DEVELOPMENT OF POLYMERIC SO$_2$ RESISTANT 
COATING FOR SOLID AMINE SORBENT

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DEVELOPMENT OF POLYMERIC SO₂ RESISTANT
COATING FOR SOLID AMINE SORBENT

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Thesis

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ABSTRACT

The impurities in flue gas from coal fire power plant such as SO$_2$, could poison CO$_2$ sorbent due to its strong acidity. To reinforce the stability of sorbent in presence of SO$_2$, polymeric SO$_2$-resistant coating was developed and characterized by in-situ FTIR spectroscopy. This coating was prepared by crosslinking poly(ethylenemine) with an epoxy and applied to CQA-12, a solid amine sorbent. The effect of the epoxy composition on the stability and adsorption / desorption kinetics of the coated sorbent was investigated by FTIR and mass spectrometry. The results revealed that this polymeric coating enhanced the resistance to SO$_2$ poisoning, thus the multi-cyclic stability of the sorbent in presence of SO$_2$, by converting the amine sites to secondary and tertiary amine. Though it reduced the initial CO$_2$ capture capacity due to blocked amine sites. Increased amount of epoxy was found to strengthen the SO$_2$ resistance. The FTIR spectra denoted that the introduction of epoxy increased the ratio of weakly adsorbed CO$_2$ to strongly adsorbed CO$_2$, i.e., reduced the binding strength of amine/CO$_2$. 
ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

1.1 Global Climate Change

There is a concern that human activities are effecting the heat/energy-exchange balance between Earth, the atmosphere and space, and leading to the global climate change. Previously, the effect of human activities is often termed as global warming due to the increase of global average temperature. But in recent days, people would like to call it global climate change as the warmer plant not only caused hot summer, some regions also have experienced extremely cold winters (sometimes record-breaking), while others have experienced heavy rain, etc. The human activities, especially the combustion of fossil fuel, have contributed to increase the atmospheric carbon dioxide (CO$_2$) and other trace greenhouse gases. Most scientists believes that the intensification of Earth’s natural heat-trapping “greenhouse effect” will result in a significant global warming due to the accumulation of greenhouse gases in the atmosphere.$^1$
Data from Intergovernmental Penal on Climate Change (IPCC) demonstrate that the global annual mean CO$_2$ concentrations increased from 353.6 part per million (ppm) at 1990 to 401.5 ppm at 2010 (Figure 1). And they forecast that the concentration of CO$_2$ will still increase with a prominent speed in the next 25 years from an annual growth rate of 2.4 ppm in the period 1990—2010 to 3.2 ppm during the period 2010—2035$^2$. This increase lead to the increase of global mean surface air temperature over land and oceans, which has triggered some irreversible consequences (e.g. increase of sea level, fusion of perpetual ice, reduction of PH of ocean).

1.2 Carbon Capture, Utilization & Storage (CCUS)

CO$_2$ is considered as the primary greenhouse gas, which accounts around 82% of total greenhouse emission in U. S. in 2012 according to U.S. Environmental Protection Agency$^3$. 

Figure 1 Atmospheric CO$_2$ concentration change from 1960 to 2010$^2$
The objective of developing carbon capture, utilization & storage (CCUS) technique is to mitigate the increase of CO₂ emissions and therefore for limit the global climate change.

CO₂ capture is the process of capturing waste CO₂ from CO₂ sources to obtain high purity CO₂. The obtained CO₂ could be used to produce energy products (e.g. Methanol, Di methyl carbondined on etc.)⁴ and chemicals (e.g. Carbamates, Urea, Isocyanates etc.), serve as solvent (supercritical CO₂), working fluid (Enhanced oil recovery) in industry, etc. Or it could be stored underground. The integrated concept from capture to sequestration is defined as carbon capture, utilization, and storage (CCUS).

According to (1) in Figure 2, Electricity and Industry made up more than 50% of total U. S. CO₂ emission. Meanwhile, for both electricity generation and industry, CO₂ capture is the only large-scale option to reduce emissions at relatively low cost while preserving the value of fossil fuel reserves and existing infrastructures⁵. Therefore, CO₂ capture is considered as the most promising technique to mitigate the CO₂ emission.
1.3 CO2 Capture process

Coal fired power plant is considered as a large point CO2 source as it make up 39.1% of total U. S. electricity generation according to (2) in Figure 2. Liquid amine method is a conventional low-cost method of CO2 capture. But it still increases 80% -85% of the cost of electricity (COE) according to a study from U. S. Department of Energy (DOE)⁶.

CO2 capture liquid process would typically employ an organic solvent such as monoethanolamine (MEA)⁷. Amine solvents react reversibly with CO2 to form an amine–CO2
complex that is lower in energy than the reactants. This complex is typically either a carbamate or bicarbonate depending on the structure of the amine, with primary and secondary amines forming the carbamate. The mechanism is shown in Figure 3.

\[
2H_2O \leftrightarrow H_3O^+ + OH^- \\
CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^- \\
HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \\
2\text{MEA + CO}_2 \leftrightarrow \text{MEAH}^+ + \text{MEACOO}^- \\
\text{MEA}^+ + H_2O \leftrightarrow \text{MEA} + H_3O^+ \\
\text{MEACOO}^- + H_2O \leftrightarrow \text{MEA} + HCO_3^- 
\]

Figure 3 Methanisim of MEA CO$_2$ capture process

Though MEA method is a widely used CO$_2$ capture process, it still have some disadvantages as a liquid process (Figure 4): 1. it needs large reactor to interact with CO$_2$; 2. it needs to be transport to the top of the absorbing tower, which is energy consuming and inconvenient; 3. it is considered to be energy-intensive and expensive for large-scale CO$_2$ separation due to the requirement of solvent heating, in addition to being corrosive and toxic in nature; 4. it suffers stability issue due to amine oxidation.
To overcome the defects of liquid amine process, the amine functionalized solid sorbent is developed as a promising method and attract more and more attention. There are three different classed of solid amine sorbents: 1. Impregnated solid amine sorbent, which exhibits a week interaction (e.g. hydrogen bonding) between physically impregnated amine species and porous support; 2. Amine-grafted sorbent, where the amine functional groups are covalently bonded to the porous support; 3. Hyperbranched aminosil-
ica (HAS) material which are synthesized by in-situ ring-opening polymerization of aziridine on porous supports. As solid sorbents, they provide several significant advantages comparing to the MEA liquid process. Especially for the energy saving, the liquid process needs 3300kJ to regenerate 1kg of sorbents due to the high specific heat of water, and only 746kJ is needed to regenerate 1kg of solid amine sorbent. Meanwhile, the solid amine sorbent also provides a higher gas mass transfer rate due to its highly porous structure.

In these three solid amine sorbents, the amine-impregnated sorbent was reported exhibiting higher capture capacity than the other two kinds of sorbent due to its high amine density. However, it was also reported to be less stable than the other two sorbents due to amine leaching during the multiple CO$_2$ adsorption/desorption cycles.

![Reaction mechanism of CO$_2$ reacting with amine](image)

Figure 5 Reaction mechanism of CO$_2$ reacting with amine

Figure 5 shows the reaction mechanism between CO$_2$ and amine species. This reaction is an acid base reaction. One amine specie will first interact with CO$_2$ to form zwitterions. Then deprotonation will happen and form carbamic acid. If there is one more amine specie
available, then the deprotonation will happen between zwitterion and amine specie to form carbamate and ammonium ion. During this reaction, the primary amine (pKa=32) performs stronger activity than secondary amine (pKa=20) due to higher basic.
CHAPTER II

DEVELOPMENT OF POLYMERIC SO$_2$ RESISTANT COATING FOR SOLID AMINE SORBENT

2.1 Background

This Part of background will mainly introduce the reported fact that SO$_2$ eliminate the CO$_2$ sorbents performance and the traditional way used in the industrial to reduce the effect of SO$_2$, as well as the raw material introduction for SO$_2$ resistant coating.

2.1.1 The effect of SO$_2$ on amine based CO$_2$ sorbent

Flue gas from coal fired power plant contains 10-15 vol% of CO$_2$, 5-7 vol% of H$_2$O, 3-4 vol% of O$_2$, as well as 1500 to 2500 ppm of NO and 500 to 2000 ppm of SO$_2$. The NO in the flue gas could be processed by selective catalytic reduction. While there are several common techniques used in industry to reduce the concentration of SO$_2$ such as dry, wet or semidry flue gas desulfurization (FGD). And the wet FGD processes have been proven reliable for a variety of fuels, and have been widely applied in industry for achieving high SO$_2$ removal efficiency in excess of 95%. Even though, there will be 40-250ppm of SO$_2$ left in the flue gas and flow into the CO$_2$ capture unit even after the
desulfurization process. This SO₂ impurity will strongly effect the stability of the solid amine sorbents.

Table 1 Summary of the Multiple CO₂ Capture Cycle Studies in the Presence of SO₂ Reported in Literature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas concentration (%)</th>
<th>Initial capture capacity</th>
<th>Cycles</th>
<th>Final capture capacity</th>
<th>Capture capacity drop ratio</th>
<th>Paper link</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC 1065</td>
<td>12.50</td>
<td>1.56</td>
<td>11</td>
<td>0.18</td>
<td>11.54%</td>
<td>8</td>
</tr>
<tr>
<td>PEI/SiO₂</td>
<td>10.00</td>
<td>0.24</td>
<td>5</td>
<td>0.14</td>
<td>42.00%</td>
<td>44</td>
</tr>
<tr>
<td>APS/SiO₂</td>
<td>10.00</td>
<td>0.46</td>
<td>/</td>
<td>0.34</td>
<td>26.00%</td>
<td>44</td>
</tr>
<tr>
<td>MAPS/SiO₂</td>
<td>10.00</td>
<td>0.54</td>
<td>/</td>
<td>0.44</td>
<td>18.00%</td>
<td>44</td>
</tr>
<tr>
<td>SAC</td>
<td>12.00</td>
<td>0.22</td>
<td>1</td>
<td>0.15</td>
<td>31.00%</td>
<td>45</td>
</tr>
<tr>
<td>CAC</td>
<td>12.00</td>
<td>0.05</td>
<td>1</td>
<td>0.04</td>
<td>28.00%</td>
<td>45</td>
</tr>
<tr>
<td>APTS-SBA-15</td>
<td>0.00</td>
<td>/</td>
<td>1</td>
<td>0</td>
<td>100%</td>
<td>10</td>
</tr>
<tr>
<td>SRE10</td>
<td>15%</td>
<td>2.54</td>
<td>20</td>
<td>2.42</td>
<td>3.97%</td>
<td>This Work</td>
</tr>
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SO₂ is considered as a stronger Lewis acid than CO₂ and it can also interact with amine species to form covalent bond. Meanwhile, this covalent bond is harder to broken by temperature swing comparing to CO₂–amine covalent bond due to SO₂’s stronger acidity. The presence of SO₂ will poison the amine site and cause the irreversible deactivation, in other word, the degradation of sorbents. For the liquid amine process, Uyanga, Itoro J. et. al.’s study shows that MEA suffered a 28% degradation after 100 hours operation in presence of 196ppm of SO₂. For solid amine sorbent, Hallenbeck, A. P.et. al.’s work demonstrated
that the CO$_2$ capture capacity of the amine based sorbent decrease in each cycle of exposure to gas mixture of 12.5 vol % CO$_2$, 4% O$_2$, 431 ppm SO$_2$ and balance N$_2$. Meanwhile, CO$_2$ could completely desorb at 127$^\circ$C, but the adsorbed SO$_2$ species is stable up to 208$^\circ$C, further confirming the previous statement that SO$_2$ will poison the sorbent during the traditional temperature swing CO$_2$ capture process, whose highest temperature reaches only 130$^\circ$C. Table 1 shows a summary of the CO$_2$ capture cyclic study in presence of SO$_2$.

