New Material Synthesis For Carbon Dioxide Capture From The Flue Gas

Major Project

Submitted in Partial Fulfillment of the Requirements

For the Degree of

Master of Technology in Chemical Engineering

By

Rajvi Mehta

(11MCHE05)

DEPARTMENT OF CHEMICAL ENGINEERING

INSTITUTE OF TECHNOLOGY

NIRMA UNIVERSITY

AHMEDABAD-382481

MAY 2013

New Material Synthesis For Carbon Dioxide Capture From The Flue Gas

Major Project

Submitted in Partial Fulfillment of the Requirements
For the Degree of
Master of Technology in Chemical Engineering
(Environment Process Design)

By
Rajvi Mehta
(11MCHE05)

Guided By
Dr. A. P.Vyas

DEPARTMENT OF CHEMICAL ENGINEERING
AHMEDABAD-382481
May 2013

Declaration

This is to certify that

1. The thesis comprises my original work towards the degree of Master of Technology in Environment Process Design at Nirma University and has not been submitted elsewhere for a degree.

2. Due acknowledgement has been made in the text to all other material used.

Rajvi .S. Mehta

Undertaking for the Originality of the work

I,Rajvi Mehta, 11MCHE05, give undertaking that the major project entitled **"New Materials for Carbon Dioxide Capture from Flue Gas "** submitted by me, towards the partial fulfillment of the requirements for the degree of master of technology in Environment Process Design of Nirma University, Ahmedabad is the original work carried out by me and I give assurance that no attempt of plagiarism had been made.

I understand, that in the event of any similarity found subsequently with any published work or any dissertation work elsewhere, it will result in severe disciplinary action.

Rajvi .S. Mehta

Signature of Student

Date:

Place:

Endorsed by

Dr. A.P. Vyas

Signature of Guide

Certificate

This is to certify that the Major Project entitled **"New Materials for Carbon Dioxide Capture from Flue Gas"** submitted by **Ms. Rajvi Mehta (11MCHE05)**, towards the partial fulfillment of the requirements for the award of Degree of Master of Technology in Chemical Engineering (Environmental Process Design) of Nirma University is the record of work carried out by her under my supervision and guidance. The work submitted has in my/our opinion reached a level required for being accepted for examination. The results embodied in this major project work to the best of my/our knowledge have not been submitted to any other University or Institution for award of any degree or diploma.

Dr. Rajeshwer Dongara
Vice President,
Reliance Technology Group
Reliance Industries Limited,
Jamnagar, Gujarat

Dr. A. P. Vyas
Professor & Guide
Institute of Technology
Nirma University
Ahmedabad, Gujarat

Dr. Satyanarayana Reddy
Senior Manager
Reliance Technology Group
Reliance Industries Limited
Jamnagar, Gujarat

Dr. J. P. Ruparelia
PG Coordinator (EPD)
Institute of Technology,
Nirma University
Ahmedabad, Gujarat

Dr. Sanjay S. Patel
HOD (Chemical Engg. Dept.)
Institute of Technology
Nirma University
Ahmedabad, Gujarat

Dr. Asit Kumar Das
HOD, Reliance Technology Group
Reliance Industries Limited
Jamnagar, Gujarat

Dr. Ketan K. Kotecha
Director, Institute Of Technology
Nirma University
Ahmedabad, Gujarat

Examiners:

Acknowledgements

It gives me immense pleasure to express my gratitude to **Dr. Rajeshwer Dongara**,Vice President, Reliance Technology Group (RTG), Reliance Industries Limited for suggesting me with this research topic and his invaluable guidance, motivation, constant inspiration and above all for his ever co-operating attitude that enabled me in bringing up this report in the present form.

I am also thanful to **Dr. A. K. Das**, Head of Department (HOD), Reliance Technology Group (RTG), for giving me as oportunity to gain knowledge from one of the leading research facility.

I would like to express my immense and deep gratitude to **Dr. Satyanarayana Reddy** for his invaluable guidance throughout my project work, by his constant help, thoughtful suggestions and co-operation have enabled me to complete this work.

I am also thankful to my guide **Dr. A.P.Vyas**, Professor, Nirma University for his support and guidence throughout the project work.

I am also thankful to **Dr. Amit Deshmukh** and entire team of Reliance Technology Group (RTG) department for their inspiration and timely help. My heartily thanks to **Ms. Priyanka Thyagrajan** for her immense help during my project work.

I take opportunity to express deep and sincere sense of gratitude towards **Dr. J. P. Ruparelia**, Professor and PG-Coordinator of Department of Chemical Engineering, Institute of Technology, Nirma University, Ahmedabad for giving support and continual encouragement throughout my Major project.

I take an oppotunity to express deep and sincere thanks to **Dr. S. S. Patel**, Head of Chemical Engineering Department, Institute of Technology, Nirma University, for providing me an opportunity to carry out my major project.

I would also like to thank **Dr K Kotecha**, Honourable Director, Institute of Technology, Nirma University, Ahmedabad for his unmentionable support by providing basic infrastructure necessary to conduct research.

Rajvi .S. Mehta

11MCHE05

Abstract

Carbon dioxide generated from fossil fuel-fired power plants is a major contributor to global warming approximately 30% of gaseous CO_2 emitted to the atmosphere comes from the fossil fuel plants. Among the approaches used, amine based chemical absorption have been used commercially for CO_2 capturing plant. However, the liquid amine based processes pose operating difficulties due to the challenge of keeping the solvent clean and operating within the process constraints of the system. This process also suffers from high regeneration energy, large equipment size, solvent leakage from piping system and also equipment corrosion problem. regenerable solid sorbents will be a promising alternative that can potentially offer several advantages over liquid amine systems such as ease in handling of solids, reduced toxicity and corrosiveness. Various porous supports impregnated with liquid amines have been reported. The key issue for adsorption separation is to develop an adsorbent with high CO_2 adsorption capacity and high CO_2 selectivity which will be the main objectives of this study. The purpose of this research is to develop a simple, cost effective technology to remove CO_2 as an essentially pure stream from flue gas using a regenerable amine-based sorbent. There are different technologies like membrane separation, cryogenic separation, absorption by liquid amines and various solid adsorbents used to functionalize for CO_2 capture by means of physical and chemical adsorption. In this research project we mainly focus on the solid adsorbents like MCM-22, Alumina and SBA-15 which will be functionalized by different amines like Tetraethylpentamine and Polyethylenimine for carbon dioxide capture capacity.The results shows that as the concentration of amines increased the surface area and pore volume decreases. Amongst all the samples 50% TEPA functionalized SBA-15 shows the maximum CO_2 adsorption Capacity i.e. 2.4 mmol/g. All the sorbents prepared for this work are regenerable at 130°C The adsorption capacities showed good correlation with well-ordered porous structure, amine loading and type of amine.

Keywords: Adsorption, Amines, Adsorbents, Functionalization, Regenerability

Contents

List of Figures

List of Tables

Chapter 1

Introduction

Environmental issues are the major cause of concern in the world of today. Greenhouse gases are an environmental concern that is continuously increasing in importance, especially the emission of carbon dioxide. Fossil fuel burning results in emission of carbon dioxide. There are too many sources for anthropogenic carbon dioxide adding to the concentration of CO_2 in the atmosphere every year, and these sources are increasing as the world becomes more industrialized. Recently industries have been taking more proactive steps to remove carbon dioxide from their emission gas streams.

Global carbon dioxide emissions exceeded 25 billion metric tons in 2003. The United States alone accounted for 23.1% of the total carbon dioxide emissions. The next closest carbon dioxide emitter was China at 14.1% of the total carbon dioxide emissions. The most abundant emission source from power plants is from coal based power plants. Coal plants account for 80% of the total carbon dioxide emissions from fossil fuel.

In 2005, the concentration of atmospheric CO_2 reached nearly 380 ppm, an increase of ~35% above the preindustrial concentration of CO_2 in the atmosphere (275285 ppm) [1]. Indian CO_2 emissions in 2005 were 1229 Mt CO_2, and almost doubled during 1990-2005. It is estimated that total annual CO_2 emissions in India will increase 2.5 times during 2005-2030 to reach 3084 Mt CO_2 in 2030, growing annually at 3.7% [2].

Different carbon capture and storage (CCS) strategies have been proposed as a means of mitigating the contribution of CO_2 emissions to global warming from power stations. However, the costs of capture and sequestration of CO_2 has been the main hurdle to overcome for the deployment of many emerging technologies. The separation of CO_2 from flue gases of coal-fired power plants can account for as much as 70-80% of the total energy cost for CO_2 CCS [4]. Therefore, the importance to develop new energy-efficient techniques for CO_2 separation has driven vast efforts from the scientific community for the development of materials and processes that can efficiently and economically capture and isolate CO_2 from flue gases.

Post-combustion capture technologies such as absorption with liquid amines or adsorption with solid adsorbents have been proposed as possible retrofits to existing PC plants that are integral to modern power generation infrastructure. Absorption processes involving CO_2 capture by liquid media are widely established [3].

Several techniques have been proposed for CO_2 separation and recovery, including chemical absorption and adsorption, physical adsorption and membrane separation. Among these techniques, chemical absorption with aqueous solutions of alkanolamines (monoethanolamine and diethanolamine, among others) is already commercially used for large scale purification of industrial gases (natural gas, syngas, etc.)[4]. The absorption is carried out in packed scrubbing columns where the CO_2 stream and aqueous amine solution are injected in a countercurrent way, allowing the reaction of CO_2 with amines and regenerating the CO_2-containing amine solution at high temperatures[5]. Despite its popularity, several concerns are associated with liquid amine absorption, including high energy requirements for solvent regeneration, extensive corrosion of the equipment[6,7], and the impact that amine solutions have on the surrounding ecosystems.

The use of membranes for CO_2 separation mainly involves the use of polymeric membranes or amine-modified inorganic membranes [8,9]. The separation is based on the high permeability of CO_2 through the membranes compared to that of nitrogen gas. This process is efficient in separating CO_2 from gas streams with high volumetric flow rates and high CO_2 concentrations[8]. For applications that fit these characteristics, membrane separation technologies are one of the most realistic and lowest energy consuming CO_2 capture methods.

Cryogenic separation is applied to CO_2 capture where the gas stream contains high CO_2 concentrations. It requires large amount of energy and is too expensive when the volume of CO_2 in the exhaust gases is too low and is at atmospheric pressure such as those encountered with typical power generation plants. However, the success of this and other emerging adsorption technologies relies upon the creation of novel sorbents with high CO_2 sorption efficiencies and low manufacture costs that allow favorable industrial processes economics and the offset of high CO_2 capture costs in coal-fired power plants.

On the other hand, pressure swing adsorption and/or temperature swing adsorption systems consisting of packed beds of novel solid sorbents are emerging technologies with great potential to reduce carbon capture costs in coal-fired power plants. They are suitable for low CO_2 concentration gas streams with large volumetric flow rates, and emerging systems using packed beds of hollow fiber hybrid sorbents have low flue gas pressure drops and low regeneration thermal requirements, allowing to reduce operational and overall CCS costs [10].

Conventional adsorbents such as zeolite molecular sieves, activated carbons, silica gels, and carbon molecular sieves have been not effective for CO_2capture from low concentrated gaseous mixtures. Therefore, significant scientific research is in progress to produce suitable adsorbents for different CO_2 emitting sources applications by using all kind of classic and novel materials. Efforts are underway in different directions, ranging from new approaches of using well known adsorbents as zeolites[11,12] and activated carbons[13,14] in the design of complex hybrid materials, to the exploration of totally new materials such as periodic mesoporous silicas[15-20] and metal organic frameworks (MOFs)[21,22].

With the aim to exploit the efficient amine-CO_2 interactions that has brought liquid amine CO_2 scrubbing to its current status of commercial technology, but avoiding the aforementioned drawbacks of this absorption system, a new generation of amine functionalized mesoporous silica adsorbents have emerged during the last years. This class of materials exhibits large surface area and pore volume, with pore size distribution in the nanometer scale that allow the introduction of amine functionalities on its surface by conventional grafting methods [20]. Due to their ordered mesoporous structure and the possibility to tailor their internal pore system, these materials have attracted the attention of researchers in many fields other than adsorption. However, certain drawbacks have been associated with amine-functionalized mesoporous silicas, like a typical non homogeneous amine surface coverage and the lost of its mesoscopic ordering. Perhaps even more important is the fact that a significant fraction of the amine groups may be inaccessible to CO_2 when embedded in the silica network [23]. Therefore, it has been found that amine groups only efficiently interact with the gas when the materials maintain an open pore structure after the grafting reactions [24].

Therefore, the development of efficient, reliable, thermally stable and cost effective sorbents for CO_2 capture from power plant flue gases is still a challenge that needs to be addressed. In order to reduce the cost of CO_2 capture and sequestration, sorbents with high sorption and long-term regeneration capacities in power-plant flue gas environments, and with low energy requirements for regeneration are needed. The use of these novel adsorbents in periodic cyclic adsorption processes is certainly a potential low cost carbon capture alternative technology that could meet the present and future economic and environmental constraints placed on CO_2 capture from coal-fired power plants.

1.1 Applications of CO_2

Gas Plants produce Carbon dioxide in mainly two forms - Liquid and Solid. Solid CO_2 is also known as "dry ice" and is used as refrigerants in food industry and for small shipments. CO_2 is widely utilized during the storage and shipping of ice cream and other frozen foods.

1. **Fire Extinguishers**: CO_2 extinguishes fires.
2. **Beverage**: This gas is used to make carbonated soft drinks and soda water.
3. **Solvent**: Liquid CO_2 is considered as a good dissolving agent for many organic compounds. Here it can be used to remove caffeine from coffee.
4. **Plants**: Plants require CO_2 to execute photosynthesis, and greenhouses can promote plant growth with additional CO_2.
5. **Pressured Gas**: It is used as the cheapest noncombustible pressurized gas. Pressured CO_2 are inside tins in life jackets. Compressed CO_2 gas is used in paintball markers, airguns, for ballooning bicycle tires.
6. **Medicine**: In medicine, up to 5% CO_2 is added to pure oxygen. This helps in provoking breathing and to stabilize the O2/CO_2 balance in blood.
7. **CO_2 Laser**: The CO_2 laser, a common type of industrial gas laser uses CO_2 as a medium. Welding: It also finds its use as an atmosphere for welding.
8. **Oil Wells**: Carbon dioxide is commonly injected into or next to producing oil wells to draw lost traces of crude oil.
9. **Chemical Industry**: It is used as a raw material in the chemical process industry, especially for urea and methanol production.
10. **Metals Industry**: It is used in the manufacture of casting influences so as to enhance their hardness.
11. **Fumigation**: Used as a fumigant to increase shelf life and remove infestations.

1.2 Converting CO_2 to Chemicals

An alternative pathway is to convert CO_2 into chemical feedstock. The entire portfolio of commodity chemicals are currently manufactured from a few primary building blocks or platform chemicals in the fossil-based chemical industry. CO_2 can be used as a source material and, utilizing renewable energy sources and water can be converted into a similar suite of building block chemicals. Insertion of CO_2 into epoxides to manufacture various polymeric materials is an exciting technology as it not only utilizes CO_2, but also avoids using fossil feedstock and creating CO_2 emissions. It has been estimated that the various chemical conversion pathways can consume approximately 0.3 to 0.7 Gt/y of CO_2 [8].

Conversion of CO_2 into inorganic minerals that may be used in building materials is being pursued by some companies. This involves a combination of electrochemical reactions to generate the alkaline reactant and necessary mineralization reactions. Initial estimates suggest that even if 10 % of the worlds building materials were to be replaced by such a source, consumption of 1.6Gt/y CO_2 would result.

1.3 The electrochemical method for CO_2 Conversion

Using metal or alloy electrodes/catalysts, various products can be produced by electrochemical reduction of CO_2, including carbon monoxide (CO), formic acid (HCOOH),oxalates (C_2O_4-), hydrocarbons (e.g., ethylene C_2H_4), and alcohols (e.g., methanol, CH_3OH). DNV selected the Electrochemical Reduction of CO_2 to Formate/ Formic Acid (ECFORM) as the process for comprehensive evaluation of the technical feasibility for CO_2 utilization because commercialization of this process was considered to be most likely to be profitable. Methanol is another attractive fuel, but requires more electrical energy than formic acid for its production from CO_2.

1.4 Application of CO_2 for Bio Use

1. Greenhouses
2. Micro Algae Bio diesel

1.4.1 Greenhouses

CO_2 has long been used to enhance the production and growth of a variety of vegetables, fruit and flowers in greenhouses throughout the world and especially in Europe. Pure CO_2 is injected via a tank into greenhouses whereby the plants within rapidly utilise the CO_2 in combination with sunlight and heat which enhances growth along with fruit and flower production even in cool climates.

1.4.2 Micro Algae Bio diesel

Algae live on a high concentration of carbon dioxide and nitrogen dioxide which are released by automobiles, cement plants, fertilizer plants, steel plants & power plants. These pollutants serve as key nutrients for the algae. Scrubbed exhaust gas from a power plant and CO_2 capture plant can be bubbled through tanks or ponds with algae. The algae extract the CO_2 from the exhaust and convert it to sugars via photosynthesis. Via further metabolism these sugars are then converted to oils and proteins, which can be extracted to form biodiesel and ethanol.

