

**Experimental and Modelling  
Investigation of CO<sub>2</sub> Adsorption on  
Silicalite-1**



**By**

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# **Experimental and Modelling Investigation of CO<sub>2</sub> Adsorption on Silicalite-1**



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**This thesis is submitted in order to fulfill the requirements for  
degree in**

**MS Chemical Engineering**

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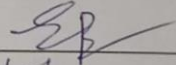
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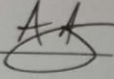
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## **Dedication**

By the mercy of the All-Powerful Allah, the Most Generous, the Most Merciful. This work is dedicated to my parents, who have consistently provided me with advice and support. To my Supervisor who taught me new things, gave me advice and encouragement, and motivated me to finish my work. And to all of the people I worked with and had good times with.

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## **List of Abbreviations**

ICDD: International Centre for Diffraction Data

MFI: Mean filling index

SEM: Scanning electron microscope

TGA: Thermogravimetric analysis

FTIR: Forrier transform infrared spectroscopy

BET: Brunauer-Emmett-Teller

TEA: Triethanol amine

FAU: Faujasite

TPOAH: Tripropyl ammonium hydroxide

TEOS: Tetra Ethyle orthosilicate

EDAX: Energy dispersive X-Ray analysis

## Abstract

CO<sub>2</sub> is present as an impurity in natural gas, flue gas, syngas, biogas and several other gas streams emitting from industrial processes. To improve the quality of natural gas, syngas, biogas, and to mitigate the greenhouse effect of CO<sub>2</sub> on the environment, the removal of CO<sub>2</sub> from such gas streams is of paramount importance. Crystalline microporous materials are promising for the adsorption of CO<sub>2</sub> owing to their high surface area and tuneable pore size. So it has its uses in many fields in chemical industry, For example, gas separation, petrochemical refining, and catalytic cracking all employ the highly porous zeolite material known as silicalite-1 as an adsorbent or catalyst. The collection and storage of carbon dioxide (CO<sub>2</sub>), a greenhouse gas that significantly contributes to global climate change, is one possible use for silicalite-1. A key tactic for lowering greenhouse gas emissions and limiting the consequences of climate change is CO<sub>2</sub> collection and storage. In this work we prepared silicalite-1 material and it is modified by the amine impregnation method. Advance characterization techniques XRD, SEM, BET, FTIR and TGA are used to examine the silicalite-1 and its successful amine modification. The experimental effort comprised measuring the CO<sub>2</sub> absorption on silicalite-1 using a high-pressure adsorption Analyzer. The device comprises of a silicalite-1-filled stainless steel cylinder that is connected to a pressure transducer and a gas supply. CO<sub>2</sub> is introduced into the cylinder using the gas supply at a specified pressure and temperature. Prior to and following the addition of CO<sub>2</sub>, the pressure within the cylinder is measured by the pressure transducer, from which the amount of CO<sub>2</sub> absorbed by silicalite-1 can be estimated. The trials were conducted at various pressures (0–15 bar) and temperatures (100°C). The quantity of CO<sub>2</sub> adsorbed as a function of pressure was used to depict the adsorption isotherms. According to the experimental findings, temperature and pressure have a significant impact on the rate of CO<sub>2</sub> adsorption on silicalite-1. It was discovered that silicalite-1's CO<sub>2</sub> adsorption capability increased with pressure and decreased with temperature. The adsorption isotherm parameters were used to model the breakthrough curves of the CO<sub>2</sub> adsorption. The

breakthrough curves also suggest a decrease in the CO<sub>2</sub> uptake (mmol/g) of the aminated silicalite-1 zeolite.



# Chapter 1

## Introduction

### 1.1 Background:

Nowadays, a large amount of CO<sub>2</sub> is being released into the atmosphere and its concentration in the atmosphere has crossed the value of 400 ppm[1]; since the industrial revolution occurred concentration of CO<sub>2</sub> is enhanced by approximately 120 ppm[2]. This happened due to the excessive use of fossil fuels[3]; the primary source of energy for industry and transport but due to its depletion and harmful effect on the environment, it is necessary to move towards green energy sources. Still, 80% of energy requirements are being met through fossil fuels causing global warming. Global warming has become a serious global issue for the survival of humanity on the planet[4]. The world is facing climate change due to calamities (floods, drought, famines, and heat waves). Renewable energy sources have been identified as an alternative source of fossil fuel [5]for industrial and transport purposes.

Considerable efforts have been made in the field of research in carbon capture processes. Nowadays, CO<sub>2</sub> separation is being done through amine-based liquid phase absorbent material at a commercial scale worldwide[6]. Despite its advantages, it has certain disadvantages like high vapor pressure, a corrosive environment, and high energy demand for regeneration. So its development at a commercial scale is a costly process[7]. Solid adsorbent material for CO<sub>2</sub> capture has the attention of researchers in recent decades to minimize the limitation of amine-based material, because it has the potential to retain some advantages of liquid phase amine such as elimination of scrubbing, chemical stability at high temperatures and pressure, good pore size and volume, and less costly and high adsorption capacity[8].

Many solid materials are used for CO<sub>2</sub> adsorption in which Silica adsorbent is one of the mesoporous materials used for CO<sub>2</sub> capturing. The CO<sub>2</sub> adsorption capacity of PEI (70%)/SiO<sub>2</sub> is 1.88 mmol/g at 1.5 bar and 25 °C, but silica also shows low stability when exposed to boiling water and sMEAm[8]. MOFs have a high surface area and volume and

show high selectivity for CO<sub>2</sub> at lower temperatures[9]. The limitation of MOFs is that their synthesis process is costly, complex, and harmed by water vapor adsorption and shows degradation on thermal treatment[10]. However, in recent years, researchers tried to develop a better process to overcome the above-discussed problems and develop a better adsorption process. So, zeolite got the attention because it has high thermal and chemical stability. Zeolites are crystalline inorganic materials that contain hydrated alumino-silicates with alkali and alkaline earth metal cations with regular three-dimensional network structures which have the capability to adsorb the material. Zeolites occur naturally in nature but are synthesized to alter their 3-dimensional shape and size to get better results and are considered as the most important class of porous compounds.

## **1.2 Zeolites:**

Zeolites are a class of minerals that can be either naturally occurring or man-made and have a distinct microporous structure[11]. They consist of a three-dimensional silica and alumina tetrahedral network with precisely sized and shaped pores and channels. Zeolites are advantageous in a variety of applications, including catalysis, ion exchange, gas separation, and water purification, thanks to these characteristics. They are efficient filters for eliminating pollutants from liquids and gases because they can selectively adsorb and desorb molecules based on their size and polarity. Detergents, petrochemicals, and other industrial goods are also made with zeolites [12].

### **1.2.1 Types of zeolite**

#### **1.2.2 A-Type zeolite**

Widely used synthetic zeolite Zeolite A features an LTA (Linde Type A) framework architecture and a sodalite-like structure. It features pores that are about 0.4 nm in size and a Si/Al ratio of 1. Zeolite A is frequently employed in the petrochemical sector as a catalyst and as a detergent builder. In laundry detergents, A-type zeolite is frequently employed as a builder. It can bond to the calcium and magnesium ions found in hard water, keeping them from obstructing the cleaning procedure.[13] This increases the detergent's efficacy while lowering the amount of water required for [14]. Due to its high pore size, A-type zeolite is effective as an adsorbent for gas separation. It can be used to separate gases like nitrogen and oxygen because it can selectively adsorb molecules of

particular sizes. Different chemical reactions can benefit from the use of a-type zeolite as a catalyst. Its strong thermal stability and [15]

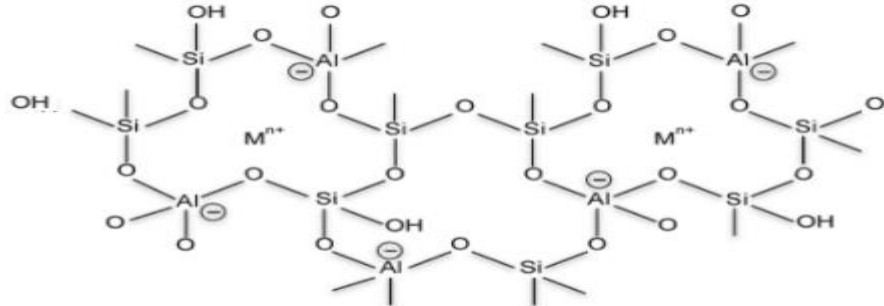


Figure 1 Zeolite A

### 1.2.2 Zeolite X

The formation of tetrahedral units of aluminum, silicon, and oxygen results in a three-dimensional network of interconnected cages and channels that makes up the structure of zeolite-X[16]. The substitution of other cations, such as sodium, potassium, and calcium, into the zeolite-X structure, can change its properties. Another man-made zeolite, Zeolite X, has a framework architecture known as FAU (Faujasite). Its and its pores are about 0.7 nm in size. Zeolite X is employed in detergent formulations as well as gas separation, adsorption, and catalytic applications[17].

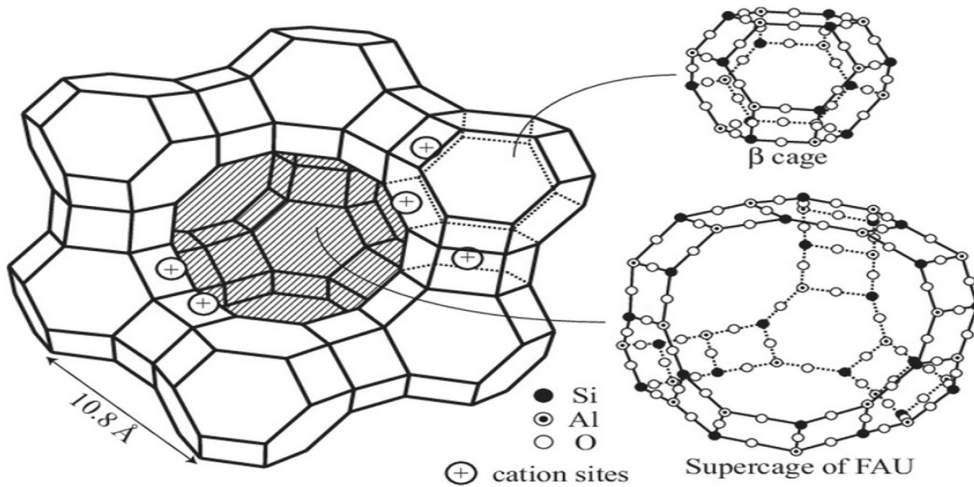


Figure 2 Zeolite X structure

### 1.2.3 Y zeolite:

Similar to Zeolite X, Zeolite Y is a synthetic zeolite with an FAU (Faujasite) framework architecture. It has a pore size of about 0.8 nm and a Si/Al ratio of 2.4–3.4. Zeolite Y is employed as an adsorbent in gas separation and as a catalyst in the refining of petroleum. A crystalline aluminosilicate substance with interconnected channels and channels in three dimensions is known as Y-type zeolite. It is a faujasite zeolite type and has a higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio than other zeolites, which makes it more durable and resistant to chemical and heat deterioration[18]. The SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra that make up the Y-type zeolite's crystal structure are connected by shared oxygen atoms. The framework has a homogeneous 0.74 nm-diameter pore size and creates a three-dimensional network of channels and cavities. big cavities connect the channels, which have three directions and a three-dimensional layout[18]. These cavities have a high surface area and permit the absorption of big molecules. There are many uses for, including as a catalyst in the manufacture of chemicals and polymers as well as chemicals and oil refining. In addition, it can be employed as an adsorbent to separate molecules according to their size and shape and to remove contaminants from gases and liquids. It is a crucial material for industrial processes because of its great stability and selectivity[19].

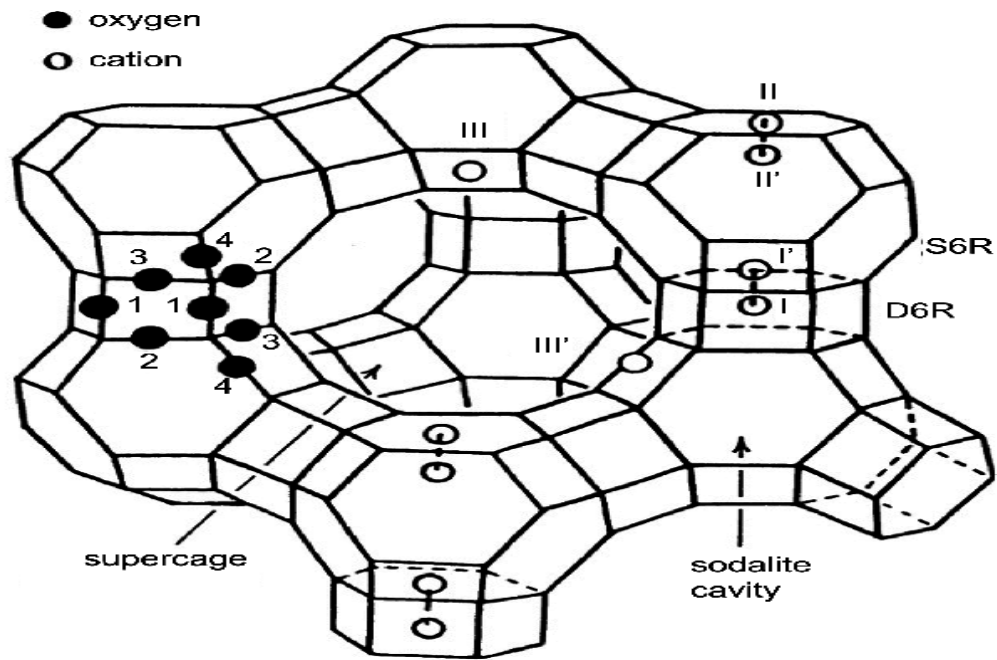


Figure 3 Y-Type Zeolite

### 1.2.4 ZSM-5

ZSM-5 is a catalyst used in a number of reactions, including isomerization and cracking, as well as in adsorption applications. ZSM-5 zeolite is frequently employed as a catalyst in the manufacturing of high-octane gasoline and other valuable compounds, such as aromatics and olefins, in the petrochemical sector. Methanol-to-olefins (MTO) process[20]. This method transforms methanol to light olefins like ethylene and propylene by using ZSM-5 zeolite as a catalyst. These olefins play a crucial role in the creation of numerous chemicals and polymers. ZSM-5 zeolite has been investigated as an efficient adsorbent for the removal of contaminants, such as heavy metals and organic compounds, from wastewater and other environmental matrices[21]. enables it to selectively catalyze reactions involving molecules of particular shapes and sizes. In the synthesis of numerous compounds, including para-xylene and styrene, this characteristic has been used[22]. There many uses for Y-type zeolite are, including as a catalyst in the manufacture of chemicals and polymers as well as chemicals and oil refining[23]. In addition, it can be employed as an adsorbent to separate molecules according to their size and shape and to remove contaminants from gases and liquids. It is a crucial material for industrial processes because of its great stability and selectivity[24].

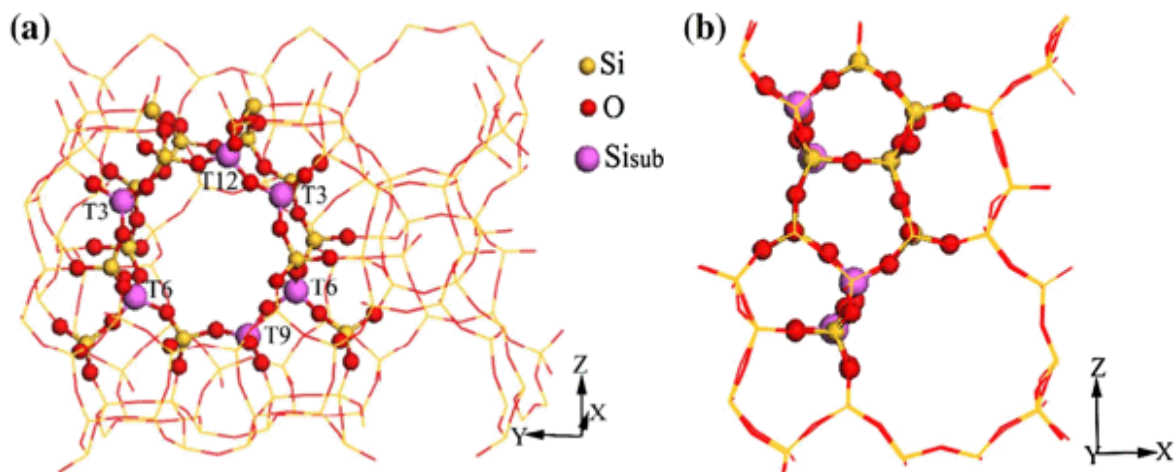


Figure 4 ZSM-5 structure

### 1.2.5 Zeolite beta

A synthetic zeolite known as beta zeolite has a framework structure known as BEA (Beta). It features a Si/Al ratio of 5-50 with pores that are between 0.6 and 1.0 nm in

size[25]. In several processes, including cracking, isomerization, and alkylation, as well as in adsorption and separation applications, beta zeolite is used as a catalyst[26].

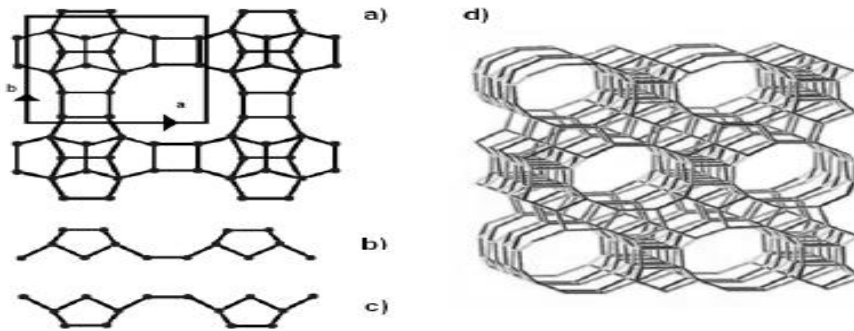


Figure 5 Beta-type zeolite

### 1.2.6 Mordenite

Natural zeolites called mordenite have a framework topology known as MOR (mordenite). Its Si/Al ratio is approximately 10–30, and its pore size is about 0.7 nm[27]. In addition to being utilized in adsorption and separation processes, mordenite is a catalyst for a number of reactions including cracking and isomerization[28].

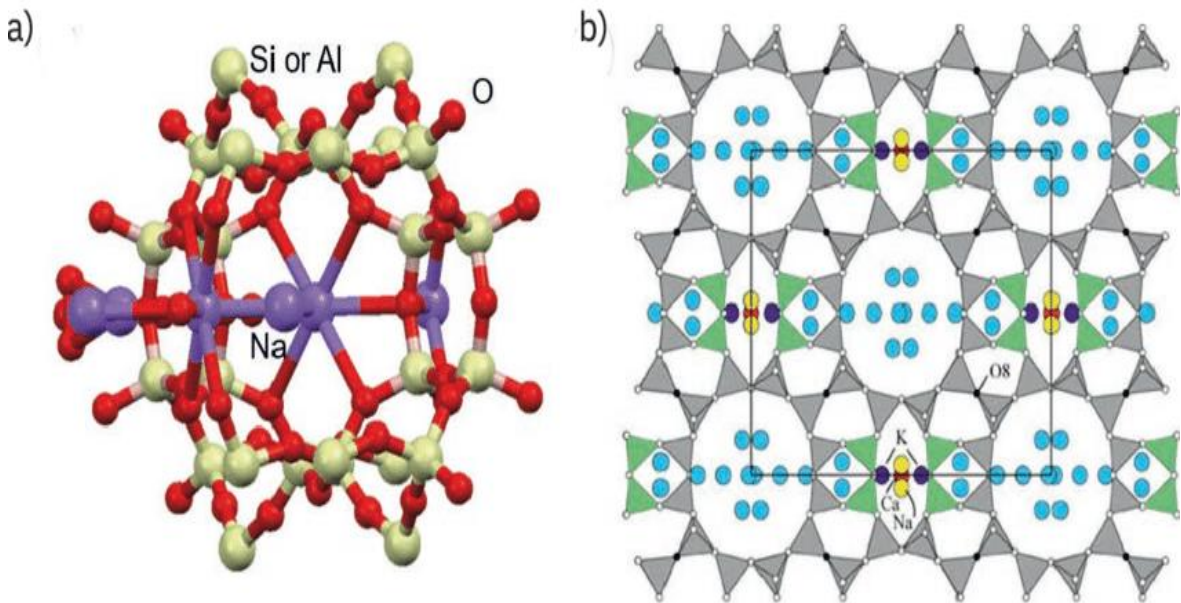


Figure 6 Mordenite Structure

### 1.2.7 Chabazite

A naturally occurring zeolite known as chabazite has a framework topology known as CHA (chabazite). It features pores that are between 0.4 and 0.6 nm in size and a Si/Al ratio of about 3 to 5[29]. In numerous processes, including hydrocracking and isomerization, as well as in adsorption and separation applications, chabazite serves as a catalyst[30].