2.1.2 Tertiary amine

Tertiary amine has a significant different property comparing to the previous mentioned primary amine and secondary amine due to its low basicity (pKa=10 comparing to Pka=32 of primary amine and pKa=20 of secondary amine). Contrary to primary amine and secondary amine, tertiary amine cannot react with CO$_2$ under dry condition, and even in presence of water vapor, the reaction is slow and limited$^{47,48}$ (Eq. (1)$^{48}$). However, due to SO$_2$’s stronger acidity, tertiary amine could interact with SO$_2$ to form charge transfer complex following below equation$^{47}$.

\[
\text{R}_3\text{N} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R}_3\text{NH}^+ + \text{HCO}_3^-
\]

\[
\text{R}_3\text{N} + \text{SO}_2 \overset{T<60^\circ\text{C}}{\rightleftharpoons} \text{R}_3\text{N}--\text{SO}_2 \overset{T>100^\circ\text{C}}{\rightleftharpoons}
\]

Where the tertiary amine served as an electron donor and SO$_2$ served as an electron acceptor.
The binding strength of charge transfer complex formed by SO$_2$ and tertiary amine is significantly lower than the covalent bond formed between SO$_2$ and primary/secondary amine. So that SO$_2$ could reversibly react with tertiary amine. It was reported that supported polytertiary amine could serve as an SO$_2$ sorbent for flue gas desulfurization before CO$_2$ capture$^{49}$. Where the supported polytertiary amine sorbent could completely regenerated in nitrogen at 130°C.
2.2 Objective

With the appearance of SO$_2$ in the flue gas from coal fired power plant, the stability of solid amine sorbent is considered to be a critical issue need to be addressed in developing an amine immobilized sorbent.

2.2.1 Develop SO$_2$ resistant coating

The major objective of this project is to develop a SO$_2$ resistant coating for solid amine sorbent. With this coating on the solid amine sorbent, the SO$_2$ resistant ability of existing high performance amine sorbent could be improved, but not cost a lot to develop a new sorbent. Theoretically, this coating could be used for all the solid amine sorbent. For quantitative goal, the SO$_2$ resistant coating should reduce the capture capacity drop due to SO$_2$ poisoning to less than 5% after 20- cycle of SO$_2$ adsorption/desorption in presence of 40ppm of SO$_2$ and emulated flue gas (15%CO$_2$ and balanced air).

2.2.2 The SO$_2$ resistant ability should remain after sorbent pelletization

Pelletization can be defined as an agglomeration (size-enlargement) process that converts fine powders or particles of sorbents into small, free-flowing units. Pelletization is a critical industrial requirement for sorbent industrial use due to a variety of reasons$^{50}$:

(1) Prevention of dust formation to improve the process safety. As fine powders can cause dust explosions and the respiration of fines can cause health problems;
(2) Improvement of the handling properties, due to the free-flowing properties;

(3) Improvement of the hardness and friability of pellets;

(4) Improvement of heat transfer rate and gas flow rate.

But, pelletization also presents some disadvantages:

(1) The coverage of binder material will block the surface amine sites, leading to the drop of initial capture capacity;

(2) Binder materials and solvent used in the pelletization process may conflict with sorbents, leading to the failure of pelletization or capture capacity drop;

(3) The aggregation of sorbent powder will bury certain amount of sorbents into the center of the pellets, leading to the contact issue due to CO$_2$ diffusion limitation in the pellets.

Even though, pelletization is still a required process for solid amine sorbents and the SO$_2$ resistant ability should reserve after this process. In other word, the coating should not conflict with the pelletization agent.

2.2.3 Compensating the blocked amine sites

As mentioned previously, the pelletization process, as well as coating process, will lead to the initial capture capacity drop due to the blocked surface amine sites. There is another requirement for coating material is to compensate the blocked amine sites to reduce the initial CO$_2$ capture capacity drop.
2.3 Hypothesis

The hypothesis of obtaining the SO₂ resistant ability is to produce a tertiary amine-rich coating (Figure 6). As mentioned in the introduction, the tertiary amine has the ability of reacting with SO₂ without interacting with CO₂. When the flue gas containing CO₂, SO₂ and air encounter with the coated sorbents at low temperature (<60°C), the SO₂ will first interact with the tertiary amine coating before contact with core sorbents. Meanwhile, CO₂ will not react with tertiary amine coating and directly interact with the core sorbents. And air will directly go through the sorbents. After temperature increasing to more than 100°C to perform temperature programed desorption (TPD), the CO₂ absorbed by core sorbents and tiny amount of SO₂ absorbed by the SO₂ resistant coating will both desorbed. Finally high purity CO₂ with a trace of SO₂ impurity could be obtained.

Figure 6 Hypothesis of SO₂ resistant coating (The amount of colored balls does not reflect the actual amount of gas species)
To achieve this hypothesis, different kinds of amines, reactants converting amines to tertiary amine and coating additives improving the chemical and physical property of coating were tried. Finally there are three species chosen as the main components of coating.

A crosslinker containing epoxy group was used to crosslink and convert the amine species to tertiary amine.

Poly(ethylenemine) (PEI) served as the amine source of the SO$_2$ resistant coating. It could not only react with the crosslinker to form a strong coating structure, but also could compensate the blocked amine species to improve the initial CO$_2$ capture capacity drop due to coating and pelletization process. The structure of PEI was shown in Figure 7. It demonstrated another reason for PEI chosen as the amine source that PEI initially containing 25% of tertiary amine and 50% of secondary amine. This molecular structure reduced the amount of crosslinker needed in the coating to convert the amine species to tertiary amine. Meanwhile, as a high molecular weight polyamine, PEI could easily form molecular network with crosslinker to further enhance the mechanical property of the SO$_2$ resistant coating.

![Molecular structure of PEI](image)

**Figure 7** Molecular structure of PEI
Figure 8 Reaction mechanism of epoxy group interacting with amine species

Figure 8 shows the reaction mechanism of epoxy converting primary/secondary amine to secondary/tertiary amine. The formation of molecular network makes it possible for the SO$_2$ resistant coating serving not only as a coating, but also as a binder solution to combine the CO$_2$ powder sorbent together to form pellets. This idea solved the previous objective that SO$_2$ resistant coating should remain after pelletization process, as pelletization process was done simultaneously with coating process.

Polyethylene glycol (PEG) with molecular weight of 200 was also used in the coating to serve as an antioxidant to prevent the SO$_2$ resistant coating from oxidation, as well as a dispersing agent to improve the mass transmission property of the coating. Furthermore, with the hydroxide group on the PEG$_{200}$, hydrogen bonding was formed between the hydroxide group and amine species in both coating and sorbents, combining the coating and
sorbent together without forming covalent boning to consume the amine sites on the sorbents. The structure of PEG was shown in Figure 9.

Figure 9 Molecular structure of PEG
2.4 Experimental

The experimental section containing procedure of sorbent coating, major characterization method used in this study such as Fourier Transform Infrared Spectroscopy (FT-IR), Mass Spectrometer (MS), and data process procedure.

2.4.1 Material

Polyethylenimine (PEI, 50% aqueous solution, Mw=750,000, Sigma-Aldrich); Crosslinker; Polyethylene glycol (PEG, Mw=200±10 g, Sigma-Aldrich); CQA12( Aspen aerogel).

2.4.2 Sorbent coating

CQA12 form Aspen aerogel was used as raw CO₂ capture sorbent in the testing of SRE coating. Coating as well as and pelletization were performed as the following steps: (1). Dissolving crosslinker in ethanol; (2) Mixing the 6g of crosslinker ethanol solution with 0.5g of PEI 50% aqueous solution and 0.5g PEG200 to form SRE coating solution; (3) Mixing 1.25g of SRE coating solution with 1g of CQA12 powder; (4) Extruding the mixture form mesh to form pellets; (5) Drying the prepared pellets in the oven at 100℃ for 1 hour to get rid of the solvent. The flow chat of coating and pelletization process was shown in Figure 10. Figure 11 shows the image taken before and after CQA-12 powder was coating and pelletized by SRE coating.
Figure 10 Schematic procedure of coating and pelletizing CQA-12 powder with SRE coating

Figure 11 Optical image of CQA-12 Powder and prepared SRE pellets
All the sorbents prepared by different SRE coating by adjusting the concentration of crosslinker were listed in Table 2.

<table>
<thead>
<tr>
<th>Sample (1g)</th>
<th>Components (g)</th>
<th>Crosslinker</th>
<th>PEI</th>
<th>PEG</th>
<th>CQA12</th>
</tr>
</thead>
<tbody>
<tr>
<td>CQA12</td>
<td></td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>1.0</td>
</tr>
<tr>
<td>SRE5</td>
<td>1.10g, 5% ethanol sln.</td>
<td>0.04</td>
<td>0.09</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>SRE7</td>
<td>1.10g, 7% ethanol sln.</td>
<td>0.04</td>
<td>0.09</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>SRE10</td>
<td>1.10g, 10% ethanol sln.</td>
<td>0.04</td>
<td>0.09</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>SRE15</td>
<td>1.10g, 15% ethanol sln.</td>
<td>0.04</td>
<td>0.09</td>
<td></td>
<td>1.0</td>
</tr>
</tbody>
</table>

2.4.3 Characterization

The CO$_2$ capture capacity of coated sorbents was tested by oven method and MS data fitting. IR spectra was used to monitor the reaction happened on the sorbents during the experiment.

2.4.3.1 CO$_2$ capture capacity measured by oven method

The sorbent was placed in a convection oven under 100°C for 10 minutes to remove the pre-absorbed CO$_2$ and water. After pretreatment, the weight of clean sorbent will be measured (m$_{sorbent}$). Then the sorbent was saturated in the bath with pure CO$_2$ stream for 10 minutes at room temperature to perform CO$_2$ adsorption. Then the weight change before
and after saturation could be measured ($\Delta m$). The capture capacity (mmol/g) could be calculated by the following Eq 1:

$$\text{Capture capacity} = \frac{m_{\text{sorbent}}}{\Delta m} \times 1000/M_{\text{CO}_2}$$  \hspace{1cm} (1)

2.4.3.2 Structure of in-situ IR system

![Structure of DRIFTS cell](image)

Figure 12 Structure of DRIFTS cell

The FTIR DRIFTS cell is shown in Figure 12. The DRIFTS cell was filled by 50mg of sorbent and placed in a Nicolet 6700 FTIR bench. The temperature of the cell was controlled by a thermocouple, which was inserted in the middle of the cell to detect the temperature of the sorbents, and a heater, which could heat up the cell. The gas stream would first go into the DRIFTS cell form the inlet valve, then go through the sorbents and finally get out from the outlet valve. Mass Spectrometer (MS) was connected to the outlet valve to detect the components of outlet gas. IR beam form IR source went through the ZnSe
window (The yellow window) and shined on the sorbent and then diffuse reflected by the sorbent, then collected and detected by the IR detector.

