of different material depends upon their crystal structure. The phenomenon to study presence, composition, or decomposition with heat flow through composite as function of temperature is known as differential scanning calorimetry DSC. It includes information of Endo-Exo thermal reaction while decomposition or formation of new crystals. The area under the curve reflects amount of heat enthalpy. As it is a function of temperature, so it get varied with the change in heating rates of temperature. The increment in heating rate provides less time for heating at some instantaneous temperature and that modifies heat of enthalpy.

Let's start with comparison of both type of calcium hydroxide presented at same heating rates. We observe calcium hydroxide to calcium oxide conversion in range of 410-425°C. In case of larger size particles, there was not much carbonate formation in pure sample for their high stability. That is why it didn't reflect any greater weight loss after that first hydroxide to oxide conversion. In case of nanoparticles, it shows a significant amount of calcium carbonate presence around 8-10 %. The conversion of calcium carbonate to calcium carbonate is done around 650°C. [52, 53]



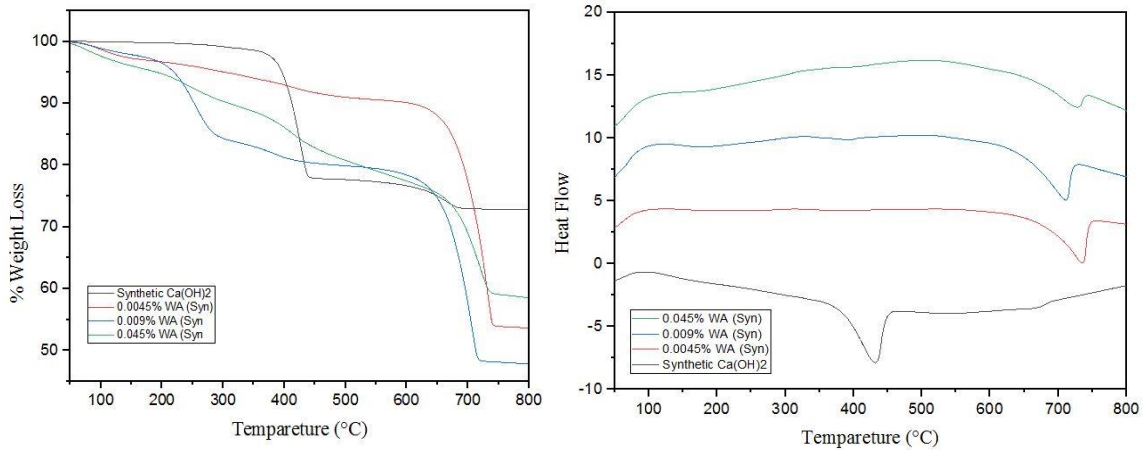
(Figure 4.18 : TGA-DSC comparison of Pure  $\text{Ca}(\text{OH})_2$  samples (Left) Thermal Gravimetric Analysis (Right) Differential Scanning Calorimetry)

The DSC results also depict Endo-Exo Thermic reaction of both conversions in respective temperature ranges. The depth of larger peak in case larger particles shows greater area under the curve and that results in higher heat of enthalpy. The conversion of calcium hydroxide to oxide only represents exothermic reaction in DSC results. At high temperature, around 950 a complete



conversion of all possible hydroxide, carbonate or even nitrate (In case if we use calcium nitrate in synthesis) got converted to calcium oxide and it stays stable for great scale temperature ranges.

Now let's differentiate the difference occur for thermochemical properties in both types of samples after coating reaction in presence and absence of ammonia.

