A Comparative Study of CO_2 Adsorption on amine Functionalized MCM-41 and Silicalite-1 Materials

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DEDICATION

By the grace of Almighty Allah, who is the most Beneficent and the most merciful

This research is dedicated to my parents, who have always been my source of guidance and support.

To my supervisor who shared his knowledge, gave advice, and encouraged me to fulfill my tasks.

And to all my fellows, with whom I worked with and shared good memories.

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ACRONYM

ICDD: International Centre for Diffraction Data

MFI: Mean filling index

SEM: Scanning electron microscope

TGA: Thermogravemetric analysis

FTIR: Forrier transform infrared spectroscopy

BET: Brunauer-Emmett-Teller

TEA: Triethanol amine

FAU: Faujasite

TPOAH: Tripropyl ammonium hydroxide

TEOS: Tertra Ethyle orthosilicate

EDAX: Energy dispersive X-Ray analysis

ABSTRACT

The primary cause of climate change is rising atmospheric carbon dioxide (CO_2) levels, which has sparked a lot of research into carbon capture and storage (CCS) technology as a vital tactic for reducing greenhouse gas emissions. In this regard, the current work compares the CO_2 adsorption capabilities of two different materials, silicalite-1 and MCM-41. These materials' distinct structural and chemical characteristics have attracted a lot of interest because of their possible use in CCS. In order to confirm the structural and functional properties of the amine-functionalized MCM-41 and Silicalite-1 materials, (XRD), (SEM), and (FTIR) were used in the experimental examination. The CO_2 adsorption capabilities of both materials were then assessed in a range of settings, such as amine functionalization levels, pressure, and temperature. The study's findings provide important new information about how CO_2 adsorbs on these materials. More specifically, better CO_2 adsorption capability was demonstrated by the amine-functionalized MCM-41 over Silicalite-1, especially at lower temperatures and higher pressures. It was also noted that amine functionalization improved CO_2 adsorption; for both materials, more amine loading led to better adsorption performance. Additionally, a detailed examination of the adsorption kinetics and isotherms for both materials yields important details about how well-suited they are for use in real-world CCS systems. These results add to the expanding body of information regarding CO_2 adsorption materials and provide insightful direction for the creation of effective and long-lasting carbon capture devices. In summary, this comparative study highlights the importance of material selection and functionalization levels in the search for efficient CCS solutions by illuminating the CO_2 adsorption capacities of amine-functionalized MCM-41 and Silicalite-1 materials. The trials were conducted at various pressures (0–15 bar) and temperatures (100°C). The quantity of CO_2 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_2 adsorption on silicalite-1. It was discovered that MCM-41 and silicalite-1's CO_2 adsorption capability increased with pressure and decreased with amine Functionalization

CHAPTER 1: INTRODUCTION

1.1. Background

Carbon dioxide excretion from human-caused sources has accelerated the rate of global warming. As a result, there is an urgent need to cut carbon dioxide emissions. This century, the only one that the world has ever known, has seen more progress than any other in human history[1, 2]. It is not easy to think about a future without the energy given by fossil fuels. Demand of energy from fossils fuels is increasing at a very high rate and is likely to be remaining as it if for the foreseeable future, growing in lockstep with the population and economy[3]. The vast majority (86%) of global energy is produced by the use of different fuels found underneath the earth Use of fossil fuels accounts for a significant amount of the carbon dioxide (CO_2) emissions emitted by various businesses, accounting for 75% of the emissions[4, 5]. These industries include synthetic ammonia facilities, cement plants, fossil energy plants, and refineries. CO_2 is the most important greenhouse gas and primary contributor in climate change and global warming[6]. CO_2 is a pollutant in the atmosphere that exists in addition to the emissions that are produced into it during the combustion of fossil fuels; CO_2 is one of the contaminants in the atmosphere. A variety of procedures, including those using fuel gas as well as natural gas, which also involve purification of gas. In addition, 40% of natural gas retains are often polluted by nitrogen and carbon dioxide, and this contamination usually happens during the extraction process. US pipelines standards has said, those types of gaseous fields can only be permitted if Carbon dioxide emissions are eradicated or lessened below 2percent mole percentage. Many methods for extracting CO_2 from gaseous based streams have come into existence, including absorption by chemical ways, separation by membrane and cryogenic based separation, and adsorption separation[7, 8]. The chemical absorption method, which employs aqueous alkanol amines as solvents, is a widely used and validated technology for the removal of carbon dioxide (CO_2). Unfortunately, this process has a number of significant drawbacks, including low CO_2 loading capacity, large equipment size, solvent deterioration, equipment corrosion, high regeneration energy, which accounts for 70% of a CO_2 capture plant's overall operating costs, the requirement to maintain a low solvent composition (less than 30% MEA) as a result of these constraints, and environmental issues caused by solvent deterioration[9]. Separation based on membrane for CO2 separation have also been developed and are now commercially accessible. CO2 separation may be advantageous if the CO2 level in the gases which came out from the channel of the post-combustion system is greater than 20%[10]. This technology has several disadvantages, including low volume and poor temperature properties, sensitivity tosulfur bases compounds and traces of other elements, decreased CO2 permeability in the existence of water, multistage separation caused by continuous use, plasticization, and deficiency of high permeability as well as selectivity. Cryogenic technique benefits gaseous streams with a rising carbon dioxide attentiveness—ideally more than 90percent of the gross. Mixture that is based on gas must be cooled to an utmost low temperature of -73.3 celsius in degree in order for CO_2 to freeze or liquefy[11, 12]. This technology has a number of disadvantages, including concerns are the high energy requirements of cooling, particularly in diluted gas streams, and the possibility of water or higher hydrocarbons blocking the heat exchanger. The coating of solid CO2 that accumulates on heat exchanger surfaces reduces process efficiency and adds to the drop in pressure that occurs during operation. Process of Adsorption is gaining popularity as a low-cost, high-efficiency technology[13-15]. It was possible to distinguish between adsorption by physical techniques and absorption by chemical processes. The majority of adsorptions are of physical varietyMesoporous silica, activated carbon, activated carbon fibre, and other physical adsorbents are examples. Physical adsorption's capacity to absorb CO2 at a given temperature, on the other hand, would be substantially smaller[16]. It is also demonstrated that capacity to selectively absorb carbon dioxide has a limit. suggested that the capacity to particularly absorb CO2 was limited[17]. To alleviate the problems associated with adsorption by physical techniques, the outer layer of the rigid adsorbent are permeate with alkanol-amines frequently used in absorption, for example (mono-ethanolamine), (di-ethanolamine), and (tri-ethanolamine)[17]. Chemical absorption studies have been conducted because these alkanolamines can selectively absorb carbon dioxide.Mesoporous silica, an adsorbent material, can absorb alkanolamines.Because of the strong amine-susceptibility of its silanol groups, amine impregnation occurs frequently in mesoporous silica.Furthermore, the size and distribution of its pores are consistent[18]. Adsorbent materials of various types have been produced with the purpose to separate carbon dioxide through process of adsorption. Beck et al. developed the siliceous mesoporous material known as Mobil Composition of Matter No. 41, or Si-MCM-41, in 1992[19]. It may also be used as adsorbent for carbon dioxide extraction because of its outstanding characteristics, for example its well-organized cylindrical structure, large volume of the pore (0.7 cm3/g), and high area of the surface (>700 m2/g), SiMCM-41 has between 40% and 60% hydroxyl (silanol) groups on its surface[20]. This may made it more simpler to modify the surface abilities of the product. Because amines have a basic nature, they are used in processes based on chemical absorptionto capture carbon dioxide. As previously stated, much research is presently being conducted on the immobilisation of amines on rigid materials as adsorbents with high carbon dioxide adsorption capacity. CO2 can be collected in both open and closed situations using amine-based solid adsorbents. Enclosed spaces include submarines, amphibious vehicles, and spacecraft. Introducing amino groups into the chemistry which relates to the surface .Si-MCM-41 may enhance the efficacy of carbon dioxide adsorption. Neverthless, in order to create new amine-functionalized materials for carbon dioxide adsorption, it is important to inquire the influence of functionalization escortedby diverse amine class[21].

Silica adsorbent is one of the mesoporous materials used for CO_2 capturing. The CO_2 adsorption capacity of PEI (70%)/SiO_2 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[22]. MOFs have a high surface area and volume and show high selectivity for CO_2 at lower temperatures. The limitation of MOFs is that their synthesis process is costly, complex, and harmed by water vapor adsorption and shows degradation on thermal treatment[23]. 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[24]. 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[25].

1.2. Silicates

Silicates are minerals and compounds made largely of silicon (Si) and oxygen (O) atoms, with additional elements such as aluminum (Al), iron (Fe), magnesium (Mg), and calcium (Ca) present in different quantities. Silicates are one of the most numerous and diversified mineral groupings on Earth, accounting for a large amount of the planet's crust. They are important in geological processes as well as in a variety of industrial, technological, and environmental applications[26, 27]. Silicate materials can be customized to have large surface areas and porosity, both of which are required for efficient gas adsorption. Porous silicates with well-defined apertures, such as zeolites and mesoporous silicas, have a huge surface area and may effectively absorb CO_2 molecules. Silicates can be altered or functionalized to increase their chemical affinity for carbon dioxide (CO_2). To facilitate adsorption, functional groups can be added to the silicate framework to produce active sites that interact strongly with CO_2 molecules[28].

1.3. Types of Silicates

1.3.1. SBA-1

SBA-1 is predominantly comprised of silicon and oxygen, resulting in the formation of a framework based on silica. This material is classified within the family of mesoporous materials, which are distinguished by their well-organized pore structures on the nanoscale. SBA-1 distinguishes itself from other mesoporous silicas due to its unique hexagonal arrangement of mesopores, which imparts it with distinctive characteristics and confers several advantages for diverse applications[29]. The mesopores of SBA-11 are famous for having a hexagonal arrangement. Because of its regular pore structure, which allows for a high degree of control over pore size and distribution, this material is excellent for applications that require a high level of precision [30].As a result of the porous structure of SBA-11, it has a significant amount of surface area. This high surface area is beneficial for processes involving adsorption, catalysis, and drug administration because it enables enhanced interactions with the molecules involved in these processes. SBA-1 is shown in Fig 1

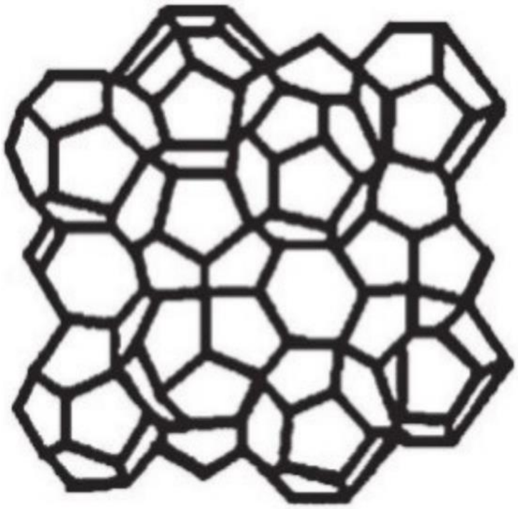

Figure 1 : SBA-1 Silicate

1.3.2. SBA-12

SBA-12 is a silicate-specific form of mesoporous molecular sieve material. It is a member of the family of SBA (Santa Barbara Amorphous) mesoporous materials. In its framework structure, SBA-12 is primarily composed of silica (SiO2) and may also contain aluminum (Al) or titanium (Ti). The precise composition can vary based on the synthesis techniques employed[31]. SBA-12 is classified as a mesoporous material, which indicates that it has a well-defined pore structure with nanometer-sized pores (typically 2-50 nm). These pores are highly organized and modifiable in terms of size and shape. P6mm denotes the characteristic hexagonal pore structure of SBA-12. SBA-

12 is beneficial for adsorption operations because to the fact that its pore size may be adjusted and that it has a high surface area[32]. It is possible to use it as an adsorbent for a wide variety of gases and liquids, as well as in the separation of gases and the removal of contaminants from wastewater.

1.3.3. SBA-15

Another type of mesoporous material belonging to the SBA (Santa Barbara Amorphous) family, SBA-15 is a silicate and counts as one of the SBA's mesoporous materials. SBA-15 has a well-ordered mesoporous structure, just like SBA-12 does; yet, its properties and uses are quite different from those of SBA-12. SBA-15 is predominantly composed of silica (SiO2), but its framework may also contain trace amounts of other elements that function as dopants. The silica framework is the primary structural component of SBA-15, which is responsible for the unique properties of the substance. The structure of SBA-15 is characterized by a hexagonal mesoporous network with well defined cylindrical pores. The pore size in SBA-15 normally ranges from 5 to 30 nanometers (nm), which enables it to be utilized in a diverse assortment of contexts. P6mm is the designation given to the hexagonal pore structure, which is quite close to SBA-12. SBA-15 is useful for adsorption applications due to the well-defined mesopores found throughout the material. It is also useful for the controlled release of compounds that have been kept as well as the removal of impurities from gases and liquids[33]. SBA-15 is shown in Fig 2

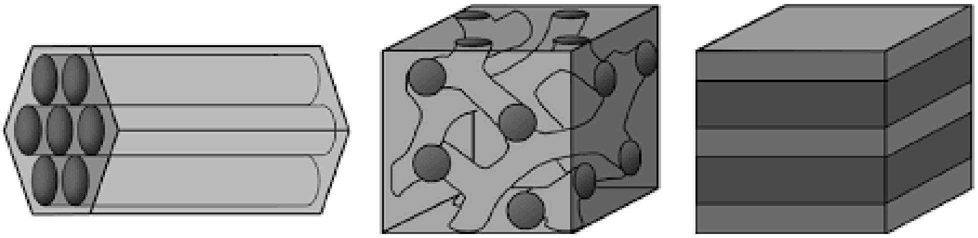

Figure 2 : Structure of Mesoporous Silica SBA-15

1.3.4. SBA-16

Mesoporous silica materials are a broader category that includes mesoporous materials like SBA-16, which is a form of mesoporous material. It is distinguished in particular by the well-ordered hexagonal arrangement of pores that it possesses as well as by the large surface area that it possesses. The abbreviation "SBA" refers to "Santa Barbara Amorphous," which was the original name given to the substance by its creators, who were scientists working at the University of California, Santa Barbara. Because it is predominantly made up of silicon and oxygen atoms, SBA-16 can be classified as a silica-based substance. In the course of its synthesis, it frequently makes use of organic surfactants and templates, both of which contribute to the organization of its pore network. The highly organized hexagonal pore structure of SBA-16 is one of the most distinguishing characteristics of this material. This regular arrangement of pores provides it a distinct edge in a variety of applications, particularly in the fields of catalysis and adsorption. In general, SBA-16 materials have a high surface area, which is essential for applications that require a large surface area, like the adsorption of gases and liquids. Because of its organized pore structure and wide surface area, SBA-16 is well suited for adsorption operations such as the purification of chemicals, the removal of pollutants from the environment, and the adsorption of gases and liquids[34]. SBA-16 is shown in Fig 3