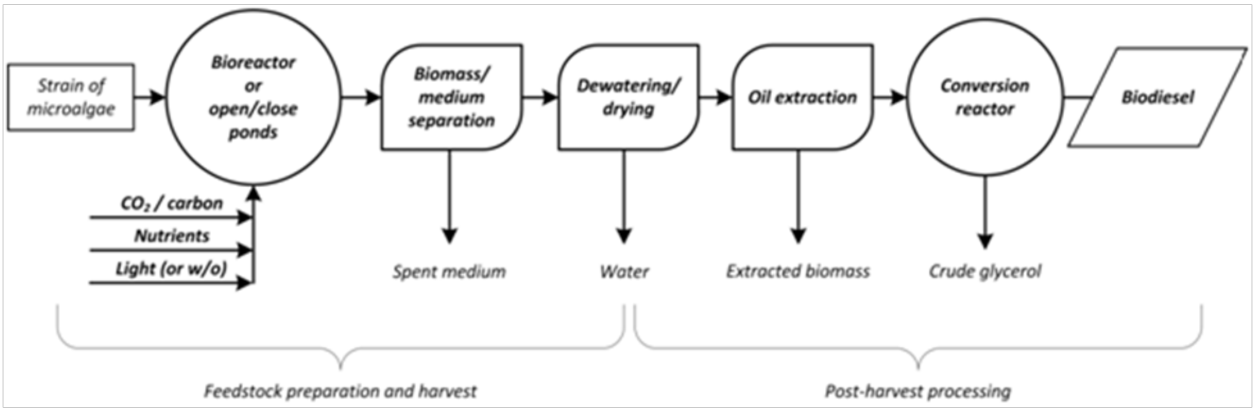


Figure 1.1: Algae to oil process

1.5 Outline of the Thesis

This thesis consists of five chapters which describes the research in a sequential order. **Chapter 1** introduces the research background on amine modified adsorbents; problems encountered by the industry, and underlined objectives to solve the problems. **Chapter 2** provides the literature review of the general aspects related to the field of research study. This includes post combustion technologies for CO_2 capture, adsorption isotherms and mechanism, fundamental of microporous and mesoporous materials, modification of adsorbents and gas adsorption characteristics. **Chapter 3** describes the materials and methods applied in the experimental study and adsorbents characterization in detail while the results and discussion of the findings are included in **Chapter 4**. Lastly, **Chapter 5** summarized the results as well as the findings of the study and some recommendations for future work.

Chapter 2

Literature Review

2.1 CO_2 capture technology

A wide range of technologies currently exist for separation and capture of CO_2 from gas streams although they have not been designed for power-plant-scale operations. They are based on different physical and chemical processes including absorption, adsorption, membranes, and cryogenics. The choice of a suitable technology depends on the characteristics of the flue gas stream, which depend mainly on the power plant technology.

The CO_2 capture technology are typically categorized into three main methods

i. Post-combustion
ii. Pre-combustion
iii. Oxyfuel combustion

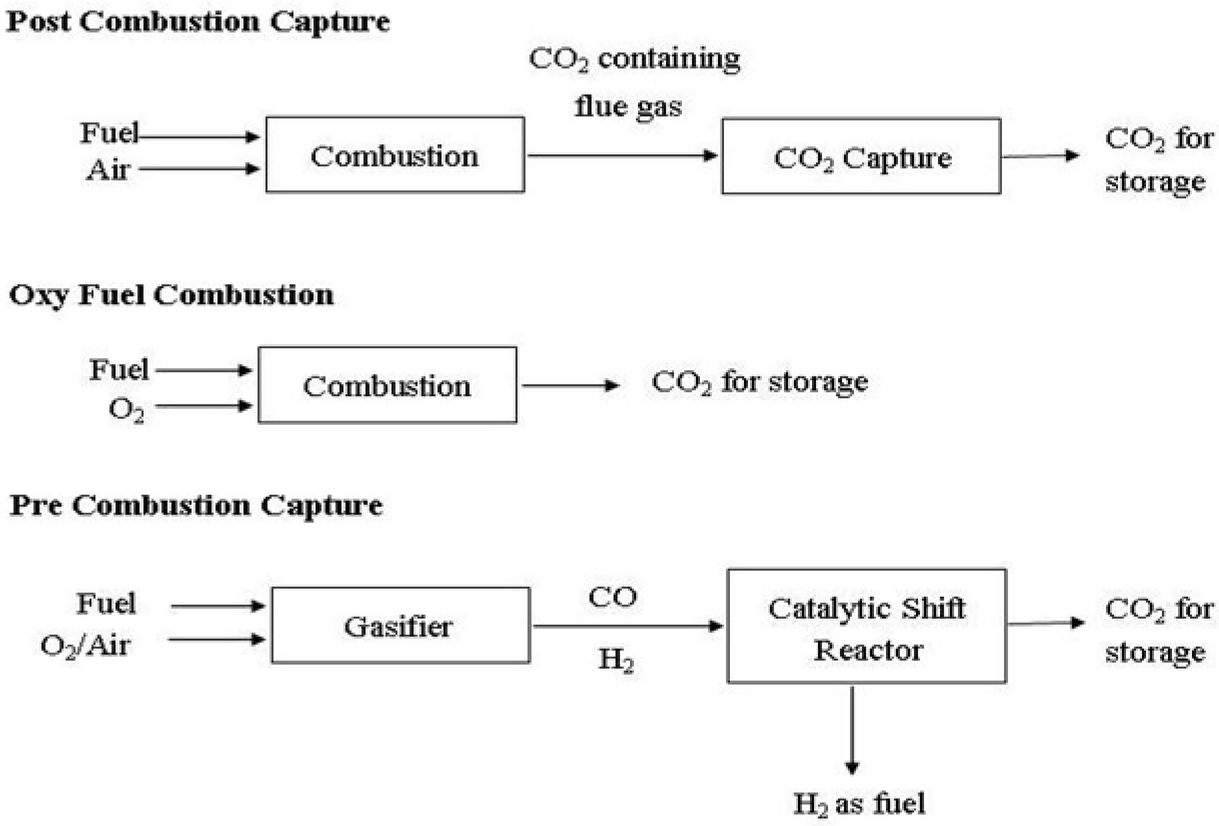


Figure 2.1: Three basic approaches to CO_2 capture

Post-combustion capture involves the removal of CO_2 from the flue gas after combustion[26,27]. Instead of being discharged directly to the atmosphere, the flue gas is passed through equipment which separates/captures most of the CO_2[26].

Pre-combustion CO_2capture refers to the capture of CO_2 prior to combustion. An alternative to capturing carbon from flue gas is to modify the combustion process so that the flue gas has a high concentration of CO_2[28]. This can be accomplished by burning the fuel in nearly pure oxygen (greater than 95%), referred to as oxy-fuel combustion or simply oxy-combustion, instead of ambient air, thereby eliminating nitrogen and this results in a flue gas that is mainly CO_2 and H_2O. Post-combustion capture applies primarily to coal-fuelled power generators that are air fired. Oxy-combustion can be applied to new plants or retrofitted to existing plants. Pre-combustion capture can be applied to gasification plants[29].

Post-combustion carbon capture has the greatest near-term potential for reducing GHG emissions, because it can be retrofitted to existing units that generate two-thirds of the CO_2 emissions in the power sector[26,29]. There are several post combustion gas separation and capture technologies being investigated, namely: Absorption, Cryogenic separation, Membrane separation, and Adsorption.

2.2 Gas Separation Methods

There are mainly 4 methods for CO_2gas separation

i. Solvent Absorption
ii. Membrane separation
iii. Cryogenic fractionation
iv. Adsorption through solid sorbents[27,30]

2.2.1 Absorption

The separation of solute gases from gaseous mixtures of noncondensables by transfer into a liquid solvent. This recovery is achieved by contacting the gas stream with a liquid that offers specific or selective solubility for the solute gas or gases to be recovered. The operation of absorption is applied in industry to purify process streams or recover valuable components of the stream. It is used extensively to remove toxic or noxious components (pollutants) from effluent gas streams [31].

It can be further divided into 2 types

i. Physical absorption
ii. Chemical absorption

2.2.1.1 Physical absorption

In physical absorption the gas CO_2 molecules are dissolved in to liquid solvent and no chemical reaction takes place. The binding between CO_2 molecules and the solvent molecules being either van der Waals force or electrostatic and is weaker than that of chemical bonds in chemical absorption. The amount of gas absorbed is proportional to its partial pressure. The physical absorption is stronger when the partial pressure of the gas absorbed is high. The amount of gas absorbed also depends on the temperature. The lower the temperature more is the gas absorbed. Typical sorbents for CO_2 are methanol, N-methyl-2-pyrrolidone, polyethylene, glycol dimethyl ether, propylene carbonate and sulfolane.

Desorption can be achieved either by lowering the pressure as in the pressure swing absorption (PSA) or by increasing the temperature as in the temperature swing absorption (TSA)[32].

2.2.1.2 Chemical absorption

In Chemical absorption of CO_2 separation from the flue gas mainly MEA is used as sorbent. Chemical absorption uses the different relativities of various gases with sorbents to separate them. The reactions need to be reversible so that the spent sorbent can be regenerated. For separating the CO_2 from the flue gas, absorption appears appropriate becauseCO_2 is acidic and the majority of the rest of flue gas, nitrogen, is not. CO_2 can be absorbed by many basic sorbents including alkali carbonate, aqueous ammonia, and alkanolamines. The attention needs to be paid is how the sorbents can be regenerated. The binding between sorbent molecules and CO_2 generally is strong and this offers a fast and effective removal of most of CO_2 in one stage of absorption. However, the strong binding between CO_2 and the sorbent molecules is also one of the causes for high regeneration energy requirement. Second concern is the control of impurities and miner components in the flue gas including SO_2, oxygen, etc. that may degrade the sorbents. These components have to be removed before the gas enters the absorber, or treated with appropriate measures. Lastly, because many sorbents are corrosive, only diluted solutions are used [33].

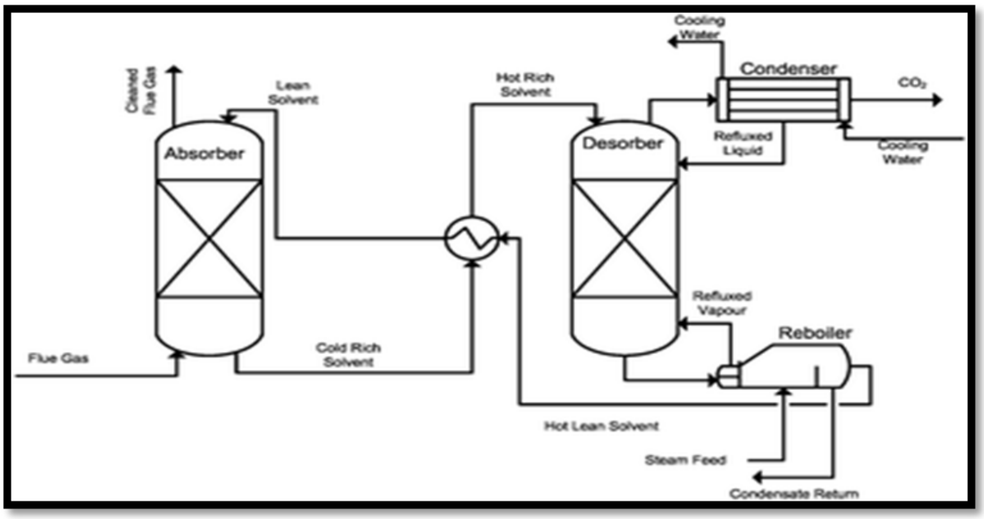


Figure 2.2: CO_2 recovery process through solvent absorption

2.2.1.3 Ionic liquids

Ionic liquids constitute another class of physical solvents which are also known to be selective for CO_2 absorption. This comprises combinations of large organic cations and smaller inorganic anions and is typically viscous liquids near room temperature. Therefore, a nonvolatile solvent that could facilitate CO_2 capture without the loss of solvent into the gas stream would be advantageous. Ionic liquids (ILs) are commonly defined as liquids which are composed entirely of ions with a melting point of less than 100°C. ILs have many unique properties in comparison to other solvents as extremely low volatility, broad range of liquid temperature, high thermal and chemical stability, and tunable physicochemical characteristics [35].

The mechanism of capture is often based on physisorption and involves weak association between ionic liquid and CO_2 molecules with heats of adsorption around -11kj/mol because of this minimal energy required for solvent regeneration. The capacity is directly proportional to the partial pressure of CO_2 and improves at pressure above 1-2 bar. Ionic liquids can also simultaneously remove CO_2 and SO2 since SO2 solubility is 8-25 times greater than that of CO_2 at the same partial pressure and as a result, ILs have been considered as a potential substitute of aqueous amine solutions for CO_2capture [36].

2.2.2 Membrane Technologies

Many membranes are made with similar materials used for physical adsorbents, because the physical quality, such as porous structure and selective gas affinity, are also useful for making membranes. Membranes are microscopic sieves. Under an applied pressure some molecules will pass through the microspores in membranes, and some molecules will be stopped. The driving forces for gas separation using membranes are generally hydrostatic pressure and concentration gradient. There has been some work done in electrically driven separation of gases via ion conduction.

Two types of membrane technologies can be used for separating CO_2 from other gases:

i. Gas separation membranes

ii. Gas absorption membranes

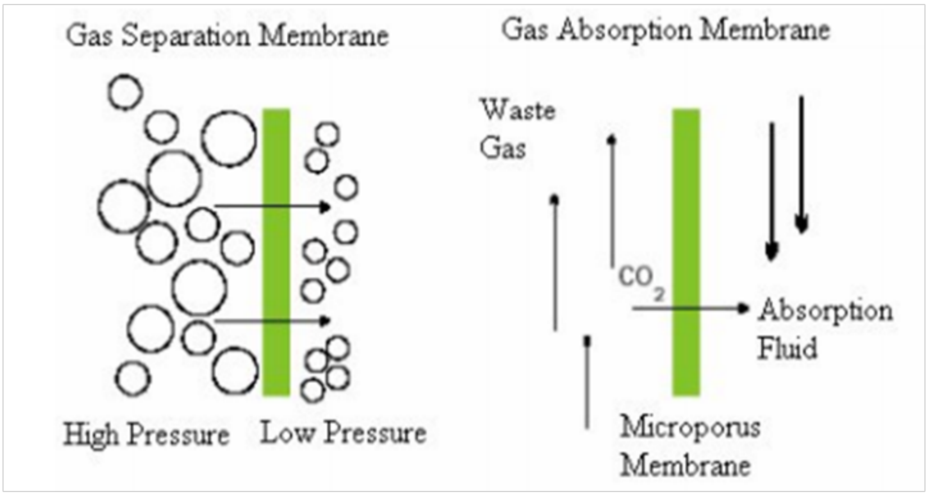


Figure 2.3: Membrane Separation

In using gas separation membranes a hydrostatic pressure is applied and the difference in permeability of gas species leads to separation of these gases. Although using separation membranes to separate CO_2 from light hydrocarbons has met with considerable success in the petroleum, natural gas and chemical industries, this technology may not be preferable to separate CO_2 from flue gas because of the large volume of the flue gas and the compression energy requirement. A study shows that a good separation using a two-stage system would cost twice much of the conventional amine separation processes.

In using gas absorption membranes, a liquid sorbent is used to carry away CO_2 molecules that diffuse through the membranes, and no high hydrostatic pressure is required. In this technology, the membranes serve as an interface between the feed gas and liquid sorbent [37].

2.2.3 Cryogenic Separation

Cryogenic separation of gas mixtures uses the difference in boiling points of various gas species to separate them. Between these temperatures, CO_2 can be liquefied by compression and cooling. The major disadvantage of cryogenic method is the high-energy consumption and costs associated with gas compression and cooling. Cryogenic separation is an energy intensive operation [33].

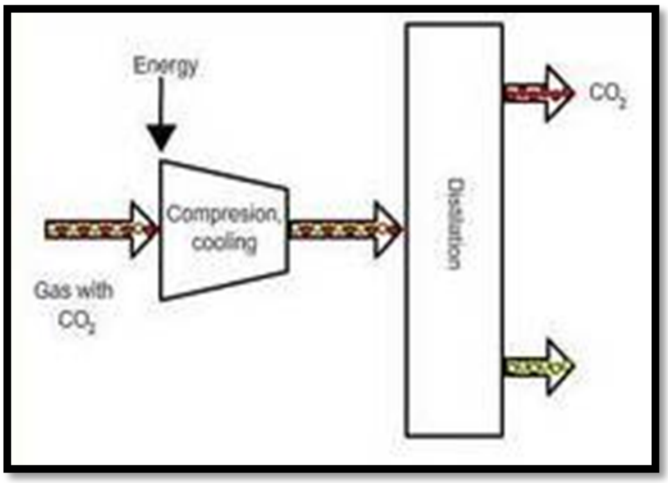


Figure 2.4: Cryogenic Distillation

2.2.4 Adsorption through solid sorbents

Adsorption is one of the promising methods that could be applicable for separating CO_2 from gas mixtures. Adsorption refers to uptake of CO_2 molecules onto the surface of a solid sorbent.CO_2adsorption involves either physisorption (van der Waals) or chemisorption (covalent bonding) interactions between the gas molecules and the surface of the material. The CO_2-laden solid is purified in stages using pressure, vacuum, or temperature swing adsorption cycles to remove and concentrate the CO_2.