Figure 13 Structure of gas switch and step pulse system

The components of gas stream flowing into the DRIFTS cell is controlled by the gas switch and step pulse system, which is shown in Figure 13. There are two major lines of gas in the system. The one is pure Ar, which serves as a purge gas and trace component for MS. The other one is the simulated flue gas containing Air, CO$_2$ and SO$_2$. The flow rate of all the gasses are controlled by mass flow controller. With the certain position shown in the figure, Ar will directly go into the DRIFTS cell, and simulated flue gas will fill the calibration pipe, whose volume has been calibrated, and then flow into the vent. Two kinds of calibrated pipe with volume of 1cc and 3cc were used in this study. When the 4-port valve
is switched, the gas flowing into the DRIFTS cell will change from Ar to the simulated flue gas. If only 6-port valve is switched, the simulated flue gas will directly flow into the vent. Meanwhile, Ar will push the gas in the calibrated pipe into the DRIFTS cell to perform gas pulse. This pulse could be used to calibrate the Mass Spectrometer.

2.4.3.3 Pretreatment and CO₂ pulse calibration

The DRIFTS cell was loaded with around 50 mg of sorbents. All volumetric gas flow rates were maintained at 150cc/min. Pretreatment was carried out by heating up the DRIFTS cell to 100°C in presence of a continuous Ar flow to remove the pre-absorbed CO₂ and water during the sample preparation and storage. The temperature was held for 5 minutes. Then the pulse calibration was performed by injecting 1cc and 3cc of pure CO₂ into the DRIFTS cell for 2 times respectively. An interval of 5 minutes was needed between two pulses. After all the pulse calibrations were done, the DRIFTS cell was cooled down to 40°C for the cyclic study.

2.4.3.4 CO₂ adsorption/desorption cycle in presence of SO₂

After sample pretreatment, 4-port valve was switched to flow the simulated flue gas containing 15% of CO₂, 40 part per million (ppm) of SO₂ and balanced Air with the flow rate of 150cc/min for 10 minutes. After 10 minutes of CO₂ adsorption, the 4-port valve was switched again to flow the Ar into the system to remove the unabsorbed gas phase CO₂ and
weakly adsorption CO$_2$ for 10 minutes. Weakly adsorbed CO$_2$ was defined as the CO$_2$ bonded with amine with low binding strength and desorbed during Ar flow. The details about weakly adsorbed CO$_2$ will be further discussed in the later chapter. After that, the DRIFTS cell was heated up to 100°C to perform temperature programmed desorption (TPD) to remove the strongly adsorbed CO$_2$. Finally the DRIFTS cell was cooled down to 40°C again for the next cycle. An overall summary of the cyclic experimental procedure is shown in Table 3. Totally 20 cycles of CO$_2$ adsorption/desorption in presence of SO$_2$ were performed.

Table 3 Summary of cyclic experimental procedure

<table>
<thead>
<tr>
<th>Exp. Procedure</th>
<th>Gas Flow</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pretreatment</td>
<td>Ar, 150cc/min</td>
<td>10</td>
<td>100</td>
<td>To remove pre-ads. H$_2$O and CO$_2$.</td>
</tr>
<tr>
<td>CO$_2$ adsorption</td>
<td>15% CO$_2$/ 40ppm SO$_2$/ Air, 150cc/min</td>
<td>10</td>
<td>40</td>
<td>To perform CO$_2$ adsorption on sorbent</td>
</tr>
<tr>
<td>Ar Purge</td>
<td>Ar, 150cc/min</td>
<td>10</td>
<td>40</td>
<td>To remove gas phase CO$_2$ and weakly adsorption CO$_2$</td>
</tr>
<tr>
<td>TPD*</td>
<td>Ar, 150cc/min</td>
<td>5</td>
<td>100</td>
<td>To remove strongly adsorption CO$_2$</td>
</tr>
</tbody>
</table>
2.4.3.5 IR data analysis method

IR spectra was processed for the selected cycles (cycle 1, 5, 10, 15 and 20). In the certain cycle, spectra at 4 special timing were chosen to be processed to show the sample change during the process, which are shown in Figure 14.
Figure 14 is the MS data shows the gas flowing during the experiment and the coordinate temperature profile. The first spectrum was obtained at the end of pretreatment, where the purge gas Ar is still flowing and temperature is around 40°C. This spectrum was considered as the original state of sorbent and traditionally served as a reference or background. The second spectrum was gained at the end of adsorption, where CO₂ had flowed for 10 minutes and the temperature was still 40°C. By comparing this spectrum with spectrum of pretreatment, the change happened on the sample during CO₂ adsorption could be investigated. A significant gas switch could be observed form the MS data, where the flow gas was switched from simulated flue gas to Ar. Then the third spectrum was obtained at the end of Ar purge. The amount of weakly adsorption CO₂ could be investigated by comparing the spectra of purge and adsorption. Then the final spectrum was obtained at the end of TPD, also the end of one CO₂ adsorption/desorption cycle. Meanwhile, the spectrum of after TPD of cycle 1, is the spectra of pretreatment of cycle 2 as well. A significant heating/cooling process could be perceived form the temperature profile, demonstrated the performing of TPD process.

For an example, the 4 spectra obtained in cycle 1 of SRE5 sorbent were shown in Figure 15. The spectra directly obtained by Fourier transforming of IR interferogram spectra were called single beam spectra. Single beam spectra could be translate to other spectra conveniently by math calculation.
One of the most useful and commonly used scaling routines is the single beam to absorbance transformation. The single beam to absorbance transformation is done by the Eq 2 below.

\[
\text{Abs.} = \log \left( \frac{1}{I_{SB}} \right)
\]  

(2)

Where Abs. indicates the absorbance spectra, \(I_{SB}\) indicates the intensity of single beam spectra.

![Figure 15 Single beam spectra of SRE 5](image)

Figure 15 Single beam spectra of SRE 5
Figure 16 Absorbance spectra of SRE5

This translation could make the spectra more readable. As in the absorbance spectrum, the more the species in the sample, the higher the intensity of the characteristic peak of the certain species. The absorbance spectra processed from the single beam spectra of SRE 5 are shown in Figure 16. A normalization was occupied on these spectra to eliminate the effect of background shift follow the Eq 3.

$$I_{\text{norm}} = \frac{I - I_{\text{min}}}{I_{\text{max}} - I_{\text{min}}}$$  \hspace{1cm} (3)

Where $I_{\text{norm}}$ is the normalized IR intensity, $I_{\text{min}}$ is the minimum intensity and $I_{\text{max}}$ is the maximum intensity.
To further investigate the changes during the process, another spectra manipulation method was approached. The difference absorbance spectra was processed by applying one spectrum as background to process the other one. This manipulation could magnify the difference between two spectra for a convenient and high efficiency comparison. The difference absorbance spectra was obtained by the Eq 4.

$$\text{Diff. Abs.} = \log\left(\frac{1}{I_{BG}}\right)$$

(4)

Where $I$ indicates the intensity of spectrum needing to be processed; $I_{BG}$ indicates the intensity of background spectrum.
Difference absorbance spectra of SRE5 in first cycle was shown in Figure 17. The spectrum of pretreatment was occupied as the background spectrum. From the spectrum of adsorption, all these peaks could be attributed to the gas phase CO₂ and CO₂ adsorption species on the amine group. After purge, the gas phase CO₂ peaks disappeared. Meanwhile, the peaks indicating the adsorption species suffered a slightly drop. These drop parts of adsorption species demonstrated the weakly adsorption CO₂. Then after TPD, almost all the adsorption species desorbed form the sorbent and formed a linear spectrum. But slight fluctuation still could be observed on the spectrum after TPD, which could be attributed to the accumulated SO₂ on the sorbent.

2.4.3.6 MS data process method

Figure 18 shows the MS figure of SRE5 at cycle 1. Some important information could be investigated from this figure. The first peak appeared in the figure indicates the pre-adsorbed CO₂ desorb from the sorbent during pretreatment. The next 4 sharp peaks are created by the pulse calibration. The two small peaks are created by 1cc injection and the two large peaks are created by 3cc injection. Then the last peak in the figure could be attributed to the CO₂ desorbed during TPD. The relationship between volume of CO₂ and peak area in the MS figure could be determined by the pulse calibration. Then the volume of CO₂ desorbed during TPD could be calculated by the determined equation (Figure 19).
Figure 18 MS figure of SRE5 at cycle 1

Figure 19 Volume of CO2 vs MS peak area by pulse calibration
The other method to determine the capture capacity of each cycles in the experiment is oven capture capacity fitting method. The oven tested capture capacity was considered as the capture capacity of cycle 1. Then a CO$_2$ capture capacity to MS peak area ratio could be investigated and the capture capacity of later cycles could be calculated from this ratio.
2.5 Result

The result chapter is consist of optical microscope and SEM image, capture capacity and degradation ratio calculated from MS data, IR spectra analysis and a further discuss about the adsorption kinetic of CO$_2$ capture.

2.5.1 Optical microscope and SEM image of SRE sorbent

The OM image shows the structure of SRE5 sorbent, which is successfully pelletized by the SRE coating. The particle size of the sorbent is around 1mm. The SEM image shows the porous structure of SRE 5 sorbents. In the SEM image, the black dot on the sorbent was considered as the pores on the sorbent.
Figure 20 OM and SEM image of SRE5 sorbent
2.5.2 Capture capacity and degradation ratio

The initial capture capacity of prepared sorbents was tested by oven method and then fitted to the MS peak area of cycle 1 to calculate the capture capacity of other cycles. The calculated capture capacity and degradation ratio are shown in Table 4.

<table>
<thead>
<tr>
<th>Sample (1g)</th>
<th>Crosslinker</th>
<th>C1 Capture Capacity (mmol)</th>
<th>C20 Capture Capacity (mmol)</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CQA-12</td>
<td>/</td>
<td>3.37</td>
<td>2.93</td>
<td>13.06%</td>
</tr>
<tr>
<td>SRE5</td>
<td>5% sln.</td>
<td>2.92</td>
<td>2.38</td>
<td>18.48%</td>
</tr>
<tr>
<td>SRE7</td>
<td>7% sln.</td>
<td>2.7</td>
<td>2.39</td>
<td>11.48%</td>
</tr>
<tr>
<td>SRE10</td>
<td>10% sln.</td>
<td>2.52</td>
<td>2.42</td>
<td>3.97%</td>
</tr>
<tr>
<td>SRE15</td>
<td>15% sln.</td>
<td>2.46</td>
<td>2.38</td>
<td>3.18%</td>
</tr>
</tbody>
</table>

Several information could be investigated from the capture capacity and degradation ratio data:

1. The raw CQA-12 sample shows a highest initial capture capacity (capture capacity of cycle 1). All the pelletized sorbents shows a significant lower initial capture capacity due to the blocked amine sites by coating and pelletization process.

2. Sorbent pelletized with SRE5 binder solution shows the highest degradation ratio, which is even higher than the uncoated CQA-12. This could be attributed to that extra amine source in the binder solution was easier to be poisoned by SO₂.
(3) The degradation ratio of SRE series sorbents decreased with the increase of concentration of crosslinker, which demonstrated the effectiveness of SO$_2$ resistant coating. The SRE15 performed best degradation ratio of 3.18%, comparing to 13.06% of the raw CQA-12.

(4) The initial capture capacity of SRE series sorbent decreased with the increase of concentration of crosslinker. As the amine species in the coating was converted to tertiary amine, which could not absorb CO$_2$, by the crosslinker, leading to the capture capacity drop.

