CO$_2$ AND SO$_2$ CAPTURE BY AROMATIC AND ALIPHATIC AMINE SORBENTS

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ABSTRACT

The emissions of CO$_2$ to the atmosphere have rapidly increased in the last decades due to the industrialization and the increasing energy demand. Due to the potential effect that CO$_2$ has as global warmer, industrialized and emerging countries are putting efforts on developing technologies to reduce emissions. Coal fired power plants produce 55% of U.S. electricity and more than 33% of global CO$_2$ emissions, representing the largest stationary source of CO$_2$. As a co-product of the combustion process of sulfur-containing coal, SO$_2$ is produced and represents between 0.2 and 0.3 v% of the power plant flue gas composition. SO$_2$ is a serious pollutant, precursor of the acid rain and particulate materials. The release of SO$_2$ to the atmosphere can cause respiratory diseases and destruction of eco-systems.

Some existing CO$_2$ capture technologies are inefficient to be applied in power plants due to the large flow rates and high concentration of CO$_2$ in the flue gas. Other technologies such as the liquid amine process are not economically viable because the energy requirements for operation and regeneration are excessive. In addition those processes cause rapid corrosion to the equipment. The adsorption on solid sorbents is potentially the most suitable process for the treatment of flue gas from power plants. The development of solid sorbents by functionalization of solid supports with amine functional groups has been recently studied. The goals during the sorbent development
are (i) a high CO$_2$ selectivity and adsorption capacity, (ii) the long term stability and cycle life, (iii) resistivity toward thermal and oxidative degradation, (iv) resistance to SO$_2$ and (iv) low cost.

In this thesis, the resistance of aliphatic amine and aromatic anime sorbents towards SO$_2$ was studied by in-situ infrared spectroscopy (IR) and mass spectrometry (MS). An operational condition to improve the CO$_2$ adsorption capacity of an amine sorbent was also studied by introducing H$_2$O in the flue gas. The hypothesis included the use of an aromatic amine to prepare a low basicity sorbent for SO$_2$ capture and to reduce the SO$_2$ poisoning on a CO$_2$ capture sorbent. In addition, it is thought that the presence of H$_2$O in the flue gas improves the adsorption capacity of an amine sorbent due to the formation of different adsorbed species. The IR and MS results showed that the aromatic amine sorbent has a weak adsorption capacity of CO$_2$ and SO$_2$, leading to CO$_2$ capture processes at low temperature. SO$_2$ strongly adsorbs on the aliphatic amine sorbent, causing accumulation of sulfate and sulfite species and reducing the availability of amine sites for CO$_2$ adsorption. The performance of CO$_2$ capture in simulated practical conditions showed the improvement in capture capacity of a sorbent by more than 60% when the flue gas is saturated with H$_2$O.
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CHAPTER I

INTRODUCTION

1.1 Environmental motivation, emissions and energy demand

The global climate changes have been attributed in great proportion to the increment of the greenhouse effect gases (GHGs) in the atmosphere. The most abundant greenhouse gas and the principal responsible for the greenhouse effect on earth is water vapor (H₂O). Water vapor is part of the natural hydrologic cycle and its concentration periodically changes due to condensation. Carbon dioxide (CO₂) is the second most abundant greenhouse gas, and the principal responsible for the so-called global warming. Methane (CH₄), ozone (O₃) and nitrous oxide (NOₓ) are other greenhouse gases present in lower concentration in the atmosphere but with a several-times greater global warming potential than CO₂. GHGs are naturally present in the atmosphere, but industrialization has changed their proportions. The concentration of CO₂ in air before industrialization was 280 ppm [1] and increased to 394 ppm at May 2011 [2]. The constant emission of non-condensable GHGs increases their concentration in air causing excessive global warming. Global warming is potentially harmful for eco-systems and earth’s life.

Due to the increasing energy demand in industrialized and emerging countries, more power plants, refineries, chemical industries and building complexes have been
built in the last decades. These stationary sources are big contributors to GHG emissions raising the CO₂ levels to concentrations that cannot be processed by plants and trees via photosynthesis. In 2005 the Kyoto protocol was established with means to reduce the concentration of greenhouse gases to levels in which they have no incidence on earth’s weather. Since then, CO₂ capture and storage technologies have been developed for treating flue gas in stationary sources [3].

Coal fired power plants produce 55% of U.S. electricity and more than 33% of global CO₂ emissions representing the largest stationary source of CO₂ [4]. The coal used in power plants contains 1 to 10 w% of sulfur [5], which accounts to generate sulfur dioxide (SO₂) concentrations up to 0.3 v% in the flue gas. SO₂ is partially responsible for the production of acid rain and particulates in air. The removal of CO₂ from coal-fired power plants is subjected to previous desulfurization or development of SO₂-resistant processes.

1.2 CO₂ capture by immobilized-amine solid sorbents

Adsorption of CO₂ on amines for storage and re-disposal is a technique developed to reduce emissions of CO₂ to the atmosphere. Porous solid particles (sorbents) can be used to capture CO₂ from flue gas through chemical or physical adsorption. Immobilization of amines on solid supports functionalizes the sorbent surface changing the adsorption modes of CO₂. During the adsorption of CO₂ on immobilized-amine solid sorbents intermediates such as carbonates and carbamic acid are formed [6]. These intermediates are IR-observable species which desorb as CO₂ by thermal or pressure swing processes. Water vapor is used to enhance the adsorption capacity of the sorbents.
because primary and secondary amines can react with CO₂ to form bicarbonates [4, 6-8]. In presence of water 1 mol of amine can capture double the amount of CO₂ than in dry conditions.

1.3 The role of SO₂ as a pollutant

Sulfur dioxide has a number of industrial applications, but is a harmful compound when present in atmospheric air. According to the U.S. Environmental protection agency (EPA), short-term exposures of SO₂ may cause adverse respiratory effects including broncho-constriction and asthma [5]. SO₂ reacts with the water present in atmosphere under the catalytic effect of NOₓ to form sulfuric acid and consequently acid rain. Animal and plants species may change in specific regions due to the exposure to SO₂ and acid rain.

Coal fired power plants are the major emissaries of SO₂ from non-natural sources. The treatment of flue gas from coal fired power plants requires an effective CO₂, and SO₂ removal in practical conditions. Although the adsorption mechanism of SO₂ on amines is similar to that of CO₂, the strength of the bonding of amine with SO₂ is higher than that of amine with CO₂. Consequently, SO₂ also plays a pollutant role in the immobilized-amine solid sorbent technologies where competes with CO₂ to adsorb on the amine sites. In a low temperature desorption process SO₂ may be considered as a poison due to the high energy requirements for desorption. High desorption temperatures may cause deactivation of the sorbent by thermal degradation, oxidation or migration of amine functional groups.
1.4 Hypothesis and objectives

The flue gas released from coal-fired power plants contains 10-15 v% of CO₂, 5-7 v% of H₂O and 0.2-0.3 v% of SO₂ (2000-3000 ppm SO₂). CO₂ is a non-condensable GHG and the principal responsible for the global warming. SO₂ is a serious pollutant which causes acid rain, particulates and health hazards. H₂O is a condensable GHG and is considered innocuous to the environment. There is a desire to reduce CO₂ and SO₂ emissions from stationary sources to fight the climate change and other environmental issues. CO₂ capture by solid amine adsorption has been studied by various authors [3, 6, 9-11]. Adsorption of CO₂ and SO₂ on amine functional groups is governed by acid-base interactions [7]. The acidity of the gas and the basicity of the amine play an important role in the adsorption/desorption process during the CO₂ capture. CO₂ (pKₐ=6.35) has an acidity several orders of magnitude lower than SO₂ (pKₐ=1.81) [12]. These two gases experience a competence towards the adsorption on the amine sites due to the high acidity of SO₂ and high driving force of CO₂ concentration. However when low desorption temperature is used, SO₂ is more likely to remain adsorbed blocking the amine sites for CO₂ adsorption.

The hypothesis for this study includes the use of two amines with different basicities; tetraethylenepentamine (TEPA, pKₐ=4.29) and m-phenylenediamine (MPD, pKₐ=9.19) [12]. The presence of both TEPA and MPD is expected to provide a balance in adsorption strength, reducing the desorption temperature of SO₂ and maintaining high CO₂ capture capacity of the sorbent. The IR and MS techniques applied for the study of CO₂ and SO₂ capture, provide information related to changes in adsorption time, chemical structure of adsorbed species and desorption energy.
The presence of H$_2$O is expected to enhance the CO$_2$ capture capacity of an amine sorbent by increasing the amine utilization due to a further reaction of carbamate species with H$_2$O. Structural changes lead to higher purity of CO$_2$ in actual operation conditions. A tubular reactor system provides information on the effect of the concentration of H$_2$O in the flue gas under simulated practical operation conditions.
BIBLIOGRAPHY


CHAPTER II

BACKGROUND

2.1 Coal-fired power plants

Coal is considered one of the most abundant and inexpensive fuel, approximately 55% of the U.S. electricity is generated using coal as fuel. Coal is projected to continue playing a significant role in the generation of electricity because of rapid economic growth [1]. In a coal-fired power plant, pulverized coal is combusted with excess air in a boiler to produce high-pressure steam, which is expanded in a steam turbine to generate electricity [2]. The process for converting heat into mechanical energy consists of a Rankine thermodynamic cycle. The Rankine cycle consists of (i) increasing the pressure of water by using a pump, (ii) heating the compressed water until all the liquid changes phase to create high pressure water vapor (steam), (iii) expansion of water vapor through a turbine to generate power and (iv) removal of heat from the vapor to obtain liquid water. After completion of processes (i) to (iv) the cycle starts over. In practice these processes are non-reversible and the overall efficiency of the cycle is lowered. The typical efficiency for the Rankine cycle is 25-35% but power plants use modifications to improve the heat recovery and power output increasing the overall efficiency of the thermodynamic cycle up to 50-60%.
Burning of coal is involved in the heating of compressed water to obtain high pressure steam. In this process the boiler is fed with pulverized coal and excess of air is pumped into the chamber to promote full combustion. The high temperature combustion gases are used as a hot fluid in a heat exchanger and water is used as a cold fluid. The effluents of the boiler are; steam that is directed to the turbine and lower temperature combustion gas, so called flue gas. The heat released by coal is equivalent to the heat of formation of \( \text{CO}_2 \) by complete combustion of carbon with oxygen (\( \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \)). As a consequence the amount of \( \text{CO}_2 \) produced by the power plant depends on the amount of steam produced to generate electricity[3] A 500 MW power plant may produce up to 8000 tons of \( \text{CO}_2 \)/day [2]. The approximate volume composition of the flue gas from a coal-fired power plant is 3-4% of \( \text{O}_2 \), 12-15% of \( \text{CO}_2 \), 5-7% of \( \text{H}_2\text{O} \), 0.2-0.3% (2000-3000 ppm) \( \text{SO}_2 \), 0.01-0.015% (150-500 ppm) NO and balance of \( \text{N}_2 \).

### 2.2 \( \text{CO}_2 \) and \( \text{SO}_2 \) capture technologies

Before the Kyoto protocol in 2005 \( \text{CO}_2 \) capture included the use of solid sorbents, the employment of liquid amines for absorption, and the utilization of a membrane separation process for natural gas treatment and removal of \( \text{CO}_2 \) from closed environments[4]. The economics of those methods was not favorable enough for \( \text{CO}_2 \) removal from flue gas at that time [5].

EPA first set standards for sulfur dioxide in 1971[6] and desulfurization processes started to be implemented in several industries to reduce \( \text{SO}_2 \) emissions. Currently the pre-combustion processes remove more than 90% of the \( \text{SO}_2 \) on most of the fuels preventing excessive \( \text{SO}_2 \) formation. Post combustion processes are mostly used for \( \text{SO}_2 \)
removal from flue gas streams. Those processes are highly efficient but produce large amounts of waste products.

2.2.1 Methods for CO\(_2\) removal

The natural CO\(_2\) cycle involves the absorption of CO\(_2\) from the atmosphere by different sources such as plants, trees, oceans and soils. In the last decades emissions of CO\(_2\) have increased due to industrialization and the natural absorption on earth has not been enough to maintain low the CO\(_2\) levels in the atmosphere. Current methods for further capturing CO\(_2\) include absorption with liquid amines, adsorption with solid sorbents, membrane separation, chemical looping and low temperature distillation [7, 8].

Separation with sorbents and solvents has been applied for more than 60 years since oil and chemical industries started emerging. Nowadays there are several processes in which amines are used to capture CO\(_2\) for industrial requirements and environmental reasons. Monoethanolamine (MEA) and diethanolamine (DEA) have been widely used for CO\(_2\) absorption in aqueous processes with recovery rates and product purity greater than 98%. The separation process using liquid amines is questioned because it involves extensive energy for regeneration, corrosion problems and fast amines oxidation [9]. Improved solvents have been studied to reduce energy requirements and slow degradation rates [10-14].

Solid sorbents such as activated carbon, alumina, silica and zeolites can be used to isolate CO\(_2\) from gas mixtures using pressure-swing adsorption (PSA), temperature-swing adsorption (TSA), and concentration-swing adsorption (CSA)[4]. PSA and TSA are commercially practiced methods for separation of CO\(_2\) in hydrogen production,
natural gas treatment and enclosed habitable environments such as submarine and spacecrafts [9]. Although adsorption is not yet considered the most attractive method for large scale CO₂ capture, the recent developments and constant studies give it the highest potential among the different methods for flue gas treatment. Advantages of the solid sorbents are; low energy requirements for regeneration, reduction on corrosion problems, low cost, high CO₂ capture capacity and high purity of the product.

Inclusion of active functional groups on solid supports has been studied for several years [5]; however functionalization with amines for CO₂ adsorption purposes has only been reported during the last two decades. Different techniques have been applied to modify the solid support surfaces such as (i) impregnation [15], (ii) chemical grafting [9, 16, 17], (iii) chemical substitution [15, 18], (iv) ammonia heat treatment [15] and (v) activation by carbonization [19].

