IN SITU FTIR AND TUBULAR REACTOR STUDIES FOR CO₂ CAPTURE OF
IMMOBILIZED AMINE SORBENTS AND LIQUID AMINE FILMS

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IN SITU FTIR AND TUBULAR REACTOR STUDIES FOR CO₂ CAPTURE OF
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ABSTRACT

In situ Fourier transform infrared spectroscopy (FTIR) and tubular reactor studies with mass spectrometry (MS) revealed the mechanisms and kinetics of CO$_2$ diffusion and adsorption/desorption for immobilized amine sorbents and liquid amine films. CO$_2$ mass transfer limitations of immobilized tetraethylenepentamine (TEPA)/silica sorbents were studied by a novel in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique using benzene as a surrogate CO$_2$ probe molecule. Results showed that (i) adsorbed CO$_2$ creates an interconnected network of ammonium-carbamate ions and carbamic acid that inhibits CO$_2$ diffusion, and (ii) readsorption of desorbed CO$_2$ along the pore wall and at the external surfaces limits the CO$_2$ removal rate from the sorbent.

CO$_2$ diffusion and adsorption/desorption for different thicknesses of TEPA films were investigated by attenuated total reflectance (ATR) and DRIFTS. Results showed that CO$_2$ strongly adsorbed to NH and NH$_2$ at the top surface of thicker films and formed a strongly bound, interconnected network that reduced the access of CO$_2$ to the bulk amines.

Adsorption/desorption of CO$_2$ onto/from immobilized amine particle and pelletized sorbents was studied in a tubular reactor set-up to investigate the sorbents’ performance under different operating conditions. Results showed enhanced CO$_2$
capture on the sorbents in the presence of H₂O vapor (wet adsorption), likely resulting from liberation of previously inaccessible amine groups of TEPA. Increasing the CO₂ partial pressure by pulsing pure CO₂ after wet adsorption, and steam regeneration of the adsorbed species in the CO₂ gas environment allows the desorbed CO₂ concentration to reach 99+%.

A novel, cross-linked porous PVA support (PPc) was synthesized and impregnated with TEPA, polyethylene glycol 200 (PEG), and other additives for testing as a low cost and stable CO₂ capture sorbent. Results showed that PPc exhibited high surface area and pore volume similar to those of silica. Increasing the PEG-OH/TEPA-N ratio of the sorbent enhanced its CO₂ capture performance due to dispersion of the NH₂ and NH groups by PEG. In situ DRIFTS studies showed a weaker binding strength of CO₂ to the amines of the PPc-supported than silica-supported sorbent, suggesting that using PPc sorbents could reduce the cost of sorbent regeneration.
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CHAPTER I

INTRODUCTION

According to the United States National Oceanic & Atmospheric Administration (NOAA), the global CO$_2$ greenhouse gas concentration has increased from 333.8 ppm in 1980 to 392.5 ppm in 2012 [1]. The National Aeronautic and Space Administration (NASA) showed that the increased atmospheric CO$_2$ concentration in 2012 is correlated with a 0.56 °C rise in the overall mean global surface temperature [2]. One study concluded that the rise in global surface temperature is responsible, in part, for the increased frequency and power of hurricanes and storms. Because 34% of CO$_2$ emissions in the U.S. result from coal combustion in power plants to produce energy [3], it is essential to develop a technology to mitigate these emissions.

Solid, immobilized amine sorbent technology has been widely studied for the removal of CO$_2$ using simulated power plant flue gas conditions (55 °C, 5-15% CO$_2$/0-10% H$_2$O vapor/air) because of the sorbents’ low heat of regeneration, reduced equipment corrosion, and enhanced CO$_2$ mass transfer compared to the conventional liquid amine technology [4-6]. Immobilized amine sorbents have been organized into three classes [7]: (1) porous supports physically loaded with amines, (2) porous supports covalently bonded to amines via silane chemistry and (3) porous polymer supports covalent attached to amine (combination of class 1 and 2). Commonly used supports include (i) silicas: MCM-41, SBA-15, precipitated, and fumed; (ii) zeolites: β-zeolite,
zeolite Y60, and zeolite 13X; (iii) carbons: activated carbon, fly ash, and carbon nanotubes and (iv) polymers: polymethylmethacrylate (PMMA), acrylonitrile, and polystyrene. Amines that are loaded onto the previously mentioned supports for class (1) sorbents include polyethyleneimine (PEI), tetraethylenepentamine (TEPA), monoethanolamine (MEA), and diethanolamine (DEA). These loaded amines contain a combination of N, NH, and NH$_2$ groups which capture CO$_2$ via nucleophilic addition of the nitrogen atoms to carbon atoms. Silanes covalently bonded to the supports for class (2) sorbents include 3-aminopropyltrimethoxysilane (APTS) and 3-aminopropyltriethoxysilane (APTES).

For practical application, the sorbent particles have to be pelletized. Pelletization of the sorbent is accomplished by mixing the sorbent with a polymer binder solution, extruding the resulting wet mixture into rods. The wet rods are placed onto a rotating metal disk set inside of a cylindrical metal chamber, which transforms the rod structure into a sphere. The polymer binder, such as polyvinyl alcohol (PVA), forms a molecular network around the outer surface of the sorbent particles through hydrogen bonding between support-OH and PVA-OH groups. The rigid network of the PVA-bonded sorbent produces pellets which are resistant to attrition during extensive cycling in various CO$_2$ capture systems.

One key issue associated with the performance of immobilized amine sorbents is the mass transfer limitations of CO$_2$ into and out of the sorbent pores. Amine structure [8] and loading [9], sorbent pore structure [10], reaction temperature [9], and the presence of additives [11] have been shown to affect the intraparticle CO$_2$ diffusion. The CO$_2$
diffusion limitations could slow the time of the adsorption-desorption cycle, resulting in higher operating costs.

Another key issue is identifying the correct adsorption/desorption mechanisms of CO$_2$ onto/from the amines, which directly affect the chemical and physical properties/structures of the adsorbed species, and also the system cycling performance. Understanding the nature of adsorbed CO$_2$ produced by the reaction with different liquid amines and amines immobilized on different supports would provide a basis for optimizing the sorbent formulation.

Numerous reactor systems utilizing immobilized amine sorbents and pellets have been developed for testing the removal of CO$_2$ from simulated flue gas under practical conditions. The most common systems are fixed bed [5, 8, 12, 13], fluidized bed [14], and circulating fluidized bed [15, 16] reactors. These reactor systems accommodate amounts of sorbent varying from 0.5 g to 2.4 kg and treat simulated flue gas with gas flow rates varying from 0.5 mL/min to 30 L/min. Concentrating the desorbed CO$_2$ to near 99% purity is essential for low cost compression and sequestration underground. CO$_2$ desorption by contacting the CO$_2$-adsorbed sorbent directly with steam, i.e. regeneration, has recently gained attention because of steam’s low cost-high energy benefit and because steam can be condensed and removed from the outlet stream, producing the high purity CO$_2$ [17]. Additional approaches to increase the desorbed CO$_2$ concentration could also include sorbent regeneration in a high purity CO$_2$ environment [16].
The outline for the projects comprising this dissertation research is shown below in Figure 1.1.

The mass transfer and adsorption-desorption mechanism of CO₂ gas within different immobilized amine sorbents and liquid amine films were studied by transient in situ infrared spectroscopy and mass spectrometry techniques. The CO₂ capture performances of immobilized amine sorbent particles and pellets using different operating conditions were also studied under practical conditions using a tubular reactor set-up.
spectroscopy elucidates the fundamental reactions occurring on the surface of the sorbents and within the amine films, and also the diffusion and reaction kinetics. Mass spectrometry monitors the gas phase concentration of reactive and inert species, revealing the adsorption-desorption characteristics of the particles and pellets and also the gas flow pattern through the system.
CHAPTER II

BACKGROUND

2.1 Overall CO2 Capture and Sequestration Costs

Because coal-fired power plants constitute a significant portion of global CO2 emissions, extensive efforts have been devoted to developing post-combustion technologies to remove these emissions. Removal of CO2 emissions from the power plants could be achieved by retrofitting the existing plants or constructing new plants equipped with this technology. A study reported by the Internal Energy Agency (IEA) reported that retrofitting the existing infrastructure is economically feasible only for plants with an efficiency above 33% [18]. Typical power plant efficiencies range between 27% and 55% [19], and can depend upon the conditions of the steam used by the turbines. Lower efficiencies around 39% have been achieved with the use of subcritical steam (538°C, 167 bar) and higher efficiencies between 42 and 47% have been achieved with supercritical (540-566 °C, 250 bar) and ultra-supercritical (580-620 °C, 270-290 bar) steam [19]. Coal-fired power plants recently commissioned in 2010 have output capacities ranging from 4 MW to 879 MW [20].

Commonly studied technologies for the remediation of CO2 emissions include (i) the post-combustion liquid monoethanolamine (MEA) absorption process, (ii) the pre-combustion oxy-fuel process, and (iii) the post-combustion chilled ammonia process.
The commercially implemented liquid (MEA) absorption process involves (i) contact of the CO₂-containing flue gas with a counter-current stream of CO₂-lean aqueous amine solution in the adsorber at 1 atm and 40-60 °C for CO₂ adsorption and (ii) transfer of the CO₂-rich solution into the desorber at 100-120 °C for desorption of CO₂ [21]. The oxy-fuel combustion process involves (i) the removal of N₂ from the flue gas by an air separator to increase the O₂ content, (ii) the combustion of coal with the O₂-rich flue gas in the furnace, and (iii) the cleaning of the flue gas and recycling of a portion of the gas back to the furnace [22]. The chilled ammonia process involves (i) the cooling of the flue gas to 0-20 °C in a chiller, (ii) the counter-current contact of the chilled flue gas with CO₂-lean ammonia solution, such as 28 wt%, at 0-20 °C and 1 atm in the absorber and (ii) the high pressure pumping of the CO₂-rich solution to the desorber at 50-200 °C and 2-136 atm [23]. Although not currently commercialized, solid immobilized amine sorbents are a viable option to remove CO₂ emissions, where adsorption occurs between 50-60 °C and 1 atm and desorption occurs between 100-130 °C.

In order to compare the costs of the different processes two economic indicators are often used, which included cost of electricity (COE) or levelized cost of electricity (LCOE) and cost of CO₂ avoided. The COE, shown below in Eq. 2.1, has been defined as the annual power plant (TC\textsuperscript{PP}) plus carbon capture (TC\textsuperscript{capture}) costs (capital plus variable operating) divided by the annual electricity production (E) [24].

Eq. 2.1: Cost of electricity, COE.

\[
\text{COE} = \frac{TC^{PP} + TC^{capture}}{E}
\]
LCOE is similar to COE, and is defined as the sum of discounted CO₂ capture costs divided by the annual production of electricity [25]. The CO₂ avoided cost is defined in Eq. 2.2

Eq. 2.2: Cost of CO₂ avoided.

\[
\text{CO}_2\text{avoided} = \frac{\text{COE}_{\text{with removal}} - \text{COE}_{\text{ref.}}}{\text{CO}_2\text{ emissions}_{\text{ref.}} - \text{CO}_2\text{ emissions}_{\text{with removal}}}
\]

Table 2.1 shows a cost comparison between the reference plants (ref.) and plants with 85 to 90 %CO₂ capture (cap.) for different CO₂ capture processes. Overall, post-combustion capture with MEA and chilled ammonia reduce the power plant efficiency by about 10-12 percentage points, however the costs for the MEA process can be slightly higher. It can also be seen that the MEA and chilled ammonia processes possess the highest electricity costs and CO₂ avoided costs, likely resulting from the high energy requirement in heating the aqueous amine solutions for desorbing CO₂.

The analysis presented for the alkalized alumina solid sorbent process was performed by incorporating bench-scale data into a modified, existing cost analysis model used for a liquid MEA process and also a capital cost analysis from Babcock&Wilcox (B&W). Results for the alkalized alumina revealed lower CO₂ capture costs compared to the MEA process, which could be attributed in part to the energy required to desorb CO₂ from the alumina (12.5-41.4 kJ/mol), which was lower than that required for the MEA solution (59.5 kJ/mol).

The objective of the analysis for the immobilized amine/SBA-15 sorbent was to analyze detailed component costs for CO₂ capture and storage [26]. It was found that for
a CO$_2$ capture capacity of 6.0 mmol/g-sorb and a low heating requirement of 620 Btu/lb CO$_2$ (sensible heat+heat of vaporization), the amine sorbent process cost of electricity was 9% lower than that of the MEA process. However, the replacement cost of the sorbent was 22 MM$/yr compared to 8.1 MM$/yr for MEA. Further detailed studies are needed to confirm the cost-effectiveness of immobilized amine sorbent technology.

Table 2.1: Cost comparison between different CO$_2$ capture technologies.

<table>
<thead>
<tr>
<th>Category</th>
<th>MEA Absorption</th>
<th>Oxy-fuel</th>
<th>Chilled Ammonia</th>
<th>Solid sorbents*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>[27]</td>
<td>[28, 29]</td>
<td>[30]</td>
<td>[29, 32]</td>
</tr>
<tr>
<td>Steam turbine</td>
<td>Super critical</td>
<td>Super critical</td>
<td>Super critical</td>
<td>Super critical</td>
</tr>
<tr>
<td>Gross plant output (MW$_e$)</td>
<td>Ref.: 580</td>
<td>Ref.: 575</td>
<td>Ref.: 865</td>
<td>Ref.: 580</td>
</tr>
<tr>
<td></td>
<td>Cap.: 662</td>
<td>Cap.: 1203</td>
<td>Cap.: 710</td>
<td>Cap.: 491</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$ capture efficiency (%)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Net plant output (MW$_e$)</td>
<td>Both: 550</td>
<td>Both: 549</td>
<td>Both: 549</td>
<td>Ref.: 550</td>
</tr>
<tr>
<td></td>
<td>Cap.: 528</td>
<td>Cap.: 454</td>
<td>Cap.: 454</td>
<td>Cap.: 590</td>
</tr>
<tr>
<td>Plant efficiency (%)</td>
<td>Ref.: 39.3</td>
<td>Ref.: 41.4</td>
<td>Ref.: 41.8</td>
<td>Ref.: 39.3</td>
</tr>
<tr>
<td></td>
<td>Cap.: 28.4</td>
<td>Cap.: 28.4</td>
<td>Cap.: 39.4</td>
<td>Cap.: 30.4</td>
</tr>
<tr>
<td>LCOE ($/MWh)</td>
<td>Ref.: 74.7</td>
<td>Ref.: 62</td>
<td>Ref.: 56.7</td>
<td>Ref.: 74.7</td>
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<tr>
<td></td>
<td>Cap.: 134.2</td>
<td>Cap.: 104</td>
<td>Cap.: 104</td>
<td>Cap.: 108.9</td>
</tr>
<tr>
<td>CO$_2$ avoided ($/ton CO$_2$)</td>
<td>69</td>
<td>58</td>
<td>35</td>
<td>41</td>
</tr>
</tbody>
</table>

*The reference plant data are derived from those used for [27].
Once captured and compressed to about 8-10 MPa, the CO$_2$ can be sequestered or used for industrial applications [35]. Sequestration of CO$_2$ begins with transport via pipelines or marine ships, tankers, and rail cars to the designated storage sites. The costs for transporting 6 MtCO$_2$/yr varies with method and distance. The costs associated with onshore and offshore pipelines increase linearly from about 3 $/tCO$_2$ at about 300 km to 32-42 $/tCO$_2$ at 3,000 km, respectively. However, marine ship costs increase at a decreasing rate from about 7 $/tCO$_2$ at 300 km to 22 $/tCO$_2$ at 3,000 km. Breakeven of the ship cost with those of the onshore and offshore pipelines occurs at about 1,000 and 1,700 km, respectively.

Sites for CO$_2$ sequestration include (i) geological-enhanced oil recovery (EOR), unused gas or oil fields, unmineable coal seams (ECBM), saline formations, and enhanced coal bed methane recovery and (ii) ocean storage-direct injection. Sequestration takes place via injection of CO$_2$ into the storage sites between 0.2 and 2 km beneath the surface, where the injected CO$_2$ is in a critical or supercritical state and can be physically trapped by layers of shale and clay. These layers inhibit the migration of CO$_2$ back to the surface. The injected CO$_2$ can displace hydrocarbon liquid or gases in the case of oil and natural gas recovery, and also react with the rock minerals to form stable compounds. Storage capacities of these sites are estimated to be 670-900 GtCO$_2$ for oil and gas fields, 3-200 GtCO$_2$ for ECBM’s, and 1,000-10,000 GtCO$_2$ for deep saline formations. The cost for geological storage of sequestered CO$_2$ could be between 0.5 and 8.0 $/ton CO$_2$, and that for ocean storage could be between 6 and 31 $/ton CO$_2$ for pipeline transport and 12-16 $/ton CO$_2$ for ship transport [35].
2.2 Reaction of CO$_2$ with Different Amines

The reaction of CO$_2$ with a primary monoamine (containing only one -NH$_2$ group) under dry conditions proceeds by two general steps shown in Eq. 2.3. Step 1 proceeds by attack of the lone electron pair of nitrogen to the carbon of CO$_2$ to form the zwitterion. In step 2, de-protonation of the zwitterion by a neighboring amine produces carbamate and ammonium ion [12, 36].

Eq. 2.3: Formation of ammonium-carbamate ion pairs.

1. $\text{CO}_2 + \text{RNH}_2 \leftrightarrow \text{RNH}_2^+\text{COO}^- \quad \text{(zwitterion)}$

2. $\text{RNH}_2^+\text{COO}^- + *\text{RNH}_2 \leftrightarrow \text{RNHCOO}^- + *\text{RNH}_3^+ \quad \text{(ion pairs)}$

According to the ion pair reaction, the maximum amine efficiency (CO$_2$/N molar ratio) for sorbents during dry adsorption is 0.5 mol CO$_2$/mol N. CO$_2$ can also adsorb onto the amines with an efficiency of CO$_2$/N=1 in the form of carbamic acid [37], according to the reaction shown in Eq. 2.4.

Eq. 2.4: Formation of carbamic acid.

1. $\text{CO}_2 + \text{RNH}_2 \leftrightarrow \text{RNHCOOH} \quad \text{(Carbamic acid)}$

The reaction of CO$_2$ with NH$_2$ under wet conditions initially proceeds through the formation of the ion pairs, followed by regeneration of NH$_2$ and formation of bicarbonate by H$_2$O as shown in Eq. 2.5.

Eq. 2.5: Formation of bicarbonate.

1. $\text{RNH}_2\text{COO}^- + \text{H}_2\text{O} \leftrightarrow \text{RNH}_2 + \text{HCO}_3^- \quad \text{(Bicarbonate)}$
Alternatively, CO₂ and H₂O can react simultaneously with NH₂. Regeneration of the amine by H₂O and direct reaction of the amine with CO₂ increases the CO₂/N efficiency to 1, and is attributed to the varying degrees of enhancement in the CO₂ capture capacity observed in several studies [12, 36, 38-42]. Additionally, the H₂O vapor could diffuse into regions of agglomerated amine molecules and disperse the NH and NH₂ groups. Dispersal of these groups by H₂O would facilitate CO₂ adsorption on previously inaccessible groups.

It was also reported that CO₂ reacts with amines and surface hydroxyl groups under dry and wet conditions to form surface-bound carbamates represented by Eq. 2.6 [43, 44], where M represents the metal/metalloid atom of the support that is bound to the surface hydroxyl.

Eq. 2.6: Formation of surface-bound carbamate.

(1) CO₂ + RNH₂ + MOH ↔ NHCOOM + H₂O (surface-bound carbamate)

It was postulated that the apparent enhancement in the CO₂ capture capacity of the sorbent in the presence of H₂O could result from the hydrolysis of the surface-bound carbamate, which regenerates the amine and allows it to adsorb more ammonium-carbamate ion pairs [44].

CO₂ adsorption onto amine molecules containing multiple NH or NH₂ groups under dry conditions also proceeds via two general steps shown in Eq. 2.7: (step 1) attack of the amine (NH₂ in this case) to CO₂ which generates the zwitterion, and (step 2) (a) de-protonation of the zwitterion by the adjacent amine group (NH) of the same molecule which forms an intramolecular ammonium-carbamate ion pair or (b) de-protonation of
the zwitterion by an NH$_2$ or NH group of a neighboring amine molecule (NH shown in this case) which forms ammonium-carbamate ion pairs [36, 45].

Eq. 2.7: Formation of ion pairs of poly-amine molecules.

$$\text{(1) } \text{CO}_2 + \text{RNHCH}_2\text{NH}_2 \leftrightarrow \text{RNHCH}_2\text{NH}_2^+\text{COO}^- \text{ (zwitterion)}$$

$$\text{(2a) } \text{RNHCH}_2\text{NH}_2^+\text{COO}^- \leftrightarrow \text{RNH}_2^+\text{CH}_2\text{NCOO}^-$$

$$\text{(2b) } \text{RNHCH}_2\text{NH}_2^+\text{COO}^- + \text{*RNHCH}_2\text{NH}_2 \leftrightarrow \text{RNHCH}_2\text{NCOO}^- + \text{*RNH}_2^+\text{CH}_2\text{NH}$$

CO$_2$ adsorption onto sorbents with isolated amine molecules is likely to proceed via step 2(a) rather than step 2(b) because there are no NH groups from neighboring amine molecules to de-protonate the zwitterion [45]. Adsorption of CO$_2$ onto these multi-amine species under wet conditions would also produce carbonate species. Carbamic acid species are also observed [45]. The reaction of secondary amines, NH, with CO$_2$ under dry and wet conditions proceeds via similar mechanisms as shown for the primary amines. Importantly, the loading, dispersion, and nature of the amine molecules (NH or NH$_2$) on the surface of the support will affect the amount of weakly and strongly adsorbed species. Weakly adsorbed CO$_2$ has been described as those species removed by pressure swing desorption, and strongly adsorbed CO$_2$ as species removed by thermal swing desorption. Importantly, it is necessary to understand the effect of different operating conditions on the CO$_2$ capture of the pelletized sorbents. Table 2.2 presents a literature review for the performance of different immobilized amine sorbents under different operating conditions.
Table 2.2: Literature review for the CO\textsubscript{2} capture of different immobilized amine sorbents under different conditions in fixed bed, fluidized bed, or circulating fluidized bed reactors.

<table>
<thead>
<tr>
<th>Sorbent(^a)</th>
<th>Ads. conditions</th>
<th>Des. conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T_{\text{ads}}) ((^\circ)C)</td>
<td>Inlet gas (vol%)</td>
<td>Method(^b)</td>
</tr>
<tr>
<td>RI-PE-MCM-41 (triamine(TRI) grafter pore expanded (PE))</td>
<td>50</td>
<td>5% CO\textsubscript{2}/95%N\textsubscript{2}</td>
<td>TS</td>
</tr>
<tr>
<td>TRI-PE-MCM-41 (triamine(TRI) grafter pore expanded (PE))</td>
<td>50</td>
<td>5% CO\textsubscript{2}/27%, 74% RH/N\textsubscript{2}</td>
<td>TS</td>
</tr>
<tr>
<td>38% PEI/silica (est.)</td>
<td>NA</td>
<td>CO\textsubscript{2}/N\textsubscript{2}</td>
<td>TS/steam</td>
</tr>
<tr>
<td>50% TEPA/Y60 zeolite</td>
<td>60</td>
<td>15% CO\textsubscript{2}/85%air</td>
<td>TS/steam</td>
</tr>
<tr>
<td>50% TEPA/Y60 zeolite (PEI-50)-silica (PQCS2129)</td>
<td>60</td>
<td>10% CO\textsubscript{2}/90%He</td>
<td>TS/steam</td>
</tr>
<tr>
<td>28 wt% TEPA/silica</td>
<td>40</td>
<td>13% CO\textsubscript{2}/87%N\textsubscript{2}</td>
<td>TS (N\textsubscript{2})</td>
</tr>
<tr>
<td>28 wt% TEPA/silica</td>
<td>40</td>
<td>13% CO\textsubscript{2}/87%N\textsubscript{2}</td>
<td>TS (CO\textsubscript{2})</td>
</tr>
<tr>
<td>18 wt% PEI/silica-A fiber</td>
<td>35</td>
<td>14% CO\textsubscript{2}/100%RH/N\textsubscript{2}/He</td>
<td></td>
</tr>
<tr>
<td>F-C-PSI, 20% PEI (post-spinning infused fiber)</td>
<td>37</td>
<td>10%CO\textsubscript{2}/100%RH/N\textsubscript{2}/He</td>
<td>TS</td>
</tr>
<tr>
<td>AX; 40 wt% PEI/silica</td>
<td>40</td>
<td>33.3% CO\textsubscript{2}/66.6%N\textsubscript{2}</td>
<td>TS</td>
</tr>
<tr>
<td>AX; 40 wt% PEI/silica</td>
<td>70</td>
<td>33.3% CO\textsubscript{2}/66.6%N\textsubscript{2}</td>
<td>TS</td>
</tr>
<tr>
<td>Compounds</td>
<td>Temperature</td>
<td>CO, Ar/He</td>
<td>Time</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>-------------</td>
<td>-----------</td>
<td>------</td>
</tr>
<tr>
<td>46 wt% PEI/silica</td>
<td>60</td>
<td>10%CO2/90%He</td>
<td>PS, TS</td>
</tr>
<tr>
<td>46 wt% PEI/silica</td>
<td>60</td>
<td>10%CO2/90%He</td>
<td>PS, TS (steam)</td>
</tr>
<tr>
<td>E-SNTs-50% TEPA (silica nanotubes)</td>
<td>75</td>
<td>10%CO2/90%N2</td>
<td>TS</td>
</tr>
<tr>
<td>E-SNTs-50% TEPA (silica nanotubes)</td>
<td>75</td>
<td>10%CO2/28%RH (25°C)/N2</td>
<td>TS</td>
</tr>
<tr>
<td>VP OC 1065 (ion exchange resin-NH2)</td>
<td>30</td>
<td>10%CO2/90%N2</td>
<td>PS, TS</td>
</tr>
<tr>
<td>VP OC 1065 (ion exchange resin-NH2)</td>
<td>70</td>
<td>10%CO2/90%N2</td>
<td>PS, TS</td>
</tr>
<tr>
<td>CA-S-PEI (&lt;57% PEI)</td>
<td>35</td>
<td>13%CO2/0, 6%H2O/N2+He</td>
<td>TS</td>
</tr>
<tr>
<td>50 wt% PEI/SBA-15</td>
<td>25</td>
<td>1%CO2/0.4%CO/2.6%Ar/He</td>
<td>PS/TS</td>
</tr>
<tr>
<td>50 wt% PEI/SBA-15</td>
<td>75</td>
<td>1%CO2/0.4%CO/2.6%Ar/He</td>
<td>PS/TS</td>
</tr>
<tr>
<td>MAG-PEI-10 (layered silicate)</td>
<td>75</td>
<td>5%CO2/95%He</td>
<td>TS</td>
</tr>
<tr>
<td>MAG-PEI-10 (layered silicate)</td>
<td>75</td>
<td>5%CO2/95%He</td>
<td>TS</td>
</tr>
<tr>
<td>95C carbon (fly ash): CPAHCl</td>
<td>25</td>
<td>10%CO2/H2O/He/</td>
<td>TS</td>
</tr>
<tr>
<td>N-enriched carbon (soybean)</td>
<td>30</td>
<td>15.4%CO2/84.6%N2</td>
<td>PS/TS</td>
</tr>
<tr>
<td>N-enriched carbon (soybean)</td>
<td>75</td>
<td>15.4%CO2/84.6%N2</td>
<td>PS/TS</td>
</tr>
<tr>
<td>T-EDA-4 (8.25 wt% N/act. carbon)</td>
<td>30</td>
<td>100%CO2</td>
<td>PS/TS</td>
</tr>
</tbody>
</table>
Table 2.2 continued.