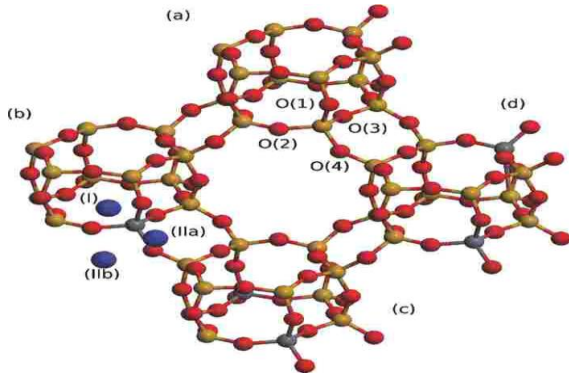


Figure 7: Chabazite

### 1.2.8 Ferrierite

A naturally occurring zeolite known as ferrierite has a framework topology known as FER (ferrierite). It features pores that are between 0.4 and 0.7 nm in size and a Si/Al ratio of about 3 to 8[31]. As a catalyst, ferrierite is employed in a number of processes.

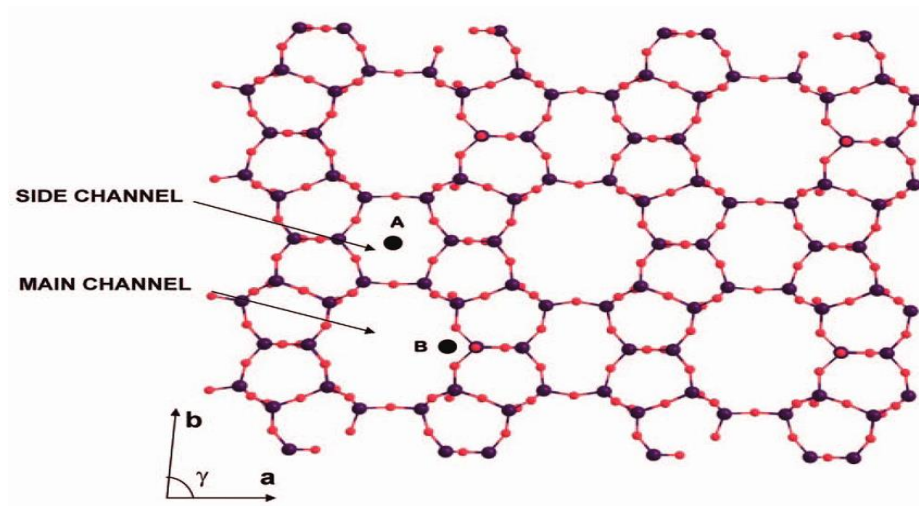


Figure 8: Ferrite unit cell

### 1.2.9 Silicalite-1

A very pure kind of zeolite made of silicon and oxygen is known as silicalite-1. It is a crystalline substance with a special pore structure that makes it practical for several processes, such as gas separation, catalysis, and molecular sieving[32]. which is smaller than the pore size of ZSM-5 zeolite. High thermal and chemical stability, one of silicalite-1's key characteristics, makes it suitable for use in challenging industrial settings. It is a favoured option for catalytic applications due to its great resistance to fouling and deactivation[33]. Silicalite-1 has been used in the pharmaceutical business to purify pharmaceuticals and other chemical substances, as well as in the petrochemical industry to convert methanol to olefins[34].

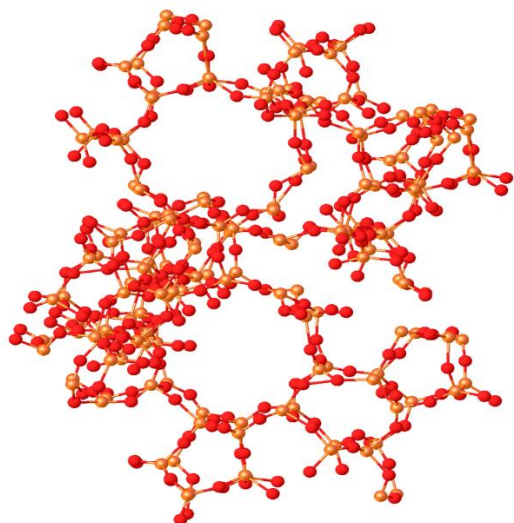


Figure 9 Silicalite (red dot indicating oxygen and orange dot indicating silicon)

### 1.3 CO<sub>2</sub> adsorption mechanism in Zeolite:

The complex mechanism involved in the adsorption of CO<sub>2</sub> on zeolites depends on a number of variables, including the zeolite's pore size and surface chemistry, the CO<sub>2</sub> concentration and pressure, and the temperature[35]. The three stages of the adsorption process are diffusion of CO<sub>2</sub> into the zeolite pores, CO<sub>2</sub> adsorption on the zeolite surface, and CO<sub>2</sub> desorption from the zeolite[36].



#### **1.4 CO<sub>2</sub> diffusion into the pores of zeolite**

Diffusion of CO<sub>2</sub> into the zeolite pores is the initial step in the adsorption process. The rate and extent of diffusion are greatly influenced by the size of the zeolite pores[37]. While zeolites with smaller pores may restrict diffusion, those with larger pores will allow CO<sub>2</sub> molecules to diffuse into the structure more easily[38]. For instance, zeolites containing a lot of aluminum atoms may have a stronger affinity for CO<sub>2</sub>, which would make diffusion more effective[39].

#### **1.5 CO<sub>2</sub> Adsorption on Zeolite Surface**

The next step is CO<sub>2</sub> adsorption on the zeolite surface after CO<sub>2</sub> molecules have diffused into the zeolite pores. The zeolite framework, which contains silicon and aluminum atoms, and CO<sub>2</sub> molecules interact during this process[40]. Van der Waals forces and electrostatic interactions are the main driving forces for the adsorption of CO<sub>2</sub> on zeolites[41]. The amount of CO<sub>2</sub> present in the environment, the temperature, and the zeolite's surface chemistry can all affect these forces[42].

#### **1.6 Zeolite CO<sub>2</sub> absorption and desorption**

Desorption of CO<sub>2</sub> from the zeolite is the last step in the adsorption process. When the amount of CO<sub>2</sub> adsorbed on the surface of the zeolite is less than the amount in the surrounding atmosphere, this process can happen on its own[43]. The temperature can also have an impact on the desorption process, with higher temperatures typically resulting in faster desorption rates[44]. To overcome the adsorption energy between the CO<sub>2</sub> and zeolite surface, desorption may occasionally necessitate the application of external energy, such as heat[45].

In general, CO<sub>2</sub> adsorption on zeolites is a complicated process that is controlled by a number of variables. It is essential to comprehend the mechanics underlying this process in order to create CO<sub>2</sub> collection methods that are both more effective and efficient[46].

#### **1.7 Chemisorption Mechanism on amine functionalised zeolite:**

The CO<sub>2</sub> molecules and amine functional groups create chemical bonds as part of the chemisorption process that causes CO<sub>2</sub> to adhere to amine zeolites[47]. A class of solid adsorbent known as amine zeolites has amine functional groups (-NH<sub>2</sub>) bonded to the

zeolite structure[48]. When these amine groups interact with CO<sub>2</sub> molecules, carbamate species are created, which are then immobilized on the zeolite's surface[49]. The CO<sub>2</sub> molecules and amine functional groups create chemical bonds as part of the chemisorption process that causes CO<sub>2</sub> to adhere to amine zeolites[50]. A class of solid adsorbent known as amine zeolites has amine functional groups (-NH<sub>2</sub>) bonded to the zeolite structure. When these amine groups interact with CO<sub>2</sub> molecules, carbamate species are created, which are then immobilized on the zeolite's surface[51].

The following reaction can be used to explain the chemisorption of CO<sub>2</sub> on amine zeolites:

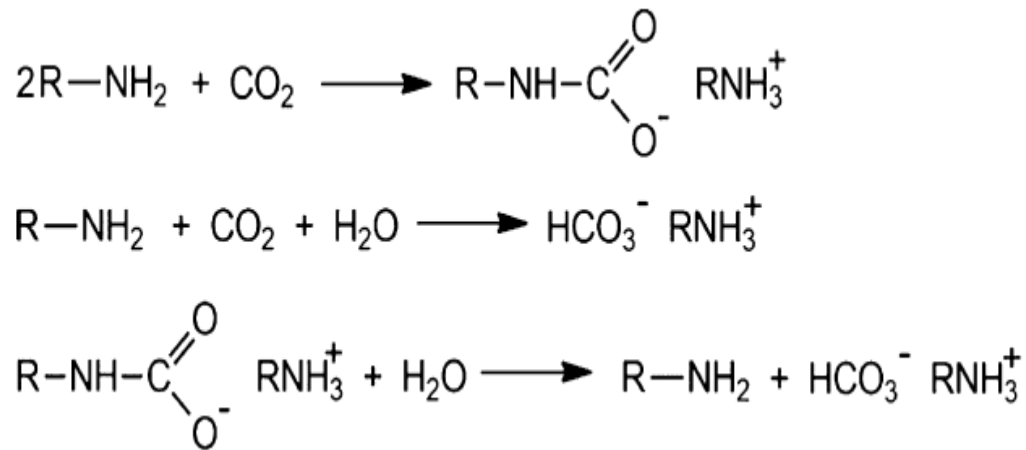


Figure 10 Reaction of CO<sub>2</sub> with amines

where R is the molecule of organic matter that is joined to the amine group. An amine-carbamate intermediate is created when the amine group works as a nucleophile and attacks the electrophilic carbon of the CO<sub>2</sub> molecule[52]. The stable carbamate species that results from subsequent reaction on this intermediate is highly adsorbed on the surface of the zeolite. The amine loading, the type of amine functional group, as well as the temperature and pressure conditions, all affect the chemisorption process. While the type of the amine functional group can affect the strength of the chemical bond formed with CO<sub>2</sub>, higher amine loadings can increase the number of active sites available for CO<sub>2</sub> chemisorption. Overall, the CO<sub>2</sub> removal process from industrial emissions is aided by the chemisorption mechanism of CO<sub>2</sub> adsorption on amine zeolites. A potential

material for carbon capture and storage applications, amine zeolites have good selectivity and capacity for CO<sub>2</sub> adsorption[53].

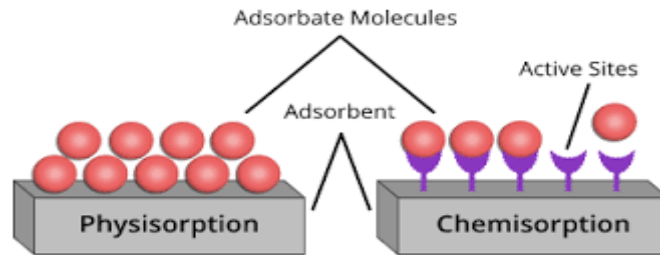


Figure 11 Physisorption and Chemisorption

### 1.8 Problem Statement:

The goal of this research is to investigate carbon dioxide (CO<sub>2</sub>) adsorption on silicalite-1, a zeolite material, using modeling and experimental methods. The objective is to gain a deeper understanding of the CO<sub>2</sub> adsorption mechanisms and behavior on silicalite-1 and to create a precise model that can forecast CO<sub>2</sub> adsorption capacity under various circumstances.

### 1.9 Research Objective:

1. to research CO<sub>2</sub>'s silicalite-1 adsorption behavior under various pressure, temperature, and concentration variations.
2. to calculate the CO<sub>2</sub> adsorption on silicalite-1's kinetic and thermodynamic characteristics.
3. to create a mathematical model that can correctly forecast the silicalite-1's ability to adsorb CO<sub>2</sub> under various circumstances.
4. to assess the model's correctness by comparing experimental results with predictions made using the model.
5. to investigate silicalite-1's possible use in carbon capture and storage procedures.
6. to advance knowledge of the CO<sub>2</sub> adsorption processes and its behavior on zeolite materials.

### 1.10 Scope of Study:

To investigate the possible application of this zeolite material in carbon capture and storage operations, the study on the experimental and modeling analysis of CO<sub>2</sub>

adsorption on silicalite-1 was conducted. A lot of research has been done on the microporous substance silicalite-1 for its use in adsorption, separation, and catalysis. In order to better understand the adsorption mechanisms and behavior of CO<sub>2</sub> on this substance, this study will concentrate on the adsorption behavior of CO<sub>2</sub> on silicalite-1 under various conditions. The goal of this work is to use both experimental and modeling methods to examine the CO<sub>2</sub> adsorption behavior on silicalite-1. In order to ascertain the CO<sub>2</sub> adsorption isotherms and kinetics on silicalite-1 under various conditions, including temperature, pressure, and concentration, experiments will be designed. A mathematical model that can precisely forecast the CO<sub>2</sub> adsorption capacity of silicalite-1 under various circumstances will be created using the experimental data. The silicalite-1 material's surface and structural characteristics will also be examined utilizing methods such as nitrogen adsorption-desorption tests, SEM, and XRD, BET surface area, TGA, FTIR, etc. These characterizations will shed light on the silicalite-1's surface area, pore size, and crystal structure as well as how these elements impact the behavior of the CO<sub>2</sub> adsorption process. The inquiry will also examine the impact of several elements, including surface area, pore size, and crystal structure, on the silicalite-1's CO<sub>2</sub> adsorption behavior. Using this knowledge can help create more effective and long-lasting carbon capture and storage systems as well as identify the ideal conditions for CO<sub>2</sub> adsorption on silicalite-1. The research will advance knowledge of the processes of CO<sub>2</sub> adsorption behavior on zeolite materials, specifically silicalite-1. The findings of this work may help to build carbon capture and storage methods that are more effective and long-lasting. The potential use of silicalite-1 in carbon capture and storage processes will be thoroughly discussed, along with the benefits and drawbacks of using it as a CO<sub>2</sub> adsorbent in comparison to other adsorbents currently in use for carbon capture and storage. The goal of this research is to investigate the CO<sub>2</sub> adsorption behavior on silicalite-1, create a mathematical model that can accurately predict CO<sub>2</sub> adsorption capacity, investigate the impact of various variables on CO<sub>2</sub> adsorption behavior, and discuss the potential use of silicalite-1 in carbon capture and storage procedures. The research will shed light on how CO<sub>2</sub> adsorbs on zeolite materials, notably silicalite-1, and how it behaves after adsorption. It may also help to design more effective and long-lasting carbon capture and storage methods.

## **1.11 Chapter Summary:**

This thesis consists of four Chapters and each chapter's summary is given below:

### **1.11.1 Chapter 1**

Chapter 1 is an introduction chapter includes includes the introduction to zeolite material and its types, Physisorption and chemisorption mechanism, Problem statement, objectives of the study and scope of study

### **1.11.2 Chapter 2**

Chapter 2 is literature review which includes the preparation methods for zeolite, types of amines used for the loading, methods used for amine loading, temperature, pressure, Si/Al ratio effect, Effect of physiochemical properties on CO<sub>2</sub> adsorption capacity of Zeolite.

### **1.11.3 Chapter 3**

Chapter 3 is materials method which includes materials description that has been used for the preparation of silicalite-1, process used in the amine loading, Characterization techniques used in this study, experimental technique used for CO<sub>2</sub> adsorption on zeolite sample.

### **1.11.4 Chapter 4**

Chapter 4 is result and discussion chapter that includes the result of different characterization techniques used in this thesis, the result of CO<sub>2</sub> adsorption on both silicalite-1 and amine functionalized silicalite-1

### **1.11.5 Chapter 5**

It includes the conclusion and the future recommendations.

# Chapter 2

## Literature review

### 2.1 Preparation methods for silicalite-1

Silicalite-1 is a type of zeolite with no aluminum content and is hydrophobic, is an effective catalyst for a variety of chemical processes, including the isomerization of organic molecules and the cracking of hydrocarbons[54]. Its homogeneous pore diameters and three-dimensional pore structure enable the selective adsorption and catalysis of particular compounds. The numerous ways to prepare silicalite-1 will be covered in this article[55].

#### 2.1.1 Hydrothermal synthesis

The most often used technique for creating silicalite-1 is called hydrothermal synthesis. In this procedure, a mixture of a template, such as tetrapropylammonium hydroxide (TPAOH), and a silica source, such as tetraethyl orthosilicate (TEOS), is heated in an autoclave under hydrothermal conditions[56]. For several days, the mixture is heated to a temperature of about 150°C and a pressure of about 15 atm. The silica and template react at this point to create the silicalite-1 structure. The template is subsequently eliminated using calcination or acid extraction[57].

#### 2.1.2 Sol-Gel Synthesis

Making silicalite-1 via the sol-gel technique is also very common. In this procedure, a template, such as TPAOH, is used to hydrolyze a silica precursor, such as TEOS, to create a sol. After adding a catalyst, such as ammonia, the sol is allowed to age at room temperature until it gels[58]. The template is then removed from the resultant gel while also forming the silicalite-1 structure[59].

#### 2.1.3 Template free Synthesis

Silicalite-1 is produced via a process called "template-free synthesis" rather than using a template. In this process, a mineralizer like sodium hydroxide is used to facilitate the hydrolysis of a silica source like TEOS[60]. The silicalite-1 structure is created by hydrothermally heating the mixture. This approach has the benefit of doing away with the

necessity for a template, which can be expensive and challenging to remove. Ionic liquid, which serves as both the solvent and the template, and a silica precursor, such as TEOS, make up the reaction mixture in ionothermal synthesis[61]. The silicalite-1 structure is created by hydrothermally heating the mixture. The advantage of this solution is that it makes use of a non-volatile template that is simple to recover and reuse.

#### **2.1.4 Microwave Synthesis**

A very recent technique for producing silicalite-1 is microwave synthesis. This technique uses microwaves to heat the reaction mixture, allowing for quicker reaction times and cooler temperatures. A template, such as TPAOH, and a silica precursor, such as TEOS, make up the reaction mixture[62]. To create the silicalite-1 structure, the mixture is heated while being exposed to microwave radiation. The benefit of using this approach over conventional hydrothermal synthesis techniques is that it is quicker and uses less energy[63].