2.3 Criteria for Selecting Adsorbent

The sorbent materials must satisfy some important criteria to be both economical and operational for CO_2capture from flue gas.

2.3.1 Adsorption capacity for CO_2 adsorption

The high capacity for CO_2 adsorption reduces both sorbent quantity and process equipment size.

2.3.2 Selectivity for CO_2

Good adsorbent materials should exhibit high CO_2 selectivity over other bulk gas components.

2.3.3 Adsorption/desorption kinetics

The overall kinetics of CO_2 adsorption on a functionalized solid sorbent is influenced by the intrinsic reaction kinetics of CO_2 with the functional group present, as well as the mass transfer or diffusion resistance of the gas phase through the sorbent structures. The porous support structures of functionalized solid sorbents also can be tailored, to minimize the diffusional resistance. The faster an adsorbent can adsorb CO_2 and be desorbed, the less of it will be needed to capture a given volume of flue gas.

2.3.4 Mechanical strength of sorbent materials

The sorbent must be morphologically stable and retain the CO_2 capture capacity during the multicycling between absorption and regeneration steps. Operating conditions, such as high volumetric flow rate of flue gas, vibration, and temperature should not cause appreciable disintegration of the sorbent particles. This could also happen via abrasion or crushing. Therefore, adequate mechanical strength of sorbent particles is critical to minimize the sorbent makeup rate and to keep CO_2 capture process cost-effective.

2.3.5 Tolerance to impurities

The amine functionalized sorbents should be stable in oxidizing environment of the flue gas and should be resistant to the common flue gas contaminants.

2.3.6 Regeneration of the sorbents

The heat of adsorption which is the measure of energy required for regeneration should be substantially low [39].

2.4 Adsorbent for CO_2 Removal

A new concept called molecular basket is being discovered to develop a high capacity, highly selective CO_2 adsorbent. A novel type of solid adsorbent has been discovered, which can serve as a molecular basket for packing CO_2 in condensed form in the nanoporous channels. To capture a large amount of CO_2 gas, the adsorbent needs to have large pore channels filled with a CO_2 capturing substance as the basket. To cause the basket to be a CO_2 molecular basket, a substance with numerous CO_2 affinity sites should be loaded into the pores of the support to increase the affinity between the adsorbent and CO_2 and as a result, the CO_2 adsorption selectivity and CO_2 adsorption capacity can be increased. In addition, the adsorption affinity to CO_2 by the CO_2 philic substance increased in the confined mesoporous environment and therefore the mesoporous molecular sieve can have a synergetic effect on the adsorption of CO_2 by CO_2 philic substance [40].

2.5 Types of Adsorption

2.5.1 Physisorption

Adsorption can result either from the universal van der Waals interactions (physical adsorption, physisorption) or it can have the character of a chemical process (chemical adsorption or chemisorption). Physical adsorption can be compared to the condensation process of the adsorptive. As a rule, it is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance. Therefore, physical adsorption is very effective particularly at a temperature close to the critical temperature of a given gas [41].

2.5.2 Chemisorption

Contrary to physisorption, chemisorption occurs only as a monolayer. Chemisorption occurs usually at temperatures much higher than the critical temperature and by contrast to physisorption is a specific process which can only take place on some solid surfaces for a given gas. Under favourable conditions, both processes can occur simultaneously or alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic [42].

2.6 Adsorption Mechanism by Porous Adsorbents

2.6.1 Physisorption by Mesoporous Adsorbents

The characteristic shape of a Type IV isotherm is the result of surface coverage of the mesopore walls followed by pore filling. The onset of capillary condensation (the pore filling process) is indicated by an upward departure of the isotherm from the multilayer Type II isotherm for the same gas-solid system. The plateau at higher p/p0 isattained when the mesopore filling is complete [41, 43].

2.7 Adsorbents

Most solid adsorbents for industrial applications possess a complex porous structure that consists of different sizes and shapes. If the pores are slit shaped, their width is consider as the size. However, for pores with cylindrical shape the term diameter is frequently used. Adsorbents or porous materials are characterized in terms of pore sizes derived from gas sorption data. Through IUPAC conventions, classification of pore sizes andgas sorption isotherms reflect the relationship between porosity and sorption[42,43].

Pores are classified according to pore diameteras follows:

i. Micropores diameters less than 2 nm;

ii. Mesoporous diameters between 2 and 50 nm;

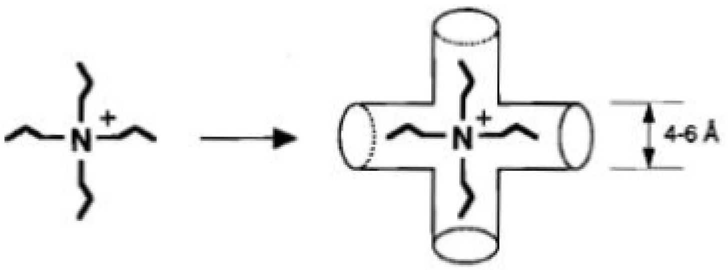
iii. Macroporous diameters more than 50 nm.

2.8 Mesoporous Materials

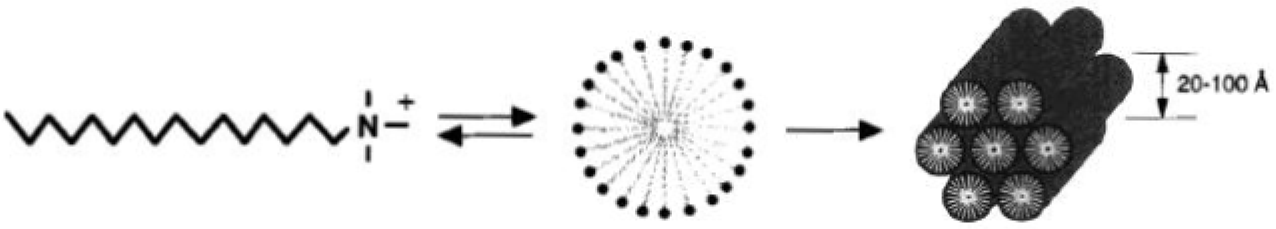
These materials, possessing pore sizes in the 2-50 nm range, have a wide range of potential applications including shape-selective catalysis and sorption of large organic molecules, chromatographic separations, and uses as hosts to confine guest molecules and atomic arrays.

2.8.1 Formation Mechanism of Mesoporous Materials

A new class of mesoporous molecular sieves, M41S, has been discovered by extending the concept of zeolite templating with small organic molecules to longer chain surfactant molecules. Rather than individual molecular directing agents participating inthe ordering of the reagents to form the porous material, assemblies of molecules, dictated by solution energetics, are responsible for the formation of these pore systems.This supramolecular directing concept has led to a family of materials whose structure, composition, and pore size can be tailored during synthesis by variation of the reactant stoichiometry, nature of the surfactant molecule, or by post synthes is functionalization techniques [43-46].



Individual Small Alkyl Chain Length Quaternary Directing Agents Generate the Formation of Microporous Molecular Sieves



Long Alkyl Chain Length Quaternary Directing Agents Self-Assemble to Supramolecular Species Which Can Generate the Formation of Mesoporous Molecular Sieves

Figure 2.5: The formation of microporous molecular sieves using individual small alkylchain length quaternary directing agents (top) and the formation of mesoporous molecular sieves use long alkyl chain length quaternary directing agents (bottom).

The formation mechanism of this mesoporous family of molecular sieves isdictated by two features. The first is the dynamics of surfactant molecules to form molecular assemblies which lead to micelle and, ultimately, liquid crystal formation.The second is the ability of the inorganic oxide to undergo condensation reactions to form extended thermally stable structures. The initial discovery involved the formation of silicates using alkyltrimethyl ammonium cationic surfactants in a basic medium. Subsequent efforts have shown these structures can also be formed in acid media and by using neutral normal amines, nonionic surfactants, and dialkyldimethyl ammonium cationic surfactants. In addition, several mechanistic studies have expanded the initial pathway studies to a more generalized view of an organic/inorganic charge balance driving force for the formation of these structures [43,46,47].

2.9 Amines

There are number of amines investigated for the impregnation onto the silica support. The amine with the maximum nitrogen content is beneficial in order to maximize the capture capacity per total weight of the adsorbent. Alkanol amines, simple combinations of alcohols and ammonia, are the most commonly used category of amine chemical solvents for CO_2 capture. Reaction rates with specific acid gases differ among the various amines. In addition, amines vary in their equilibrium absorption characteristics and have different sensitivities with respect to solvent stability and corrosion.

Alkanolamines can be divided into three groups

i. Primary amines
ii. Secondary amines
iii. Tertiary amines

2.9.1 Mechanism of amines reacting CO_2

Amines are the most common solvents used for CO_2absorption and therefore different possible reactions for absorbing CO_2 in amines are studied. The interaction of CO_2 with amines can be governed by several different mechanisms. Primary and secondary amines can react directly with CO_2 to produce carbamates through the formation of zwitterionic intermediates [48]. In the first step the lone pair on the amine attacks the carbon on CO_2 to form the zwitterion. Free base deprotonates the zwitterion to form the carbamate. In an aqueous amine the base can be H_2O or OH. The same mechanism is applicable to the secondary amines also [49]. Tertiary amines do not react directly with CO_2 but primary and secondary amines do react directly with CO_2. They lack the free proton needed in the deprotonation step. Instead of reacting directly with CO_2, tertiary amines catalyze the formation of bicarbonate.

In the first step, the tertiary amine dissociates H_2O to form a quaternary cationic species and OH. Hydroxide ion then attacks $CO_2$to form the bicarbonate anion. The last step is then the ionic association of the protonated amine and bicarbonate [50]. The formation of bicarbonate allows a high equilibrium capacity. For CO_2capture from the flue gas the immobilization of amines onto the solid support has many advantages. A large energy cost is paid to heat H_2O in the aqueous amine solution during the amine-regenerating, CO_2 stripping step.

A portion of this process cost can be avoided by eliminating H_2O in exchange for a solid silica support (SBA-15, MCM-41) with lower heat capacity. By using the solid support there is no issue of degradation due to evaporation loss and due to poor contact between the solid-solid surface vessel corrosion is less [13].

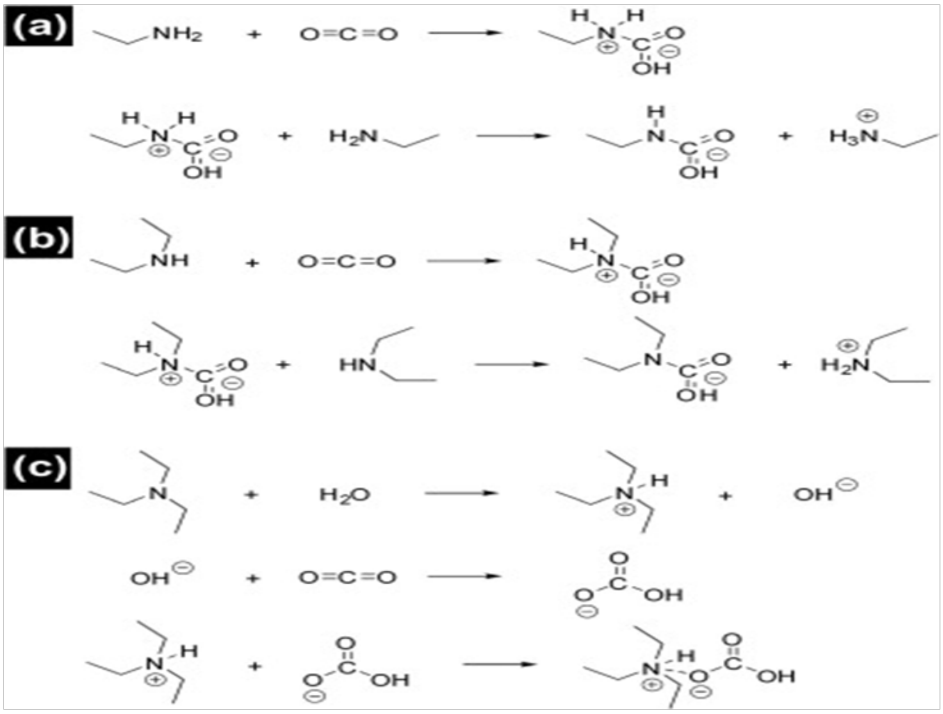


Figure 2.6: General reaction scheme for the chemical absorption of primary amines, secondary amines and tertiary amines respectively.

2.10 Adsorbents for CO_2 Capture

A large variety of adsorbents are found for CO_2 capture including activated carbon, zeolites or molecular sieves, silica gel, and activated alumina. Others include mesoporous materials such as MCM-41 and SBA-15, oxides, and metal-organic frameworks (MOFs). Carbon-based porous materials, especially activated carbon find many applications as adsorbents or supports for various catalysts.

Activated carbons have microcrystalline structures and their adsorptive properties are due to their microporous structure, high surface area and high surface reactivity. They have adequate adsorption capacity for CO_2at ambient temperature and atmospheric pressure.

Zeolites are crystalline alumino silicates of metals like sodium, potassium, magnesium, or calcium. The framework structure of zeolites are composed of a three dimensional network of basic structural units consisting SiO_4 and AlO_4 tetrahedra linked through oxygen atoms.

In general, zeolites have higher adsorption capacity and higher selectivity for CO_2adsorption as compared to carbon based sorbents. But zeolites have high isosteric heat of adsorption for CO_2 adsorption and very strong nature of adsorption makes desorption difficult. CO_2 adsorption capacity of activated carbon was found to be about 2.5 mmol/g at 25°C and 1 atm CO_2 partial pressure. It has been reported that the CO_2adsorption capacities of activated carbons decrease with increasing adsorption temperature due to the physical nature of the adsorption process.

Thus, activated carbons need to be modified so as to facilitate chemical adsorption and hence improve the CO_2 adsorption capacity at high temperatures. Their surface chemistry can be efficiently modified by chemical impregnation which together with the intrinsic nature of the activated carbon can highly increase the adsorption capacity. The impregnation of carbon with various compounds may result in some negative effects, such as decrease in surface area and pore blocking in the structure of activated carbon. But there is an increase in the adsorption capacity of activated carbons at high temperatures.

Materials like zeolites and activated carbons have high surface areas ($>$1500 m^2/g) and adsorb selectively different gases depending on their surface area, pore size, pore volume and surface chemistry. They can reversibly adsorb a large quantity of CO_2 at room temperature but their capacity diminishes quickly at elevated temperatures.

Their selectivity for CO_2 in the presence of water is also poor. They require large pressure and/ or temperature gradient between the adsorption and desorption stages to enable both efficient adsorption performances and near complete desorption of CO_2

Thus, these adsorbents need to be modified so as to facilitate chemical adsorption in these adsorbents. Hence, there is an increasing demand to design highly selective adsorbents, which can operate at such high temperatures. This can be achieved by modification of adsorbents [51].

2.11 Amine Functionalized Solid Sorbents

A variety of mesoporous materials loaded with basic nitrogen functionality, more specifically, organic amine functionality has been synthesized and characterized to chemisorb CO_2 from flue gas streams. Supported amine sorbents have been classified into three classes:

Class 1: This class of supported sorbents is prepared by physically loading monomeric or polymeric amine species into or onto the porous support (typically, the porous silica by impregnation technique).

Class 2: This class of supported adsorbents is that in which the amine, mainly amine containing silane is covalently tethered to a solid support, such as porous silica. This is accomplished by binding amines to oxides via the use of silane chemistry or via preparation of polymeric supports with amine-containing side chains. This provides covalently tethered amine sorbents with the potential to be completely regenerable through multicycle adsorption/desorption uses.

Class 3: These supported adsorbents are based on porous supports upon which monopolymers are polymerized in situ. This category of supported sorbents can be considered a hybrid of the other two classes [52].

2.12 Modification of Adsorbents

A promising approach for CO_2 adsorbents that has been successfully developed in recent years is the incorporation of amines into a high surface area support, combining good capacity and selectivity at moderate temperature. Adsorbents containing basic nitrogen functional groups have increased adsorbent/adsorbate interaction, thereby providing such materials with a selective affinity for CO_2 via the formation of ammonium carbamate species under anhydrous conditions and, in addition, via transformation to ammonium bicarbonate and carbonate species in the presence of water.

Zeolite 13X had been modified with monoethanol amine (MEA) using methanol as the solvent. The CO_2 adsorption capacity of adsorbents was evaluated using the breakthrough adsorption method in the temperature range of 30-120°C. The adsorbents showed improvement in CO_2 adsorption capacity over the unmodified zeolite by a factor of ca. 1.6 at 30°C, whereas at 120°C the efficiency improved by a factor of 3.5. The adsorbent was also studied for CO_2 selectivity over N_2 at 75°C. The MEA modified adsorbent had selectivity for CO_2 over N_2 1.4 times more compared to bare zeolite 13X. The performance of the adsorbent was also satisfactory in repeated cycles of adsorption.

In another work, novel functionalized adsorbents had been synthesized by immobilization of various amines like monoethanol amine, ethylene diamine and isopropanol amine on synthetic zeolite 13X.

Effect of various parameters like effect of solvent, shaking time, synthesis temperature, and wetting of pellets prior to amine loadings was also studied. The adsorption capacities obtained were 0.36 mmol/g of CO_2 for unmodified zeolite 13X and 0.45, and 0.52 mmol/g of CO_2 for zeolite modified with monoethanol amine, and isopropanol amine.