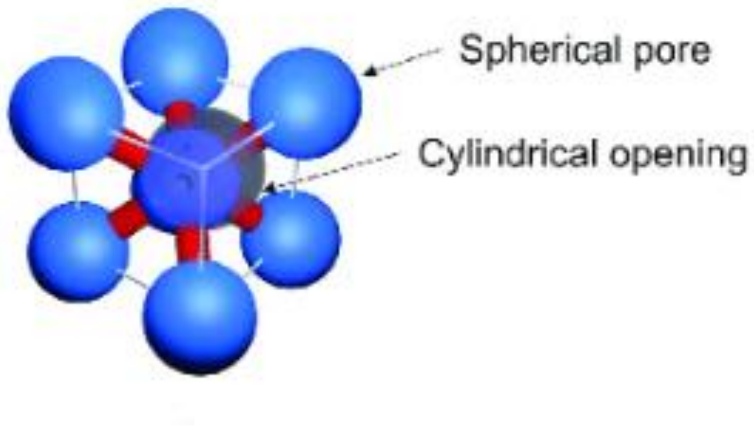

Figure 3 : Structure of Silica SBA-16

1.3.5. KIT-5

The mesoporous silica material known as KIT-5 is a type of material that belongs to a family of materials that are utilized in a variety of scientific and industrial applications. Mesoporous materials like KIT-5 are well-known for having well-defined pore architectures and high surface areas, both of which make them useful in fields such as catalysis, adsorption, and drug delivery. Because it is predominantly made up of silicon and oxygen atoms, KIT-5 can be classified as a silica-based substance. Its structure often consists of well defined mesopores that are arranged in a predictable pattern. The KIT-5's organized and modifiable pore structure is one of its most distinguishing characteristics. During the synthesis process, the size and shape of these pores can be altered, and they commonly exhibit a hexagonal or cubic array of pores. commonly, the pores are arranged in a grid. In applications requiring adsorption, catalysis, and drug delivery, one of the most important characteristics required is a material with a high surface area, which KIT-5 materials are known to possess. Because of the vast surface area, there are many of active sites available for interactions with molecules. In order to successfully synthesize KIT-5, it is customarily necessary to make use of control agents, silicate sources, and surfactants. To drive the production of the mesoporous structure, these components are carefully selected and regulated before the process begins. It is possible to fine-tune the material's properties, such as its pore size and surface area, by altering the conditions under which the material was synthesized. Because of its clearly defined mesoporous structure as well as its large surface area, KIT-5 is an excellent candidate for adsorption operations. It is useful in applications such as environmental remediation and purification because it may be used to adsorb gases, liquids, and pollutants[35]. KIT-5 is shown in Fig 4

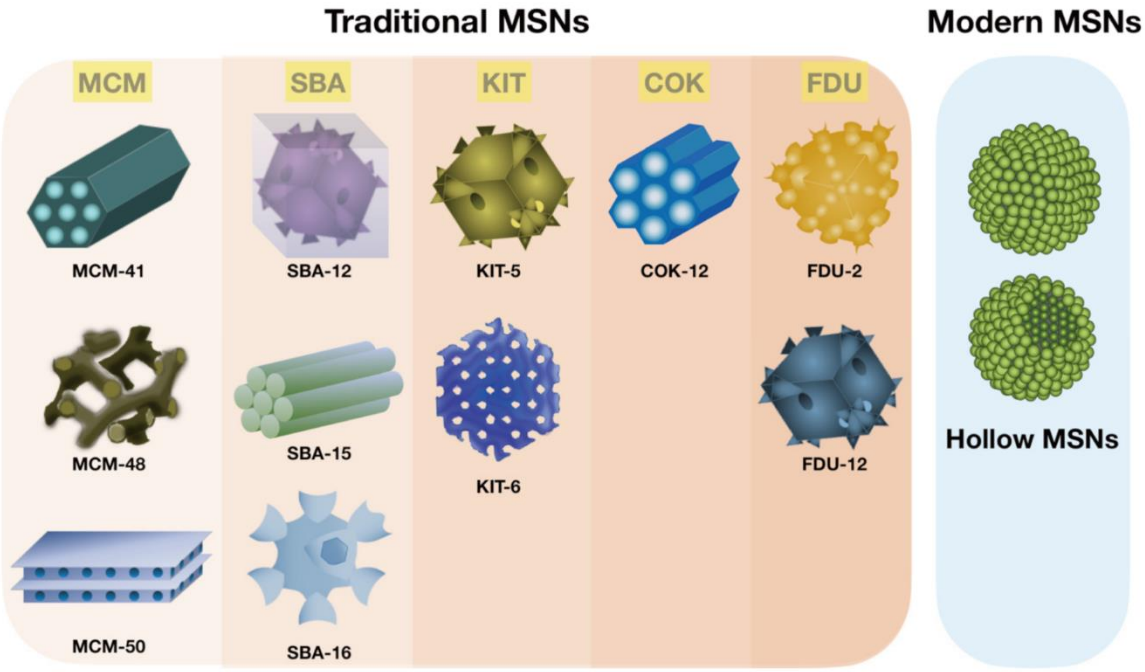

Figure 4 : The Construction of MSNs via different strategies

1.3.6. FDU-12

The mesoporous silica material known as FDU-12 is a form of mesoporous material that belongs to the family of mesoporous materials that are noted for their clearly defined pore architectures and high surface areas. In the same way as other mesoporous silica materials do, FDU-12 possesses exceptional qualities that make it useful in a wide variety of scientific and commercial applications. Because it is predominantly made up of silicon and oxygen atoms, FDU-12 can be classified as a silica-based substance. Its structure often consists of well-defined mesoporous that are arranged in a predictable pattern. The organized and adaptable pore structure of FDU-12 is one of the most notable characteristics of this material. During the synthesis process, the size and shape of these pores can be altered, and they commonly exhibit a hexagonal or cubic array of pores. commonly, the pores are arranged in a grid. In applications requiring adsorption, catalysis, and drug delivery, one of the most important characteristics required is a material with a high surface area, which FDU-12 materials are known to possess. Because of the vast surface area, there are many of active sites available for interactions with molecules. Because of its well-defined mesoporous structure as well as its large surface area, FDU-12 is an excellent material for adsorption operations. It is useful in applications such as environmental remediation and purification because it may be used to adsorb gases, liquids, and pollutants[36, 37]. FDU-12 is shown in Fig 5

Figure 5 : Pore ordering and surface properties of FDU-12

1.4. Zeolites

Zeolites are a class of minerals that can be either naturally occurring or man-made and have a distinct microporous structure. 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[38].

1.5. Types of zeolite

1.5.1. A-Type zeolite

Widely used synthetic 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. This increases the detergent's efficacy while lowering the amount of water required for. Due to its high pore size, A-type zeolite is effective as an adsorbent for gas separation[39, 40]. 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. A-type zeolite is shown in Fig 6

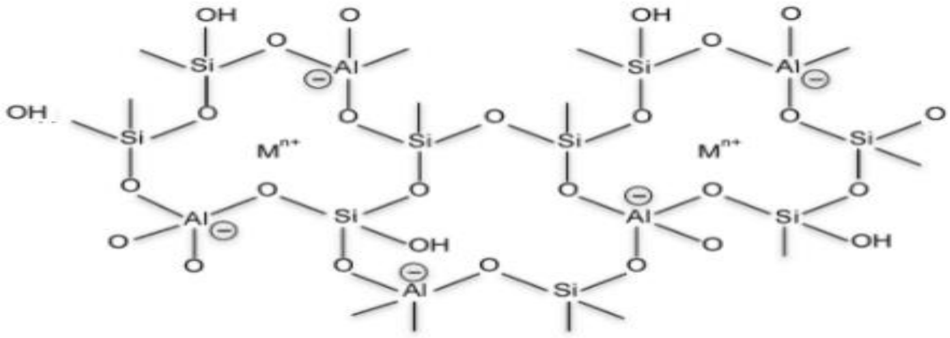

Figure 6 : ***A-type zeolite***

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-A. The substitution of other cations, such as sodium, potassium, and calcium, into the zeolite-X structure, can change its properties[41].Another man-made zeolite, Zeolite X, has 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[42] Zeolite X structure is shown in Fig 7

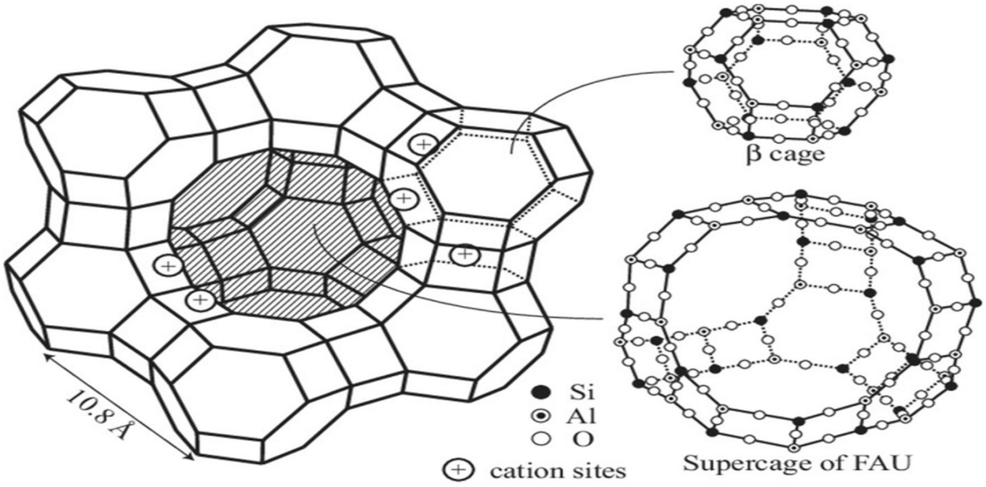

Figure 7: Zeolite X structure

1.5.3. Y zeolite

Similar to Zeolite X, Zeolite Y is a synthetic zeolite with 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 SiO2/Al2O3 ratio than other zeolites, which makes it more durable and resistant to chemical and heat deterioration. The SiO4 and AlO4 tetrahedral 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. These cavities have a high surface area and permit the absorption of big molecules[43]. 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[44]. Y-type zeolite is shown in Fig 8

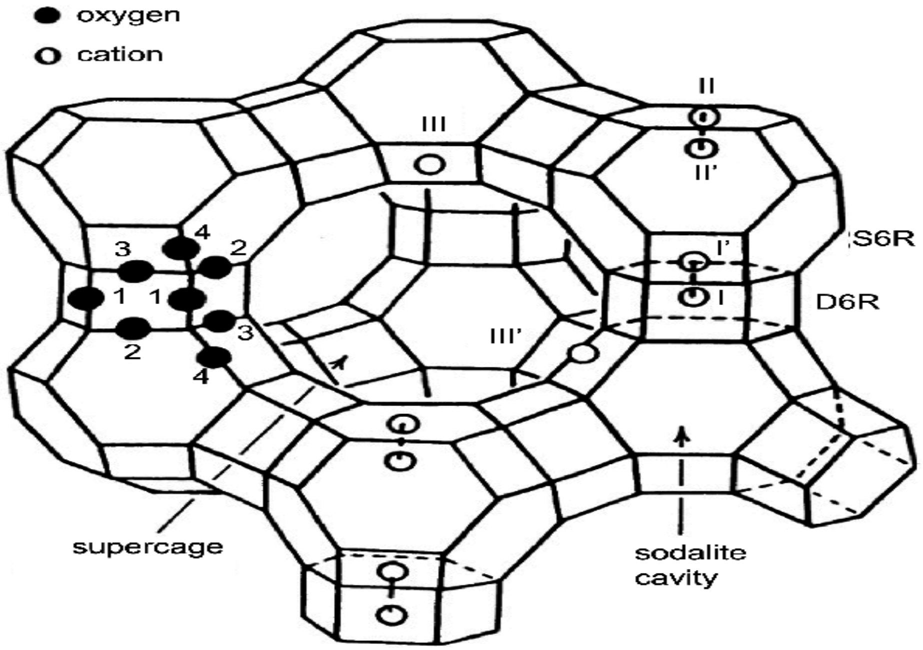

Figure 8 : Y-Type Zeolite

1.5.4. 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. 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[45].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. 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[46]. 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. 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. Solvent free synthesis of ZSM-5 is shown in Fig 9

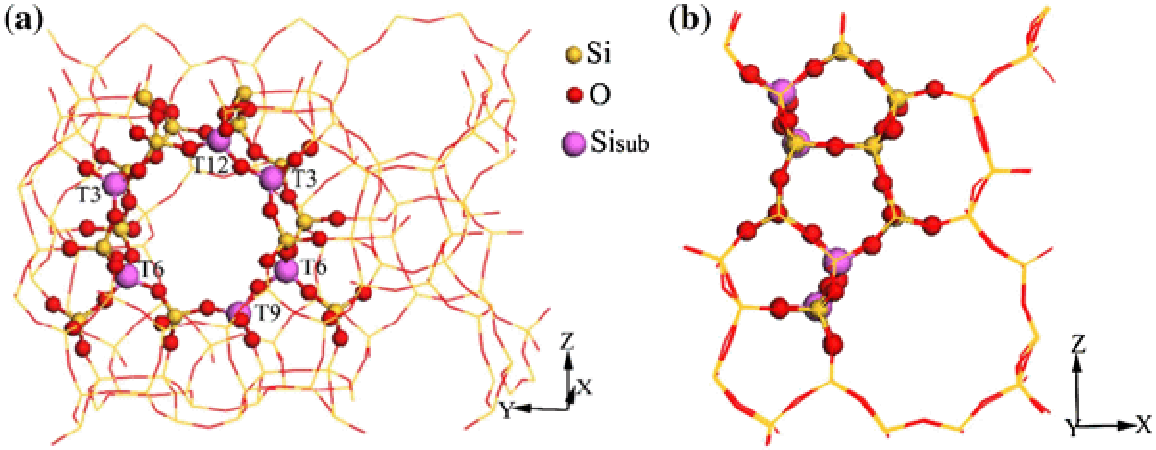

Figure 9 : Solvent Free Synthesis of ZSM-5

1.6. CO_2 Adsorption Mechanism on Pure Silicate

Depending on the particular silicate type and the circumstances, the adsorption of CO_2 on pure silicate materials predominantly takes place through physical adsorption and chemical reactions. Quartz (SiO_2) and other silicate minerals have surfaces that can interact with CO_2 molecules[47]. Here is a quick summary of the contributing mechanisms: This is shown in Fig 10

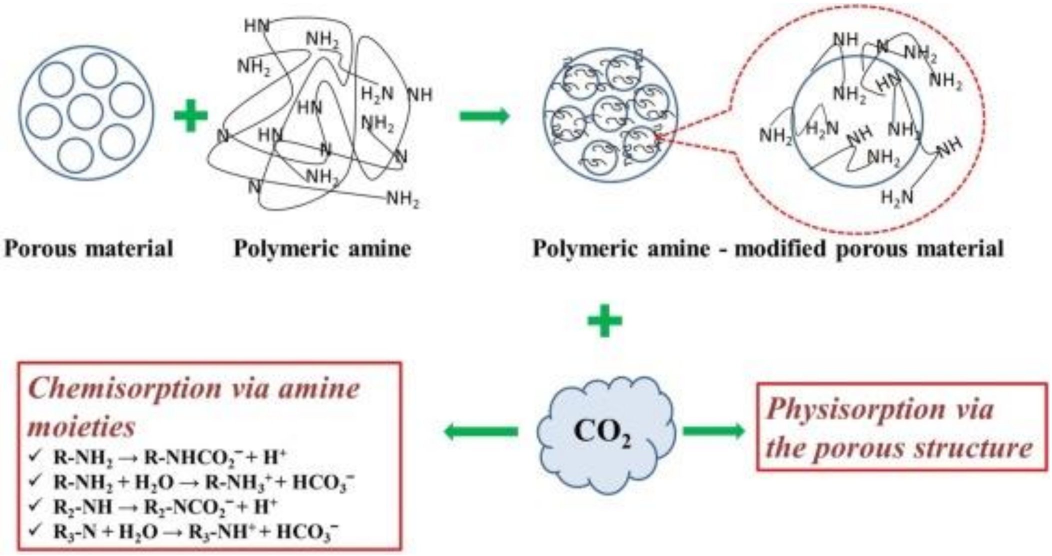

Figure 10 : CO_2 capture adsorbents functionalized by Amine

1.6.1. Diffusion Mechanism

Interstitial Diffusion: Through the pores or the interstitial spaces between the crystal lattices, CO_2 molecules can diffuse into the porous structure of silicate materials.

Surface Diffusion: CO_2 atoms can also travel along the silicate material's surface. pressure, Temperature, and the existence of other gases are only a few variables that affect how quickly gases diffuse onto surfaces.

Knudsen Diffusion: In materials with very small pores, such as microporous silicates, CO_2 molecules may display Knudsen diffusion, a type of diffusion where pore wall collisions play a major role. In zeolites and other nanoporous materials, it is crucial.