## **2.2 Types of Amines used for amine modification**

Zeolites have a large surface area, are thermally stable, and have adjustable pore sizes, making them a popular choice for carbon dioxide (CO<sub>2</sub>) extraction. However, by altering their surface chemistry by adding amine functional groups, zeolites can be made more selective and effective at capturing CO<sub>2</sub>[64]. The alteration of zeolites for CO<sub>2</sub> capture can be done using a variety of amines, including primary, secondary, and tertiary amines. The simplest and most popular kind of amine for zeolite alteration is a primary amine[65]. They have only one amino (-NH<sub>2</sub>) group, and a silane coupling agent can covalently attach them to the surface of the zeolite. To boost the zeolite surface's amine functional group density and the material's ability for CO<sub>2</sub> adsorption, primary amines are frequently utilized[66]. However, primary amines frequently experience unfavorable side effects like oxidation and deamination, which can gradually reduce their efficacy. Another kind of amine that can be used to modify zeolite is a secondary amine. They can be covalently joined to the surface of the zeolite using a bifunctional coupling agent and have two amino (-NH<sub>2</sub>) groups. In comparison to primary amines, secondary amines exhibit a higher resistance to oxidation and deamination, making them more stable when used over an extended period of time. Two amino groups on the surface may cause


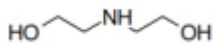

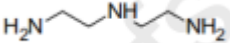
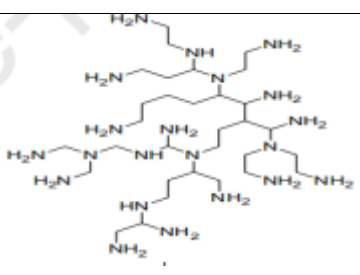
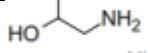
undesirable interactions with other molecules, though. The most stable and resistant to oxidation and deamination of the three types of amines, tertiary amines have three amino (-NH<sub>2</sub>) groups. Through the use of a trifunctional coupling agent, they can be covalently joined to the surface of the zeolite. Additionally, tertiary amines can benefit from selective CO<sub>2</sub> adsorption over other gases like nitrogen and methane. However, the increased functionalization can result in steric hindrance, which reduces their CO<sub>2</sub> adsorption capacity. In conclusion, all three types of amines—primary, secondary, and tertiary—can be utilized to modify zeolites for CO<sub>2</sub> capture. Primary amines have a high adsorption capacity, secondary amines have increased stability, and tertiary amines have selective CO<sub>2</sub> adsorption. The particular application and required performance characteristics will determine which sort of amine is best.

Table 1: Different Amines Used for loading on Zeolite

<b>Amine name</b>	<b>Molecular weight (g/mole)</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Reference</b>
Triethanolamine	149.188	1.133	[67]
Ethylenediamine	60.10	1.09	[68]
Triethylenetetramine	103.17	0.95	[69]
Triethylenepentamine	146.25	0.97	[70]
Piperazine	189.33	0.98	[71]
N-Methylepiperazine	86.14	1.03	[72]
N,N-Dimethylepiperazine	100.16	0.96	[73]
Cyclohexalamine	114.19	0.92	[74]
N-methyldiethanoleamine	119.16	0.81	[75]



Table 2: Amines with Structure

Amine type	Abbreviation	Structure
Monoethanolamine	MEA	
Diethanolamine	DEA	
Ethanediamine	EDA	
Diethylenetriamine	DETA	
Polyethyleneimine	PEI	
Iso propanol amine	IPA	

## 2.3 Methods used for Amine loadings

### 2.3.1 Impregnation method

To create an amine-functionalized CO<sub>2</sub> adsorbent, organic amine species are wet impregnated into the mesoporous support material's pores and on its surface. A greater amine-based loading can be obtained by using the impregnation approach, which can introduce huge amounts of amine species[76]. The impregnation-method adsorbent has been categorised as Class 1. Fig. 4 depicts the preparation process for 8 in detail. As shown in Table, there are numerous amine types from which to choose when creating amine-base solid adsorbents in order to produce an adsorbent with good performance. Due to their excellent stability and nitrogen content, PEI and TEPA are the most popular amine species[77]. The total pore volume of the porous material and the amine density define how much amine is put into the porous material. The support's pore volume and the amine density can be used to determine the theoretical loading amount of the organic amine[78]. The status of the prepared adsorbent makes it evident that amine species will

be attached to the support's outer surface if the amount of loaded amine exceeds the theoretical loading of the support. The typical form of a well manufactured solid amine adsorbent is a flowing powder. If an amine species is overloaded, it will agglomerate on the support's surface, adhering to tiny particles of porous material to create bigger agglomerated powders. Even the slurry mixture will become visible. At this moment, the adsorbent's accessible amine active sites are actually diminished. Adsorbents with the proper amine loading can therefore offer a lot of amine active sites that are available and increased amine utilisation for CO<sub>2</sub> collection. As a result, the distribution and loading of the amine group have a significant impact on the adsorption performance of the adsorbent[79]. In other words, the carrier's pore structure characteristics have a significant impact on how well the amine modified adsorbent captures particles. Below is a detailed explanation of how the support structure property affects the performance of the adsorbent. The procedure of impregnation has several benefits. For instance, the 9 adsorbent is rather easy to prepare, and the amine is loaded heavily. [80]. However, because the supported amine takes up a large portion of the internal pores of the support material, the transfer of carbon dioxide within the adsorbent is restricted and the amine utilisation is lower. Simultaneously, the volatile organic solvent such as methanol is typically used in the preparation of amine-impregnated solid amine adsorbent. In order to prepare an adsorbent, the organic solvent is typically removed using the heat drying process. This process uses energy and can cause amine loss and pore structure collapse when heated. Wang et al. recently prepared the adsorbents using freeze-drying method to get beyond the aforementioned drawbacks. When making the adsorbent by freeze-drying, water is used as the organic amines' solvent. Liquid nitrogen was applied to the resulting support and amine species combinations. Sublimation is then used to remove the frozen water. Due to the removal of water during the freeze-drying process, the method used to prepare the adsorbent not only uses less energy but also creates new voids in the loaded organic amine layer, facilitating gas diffusion and exposing the organic amine's active site. The carrier material is very applicable to the impregnation technique. Therefore, a variety of carriers, including zeolite molecular sieves, porous carbon materials, mesoporous molecular sieves, and MOF materials, can be used as carriers for the preparation of adsorbents by impregnation method[81].



Figure 12 Impregnation method

### 2.3.2 Grafting method:

Grafting is a process that involves covalently bonding a functional group to an inorganic surface, most frequently zeolites. This technique is used to modify zeolites for a variety of purposes, including as the impregnation of amines. Because they have a strong affinity for  $\text{CO}_2$ , amines, which are organic compounds with nitrogen atoms, are frequently used as sorbents for  $\text{CO}_2$  capture. Zeolites' efficiency and selectivity for  $\text{CO}_2$  capture can be enhanced by grafting amines onto them. Zeolites are crystalline aluminosilicates with a porous structure that make them excellent for a variety of uses, such as gas separation and catalysis. However, they might not always be appropriate for particular applications, like  $\text{CO}_2$  capture, due to their pore size and surface chemistry. Zeolites' pore size and surface chemistry can be changed by grafting functional groups onto their surface, making them better suited for particular purposes. A number of stages are necessary to graft amines onto zeolites, including surface modification of the zeolite, amine activation, and amine attachment to the zeolite surface. The zeolite must first have its surface modified, which entails the elimination of contaminants and the formation of a clear, reactive surface. Acid treatment is often used to complete this stage, which cleans up any impurities and activates the zeolite surface. Surface flaws and silanol groups are produced as a result of acid treatment, and these features offer the amine reactive sites for attachment. The amine must then be activated, which entails changing it into a reactive species that can interact with the surface of the zeolite. This phase is often accomplished by creating an amine

salt, which can subsequently interact with the surface of the zeolite. The amine is combined with an acid, such as sulfuric or hydrochloric acid, to create the amine salt. The finished amine salt can then be combined with the zeolite after being dissolved in a solvent like water or ethanol. The attachment of the amine to the zeolite surface, which requires an interaction between the amine salt and the zeolite surface, is the last stage. The silanol groups on the zeolite surface and the amine salt normally react by condensation to complete this step. Covalent bonds between the amine and the zeolite surface can be formed by heating the mixture for a predetermined amount of time and temperature to start the reaction. The kind of zeolite, the type of amine, and the circumstances utilised during the grafting process are only a few of the variables that affect how efficient the grafting method for amine impregnation on zeolite is. The pore size and surface chemistry of the zeolite can vary depending on its type, which can change how well the amine adheres to the zeolite surface. Since different amines have different reactivity and solubility characteristics, the type of amine used can also have an impact on how effective the grafting technique is. The grafting procedure's efficiency may also be impacted by the environmental factors used. The concentration of the amine salt, the solvent employed, the reaction temperature and time, as well as the mixture's pH, can all affect how well the amine adheres to the surface of the zeolite. A stable and efficient amine-impregnated zeolite can form if these parameters are improved.

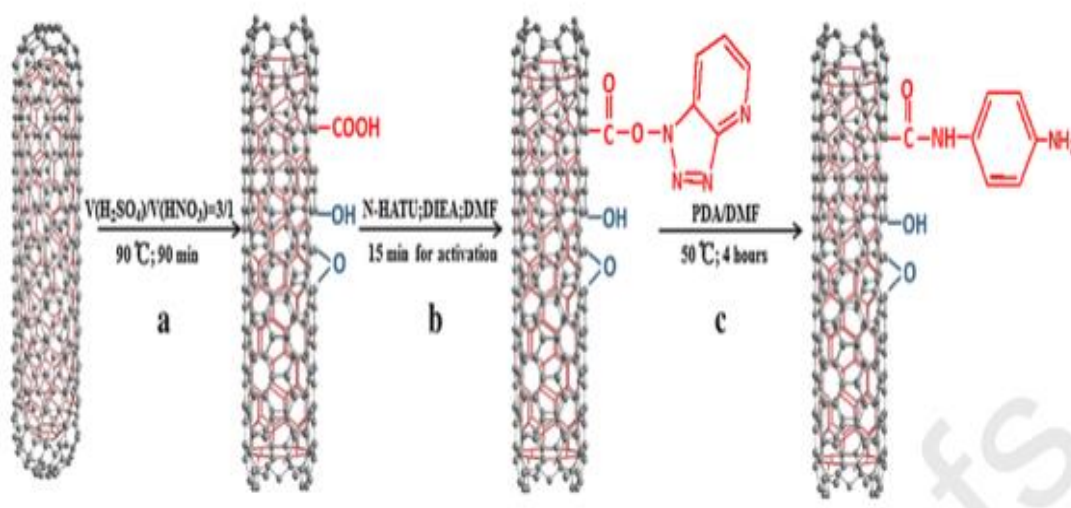


Figure 13 Grafting of PDA

### **2.3.3 Direct synthesis method**

In a one-step synthesis procedure, amine functional groups are added to the surface of porous materials in the direct synthesis of amine-modified porous materials. Due to the growing need for porous materials with particular properties for applications in catalysis, gas separation, and drug administration, among other things, this technique has been extensively investigated in recent years. Due to their high surface area, huge pore volume, and variable pore size, porous materials like metal-organic frameworks (MOFs), zeolites, and mesoporous silica have been widely employed as adsorbents and catalysts. These materials' selectivity and activity for particular uses, such as CO<sub>2</sub> capture and catalytic processes, can be enhanced by adding amine functional groups to their surfaces. The direct synthesis of amine-modified porous materials can be accomplished in a number of ways, such as co-condensation, post-synthesis modification, and template-directed synthesis. In post-synthesis modification, the amine functional group is added to the material's surface after synthesis, as opposed to co-condensation, which includes the simultaneous creation of the porous material and the amine functional group during synthesis. In template-directed synthesis, the insertion of the amine group and the production of the porous substance are guided by a template molecule. A popular technique for the direct production of amine-modified porous materials is co-condensation. In this process, a base and a solvent are present while a metal precursor, an organic linker, and an amine precursor simultaneously react. A metal-organic framework or a hybrid material with amine functional groups inserted into the framework structure is created when the amine precursor interacts with the metal precursor and the organic linker. Another approach for the direct synthesis of amine-modified porous materials is post-synthesis modification. In this technique, the amine functional group is added to the porous material's surface following synthesis. The amine group is first removed from the porous material during initial synthesis, and it is then functionalized with an amine precursor utilising a variety of techniques, including grafting, impregnation, or covalent bonding. While impregnation entails the diffusion of the amine precursor into the material's pores, grafting entails attaching the amine precursor to the surface of the porous material through a covalent bond. The process of creating a covalent bond comprises the reactivity of the amine precursor with the surface functional groups of the

porous material. Another technique for the direct synthesis of amine-modified porous materials is called template-directed synthesis. In this technique, the introduction of the amine group and the production of the porous material are guided by the use of a template molecule. The surfactant or polymer that produces a micelle or a template around which the porous material is created is usually the template molecule. The reaction is then allowed to continue once the amine precursor is introduced to the template, resulting in the formation of a porous material with amine functional groups incorporated into the structure. The kind of porous material, the kind of amine precursor, and the reaction conditions utilised during synthesis are all aspects that affect how well amine-modified porous materials may be produced directly. The characteristics of the finished material, including pore size, surface area, and stability, can vary depending on the type of porous material used. The efficiency of the procedure can also be influenced by the type of amine precursor used, as various amines have various reactivity and solubility characteristics. The efficiency of the approach can also be impacted by the reaction conditions utilised during synthesis. The creation and qualities of the resulting substance can be affected by a number of variables, including the reactant content, the solvent employed, the reaction temperature and time, and the mixture's pH. An amine-modified porous material that is stable and efficient can be created by improving these parameters.

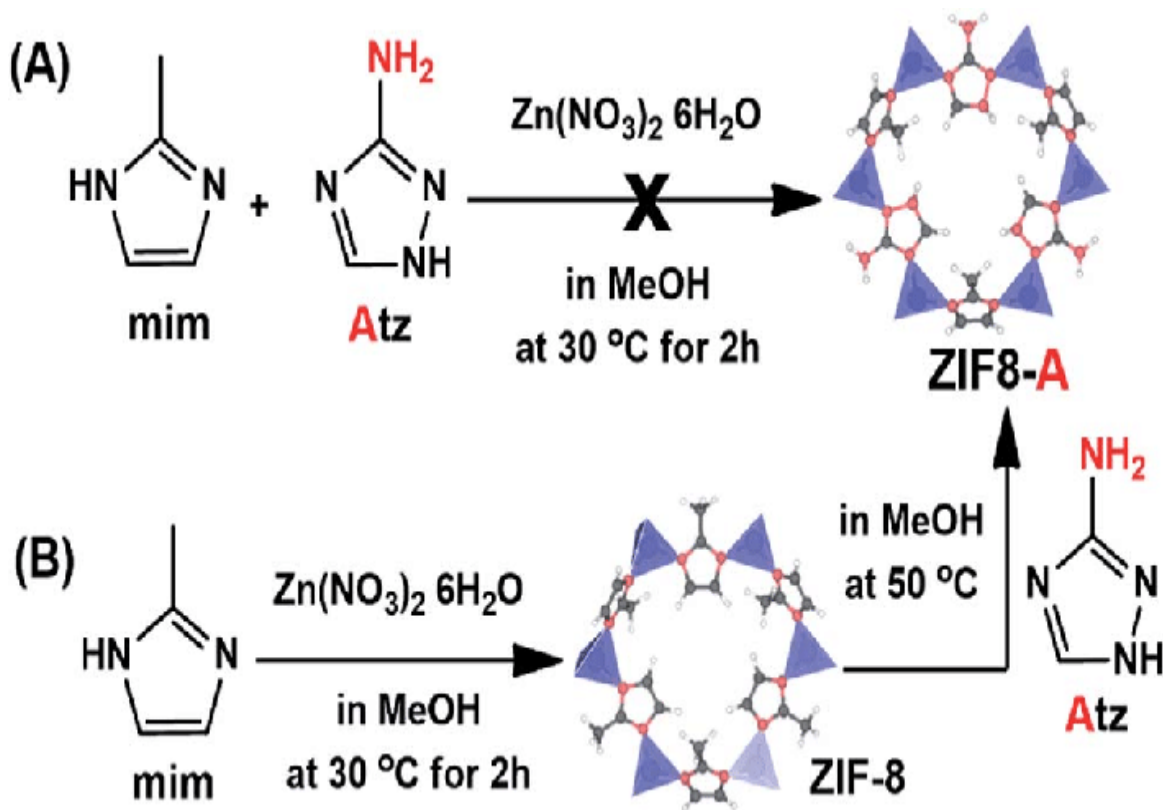


Figure 14: Direct Synthesis method

## 2.4 Factors affecting the CO<sub>2</sub> adsorption on zeolite

The kind of zeolite, its crystal structure, the size and shape of the pores, the Si/Al ratio, and the temperature and pressure of the adsorption process are some of the variables that affect the adsorption of CO<sub>2</sub> over zeolites. Since some zeolites have a higher affinity for CO<sub>2</sub> than others, the type of zeolite used can have an impact on a material's ability to adsorb CO<sub>2</sub>. As some zeolite crystal structures have more open pores and channels than others, this can increase the surface area available for CO<sub>2</sub> adsorption. The zeolite's pore size and shape can also affect how well it can absorb CO<sub>2</sub>. Smaller pores might offer a more selective adsorption mechanism, while larger pores might facilitate simpler CO<sub>2</sub> molecule passage into the zeolite. Higher Si/Al ratios may create a more acidic surface for CO<sub>2</sub> adsorption, which can have an impact on the zeolite's ability to absorb CO<sub>2</sub>. Finally, CO<sub>2</sub> adsorption over zeolites can be affected by the temperature and pressure of the adsorption process. The amount of CO<sub>2</sub> adsorbed can often be increased

by increasing pressures and temperatures, but the ideal circumstances will vary depending on the particular zeolite and its characteristics.

Following are the factors that has been discussed here.

#### **2.4.1 Effect of Framework on CO<sub>2</sub> adsorption**

Crystalline aluminosilicates called zeolites have an unusual porous structure. According to the size, shape, and polarity of the molecules, they can adsorb and separate them using a three-dimensional network of interconnecting channels and cavities. Due to their large surface area, thermal stability, and selectivity, zeolites are frequently used in a wide range of industrial applications, including catalysis, adsorption, and separation. Due to zeolites' high affinity for CO<sub>2</sub> molecules, its usage for CO<sub>2</sub> adsorption has attracted a lot of attention recently. The polarity and tiny size of the CO<sub>2</sub> molecule make it the perfect option for adsorption in the zeolite channels[82]. The distinct porous structure of zeolites creates the perfect environment for CO<sub>2</sub> molecule adsorption, leading to great selectivity and capacity. Two primary processes—physisorption and chemisorption—can be used to explain the CO<sub>2</sub> adsorption mechanism in zeolites. CO<sub>2</sub> molecules bind weakly and irreversibly with the surface of zeolite channels by physisorption. In contrast, in chemisorption, CO<sub>2</sub> molecules form chemical connections with the active sites of the zeolite framework. The size and form of zeolite channels, the existence of active sites, as well as the temperature and pressure conditions, all affect the kind of CO<sub>2</sub> adsorption mechanism. Several factors, including adsorption capacity, selectivity, and stability, can be used to analyze the impact of zeolite frameworks on CO<sub>2</sub> adsorption[83]. The number of CO<sub>2</sub> molecules that may be adsorb per unit weight or volume of zeolite is referred to as the adsorption capacity. The term "selectivity" describes a material's capacity to absorb CO<sub>2</sub> molecules above others, such as nitrogen (N<sub>2</sub>) and methane (CH<sub>4</sub>). The stability of zeolite is defined as its capacity and selectivity for adsorption during a number of adsorption-desorption cycles. Several methods, including modifying the zeolite framework's structure, functionalizing the zeolite surface with particular groups, and optimizing the temperature and pressure conditions, can increase the adsorption capacity of zeolites for CO<sub>2</sub>. In order to increase the accessibility and diffusion of CO<sub>2</sub> molecules, it is possible to modify the zeolite structure by creating zeolites with bigger pore



diameters, adding secondary pores, or creating channel defects. For instance, compared to traditional microporous zeolites, the use of hierarchical zeolites, which contain a combination of micro- and mesopores, has demonstrated to improve the CO<sub>2</sub> adsorption capacity. By adding more places for CO<sub>2</sub> molecules to interact with the zeolite surface, the functionalization of zeolite surfaces with certain groups, such as amino, carboxylic, or hydroxyl groups, can also increase the CO<sub>2</sub> adsorption capacity. There are several ways to functionalize a compound, including post-synthesis modification, ion-exchange, and covalent attachment. For instance, it has been demonstrated that functionalizing zeolites with amine groups increases the CO<sub>2</sub> adsorption capacity and selectivity because stable carbamate bonds occur between CO<sub>2</sub> molecules[84].