Figure 2.1 Schematic diagram of a CO₂ capture unit that uses the TSA method. Left: the flue gas flows through the sorbent bed and CO₂ is adsorbed at low temperature. Right: CO₂ is desorbed at high temperature and concentrated using steam.
2.2.2 Adsorption, desorption and CO₂ capture process

CO₂ capture by solid sorbents occurs by adsorption and desorption processes. Adsorption is the process in which a molecule (adsorbate), is attached to an atom or a surface (sorbent). This process is classified by the heat of adsorption (binding energy) between the adsorbate and the sorbent into (i) physisorption and (ii) chemisorption. Physisorption is a physical attachment with heat of adsorption between 1 and 15 kcal/mol, the binding energy is low and the bonding is easily broken. The interactions between the adsorbate and the sorbent are Van der Waals forces present on two permanent dipoles, a permanent dipole and an induced dipole, or between neutral atoms and molecules[20]. Chemisorption is a chemical attachment in which the molecule changes its nature to create a covalent bonding with the surface. The heat of adsorption in chemisorption is between 40 and 400 kcal/mol, similar to a typical heat of reaction and orders of magnitude higher than that of physisorption [20]. Chemisorption is able to affect the rate of a chemical reaction because when a molecule is chemically adsorbed its atomic and electronic configurations are perturbed, making it highly reactive. When no chemical reaction has occurred and sufficient energy is applied to the surface, the bond breaks and the molecule detach recovering its initial structure. This process is called desorption and is usually driven by increasing the temperature or reducing the pressure.

CO₂ capture takes place at the interface between the flue gas and the immobilized-amine solid sorbent. The CO₂ capture process involves six steps, one less than a catalytic chemical reaction. At initial conditions of temperature, pressure and concentration the CO₂ (1) travels from the flue gas bulk to a stagnant region close to the solid sorbent, (2) diffuses through the stagnant region inside of the pores and proximate
the solid surface and (3) adsorbs on the sorbent. By applying a change in temperature, pressure or concentration the CO₂ (4) desorbs from the surface, (5) diffuses through the stagnant region and (6) returns to the bulk gas. CO₂ is selectively chemisorbed on amines forming carbonate, bicarbonate and carbamic acid species[9].

2.2.3 Methods for SO₂ removal

The most common method for removal of SO₂ involves wet scrubbers that use limestone, seawater and other alkaline sorbents. The wet scrubber method is highly efficient but tend to require large capital investment and produces large amounts of water and solid wastes [21]. Semi-wet and dry processes have been proposed using carbonates slurries, activated carbon and metal oxide sorbents. For metal oxide sorbents the desorption temperature is very high resulting in high cost for regeneration [22].

2.3 Adsorption of CO₂ and SO₂ on amine functional groups

Adsorption of CO₂ and SO₂ on amine functional groups is governed by the acid-base interaction between the gases and the sorbent [23]. These interactions cause the formation of IR-observable intermediate species such as carbamate, carbonate, bicarbonate and carbamic acid for CO₂ and sulfates, sulfites, bisulfate and sulfonic acid for SO₂ [3, 24-28].

Carbamate and ammonium ion are formed by the reaction of two amine molecules with one molecule of CO₂. The presence of H₂O can increase the CO₂ capture capacity of amine sorbents because the carbamate formed in dry conditions can further react with H₂O and CO₂ to form bicarbonate and another ammonium ion [4, 23, 26]:
\[2R_1R_2\text{NH}+\text{CO}_2 \leftrightarrow R_1R_2\text{NH}^++R_1R_2\text{NCOO}^-\]

\[R_1R_2\text{NCOO}^-+\text{CO}_2+\text{H}_2\text{O} \leftrightarrow R_1R_2\text{NH}^++\text{HCO}_3^-\]

Table 2.1 Proposed band assignment for identification of adsorbed species of \(\text{CO}_2\) and \(\text{SO}_2\) on TEPA and MPD by IR spectroscopy.

<table>
<thead>
<tr>
<th>Species</th>
<th>Functional groups</th>
<th>Wavenumbers (cm(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia ion</td>
<td>(\text{NH}_3^+)</td>
<td>1510, 1625, 3025</td>
<td>[29, 30]</td>
</tr>
<tr>
<td>Carbamate</td>
<td>(\text{C}=\text{O})</td>
<td>1530, 1635</td>
<td>[8, 27, 30, 31]</td>
</tr>
<tr>
<td>Carbonate</td>
<td>(\text{CO}_3^=)</td>
<td>1337, 1390, 1575</td>
<td>[9, 26]</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>(\text{HCO}_3^-)</td>
<td>1432, 1493, 1634</td>
<td>[9, 26]</td>
</tr>
<tr>
<td>Carbamic acid</td>
<td>(\text{HNCO}_2^-)</td>
<td>1330, 1441, 1595</td>
<td>[9, 27]</td>
</tr>
<tr>
<td>Sulfate</td>
<td>(\text{SO}_4^{=})</td>
<td>1100, 1149, 1462, 1520</td>
<td>[24, 28, 32]</td>
</tr>
<tr>
<td>Bisulfate</td>
<td>(\text{HSO}_4^-)</td>
<td>805, 897, 979, 1010, 1100, 1170, 1220, 1569</td>
<td>[24, 33]</td>
</tr>
<tr>
<td>Sulfite</td>
<td>(\text{SO}_3^{=})</td>
<td>963, 1025, 1135, 1462</td>
<td>[24, 28, 30]</td>
</tr>
<tr>
<td>Metabisulfite</td>
<td>(\text{S}_2\text{O}_5^-)</td>
<td>979, 1060, 1170, 1385, 1462</td>
<td>[32, 34]</td>
</tr>
<tr>
<td>(\text{SO}_2--\text{NH}_2)</td>
<td>(\text{N-O})</td>
<td>1510, 1643</td>
<td>[3, 26, 30]</td>
</tr>
</tbody>
</table>

2.4 Aliphatic and aromatic amines

Amines are organic derivatives of ammonia (\(\text{NH}_3\)) in which one, two or three of the hydrogen atoms have been substituted by an organic radical. The structure of amines is similar to that of ammonia, the nitrogen is \(\text{sp}^3\) hybridized, with the three substituents occupying three corners of a tetrahedron and a lone pair of electron occupying the fourth corner [35]. Amines classify according to the number of substituents as primary, secondary or tertiary amines. The nature of the substituent provides another classification as aliphatic amines, when the substituent is an alkyl group and aromatic amines, when the substituent is an aryl group.
As ammonia, amines have basic and nucleophilic properties. The lone electron pair that gives ammonia its basic properties is also present in amines making them an electron pair donor and likely to combine with hydrogen ions (H\(^+\)). The electron pair is attached to the nitrogen atom, which is very electronegative, these electrons can attract the positive part an ion to form polar bondings. Amines react with acids to form ammonium ions and consequently acid-base salts. These are the type of reactions more likely to occur during the adsorption of CO\(_2\) and SO\(_2\) on amine sorbents. The basicity of an amine can be measured by defining an analogous basicity constant (K\(_b\)), for the reaction [35]:

\[
\text{RNH}_2 + \text{H}_2\text{O} \leftrightarrow \text{RNH}_3^+ + \text{OH}^-
\]

\[
K_b = \frac{[\text{RNH}_3^+][\text{OH}^-]}{[\text{RNH}_2]} \quad \text{pK}_b = -\log K_b
\]

Similarly, the acidity of a compound such as CO\(_2\) or SO\(_2\) can be measured to obtain the acidity constant (K\(_a\)) and pK\(_a\). Similarly to the pH definition, pK\(_a\)+pK\(_b\)=14. The larger the basicity constant and the smaller the value of pK\(_b\); the stronger the base.

Aliphatic amines are stronger bases than aromatic amines. In an aliphatic amine, the alkyl substituent plays a role similar to the hydrogen in ammonia, and the lone electron pair of the nitrogen remains unchanged in an sp\(^3\) orbital. In an aromatic amine there is an interaction between the delocalized electrons in the benzene ring and the lone pair in the nitrogen atom. The lone electron pair changes its electronic configuration to sp2, loosing part of its s character and decreasing its availability for bonding[35]. The
share of the lone electron pair into the benzene ring increases the electron density around the ring making it more reactive.

2.4.1 Tetraethylenepentamine (TEPA)

Tetraethylenepentamine is a linear amine-hydrocarbon molecule that contains three secondary amines and two primary amines, one at each end. TEPA is used in the fabrication of oil additives, corrosion inhibitors, epoxy resins, pesticides, catalysts and solid sorbents. TEPA can be impregnated on silica supports because easily creates hydrogen bonding with the silanol groups of silica (SiO₂). TEPA is a medium strength base with pKₐ=4.29. The boiling point of pure TEPA is 288 °C, at this temperature TEPA starts experiencing thermal and oxidative degradation.

![Molecular structure of tetraethylenepentamine (TEPA).](image)

**Figure 2.2** Molecular structure of tetraethylenepentamine (TEPA).

**Table 2.2** Proposed band assignment for identification of TEPA by IR spectroscopy.

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Vibration</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H</td>
<td>Asymmetric stretch</td>
<td>3356 - 3338</td>
<td>[8, 26, 35]</td>
</tr>
<tr>
<td>N-H</td>
<td>Symmetric stretch</td>
<td>3300 - 3290</td>
<td>[8, 26, 35]</td>
</tr>
<tr>
<td>C-H</td>
<td>Asymmetric stretch</td>
<td>2910-2920</td>
<td>[9, 23]</td>
</tr>
<tr>
<td>C-H</td>
<td>Symmetric stretch</td>
<td>2860-2870</td>
<td>[3, 31]</td>
</tr>
<tr>
<td>H-N-H</td>
<td>Scissoring/wagging</td>
<td>797, 1509, 1606, 3208</td>
<td>[35, 36]</td>
</tr>
<tr>
<td>C-N</td>
<td>Stretching</td>
<td>1240-1255</td>
<td>[32]</td>
</tr>
<tr>
<td>H-C-H</td>
<td>Twisting</td>
<td>1348, 1459, 3200</td>
<td>[35, 36]</td>
</tr>
</tbody>
</table>
2.4.2 m-phenylenediamine (MPD)

m-phenylenediamine is an aromatic amine that consists of two primary amine functional groups attached to an aromatic benzene ring in meta-position. MPD is used in the fabrication of polymers, epoxy resins and dyes. Due to the aromatic ring MPD is a weak base with pKb=9.19.

![Molecular structure of m-phenylenediamine (MPD).](image)

Figure 2.3 Molecular structure of m-phenylenediamine (MPD).

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Vibrations</th>
<th>Wavenumbers (cm⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H</td>
<td>Asymmetric stretch</td>
<td>3356 - 3338</td>
<td>[8, 26, 35]</td>
</tr>
<tr>
<td>H-N-H</td>
<td>Scissoring/wagging</td>
<td>797, 1509, 1606, 3208</td>
<td>[35, 36]</td>
</tr>
<tr>
<td>-C=C- from aromatic ring</td>
<td>Stretching</td>
<td>1503, 1640, 1653</td>
<td>[26, 32]</td>
</tr>
<tr>
<td>C-N</td>
<td>Stretching</td>
<td>1240-1255</td>
<td>[32]</td>
</tr>
<tr>
<td>C-H</td>
<td>Asymmetric stretch</td>
<td>2910-2920</td>
<td>[9, 23]</td>
</tr>
<tr>
<td>C-H</td>
<td>Symmetric stretch</td>
<td>2860-2870</td>
<td>[3, 31]</td>
</tr>
<tr>
<td>C-H from aromatic ring</td>
<td>Stretching</td>
<td>3035-3050</td>
<td>[32]</td>
</tr>
</tbody>
</table>


27. Tanthana, J., Study of Amine Impregnated on Silica Support for CO2 Capture, in Department of Chemical and Biomolecular Engineering. 2008, The University of Akron: Akron, OH.


CHAPTER III

EXPERIMENTAL

3.1 Sorbent Preparation

Aromatic an aliphatic amine solid sorbents were prepared and used for CO₂/SO₂ capture studies. The solid sorbents were prepared by incipient impregnation of amine species on a solid support. Amorphous silica (SiO₂) was selected as a support because of its high surface area, low acidity, high thermal conductivity and low cost. High surface area yields to a large concentration of adsorption sites, SiO₂ large pores facilitate the diffusion and mass transport of CO₂ into and off the active sites. Low acidity is desired to prevent direct interaction of the basic amine group with the surface, avoiding blocking of CO₂ adsorption sites. High thermal conductivity is important for the solid sorbent technologies because it allows the rapid heating/cooling process, decreasing the energy requirements for regeneration. The two amines selected for this thesis are tetraethylenepentamine (TEPA) and m-phenylenediamine (MPD). TEPA is an aliphatic molecule with low toxicity, low cost and high availability in the market. The five amine functional groups of TEPA offer high concentration of adsorption sites for interacting with CO₂. MPD is an aromatic molecule with two amine functional groups. The lone electron pairs from the amine groups interact with the aromatic ring of MPD decreasing
the basic strength for adsorption of CO$_2$ and SO$_2$ [1]. SO$_2$ is expected to be desorbed more easily from MPD than from TEPA.

The stability of the sorbents is enhanced with the addition of (i) PEG, used as an amine dispersant [2], (ii) a polymeric linker, used for immobilization of amine molecules to silica, and (iii) an inorganic additive, used as an antioxidant. Figure 3.1 shows the procedure to impregnate TEPA and MPD on SiO$_2$. The amine species are mixed with PEG and the polymeric linker in one beaker at 60 °C. In a separate beaker, the inorganic additive is dissolved in water and ethanol obtaining a dilute solution. The content of the two beakers are combined and mixed until obtaining a homogeneous solution. Silica is added to the solution and stirred for 5 min resulting in white slurry. The slurry is spread on a tray and dried in oven at 100 °C until obtaining a white powder. The loading of amine, PEG, and other additives is shown in Table 3.1.

Figure 3.1 Procedure to impregnate TEPA and MPD on SiO$_2$ by incipient impregnation method.
Table 3.1 Loading of amine, PEG and other additives for preparation of sorbents. Amounts in grams, based on 10 g of SiO\textsubscript{2} as a support.