1.6.2. Physical Adsorption

Van der Waals forces, sometimes referred to as physisorption, are a weak interchange between carbon dioxide molecules and the silicate layers. Due to the polarizability of CO_2 molecules, small attractive forces are produced when they create transient dipoles and induce dipoles in the silicate surface. This adsorption process is often reversible and is influenced by pressure and temperature. It is crucial in the earlier stages of CO_2 capture[48]. Due to the polarizability of CO_2 molecules, small attractive forces are produced when they create transient dipoles and induce dipoles in the silicate surface. This adsorption process is often reversible and is influenced by pressure and temperature. It is crucial in the initial stages of CO_2 capture[49]. Physical and Chemical Adsorption is shown in Fig 11

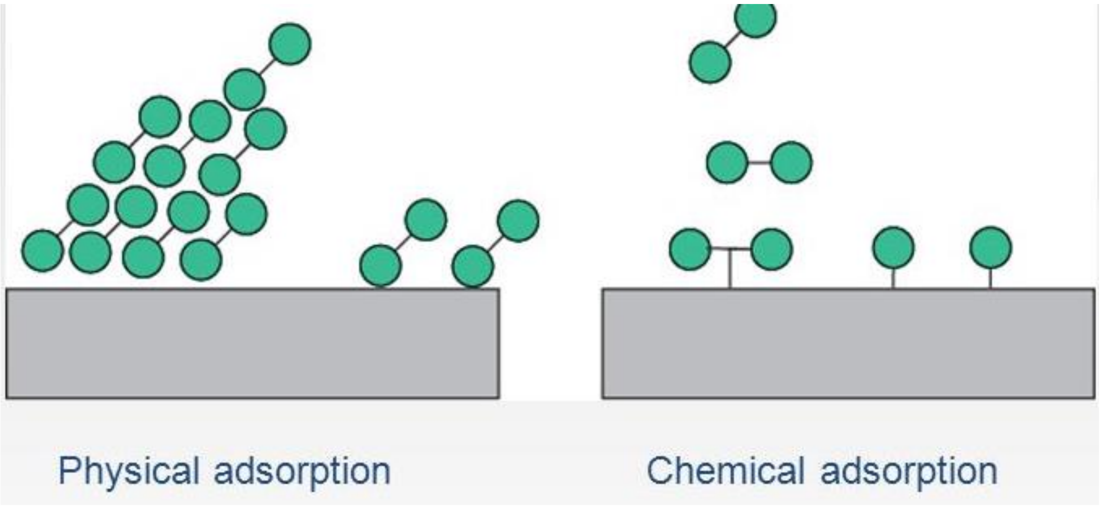

Figure 11 : Physical and Chemical Adsorption

1.6.3. Chemisorption mechanism on amine functionalized silicate

A critical phase in the carbon dioxide (CO_2) capture process is chemisorption on amine-functionalized silicate materials. These substances are frequently employed as sorbents to pick out CO_2 from gas streams. The amine functional groups and CO_2 molecules undergo chemical reactions as part of the chemisorption mechanism[50]. The chemisorption mechanism on amine-functionalized silicates is described in more depth below

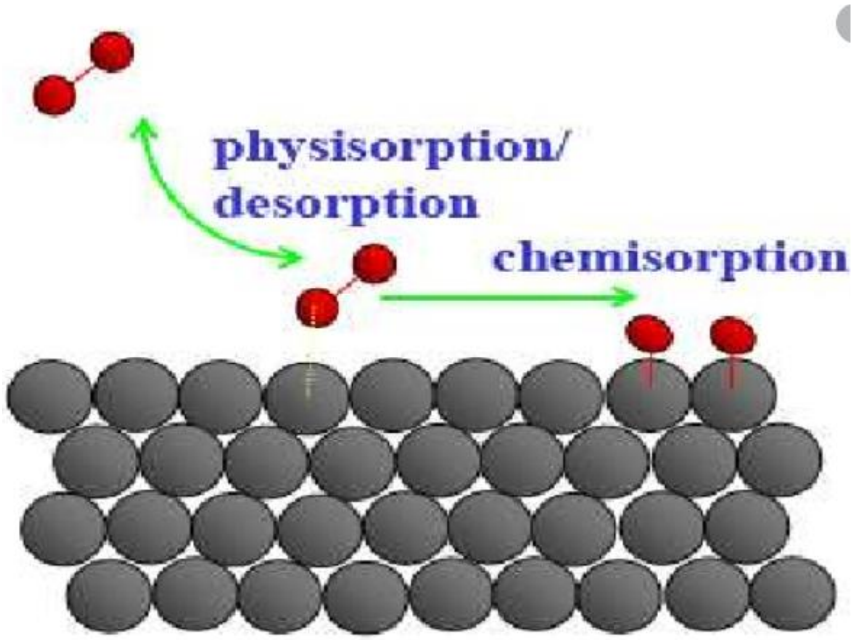

Figure 12 : Physisorption vs. Chemisorption

1.7. Amine Functionalization

Silicate materials, like silica (SiO_2), are altered by adding amine functional groups to their surfaces, such as -NH2, -NH, or -NHR, where R is an organic group. Typical amine-functionalized silicate materials include mesoporous silicates with amine grafts, amine-modified zeolites, and silica gel[51].

1.7.1. Chemical Reaction

When CO2 molecules come into touch with the amine-functionalized surface, chemisorption takes place. The production of Carbamate or bicarbonate species is the main chemical process involved in CO_2 chemisorption on amine-functionalized silicate. Carbamate formation occurs When CO_2 and the amine functional group (NH_2) interact, a carbamate species (RNHCOO-) is created.

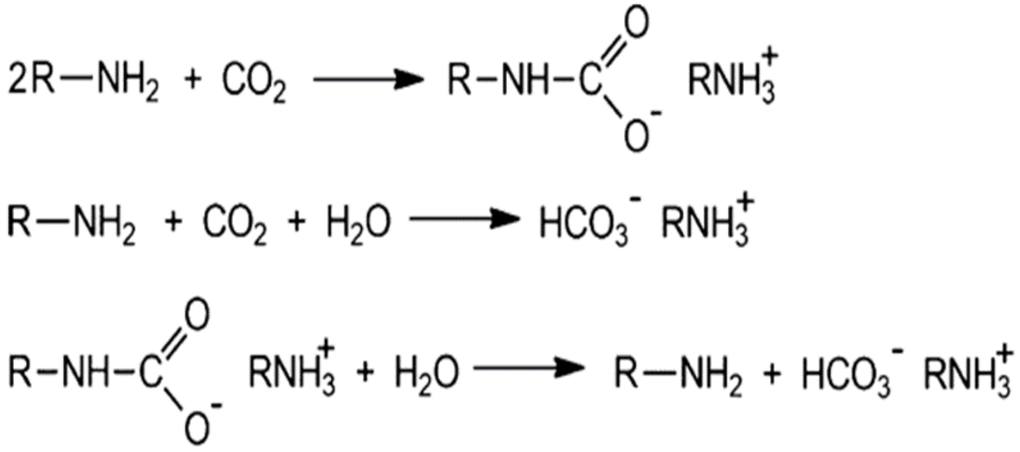

Figure 13 : Amine reaction with carbon dioxide

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_2 molecule[52]. The stable carbamate species that results from subsequent reaction on this intermediate is highly adsorbed on the outer layer of the zeolite. Loading of the amine, the types 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_2, higher amine loadings can increase the number of active sites available for CO_2 chemisorption. Overall, the CO_2 removal process from industrial emissions is aided by the chemisorption mechanism of CO_2 adsorption on amine zeolites. A potential material for carbon capture and storage applications, amine zeolites have good selectivity and capacity for CO_2 adsorption.

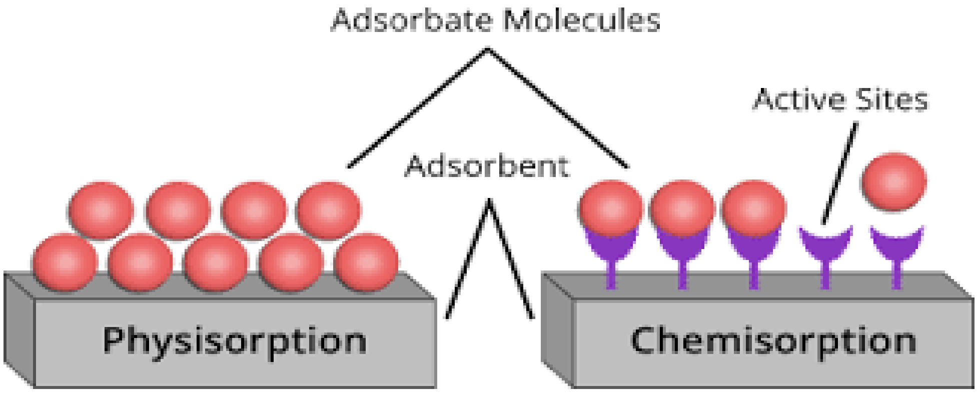

Figure 14 : Physisorption vs. Chemisorption

1.8. Problem statement

In this investigation, the CO_2 adsorption capacities of Silicalite-1 and MCM-41 materials functionalized with amine are compared in terms of effectiveness. The study addresses the need for a thorough analysis of these materials to help guide their use in carbon capture and environmental remediation technologies.

1.9. Research Objectives

To thoroughly analyze the structural characteristics, surface chemistry, and amine functionalization of amine-functionalized MCM-41 and Silicalite-1 materials in order to comprehend their fundamental differences and similarities.

To examine and contrast the amine-functionalized MCM-41 and Silicalite-1 CO_2 adsorption kinetics and capacities at various pressures and temperatures in order to assess the effectiveness of their CO_2 adsorption.

Silicalite-1 and amine-functionalized MCM-41 should be thoroughly compared in order to determine whether material performs better at CO_2 adsorption and the main variables behind those differences.

To provide information on the practical usage and possible industrial applications of the best material for CO_2 capture, taking into account aspects like cost-effectiveness and scalability.

Through the selection and optimization of adsorbents for CO_2 mitigation measures, this study intends to advance knowledge in the fields of carbon capture and environmental sustainability.

1.10. Scope of the Study

The objective of the study, "A Comparative Study of the CO_2 Adsorption on Amine Functionalized MCM-41 and Silicalite-1 Materials," is to compare the CO_2 adsorption performance of these two different materials in great detail. A thorough analysis of the structural characteristics (such as pore size, pore volume, and surface area), surface chemistry, and amine functionalization of MCM-41 and Silicalite-1. This will use methods including scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption isotherms (BET analysis), and X-ray diffraction (XRD). To ascertain the CO_2 adsorption capabilities of Silicalite-1 and MCM-41 with amine functionalization, rigorous adsorption tests were performed under regulated conditions. To comprehend their adsorption effectiveness and equilibrium behavior, experiments will be performed at varied temperatures, pressures, and CO2 concentrations. A thorough evaluation of the CO_2 adsorption capacities of Silicalite-1 and MCM-41 with amine functionalization. determining the differences between the two materials and how these differences may affect their practical applications, such as adsorption capacity, kinetics, and stability. drawing judgments about the relative performance of different materials based on the analysis and interpretation of experimental data. To confirm the validity of the results, statistical analysis will be used in this process. offering suggestions based on research findings, including details on prospective CO_2 capture material optimization options. Discovering potential areas for additional study and advancement in this area. Creating a thorough research report that summarizes every aspect of the study, along with presentations and visual aids to effectively convey the findings to audiences both inside and outside of the scientific community. Examining the study's practical applications, including potential industrial uses of the improved material in carbon capture and storage (CCS) and other pertinent technologies. The goal of this study is to provide a thorough understanding of the CO_2

adsorption behavior of MCM-41 and Silicalite-1 that will add to the body of knowledge in the field of carbon capture and offer insightful information for scientists, engineers, and decision-makers engaged in environmental sustainability and greenhouse gas mitigation.

1.11. Chapter Summary

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

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

Chapter 2 is literature review which includes the preparation methods for zeolite and silicates, types of amines used for the loading, methods used for amine loading, temperature, pressure, Si/Al ratio effect, Effect of physiochemical properties on CO_2 adsorption capacity of Zeolite.

Chapter 3 is materials method which includes materials description that has been used for the preparation of silicalite-1 and MCM-41, process used in the amine loading, Characterization techniques used in this study, experimental technique used for CO_2 adsorption on both sample.

Chapter 4 is result and discussion chapter that includes the result of different characterization techniques used in this thesis, the result of CO_2 adsorption on silicalite-1, MCM-41 and their aminated derivatives.

Chapter 5 includes the conclusion and the future recommendations.

CHAPTER 2: LITERATURE SURVEY

Chen et al., [2010] study compares two methods (impregnation and grafting) for incorporating amine groups onto MCM-41 for CO2 capture. Impregnation resulted in higher CO2 uptake but lower thermal stability compared to grafting. [110]

Wang et al., [2014] This research investigates the impact of synthesis methods (sonication vs. conventional) on Silicalite-1's CO2 and CH4 adsorption. Sonicated samples showed higher CO2/CH4 selectivity at low pressures, while conventionally prepared samples exhibited a larger overall adsorption capacity for both gases. [87]

Li et al., [2011] This work explores the influence of pore size and framework structure in amine-modified mesoporous silicas (including MCM-41) on CO2 adsorption. The study revealed a complex interplay between pore accessibility, amine density, and CO2 capture capacity. [81]

Yang et al., [2012] This research examines the CO2 adsorption performance of MCM-41 modified with different amine groups. The type of amine significantly impacted the adsorption capacity, with some amines exhibiting superior CO2 uptake compared to others. [80]

Yu et al., [2012] This study investigates the CO2 capture potential of amine-functionalized Silicalite-1 from simulated flue gas. The research explores regeneration techniques and analyzes the material's stability over multiple adsorption-desorption cycles [86]

Serna-Morales et al., [2010] This research introduces a concept of "CO2 capture working capacity" and analyzes it for various amine-functionalized MCM-41 materials. The study emphasizes the importance of considering both adsorption capacity and regeneration energy requirements. [75]

Zhang et al., [2013] While not directly comparing MCM-41 and Silicalite-1, this paper explores amine-modified Periodic Mesoporous Organosilicas (PMOs) for CO2 capture. It offers valuable insights into the design of amine-functionalized porous materials for CO2 adsorption. [71]

(Huang et al., [2010] this study focuses on CO2 capture using amine-functionalized SBA-15 (another mesoporous silica). It investigates the impact of amine chain length and grafting density on the adsorption performance, providing valuable knowledge applicable to MCM-41 and Silicalite-1 as well. [68]

Lu et al., [2012] This research explores the feasibility of capturing CO2 from flue gas using amine-functionalized mesoporous silicas. The study emphasizes the importance of material properties (pore size, amine type) and operating conditions (temperature, pressure) on CO2 capture efficiency. [66]

Zhao et al., [2013] This study investigates the influence of amine loading and pore size in amine-modified Silicalite-1 for CO2 capture. The findings demonstrate the need for optimization between these factors to achieve optimal CO2 adsorption performance. [65]

Li et al. [2019] studied the impact of solvent and synthesis conditions on amine-modified MCM-41 for CO2 capture. The research explores the influence of synthesis parameters on the structural properties and adsorption performance of these materials. [64]

Wang et al. [2017] conducted experimental and modeling studies to investigate the CO2 adsorption kinetics on amine-functionalized Silicalite-1. The research provides insights into the dynamic behavior of CO2 molecules during adsorption processes. [61]

Xu et al. [2018] optimized the amine loading in MCM-41 materials to enhance CO2 capture efficiency. The study explores the relationship between amine content and adsorption performance, aiming to maximize CO2 uptake while minimizing energy consumption. [58]

CHAPTER 3: EXPERIMENTAL SECTION

3.1 Synthesis Methods for Silicalite-1

A hydrophobic zeolite known as silicalite-1 that contains no aluminum is a powerful catalyst for a number of chemical reactions, including the isomerization of organic molecules and the cracking of hydrocarbons. Its homogenous pore widths and three-dimensional pore structure make it possible for specific molecules to be selectively adsorb on it and be catalyzed. This page will describe the various ways to make silicalite-1[53].