Table 3: Effect of Framework on CO<sub>2</sub> Adsorption

Type of Zeolite	Adsorption Capacity mmole/g	Selectivity CO <sub>2</sub> /N <sub>2</sub>	Stability Number of cycle
ZSM-5	3.6	37	6
SAPO-34	4.2	45	10
Beta	2.8	50	8
Y	2.2	23	5
MFI	3.9	42	9

In this illustration, the table lists five distinct research that looked into how various zeolite frameworks affected CO<sub>2</sub> adsorption. The table's rows represent various studies, and its columns list the zeolite type that was employed, the amount of CO<sub>2</sub> that it can bind to each gram of zeolite in millimoles, the selectivity of CO<sub>2</sub> over nitrogen (N<sub>2</sub>), and the stability of the zeolite over a predetermined number of adsorption-desorption cycles.

The results shown in the table indicate that the selectivity, stability, and capacity of CO<sub>2</sub> adsorption vary among different zeolite frameworks. For instance, among the zeolites given in the table, SAPO-34 had the highest CO<sub>2</sub> adsorption capacity and selectivity,

whilst Y demonstrated the lowest. The stability of the zeolites also varied, with exhibiting the highest and lowest levels, respectively, of stability. The zeolite structure, pore size, active sites, as well as the temperature and pressure settings utilized in the studies, could all be responsible for these variations[83].

#### **2.4.2 Influence of temperature pressure on adsorption capacity of zeolite:**

Zeolites have crystalline structures and are extremely porous, which makes them perfect for a variety of uses, including gas adsorption. The adsorption of CO<sub>2</sub> by zeolites has generated a lot of interest since carbon dioxide (CO<sub>2</sub>) is a substantial greenhouse gas that contributes greatly to climate change. Temperature and pressure are two variables that can affect the ability of zeolites to adsorb CO<sub>2</sub>. The effects of temperature and pressure on the CO<sub>2</sub> adsorption capacity of several zeolites will be covered in this article. Temperature has a significant impact on zeolites' ability to adsorb CO<sub>2</sub>. The ability of the system to adsorb CO<sub>2</sub> typically decreases as system temperature rises. This is because the adsorbate molecules have more kinetic energy at higher temperatures, which increases their propensity to desorb from the surface of the zeolite. Higher temperatures can also modify the zeolite's structure, which can impact its surface area and pore size distribution and eventually reduce its ability for CO<sub>2</sub> adsorption. Numerous studies have demonstrated that as the system temperature rises, zeolites' ability to adsorb CO<sub>2</sub> decreases. For instance, [83] evaluated the CO<sub>2</sub> adsorption capability of zeolite ZSM-5 at various temperatures ranging from 303 to 363 K. The findings demonstrated that as the system's temperature rose, CO<sub>2</sub>'s ability to adsorb became less effective. In a research on the CO<sub>2</sub> adsorption by zeolite Na-Y at various temperatures ranging from 293 to 333 K, [84] noted a similar pattern. Another significant element that might affect zeolites' ability to adsorb CO<sub>2</sub> is pressure. The ability of the system to adsorb CO<sub>2</sub> typically increases as system pressure rises. This is because more CO<sub>2</sub> molecules are accessible for adsorption as a result of greater pressures increasing the concentration of CO<sub>2</sub> in the gas phase. However, the adsorption capacity of zeolites has a limit beyond which it becomes saturated. At this stage, additional pressure increases do not significantly boost adsorption. Numerous studies have demonstrated that as system pressure rises, zeolites' ability to adsorb CO<sub>2</sub> increases. For instance, Dai et al. (2018) examined the adsorption of CO<sub>2</sub> by zeolite Y at various pressures ranging from 0.1 to 1.0 MPa. The outcomes

demonstrated that the system's pressure grew together with the CO<sub>2</sub>'s adsorption capability. In a research on the adsorption of CO<sub>2</sub> by zeolite X at various pressures ranging from 0.1 to 1.0 MPa, Khezami et al. (2017) noted a similar pattern. Different zeolites have different effects at different temperatures and pressures on their ability to absorb CO<sub>2</sub> depending on their structural and chemical characteristics. For instance, the zeolite's ability to adsorb CO<sub>2</sub> can be influenced by the sort of cation that is present in it. In comparison to zeolites containing alkaline earth metals like calcium or magnesium, those containing alkali metals like potassium or sodium have a higher potential to absorb CO<sub>2</sub>. This is due to the stronger interactions that alkali metal cations may have with CO<sub>2</sub> molecules, which improves their capacity for adsorption. Zeolites' ability to absorb CO<sub>2</sub> can also be impacted by the size of their pores and surface area. Zeolites with more surface area and smaller pore diameters often have greater CO<sub>2</sub> adsorption capacities.

Table 4: Effect of Temperature and Pressure on Adsorption capacity of Zeolite

Zeolite	Temperature °C	Pressure (bar)	Adsorption Capacity mmole/g	Reference
Na-ZSM-5	24	0.71	1.90	[85]
	30	2	1.20	
	60	2	1.43	[86]
Li-ZSM-5	30	2	1.41	[86]
	60	2	1.37	[86]
Cs-ZSM-5	30	2	1.33	[86]
	60	2	1.25	[86]
Rb-ZSM-5	30	2	1.33	[86]
	60	2	1.45	[86]
K-ZSM-5	30	2	1.20	[86]
	60	2	1.50	[86]
MCM-41	50	1.013	0.325	[87]
	75	1.013	0.195	[87]
	100	1.013	0.150	[87]

### **2.4.3 Effect of Si/Al ratio, Temperature and Pressure of CO<sub>2</sub> adsorption of Zeolite.**

Zeolites' Si/Al ratio significantly affects their ability to adsorb substances. The number of silicon (Si) atoms to aluminium (Al) atoms in the zeolite framework is what is used to define it[88]. The zeolite's acidity, which in turn impacts its capacity to absorb CO<sub>2</sub>, is influenced by the Si/Al ratio. In comparison to zeolites with a low Si/Al ratio, those with a high Si/Al ratio are more acidic and have a greater affinity for CO<sub>2</sub>[89]. The impact of the Si/Al ratio on the ability of zeolites to adsorb CO<sub>2</sub> has been examined in a number of research. As an illustration, Zhou et al. (2018) produced a variety of ZSM-5 zeolites with Si/Al ratios ranging from 22 to 205 and assessed their CO<sub>2</sub> adsorption capability at room temperature and atmospheric pressure. They discovered that when the Si/Al ratio grew, the capacity for CO<sub>2</sub> adsorption increased as well, peaking at a Si/Al ratio of around 80, and subsequently declining at higher Si/Al ratios. The balance between the quantity of active sites and the potency of CO<sub>2</sub> adsorption was cited by the authors as the cause of this tendency. Similar to this, Wang et al. (2017) created a variety of H-ZSM-5 zeolites and tested their CO<sub>2</sub> adsorption capacity at 298 K and 1 bar using Si/Al ratios ranging from 15 to 400. The highest CO<sub>2</sub> adsorption capacity was discovered at a Si/Al ratio of around 80. They discovered that the CO<sub>2</sub> adsorption capacity rose with increasing Si/Al ratio up to a certain point and then plateaued[90]. The authors hypothesised that the rise in Brnsted acid sites, which are in charge of CO<sub>2</sub> adsorption, was the cause of the increase in CO<sub>2</sub> adsorption capacity with increasing Si/Al ratio. Another significant element that influences zeolites' ability to absorb CO<sub>2</sub> is temperature. As the interaction between the CO<sub>2</sub> molecule and the zeolite surface weakens at higher temperatures, the adsorption capacity of zeolites typically declines[91]. However, the particular zeolite and the operating circumstances can also have an impact on how temperature affects CO<sub>2</sub> adsorption capacity. For instance, Li et al. (2016) examined the impact of temperature on the NaX zeolite's ability to adsorb CO<sub>2</sub> at various pressures. They discovered that the NaX zeolite's ability to adsorb CO<sub>2</sub> reduced as temperature rose, while the rate of decline was slower at higher pressures. The authors proposed that the interaction between CO<sub>2</sub> and the zeolite surface was greater at higher pressures, resulting in a slower[92].

Table 5: Effect of Si/Al ratio on CO<sub>2</sub> adsorption

Zeolite type	Si/Al Ratio	Temperature °C	Pressure (bar)	Adsorption Capacity mmole/g	Reference
ZSM-5	15	7	0.81	2.14	[93]
	15	20	0.91	2.11	[93]
	30	7	0.94	1.87	[93]
	30	20	0.92	1.66	[93]
	60	7	0.52	1.37	[93]
	60	20	0.81	1.27	[93]
	280	40	1.013	1.24	[94]

#### 2.4.4 Effect of Basicity on CO<sub>2</sub> adsorption (As CO<sub>2</sub> is an acidic gas)

The basicity of the zeolite is a significant component that influences the adsorption of CO<sub>2</sub> on zeolites. Basicity, which describes a substance's capacity to give or take electrons, is correlated with the potency of the Bronsted-Lowry acid sites in zeolites. Through the process of chemisorption, in which CO<sub>2</sub> reacts with the surface of the zeolite to form a chemical bond, these acid sites are in charge of the adsorption of CO<sub>2</sub>. Studies have revealed that zeolites' basicity has a sizable impact on the adsorption of CO<sub>2</sub>. The ability of zeolites to adsorb CO<sub>2</sub> has been observed to increase with basicity. This is due to the fact that the basicity of the zeolite surface raises the adsorbate's electron density, which raises the intensity of the adsorption interaction. The CO<sub>2</sub> molecule serves as an electron acceptor, and the Bronsted-Lowry acid sites on the zeolite surface serve as electron donors. As a result, a chemical interaction is created between the CO<sub>2</sub> molecule and the surface of the zeolite[95]. Basic sites or Lewis base sites on a surface are what define a material's basicity, or its capacity to take or donate electrons. Lewis acid sites, which have the potential to serve as electron acceptors, are known to exist on the surface of zeolites. The surface of some zeolites, including ZSM-5, also has basic sites that can serve as electron donors[96]. The presence of alkali or alkaline earth metal cations in the zeolite framework is often linked to these basic sites. Group 1A cations boost the basic strength of cationic zeolites in the following ways: Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. The

capacities and rate of CO<sub>2</sub> adsorption of natural hershelite-sodium chabazite (sodium aluminosilicate), clinoptilolite (sodium aluminosilicate), and clinoptilolite (potassium calcium sodium aluminosilicate) have also been discovered through research on these three zeolites. Additionally, it has been noted that replacing Na<sup>+</sup> cations with Ba<sup>2+</sup> cations significantly reduces the basicity of oxygen atoms in the NaX and NaY zeolites' frameworks[97]. The partial negative charge of oxygen atoms close to Ba<sup>2+</sup> cations may have decreased, which could be the source of this event. In this case, a study of the CO<sub>2</sub> adsorption on the zeolites KX, BaX, and LaX has successfully demonstrated that KX was the most basic of the three zeolite. The replacement of Na<sup>+</sup> and K<sup>+</sup> by Ca<sup>2+</sup>, on the other hand, resulted in a rise in the basicity of the framework oxygen functioning as basic center, according to a research of CO<sub>2</sub> adsorption on the clinoptilolite[97]. By occluding alkali metal oxides, zeolites' fundamental strength and CO<sub>2</sub> adsorption capability may also be greatly enhanced. Basic metal oxides such rare earth and alkaline earth oxides are thought to have more strongly basic sites than ion-exchanged zeolites[98]. The basicity and capacity of CO<sub>2</sub> adsorption on the zeolites NaX and NaY increased as a result of the cesium oxides (CsOx) being occluded, and the increase in the capacity of CO<sub>2</sub> adsorption was proportional to the amount of occluded CsOx. The impact of basicity on CO<sub>2</sub> adsorption on zeolites has been examined in several experimental experiments. Wang et al.'s (2013) investigation on the ZSM-5 zeolite's ability to absorb CO<sub>2</sub> looked at the impact of alkaline metal cations (Na<sup>+</sup> and K<sup>+</sup>). The findings demonstrated a considerable increase in the CO<sub>2</sub> adsorption capacity when Na<sup>+</sup> or K<sup>+</sup> cations were present in the zeolite framework, which was attributable to the basicity of the metal cations[99]. The research also demonstrated that the stability of CO<sub>2</sub> adsorption on the zeolite surface was enhanced by the presence of basic sites. Chen et al. (2015) also looked at the impact of basicity on CO<sub>2</sub> adsorption on Y-type zeolites that had been altered with various alkaline metal cations[43]. The outcomes demonstrated that as the basicity of the zeolite surface grew, so did the CO<sub>2</sub> adsorption capability. The research also shown a high correlation between the quantity of basic sites on the zeolite surface and the CO<sub>2</sub> adsorption capacity[100].

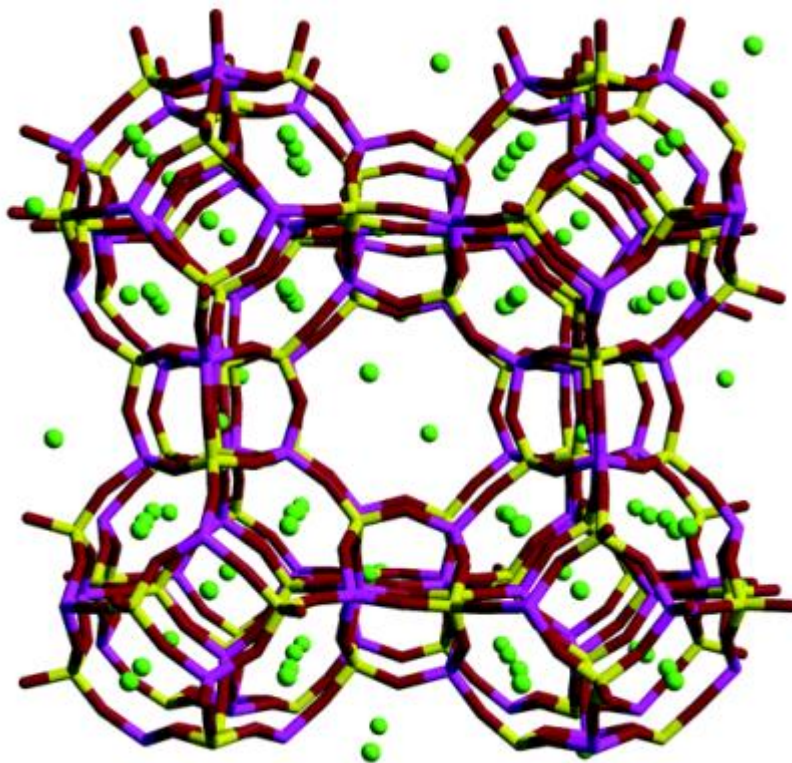


Figure 15: Green dots indicating sodium increasing basicity

## **2.5 EFFECT OF THE PHYSICOCHEMICAL PROPERTIES ON THE BEHAVIOUR OF ZEOLITES AS CO<sub>2</sub> ADSORBENTS**

### **2.5.1 Effect of enthalpy of adsorption**

An essential element that can affect how carbon dioxide (CO<sub>2</sub>) adheres to zeolites is the enthalpy of adsorption. Enthalpy of adsorption, which measures the strength of the interaction between the adsorbate and the adsorbent, is the quantity of energy released or absorbed when a molecule is adsorbed onto a surface. A higher enthalpy of adsorption for CO<sub>2</sub> on zeolites often denotes a stronger binding relationship and a larger adsorption capacity. The impact of the enthalpy of adsorption on CO<sub>2</sub> adsorption on zeolites has been studied in numerous publications, utilizing a variety of experimental approaches like isothermal adsorption measurements, calorimetry, and computer models. Table 1 lists a few of the published CO<sub>2</sub> enthalpy of adsorption values for several zeolites types.

Table 6: Effect of Enthalpy of adsorption

Zeolite Type	Enthalpy of adsorption (kJ/mol)
ZSM	-30 to -50
Beta	-40 to -70
Y	-45 to -60
Mor	-44 to -60
FAU	-37 to -70

The table shows that the usual range of the enthalpy of adsorption for CO<sub>2</sub> on zeolites is between -30 and -70 kJ/mol. The stated values do, however, exhibit significant fluctuation, which can be related to a number of variables, including the particular zeolite type, the presence of other gases, the temperature and pressure conditions, and the testing method employed. The Si/Al ratio and pore size of ZSM-5 zeolites were examined by Yang et al. (2015) in one study to see how they affected the enthalpy of CO<sub>2</sub> adsorption. They discovered that while increasing the pore size increased the enthalpy of adsorption, they discovered that increasing the Si/Al ratio decreased it. This results from a higher density of acidic sites on the zeolite surface caused by a higher Si/Al ratio, which can reduce the interaction between CO<sub>2</sub> and the zeolite [101]. On the other hand, more accessibility to the acidic sites is made possible by larger pores, which can enable a stronger interaction between CO<sub>2</sub> and the zeolite surface. Wang et al. (2017) also looked at the impact of cation type and concentration on the enthalpy of CO<sub>2</sub> adsorption on NaX and CaX zeolites in another study. They discovered that raising the cation concentration increased the adsorption enthalpy for both NaX and CaX, with CaX exhibiting a greater rise. This is because cations and CO<sub>2</sub> molecules can interact through ion-dipole interactions, which can enhance the binding relationship between CO<sub>2</sub> and the zeolite surface. The impact of the enthalpy of adsorption on CO<sub>2</sub> adsorption on zeolites has also been studied using computational models in addition to experimental experiments. For instance, Tang et al.'s (2018) study examined the impact of pore size on the enthalpy of CO<sub>2</sub> adsorption on MFI zeolites using molecular dynamics simulations. Because larger



pores may result in a weaker confinement effect and a lower density of acidic sites, they discovered that increasing the pore size resulted in a decrease in the enthalpy of adsorption. In conclusion, the adsorption behavior of CO<sub>2</sub> on zeolites can be significantly influenced by the enthalpy of adsorption[102].

### **2.5.2 Effect of adsorbate characteristic on adsorption on Zeolite**

The process of adhering molecules or atoms to the surface of a solid, liquid, or gas is known as adsorption. Adsorption is a crucial characteristic of zeolite because of its porous structure and capacity to only adsorb particular molecules. A group of crystalline aluminosilicates known as zeolites have a vast surface area for adsorption due to their 3D structure of linked channels and cavities. The adsorption process on zeolite depends critically on the adsorbate property. The impact of adsorbate characteristics on zeolite adsorption will be covered in this paper. The physicochemical parameters of the adsorbing species are referred to as adsorbate characteristics. These characteristics include the size, shape, charge, polarity, and presence of functional groups in the molecules. These characteristics control how the adsorbate and zeolite interact, which in turn influences the adsorption procedure[103].

### **2.5.3 Effect of molecular Size**

Adsorption is the process of attaching or accumulating a substance onto the surface of a solid or liquid. In the context of zeolite, adsorption refers to the ability of the material to selectively trap and retain specific molecules within its pore structure. The adsorption process is influenced by various factors, such as the physicochemical properties of the adsorbent and adsorbate molecules, temperature, pressure, and the size of the adsorbate molecule. This article focuses on the effect of adsorbate molecular size on adsorption on zeolite. Zeolites are crystalline aluminosilicate materials with a unique three-dimensional pore structure that provides a large surface area for adsorption. The pore structure of zeolites is typically in the range of 3-10 Å, which makes them ideal for adsorbing small molecules such as water, carbon dioxide, and nitrogen. The size of the adsorbate molecule plays a crucial role in determining the adsorption capacity of zeolites. Smaller Molecules Have Higher Adsorption Capacities The size of the adsorbate molecule is a critical factor that affects its adsorption capacity on zeolite. Smaller molecules can easily

penetrate into the pores of zeolites, leading to higher adsorption capacities. The pore size of zeolites is typically in the range of 3-10 Å, which makes them ideal for adsorbing small molecules[104]. As the size of the adsorbate molecule increases, its ability to penetrate into the zeolite pores decreases, leading to a lower adsorption capacity. For example, the adsorption capacity of water molecules on zeolite 4A, which has a pore size of 4 Å, is approximately 20% by weight. On the other hand, the adsorption capacity of larger molecules such as hexane, which has a molecular diameter of 5.1 Å, is only 0.5% by weight. This shows that the size of the adsorbate molecule plays a crucial role in determining its adsorption capacity on zeolite.