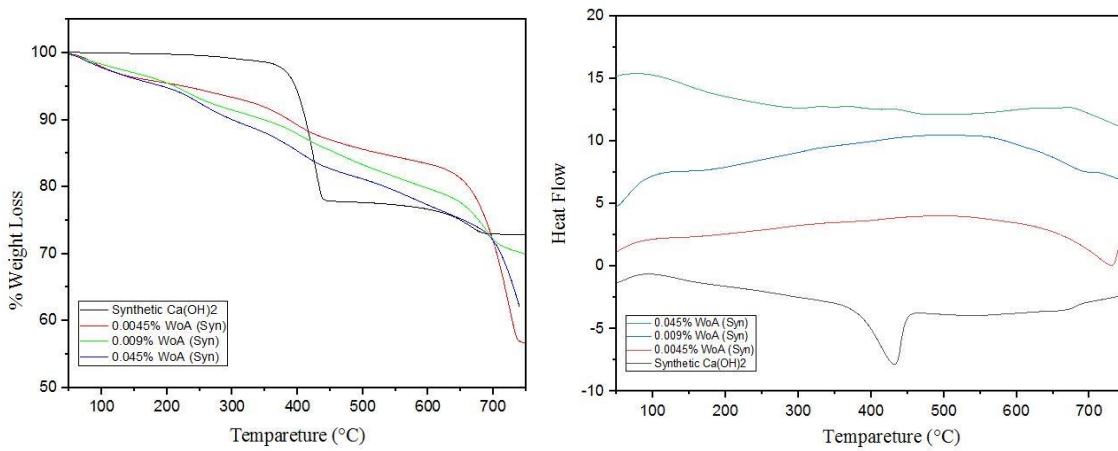


(Figure 4.19 : TGA-DSC Results of synthetic coated samples in the presence of Ammonia  
(Left) Thermal Gravimetric Analysis (Right) Differential Scanning Colometry)

A clear observation noticed that the decrease in calcium hydroxide as the weight drop is reduced around 425°C. On the other hand, weight drop around 730 -750°C clearly shows the conversion of calcium hydroxide to calcium carbonate. Its already found from previous results that calcium carbonate was present in pure samples. It was noticed clearly that most of the weight loss in calcium carbonate range for the lowest silica coated value. As with the increase in the silica value up to ten times then particles show more stability and less carbonate formation. This refers enough even extra amount of silica availability. This excessive silica can cover agglomerated nano-particles easily. The central value exhibit a little different behavior as compared to upper and lower values. The difference is cleared from start where in between range of 250-300°C. [54] The weight loss of ethyl groups of TEOS. On losing these groups early, the remaining silica plays a different role in the crystal formation of calcium carbonate. The difference between calcite, aragonite and vaterite clearly got depicted in the range of 700-750 °C. [55]

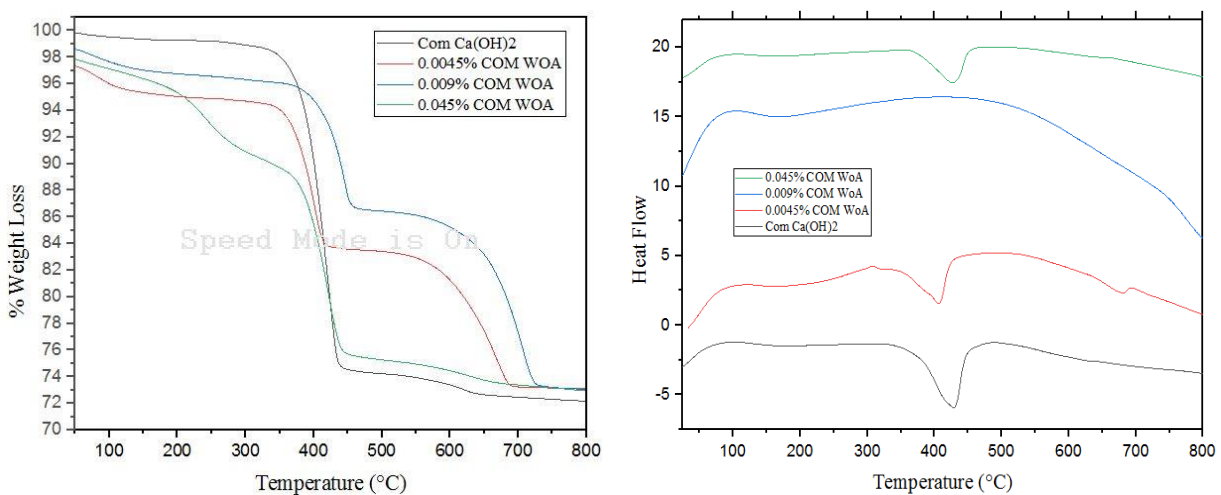
The DSC curves clearly shows the difference of silica coating has changed. At less silica, we have gained 65% of original heat of enthalpy. As we have increased silica quantity in other two samples, that results in decrease of heat of enthalpy for these composites. The difference in temperature ranges of first two samples. But for the highest value, the peak got shifted towards

right side. This represents heavy amount of silica. That almost has covered all the agglomerated calcium hydroxide.