A new type of composite adsorbent was synthesized by incorporating monoethanol amine into zeolite. The adsorption behavior of carbon dioxide, methane, and nitrogen on these adsorbents was investigated at 30°C. The results showed that the structure of zeolite did not deteoriate after MEA modification. In comparison with CH_4 and N_2, $CO_2$was preferentially adsorbed on the adsorbents investigated [53].

2.13 Impregnation Method

The simplest and probably the most common procedure for dispersing a catalytic species on a carrier involve impregnating the predried support to incipient wetness with an aqueous or non-aqueous solution containing a salt (precursor) of the catalytic element or element. The precursor salt is dissolved in a volume of solvent equal to the catalyst pore volume and this solution is added slowly (sometime drop wise) to the support in which capillary forces of up to several hundred atmosphere draw the liquid into the pores. Addition of solution continues until the pores of the support are saturated, as evident by the beading of the excess solvent. In this manner, the precise amount of catalytic species is assured to be present in the carrier.

2.14 Amines Covalently Tethered to Oxide Supports

The second main class of silica supported amines used as solid CO_2 adsorbents are those in which the amine is covalently bound to the silica support, usually through alkylsilyl linkages. These adsorbents have a clear advantage over amine impregnated silicas in that they cannot leach amines unless conditions are strong enough to break covalent bonds. This gives covalently tethered amine adsorbents (CTA) the potential to be fully regenerable through repeated adsorption and desorption cycles.

2.14.1 Amine-containing Silanes

The most commonly reported method for synthesizing CTAs is through the use of silane chemistry. A general synthetic scheme is presented where R1 is often an aminoaklyl group. In it, an aminoalkyltrialkoxysilane is reacted with a silica surface, typically in an organic solvent. The alkoxysilyl groups condense with surface silanol groups to form new Si-O-Si linkages while liberating alcohols. Trialkoxysilanes are typically used to create as many new linkages to the silica surface as possible. The R2 groups in the alkoxy functionalities are most often methyls since they have been shown to be more reactive than bulkier groups such as ethyls or propyls. The average number of surface bonds actually formed depends on the density of silanols on the silica support, the R1 and R2 groups used, and reaction conditions such as silane concentration, temperature, and time.

The choice of amine used for synthesizing CTAs directly impacts the resulting materials adsorptive properties. Primary and secondary amines have been shown to capture CO_2 more efficiently than tertiary amines, as noted above. As previously discussed, the nitrogen density of supported amines is also critical from a CO_2 capacity per weight perspective. Thus, the logical choice for an amine-containing silane would be one with a maximum density and quantity of accessible primary and secondary amines.

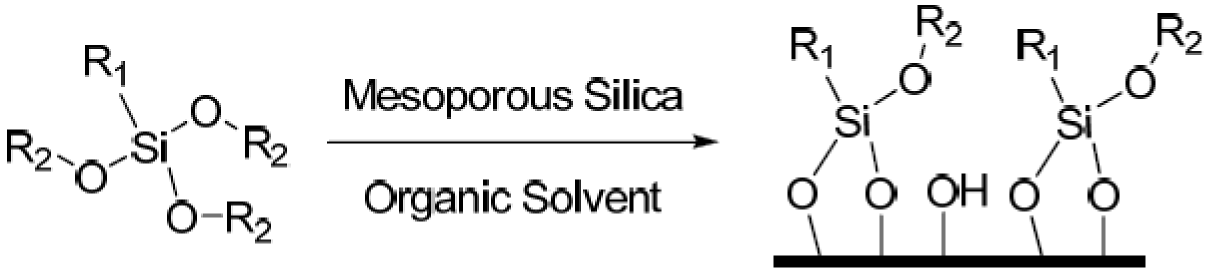


Figure 2.7: Scheme for the reaction of silane with silica. R1 can be either alkyl or aminoalkyl group, and R2 is typically a methyl or ethyl group.

By far, the three most common aminosilanes used in the CTA literature are:

1. 3-aminopropyltrimethoxysilane (mono silane)
2. 3-(2-aminoethyl)aminopropyltrimethoxysilane (di silane)
3. [2-(2-aminoethyl) aminoethyl] aminopropyltrimethoxysilane (tri silane)

These silanes have one, two, and three amines respectively. Monosilane only has a primary amine end group, while di and triaminosilanes have secondary amines in their linkers and are terminated with primary amines [71].

2.15 Amine functionalized Mesoporous Silica (SBA-15, MCM-41)

Several research groups had reported excellent performances of mesoporous silica materials incorporated with an amine-type capturing agent for CO_2 removal by sorption processes. CO_2 adsorption properties were examined in which adsorption isotherms were collected by TGA measurements and adsorption capacity was measured using fixed bed flow system. The result showed that EDA-SBA-15 adsorbs around 20mg/g of CO_2 in N_2 at 25°C and 1 atmosphere total pressure. In pure CO_2

at 1 atmosphere its adsorption capacity is 86 mg/g at 22°C. EDA-SBA-15 is fully regenerable by thermal swings. Desorption of CO_2 occurs at 110°C and the sorbent is stable in air upto 200°C and CO_2 uptake is not influenced by humidity [54].

Mesoporous silica with different pore sizes (33Å small pore size for MCM-41, 38Å for SBA-12,71 Å large pore size for SBA-15) and pore connectivity (2D for MCM-41 & SBA-15, 3D for SBA-12 material) were prepared and functionalized with aminopropyl ligands. Large pore silica showed the largest CO_2 sorption capacity (1.5 mmol/g) having highest amine density. SBA-12 resulted in faster response to CO_2 uptake in comparison with MCM-41 & SBA-15 [55].

SBA-15 functionalized with PEI containing 15.1 v/v% CO_2 in temperature range of 30-75°C. SBA-15 with largest pore volume (1.14cm^3/g) exhibited largest CO_2 adsorption capacity (105.2mg/g) adsorbent in N_2 at 75°C and atmospheric pressure [56].

The new adsorbents show excellent stability in cyclic adsorption desorption operations, even under dry conditions in which aminosilica adsorbents are known to lose capacity due to urea formation. The adsorbents of this type can be considered promising materials for the direct capture of $CO_2$from ultra-dilute gas streams such as ambient air.

SBA-15 modified with triethanol amine (TEA) showed promising performance in separating $CO_2$from its mixture CH_4 to enhance the selectivity for CO_2. This modification enlarged the difference between equilibrium adsorption of CO_2 and that of the other gases. The separation coefficient between CO_2 & CH_4 was evaluated on the basis of breakthrough curve enlarged as much as seven times due to modification. Saturated adsorbent was regenerated at ambient temperature either by purging it with purified gas or by vaccuming [57].

SBA-15 grafted with c-(aminopropyl) triethoxysilane (APTS) having pore size of 21nm and surface area of 200-230 m^2/g. it adsorbs CO_2 as carbonates and bicarbonates with total capacity of 200-400mol/g. Heat of desorption was 3.2-4.5 KJ/mol in presence of H_2O and 6.6-11.0 KJ/mol in absence of H_2O during the temperature programmed desorption. SBA-15 possesses low mechanical strength compared to MCM-41. SBA-15 contains significant amount of micropores in addition to the hexagonal arrangement of large mesopores. The study showed that SBA-15 synthesized at temperature higher than 120°C contains almost no pores [58].

Amines were anchored onto the silica surface in order to increase the MCM-41-CO_2 sorption capacity by 2.48 mmol/g. amine functionalized material exhibited higher uptake to CO_2 at very low pressure compared to non-grafted material.

Modified material presented heat of adsorption of -32 KJ/mol for MCM-41 at low pressures. Mode of CO_2 uptake in MCM-41-NH_2 was both chemisorption at low pressures and physisorption at high pressures. This material has a potential for CO_2 recovery at low pressures/concentrations [59].

MCM-41 modified with PEI for CO_2 adsorption from simulated flue gas CO_2, O_2, N_2 with and without moisture. CO_2 adsorption capacity and CO_2 separation selectivity of MCM-41 were greatly improved by loading PEI into its nano sized pore channel. CO_2 adsorption capacity of MCM-41-PEI for the simulated flue gas was higher than that of the simulated dry flue gas. CO_2 sorption capacity was also improved in presence of moisture. The results of adsorption/desorption separation cycles showed that MCM-41-PEI adsorbent was stable over 10 cycles of adsorption/desorption cycles [60].

Adsorption of CO_2 on pore expanded MCM-41 grafted with Triamine, TRI-PE-MCM-41wasinvestigated from very low pressure to 1 bar at four temperature (298, 308, 318, and 328 K) using gravimetric measurements. It has high selectivity for CO_2 over N_2, CH_4, H_2 and O_2 at very low CO_2 concentration [61].

Highest CO_2 capacity (1.95 mmol/g) and the fastest desorption rate (9.82 * 10^-4 mmol/g.sec)occurred when desorption was carried out at 150°C. If vacuum is applied regeneration can be achieved at a temperature as low as 70°C with only 13% penalty in terms of working adsorption capacity TRI-PE-MCM-41 is stable over 100 adsorption-desorption cycles [62].

2.16 Amine functionalized Carbonaceous Materials

The optimal PEI loading was fixed to be 65 wt. % with a CO_2 sorption capacity of 4.82 mmol-CO_2/g-sorbent in 15% CO_2/N_2 at 75, owing to low mass-transfer resistance and high utilization ratio of the amine compound (63%). Moisture had a promoting effect on the sorption separation of CO_2. In addition, the developed sorbent can be regenerated easily at 100°C, and it exhibited excellent regenerability and stability. These results indicate that this PEI-loaded mesoporous carbon sorbent should have a good potential for CO_2 capture in the future [63].

The surfaces of activated carbon were functionalized by 3-chloropropyltrimethoxy silane, which was subsequently grafted with amine compounds tris-(2-aminoethyl) amine and tri-ethylene tetramine and subjected to comparison. Carbon dioxide adsorption behaviors of the amine grafted activated carbons were examined via the amounts of carbon dioxide adsorption at 298 K and 1.0 atm. From the results, tris-(2-aminoethyl) amine grafted activated carbons showed 43.8 cm^3/g of carbon dioxide adsorption while non-treated activated carbons and triethylenetetramine grafted activated carbons showed less carbon dioxide adsorption. These results were thought to be due to the presence of isolated amine groups in the amine compounds.

Here we report carbon-based composites polyethylenimine mesocarbon (PEI-CMK-3) and polyvinyl amine mesocarbon (PVA-CMK-3) that can be used to capture and rapidly release CO_2. CO_2 uptake by the synthesized composites was determined using a gravimetric method at 30°C and 1 atm; the 39% PEI-CMK-3 composite had 12 wt % CO_2 uptake capacities and the 37% PVA-CMK-3 composite had 13 wt % CO_2 uptake capacities. A desorption temperature of 75°C was sufficient for regeneration. The CO_2 uptake was the same when using 10% CO_2 in a 90% CH_4, C_2H_6, and C_3H_8 mixture, underscoring this composites efficacy for CO_2 sequestration from natural gas [64].

The adsorbents activated carbon synthesized from bagasse (BAC) and from rice husk (RAC) were investigated. The synthesized BAC and RAC showed high thermal stability with the weight loss less than 0.1% for the temperatures below 150°C. N_2 adsorption isotherm analysis indicates that BAC and RAC are microporous. The BET surface areas were 923 and 927 m^2/g for BAC and RAC respectively. The total pore volumes were 0.53 and 0.56 cm^3/g, and pore sizes were 0.8 and 0.8, for BAC and RAC respectively. At 30°C these materials were able to adsorb 76.89 and 57.13 mg CO_2/g-adsorbent, respectively. When the adsorption temperature increased, adsorption capacity of BAC and RAC was decreased. This implied that physical process was the main mechanism of CO_2 adsorption [65].

2.17 Amine Functionalized Polymeric Material

Amidine and guanidine functional groups increase the capacity of CO_2 binding. Several amidine containing compounds and guanidine containing compounds have been synthesized and show increased binding capacity of CO_2 compared to conventional liquid systems. By reducing the molecular weight of non-binding portion of the polymer, an amidine polymer can bind two times that of the other created adsorbents.

Polyamidine bound 9.30 molCO_2/kg polymers while polyguanidine bound over 6 molCO_2/kg polymer. These experiments were done in 10ml batch reactor at 45 psi at room temperature. Water was added prior to experiment at 1:1 molar ratio with binding sites of polymers [66].

Porous organic polymers containing nitrogen-rich building units are among the most promising materials for selective CO_2 capture and separation which can have a tangible impact on the environment and clean energy applications. Synthesis and characterization of four new porous benzimidazole-linked polymers (BILPs) and evaluate their performance in small gas storage (H_2 ,CH_4, CO_2) and selective CO_2 binding over N_2 and CH_4.

BILPs were synthesized in good yields by the condensation reaction between aryl-o-diamine and aryl-aldehyde building blocks. The resulting BILPs exhibit moderate surface area, high chemical and thermal stability, and remarkable gas uptake and selectivity. The highest selectivity based on initial slope calculations at 273 K was observed for BILP-2:CO_2/N_2 (113) and CO_2/CH_4 17), while the highest storage capacity was recorded for BILP-4:CO_2 (24 wt % at 273 K and 1 bar)and H_2 (2.3 wt % at 77 K and 1 bar).

These selectivities and gas uptakes are among the highest by porous organic polymers known to date which in addition to the remarkable chemical and physical stability of BILPs make this class of material very promising for future use in gas storage and separation applications.Three porous polymer networks (PPNs) have been synthesized by the homocoupling of tetrahedral monomers. Like other hyper-cross-linked polymer networks, these materials are insoluble in conventional solvents and exhibit high thermal and chemical stability. Their porosity was confirmed by N_2 sorption isotherms at 77 K.

One of these materials, PPN-3, has a Langmuir surface area of 5323 m^2/g. Their clean energy applications, especially in H_2, CH_4, and CO_2 storage, as well as CO_2/CH_4 separation, have been carefully investigated. Although PPN-1 has the highest gas affinity because of its smaller pore size, the maximal gas uptake capacity is directly proportional to their surface area. PPN-3 has the highest H_2 uptake capacity among these three (4.28 wt%, 77 K). Although possessing the lowest surface area, PPN-1shows the best CO_2/CH_4 selectivity among them.

Two different types of cellulose acetate-based sorbents for CO_2 capture have been developed. A low-acetyl content cellulose acetate/titanium(IV) oxide hybrid sorbent has been designed in the form of a film that is capable to adsorb up to 13.60 cc (STP) CO_2/ cc sorbent at 1 atm of pressure and 49.27 cc(STP) CO_2/ cc sorbent at equilibrium pressures of 5 atm.

This represents an additional capture of about 0.22 mmol CO_2/g sorbent at 1 atm and 0.97 mmol CO_2/g sorbent at 5atm after the titanium modification of cellulose acetate. However, the sorbent dissolves in water.

An amino silane functionalized cellulose acetate sorbent in powder form has been tailored to adsorb up to 27 cc (STP) CO_2/ cc at 1 sorbent atm and about 39.2 cc

(STP) CO_2/ cc sorbent at 5 atm. Its amine loading is about 5.18 mmol amine (nitrogen)/g sorbent. The sorbent captured an additional amount of CO_2 in the order of 0.78 mmol CO_2 per gram of sorbent at 1 atm and 0.84 mmol CO_2 per gram of sorbent at 5 atm.

The exposure of the sorbent to water vapor slightly increases its sorption capacity on a second CO_2 sorption cycle. The new capacity of the sorbent reached 30 cc(STP) CO_2/cc sorbent at 1atm and 44.5 cc (STP) CO_2/cc sorbent at 5 atm. Moreover, in the presence of humidity, further increases in sorption capacity are expected based on higher amine efficiencies known to occur in humid environments [29].

Amine impregnated monolith silica exhibited significantly higher CO_2 adsorption capacity than other silica-supported amine sorbents, and produced a reversible and durable sorption performance. In particular, the PEI/monolith exhibited very reversible and durable CO_2 capturing performance (4.77 mmol/g of CO_2 at 75 řC), and also showed excellent performances in both diluted and moisture-containing CO_2 conditions.

A novel adsorbent was developed by coating polyethylenimine (PEI) on glass fiber matrix and using epichlorohydrin as cross-linking agent. The physicochemical properties of the fibrous adsorbent were characterized. The experimental results showed that this fibrous PEI adsorbent exhibited much higher adsorption capacity of 3.98 mmolCO_2/g of adsorbent at 30°C. Factors that affect the adsorption capacity of the fibrous adsorbent were studied [67].The adsorbent can be completely regenerated at 120°C. This PEI modified fibrous adsorbent had high thermal stability (about 250°C) and is stable in the presence of moisture.

Two approaches, thermal swing adsorption (TSA) cycles over a range of temperatures and time in an atmosphere of CO_2 and thermally assisted pressure swing desorption, are explored for the regeneration of the polyethylenimine (PEI) based adsorbents. Thermal swing regeneration was demonstrated to give good cyclic regeneration capacities (2 mmol/g). The reactions occurring during the TSA regeneration of PEI based adsorbents in an atmosphere of CO_2, especially the formation of a thermostable complex between PEI and CO_2 above 130°C are described [69].