<table>
<thead>
<tr>
<th>Sorbent description</th>
<th>Name</th>
<th>SiO\textsubscript{2}</th>
<th>TEPA</th>
<th>MPD</th>
<th>PEG</th>
<th>Water</th>
<th>Ethanol</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEPA/additives/SiO\textsubscript{2}</td>
<td>TAS</td>
<td>10</td>
<td>5.62</td>
<td>-</td>
<td>3.75</td>
<td>20</td>
<td>20</td>
<td>1.3</td>
</tr>
<tr>
<td>TEPA/MPD/additives/SiO\textsubscript{2}</td>
<td>TMAS</td>
<td>10</td>
<td>5.62</td>
<td>0.1</td>
<td>3.75</td>
<td>20</td>
<td>100</td>
<td>1.3</td>
</tr>
<tr>
<td>MPD/PEG/SiO\textsubscript{2}</td>
<td>MPS</td>
<td>10</td>
<td>-</td>
<td>1</td>
<td>3</td>
<td>-</td>
<td>120</td>
<td>-</td>
</tr>
</tbody>
</table>

The three sorbents prepared were given a short name based on the type of amine used; (i) TAS stands for silica impregnated with TEPA and additives, (ii) MPS stands for silica impregnated with MPD and PEG and (iii) TMAS stands for silica impregnated with TEPA, MPD and additives.

3.2 Experimental Techniques

Different experimental techniques were applied to study the CO\textsubscript{2} adsorption on immobilized-amine solid sorbents and the effect of the flue gas components over the CO\textsubscript{2} capture capacity. In-situ infrared spectroscopy (IR) and mass spectrometry (MS) were the main techniques used for quantification of CO\textsubscript{2} and determination of adsorbed species. Coupling of IR and MS techniques permitted the real-time monitoring of the CO\textsubscript{2} capture process under practical operating conditions. Temperature controllers connected to in-situ thermocouples permitted the continuous control and monitoring of the sorbent bed temperature throughout the process. Psychrometer, CO\textsubscript{2} sensor and mass flow controllers (MFC) were used to monitor other variables such as humidity, concentration and flow rate. In-situ infrared study of the solid sorbents was performed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), which is a well-established technique in the analysis of solid surfaces. Residence time distribution, mass...
and heat transfer effects were studied in a tubular reactor in which the effluents in gas phase were analyzed by infrared and mass spectrometry.

In-situ studies were complemented with transient techniques during the study of CO₂ capture and for calibration purposes. Step switching and pulse input were performed to cause a perturbation in the composition of the inlet gases, creating transient responses. Temperature programmed desorption (TPD) was performed by increasing the sorbent temperature to cause CO₂ desorption.

3.2.1 Testing conditions

To emulate the low concentration of H₂O and SO₂ in the flue gas from a coal-fired power plant, precise control of gas flow and accurate measurement of gas-phase concentration are required. The flue gas was simulated by a stream consisting of 70-80 v% clean air (15-17 v% O₂ in the total flow), 10-15 v% CO₂, 0-10 v% H₂O and 0-0.3 v% (0-3000 ppm) SO₂. Argon (Ar) was used as a carrier gas for the DRIFTS reactor and air was the carrier gas in the tubular reactor. Due to its inertness and non-adsorbing nature, methane (10 v% CH₄) was used as a tracer to evaluate the flow patterns and residence time distribution of the tubular reactor. Prior to CO₂ adsorption the sorbent was heated to 100 °C and held for 5 min under the flow of the carrier gas to remove pre-adsorbed H₂O and CO₂. Adsorption was carried out at 55 °C by a step switch from carrier gas to the flue gas mixture. When adsorption reached a steady state condition, a step switch changed the flow back from the flue gas mixture to carrier gas. Temperature programmed desorption (TPD) was performed by heating the sorbent from 55 to 100 °C and (i) flowing argon (Ar) in the case of DRIFTS reactor or (ii) performing a steam pulse followed by flowing air in the case of tubular reactor.
3.2.2 Step switching and pulse input

Switching the reactor inlet flow from pure air to flue gas mixture may cause an instant pressure drop or concentration spike in the process lines. Pressure drop and concentration spikes affect the process, creating difficulties in data analysis or suppressing valuable information from the transient responses. To prevent such disturbances it is necessary to use a 4-port valve. A 4-port valve allows switching between two gas streams maintaining a constant flow rate and producing nearly-ideal step changes in concentration. Figure 3.2 shows the configuration of the 4-port valve which consists of two inlets and two outlets. In position A, the inlet stream connected to the carrier gas, is directed through the reactor while the flue gas mixture flows to a vent. In position B the outlets are switched redirecting the carrier gas to the vent and the flue gas mixture through the reactor. Step switching is used to determine the rate of adsorption and the residence time distribution as well as to perform concentration steps for calibration.

A pulse input is generated by injecting a known amount of CO$_2$ or any quantifiable gas into the process lines. The magnitude and shape of the pulse strongly depend on the volume and rate of injection. A 6-port valve is be used to inject a known volume of gas with accuracy and reproducibility. Figure 3.2 shows the configuration of a 6-port valve which consists of two inlets, two outlets and a volumetric loop. In position A (charge) the carrier gas is directed through the reactor while pure CO$_2$ fills the volumetric loop and flows to a vent. In position B (discharge), the carrier gas is redirected through the volumetric loop before entering the reactor carrying the CO$_2$. 

26
previously accumulated in the loop, while pure CO₂ is directly sent to the vent. Pulse input is used to quantify the amount of CO₂ (or SO₂).

A transient technique applied through the reactor will cause a transient response based on the reactor space-time velocity and on the interaction of the gases with the sorbent bed (i.e. adsorption or chemical reaction). A transient technique applied down-stream or by-passing the reactor will cause a response only based on space-time velocity of the process lines.

![Diagram of 4-port and 6-port valves](image)

Figure 3.2 Configuration of the 4-port and 6-port valves used for step switching and pulse input.

3.2.3 Temperature-Programmed Desorption (TPD)

The binding energy of adsorbed species on a solid surface can be determined by performing a TPD. At low temperature, a given amount of adsorbate reaches the state of adsorption equilibrium with the solid surface. As the sorbent temperature increases, part
of the energy is transferred to the adsorbate until the binding energy is overcome, causing desorption of adsorbed species. TPD is performed by heating up the sorbent at a controlled heating rate. At the highest temperature the sorbent is believed to be totally free of adsorbate or at a very low state of adsorption equilibrium. This technique requires an analytic device to measure the amount of desorbed species and a precise control of temperature.

3.2.4 Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Diffuse reflectance is a multi-modal technique that uses three types of reflections to create an infrared spectrum of a solid sample; (i) specular reflectance is the portion of the light that is reflected only by the surface, (ii) diffuse specular reflectance is the portion of the light that penetrates the solid crystals and (iii) ‘true’ diffuse reflectance is the portion of the light that penetrates into the crystals and the solid matrix structure. The solid sample is usually a powder diluted in non-observable IR species such as KBr. Dilution of the powder to a concentration between 5 and 10 w% augments the proportion of ‘true’ diffuse reflectance, offering higher spectrum definition but decreasing the total load capacity of the reactor [3]. Low sample loads result in weak responses to the transient methods. In a DRIFTS reactor the incident light beam is directed to the sample and the scattered beams are collected and refocused by ellipsoidal mirrors and directed to the IR detector.

Figure 3.3 shows the DRIFTS reactor which is a closed chamber placed in a casing collector and connected to a temperature control unit. DRIFTS reactor consists of a sample holder, heating element and inlet/outlet gas lines. The reactor closes using a gas-tight dome with two ZnSe windows that allow the transmission of the IR beam in the
mid-IR region. The casing collector contains the arrangement of optical instruments to
direct and collect the IR beams and a purge air inlet to reduce the CO₂ and H₂O
background. The temperature controller monitors the temperature of the sorbent and
regulated the output signal sent to the heating element.

3.2.5 FTIR Transmission cell

Transmission spectroscopy is a well known and widely applied infrared method.
In this technique the incident IR beam passes through a sample and is absorbed at
specific wavelengths before it reaches the detector. The sample can be present in solid,
liquid or gas phase and is usually placed in a closed transmission cell. Figure 3.4 shows
the gas phase transmission cell. The gas phase transmission cell consists of (i) a tubular
compartment closed in both ends by CaF₂ rods which allow the transmission of the IR beam in most part of the mid-IR region and (ii) a heating element connected to a Variac transformer to control the cell temperature. The transmission cell is located into the FTIR chamber with a purge air inlet to reduce CO₂ and H₂O background. The length of the tubular compartment and the separation of the CaF₂ rods determine the pathlength of the beam. The pathlength determines the grade of beam saturation and hence the strength of the signal at the detector. Due to the low density of gas samples, the pathlength for the gas transmission cell must be greater than those for solid and liquid samples.

3.2.6 Mass Spectrometry

Mass spectrometry provides information on the molecular weight and molecular
formula of a sample. This technique is commonly used to complement information
obtained from spectroscopic methods such IR and Raman, but is fundamentally different
from spectroscopy because does not involve light, absorption or emission. A mass
spectrometer ionizes the sample in a high vacuum and sorts the ions according to their masses by using electric and magnetic fields. The relative number of ions of each mass is measured from the ionized particles and the abundance of each mass-to-charge ratio is registered [4].

3.3 Experimental Apparatus

To test the sorbents, apply the transient techniques, simulate the flue gas and measure the response variables, the DRIFTS and tubular reactors were connected to process lines, utilities and analytic devices. This section shows the configuration of the DRIFTS and tubular reaction systems and details how they operate.

3.3.1 Milligram-Scale DRIFTS Reaction System

The experimental setup for the milligram-scale DRIFTS reaction system, shown in Figure 3.3, consists of (i) gas flow controller manifolds, four and six port valves, (ii) a Harrick Praying Mantis in-situ DRIFT cell reactor, with sorbent capacity of 50 mg, attached to a Thermo Nicolet 6700 FTIR (IR), and (iii) a Pfeiffer QMS 200 quadruple mass spectrometer (MS). Ar, CO$_2$, pure air and a mixture of 1 v% SO$_2$ in air 10000 ppm SO$_2$/air) and were connected to mass flow controllers (MFC) for precise control of the flow rate and composition. The four-port valve switched the gas inlet to the DRIFTS reactor between Ar and CO$_2$/SO$_2$/air. The six-port valve was used to inject a known volume of gases for calibration. Inside the DRIFTS reactor the gases were restricted to flow from top to bottom of the sorbent bed. The temperature of the sorbent bed was monitored and controlled by a K-type thermocouple, located in the center of the DRIFTS sample holder. A series of IR spectra of the sorbent was collected during the CO$_2$ capture
process. Every IR spectrum was formed by 32 co-added scans with resolution of 4 cm\(^{-1}\), which take 16 second to be recorded. The composition of the reactor effluent was monitored by MS for N\(_2\) (m/e=14 and 28), O\(_2\) (m/e=16 and 32), Ar (m/e= 40), CO\(_2\) (m/e=44) and SO\(_2\) (m/e=48 and 64).

Figure 3.3  Experimental setup for the milligram-scale DRIFTS reaction system.

3.3.2 Gram-Scale Tubular Reaction System

The experimental setup for the gram-scale tubular reaction system, shown in Figure 3.4, consists of (i) gas flow controller manifolds, four and six port valves, (ii) H\(_2\)O saturator, psychrometer and in-line air heater, (iii) a jacketed fluidized bed adsorber with load capacity of 10 g and utility services of steam and cooling water, (iv) a Pfeiffer QMS 200 quadruple mass spectrometer (MS) and (v) an in-house tailored Transmission cell placed in Thermo Nicolet 6700 FTIR (IR). Air, CO\(_2\) and CH\(_4\) lines were connected to
mass flow controllers (MFC) for precise control of the flow rate. The four-port valve switched the inlet gas to the reactor between purge air and a mixture of 10 v% CO$_2$, 10 v% CH$_4$ and 80 v% air. The stream containing CO$_2$, CH$_4$ and air can be selected to bypass or flow through a 500 ml H$_2$O saturator by using an arrangement of three-way valves. The sorbent bed was fluidized by flowing the inlet gas from bottom to top in the adsorber. The temperatures of the H$_2$O saturator and the sorbent bed were monitored and controlled by three K-type thermocouples located at (1) the liquid in the H$_2$O saturator, (2) the center of the sorbent bed, r=0 and (3) touching the inner wall in the reactor, r=R. The composition of the effluent gas was monitored by MS for N$_2$ (m/e=14 and 28), O$_2$ (m/e=16 and 32), CH$_4$ (m/e=15 and 16), H$_2$O (m/e=18) and CO$_2$ (m/e=44). IR was also used to analyze the effluent gas composition for CO$_2$ (2356 and 3727 cm$^{-1}$), CH$_4$ (1305 and 3014 cm$^{-1}$) and H$_2$O (1646 and 3401 cm$^{-1}$). Pure CO$_2$ pulses were injected using the six-port valve for calibration of the gases.

Figure 3.4 Experimental setup for the gram-scale tubular reaction system.
3.4 Calibration and CO₂ capture determination

To determine the CO₂ capture capacity of a sorbent using the experimental apparatus described in section 3.3, calibration of the analytical instruments response to CO₂, H₂O and SO₂ under continuous gas flow is required. The calibration of the instruments was performed by step-switching the concentration of CO₂ from 0 to 100 v%, H₂O from 0 to 10 v% and SO₂ from 0 to 1 v%. Pulse calibration was performed for CO₂ by pulsing 1, 3 and 5 cm³ of pure CO₂ in the DRIFTS reaction system and 30, 50 and 100 cm³ of pure CO₂ in the tubular reaction system. SO₂ was calibrated by pulsing 3, 5 and 10 cm³ of 1 v% SO₂ into the DRIFTS reaction system. Step calibration for H₂O was recorded simultaneously by psychrometer, MS and IR as shown in section 3.4.2.