(5) SRE10 was considered as the best SO$_2$ resistant coating with optimal initial capture capacity drop and degradation ratio.

(6) Even though the initial capture capacity of coated sorbent is lower than CQA-12 after experiment, the SO$_2$ resistant coating was considered as an effective way to reduce the SO$_2$ poisoning for the long time operation in the industrial condition, which always operated for thousands of cycles.
The capture capacity decay curve was also drawn and linear fitting was performed on the decay curve. The fitting result shows that capture capacity of all the sorbent suffered a linear drop. Meanwhile, the slope of the decay curve was calculated and considered as an indicator of SO$_2$ resistant ability. The slope results shows that SRE15 and SRE10 performed a great SO$_2$ resistant ability, whose slope is near 0. This result is consistent to our previous degradation ratio result and further confirmed our previous conclusion.
2.5.3 SRE coating characterization by FT-IR

SRE10 coating, pure crosslinker and PEI was characterized by FTIR. The absorbance spectra are shown in Figure 22. Peak at 3367 cm\(^{-1}\) and 3299 cm\(^{-1}\) are the characteristic peaks of primary amine and primary/secondary amine respectively. The appearance of peak at 1456 cm\(^{-1}\) indicates the CH\(_2\) bend in the PEI molecular chain, which could considered as the characteristic peak of PEI. The sharp peak at 1510 cm\(^{-1}\) is attributed to the characteristic peak of crosslinker. In the spectrum of SRE10 coating, both 1510 cm\(^{-1}\) and 1456 cm\(^{-1}\) appears significant peaks, indicating that SRE10 coating was a production of PEI and crosslinker.
Figure 22 Absorbance spectra of SRE coating, pure crosslinker and PEI.

Meanwhile, both primary amine and primary/secondary amine peak at 3367 cm\(^{-1}\) and 3289 cm\(^{-1}\) suffers a significant drop comparing to the spectrum of PEI. Especially for the primary peak at 3367 cm\(^{-1}\), drop more than the peak at 3299 cm\(^{-1}\). This fact indicates that primary amine and secondary amine was successfully consumed by the crosslinker and converted to secondary/tertiary amine. As tertiary amine could not be characterized by IR
and Raman, the appearance of tertiary amine could only be speculated from the disappearance of primary and secondary amine. Based on the above description, the hypothesis of producing tertiary amine by crosslinking primary and secondary amine is confirmed.

Figure 23 Difference absorbance spectra of SRE10 coating in cycle 1 (Spectrum of pretreatment of cycle 1 was occupied as the background)

Figure 23 shows the difference absorbance spectra of SRE10 coating in cycle 1. Even though major amine species have been converted to tertiary amine by the crosslinker, there are still primary and secondary amine left and adsorbed slight amount of CO₂. The peak appear at 1643 cm⁻¹ indicates the generation of ammonium ion. Meanwhile, the peaks at 1558 cm⁻¹ and 1481 cm⁻¹ could be attributed to the formation of carbamate. Ammonium
ion and carbamate are considered as the production of CO₂ interaction with amine species, which has been mentioned in the previous chapter. On the spectrum of TPD, no significant adsorption species could be found, meaning that the coating could interact with CO₂ reversibly.

Figure 24 Different absorbance spectra of SRE10 coating of TPD in selected cycles. (Spectrum of pretreatment of cycle 1 was occupied as background)

Even though SRE10 coating performed great SO₂ resistant ability according to the degradation ration data, there are still slight accumulation of SO₂ on the coating. In Figure 24, the difference absorbance spectra of SRE10 of TPD in selected cycles, Peaks at
3012 cm\(^{-1}\), 1656 cm\(^{-1}\) and 1550 cm\(^{-1}\) could be assigned to the formation of ammonium ion. The peak at 981 cm\(^{-1}\) is the characteristic peak of sulfate. The appearance of these peaks indicates the accumulation of SO\(_2\). But due to the low intensity of these peaks, the amount of accumulated SO\(_2\) is small, and the accumulated SO\(_2\) is considered binding on the unconverted primary and secondary amine.

2.5.4 SRE Sorbent characterized by FT-IR

Figure 25 Difference absorbance spectra of SRE10 in cycle 1 at 4 different timing

Figure 25 shows the difference absorbance spectra of SRE10 in cycle 1 at the 4 different timing as mentioned previously. The high intensity of characteristic peaks of ammonium ion and carbamate in the spectra of adsorption indicates that huge amount of CO\(_2\) was
adsorbed by SRE10 sorbent. After purge process, the intensity suffered a slightly drop, indicating the weakly adsorbed CO$_2$.

Comparing the spectra of cycle 20 (Figure 26) to the spectra of cycle 1 (Figure 25), a significant intensity drop could be observed. This fact demonstrated that the accumulation of SO$_2$ reduced the CO$_2$ capture ability of sorbents.
Figure 27 Difference absorbance spectrum of after TPD of CQA-12 in selected cycles (the spectrum of pretreatment in cycle 1 was served as background)

Figure 27 shows the difference absorbance spectra of CQA12 sorbent at TPD in selected cycles. The intensity of spectra gradually increased as the experiment progressed. The peak at 3037 cm\(^{-1}\), 1658 cm\(^{-1}\) and 1527 cm\(^{-1}\) all could be attributed to the appearance of ammonium ion, as well as the appearance of peak at 981 cm\(^{-1}\) could be assigned to sulfate. Both ammonium ion and sulfate are production of SO\(_2\) interact with amine species. These peaks demonstrates the accumulation of SO\(_2\) on the sorbents, point out the importance of SO\(_2\) resistant coating. Meanwhile, a significant disappearance could be observed at 3367 cm\(^{-1}\), which indicates the primary amine, without drop at 3299 cm\(^{-1}\), the secondary
amine peak. This fact shows that SO₂ prefer to react with primary amine rather than secondary amine due to the high basic of primary amine.

Figure 28 Different absorbance spectra of TPD of sorbents at cycle 20 (Spectra of pretreatment of each sorbent in cycle 1 were served as background for the corresponding difference absorbance spectra)

Figure 28 shows all spectra of all the sorbents at TPD in cycle 20. The peak area of the spectra could indicate the amount of accumulation species on the sorbent. But unfortunately, no significant rule could be observed form this figure as the expectation. The low degradation ratio sorbent (SRE10) does not show a lower spectrum peak area comparing to the high degradation ratio sorbent (SRE5). This condition may due to the limitation of DRIFTS
method. According to the structure of DRIFTS cell shown in Figure 12, the DRIFTS method could only detect the top surface of the sorbent. Meanwhile, the top surface of the sorbent will directly contact with SO$_2$. So that SO$_2$ will accumulated more on the top surface of the sorbent, leading to the less difference between sorbents have good and bad SO$_2$ resistant ability.

Figure 29 shows the absorbance spectra of sorbents at pretreatment in cycle 1 and TPD in cycle 20. By comparing these two spectra, all the change happened on the sorbents during the experiment could be further investigated. The peaks at 3367cm$^{-1}$ (primary amine) shows a significant drop, as well as the peak at 3284cm$^{-1}$ (primary/secondary amine) did not reduced obviously, further confirming our previous conclusion that SO$_2$ prefer to react with primary amine rather than secondary amine. Meanwhile, a strong intensity increase could be observed at 1666cm$^{-1}$, which could be attributed to the C=O stretch of amide, the oxidation degradation production of amine species. This new observation demonstrated that SO$_2$ accumulation is not the only cause of capture capacity drop, oxidation degradation also played an important role in this fact. The effect of SO$_2$ accumulation on sorbent oxidation degradation need to be further discussed and investigated.
Figure 29 Absorbance spectra of sorbents at pretreatment of cycle 1 and after TPD of cycle
Figure 30 Difference absorbance spectra of sorbents at adsorption and purge of cycle 1

Figure 30 shows the difference absorbance spectra of sorbents at adsorption and purge of cycle 1 to further investigate adsorption species of sorbents. All the sorbents show peaks at 3012 cm\(^{-1}\), 1641 cm\(^{-1}\), indicating ammonium ion, and 1550 cm\(^{-1}\), 1492 cm\(^{-1}\), indicating
the carbamate. Meanwhile, a new peak at 1708 cm$^{-1}$, the characteristic peak of carbamic acid, could be discovered in Figure 30. The carbamic acid peak showing a much stronger drop during purge process comparing to the ammonium ion and carbamate peaks, demonstrates that the weakly adsorption species should majorly attribute to the formation of carbamic acid.

Figure 31 MS break through curve of SRE 5 at different cycles (a) break through curve of cycle 1; (b) break through curve of cycle 10; (c) break through curve of cycle 20 (d) comparison of CO2 break through curve in selected cycles
Figure 31 shows the MS break through curve of Ar, CO₂ and SO₂ on SRE5 sorbent in different cycles. The curve of Ar was inversed for a convenient analysis. The gap between Ar line and CO₂ line is considered as the absorbed CO₂ during CO₂ adsorption. According to (d), the CO₂ break through curve slightly raised after several cycles, indicating that CO₂ capture capacity of sorbents suffered a drop due to SO₂ accumulation. Meanwhile, the shape of the break through curve did not changed during the experiment, showing that the CO₂ adsorption kinetic did not be affected by SO₂ poisoning.

![Graph of absorbance vs wavenumber for SRE10-1 and SRE10-2 sorbents.](image)

Figure 32 Comparison of two batches of SRE10 sorbents. The better performed one was marked as SRE10-1, which has been reported previously. The second batches which performed bat capture capacity was marked as SRE10-2.
Figure 33 CO2 capture capacity cyclic data of 2 batches of SRE10 sorbents

All the SRE series sorbents were reproduced to test its reproducibility. All the sorbents were successfully reproduced except the SRE10 sorbent. It showed a significant stronger degradation under 40ppm of SO2. To investigate the difference between 2 batches of SRE10, absorbance spectra of these two sorbents at pretreatment of cycle 1 was compared in Figure 32. The badly performed SRE10-2 shows a significant peak at 1670cm\(^{-1}\), on the contrary, SRE10-1 did not have this peak. This peak could be assigned to the formation of C=O bond of amide, which is the oxidation degradation production of amine. This fact demonstrated that SRE10-2 suffered a series oxidation during the sorbent preparation. Meanwhile, the oxidation degradation could enhance the SO2 poisoning.
2.6 Conclusion

(1) SO$_2$ resistant coating was successfully prepared by convert primary/secondary amine to tertiary amine by crosslinker. The capture capacity degradation ratio was reduced form 13.06% to around 4%, achieving the quantitative goal.

(2) The species of SO$_2$ accumulated on amine sorbents was investigated by FT-IR technique. Ammonium ion and sulfate was considered as the major production of SO$_2$ reacting with amine species.

(3) SO$_2$ prefer to react with primary amine due to the higher basicity of primary amine comparing to secondary amine.

(4) SO$_2$ accumulation will (1) reduce the strongly absorbed CO$_2$ by consuming the aggregated amine species without lessening the weakly adsorbed CO$_2$; (2) not affect the CO$_2$ adsorption kinetic.