<table>
<thead>
<tr>
<th>Material</th>
<th>CO_2 (%)</th>
<th>N_2 (%)</th>
<th>Method</th>
<th>Temperature (°C)</th>
<th>PS/TS</th>
<th>TS (%CO2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-DETA-4 (6.94 wt%N carbon)</td>
<td>30</td>
<td>100</td>
<td>PS/TS</td>
<td>120</td>
<td></td>
<td>0.7</td>
</tr>
<tr>
<td>PEI(50)/C4 (coal-based carbon black)</td>
<td>75</td>
<td>15%</td>
<td>PS/TS</td>
<td>100</td>
<td></td>
<td>3.1</td>
</tr>
<tr>
<td>PEI(50)/C4 (coal-based carbon black)</td>
<td>75</td>
<td>15%</td>
<td>PS/TS</td>
<td>100</td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>CNT(45 wt%APS) (carbon nanotube)</td>
<td>25</td>
<td>15%</td>
<td>TVS</td>
<td>130</td>
<td></td>
<td>42.6</td>
</tr>
<tr>
<td>CNT(45 wt%APS) (carbon nanotube)</td>
<td>25</td>
<td>15%</td>
<td>TVS</td>
<td>150</td>
<td></td>
<td>69.2</td>
</tr>
<tr>
<td>CNT(45 wt%APS) (carbon nanotube)</td>
<td>25</td>
<td>15%</td>
<td>TVS</td>
<td>150</td>
<td></td>
<td>82.2</td>
</tr>
<tr>
<td>IG-MWCNTs-10 (multi-walled carbon nanotube)</td>
<td>20</td>
<td>10%</td>
<td>TVS</td>
<td>0.44</td>
<td></td>
<td>0.44</td>
</tr>
<tr>
<td>IG-MWCNTs-30 (multi-walled carbon nanotube)</td>
<td>20</td>
<td>10%</td>
<td>TVS</td>
<td>1.73</td>
<td></td>
<td>1.73</td>
</tr>
<tr>
<td>IG-MWCNTs-50 (multi-walled carbon nanotube)</td>
<td>20</td>
<td>10%</td>
<td>TVS</td>
<td>2.15</td>
<td></td>
<td>2.15</td>
</tr>
<tr>
<td>IG-MWCNTs-50 (multi-walled carbon nanotube)</td>
<td>70</td>
<td>10%</td>
<td>TVS</td>
<td>3.09</td>
<td></td>
<td>3.09</td>
</tr>
</tbody>
</table>

a. DETA=diethylenetriamine, EDA=ethylenediamine

b. TS=temperature swing, PS=pressure swing, TVS=temperature/vacuum swing
Because the amine loading of the powder and pelletized sorbent can affect the structure and binding strength of the CO\textsubscript{2} adsorbed species, understanding the adsorption characteristics of CO\textsubscript{2} on unsupported amines could provide a basis for optimizing the sorbents. It is believed that adsorption and desorption processes occurring on different thicknesses of amine films could resemble those occurring on sorbents with different amine loadings.

2.3 Bulk CO\textsubscript{2} Gas Mass Balance

The CO\textsubscript{2} mass transfer processes are described for flowing a 10-15 vol\% CO\textsubscript{2}/air mixture through a fixed bed reactor filled with an immobilized amine/silica particle sorbent. Properties of the sorbent can vary, and include: sorbent particle diameter of 0.05-300 μm, TEPA or PEI loading of 5-60 wt%, sorbent pore volume<1 cm\textsuperscript{3}/g, and mesoporous silica pore size of 2-50 nm. Some of the key assumptions for the system include, (i) no pressure drop across the bed, (ii) isothermal operation, (iii) no radial gradient for gas phase CO\textsubscript{2} concentration, (iv) uniform spherical particles, (v) equilibrium between gas phase and adsorbed CO\textsubscript{2} within the pore, and (vi) the external diffusion is modeled according to the linear driving force (LDF) model [62].

Describing the CO\textsubscript{2} mass transfer processes begins with the overall mass balance for the bulk gas phase CO\textsubscript{2} concentration within the tubular reactor, shown in Figure 2.1 [62]. The equation in Figure 2.1 shows that the rate of change in the bulk CO\textsubscript{2} concentration at any z-axial position is governed by the (i) rate of convection, (ii) axial dispersion through the bed, and (iii) external diffusion from the bulk to the particle surface [62]. The convection term is governed by the bulk flow rate of CO\textsubscript{2} into the
reactor, which depends upon the total volumetric flow rate \( V \) and \( C_B \). Since \( C_B \) is essentially fixed between 10 and 15% because of the simulated flue gas conditions, increasing the total flow rate would enhance convection.

Figure 2.1: Overall mass balance for the bulk CO\(_2\) concentration \( C_B \), with identified parameters and variables; (I) represents independent variables and (D) represents dependent variables.

Although it is assumed there is no pressure drop across the bed, it is important to know how a pressure drop would affect mass transfer. Because the driving force for convection through the bed is the pressure difference between the inlet gas and the outlet of the reactor (usually ambient at 1 atm), a pressure drop across the bed resulting from friction losses would decrease the total flow rate. Pressure drop could be adjusted by varying the particle size of bed height.
The driving force for axial dispersion of CO$_2$ is the concentration gradient in the z-direction. Axial dispersion is characterized by the axial diffusion coefficient for CO$_2$ in air, $D_z$. Large values for $D_z$ facilitate rapid CO$_2$ diffusion in the z-direction, dispersing the gas along the length of the bed and reducing the concentration gradient in the z-direction. Because $D_z$ is a function of the Reynold’s number, $N_{Re}$, and the reciprocal of the bed void, $1/\epsilon_c$, axial dispersion/diffusion would be enhanced by increasing the gas velocity through the bed and reducing the bed void volume. Reynold’s number for a packed bed is defined as shown in Eq. 2.8 [63], where D is the reactor inner diameter, $\rho$ is the gas density, and $\mu$ is the gas viscosity.

Eq. 2.8: Reynold’s number for a packed bed.

$$N_{Re} = \frac{D\cdot \rho \cdot \mu}{(1-\epsilon_c)\cdot \mu}$$

It was mentioned that axial dispersion is significant when the Peclet number, $N_{Pe}=N_{Re}N_{Sc}$ is less than 2 [8]. The Schmidt number for a gas mixture, $N_{Sc}$, is defined below in Eq. 2.9, where $D_{AB}$ is the diffusivity of CO$_2$ in the gas mixture.

Eq. 2.9: Schmidt number for gases.

$$N_{Sc} = \frac{\mu}{\rho D_{AB}}$$

According to the LDF model, the concentration gradient between the bulk CO$_2$ and the external particle surface (pore entrance) is the driving force for external diffusion. The external diffusion is characterized by the external film mass transfer coefficient $k_f$ and is dependent upon the particle radius as $1/r_p$. The coefficient $k_f$ is a function of $N_{Re}$, where increasing the gas velocity increases $k_f$ and the external diffusion.
Solving the equation for \( C_B \) requires the following initial (IC) and boundary (BC) conditions:

1. IC1: \( C_B = 0 \) at \( t=0 \) and \( z\geq 0 \); no CO\(_2\) present at \( t=0 \)

2. IC2: \( C_B = C_{B,\text{inlet}} \) at \( z=0 \) and \( t\geq 0 \); entering CO\(_2\) concentration is constant

3. BC2: \( \partial C_B / \partial z = 0 \) at \( z=L \) and \( t\geq 0 \); no CO\(_2\) exiting the reactor

2.4 Pore Mass Balance

With the mass balance equation for \( C_B \) established, the mass balance for gas phase and adsorbed CO\(_2\) within the pore of the particle is considered next. Once CO\(_2\) diffuses from the bulk phase to the particle surface it undergoes intra-particle diffusion into the pores where it reacts with the NH\(_2\) and NH groups of the amine; tetraethylenepentamine (TEPA) as an example. The equation in Figure 2.2 shows that the rate of change of gas phase CO\(_2\) concentration within the particle \( C_p \) at any radial position \( r \) is governed by the (i) intra-particle diffusion and (ii) reaction rate. The driving force for intra-particle diffusion is the CO\(_2\) concentration gradient within the pores, and is characterized by the effective diffusivity \( D_{\text{eff}} \) and Knudsen diffusivity \( D_{\text{Kn}} \). The \( D_{\text{eff}} \) parameter is a function of the CO\(_2\) molecular diffusion coefficient \( D_M \), particle void fraction \( \varepsilon_p \), and pore tortuosity \( \tau \). Since \( D_M \) is an inherent property of CO\(_2\) in this gas mixture under isothermal conditions, \( D_{\text{eff}} \) is primarily affected by the sorbent particle properties, \( \varepsilon_p \) and \( \tau \) [63]. These particle properties may be adjusted by choosing different support materials and amines for preparing the sorbent, or varying the amine loading. The Knudsen diffusion is a function of the pore radius \( r_{\text{pore}} \), temperature \( T \), and molecular weight of CO\(_2\). This diffusion process is significant when the Knudsen number, \( Kn = \lambda / D \), is above 1 where \( \lambda \) is
the mean free path and D is the pore diameter. Because the calculated mean free path of CO₂ at a typical adsorption temperature of 55 °C is 1.4 nm, Knudsen diffusion is only relevant for sorbent particles containing pores <1.4 nm in diameter.

The reaction of CO₂ with NH and NH₂ groups to form carbamate and ammonium ion species as previously described is well studied, and occurs by Eq. 2.10 [4, 64].

Eq. 2.10: Formation of ammonium-carbamate ion pairs on amines.

(A) 2RNH₂ + CO₂ ↔ RNH₃⁺ + RNHCOO⁻ (primary amine)
(B) 2RNH + CO₂ ↔ R₂NH₂⁺ + R₂NCOO⁻ (secondary amine)

Rather than deriving a rate law based upon the reaction presented above, a simpler approach involves choosing an adsorption isotherm and incorporating it into an empirical kinetic model. It was reported that the equilibrium CO₂ adsorption onto an amine sorbent follows the Toth isotherm [65] and that kinetic adsorption follows the Avrami model [8]. The Toth isotherm, which models adsorption of an energetically non-homogeneous surface, is described by Eq. 2.11 [5].

Eq. 2.11: Toth adsorption isotherm.

\[ q_e = \frac{n_2 b C_p RT}{(1+(b C_p RT)^t')^{1/t'}} \] (Toth isotherm)

The \( q_e \) term is the equilibrium amount adsorbed, \( C_p \) is the CO₂ concentration inside of the pore, \( n_2 \) is the amount adsorbed (mmol/g) on each site, \( b \) is a constant governed by the heat of adsorption near 0% coverage, \( t' \) is a parameter to model non-homogeneity, \( R \) is the ideal gas constant, and \( T \) is temperature. The kinetic Avrami model is shown in Eq. 2.12.
Eq. 2.12: Avrami kinetic model.

\[ \frac{\partial C_{\text{Ads}}}{\partial t} = k^A_A t^{n-1} (q_e - q) \quad \text{(Avrami model)} \]

The \( k^A_A \) is the rate constant corresponding to the reaction of order \( n \), \( t \) is time, and \( q_e \) is the equilibrium adsorption capacity corresponding to \( C_p \) that is determined by the Toth isotherm, and \( q \) is the amount adsorbed at time \( t \). Increasing the adsorption temperature would enhance the reaction rate constant and the overall rate of reaction and then decrease the overall reaction rate because of the shifted equilibrium.

Intra-particle diffusion

\[ \varepsilon_p \frac{\partial C_p}{\partial t} = D \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial C_p}{\partial r} \right] \right) \]

\[ \frac{1}{D} = \frac{1}{D_{\text{eff}}} + \frac{1}{D_{Kn}} \]

\[ D_{\text{eff}} = f(D_M, \varepsilon_p, \tau) \]

\[ D_{Kn} = f(r_{pore}, T, MW) \]

Ex: CO\(_2\) ads. onto tetraethylenepentamine (TEPA)

\[ \frac{\partial C_{\text{Ads}}}{\partial t} = f(\text{ToF, Avrami}) \]

Figure 2.2: Overall mass balance equation for gas phase CO\(_2\) and adsorbed CO\(_2\), \( C_p \) and \( C_{\text{Ads}} \) respectively, within the particle pore.
The equations for $C_p$ and $C_{Ads}$ may be solved with the following initial and boundary conditions:

1. **IC1**: $C_p=0$ at $t=0$ and $r\geq 0$; no CO$_2$ initially present inside the pore

2. **BC1**: $D*\frac{\partial C_p}{\partial r}=k_r^*(C_B-C_p)$ at $r=r_p$ and $t\geq 0$; equal mass transfer rate as ext. diff.

3. **IC2**: $C_{Ads}=0$ at $t=0$; no CO$_2$ initially adsorbed

It is often assumed that intraparticle diffusion rather than the rate of adsorption is the rate limiting step to CO$_2$ mass transfer into the sorbent because of the rapid adsorption kinetics. A rough estimate to determine whether or not mass transfer is intraparticle diffusion limited or reaction limited is the Weisz-Prater criterion [66], $C_{WP}=\phi^2\eta^2$, where $\phi$ is the Thiele modulus and $\eta$ is the internal effectiveness factor. $C_{WP}$ values $<<1$ show reaction limited kinetics of the pellet and $C_{WP}>>1$ shows diffusion limited kinetics. The $\phi$ value is the ratio of a surface reaction rate to a pore diffusion rate [66], where the equation describing $\phi$ depends upon the reaction order. The $\eta$ value is the ratio of an observed (actual) reaction rate to a theoretical rate in which the internal pore surfaces are exposed to external surface reaction temperature and gas concentrations [66].

Pelletization of the sorbent particles with the PVA polymer binder, shown in the Figure 2.3, introduces additional diffusion limitations for CO$_2$ through the PVA molecular network. The additional limitations are presented intraparticle (within the pore) and interparticle (between neighboring particles). These limitations would reduce working capacity of the sorbent in practical applications.
Figure 2.3: Schematic of how pelletization of a TEPA/silica particle sorbent with a PVA binder solution adds additional CO$_2$ diffusion limitations.

The intraparticle component can be lumped into the $D$ parameter without adding an additional diffusion term to the mass transfer equation. However, the inter-particle component should be accounted for with an additional mass balance equation for CO$_2$ transport through the PVA network.

Not assuming isothermal operation of the reactor dictates that energy balance equations be included with the mass balance equations to accurately model the system. Energy balance equations would be applied to (i) the bulk gas phase, (ii) the pellet, and (iii) the walls of the column [62]. The balance around the bulk gas phase includes terms for axial conduction through the bed, transfer between the bulk phase and particle
surface, convection from the bulk flow, and transfer to the column wall. The balance around the particle accounts for the gas within the pores and the amine-functionalized solids, and includes terms for heat conduction within the pellet and the heat of CO₂ adsorption. The balance around the column accounts for transfer from the bulk flow to the wall and from the wall to the external surface. Because this is a gas adsorption process, non-isothermal operation will affect the gas velocity, CO₂ concentration, diffusion rate; and reaction rate throughout the bed.

Ultimately, the kinetics of CO₂ adsorption and the equilibrium adsorption capacity of CO₂ onto the amines will be affected both by mass transfer and heat transfer processes. Understanding mass and heat transfer processes is essential for optimizing the sorbent formulation, and the design and operation of the system.

2.5 Polymer Supported Sorbents for CO₂ Capture

Previous work showed that hydrogen bonding of NH and NH₂ groups of immobilized TEPA with the OH groups of polyethylene glycol helps to disperse the amines, effectively (i) enhancing the CO₂ capture capacity and CO₂/N efficiency of the sorbent, (ii) reducing the poisoning of TEPA’s amine sites by carboxylate species, and (iii) inhibiting oxidative degradation of TEPA [6, 67]. These results introduce the possibility of incorporating other hydroxyl-containing additives into the sorbent that could further enhance the sorbent performance, such as polyvinyl alcohol (PVA).

PVA is a semi-crystalline polymer prepared by hydrolyzing the -[CH₂CH(OH)]ₙ-monomeric units of polyvinyl acetate (80-99+% complete hydrolysis), producing the repeating -[CH₂CH(OH)]ₙ- units of PVA. The high molecular weight of solid PVA
(Mw=10,000 to 185,000 g/gmol) allows the added benefit for the polymer to resist migration from the sorbent at the CO$_2$ desorption temperature because of its high viscosity relative to PEG. More importantly, because PVA is a solid at room temperature it is possible that it can replace silica as the support of the immobilized amine sorbents. Replacing silica with PVA has the potential advantage of further enhancing (i) the sorbent particle CO$_2$ capture performance and (ii) the attrition resistance of a flexible polymer-based pellet sorbent. However, because of the low surface area and porosity of the raw PVA, further modification of the material is needed to make suitable as a support.

Porous PVA-based materials have a wide variety of applications, including H$_2$O purification [68-73]; drug delivery [74, 75], microorganism and enzyme immobilization [76-78]; various biomaterials [79-82]; basic catalysis [83-86], and CO$_2$ gas separation [87-91]. The physical structure of porous PVA materials can be divided into several categories: (i) nanofibers [70, 92, 93], (ii) foams [69, 94, 95] and monoliths [96, 97], (iii) hydrogels [75, 78-80, 98-111], (iv) membranes [68, 87-91, 112-134], and (v) beads and particles [71, 73, 76, 77, 84-86, 135-139].

In general, stable porous PVA materials are prepared by templating, gelling/phase separating, and chemically cross-linking. Templating involves the addition of a pore-forming molecule to an aqueous PVA solution to separate the PVA polymer chains, where the pore-former/template could include liquid polyethylene glycol 400 [80], solid polyethylene glycol 10,000 [126], a solid carbonate that reacts with an acid to produce CO$_2$ gas bubbles [95, 99], or even H$_2$O [140]. The PVA+template solution is cast into a specific geometry and then phase separated into PVA rich and PVA poor regions by (i) submersing in a precipitate bath (immersion precipitation) [141], such as acetone (phase
inversion) or aqueous sodium sulfate, or (ii) thermally inducing (TIPS) [141] (cooling or freezing-thawing). Phase inversion here involves displacement of H₂O by the acetone, which also serves to wash out the template to create the pore. Figure 2.4 illustrates the scheme for the gelling and phase inversion of a templated PVA solution. Addition of the template/gelling agent causes the PVA chains to precipitate and physically cross-link around the template into an amorphous gel. Phase inversion of the amorphous gel using a non-solvent such as acetone removes H₂O and the template, producing an amorphous porous structure.

![Diagram](image)

Figure 2.4: Schematic of the formation of porous PVA particles by gelling and phase inversion, adapted from [80].

Chemical cross-linking of the porous PVA material involves covalently attaching the PVA chains through reaction of the hydroxyl groups with aldehydes (formaldehyde and glutaraldehyde) to form C-O-C linkages [110, 120], carboxylic acid, or boric acid.
groups [76, 102]. A literature review for the preparation and application of different porous PVA materials is summarized in

Table 2.3. The low PVA cost of about $33/kg at lab scale and $5.50/kg at industry scale compared to other raw materials used to prepare porous polymer CO$_2$ capture sorbents makes PVA an attractive material. Table 2.4 shows a literature review summarizing the cost and performance of various non-PVA polymer sorbents for CO$_2$ capture. Although the polymer sorbents typically capture between 0.9 and 4.3 mmol CO$_2$/g-sorb, the sorbents are not feasible for industrial application because of their excessive costs.

Table 2.3: Literature review for the preparation and application of porous PVA materials.

<table>
<thead>
<tr>
<th>Precursor solutions. and reaction conditions</th>
<th>Preparation procedure</th>
<th>Material properties</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Aqueous soln: 2.5 wt% PVA, pH=1 with HCl</td>
<td>*Mix 5.0 mL of soln 1 to 95 g of soln 2, then add soln 3 and react</td>
<td>Nano-spherical beads-Modification of low-fouling membranes for biological systems; *Bead diam.=150-1500 nm,</td>
<td>[135]</td>
</tr>
<tr>
<td>(2) Organic soln: paraffin oil/Span 80/OP-10 (organic: aqueous=1:19)</td>
<td>*Add 2 mL EtOH to destabilize, wash with ethanol and isopropanol, then dry at 45 °C.</td>
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<tr>
<td>(3) Cross-linking soln: GA (50-100% aimed cross-linking)</td>
<td>*Cond’s:Cross-link:T=50 °C, t=3 h</td>
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<tr>
<td>(1) Pore former soln: HCl=stoichiometric to CaCO$_3$</td>
<td>*Add soln 2 to soln 1 to produce foam, then freeze/thaw foam and cut into 0.5 cm$^3$ cubes.</td>
<td>Porous PVA-chitosan foams-Heavy metal and organic removal from H$_2$O; *Surface area=17-40 m$^2$/g, *Pore size=5-200 um, *H$_2$O regain%=42-67%, Cu(II) ads=38 um/g(500 min)</td>
<td>[69]</td>
</tr>
<tr>
<td>*Conditions: Freeze: T=-20°C, t=overnight Thaw: T=25°C</td>
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<tr>
<td>(2) Pore former soln: HCl=stoichiometric to CaCO$_3$</td>
<td>*Mix 5.0 mL of soln 1 to 95 g of soln 2, then add soln 3 and react</td>
<td>Nano-spherical beads-Modification of low-fouling membranes for biological systems; *Bead diam.=150-1500 nm,</td>
<td>[135]</td>
</tr>
<tr>
<td>*Conditions: Freeze: T=-20°C, t=overnight Thaw: T=25°C</td>
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<tr>
<td>(1) Polymer soln: PVA/CaCO$_3$/chitosan=(10-15)/(7.5-10)/(3-4.5) wt</td>
<td>*Add soln 2 to soln 1 to produce foam, then freeze/thaw foam and cut into 0.5 cm$^3$ cubes.</td>
<td>Porous PVA-chitosan foams-Heavy metal and organic removal from H$_2$O; *Surface area=17-40 m$^2$/g, *Pore size=5-200 um, *H$_2$O regain%=42-67%, Cu(II) ads=38 um/g(500 min)</td>
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<td>(2) Pore former soln: HCl=stoichiometric to CaCO$_3$</td>
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<td>[69]</td>
</tr>
<tr>
<td>*Conditions: Freeze: T=-20°C, t=overnight Thaw: T=25°C</td>
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<tr>
<td>(1) PVA soln: 12 wt% PVA</td>
<td>*Cast 90 um layer of soln 1 onto glass, immerse into coagulation bath of 8 wt% Na$_2$SO$_4$ and 4 wt% NaOH, remove and let sit 24 h. *Wash membrane with H$_2$O, cross-link in soln 2, wash with H$_2$O, and dry.</td>
<td>Asymmetric porous membrane-H$_2$O purification; *Pore size=0.03-0.1 um, *H$_2$O flux= 0.01-0.025 g/cm$^2$*min</td>
<td>[68]</td>
</tr>
<tr>
<td>(2) Cross-link soln: 1.3 g/l GA, 10 g/l H$_2$SO$_4$ catalyst,45 g/lNa$_2$SO$_4$ *Cond’s: Cross-link: T=25 °C, t=0.5-2.0 h</td>
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<tr>
<td>*Cast 90 um layer of soln 1 onto glass, immerse into coagulation bath of 8 wt% Na$_2$SO$_4$ and 4 wt% NaOH, remove and let sit 24 h. *Wash membrane with H$_2$O, cross-link in soln 2, wash with H$_2$O, and dry.</td>
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</table>
Table 2.3 continued.

| (1) Polymer soln: 10 wt% PVA, 0.8 wt% Na-Alg, yeast cells | *Extrude soln 1 through 450 or 270 um needle into soln 2 for cross-linking, and then immerse resulting beads into soln 3. *Wash beads with distilled water. | Gel beads-cell immobilization; *Bead diameter=2-3 mm, *H2O swelling ratio=175-520% after 3h. | [76] |
| (2) Cross-linking soln: 100 mM CaCl in sat'd boric acid soln and (3) Inducer soln: 0.5-1.5 M Na2SO4 soln. *Conditions: Cross-link: T=30 °C, t=1.5 h Induce: T=25 °C, t=1.5 h | | | |

| (1) Polymer soln: 9.1 wt% (2) HTCC soln: precipitated chitosan, isopropanol, glycidyl trimethylammonium chloride (HTTC:PVA=0:100-40:60 wt) (3) Cross-linking soln: 0-2.4 wt% GA * Conditions: Cross-link: T=70 °C, t=15 min | *Mix solns 1 and 2 at 100 °C and cool, then add soln 3 and react. *Pour resulting soln into dish and dry at 25 °C. | Antibacterial films-drug delivery and wound dressing; *H2O swelling degree=100-210 % at 250 min and pH=7.4, | [115] |
| (1) Polymer soln: polyethyleneimine (PEI) soln:PVA soln=1/3 wt (PVA+PEI=8, 10, 12 wt%) (2) Cross-linking soln: isopropanol/H2O/conc. HCl/GA soln=30/3/0.3/4 vol. *Conditions: Liquid cross-link: est. T=25 °C, t=1 h, Vapor cross-link: est. T=25 °C, t=24 h | *Electro spin soln 1 with flow rate=0.1-0.5 mL/h and distance=20 or 25 cm. *Perform liquid phase (soln 2) or vapor phase (vacuum) cross-linking and wash with H2O. | Porous PVA-PEI nanofiber mats-dye adsorption/H2O remediation; *Porosity=65.5% *Young's module=162.4 *Dye ads.=218.8 mg/g after 60 min at 25 °C with Cmat=0.25 g/L | [70] |
| (1) Polymer soln: 12 wt% of PVA:PEI=3:1 wt Cross-linker: GA vapor (2) Dopant soln: 0.5 mM AuCl (3) Reduction soln: 2 mM NaBH4 *Conditions: Vapor cross-link, vacuum: T=25 °C, t=24 h | *Electron spin PVA+PEI soln with flow rate=0.3 mL/h, distance=25 cm, needle tip=0.8 mm, and 18.6 kv to produce fibers. Vapor-cross-link fibers then H2O wash. *Place fibers in 20 ml of soln 2 for 1 h, H2O wash, and 24 h vacuum dry. *Place doped fibers in soln 3 for 2 h, H2O wash, and 24 h vacuum dry at 25 °C. | Porous, Au-doped PVA-PEI nanofiber mats-basic catalysis; *Porosity=41.5-61.5 %, *Avg. fiber diameter=10.1-675 nm | [92] |
| (1) Polymer soln: 6 wt% PVA, PEI (PEI:PVA=20:80-95:5), 0.1 wt% sodium dodecyl benzene sulfonate (2) Cross-linking soln: GA soln:N,N-dimethylformamide (1:20 vol) *Conditions: Electro-spin and cross-link: T=25 °C, t=3 h | *Electro-spin soln 1 with flow rate=0.36 mL/h onto rotary drum, which rotates into soln 2 for cross-linking. *Vacuum dry at 40 °C until constant weight. | Porous PVA-PEI nanofiber mats-heavy metal removal from H2O; *Fiber diameter=220-550 nm *Ion ads=20-110 mg/g of Cu(II) Pb(II), or Cd(II) at 100 mg/L ion conc. | [116] |
Table 2.3 continued.