However, further reaction of the regenerable carbamate ion to form urea linkages, significantly reduces cyclic capacity and therefore the lifetime of the adsorbent. Regeneration of this secondary reaction product at elevated temperatures was attempted in a nitrogen atmosphere, and whilst recovering some of the original capacity did not fully regenerate the adsorbent. Adsorbent regeneration with nitrogen as a stripping gas was used as an alternative regeneration method, the results of which suggest that steam stripping may be a potential method for adsorbent regeneration [70].

Chapter 3

Experimental Methods

The experimental work is divided into three sections: adsorbent preparation, characterization and evaluation. The compositional data of prepared samples are also recorded in this section. The methodology for analytical techniques like BET surface area. The evaluation section describes the reactor configuration, techniques used for product compositional analysis and procedure of experimental run.

3.1 Experimental Methods

3.1.1 Introduction

The characterization of the catalysts is an important aspect in order to obtain information about molecular nature and structure of the active component to prepare the catalysts and also helps in optimizing industrial catalytic processes. No single technique is available to get the complete information about the surface structure of the active component and it is an impossible task to a single discipline of the subject to get comprehensive overview of the molecularities of the surface. In many cases, however, the catalysts utilized in chemical industry consistof two or more components. This chapter also deals with experimental section of adsorbent evaluation for the CO_2 adsorption studies.

3.1.2 Materials

Tetraethylpentamine(TEPA), Polyethylenimine (PEI, 50%), were obtained from Sigma Aldrich. Methanol (CH_3OH) was obtained from Merck. All these chemicals were used without further purification. The supports used were SBA-15, MCM-22 and Alumina.

3.1.3 Preparation of adsorbents

Many preparation methods have been developed by researchers for the synthesis of MCM-41 and SBA-15 General flow sheet of the procedures adopted is shown in Figure

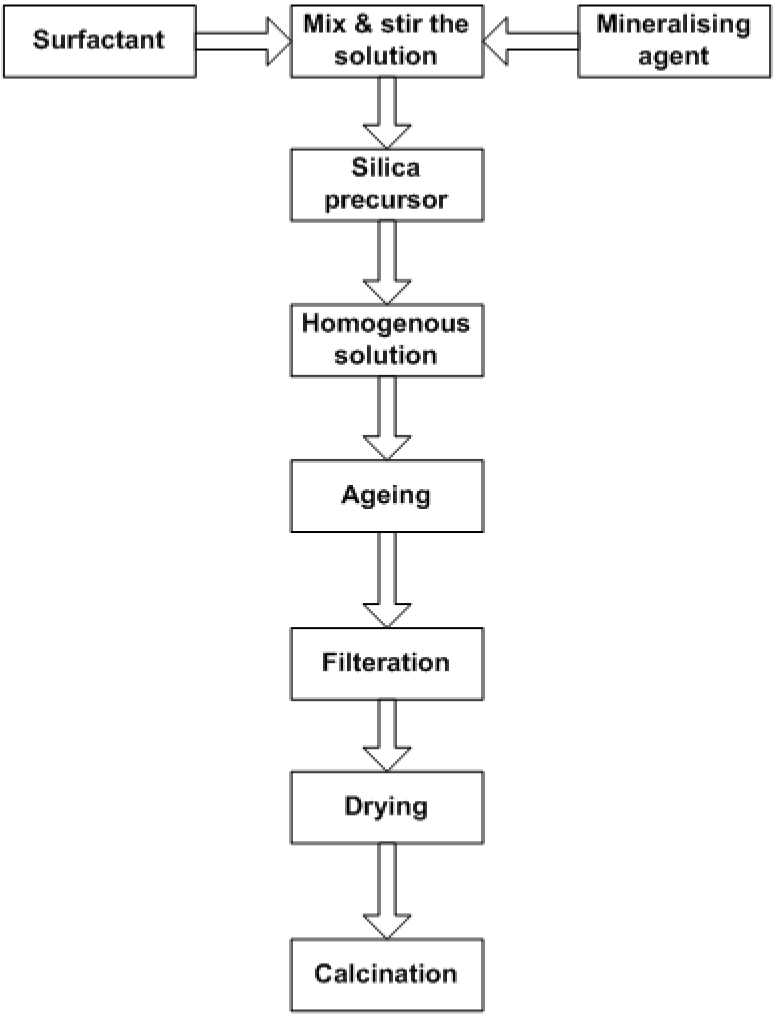


Figure 3.1: Preparation of modified adsorbents

3.2 Preparation of adsorbent

3.2.1 MCM-22 Preparation

Initially, 43.89 g of sodium silicate (26.5% SiO_2, 10.6% Na_2O, 62.9% H_2O, Aldrich) was mixed with 22.2 g of de-ionized water. To this solution, 8.81 g of hexamethyleneimine(99%, Aldrich) was added. Then, a solution of 4.41 g of aluminumsulfate (98%, Aldrich) and 3.63 g of sulfuric acid (95%, Aldrich) in 110 g of de-ionized water were added slowly. Hydrothermal reaction was then conducted at 423 K under mechanical stirring for 80 h. The obtained product MCM-22(P) was washed with sufcientde-ionized water and dried at 393 K for 6 h. The dried product was nally calcined at 823 K for 6 h to remove the organic template.

3.2.2 SBA-15 Preparation

Method for synthesizing of SBA-15 was in accordance to literatures reviewed 4.0 g of Pluronic P123 was dissolved in 30ml of deionised water. Then, 120ml of 2.0 M HCl was added into the solution and stirred at room temperature for 2 hours. The resulting solution was then transferred into a container and stirred at 40°C. After that, 8.5g of TEOS was added drop by drop into the solution while stirring for 30 minutes. Then, slowing down the stirring rate to around 120 rpm and stirred for another 20 hours at the same temperature. After that, ageing of the solution was done in an oven at 100°C for 48 hours without stirring. The final product was filtered, washed with deionised water and dried for 24 hours at 80žC. Finally, the calcination was done at 550°C for 5 hours under flowing air.

3.2.3 Preparation of mesoporous alumina by sol-gel process

$Al(NO_3)_3$, $9H_2O$ (35 g) was dissolved in 35 mL distilled deionized water at 22°C under magnetic stirring. Urea (72 g) was added keeping the molar ratio of Al_3+/urea at 1/13. The solution mixture was maintained at 22°C for 1 h and then filtered to remove any insoluble impurity. The aluminium/urea saturated solution was heated at 90°C for around 12 h. The pH of the solution mixture was initially 2.0. As the reaction proceeds the pH gradually increased and rose sharply from 3 to 6 producing alumina sol. The sol was heated for another 3 h to a transparent gel. The freshly prepared alumina gel was dried at 280°C for 1 h in presence of air to eliminate the remaining urea and nitrate and resulted in porous, amorphous -alumina powder.

3.3 Amine functionalized Adsorbents

Modifying MCM-22 and SBA-15 using amines as functional groups utilize the same conventional method which is known as wet impregnation method. Methanol was used as solvent to allow amine solution dissolved in the mixture before adding to the calcined MCM-22/SBA-15. Then, the resultant slurry was stirred and dried at 80°C for 16 hours in hot oven.

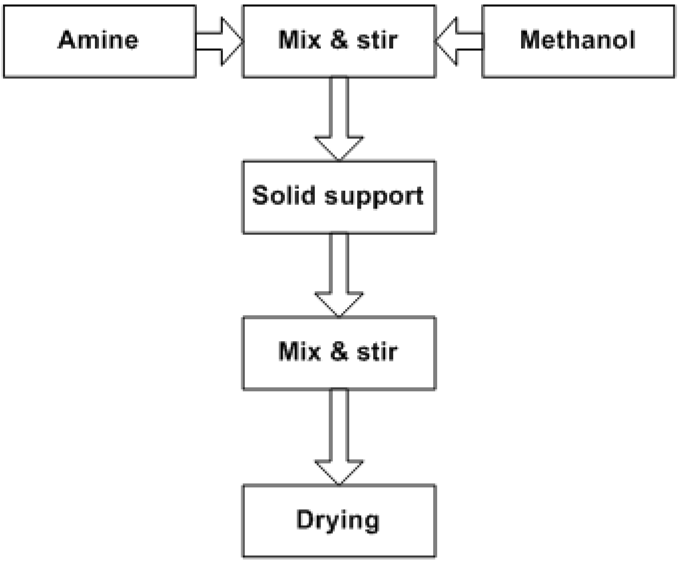


Figure 3.2: Preparation method for modified adsorbents

3.3.1 Functionalization of Alumina with TEPA via physical impregnation

To Prepare 20%, 30% 40%, 50% TEPA functionalized on alumina and making total volume of 20 gm. Take 4, 6, 8, 10 ml of TEPA in a conical flask and add 100 ml of methanol as a solvent into each flask. Add 16, 14, 12, 10 gm of dried alumina in to each flask respectively. Sonicate the sample first into sonicator for making the solution uniform. Place the solution under stirring condition at around 600 rpm at room temperature for 6 hours. Also sonicate the sample every1 hour. Keep the solution for drying at 80°C overnight in vacuum oven. Collect the sample, measure the volume and label it.

3.3.2 Functionalization of SBA-15 with TEPA via physical impregnation

To Prepare 20%, 30% 40%, 50% TEPA functionalized on SBA-15 and making total volume of 2 gm. Take 0.4, 0.6, 0.8, 1.0 ml of TEPA in a conical flask and add 15 ml of methanol as a solvent into each flask. Add 1.6, 1.4, 1.2., 1.0 gm of dried SBA-15 in to each flask respectively. Sonicate the sample first into sonicator for making the solution uniform. Place the solution under stirring condition at around 160-180 rpm at room temperature for 6 hours. Also sonicate the sample every1 hour. Keep the solution for drying at 80°C overnight in vacuum oven. Collect the sample, measure the volume and label it.

3.3.3 Functionalization of MCM-22 with TEPA via physical impregnation

To Prepare 20%, 30% 40%, 50% TEPA functionalized on alumina and making total volume of 15 gm. Take 3, 4.5, 6, 7.5 ml of TEPA in a conical flask and add 100 ml of methanol as a solvent into each flask. Add 12, 10.5, 9, 7.5 gm of dried MCM-22 in to each flask respectively. Sonicate the sample first into sonicator for making the solution uniform. Place the solution under stirring condition at around 600 rpm at room temperature for 6 hours. Also sonicate the sample every1 hour. Keep the solution for drying at 80°C overnight in vacuum oven. Collect the sample, measure the volume and label it.

3.3.4 Functionalization of MCM-22 with PEI via physical impregnation

To Prepare 20%, 30% 40%, 50% PEI functionalized on alumina and making total volume of 5 gm. Take 1.84, 2.76, 3.7, 4.62 ml of PEI in a conical flask and add 100 ml of methanol as a solvent into each flask 4.08, 3.92, 3.15, 2.69 gm of dried MCM-22 in to each flask respectively. Sonicate the sample first into sonicator for making the solution uniform. Place the solution under stirring condition at around 600 rpm at room temperature for 6 hours. Also sonicate the sample every1 hour. Keep the solution for drying at 80°C overnight in vacuum oven. Collect the sample, measure the volume and label it.

3.4 Characterization Equipment and Procedures

3.4.1 Surface Area

Surface area determination is an important factor in determining the catalyst performance, a method of assessing the efficiency of catalyst supports and promoters. The surface area measurements can be used to predict catalyst poisoning and provide reasons for the deactivation of the catalyst either due to poisoning or due to sintering. The BET (Brunner, Emmett and Teller) equation is based on the extension of Langmuir theory to multilayer adsorption. The basic equation to find the surface area is as follows

$$\frac{P}{V_{ads}(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0}$$

Where
P= equilibrium adsorption pressure
P0= saturated vapour pressure of the adsorbent
Vads= volume (in ml) adsorbed at STP at pressure P
Vm = volume of adsorbate required to form a monolayer coverage
C = Constant related to heat of adsorption

According to the BET method a plot of $\frac{P}{V_{ads}(P_0-P)}$ Vs $\frac{P}{P_0}$ is a straight line (in the range of P/P0: 0.05 -0.3) with slope (C-1)/VmC and intercept 1/VmC. By knowing these intercept and slope values Vmcan be calculated and further specific surface area can be calculated as follows

Specific surface area (m^2/g) = [(Vmx NA)/(22414 x Wt)] x Am
Where Vm= monolayer volume in ml at STP
NA= Avogadro number
Am = mean cross sectional area of adsorbate molecule (0.162 nm^2 for N_2)
Wt= weight of the catalyst in grams

Surface area and pore volume of the support and calcined catalysts were measured on a Micromeritics Autochem 2020 instrument. The instrument is located at RIL, Jamnagar. The sample (0.15 g) was evacuated at 80°C for 4 h prior to measurement. In the next step, nitrogen adsorption and desorption isotherms were measured at liquid nitrogen temperature. The Brunauer-Emmett-Teller (BET) area was estimated by N_2 adsorption at relative pressures (P/P0) between 0.06 and 0.2, where P and P0 are the measured and equilibrium pressures, respectively. The total pore volume was calculated from the amount of vapor adsorbed at a relative pressure close to 0.995. The nitrogen desorption isotherm was chosen for the pore size analysis. The pore size distribution was established by applying the Barrett-Joyner-Halenda (BJH)method.

Figure 3.3: Surface Area Analyzer

3.5 Experimental Reaction Setup and Procedure for Adsorbent Evaluation

The experiments were performed in gas chromatography supplied by PerkinElmer at RIL. The detector used was thermal conductivity detector (TCD) for CO_2 capacity.

3.5.1 Equipment description

Gas Chromatography is used to analyze the CO_2 adsorption studies. The manufacture of lab scale catalyst testing unit is provided by PerkinElmer.

3.5.1.1 Gas Chromatography

Gas chromatography: PerkinElmer Column:
Packed GC column Column size: 2 m (ID -1 mm; OD-1/6 inch dia)
Oven temperature: 30-130°C (temperature programme)
Carrier gas flow rate: 60 SCCM
Detector: Thermal Conductivity Detector Detector
Temperature: 150°C

3.5.2 Gas Chromatography Set-up

Figure 3.4: Gas Chromatography

The unit has Physical Components that involve inlet port, Adsorption column, detector port, flow controller (to control the flow of carrier gas), etc. the CO_2gas is allowed to pass through the 6-port valve to the packed bed column and then to the detector. The detector used here is thermal conductivity detector and the reference gas used is helium (He).

3.6 Experimental reaction procedure

3.6.1 Reactor Loading

The stainless-steel reactor tube is cleaned and dried thoroughly prior to each loading. Typically, about 200mg of the adsorbent is loaded in the column for each run. The bed comprises of the adsorbent, carefully embedded between two stubs of quartz wool. The column is fixed and the system is then checked for leaks by soap water.

3.7 Method for CO_2 adsorption

3.7.1 Adsorption of CO_2

The reaction is started by adjusting the required flows of the feed gases and setting the required temperatures with the manually. However, the reaction pressure has to be set manually, by means of the back pressure regulator. The software is preset for a certain GC analysis period. For all the runs, the analysis time was fixed for a period of twenty minutes after prior calibration and optimization. Adsorption of CO_2 in GC was studied at 30°C for all the adsorbents. The adsorbent with the best result was analyzed further for 50°C and 70°C.

The flow path is controlled by closing or blocking the fluid passage between valves ports. The sample injection was done with the 6-port valve. With the valve in Position A, sample flows through the external loop while the carrier flows directly through to the chromatographic column. When the valve is switched to Position B, the sample contained in the sample loop and valve flow passage is injected onto the column.

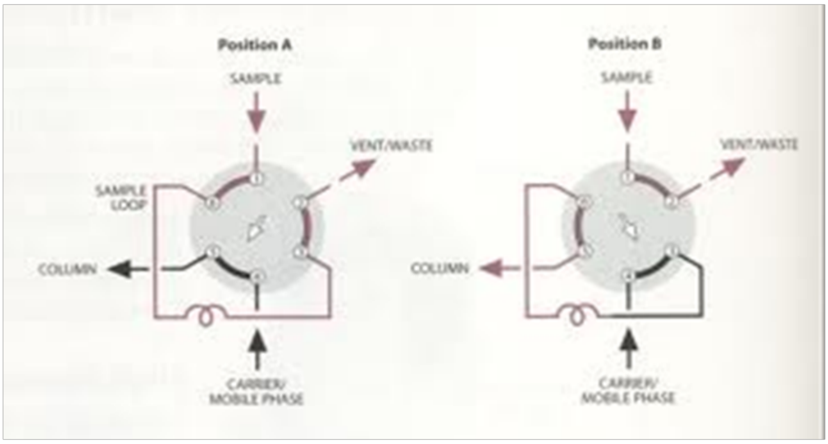


Figure 3.5: Gas Sampling Valve

Regeneration of CO_2 was carried out at temperature of 130°C for a time period of around 25 min.The detector used is thermal conductivity detector having the temperature conditions of 150°C. TPD is the technique that allows one to observe desorption of absorbed specie as a function of temperature. First, the sorbent is introduced to the absorbed specie. The gas flow is switched to inert for some time in order to reach the system equilibrium as determined by gas chromatography. Temperature programmed desorption is carried out at 30-300°C having the rate of 10°C/min.