**Shape of the Molecule Also Affects Adsorption**

The shape of the adsorbate molecule also plays a critical role in determining its adsorption capacity on zeolite[105]. Linear and planar molecules can easily fit into the zeolite pores, leading to higher adsorption capacities. Bulky or irregularly shaped molecules may not fit into the zeolite pores or may only be partially adsorbed, resulting in lower adsorption capacities. For example, methane, which is a small linear molecule, has a high adsorption capacity on zeolite due to its ability to easily penetrate into the pores. On the other hand, molecules such as cyclohexane, which have a bulky cyclic structure, have a lower adsorption capacity on zeolite due to their inability to fit into the zeolite pores.

**Pore Structure of Zeolite Determines Adsorption Capacity**

The pore structure of zeolite is an essential factor that determines the adsorption capacity of the material. Zeolites have a unique three-dimensional structure that provides a large surface area for adsorption. The pore size and shape of zeolite can be tailored to selectively adsorb specific molecules. For example, zeolite 13X, which has a pore size of 10 Å, is ideal for adsorbing large molecules such as n-hexane and carbon dioxide. Zeolite 4A, which has a pore size of 4 Å, is ideal for adsorbing small molecules such as water and ammonia. The pore structure of zeolite can be modified by changing the ratio of aluminum to silicon atoms in the material. This allows for the creation of materials with tailored pore structures that can selectively adsorb specific.

#### **2.5.4 Effect of Shape of molecule**

Another crucial factor that influences adsorption on zeolite is the form of the adsorbate molecule. Higher adsorption capabilities result from the ease with which planar and linear molecules can fit into zeolite pores. Lower adsorption capacities are caused by

molecules that are bulky or have irregular shapes that may not fit into the zeolite pores or may only be partially adsorbed. The adsorption of specific compounds can also be impacted by the zeolite pores' shape. For instance, cylindrical zeolites work best for adsorbing linear molecules, while spherical zeolites work best for adsorbing bulky molecules. Adsorption is the process by which atoms or molecules are drawn to and retained on the surface of a solid or liquid substance. The porous nature of zeolites, a form of aluminosilicate material, makes it the perfect substance for adsorption procedures. The adsorption process on zeolite is significantly influenced by the shape of the adsorbate molecule. The impact of adsorbate molecule shape on adsorption on zeolite will be covered in this article. The 3D configuration of atoms in a molecule is known as its molecular form. It is a crucial property that impacts how the adsorbate and zeolite surface interact. The size and orientation of the adsorbate molecule as it approaches the zeolite surface depend on its shape. This finally affects the adsorption procedure by affecting the type and strength of interactions between the molecule and the zeolite surface. A vast surface area for adsorption is produced by the framework structure of interconnected channels and voids found in zeolites. The adsorption of specific compounds can be impacted by the zeolite's pore structure. For instance, cylindrical zeolites work best for adsorbing linear molecules, while spherical zeolites work best for adsorbing bulky molecules. The chances of molecules being adsorbed are often higher for molecules that can readily fit into the zeolite pores than for molecules that cannot. Lower adsorption capacities are caused by molecules that are bulky or have irregular shapes that may not fit into the zeolite pores or may only be partially adsorbed. In contrast, the zeolite pores can accommodate planar and linear molecules with ease, resulting in larger adsorption capabilities. The degree of interaction between a molecule and the zeolite surface depends on the size and shape of the zeolite pores as well as the shape of the adsorbate molecule. The orientation of the adsorbate molecule on the zeolite surface has an impact on the adsorption process as well. The degree of interactions between a molecule and the surface of a zeolite can be influenced by the orientation of the molecule. For instance, a molecule adsorbed on the surface with its polar end facing the zeolite surface will interact with the surface more strongly than a molecule adsorbed with its non-polar end. The type of interactions between the molecule and the zeolite surface can

also be influenced by the shape of the adsorbate molecule. Electrostatic and van der Waals interactions are the two basic categories of interactions. Van der Waals interactions happen between molecules with no net charge, whereas electrostatic interactions happen between molecules with opposite charges. Polar molecules can interact strongly electrostatically and charge-separately with the zeolite surface. On the other hand, nonpolar molecules can only establish weak van der Waals interactions with the zeolite surface. The adsorption capacity of the zeolite can also be impacted by the form of the adsorbate molecule. Lower adsorption capabilities may result from larger molecules being unable to fit into zeolite pores. The selectivity of the zeolite for particular compounds can also be influenced by the shape of the adsorbate molecule. Based on their size, shape, and polarity, certain compounds can be selectively adsorbed by zeolites. For instance, cylindrical zeolites work best for adsorbing linear molecules, while spherical zeolites work best for adsorbing bulky molecules.

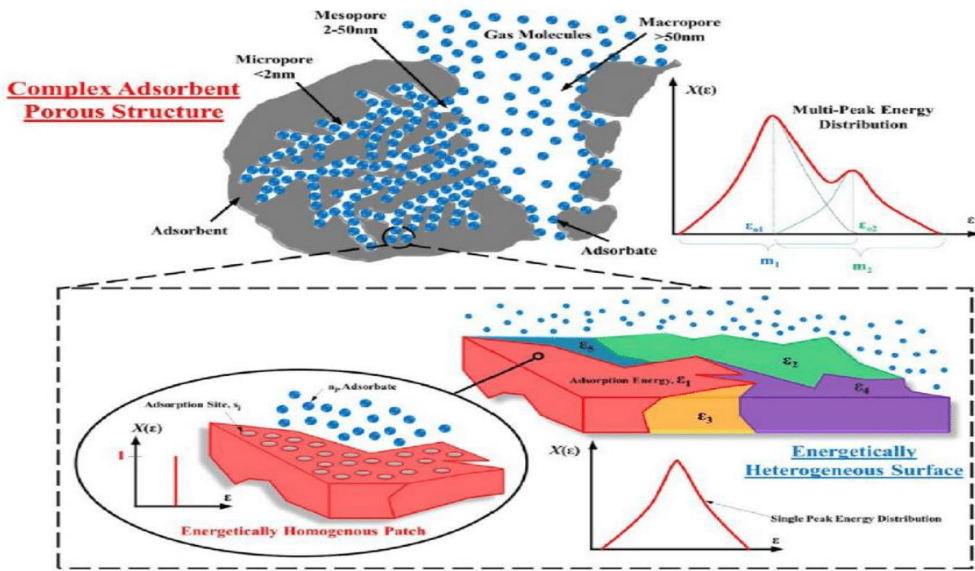


Figure 16: Effect of Shape of molecule on impregnation

# Chapter 03

## Materials and Methods

### 3.1 Materials

All the chemicals, such as methanol ( $\text{CH}_3\text{OH}$ , 99.7%), TPOAH (tripropyl ammonium hydroxide), TEOS (Tetra Ethyl orthosilicate), TEA (Triethanol Amine) and Distilled water were acquired from Sigma-Aldrich and employed as received in this study.

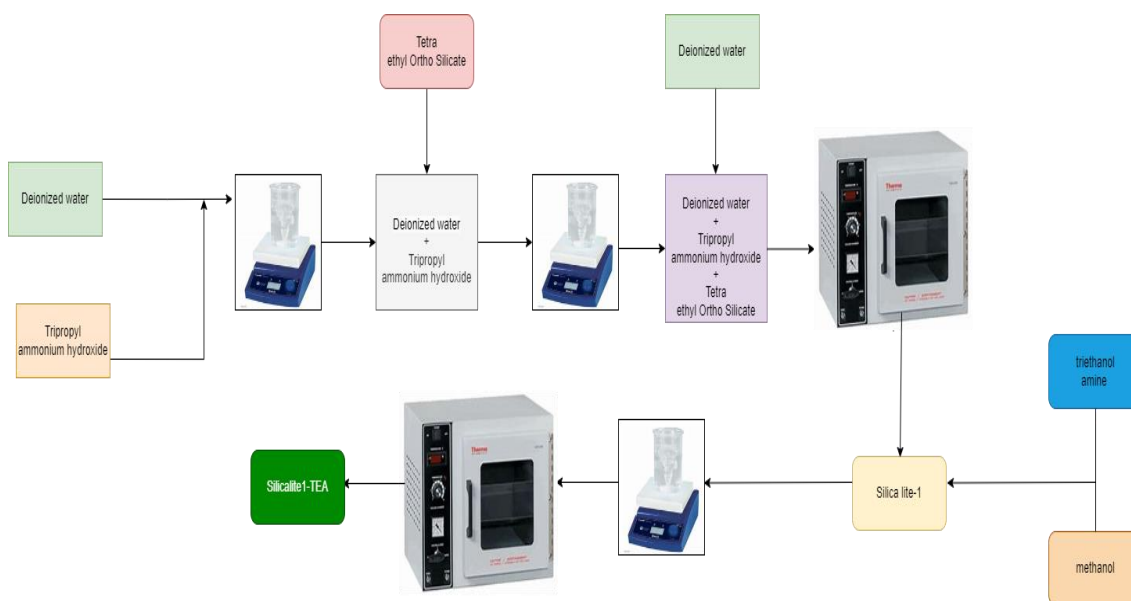


Figure 17: Methodology adopted

### 3.2 Preparation of Silicalite-1:

Silicalite-1 is prepared according to following method

- Mix TEOS(tetraethyl orthosilicate), TPAOH and  $\text{H}_2\text{O}$  in right quantity.
- Stir the mixture at the room temperature for 24 hours.
- Heat the mixture at  $90^\circ\text{C}$  for 3-5 days in the oven.
- Separate the Powder in centrifuge machine.
- Dry in the oven.
- Calcine the sample.

### 3.3 Amine functionalization of Silicalite-1:

Silicalite-1 is modified with TEA according to following method:

- Impregnation is a process that introduces amine molecules into the pores of a porous material.
- To do this, the amine (TEA) was first dispersed in a methanol and Stirred for half hour.
- Then the silicalite-1 material was dissolved in the solution and stirred for 24 hours.
- Thereafter, the Methanol was vaporized by drying in vacuum oven.
- such that only the amine was now left inside the pores of material, resulting in the amine-impregnated zeolite

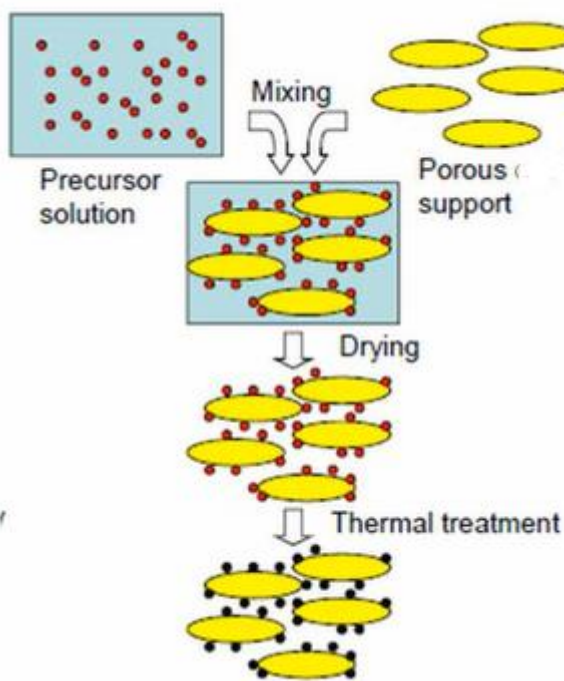


Figure 18: Amine impregnation method

## **3.4 Characterization Techniques:**

### **3.4.1 XRD**

The X-ray diffraction patterns of silicalite-1 and amine-functionalized silicalite-1 were attained from an X-ray diffractometer (Bruker D<sub>2</sub> Phaser Germany) by utilizing a radiation source of Cu K $\alpha$  ( $\lambda=1.5418\text{\AA}$ ). A  $2\theta$  ranges from  $2^\circ$ - $50^\circ$ .

### **3.4.2 SEM**

Scanning electron microscopy (SEM) is used to study the surface morphology of the silicalite-1 and amine-functionalized silicalite-1 by using a scanning electron microscope (JEOL JSM-6490A). SEM worked at 20KV. SEM is equipped with EDAX (METEK Z2-i7) to check the elemental composition of the silicalite-1. The SEM images are taken at magnifications of  $1\mu\text{m}$ ,  $2\mu$ , and  $5\mu\text{m}$ .

### **3.4.3 FTIR**

Fourier-Transform infrared spectroscopy is performed to study the chemical bonds and functional groups by utilizing an FTIR spectrometer (Perkin Elmer spectrum 100). The crystalline structure of adsorbents is determined by XRD machine linked to a computer interface.

### **3.4.4 BET**

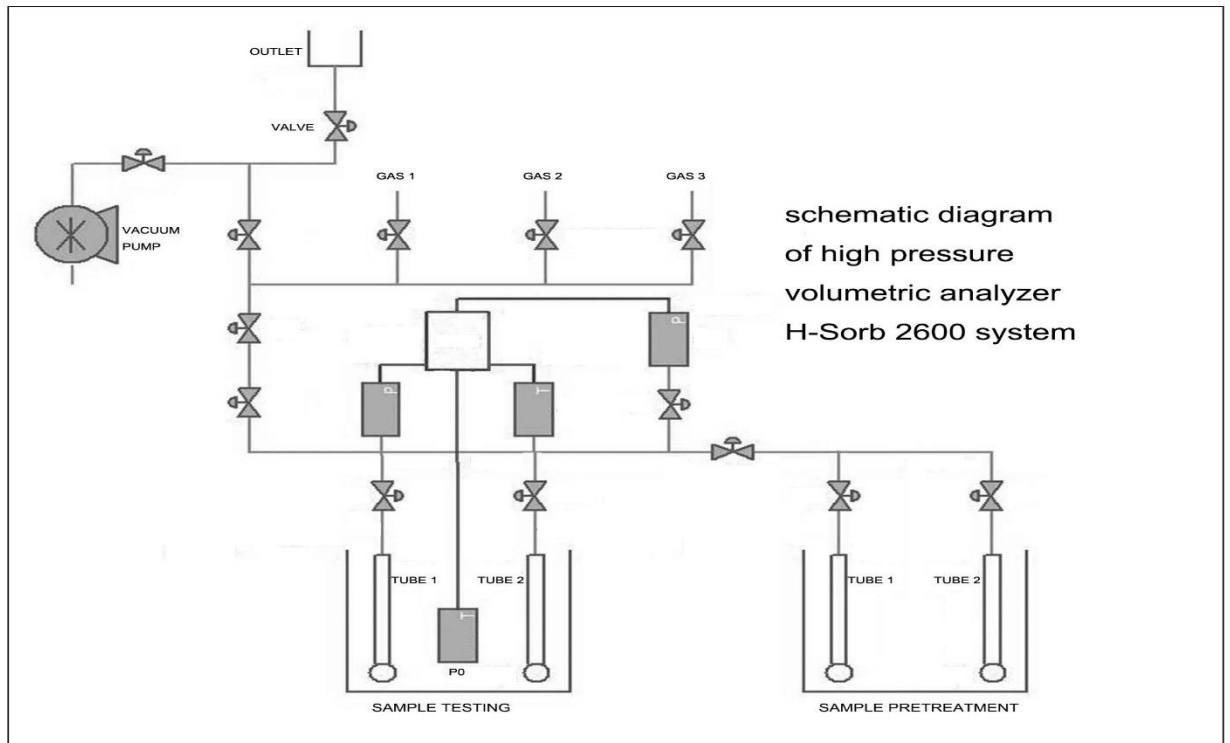
The specific surface area and pore size distribution are obtained by Brunauer-Emmett-Teller (BET). Pure nitrogen is used for adsorption and we got the specific surface area and pore size distribution.

### **3.4.5 TGA**

Thermogravimetric analysis is done in order to check the stability of the silicalite-1 is checked upto 600 degree centigrade. Then the stability of silicalite -1-TEA is checked. Both these compounds showed their stability at working temperature which is 100 degree centigrade.

### 3.5 CO<sub>2</sub> adsorption

Experiments with CO<sub>2</sub> adsorption were performed on a high-pressure gas adsorption analyzer (H-sorb 2600), and the software VxComm utility was used (TDS-734 module). Firstly, to remove all of the moisture from the sample, it was first baked in a vacuum at 100 °C for twenty-four hours. In the second step of the process, a sample of silicate-1-TEA and its composites weighing up to 5 g was collected. The samples were degassed for ten hours at a temperature of 150 °C and a Hoover before the CO<sub>2</sub> adsorption tests were performed. The temperature of the sorption tests was kept constant at 45 °C, and the flow rate of CO<sub>2</sub> was kept at 18 cm<sup>3</sup> min<sup>-1</sup>. The pressures ranged from 0 to 15 bar.