<table>
<thead>
<tr>
<th>Polymer soln: 17 wt% PVA, 0-30 wt% dextran</th>
<th>*Freeze/thaw PVA+dextran soln, freeze in liquid N(_2) for 6 min, lyophilize at -50°C for 58h, then soak in H(_2)O for 72h.</th>
<th>Porous PVA-dextran Xerogels-bioapplications; *Pore size=1-20 um</th>
<th>[101]</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Conditions: Freeze: T=(-20) °C, t=20 h Thaw: T=(25) °C, t=4 h</td>
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<tr>
<td>(1) PEI soln: 0.1 wt% PEI adjusted to pH=10, 8, 7, and 4 with 1.0M HCl (2) Polyacrylic acid (PAA): 0.2 wt% pH adjusted with NaOH (3) Cross-linking soln: 1 wt% GA Substrate: silicon wafer, poly(ethylene terephthalate) (PET), and polystyrene (PS) films *Conditions: PEI and PAA deposit: T=25 °C, t=5 min, Cross-link: not specified</td>
<td>*Dip substrates into soln 1 then 30 s H(_2)O wash, followed by drying. *After drying, repeat process for soln 2. After 10 PEI+PAA layers, dip into soln 3 then wash.</td>
<td>Cross-linked PEI-PAA films (C=N linkage)-electronics and food packaging material; *PEI+PAA thickness (30 layers)=90 nm to 5 um *O(_2) permeability=0.005-8.48 cm(^3)/(m(^2) day atm)</td>
<td>[142]</td>
</tr>
<tr>
<td>(1) Polymer soln: (a) PVA, sodium alginate, 0.2-0.6 wt% NaHCO(_3) or (b) PVA, sodium alginate, activated sludge, 0.2-0.6 wt% NaHCO(_3) (2) Cross-linking soln: sat'd boric acid, CaCl(_2) *Conditions: Cross-link: T=25 °C, t=1 h</td>
<td>*Drip soln 1 into soln 2 to form beads and react. *Wash cross-linked beads with H(_2)O.</td>
<td>Cross-linked, porous PVA gel beads-microorganism immobilization; *10 h H(_2)O swelling ratio=150-350% *est. macropore size=1-30 um,</td>
<td>[99]</td>
</tr>
<tr>
<td>(1) Polymer soln: PVA/CaCO(_3)/chitosan = (4-8)/(7.5-10)/(0-7.5) wt, Na-Alg/H(_2)O=1.3 g/150 mL (2) Cross-linking soln: 3 wt% sat'd CaCl(_2)-boric acid (3) Macroreticular pore former: 1 M HCl Conditions: *Cross-link: est. T=25°C, t=48 h</td>
<td>*Add chitosan to PVA/Na-Alg/CaCO(_3) soln at 90 °C and mix for 6 h to form soln 1. *Extrude soln 1 through 3 mm diameter nozzle into soln 2, react for 48 h, then add soln 3 until no bubbles form. *Wash beads with H(_2)O.</td>
<td>Porous, cross-linked PVA/Na-alg/chitosan beads-heavy metal removal from H(_2)O; *Surface area=16-27 m(^2)/g *Avg bead size=2 mm *Pore volume=0.03 mL/g *Avg pore diameter=27 nm *Est. macro pore size=2-10 um, *Ion ads=238 Cu(^{2+}), 126 Cd(^{2+}), 166 Pb(^{2+}), and 74 Zn(^{2+}) (mg/g)</td>
<td>[73]</td>
</tr>
<tr>
<td>(1) PVA soln: 5-15 wt% PVA (2) Cross-linking soln: GA soln (GA:PVA=0.5:1-1.5:1 wt) (3) Catalyst soln: 0.1-0.4 N HCl Conditions: Cross-link: T=25 °C, t=5-10 min</td>
<td>*Mix soln 2 with soln 1, then add 100 mL of PVA+H(_2)O+Glut soln to 150-250 mL soln 3 and let react. *If precipitate formed then filter, H(_2)O wash, dry, and sieve.</td>
<td>Gel, or white amorphous precipitate-tablet disintegrant for drug delivery; *Pore volume=0.03-0.46 m(^3)/g</td>
<td>[143]</td>
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</table>
Table 2.3 continued.

| (1) Aqueous: 4 wt% PVA, 9.8 vol% GA, 12.2 vol% 1.0 M HCl | *Mix aqueous soln with organic soln under stirring at and cross-link. | AlCl₃ functionalized, spherical beads-FC acylation; *Avg. diameter=160 µm *Al content: 0.25-2.0 mmol Al/g beads [85] |
| (2) Organic: liquid paraffin/sorbitan monostearate (SM) (organic: aqueous=2/1) Additive: AlCl₃ powder Conditions: Cross-link: T=65, t=6.5 h AlCl₃ deposit: T=40, t=1-8 h | *Wash resulting beads with ether and H₂O to obtain porous beads. *Mix beads with chloroform and the AlCl₃ additive then dry. | |

| (1) Polymer soln: 10-15 nominal wt% PVA, 5-15 nominal wt% CaCO₃, 5 M HCl stoichiometric to CaCO₃ as pore former (2) Cross-linking soln: 0.5 wt% Epi, 1.0 M NaOH *Conditions: Cross-link: T=35 °C, t=2 h | *Mix PVA with CaCO₃ and add HCl to produce foam. *Freeze foam at -20 °C, cut into 2 cm cubes, and place into 200 ml of soln 2. | Macroporous PVA foam-microorganism immobilization; *Pore size<500 um *Specific surface area=177.5 m²/g [94] |

| (1) PVA soln: 10 wt% PVA (2) Cross-linking soln: malic acid, citric acid, tartaric acid (acid:PVA=10:1.5-10:10 wt) (3) Catalyst soln: 1 M H₂SO₄ Conditions: Cross-link/dry: T=80 °C, t=2 h | *Mix soln 2 and soln 3 with soln 1 at 25 °C, pour mixture onto plate and cross-link/dry in oven, then wash film with H₂O. | Cross-linked PVA film-microbial engineering, food packaging, pharmaceuticals; *Degree of swelling=30-175% in H₂O after <30 min. [102] |

| (1) Aqueous soln: 12.5 wt% PVA soln, chitosan soln with 2 wt% acetic acid (PVA:chitosan=2:1), pH=2 with HCl (2) Organic soln: toluene:chlorobenzene (1:3 vol), 1.5 g Tween 80 (organic: aqueous=1/1 vol) (3) Cross-linking soln: 2 wt% GA *Conditions: Cross-link: T=25 °C, t=8 h | *Mix solution 1 with solution 2 at 90 °C under 190 rpm of stirring, cool to 25 °C, and add soln 3 to produce beads. *Filter beads with acetone and H₂O, neutralize with 0.1 M NaOH, then wash with H₂O. | PVA-chitosan gel beads-heavy metal removal from H₂O; *H₂O swelling=40.3 wt% *Cd(II) Ion ads=40 mg/g at CCd(II)=50 gm/l, pH=6, t=6.7 h [71] |

| (1a)Aqueous soln: 1.5 wt% PVA with NaCl (1b) Organic: vinyl acetate/DVB/azobisisobutyronitrile=10/3.1 (vol/vol/wt), organic/aqueous=1.3/10 | *Mix soln 1a and sol 1b and react under N₂ to produce microspheres, the dry. *Add spheres to soln 2 and react. *Add treated spheres to soln 3 and react under N₂ for grafting, collect, and H₂O wash. | PVA-acrylamide beads-varied; *Est. bead size=150-225 um, *Fe³⁺ ion ads=21mg/g at 0.55 g/L, 30 °C, pH=4.0 [144] |
| (2) Alcoholysis soln: MeOH+NaOH(4%), beads/alcohol=5 g/30 mL (3) Grafting soln: 3.7 wt% acrylamide, H₂SO₄=0.1-0.5 M, cerium salt=3-10 x10⁻³ M (4)Hoffman deg soln: DMSO +H₂O/14 wt% NaOH/NaOCl | | |

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Table 2.3 continued

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<tr>
<td>(1) Polymer soln: 5-10 wt% PVA, pH adjusted to 2 with 1.0M HCl</td>
<td>(2) Cross-linking soln: GA soln (GA:PVA=1:20-5:20)</td>
<td>*Add soln 2 to soln 1 and pour onto plate. Let dry and react.</td>
<td>Gel film-drug delivery; *H2O swelling degree=50-175%</td>
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<tr>
<td>(1) Polymer soln: 10 wt% PVA soln, 5-sulfosalicylic acid drug (drug:PVA=1:10 wt)</td>
<td>(2) Cross-linking soln: 25 wt% GA soln (0.5 mol GA/mol OH from PVA), 10 wt% H2SO4/50 wt% MeOH/10 wt% acetic acid=1/2/3.</td>
<td>*Mix solutions 1 and 2, cast mixture into mold with diameter=9 cm and thickness=0.45-0.50 mm, and cross-link.</td>
<td>Thin, porous PVA hydrogels-drug delivery; *Buffer soln swelling degree=150-1100% after 5 days *Diff Coef=2.76x10-10 to 7.4 x10-9</td>
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<tr>
<td>PVA soln: 15 wt% PVA, PEG 400 (PEG:PVA=2:1)</td>
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<td>*Pour PVA+PEG soln into 45 mm x 70 mm x 7 mm mold at 90 ºC, cool to 25 ºC and sit/react for 24 h to produce gel. *Vacuum dehydrate gel, anneal some at 160 ºC for 1 hr under Ar then rehydrate with saline.</td>
<td>PVA-PEG hydrogel-biomaterials; *equilibrium H2O content=55-91%, pore size&lt;20 um.</td>
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<tr>
<td>(1) PEI soln: 2 mg PEI/mL in 0.5 M NaCl, pH=9</td>
<td>(2) Cross-linking soln: 0.5 wt% GA</td>
<td>*Dip MnCO3 particles in soln 1, 5 min centrifuge, then H2O wash x 3. *Dip MnCO3+PEI in soln 2, then H2O wash x 3 *Repeat previous 2 steps x 10, dip in soln 3 to remove MnCO3, wash with 0.01 M EDTA, then H2O wash.</td>
<td>Hollow PEI microcapsules-biotechnology, basic catalysis, etc.; *Capsule size=about 10-20 um</td>
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<tr>
<td>(1) Polymer soln: (a) 10-18 wt% PVA, GA (50 wt% GA soln:PVA=2:10 wt), 2 wt% PVAc-PEG-PVAc surfact., (b) 15 wt% of PVA:PEG 400=75/25 or (c) PVA:PEG 400=50/50 with GA soln and surfact., and (d) 0.4 or (e) 0.6 wt% chitosan with GA soln and surfact. (2) Catalyst soln: 0.1 mL of 2.0 N HCl</td>
<td>(3) Acid soln: 0.1 M HCl</td>
<td>*Load soln 1 into reactor, 15 min CO2 purge and pressurize with CO2, then begin stirring and add soln 2 after 10 min. *React mixture then 24 h freeze dry or ambient dry.</td>
<td>Porous, cross-linked PVA or chitosan hydrogels-separation materials, tissue scaffolds, controlled drug release; *Pore volume (PVA gel)=8-19.1 cm3/g *Avg pore size=3.1-12.3 um</td>
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Table 2.3 continued.

<table>
<thead>
<tr>
<th>Conditions: Cross-link: T=35-55 °C, *Conditions: Cross-link: T=25 °C, t=5-30 min Heat treat: T=120 °C, t =1-3 h</th>
<th>*Pour PVA solution into circular mold with diameter=2 cm and H=200-3400 um then place mold into reactor. *Fill reactor with supercritical CO$_2$ in batch for 30 min, then set in continuous mode and flow 1.5 kg/h CO$_2$ for 30 min. *Depressurize for 10 min.</th>
<th>Porous PVA membrane-ultra and nanofiltration, drug release material, catalyst support; * Est. pore size=0.2-2 um [127]</th>
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</thead>
<tbody>
<tr>
<td>PVA soln: 1-35 wt% PVA in DMSO or DMSO:acetone=65:20, 70:15, 80:5 wt</td>
<td>*Conditions: Cross-link: T=35-55 °C, Ptot=100-200 bar, PCO$_2$=300-900 kg/m$^3$</td>
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<tr>
<td>(1) Polymer soln: 10 wt% PVA, 0.5 wt% PEG 10,000 (2) Cross-linking soln: 27.5 wt% Na$_2$SO$_4$, 3 wt% GA, and 5 wt% H$_2$SO$_4$</td>
<td>*Cast PVA soln onto glass plate, immerse in acetone for phase inversion, and dry in vacuum at 25 °C for 1 h. *Cross-link or heat treat membrane.</td>
<td>Porous PVA film-filtration membrane; *Porosity=0.42-0.65 *Est. pore size=3-15 um [126]</td>
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<tr>
<td>(1) PVA soln: 10 wt% PVA (2) Cross-linker: 10-60 wt% maleic acid</td>
<td>*Mix soln 2 with soln 1, cast mixture soln onto glass plate, dry at ambient temperature, and cure.</td>
<td>Cross-linked PVA hydrogel/film-film in paper industry, textile sizing, emulsifier; *H$_2$O swelling=up to 135% at 85 °C after 24 h [145]</td>
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<tr>
<td>(1) PVA soln: 13.6 wt% PVA (2) Catalyst soln: NaOH (NaOH: solid PVA=2:3 wt%) (3) Organic soln: 250 mL paraffin oil/0.4 g Span 80 (add.:PVA=4:25 vol) (4) Cross-linking soln: epichlorohydrin (Epi) (Epi:PVA=1:8-1:4)</td>
<td>*Add 251 g of soln 3 to 45-50 g of soln 1+soln 2. *Add soln 4 to soln 1+soln 2+soln 3 and let react to produce beads. *Wash beads with ether, methanol, water, and acetone, then freeze dry and sieve.</td>
<td>Solid, porous beads-basic catalysis, absorption, and separation; *Pore volume=0.5-4.7 mL/g *Pore size=1-15 um [84]</td>
</tr>
<tr>
<td>(1) PVA soln: 2 wt% PVA in H$_2$O or DHF (2) Cross-linker: 5-10 mM GA (3) pH adjust soln: pH=3.2 (phosphoric acid/sodium dihydrogen phosphate buffer) or 4.7 (citric acid/disodium phosphate buffer), with NaCl</td>
<td>*Mix all solns together and react in nmr set-up.</td>
<td>Cross-linked PVA gel-basic research/varies; *Reaction order: H$^+$ and GA=1, *Activation energies=40-66 kJ/mol. [110]</td>
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**Table 2.3 continued.**

| Conditions: | Cross-link: T=20-60 °C, t=60 min | Cross-linked PVA membrane—basic research/varies;
*Reaction order: PVA, GA, and H₂SO₄=1 | [133] |
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<tr>
<td>Cross-linking soln: 0.015-0.06 M GA, 0.1-0.4 M H₂SO₄ catalyst, 0.96 M Na₂SO₄</td>
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<tr>
<td>*Add soln 2 to membrane for cross-linking.</td>
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<tr>
<td>*Cast PVA solution into W=120 mm x L=250 mm x D=0.5 mm, dry for 120 min at 25 °C, and place into coagulation bath (1.5 M Na₂SO₄ and 0.3 M NaOH) for 60 min to form PVA membrane.</td>
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<tr>
<td>*Reaction order: PVA, GA, and H₂SO₄=1</td>
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**Patent example 1:**

(1) Aqueous soln: 8.3 wt% PVA, 8.3 wt% NaCl
(2) Organic soln: 0.5 g cellulose acetate butyrate/250 mL dichloroethane
(3) Cross-linking soln: 20 wt% NaCl/25 wt% GA/1N HCl/5N HCl=5/1.2/0.1/1 vol

*Conditions: Gelation: T=25 °C, t=92 h, Cross-link: T=65 °C, t=4 h
*Add soln 3 to the gel and react.
*MeOH and H₂O wash, then distill off dichloroethane in 700 mL H₂O at 95 °C for 1 h.
*Reaction order: PVA, GA, and H₂SO₄=1

<table>
<thead>
<tr>
<th>Polymer sorbent</th>
<th>Reagent costs</th>
<th>CO₂ ads. cond.’s</th>
<th>CO₂ ads. (mmol/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMP-1-COOH</td>
<td>2,5-dibromobenzoic acid; $207.91/25 g (VWR) 1,3,5-triethynylbenzene; $466/5 g (VWR)</td>
<td>T=25°C CO₂=1 bar Method: grav./vol.</td>
<td>est. 0.94</td>
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<tr>
<td>CMP-1-NH₂</td>
<td>2,5-dibromoaniline; $111.5/25 g (VWR), 1,3,5-triethynylbenzene; $466/5 g (VWR)</td>
<td>T=25°C CO₂=1 bar Method: grav./vol.</td>
<td>est. 0.94</td>
<td>[147]</td>
</tr>
<tr>
<td>CMP-1</td>
<td>1,4-diiodobenzene; $103.05/50 g (VWR), 1,3,5-triethynylbenzene; $466/5 g (VWR)</td>
<td>T=25°C CO₂=1 bar Method: grav./vol.</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>PAF-1</td>
<td>Tetrakis(4-bromophenyl)methane Bis(1,5-cyclooctadiene)nickel(0); $59.5/2 g (Aldrich) 2,2'-Bipyridyl; $198.5/100 g (Aldrich)</td>
<td>T=25°C CO₂=1 bar Method: grav./vol.</td>
<td>[148]</td>
<td>1.15</td>
</tr>
</tbody>
</table>

**Table 2.4: Literature review of porous polymer sorbents for CO₂ adsorption.**
<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAF-3</td>
<td>Tetrakis(4-bromophenyl) silane; $100/50 mg (Aldrich)</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol.</td>
<td>[148]</td>
</tr>
<tr>
<td></td>
<td>Bis(1,5-cyclooctadiene)nickel(0); $59.5/2 g (Aldrich)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,2'-Bipyridyl; $198.5/100 g (Aldrich)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tetrakis(4-bromophenyl) germane; $100/50 mg (Aldrich)</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol.</td>
<td>1.98</td>
</tr>
<tr>
<td></td>
<td>Bis(1,5-cyclooctadiene)nickel(0); $59.5/2 g (Aldrich)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,2'-Bipyridyl; $198.5/100 g (Aldrich)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOP-C</td>
<td>Tetrakis(4-azidophenyl)methane</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol.</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>Tetrakis(4-ethynylphenyl)methane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOP-E</td>
<td>Tetraphenyldimethane; $74.22/1 g (VWR)</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol.</td>
<td>1.77</td>
</tr>
<tr>
<td>BILP-3</td>
<td>Tetrakis(4-formylphenyl)methane</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol.</td>
<td>3.30</td>
</tr>
<tr>
<td>BILP-4</td>
<td>1,2,4,5-benzenetetramine tetrahydrochloride; $217.5/5 g (Aldrich)</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol.</td>
<td>3.59</td>
</tr>
<tr>
<td>PPN-6-CH2 DETA (impregnated)</td>
<td>Tetrakis(4-bromophenyl)methane, Bis(1,5-cyclooctadiene)nickel(0); $59.5/2 g (Aldrich)</td>
<td>T=24°C</td>
<td>PCO₂=400 ppm</td>
<td>Method: calc., fixed bed</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>2,2'-Bipyridyl; $198.5/100 g (Aldrich)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPN-6-CH2 EDA (impregnated)</td>
<td>Tetrakis(4-bromophenyl)methane, Bis(1,5-cyclooctadiene)nickel(0); $59.5/2 g (Aldrich)</td>
<td>T=24°C</td>
<td>PCO₂=400 ppm</td>
<td>Method: calc.</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>2,2'-Bipyridyl; $198.5/100 g (Aldrich)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BILP-1</td>
<td>Tetrakis(4-for-mylphenyl)methane 2,3,6,7,10,11-hexaaminotriphenylene</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol.</td>
<td>2.98</td>
</tr>
<tr>
<td>COP-1</td>
<td>Cyanuric chloride; $18.5/250 g (Aldrich)</td>
<td>T=45°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol.</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>Piperazine; $54.6/500 g (Aldrich)</td>
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Table 2.4 continued

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<tr>
<th>COP-2</th>
<th>Cyanuric chloride; $18.5/250 g (Aldrich) 4, 4’-bipiperidine; $9.2/1 g (Aldrich)</th>
<th>T=45°C</th>
<th>PCO₂=1 bar</th>
<th>Method: grav./vol. 0.93</th>
<th>[153]</th>
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<tr>
<td>COF-102</td>
<td>Tetra(4-dihydroxyborylphenyl)methane</td>
<td>T=25°C</td>
<td>PCO₂=55 bar</td>
<td>27.27</td>
<td>[154]</td>
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<tr>
<td>COF-103</td>
<td>Tetra(4-dihydroxyborylphenyl)silane</td>
<td>T=25°C</td>
<td>PCO₂=55 bar</td>
<td>27.05</td>
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</tr>
<tr>
<td>MPI-1</td>
<td>Tetrakis(4-aminophenyl)methane; $256.16/500 mg (VWR) Pyromellitic dianhydride; $108/500 g (J-K sci.)</td>
<td>T=0°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol. 3.82</td>
<td>[155]</td>
</tr>
<tr>
<td>MPI-2</td>
<td>Tetrakis(4-aminophenyl)methane; $284/5 g (tci) Pyromellitic dianhydride; $108/500 g (J-K sci.)</td>
<td>T=0°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol. 3.14</td>
<td></td>
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<tr>
<td>PAF-18-OH</td>
<td>Tetrakis(4-ethynylphenyl)methane 2,4,6-tribromo-benzene-1,3,5-triol Tetrakis-(triphenphosphine)palladium</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol. 1.50</td>
<td>[156]</td>
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<tr>
<td>PAF-18-OLi</td>
<td>Tetrakis(4-ethynylphenyl)methane 2,4,6-tribromo-benzene-1,3,5-triol Tetrakis-(triphenphosphine)palladium Lithium-naphthalenide</td>
<td>T=25°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol. 2.02</td>
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<td>Torlon (63 mg)/[Im21OH][Tf2N]-DBU</td>
<td>Torlon 4000T polyamide-imide</td>
<td>T=35°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol. est. 1.35</td>
<td>[157]</td>
</tr>
<tr>
<td>Torlon (62 mg)/[Im21OH][Tf2N]-DBU (48 mg) (impregn. ionic liquid)</td>
<td>Torlon 4000T polyamide-imide</td>
<td>T=35°C</td>
<td>PCO₂=1 bar</td>
<td>Method: grav./vol. est. 0.81</td>
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<td>PPN-6-CH₂ EDA (impreg.)</td>
<td>Tetrakis(4-bromophenyl)methane, Bis(1,5-cyclooctadiene)nickel(0); $59.5/2 g (Aldrich) 2,2’-Bipyridyl; $198.5/100 g (Aldrich)</td>
<td>T=22°C</td>
<td>PCO₂= est. 1.04 bar</td>
<td>Method: grav./vol. est. 3.3</td>
<td>[158]</td>
</tr>
<tr>
<td>PPN-6-CH₂ DETA (impreg.)</td>
<td>Tetrakis(4-bromophenyl)methane, Bis(1,5-cyclooctadiene)nickel(0); $59.5/2 g (Aldrich) 2,2’-Bipyridyl; $198.5/100 g (Aldrich)</td>
<td>T=22°C</td>
<td>PCO₂= est. 1.04 bar</td>
<td>Method: grav./vol. est. 4.3</td>
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Table 2.4 continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>Components</th>
<th>Method</th>
<th>Temp</th>
<th>Pressure</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPN-6-CH₂ TETA (impreg.)</td>
<td>Tetrakis(4-bromophenyl)methane, Bis(1,5-cyclooctadiene)nickel(0); $59.5/2$ g (Aldrich) 2,2′-Bipyridyl; $198.5/100$ g (Aldrich)</td>
<td>grav./vol.</td>
<td>$22^\circ$C</td>
<td>1.04 bar</td>
<td>est. 3.2</td>
</tr>
<tr>
<td>PPN-6-CH₂ TAEA (impreg.)</td>
<td>Tetrakis(4-bromophenyl)methane Bis(1,5-cyclooctadiene)nickel(0); $59.5/2$ g (Aldrich) 2,2′-Bipyridyl; $198.5/100$ g (Aldrich)</td>
<td>grav./vol.</td>
<td>$22^\circ$C</td>
<td>1.04 bar</td>
<td>est. 3.6</td>
</tr>
<tr>
<td>TP[PPc]ENa₁%_+T/P 1 (impreg.)</td>
<td>Polynvinyl alcohol (MW=75k, 99+% hydrolyzed); $33.0$ kg (DuPont) Glutaraldehyde (25 wt%); $87.48/2.5$ L (VWR) Tetraethylenepentamine; $88.4$ kg (Aldrich)</td>
<td>grav.</td>
<td>$25^\circ$C</td>
<td>1 bar</td>
<td>2.46</td>
</tr>
</tbody>
</table>

2.6 Cross-linking Reaction Mechanisms

This section describes the reaction mechanisms for amines and alcohols with aldehydes.