The CO₂ capture capacity of the sorbents was determined by measuring the area under the CO₂ profile during the TPD and the amount of sorbent loaded into the reactor. The calculation for CO₂ capture capacity involves the equation of a straight line and the equation of the ideal gas:

\[
\text{Vol CO}_2 [\text{cm}^3] = \text{TPD area} \times \text{Cal. factor [cm}^3] + \text{intercept}
\]

\[
\mu \text{mol CO}_2 = \frac{PV}{RT} = \frac{1 \text{ atm} \times \text{Vol CO}_2 [\text{cm}^3] \times 1000}{0.0821 \text{ atm} \times \text{cm}^3 \times \text{mmol CO}_2 \times \text{K}} \times 298 \text{ K}
\]

\[
\text{CO}_2 \text{ capture capacity} \left[ \frac{\mu \text{mol CO}_2}{\text{g-sorbent}} \right] = \frac{\mu \text{mol CO}_2}{\text{mass of sorbent [g]}}
\]
3.4.1 Calibration of CO$_2$ and SO$_2$ in DRIFTS reaction system

Figure 3.5 (a) shows the MS profile for SO$_2$ and CO$_2$ during the pulse input calibration. Each pulse produced a peak response profile consistent of an instant increase in MS intensity following a trailing profile. Increments in the injected volume increased the height and area under the peaks. Each injection was repeated three times to confirm reproducibility and accuracy in the calibration process. The area of each peak was measured and correlated with the injected volume as shown in Figure 3.5 (b). The injected volume vs. peak area correlation follows a nearly linear trend in which the slope is the so-called calibration factor used for CO$_2$ capture determination.

![SO$_2$ and CO$_2$ MS profiles](image)

Figure 3.5 (a) MS profile for SO$_2$ and CO$_2$ during the pulse input calibration. (b) Correlation of the peak area with the injected volume.
The detection limit of the mass spectrometer with respect to \( \text{SO}_2 \), at the working conditions, was determined by a step calibration. Figure 3.6 (a) shows the MS profile for Ar and \( \text{SO}_2 \) as well as the corresponding concentration of \( \text{SO}_2 \) for each step. Switching the flow from Ar to \( \text{SO}_2/\text{air} \) caused an immediate increase in \( \text{SO}_2 \) MS intensity until steady state was reached. Switching the flow back from \( \text{SO}_2/\text{air} \) to Ar caused the intensity of \( \text{SO}_2 \) to decrease creating a nearly-rectangular profile response. The concentration of \( \text{SO}_2 \) was correlated with the height of each rectangular step, as shown in Figure 3.6 (b). The detection limit of the MS towards \( \text{SO}_2 \) was found to be 0.25 v%.

![Figure 3.6](image)

**Figure 3.6** (a) MS profile for Ar and \( \text{SO}_2 \) during step switch calibration. (b) Correlation of the MS intensity with the concentration of \( \text{SO}_2 \).

### 3.4.2 Calibration of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) in Tubular Reaction System

Figure 3.7 (a) shows the MS profile for \( \text{CO}_2 \) during the step switch and pulse input calibration. The height of each rectangular step is related with the concentration of \( \text{CO}_2 \) and the area of each pulse input is related with the injected volume as shown in Figure 3.7 (b). The calibration factor is the slope of the correlation for injected volume.
vs. peak area. The amount of water in the flue gas mixture was determined by a step switch calibration. The step switch calibration was performed by directing the dry air through the H₂O saturator for 5 min and switching back to by-pass position to cause a rectangular shape profile. The H₂O saturator was set at different temperatures to obtain different concentrations of H₂O in the stream. Figure 3.8 shows (i) the water temperature in the saturator, (ii) the wet bulb temperate and relative humidity (RH), (iii) the MS profile for H₂O (m/e=18) and (iv) the IR profile for H₂O (1646 and 3401 cm⁻¹) during the step switch calibration. The concentration of H₂O was calculated using a psychrometric chart and was correlated with the temperature of the H₂O saturator, as shown in Figure 3.8. Although a psychrometer is meant to be used with only air/H₂O mixtures, MS and IR profiles were correlated with the information from the psychrometer to proof the veracity of the quantification.
Figure 3.7 (a) MS profile for CO$_2$ during the step switch and pulse input calibration. (b) Correlation of the MS intensity with the concentration of CO$_2$. 

- **Graph (a)**: 
  - CO$_2$ concentration (v%) range from 10 to 100. 
  - CO$_2$ MS intensity levels are 1x10$^{-10}$, 2x10$^{-10}$, 3x10$^{-10}$, and 4x10$^{-10}$. 
  - Time (min) range from 0 to 40.

- **Graph (b)**: 
  - CO$_2$ concentration (v%) range from 0 to 100. 
  - CO$_2$ volume (cm$^3$) range from 0 to 100. 
  - Calibration factor: Slope = 2.925x10$^{11}$ ± 5.9x10$^9$, Intercept = 0.13 ± 1.19. 
  - Slope = 7.249x10$^{12}$ ± 2.2x10$^{11}$, Intercept = 0.23 ± 2.0.
Figure 3.8 Temperature, relative humidity, MS and IR intensities during the step switch calibration for H$_2$O.


CHAPTER IV

RESULTS AND DISCUSSION

4.1 Sorbents characterization

Figure 4.1 shows the IR single beam spectra of the three sorbents prepared for this thesis; TAS, TMAS and MPS. The labeled bands are contribution from the different functional groups in TEPA, MPD and SiO$_2$. The bands corresponding to SiO$_2$, show the unassociated silanol group (Si-OH) at 3779 cm$^{-1}$ and the chemical bonding Si-O-Si at 1256 and 884 cm$^{-1}$. The three sorbents show absorption at the band corresponding to N-H asymmetric stretching located at 3356 cm$^{-1}$, and TAS and TMAS show one more absorption band at 3297 cm$^{-1}$ which is due to the N-H symmetric stretching. MPS does not show absorption at 3297 cm$^{-1}$ because it has no secondary amines in its structure.

The band present at 2915 cm$^{-1}$ corresponds to C-H asymmetric stretching and that present at 2865 cm$^{-1}$ corresponds to C-H symmetric stretching. These C-H bands are broader for MPS because of the deformation caused by the NH$_2$ group on the aromatic ring. The absorption at 2530 cm$^{-1}$ is only shown by MPS. NH$_2$ scissoring and wagging is evidenced by those bands at 1606, 1509 and 797 cm$^{-1}$. These three bands are broader and slightly shifted to the sides for MPS sorbent because of the insaturations on the aromatic ring.

The C=C bonding presents absorption at 1640 cm$^{-1}$. The CH$_2$ twisting present in TEPA
molecules is characterized by the absorption at 1459 and 1348 cm$^{-1}$. The spectrum of MPS shows weaker absorption on a number of bands due to the low concentration of MPD impregnated and some other bands are occluded by the chemical bonding from PEG and H$_2$O. TAS and TMAS spectra present no evident differences because the characteristic bands from MPD in TMAS are very weak and overlapped with those from TEPA, which is in higher concentration.

Figure 4.1 IR single beam spectra of TAS, TMAS and MPS taken at 55 °C under 120 cm$^3$/min of flowing Ar. The labeled bands are contribution from the different functional groups in TEPA, MPD and SiO$_2$. 
4.2 Adsorption of SO₂ on aliphatic and aromatic amine sorbents

Two experiments were performed to evaluate the adsorption-desorption characteristics of SO₂ on solid amine sorbents. The first experiment consisted on studying the SO₂ capture on sorbents prepared with aliphatic amine (TEPA) and aromatic amine (MPD). Under similar conditions of adsorption and desorption, those sorbents prepared using MPD presented shorter adsorption times and weaker interaction between SO₂ and amine functional group than the sorbent prepared with only TEPA. The second experiment consisted on studying the effect of the SO₂ desorption temperature by temperature programmed desorption. MPS sorbent was subjected to three consecutive cycles of SO₂ capture with similar adsorption conditions and desorption temperature of 110 °C for the first cycle, 130 °C for the second cycle and 150 °C for the third cycle. The adsorption time decreased throughout the cycles and the SO₂ capture capacity increased with increments in the desorption temperature.

A number of SO₂ adsorbed species remain after the TPD, causing accumulation on the sorbent and potentially blocking the amine sites. To completely remove the SO₂ adsorbed species, higher desorption temperature is required.

4.2.1 SO₂ capture for sorbents with different load of MPD and TEPA

Figure 4.2 shows the normalized MS profiles for Ar, N₂ and SO₂ during one cycle of SO₂ capture on three sorbents with different load of MPD and TEPA; (a) MPS, (b) TAMS and (c) TAS. Each sorbent was placed on DRIFTS reactor and Ar was flown during pretreatment until steady state was reached. Switching the flow from Ar to SO₂/air caused the immediate increase in N₂ intensity and the decrease in Ar intensity.
The steady state for N₂ and Ar was achieved about 1 min after the switching, following a nearly perfect step change and indicating no significant adsorption of N₂ and Ar on the sorbent. The SO₂ intensity started increasing after a breakthrough time (τ₀) of 2.19 min for MPS and 4.83 min for TMAS. Although longer adsorption time was allowed for TAS, no increment in SO₂ intensity was observed, suggesting that τ₀>15min for this sorbent. During the breakthrough time the sorbents were able to effectively capture all the SO₂ flown through the reactor. The higher load of amine caused longer breakthrough times for TMAS and TAS. The SO₂ intensity did not reach steady state, indicating that the sorbent did not get completely saturated by SO₂ during the adsorption stage.

After adsorption the flow was switched back to Ar, causing immediate drop in N₂ intensity and increase in Ar intensity. The SO₂ intensity for MPS and TMAS slowly decreased, reaching the baseline intensity about 5 min after the switching. The slower reduction in SO₂ intensity points the removal of physisorbed SO₂ and slow diffusion of gas phase SO₂ through the sorbent bed. SO₂ can physically adsorb on weak amine sites and via hydrogen bonding; N-H—O (1.9 kcal/mol) or OH—O (5 kcal/mol).

Desorption stage was performed by a TPD with maximum temperature of 130 ℃. A small, broad peak was observed for SO₂ intensity during the desorption, representing a small amount of SO₂ released by the sorbents due to the increase in temperature. The SO₂ capture capacity of the sorbents increased with the load on MPD and decreased with the load of TEPA as MPS>TMAS>TAS. This result shows that a small concentration of aromatic amine is able to reduce the bonding energy of SO₂ on the sorbent facilitating the desorption.
Figure 4.2 Normalized Ar (m/e=40), N\textsubscript{2} (m/e=28), and SO\textsubscript{2} (m/e=64) MS profiles during one cycle of SO\textsubscript{2} capture on (a) MPS, (b) TMAS, and (c) TAS. Adsorption at 55 °C under 120 cm\textsuperscript{3}/min of 0.25 v\% SO\textsubscript{2} in air. Desorption by TPD at 130 °C.

Figure 4.3 shows the IR single beam and absorbance spectra (a) prior to SO\textsubscript{2} adsorption, (b) during the SO\textsubscript{2} adsorption, (c) prior to TPD and (d) after TPD for the SO\textsubscript{2} cycle over MPS. The absorbance spectra was obtained by Abs=-\log(I/I\textsubscript{0}) where I is the single beam taken at any time of the cycle and I\textsubscript{0} is the single beam taken prior to SO\textsubscript{2} adsorption. In the absorbance spectra changes between two single beams become more evident; the bands pointing up represent the formation or accumulation of species (stronger absorption) and the bands pointing down represent the consumption or depletion of species (weaker absorption).
Figure 4.3 IR single beam and absorbance spectra of MPS during an SO$_2$ capture cycle. Absorbance is obtained by Abs=$-\log(I/I_o)$ where I is the single beam taken at any time of the cycle and $I_o$ is the single beam taken prior to SO$_2$ adsorption.

The single beam spectra show the characteristic bands discussed in section 4.1 but the difference between (a), (b), (c) and (d) is difficult to tell by simple inspection. The absorbance spectra show a nearly flat spectrum for (b) and (c) and pronounced changes in (d). The broad band between 2950 and 3600 cm$^{-1}$ represents the physisorption of SO$_2$ by hydrogen bonding on the OH groups of PEG and on the NH$_2$ groups of MPD. The band at 3713 cm$^{-1}$ shows that physisorption also takes place on silanol groups from SiO$_2$. The increase of 1551 cm$^{-1}$ on (d) can be attributed to a N-O stretching of the remaining
adsorbed SO$_2$ on NH$_2$. The spectrum (d) shows the depletion of 3042, 1638, and 1494 cm$^{-1}$, which are characteristic bands for MPD, and the augment of unassociated silanol groups at 3713 cm$^{-1}$. These two facts are an indicative of potential degradation of the sorbent due to decrease of MPD concentration.

Figure 4.4 shows the single beam and absorbance spectra during the SO$_2$ cycle over TMAS. The single beam spectra shows the presence of functional groups of TEPA, MPD and SiO$_2$ and the absorbance spectra shows the differences among the stages of the cycle. Spectra (b) and (c) show pronounced variations with respect of the fresh sorbent and (d) shows that some species remain adsorbed on the sorbent even after TPD. The bands at 3369 and 3312 cm$^{-1}$ show a significant drop in (b) and (c) due to the adsorption of SO$_2$ on amine sites, the stronger absorption at 3369 cm$^{-1}$ suggests that SO$_2$ is more likely to interact with primary amines. The band at 1531 cm$^{-1}$ confirms the adsorption of SO$_2$ on amine by the increment of N-O stretching and those at 1005, 955 and 893 cm$^{-1}$ confirm the adsorption of SO$_2$ via formation of C=O bonding present in bisulfate, sulfite and sulfate species. All the described bands tend to return to its original state, showing smaller peaks in (d). The peaks remaining in (d) are caused by the accumulation of adsorbed species that could not been removed by TPD.

Adsorption of SO$_2$ on TAS shows a very similar character as that on TMAS. The difference in adsorbed species on TAS compared with TMAS are (i) a less pronounced peak at 3312 cm$^{-1}$ due to the lesser concentration of secondary amine groups, (ii) broader bands at the 900-1000 cm$^{-1}$ region indicating the higher concentration of sulfite and sulfate adsorbed species and (iii) the less efficient removal of SO$_2$ adsorbed species evidenced by remaining bands at 1531 and 975 cm$^{-1}$ after TPD, as shown in Figure 4.5.
TMAS and TAS show the broad band around 3005 cm\(^{-1}\) in which the formation of ammonia ion (NH\(_3^+\)) and the hydrogen bond interactions overlap. The remaining ammonia ion confirms the inefficient removal of sulfates and sulfites.