# Chapter 4

## Results and Discussion

### 4.1 Characterization of Silicalite-1 and Silicalite-1-TEA:

#### 4.1.1 XRD:

Silicalite-1 has a three-dimensional microporous structure made of silicon and oxygen atoms. A common method for examining the crystal structure of materials, including zeolites, is X-ray diffraction (XRD). Below experimental data has been discussed, I described the typical XRD pattern and structural details for silicalite-1 comparing with information that is already known. For the purpose of examining the crystal structure of materials,

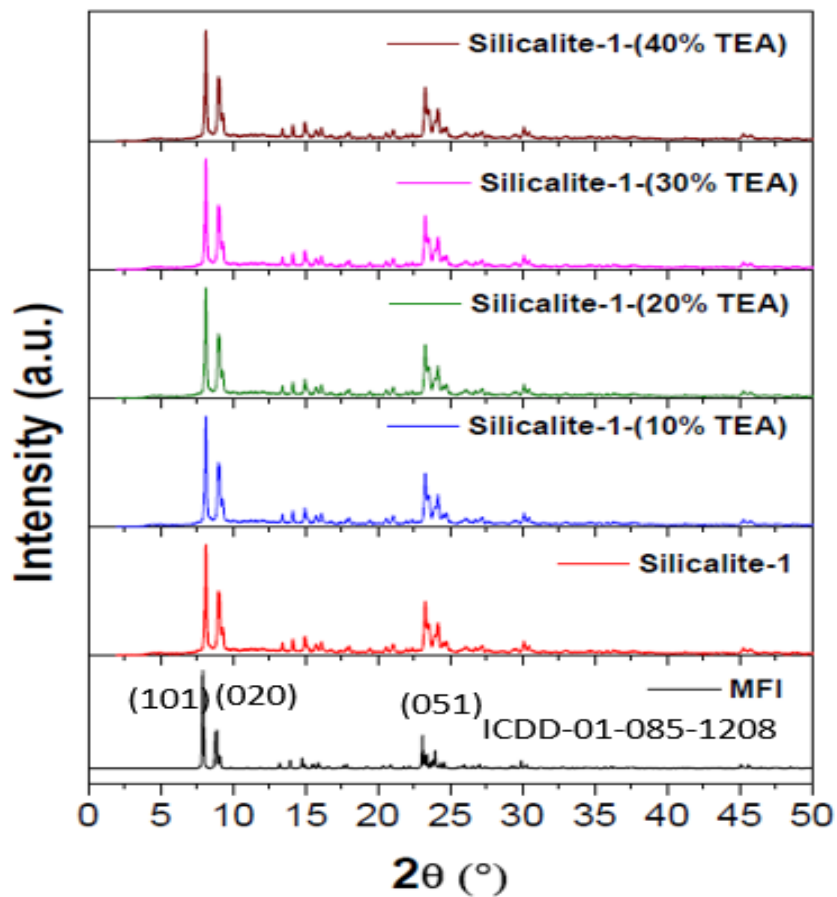


Figure 19: XRD of silicalite-1 and Silicalite-1 (amine modified)

the XRD angle range of 2–50 degrees is frequently utilized. X-ray interactions with the material's crystal lattice planes cause diffraction peaks to appear during XRD examination. The distance between the lattice planes and the X-ray wavelength employed determine the angle at which these peaks appear. It guarantees that a sufficient number of diffraction peaks are captured for examination by setting the angle range to 2 to 50 degrees. As the scattering angle increases, the intensity of the diffraction peaks decreases. It concentrates on the area where the majority of the intense peaks are located by limiting the angle range to 2–50 degrees, resulting in clearer and more pronounced diffraction signals. Instrumental artifacts and background signals from non-crystalline or amorphous components of the sample are frequently present in XRD measurements. It reduces the effect of background noise and improves the visibility of the diffraction peaks by limiting the angle range to 2–50 degrees. The 2–50 degree angle range diffraction pattern can be utilized for additional research, such as indexing the crystal lattice, figuring out the properties of the unit cells, and solving the crystal structure using techniques like Rietveld refinement or direct approaches. This angle range enables the identification of diffraction peaks matching to the crystal lattice planes and offers details on the atom arrangement inside the substance. illustrates the XRD patterns of synthetic silicalite-1 and Silicate-1 Tri-ethanol amine-20 and 40. The diffraction patterns reveal that the samples have a high degree of crystallinity because they show high-intensity reflections in the 2theta between 7 and 9°, 23 and 25°. The same pattern of Silicate-1 was found in the literature. Silicalite-1 has an XRD pattern that often correlates well with the reference pattern for the MFI framework type provided by the ICDD (International Centre for Diffraction Data). Zeolites are included in the extensive database of XRD patterns kept by the ICDD for numerous materials. For MFI-type zeolites like silicalite-1, the ICDD reference pattern has a collection of distinctive diffraction peaks that match the crystal structure of the substance. Through experimental measurements and examination of known materials, several peaks have been identified. The positions and intensities of the diffraction peaks can be compared when comparing the XRD pattern of a synthetic or commercial sample of silicalite-1 with the ICDD reference pattern for MFI to determine how closely the two patterns match. The presence of the MFI framework type in the sample is confirmed by a good match between the experimental and reference patterns,

which denotes the development of silicalite-1. It's important to keep in mind that while the ICDD reference pattern offers a trustworthy benchmark, there may be very minor changes in peak locations and intensities as a result of things like sample preparation, instrumentation, and lattice strain. In this experiment there is precise match between the experimental and reference patterns. Which indicates that the silicalite-1 has clearly been developed successfully.

#### **4.1.2 Forrier Transform Infrared spectroscopy(FTIR)**

An approach that can be used to examine the vibrational modes and functional groups contained in a material is called Fourier Transform Infrared Spectroscopy (FTIR). Silicalite-1 has hydroxyl groups bonded to the silicon atoms known as silanol (Si-OH) groups. These groups have broad, strong absorption bands between 2700 and 3200  $\text{cm}^{-1}$ , which point to the O-H bond's stretching vibration.  $\text{SiO}_4$  tetrahedra are joined to one another to form silicalite-1's framework. In the range of 1300-1000  $\text{cm}^{-1}$ , the Si-O-Si bonds' stretching vibrations may be seen. Depending on the unique structure and Si/Al ratio of the silicalite-1 sample, the exact locations and intensities of these bands may change. Specific species on the exterior surface of Silicalite-1 may have been adsorbed there as a result of interactions with the synthesis environment or exposure to the atmosphere. These species may consist of leftover organic molecules, water molecules, or other contaminants. Depending on the concentration and make-up of the adsorbates, their associated vibrational modes may manifest as extra spectral bands. It's crucial to remember that the precise location, strength, and shape of the absorption bands in the FTIR spectrum might change based on a number of variables, including how the sample was prepared, the synthesis circumstances, and the presence of contaminants. It is best to refer to experimental data or study literature sources that provide specific spectral information for this material in order to obtain a more exact and accurate FTIR spectrum of silicalite-1.

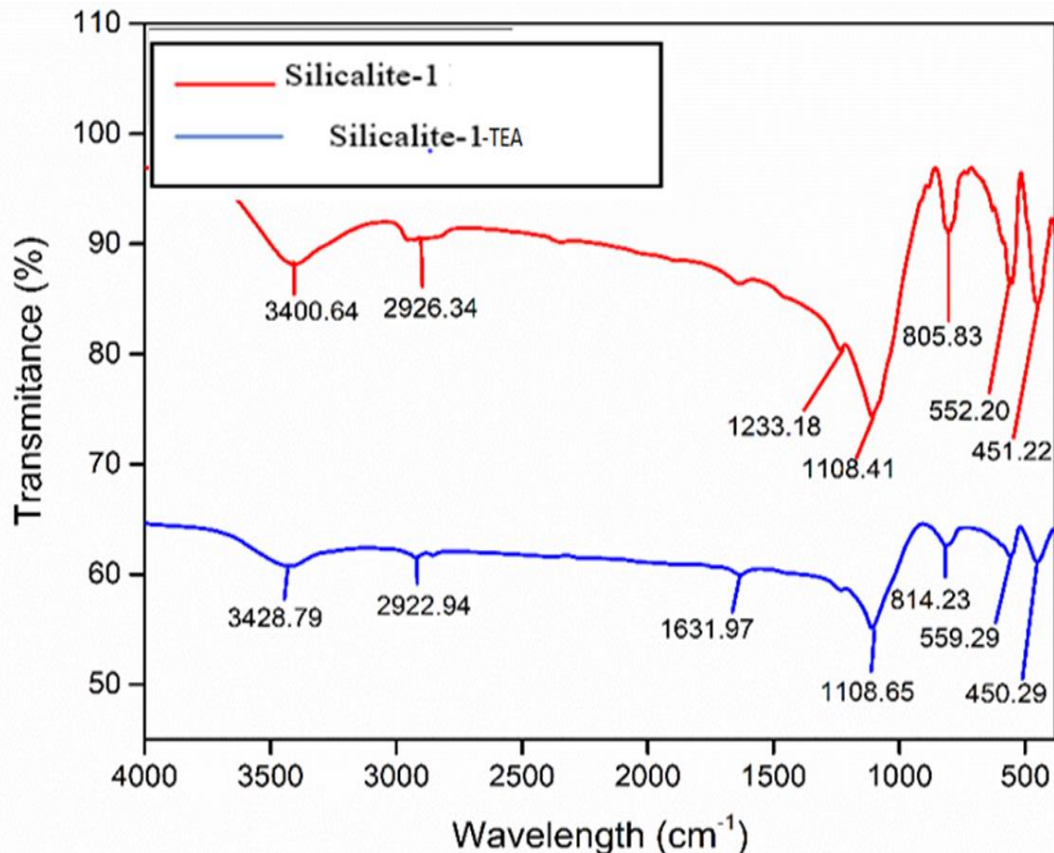


Figure 20: FTIR of Silicalite-1 and Silicalite-1-TEA.

The O–H bond stretching vibration was represented by the broad bands between 3200 and 3600  $\text{cm}^{-1}$  in the FTIR spectrum of the silicalite-1 particles, and the O–H bond bending vibration of the absorbed  $\text{H}_2\text{O}$  was represented by the spectra lie between 1600 and 1700  $\text{cm}^{-1}$ . The FTIR Peak at 814.29 shows the presence of Si-O-Si. The bands that were observed at 559.29 and 1108.65  $\text{cm}^{-1}$  corresponded to five-membered ring chains and structures, respectively[106][106][105][104]. The FTIR of Silicalite-1 TEA show the shift of frequency value 3428.79, 2922.94, 814.23, 559.29 and 450.29  $\text{cm}^{-1}$  to 3400.64, 2926.34, 805.83, 552.20 and 451.22  $\text{cm}^{-1}$ . The absorption peak was observed at 1233.18, which characterizes the presence of TEA. Examine the FTIR spectrum of the amine-modified silicalite-1 that was obtained. Look for distinctive absorption peaks or bands that match the functional groups of amines. The N-H stretching vibrations (3000-3500  $\text{cm}^{-1}$ ), C-N stretching vibrations (1000-1300  $\text{cm}^{-1}$ ), and maybe additional functional group-specific regions are typical regions of interest. However, this depends on the type

of amine alteration. Based on the observed absorption peaks and their assigned values, interpret the FTIR results. To find any changes or new peaks brought about by the amine functionalization, compare the spectra of the amine-modified and untreated silicalite-1. This can reveal whether amine groups were successfully incorporated into the surface of the zeolite.

#### **4.1.3 Scanning Electron microscope**

Set up the SEM instrument first. For optimum performance, make sure the device is calibrated and maintained correctly. Depending on the unique needs of the analysis, adjust the working distance, accelerating voltage, and beam current. Install the prepared sample, making sure it is firmly fastened, onto the SEM sample holder or stage. The sample should be placed so that it is easily accessible from the area of interest. To reduce contamination and electron scattering, create a vacuum inside the SEM chamber. To get the desired resolution and image quality, adjust the electron beam's parameters, such as its energy and spot size. Start using the SEM to image the silicalite-1 submicron spherical particles. Start with a modest magnification to find the important particles, and then gradually boost it for a thorough analysis. To get a complete view of the particles, take many pictures from various perspectives. Energy-dispersive X-ray spectroscopy (EDS) can be used to gather the necessary data on elemental composition. The sample's elements can be analyzed qualitatively and quantitatively using EDS detectors attached to the SEM. This makes it easier to determine which elements are present in the particles. To glean important details about the silicalite-1 particles, examine the acquired SEM pictures and EDS spectra. Take measurements of the particle size, shape, surface morphology, and any other relevant parameters. If an EDS study was done, quantify the distribution and composition of the elements. Interpret the SEM findings in light of the particular study or application. To evaluate the quality and appropriateness of the particles for their intended application, compare the measured features with the predicted silicalite-1 qualities. It is significant to note that the aforementioned stages offer a general framework for SEM investigation of spherical silicalite-1 particles. Depending on the instrument used, the methods used to prepare the samples, and the goals of the analysis, the specifics may change. For accurate and trustworthy results, it is advised to refer to the instrument's user manual and seek advice from skilled SEM operators.

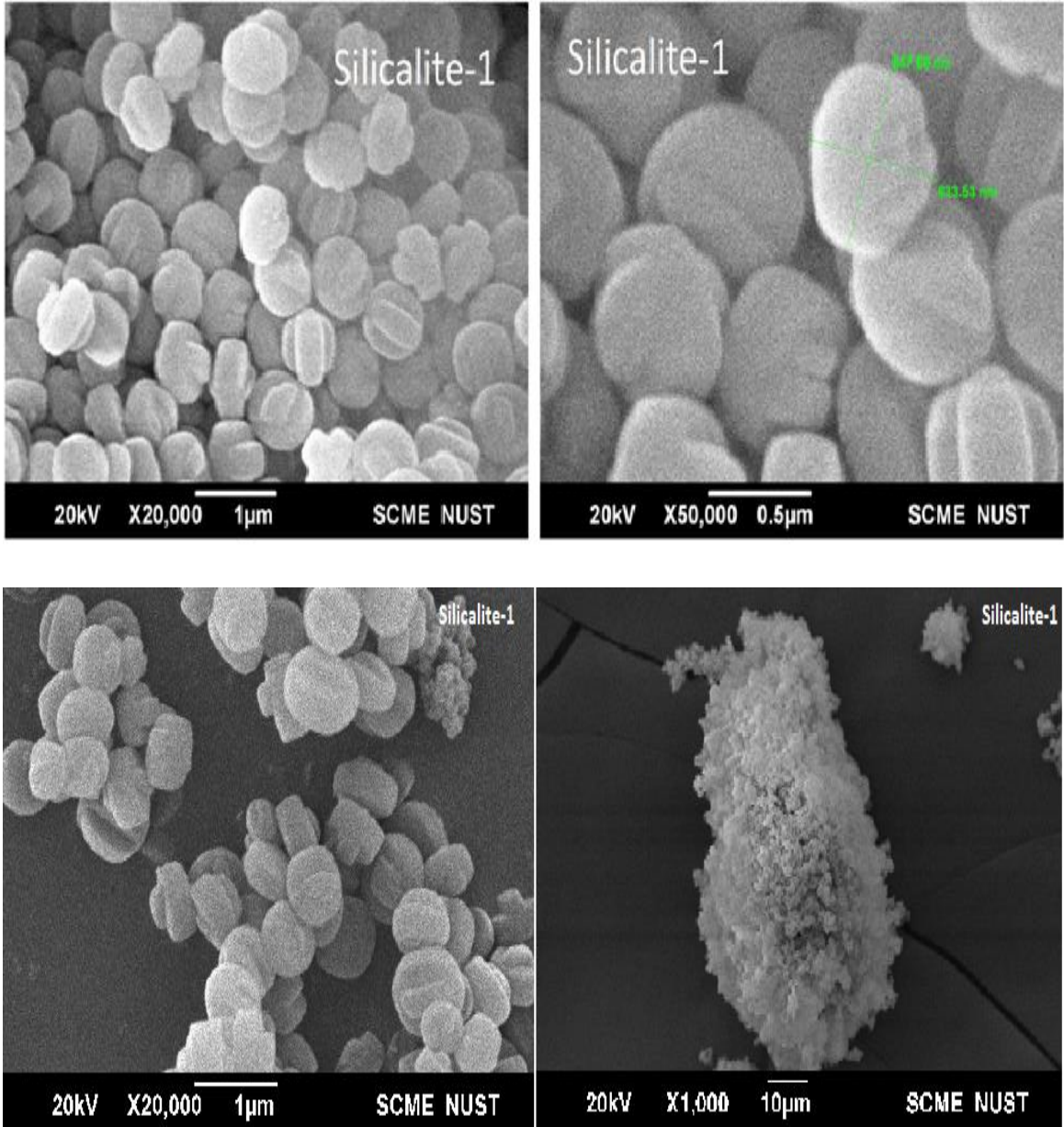


Figure 21: SEM analysis of Silicalite-1



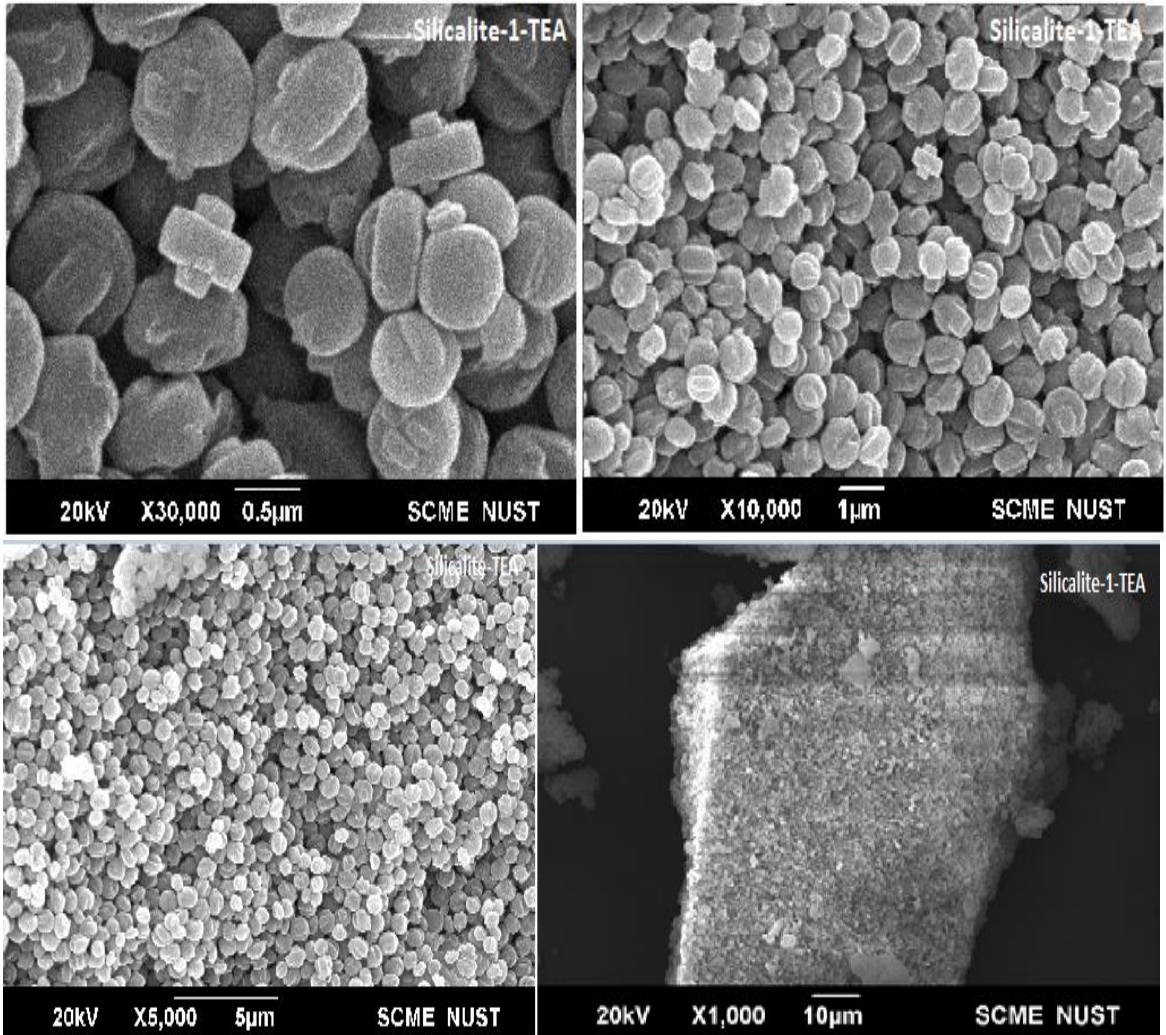


Figure 22: SEM analysis of amine modified silicalite-1

Utilize specialized software or tools to analyze the collected EDX spectra. Finding the characteristic peaks associated with the various elements in the sample involves doing this. By comparing the experimental spectrum to reference spectra or databases, the peaks are often identified. If quantitative analysis is desired, known samples with known compositions or calibration standards can be employed. The range of elements included in the silicalite-1 sample should be covered by these standards. The quantitative elemental composition of the sample can then be calculated by correlating the intensity of the distinctive peaks in the EDX spectrum with the known compositions.