2.6.1 Reaction Mechanism of Aldehydes with Amines

The reaction of primary amines with aldehydes in the liquid phase to produce imines is one pathway of cross-linking. Primary amines, R’NH₂, react with aldehydes, RCH=O in the presence of acid or base catalysts in two key steps, illustrated in Figure 2.5. Step 1 involves nucleophilic addition of R’NH₂ to RCH=O, forming a carbinolamine. Addition begins with electron transfer from the nitrogen to the carbon, and from the carbon to the oxygen producing the first intermediate. The intermediate is protonated by H₂O forming the carbinolamine. Step 2 involves dehydration of the carbinolamine, eliminating H₂O to form the N-substituted imine and H₂O. The dehydration is initiated by protonation of the oxygen on the carbinolamine. The
protonated carbinolamine then loses H₂O, forming a carbocation which is stabilized by the lone electron pair of nitrogen. De-protonation of the carbocation by H₂O produces the imine.

The pH of the solution is an important factor which affects the reaction rate and is commonly adjusted using buffer solutions [159] or HCl [83]. Solutions with excessively low pH will protonate the R’NH₂ groups via interaction with the lone electron pair of nitrogen, reducing the rate of the nucleophilic addition step. Excessively high pH will slow the rate of the dehydration step. The optimum pH value will depend upon the particular aldehyde and amine reacting.

Figure 2.5: Scheme for the (a) general reaction between primary amine groups and aldehydes and (b) specific reaction between polyethyleneimine and glutaraldehyde.
(adapted and re-drawn from [142] and [160]. The PEI molecule was re-drawn based upon Sigma-Aldrich).

Polyethyleneimine, PEI, is a water soluble liquid polymeric amine possessing primary, R’NH\(_2\), secondary, R’NH, and tertiary, R’N, amine groups. PEI is commonly cross-linked with glutaraldehyde to produce membranes or capsules for many biological applications. The reaction of glutaraldehyde with PEI occurs via nucleophilic addition/elimination between the RHC=O and R’NH\(_2\) groups [160]. The R’NH and R’N groups do not participate in cross-linking because they are weaker nucleophiles than R’NH\(_2\). Cross-linking is accomplished through simultaneous reaction of both RCH=O groups on one glutaraldehyde molecule with R’NH\(_2\) groups of two different PEI molecules, illustrated in Figure 2.5 (b) [142]. The two H\(_2\)O molecules formed are by-products of cross-linking. The common pH range for cross-linking is 4-10, however 9-10 produced the best results [83, 142]. Spectroscopic techniques, such as FTIR and NMR, verify the formation of the C=N bond and the reduction of the C=O and N-H bonds resulting from cross-linking.

2.6.2 Reaction Mechanism of Aldehydes with Alcohols

The reaction of alcohols with aldehydes in the liquid phase to produce di-acetals is another pathway of cross-linking. Primary alcohols, R’OH, react with aldehyde, RCH=O, in the presence of an acid catalyst in two key steps, illustrated in Figure 2.6. Step 1 involves nucleophilic addition of the RCH=O to the R’OH, producing a hemiacetal. The addition begins with protonation of the C=O oxygen to form the conjugate acid of the aldehyde. The R’OH nucleophilically adds to the C=O carbon of the conjugate acid, where the added R’OH is then de-protonated to form the hemiacetal. The hemiacetal reacts with a second R’OH to produce the di-acetal and H\(_2\)O in step 2.
Di-acetal formation begins with protonation of the C-OH oxygen of the hemiacetal, where H₂O is eliminated to produce a carbocation intermediate. The second R’OH molecule nucleophilically adds to the carbocation, producing another conjugate acid. The conjugate acid is protonated, producing the final di-acetal. The overall reaction equilibrium favors di-acetal formation in the presence of excess alcohol. However, excess water may hydrolyze the di-acetal to regenerate the alcohol and aldehyde.

Figure 2.6: Scheme for the (a) general reaction between primary alcohols and aldehydes and (b) specific reaction between polyvinyl alcohol and glutaraldehyde (adapted and redrawn from [142] and [103]).

Polyvinyl alcohol is a water soluble solid polymeric alcohol, possessing secondary, R₂’OH groups. The R₂’OH groups of PVA also react with aldehydes to form di-acetals [103]. PVA is commonly cross-linked with glutaraldehyde to produce
hydrogels for cell immobilization and drug delivery. PVA must be dissolved into a solvent, such as H₂O, to participate in the liquid phase reaction. Cross-linking is accomplished through simultaneous reaction of both RCH=O groups on one glutaraldehyde molecule with two R₂’OH groups of two different PVA molecules, illustrated in Figure 2.6. The reaction is typically carried out at 25-60 °C with low pH values, 1-3. The pH values are adjusted with H₂SO₄, HCl, or acetic acid [103, 133]. FTIR verifies the formation of C-O-C acetal bonds and the reduction of C=O and O-H bonds resulting from cross-linking [103].

2.7 Summary and Hypotheses

Numerous studies have provided valuable insight into the various factors affecting CO₂ diffusion, including amine loading and type, temperature, and pore structure of the sorbent. However, one key factor that has not been considered is the diffusion limitation caused by chemically adsorbed CO₂ species. Additionally, readsorption of the desorbed species could also slow CO₂ removal from the sorbent. Because benzene has been shown to adsorb onto the isolated hydroxyl groups of silica and not the NH₂ and NH groups of amines, we could use the hydroxyl profile as an index to measure benzene diffusion. These factors generate hypothesis 1:

1. Benzene can serve as a surrogate molecule to probe the diffusion of CO₂ within immobilized amine sorbents, allowing diffusion and a desorption/re-adsorption mechanism to be decoupled.

Benzene and benzene/CO₂ adsorption-desorption studies will be performed on silica and TEPA/silica and PEI/silica sorbents in situ using diffuse reflectance infrared Fourier
transform spectroscopy (DRIFTS). The integrated absorbance profiles of the isolated and
geminal Si-OH on silica and the sorbents will be compared during adsorption and
desorption in the presence and absence of adsorbed CO₂

The success of solid amine sorbent technology relies on the fundamental chemical
interactions between CO₂ and amine groups in different environments. To date, little
research has been done to investigate the transient nature of CO₂ adsorption onto and
desorption from amine thin films. Understanding the fundamental interactions of CO₂
with the unsupported amines and also the CO₂ mass transfer characteristics could assist in
developing a more effective solid sorbent. These factors generate hypothesis 2:

2. Adsorption of CO₂ onto a thick amine film produces a strongly bound, inter-
connected CO₂-amine network near the top surface, which inhibits the diffusion
and adsorption/desorption of CO₂ into and from film.

In-situ Fourier transform infrared spectroscopy (FTIR) is an excellent technique that can
elucidate the chemical bonding of CO₂ to the NH and NH₂ groups of unsupported amine
films as a function of time. This in-situ FTIR technique will be used to show the
adsorption and desorption of weakly and strongly adsorbed CO₂ species from different
thicknesses of amine thin films. Attenuated total reflectance (ATR) and diffuse
reflectance infrared Fourier transform spectroscopy (DRIFTS) will be used to perform
the in-situ study. It is expected that these accessories can reveal the nature of the
adsorbed species at different locations within the films because of their different scanning
modes.
Provided with the basic understanding of CO$_2$ adsorption onto the unsupported amines, the nature of CO$_2$ adsorption onto pelletized immobilized amine sorbents under different operating conditions can be investigated. Studying the nature of CO$_2$ adsorption and desorption for pelletized amine sorbents under practical conditions is key to optimizing the pellet formulation. Because highly pure CO$_2$ is essential for its sequestration underground, it is worthwhile to investigate different operating conditions that could enhance the pellet CO$_2$ capture capacity and concentrate the desorbed CO$_2$. These factors generate hypothesis 3:

3. Adsorption of CO$_2$ gas onto immobilized amine sorbents in the presence of H$_2$O vapor followed by purging with 100% CO$_2$ enhances the total CO$_2$ capture capacity, resulting in greater than 98% concentrated CO$_2$ generated during steam regeneration.

Adsorption by flowing CO$_2$ onto sorbent particles followed by (i) CO$_2$ pulsing, (ii) air flowing, or (iii) air pulsing and then steam regeneration will be performed in a tubular reactor set-up to evaluate the effect of different operating conditions on the amount and concentration of weakly and strongly adsorbed CO$_2$. Adsorption by pulsing CO$_2$ will be performed to examine the temperature rise, i.e. binding strength, of CO$_2$ at different loadings of adsorbed species. Lastly, the effect of H$_2$O vapor on CO$_2$ capture capacity of sorbent pellets will be investigated.

Incorporating additional hydroxyl groups (PEG) into immobilized amine sorbents was shown to enhance the CO$_2$/amine efficiency and reduce the oxidative degradation of the NH and NH$_2$ groups by dispersing the amine molecules. Therefore, it is reasonable to
assume that other hydroxyl-containing polymers can enhance the performance of solid amine sorbents. Because PVA possess a higher hydroxyl content per gram of sample than most silica grades, and because the porosity and both chemical and physical stabilities can be enhanced through templating and cross-linking, it is an attractive support for solid amine sorbents and pellets. These factors generate hypothesis 4:

4. Interactions between the PVA-OH groups and the amine groups of impregnated TEPA decreases the binding strength of CO$_2$ to the NH and NH$_2$ sites, producing more weakly adsorbed CO$_2$ species.

PEG is soluble in aqueous PVA solution, making it an excellent template. PEG with different molecular weights will be used to produce a templated PVA hydrogel, where the hydrogel will be further treated by vacuum drying or phase inversion to produce a porous solid material. The porous material will be cross-linked with different amounts of glutaraldehyde to reduce the H$_2$O solubility. FTIR, SEM, BET, and other techniques will be used to characterize the porous structures. Once the best cross-linked porous PVA material is synthesized, it will be impregnated with different amounts of an amine and other additives to prepare the PVA-immobilized sorbents. In situ CO$_2$ adsorption over the PVA-immobilized amine sorbents will be performed in DRIFTS and the results will be compared with those for adsorption on silica-supported sorbents to determine the effect of the PVA hydroxyls on the amount of strongly and weakly adsorbed CO$_2$.
3.1 Immobilized Amine Sorbent Preparation

Immobilized amine sorbents were prepared by the following general procedure:

(i) preparation of an impregnation solution, (ii) mixture of the impregnation solution with silica (Tixosil 68 or Tixosil 6i8B, Rhodia) or cross-linked porous polyvinyl alcohol particles (PPc) to produce a wet paste, (iii) distribution of the wet paste into a steel pan and heating at 100-130 °C for 1-2 h to evaporate solvent, and (iv) grinding the resulting with solid into a fine powder. The impregnation solution was prepared by mixing different concentrations of (i) tetraethylenepentamine (TEPA, tech. 98%, Sigma-Aldrich) or polyethyleneimine (Mw=750,000, Sigma-Aldrich) in ethanol and (ii) TEPA, polyethylene glycol (PEG Mw=200, Sigma-Aldrich), epoxy (E), and antioxidant (A) in deionized H₂O and ethanol. Pelletization of the powder sorbent prepared from Tixosil 68B was accomplished by (i) mixing the sorbent with a polymer binder solution, (ii) extruding the sorbent+binder dough mixture into rods, (iii) and then placing the rods into a spheronizer followed by drying to produce the round pellets. The detailed procedure for preparing the sorbents and pellets can be found in CHAPTERS IV-VII.
3.2 Preparation of Porous Polyvinyl Alcohol Materials

An array of 70 templated polyvinyl alcohol (Elvanol 71-30, fully hydrolyzed, est. Mw=75,000 (PVA)) precursor solutions, each of 50.0 g, was prepared by first dissolving 2.0-7.5 g of PVA in DI H₂O at 100 °C for 60 min and then adding the following templates: ethylene glycol=1-25 wt%; polyethylene glycol (Mw=200, Sigma-Aldrich, (PEG 200)) =7-72%; PEG 400=7-38 wt%, PEG 600=13-73%; or PEG 900=13-25 wt%.

The final wt% of PVA in the solutions ranged from 4 to 15 wt%. The remaining procedure for synthesizing porous polyvinyl alcohol materials from the templated PVA gels can be divided into four groups and according to the methods of gelling, drying, and template removal that were used. Figure 3.1 summarizes the preparation procedures of the Group 1-3 porous PVA materials.

**Group 1.** Porous PVA materials were prepared using a modified approach as reported elsewhere [80], in which the templated PVA precursor solutions were poured into circular aluminum molds (diameter=2”) and allowed to cool for 16 h to 25 °C, which caused the solutions to form flexible hydrogels. The hydrogels were then dehydrated by drying at 50 °C in a 27 inch Hg vacuum for 24 h, producing rigid solids. The rigid solids were annealed in an oven at 160 °C under a 10 inch Hg vacuum in the presence of Ar for 1 hr. The template was then rinsed from the annealed rigid solid by submerging in 100 mL of DI H₂O at 25 °C for 24 h, and then H₂O absorbed by the solid was removed by drying at 50 °C under a 27 inch Hg vacuum for 24 h.
Figure 3.1: Summary of preparation for the Group1-3 porous PVA materials.

**Group 2.** The templated PVA precursors solutions were poured into a multi-compartment steel mold (diameter=2”), and then the solutions underwent two cycles of freezing-thawing. A freezing-thawing cycle was performed by (i) submerging the bottom half of the mold containing precursor solutions into a dry ice/acetone bath at -79 °C for 30 min for freezing and then (ii) heating at 50 °C for 25 min for thawing the frozen solutions. Freezing-thawing in this way produced hydrogels similar to those described for group 1. After two freezing-thawing cycles, the hydrogels were then vacuum dried, annealed, rinsed, and then dried again similar to the group 1 materials.
**Group 3.** The templated PVA precursor solution underwent two freezing-thawing cycles similarly as the group 2 materials. The resulting hydrogels were then placed into a hot vegetable oil bath at 100-200 °C for 3 min to boil-off and remove the H₂O, followed by rinsing in 100 mL of acetone at 50 °C for 24 h to remove the oil and the template. Acetone was then removed from the rinsed samples by heating at 90 °C for 1 h.

The detailed description for the preparation of the Group 4 porous PVA materials is found in CHAPTER VIII. These group 4 materials were used to prepare PPC-based immobilized amine sorbents.

### 3.3 Experimental Techniques

This section describes the in situ infrared spectroscopy accessories, tubular reactor system, mass spectrometer, and additional techniques used for material characterization.

#### 3.3.1 FTIR Accessories

In situ infrared studies were performed using (a) a diffuse reflectance infrared Fourier transform spectroscopy, (b) an attenuated total reflectance, or (a) a transmission cell placed inside of a Nicolet 6700 FT-IR spectrometer (Thermo Scientific). Figure 3.2 shows the images of the spectrometer and the different IR cells. The DRIFTS technique can be used to observe heterogeneous (i) gas-solid reactions occurring at the external surface and internal surfaces (pore walls) of porous and nonporous solid particles, and (ii) gas-liquid reactions occurring near the gas/liquid interface and within the bulk of a liquid film cast onto a reflective metal surface. The (a) DRIFTS cell is mounted onto a y-axis-
adjustable stage attached to an accessory box equipped with fixed parabolic and adjustable plane mirrors. The y-axis stage and plane mirrors are used to align the incident IR beam onto the sample to achieve the maximum detector signal intensity.

Figure 3.2: Camera images of the FT-IR and IR accessories for in situ studies.

The majority of the infrared light contacts the top sample surface and penetrates into the bulk, which is about 0.5-1.0 mm into a packed particle bed and about 10 μm into a liquid film. The penetrated light is then refracted through the sample and is scattered (diffusely reflected) by reflection, refraction, and diffraction [161]. A portion of the infrared light is absorbed by the sample at different wavenumbers, which correspond to different molecular functional groups (hydroxyl, amine, aldehyde, etc.), and the
nonabsorbed diffusely reflected light is collected by the parabolic mirrors and sent to the detector, which generates the IR spectrum.

The (b) ATR cell is commonly used to observe homogeneous liquid phase and heterogeneous gas-liquid reactions occurring within a 2 μm region of a thick liquid film. The incident IR beam reflects off of a 45 ° angle plane mirror and refracts up into a ZnSe window contained inside of a widow. Entering the window at greater than the critical angle (ZnSe=40 °) results in total internal reflection of the IR beam, which allows the beam to propagate horizontally through the window and then exit at the window down to another plane mirror, which reflects the beam to the detector. The electric field of the incident IR beam (evanescent wave) extends into the sample film (penetration depot) and decays exponentially with thickness. The penetration depth of the evanescent wave is described in Eq. 3.1 as

Eq. 3.1: Penetration depth of ATR.

$$d_p = \frac{\lambda}{2\pi n_1 \sin^2 \theta - (n_2/n_1)^2}$$

where λ is the penetrating wavelength, n₁ and n₂ are the refractive indices of ZnSe (2.4) and the film respectively, and θ is the angle of incidence of the IR beam [161].

The transmission cell (c) is also used to observe both homogeneous and heterogeneous reactions through the entire thickness of a liquid film or a solid wafer/disk that pressed from a powder. Liquid films are prepared by casting a solute/solvent mixture, such as amine/ethanol, onto the window and evaporating the solvent. Self-sustaining disks can be prepared by mixing the sample powder with KBr or other IR
transparent salt and pressing the mixture at 1,000-10,000 psi. A metal grid can be incorporated into the disk for added support and better thermal conductivity. One advantage of using the transmission cell is the ability to quantify adsorbed-phase and gas-phase reactants and products by using Beer’s law as shown below in Eq. 3.2 [161].

Eq. 3.2: Beer’s law.

\[ A = \log \left( \frac{I_0}{I} \right) = \varepsilon lc \]

The absorbance or integrated absorbance intensity value, \( A \), at one wavenumber or a range of wavenumbers, respectively, is calculated by taking the logarithm of the IR ratio for the background and sample intensities. The value of \( A \) is proportional to the molar absorption coefficient \( \varepsilon \) (L·mmol⁻¹·cm⁻¹), path length through the sample \( l \) (cm), and the sample concentration \( c \) (mmol/cm³).

3.3.2 Mass Spectrometer

A Pfeiffer QMS quadruple mass spectrometer (MS) was used to measure the effluent gas from the tubular reactor system and IR cells, allowing the signal intensity profiles for species to be converted into concentration profiles. The MS was operated under high vacuum in the range of 10⁻⁵ to 10⁻⁶ mbar, and monitored the following mass/charge (m/e) ratios corresponding to each gas of interest: 18=H₂O, 28=N₂, 32=O₂, 40=Ar, 44=CO₂, and 78=C₆H₆.

3.3.3 Tubular Reactor System

The key components for the tubular reactor system used for performing the in-situ CO₂ adsorption desorption studies are shown in Figure 3.3, and consist of a (i) aluminum tubular reactor (ID=1.3 cm, L=27.5 cm) with a 30.0 g sorbent capacity; (ii) process steam
generator (Electro-Steam, Model LG-20) with a saturated steam (212°F) capacity of 69 lb/hr; (iii) 226 cm³ stainless steel pressure vessel with a 30 psi capacity; (iv) jacked H₂O vapor condenser with 0.5 L/min H₂O (25°C) flowing through the jacket; and (v) Pfeiffer QMS quadruple mass spectrometer for monitoring effluent gases.

Figure 3.3: Key components of the tubular reactor system used for performing in situ CO₂ adsorption-desorption studies.

3.4 In situ Experimental Procedures

This section describes the procedures for performing in situ CO₂ adsorption-desorption studies in the IR cells and tubular reactor.
3.4.1 In Situ Benzene/CO$_2$ Adsorption-Desorption of Immobilized Amines Sorbents

The procedure for performing in situ benzene and benzene/CO$_2$ adsorption-desorption is illustrated in Figure 3.4.

**Figure 3.4**: Experimental procedure for performing in situ benzene and benzene/CO$_2$ adsorption-desorption on silica and TEPA/silica sorbents.
Briefly, the sorbents are first pretreated at 110 °C in flowing Ar to remove H₂O and CO₂ adsorbed from the ambient atmosphere and onto the hydroxyl and amine groups. Benzene adsorption at 40 °C for 3 min with 6.8% C₆H₆ vapor is then performed by flowing Ar through the benzene saturator, where the concentration of benzene was determined by the increased volumetric flow rate of benzene/Ar compared to Ar.

Benzene was then desorbed by flowing Ar for 12 min. Benzene/CO₂ adsorption was performed by flowing 10%/CO₂/6.8% through the sorbent, which was followed 10 min of Ar purging and then heating at 100 °C to remove strongly and weakly adsorbed species.

3.4.2 In situ CO₂ Adsorption-Desorption of TEPA Films

Figure 3.5 shows the experimental procedure for performing in situ CO₂ adsorption-desorption of TEPA thin films, which consisted of (1) pretreating by heating at 100 °C for 5 min in flowing Ar, (2) adsorbing CO₂ by flowing 10%CO₂/air over the films at 50 °C, and (3) desorbing weakly adsorbed CO₂ by flowing Ar for 10 min and then heating at 100 °C to desorb strongly adsorbed CO₂.

The calibration for estimating the amount of adsorbed CO₂ on the films in the DRIFTS was performed on a 4 μm TEPA film. Different volumes of 100% CO₂ were sequentially injected through a septum and into the DRIFTS cell at 50 °C. Adsorption of an injected volume of CO₂ by the film was evidenced by the increase in IR band intensities of the adsorbed species and by the absence of a gas phase CO₂ IR band.
Figure 3.5: Experimental procedure for performing in situ CO\textsubscript{2} adsorption-desorption on TEPA thin films.

The sequential amounts of CO\textsubscript{2} gas adsorbed on the film were correlated with the increased band intensities of the adsorbed CO\textsubscript{2} species until gas phase CO\textsubscript{2} was detected.
by the IR. Calibration factors were calculated by dividing the amount of CO$_2$ by the adsorbed CO$_2$ band intensities. These calibration factors were used to estimate the amount of adsorbed CO$_2$ on all films in the DRIFTS during the adsorption-desorption experiments.

3.4.3 In situ CO$_2$ Adsorption-Desorption onto Sorbent Particles and Pellets in the Tubular Reactor

Figure 3.6 and Figure 3.7 shows the experimental procedures for performing the adsorption-desorption studies on the sorbent particles and pellets in the tubular reactor system, respectively. The study for retaining and concentrating weakly adsorbed CO$_2$ from sorbent particles during desorption was studied by performing three different operations after adsorption: pulsing air, flowing air, and pulsing CO$_2$. Pulsing and flowing air reduces the partial pressure inside the reactor, causing weakly adsorbed CO$_2$ species to be removed. However, pulsing CO$_2$ should remove residual air present after adsorption which increases the CO$_2$ partial pressure. Increasing the total CO$_2$ gas concentration inside the reactor system should allow desorbed CO$_2$ from the sorbent to be highly concentrated.

Desorption of CO$_2$ was performed by steam regeneration, where saturated steam at 130 °C and 70 psi was provided by a commercial lab-scale generator and pulsed into the reactor and then purged with hot air. Steam regeneration allows CO$_2$ to be concentrated to high purity because the steam can be removed by condensation. Pulse adsorption of CO$_2$ onto the sorbents particles was performed in order examine the effect of adsorbed CO$_2$ loading on the resulting heat released, i.e. CO$_2$ bond strength.
Figure 3.6: Experimental procedure for performing CO₂ adsorption-desorption studies of sorbent particles in the tubular reactor system.

Pulse adsorption was performed by introducing 15 pulses of 226 cm³ of 100% CO₂ at 30 psi into the reactor and allowing a 10 min equilibration time between each pulse.
In situ Tubular CO$_2$ Adsorption-Desorption (Pellets)

Sorbent:
* TPSENa pellets

(C) CO$_2$ Adsorption in the Presence of H$_2$O Vapor

(1) Pretreatment
A. Air; 4.2 L/min
B. 110 °C
C. 5 min

(2.1) CO$_2$ ads.-dry
A. 10%CO$_2$/10%CH$_4$/air; 4.2 L/min
B. 55 °C
C. 5 min

(2.1) CO$_2$ ads.-wet
A. 10%CO$_2$/10%CH$_4$/100% RH at 45 °C/air; 4.2 L/min
B. 55 °C
C. 5 min

(3) CO$_2$ des. retention weakly ads.
A. 100% CO$_2$ pulse; 226 cm$^3$, 30 psi
B. 55 °C
C. 10 min equilibration

(4) CO$_2$ des.-steam regeneration
(i) A. No flow
B. 110 °C
C. 1
(ii) A. Air; 4.2 L/min
B. 110 °C; 8 min
C. 55°C cooling

Figure 3.7: Experimental procedure for performing CO$_2$ adsorption-desorption studies of sorbent pellets in the tubular reactor system.
CO₂ adsorption-desorption onto the pellet sorbent was performed under dry conditions similarly as the particle sorbent, followed by CO₂ pulsing and steam regeneration. Wet adsorption, i.e. adsorption in the presence of H₂O vapor, was tested by flowing a 10%CO₂/10%CH₄/air flow through a water saturator maintained at 45-50 °C for 5 min, followed by pulsing with 100% CO₂ and performing steam regeneration.
CHAPTER IV

PROBING THE ADSORPTION/DESORPTION OF CO$_2$ ON AMINE SORBENTS BY TRANSIENT IR STUDIES OF ADSORBED CO$_2$ AND C$_6$H$_6$.