Chapter 4

Results and Discussions

Amine based solid materials showed several advantages over traditional adsorbents for CO_2 capture capture. These eliminate potential corrosion problems and lower energy cost for sorbent regeneration. Amine based solids prepared by immobilization of tetraethylenepentamine (TEPA) and polyethyleneimine (PEI) in porous materials like SBA-15, MCM-22 and Alumina. Sorbents with large pore size exhibit high CO_2 adsorption capacities. This is the result of the support's greater capacity to retain large amounts of amine while also allowing effective CO_2 transportation within the sorbent. In this study, effect of support materials with different pore dimensions and size for amine immobilization was investigated on the CO_2 adsorption capacity.

4.1 Textural properties of the Sorbents

4.1.1 Preparation and characterization of amine based sorbents

SBA-15, MCM-22 and alumina with different TEPA and/or PEI loadings were prepared by wetness impregnation using methanol as solvent at room temperature. The sorbents were characterized by surface area, pore volume and pore size by N_2 adsorption-desorption.

4.1.1.1 Surface area pore volume and pore diameter of the supports

Table 4.1: Textural Properties of Fresh Support

Sr. No.	**Support**	**Surface Area (m^2/g)**	**Pore Volume (cc)**	**Avg. Pore Diameter (A^o)**
1	SBA-15	714	1.2	66
2	MCM-22	388	0.6	118
3	Alumina	242	0.55	71

Table 4.1 shows the textural properties of the fresh support materials used for amine loadings. Porous structure of the support plays a significant role in determine the loading capacity of the active ingredient and performance of the sorbents. SBA-15 a mesoporous material is appropriate support for amine loading as it has large pores, thicker wall and higher thermal stability. The specific surface areas of the supports were estimated by BET equation from nitrogen adsorption measurement and the pore size distribution from the desorption branch of the isotherm using BJH method. SBA-15 exhibits high BET surface area of 714 m^2/g and pore volume of 1.2 ml/g, while MCM-22 and alumina shows surface areas of 388 and 242 m^2/g, respectively. Pore volumes were 0.6 and 0.5 ml/g for MCM-22 with Si/Al ratio 30 and alumina, respectively. Pore sizes of these three supports followed in the order of MCM-22>SBA-15>Alumina (118>71>66 A^o). The large pore volume and larger pore size are expected to allow higher loading of amine and facilitates effective diffusion of CO_2. MCM-22 with silica to alumina ratio 30 shows BET surface area, pore volume and pore diameter of 388 m^2/g, 0.6 ml/g and 118 A. Alumina exhibited mercury pore volume of 2.2 ml/g.

4.1.2 N_2 Adsorption isotherms of SBA-15, MCM-22 and Alumina

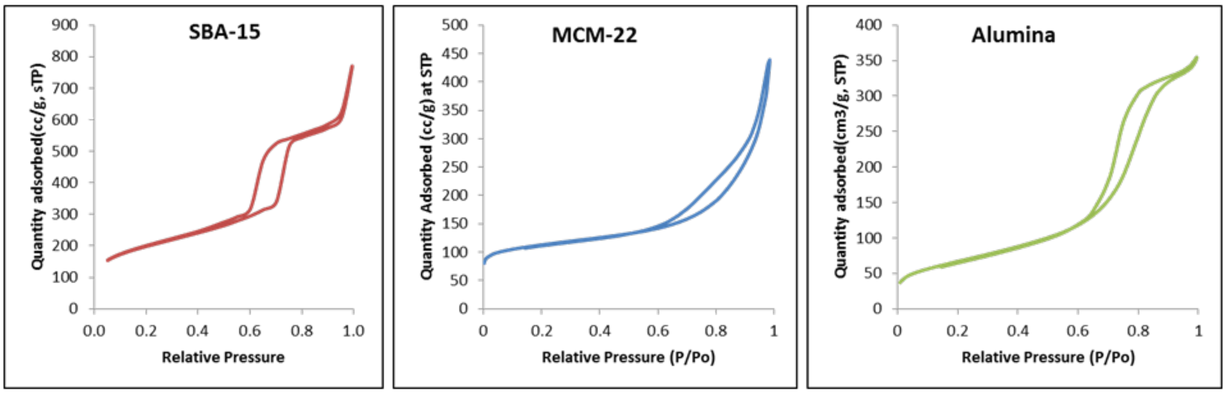


Figure 4.1: N_2 adsorption isotherms at 77 K for SBA-15, MCM-22 and alumina supports

Fig. 4.1 shows nitrogen adsorption isotherms at 77 K for the supports used in this study. The isotherm for SBA-15 shows type IV (IUPAC nomenclature) with a sharp step with a hysteresis loop (type H1) corresponding to the filling of ordered mesopores. Hysteresis loops with sharp adsorption and desorption branches are indicative of a narrow pore size distribution. Isotherm of MCM-22 (Fig.4.1b) can be classified as a type I + IV isotherm, pointing out that this solid, along with the characteristic microporous zeolite framework there is a mesoporous structure. MCM-22 has a peculiar pore structure of tridimensional and bidimensional pore system formed with 10 membered ring openings that give access to two independent pore systems. Isotherm of alumina is evident for type IV with H4 type hysteresis loop at high relative pressures indicating the presence of slit shaped pores. It is clear from the isotherms of the supports that all the materials exhibited hysteresis during N_2 adsorption-desorption indicating the presence of mesopores in all the three supports with different size and type of pores.

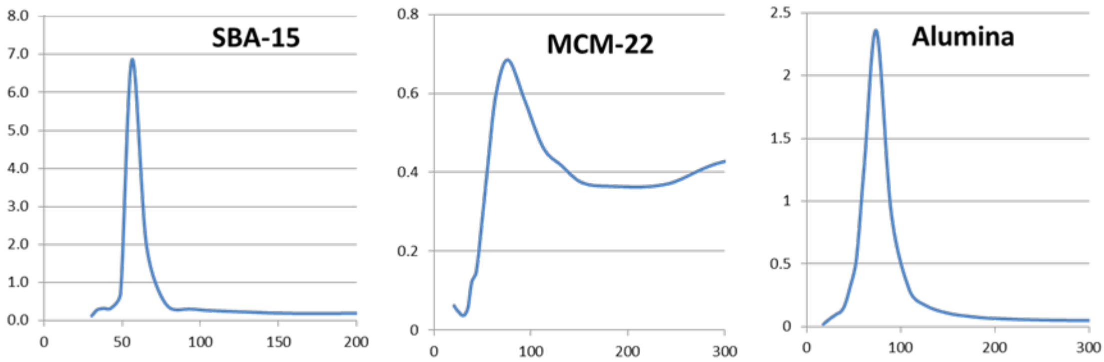


Figure 4.2: Pore Size Distribution of SBA-15, MCM-22 and Alumina by BJH method

Fig.4.2 shows the pore size distribution of the supports used for the preparation of amine based sorbents. SBA-15, a Mesoporous silica, exhibits narrow pore size distribution between 40-100 A°.SBA-15 exhibits higher thickness of the pore wallwhich gives advantage the materialwith higher hydrothermal and mechanical stability compared to MCM-41. Similarly, MCM-22 consists of mesopores of sizebetween 50-150 A° along with some micropores. Pore size distribution results indicate that MCM-22 consist of mesopore with different sizes.Alumina revealed the presence of mesoporewith narrow size distribution between 40-120A°. All the supports used in this studycontain mesopores of variable sizes;however the type of pores is and size distribution is different.

4.2 Textural properties of amine based sorbents

The pore size, surface area and pore volume of SBA-15, MCM-22 and alumina after loading the TEPA and PEI were obtained from the nitrogen adsorption/desorption isotherms and listed in Table 4.2. Surface area and pore volume of SBA-15 with 20% TEPA loading decreased to 193 m^2/g from 714 m^2/g and 1.2ml/g to 0.06 ml/g, respectively of the fresh support. It indicates that SBA-15 pore channels were nearly filled with 50 wt% TEPA as pore volume was reduced drastically. The surface area of the sorbents, 30 and 40%TEPA loading on SBA-15, shows 98 m^2/g, 0.2 cc/g, respectively. Pore volume was about 81 m^2/g and 0.17 ml/g, respectively.

Table 4.2: Textural properties of functionalized supports

Sr. No.	**Amine based sorbents**	**Surface Area (m^2/g)**	**Pore Volume (cc)**	**Avg. Pore Diameter (A^o)**
1	20% TEPA/SBA-15	193	0.37	77
2	30% TEPA/SBA-15	98	0.2	83
3	40% TEPA/SBA-15	81	0.17	84
4	50% TEPA/SBA-15	25	0.06	93
5	20% TEPA/MCM-22	64	0.18	117
6	30% TEPA/MCM-22	31	0.1	128
7	40% TEPA/MCM-22	19	0.04	83
8	50% TEPA/MCM-22	07	0.0055	32
9	20% TEPA/Alumina	121	0.48	160
10	30% TEPA/Alumina	98	0.38	153
11	40% TEPA/Alumina	34	0.16	186
12	50% TEPA/Alumina	13	0.04	127
13	20% PEI/MCM-22	45	0.13	119
14	30% PEI/MCM-22	23	0.05	93

The surface area and pore volume of TEPA loaded on MCM-22 and alumina samples exhibited a same trend as that of TEPA/SBA-15 samples. The surface area and pore volume of MCM-22 after 20% TEPA loading decreased to 64 from $388m^2/g$ and 0.18 from 0.6 ml/g, respectively. With further increase of TEPA surface area decreased to 31, 19, and $7m^2/g$ for 30, 40 and 50% TEPA loadings respectively. Similarly, upon 20 and 50% TEPA loading on alumina showed drastic reduction in surface area and pore volumes due to pores filling.

Likewise, PEI loaded on MCM-22 followed a sametrend of decrease in surface area, pore volume and pore size with the increase of loading amount as presented in Table 4.2. It is observed that, with 20%PEI loading the surface area and pore volume decreased sharply compared to 20% TEPA loading on MCM-22, which indicates that polymeric molecules are fully entering into mesoporechannels and restricting the access of nitrogen. Amine molecules remain adsorbed on the external surface of the support particles once the pores of the supports are filled and form a gel-like material with higher loadings.

4.3 CO_2 adsorption measurements

4.3.1 Effect of support

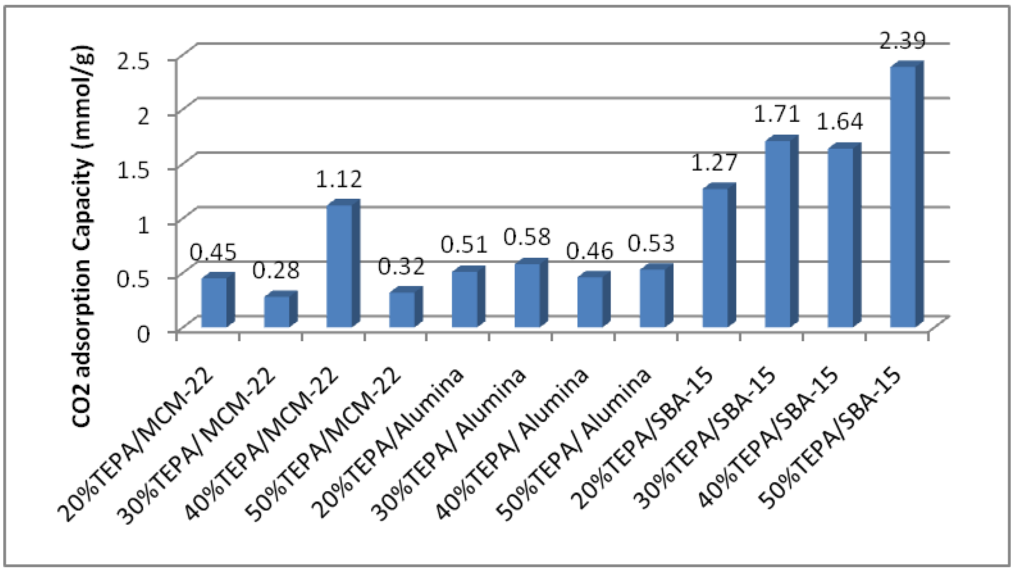


Figure 4.3: CO_2 adsorption capacities of TEPA and PEI loaded on SBA-15, MCM-22 and alumina supports at 30°C.

Reaction conditions: (CO_2 flow rate 60ml/min, carrier gas flowrate= 50ml/min, loop volume =1ml, adsorption period= 20 minutes, oven Temperature=30°C, TCD temperature =150°C)

Solid supports with different pore structures for TEPA and PEI loading were prepared and evaluated for CO_2 uptake by pulse chemisorption using GC with pure CO_2. The total CO_2 adsorption capacity was measured at 30°C after saturation of the sorbent in 16 CO_2 pulses (loop volume is 1 mL) is shown in Fig.4.3. Among different sorbents prepared in this study, the 50%TEPA/SBA-15 sorbent showed highest CO_2 adsorption capacity i.e 2.4 mmol/g compared to TEPA loaded on alumina or MCM-22 for a given loading under identical reaction conditions. However, the adsorption capacities are not increasing with the amine loading on a given support. The decrease in the adsorption capacity in case of alumina and MCM-22 could be attributed to blockage of pores, evidenced by pore size reduction from Table 2. Pores filled with liquid amine molecules limitdiffusion of CO_2 to the active sites.

When the amine loading was low, the pore size of the adsorbent retained to facilitate interaction with the CO_2 while higher amine loadings results deposition of amine on the external surface of the particles. It was reported that only amines loaded in mesopores have strong synergic effect on CO_2 adsorption. In case of SBA-15, due to its high pore volume and surface area upto 50 wt% TEPA could be loaded into the mesopores resulting linear increase in the adsorption capacity. The adsorption capacities for 50%TEPA/SBA-15, 40%TEPA/MCM-22 and 30%TEPA/alumina are 2.4, 1.2 and 0.4 mmol/g respectively. It can be deduced from the results that the supports with well-defined mesoporous structurei.e SBA-15 in this study, with high pore volume can be a better support that will allow higher amine resulting proportionate increase in adsorption capacity.

4.3.2 Comparison of theoretical value with the Actual values of CO_2 adsorption

Table 4.3: Comparison of Theoretical value with the Actual values of CO_2 adsorption

Adsorbent	**Amount of Amine (mmol/g)**	**Theoretical Capacity (mmol/g)**	**Actual Capacity (mmol/g)**	**% Adsorption**
20% TEPA/MCM-22	5.2	2.6	0.48	17.30
20% TEPA/MCM-22	7.9	3.96	0.28	7.07
20% TEPA/MCM-22	10.4	5.2	1.12	21.53
20% TEPA/MCM-22	13.2	6.6	0.32	4.84
20% TEPA/MCM-22	5.2	2.6	0.51	19.61
20% TEPA/MCM-22	7.9	3.96	0.58	14.64
20% TEPA/MCM-22	10.4	5.2	0.46	8.84
20% TEPA/MCM-22	13.2	6.6	0.53	8.03
20% TEPA/MCM-22	5.2	2.6	1.27	48.84
20% TEPA/MCM-22	7.9	3.96	1.77	48.18
20% TEPA/MCM-22	10.4	5.2	1.61	30.96
20% TEPA/MCM-22	13.2	6.6	2.4	36.36

4.4 Effect of type of amine

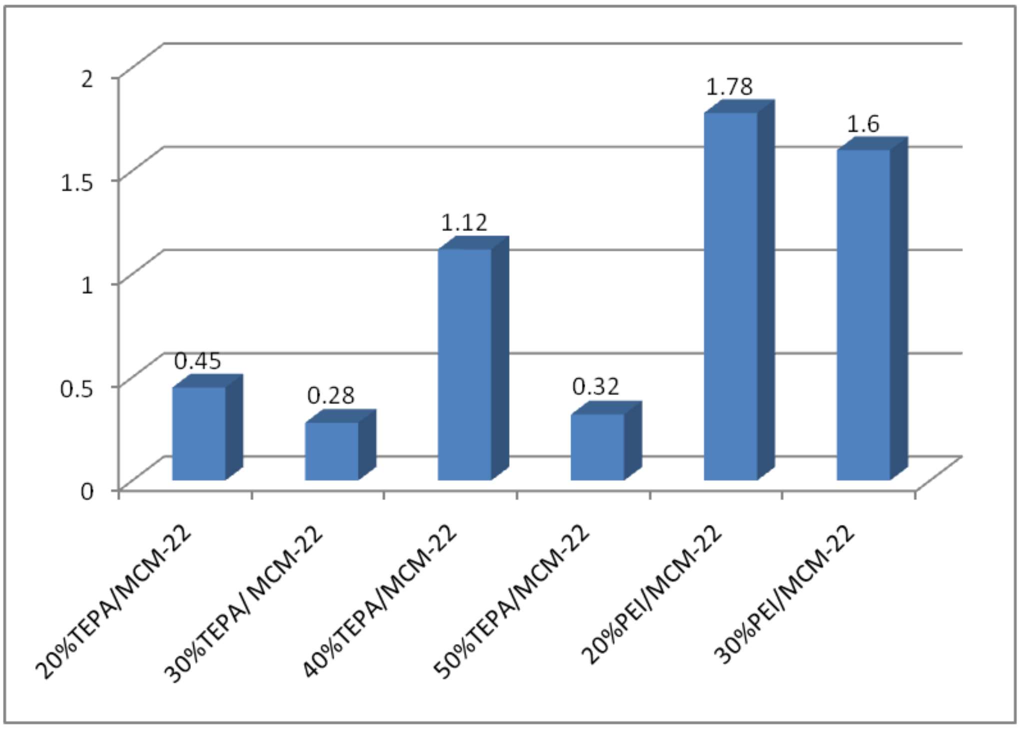


Figure 4.4: Comparison of CO_2 adsorption capacities of TEPA and PEI on MCM-22.