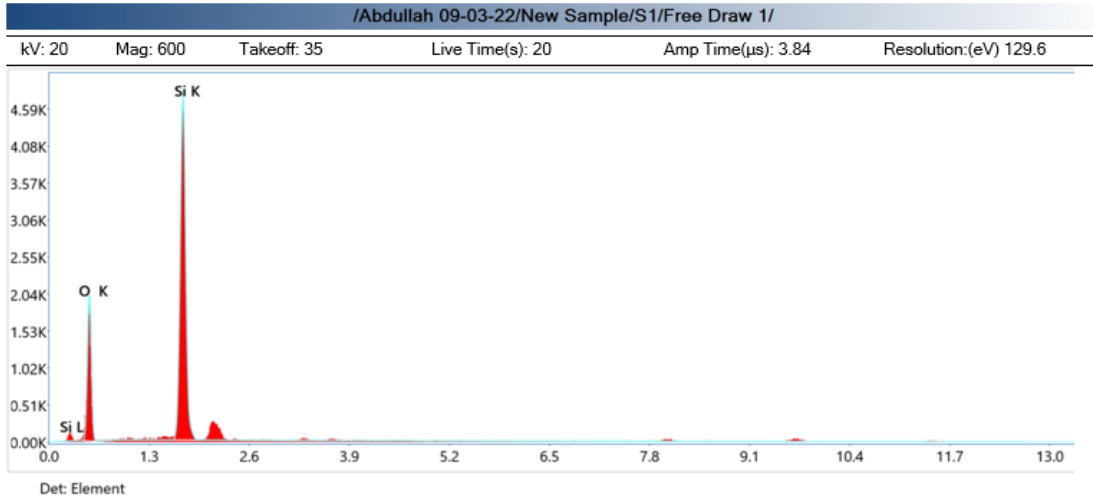
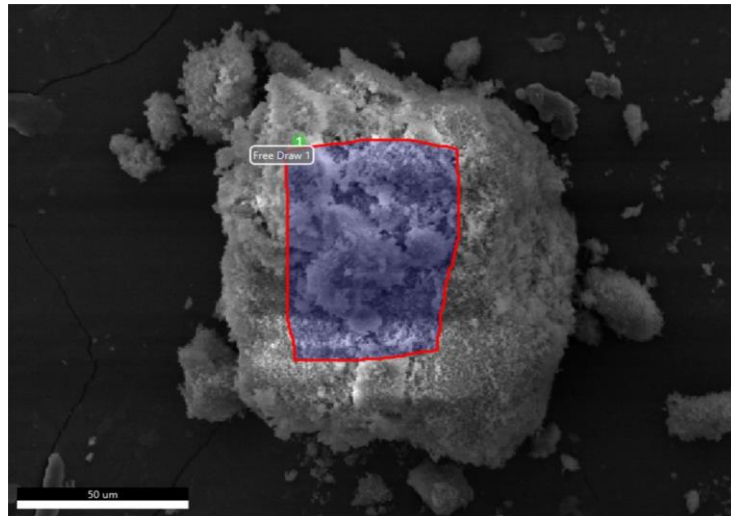


Figure 23: Elemental analysis graph for silicalite-1



**eZAF Quant Result - Analysis Uncertainty: 27.95**

Element	Weight %	% MDL	Atomic %	Error %
O K	51.1	0.27	64.7	10.1
Si K	48.9	0.15	35.3	4.6

Table 7: Elemental percentage in Silicalite-1



EDX accurately showing the presence of only two elements oxygen and silicone which are the building blocks of silicalite-1.

#### **4.1.4 Thermogravimetric Analysis:**

Thermogravimetric analysis, or TGA, is a method for analyzing how a substance decomposes as a function of temperature and its thermal stability. TGA can be performed to examine the thermal stability of silicalite-1 and the presence of adsorbed or occluded species inside its pores. The sample is put through a controlled temperature ramp as part of the TGA analysis, and the mass changes brought on by decomposition, desorption, or other thermal events are tracked. To get rid of any volatile contaminants or moisture that has been absorbed, the silicalite-1 sample is typically dried thoroughly. Making sure the sample is uniform and representative is crucial. A sample pan or crucible with the silicalite-1 sample loaded onto it is placed into the TGA instrument. To obtain precise measurements, the device is calibrated using reference materials. The sample is subjected to a regulated temperature ramp by the TGA equipment, typically from ambient temperature to high temperatures. The required particular analysis will determine the ramp rate and temperature range. The mass of the sample is continually tracked by the TGA device as a function of temperature. Different processes, such as desorption, breakdown, or oxidation, might be indicated by mass changes. The temperature ranges at which mass changes take place and the related mass loss or gain are identified through analysis of the TGA data. Different thermal events, such as the release of adsorbed water or the decomposition of organic contaminants, can be blamed for these modifications. It is possible to ascertain silicalite-1's thermal stability, spot weight gain or loss incidents, and comprehend its behavior at various temperatures by studying the TGA data. This knowledge is useful for determining if silicalite-1 is appropriate for use in certain processes, such as catalysis or gas adsorption, where heat stability is important. A well-known zeolite material called silicalite-1 has a high silica to aluminum ratio and a silica tetrahedral three-dimensional framework structure. One of its important characteristics is thermal stability, which makes it valuable for numerous applications at high temperatures. Silicalite-1 is typically stable up to temperatures of about 600 degrees

Celsius (°C). The material maintains its desirable characteristics and structural integrity at these temperatures. It's crucial to remember that the precise thermal stability of silicalite-1 can vary depending on a number of variables, including the technique of synthesis, impurities, and other circumstances. Graph shows 2% reduction in mass which is actually the water vapours.

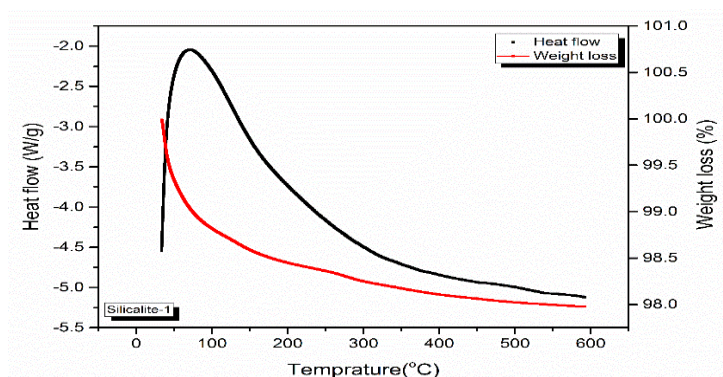


Figure 24: TGA of silicalite-1

Triethanolamine-functionalized A modified form of silicalite-1 is known as silicalite-1, and it has triethanolamine (TEA) groups functionalized on its surface. This alteration may add new qualities or improve already-existing ones. However, the addition of organic functional groups occasionally has an impact on the material's thermal stability. The fact that triethanolamine-functionalized silicalite-1 demonstrated stability in a thermogravimetric analysis (TGA) up to 150 degrees Celsius (°C) shows that the presence of the TEA functional groups may have decreased the material's overall thermal stability in comparison to unprocessed silicalite-1. This discovery might be explained by the deterioration or disintegration of the organic functional groups at lower temperatures. It's crucial to keep in mind that the precise TGA results can change based on the synthesis process, TEA loading quantity, and other experimental circumstances. If the thermal stability of triethanolamine-functionalized silicalite-1 has undergone any recent changes or research.

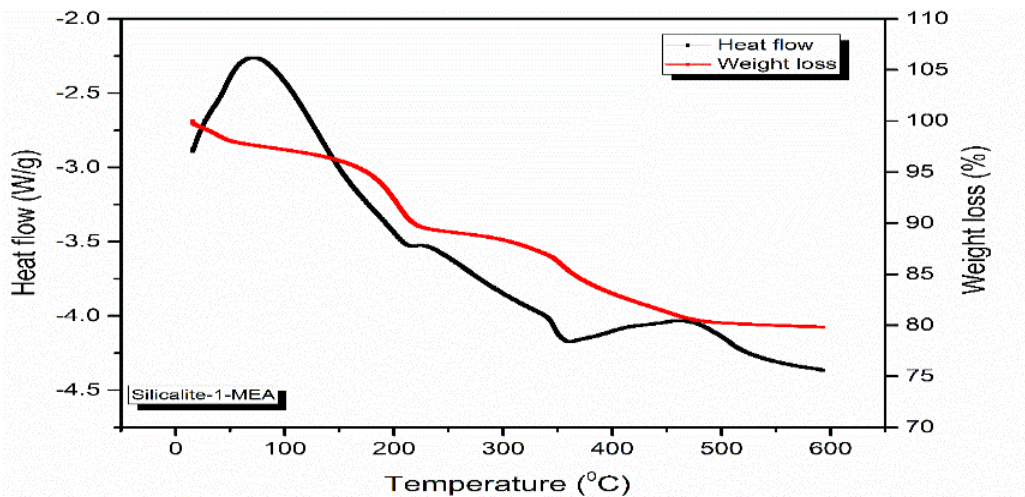


Figure 25: TGA of silicalite-1 (amine modified)

#### 4.1.5 Brunauer-Emmett-Teller (BET) surface area:

A popular material for many uses, particularly in catalysis and adsorption, silicalite-1 is noted for having a high surface area. Silicalite-1's specific surface area can change based on variables like the synthesis circumstances and post-treatment techniques. The surface area of silicalite-1 is typically high, ranging from 300 to 600 square meters per gram ( $\text{m}^2/\text{g}$ ). It's crucial to remember that the stated results can change based on the measuring methods and particular experimental setups utilized to calculate the surface area. It is usual practice to quantify the surface area of porous materials like silicalite-1 using the BET (Brunauer-Emmett-Teller) method. It involves the adsorption of nitrogen gas and determines the surface area using information from the adsorption isotherm. The silicalite-1 BET surface area is frequently claimed to fall within the aforementioned range. The specific surface area of silicalite-1 calculated in this study is  $354 \text{ m}^2/\text{g}$ .

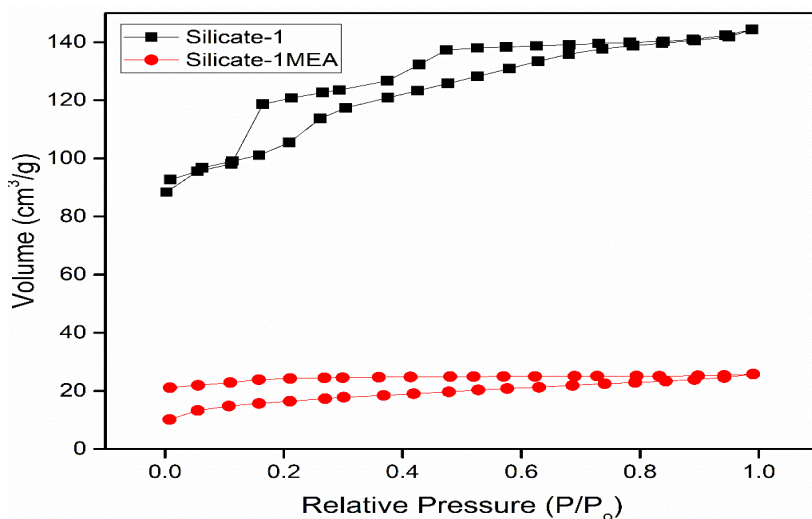


Figure 26: Nitrogen adsorption graph

The BET surface area of triethanolamine-functionalized silicalite-1 material, reported as 54 m<sup>2</sup>/g, indicates that the surface area has decreased in comparison to unprocessed silicalite-1. Triethanolamine functionalization has the ability to add organic groups to the material's surface, perhaps taking up some of the open surface sites and lowering the material's overall surface area. It's crucial to remember that the precise surface area can change based on the synthesis process, the triethanolamine loading quantity, and other experimental circumstances. The surface area of the triethanolamine-functionalized silicalite-1 material generated under the specified circumstances is shown by the reported value of 54 m<sup>2</sup>/g.

Table 8: BET surface area for Silicalite-1 and Silicalite-1-TEA

Adsorbent	BET Surface Area(m <sup>2</sup> /g)	Total Pore Volume (cm <sup>3</sup> /g)	Pore diameter (Å)
Silicalite-1	354.5	0.039	5.5
Silicalite-1 TEA (20%)	54.7	0.017	1.9

## 4.2 CO<sub>2</sub> Adsorption:

### 4.2.1 Silicalite-1

Samples of silicalite-1 tested for the CO<sub>2</sub> adsorption. The CO<sub>2</sub> absorption capacity of silicalite-1 was precisely measured during high-pressure CO<sub>2</sub> adsorption tests utilizing a cutting-edge adsorption analyzer. To evaluate the material's performance at high temperatures, trials were run at 100°C. A CO<sub>2</sub> adsorption capacity of 42 mmol/g was determined by the high-pressure adsorption study of silicalite-1 at 100°C. According to this finding, silicalite-1 has a sizable affinity for CO<sub>2</sub> molecules under the given circumstances. The silicalite-1's potential as an efficient adsorbent for CO<sub>2</sub> capture applications is highlighted by the adsorption capacity that was measured. The measured CO<sub>2</sub> adsorption capacity of 42 mmol/g at 100 °C indicates that silicalite-1 performs exceptionally well at capturing CO<sub>2</sub>. The silicalite-1's potent ability to adsorb CO<sub>2</sub> molecules is probably due to its large surface area and clearly defined pore structure.

Furthermore, the material's stability and adaptability for real-world applications are demonstrated by the elevated temperature of 100°C, which represents an important working condition for CO<sub>2</sub> capture systems. silicalite-1 has a considerable CO<sub>2</sub> adsorption capacity of 42 mmol/g when tested at 100°C using a high-pressure adsorption analyzer. This discovery highlights silicalite-1's potential as a successful CO<sub>2</sub> adsorbent. To improve the material's practical usefulness in CO<sub>2</sub> capture operations, additional research can include refining the synthesis parameters, examining the material's long-term stability, and investigating its regeneration capacity.

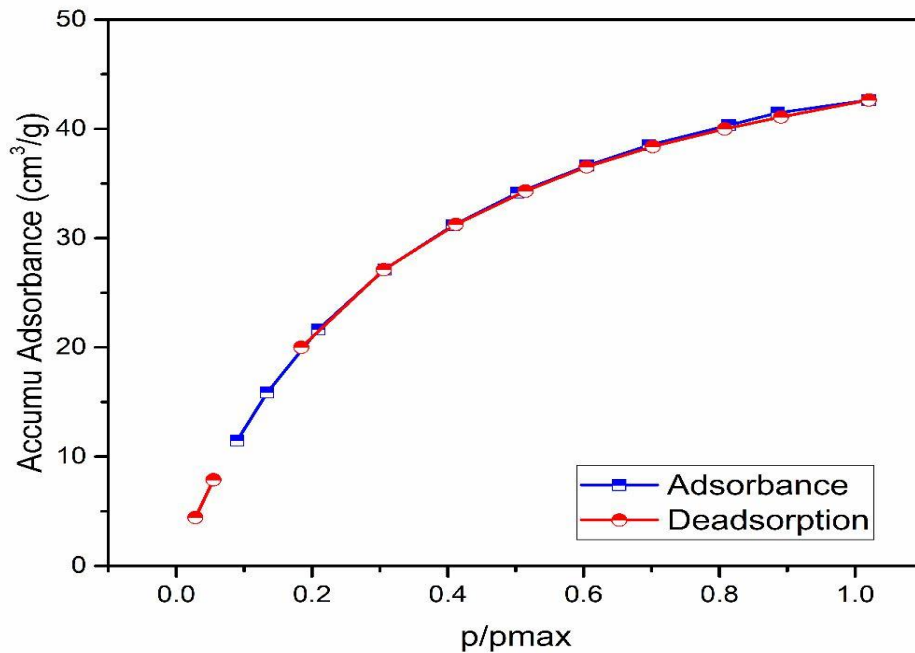


Figure 27: CO<sub>2</sub> adsorption on silicalite-1

Table 9: CO2 adsorption data on Silicalite-1

Equilibrium Ads. Data Sheet

P/Pmax	Absolute Pressure(bar)	Incr.Absorbed (cm <sup>3</sup> /g,STP)	Cumu.Absorbed (cm <sup>3</sup> /g,STP)	Cumu.Absorbed (mmol/g,STP)
1.019980	15.299702	1.557043	42.645449	1.902626
0.890659	13.359880	1.094639	41.088406	1.833158
0.807746	12.116192	1.606990	39.993767	1.784321
0.701781	10.526719	1.849523	38.386777	1.712625
0.604637	9.069555	2.229372	36.537253	1.630109
0.514385	7.715768	3.061343	34.307881	1.530645
0.411937	6.179052	4.138578	31.246538	1.394063
0.305755	4.586328	7.102142	27.107960	1.209421
0.184383	2.765743	7.532060	20.005818	0.892559
0.096261	1.443908	4.596744	12.473758	0.556516
0.054895	0.823430	3.450446	7.877014	0.351433
0.028340	0.425105	4.426567	4.426567	0.197491

Table 10: Desorption data for CO<sub>2</sub> adsorption on Silicaite-1

Equilibrium Des. Data Sheet

P/P <sub>max</sub>	Absolute Pressure(bar)	Incr.Absorbed (cm <sup>3</sup> /g,STP)	Cumu.Absorbed (cm <sup>3</sup> /g,STP)	Cumu.Absorbed (mmol/g,STP)
1.019980	15.299702	1.557043	42.645449	1.902626
0.885761	13.286417	-1.174487	41.470962	1.850226
0.813789	12.206829	-1.129356	40.341606	1.799840
0.696399	10.445978	-1.828308	38.513299	1.718270
0.604709	9.070637	-1.886997	36.626302	1.634081
0.502341	7.535118	-2.491781	34.134521	1.522911
0.407690	6.115346	-2.966271	31.168250	1.390571
0.306924	4.603867	-4.028623	27.139627	1.210834
0.209057	3.135852	-5.509890	21.629737	0.965010
0.134014	2.010216	-5.775525	15.854211	0.707335
0.089498	1.342476	-4.394086	11.460126	0.511293
0.061654	0.924816	-3.266200	8.193925	0.365572
0.043410	0.651154	-2.332747	5.861178	0.261496

#### **4.2.2 Silicalite-1-TEA:**

Samples of silicalite-1 that have been functionalized with triethanolamine were created using [insert functionalization technique]. The structural and surface properties of the material were examined using characterization techniques including [insert techniques]. A cutting-edge adsorption analyzer was used in high-pressure CO<sub>2</sub> adsorption studies to precisely measure the functionalized silicalite-1's CO<sub>2</sub> absorption capacity. To assess the material's performance at high temperatures, trials were conducted at 100°C. A CO<sub>2</sub> adsorption capacity of 16 mmol/g was found in the high-pressure adsorption study of triethanolamine-functionalized silicalite-1 at 100°C. This discovery proves the substance's ability to adsorb CO<sub>2</sub> molecules under the required circumstances. Due to its triethanolamine functionalization, silicalite-1 may be a useful adsorbent for CO<sub>2</sub> capture applications, according to the reported adsorption capability. According to the measured CO<sub>2</sub> adsorption capacity of 16 mmol/g at 100 °C, triethanolamine-functionalized silicalite-1 displays acceptable CO<sub>2</sub> capture adsorption ability. The silicalite-1 surface contains triethanolamine functional groups, which probably improves the substance's affinity for CO<sub>2</sub> molecules. The functionalized material's performance at 100°C also demonstrates its stability and applicability for CO<sub>2</sub> capture methods that operate at high temperatures. A CO<sub>2</sub> adsorption capacity of 16 mmol/g was discovered when triethanolamine-functionalized silicalite-1 was tested for CO<sub>2</sub> adsorption utilizing a high-pressure adsorption analyzer at 100°C. These findings show the material's potential to operate as a powerful adsorbent for CO<sub>2</sub> collection applications. To increase the practical practicality of triethanolamine-functionalized silicalite-1 in CO<sub>2</sub> capture technologies, future study can concentrate on streamlining the functionalization procedure and investigating the material's long-term stability and regeneration capacity.