4.1 Summary

CO$_2$ diffusion limitations and re-adsorption of desorbed CO$_2$ during removal from immobilized amine sorbents could significantly reduce the effectiveness of CO$_2$ capture processes. To decouple CO$_2$ diffusion from desorption/re-adsorption on silica and tetraethylenepentamine (TEPA)/silica sorbents, a new transient diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) method was carried out by using benzene as a surrogate probe molecule. Comparison of the infrared intensity profiles of adsorbed CO$_2$ and Si-OH (which adsorbs benzene) revealed that slow rates of CO$_2$ uptake and desorption are a result of (i) CO$_2$ diffusion through an inter-connected network produced from CO$_2$ adsorbed inside of the amine/silica sorbent pores and (ii) re-adsorption of CO$_2$ on the amine sites inside of the pores and at the external surface of the sorbents. High rates of CO$_2$ adsorption/desorption onto/from the immobilized amine sorbents could be achieved by sorbents with low amine density at the external surfaces and pore mouths.
4.2 Introduction

Immobilized amine sorbents are widely studied for the removal of carbon dioxide from the flue gas of coal-fired power plants in order to reduce anthropogenic CO$_2$ emissions. Advantages of immobilized amine sorbent technology over conventional aqueous amine processes could include low heat of regeneration, reduced equipment corrosion, and enhanced CO$_2$ mass transfer kinetics. Among the most commonly studied sorbents are those consisting of impregnated amines such as tetraethylenepentamine (TEPA) and polyethylenimine (PEI) or grafted amines such as 3-aminopropyltriethoxysilane (APTES) on hydroxyl-containing porous supports, for instance silicas [6, 9-11, 16, 44, 45, 67, 162, 163] and zeolites [12, 164, 165]. One issue with the use of immobilized amine sorbents is the CO$_2$ mass transfer limitations, specifically for intra-particle diffusion. Slow diffusion of CO$_2$ into and out of the sorbents could extend the overall CO$_2$ capture cycling time, reducing the effectiveness of the process.

Thermal Gravimetric Analysis (TGA) studies conducted by Sayari’s group have attempted to identify amine dispersion [9] and pore length [10] as contributing factors to CO$_2$ diffusion limitations during adsorption onto PEI/MCM-41 sorbents. High CO$_2$ uptake was observed for sorbents (i) containing surfactant, (ii) containing low amine loading, and (iii) adsorbing CO$_2$ at high temperature. The high uptakes were attributed to better amine dispersion, which reduced CO$_2$ diffusion limitations [9]. Higher CO$_2$ uptake capacities and faster uptake kinetics were also observed for PEI sorbents containing short pores (0.2 µm) than those containing long pores (24-40 µm) and were attributed to a reduced diffusion path (less diffusion resistance) for CO$_2$ [10]. Other studies showed that
enhancement in the CO\textsubscript{2} uptake of different PEI/silica sorbents was achieved by adding 3-aminopropyltriethoxysilane (APTES) [47] or polyethyleneglycol-400 [11] to the sorbent, which was further attributed to better amine dispersion by the additives. It was also observed from TGA that the rate of CO\textsubscript{2} removal from PEI/MCM-41 in N\textsubscript{2} flow under isothermal conditions decreased with temperature (100 to 75 °C)[162]. The incomplete regeneration of the sorbent at 75 °C was attributed to both strong binding of CO\textsubscript{2} to the amine and diffusion limitations. A fluidized bed study has also been conducted in an attempt to model the nonisothermal desorption of CO\textsubscript{2} from PEI/Silica sorbents in the presence of gas-phase CO\textsubscript{2} and with varying sorbent heating rates [166]. It was reported that the apparent CO\textsubscript{2} desorption activation energy increased with conversion \(X\) for \(0.05 \leq X \leq 0.30\), i.e. CO\textsubscript{2} desorption, which was attributed, in-part, to competition between CO\textsubscript{2} adsorption and desorption.

Other TGA studies have been conducted in which kinetic models were applied to CO\textsubscript{2} uptake profiles of immobilized amine sorbents to describe adsorption and diffusion kinetics [8]. Analysis of the CO\textsubscript{2} breakthrough curve was conducted using pseudo-first order kinetic models to calculate lumped adsorption/diffusion constants for impregnated PEI-PE-MCM-41 and grafted TRI-PE-MCM-41 sorbents during adsorption at 25-70 °C. This analysis revealed that CO\textsubscript{2} uptake on the TRI (2-[2-(3-trimethoxysilylpropylamino)ethylamino]-ethylamine) sorbent exhibited faster kinetics than on the PEI sorbent for all temperatures. Faster kinetics were attributed, in part, to the open pore structure of the grafted TRI sorbent. A modified weight gain technique has also been used in an attempt to decouple the adsorption and diffusion processes which govern the overall CO\textsubscript{2} uptake kinetics of sorbents consisting of N-(3-
(trimethoxysilyl)propyl)ethane-1, 2 amine (APAETMS) functionalized onto mesoporous silicas with different pore diameters [167]. A double exponential function was fit to the CO$_2$ uptake profile of the sorbents, where separate time constants for adsorption ($\tau_1$) and diffusion ($\tau_2$) processes were calculated. The authors reported higher values of $\tau_2$ than $\tau_1$ for all sorbents, which were attributed to diffusion-limited CO$_2$ uptake. Additionally, increased values of $\tau_1$ with decreased pore diameters were attributed to diffusion limitations resulting from the narrow pores. Packed bed experiments for CO$_2$ adsorption onto zeolite 13X and 3-aminopropyltrimethoxysilane (APTMS)/SBA-15 sorbents conducted by Jones’ group revealed a gradual breakthrough profile for gas-phase CO$_2$, i.e. small linear driving force constant, for the zeolite compared to sharp profiles for the ATPMS sorbents [168]. The authors ascribe the gradual CO$_2$ breakthrough to slow access of CO$_2$ to the adsorption sites of zeolite compared to those of APTMS sorbents, resulting from the small pore structure of the zeolite.

These studies provide valuable insight into the various factors affecting CO$_2$ diffusion, including amine loading and type, temperature, and pore structure of the sorbent. However, one key factor that has not been considered is the diffusion limitation caused by chemically adsorbed CO$_2$ species. It is well know that CO$_2$ adsorbed on liquid amines increases the amine viscosity, which could result in diffusion limitations for CO$_2$ adsorbed on immobilized amines. The objective of this work is to use an in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique to study the diffusion kinetics of CO$_2$ gas within a TEPA/Silica sorbent in the presence of adsorbed CO$_2$. Because of the high affinity of CO$_2$ to the amines, we used benzene as a surrogate molecule to probe the CO$_2$ diffusion. We found that CO$_2$ adsorbed as
carbamate/ammonium pairs, ammonium-carbamate zwitterions, and carbamic acid decreases the rate of benzene (CO₂ gas) diffusion from the sorbent. We also found that a desorption/re-adsorption mechanism limits the rate of CO₂ removal from the sorbent.

4.3 Experimental Section

This section describes the procedures for preparing the sorbents and performing the benzene and benzene/CO₂ adsorption-desorption experiments.

4.3.1 Sorbent Preparation

A 5.0 g sample of amorphous silica (Tixosil 68, Rhodia) was impregnated with 14.5 g of 20 wt% tetraethylenepentamine (TEPA tech. 98%, Sigma-Aldrich) in ethanol and dried at 100 °C for 60 min. The dried sorbent was a white granular powder containing 37 wt% TEPA, labeled 37 wt% TEPA/Silica. A 12 wt% TEPA/Silica sorbent was prepared by impregnating 5.0 g of silica with 14.5 g of 4.8 wt% TEPA in ethanol. The amine loadings of the sorbents were determined by the weight increase of silica after TEPA impregnation.

The particle diameter of silica (160-510 µm; avg.=360 µm) and the amine sorbents (120-660 µm; 12 wt% TEPA/Silica avg.=320 µm, 37 wt% TEPA/Silica avg.=260 µm) was determined by scanning electron microscopy (SEM, Hitachi TM-3000), and the amine distributions on the external and internal surfaces of the sorbents were determined by energy-dispersive X-ray spectroscopy (EDS, Quantax 70). The surface area of silica (S_BET=252 m²/g) was obtained from a nitrogen adsorption isotherm at 77 K using data in the region of P/P₀=0.10-0.34 (Micromeritics ASAP 2020). Silica was pretreated at 200 °C for 16 h prior to analysis. Ethanol uptake values of silica and
the TEPA/Silica sorbents were used to compare the sorbents’ pore volumes. The uptake was performed by adding ethanol to 0.5 g samples of the sorbents until the samples became saturated, then decanting any excess.

4.3.2 Benzene Adsorption

Figure 4.1 shows the experimental set-up consisting of (i) a gas manifold with mass flow controllers, 4-port valve, and benzene (C₆H₆ anhydrous 99.8%, Sigma-Aldrich) saturator, (ii) a DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) cell loaded with 30-50 mg of silica or TEPA/Silica sorbent and with gas flow directed from top-to-bottom placed inside of a Nicolet 6700 FTIR bench (IR), (iii) a Pfeiffer QMS 200 quadruple mass spectrometer (MS), and (iv) Labview computer software to control and monitor DRIFTS cell temperature and heating rate. Prior to benzene adsorption, 150 cm³/min of Ar were flowed through the benzene saturator for 20 min to purge residual ambient gas. Benzene adsorption onto silica and TEPA/Silica sorbents was performed by (i) pretreating at 110 °C for 10 min in a 150 cm³/min Ar flow for the removal of H₂O and CO₂ adsorbed from ambient, (ii) adsorbing benzene at 40 °C for 3.0 min by switching the Ar flow to a 6.8 vol% benzene flow from the benzene saturator, and (iii) removing gas-phase and adsorbed benzene for 12.0 min with Ar flow. Single-beam spectra, I, from 32 co-added scans with a resolution of 4 cm⁻¹ were obtained every 10 s at a rate of 6 scans/min.

The reference IR spectrum of gas-phase benzene was obtained by flowing Ar/C₆H₆ through the DRIFTS cell with a metal cup placed on the sample holder. The reference IR spectrum of liquid benzene was obtained by Attenuated Total Reflectance (ATR). The IR absorbance spectra of the benzene references were obtained by
abs = \log{\frac{I_{\text{background}}}{I_{\text{reference}}}}, \text{ where } I_{\text{background}} \text{ was the spectrum of the blank ZnSe window (ATR) or the metal cup (DRIFTS) and } I_{\text{reference}} \text{ was the spectrum of gas-phase or liquid benzene.}

![Diagram](image)

Figure 4.1: Experimental set-up used for the benzene and benzene/CO$_2$ adsorption-desorption studies.

4.3.3 CO$_2$ and Benzene Adsorption

The adsorption and desorption of CO$_2$ and benzene were performed on 37 wt% TEPA/Silica by (i) pretreating at 110-120 °C for 10 min in a 150 cm$^3$/min Ar flow, (ii) cooling to 40 °C and adsorbing CO$_2$ and benzene for 3 min by step switching from Ar to a 150 cm$^3$/min flow of 10% CO$_2$/6.8% benzene/air via the 4-port valve, (iii) removing gas-phase and weakly adsorbed species by switching back to the Ar flow for 10 min, and (iv) heating to 110 °C at 10 °C/min in Ar and holding for 10 min for temperature programmed desorption (TPD) of strongly adsorbed CO$_2$. 

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4.4 Results and Discussion

Figure 4.2 shows the IR absorbance spectra (abs=log(1/I)) of silica and the TEPA/Silica sorbents at 40 °C before adsorption, and the inset table shows their physical properties. The spectrum of silica shows the characteristic Si-OH stretching of geminal groups at 3730 cm\(^{-1}\) [169] and H-bonded Si-OH groups at 3670 cm\(^{-1}\) [6]. The Si-OH stretching band of isolated groups at 3743 cm\(^{-1}\) [169] is overlapped with the bands of geminal and H-bonded groups. Adsorbed H\(_2\)O remaining on the surface after pretreatment is evidenced by the broad O-H stretching band between 3500 and 2500 cm\(^{-1}\) and the O-H bending band at 1630 cm\(^{-1}\).

Figure 4.2: Physical properties of silica and TEPA/silica sorbents, and their IR absorbance spectra before benzene adsorption.

Impregnating TEPA onto silica, i.e. 12 wt% TEPA/Silica, decreased the intensity of the isolated and geminal Si-OH stretching bands and produced asymmetric and symmetric N-H stretching bands at 3360 and 3295 cm\(^{-1}\), asymmetric and symmetric C-H stretching...
bands at 2930 and 2814 cm$^{-1}$, an NH$_2$ deformation band at 1603 cm$^{-1}$, and a CH$_2$
deformation band at 1458 cm$^{-1}$.

Partial removal of adsorbed H$_2$O by impregnated TEPA is evidenced by the
reduction in the O-H stretching and bending bands of H$_2$O. Increasing the TEPA loading
to 37 wt% further decreased the isolated and geminal Si-OH stretching bands and
increased the intensity ratio of the N-H to C-H vibration bands. The amount of isolated
plus geminal Si-OH groups on the silica surface is calculated to be 0.7 mmol Si-OH/g-
silica, based upon an estimated 1.7 Si-OH/nm$^2$-silica [170, 171] and silica surface area of
$S_{\text{BET}}=252$ m$^2$/g-silica. The TEPA/Si-OH molar ratios of 1.1 (12 wt% TEPA/silica) and
4.6 (37 wt% TEPA/silica) suggest a TEPA coverage greater than one monolayer on the
silica surface at the higher loading. Low ethanol (EtOH) uptake values of 2.9 and 1.8 mL
EtOH/g*sorbent for 37 and 12 wt% TEPA/Silica compared to 3.2 mL EtOH/g*silica
confirms that TEPA was impregnated inside of the silica pores.

The transmission electron microscopy (TEM, JEOL 1230) images of silica in
Figure 4.7 in the Supporting Information revealed that the porous structure of silica was
formed by agglomeration of non-porous particles of which the diameter is in the range of
10 to 20 nm. The void spaces between the particles constitute the pores. The pore size
distribution of silica obtained by BET measurements revealed a 1.9 nm average diameter
for the small pores and an 80 to 120 nm average diameter for the large pores, which were
observed by TEM. The TEM images of 37 wt% TEPA/Silica shown in Figure 4.7
unraveled that TEPA occupied the voids (pores) between the silica particles, reducing the
overall pore diameters. BET measurements of the TEPA sorbents were not obtained due
to evaporation of TEPA. However, other BET results have reported that the
impregnation of SBA-15 with about 31 wt% PEI reduced the pore diameter by 14% [172]. Assuming a 14% reduction in the pore diameter of silica upon impregnation with 37 wt% TEPA, the average diameters of the sorbent presented in this work are estimated to be 9-17 nm for small pores and 69-103 nm for large pores.

Figure 4.3 shows the SEM images of the spherical TEPA/Silica sorbent particles and the EDS mapping of elemental N (red), which reveals the amine distribution on both the external and internal surfaces. The displayed N/Si ratios for the internal and external surfaces describe the relative amine (NH and NH$_2$) density on the sorbent particles resulting from impregnated TEPA. Higher ratios at the external than internal surfaces of the particles, especially for 37 wt% TEPA/Silica, show a gradual decrease of amine density in the radial direction.

12 wt% TEPA/Silica

<table>
<thead>
<tr>
<th>External surface</th>
<th>Internal surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/Si=0.17</td>
<td>N/Si=0.24</td>
</tr>
</tbody>
</table>

37 wt% TEPA/Silica

<table>
<thead>
<tr>
<th>External surface</th>
<th>Internal surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/Si=0.26</td>
<td>N/Si=0.65</td>
</tr>
</tbody>
</table>

MAG: 800 N 50 µm
MAG: 2000 N 20 µm

Figure 4.3: SEM images of spherical TEPA/Silica sorbent particles and EDS mapping of elemental N on the particles’ external and internal surfaces. The internal surfaces were exposed by breaking the full particle into two nearly equal size sections.
Figure 4.4: (a) IR absorbance spectra of adsorbed benzene on silica and the TEPA/Silica sorbents after 0.2 and 3.0 in Ar/C₆H₆ flow and after 13.0 min in Ar flow, (b) normalized integrated absorbance profiles showing the formation and removal of adsorbed benzene from the isolated and geminal Si-OH groups.

The higher amine density on the external surface suggests the presence of thick multilayers, which could block pore entrances and inhibit CO₂ and benzene diffusion. The 37 wt% TEPA/Silica exhibited higher amine densities at both surfaces compared to 12 wt% TEPA/Silica, evidenced by the larger N/Si ratios. The great difference in the amine density between the external and internal surfaces for the 37 wt% amine loading resulted from impregnation of silica with a highly concentrated TEPA solution.
Figure 4.4 (a) shows the IR absorbance spectra collected during benzene adsorption onto and desorption from silica at 40 °C. Diffusion of benzene into the pores and adsorption onto the isolated hydroxyl groups of silica was observed after 0.2 min, producing the sharp negative Si-OH band at 3743 cm\(^{-1}\) [173-175]. Less extent of splitting of the (i) C-H in-plane (\(v_{20}\))/C-C stretching combination bands at 3038 and 3092 cm\(^{-1}\) and (ii) C-C in-plane stretching (\(v_{19}\)) bands at 1481 cm\(^{-1}\) than those for reference gas-phase benzene have been observed elsewhere [173-175] and can be attributed to restriction of the free rotational motion, indicating the adsorbed state of benzene.

Adsorption of gas-phase benzene has also been shown to (i) red shift the C-C stretching band to 1478 cm\(^{-1}\) or 1479 cm\(^{-1}\) [173, 176] (liquid benzene position), and (ii) blue shift the out-of-plane C-H deformation band to 685 cm\(^{-1}\) resulting from interaction of the pi-electrons with Si-OH [174]. We did not observe these features in our spectra because of the overlapping of adsorbed and gas-phase benzene. Interestingly, Monte Carlo simulations have shown that adsorbed benzene molecules are typically oriented between 0 and 50° relative to the silica surface at a monolayer of coverage, depending upon the degree of hydroxylation [177].

Formation of perturbed (hydrogen bonded) Si-OH groups was revealed by the broad Si-OH band at 3622 cm\(^{-1}\), and has been previously observed for benzene adsorption on different silica grades [174], porous glass [175], and beta zeolite [173]. It has been suggested that these Si-OH groups are formed due to clustering of benzene inside the pores, which forces Si-OH groups to interact [173]. Trace amounts of H\(_2\)O in the Ar/benzene flow were adsorbed on silica, indicated by the broad O-H bending band at 1630 cm\(^{-1}\). Figure 4.8 in the Supporting Information shows that the trace H\(_2\)O was
estimated to be <0.005 vol%, which was calculated based upon the MS intensity ratio of H₂O/N₂ for ambient air and for the gases pulsed in during benzene adsorption.

Benzene continued to diffuse and adsorb onto silica, interacting with isolated Si-OH up to 3.0 min, evidenced by the increase in all band intensities. The accompanying 5 cm⁻¹ red shift of the 3743 cm⁻¹ band down to 3738 cm⁻¹ resulted from weakening of the Si-OH bond by adsorbed benzene. Further adsorption of H₂O on the Si-OH produced the broad band between 3500 and 2500 cm⁻¹; increased the 1630 cm⁻¹ band intensity; and generated the Si-O stretching band at 955 cm⁻¹ for Si-OH with adsorbed H₂O [178]. Figure 4.9 in the Supporting Information shows that H₂O would adsorb on <15% Si-OH groups, which was estimated from the integrated absorbance of the O-H bending band and the negative Si-OH band during pretreatment and benzene adsorption. Emergence of a broad band at 1676 cm⁻¹ for the O-H bending could indicate that some of the adsorbed H₂O experienced less hydrogen bonding in the presence of benzene. This O-H band was not observed in the absence of benzene, suggesting that it resulted from weak interactions between H₂O and layers of adsorbed benzene. Additionally, the 1676 cm⁻¹ band could indicate that some of the H₂O remaining on silica after pretreatment was displaced by adsorbed benzene, where the displaced H₂O would also interact with the benzene layers. Flowing Ar caused desorption and diffusion of nearly all adsorbed benzene and H₂O from silica after 13.0 min. The remaining Si-OH and H₂O bands show that some of the adsorbed H₂O was not completely removed from SiO₂.

The absence of a decrease in the geminal Si-OH band of both 12 and 37 wt% TEPA/Silica after 0.2 min, in contrast to the appreciable decrease of the Si-OH on SiO₂, indicates that benzene did not adsorb on the silica surface and suggests that a high driving
force was needed to overcome the diffusion limitations caused by TEPA. Formation of
the negative Si-OH band at 3725 cm\(^{-1}\) on both sorbents after 3.0 min indicates that
benzene diffused through the TEPA filled pores and adsorbed onto the silica surface.
The integrated absorbance of the negative Si-OH band for 12 wt\% TEPA/Silica was 72% less than that for silica after 3.0 min of benzene adsorption, revealing that most of the Si-
OH groups on the TEPA/Silica sorbent were bonded to the amine groups of TEPA. The Si-OH absorbance further decreased by only 9\% for 37 wt\% TEPA/Silica, indicating that the additional impregnated amine formed multi-layers on the external silica surface and inside of the pores.

Stronger interaction of benzene with oxygen-bonded protons than nitrogen-
bonded protons [179] suggests that benzene is less likely to adsorb on the NH and NH\(_2\) of TEPA than the Si-OH of silica. It was reported that no adsorption of benzene occurred on the amines of a TEPA/beta zeolite sorbent, further indicating that benzene adsorption on TEPA is unlikely to occur [180]. The spectra also show the adsorption of H\(_2\)O on Si-
OH groups, as well as adsorption on amine groups of TEPA evidenced by the negative
NH stretching bands. Lower \( I_{955}/I_{1630} \) band intensity ratio for the sorbents than silica was
observed along with the negative amine bands, indicating that H\(_2\)O adsorbed more on the amines than the Si-OH. Small amounts of adsorbed H\(_2\)O and possibly benzene remained on the sorbents after Ar purge.

The normalized integrated absorbance profiles for isolated and geminal Si-OH
groups in Figure 4.4 (b) unraveled the diffusion kinetics of benzene into and out of silica
and the TEPA/Silica sorbents during adsorption and desorption, respectively.
Normalized integrated absorbance was calculated by abs=(\( A_t - A_{\min} \))/(\( A_{\max} - A_{\min} \)), where \( A_t \)
is the integrated absorbance intensity at time \( t \) for the profile of interest, \( A_{\text{max}} \) is the maximum profile intensity, and \( A_{\text{min}} \) is the minimum profile intensity. The change in the IR intensity of Si-OH groups served as an index to monitor benzene diffusion because the IR features of adsorbed benzene were overlapped with those of the gas phase, and because the adsorption of benzene decreased the Si-OH intensity. Yates, et. al. used the isolated Al-OH groups as an index to monitor the diffusion of 2-chloroethylsulfide (2-CEES) into Al\(_2\)O\(_3\) particles [181]. During benzene adsorption the Si-OH profile of both amine sorbents required about 55 s to decay 50\%, i.e. adsorption half time, compared to 24 s required for the profile of silica. Expectedly during desorption the Si-OH profiles of the amine sorbents required longer time than that of silica to regenerate 50\%, i.e. desorption half time; 174 s for 12 wt\% TEPA/Silica, 258 s for 37 wt\% TEPA/Silica, and 42 s for silica. These results show that impregnated TEPA blocks the pores and inhibits the diffusion of benzene, which is more evident during benzene desorption than adsorption.

Figure 4.13 (a) shows the absorbance spectra of adsorbed CO\(_2\) and benzene on the amine sorbent in the 10% CO\(_2\)/6.8% C\(_6\)H\(_6\)/air flow after 3 min and in the Ar flow after 13 min. Adsorption of CO\(_2\) on the amine sites of impregnated TEPA produced (i) COO\(^-\) and C-N stretching bands at 1495 and 1410 cm\(^{-1}\) [45, 182] respectively, and NH\(_3^+\) deformation and stretching bands at 1632 and 3056 cm\(^{-1}\) [44, 45] for carbamate/ammonium ion pairs; (ii) a broad NH\(_3^+\) stretching band between 2792 and 1876 cm\(^{-1}\) for ammonium-carbamate zwitterions [45]; and (iii) a C=O stretching band at 1706 cm\(^{-1}\), which is in the region of carbamic acid [45] and surface-bound carbamate.
Because of the higher affinity of CO$_2$ to amines than Si-OH, we tentatively assign the 1706 cm$^{-1}$ band to carbamic acid.

Figure 4.5: (a) IR absorbance spectra of adsorbed CO$_2$ and benzene on 37 wt% TEPA/Silica in a 10% CO$_2$/6.8% C$_6$H$_6$/air flow after 3 min and in an Ar flow after 13 min, (b) integrated absorbance profiles showing the adsorption and desorption of CO$_2$ and benzene from the amine sorbent. The full profiles can be found in Figure 4.10 in the Supporting Information.

Furthermore, it was shown that the high absorbance intensity ratio of the 2792-1876 cm$^{-1}$ region/1750-1250 cm$^{-1}$ region corresponded to the adsorption of CO$_2$ on secondary amine sites [45]. The authors suggest that adsorption onto secondary amine sites can form carbamic acid because of the lack of neighboring primary amine sites to accept the acidic proton [45], which supports our assignment of 1706 cm$^{-1}$.

Although the total amount of adsorbed CO$_2$ inside of the pores should be greater than the amount adsorbed on the external surface, the density of adsorbed species should be greater on the external surface because of the higher N/Si ratio (amine density) as shown by EDS. It is suggested that the adsorbed CO$_2$ species on the external surface
should exhibit a larger ratio of ammonium-carbamate zwitterions/ion pairs than those adsorbed on the internal surface because of the higher amine density. Importantly we also observed the adsorption of benzene from the negative Si-OH band, showing that benzene could serve as a surrogate probe molecule for CO$_2$. The CO$_2$ molecule does not compete significantly with benzene for adsorption on the Si-OH because CO$_2$ has a higher affinity to the amines.