3.1.1 Hydrothermal synthesis

Hydrothermal synthesis is the process that produces silicalite-1 the most frequently. In this process, an autoclave is heated under hydrothermal conditions while a mixture of a template, such as tetrapropylammonium hydroxide (TPAOH), and a silica source, such as tetraethyl orthosilicate (TEOS), is heated. The mixture is heated for several days to a temperature of roughly 150°C and a pressure of roughly 15 atm. At this moment, the silica and template react to form the silicalite-1 structure. The template is then removed using acid extraction or calcination[54].

3.1.2 Sol-Gel method

Utilizing the sol-gel method to create silicalite-1 is also highly prevalent. In this process, a silica precursor, such TEOS, is hydrolyzed using a template, like TPAOH, to produce a sol. A catalyst, like ammonia, is added, and the sol is then let to mature at room temperature. heat till the gels[55].

3.1.3 Template free synthesis

Instead of utilizing a template, "template-free synthesis" is the method used to create silicalite-1. In this procedure, a silica source such as TEOS is hydrolyzed with the help of a mineralizer, such as sodium hydroxide. The silicalite-1 configuration is produced by heating the mixture hydrothermally. One advantage of this method is that it eliminates the need for a template, which may be costly and difficult to remove. Ion thermal synthesis uses an ionic liquid as the solvent and template, along with a silica precursor like TEOS, to form the reaction mixture. The mixture is heated hydrothermally to produce the silicalite-1 structure. This technique has the benefit of using a non-volatile template that is easy to recover from and reuse[56].

3.1.4 Microwave synthesis

Microwave synthesis is a relatively new method of making silicalite-1. With this method, the reaction mixture is heated using microwaves, enabling faster reaction times and lower temperatures. A forerunner of silica, like TEOS, and a template, like TPAOH, the reaction mixture is composed of. In order to form the structure of silicalite-1, the mixture is heated as a result of microwave exposure. The advantage of employing this strategy advantages over traditional hydrothermal synthesis methods include speed and reduced energy consumption[57].

3.2 Methods used for the synthesis of MCM-41

A well-known mesoporous material called MCM-41 is distinguished by its well-organized, hexagon-shaped pore structure, which is made up of a web of cylindrical channels. Because of its distinctive architecture and homogeneous pore diameters, which normally range from 1.5 to 10 nanometers, it has excellent qualities and a broad range of applications in many different disciplines. Although silica makes up the majority of this material, it can also incorporate other metal oxides, offering a flexible platform for customized functionalization and modification. With its consistent pore size distribution, huge pore volume, and high surface area, MCM-41 is a great option for drug delivery, adsorption, catalysis, and as a host material for encapsulating different compounds.

3.2.1 Direct synthesis method

In the direct technique, an alkaline mixture of a silica precursor (such as tetraethyl orthosilicate, TEOS) and a cationic surfactant (such as cetyltrimethylammonium bromide, CTAB) is usually used. The silica precursors condense around the micelles that the surfactant molecules self-assemble form. The mesoporous structure is obtained by removing the surfactant following further treatment and aging[57].

3.2.2 Template assisted synthesis

According to the intended pore structure, a template—typically a sacrificial material—is chosen in this process. Carbon spheres, polymers, and other materials that can be eliminated or broken down following the synthesis process are examples of common templates. A precursor material (often a silica source such as tetraethyl orthosilicate, or TEOS) is coated or impregnated onto the selected template. The mesoporous structure will form around the scaffolding that is the template. The template structure is exposed to regulated circumstances, such as the presence of a catalyst or a particular pH, to allow the silica precursor to condense and polymerize around it. This makes it possible to create a mesoporous framework that is organized. The template material is eliminated once the mesoporous structure has developed. This is frequently accomplished by extraction, calcination, or breakdown, which leaves the ordered MCM-41 structure with its network of hexagonally organized pores intact. In comparison to the direct synthesis approach, template-assisted synthesis has several advantages, especially when it comes to managing pore size, structure, and morphology. It gives you more freedom to create various pore geometries by changing the size, shape, or composition of the template material. To fully eliminate the template, this approach could necessitate extra procedures, which occasionally might have an impact on the MCM-41 material's ultimate properties. The final pore properties and the general quality of the mesoporous material are greatly influenced by the template selection and the conditions under which the synthesis is carried out. The final pore properties and the general quality of the mesoporous material are greatly influenced by the template selection and the conditions under which the synthesis is carried out. In order to customize MCM-41 structures and produce distinct pore topologies and forms that are useful for a variety of applications including catalysis, adsorption, and controlled release systems, template-assisted synthesis is still a crucial technique[58].

3.2.3 Post synthetic grafting method

The surface and structural characteristics of pre-existing mesoporous materials, such as SBA-15, are modified or altered as part of the post-synthetic grafting process to create MCM-41. With this technique, when the material is first synthesized, specific properties, like surface functionality or pore size, can be changed. Start with a mesoporous material that has already been synthesized; this is usually SBA-15, which has a different pore structure or surface characteristics than MCM-41. To change the surface chemistry of the pre-existing material, apply different reagents or functional groups to it. For example, the removal of specific structural units or the introduction of new functional groups through chemical alteration utilizing acids or bases or alkali treatment. The material's structure is altered during the treatment or modification in an effort to reorganize the pores and surface properties to more closely match MCM-41. To obtain the distinctive hexagonal pore structure of MCM-41, this may entail adjusting the pore layout or size. To determine whether the changed material now more closely resembles the features of MCM-41, it is subjected to a variety of characterization techniques (including X-ray diffraction, NMR, BET surface area analysis, etc.) to evaluate its structure and pore properties. A way to alter current mesoporous materials to replicate the characteristics of MCM-41 is through the post-synthetic grafting technique. It enables modifications to surface functioning and pore structure without requiring whole material synthesis. This approach can be more economical and environmentally beneficial because it does not require a full synthesis procedure[59, 60].

3.2.4 Seed assisted growth method

Pre-formed MCM-41 particles or seeds are used as templates for the creation of new MCM-41 structures in the seed-assisted growth technique of MCM-41 preparation. This method uses the existing MCM-41 particles as a foundation for continued growth, allowing for the construction of larger structures or other morphologies. Start by creating or acquiring MCM-41 particles or seeds. These seeds act as the starting point, or template, around which further MCM-41 material grows. Introduction of Precursor: Add the silica precursor to a solution containing MCM-41 seeds. TEOS is a common example of this precursor. The building blocks for the development of new MCM-41 material are provided by this predecessor[61, 62].

3.2.5 PH adjustment method

The creation and attributes of MCM-41 are significantly influenced by the pH of the synthesis solution, which also affects the pore size, structure, and other features of the final product. Generally speaking, the sol-gel process involves controlling the pH level, particularly when producing MCM-41 via the direct synthesis method. Adding acids or bases to the reaction mixture during synthesis is the usual method used to modify the ph. However, depending on the particular synthesis procedure and required

MCM-41 material characteristics, the precise pH levels may change. A typical pH control strategy in the direct synthesis method could be the synthesis starts with a combination that contains a structure-directing agent (like cetyltrimethylammonium bromide, CTAB), a silica source (like tetraethyl orthosilicate, TEOS). Initially, the alkaline catalyst is added to the solution to maintain a basic pH (pH > 7). The synthesis of the MCM-41 structure is triggered by the hydrolysis and condensation of the silica precursor surrounding the surfactant micelles, which is aided by this alkaline environment. The creation of the appropriate pore size and structure depends on pH regulation. The process of aging and gelation involves adjusting the pH within certain ranges, which has an impact on the distribution and size of pores in the final MCM-41 material[63]. To encourage more silica species condensation and aid in the formation of the ordered mesoporous structure, the solution is left to mature under carefully regulated pH conditions.

3.3 Types of amine used for amine modification

Zeolites are widely used for carbon dioxide (CO_2) extraction because of their enormous surface area, thermal stability, and tunable pore diameters. However, zeolites can be made more porous by adding amine functional groups to change the surface chemistry of the material. Capturing CO_2 is both efficient and selective. Zeolites' modification for CO_2 collection can be carried out using primary, secondary, and tertiary amines, among other amines[64]. A primary amine is the most widely used and least complicated type for zeolite modification is ammonia. They have a single amino ($-NH_2$) group, and they can be covalently attached to the zeolite surface by a silane coupling agent. Primary amines are added to the zeolite surface to increase the amine functional group density and the material's capacity for CO_2 adsorption regularly employed[65]. However, adverse side effects are common with primary amines impacts such as oxidation and deamination, which may progressively lessen their effectiveness. A secondary amine is an additional type of amine that can be utilized to alter zeolite. They are able to become covalently attached to the zeolite's surface by means of a functional coupling agent and possess two amino groups (-NH_2). Secondary amines are different from primary amines in that demonstrate a greater ability to withstand oxidation and deamination, rendering them more stable when utilized for a prolonged length of time. However, two amino groups on the surface could interact with other molecules in an undesired way 16... The most resilient and steady tertiary amines include three amino acids due to the oxidation and deamination of the three types of amines (-NH_2) units. They are covalently bondable when a trifunctional coupling agent is used attached to the zeolite's surface. Furthermore, tertiary amines might gain from preferential adsorption of CO_2 over methane and nitrogen. Still, the Steric hindrance brought on by increasing functionalization can lower their CO_2 adsorption potential. In conclusion, the primary, secondary, and triamint categories of amines tertiary—is useful for modifying zeolites to absorb CO_2, which is shown in Table 1 and Table 2

Table 1: Different amines used for CO_2 Capturing

Amine Name	**Molecular Weight (g/mole)**	**Density** $(\frac{g}{cm^3})$
1-amino-2-propanol(1A2P	75.90166	973(kg/m^3)
2-amino-1-butanol(2A1B)	89.14	973
Sec-butylamine(SBA)	408.532Da	724
Isobutylamine(IBA)	73.14	736
Triethanolamine	149.188	1.124

Table 2: Different amines and their structure

Amine Type	**Abbreviation**	**Structure**
Sec-butyl amine	(SBA)	$CH_3CH_2CH(NH_2)CH_3$
Isobutyl amine	(IBA)	$(CH_3)_2CHCH_2NH_2$

2-amino-1-butanol	(2A1B)	$C_2H_5CH(NH_2)CH_2OH$
1-amino-2-propanol	(1A2P)	$CH_3CH(OH)\ CH_2\ NH_2$
N-methyldimethanolamine	MDEA	$CH_3N(C_2H_4OH)_2$

3.4 Types of method used for amine loading

3.4.1 Impregnation Method

Organic amine species are wet impregnated into the pores and surface of the mesoporous support material to form an amine-functionalized CO_2 adsorbent. The impregnation method might produce a higher amine-based loading, which can add massive concentrations of amine species. Adsorbent used in the impregnation process has been assigned to Class 1[66]. The detailed preparation method for 8 is shown in Fig. 4. As seen in Table, there are a variety of amine types available for use in amine-base solid adsorbents in order to generate an effective adsorbent. PEI and TEPA are the most often used because of their superior stability and nitrogen content of amines. .. The amount of amine incorporated into the porous material is determined by the amine density and the overall pore volume of the substance[67]. The potential loading amount of the organic material can be ascertained by utilizing the amine density and the pore volume of the support. It is clear from the state of the produced adsorbent that amine species will eighteen be affixed to the exterior of the support if the loaded amine quantity surpasses the theoretical weighting of the backing. The usual form of a solid amine that is made well adsorbent is a powder that flows. An amine species will clump together if it gets overwhelmed. the surface of the support, binding to minuscule porous material particles to form larger finely divided powders. It will even make the slurry mixture visible. The amount of accessible amine active sites on the adsorbent is currently reduced. Therefore, adsorbents with the appropriate amine loading can provide a large number of accessible amine active sites[68]. However, the transfer of carbon dioxide within the adsorbent is constrained and the amine utilization is decreased as a result of the supported amine occupying a significant fraction of the interior pores of the support material. The process of preparing amine-impregnated solid amine adsorbent usually involves the simultaneous use of a volatile organic solvent, such as methanol. Heat drying is usually used to remove the organic solvent in order to prepare an adsorbent. When heated, this mechanism can result in amine loss and pore structure collapse. It also consumes energy. Water is employed as the solvent for the organic amines while creating the adsorbent through freeze-drying. The resultant combinations of amine species and support were treated with liquid nitrogen. The frozen water is subsequently removed by sublimation. The approach used to make the adsorbent requires less energy since water is removed during the freeze-drying process. This also forms new voids in the loaded organic amine layer, which facilitate gas diffusion and reveal the active site of the organic amine. The impregnation process is highly suited to the carrier material. As a result, a range of carriers can be utilized to manufacture adsorbents via impregnation approach, such as zeolite molecular sieves, porous carbon materials, mesoporous molecular sieves, and MOF materials[68].

3.4.2 Grafting Method

Covalently attaching a functional group to an inorganic surface—most commonly, zeolites—is the process known as grafting. Zeolites can be modified using this method for a number of uses, such as impregnating amines. Amines are organic compounds containing nitrogen atoms that are commonly utilized as sorbents for CO2 collection due to their great affinity for CO2. Zeoes can be modified to increase their CO2 collection efficiency and selectivity by the amine grafting process. Zeolites are porous crystalline aluminosilicates that are good for a wide range of applications, including gas separation and catalysis[69]. However, because of their pore size and surface chemistry, they might not always be suitable for specific applications, such as CO2 capture. By adding functional groups to their surface, zeolites' pore size and surface chemistry can be altered to better fit their intended uses. Grafting amines onto zeolites requires several steps, such as modifying the zeolite's surface, activating the amine, and attaching the amine to the surface. The surface of the zeolite must first be adjusted, which comprises cleaning the surface to remove impurities and creating a reactive, transparent surface[70]. This stage is often finished with an acid treatment, which removes any contaminants and activates the zeolite surface. Acid treatment results in the production of silanol groups and surface defects, which provide the amine with reactive sites for attachment. The next step is to activate the amine, which involves transforming it into a reactive species that can engage with the zeolite's surface. Usually, this stage is completed by making an amine 20 salt, which can then interact with the zeolite's surface. To make the amine salt, the amine is mixed with an acid, such as hydrochloric or sulfuric acid. After being dissolved in a solvent such as water or ethanol, the completed amine salt can then be mixed with the zeolite. The next step is the attachment of the amine to the zeolite surface, which necessitates a reaction between the amine salt and the surface. This process is often completed by a condensation reaction between the amine salt and the silanol groups on the zeolite surface. Heating the combination to a specific temperature and time can initiate a process that forms covalent bonds between the amine and the surface of the zeolite. A few factors that influence how effective the grafting method for amine impregnation on zeolite is include the kind of zeolite, the type of amine, and the conditions used during the grafting process. Depending on the type of zeolite, the pore size and surface chemistry can differ, which can affect how well the amine sticks to the zeolite surface. The kind of amine employed can also affect how successful the grafting procedure is since different amines have varying reactivity and solubility characteristics[71]. The setting in which the grafting process is carried out may also have an effect on its effectiveness. How strongly the amine sticks to the zeolite's surface can be influenced by a number of factors, including the concentration of the amine salt, the solvent used, the reaction temperature and duration, and the pH of the mixture. If these parameters are adjusted, an amine-impregnated zeolite can form that is both stable and effective[72].