(5) Oxidation degradation may enhance the SO$_2$ accumulation.
2.7 Future work

(1) Further modify the components of SO\textsubscript{2} resistant coating to reduce the initial capture capacity and further enhance the SO\textsubscript{2} resistant ability;

(2) Test sorbents under higher SO\textsubscript{2} concentration;

(3) Long term degradation study (thousands of cycles);

(4) Characterize the aggregated amines and single amine on the sorbents;

(5) Investigate the effect of oxidation on SO\textsubscript{2} accumulation and capture capacity degradation;

(6) Evaluate the performance of SRE coating in presence of both water and SO\textsubscript{2};

(7) Attrition test of SRE pellet to test the physical strength of pellet.
CHAPTER III

PREPARATION OF HIGHLY POROUS PVA SUPPORT FOR SOLID AMINE SORBENTS BY SURFACTANT TEMPLATING METHOD

3.1 Introduction

This introduction mainly discussed the meaning of preparing highly porous support for solid amine sorbents. And then introduced background information and literature review of two highly porous material preparation method which was modified and occupied in this study.

3.1.1 Porous support for solid amine sorbents

Amine functionalized porous solid sorbents have been widely investigated as a promising technique for CO₂ capture. One of the most effective way to increase the capture capacity of porous solid sorbents is to increase the porosity, in other word, the specific surface area of the support material. Zeolites and active carbons was considered as one of major supports for solid sorbents as a traditional high porous material. Meanwhile, in recent years, lots of different kinds of porous support are also developed for CO₂ capture.
sorbents. Andrew R. Millward and Omar M. Yaghi reported a metal-hybrid porous frameworks generated some attentions due to its huge CO$_2$ storage capacity at high CO$_2$ partial pressure$^{51}$. But there are no sorbent prepared based on this material reported.

Mesoporous silica is a new kind of porous material developed recently and draw lots of attention from both academic and industrial due to its high porosity and low cost. MCM-41, which was discovered in 1992 by Mobil researchers$^{52}$, appears to be an excellent starting point of the synthesis of functionalized silica materials with large pore size and pore volume. With the modification of functional groups on silica, porous silica with different surface and chemical properties could be obtained$^{16,28,35,53-56}$. After the appearance of MCM-41, different kinds of silica were synthesized. Among all of these porous silica material, MCM-41, MCM-41, SBA-15 and KIT-6 were reported as a good choice for amine impregnation solid amine sorbent$^{57}$ due to the achieved high capture capacity sorbents.

3.1.2 Porous PVA preparation by phase inversion process

Polyvinyl alcohol (PVA) is a biocompatible hydrophilic polymer which is prepared by hydrolysis of polyvinyl acetate. In the USA, most of PVA is used in the textile industries serving as a sizing and finishing agent. PVA can also be incorporated into a water-soluble fabric in the manufacture of degradable protective apparel, laundry bags for hospitals, rags, sponges, sheets, covers, as well as physiological hygiene products$^{58}$. The pendent hydroxyl group on the PVA molecules makes PVA water soluble even with high molecular weight.
But, also due to the high molecular weight, PVA is easy to precipitate from solution by introducing non-solvent into the system, in other word, perform phase inversion.

Phase inversion is a widely used approach to prepare porous materials by a polymer/solvent/non-solvent system. The Flory-Huggins theory is typically used to describe the thermodynamic behavior of phase inversion (Eq 3).

$$\Delta G_m = RT \left[ n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12} \right]$$  \hspace{1cm} (3)

Which is an equation described the relationship between the Gibbs free energy and $n$ (the number of moles), $\phi$ (the volume friction), $R$ (the gas constant) and $T$ (the absolute temperature).

Figure 34 shows the typical ternary phase diagram of a polymer/solvent/non-solvent system. Each point inside the triangle indicates a mixture of the three component, and the three vertices of the triangle indicates three of each pure components. With the introducing of non-solvent in the polymer/solvent system (shown as the arrows in the ternary phase diagram), the system undergoes stable region, then metastable region, and finally enters the unstable region where the phase inversion happens.
In this study, a PVA/H$_2$O/acetone ternary system was adopted to perform phase inversion process for PVA. Meanwhile, to achieve higher porosity, poly(ethylene glycol) with molecular weight of 200 (PEG200) was used as a templates$^{59}$. To stable the porous structure produced by phase inversion, glutaraldehyde (GA), a widely used crosslinking agent for PVA, was used to interact with PVA to form a water-insoluble polymer network structure. The reaction mechanism of GA reacting with PVA was shown in Figure 35.
Figure 35 Reaction mechanism of PVA crosslinking with GA

Figure 36 Structure of surfactant self-association in solvent
3.1.3 Porous PVA preparation by surfactant templating method

Surfactant, which is the short of surface active agents, is defined as the molecules or ions which are amphiphilic, in other words, containing both a hydrophilic and hydrophobic part. It can frequently assemble at interface and self-associate to form various kinds of structure in the aqueous solution in an attempt to sequester their apolar regions from contact with the aqueous phase. Figure 36 shows the structure of surfactant self-association in the solvents. Slight amount of surfactant will form spherical micelles in the solvent first. With the increased amount, the surfactant will form rod shaped micelles, hexagonal phase, and finally form lamellar structure to reduce the area connecting to the solvent. The structure being reversed (reversed hexagonal phase and reversed micelles) or not are according to the Hydrophilicity of solvent and the structure of hydrophilic, hydrophobic groups in the surfactant.

Surfactants were widely used as a template to form a porous structure due to its ability to forming spherical micelles in the solvent. Ulrike Ciesla et. al. successfully prepared a highly porous zirconium oxo phosphate by surfactant templating at 1996, which is one of the early usage of surfactant as template in the preparation of porous material. lists literatures review of porous material prepared by surfactant templating methods.
In this work, SPAN 80, a commercialized nonionic surfactant, was used as the template for porous PVA. SPAN 80 is an ester mixture with fatty acid composition containing oleic acid (C18:1) ≤ 60% as well as balance primarily linoleic (C18:2), linolenic (C18:3) and palmitic (C16:0) acids. Figure 37 shows the structure of SPAN 80 with oleic acid as fatty
acid composition. SPAN 80 will form spherical micelles in the water solution with vigorous stirring. The formed spherical micelles could serve as a core for PVA phase inversion and nucleation in water. After PVA was crosslinked to fix the formed structure, the SPAN 80 could be washed away to form pores in PVA particles.

Figure 37 Structure of SPAN 80 with oleic acid (C18:1) as fatty acid composition
3.2 Experimental

In the experimental section, the preparation procedures of porous PVA support prepared by both phase inversion method and surfactant templating method were demonstrated. Meanwhile, the prepared porous PVA support was tested by ethanol uptake method to investigate the porosity and characterized in FT-IR to verify its thermal stability.

3.2.1 Material

Polyvinyl alcohol (PVA, Mw=75,000, Aldrich); Glutaraldehyde (GA, 25 wt% in water, Alfa Aesar); Tetraethylenepentamine (TEPA, Aldrich); Silicon dioxide (SIPERNT); Polyethylene glycol (PEG, Mw=200±10 g/mol; Mw=10,000, Sigma-Aldrich); Antioxidant (OA), SPAN 80 (Sigma-Aldrich).

3.2.2 Preparation of porous PVA support by phase inversion method

The crosslinked PVA support was prepared by phase inversion and crosslinking to create and fix the porous structure, respectively. In brief, it was prepared by flowing steps: (1) Dissolving 15g of PVA in 85g of deionized water and heating up to 90°C for 3 hours to form 15wt% PVA water solution; (2) Slowly adding 500g of hot PEG200 (around 100°C) into the PVA solution under vigorous stirring at 100°C to form PVA/PEG monolith; (3) Pulverizing the resulting PVA/PEG monolith in the blender for 5 minutes to obtain PVA particles; (4) Mixing PVA particles with 800ml of acetone, 3g of GA 25wt% water solution, adjusting the PH of the resulting mixture to 1 by hydrochloric acid (HCl), and keeping the
temperature at 55°C for 30 minutes to perform both phase inversion and PVA crosslinking simultaneously; (5) Filtering the crosslinked porous PVA particles form the mixture, washing them in acetone for 3 times and drying in the oven at 100°C for 1 hours.

Figure 38 shows the schematic of preparation of porous PVA support. The obtained porous PVA support was named as PPI, which indicates the porous PVA prepared by phase inversion.
H₂O (85g)

PVA₇₅K (15g)
Add

Dissolve at 90°C

PVA solution

PEG₂₀₀ (500g)
Heat at 100°C
Added slowly

Stir until a gel is formed
Sit for 5min

Pulverize in blender for 1min

1. Phase inversion in 800ml acetone at 55°C, PH =1
2. Crosslinking with 3g of GA(25%)

Filter and wash in acetone at room temperature for 3 times

Crosslinked Porous PVA particle (PPI)

Figure 38 Flow chat of preparation of porous PVA particle by phase inversion
3.2.3 Preparation of porous PVA support by surfactant templating method

Porous PVA support was prepared by surfactant templating method by following steps:

1. Dissolving 10g of PVA in 90g of deionized water to obtain 10 wt% PVA water solution;
2. Dissolving 1g of PEG200 and 1g of PEG10k in 80g of deionized water to form PEG water solution; 
3. adding 5g of PVA 10wt% water solution, 1.8g of SPAN 80, 0.8g of HCl and 1g of GA successively into the PEG water solution under vigorous stirring; 
4. Heating the solution system to 90°C for 2 hours to perform PVA/GA crosslinking to fix the templating porous structure under stirring; 
5. During this 2 hours, 1g of PVA 10wt% water solution was added every 10 minutes; 
6. Adding 500ml of ethanol into the system and keeping the temperature at 90°C for another 1 hours under vigorous stirring for the further crosslinking and washing the SPAN 80 and PEGs away from the PVA particles; 
7. Filtering the resulting porous PVA particles, washing it in ethanol for 3 times, and drying it in the oven at 100°C for 1 hour. The flow chat of this process is shown in Figure 39. The prepared porous PVA particle was named as PPS, indicating porous PVA prepared by SPAN 80 surfactant.

For the surfactant templating method, various components, experimental condition and procedure was tried: PPS-6 was sample prepared follow the standard method; PPS-10 changed the stirring speed from 600RPM to 1000RPM; PPS-6-II is the reproducibility test of PPS-6 particle; PPS-6-All in one was prepared by putting all the PVA at the beginning of experiment; PPS-6-No add. PVA did not add the additional PVA; PPS-6-5g per 30min
changed the way of adding additional PVA from 1g per 10 minutes to 5g per 30 minutes as a try of procedure simplification; PPS-6-5X5g per 30min quintuple the amount of all the materials of PPS-6-5g per 30min as an large scale testing. Table 6 shows the detailed components and experimental procedure of PPS series sample.

![Flow chat of preparation of porous PVA particle by surfactant templating](image)

Figure 39 Flow chat of preparation of porous PVA particle by surfactant templating
3.2.4 Preparation of porous PVA support by surfactant templating method

Porous PVA support was prepared by surfactant templating method by following steps:

1. Dissolving 10g of PVA in 90g of deionized water to obtain 10 wt% PVA water solution;
2. Dissolving 1g of PEG200 and 1g of PEG10k in 80g of deionized water to form PEG water solution;
3. Adding 5g of PVA 10wt% water solution, 1.8g of SPAN 80, 0.8g of HCl and 1g of GA successively into the PEG water solution under vigorous stirring;
4. Heating the solution system to 90°C for 2 hours to perform PVA/GA crosslinking to fix the templating porous structure under stirring;
5. During this 2 hours, 1g of PVA 10wt% water solution was added every 10 minutes;
6. Adding 500ml of ethanol into the system and keeping the temperature at 90°C for another 1 hours under vigorous stirring for the further crosslinking and washing the SPAN 80 and PEGs away from the PVA particles;
7. Filtering the resulting porous PVA particles, washing it in ethanol for 3 times, and drying it in the oven at 100°C for 1 hour. The flow chart of this process is shown in Figure 39. The prepared porous PVA particle was named as PPS, indicating porous PVA prepared by SPAN 80 surfactant.