Figure 4.4 IR single beam and absorbance spectra of TMAS during an SO\(_2\) capture cycle. Absorbance is obtained by Abs = -log(I/I\(_o\)) where I is the single beam taken at any time of the cycle and I\(_o\) is the single beam taken prior to SO\(_2\) adsorption.
Figure 4.5 IR single beam and absorbance spectra of TAS during an SO$_2$ capture cycle. Absorbance is obtained by Abs=$-\log(I/I_o)$ where $I$ is the single beam taken at any time of the cycle and $I_o$ is the single beam taken prior to SO$_2$ adsorption.

4.2.2 The effect of temperature on the desorption of SO$_2$

Figure 4.6 shows the MS profiles for Ar, N$_2$ and SO$_2$ for three consecutive cycles of SO$_2$ capture on MPS. Desorption temperature for the first cycle (a) was 110 °C, for the second cycle (b) was 130 °C and for the third cycle (c) was 150 °C. The breakthrough time in (a) was 4.02 min, which is significantly larger than that for (b) $\tau_o=2.19$ min and (c) $\tau_o=2.40$. In none of the cycles saturation of SO$_2$ on the sorbent was reached but the adsorption curve became more convex throughout the cycles, indicating faster adsorption.
The decrease in SO$_2$ intensity after adsorption was similar for the three cycles and reached the initial baseline in about 5 min. For (a) there was no evidence of desorbed SO$_2$, which means that the energy provided by the TPD at 110 °C was not enough to overcome the bonding energy of SO$_2$ adsorbed species on the sorbent. Raising the desorption temperature to 130 °C in (b) produced an observable peak for TPD in SO$_2$ intensity that represents the amount of SO$_2$ desorbed. Further increment in desorption temperature to 150 °C in (c) produced a more evident desorption peak than that in (b).

Figure 4.6  Normalized Ar (m/e=40), N$_2$ (m/e=28), and SO$_2$ (m/e=64) MS profiles during three consecutive cycles of SO$_2$ capture on MPS. Adsorption at 55 °C under 120 cm$^3$/min of 0.25 v% SO$_2$ in air. Desorption by TPD at (a) 110 °C, (b) 130 °C and (c) 150 °C.
The reduction of \( \tau_0 \) from (a) to (b) can be attributed to the reduction of available sites for \( \text{SO}_2 \) adsorption after the first cycle. This reduction was significant because all the strongly adsorbed \( \text{SO}_2 \) species remained on the sorbent after the TPD at 110 °C. A slight increase in \( \tau_0 \) from (b) to (c) demonstrates that the TPD at 130 °C partially removed the strongly adsorbed species from the sorbent, creating more amine available sites for \( \text{SO}_2 \) adsorption in (c). The increase in amount of \( \text{SO}_2 \) desorbed throughout the cycles evidences that higher desorption temperature yields to a more efficient removal of adsorbed \( \text{SO}_2 \). Although a higher desorption temperature is needed to completely desorb the \( \text{SO}_2 \) from the sorbent, it is not feasible to carry out the desorption at very high temperature due to the thermal degradation of the sorbent. Figure 4.6 also shows a comparison of (i) the total amount of \( \text{SO}_2 \) adsorbed, represented by the area between \( \text{SO}_2 \) intensity and \( \text{N}_2 \) intensity during adsorption, (ii) the weakly adsorbed \( \text{SO}_2 \) removed during the purge, represented by the area between \( \text{N}_2 \) intensity and \( \text{SO}_2 \) intensity and (iii) the strongly adsorbed \( \text{SO}_2 \) removed during desorption, represented by the area under TPD curve. The total \( \text{SO}_2 \) adsorbed is larger than the sum of the weakly and strongly adsorbed \( \text{SO}_2 \) removed from the sorbent. For the three cycles (i) was greater than (ii)+(iii), however this difference became lower with the increments in desorption temperature. The diminution in the difference between (i) and (ii)+(iii) is due to the lesser total adsorption capacity caused by the accumulation of species and the more effective removal of adsorbed species caused by the increments in desorption temperature.

The IR analysis of the effect of desorption temperature is illustrated in Figure 4.7. The single beam spectra and absorption spectra for the fresh sorbent and after the three cycles with desorption temperature of (a) 110 °C, (b) 130 °C and (c) 150 °C show the
difference on the sorbent due to degradation and accumulation of SO₂ adsorbed species.

The single beam spectra show the characteristic bands for MPD

Figure 4.7 IR single beam and absorbance spectra of fresh MPS sorbent and after three consecutive cycles of SO₂ capture with desorption temperature of (a) 110 °C, (b) 130 °C and (c) 150 °C. Absorbance is obtained by Abs=−log(I/I₀) where I is the single beam of the fresh sorbent and I₀ is the single beam of the sorbent after TPD for each cycle.

The absorbance spectra show the increment of SO₂ adsorbed species throughout the cycles via S=O vibration from bisulfate at 1005 cm⁻¹, and sulfate 1419 cm⁻¹. The accumulation of SO₂ is also evidenced by the N-O stretching at 1551 cm⁻¹ from SO₂-N interaction. The migration of MPD from the sorbent surface is evidenced by the
depletion in the characteristic bands such as 2530 cm\(^{-1}\), C-H stretching at 3042 cm\(^{-1}\), C=C stretching at 1638 cm\(^{-1}\), NH\(_2\) stretching at 1591 cm\(^{-1}\) and C-N stretching at 1237 cm\(^{-1}\).

The excessive heating of the sorbent may have caused the removal of MPD (boiling point 283 °C) from the sorbent. The increase in absorption band at 3713 cm\(^{-1}\) is sign of the increment of unassociated silanol groups of SiO\(_2\), further confirming the removal of MPD from SiO\(_2\) support. The bands labeled in Figure 4.7 became stronger throughout the cycles, suggesting that higher temperature is needed to remove the SO\(_2\) adsorbed species from the sorbent. However higher temperature also causes degradation of the sorbent by removal of MPD species. A possible approach to solve this issue is the immobilization of MPD by using a linker. Section 4.3 shows the performance of the sorbents with content of aromatic amine for CO\(_2\) capture in presence of SO\(_2\).

4.3 Effect of SO\(_2\) on the CO\(_2\) capture capacity

Five consecutive CO\(_2\) capture cycles on MPS and TMAS were performed to evaluate the effect of SO\(_2\) on CO\(_2\) adsorption and desorption process. Each sorbent was subjected to (i) an initial CO\(_2\) capture cycle in absence of SO\(_2\), (ii) three consecutive CO\(_2\) capture cycles under the presence of 0.25 v% SO\(_2\) and (iii) a last CO\(_2\) capture cycle in absence of SO\(_2\). The study on MPS shows a low CO\(_2\) capture capacity compared with that of TMAS and no desorption of SO\(_2\) was observed during the TPD. The capture capacity of the two sorbents rapidly decreased throughout the cycles for a total degradation of 64 % for MPS and 31 % for TMAS. Table 4.1 shows the CO\(_2\) capture capacity and degradation percentage for the CO\(_2\) capture cycles for the study of the effect of SO\(_2\) during the CO\(_2\) capture.
Table 4.1 CO₂ capture capacity and degradation percentage for the CO₂ capture cycles for the study of the effect of SO₂ during the CO₂ capture.

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<th>Sorbent</th>
<th>Cycle</th>
<th>Adsorption</th>
<th>CO₂ capture (µmol CO₂/g-sorb)</th>
<th>Loss in CO₂ capture (µmol CO₂/g-sorb)</th>
<th>% Degradation</th>
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<td>-</td>
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<td>321</td>
<td>31.10%</td>
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</tbody>
</table>

4.3.1 MPS sorbent

Figure 4.8 shows the normalized MS profiles for Ar, N₂, SO₂ and CO₂ for the first and fourth cycles of CO₂ capture on MPS during the study of the effect of SO₂ on CO₂ capture. Part (a) illustrates the first cycle in which Ar was flown during pretreatment until reached steady state. The switching from Ar to CO₂/air caused the immediate increase in CO₂ and N₂ intensities and the decrease in Ar intensity. After the switching, N₂ and Ar reached the steady state in about 1 min and CO₂ in 2.5 min indicating the selective adsorption of CO₂ on the sorbent. After adsorption the flow was switched back to Ar, causing the immediate drop in N₂ intensitiy and the increase in Ar intensity. The CO₂ intensity decreased slightly slower due to the removal of weakly adsorbed CO₂. As temperature increased to perform desorption, the intensity of CO₂ increased until showing a maximum at 69 °C, 1.4 min after the TPD started. Although the temperature further increased, the intensity of CO₂ started decreasing until reaching the original baseline. The intensity for Ar, and N₂ remained steady during the desorption stage. The area under
the peak formed by CO$_2$ during desorption is proportional to the CO$_2$ capture capacity, which was calculated as 222 µmolCO$_2$/g-sorb. The SO$_2$ intensity did not show any changes because this gas was not present during the first cycle.

Figure 4.8 Normalized Ar (m/e=40), N$_2$ (m/e=28), SO$_2$ (m/e=64) and CO$_2$ (m/e=44) MS profiles for two selected cycles of CO$_2$/SO$_2$ capture on MPS. Adsorption at 55 °C and desorption by TPD at 110 °C. (a) Cycle 1 adsorption in presence of 10 v% CO$_2$ in air. (b) Cycle 4, adsorption in presence of 10 v% CO$_2$ and 0.25 v% SO$_2$ in air. CO$_2$ intensity during TPD magnified x100.

Part (b) illustrates the fourth cycle, in which 0.25 v% SO$_2$ was present during adsorption. The intensities for Ar and N$_2$ show the same behavior as in the first cycle. The intensity for CO$_2$ in (b) shows small differences with respect to that in (a), such as (i) reduction in time reaching the steady state after the switching from Ar to CO$_2$/SO$_2$/air to
about 1 min and (ii) the smaller area under the TPD curve, with the maximum at 63 °C, 0.8 min after the TPD started. These differences in the CO₂ profile demonstrate the reduction of the CO₂ capture capacity of the sorbent. The maximum of CO₂ profile during the TPD curve represents the minimum temperature required to desorb the CO₂ species from the sorbent. The low temperature observed for sorbent MPS confirms the weaker bonding between CO₂ and aromatic amine. The SO₂ intensity started increasing 1 min after the switching (τ₀=1 min) and did not saturate the sorbent during the 5 min given for adsorption. SO₂ intensity showed τ₀=1.8 min for the second cycle and τ₀=1.2 min for the third cycle, indicating the accumulation of adsorbed species on the sorbent.

Figure 4.9 shows the IR absorbance for cycle 1 and 4 during the different stages of the cycles. Similarly to the results shown in section 4.2, spectrum (b) for cycle 1 is almost flat for the fingerprint region, indicating that CO₂ was mostly physisorbed on the sorbent. The spectrum (d) for cycle 1 shows the migration of MPD by the reduction of intensity in 3042, 2522, 1638, 1594 and 1494 cm⁻¹. The increment of unassociated silanol groups further confirms the removal of MPD from the sorbent. The spectra (b) and (c) for cycle 4 only show the broad band in the hydrogen bonding region, confirming that the CO₂ capture of the sorbent is due to physically adsorbed CO₂. The bonding of physically adsorbed CO₂ is strong enough to remain after the purge with Ar, but weak enough to get desorbed at very low temperature. Spectrum (d) shows a nearly flat profile, indicating that the sorbent did not degrade further after cycle 4. A comparison of the spectrum after TPD throughout the cycles is illustrated in Figure 4.12. The only significant change of the sorbent is the further removal of MPD, evidenced by the reduction of the bands at 1638 and 1594 cm⁻¹.
4.3.2 TMAS sorbent

Figure 4.10 shows the normalized MS profiles for Ar, N$_2$, SO$_2$ and CO$_2$ for the first and fourth cycles of CO$_2$ capture on TMAS. For the first cycle, part (a), the CO$_2$ intensity slowly increased after the switching from Ar to CO$_2$/air indicating a large amount of total CO$_2$ adsorbed. The larger adsorption of CO$_2$ on TMAS is due to the higher concentration of amine sites in this sorbent compared with MPS. The CO$_2$ intensity did not reach the steady state during the five minutes of adsorption, suggesting
that the sorbent did not get completely saturated. Switching the flow back to Ar caused a
slower decrease in the CO$_2$ intensity than that of N$_2$ intensity, as an indicative of the
removal of weakly adsorbed CO$_2$. As temperature increased during the TPD, the
intensity of CO$_2$ increased until showing a maximum at 88 °C, 3.3 min after TPD started
and then decreased to the baseline. The fourth cycle is illustrated in part (b), the
significant differences in CO$_2$ profile indicate (i) a lower amount of total adsorbed CO$_2$,
(ii) the lower release of weakly adsorbed CO$_2$ and (iii) The smaller desorption peak,
showing the maximum at 64 °C, 0.9 min after the TPD started. The shifting of the
desorption peak to the left indicates that the strong basic amine sites from the sorbent
have disappeared and only weak adsorption is happening on the sorbent. The IR analysis
for this section further tells the reason for the desorption peak shifting. The SO$_2$ profile
in (b) shows a similar trend as that in Figure 4.8 (b). The breakthrough time for SO$_2$ was
4.2 min for the second cycle, 2.3 min for the third cycle and 1.6 min for the fourth cycle.

Figure 4.11 shows the IR absorbance for cycles 1 and 4 during the different stages
of the cycles. For the first cycle the spectra shows the characteristic bands for CO$_2$
adsorbed species, which are almost totally removed after the TPD. Those adsorbed
species correspond to (i) carboxamid (C-N) that absorbs at 1626 and 1531 cm$^{-1}$, (ii)
carbonate (CO$_3^{2-}$) that absorbs at 1626 and 1332 cm$^{-1}$, (ii) bicarbonate (HCO$_3^-$) that
absorbs at 1626, 1475 and 1432 cm$^{-1}$ and (iv) ammonia ion (NH$_3^+$) that is a co-product of
the formation of (i), (ii) and (iii) and absorbs at 3005 cm$^{-1}$.
Figure 4.10 Normalized Ar (m/e=40), N\textsubscript{2} (m/e=28), SO\textsubscript{2} (m/e=64) and CO\textsubscript{2} (m/e=44) MS profiles for two selected cycles of CO\textsubscript{2}/SO\textsubscript{2} capture on TMA\textsubscript{S}. Adsorption at 55\textdegree C and desorption by TPD at 110\textdegree C. (a) Cycle 1, adsorption in presence of 10 v\% CO\textsubscript{2} in air. (b) Cycle 4, adsorption in presence of 10 v\% CO\textsubscript{2} and 0.25 v\% SO\textsubscript{2} in air. CO\textsubscript{2} intensity during TPD magnified x10.