3.4.3 Direct synthesis method

The direct synthesis of amine-modified porous materials involves the addition of amine functional groups to the surface of porous materials in a single step. This approach has been thoroughly studied in recent years due to the increasing need for porous materials with specific properties for applications in medication administration, gas separation, and catalysis, among other things. Porous materials, such as metal-organic frameworks (MOFs), zeolites, and mesoporous silica, have been widely used as adsorbents and catalysts because of their large pore volume, high surface area, and variable pore size. By adding amine functional groups to their surfaces, these materials' selectivity and activity for specific applications, like CO2 capture and catalytic processes, can be improved[73]. There are several methods for achieving the direct synthesis of amine-modified porous materials, including co-condensation, template-directed synthesis, and post-synthesis modification. Unlike co-condensation, which involves the simultaneous synthesis of the porous material and the amine functional group, post-synthesis modification adds the amine functional group to the material's surface after synthesis has completed. In template-directed synthesis, a template molecule directs the insertion of the amine group and the creation of the porous material. Co-condensation is a widely used method for the direct synthesis of porous materials modified with amines. This procedure involves the simultaneous reaction of a metal precursor, an organic linker, and an amine precursor in the presence of a base and a solvent[74]. When the amine precursor interacts with the metal precursor and the organic linker, a metal-organic framework or a hybrid material with amine functional groups inserted into the framework structure is formed. Post-synthesis modification is an additional method for the direct synthesis of amine-modified porous materials. This method adds the amine functional group to the surface of the porous material after production. During initial synthesis, the amine group is first extracted from the porous material. It is then functionalized with an amine precursor by a number of methods, such as covalent bonding, grafting, or impregnation[75]. Grafting involves attaching the amine precursor to the surface of the porous material through a covalent bond, as opposed to impregnation, which involves the diffusion of the amine precursor into the material's pores. The interaction of the amine precursor with the surface functional groups of the 22 porous substance is what initiates the formation of a covalent bond. Template-directed synthesis is an additional method for the direct synthesis of amine-modified porous materials. This method uses a template molecule to guide the insertion of the amine group and the creation of the porous substance. Usually, the template molecule is a surfactant or polymer that forms a micelle or template around which the porous material is formed. After adding the amine precursor to the template, the reaction is then let to proceed, forming a porous material with amine functional groups integrated into the structure. The synthesis conditions, type of amine precursor, and type of porous material are the factors that determine the degree to which amine-modified porous materials can be directly synthesized. Depending on the kind of porous material employed, the final product's properties, such as pore size, surface area, and stability, may change. Because different amines have different reactivity and solubility characteristics, the type of amine precursor employed can also affect the procedure's efficiency. The synthesis process's reaction conditions can also have an effect on the method's effectiveness. Many factors, including as the amount of reactant used, the solvent used, the temperature and duration of the reaction, and the pH of the combination, can influence the formation and properties of the resultant material. By enhancing these variables, a stable and effective amine-modified porous material can be produced[76].

3.5 Factors affecting the CO_2 adsorption on porous material

The variables that impact CO_2 adsorption over zeolites include 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. The type of zeolite utilized can affect a material's capacity to absorb CO_2, as certain zeolites have a stronger affinity for CO_2 than others. It is possible for the surface area available for CO_2 adsorption to grow in zeolite crystal structures with more open pores and channels than in other configurations. The zeolite's capacity to absorb CO_2 can also be influenced by the size and shape of its pores. 2. Reduced pore size may provide a bigger holes could provide a simpler CO_2 adsorption method, but more selective adsorption entry of molecules into the zeolite[77]. Lastly, the temperature and pressure of the adsorption process might have an effect on CO_2 adsorption over zeolites. Higher Si/Al ratios may produce a more acidic surface for CO_2 adsorption, which can influence the zeolite's ability to absorb CO_2. Increasing pressures and temperatures can frequently increase the quantity of CO_2 adsorbed, although the ideal conditions will differ based on the specific zeolite and its properties.

Following are the factors that has been discussed below:

3.5.1 Effect of framework on CO_2 adsorption

An important factor in CO_2 adsorption is the structure of silicates, a family of minerals made of silicon, oxygen, and other elements. Silicates are interesting materials for carbon capture and storage (CCS) applications because of their ability to adsorb CO_2 molecules and their porous structure, which may be modified at the molecular level. It is possible to alter the silicate framework to produce porous structures with large surface areas[78]. There is plenty of room for CO_2 molecules to be trapped because of this porous nature. The capacity for C_{O2} adsorption increases with surface area and well-defined pore structure. It is possible to change the silicate framework's unique chemical makeup and functional groups to improve the way that CO_2 molecules interact with the material's surface. The silicate structure can be modified to include functional groups like amine (-NH2) or hydroxyl (-OH) to boost the affinity for CO_2 and facilitate adsorption. Because silicate frameworks frequently exhibit thermal stability, they can tolerate challenging circumstances throughout the CO_2 adsorption process[79]. Regeneration of the material for several adsorption cycles depends on its capacity to tolerate high temperatures without experiencing structural damage. A more effective separation procedure can be made possible by designing the framework structure to preferentially absorb CO_2 over other gases. In industrial applications where CO_2 needs to be extracted from flue gases or other emission sources, this selectivity is essential. The rate at which CO_2 is adsorbed can be affected by the structure of silicates. Optimized surface functions and pore sizes in well-designed frameworks can improve adsorption kinetics and increase process efficiency. Silicate frameworks may provide a more affordable and scalable CO_2 capture option than some traditional techniques if they are made for large-scale production[80]. Their practical applicability may be aided by their natural abundance and possible simplicity of synthesis. By modifying their composition and structure, they can better trap CO_2, be more selective, and regenerate, which makes them attractive options for reducing CO_2 emissions and halting climate change. The goal of this field's ongoing research and development is to further enhance materials based on silicates for CO_2 capture methods that are both effective and profitable. This is shown in Table 3

Table 3: Effect of framework on CO_2 adsorption

Type of Silicate	Adsorption Capacity(mg/g)	Selectivity(CO_2/N_2)	Stability(Number of Cycle)
13X-C	265	29	7
13X-M	255	14	4
Zeolite 13x	211	45	8
MOF 5	38	25	3
Activated carbon	99	45	6

3.5.2 Effect of temperature and pressure on CO_2 adsorption.

The two main factors affecting carbon dioxide (CO_2) adsorption on silicate materials are temperature and pressure. Because silicate materials are porous and have the ability to adsorb CO_2, researchers have looked at their potential for CO_2 capture and storage. In general, a rise in temperature can lessen CO_2's ability to adsorb on silicate materials. The thermodynamics of adsorption is responsible for this phenomenon's observation.

Elevated temperatures have the potential to decrease CO_2 molecules' attraction for the silicate surface, hence reducing the adsorption capability[81]. High temperatures have the potential to accelerate CO_2 desorption from the silicate surface. Because it facilitates the release of the absorbed CO_2 for storage or other purposes, this feature may be helpful for regeneration in a cyclic adsorption-desorption process. Generally speaking, higher pressures can promote CO_2 adsorption on silicate materials. More CO_2 molecules are available at higher pressures, which increase the likelihood of contact with the silicate surface and, as a result, improve adsorption. Pressure is necessary to bring the adsorbed and gas-phase CO_2 into equilibrium. Higher pressures may allow for the adsorption of more CO_2 until equilibrium is reached. There are a number of models that may be used to explain how temperature, pressure, and CO_2 adsorption on silicates relate to one another. These models include Freundlich or Langmuir isotherms, which depict the adsorption process and its dependency on these variables. The kind of silicate, its porosity, surface area, and the kind of CO_2 being adsorbed can all affect the particular behavior. Studies are frequently carried out by researchers to gain a deeper understanding of these linkages and to use silicates to maximize CO_2 capture settings. For carbon capture and storage technology to be used effectively, it is imperative to determine the optimal temperature and pressure to optimize CO_2 adsorption while taking energy costs and practicality into account[82]. It is Shown in the Table 4 below:

Table 4: Effect of temperature and pressure on adsorption capacity of zeolite

Zeolite Type	Temperature °C	Pressure (bar)	Adsorption Capacity mmole/g
13x	393	0.15	0.7
5A	393	0.15	0.38
4A	393	0.15	0.5
WEG-592	393	0.15	0.6

APG-II	393	0.15	0.38
NA-Y	273	0.1	4.9
NA-X	373	1	1.24
Na-X-h	293	1	2.52
Na-X-h	373	1	1.37
Na-X-C	323	1	2.14
Na-X-C	373	1	1.41
Cs-X-h	323	1	2.42
Cs-X-h	373	1	1.48
Cs-X-c	323	1	1.76
Cs-X-c	373	1	1.15

3.6 Effect of physiochemical properties on CO_2 adsorption

3.6.1 Effect of enthalpy of adsorption

Mesoporous material MCM-41 has been investigated for its potential in adsorption applications, such as CO_2 adsorption. One important aspect affecting how the adsorbent and the adsorbate (CO_2) interact is the enthalpy of adsorption (MCM-41).The energy produced or absorbed when a molecule (like CO_2) sticks to the surface of the adsorbent material (MCM-41 in this example) is known as the enthalpy of adsorption[83]. It is a measurement of how strongly the adsorbate and adsorbent surface interact. CO_2 and the MCM-41 surface often interact more strongly when the enthalpy of adsorption is larger. The material may adsorb CO_2 more steadily as a result of this stronger binding. An enhanced capacity for CO_2 adsorption is frequently correlated with a higher enthalpy of adsorption. This is due to the fact that a higher enthalpy denotes a more advantageous adsorption process, which permits a greater number of CO_2 molecules to stick to the MCM-41 surface. One of the most important factors to take into account when evaluating MCM-41's effectiveness for CO_2 adsorption is its enthalpy of adsorption. Enthalpy of adsorption can be regulated to allow for efficient CO_2 collection and subsequent release during desorption operations, provided that it is not too high or too low. In order to understand the thermodynamics of the adsorption process and to optimize the settings for CO_2 capture using MCM-41, researchers investigate the enthalpy of adsorption[84]. It's a crucial factor to consider when developing and choosing materials for CO_2 capture because it has a direct impact on how well the adsorption-desorption cycle works in applications involving carbon capture and storage. This is shown in table 5

Table 5: Enthalpy of adsorption of different zeolites

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

3.6.2 *Effect of absorbate characteristics on CO_2 adsorption of silicate*

Both the silicate material's inherent qualities and the features of the absorbate, or CO_2 molecules, have an impact on the adsorption of carbon dioxide (CO_2). The way that the CO_2 molecule interacts with the silicate surface depends on its size and structure. Smaller molecules may be more likely to be adsorbed on silicate materials with particular pore diameters. Because it is a very tiny molecule, CO_2 can interact with some silicate structures in a positive way. The adsorption capacity on silicate surfaces can be affected by increased CO_2 concentrations or pressures. A higher CO_2 concentration can encourage more molecules to interact and adsorb onto the silicate's surface. CO_2 molecule energy is dependent on temperature. Because of the molecules' decreased attraction for the surface, higher temperatures may diminish CO_2's ability to adsorb on silicate surfaces. However, higher temperatures may aid in the desorption process. The polarity and interaction potential of CO_2 are two of its chemical characteristics that affect how it adsorbs to silicates. Silicates may influence adsorption by interacting more favorably with the polar CO_2 molecule due to certain functional groups or surface characteristics.

3.7 Materials

All of the chemicals used in this work, including distilled water, TEOS (Tertra ethylene orthosilicate), TPOAH (tripropyl ammonium hydroxide), methanol (CH3OH, 99.7%), and TEA (Triethanol amine), were purchased from Sigma-Aldrich.

3.8 Preparation of Silicalite-1

Silicalite-1 is made using the procedure listed below.

- Combine H_2O, TPAOH, and TEOS (tetraethyl orthosilicate) in the proper amount.
- For a full day at room temperature, stir the mixture.
- heat the mixture at $90^{O}C$ for 3-5 days.
- Use a centrifuge machine to separate the powder.
- In the oven, dry.
- Calcine the remaining specimen [85].

3.9 Preparation of MCM-41

In accordance with the literature, MCM-41 is formed by addition of 2.5 grams of (CTABr) i.e. n-hexadecyltrimethylammonium bromide in deionized water which weighs 50 grams to diffuse it. After that, surfactant solution was added to to 13.2 grams of ammonia solution (32 wt.%) and 60.0 g of pure Ethyl alcohol. The mixture was stirred at 250 revolutions per minute for 15 minutes, after that 4.7 g of TEOS (Tetraethyl orthosilicate) was added in the above solution drop after drop, then the solution was made stirred for approximately 120minutes. White precipitates were collected after whisking, centrifuge, and clean it with 100 mL of deionized water and 100 mL of ethyl alcohol. At a temperature of 90 ^{o}C, the prepared MCM-41 was desiccated to stay for a night at some particular place. High temperature heating was done for 120 min at a temperature of 550 ^{o}C [86].

3.10 Amine functionalization of Silicalite-1 and MCM-41

The following procedure is used to modify silicalite-1 with TEA: • Impregnation is the introduction of amine molecules into a porous material's pores.

This was accomplished by first dispersing the amine (TEA) in methanol and stirring for

30 minutes.

- After that, the solution containing the silicalite-1 material was dissolved and agitated for 24 time.

- The methanol was then dried in a vacuum oven until it evaporated.

- so that the material's pores contained only the amine, resulting in the zeolite treated with amine[87]

4 CHAPTER 4: CHARACTERIZATION TECHNIQUES

4.1 XRD

Using a radiation source of Cu Kα (λ=1.5418Å), the X-ray diffraction patterns of silicalite-1 and amine-functionalized silicalite-1 were obtained from an X-ray diffractometer (Bruker D2 Phase Germany). A 2θ spans 2° to 50°.

4.2 SEM

Using a scanning electron microscope (JEOL JSM-6490A), scanning electron microscopy (SEM) is utilized to analyze the surface morphology of silicalite-1 and amine functionalized silicalite-1. At 20KV, SEM operated. SEM is outfitted with EDAX (METEK Z2-i7) to verify the silicalite-1's elemental composition. The SEM pictures are captured at 1µ, 2µ, and 5µm magnifications.

4.3 FTIR

An FTIR spectrometer (Perkin Elmer spectrum 100) is used to examine chemical bonds and functional groups through Fourier-Transform infrared spectroscopy. An XRD machine connected to a computer interface determines the crystalline structure of adsorbents.

4.4 BET

Using Brunauer-Emmett-Teller (BET), the specific surface area and pore size distribution are determined. We obtained the specific surface area and pore size distribution by using pure nitrogen for adsorption.

4.5 TGA

The stability of silicalite-1 is tested by thermo gravimetric analysis, which is performed up to 600 degrees Celsius. Next, the silicate -1-TEA's stability is examined. At 100 degrees Celsius, which is the operating temperature, both of these compounds demonstrated stability in Celsius.

4.6 CO_2 Adsorption

CO_2 adsorption experiments were conducted using the VxComm software (TDS-734 module) and a high-pressure gas adsorption analyzer (H-sorb 2600). Initially, the sample was baked under vacuum for twenty-four hours at 100 0C in order to completely evaporate any remaining moisture. A sample of silicate-1-TEA and its composites weighing up to 5 g was gathered in the second step of the procedure. Before the CO2 adsorption tests were conducted, the samples were hoovered and degassed for ten hours at 150 0C. The sorption tests were conducted at a constant temperature of 45 0C and a constant CO_2 flow rate of 18 cm3 min-1. There was a range of pressures from 0 to 15 bar.