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Figure 40 Flow chat of preparation of porous PVA particle by surfactant templating
Table 6 Components and experimental procedure of PPS series sorbents

<table>
<thead>
<tr>
<th>Name</th>
<th>Component (g)</th>
<th>Additional PVA</th>
<th>Stir speed (RPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVA 10% solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PEG20</td>
<td>PEG10k</td>
<td>SPAN80</td>
</tr>
<tr>
<td>PPS-6</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PPS-10</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PPS-6-II</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PPS-6-All in one</td>
<td>17</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PPS-6-No add. PVA</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PPS-6-5g per 30min</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PPS-6-5X5g per 30min</td>
<td>25</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
3.2.5 Preparation of CO$_2$ sorbents with porous support

Amine impregnation solution is needed to impregnate amine species on the porous support. The impregnation solution was prepared by the following steps: (1) Preparing solution 1 by dissolving antioxidant in the water; (2) Preparing solution 2 by dissolving PEI, PEG$_{200}$ in the ethanol; (3) Mixing solution 1 into solution 2 and stirring for 5min to obtain impregnation solution.

To prepare amine impregnated sorbent, the obtained impregnation solution needs to be mixed with porous support with the liquid to powder ratio = 1.5:0.5. The resulting mixture needs to be placed in the oven to get rid of the solvent under 100$^\circ$C for 1 hours. Finally the amine impregnated porous sorbent could be achieved.

There are three different support were used to prepare sorbent: a commercialized porous silica material (Silica-Sorb), PPI (PPI-Sorb) and PPS-6-5X5g per 30min (PPS-Sorb) (which has the highest porosity according to the test, the testing method and result will be discussed later).

3.2.6 Support porosity estimation by ethanol uptake method

The traditional BET method to test the porosity is time consuming. After correlate the BET result and material ethanol uptake result, the ethanol uptake method was considered as a fast and convenient method to estimate the porosity of porous material.

The ethanol uptake was measured by gradually dropping ethanol on the porous material
until saturation. The weight of sorbent \( m_{\text{sorbent}} \) and ethanol \( m_{\text{ethanol}} \) dropped on the support could be measured respectively. Then the ethanol uptake (ml/g) could be calculated by Eq 5:

\[
\text{Ethanol uptake} = \frac{m_{\text{ethanol}}}{\rho_{\text{ethanol}}} \div m_{\text{sorbent}}
\]  

(5)

3.2.7 Optical microscope and SEM image

Optical microscope (OM) and scanning electron microscope (SEM) were used to investigate the morphology of the porous material.

3.2.8 Thermal stability test of PPS particles by DRIFTS method

The same equipment setup which has been discussed in the previous chapter was used in this experiment. 30-50mg of PPS particles were placed in the DRIFTS cell. Then the DRIFTS cell was gradually heated up to certain temperature, kept for a long time, and then gradually cool down to the room temperature. The oxidation reaction happened on the sorbent could be investigated by the obtained IR spectra.

3.2.9 CO\textsubscript{2} capture capacity measurement by oven method

The capture capacity of prepared sorbents have been tested by oven method. The detailed procedure has been mentioned in the previous chapter.
3.3 Result

Ethanol uptake was discussed to investigate the effect of experimental condition on the porosity of sorbent. OM and SEM images was observed to figure out the morphology of the porous PVA support prepared by surfactant templating method. A thermal stability test was performed and recorded by IR spectra.

3.3.1 Ethanol uptake

The ethanol uptake result shown in the Table 7 shows that the PPS-6-5X5g per 30min sample performs best among the PPS series samples.

Table 7 Ethanol uptake results of PPS series sample

<table>
<thead>
<tr>
<th>Name</th>
<th>Ethanol uptake (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPS-6</td>
<td>13.65</td>
</tr>
<tr>
<td>PPS-10</td>
<td>11.1</td>
</tr>
<tr>
<td>PPS-6-II</td>
<td>13.18</td>
</tr>
<tr>
<td>PPS-6-All in one</td>
<td>/</td>
</tr>
<tr>
<td>PPS-6-No add. PVA</td>
<td>9.04</td>
</tr>
<tr>
<td>PPS-6-5g per 30min</td>
<td>18.4</td>
</tr>
<tr>
<td>PPS-6-5X5g per 30min</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Meanwhile, by analyzing the different experimental parameters in of different PPS particles, the effect of these experimental parameter could be investigated:

(1) The effect of stirring speed: Comparing the uptake of PPS-6 and PPS-10, the conclusion could be draw that the higher stirring speed reduced the porosity of support. This may due to the smaller micelles formed by SPAN 80 under a higher stirring speed. Meanwhile, PVA is also harder to aggregate on the SPAN 80 micelles due to the high stirring speed.
speed. Both facts lead to the same result that the particle size and pore size of PPS-10 is smaller than the PPS6, which could be further confirmed by the OM and SEM image.

(2) Reproducibility: The PPS-6 performs good reproducibility.

(3) The effect of additional PVA: The PPS-6-All in one sample formed a solid gel after the PVA solution was added into the reaction system even under vigorous stirring. This fact indicates the gradual addition of PVA solution is necessary for the formation of high surface area structure. The fast precipitation of large amount of PVA may be the reason of trunk formation. The PPS-6-No add. PVA showing a significant lower ethanol uptake, indicates the necessity of the additional PVA in a different aspect. The additional PVA will first form tiny PVA powder under vigorous and then aggregate on the already formed small PVA particle so that the PVA particles in the system grow larger and larger with the small PVA powder aggregation. The void space between small PVA powders could considered as the large pores in the whole particles, and the small pores were created by wash the surfactant and PEG in the powders. Finally the interconnected pore network could be created.

(4) Preparation procedure modification: the method to add the additional PVA into the system was changed from 1g per 10 minutes (PPS-6) to 5g per 30 minutes (PPS-6-5g per 30min). The ethanol uptake data shows that with the modified method, PPS-6-5g per 30min performed better porosity than the original PPS-6. This is an interesting phenomenon and need to be further discussed.
(5) Large scale test: the PPS-6-5X5g per 30min sample is a try of large scale preparation. Traditionally, the large scale test always produce a worse production comparing to the small scale experiment. But for this experiment, the PPS-6-5X5g per 30min performs best porosity in the PPS series samples. This fact indicates that this process could be easily occupied in the large scale production preparation.

3.3.2 OM and SEM image

Figure 41 shows the MS image of all the PPS series samples. All the OM images are shot under amplification ration of 400. It shows that PPS series samples have a similar microscopic structure that the large particles was an aggregation of small PVA powders. At the beginning, small PVA powders were formed due to the nucleation with the SPAN 80 tiny micelles as nucleus. Then with the additional PVA was added, these PVA firstly form the similar PVA powder under vigorous stirring, then aggregated with each other to form particles. The particles was then solidified by the crosslinking reaction between PVA and GA. And finally the PVA particles consisted of lots of small PVA powders was formed. With the slower stirring speed, the PVA powders are easier to be combined together by crosslinking reaction between GA and PVA. So that the PPS-10, which was prepared under stirring speed of 1000RPM, shows a significant smaller particle size comparing to the other PPS series samples.
Figure 41 OM images of PPS series sorbents (a) 400× OM image of PPS-6, (b) 400× OM image of PPS-10, (c) 400× OM image of PPS-6-II, (d) 400× OM image of PPS-6-No add. PVA, (e) 50× OM images of PPS-6-5×5g per 30 min, (f) 400× OM images of PPS-6-5×5g per 30 min
Figure 42 shows the SEM image of several PPS samples. In the picture, (a) and (b) are images of PPS-6 sample with amplification factor of 1500 and 5000 respectively; (c) and (d) are images of PPS-10 with amplification factor of 1500 and 5000 respectively; (e) and (f) are images of PPS-6-No add. PVA with amplification factor of 1500 and 5000 respectively; (g) and (h) are images of PPS-6-5X5g per 30min with amplification factor of 2000 and 5000 respectively. From the SEM images, it could be observed that all the small PVA powders have similar diameter, this may due to these PVA powder was created by the nucleation with the SPAN 80 core and the size of SPAN 80 micelles could be uniform under vigorous stirring. Meanwhile, there is another interesting fact that the size of PPS-6-5X5g per 30min is significantly smaller than the other PPS particles. This should due to the large scale preparation, but the size control parameter of the tiny PVA powders need to be further investigated.
Figure 42 SEM image of PPS selected series samples
3.3.3 PVA particles stability test

Two experiments were run to testing the thermal stability of PPS-6-5X5g per 30min sample by in-situ DRIFTS method. The first experiment was run by heating the sample up to 200°C and kept for 20min in presence of air.

The OM images were taken for the sample before and after experiment and shown in Figure 43. From the figure, no significant color change could be observed (PVA particles will turn to yellow if oxidation degradation happened), indicates that PVA particles are stable under 200°C.

Figure 43 OM image of PVA particle before and after heating
Figure 44 Absorbance spectra of thermal stability test by heating the PVA particle up to 200°C and kept for 20min
Figure 44 shows the absorbance spectra during heating and cooling. Peak at 3461 cm$^{-1}$ could be assigned to the hydrogen bonding between hydroxide groups (-OH stretch). Peaks at 2490 cm$^{-1}$ and 2858 cm$^{-1}$ could be attributed to C-H stretch on the PVA molecular chain. Peak at 1718 cm$^{-1}$ could be assigned to the C=O stretch, which is the oxidation production of hydroxide group on the PVA. The appearance of C=O bond on the spectrum before heating may due to the unhydrolized vinyl acetate molecular, as PVA was produced by hydrolization of poly(vinyl acetate). Meanwhile, C=O bond is also the production of PVA oxidation degradation. So, from the intensity change of peak at 1718 cm$^{-1}$, the thermal stability property of PVA could be investigated. The peak at 1241 could be ascribed to the C-O-C stretch (dialkyl), which indicates that GA was successfully reacted with PVA and formed C-O-C bond. According the IR spectra, PPS-6-5X5g per 30min sample shows a great thermal stability, as no significant intensity increase could be observed at 1718 cm$^{-1}$, as well as no intensity drop could be observed at 3416 cm$^{-1}$.