For the cycle 4, Figure 4.11 shows the same bands as for cycle 1 in the region between 1650 and 1330 cm\textsuperscript{-1}. In addition the adsorbed species for SO\textsubscript{2} are present in the region of lower wavenumbers as (i) sulfate (SO\textsubscript{4}\textsuperscript{2-}) that absorbs at 1011 cm\textsuperscript{-1}, (ii) bisulfate (HSO\textsubscript{4}\textsuperscript{-}) that absorbs at 1011, 897 and 816 cm\textsuperscript{-1} and (iii) metabisulfate (S\textsubscript{2}O\textsubscript{5}\textsuperscript{-}) that absorbs at 980 cm\textsuperscript{-1}. Some SO\textsubscript{2} adsorbed species also absorb in the CO\textsubscript{2} adsorbed species region, resulting in overlapping of the bands. Ammonia ion is also present for cycle 4, with stronger absorption, indicating that it is also a co-product for SO\textsubscript{2} adsorbed species.
Figure 4.11 IR absorbance spectra of TMAS during the first and fourth cycles of CO\textsubscript{2} capture in presence of SO. Absorbance is obtained by \( \text{Abs} = -\log(I/I_o) \) where \( I \) is the single beam taken at any time of the cycle and \( I_o \) is the single beam taken prior to CO\textsubscript{2}/SO\textsubscript{2} adsorption.

Figure 4.12 shows the comparison of the spectrum after TPD throughout the cycles for MPS and TMAS. The spectra for MPS does not have significant changes, except for the reduction in absorption at 1638 and 1595 cm\textsuperscript{-1} as discussed in section 4.3.1. The spectra for TMAS show small peaks for cycles 1 and 2 and pronounced peaks for cycles 3, 4 and 5 in the region from 1650 to 750 cm\textsuperscript{-1}. Those peaks are product of the remaining SO\textsubscript{2} species on the sorbent. The band at 1628 cm\textsuperscript{-1} is overlapped with 1604 cm\textsuperscript{-1}, the small band shifted to the right in cycle 1, which corresponds to CO\textsubscript{2} adsorbed.
species only. Some other bands overlapped make visible throughout the cycles such as 1502, and 1278 cm\(^{-1}\), that correspond to sulfates and sulfites adsorbed on the sorbent.

The appearance of these bands demonstrates that the accumulation of adsorbed SO\(_2\) is more significant than the accumulation of adsorbed CO\(_2\). The depletion in 3369 and 3312 cm\(^{-1}\) is evidence of the loss of amine groups.

Figure 4.12 IR absorbance spectra of MPS and TMAS after the five cycles of CO\(_2\) capture in presence of SO\(_2\). Absorbance is obtained by Abs=-log(I/I\(_0\)) where I is the single beam taken after the TPD of each cycle and I\(_0\) is the single beam of the fresh sorbent.
4.4 CO₂ capture in presence of H₂O simulating practical operation conditions.

The presence of H₂O during adsorption in a CO₂ capture process is believed to enhance the CO₂ capture capacity of the sorbent due to the further reaction of adsorbed species with CO₂ and H₂O from carbamate to carbonate, shown in section 2.3. The amount of H₂O entering the reactor is proportional to the temperature of H₂O in the saturator and the flow rate of the flue gas. The tubular reaction system was used to evaluate the effect of water on the CO₂ capture capacity of TAS. Three CO₂ capture cycles were run using different degrees of H₂O saturation in the flue gas stream; (i) dry flue gas, (ii) flue gas saturated by H₂O at 30 °C and (iii) flue gas saturated by H₂O at 55 °C. The effluent gas from the reactor was analyzed by MS and IR and the gradient of temperature inside the reactor was measured throughout the process. The results show that the CO₂ capture capacity of TAS is enhanced by 21% when using 4.5 v% of H₂O and 65% when using 10.9 v% of H₂O.

Figure 4.13 shows the normalized CO₂ and H₂O MS profiles and the sorbent temperature profile during the three cycles of CO₂ capture. Part (a) shows that switching the inlet gas from air to CO₂/CH₄/air caused an immediate increase in CO₂ intensity, followed by a short concentration spike and rapidly reaching the steady state. The concentration spike is caused by the remaining CO₂ in the lines from earlier calibration. The H₂O MS profile remained unchanged indicating that the flue gas was dry. A temperature rise of 23 °C was observed at the center of the adsorber during the adsorption stage due to the exothermic nature of the adsorption process. A lower temperature rise of 9 °C was observed at the adsorber wall, evidencing that the heat was released by the sorbent and partially removed through the wall.
Figure 4.13 Three cycles of CO₂ capture on TAS. Up: normalized CO₂ (m/e=44) and H₂O (m/e=18) MS profiles. Down: temperature profiles at the center and at the wall of the reactor. Adsorption in presence of 10 v% CO₂ under (a) dry conditions, (b) 4.5 v% H₂O and (c) 10.9 v% H₂O. Desorption by temperature swing and steam pulse.
Switching the flow back to air caused the CO₂ and temperature profile to decrease and reach the baseline after 3 min, due to the removal of weakly adsorbed CO₂.

Desorption of strongly adsorbed CO₂ was performed by heating the adsorber to 100 °C using the heating jacket. The heating stage caused a rapid increment in temperature at the adsorber wall and a slower increment at the center. This gradient in temperature happened because the reactor is closed at this time and the heat transfer from the wall to the sorbent is only by conduction and natural convection. After the heating, steam was pulsed through the adsorber producing a very sharp peak in the CO₂ profile, the high and narrow CO₂ peak indicates that all the desorbed CO₂ was rapidly concentrated and removed from the reactor. The steam used during desorption caused the H₂O intensity to show a high, broad peak. The broadness of the H₂O peak is due to the adhesive and cohesive properties of H₂O which caused the slow diffusion of H₂O out of the reactor, through the process lines and into the MS chamber. After desorption, the reactor was cooled down using the jacket, gradually reducing the temperature to 55 °C.

Figure 4.13 (b) shows MS and temperature profiles for cycle 2, using the H₂O saturator at 30 °C. The CO₂ intensity shows a similar behavior to that for the dry cycle. The H₂O intensity shows a step increase during adsorption, indicating that 4.5 v% H₂O was present in the flue gas. The H₂O intensity decreased during the purge and reached the baseline. The temperature rise during CO₂ adsorption in cycle 2 was 40 °C, indicating that more heat was released. The higher temperature spike suggests that more CO₂ was adsorbed in cycle 2 than in cycle 1. Due to the exothermic nature of the adsorption, it is desirable to remove the heat released, to avoid self-desorption of CO₂. Adsorption at high temperature decreases the adsorption equilibrium of CO₂ on the
sorbent. The high and narrow peak for CO₂ was observed during desorption stage, similar to that in cycle 1. An even broader H₂O peak was observed for desorption in cycle 2 compared to that in cycle 1.

Figure 4.13 (c) shows the CO₂ capture cycle when the H₂O saturator was used at 55 °C. The higher step for H₂O intensity during adsorption stage represents the 10.9 v% H₂O in the flue gas. The temperature spike for this cycle was 40 °C, the same as in cycle 2, however the CO₂ capture capacity for cycle 3 was higher than that for cycle 2. The CO₂ capture capacity increased from 1560 µmol CO₂/g-sorb in the dry condition to 1890 µmol CO₂/g-sorb using 4.5 v% of H₂O and to 2.58 µmol CO₂/g-sorb using 10.9 v% of H₂O.

Table 4.2 Summary of the results for CO₂ capture in presence of H₂O simulating practical operation conditions.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Cycle</th>
<th>H₂O saturator temperature. (°C)</th>
<th>H₂O content (v%)</th>
<th>Temperature spike (°C)</th>
<th>CO₂ capture capacity (µmol CO₂/g-sorb)</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>By-passed</td>
<td>0</td>
<td>23</td>
<td>1560</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>4.5</td>
<td>40</td>
<td>1890</td>
<td>21%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>10.9</td>
<td>40</td>
<td>2580</td>
<td>65%</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER V

CONCLUSIONS

The background of this thesis shows a current problematic of global warming and pollution due to CO₂ and SO₂ emissions and the lack of an efficient process to remove both gases from the flue gas released by coal-fired power plants. The hypothesis included (i) the use of IR and MS techniques to study the capture of CO₂ and SO₂ on balanced-basicity sorbents prepared by a combination of aromatic amine (MPD) and aliphatic amine (TEPA), and (ii) the use of a reactor with simulated practical operation conditions to study the influence of the presence of H₂O in the flue gas over the CO₂ capture capacity of the sorbent. The successful impregnation of MPD and TEPA on a silica support was verified by FT-IR characterization. The spectra of the prepared sorbents showed the characteristic bands for primary and secondary amines and those characteristic bands for hydrocarbon stretching produced by the aliphatic chains of TEPA and the aromatic ring of MPD.

In-situ SO₂ capture study on the prepared sorbents was studied by using the actual concentration of SO₂ on flue gas. The MS profiles for SO₂, Ar and N₂ during the SO₂ capture cycle showed particular differences between the aromatic and aliphatic amine sorbents. The sorbent prepared with TEPA adsorbed a larger amount of SO₂ than that
prepared with MPD, however desorption of SO$_2$ was more efficient for MPD sorbent than for TEPA sorbent. The inclusion of a small concentration of MPD in TEPA sorbent decreased the strength of SO$_2$ adsorbed species, providing the sorbent the ability to desorb SO$_2$ for regeneration of the amine sites. The SO$_2$ capture capacity for TEPA sorbent was 300 µmol SO$_2$/g-sorb and was improved to 550 sorbent µmol SO$_2$/g-sorb by the addition of 5mg of MPD by gram of sorbent. The SO$_2$ capture capacity for MPS was 870 µmol SO$_2$/g-sorb when the desorption temperature was 150 °C and 590 µmol SO$_2$/g-sorb when the desorption temperature was 130 °C. No desorption was observed by using desorption temperature of 110 °C. The SO$_2$ adsorbed species were observed by IR spectroscopy and matched according to a literature review as sulfates, sulfites, bisulfates and bisulfites. For weak adsorption of SO$_2$ the IR bands corresponding to hydrogen bonding were observed.

The study of CO$_2$ capture in presence of SO$_2$ showed that the MPD sorbent is not suitable for CO$_2$ because of its low CO$_2$ capture capacity of 222 µmol SO$_2$/g-sorb and fast degradation of 64.3 %. Different from MPD sorbent, TEPA sorbent with addition of MPD has a high capture capacity of 1152 µmol SO$_2$/g-sorb and lower degradation of 31.1 % throughout the CO$_2$/SO$_2$ capture cycles. The adsorbed species observed by IR, indicate the progressive accumulation of sulfates, bisulfates, sulfites and bisulfites on TEPA/MPD sorbent while carbonates, bicarbonates and carbamate do not significantly accumulate. MPS sorbent adsorbs the CO$_2$ via hydrogen bonding, but progressively degrades throughout the cycles due to the insufficient immobilization of MPS on silica support.
Actual operational process conditions where simulated on a gram-scale tubular reactor. The study of the influence of H$_2$O on the flue gas showed that the CO$_2$ capture capacity increased from 1560 µmol CO$_2$/g-sorb in the dry condition to 1890 µmol CO$_2$/g-sorb using 4.5 v% of H$_2$O and to 2.58 µmol CO$_2$/g-sorb using 10.9 v% of H$_2$O. The greater improvement represents 65% more capture capacity for the sorbent when the flue gas is saturated with H$_2$O.

Further studies of the influence of SO$_2$ and H$_2$O on the CO$_2$ capture process are expected to focus on the fine-tuning of the sorbent composition, the mechanistic study of CO$_2$/H$_2$O adsorption and the inclusion of H$_2$O in the SO$_2$-containing flue gas. The fine-tuning of the sorbent requires the optimization of the concentration and the proper immobilization of aromatic amine species. The preparation method of the sorbents may be modified to increase the exposure of aromatic amine sites, preventing the poisoning of SO$_2$ on aliphatic amine sites.
APPENDIX A

STEAM DEGRADATION STUDY OF TAS SORBENT

Objective

To study the degradation of sorbent TAS under high temperature steam.

Steam degradation and CO₂ capture of the sorbent

Steam degradation was done under O₂ free environment to prevent oxidative reactions. Oxidative reactions may cause other type of degradation in the sorbent occluding the real effect of high temperature steam. The effluent steam of the reactor was condensed and collected for further IR study.

The operational steps include (i) loading of 2 g of TAS into the reactor, (ii) flowing 500 cm³/min of N₂ for 5 min to purge out O₂, (ii) heating the reactor from room temperature to 110°C to prevent steam condensation, (iii) switching the flow from N₂ to 35 psi steam, (iv) holding the steam flow for 30, 60 and 90 min, (v) switching the flow back to preheated N₂ for 5 min to purge out steam and (vi) cool the reactor to 60°C to take a sorbent sample.

CO₂ capture measurements for the solid sorbent were performed using a weight difference method. The measurement consisted of (i) heating the sorbent in oven at 120
°C for 7 min to remove CO₂ and H₂O pre-adsorbed from ambient atmosphere, (ii) measuring the weight of the sorbent after heating, (iii) saturating the sorbent in pure CO₂ bath at a flow rate of (500 cm³/min) for 10 min and (iv) measuring the weight of the sorbent after CO₂ capture. The weight gain of the sorbent before and after the CO₂ saturation is estimated as the amount of CO₂ captured by the sorbent.