CHAPTER 5: RESULTS AND DISCUSSIONS

5.1 Characterization of MCM-41, Silicalite-1 AND MCM-41-TEA.Silicalite-1-TEA

After synthesis of sample, different techniques are used to understand its properties and morphology. X-ray Diffraction, scanning electron microscopy, energy dispersive x-ray spectroscopy, and Fourier Transform Infrared are some of few examples of different spectroscopic approaches. These characterization approaches were skillfully applied for the inquiry in order to thoroughly understand the characteristics, configuration, and structure of samples. The analysis included the use of XRD, SEM, and EDX techniques to examine the sample morphology and construction. The identification of functional groups and bonding types in our specimens was also made easier by the FTIR approach. Pressure conditions were purposefully changed throughout the experiment of CO2 adsorption. Under CO2 adsorption conditions, each sample underwent a thorough inspection. The full results of the characterization approaches and the unique CO2 captureanalysis for each sample are discussed in more detail in the following sections

5.2 X-Ray Diffraction (XRD)

X-ray diffraction was used to determine the crystalline structure of Silicalite-1 and Silicalite-1 functionalized with amine groups. The results are shown in Figure 15. The graph also includes an XRD pattern of a typical MFI-type material for comparison's sake. The Silicalite-1 sample's diffraction pattern showed characteristic peaks between 7.5-9 ° and 22.5-25 °, which are usually associated with the MFI-type structure. As a result, the XRD data showed that the Silicalite-1 sample had MFI-topology and that it lacked any more reflection peaks, a sign that the sample contained no more crystalline phase. The XRD patterns of the amine-functionalized samples resemble those of the conventional MFI-type material, suggesting that the amine functionalization did not change Silicalite-1's crystalline structure**.**

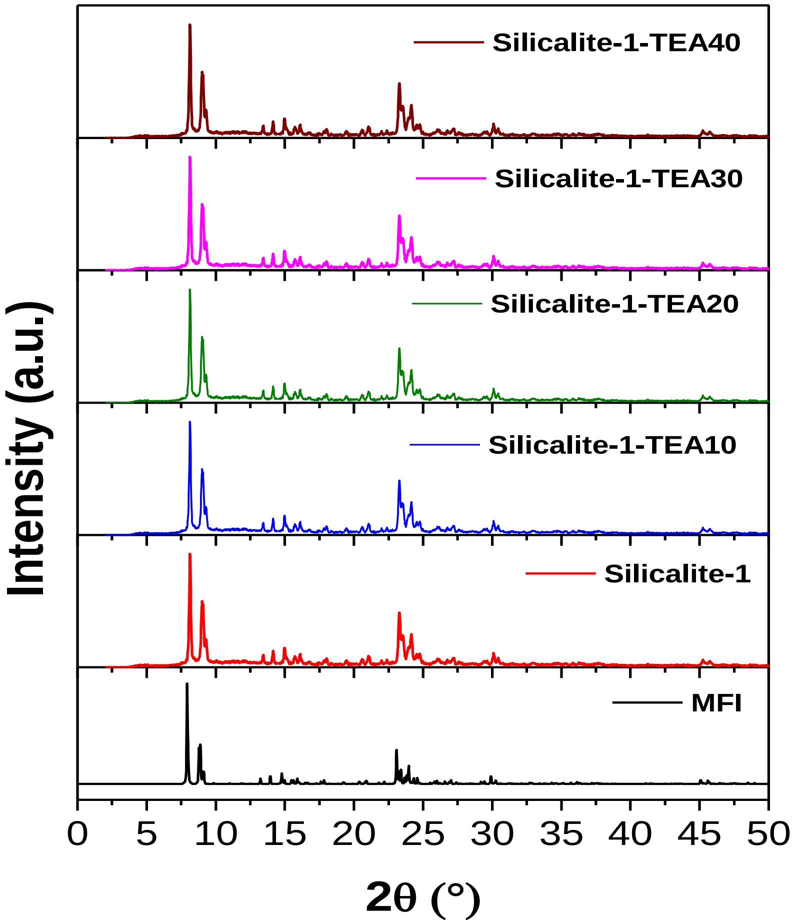

Figure 15 : X-ray diffraction patterns of Silicalite-1 and Silicalite-1 functionalized with 10, 20, 30 and 40 wt.% of triethanolamine

Then, before any modifications, XRD was used to characterise the mesoporous molecular sieve, or MCM-41 samples. Fig. 16 shows examples of X-ray diffractograms before and after calcination at 550 °C in the air. The release of the organics from the silica structure following the calcination step is shown by a comparison of the XRD peaks in Figs. 1a and 1b, which are sharper and more intense (crystalline). In the low 2θ degrees of 2 ^{0}-7 ^{0}, the diffractogram in Fig. 1(a) reveals the presence of three weak peaks in addition to one high intensity peak. Four diffraction peaks can be identified in the XRD pattern, and they correspond to the reflections (100), (110), (200), and (210). These are the properties of the long range ordered hexagonal mesoporous phase in MCM-41. The parent MCM-41 displays three small peaks at 21.31 Å, 18.55 Å, and 14.14 Å, which are caused by the (100), (110), (200), and (210) reflections, respectively. The parent MCM-41 also displays a narrow and strong peak at 37.19 Å.

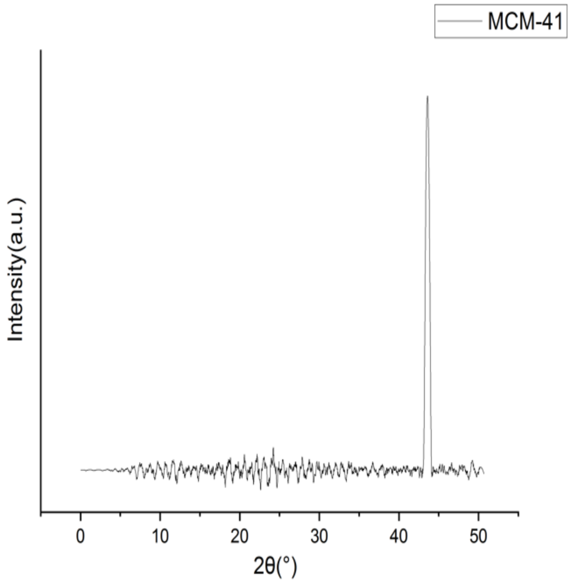

Figure 16 : *X-Ray Diffraction Patterns of MCM*-41

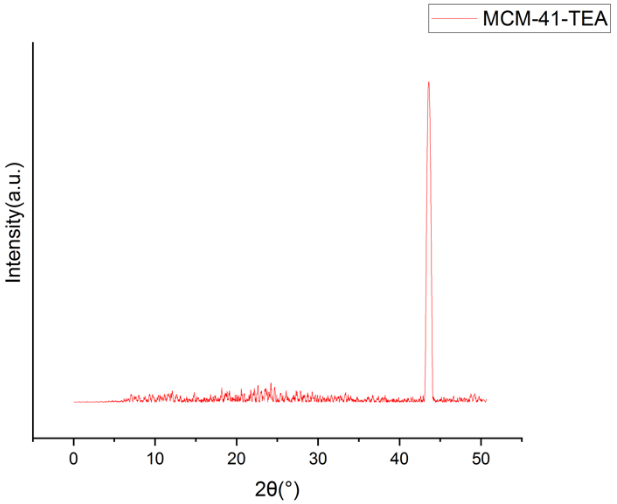

Figure 17 : X-Ray Diffraction Patterns of MCM-41functionalized with 20wt%. of triethanolamine

5.3 Scanning Electron Microscope (SEM)

Figure 15 shows results of the zeolite, silicalite-1, SEM images of silicalite-1 shows that Silicalite-1 particles have a high degree of structural cohesion, looking mainly intact and free of obvious evidence of disintegration or deterioration. This shows that the synthesis method used produced well-formed and resilient particles. The Silicalite-1 particles' surfaces appear rough and uneven. These surface characteristics contribute to the material's enhanced surface area, which is required for high CO2 adsorption capability. The detected particles had a spherical or polyhedral form, implying crystalline structure. The spherical-like shape could be due to the intergrowth of several smaller crystallites, which contribute to the overall particle shape [88].

Silicalite-1 has been functionalized, resulting in SEM pictures that closely replicate the morphology of the parent or starting sample. This remarkable result not only illustrates the structural durability of Silicalite-1 after functionalization, but it also has significant implications for its application during CO_2 adsorption [89].

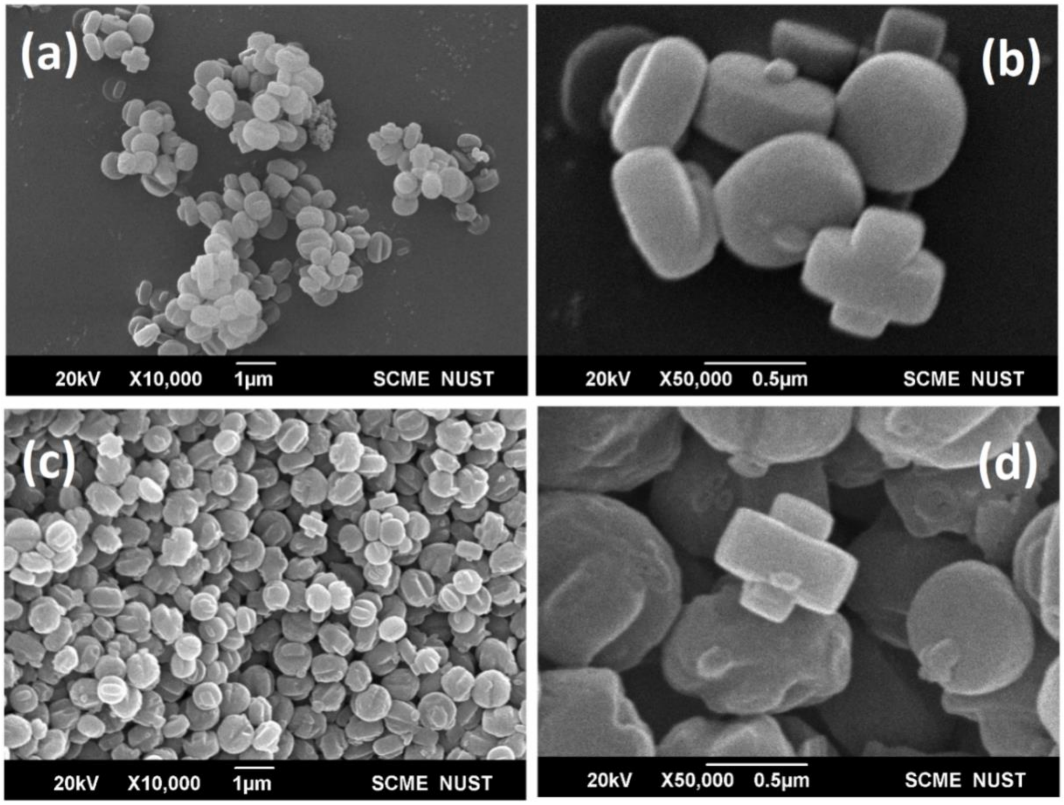

Figure 18 : SEM micrographs of samples (a) Silicalite-1 at low magnification of 10Kx, (b) Silicalite-1 at 50Kx, (c) Silicalite-1-TEA20 at low magnification of 10K and (d) Silicalite-1-TEA20 at 50Kx

The outermost geometries of MCM-41 and 20%TEA-MCM-41 samples are depicted in Figure 16. The sphere short rod-like stacking morphology and a big exterior pore are depicted in the figure. The micrograph of Si-MCM-41 displays spheroidal shaped particles as well as the production of agglomerates. When pristine Si-MCM-41 was modified with 20% TEA (Triethanolamine), the surface morphology of MCM-41 gets a change. After modification of SI-MCM-41 it started to form agglomerates. Furthermore it has been observed that after increasing amine percentage on Si-MCM-41, particles tend to form agglomerates of different shapes and sizes. The change in surface morphology of Si-MCM-41 can be described as, at initial loading of amine onto the Si-

MCM-41 molecules are distributed into the pores and later on as the amine loading increases, amine particles spillover on the outer surface which results in the agglomeration of particles.

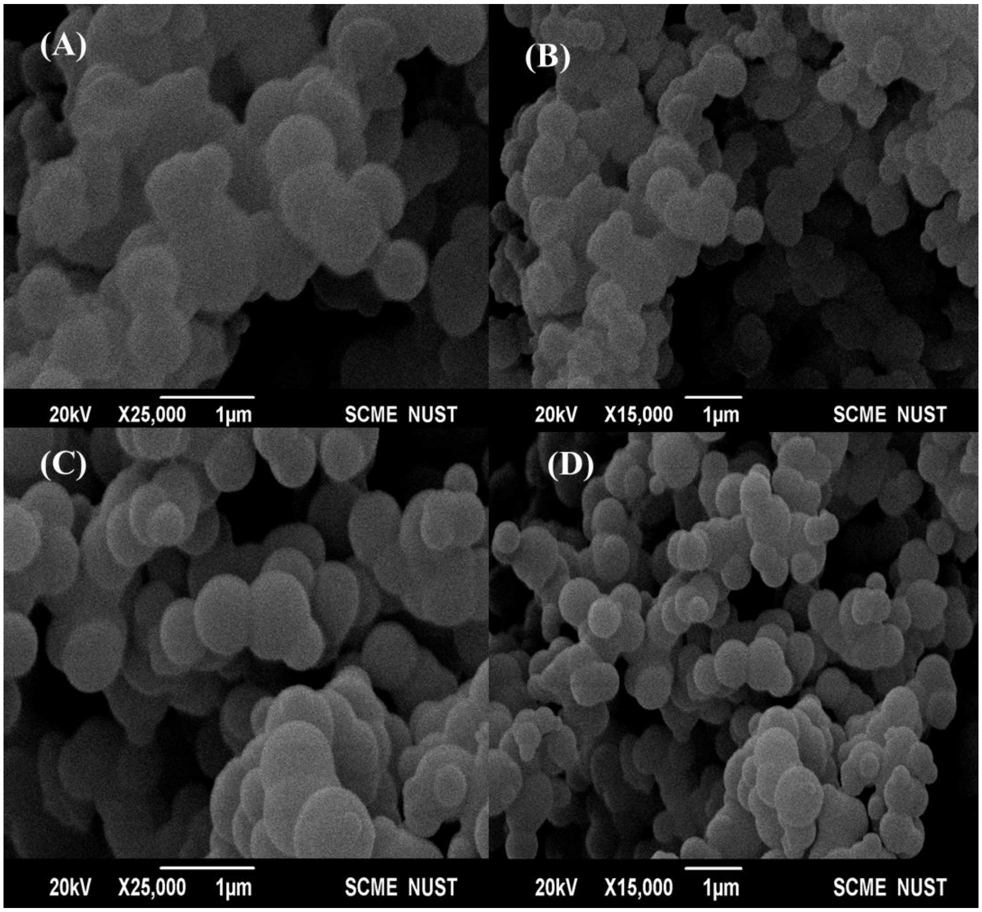

Figure 19 : SEM micrographs of samples **(a)** MCM-41 at low magnification of 25Kx, **(b)** MCM-41 at15Kx, **(c)** MCM-41 -TEA20 at low magnification of 25KX and **(d)** MCM-41 -TEA20 at 50Kx

5.4 Thermogravimetric (TGA) Analysis

The Q50 TA Instrument is used for thermogravimetric analysis of MCM-41 and amine impregnated materials. TGA curves for experimental materials are depicted in The curves are presenting the % change in weight of the sample with the rise in temperature.

Figure 17 shows that all three samples lost weight in two different ways: between 20 and 100 °C and above 550 °C. The weight loss in 20-100 °C was caused by water or CO_2 in the air being released which tells that the prepared sample is thermally stable [89]. At above 500 °C, TEA was totally degraded. Condensation of surface silanol groups (Si–OH) contributes to the weight loss at high temperature (500°C)[90]. Weight loss from 150°C to 500°C occurs gradually because of the condensation of silanol groups, which causes the breakdown of hydrocarbon bonds and the loss of water molecules.

The MCM-41-20% -TEA sample lost weight rapidly between 100 °C and 200°C and 200-300°C. A gradual weight loss curve is found above 400°C. The weight loss between 100 and 300 C is primarily due to silanol group condensation across two stages (100-200 °C and 200-300 °C). In addition to the elimination of silanol groups, TEA breakdown has happened at temperatures ranging from 200 to 400 °C. At 450°C, the amine is entirely dissolved. The weight loss between 450 and 500 °C is due to surfactant tem plate degradation. At 500 °C, the surfactants totally disintegrate[91].