Reaction conditions:CO_2 flow rate 60ml/min, carrier gas flowrate= 50ml/min, loop volume =1ml, adsorption period= 20 minutes, oven Temperature=30°C, TCD temperature =150°C)

Other than the structure of the support, the effect of amine type on the adsorption capacity was investigated using two different amines, PEI and TEPA. A higher CO_2 capacity obtained from PEI than TEPA at the same amine loading and the stoichiometry of CO_2 and amine (CO_2/N) was improved to 0.33. We suspect that the higher density ofamino groups of PEI compared to TEPA provide more reactive sites for CO_2 and thus a higher overalladsorption capacity.

The structure and nitrogen atom density in amine molecules plays an important role in determining the adsorption capacity of the sorbent. Hence, the main requisite for developing more efficient amine based sorbent is to increase the density of nitrogen atoms in the active component. In this study, owing to understand the effect of density of nitrogen atoms in amine molecule and the role of primary and secondary amine groups TEPA and PEI load MCM-22 were prepared. TEPA consists of both primary and secondary amine functionalities, while PEI, a polymeric molecule contains only secondary amines.

The CO_2 adsorption capacities of TEPA and PEI, impregnated MCM-22 are shown in Fig.4.4. CO_2 adsorption capacity of PEI based sorbent is higher than TEPA counterpart at the given loading. Incontrast to TEPA sorbents, the increase of PEI loading resulted in the decrease of CO_2 adsorption. This is mainly due to more addition of PEI into the support limits entering of polymeric molecules into the porous structure. It was observed that sorbents with 40 and 50% PEI loading become gelatinous materials. In addition, PEI based sorbent showed no adsorption at 30°C, but adsorbed considerable amount of CO_2 at 70°C. This can be explained based on the fact that diffusion of CO_2 required higher energy to accessactive sites on the polymeric amine.

4.5 Effect of Temperature

The effect of temperature was studied for three different adsorbents showing the maximum adsorption capacity. The temperature effect was studied for 30°C, 50°C and 70°C for 20% TEPA/ MCM-22, 50% TEPA/SBA-15 and 20% TEPA/Alumina.

4.5.1 Effect of Temperature on 20% PEI/MCM-22

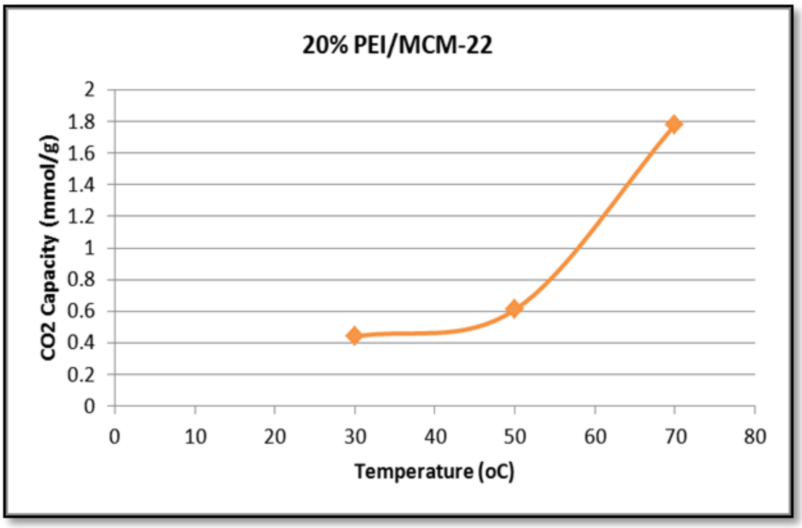


Figure 4.5: Effect of Temperature on 20% PEI/MCM-22

The CO_2 adsorption capacity of 20% PEI/MCM-22 increases with the increase in temperature. It gives the maximum capacity 0.44 mmol at 30°C. The capacity at 50°C and 70°C are 0.61 and 1.78 mmol respectively. It shows that polymeric compound gives better diffusivity at higher temperature.

4.5.2 Effect of Temperature on 50% TEPA/SBA-15

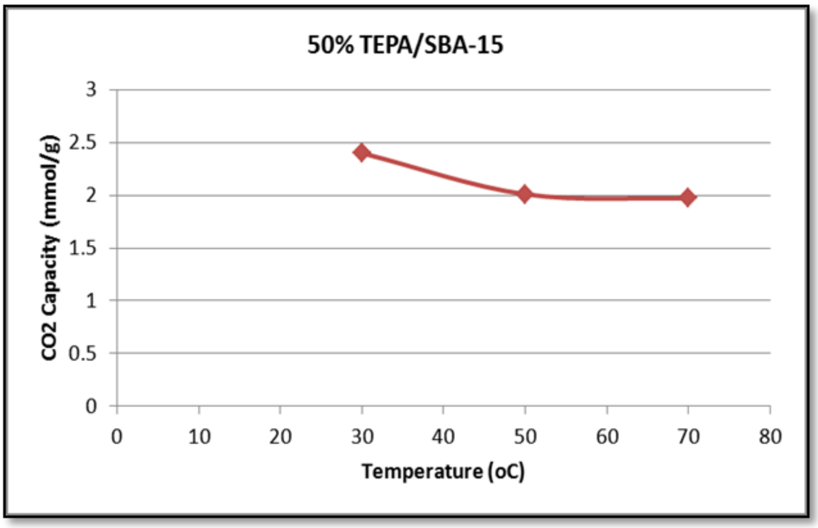


Figure 4.6: Effect of Temperature on 50% TEPA/SBA-15

The adsorption capacity of CO_2 is 2.4mmol/g at 30°C, 2.01mmol/g at 50°C and 1.97 mmol/g at 70°C.the adsorption capacity of 50% TEPA/SBA-15 reduces as the temperature increases.

4.6 Regenerability studies

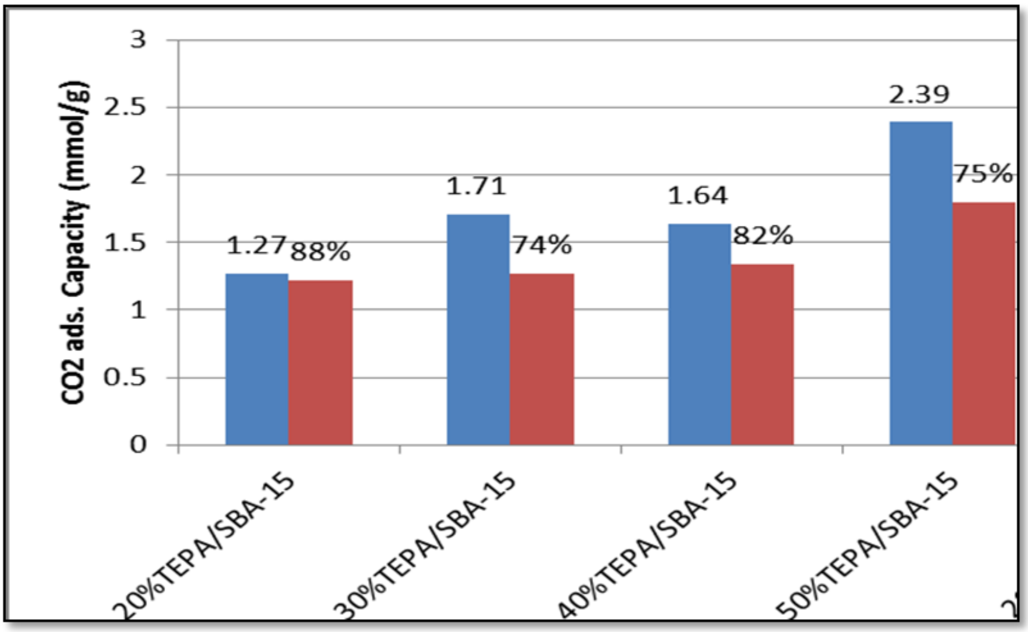


Figure 4.7: Regenerability of TEPA loaded sorbents at 130°C.

Reaction conditions: Oven Temperature=30-130°C,Regeneration period=25 min, TCD temperature =150°C)

For potential practical applications, in addition to high CO_2 capturing capacity, the sorbent must possess long-term stability and regenerability with a minimum difference in adsorption/desorption temperatures would determine their efficiency, cost and therefore feasibility for use. At the same time, a short cycle time is generally preferred. To this end, Thermal swing regeneration is an attractive method for the regeneration of the adsorbent. Temperature swing was used to evaluate the stability and regenerability of the TEPA and PEI based sorbents. The regenerability after first cycle using nitrogen as sweep gas at 130°C is presented in Fig. 4.5. Cyclic adsorption capacity of 50%TEPA/SBA-15 is measured as a percentage during the first adsorption cycle therefore, 100% corresponds to adsorption of 2.4 mmol/g of CO_2.

The extent of regeneration of the sorbent greatly depends on the amount of amine loading and nature of the support. It is seen that lower amine loadings showed better regeneration capacity than higher loading for a given amine. 20%TEPA/SBA-15 showed regeneration upto 88% while 50%TEPA/SBA-15 could be regenerated about 75% indicating amount of loading influenced the extent of regeneration. Same trend is observed in case of PEI loaded sample. This is mainly due to the reaction between amine functionalities and CO_2 forming carbamates which have more viscosity than the original amine. These carbamate complexes limit diffusion of the gases and require higher regeneration temperatures.

4.7 CO_2 Adsorption-Desorption study

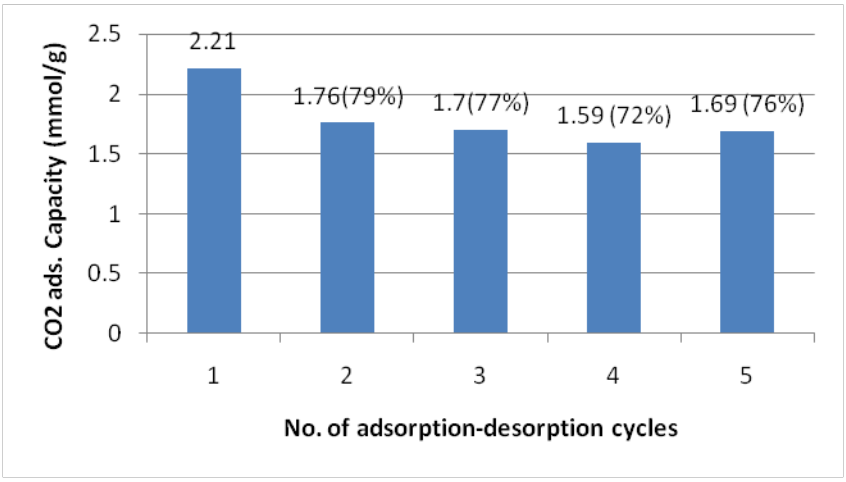


Figure 4.8: CO_2 adsorption-desorption cycle study on 50%/TEPA/SBA-15,

Reaction conditions:For Adsorption: CO_2 flow rate 60ml/min, carrier gas flowrate= 50ml/min, loop volume =1ml, adsorption period= 20 minutes, oven Temperature=30°C, TCD temperature =150°C. For Desorption: Oven Temperature=30-130°C, Regeneration period=25 min, TCD temperature =150°C.

The extent of regenerability of 50%TEPA/SBA-15, the best sample with initial highest adsorption capacity was investigated,up to 5 cycles as shown in the Fig.4.6.The adsorption capacity decreased to 79% after first regeneration and the sorbent could be regenerated in subsequent cycles. The adsorption capacity of this sorbent retained for five cycles without any significant drop in the extent of regeneration. The initial decrease in the adsorption can be attributed to the formation of the thermostable complex, which is crucial factor for the regeneration of the adsorbents. Regeneration temperatures above 145°C whilst recovering approximately 90% of the original adsorption capacity, results in considerable decrease from the first to the second regeneration cycle, leading to a 20 % loss in capacity between thetwo cycles at 120°C. This destructive effect of the thermostable complex on adsorption capacity was not observed in the subsequent cyclesatleast up to 5. Extent of regeneration can be improved by adopting different methods of amine loading to attain better dispersion of amine molecules.

4.8 Temperature programmed desorption 50%TEPA/SBA-15 after CO_2 adsorption

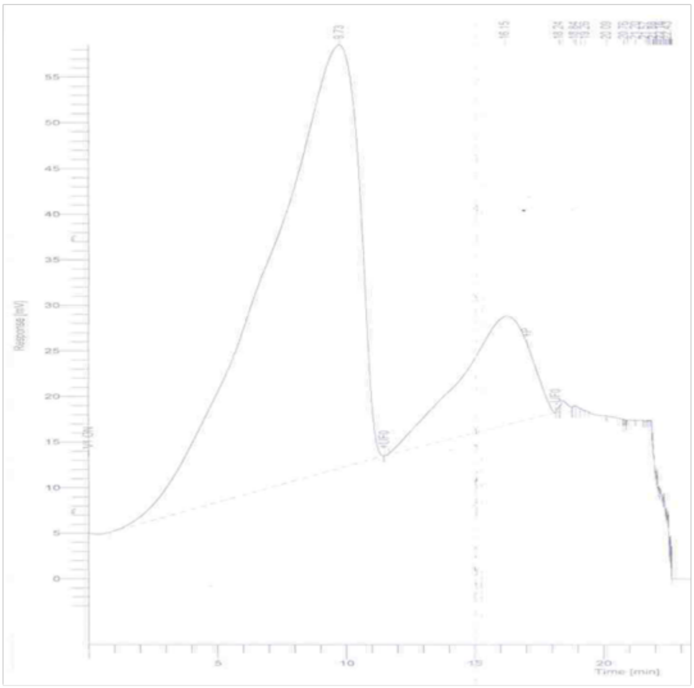


Figure 4.9: Temperature Programmed Desorption of 50% TEPA/SBA-15

Reaction conditions: CO_2 adsorption temp, 30-300°C, time=40 min

Amine based sorbents adsorb CO_2 and forms thermostable complexes, whose decomposition temperatures vary depending up on the structure and nature of the amine group. In Fig. 4.7 TPD of CO_2 adsorbed on TEPA was investigated in presence of N_2 flow. After CO_2 adsorption at 30°C the sorbent was subjected to desorption while increasing the temperature up to 300°C. It is observed that release of CO_2 initiated at 50°C and continued up to 130°C. However, the maximum desorption of CO_2 peak was observed at 120°C. Another peak at 170°C was observed could be due to decomposition of TEPA[72]. This TPD data collaborates the regenerability of the sorbents shown in Fig.4.5 and 4.6.

More importantly the amine based composite sorbents show an extraordinary capacity up to 7.9 mmol/g at 75°C under simulated flue gas conditions (pre-humidified 10% CO_2) [72]. This mesoporous capsules based sorbents with amine loading greatly enhances amine incorporation and facilitates transport of CO_2 inside the sorbent leading to exceptional capture capacity of 6.6 mmol/g under 1 atm dried CO_2 gas at 75°C. A hyperbranched aminosilicate material by a one-step reaction between aziridine and SBA-15, and achieved a capacity about 3.1 mmol/g at 25°C in simulated flue gas conditions. In this study, 50%TEPA/SBA-15 showed maximum adsorption capacity. Improvement of the CO_2 capture capacity of the sorbents has become challenging because of limitations with the amount of amine loaded and the availability of active sites for CO_2 capture in the sorbents. As support, amine characteristics and method of preparation greatly determine the CO_2 adsorption capacities. As adsorption capacity, thermal stability and regenerability significantly depend on the support properties, pore structure and nature and type of amine functionalities further optimization of amine loading and evaluation would provide more insights in improving the adsorption capacities of the sorbents prepared for this thesis.

Chapter 5

Conclusions

Various amines based solid adsorbents with different loadings of TEPA or PEI on SBA-15, MCM-22 and alumina were investigated for CO_2 capture. The surface area, pore volume and pore size of the supports before and after amine loading by N_2 adsorption. These textural properties found to be decreased with increase of amine loading drastically. The CO_2 adsorption capacities were measured by using pulse chemisorption using GC with TCD. The adsorption capacities showed good correlation with well-ordered porous structure, amine loading and type of amine. Among the sorbents, 50%TEPA/SBA-15 showed highest adsorption capacity i.e 2.4 mmol/g at 30°C. All the sorbents prepared for this work are regenerable at 130°C and the extent of regenerability depends on nature of the amine for a given loading. Temperature programmed desorption of CO_2 adsorbed amines also corroborated decomposition temperature of carbamate complex about 130°C.

Bibliography

[1] Chatti R., Bansiwal A. K., Thote J. A., Kumar V., Jadhav P., Lokhande S. K., Biniwale R. B., Labhsetwar N. K., and Rayalu S. S. (2009), Amine Loaded Zeolites for Carbon Dioxide Capture: Amine Loading and Adsorption Studies, Microporous and Mesoporous Materials, 121, 84-89.

[2] Garg A., and Shukla P. R. (2009), Coal and Energy Security for India: Role of Carbon Dioxide (CO_2) Capture and Storage (CCS), Energy, 34, 1032-1041.

[3] Deanna M. DAlessandro, BerendSmit, Jeffrey R. Long, Carbon Dioxide Capture: Prospects for New Materials, AngewandteChemie, 2010, 49, 6058-6082.