IR studies

The IR study of the fresh and degraded sorbent was performed by placing 50 mg of TAS in DRIFTS (Diffuse Reflectance Infrared Fourier Transform, Spectra-Tech) cell on a Nicole-6700 FT-IR. The IR-spectra of the fresh and degraded sorbent was collected at 30° C. The single beam spectra were collected by 32 co-adding scans and a resolution of 4 cm⁻¹ at a rate of 6 scans/min. The absorbance spectra were obtained by the equation: Abs = log (1/I) where I is single beam spectrum of interest. The condensed outlet was collected and scanned using ATR accessory on a Nicolet-6700 FT-IR.
Figure A.1 Single beam spectra of the sorbent after steam degradation for 30, 60 and 90 min.

Figure A.2 IR absorbance spectra of the sorbent after steam degradation.
Figure A.3 Single beam spectra of the dry condensed outlet.

Figure A.4 Absorbance spectra of the dry condensed outlet
Figure A.5. Difference spectra of dry condensed outlet subtracted with air
CO₂ Capture Results, discussion and problems

Table A.1  CO₂ capture capacity of the sorbents after 30, 60, and 90 min of steam degradation.

<table>
<thead>
<tr>
<th>Degradation time(min)</th>
<th>CO₂ capture capacity(mmol/g.sorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.235</td>
</tr>
<tr>
<td>30</td>
<td>2.080</td>
</tr>
<tr>
<td>60</td>
<td>1.954</td>
</tr>
<tr>
<td>90</td>
<td>1.873</td>
</tr>
</tbody>
</table>

-IR results from Figure A.4 show that the outlet steam contained a detectable amount of TEPA, PEG, and polymeric linker, this is an evidence of the washing effect that steam has on the sorbent and incomplete immobilization on the species. The decrease in capture capacity shows the rapid degradation of the sorbent due to steam effect.

-The condensed outlet of from the reactor was a blue liquid. Also, the sorbent in the reactor after the degradation was light blue. This could be due to oxidation of copper from the steam lines.

-The aluminum rings to hold the sorbent, deformed after heated at high temperature for a long time and stuck to the inside of the reactor.
APPENDIX B

EARLY STUDY OF CO$_2$ AND SO$_2$ CAPTURE IN THE GRAM-SCALE REACTOR

Summary

A fluidized bed reactor was used to evaluate TAS sorbent in gram scale; the sorbent was tested for CO$_2$ and SO$_2$ in different runs. The CO$_2$ capture capacity for the sorbent in this system was 2.2 mmolCO$_2$/g-sorb. It was found that this reactor needs a more efficient heat transfer system and an accurate method for the SO$_2$ calibration.

Objectives

To evaluate the CO$_2$ capture capacity of the sorbent in the gram-scale system

To evaluate the operational convenience of this reactor to be used with SO$_2$.

Experimental

The sorbent was sieved and 7.1 g of the retained particles were used in the fluidized bed system for CO$_2$ capture. The sorbent was mixed with 0.9 g of aluminum foil particles for a total load of 8 g and placed in the reactor for SO$_2$ capture test.
CO₂ capture: A volumetric mixture of air, 10 v% CO₂ and 10 v% CH₄ at 55 °C was used for the adsorption stage with a total flow rate of 18 L/min. Purge air at 22 L/min was used during purge and desorption stages.

SO₂ capture: A volumetric mixture of air and SO₂ (1 v%) at 55 °C was used for the adsorption stage. Purge air at 22 L/min was used during purge and desorption stages.

Steam, from the steam generator at 70 psi (~155 °C) was used for external heating and for the desorption stage. IR transmission series were collected during the assays to analyze the system effluents.

The general procedure is shown below:

To start the system:

Turn on the main wall breaker and the power to the system
Open air, water, CO₂ and CH₄ valves and verify the flow rate of each
Flow purge air to the system
Open the temperature monitor and Omnic and check IR alignment

Adsorption stage:

When average temperature in the reactor is 55°C, switch the inlet to mixture, make the flow pass through the water saturator and let adsorb for 10 min (when flowing SO₂ the saturator is by-passed)
Switch inlet to purge air until CO₂ reaches the baseline, then close and heat the reactor to 100 °C

Desorption stage:

Flow steam to the reactor for 5 seconds and flow purge air
Cool down the reactor to 55 °C, perform the calibration and start a new cycle
Results

Figure B.1 shows the total intensity and CO\textsubscript{2} and CH\textsubscript{4} bands for the CO\textsubscript{2} capture test. Figure B.2 shows the single beam for the different stages of the process.

Figure B.3 shows the total intensity and SO\textsubscript{2} band for the SO\textsubscript{2} capture test. Figure B.4 shows the single beam for the different stages of the cycle and Figure B.5 shows the picture of the sorbent after the SO\textsubscript{2} capture cycle.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>CO\textsubscript{2} capture capacity mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2} capture test</td>
<td>2.2</td>
</tr>
<tr>
<td>SO\textsubscript{2} capture test</td>
<td>Calibration not visible</td>
</tr>
</tbody>
</table>

It was found that the addition of foil improved the heat transfer in the reactor, however the foil particles were too big and they remained in the bottom of the reactor causing hot spots during the SO\textsubscript{2} cycle. Figure 7 shows the aspect of the sorbent and the screen used as a support after this test.

Conclusions

The heating system of the reactor must be improved to obtain a faster heating up/and cooling down during the cycles. The CO\textsubscript{2} capture capacity for the sorbent at the conditions of the system is 2.2 mmol/g. SO\textsubscript{2} is an IR detectable gas with absorbance at the band 1373 cm\textsuperscript{-1}. However the detection limit is lower than the amount for calibration and SO\textsubscript{2} capture capacity could not been calculated.
Figure B.1  Total IR intensity and intensity for CO$_2$ and CH$_4$ bands during the CO$_2$ capture test
Figure B.2 IR single beam spectra during the CO₂ capture test and calibration
Figure B.3 Total IR intensity and SO$_2$ band intensity for the SO$_2$ capture in the 5 g system.
Figure B.4 IR single beam spectra for the \( \text{SO}_2 \) capture in the gram-scale system.
Figure B.5 Picture of the sorbent and the screen after the SO$_2$ capture.
APPENDIX C

CONFIGURATION AND DESCRIPTION OF THE TUBULAR REACTION SYSTEM

The gram-scale reaction system has been used for running CO$_2$ capture over different sorbents using 5 and 10 grams. However its size and configuration make it very flexible and may be used for preparation, drying and steam degradation of sorbents. The present report shows some features of the system in order to be used to prepare, dry, test and degrade sorbents as one continuous process. The flexibility of the system gives the possibility to perform each step at a time.

Objectives

- To show the main features in the gram-scale reaction system.
- To describe the main potential applications of the whole system.

Experimental

The reaction system is composed by 4 sequential sections as shown in Figure C.1; (1) Utilities and gas lines, (2) Reactor, (3) Condenser and (4) IR spectrometer. Each part of the system may be used, modified or skipped and there is the possibility to work in a wide range of variables such as:
The outline of the system and its configuration allow us to record specific data such as temperature, flow, mass, and IR spectra of the outlet gas stream. By measuring these variables there is the possibility to make deeper studies over a sorbent.

Utilities and gas lines

The reaction system counts with the possibility to work with up to 5 gases, they may be introduced to the reactor pure or mixed in any proportion. Due to all the lines are heated, the gases can be conditioned to reach any desired temperature before entering the reactor. These lines also have a liquid saturator (water saturator) that may be used or bypassed according to the necessities of the process. There are some auxiliary units such as steam generator, purge air generator, and temperature controlled heating tapes that provide:

- Low and medium pressure steam
- Purge clean air
- Electric heating
- Cooling water
Table C.1 shows some important data about flow, temperature and availability of utilities and gases and figure 2(1) shows the schematic of this section of the process.

Table C.1 Important features for utilities and gas lines.

<table>
<thead>
<tr>
<th>Available gases</th>
<th>Channel in FC</th>
<th>Max Flow (L/min)</th>
<th>Heating</th>
<th>Water saturation</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1</td>
<td>30</td>
<td>Yes</td>
<td>Yes</td>
<td>From purge air generator</td>
</tr>
<tr>
<td>CO₂</td>
<td>2</td>
<td>10</td>
<td>Yes</td>
<td>Yes</td>
<td>Cylinder (99.9%)</td>
</tr>
<tr>
<td>CH₄</td>
<td>3</td>
<td>10</td>
<td>Yes</td>
<td>Yes</td>
<td>Cylinder (99.9%)</td>
</tr>
<tr>
<td>SO₂/N₂/He</td>
<td>4</td>
<td>10</td>
<td>Yes</td>
<td>Yes</td>
<td>Cylinder (Auxiliary gas)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Utility</th>
<th>Main features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
<td>Saturated steam</td>
</tr>
<tr>
<td></td>
<td>Low and medium pressure (0 to 100 psig)</td>
</tr>
<tr>
<td></td>
<td>Temperature from 100 to 165 °C</td>
</tr>
<tr>
<td></td>
<td>Possible to send through jacket or inside the reactor</td>
</tr>
<tr>
<td>Electric heating</td>
<td>Heating tapes with self-temperature controller</td>
</tr>
<tr>
<td></td>
<td>Max temperature operation 200 °C</td>
</tr>
<tr>
<td>Purge air</td>
<td>Wet applications resistant</td>
</tr>
<tr>
<td></td>
<td>50 and 80 cm long</td>
</tr>
<tr>
<td></td>
<td>Max flow of 50 L/min</td>
</tr>
<tr>
<td>Cooling water</td>
<td>Pressure 70 psig (@ source)</td>
</tr>
<tr>
<td></td>
<td>Low humidity</td>
</tr>
<tr>
<td></td>
<td>Use in process and spectrometer</td>
</tr>
<tr>
<td></td>
<td>Available from sink at room temperature</td>
</tr>
<tr>
<td></td>
<td>For use through jacket</td>
</tr>
</tbody>
</table>

Note: Max flows and compositions are subject to the flow controller, pressure and cylinders, the reported values are for the current configuration.

Reactor

Utilities and gas lines are connected and organized in order to meet all the requirements of the reaction or process, any of the potential process that may be carried out in the system occurs inside of the reactor. The reactor is an aluminum vessel equipped with a heating-cooling jacket, O-ring compartments in which the sorbent may be placed, and thermocouples in different locations. Table 2 shows some important
features and descriptions about the reactor and figure 2(2) shows a schematic of this section of the process.

Table C.2 Features and dimensions of the reactor.

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<th>Main features</th>
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<tr>
<td><strong>Dimensions</strong></td>
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<tr>
<td>Internal diameter: 5 cm</td>
</tr>
<tr>
<td>Jacket external diameter: 10cm</td>
</tr>
<tr>
<td>Total height: 24 cm</td>
</tr>
<tr>
<td>11 rings that allow up to 9 individual compartments to place the sorbent</td>
</tr>
<tr>
<td><strong>O-ring features</strong></td>
</tr>
<tr>
<td>Material: Aluminum</td>
</tr>
<tr>
<td>Internal diameter</td>
</tr>
<tr>
<td>External diameter</td>
</tr>
<tr>
<td>Nylon screen may be placed between the rings</td>
</tr>
<tr>
<td>Design steam pressure: 70 psig</td>
</tr>
<tr>
<td><strong>Jacket and insulation</strong></td>
</tr>
<tr>
<td>Bottom: Inlet and drain valve</td>
</tr>
<tr>
<td>Top: Outlet and pressure release valve</td>
</tr>
<tr>
<td>External electric heating</td>
</tr>
<tr>
<td>External wet-pad insulation</td>
</tr>
<tr>
<td><strong>Fittings</strong></td>
</tr>
<tr>
<td>All ¼” Swagelok fittings</td>
</tr>
</tbody>
</table>

Condenser

For process like drying and CO₂ capture capacity it is necessary to collect the volatile species leaving the reactor; either for avoiding noisy signal in the transmission cell, concentrate one of the products (CO₂) or collect samples for ATR studies. There is a condenser that works with cold water, the outlet may be connected either to the IR transmission cell or to a liquid collection vessel. Figure C.2 shows a schematic of the condenser in the process.
IR transmission cell

At the end of the process, the outlet stream is connected to a transmission cell in which the gas species leaving the reactor may be identified. The cell is connected and aligned to the IR spectrometer and may be heated as well as the gas lines connected to it. The outlet stream is directed to a hood for its final disposition. Figure C.2 shows a schematic of this section of the process.

Figure C.2  Schematic flow and equipments diagram for the reaction system in lab 405.
Figure C.3 Pictures for the reactor, O-ring and thermocouples in the reaction system in lab 405.
APPENDIX D

TEPA-POLYMERIC LINKER SILICA BASED CATALYSTS

Summary

SBA-15 mesoporous material was prepared from sodium silicate using a low cost technique. Two final materials were obtained after preparation; (i) as prepared and (ii) calcined. The final form of the supports was impregnated with crosslinked TEPA/Polymeric linker solution. This material is intended to be used as basic catalyst in different reactions such as deoxygenation and esterification.

Experimental

Figure D.1 shows the preparation procedure of (1) SBA-15 and (2) basic catalyst. SBA-15 was prepared by dissolving surface agent P123 copolymer in water at 30 °C for 2 h. Acetic acid was added to the water solution to decrease the pH to ~5. Sodium silicate was added to the acidic solution and stirred vigorously for 24 h at 30 °C. The homogeneous mixture was aged in closed vessels with no stirring at 100 °C for 24 h. The solids resulting from aging were washed repeated times using water to remove the excess acid and dried in oven at 100 °C. The resulting white powder was labeled as “As prepared SBA-15”. A portion of the as prepared SBA-15 was calcined at 500 °C under the presence of air for 12 h and was labeled as “Calcined SBA-15”.

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Commercial SiO$_2$, as prepared and calcined SBA-15 were used to prepare the TEPA/Polymeric linker basic catalysts. TEPA and Polymeric linker were mixed in 1:1 weight ratio and crosslinked at 100 °C for 5 min. The crosslinked species were dissolved in ethanol at room temperature to get a 4 w% solution. TEPA/Polymeric linker solution was impregnated on each of the silica supports by stirring for 1 h and drying in oven at 100 °C for 12 h.