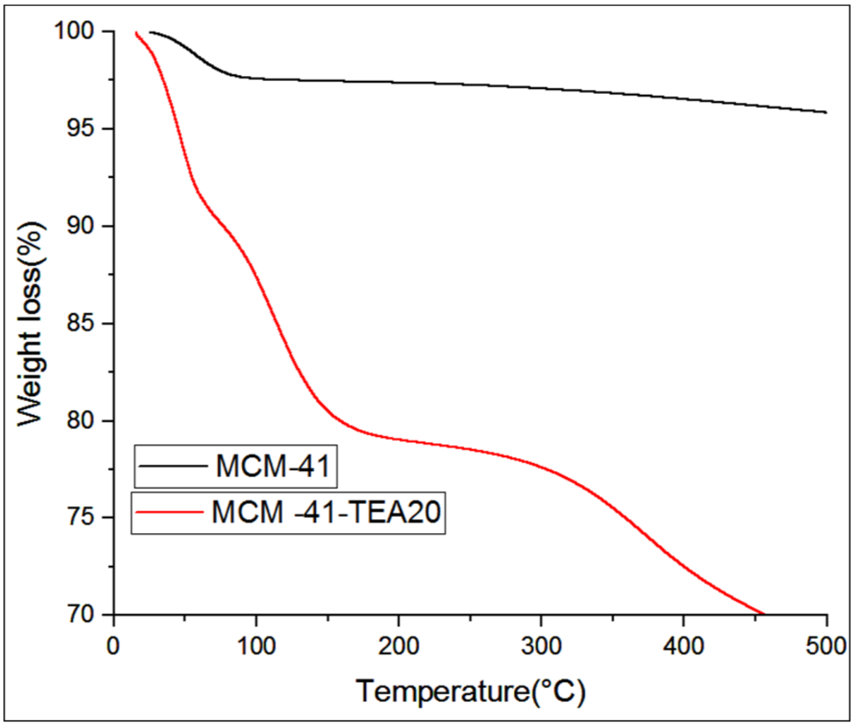

Figure 20 : TG analyses of MCM-41 and MCM-41-TEA20

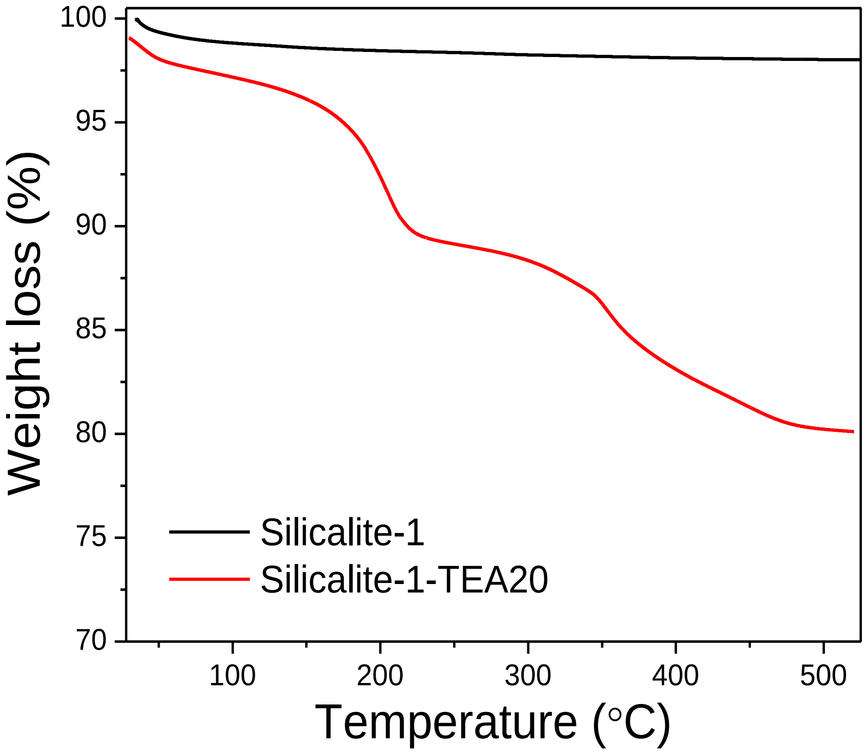

Figure 21 : TG analyses of Silicalite-1 and Silicalite-1-TEA20

The TGA curve demonstrates a relatively little mass loss as the temperature rises in the case of a fresh sample, Silicalite-1. The lack of considerable weight loss throughout the temperature range of 30 to 500 °C indicates that the fresh Silicalite-1 sample does not experience significant decomposition or chemical transformations at the studied conditions, indicating that the material is relatively thermally stable[92].

When compared to the fresh sample, the aminated Silicalite-1 sample (Silicalite-1-TEA20) shows more noticeable mass changes on the TGA curve. The TGA curve notably exhibits three distinct troughs at roughly 100 °C, 200 °C, and 350 °C. These troughs show weight losses linked to the elimination of particular substances[93]. Alcohol and volatile moisture that might have been added during the amination process are thought to have been removed, as evidenced by the first fall in the TGA curve, which happened at 100°C. Further elimination of water molecules and maybe other volatile substances is indicated by the second dip, which was seen at about 200 °C. About 350 °C is the estimated temperature of the third dip, which is probably related to the breakdown or removal of amines that were grafted onto the Silicalite-1 surface during the amination process. A continuous weight loss with discrete portions of weight loss is also seen by the TGA curve between 30 °C and 500 °C[94, 95]. A nearly 4% weight loss is seen between room temperature and 150 °C. An extra 6% of body weight is lost between 150 and 250 degrees. The weight loss keeps going, and between 250 and 550 degrees Celsius, it approaches 10%. Over the whole temperature range of 30 °C to 500 °C, the cumulative weight loss is about 20%. The TGA curve shows no discernible change above 500 °C, indicating that the material has completed its initial stages of disintegration.

The decomposition temperature is strongly influenced by the length of the amine chain, hence the temperature at which breakdown occurs can vary. Because amines coated on the outside surface enhance the resistance towards the heat and mass transfer of the decomposed product, the decomposition temperature rises as the amine chain length grows. Longer chain amines tend to form a coating on the surface and are thus unable to permeate the pores. TEA has a boiling point of 335 ^{o}C.A more resilient amine (TEA) with a higher boiling point is advantageous for industrial applications. Overall, the impregnated amines result in adsorbents that are thermally stable up to 100 degrees Celsius, with the thermal stability increasing with amine chain length and boiling point.

$$\boldsymbol{\eta = \frac{z}{50\%} * 100\%} \qquad (1)$$

Where z was the TGA-measured amine loading [96]

5.5 Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR spectroscopy was used to analyse the vibrations of molecules and functional categories on the outer layer of MCM-41, MCM-41-TEA-20, Silicalite-1 and Silicalite-

1-TEA20. In the instance of MCM-41 and Silicalite-1, FTIR examination of both fresh and aminated samples reveals chemical changes that occur during surface functionalization. The FTIR spectra display unique bands and peaks that shed light on chemical interactions and functional group changes [97].

The MCM-41 and amine functionalized materials are characterized using FT-IR spectroscopy in the mid-infrared range, which spans 400 cm^{-1} to 4000 cm^{-1}. The appearance of a broad absorption band at 3445 cm can be attributed to H-bonded silanol groups (Si–OH), whereas a peak at 1635 cm^{-1} is reflected from the bending vibration caused by water molecules adhering to a silica surface[98]. The Si–O–Si connections' symmetric and asymmetric bending and stretching vibrations are shown by the small peaks at 1050 cm^{-1} and 800 cm^{-1}. The 968 cm^{-1} peak is caused by symmetric vibrations of stretching of Si-OH groups. Weak peaks at 2020 cm^{-1} and 1879 cm^{-1}depict the bending vibration of water molecules adsorbed on the silica structure's surface. The amine impregnated samples also showed the three bands at 1080 cm^{-1} (from the bending vibration), 968 cm^{-1} (from the symmetric stretching vibration of Si-O-Si in MCM-41), and 800 cm^{-1} (from the asymmetric stretching vibration of Si-O-Si in MCM-41)[98]. The presence of silanol groups (Si-OH) in MCM-41 impregnated with 20% TEA is indicated by spectral peaks at 3428 cm^{-1}. These signature peaks indicate that the amines did not alter MCM41's main structure in the sample that was impregnated with amines.

. The H-O-H band is connected to the 1660 c band. The creation of carbamates is attributed to the appearance of a low intensity peak at 1391, a medium intensity peak at 1659, and a sharp and narrow peak at 3428. N-CO-O symmetric stretching is responsible for a weak intensity peak at 967, which indicates the creation of Carbamate[99]. These findings provide proof that carbamates are formed through chemisorption.

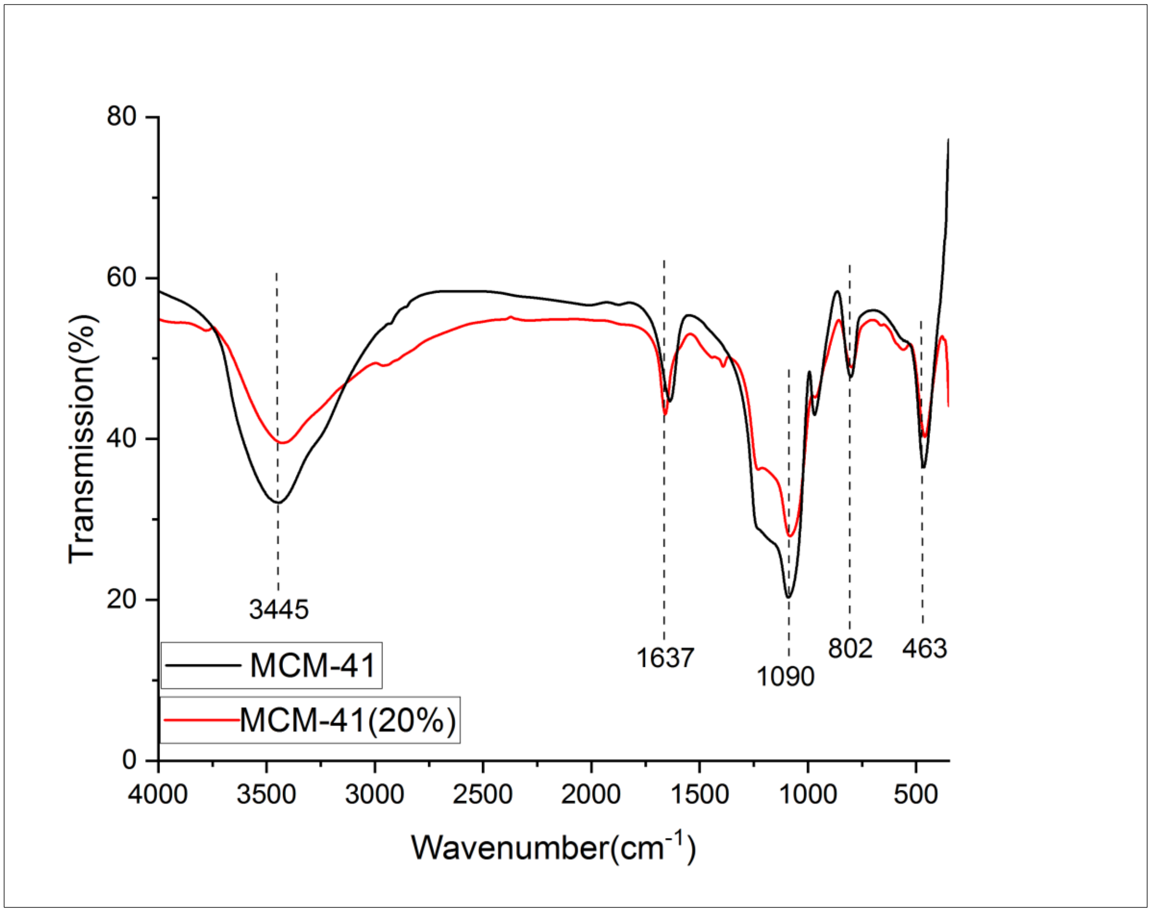

Figure 22 : FTIR spectra of MCM-41 and MCM-41-TEA20

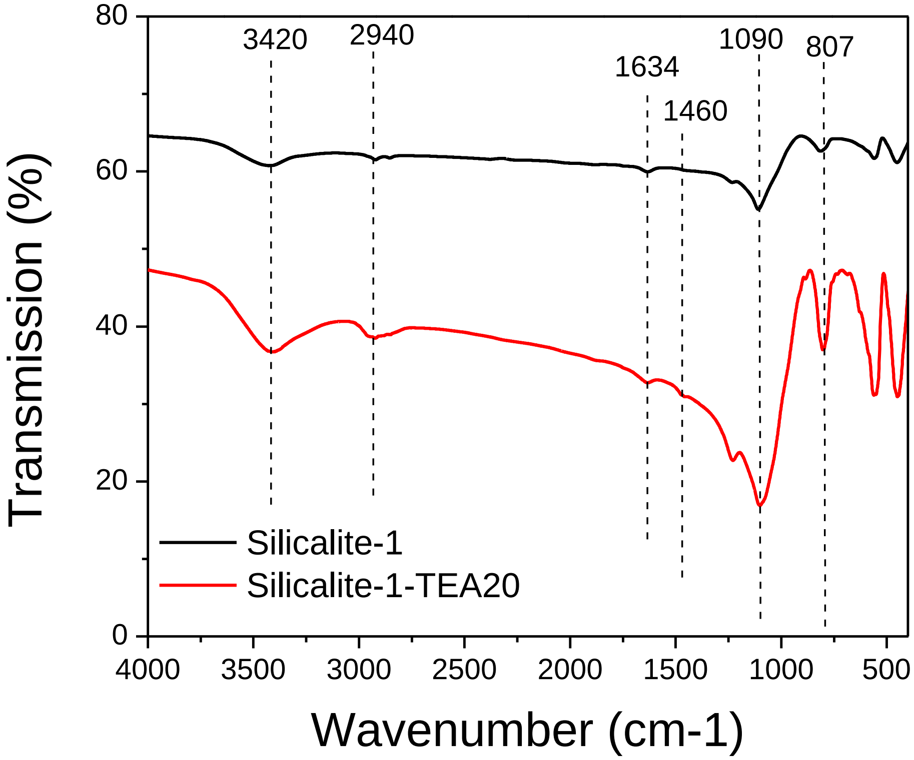

Figure 23 : FTIR spectra of Silcalite-1 and Silicalite-1-TEA20

There are multiple prominent peaks in the FTIR spectrum of the fresh Silicalite-1 sample, each of which is indicative of a different set of chemical vibrations and interactions. Owing to the stretching vibrations of hydroxyl groups (H-OH) and hydrogen bonding, the broad band at 3420 cm^{-1} is explained by the presence of adsorbed water molecules on the surface of Silicalite-1. Many porous materials share the characteristic of adsorbed water, which increases the total capacity for CO_2 adsorption[100]. Adsorbed water molecules are further confirmed by the peak at 1634 cm^{-1}, which is representative of the H-OH bending and stretching vibrations. The Si-O asymmetric stretching vibration of Silicalite-1's framework is linked to the strong band at 1090 cm^{-1}. It illustrates the presence of the distinctive Si-O-Si framework linkages found in Silicalite-1, which characterize its crystalline structure. An additional indication of the zeolite's framework structure, the peak at 807 cm^{-1} correlates to the Si-O symmetric stretching vibration and validates the integrity of the Silicalite-1 structure[101].

The FTIR spectrum of the aminated Silicalite-1 sample shows clear changes in vibrational modes after the amination process using triethylamine (TEA), showing the introduction of new functional groups. The asymmetric and symmetric stretching modes of $C\text{-}H_2$ are responsible for the peaks that arise in the range of 2940 cm^{-1}. This implies that the amination procedure was successful in incorporating organic groups onto the zeolite surface. The surface chemistry is being altered in part by these organic moieties. Weak bands at approximately 1460 cm^{-1} are suggestive of $N\text{-}H_2$ vibration, more precisely connected to the primary amine group (RNH_2). This peak opens up a new possibility for CO_2 adsorption by confirming that amine functional groups were successfully grafted onto the Silicalite-1 surface.