Rapid CO$_2$ uptake by the sorbent within the first 15 s (85% total capacity) was observed by the sharp increase in the integrated absorbance profile of all CO$_2$ adsorbed species, shown in Figure 4.13 (b), and was followed by slow CO$_2$ uptake up to 3.0 min. Rapid diffusion and adsorption of benzene produced the sharp decrease in the Si-OH profile, beginning at 10 s because of the overlapping with the positive CO$_2$ overtone bands. Similar behavior of the CO$_2$ uptake profiles for TEPA/SBA-15 [183] and PEI/Silica capsule [184] sorbents compared with our results has been previously observed. The authors postulated that the decreased CO$_2$ uptake kinetics of these sorbents resulted from diffusion limitations caused by an increase in PEI viscosity, where increased viscosity was observed by bubbling CO$_2$ through liquid PEI. It has also been reported that enhanced viscosity, even gel formation, in amine-functionalized ionic liquids corresponds to the formation of carbamate species [185].

The basis for postulating that the diffusion of CO$_2$ into our TEPA/Silica sorbents is limited by an inter-connected network of ammonium-carbamate ion pairs and hydrogen bonded carbamic acid within the pores is supported by (i) the IR spectra of carbamate/ammonium bridges (ion pairs) and carbamic acid produced by adsorption of CO$_2$ onto multi-layers of immobilized amines and (ii) the slow formation of adsorbed
CO₂ species. Rudkevic et. al. have shown that the adsorption of CO₂ by solutions of calix[4]arene tetraurea can form supramolecular 3D gel networks, in part by the formation of carbamate/ammonium ion (NHCOO⁻ - NH₃⁺) salt bridges [186], which was verified by ¹H COSY and ¹³C NMR spectroscopy.

Figure 4.6: Integrated absorbance profiles for regeneration of isolated and geminal Si-OH groups during removal of benzene and CO₂ from silica, the neat amine sorbent, and the CO₂-adsorbed amine sorbent. The initial slopes were calculated from estimated linear regions of the profiles.
The formation of carbamic acid was also shown to increase the viscosity of an NH$_2$-containing ionic liquid because of hydrogen bonding of the acid with a neighboring amine molecule [187].

Figure 4.6 compares the Si-OH integrated absorbance profiles during the removal of benzene and CO$_2$ from the CO$_2$-adsorbed amine sorbent (37 wt% TEPA/Silica) and during the removal of benzene from the neat amine sorbent in a CO$_2$ free environment. Because of the overlapping between the negative Si-OH band and the positive gas-phase CO$_2$ overtone bands, the Si-OH profiles are plotted after 3.4 min when gas-phase CO$_2$ was removed and are vertically centered inside of the graphs for easy comparison. The profile of the Si-OH shows a slower recovery in its intensity on the CO$_2$-adsorbed sorbent than the neat sorbent, confirming that the network of carbamate/ammonium ion pairs and hydrogen bonded carbamic acid, and ammonium-carbamate zwitterions blocked the diffusion of benzene (CO$_2$ gas) within the pores.

Furthermore, slow removal of adsorbed CO$_2$ compared to fast regeneration of Si-OH, i.e. benzene (CO$_2$ gas) diffusion, was evidenced by the small slope for adsorbed CO$_2$ during desorption of adsorbed CO$_2$ and benzene from TEPA/SiO$_2$. According to the behavior of the Si-OH and CO$_2$ profiles; the EDS mapping of N (Figure 4.3); and the IR absorbance spectra of adsorbed CO$_2$ (Figure 4.13); we propose a general two-step CO$_2$ desorption/re-adsorption mechanism for the amine sorbents. In step 1, the CO$_2$ partial pressure is reduced which causes adsorbed CO$_2$ (carbamate/ammonium zwitterions and pairs, and carbamic acid) on the external particle surface to desorb. Desorption of these species breaks the inter-connected TEPA-CO$_2$ network clogging the pores. In step 2, CO$_2$ adsorbed inside of the pores is desorbed and gradually diffused out through the network
to the external particle surface. The desorbed CO\textsubscript{2} can re-adsorb on newly regenerated amine sites along the pore wall or on the external particle surface, re-forming the network. The above analysis for 37 wt\% TEPA/SiO\textsubscript{2} is consistent with the observation on 36 wt\% PEI/SiO\textsubscript{2}, which is illustrated in the Supporting Information. The negative slopes of the ads. CO\textsubscript{2} intensity profile and positive slopes of the geminal Si-OH, corresponding to the rates of CO\textsubscript{2} desorption and benzene diffusion, respectively, are summarized in Table 4.1. Note that benzene was used as a surrogate molecule to probe the CO\textsubscript{2} diffusion. These results suggest that it is possible to quantitatively decouple a CO\textsubscript{2} desorption/re-adsorption mechanism from diffusion by closely examining adsorbed CO\textsubscript{2} and Si-OH profiles during transient conditions.

Table 4.1: Calculated slopes for geminal Si-OH and ads. CO\textsubscript{2} integrated absorbance profiles during benzene and benzene/CO\textsubscript{2} desorption from neat and CO\textsubscript{2}-adsorbed TEPA/Silica and PEI/Silica sorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Neat Gem Si-OH</th>
<th>Neat Gem Si-OH</th>
<th>Ads. CO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>37 wt% TEPA/Silica</td>
<td>0.15</td>
<td>0.12</td>
<td>-0.06</td>
</tr>
<tr>
<td>36 wt% PEI/Silica</td>
<td>0.09</td>
<td>0.02</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

4.5 Conclusions

The mass transfer of benzene and CO\textsubscript{2} within TEPA/Silica sorbents was studied by a new DRIFTS method, where benzene served as a surrogate molecule to probe the kinetics of CO\textsubscript{2} diffusion within the sorbents. EDS and EtOH uptake results show that impregnated TEPA distributes more on the external particle surface than its interior. Adsorption of benzene on silica and the sorbents indicated that 12 wt\% and 37 wt\%
TEPA consumed 72% and 81% of the Si-OH groups, respectively, suggesting the formation TEPA multilayers inside of the pores especially at high loading.

Slow responses in the transient Si-OH profiles of the sorbents compared to that for silica during benzene adsorption and desorption suggested that blockage of the pores by TEPA slowed the diffusion of benzene. More importantly, slower response in the Si-OH profile of the CO$_2$-adsorbed sorbent than that of the neat sorbent in a CO$_2$-free environment during benzene and CO$_2$ desorption confirmed that an inter-connected network of (i) carbamate/ammonium ion pairs; (ii) ammonium-carbamate zwitterions; and (iii) carbamic acid inhibits the diffusion of benzene (CO$_2$ gas) from the amine sorbent. Furthermore, the slow removal of adsorbed CO$_2$ compared to fast regeneration of Si-OH (benzene/CO$_2$ diffusion) during desorption allows us to propose the following general two-step CO$_2$ desorption/re-adsorption mechanism for immobilized amine sorbents: (i) desorption of adsorbed CO$_2$ from the external particle surface and (ii) desorption and diffusion of adsorbed CO$_2$ from inside the pores through the network, where desorbed CO$_2$ re-adsorbs along the pore walls and on the external particle surface to re-form the network.

Overall, our results show that this new technique can be used to better understand the mass transfer issues related to CO$_2$ capture by immobilized amine sorbents, as well as to understand the issues associated with other gas-solid reactions involving porous materials. The results of this study suggest that favorable adsorption/desorption and diffusion kinetics could be achieved by the sorbents with low amine density at the external surface of the sorbent particles.
4.6 Supporting Information

This section describes the supporting information for the CO₂/benzene adsorption-desorption studies.

4.6.1 Figures for Adsorption-Desorption Studies on TEPA/Silica Sorbents

Figure 4.7: SEM and TEM images of (a) silica and (b) 37 wt% TEPA/Silica, along with the pore size distribution of silica. The illustrations show the pore structure and pore sizes of silica and the TEPA/Silica sorbent. *Assuming a 14% reduction in pore diameter by impregnated TEPA.
Figure 4.8: MS profiles of (a) ambient air and (b) N₂, O₂, and H₂O during benzene adsorption on silica at 40 °C.

Pre-treatment, 40°C:
A₃₇₂₅⁺₃₇₄₃ area=2.9
A₁₆₃₀ area=4.7

Benz. ads., 3 min:
A₃₇₂₅⁺₃₇₄₃ area=20.3
A₁₆₇₆⁺₁₆₃₀ area=4.6
Si-OH with ads. H₂O<15%

Figure 4.9: IR absorbance spectra of H₂O adsorbed on silica at different temperatures during pretreatment. The spectra were obtained by abs=log(I_{cooling}/I_{heating}), where I_{heating} is the single beam spectrum of silica (contains ambient adsorbed H₂O) at different temperatures during heating to 110 °C in 150 cm³/min Ar flow and I_{cooling} is the corresponding single beam spectrum of silica at the same temperature during cooling.
Figure 4.10: Complete IR integrated absorbance profiles during CO$_2$/benzene adsorption onto and desorption from 37 wt% TEPA/Silica

4.6.2 Benzene and Benzene/CO$_2$ Adsorption-Desorption of PEI/Silica

Additional benzene and benzene/CO$_2$ adsorption-desorption studies were performed on 36 wt% and 12 wt% polyethyleneimine (branched PEI, Mw=750,000)/Silica sorbents to further check the validity of probing the CO$_2$ adsorption/desorption process with adsorbed benzene. The EDS N mapping on the PEI sorbent particles is presented in Figure 4.11 and shows higher amine density on the internal surfaces, i.e. inside the pores, than external surface. This is in contrast to TEPA/Silica sorbents which show higher density on the external surface. The N/Si ratios of PEI/Silica are summarized in Table 4.2. Table 4.2 shows that the sorbents with the same amine loading of PEI/Silica and TEPA/Silica have similar values in the intensity of
Iso. (isolated) Si-OH, Gem. (geminal) Si-OH, and the sum of these two intensities (Iso + Gem.). These values indicate the sorbents with the same level of amine loading possessed approximately same quantities of available Si-OH groups on the sorbents to adsorb benzene.

![Figure 4.11: IR absorbance spectra (log (1/I)) of fresh TEPA/Silica and PEI/Silica sorbents, and EDS N mapping on PEI/Silica.](image)

Table 4.2: IR absorbance intensities, integrated absorbances, and EDS results for silica and the amine sorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Fresh (abs. int. [log(1/I)])</th>
<th>Benz.-ads. (integ.abs.)</th>
<th>N/Si ratio (EDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iso. Si-OH</td>
<td>Gem. Si-OH</td>
<td>Iso.+Gem</td>
</tr>
<tr>
<td>Silica</td>
<td>0.66</td>
<td>0.78</td>
<td>1.44</td>
</tr>
<tr>
<td>12 wt% TEPA/Silica</td>
<td>0.17</td>
<td>0.31</td>
<td>0.48</td>
</tr>
<tr>
<td>37 wt% TEPA/Silica</td>
<td>0.1</td>
<td>0.22</td>
<td>0.32</td>
</tr>
<tr>
<td>12 wt% PEI/Silica</td>
<td>0.14</td>
<td>0.32</td>
<td>0.46</td>
</tr>
<tr>
<td>36 wt% PEI/Silica</td>
<td>0.13</td>
<td>0.28</td>
<td>0.41</td>
</tr>
</tbody>
</table>
Figure 4.12 (a) revealed the intensity of the negative geminal Si-OH on the PEI/Silica sorbents is less than that of negative Si-OH on silica and the TEPA/Silica sorbents (Figure 4.12), confirming that PEI inside the pores prevented full access of benzene to the available Si-OH. The slow responses in the Si-OH intensity profiles during adsorption onto and desorption from the sorbents shown in Figure 4.12 (b) confirm the diffusion of benzene is limited by the PEI which filled the pores of the support.

Figure 4.12: (a) IR absorbance spectra of adsorbed benzene on silica, 12 wt% PEI/Silica, and 36 wt% PEI/Silica at 40 °C after 0.2 and 3.0 in Ar/C₆H₆ flow and after 13.0 min in Ar flow, (b) normalized integrated absorbance profiles showing the formation and removal of adsorbed benzene from the isolated and geminal Si-OH groups of silica and the amine sorbents.
Adsorption of CO$_2$ and benzene onto 36 wt% PEI/Silica shown in Figure 4.13 (a) produced carbamate/ammonium zwitterions and pairs and carbamic acid similar to adsorption on TEPA/Silica, confirming the formation of the inter-connected network.

Figure 4.13: (a) IR absorbance spectra of adsorbed CO$_2$ and benzene on 36 wt% PEI/Silica at 40 °C in a 10% CO$_2$/6.8% C$_6$H$_6$/air flow after 3 min and in an Ar flow after 13 min, (b) integrated absorbance profiles showing the adsorption and desorption of CO$_2$ and benzene from the amine sorbent.

The negative geminal Si-OH band was not observed in Figure 4.13 (a) because of overlapping with CO$_2$ gas overtones. The intensity profile of adsorbed CO$_2$ on PEI/Silica in Figure 4.14 (b) revealed that 85% adsorption capacity was reached after 48 s compared to 15 s for adsorption on TEPA/Silica, shown in Figure 4.5 (b), confirming that impregnated PEI resulted in a greater diffusion limitations through the sorbents pores than impregnated TEPA.

Figure 4.13 (b) shows that purging CO$_2$ from PEI/Silica by flowing Ar caused fast decay in the adsorbed CO$_2$ profile (slope=−0.06) compared to slow regeneration in the Si-OH profile (slope=0.02), where the magnified features between 4000-3500 cm$^{-1}$ of Figure 4.14 confirm the presence of the negative Si-OH band. The negative S-OH band
emerged as soon as gaseous CO$_2$ was removed. These results indicate that the removal of adsorbed CO$_2$ from immobilized, highly viscous PEI or other viscous amine sorbents could occur by “site-hopping” across NH$_2$ and NH sites (surface diffusion) of amine multi-layers, rather than desorbing into the gas phase and diffusing through or re-adsorbing within the blocked pores. Alternatively, sorbents with higher amine density inside of the pores than on the external particle surface could produce a longer CO$_2$ diffusion path through the inter-connected network, i.e. more diffusion limitations. However, further evidence is needed to support this.

Figure 4.14: IR absorbance spectra of adsorbed CO$_2$ and benzene on 36 wt% PEI/Silica at different times during adsorption.
CHAPTER V

THE EFFECT OF TEMPERATURE ON THE DIFFUSION OF BENZENE WITHIN IMMOBILIZED AMINE SORBENTS

5.1 Summary

Understanding the effect of temperature on the diffusion of benzene (CO₂ surrogate molecule) into immobilized amine sorbents could provide the basis for improving their overall mass transfer kinetics. In this work, benzene and desorption and was performed on different porosity silicas and tetraethylenepentamine (TEP)/silica sorbents at different temperatures using an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) technique. Benzene diffusion coefficients were determined according to a Fickian slab model, and the amount of adsorbed benzene was calculated from the mass spectrometer (MS) gas tracer (1/Ar) and benzene gas profiles. Our results confirmed that benzene adsorption onto the Si-OH sites of porous silica was diffusion controlled, where the coefficient D=9.4 x 10⁻⁶ at 40 °C. Impregnation of 12 and 37 wt% TEPA into porous silica decreased the D value by up to 49%, which is attributed to pore blockage of the sorbents by the amine and removal of potential Si-OH surface diffusion sites. Raising the diffusion temperature enhanced nearly all D values because of the increased mobility of benzene molecules into the pore and across the surface of SiO₂.
5.2 Experimental

This section describes the procedures for preparing low porosity silica particles and immobilized amine sorbents, and for performing the benzene adsorption-desorption studies.

5.2.1 Preparation of Sorbents and Low Porosity Silica Particles, SiO$_2$-lp

The preparation procedure and physical properties of 12 and 37 wt% tetraethylenepentamine (TEPA)/silica sorbents have been reported in our previous work [188]. Briefly, two 5.0 g amounts of silica (Tixosil 68) were impregnated with 4.8 and 20 wt% TEPA in ethanol solutions, and then the wet sorbent mixtures were dried at 100 °C for 60 min. The resulting sorbents contained 12 and 37 wt% TEPA, and exhibited average particle sizes of 320 and 260 μm, respectively.

Low porosity SiO$_2$ particles, labeled SiO$_2$-lp, were prepared by a sol-gel method. A 10.0 g amount of 27 wt% Na$_2$SiO$_3$/H$_2$O solution (Aldrich) was diluted to 10 wt% with DI H$_2$O, then pH adjusted to 7 at 60 °C using 10 wt% acetic acid solution. The resulting hydrolyzed gel was crushed and pH adjusted to 11 by adding 10 wt% NaOH solution. The resulting mixture was heated at 70 °C for 2 hr to form SiO$_2$ gel particles. The gel particles were crushed, washed with 100 mL each of H$_2$O and EtOH, and dried at 100 °C for 60 min to produce rigid particle. The rigid particles were washed again with H$_2$O and EtOH then dried. The average particle size of SiO$_2$-lp is 370 μm (optical microscope).

5.2.2 Benzene Adsorption

An identical experimental set-up and procedure to those reported in our previous work [188] was used to perform benzene adsorption-desorption on the silicas and
TEPA/silica sorbents. Briefly, the set-up consists of (i) a gas manifold with mass flow controllers, 4-port valve, and benzene (C₆H₆) saturator, (ii) a DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) cell loaded with 30-50 mg of silica or TEPA/Silica sorbent and with gas flow directed from top-to-bottom placed inside of a Nicolet 6700 FTIR bench (IR), (iii) a Pfeiffer QMS 200 quadruple mass spectrometer (MS), and (iv) Labview software to control and monitor DRIFTS cell temperature and heating rate.

Benzene adsorption-desorption studies of silicas and amine sorbents pretreated at 110 °C in Ar flow was performed by (i) adsorbing benzene at 40 °C for 3.0 min by switching the Ar flow to a 6.8 vol% benzene flow from a benzene saturator and (ii) removing gas-phase and adsorbed benzene for 12.0 min with Ar flow. Adsorption was further performed at 70 and 120 °C by repeating steps (i) and (ii). Single-beam spectra, $I$, from 32 co-added scans with a resolution of 4 cm⁻¹ were obtained every 10 s at a rate of 6 scans/min. The composition of the DRIFTS effluent was monitored by MS.

5.3 Results and Discussion

This section describes the results of the benzene adsorption and desorption studies performed on the silica particles and TEPA/silica sorbents.

5.3.1 Benzene Adsorption onto Silica and SiO₂-lp Particles

Figure 5.1 shows the IR absorbance spectra and physical properties of pretreated SiO₂-lp, silica, and TEPA/Silica sorbents at 40 °C.
Figure 5.1: IR absorbance spectra and physical properties of pretreated SiO$_2$-lp, silica, 12 wt% TEPA/Silica, and 37 wt% TEPA/Silica

Because the detailed analysis of the IR bands for silica and the amine sorbents can be found in our previous work, we present only a brief discussion of their features. The IR spectrum of silica shows the characteristic Si-OH stretching of (i) free geminal groups at 3730 cm$^{-1}$ [169], (ii) H-bonded Si-OH groups at 3670 cm$^{-1}$ [6, 189], and (iii) free isolated groups at 3743 cm$^{-1}$ [169, 189, 190], which is overlapped with the bands of geminal and H-bonded groups. Strongly adsorbed H$_2$O remaining on the surface after pretreatment produces the broad O-H stretching band between 3500 and 2500 cm$^{-1}$ and the O-H bending band at 1630 cm$^{-1}$, and does not interfere with benzene adsorption. Impregnating 12 and 37 wt% TEPA onto the external silica surface and inside of the pores silica consumed 72 and 81% of the free hydroxyl groups, which decreased the intensity of the hydroxyl IR bands and produced N-H stretching bands at 3360 and 3295 cm$^{-1}$. Evaporation of TEPA produces erroneous BET data.
cm\(^{-1}\), C-H stretching bands at 2930 and 2814 cm\(^{-1}\), an NH\(_2\) deformation band at 1603 cm\(^{-1}\), and a CH\(_2\) deformation band at 1458 cm\(^{-1}\) [191, 192].

The spectrum of SiO\(_2\)-lp shows a sharp Si-OH stretching band at 3737 cm\(^{-1}\) for either free isolated or free geminal groups, and a broad Si-OH band between 3500 and 2500 cm\(^{-1}\) for H-bonded Si-OH groups. The SiO\(_2\)-lp exhibits a lower IR intensity ratio of free Si-OH/H-bonded Si-OH than silica, corresponding to smaller BET surface area; 

\[ S_{\text{BET}} = 190 \text{ m}^2/\text{g} \] for SiO\(_2\)-lp and 

\[ 252 \text{ m}^2/\text{g} \] for silica. The SiO\(_2\)-lp (0.67 cm\(^3\)/g) also has 50\% lower pore volume than silica (1.37 cm\(^3\)/g), suggesting that the Si-OH of SiO\(_2\)-lp are located either (i) inside of more shallow pores or (ii) on a rougher external particle surface.

Figure 5.2 shows the IR absorbance spectra of adsorbed benzene on silica and low porosity SiO\(_2\)-lp after 3.0 min in flowing Ar/C\(_6\)H\(_6\). Adsorption of benzene onto the isolated Si-OH of silica and SiO\(_2\)-lp produced the sharp negative band at 3743 cm\(^{-1}\). The integrated absorbance of the Si-OH band for SiO\(_2\)-lp was about 90\% less than the value for silica, showing significantly fewer adsorption sites. Fewer adsorption sites corresponded to the lower \( S_{\text{BET}} \) for SiO\(_2\)-lp than silica. The C-H in plane (\( \nu_{20}\))/C-C combination stretching bands at 3038 and 3092 cm\(^{-1}\) and the C-C in-plane stretching (\( \nu_{19}\)) bands of adsorbed benzene were overlapped with those of the gas phase. Formation of the H-bonded Si-OH band on both silica and SiO\(_2\)-lp suggests the clustering of benzene inside of the pores. Adsorption of H\(_2\)O on silica’s isolated Si-OH was evidenced by (i) the 1630 cm\(^{-1}\) and 1676 cm\(^{-1}\) O-H stretching band for H\(_2\)O and (ii) the 955 cm\(^{-1}\) Si-OH· · · H\(_2\)O band for SiO\(_2\), which is in contrast to adsorption of H\(_2\)O on SiO\(_2\)-lp which produced only the 1630 cm\(^{-1}\) band.
Figure 5.2: IR absorbance of adsorbed benzene on silica and SiO$_2$-lp particles at 40 °C after 3.0 min in flowing Ar/C$_6$H$_6$. The inset shows the normalized integrated absorbance profiles for gas-phase and adsorbed benzene.

The absence of both the 1630 cm$^{-1}$ stretching band of H$_2$O and the 955 cm$^{-1}$ Si-OH···H$_2$O band for SiO$_2$-lp suggests that H$_2$O did not adsorb significantly onto the isolated Si-OH, i.e. H$_2$O adsorbed primarily onto the H-bonded Si-OH. These results indicate that benzene does not compete with H$_2$O for adsorption onto the isolated Si-OH groups of SiO$_2$-lp, which could enhance the reaction rate of benzene with SiO$_2$-lp.
The inset of Figure 5.2 shows the normalized integrated absorbance profiles of 1481 cm\(^{-1}\) for gas-phase/adsorbed benzene and of 3743 cm\(^{-1}\) for isolated Si-OH of porous silica and low porosity SiO\(_2\)-lp during adsorption. The slow decay of the silica Si-OH profile compared to the rapid increase in the benzene profile showed gradual diffusion of benzene vapor into the pores and adsorption onto the Si-OH sites. In contrast to the profiles of silica, the sharply inverse responses of the benzene and Si-OH profiles for SiO\(_2\)-lp indicates negligible diffusion limitations for benzene to access the Si-OH adsorption sites of the low porosity material. The Si-OH profile of the porous silica required 24 s to decay by 50%, i.e. adsorption half time, compared to 3 s required for the profile of SiO\(_2\)-lp. Despite an estimated 10 times higher isolated Si-OH concentration for porous silica than low porosity SiO\(_2\)-lp, the rate of benzene adsorption onto the more porous SiO\(_2\) was 88% slower than that for the low porosity SiO\(_2\). These results indicate that the rate of benzene adsorption onto the isolated Si-OH of the porous silica is controlled by the rate of benzene diffusion through the pores.

5.3.2 Modeling Benzene Diffusion

Diffusion of gases into porous solids occurs by molecular gas diffusion and surface diffusion mechanisms, where the driving forces are concentration gradients of gas-phase and adsorbed species along the axis of diffusion [193]. Fick’s second law of diffusion describing the time-dependencies of ideal gas-phase and adsorbed species concentrations inside of the pores is written below in Eq. 5.1.

Eq. 5.1: Fick’s second law of diffusion.

\[
\frac{\partial}{\partial t} (C + \beta n) = \left[ 1 + \beta \left( \frac{dn}{dc} \right) \right] \frac{\partial C}{\partial t} = \nabla \cdot \left[ D_g + \beta \left( \frac{n}{C} \right) D_s \right] \nabla C
\]
Here, $C$ is the gas phase concentration inside of the pores; $t$ is time; $\beta$ is the surface to volume ratio of the pores; $n$ and $c$ are the adsorbed and gas phase concentrations from the adsorption isotherm; and $D_g$ and $D_s$ are the gas-phase and surface diffusion coefficients [193]. Assuming the bracketed term containing $D$ and $D_s$ remains constant with $t$, the previous equation becomes

Eq. 5.2: Simplified Fick’s law.

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

where $D$ is the apparent diffusion coefficient defined by Eq. 5.3.

Eq. 5.3: Apparent diffusion coefficient, $D$.

$$D = \frac{D_g + \beta (n/c) D_s}{1 + \beta \left( \frac{dn}{dC} \right)}$$

Spherical and rectangular coordinates have been applied to equation 3 to model gas diffusion into porous spherical particles [194] and slabs [181], respectively. Because the Ar/C$_6$H$_6$ gas flow in our system is directed top-to-bottom through the sample bed, we model diffusion of benzene through a slab that follows Eq. 5.4.

Eq. 5.4: Fick’s second law for diffusion through a slab.

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial^2 x}$$

Gas-phase benzene present at the top ($x=0$) and bottom ($x=l$) (due to voids) of the slab produces the initial and boundary conditions as reported elsewhere [181]. The resulting
equation Eq. 5.5 is used to model the diffusion of benzene into the porous silica and amine sorbent slabs.

Eq. 5.5: Equation for modeling benzene diffusion through samples in DRIFTS.

$$\frac{A_t}{A_{\infty}} = 1 - \frac{8}{(2n + 1)^2 \pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \exp \left( - \frac{D(2n + 1)^2 \pi^2 t}{l^2} \right)$$

The $A_t$ and $A_{\infty}$ terms are the integrated absorbance intensities of isolated plus geminal Si-OH groups at time $t$ and adsorption equilibrium (3.0 min) that correspond to the concentration of the $n$, respectively, $n=100$ is the number of summed terms, $D$ is the apparent diffusion coefficient, and $l$ is the slab thickness.