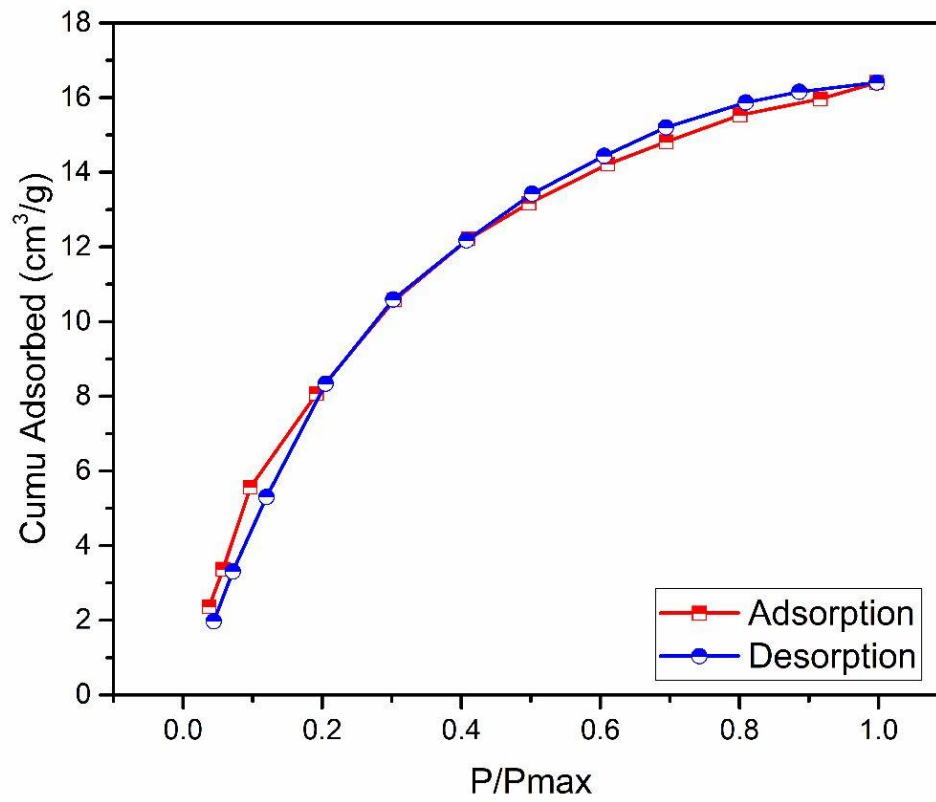


Figure 28: CO<sub>2</sub> adsorption on Silicalite-1-TEA

Table 11: Adsorption of CO2 on silicalite-TEA

Equilibrium Ads. Data Sheet

P/Pmax	Absolute Pressure(bar)	Incr.Absorbed (cm <sup>3</sup> /g,STP)	Cumu.Absorbed (cm <sup>3</sup> /g,STP)	Cumu.Absorbed (mmol/g,STP)
0.997754	14.966316	0.438877	16.408213	0.732052
0.916670	13.750052	0.435469	15.969336	0.712471
0.801187	12.017801	0.715867	15.533867	0.693043
0.694927	10.423906	0.603661	14.818000	0.661105
0.610464	9.156967	1.040437	14.214339	0.634172
0.497612	7.464178	0.962231	13.173901	0.587753
0.410418	6.156274	1.638745	12.211670	0.544823
0.303900	4.558499	2.497839	10.572926	0.471711
0.192198	2.882963	3.069411	8.075087	0.360270
0.096981	1.454721	1.638673	5.005676	0.223328
0.057511	0.862668	1.007910	3.367003	0.150219
0.037213	0.558190	2.359093	2.359093	0.105251

Table 12: Desorption of CO<sub>2</sub> on Silicalite-1-TEA

Equilibrium Des. Data Sheet

P/Pmax	Absolute Pressure(bar)	Incr.Absorbed (cm <sup>3</sup> /g,STP)	Cumu.Absorbed (cm <sup>3</sup> /g,STP)	Cumu.Absorbed (mmol/g,STP)
0.997754	14.966316	0.438877	16.408213	0.732052
0.886011	13.290171	-0.252608	16.155605	0.720782
0.809053	12.135790	-0.285420	15.870185	0.708048
0.694341	10.415121	-0.668637	15.201547	0.678217
0.605997	9.089959	-0.763589	14.437959	0.644149
0.501817	7.527249	-1.013323	13.424636	0.598940
0.407827	6.117403	-1.245847	12.178789	0.543356
0.302271	4.534070	-1.582460	10.596329	0.472755
0.205160	3.077406	-2.257109	8.339220	0.372054
0.119987	1.799804	-3.036528	5.302691	0.236579
0.071614	1.074205	-1.972044	3.330648	0.148597
0.044144	0.662161	-1.357809	1.972839	0.088018

### 4.3 Langmuir Fit Model

The adsorption of gases on solid surfaces, particularly the adsorption of CO<sub>2</sub> on substances like silicalite-1, is frequently described by the Langmuir model. According to the Langmuir isotherm, adsorbate molecules attach to particular adsorption sites on the surface of the adsorbent in a monolayer adsorption process.

The Langmuir equation has the following form:

$$q = (Q_{max} \times C) / (1 + C \times K)$$

Where:

- $q$  is the amount of gas adsorbed (in moles or grams per unit mass of adsorbent) at a specific equilibrium pressure.
- The maximum adsorption capacity, measured in moles or grams per unit mass of adsorbent, is known as  $Q_{max}$ .
- The gas's equilibrium concentration (in units of pressure or concentration) is denoted by the letter  $C$ .
- The adsorption equilibrium constant, or Langmuir constant (in units of concentration or pressure), is  $K$ .

Experimental data of CO<sub>2</sub> adsorption at various equilibrium pressures can be gathered to establish the maximum adsorption capacity ( $Q_{max}$ ). The values of  $Q_{max}$  and  $K$  can then be calculated by fitting the Langmuir equation to the data using a nonlinear regression technique, such as the least squares method.

The steps for fitting the Langmuir model to experimental data are as follows:

Gather data from experiments: Calculate the quantity of CO<sub>2</sub> that has been absorbed by silicalite-1 at various equilibrium pressures or concentrations.

Make a data plot: Make a graph with the amount of CO<sub>2</sub> adsorbed on the y-axis and the equilibrium pressure or concentration on the x-axis.

Nonlinear regression: Apply the Langmuir equation to the experimental data and do a nonlinear regression analysis using the appropriate software or computer language. The  $Q_{max}$  and  $K$  values that best suit the data will be estimated by the software.

Consider statistical indicators like the coefficient of determination ( $R$ -squared) or the sum of squared residuals to evaluate the fit. A better fit is indicated by a greater  $R$ -squared value or a lower sum of squared residuals.

Find the maximum adsorption capacity: The maximum adsorption capacity of  $CO_2$  on silicalite-1 under the specified experimental conditions is represented by the estimated value of  $Q_{max}$  from the regression analysis.

The Langmuir model relies on ideal conditions and a uniform adsorbent surface, which may not necessarily be true in real-world systems. Further evidence for a more thorough knowledge of the adsorption behavior can come from experimental data at various pressures and temperatures.

#### 4.4 Langmuir data for $CO_2$ adsorption on silicalite-1:

Langmuir fit model where  $R^2$  value is showing that it is highly fit model.

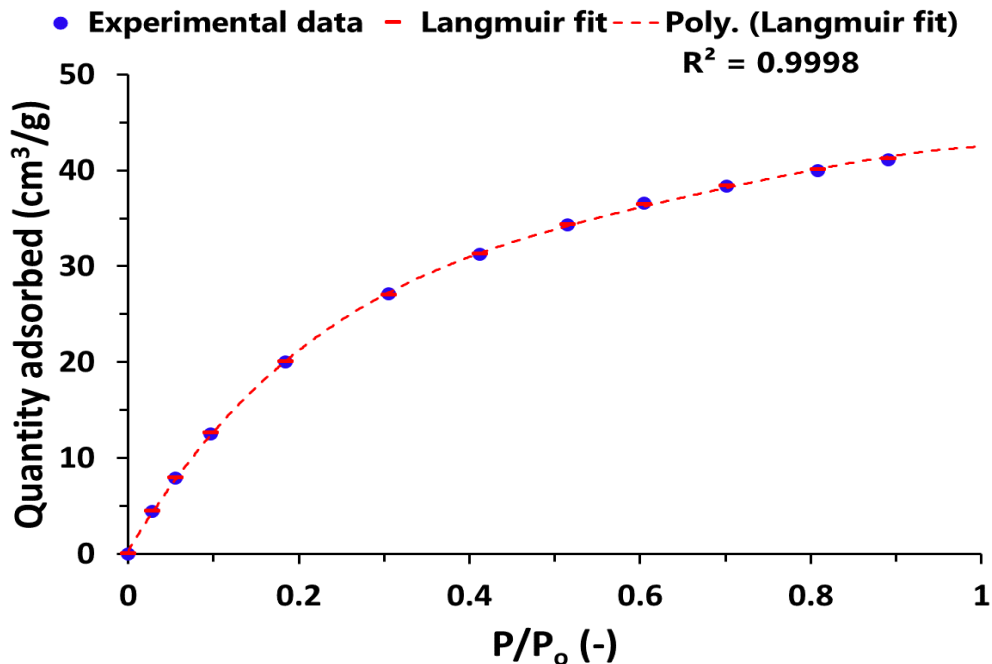


Figure 29: Langmuir Fit model

Table 13: Langmuir Data for Silicalite-1

	Slope	Intercept	$V_L$ ( $\text{cm}^3/\text{g}$ )
Silicalite-1	0.0176	0.0893	56.8

#### 4.5 Langmuir fit model for CO<sub>2</sub> adsorption on amine functionalised silicalite-1:

Langmuir model can be more suited depending on the precise properties of the adsorbent and the adsorbate. For a thorough knowledge of the adsorption behavior on amine silicalite-1 experimental data at various pressures and temperatures are helpful.

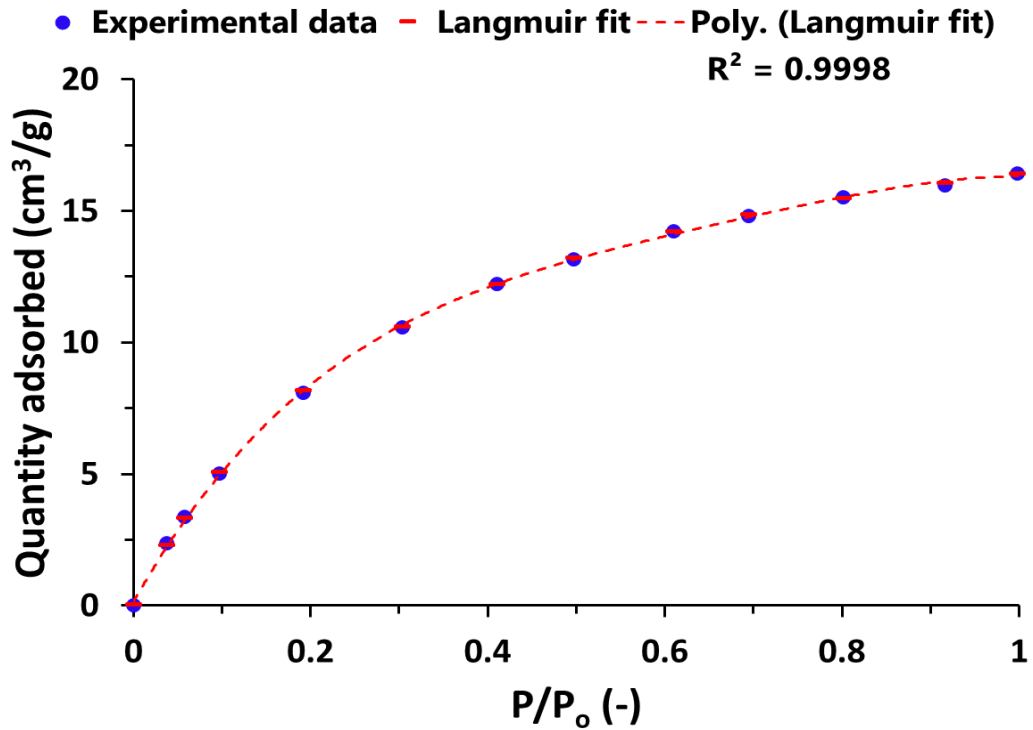


Figure 30: Langmuir Fit model of silicalite-1-TEA

Table 14: Langmuir data for silicalite-1-TEA

	Slope	Intercept	$V_L$ ( $\text{cm}^3/\text{g}$ )
Silicalite-1	0.04652	0.02180	21.49
TEA			

#### 4.6 Breakthrough curves for CO<sub>2</sub> adsorption:

The amount of the adsorbate (in this case, CO<sub>2</sub>) in the effluent stream as a function of time is shown as a function of time on a breakthrough curve, which is a graph illustrating the adsorption process over time. The CO<sub>2</sub> adsorption on silicalite-1 breakthrough curve depicts the dynamic behavior of the adsorption process up until the breakthrough point, where the concentration of CO<sub>2</sub> in the effluent starts to significantly increase.

Here are the parameters that are used in this modelling:

Assumptions:

- The system operates under isothermal condition.
- Negligible pressure drop through the adsorbent bed.
- Velocity is assumed to be constant throughout the bed.
- Langmuir isotherm is valid for the system.
- there is no axial or radial dispersion.
- The bed is clean initially.

Table 15: Parameters for Modelling

Parameters	(Units)	Values
Bed Length	(cm)	3
Porosity	(-)	0.4
Velocity	(m/s)	0.12
B	(m <sup>3</sup> /Kg)	0.09, 0.021
q <sub>m</sub> (max. adsorption capacity)	(cm <sup>3</sup> /g)	56.8, 21.49
C <sub>0</sub> (inlet concentration of CO <sub>2</sub> )	(Kg/kg)	0.999
ρ <sub>p</sub>	(Kg/m <sup>3</sup> )	1.87

Equation Solved in Matlab

$$u \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} + \frac{1 - \epsilon}{\epsilon} \rho_p \frac{15 D_e}{R_p^2} \left( \frac{q_m b c}{1 + b c} - q \right) = 0$$

$$\frac{\partial q}{\partial t} = \frac{15 D_e}{R_p^2} \left( \frac{q_m b c}{1 + b c} - q \right)$$



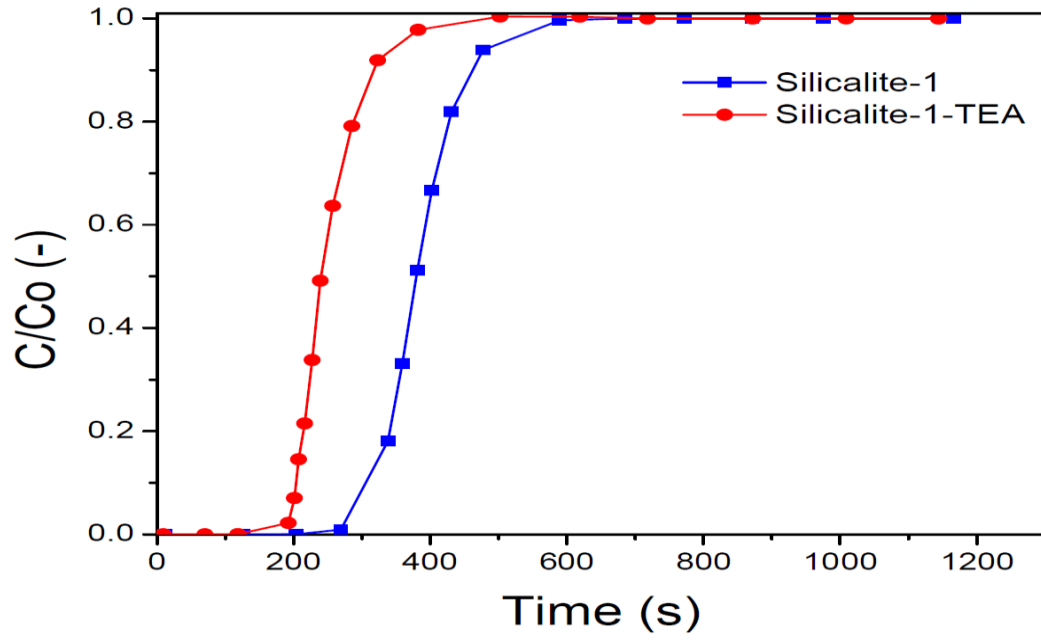


Figure 31: Breakthrough Curves 4.7 Modelling Code:

```

clear
clc
close all

%input data
eps=0.8f
u=0.01f
%1500/Rp^2=1
a=0.05f
b=0.75f
qm=0.01425f
co=1f
thop=1000f

%increment for length
L=0.5f
Ns=100f
z= linspace(0, L, Ns)
dz=z(2)-z(1);

%time
t=0:1200f

%initial condition
IC=zeros(1,Ns); %PPF
ICb=zeros(1,Ns); %O2C
IC=ICa, ICb);

%ODE solver
[c y]=ode15s(@f, c, IC, [1, eps, u, a, b, qm, co, thop, Ns, dz]);

%extract results
c=y(:,1:Ns);
qm=y(:,Ns+1:2*Ns);

%input BC
c(1,1)=co;
c(1,end)=(4*c(1,end-1)-c(1,end-2))./3; %use backward secondary order error
q(1,end)=(4*q(1,end-1)-q(1,end-2))./3;

%visual
figure(1)
imagesc(c,c)
colormap jet
title('concentration')
xlabel('time')
ylabel('Length of Bed (m)')
figure(2)

%plot breakthrough curve
c=end-c(:,end);
plot(c,:,'r');
hold on;
plot(c,:,'b');
title('Breakthrough Curve')
xlabel('time')
ylabel('c/co')

%function
function dydt=f(t,y,eps,u,a,b,qm,co,thop,Ns,dz)
dydt=zeros(length(y),1);
dodt=zeros(Ns,1);
dqdt=zeros(Ns,1);

%define values
c=y(1:Ns);
qm=y(Ns+1:2*Ns);

%boundary condition
c(1)=co;
c(end)=(4*c(end-1)-c(end-2))./3; %use backward secondary order error

%interior
for l=2:Ns-1
dqdt(l)=a*(qm.*b.*c(l)./(1+b.*c(l))-q(l));
dodt(l)=(c(l+1)-c(l-1))./2./dz;
dodt(l)=-u*(dodt(l))-thop*(1-eps)./eps.*dqdt(l);
end
dydt=[dodt;dqdt];
end

```

## Conclusion and Recommendation

Numerous studies have been conducted on Silicalite-1, a zeolite material with a high surface area and homogenous pore structure, to determine its adsorption capabilities. In this investigation, the Langmuir fit model was used to assess and contrast the adsorption capabilities of pure silicalite-1 and silicalite-1 that had been modified with amines. The results showed that amine modification significantly increased adsorption per unit area, suggesting that amine-functionalized silicalite-1 may be an effective adsorbent. Pure silicalite-1 and silicalite-1 treated with amine were found to have initial adsorption capabilities of 1.9 mmole/g and 0.7 mmole/g, respectively. According to these findings, the amine alteration resulted in a reduction in adsorption capacity. It is crucial to remember that comparing adsorption capabilities does not, by itself, give a complete picture of the performance of the adsorbent. To determine the adsorption effectiveness per unit surface area, more research is necessary. The equilibrium between the adsorbent and adsorbate systems was investigated using the Langmuir fit model. The maximum adsorption capacity and the affinity of the adsorbate-adsorbent interactions are revealed by this model, which assumes a monolayer adsorption process. The adsorption capabilities of the materials were determined by fitting the experimental data to the Langmuir model while accounting for the surface area available for adsorption.

Adsorption per Unit Surface Area: Pure silicalite-1 had an adsorption per unit surface area of 0.0053 mmol/m<sup>2</sup>, but silicalite-1 that had been treated with amine had an adsorption per unit surface area of 0.013 mmol/m<sup>2</sup>. This considerable increase in adsorption per unit area following amine modification indicates that silicalite-1's adsorption effectiveness was improved by the addition of amine functional groups. The results of comparing the adsorption capacities of pure silicalite-1 with silicalite-1 that had been treated with amine showed that the latter had less adsorption capacity. However, the amine-modified silicalite-1 showed a much greater adsorption effectiveness compared to the pure form when taking into account the adsorption per unit surface area. This finding emphasizes how crucial it is to evaluate adsorbents based on their performance per unit surface area as opposed to just considering their overall adsorption capacity. Future recommendation is to explore the amine functionalized silicalite-1 material for the selectivity and study the detail kinetics for the CO<sub>2</sub> reaction with the amines.

Table 16: Comparison for Whole Study

	Surface area (m <sup>2</sup> /g)	Adsorption capacity (mmole/g)	Adsorption capacity (mmole/m <sup>2</sup> )
<b>Silicalite-1</b>	354.7	1.92	0.0053
<b>Silicalite-1-TEA</b>	54.7	0.732	0.013

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