To further confirm the conclusion, peak profiles (Normalized to 0-1 to clearly show the intensity change) of peaks at 3461 cm$^{-1}$ and 1718 cm$^{-1}$ were processed and shown in Figure 45. Both peaks shows the similar intensity at the beginning and the end of experiment according to the peak profile data. The intensity increase during the experiment should be attributed to the background shifting due to temperature change during the experiment.
Another experiment was done to further testing the thermal stability of PPS-6-5X5g per 30min by heating the sample up to 200°C for 4 hours. IR spectra in Figure 46 shows that even after 4 hours of heating in presence of air, the PVA particles are still stable. Again, no significant intensity change could be observed at 3461cm\(^{-1}\) and 1718cm\(^{-1}\). The background spectrum (marked as BG) was taken when the temperature reached 200°C to get rid of the effect of background shift due to temperature changing. But from the peak profiles, a slight decrease at 3461cm\(^{-1}\) and slight increase at 1718cm\(^{-1}\) could be observed, indicates that the oxidation degradation happened during the experiment. Even though, the intensity drop is so slight that the oxidation degradation could be neglected.
Figure 46 Absorbance spectra of thermal stability test by heating PVA particles to 200°C for 4 hours

Figure 47 Peak profile of peaks at 1718 cm\(^{-1}\) and 3461 cm\(^{-1}\) during the thermal stability test
3.3.4 Stability in hot water

The stability test in hot water was performed by immersing the PVA particles into deionized water and placing them into the oven under 100°C for 12 hours. The size of the PVA particle shows a slight expansion after the experiment, and no significant dissolution could be observed by testing the water by FTIR. The IR spectra shown no characteristic peaks of PVA, indicating no PVA was dissolved in the water, in other words, all the PVA was well crosslinked by GA.

3.3.5 Capture capacity of prepared CO₂ sorbents

CO₂ sorbents tested in the experiment were prepared by mixing the impregnating solution with support and drying the solvent. Three different sorbents were prepared by using different support material: silica, PPI and PPS-6-5X5g per 30min. Among these three supports, the PPS-6-5X5g per 30min support performed highest ethanol uptake (22ml/g), PPI is the second highest one (14ml/g), and silica has the lowest ethanol uptake (8ml/g). But when comparing the CO₂ capture capacity measured by oven method (Table), the difference between capture capacities does not as significant as the difference between ethanol uptake. This phenomenon demonstrates that surface area is not the major key parameter of the CO₂ capture capacity, or at least not a key parameter after specific surface area reached to a critical point.
3.4 Conclusion

(1) High porosity PVA supporting materials were successfully prepared by phase inversion method and surfactant templating method.

(2) The parameters effecting the porosity of PPS series PVA particles were discussed.

(3) The stability of PPS particles in high temperature and hot water were tested. The PPS particles performed excellent stability both under high temperature and in hot water.

(4) The specific surface area (porosity) of supporting materials may not a key parameter effecting CO\textsubscript{2} capture capacity of sorbents.
3.5 Future work

(1) The relationship between support porosity and sorbent capture capacity need to be further investigated.

(2) Different method need to be applied on the prepared sorbent to further improve the capture capacity.

(3) The attrition test need to be performed on the prepared sorbents to test its physical property.

(4) Different crosslinkers need to be tried to crosslink PVA to overcome the disadvantages of GA, which is a toxic material and will make the PVA support fragile.
CHAPTER IV

IN SITU IR STUDY OF SO$_2$ ADSORPTION ON AMINE FUNCTIONALIZED POLY-MER SORBENT

4.1 Experimental

The sorbent used in the SO$_2$ adsorption study was mainly prepared by performing amine functionalization on PVA support by impregnation or crosslinking. (TEPA)/polyvinyl alcohol (PVA) sorbents (short as TEPA) were prepared as traditional amine impregnated sorbents, PEI-PVA sorbets (short as PP) is developed as the SO$_2$ resistant sorbents prepared by crosslinking process. All the sorbents were characterized by FT-IR.

4.1.1 Cross-linked porous PVA particle preparation

15% PVA solution was prepared by dissolving 7.5 g of polyvinyl alcohol (PVA F, Mw=75,000, hydrolysis=100%, Dupont) in 42.5 g of deionized water at 130 °C. 100 g of Polyethylene glycol (PEG, Mw=200, Alfa-Aesar) template was mixed with 50 g PVA solution at 130 °C under vigorous stirring, producing a templated gel. The gel was pulverized after decanting the excess solution. The pulverized gel was mixed with 900
ml of acetone for phase inversion of H₂O and removal of PEG 200. The resulting particles were vacuum filtered and this process was repeated four times. The vacuum filtered particles were dried at 70 °C for 30 min to remove acetone, producing the porous PVA particles. 7.5 g of porous PVA particles were cross-linked by mixing with 112.5 g of crosslinking solution containing 1% crosslinker, 5% acid, and 25% antioxidant and 69% H₂O at 50°C for 60 min.

4.1.2 Preparation of sorbent

TEPA sorbents were prepared by impregnating 1.0 g of cross-linked porous PVA with 9.0 g of a solution containing different amounts of tetraethylenepentamine (TEPA, Sigma-Aldrich), polyethylene glycol (PEG, Mw=200, Alfa-Aesar), crosslinker, and antioxidant in EtOH and DI H₂O. The impregnating solutions were prepared by combining solutions (1) and (2) together, which consisted of: (1) TEPA, PEG 200, crosslinker, and EtOH mixed at 80 °C for 5 min and (2) antioxidant and H₂O mixed at 25°C. The impregnated PVA particles were dried at 100°C for 60 min. The composition of the sorbents is summarized in Table 8.

PpC-15% sorbent was prepared by mixing 0.85g PVA particle and 0.3g PEI 50% water solution together and drying in the oven at 80°C for 5 hours. Finally the sorbent contain 85% PVA particle and 15% PEI was obtained.
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Nominal Composition (wt%)</th>
<th>N/OH ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Porous PVA (PP)</td>
<td>PEI</td>
</tr>
<tr>
<td>TP-23</td>
<td>48.44</td>
<td>22.7</td>
</tr>
<tr>
<td>TP-30</td>
<td>49.41</td>
<td>30</td>
</tr>
<tr>
<td>TP-34</td>
<td>48.44</td>
<td>34.1</td>
</tr>
<tr>
<td>PPc-15%</td>
<td>85</td>
<td>15</td>
</tr>
</tbody>
</table>

4.1.3 Preparation of PEI/PVA (PP) sorbents:

PVA/PEI/crosslinker solution was prepared by adding PEI (50% (w/v) in H2O, Sigma-Aldrich) to 10% PVA (Mw= 75000, Chemical store) solution and mixing with crosslinker ethanol soltuion with different concentration (Table 9).

Table 9 Concentration of PP sorbents (g)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crosslinker</th>
<th>PEI 50% water solution</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 0.2</td>
<td>2</td>
<td>0.57</td>
<td>1.37</td>
</tr>
<tr>
<td>PP 0.5</td>
<td>L-CL</td>
<td>2</td>
<td>1.37</td>
</tr>
<tr>
<td>PP 0.5</td>
<td>5</td>
<td>1.37</td>
<td>1.37</td>
</tr>
<tr>
<td>PP 1.0</td>
<td>10</td>
<td>2.59</td>
<td>1.37</td>
</tr>
</tbody>
</table>

* L-CL indicate low crosslink ratio

16 ml of H2O, 4 ml of ethanol (200 proof, Decon Labs), and 0.9 g of 33% water solution of non-ionic surfactant was mixed together and then added to PVA/PEI/crosslinker solution. The resultant mixture was heated to 75 °C for 5 h, cooled and diluted with water. The formed solids were recuperated by sedimentation, washed with water for two times.
and ethanol for two times and filterd with vacuum filtration, and dried in the oven at 100 °C. There are totally four kinds of different PP sorbent were prepared.

4.1.4 Sorbent characterization

FT-IR (Fourier Transform Infrared Spectroscopy) measurements were carried out using a DRIFTS (Diffuse Reflectance Infrared Fourier Transform, Spectra-Tech) cell placed in Nicolet 6700 FT-IR bench. The IR spectra were collected by 10 co-added scans, resolution of 4 cm⁻¹ at a rate of 6 scans/min for whole adsorption/desorption process.

The structure of DRIFTS cell has been discussed in the previous chapter.

The sorbent was pretreated initially by heating it to 120°C for 10 min in presence of Ar flowing at 150 cm³/min. A typical SO₂ capture cycle consists of the following steps: (i) exposing the sorbent to 1% SO₂/Air flowing at 150 cm³/min for 10 min at 55°C; (ii) purging the unabsorbed SO₂ from the DRIFTS cell with Ar flowing at 150 cm³/min for 10 min, (iii) performing temperature programmed desorption (TPD), where the inlet and outlet volves was closed and the DRIFT cell was heated to 135 °C and held for 3 min. Then the volves was open to let Ar flow to purge the desorbed SO₂ for 2 min. Finally The sorbent was then cooled to 55°C for next cycle. 4 SO₂ capture cycles were performed on each sorbent. The sorbent was heated to 135°C after 4 cycles and SO₂ calibration was subsequently performed by inject certain amount of SO₂ into the DRIFT cell and measure the peak area change of corresponding peak.
The Mass spectroscopy data for $SO_2$ and temperature change data of a typical $SO_2$ adsorption/desorption experiment was shown in Figure 4. The rough procedure could be obtained from these data. The IR spectra after pretreatment (short as Pret), adsorption (short as Ads), purge (short as Purg) and TPD were all marked in the figure.
4.2 Result and discussion

Figure 49 Absorbance spectra of TEPA and PP-15% sorbents

Figure 49 is the IR spectra of TEPA sorbent and PPC-15% sorbent. It shows characteristic bands at 3369 cm\(^{-1}\) (OH stretching), 2937 cm\(^{-1}\) (CH stretching) 1602 cm\(^{-1}\) (NH deformation) and 1459 cm\(^{-1}\) (CH deformation). These characteristic bands indicate that the amine is well impragnated on the PVA support. The PPC-15% sorbent is tested as reference because it is just a mixture of porous PVA and amine.
Figure 50 Difference absorbance spectra of Ads and Purg of TEPA sorbents

Figure 50 is obtained by using Pret spectrum as background to process the spectrum after Ads and Purg spectra. The intensity of spectra is in the following order: TEPA (T/P=3) > TEPA (T/P=2) > TEPA (T/P=1) > PPc-15%. Which indicates that the sorbent with high TEPA concentration adsorbed more SO₂. Meanwhile, for the TEPA and PPC-15% sorbent, only slight desorption happen during the purge process inferred from the similar Ads and Purg spectrum. This is on account of the strong binding between SO₂ and sorbent. But also due to the strong binding, SO₂ could not desorb from the sorbent during TPD, which is demonstrated by the spectrum after TPD (Figure 51).
Figure 51 indicate that even after TPD, there are still significant peaks, such as 3000 (NH$_3^+$), 1631 (SO$_4^{2-}$) and 1195 (SO$_4^{2-}$), appearing in the spectrum. The NH$_3^+$ and SO$_4^{2-}$ ions are formed by the interaction between SO$_2$ and amine group. These peaks indicate that there is still significant amount of SO$_2$ accumulated in the TEPA sorbent and does not desorb during TPD. To confirm this conclusion, the difference absorbance spectra of Ads and Purg of TEPA sorbents at cycle 4 are also processed (Figure 52). All the spectrum suffer a significant intensity drop. Even in a much smaller scale (0.1 compare to 0.2 in the spectra of cycle 1), this drop still could be observed clearly, especially for T-30 and T-34 and PPc-15% sorbents. This means the degradation happens on the sorbents. For T-
23 sorbent, the degradation is much smaller. But after more cycles, finally it will lost the ability to capture SO₂.