A DRIFTS depth penetration experiment was conducted on silica, shown in Figure 5.5 in the Supporting Information, and it was found that the IR light penetrated about 520 μm into the bed, so the slab thickness used in the diffusion equation is $l=520$ μm. The diffusion coefficients were obtained by iterating for $D$ in the model equation until the minimum standard deviation, $\sigma$, between the model and experimental data was achieved. Application of the final diffusion to the isolated plus geminal Si-OH decay profiles requires a linear relationship between the absorbance intensities and concentrations of the groups.

5.3.3 Benzene Adsorption at Different Temperatures

Figure 5.3(a) shows the IR absorbance spectra produced after 3.0 min of benzene adsorption onto silica and the TEPA/Silica sorbents at 40, 70, and 120 °C. Increasing the adsorption temperature from 40 to 120 °C for all samples decreased the amount of adsorbed benzene; H-bonded Si-OH; and adsorbed H$_2$O; which was evidenced by the
reduced band intensities for nearly all species. The decreased adsorption capacities of all samples at high temperatures shown by the IR were confirmed by the amounts calculated from the C₆H₆ and 1/Ar MS profiles, which is shown in the Supporting Information.

Figure 5.3: (a) IR absorbance spectra of adsorbed benzene on silica and the TEPA/silica sorbents after 3.0 min in Ar/C₆H₆ flow at 40, 70, and 120 °C and (b) diffusion modeling of the Si-OH integrated absorbance intensity profiles.

The amount of benzene adsorbed by silica and the sorbents are included in Figure 5.3(a) next to their respective IR spectra. An increase in the 1495 cm⁻¹ rotation-vibration band with temperature relative to the primary vibration band at 1481 cm⁻¹ in the IR spectra.
shows that gas-phase benzene contributes more to the spectra than adsorbed benzene at high temperature because there are less adsorbed species. The spectra of silica show a 73% reduction in the integrated absorbance of isolated Si-OH from 40 °C to 120 °C, confirming less adsorption by the groups at high temperature. The spectra of 12 and 37 wt% TEPA/Silica sorbents show a 78% and 88% reduction in the geminal Si-OH intensity, respectively. Both silica and the sorbents exhibited decreasing intensity of the 1630 and 1676 cm\(^{-1}\) bands for adsorbed H\(_2\)O with increasing temperature, showing a reduction in the number of adsorbed H\(_2\)O layers. Slight red-shifting of the 1630 cm\(^{-1}\) band at 40 °C to 1622 cm\(^{-1}\) at 120 °C for silica shows weakening of the H-O-H bonds, indicating that only strongly adsorbed H\(_2\)O remained on the surface at high temperature.

The normalized integrated absorbance decay profiles of isolated and geminal Si-OH were used to model the diffusion of benzene into silica and the sorbents during adsorption at different temperatures. The IR profile of isolated -OH groups has been previously used as an index to model the diffusion of 2-chloroethylethyl sulfide (2-CEES) into γ-Al\(_2\)O\(_3\) with different particle sizes [181]. Excellent agreement between the experimental data and the model for benzene diffusion into silica was achieved with 

\[
D = 9.4 \times 10^{-6} \text{ cm}^2/\text{s} \text{ at } 40 \degree \text{C (σ<0.02)}, \text{ which increased to } D = 1.2 \times 10^{-5} \text{ cm}^2/\text{s (σ<0.05) at 120 °C.} \]

The model was fit to the 40 °C profile after 9 s of adsorption. Enhancement of the diffusion coefficient at 120 °C may result from increased velocity of gas-phase molecules (gas diffusion) and activation of chemisorbed molecules to a mobile precursor state (surface diffusion) [195]. In was found that both the increasing the temperature from 15 to 57 °C enhanced both the pore and surface diffusion coefficients for benzene diffusion into ink-bottle-like MCM-41 [196]. Importantly, the \(D\) values we obtained here
are in the range of those reported by others that used different techniques to measure benzene diffusion into different silica materials, which are shown in Table 5.1.

Table 5.1: Literature review of benzene uptake and diffusion coefficients for different porous materials.

<table>
<thead>
<tr>
<th>Porous material</th>
<th>SA (m²/g)</th>
<th>T_ads (°C)</th>
<th>Static/Dynamic uptake (mmol/g)</th>
<th>Technique</th>
<th>D (cm²/s)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon cloth</td>
<td>1705</td>
<td>25</td>
<td>7.2/na</td>
<td>Grav.</td>
<td></td>
<td>[197]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>1120</td>
<td>25</td>
<td>est. &lt;9.0/na</td>
<td>Vol.</td>
<td></td>
<td>[196]</td>
</tr>
<tr>
<td>Pore-opened MCM-41</td>
<td>886</td>
<td>25</td>
<td>7.4/na</td>
<td>Vol.</td>
<td>D_pore=2.05x10⁻², D_surface=1.56x10⁻⁴</td>
<td>[196]</td>
</tr>
<tr>
<td>Benzene-funct. MCM-41</td>
<td>1013</td>
<td>35</td>
<td>5.7/na</td>
<td>Grav.</td>
<td></td>
<td>[198]</td>
</tr>
<tr>
<td>Benzene-imprint. MCM-41</td>
<td>918</td>
<td>35</td>
<td>6.5/na</td>
<td>Grav.</td>
<td>est. 0.83-1.15x10⁻⁵ (surface)</td>
<td>[198]</td>
</tr>
<tr>
<td>Silica</td>
<td>200</td>
<td>23</td>
<td></td>
<td>NMR</td>
<td></td>
<td>[199]</td>
</tr>
<tr>
<td>Methylated silica</td>
<td>23</td>
<td></td>
<td></td>
<td>NMR</td>
<td>est. 1.15-2.7x10⁻⁵ (surface)</td>
<td>[199]</td>
</tr>
<tr>
<td>Cr-based MOF; MIL-101</td>
<td>3054</td>
<td>23</td>
<td>15/na</td>
<td>Grav.</td>
<td>4.3x10⁻⁹ (intracrystalline)</td>
<td>[200]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>698</td>
<td>35</td>
<td>10.6/0.91</td>
<td>Grav./FB</td>
<td></td>
<td>[201]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>1210</td>
<td>35</td>
<td>9.4/0.98</td>
<td>Grav./FB</td>
<td></td>
<td>[201]</td>
</tr>
<tr>
<td>Toluene funct. MCM-48</td>
<td>1164</td>
<td>35</td>
<td>8/0.78</td>
<td>Grav./FB</td>
<td></td>
<td>[201]</td>
</tr>
<tr>
<td>Aerogel</td>
<td>726</td>
<td>45</td>
<td>7.3/0.88</td>
<td>Grav./FB</td>
<td></td>
<td>[202]</td>
</tr>
<tr>
<td>2 wt% act. carbon/aerogel</td>
<td>727</td>
<td>45</td>
<td>5.1/1.58</td>
<td>Grav./FB</td>
<td></td>
<td>[202]</td>
</tr>
<tr>
<td>H-ZSM-5 zeolite</td>
<td>122</td>
<td></td>
<td>0.16/na</td>
<td>FTIR</td>
<td>6.8x10⁻¹⁰</td>
<td>[203]</td>
</tr>
<tr>
<td>Microporous silica</td>
<td>600</td>
<td>27</td>
<td></td>
<td>NMR</td>
<td>5.7-9.5x10⁻⁷ (self)</td>
<td>[204]</td>
</tr>
<tr>
<td>Octadecyl-silyl silica gel</td>
<td>50</td>
<td></td>
<td></td>
<td>GC</td>
<td>D_pore=4.3x10⁻⁴, D=5.7x10⁹</td>
<td>[205]</td>
</tr>
<tr>
<td>Crystalline silicalite</td>
<td>20</td>
<td>1.42/na</td>
<td></td>
<td>Grav.</td>
<td>0.86x10⁻¹¹</td>
<td>[206]</td>
</tr>
<tr>
<td>Silica</td>
<td>252</td>
<td>40</td>
<td>/10.4</td>
<td>FTIR</td>
<td>9.4x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>12 wt% TEPA/Silica</td>
<td>40</td>
<td>/7.8</td>
<td></td>
<td>FTIR</td>
<td>5.0x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>37 wt% TEPA/Silica</td>
<td>40</td>
<td>/2.0</td>
<td></td>
<td>FTIR</td>
<td>4.9x10⁻⁶⁴</td>
<td>This work</td>
</tr>
</tbody>
</table>

99
Reduction in the diffusion coefficients of 12 wt% TEPA/Silica to $D = 5.0 \times 10^{-6}$ cm$^2$/s at 40 °C and $D = 5.5 \times 10^{-6}$ cm$^2$/s 120 °C relative to those for silica could be attributed to pore blockage and removal of surface transport sites by impregnated TEPA. A 17 s lag for benzene to diffuse into the amine sorbent was observed, resulting from an insufficient driving force for benzene to overcome the limitations caused by TEPA. Further increasing the amine loading of the sorbent to 37 wt% TEPA/Silica slightly reduced the diffusion coefficient at 40 °C to $D = 4.9 \times 10^{-6}$. Raising the temperature to 120 °C increased $D$ to $1.0 \times 10^{-5}$ and could be caused by the migration of agglomerated TEPA from the back of the pore to the front, which would decrease the diffusion length of benzene into the pore. A shortened pore length has been attributed to reduced diffusion limitations of CO$_2$ into immobilized PEI sorbents [10].

Interestingly, there was a 47% reduction in $D$ from 0 wt% (silica) to 12 wt% TEPA/Silica and only a 1% reduction from 12 wt% to 37 wt% TEPA/Silica, which is attributed to the surface coverage of silica by TEPA. Table 5.2 shows that increasing the TEPA/free isolated plus geminal Si-OH molar ratio from 0 (silica) to 1.1 (12 wt% TEPA) produced a sharp drop in $D$.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>mol TEPA/mol free Si-</th>
<th>% available Si-OH (40 °C)</th>
<th>$D$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>0</td>
<td>100</td>
<td>$9.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>12 wt% TEPA/Silica</td>
<td>1.1</td>
<td>28</td>
<td>$5.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>37 wt% TEPA/Silica</td>
<td>4.6</td>
<td>19</td>
<td>$4.9 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

A molar ratio of 1.1 corresponds to 28.3% of the initial isolated plus geminal Si-OH groups on silica that remained available for benzene adsorption after TEPA.
impregnation. Further increasing the molar ratio to 4.6 (19% Si-OH groups available) produced only a slight decrease in $D$. These results indicate that the limited diffusion of benzene into the sorbents is partially attributed to the removal of the Si-OH adsorption sites, which could also serve as the sites for surface diffusion. At high amine loading it is likely that gas diffusion is dominant over surface diffusion. Overall, the results for both benzene diffusion and adsorption capacity follow silica>12 wt% TEPA/Silica>37 wt% TEPA/silica, which is primarily consistent for all temperatures.

5.4 Conclusions

Benzene adsorption-desorption studies of SiO$_2$ with different porosities and TEPA/SiO$_2$ sorbents were performed between 40 and 120 °C under transient conditions using DRIFTS. Flowing Ar/C$_6$H$_6$ over SiO$_2$-lp for adsorption at 40 °C produced strongly inverse responses in the transient IR profiles of isolated Si-OH adsorption sites and gas phase benzene, indicating rapid adsorption in the absence of diffusion limitations. The Si-OH profile of porous silica exhibited a large adsorption half time relative to that for low porosity SiO$_2$-lp, indicating that the rate of benzene adsorption onto Si-OH within the pores is diffusion limited. A diffusion coefficient for silica of $D=9.4 \times 10^{-6}$ cm$^2$/s was obtained by fitting the isolated Si-OH profile to a Fickian diffusion equation for a 520 μm thick slab. Impregnating 12 and 37 wt% TEPA into porous silica consumed free isolated and geminal Si-OH groups (1.1 and 4.6 mol TEPA/mol Si-OH), leaving only 28% and 19% of the initial groups free to adsorbed benzene, respectively. Consumption of the adsorption sites and blockage of the pores by impregnated TEPA diminished the surface and gas phase pore diffusion of benzene, where $D=5.0 \times 10^{-7}$ cm$^2$/s and $D=4.9 \times 10^{-7}$ cm$^2$/s for 12 and 37 wt% TEPA/Silica, respectively. Increasing the adsorption temperature
decreased the amount of adsorbed benzene for silica and the sorbents, and enhanced the
diffusion of benzene into silica because of the increased mobility of the molecules.
These results suggest that rapid diffusion of CO$_2$ into the sorbent pores could be achieved
by performing CO$_2$ adsorption at elevated temperatures.

5.5 Supporting Information

This section describes (i) the procedure for and results of the IR penetration depth
experiment and (ii) the results of benzene adsorption-desorption on silica in transmission
mode.

5.5.1 DRIFTS Penetration Experiment

Figure 5.4: Schematic of the DRIFTS cup, illustrating how the penetration depth
experiment was performed.

Figure 5.4 shows the schematic of the DRIFTS cup, containing a sheet of paper
placed onto stainless steel disk studs (1.0 mm thickness) and stainless steel disk spacers
(114 µm thickness), and different amounts of silica (114-1140 µm bed depth). The
penetration depth experiment was performed on silica at 25 °C by, (i) placing two steel
studs and 10 spacers into the DRIFTS cup, covering with the dome, aligning the vertical position of the DRIFTS cell to achieve maximum intensity, and taking a scan with no sample; (ii) removing the dome and one spacer, filling with silica, and pressing lightly on the sample for light packing; and (iii) replacing the dome, aligning, and taking an IR scan. The silica sample was then discarded and another spacer was removed, and then a new sample of silica was loaded into the DRIFTS cup. This procedure was continued until all spacers were removed. Removing spacers produces different silica bed heights, allowing us to collect the IR spectra for different depths and determine the maximum IR penetration. Optical microscope was used to verify consistent surface morphology for the samples’ surfaces. Results of the penetration depth experiment, shown in Figure 5.5, reveal that the IR band for the paper at 2134 cm\(^{-1}\) was concealed by a silica bed height of about 570 μm, which was determined to be the DRIFTS IR penetration depth.

5.5.2 Determining the Amount of Adsorbed Benzene by MS

The amount of benzene adsorbed by silica and the TEPA/silica sorbents at different temperatures was calculated from the 1/Ar and benzene gas profiles, shown in Figure 5.6, according to Eq. 5.6

Eq. 5.6: Determining the amount of adsorbed benzene from MS profiles.

\[
Q_{ads} = \frac{\int_0^t M_{tracer} (t)dt - \int_0^t M_{benzene} (t)dt}{\int_0^t M_{tracer} (t)dt} (F \cdot C_B \cdot t)
\]

where \(Q_{ads}\) is the amount of adsorbed benzene (mmol), \(M_{tracer}(t)\) is the 1/Ar tracer MS profile, \(M_{benzene}(t)\) is the benzene MS profile, \(F\) is the total inlet gas flow rate (cm\(^3\)/min), \(C_B\) is the inlet concentration of benzene (mmol/cm\(^3\)), and \(t\) is the total time for adsorption (3 min).
Figure 5.5: IR absorbance spectra of different bed depths of silica placed on top of a piece of paper.

The integrated area below the $1/\text{Ar}$ profile ($M_{\text{tracer}}$) in the denominator represents the total amount of benzene flowed, and the difference in the area below the $1/\text{Ar}$ and benzene
profiles ($M_{benzene}$) in the numerator represents the amount of benzene adsorbed by silica or the sorbents.

![Graph showing MS profiles of benzene adsorption onto silica and amine sorbents.](image)

**Figure 5.6**: MS profiles of the 1/Ar tracer and benzene during adsorption onto silica and the amine sorbents.

5.5.3 Transmission Study of Benzene Adsorption-Desorption

In order to compare the nature of benzene adsorption and desorption from silica using different IR techniques, an experiment was performed on silica in transmission cell. Briefly, a 100.0 mg amount of a 10 wt% silica/KBr powder mixture was hydraulically pressed into a self-sustaining disk, which was placed into a transmission cell equipped with ZnSe windows and a heating tape for controlling the cell temperature. Benzene adsorption-desorption of the silica disk in transmission was performed at 40 °C.
identically to that of silica powder in DRIFTS. The DRIFTS and transmission absorbance spectra of the fresh films are compared in Figure 5.7 and show identical band positions for all Si-OH and H$_2$O vibrations. The transmission spectra exhibited a 93% smaller band intensity ratio for the combined vibrations of Si-OH (isolated+geminal+H-bonded)/Si-O-Si than that of the DRIFTS, showing that the transmission observed more of the bulk features of SiO$_2$ compared to DRIFTS due to complete penetration through of the IR beam through the disk.

![Figure 5.7: IR absorbance spectra of fresh silica in DRIFTS and transmission modes at 40 °C.](image-url)
The transmission spectra of the silica disk showed a 16% larger intensity ratio for H-bonded Si-OH/(isolated+geminal) Si-OH than that for the silica particles in DRIFTS, suggesting that compression of the disk under high pressure collapsed the porous structure of SiO₂ and forced free Si-OH to interact. Collapse of the pores could reduce the amount of isolated and geminal Si-OH available for benzene adsorption on the disk relative to those for adsorption on the silica particles.

Figure 5.8: Comparison of (a) the IR absorbance spectra of adsorbed benzene on silica in DRIFTS and transmission mode after 3.0 min in Ar/C₆H₆ and (b) the corresponding normalized integrated absorbance profiles during adsorption-desorption of the isolated Si-OH groups.

Figure 5.8(a) compares the DRIFTS and transmission absorbance spectra of adsorbed benzene on silica after 3.0 min in Ar/C₆H₆. The transmission spectra expectedly showed, (i) the adsorption of benzene to the isolated Si-OH groups of the disk by the negative 3743 cm⁻¹ Si-OH band, (ii) the clustering of benzene by the formation of the 3622 cm⁻¹ band, and (iv) the adsorption of trace amounts of H₂O in the Ar/C₆H₆ flow.
by the 1630 and 955 cm\(^{-1}\) bands. The weaker 3743 cm\(^{-1}\) band intensity in transmission than DRIFTS after adsorption could result from a shorter IR beam path through the disk than the particles, and also the lower concentration of silica in the former (10 wt\%) than that the latter (100%).

Interestingly, the Si-OH absorbance profiles in Figure 5.8(b) reveal a faster benzene adsorption half time of 5 s for the disk in transmission compared to 24 s for the particles in DRIFTS. These results indicate rapid access of benzene to more Si-OH groups located on external SiO\(_2\) surfaces of the disk compared to access of more internal pores surfaces of the particles. Because we observed faster benzene adsorption onto low porosity SiO\(_2\)-lp particles than porous silica particles, the rapid kinetics observed for the silica disk are further attributed to the accessible external Si-OH sites.
CHAPTER VI

IN SITU ATR AND DRIFTS STUDIES OF THE NATURE OF ADSORBED CO$_2$ ON TETRAETHYLENEPENTAMINE FILMS

6.1 Summary

CO$_2$ adsorption/desorption onto/from tetraethylenepentamine (TEPA) films of 4, 10, and 20 μm thicknesses were studied by in situ attenuated total reflectance (ATR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) techniques under transient conditions. Molar absorption coefficients for adsorbed CO$_2$ were used to determine the CO$_2$ capture capacities and amine efficiencies (CO$_2$/N) of the films in the DRIFTS system. Adsorption of CO$_2$ onto surface and bulk NH$_2$ groups of the 4 μm film produced weakly adsorbed CO$_2$ which can be desorbed at 50 °C by reducing the CO$_2$ partial pressure. These weakly adsorbed CO$_2$ exhibit low ammonium ion intensities and could be in the form of ammonium-carbamate ion pairs and zwitterions. Increasing the film thickness enhanced the surface amine-amine interactions, resulting in strongly adsorbed ion pairs and zwitterions associated with NH and NH$_2$ groups of neighboring amines. These adsorbed species may form an interconnected surface network, which slowed CO$_2$ gas diffusion into and diminished access of the bulk amine groups by up to 65%. Desorption of strongly adsorbed CO$_2$ comprising the surface network could occur via dissociation of NH$_3^+$/NH$_2^+$···NH$_2$/NH ionic hydrogen bonds beginning from 60 to 80 °C, followed by decomposition of NHCOO$^-$/NCOO$^-$ at 100 °C. These results suggest that
faster CO₂ diffusion and adsorption/desorption kinetics could be achieved by thinner layers of liquid or immobilized amines.

6.2 Introduction

A 15% increase in atmospheric CO₂ concentration over the last twenty years[207] to 398 ppm in 2014 and its recognized impact on climate changes have promoted extensive research for the development of effective approaches in controlling CO₂ emissions from the power plants and other point sources. Amine functional groups in the form of (i) aqueous amines: monoethanolamine (MEA) [21, 208-212] and 2-amino-2-methyl-1-propanol (AMP) [213-215]; (ii) amine-based ionic liquids (IL’s): lysine-based [N₆₆₆₄][Lys] [216] and [EMIM][Lys] [217], anionic [P₆₆₆₄][ρ-AA] [187], and glycinate-based [P₄₄₄₄][Gly] [218]; and (iii) immobilized amines for sorbents and membranes: tetraethylenepentamine (TEPA) [13, 51, 183, 219, 220] and polyethyleneimine (PEI) [47, 48, 55, 166, 221, 222] have been widely studied for capturing the emitted carbon dioxide. Aqueous amines and IL’s used for CO₂ absorption have also been incorporated into the sorbents and membranes for CO₂ adsorption.

The reaction mechanisms of CO₂ with aqueous or immobilized primary and secondary amine groups could occur via two general steps [36, 223, 224] shown in Eq. 6.1 [36, 223, 224], where *R-NH₂ represents a second amine molecule. Step (1) proceeds by nucleophilic addition of 1 mol of R-NH₂ (primary) or R₁-NH-R₂ (secondary) amine groups to the carbons of 1 mol of CO₂, forming 1 mol of carbamate-ammonium zwitterion intermediates. The zwitterions are then deprotonated in Step (2) by 1 mol of free amine groups, producing 1 mol of ammonium-carbamate ion pairs. Alternatively, 1
mol of CO$_2$ could react with 1 mol of primary or secondary amine to form the zwitterion followed by carbamic acid (NHCOOH or NCOOH).

Eq. 6.1: Formation of ammonium-carbamate ions on NH and NH$_2$.

Primary amine:

$$R\text{-NH}_2 + CO_2 \rightarrow R\text{-NH}_2^+COO^- \quad (zwitterion) \quad (1)$$

$$R\text{-NH}_2^+COO^- + *R\text{-NH}_2 \rightarrow R\text{-NHCOO}^- + *R\text{-NH}_3^+ \quad (ion \ pair) \quad (2)$$

Secondary amine:

$$R_1\text{-NH-R}_2 + CO_2 \rightarrow R_1\text{-NH}^+COO^-\text{-R}_2 \quad (zwitterion) \quad (1)$$

$$R_1\text{-NH}^+COO^-\text{-R}_2 + *R_1\text{-NH-R}_2 \rightarrow R_1\text{-NCOO}^-\text{-R}_2 + *R_1\text{-NH}_2^+\text{-R}_2 (ion \ pair)(2)$$

It has been reported that carbamic acids are stabilized through the formation of dimers or through hydrogen bonding with neighboring amine groups [44, 45], which has been supported by density functional theory (DFT) calculations [187]. The proposed reactions of CO$_2$ with the primary amine are further illustrated in Figure 6.1.

**Figure 6.1:** Proposed reaction mechanisms of CO$_2$ with a primary amine.
CO₂ diffusion within immobilized polyethyleneimine (PEI)/silica sorbents could resemble the facilitated CO₂ diffusion across the amine-containing membranes [128, 225]. This type of diffusion has been examined in detail by thermodynamic and kinetic modeling of thermogravimetric analysis (TGA) profiles for adsorbed CO₂ and by performing DFT calculations of different CO₂/amine systems [226]. The mass transfer of CO₂ through the PEI layers was modeled in two steps: (i) the formation of ammonium/carbamate zwitterions (reactive intermediates) and ion pairs at the gas-amine interface followed by (ii) the facilitated diffusion of zwitterions into the bulk. The model revealed that the zwitterion stability (enthalpy and entropy of formation) and its dissociation with an activation energy barrier could control the overall CO₂ uptake kinetics and capacity of the amine sorbent.

Our previous results from a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study showed that CO₂ adsorption onto immobilized TEPA/silica sorbents with a high density of amine sites produced ammonium-carbamate ion pairs and carbamic acid, which inhibited the diffusion of CO₂ gas within the sorbent [188]. Higher density of these ion pairs and acid was envisioned at the external pore mouths of the sorbent rather than inside of the pores for the sorbents with higher amine density at the external particle surface. These results could aid our understanding of the factors in controlling CO₂ gas diffusion into liquid amines. During CO₂ adsorption, a concentration gradient of adsorbed species is formed along the direction of diffusion through liquid and supported amines. A better understanding of the nature of these adsorbed species at different locations within the amine film could provide the scientific basis for the design of more efficient amine sorbents and membranes.
The nature of adsorbed CO\textsubscript{2} at the top surface (7-9 nm) and within the bulk of a 100 \textmu m layer of an NH-containing ionic liquid, dihydroxyethylidimethylammonium taurinate, has been examined by attenuated total reflectance (ATR) and X-ray photoelectron spectroscopy (XPS) [227]. The XPS results showed a higher amount of carbamic acid (0.43 mol CO\textsubscript{2}/mol IL) than carbamate (0.15 mol CO\textsubscript{2}/mol IL) at the top surface than in the bulk of the IL after exposure to 0.9 mbar of CO\textsubscript{2}. The ATR and \textsuperscript{13}C NMR results confirmed the presence of only carbamate species within the bulk after exposure of the IL to 1 bar of CO\textsubscript{2}. It was postulated that CO\textsubscript{2} adsorption occurred first at the top surface of the IL by forming carbamic acid followed by carbanates, which then diffused into the bulk. XPS results also showed that CO\textsubscript{2} adsorption onto a 15 \textmu m diameter jet of 30 wt\% aqueous MEA solution resulted in neutral MEA molecules at the outer surface layers and carbamate plus carbamic acid species within the bulk layers [228]. It was postulated that CO\textsubscript{2} adsorbed onto the surface of MEA as the carbamate and acid, which diffused (facilitated diffusion) into the bulk.