(Figure 4.20 : Synthetic  $\text{Ca}(\text{OH})_2$  and its coated samples in the absence of Ammonia (Left) Thermal Gravimetric Analysis (Right) Differential Scanning Colometry)

Now let's see the coating on micro-sized particles and their intend towards forming other compounds like calcium carbonate or calcium silicate. From figure 4.14 we can easily conclude that there is very less reactivity of calcium hydroxide micro-sized particles with air to form calcium carbonate. So, it shows negligible amount of calcium carbonate present in commercial samples before using for coating reaction. Now let's move to figure 4.17, where we commercial sample coated in the absence of ammonia.

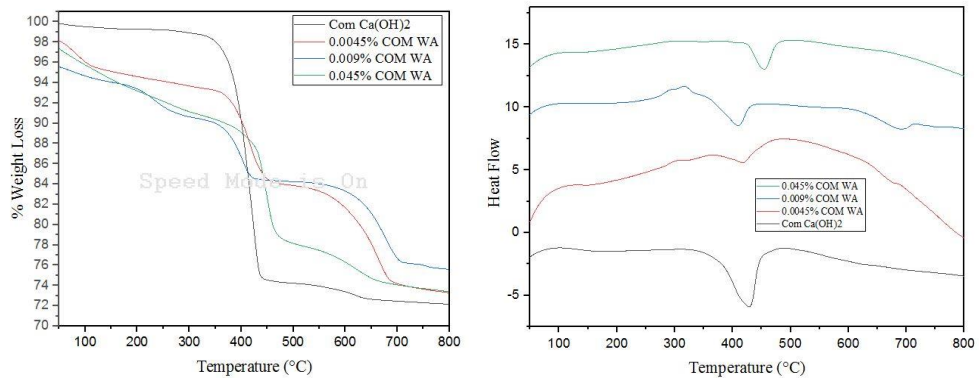


(Figure 4.21 : TGA-DSC results of calcium hydroxide commercial samples (Left) Thermal Gravimetric Analysis (Right) Differential Scanning Colometry (DSC))

The first difference is the clearly shown by stability of greater sized particles as compared to nanoparticles. The more weight loss around 425°C gives more presence of calcium hydroxide. Then before discussion about 10uM sample from other two extreme values, a clear conclusion can get obtained about of size of these particles and the comparative TEOS amount coated. Now as the size is in micro range now so can see that 5uM, the amount of silica was not enough. So, it gets converted into calcium silicate after reacting with silicate.<sup>[56]</sup> The presence of small amount of calcium carbonate was already present in pure sample. After getting maximum reaction of silica with calcium hydroxide, the rest of the broken calcium hydroxide gets converted into calcium carbonate. Both calcium silicate and calcium carbonate shows weight loss after 650°C. The combined weight loss gives a less sharp slop as compared with nanoparticles case. Now in case of 50uM, we have extra amount of TEOS available. The first thing shows initial weight loss around 250 for broken ethyl groups of TEOS. In next phase change, most of the weight loss around 425°C, which can easily describe the amount of calcium hydroxide preserved inside silica. This not only stop the external reaction with carbon dioxide to prevent from calcium carbonate formation, but the silica also stay non-reactive after its formation.

So, there is only one last conversion of calcium hydroxide to calcium oxide is remaining and then both silica and calcium oxide stays stable, and excess of silica also stop calcium carbonate formation during coating reaction. The central term of 10uM, shows an intermediate behavior. Initially a little weight loss shown by TEOS but rest of the TEOS and silica tried to cover whole sample. But as the temperature increase the broken water molecules leave the sample. But both conversions didn't show sharp changes. A sharp change can get observed on reduction of heating rate but in comparison of other samples, these results show some of the coating effects that were not enough really to prevent sample from formation of carbonation. Secondly, the incomplete weight loss of TEOS in this case didn't show clear formation of either calcium silicate or the effect of non-reactive silica presence also gets reduced because of less amount used for TEOS.