Results

Figure D.2 shows the IR single beam of the silica supports; SiO$_2$, as prepared and calcined SBA-15 and the TEPA/Polymeric linker catalysts at 35 °C. Figure D.2 shows the IR single beam of those species at 105 °C after water was partially removed from the surface. For calcined SBA-15 a prominent peak appears at 3746 cm$^{-1}$ which is not observed in SiO$_2$ and as prepared SBA-15. As prepared SBA-15 shows a broad peak at 1730 cm$^{-1}$ that suggests the presence of carboxylic acid and other species containing C=O bonding on the surface. For the three catalysts bands at 3368 and 3301 cm$^{-1}$ are observed confirming the presence of NH$_2$ groups from TEPA and the peak at 830 cm$^{-1}$ is evidence of groups from Polymeric linker.

Figure D.4 shows the absorbance spectra for TEPA/Polymeric linker catalysts, using the raw material as a background. For SiO$_2$ and as prepared SBA-15 the presence of OH groups is more notorious according to the higher and broader 3520 cm$^{-1}$ band. Bands at 2812, 2879, 2929 and 2961 cm$^{-1}$ show the evidence of the C-H stretching from TEPA and Polymeric linker. The peaks 3056 and 3036 cm$^{-1}$ show the N-H stretching from TEPA.
Figure D.1 Preparation procedure for (1) SBA-15 and (2) TEPA-Polymeric linker/Silica based catalyst.
Figure D.2: Normalized IR single beam for silica supports (black lines) and TEPA-Polymeric linker silica based catalysts (red lines). Spectra taken at 35°C.
Figure D.3: Normalized IR single beam for silica supports (black lines) and TEPA-Polymeric linker silica based catalysts (red lines). Spectra taken at 105°C.
Figure D.4: Absorbance spectra for TEPA-Polymeric linker silica based catalysts at 35 and 105°C. Abs = -log₁₀(I_{cat}/I_{raw}) where I_{cat} is the normalized single beam of the catalyst and I_{raw} is the normalized single beam of the raw support.

Conclusions

Basic catalysts with evident presence of TEPA/Polymeric linker on their surface were prepared on in-house prepared SBA-15 and commercial SiO₂. The three silica supports used for the study; SiO₂, as prepared SBA-15 and calcined SBA-15 show pronounced differences in their structures.
APPENDIX E

BLANK TESTS ON SILICA FOR CO₂ AND SO₂ CAPTURE

CO₂ and SO₂ capture were measured on blank silica samples to determine the adsorption capacity of the support without the active amine sites. Pure silica has silanol groups and is expected to weakly adsorb a small amount of CO₂ and SO₂ by its own.

The blank test was performed in the DRIFTS reaction system using similar conditions as CO₂ and SO₂ capture set for the solid amine sorbents. Adsorption at 55 °C under 15 v% CO₂ in Air stream was performed by step switch of flow for 5 min and CO₂ desorption was performed by TPD at 110 °C. A 0.25 v% SO₂ in air stream was used for SO₂ capture experiment and the desorption temperature was 130 °C.

Amorphous powder silica (27.5 mg) was placed in DRIFTS reactor and heated to 110 °C for CO₂ calibration previous to adsorption of CO₂. After the CO₂ capture cycle, a SO₂ capture cycle was performed and SO₂ calibration was done at the end of the run to prevent contamination of the sample.

Figure E.1 shows the MS CO₂ profile for the CO₂ capture cycle on blank silica. During the calibration two sharp peaks were generated by pulsing 3 and 1 cm³ of pure CO₂. The adsorption step switch shows that blank silica adsorbs a small amount of CO₂ and the purge step switch shows the removal of most of the CO₂ adsorbed, suggesting the
weak interaction between silica and CO$_2$. The desorption stage shows a very small TPD curve, observable by magnification of the CO$_2$ profile. The area under the TPD curve shows that the CO$_2$ capture capacity of blank silica is 6 $\mu$mol CO$_2$/g-SiO$_2$.

Figure E.1 Normalized CO$_2$ (m/e=44) MS profile for one cycle of CO$_2$ capture on blank silica. Adsorption at 55 °C and desorption by TPD at 110 °C. Inset a x3500 magnification of the TPD curve.

Figure E.2 shows the SO$_2$ MS profile for the SO$_2$ capture cycle performed on blank silica. The adsorption curve suggests a significant amount of SO$_2$ was adsorbed by silica and the tail shape during the purge stage indicates the removal of the weakly adsorbed SO$_2$. The area under desorption curve shows that the SO$_2$ capture capacity of blank silica is 12 $\mu$mol SO$_2$/g-SiO$_2$. 

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Figure E.2  Normalized SO$_2$ (m/e=64) MS profile for one cycle of CO$_2$ capture on blank silica. Adsorption at 55 °C and desorption by TPD at 130 °C. Inset a x50 magnification of the TPD curve.

The results indicate that silica has very low CO$_2$ and SO$_2$ capture capacity and does not have a significant contribution to the solid anime sorbent total capacity. The role of silica is to provide surface area and support the amine sites.
APPENDIX F

RESIDENCE TIME DISTRIBUTION ON TUBULAR REACTION SYSTEM AND EFFECTIVENESS FACTOR FOR CO₂ ADSORPTION ON POWDER SORBENT

Residence time distribution

During the operation of the tubular reaction system, methane (CH₄) was used as a tracer to evaluate the residence time distribution (RTD) of gas species in the reactor and process lines. Due to its inertness and non-adsorption nature on amine sorbents, the concentration of CH₄ in the effluent after a step switch can be registered throughout the time and used to calculate the mean residence time (tₘ) of a species into the reactor. The concentration of CO₂ in the effluent as a function of time can be used to evaluate the adsorption half-time (τ₀⁺) of CO₂ on the sorbent.

Figure F.1 shows the external age E(t) and cumulative F(t) residence time distribution functions determined experimentally by a CH₄ step input in the tubular reaction system. E(t), F(t) and tₘ time were obtained by using the equations:

\[ F(t) = \frac{C(t)}{C_0} \]

\[ E(t) = \frac{d}{dt}[F(t)] \]
Where $C(t)$ is the concentration of CH$_4$ as a function of time and $C_0$ is the equilibrium concentration of CH$_4$ after the step switch (10 v%). The values for $\tau_{0.5}$ and $\tau_{0.95}$ for CO$_2$ adsorption can be graphically calculated.

Figure F.1 In red: External age $E(t)$ and cumulative $F(t)$ residence time distribution functions determined experimentally by a CH$_4$ step input in the tubular reaction system. In black: Cumulative adsorption curve of CO$_2$ on amine sorbent.
The mean residence time and half-CO$_2$ adsorption time were calculated to be 0.37 min indicating that CO$_2$ rapidly adsorbs at least half of the CO$_2$ during the first 0.37 min. In addition, this is the mean time that a molecule stays in the reactor before reaching the IR and MS analyzers.

The value of $t_{0.95}$ represents that 0.62 min are necessary for eluding 95% of the species in the reactor. This value is almost twice the value of $t_m$. The value of $\tau_{0.95}$ represents that 2.5 min are necessary to reach 95% saturation of CO$_2$ on the sorbent. The large value for $\tau_{0.95}$ indicates that adsorption of CO$_2$ becomes slower throughout the sorbent gets saturated.

Effectiveness factor

The overall effectiveness factor for adsorption of CO$_2$ on the sorbent was calculated. Due to the lack of surface reaction and the constant concentration of CO$_2$ in the feed during the semi-batch adsorption process, assumptions were made to reach the calculation. The assumptions made for this section are: (i) The concentration of CO$_2$ in the fed decreases thought the adsorption time at the same rate of CO$_2$ is adsorbed on the sorbent surface (CO$_2$-S), (ii) the reaction rate ($-r_{CO_2}$) and reaction rate constant ($k''$)are function of time and only account for the adsorption reaction, (ii) the adsorption happens in presence of only CO$_2$ and air and at constant temperature of 55°C.

The concentration of CO$_2$ on the sorbent was calculated by using the adsorption curve shown in Figure F.1 and assuming that the capture capacity of the sorbent is 1500 $\mu$mol CO$_2$/g-sorb. The concentration of CO$_2$ in the fed was calculated by subtraction of the concentration of CO$_2$-S from the initial fed concentration. The adsorption rate is the
instant derivative of CO$_2$ concentration with respect to time and k” is the ration – rCO$_2$/CO$_2$. The units for k” were adjusted by using the density and surface area of the sorbent.

Thiele modulus (Φ), internal effectiveness factor (η), external mass transfer coefficient (k$_c$) and overall effectiveness factor (Ω ) were calculated as follows; the results for the instant calculations in the semi-batch process are shown in Table F.1.

\[ Φ = \frac{d_p}{2} \sqrt{\frac{k'' \rho_p s_a}{D_e}} \]

\[ η = \frac{3}{\Phi^2} \left( \Phi coth \Phi - 1 \right) \]

\[ k_c = \frac{1 - \phi}{\phi} \left( \frac{D_{AB}}{d_p} \right) \left( \frac{U d_p}{1 - \phi} \right)^{0.5} \left( \frac{\nu}{D_{AB}} \right)^{0.33} \]

\[ Ω = \frac{η}{1 + η k'' s_a \rho_b / k_c a_c} \]

Where:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
</tr>
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<tr>
<td>S$_a$ (m$^2$/g)</td>
<td>40</td>
<td>Surface area</td>
</tr>
<tr>
<td>ν (m$^2$/s)</td>
<td>1.64E-05</td>
<td>Kinematic viscosity</td>
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<tr>
<td>D$_{AB}$ (m$^2$/s)</td>
<td>2.03E-05</td>
<td>Diffusivity CO$_2$/air</td>
</tr>
<tr>
<td>D$_e$ (m$^2$/s)</td>
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<td>Effective diffusivity</td>
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<td>ρ$_p$ (g/m$^3$)</td>
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<td>φ</td>
<td>0.62</td>
<td>Particle porosity</td>
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<td>P$_b$ (g/m$^3$)</td>
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<td>a$_c$</td>
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<td>U</td>
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<td>k$_c$</td>
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<td>External mass transfer coefficient</td>
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The results in Table F.1 show that despite the CO\textsubscript{2} concentration and adsorption rate the internal and overall effectiveness factor are equal to one. The very high diffusion efficiency is due to the very high velocity (flow rate) and very small particle size. The difference in concentration between the particle surface and the inside of the pores is negligible.
Table F.1 Calculation of effectiveness factor for CO$_2$ adsorption on powder amine sorbent.

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<tr>
<th>Time (s)</th>
<th>CO$_2$-S (mol/m$^3$)</th>
<th>CO$_2$ (mol/m$^3$)</th>
<th>-rCO$_2$ (mol/m$^2$.s)</th>
<th>k” (m$^3$/m$^2$.s)</th>
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APPENDIX G

THERMAL DEGRADATION STUDY ON TAS SORBENT

Thermal degradation was studied in DRIFTS reactor by heating 57 mg of TAS sorbent from 55 to >500 °C under the flow of Ar. The inert gas Ar was used to prevent the oxidative degradation of the sorbent and as a carrier of degraded species. The sorbent surface was monitored by IR spectroscopy and the effluent gas from the DRIFT reactor was analyzed by MS spectroscopy. Two experiments with different heating rate were performed (i) using a fast heating causing rapid degradation of the sorbent and (ii) a slow heating to analyze the evolution of species along the temperature (as a function of time).

Figure G.1 shows the temperature profile for the two degradation experiments. The heating rate for the rapid heating experiment was of 150 °C/min, for which the changes in the sorbent are expected to be noticed at higher temperature than the actual change. The slow heating experiment had a heating rate of 28 °C/min and the changes in IR spectra and MS profiles are expected to be observed closer to the actual temperature of the sorbent.
Figure G.1 Temperature profile for the (a) Rapid heating and (b) Slow heating thermal degradation experiments.

Figure G.2 shows the MS profiles for different species present in the effluent or the DRIFTS reactor. For the rapid heating experiment the MS intensities of all the species are at steady state. By starting the heating process CO₂ intensity increased showing a peak between 80 and 180 °C that may be caused by the desorption of pre-adsorbed CO₂ from environment. After 180 °C the intensities of O₂, N₂, H₂O and CO₂ started increasing, showing a broad peak with maximum between 300 and 600 °C. The presence of these species in the reactor effluent indicates (i) the degradation of the sorbent by decomposition of amine molecules and additives to CO₂ and N-compounds and (ii) the desorption of trapped H₂O that does not leave the sorbent at low temperature. After 200 °C in the cooling stage, the changes in the effluent composition are very small and do not represent changes due to thermal degradation of the sorbent.
The slow heating experiment shows more details about the progressive decomposition of the sorbent throughout the temperature. CO$_2$ was desorbed from 70 to 120 °C and does not appear further with increments in temperature. The N$_2$ and NH$_3$ intensities show the degradation of amine to ammonia and N-compounds starting at 200 °C until 500 °C. H$_2$O was desorbed at 250 °C along with the formation of NH$_3$.

![MS profile](image)

Figure G.2 Normalized MS profiles for (a) Rapid heating and (b) Slow heating thermal degradation experiments.

Figure G.3 shows the IR absorbance spectra of the sorbent during the thermal degradation experiments. The bands at 3360 and 3300 cm$^{-1}$ show a gradual decrease with increments in temperature, suggesting the removal or decomposition of primary and secondary amine sites. The bands in the fingerprint region show the depletion of C-H and N-H chemical groups and the shifting in characteristic peaks of TEPA, suggesting the
formation of N-compounds and the breaking of C-C and C-N bonding. The two bands at 930 and 770 cm⁻¹ show the depletion of N-H groups. The formation of gas phase CO₂ at low temperatures is caused by the desorption of pre-adsorbed CO₂.

According to these results, the sorbent is expected to lose most of its active species after 150 °C, indicating that the sorbent can be more stable by using desorption temperatures lower than 150 °C. The use of low desorption temperature is possible due to the complete removal of CO₂ adsorbed species between 80 and 140 °C.

![Figure G.3](image-url) Absorbance spectra for TAS during the (a) Rapid heating and (b) Slow heating thermal degradation experiments. Abs=−log₁₀(I/I₀) where I is the normalized single beam at one selected temperature during the heating and I₀ is the normalized single beam at the same temperature during the cooling.