[4] Holly M. Krutka, Sharon Sjostrom, C. Jean Bustard, Mike Durham, Ken Baldrey, Robin Stewart, Summary of Post-Combustion CO_2Capture Technologies for Existing Coal-fired Power Plants

[5] Sean I. Plasynski, Zhong-Ying Chen, Review of CO_2capture technologies and some improvement opportunities, PCS, acsfuel, 45,644-649.

[6] Harlick, P.J.E., Sayari, A., Applications of Pore-Expanded Mesoporous Silica. 3. Triamine Silane Grafting for Enhanced CO_2 Adsorption. Industrial and Engineering Chemistry Research 2006. 45: p. 32-48.

[7] Khatri, R.A., Chuang, S. S. C., Soong, Y., Gray, M. , Thermal and Chemical Stability of Regenerable Solid Amine Sorbent for CO_2 Capture. Energy & Fuels, 2006. 20: p. 1514-1520.

[8] Feng, B., Du, M., Dennis, T. J., Anthony, K., Perumal, M. J., Reduction of Energy Requirement of CO_2 Desorption by Adding Acid into CO_2-loaded Solvent. Energy Fuels, 2010. 24: p. 213219.

[9] Li, Y., Study on Corrosion and Material Selection for Desulphurization Unit in Refinery. Petroleum Refinery Engineering, 2008. 38: p. 24-27.

[10] Veltman, K., Singh, B., Hertwitch, E.G., Human and Environmental Impact Assessment on Postcombustion CO_2 Capture Focusing on Emissions from Amine based Scrubbing Solvents to Air. Environmental Science and Technology 2010. 44: p. 14961502.

[11] Bredesen, R., Jordal, K., Bolland, O., High-temperature Membranes in Power Generation with CO_2 Capture. Chemical Engineering and Processing 2004. 43(9): p. 1129-1158.

[12] Kim, S., Ida, J., Guliants, V. V., Lin, Y. S., Functionalised Mesoporous Silica Membrane for the Separation of Carbon Dioxide. International Journal of Environment Technology and Management, 2004. 4(1-2): p. 21.

[13] Lively, R.P., Chance, R. R., Kelley, B. T., Deckman, H. W., Drese, J. H., Jones, C. W., Koros, W. J. , Hollow Fiber Adsorbents for CO_2 Removal from Flue Gas. Industrial and Engineering Chemistry Research, 2009. 48: p. 73147324.

[14] Su, F., Lu, C., Kuo, S. C., Zeng, W. , Adsorption of CO_2 on Amine-functionalized Y-type Zeolites. Energy Fuels, 2010. 24: p. 14411448.

[15] Plaza, M.G., Pevida, C., Arias, B., Casai, M. D., Martin, C. F., Fermoso, J., Rubiera, F., Pis, J. J., Different Approaches for the Development of Low-cost CO_2 Adsorbents. Journal of Environmental Engineering, 2009. 135: p. 426432.

[16] Czakkel, O., Onyestyák, G., Pilatos, G., Kouvelos, V., Kanellopoulos, N., Lászlló, K. , Kinetic and Equilibrium Separation of CO and CO_2 by Impregnated Spherical Carbons. Microporous and Mesoporous Materials 2009. 120: p. 7683.

[17] Huang, H.Y., Yang, R. T., Chinn, D., Munson, D. L., Amine-Grafted MCM-48 and Silica Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas. Industrial and Engineering Chemistry Research 2003. 42(2427).

[18] Knowles, G.P., Delaney, S. W., Chaffee, A. L., Amine-Functionalised Mesoporous Silicas as CO_2 Adsorbents. Studies in Surface Science and Catalysis, 2005. 156: p. 887.

[19] Zheng, F., Tran, D. N., Busche, B. J., Fryxell, G. E., Addleman, R. S., Zemanian, T. S., Aardahl, C. L., Ethylenediamine-Modified SBA-15 as Regenerable CO_2 Sorbent. Industrial and Engineering Chemistry Research, 2005. 44: p. 3099.

[20] Yue, M.B., Chun, Y., Cao, Y., Dong, X., Zhu, J. H., CO_2 Capture by Asprepared SBA-15 with an Occluded Organic Template. Advanced Functional Materials 2006. 16: p. 17171722.

[21] Knöfel, C., Martin, C., Hornebecq, V., Llewellyn, P. L., Study of Carbon Dioxide Adsorption on Mesoporous Aminopropyl silane-Functionalized Silica and Titania Combinig Microcalorimetry and in Situ Infrared Spectroscopy. Journal of Physical Chemistry C, 2009. 113: p. 21726-21734.

[22] Harlick, P.J.E., Sayari, A., Applications of Pore-Expanded Mesoporous Silica. Triamine Grafted Material with Exceptional CO_2 Dynamic and Equilibrium Adsorption Performance. Industrial & Engineering Chemistry Research, 2007. 46(2): p. 446-458.

[23] Couck, S., Denayer, J. F. M., Baron, G. V., Remy, T., Gascon, J., Kapteijn, F. , An Aminefunctionalized MIL-53 Metal-organic Framework with Large Separation Power for CO_2 and CH_4. Journal of the American Chemical Society, 2009. 131: p. 63266327.

[24] Yazaydin, A.O., Snurr, R. Q., Park, T. H., Koh, K., Liu, J., LeVan, M. D., Benin, A. I., Jakubczak, P., Lanuza, M., Galloway, D. B., Low, J. J., Willis, R. R. , Screening of Metal-organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach. Journal of the American Chemical Society, 2009. 131(1819818199).

[25] Rosenholm, J., Penninkanga, A., Linden, M., Amino-functionalization of Large pore Mesoscopically Ordered Silica by a One-step Hyperbranching Polymerization of a Surface-grown Polyethyleneimine. Chemical Communications 2006: p. 39093911.

[26] Serna-Guerrero, R., Belmabkhout, Y., Sayari, A. , Modeling CO_2 Adsorption on Amine-functionalized Mesoporous Silica: 1. A Semi-empirical Equilibrium Model. Chemical Engineering Journal, 2010. 161: p. 173181.

[27] Plasynski S. I., Litynski J. T., McIlvried H. G., and Srivastava R. D. (2009), Progress and New Developments in Carbon Capture and Storage, Critical Reviews in Plant Sciences, 28 (3), 123-138.

[28] Thiruvenkatachari R., Su S., An H., and Yu X. X. (2009), Post Combustion CO_2 Capture by Carbon Fibre Monolithic Adsorbents, Progress in Energy and Combustion Science, 35, 438-455. 28 Herzog H., Meldon J., and Hatton A. (2009), Advanced Post Combustion CO_2 Capture.

[29] Figueroa J. D., Fout T., Plasynski S., McIlvried H., Srivastava R. D. (2008), Advances in CO_2 Capture Technology-The U.S. Department of Energys Carbon Sequestration Program, International Journal of Greenhouse Gas Control, 2, 9-20.

[30] Kanniche M., Gros-Bonnivard R., Jaud P., Valle-Marcos J., Amann J.-M., and Bouallou C. (2009), Pre-Combustion, Post-Combustion and Oxy-Combustion in Thermal Power Plant for CO_2 Capture, Applied Thermal Engineering.

[31] Lei Li, Ning Zhao, Wei Wei, Yuhan Sun, A review of research progress on CO_2capture, storage, and utilization in Chinese Academy of Sciences, FUEL, august 2011.

[32] Adsorbent materials for carbon dioxide capture from large anthropogenic point sources, by Sunho Choi, Je_rey H. Drese, and Christopher W. Jones, published in ChemSusChem, in 2009, volume 2, pages 796- 854.

[33] Sean I. Plasynski, Zhong-Ying Chen, Review of CO_2 capture technologies and some improvement opportunities, PCS, acsfuel, 45,644-649.

[34] Holly M. Krutka, Sharon Sjostrom, C. Jean Bustard, Mike Durham, Ken Baldrey, Robin Stewart, Summary of Post-Combustion CO_2Capture Technologies for Existing Coal-fired Power Plants.

[35] Lei Li, Ning Zhao, Wei Wei, Yuhan Sun, A review of research progress on CO_2capture, storage, and utilization in Chinese Academy of Sciences, FUEL, august 2011.

[36] Deanna M. DAlessandro, BerendSmit, Jeffrey R. Long, Carbon Dioxide Capture: Prospects for New Materials, AngewandteChemie, 2010, 49, 6058-6082.

[37] Sean I. Plasynski, Zhong-Ying Chen, Review of CO_2capture technologies and some improvement opportunities, PCS, acsfuel, 45,644-649.

[38] Carbon Dioxide (CO_2) Capture at Coal-Fired Power Plants Presented By Brian McNamara

[39] ArunkumarSamanta, An Zhao, George K. H. Shimizu, ParthaSarkar, and Rajender Gupta, Post-Combustion CO_2Capture Using Solid Sorbents: A Review, IECR, 2012, 51, 1438-1463.

[40] X. C. Xu, C. S. Song, J. M. Andresen, B. G. Miller, A. W. Scaroni, Energy & Fuels 2002, 16, 1463.

[41] Sing, K. S. W. (1998). Adsorption Methods for the Characterization of Porous Materials. Adv. Colloid Interface Sci. 76-77: 3-11.

[42] Dabrowski, A. (2001). Adsorption- From Theory to Practice. Adv. Colloid Interface Sci. 93: 135-224.

[43] Barton, T. J., Bull, L. M., Klemperer, W. G., Loy, D. A., McEnaney, B., Misono, M., Monson, P. A., Pez, G., Scherer, G. W., Vartuli, J. C., and Yaghi, O. M. (1999). Tailored Porous Materials. Chem. Mater. 11: 2633-2656.

[44] Beck, J. S. and Vartuli, J. C. (1996). Recent Advances in The Synthesis, Characterization and Applications of Mesoporous Molecular Sieves. Current Opinion in Solid State & Materials Science. 1: 76-87.

[45] Boger, T., Roesky, R., Gläser, R., Ernst, S., Eigenberger, G., and Weitkamp, J. (1997). Influence of The Aluminum Content on The Adsorptive Properties of MCM-41. Micropor. Mater. 8: 79-91.

[46] Zhao, X. S., Lu, G. Q., and Millar, G. J. (1996). Advances in Mesoporous Molecular Sieve MCM-41. Ind. Eng. Chem. Res. 35: 2075-2090.

[47] Zhao, X. S., Lu, G. Q., and Hu, X. (2000). Characterization of the Structural and Surface Properties of Chemically Modified MCM-41 Material. Micropor. Mesopor. Mater. 41: 37-47.

[48] M. Caplow, Journal of the American Chemical Society 1968, 90, 6795. 49 G. Sartori, D. W. Savage, Industrial & Engineering Chemistry Fundamentals 1983, 22, 239.

[49] T. L. Donaldson, Y. N. Nguyen, Industrial & Engineering Chemistry Fundamentals 1980, 19, 260.

[50] FengZheng, Diana N. Tran, Brad J. Busche, Glen E. Fryxell, R. Shane Addleman, Thomas S. Zemanian, and Christopher L. Aardahl, Ethylenediamine-Modi_ed SBA- 15 as Regenerable CO_2SorbentIndustrial & Engineering Chemistry Researc H_2O 05, 44, 3099-3105.

[51] V. Zelenáka, M. Badanicováa, D. Halamováa, J. Cejkab, A. Zukalb, N. Murafac, G. Goerigkd, Amine-modi_ed ordered mesoporous silica: E_ect of pore size on carbon dioxide capture, Chemical Engineering Journal 144 (2008) 336-342.

[52] Sunho Choi, McMahan L. Gray and Christopher W. Jones, Amine-Tethered Solid Adsorbents Coupling High Adsorption Capacity and Regenerability for CO_2 Capture From Ambient Air, ChemSusChem 2011, 4, 628-635.

[53] XiuwuLiua, Li Zhoua, XinFub, Yan Suna,WeiSua, YapingZhoub, Adsorption and regeneration study of the mesoporous adsorbent SBA-15 adapted to the capture/ separation of CO_2 andCH_4, Chemical Engineering Science 62 (2007) 1101-1110.

[54] Alex C. C. Chang, Steven S. C. Chuang, McMahan Gray, and Yee Soong, In-Situ Infrared Study of CO_2Adsorption on SBA-15 Grafted

with ç- (Aminopropyl)triethoxysilane, Energy & Fuels 2003, 17, 468-473.

[55] XiaochunXu, Chunshan Song, Bruce G. Miller, and Alan W. Scaroni, Influence of Moisture on CO_2 Separation from Gas Mixture by a Nanoporous Adsorbent Based on Polyethylenimine-Modified Molecular Sieve MCM-41, Industrial & Engineering Chemistry ResearcH_2O05, 44, 8113-8119.

[56] Gregory P. Knowles, Seamus W. Delaney, and Alan L. Chafee, Diethylenetriamine[propyl(silyl)]-Functionalized (DT) Mesoporous Silicas as CO_2 Adsorbents, Industrial & Engineering Chemistry Research. 2006, 45, 2626- 2633.

[57] Xinlong Yan, Lei Zhang, Ying Zhang, Guidong Yang, and Zifeng Yan, Amine-Modified SBA-15: E_ect of Pore Structure on the Performance for CO_2 Capture, Industrial & Engineering Chemistry Research. 2011, 50, 3220-3226.

[58] Wha-SeungAhn, Won-Jin Son, and Chao Chen, CO_2Capture Using Amineimpregnated Mesoporous Silica, Department of Chemical Engineering, Inha University, Incheon 402-751.

[59] Marília R. Mello, DelphinePhanon, Gleiciani Q. Silveira, Philip L. Llewellyn, Célia M. Ronconi, Amine-modified MCM-41 mesoporous silica for carbon dioxide capture, Microporous and Mesoporous Materials 143 (2011), 174-179.

[60] Youssef Belmabkhout, Rodrigo Serna-Guerrero, and Abdelhamid-Sayari, Adsorption of CO_2-Containing Gas Mixtures over Amine-Bearing Pore-Expanded MCM- 41 Silica: Application for Gas Purification, Industrial & Engineering Chemistry Research 2010, 49, 359-365.

[61] Chih-Chau Hwang, Zhong Jin, Wei Lu, Zhengzong Sun, Lawrence B. Alemany, Jay R. Lomeda and James M. Tour, In situ Synthesis of Polymer-Modified Mesoporous Carbon CMK-3 Composites for CO_2 Sequestration, ACS Applied Materied Interfaces 2011, 3, 4782-4786.

[62] Dong-Il Jang and Soo-Jin Park Bull, In_uence of Amine Grafting on Carbon Dioxide Adsorption Behaviors of Activated Carbons, Korean Chem. Soc. 2011, Vol. 32, 93-377.

[63] Mohammad GulamRabbani and Hani M. El-Kaderi, Synthesis and Characterization of Porous Benzimidazole-Linked Polymers and Their Performance in Small Gas Storage and SelectiveUptake, Chemistry of Materials, 2012, 24, 1511-1517.

[64] Hestekin, J.A., Bachas, L. G., Bhattacharyya, D., Poly(amino acid)-Functionalized Cellulosic Membranes: Metal Sorption Mechanisms and Results. Industrial & Engineering Chemistry Research 2001, 40, 2668-2678.

[65] Weigang Lu, Daqiang Yuan, Dan Zhao, Christine Inge Schilling, Oliver Plietzsch, Thierry Muller, Stefan Brease, Johannes Guenther, Janet Bleumel, Rajamani Krishna, Zhen Li, and Hong-Cai Zhou, Porous Polymer Networks: Synthesis, Porosity, and Applications in Gas Storage/Separation, Chemistry of Materials 2010, 22, 5964-5972.

[66] Li P., Ge B., Zhang S., Chen S., Zhang Q., and Zhao Y. (2008a), CO_2 Capture by Polyethylenimine-Modified Fibrous Adsorbent, Langmuir, 24, 6567-6574. 68 Li P., Zhang S., Chen S., Zhang Q., Pan J., and Ge B. (2008b), Preparation andAdsorption Properties of Polyethylenimine Containing Fibrous Adsorbent for Carbon Dioxide Capture, Journal of Applied Polymer Science, 108, 3851-3858.

[67] Drage T. C., Arenillas A., Smith K. M., and Snape C. E. (2008), Thermal Stability of Polyethylenimine Based Carbon Dioxide Adsorbents and Its Influence on Selection of Regeneration Strategies, Microporous and Mesoporous Materials, 116, 504-512.

[68] Drage T. C., Arenillas A., Smith K. M., Pevida C., Piippo S., and Snape C. E. (2007), Preparation of Carbon Dioxide Adsorbents from the Chemical Activation of Urea- Formaldehyde and Melamine-Formaldehyde Resins, Fuel, 86, 22-31.

[69] C. J. Brinker, G. W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol- Gel Processing, Academic Press, Inc., San Diego 1990.

[70] R. A. Khatri, S. S. C. Chuang, Y. Soong, M. Gray, Industrial & Engineering Chemistry Research 2005, 44, 3702.

[71] M. L. Gray, Y. Soong, K. J. Champagne, H. Pennline, J. Baltrus, International Journal of Environmental Technology and Management 2004, 4, 82.

[72] J. C. Hicks, J. H. Drese, D. J. Fauth, M. L. Gray, G. G. Qi and C. W. Jones, J. Am. Chem. Soc., 2008, 130, 29022903.