Now let's see the effect of ammonia catalyst that how it effects the conversion and TEOS weight loss for ethyl groups before any sample conversion. Ammonia also plays a vital role in improvement of coating pure silica to prevent further side reactions. The lowest 5uM value shows a similar result like the previous one to give less amount of silica present for coating. However, the 10uM sample the coating gets enhanced and we can see clear difference between TEOS, calcium hydroxide and calcium carbonate/silicate. But in 50uM, we can clearly see that excessive silica presence reduced further reaction for calcium silicate or carbonate.

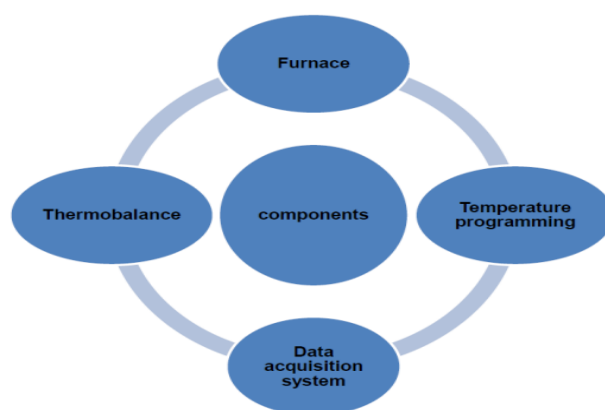


(Figure 4.22 : Coating results of calcium hydroxide in the presence of ammonia (Left) Thermal Gravimetric Analysis (Right) Differential Scanning Calorimetry)

### 5.1 FUTURE RECOMMENDATIONS

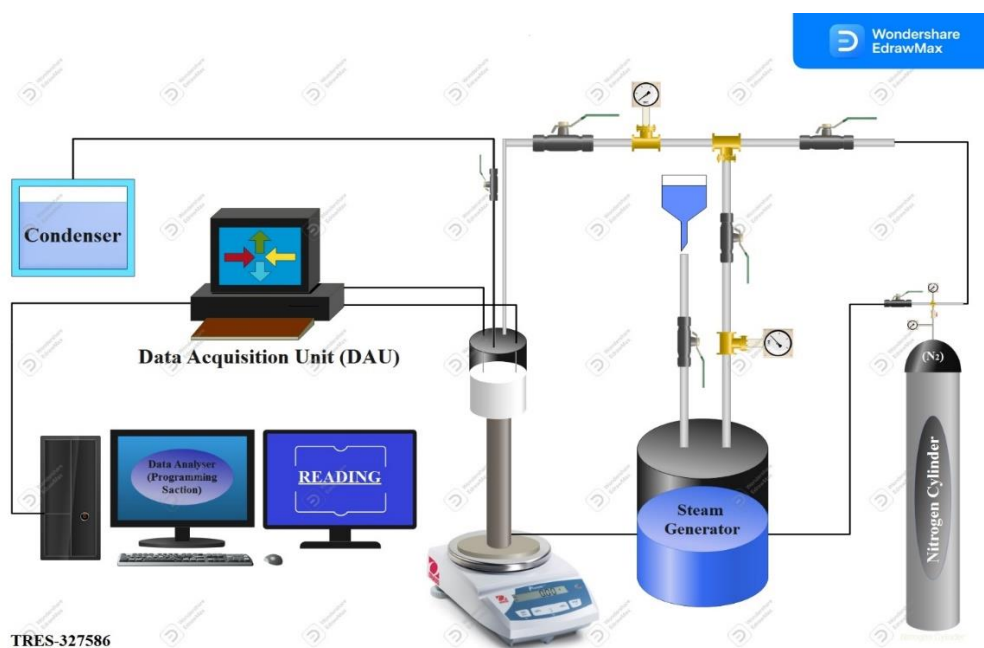
Until now we have seen properties of material and its ability to store specific amounts of energy. But in practical view or testing in recycling our samples and checking its viability for multiple runs, we were unable as we can't add water vapors in our locked TGA-DSC 650 version. The decomposed water vapors gets removed with the help of nitrogen flow to form an inert atmosphere. After that we can't pull them back while condensation process.