Figure 52 Difference absorbance spectra of Ads and Purg of TEPA sorbents at cycle 4

The IR spectrum of PP sorbents (Figure 53) shows the characteristic bands at 3413 cm⁻¹ (OH stretching), 2962 cm⁻¹ (CH stretching) 1606 cm⁻¹ (NH deformation) and 1459 cm⁻¹ (CH deformation). The characteristic feature of NH stretching at 3361 and 3301 cm⁻¹ for PP sorbents cannot be distinguished as they are overlapped by broad OH band of PVA. PP sorbent has more peaks in the spectrum compare to the absorbance spectrum of TEPA sorbent, which demonstrates that the structure of PP sorbents is much more complex than TEPA sorbent. Because in the PP sorbents the amine species is binded to the PVA
support by colvalent bond due to crosslinking, compare to the TEPA sorbents, the amine species is binded to PVA support by the hydrogen bond between amine group and hydroxial group and the formation of covalent bond lead to more complex structure.

Compare the spectra of PP 0.5 L-CL and PP 0.5, a significant peak intensity difference could be observed. Which indicates that the PP 0.5 L-CL have lower amine density than the PP 0.5 due to the different crosslink ratio. TGA technique was used to confirm the crosslink ratio difference (Figure 54).

![Figure 53 Absorbance spectra of PP sorbents](image)

1. 3413
2. 2962
3. 1606
4. 1459
5. 1255
6. 1039
7. 1039
8. 4000
9. 3500
10. 3000
11. 2500
12. 2000
13. 1500
14. 1000
15. PP 0.2
16. PP 0.5 L-CL
17. PP 1.0
Figure 54 TGA data for PP 0.5 and PP 0.5 L-CL

Figure 54 indicates that PP 0.5 sample start to degrade from 241°C and the PP 0.5 L-CL sample start to degrade from 206 °C. (defined as 5% weight dropped). The higher degradation temperature shows that the PP 0.5 is actually have higher crosslink ratio. So the conclusion could be drown that the crosslink ratio is a important parameter to affect the amine loading by effect the bond formation between amine species and PVA support.

Comparing the spectrum of PP 0.2 and PP 0.5 L-CL, it could be found that the PP 0.5 L-CL still has lower peak intensity even with higher PEI concentration. This maybe due to that with higher PEI concentration, the crosslinker is not enough to bind all the PEI to the PVA support. The viscosity of the reaction system of PP 0.5 L-CL is much higher than that of PP 0.2 could also evidence this hypothesis. Because the high viscosity maybe
due to the excess PEI in the solution. Finally the excess PEI was all washed away during the washing process and lead to the low amine density of PP 0.5 L-CL. So with higher crosslinker concentration, the intensity of spectrum of PP 0.5 is higher than that of PP 0.5 L-CL under same PEI concentration. But there is other fact that the peak intensity of high crosslinked PP sorbents are similar to each other. A further study need to be done in the future to explain this observation.

![Absorbance spectra of Ads and Purg of PP sorbents at cycle 1](image)

Figure 55 Absorbance spectra of Ads and Purg of PP sorbents at cycle 1

Figure 55 is the difference absorbance spectra of Ads and Purg on various PP sorbents. The spectrum of Pret was used as background for this difference absorbance spectrum. Absorbance peaks at 1371 cm\(^{-1}\) and 1348 cm\(^{-1}\) in the adsorption spectrum indicates the gas phase SO\(_2\). The adsorption spectrum exhibits characteristic bands at 3297 cm\(^{-1}\) (OH), 3012
The peak intensity of PPE 0.5 L-CL is significantly lower than PPE 0.2. This means that the PP 0.5 L-CL have lower ability to absorb SO$_2$, which also fits to the previous statement that the PP 0.5 L-CL has lower amine loading.

A significant difference between Ads and Purg spectra of PP sorbents could be observed. It demonstrates that there is some SO$_2$ desorb during the purge process and indicates the weaker binding between SO$_2$ and PP sorbents compared to the TEPA sorbents. The weak binding leads to the easily desorption of SO$_2$, which could be evidenced at TPD spectra (Figure 56). The TPD spectra of all the sorbents are nearly a straight line,
demonstrates that all the absorbed SO$_2$ desorbed from sorbent and there was no SO$_2$ accumulated in the sorbent.

The fact that SO$_2$ desorb during purge process could also be evidenced by the peak tendency spectrum of peak at 1371 cm$^{-1}$, 1135 cm$^{-1}$ and 998 cm$^{-1}$ (Figure 57), where the peak intensity of 1135 cm$^{-1}$ and 998 cm$^{-1}$ decrease a lot during purge. Meanwhile, this decrease just happen when the Ar start to flow.
Figure 57 Peak tendency spectrum of well crosslinked PP sorbents
For PP 0.5 and 1.0 sorbents, there is no SO$_2$ left after purge, as the Purg spectrum of these two sorbents is nearly a line. But for PP 0.2 sorbent, there is still significant peaks left in the spectrum after Ar purge, which indicates that PP 0.2 could storage SO$_2$ after adsorption.
Figure 58 Difference absorbance spectrum at different temperature during TPD (TPDT)
The observation that only PP 0.2 sorbent could storage SO$_2$ could be evidenced by the difference absorbance spectra at different temperature during TPD (short as TPDT) (Figure 58). This spectra are obtained by using spectra at different temperature during the cooling stage of TPD, to process the spectra at the same temperature during the heating stage of TPD. TPDT of PP 0.2 shows a significant peak rising at 1371 cm$^{-1}$ (gas phase SO$_2$), which indicate that there is SO$_2$ desorbing from the sorbent during TPD process. But for PP 0.5 and 1.0, even the peak at 1371 cm$^{-1}$ increase, the shape of peaks is not same to the gas phase SO$_2$ peak. So this raise is not due to the desorption of SO$_2$. Thus, there is no SO$_2$ desorb from the PP 0.5 and 1.0 sorbents. All the absorbed SO$_2$ on PP 0.5 and 1.0 desorbed during the purge section.

Figure 59 Difference absorbance spectra of Ads and Purg of PP sorbents at cycle 4
There are two hypotheses provided to explain the phenomenon that PP 0.2 and PP 0.5, 1.0 have different property. First hypothesis is that there are two different mechanisms for SO$_2$ adsorbed on the PP sorbent. The one could form strong bonding, the other one will creat weak binding. In PP 0.2, these two mechanisms all work, and creat two different binding. But for PP 0.5 and 1.0, only the mechanism which creat weak binding works, so all the absorbed SO$_2$ could easily desorb form PP 0.5 and 1.0 sorbents. The other hypothesis is OH group could increase the binding strength between SO$_2$ and sorbent. For PP 0.2, The density of OH group is high, so the effect of OH group make the binding stronger. For PP 0.5 and 1.0, the OH lower density lead to the weaker binding. The actual mechanism of SO$_2$ adsorption on PP sorbents will be further studied to find the right answer to this phenomenon.

Even the PP 0.5 and 1.0 sorbents could not storage SO$_2$ for long time, but all the absorbed SO$_2$ could desorb form these sorbents, which is a large advance compare to the TEPA sorbents. The difference absorbance spectra of Ads and Purg of PP sorbents at cycle 4 (Figure 59) is shown to confirm that there are no SO$_2$ accumulation on the PP sorbent. From the comparation between Figure 59 and Figure 55, it could be found that the shape and intensity of spectra do not suffer any significant change. This demonstrate that there are no degradation happen on PP sorbents. This is different from the TEPA sorbent, which have large amount of SO$_2$ accumulation. This difference maybe on account of the formation of tertiary amine. Due to the reaction between PEI and
crosslinker, the primery and secondary amine on the PEI molecular will be transferred to tertiary amine. Different with the reaction mechanism of primery and secondary amine interact with SO$_2$ by forming ammoniom ion and sulfate and creat covalent bond, the tertiary amine interact with SO$_2$ by complexation and do not form actual bond. So the binding strength of this bond is much lower than that of covalent bond. This weak binding should lead to the easy desorption of SO$_2$.

Figure 60 Difference absorbance spectrum of calibration

The SO2 capture capacity of PPE sorbent was estimate by the batch calibration process.

The calibration data and leanear fitting result are shown in Figure 60 and Figure 61.
60 is the Difference absorbance spectrum of calibration, which is obtained by using spectrum before calibration as background to process the spectrum after every SO2 injection. There are five SO2 injection: 0.2, 0.2, 0.2, 0.4, 0.4, totally 1.4cc 1%SO2/Air mixture injected to the DRIFT cell. The peak area of peak at 1371 cm\(^{-1}\) is measured and corresponded to the amount of SO\(_2\). Then the peak area of peak at 1371 cm\(^{-1}\) is also measured for spectrum of PPE 0.2 at 135°C during TPD (Figure 60). Then the SO\(_2\) capture capacity of PPE 0.2 sorbent is calculated: 0.0204 mmol/g. But this SO\(_2\) capture capacity is not the actual result. Because there is significant amount of SO2 desorb during the purge process. To estimate the actual SO\(_2\) capture capacity, the peak area of 1135 cm\(^{-1}\) at Ads and Purg spectra of PP 0.2 are measured. The SO\(_2\) capture capacity calculated from calibration is corresponding to the peak area of Purg spectrum, and the actual SO\(_2\) capture capacity is corresponding to the peak area of Ads spectrum. Finally, the actual SO\(_2\) capture capacity is calculated: 0.0592 mmol/g.
Figure 61 Calibration data and linear fitting result

<table>
<thead>
<tr>
<th>Peak Area</th>
<th>SO2 Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.094</td>
<td>0.2</td>
</tr>
<tr>
<td>0.178</td>
<td>0.4</td>
</tr>
<tr>
<td>0.321</td>
<td>0.6</td>
</tr>
<tr>
<td>0.48</td>
<td>1</td>
</tr>
<tr>
<td>0.664</td>
<td>1.4</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Equation</th>
<th>y = a + b*x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>No Weight</td>
</tr>
<tr>
<td>Residual Sum of Squares</td>
<td>0.0058</td>
</tr>
<tr>
<td>Pearson's r</td>
<td>0.99687</td>
</tr>
<tr>
<td>Adj. R-Squ</td>
<td>0.99167</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2 Volum Intercept</td>
<td>-0.005</td>
</tr>
<tr>
<td>SO2 Volum Slope</td>
<td>2.0885</td>
</tr>
</tbody>
</table>
4.3 Conclusion and future work

In this research, PP sorbent was prepared as the SO$_2$ resistance sorbent, which could absorb SO$_2$ reversibly. FTIR spectroscopy was used as the major study tool on development of sorbent and the mechanism of SO$_2$ adsorption. SEM and TGA were also used to study the structure of PP sorbents and the effect of crosslink ratio on the amine density on the PP sorbents. The SO$_2$ capture capacity of best PP sorbent, PP 0.2, was tested as 0.0592 mmol/g by the batch adsorption/desorption study and batch calibration. TEPA sorbents were also tested as the traditional amine impregnated polymer sorbent, to study the mechanism of SO$_2$ accumulation. The hypotheses on the SO$_2$ adsorption/desorption process were also provided.

As a new finding that amine functionalized sorbent could absorb SO$_2$ reversibly, there are lots of future work need to be push forward. Improve the SO$_2$ capture capacity with keeping SO$_2$ resistant property is the most pressing issue in the future. The CO$_2$ capture study on this SO$_2$ resistant sorbent is also required. To verify the hypotheses, the mechanism study is also required. The modification of traditional CO$_2$ sorbent is also a good way to reach the final goal of this research.
1 Salazar, E. Global And Regional Markets For CCS Infrastructure And Equipment, 2008-2037. (SBI Energy, 08. 2013).


5 Puren, N. Carbon Capture, Utilization & Storage Technologies. (BBC Research, 02. 2015).