5.6 N_2 Adsorption/desorption isotherm

MCM-41 and impregnated samples' nitrogen adsorption-desorption isotherms are similar to type IV isotherms, mainly because of the mesoporous structure's capillary condensation effect. The adsorption isotherm rises sharply during the capillary condensation phase, and this is seen here at relative pressures between 0.08 and 0.15 and between 0.22 and 0.32[102]. Adsorption isotherms of MCM-41 and functionalized materials show a reversible and almost contemporaneous adsorption and desorption curve, with a very short type 4 hysteresis loop. H4-type hysteresis loops, which are connected to the existence of narrow slit pores in mesoporous materials, are shown in Figure 9This is in line with the pore size distribution data (shown in Fig. 10), which for MCM-41 and MCM-41 impregnated with 20% TEA, respectively, shows a very narrow pore size distribution with pores centred at 1.60 nm[13].The quantity of adsorption increases sharply below 0.35 in the amine-impregnated MCM-41 adsorption isotherm, suggesting a strong pore-filling effect.In the relative pressure range of 0.35-1.0, adsorption increases gradually with pressure, leading to a bimodal pore size distribution.

MCM-41 has a homogeneous mesoporous structure, as indicated by the reversible steep rise behaviour observed, which supports the BJH pore size distribution data. The amine modification of MCM-41 samples does not alter the presence of ordered mesoporous structure, as evidenced by the similar isotherm patterns observed in the adsorption isotherms of the modified samples and MCM-41. The fact that there is virtually no hysteresis loop in the isotherms of the amine-modified MCM-41 indicates that the amines have filled the pores, causing a reduction in both surface area and chamber volume. According to Table 1's structural properties, MCM-41 has a specific surface area of 958.859 m2/g and a total pore volume of 0.5102. We obtain 618.838 m^2/g for the specific surface area and 0.3321 cc/g for the total pore volume for MCM41-20%-TEA. The specific surface area and pore volume of TEA-impregnated MCM-41 may be reduced since TEA is on the silica's surface and all of the pores are filled.The pore size distribution reveals that amine-modified MCM-41 samples exhibit little to no microporosity, while post-impregnation materials maintain their mesoporosity. The aforementioned findings demonstrate that MCM-41's structural stability and homogeneity persist during impregnation, indicating that the amine was successfully infused into the material [14].

Figure 21 shows the N_2 adsorption-desorption isotherms for the samples of Silicalite-1 and amine-functionalized Silicalite-1. The nitrogen sorption isotherm for Silicalite-1 shows a type I isotherm with a hysteresis at P/Po>0.02, indicating the presence of some intercrystalline mesoporosity, and strong nitrogen uptake at a low relative pressure (P/Po), which is often attributed to the microporosity. The N_2 sorption isotherm of Silicalite-1-TEA20 indicates a decrease in microporosity caused by the amine functionalization. It shows comparatively less N_2 absorption at a relatively low relative pressure (P/Po) than the Silicalite-1 sample [103].

The BET surface area of the Silicalite-1 and amine-functionalized Silicalite-1 samples was determined using the N_2 adsorption isotherm, and the results are shown in Table 1. A typical MFI-type zeolite with a high BET surface area (~350–400 m^2/g) is Silicalite-1. The BET surface area of the Silicalite-1 employed in this investigation was 355.6 m^2/g; however, following amine functionalization, it dropped to 55.1 m^2/g. Since it is well known that micro porosity increases a microporous material's total surface area, a decrease in the BET surface area of Silicalite-1-TEA20 suggests that the Triethanolamine inhibited Silicalite-1's microspores [104]

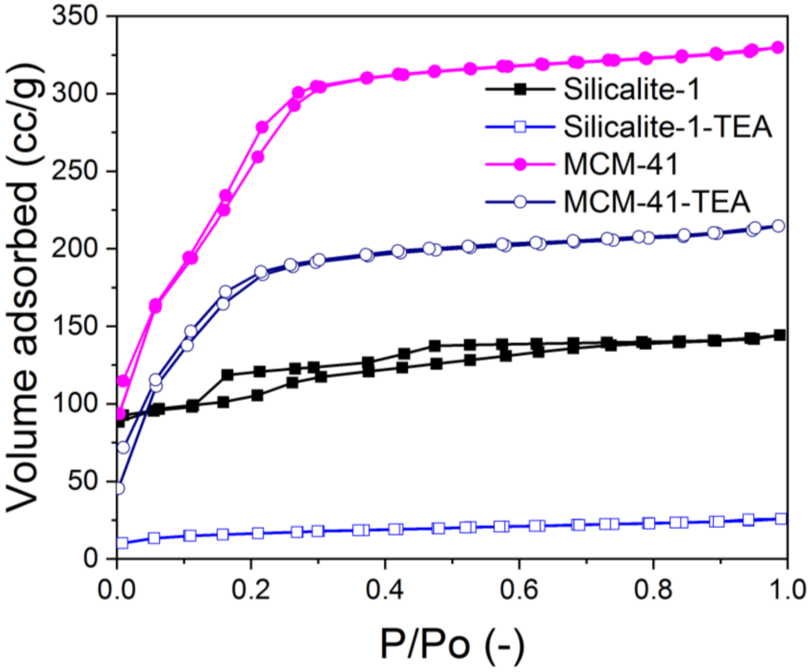

Figure 24 : N_2 adsorption-desorption isotherms of MCM-41.MCM-41-TEA & Silicalite-1,Silicalite-1-TEA20

Table 6: BET surface area of MCM-41.MCM-41-TEA & Silicalite-1,Silicalite-1-TEA20

Adsorbent	BET Surface Area(m^2/g)	Total Pore Volume (cc/g)	Pore diameter (Å)
MCM-41	958.859	0.5102	5.5
MCM-41 TEA (20%)	618.838	0.3321	1.9
Silicalite-1	354.5	0.039	5.5

Silcalite-1 TEA (20%)	54.7	0.017	1.9

5.7 CO_2 Adsorption

The CO_2 adsorption behaviour of both fresh and aminated MCM-41, Silicalite-1 samples was tested at 100°C and pressures ranging from 0 to 15 bar to gather essential information regarding materials for carbon dioxide capture and storage, and the results are shown in Figure 7. This is an important aspect for solving environmental and energy-related issues. The adsorption capabilities and surface areas of the samples are critical in determining their suitability for carbon capture applications[105].

Si-MCM-41 was functionalized with 20 wt% Triethanolamine (TEA) in order to investigate the impact of tertiary amine on Si-MCM-41 for CO_2 adsorption. As TEA contains three alkyl groups on its fundamental "N" atom, its molecular structure is larger. CO_2 adsorption behavior at 20 wt%TEA-Si-MCM-41 at 100C and 0–15 bar of pressure is shown. The adsorption capacity of Si-MCM-41 at a pressure of 15 ($P/P_0=1$) is 1.12cmmol/g. CO_2 adsorption capacity of 20 wt.%TEA-Si-MCM-41 is 0.83 mmol/g at 100°C and 15 bar, which is lower than Si-MCM-41[106]. This shows that the unmodified material has a reasonably high capacity for CO_2 adsorption. The fresh MCM-41 sample has a surface area of 958.859 m2/g, which contributes to its adsorption potential. The high capacity of MCM-41 to adsorb CO_2 molecules is most likely due to its enormous surface area and well-defined pore structure. Furthermore, the elevated temperature of 100°C, which represents an important operating condition for CO_2 collection systems, demonstrates the material's resilience and flexibility for real-world applications.

Surprisingly, the aminated MCM-41 sample has lower CO_2 adsorption capability than the fresh sample. The aminated sample had an adsorption capacity of 0.835 mmol/g under the same conditions (100°C and p/po = 1). The surface area of the aminated MCM-41 sample is also significantly reduced, at 618.838 m2/g. When calculating the mmol/m2 performance, the adsorption capacity relative to the surface area must be taken into account. MCM-41 has a CO_2 adsorption capability of 0.0011 mmol/m^2 due to its increased adsorption capacity and surface area. AminatedMCM-41 performs better in terms of adsorption capacity per unit surface area, registering at 0.0013 mmol/m2, although having a lower absolute adsorption capacity.Reduced CO_2 adsorption may arise from steric barrier to interaction with CO2 molecules caused by the presence of three alkyl groups on the core "N" atom. The 20 weight percent TEA-Si-MCM-41 CO_2 adsorption isotherm at 100 C shows a sharp absorption of CO_2 at low pressure region (0.1 bar) and steep slope, showing a high affinity to collect CO_2 molecules. These results suggest that the CO_2 adsorption capacity of the amine-functionalized Si-MCM-41 adsorbent is significantly influenced by the type and structure of the amine molecule[107].

Another tertiary amine that is impregnated on Si-MCM-41 is Triethanolamine (TEA). It is suggested that whereas tertiary amines do not produce Carbamate when absorbing CO_2, a base-catalyzed hydration mechanism can account for the reaction. On the other hand, tertiary amine-mediated CO_2 adsorption may work via a different mechanism. It might be a direct response between the functions of tertiary amines and CO_2 molecules. It's possible that van der Walls forces and electrostatic attraction prevent the tertiary amine from going through the zwitterion deprotonating procedure for CO_2 interaction. The interaction between CO_2 and tertiary amines works like this:

First step: $R_3N + CO_2$ ----- $R_3N + COO^-$ **(2)**

Second step: $R_3N + COO^- + R_3N$ ---- $R_2NCOO^- + R_4N^+$ **(3)**

The CO_2 adsorption isotherm of the fresh Silicalite-1 sample demonstrates its ability to adsorb CO_2 at 100°C. At a pressure of 15 bar ($p/p_o = 1$), the adsorption capacity of the fresh sample was measured as 1.90 mmol/g. This indicates that the unmodified material possesses relatively good CO_2 adsorption capability[107]. The surface area of the fresh Silicalite-1 sample, measured as 355.6 m^2/g, contributes to its adsorption potential. Silicalite-1's potent ability to adsorb CO_2 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_2 capture systems. Interestingly, the aminated Silicalite-1 sample exhibits a lower CO_2 adsorption capacity compared to the fresh sample. At the same conditions (100°C and $p/p_o = 1$), the aminated sample showed an adsorption capacity of 0.732 mmol/g. The surface area of the aminated Silicalite-1 sample is notably lower as well, measured at 54 m^2/g. When considering the $mmol/m^2$ performance, it is important to account for the adsorption capacity relative to the surface area. Silicalite-1, with its higher adsorption capacity and surface area, has a CO_2 adsorption capacity of 0.00536 $mmol/m^2$. On the other hand, aminated Silicalite-1, despite its lower adsorption capacity in absolute terms, demonstrates superior performance in terms of adsorption capacity per unit surface area, measuring at 0.0135 $mmol/m^2$[108].

From the above results we see that adsorption capacity of a silicate is also temperature dependent. This phenomena can be explained as follows: at higher temperatures, CO_2 molecules have higher kinetic energy, resulting in an unfavourable interaction between CO_2 molecules and amino sites, resulting in a decrease in CO_2 adsorption capacity.

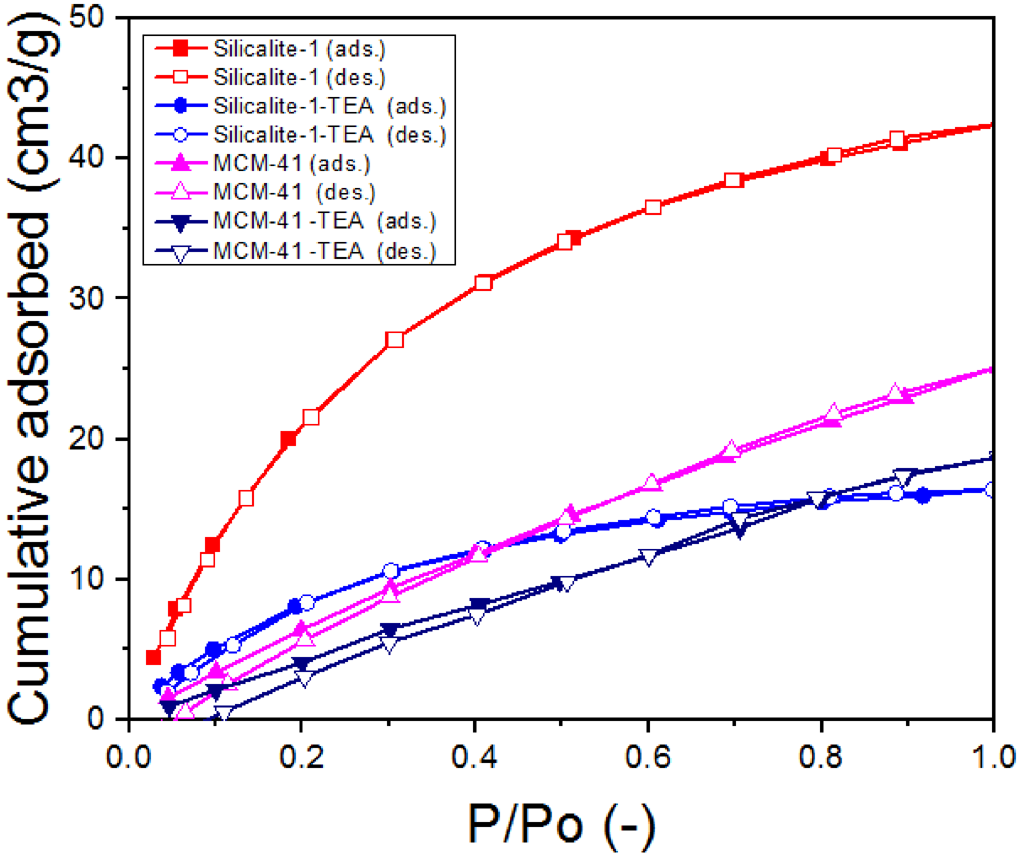

Figure 25 : CO_2 adsorption isotherms of MCM-41.MCM-41-TEA & Silicalite-1,Silicalite-1-TEA20

6 CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 FUTURE RECOMMENDATIONS

Numerous studies have been conducted on MCM-41, a silicate material and silicalite-1, a zeolite with a high surface area and homogenous pore structure, to determine its adsorption capabilities. In this investigation, Amination process was used to assess and contrast the adsorption capabilities of pure MCM-41, silicalite-1 and MCM-41, silicalite-1 that had been modified with amines. Both materials' adsorption rates per unit surface area were calculated. The results showed that amine modification significantly increased adsorption per unit area, suggesting that amine-functionalized MCM-41, silicalite-1 may be an effective adsorbent. Pure MCM-41, silicalite-1 and MCM-41,silicalite-1 treated with amine were found to have initial adsorption capabilities of 1.12 mmole/g,1.90mmol/g and 0.83 mmole/g,0.732mmol/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. Adsorption per Unit Surface Area: Pure MCM-41, silicalite-1 had an adsorption per unit surface area of 0.0011 mmol/m2 and 0.00536mmol/m^2, but MCM-41,silicalite-1 that had been treated with amine had an adsorption per unit surface area of 0.013 mmol/m2 and 0.0135 mmol/m^2. This considerable increase in adsorption per unit area following amine modification indicates that MCM-41's, silicalite-1 adsorption effectiveness was improved by the addition of amine functional groups. The results of comparing the adsorption capacities of pure MCM-41, silicalite-1 with MCM-41, silicalite-1 that had been treated with amine showed that the latter had less adsorption capacity. However, the amine-modified MCM-41, silicalite-1 showed 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 MCM-41, silicalite-1 material for the selectivity and study the detail kinetics for the CO_2 reaction with the amines. Table 7 shows

Table 7: Comparison of Whole Study

Silicate & Zeolite	Surface area (m^2/g)	Adsorption capacity (mmole/g)	Adsorption capacity ($mmole/m^2$)
MCM-41	958.859	1.12	0.0011
MCM-41 Comparison with literature[109]	750	0.89	0.0011
MCM41-TEA	618.838	0.83	0.0013
MCM41-TEA Comparison with literature[109]	589	0.62	0.0010
Silicalite-1	354.7	1.92	0.0053
Silicalite-1 Comparison with literature[110]	238	1.64	0.0068
Silicalite-1-TEA	54.7	0.732	0.013
Silicalite-1-TEA Comparison with literature[110]	94	0.810	0.0086

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