The major components can get divided in four main steps or requirements for complete recycling. The first step is a requirement of a close furnace, which should include inert atmosphere availability for avoiding any additional reaction with elements present in normal atmosphere. The thermostat should have at least 200°C above then maximum temperature required for the breakdown of given samples. Secondly, the furnace design will include the addition of decomposed components set-up for recycling. In next step, we require a temperature programing. Normally we use thermocouples to find instantaneous temperature of samples (Material). So, programming about temperature scale through automation and signals in form of voltage can get converted into given set-up ranges. The one scale shift adjustment helps us to find the change in temperature with respective value of one scale shift. In next step, we require a data acquisition unit that can record, save, and analyze the received data. In this section usually programming gets instructions about plotting graphs, finding slops, finding derivatives (By finding area under the curve), and analyses inside different ranges about temperature from X-axis. In last section, we must attach a separate set-up to notice weight changes in both cases while decomposition or recombination. This section gets related to weight loss and checking efficiency of specific sample for recycling multiple times. <sup>[57]</sup>



(Figure 5.1 : Major components for recycling of Thermally Decomposed Materials )

To resolve this issue, we have managed to build a separate set-up for verifying recycling ability of our samples in same inert atmospheric conditions. Initially we chose a high-quality steel cylinder to make a chamber for our sample. Then we design it upper and lower lids to incorporate Thermocouples and steam in & out from upper side and nitrogen purging from bottom lid. We have also connected another nitrogen connection with incoming steam to make inner atmosphere perfectly inert.



(Figure 5.2 : Practical set-up formed for checking recycling ability of desired samples)

The thermocouples are directly connected with Data Acquisition Unit (DAU) which can receive updated temperature reading manually and we can record it for further analysis. On the bottom of reactor, we have placed a weight balance to notice weight changes manually. In case of long reactions, we can feel it difficult to take continuous reading. To resolve this issue, we attached a condenser at the end of the pipe of outgoing steam. By finding weight gained on that side, we can see the manual change occurred inside reactor. We can attach a designed set-up based on Arduino device to save instantaneous results as well as continuous analyses.

After finding these practical results, we can compare them with our one time run sample in TGA and confirm the ability to recycle our samples on given conditions. Secondly it can help us to prepared different material (e.g., Nano-Particles of calcium hydroxide) to avoid side reactions.

## 5.2 CONCLUSION

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 behavior  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2/\text{SiO}_2$  composite have been synthesized successfully via sol gel method. On larger side particles, we didn't face issues of agglomeration. The structural analysis was confirmed by using XRD and morphological analysis indicated the attachment of silica nanoparticles on the surface of  $\text{Ca}(\text{OH})_2$ .  $\text{Ca}(\text{OH})_2/\text{SiO}_2$  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  $\text{Ca}(\text{OH})_2$  confirmed the bonding with extra  $\text{CO}_3$  bond. The band in range of  $791\text{ cm}^{-1}$  confirmed the presence of Si- O-Si in composite sample while EDX analysis was used to determine the composition of the samples and presence of different elements which are nearly equal to the inputs in practical reactions. Thermogravimetric analyses were used to determine the thermal behavior of pure  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2/\text{SiO}_2$  to confirm the decomposition. TGA analysis showed decomposition of  $\text{Ca}(\text{OH})_2$  into  $\text{CaO}$ . As we decrease the concentration of silica nanoparticles, change in mass decreases and which effect the decomposition of the material. But after a certain limit it allows agglomeration in nanoparticles and from value of 0.009%, we observe a different behavior was shown by both sized cases. 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 calculate concentration of silica coated and its impact on decomposition.
- To change the concentration of catalyst to find more closer results for catalytical activity.
- As this 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 materials which are having thermal conductivity higher.
- The kinetics study of de – & rehydration of composite for thermochemical energystorage.

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