The objective of this study was to investigate the nature of adsorbed CO\textsubscript{2} on tetraethylenepentamine (TEPA) films. TEPA was selected because it has been widely used for immobilized amine sorbents [13, 15, 61, 183, 229]. We compared the attenuated total reflectance (ATR) and diffuse reflectance (DRIFTS) infrared spectroscopy of adsorbed species during CO\textsubscript{2} adsorption onto and desorption from TEPA films with different thicknesses under transient conditions. Because ATR and DRIFTS scan the bottom and top layers of the amine films, respectively, the results obtained from these IR studies provide insights into the mechanisms of the reaction and mass transfer processes occurring near the film surface and within the bulk. We found that adsorption of CO\textsubscript{2}
onto TEPA films produced a thick, interconnected network of ammonium-carbamate ion pairs near the film surface, which slowed down CO$_2$ gas diffusion into and adsorption onto the bulk NH$_2$ groups. We also estimated the DRIFTS molar absorption coefficients of carbamate and ammonium ions and determined the CO$_2$/N efficiency of the films. The latter was found to decrease with increasing thickness, which confirmed the inability of CO$_2$ to access all available NH and NH$_2$ groups within the bulk because of the diffusion limitations imposed by the surface network.

### 6.3 Experimental

This section describes the procedures for preparing the tetraethylenepentamine (TEPA) thin films and for performing the CO$_2$ adsorption-desorption studies.

#### 6.3.1 Preparation of Amine Films

Tetraethylenepentamine (TEPA) (Sigma-Aldrich, technical grade) films with thicknesses of 4, 10, and 20 µm were deposited onto (i) the ZnSe crystal of an attenuated total reflectance (ATR) FTIR cell and (ii) a stainless steel metal disk set inside of a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell for CO$_2$ adsorption/desorption studies. Different amounts/concentrations of TEPA/ethanol solutions were injected onto the ZnSe crystal and metal disk, which were heated at 80 to 100 °C under a 150 cm$^3$/min Ar flow to evaporate ethanol. The total amount of TEPA/ethanol solution required to deposit the 4, 10, and 20 µm films are as follows: 200 µL of 0.084, 0.210 and 0.419 M for the 8 cm$^2$ ATR ZnSe crystal and 5 µL of 0.23, 0.58, and 1.16 M for the 0.55 cm$^2$ DRIFTS metal disk.
6.3.2 CO$_2$ Adsorption and Desorption Studies

Figure 6.2 shows the experimental set-up used for the CO$_2$ adsorption and desorption studies, consisting of (i) a gas manifold with mass flow controllers and a 4-port valve for switching the gases between 15% CO$_2$/air and Ar; (ii-a) an attenuated total reflectance (ATR, Harrick Scientific) accessory with a ZnSe crystal or (ii-b) a stainless steel metal cup set inside of a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, Thermo Scientific) cell; and (iii) a Labview DAQ module to operate the 4-port valve and to control and monitor the IR cell temperature. The IR cells and accessories were placed inside of a Fourier transform infrared spectrometer (Nicolet 6700 FTIR, Thermo-Nicolet).

![Diagram of experimental set-up](image)

Figure 6.2: Experimental set-up for conducting the CO$_2$ adsorption-desorption studies.

The schematic at the right of Figure 6.2 illustrates the method for investigating CO$_2$ adsorption onto and diffusion through the TEPA films by incorporating both IR
techniques. Briefly, DRIFTS spectra allowed observation and elucidation of processes of CO$_2$ gas adsorption at the CO$_2$/TEPA interface and diffusion into the top of the film. Adsorbed CO$_2$ continues to diffuse through the middle of the film and reach the bottom of the film, which is shown by the ATR spectra.

In-situ CO$_2$ adsorption and desorption studies of the TEPA films consists of the following steps: (i) pretreating at 100 °C for 5 min in a 150 cm$^3$/min Ar flow and cooling to 50 °C, (ii) adsorbing CO$_2$ for 10 min by step switching to a 150 cm$^3$/min flow of 15% CO$_2$/air via the 4-port valve, (iii) removing gas-phase and weakly adsorbed CO$_2$ by switching back to the Ar flow for 10 min, and (iv) heating to 100 °C at 10 °C/min in Ar flow and holding for 10 min for temperature programmed desorption (TPD) of strongly adsorbed CO$_2$. Single-beam spectra, $I$, with a resolution of 4 cm$^{-1}$ were obtained every 10 s, where each spectrum was averaged from 32 co-added scans.

6.4 Results and Discussion

This section describes the results of the adsorption-desorption studies performed on the TEPA films.

6.4.1 IR Spectra of Fresh Films

Figure 6.3 shows the IR absorbance spectra (log(1/I)) of TEPA films with thicknesses of 4, 10, and 20 µm in ATR and DRIFTS at 50 °C after pretreatment at 100 °C. The spectra of TEPA resembles those of organic amines which show the characteristic (i) asymmetric and symmetric N-H stretching bands at 3354 and 3282 cm$^{-1}$ and N-H deformation band at 1595 cm$^{-1}$ for primary amines, NH$_2$; (ii) asymmetric and symmetric C-H stretching bands at 2929 and 2809 cm$^{-1}$, C-H deformation band at 1456
cm\(^{-1}\), and H-C-H twisting band at 1302 cm\(^{-1}\) and for CH\(_2\); and (iii) C-N stretching band at 1125 cm\(^{-1}\) for -CH\(_2\)-NH\(_2\) [191, 192]. The N-H stretching band of secondary amines, NH, is overlapped with that of the symmetrical stretching of NH\(_2\) [192]. The secondary amine band assignment for TEPA is further supported by the N-H stretching band observed at 3283 cm\(^{-1}\) for N,N'-dimethylethylenediamine [230].

![Figure 6.3: IR absorbance spectra of 4, 10, and 20 µm TEPA films at 50 °C in ATR and DRIFTS before CO\(_2\) adsorption.](image)

The ATR spectra of TEPA for different film thicknesses show nearly identical intensities and shapes for all bands, resulting from the same penetration depth of the IR
beam into these various thickness films. The penetration depth is determined by the incident angle of the IR beam and the refractive indices of TEPA and the ZnSe ATR crystal (See Supporting Information). In contrast, the DRIFTS spectra showed a significant variation in their intensity with film thickness. The 4 µm film has a low intensity ratio of N-H/C-H bands which could be attributed to the interaction between the Al surface and the N-H of TEPA. Increased N-H/C-H stretching (3355 and 3284 cm\(^{-1}\)/2929 cm\(^{-1}\)) and deformation (1595 cm\(^{-1}\)/1456 cm\(^{-1}\)) band intensity ratios with film thickness may be explained by the diminishing effect of the surface on TEPA at the top layers of the thicker films. The broadened N-H stretching bands from 4 to 20 µm thicknesses could result from enhanced amine-amine hydrogen bonding near the top layer of the 20 µm thick films. The flat C-H and N-H bands show that the detector was saturated due to the long IR path through the thicker films.

We further demonstrated that the DRIFTS primarily observes the top surfaces of the amine films by depositing various thickness of TEPA onto a 4 µm polyvinyl alcohol (PVA) film. Figure 6.8 of the Supporting Information reveals that the IR features of PVA were nearly diminished by applying 12 µm of TEPA film onto the PVA. The 12 µm depth is the DRIFTS detection limit for the amine film. By utilizing ATR and DRIFTS techniques, each with different penetration depths, we could study the structures and kinetics of adsorbed CO\(_2\) at different locations within the TEPA film.

### 6.4.2 Calculation of Film CO\(_2\) Capture Capacities

The molar absorption coefficients of adsorbed CO\(_2\) (\(\varepsilon_{\text{Ads.}}\)), i.e. ammonium ions and carbamates, were determined by the detailed procedure in the Supporting Information, and are shown in Table 6.1. Beer’s law, \(c_{\text{Ads.}} = A_{\text{Ads.}}/(l_{\text{TEPA}} \cdot \varepsilon_{\text{Ads.}})\) [161], was
used to calculate the concentration of adsorbed CO$_2$ (capture capacity, $c_{\text{Ads.}}$) for each film in DRIFTS from the following: (i) the IR path length through each TEPA film ($l_{\text{TEPA}}$, Supporting Information), (ii) the 1575/1525 cm$^{-1}$ carbamate absorbance intensity ($A_{\text{Ads.}}$) after CO$_2$ adsorption, and (iii) the corresponding $\varepsilon_{\text{Ads.}}$ value for 1575/1525 cm$^{-1}$ from Table 6.1. The CO$_2$ capture capacities and amine efficiencies (CO$_2$/N) of the DRIFTS TEPA films are shown in Table 6.3.

Table 6.1: Average molar absorption coefficients of adsorbed CO$_2$ in the DRIFTS.

<table>
<thead>
<tr>
<th>IR band</th>
<th>Assignment</th>
<th>Molar absorption coefficient $\varepsilon_{\text{Ads.}}$* $(\sigma, \text{STD})$</th>
<th>(\text{L} \cdot \text{mmol}^{-1} \cdot \text{cm}^{-1} %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1575/1525</td>
<td>COO$^-$</td>
<td>0.052 (9.8)</td>
<td></td>
</tr>
<tr>
<td>1477</td>
<td>COO$^-$</td>
<td>0.047 (10.1)</td>
<td></td>
</tr>
<tr>
<td>1405</td>
<td>NCOO$^-$</td>
<td>0.033 (7.1)</td>
<td></td>
</tr>
<tr>
<td>1630</td>
<td>$\text{NH}_3^+$</td>
<td>0.034 (9.4)</td>
<td></td>
</tr>
</tbody>
</table>

*Average $\varepsilon_{\text{Ads.}}$ values were calculated for $c_{\text{Ads.}}$ values between 3.54 and 17.71 mmol CO$_2$/g-TEPA.

6.4.3 Spectra of Adsorbed CO$_2$

Figure 6.4 (a) shows the ATR absorbance spectra of adsorbed CO$_2$ on the TEPA films after 10 min in a 15%CO$_2$/air flow. The band assignments for adsorbed CO$_2$ species were reported in the literature and are tabulated in Table 6.2. Adsorption of CO$_2$ onto all TEPA films in ATR produced the characteristic: (i) NCOO$^-$ skeletal vibration band at 1305 cm$^{-1}$, COO$^-$ stretching bands at 1563 and 1486 cm$^{-1}$, and C-N stretching band at 1405 cm$^{-1}$ for carbamates and (ii) $\text{NH}_3^+$ deformation and stretching bands at 1630
and 2975 cm\(^{-1}\), respectively, for primary ammonium ions. The NH\(_3^+\) was produced by proton transfer from the R-NH\(_2^+\)COO\(^-\) intermediate to a neighboring R-NH\(_2\) group, giving the negative 3366 cm\(^{-1}\) N-H band as illustrated in Figure 6.1. The C-N stretching band for the resulting R-NHCOO\(^-\) was observed at a lower wavenumber than that for a TEPA/silica sorbent [45], suggesting weaker binding of CO\(_2\) to NH\(_2\) in a liquid amine environment.

Figure 6.4: IR absorbance spectra of adsorbed CO\(_2\) on 4, 10, and 20 \(\mu\)m TEPA films in (a) ATR and (b) DRIFTS modes after 10 min in a 15% CO\(_2\)/air flow. Absorbance = \(\log(I/I_0)\), where \(I_0\) was the single beam spectrum before CO\(_2\) adsorption and I was the single beam spectrum during adsorption.
The N-H···N-H hydrogen bonding of ammonium ions produced the broad N-H combination bands between 2750 and 1750 cm$^{-1}$, with a maximum intensity at 2619 cm$^{-1}$ for NH$_3^+$. The NH$_3^+$ could also be formed by deprotonation of R-NH$^+$COO$^-$R by NH$_2$ of the same TEPA molecule to form ammonium/carbamate zwitterions. The broad band at 2184 cm$^{-1}$ is likely due to N-H combination bands of secondary ammonium ions, NH$_2^+$, which were produced by deprotonation of -NH$^+$COO$^-$ by secondary amines. A general trend for NH$_2^+$ giving lower wavenumber bands than NH$_3^+$ can be observed for various organic amine salt [231]. The assignment of NH$_2^+$ for TEPA is further supported by weak combination bands specifically reported at 2140 and 2160 cm$^{-1}$ for piperazine hydrochloride and dimethylamine hydrochloride, respectively [232].

Table 6.2: IR Band assignments for adsorbed CO$_2$ species.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
<th>Species</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3075-2975</td>
<td>NH$_3^+$ stretching</td>
<td>primary ammonium ions</td>
<td>[45, 182]</td>
</tr>
<tr>
<td>2750-1750</td>
<td>N-H stretching</td>
<td>primary/secondary ammonium ions</td>
<td>[45, 231, 232]</td>
</tr>
<tr>
<td>1696</td>
<td>C=O</td>
<td>dimer carbamic acid</td>
<td>[44, 45]</td>
</tr>
<tr>
<td>1670-1630</td>
<td>NH$_3^+$ deformation</td>
<td>primary ammonium ions</td>
<td>[44, 45, 182]</td>
</tr>
<tr>
<td>1575-1525</td>
<td>COO$^-$ stretching</td>
<td>carbamate</td>
<td>[44, 45, 182]</td>
</tr>
<tr>
<td>1486-1477</td>
<td>COO$^-$ stretching</td>
<td>carbamate</td>
<td>[45, 233]</td>
</tr>
<tr>
<td>1405</td>
<td>C-N stretching/NCOO$^-$</td>
<td>carbamate</td>
<td>[182, 234]</td>
</tr>
<tr>
<td>1324-1305</td>
<td>NCOO$^-$ skeletal vibration</td>
<td>carbamate</td>
<td>[45, 182, 233]</td>
</tr>
</tbody>
</table>
The band intensities of the carbamate at 1563 cm\(^{-1}\) (1.3) and ammonium ion at 1630 cm\(^{-1}\) (0.7) for the 20 µm film were 23 and 33% less, respectively, than those for 4 µm, reflecting lower concentration of adsorbed CO\(_2\) at the bottom layers of the thicker film. Lower adsorbed CO\(_2\) concentration for the thicker film could be correlated with lower uptake of PEI/silica sorbents containing longer pores (24-40 µm) than those containing shorter pores (0.2 µm) [10], which was attributed to high CO\(_2\) diffusion resistance through more amine layers. Interestingly, the ATR spectra of adsorbed CO\(_2\) resembles the DRIFTS spectra for low concentration of adsorbed CO\(_2\) on 4 µm at 0.1 min (Figure 6.5(a)), where the surface amine layers were exposed to low CO\(_2\) partial pressure upon switching to the CO\(_2\)/air flow.

The DRIFTS spectrum of adsorbed CO\(_2\) on the 4 µm film in Figure 6.4 (b) exhibited shifts in the carbamate band positions and a reduced 2619 cm\(^{-1}\)/2975 cm\(^{-1}\) intensity ratio compared to those in the ATR spectrum. These results suggest diminished hydrogen bonding of ammonium-carbamate species with the reduced available NH\(_2\) near the TEPA/Al interface. In other words, NH\(_2\) groups interacting with Al are unable to further stabilize adsorbed CO\(_2\). The negative NH\(_2\) band at 3366 cm\(^{-1}\) indicates that the adsorbed CO\(_2\) was associated more with primary than secondary amines throughout the thinnest film. Intramolecular proton transfer of the R-NH\(_2\)’COO\(^{-}\) intermediate could produce NHCOOH (carbamic acid) at the top layers of the TEPA film, and has been observed within 9 nm of a CO\(_2\)/ionic liquid (NH\(_2\)) film interface by XPS [227]. Carbamic acid was not observed on TEPA because of complete penetration of the DRIFTS IR beam into the film. The calculated CO\(_2\) capture capacity of 10.7 mmol CO\(_2\)/g-TEPA, i.e. amine efficiency of 0.40 mol CO\(_2\)/mol N, shown in Table 6.3, is close
to the theoretical 0.5 value for ammonium-carbamate formation and shows effective utilization of surface and bulk amine sites to adsorb CO$_2$.

Increasing the TEPA film thickness increased the intensity ratio of the 2750-1750 cm$^{-1}$/1750-1000 cm$^{-1}$ region and shifted/merged the carbamate bands, suggesting enhanced CO$_2$ adsorption onto secondary amines [45]. Proton transfer from the R-NH*COO$^-$-R intermediate to neighboring amines generated the negative NH band at 3284 cm$^{-1}$, shifted the positions of the ammonium ion bands, and produced more prominent features for NH$_2^+$ at 2184 cm$^{-1}$ than NH$_3^+$ at 2531 cm$^{-1}$.

Table 6.3: CO$_2$ capture capacities and amine efficiencies of the TEPA films in DRIFTS.

<table>
<thead>
<tr>
<th>Film thickness (µm)</th>
<th>CO$_2$ capture capacity (mmol CO$_2$/g-TEPA)</th>
<th>Amine efficiency (CO$_2$/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>10.7</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>7.1</td>
<td>0.27</td>
</tr>
<tr>
<td>20</td>
<td>3.8</td>
<td>0.14</td>
</tr>
</tbody>
</table>

These results indicate more association of NH in the surface regions of the thicker than thinner films in forming ammonium-carbamate ion pairs and zwitterions. We further speculate a higher availability of NH$_2$ sites at the surface compared to the bulk for deprotonation of R-NH$_2^+$COO$^-$ intermediates, converting the amine sites into ammonium ions. CO$_2$ adsorption onto 15 and 50 wt% polyethyleneimine (PEI)/SBA-15 [182] (0.2 and 1.0 nm of amine) produced similar IR features for ammonium-carbamate species as those for 4 and 10 µm TEPA films. These results suggest that the CO$_2$ adsorption
mechanisms for liquid amine films can be used to explain the behavior of immobilized amine layers.

A 40% and 65% decreased amine efficiencies of the 10 and 20 μm films, respectively compared to that of 4 μm confirms that surface diffusion limitations by the adsorbed species restricted the access of CO₂ to all available amine sites. The adsorbed species are stabilized by hydrogen bonding with neighboring amines to form an interconnected network [188], which slowed CO₂ diffusion to the bulk amine groups. Ab intio calculations revealed stronger binding energy of CO₂ to the NH (20.4 kJ/mol) than NH₂ (14.5 kJ/mol) groups of TEPA [220], suggesting that slow CO₂ diffusion through the network occurred mainly by solution-diffusion (gas-phase) rather than facilitated transport across the NH sites. Diminished CO₂/N efficiency for TEPA/SBA-15 with increased amine loading [183] further supports limited CO₂ diffusion through more amine layers.

Interestingly, the formation of the interconnected surface network is associated with the high degree of amine-amine hydrogen bonding of the films before adsorption. In the words, the mechanism for CO₂ adsorption onto amine films could be predicted by the DRIFTS spectra of the fresh films.

6.4.4 CO₂ Adsorption in DRIFTS

Figure 6.5(a) compares the DRIFTS absorbance spectra of adsorbed CO₂ as a function of time on 3 different thickness films. The spectra of adsorbed CO₂ on 4 μm shows identical features for band positions and shapes with increasing intensity, indicating a homogeneous distribution of surface and bulk species. The spectra of
adsorbed CO$_2$ for 10 and 20 μm showed an appreciable difference in the IR band intensity growth. The spectrum at 0.1 min, which represents adsorbed CO$_2$ on primary amines at low concentration, resembled that obtained for 4 μm. As CO$_2$ exposure time increases, the growth of NH$_3^+$ and NH$_2^+$ ammonium ion band intensities at 2431 and 2184 cm$^{-1}$ and shifted/merged carbamate bands suggest further association of adsorbed CO$_2$ with secondary amines.

Figure 6.5: (a) IR absorbance spectra of adsorbed CO$_2$ on the TEPA films in DRIFTS mode during CO$_2$ adsorption and (b) normalized IR absorbance intensity profiles of adsorbed and gas-phase CO$_2$. The insets of (b) show the relative rates of CO$_2$ adsorption (ΔI/Δt) onto each film as a function of time. Norm. abs. int.=(I$_t$-I$_{min}$)/(I$_{max}$-I$_{min}$), where I$_t$ is the absorbance intensity at time t for the profile of interest, I$_{max}$ is the maximum profile intensity, and I$_{min}$ is the minimum profile.
Figure 6.5(b) plots the intensities of ammonium ion and carbamate bands with time during flowing CO$_2$/air. The ammonium ion and carbamate intensities increased at the same rate on the 4 μm film, compared to leading of the ammonium ion profile relative for that for carbamate for 10 and 20 μm. The NH$_2^+$ band around 2184 cm$^{-1}$ emerged at 0.5 min on these thicker film. The adsorbed CO$_2$ spectra and intensity profiles suggest two possible pathways for ammonium ion formation: (i) CO$_2$ adsorption onto NH$_2$ sites first to produce primary NH$_3^+$- NHCOO$^-$ ion pairs and then onto the NH sites or (ii) migration of an NH$_3^+$ proton to NH for regeneration of the NH$_2$ to adsorbed incoming CO$_2$. The migration of these protons is diffusion limited, evidenced by the increased lag between the ammonium ion and carbamate profiles with film thickness.

The derivative intensity profiles of the adsorbed species ($\Delta I/\Delta t$) for 4 μm, shown in the inset, increased sharply up to a maximum relative rate of $\Delta I/\Delta t=4.0$ at 0.3 min, and then symmetrically decreased until 1 min. These results confirm negligible CO$_2$ diffusion limitations through the entire film. In contrast the $\Delta I/\Delta t$ profiles for 10 and 20 μm rapidly increased to maximum relative rates of 2.5 and 1.8-4.0 around 0.45 min, respectively, and then steadily decreased until 2.0 min. These asymmetrical intensity profiles reveal slow CO$_2$ diffusion through the interconnected surface network and to the bulk amines. Asymmetrical CO$_2$ uptake profiles for amine/silica sorbents [182, 223] have been attributed to fast adsorption onto external amine layers followed by slow diffusion into bulk layers. It was further postulated that slow bulk diffusion resulted from the formation of an ionic carbamate gel at the amine surface layers [235].
6.4.5 CO₂ Desorption in DRIFTS

Figure 6.6(a) shows the DRIFTS absorbance spectra of adsorbed CO₂ after Ar purge and during TPD from the TEPA films. Reducing the partial pressure of CO₂ by switching to the Ar flow at 50 °C desorbed about 20% of the adsorbed CO₂, evidenced by the reduced carbamate and ammonium ions band intensities.

![Absorbance Spectra](image)

Figure 6.6. (a) IR absorbance spectra of adsorbed CO₂ after Ar purge and during TPD, and (b) normalized IR intensity profiles of adsorbed and gas-phase CO₂. The insets of (b) show the relative rates of CO₂ desorption from each film as a function of temperature.

These species desorbed at zero CO₂ partial pressure and constant temperature are considered as weakly adsorbed CO₂. Increasing the temperature accelerated the removal
of these adsorbed CO$_2$, beginning at 60 °C. The spectra during desorption resembles those during adsorption, further supporting that the adsorbed species were reversibly adsorbed to the amine groups.

In contrast to 4 μm, adsorbed CO$_2$ on the 10 and 20 μm films required a higher desorption temperature (100 °C) than that of 4 μm. Higher desorption temperature for the thicker films show stronger binding of the ion pairs and zwitterions to NH groups that comprise the hydrogen bonded surface network. The IR features of adsorbed CO$_2$ being desorbed at 100°C resemble those at 0.1 min of CO$_2$ adsorption (Figure 6.5(a)), suggesting the removal of bulk species associated with primary amines trapped beneath the network.

Figure 6.6(b) shows increased lead times of the ammonium ion profiles relative to the carbamate profiles with increased film thickness during thermal desorption. It is interesting to observe the reversed lead-lag trend for the ammonium and carbamate ion profiles when comparing with those for adsorption in Figure 6.5(b). Faster reduction of the ammonium ion than carbamate profiles suggests that deprotonation precedes the decomposition of carbamate during CO$_2$ desorption.

The thermally desorbed CO$_2$ can be considered as a strongly adsorbed species. The key differences in the IR spectra between strongly and weakly adsorbed CO$_2$ are the intensities of ammonium ions and the variations in the carbamate bands. These differences can be, in part, attributed to the availability of -NH$_2$/NH sites for protonation, especially -NH$_2$. The high fraction of the NH$_2$, primary amines, on TEPA interacting with the Al surface for the 4 μm film would produce more weakly adsorbed CO$_2$ than the
high fraction of available primary amine sites for 10 and 20 μm. It is likely that a high fraction of carbamate on the 4 μm film near the TEPA/Al interface is associated with the secondary amine sites.

The 10 and 20 μm films exhibited slow reduction in the 2531 cm$^{-1}$ ammonium ion profile beginning at 65°C prior to CO$_2$ desorption, which could result from dissociation of ionic hydrogen bonds (IHB) between NH$_3^+$ and NH$_2$/NH. A reported lower ionic hydrogen bond (IHB) strength of 86.8 kJ/mol for CH$_3$NH$_3^+$···H$_2$NCH$_3$ (gas-phase) [236] than a 155-45 kJ/mol CO$_2$ binding strength for silica-immobilized aminopropylsilane (APS) [237] further supports this hypothesis.

The higher fraction of weakly adsorbed ammonium ion and carbamate species on the thinner 4 μm film gave the broad $\Delta$I/$\Delta$t profiles with respect to temperature, reflecting a wide distribution of CO$_2$-amine binding strengths throughout the film. In contrast, the higher fraction of strongly adsorbed species comprising the surface network of 10 and 20 μm gave narrower $\Delta$I/$\Delta$t profiles, which showed faster CO$_2$ desorption kinetics at higher temperature.

Figure 6.7 compares the intensity profiles of ATR (1563 cm$^{-1}$) and DRIFTS (1575, 1525 cm$^{-1}$) for COO$^-$ during TPD. Slower decay in the 1577/1525 cm$^{-1}$ carbamate ATR profile than that of DRIFTS for the 4 μm film indicates that weakly adsorbed CO$_2$ removal was limited by the slow rate of facilitated transport/diffusion through the bulk amines. Increasing the TEPA film thickness inhibited bulk diffusion and delayed surface desorption of strongly adsorbed CO$_2$, which is evidenced by the slow responses in the
respective ATR and DRIFTS profiles. Note that ATR observed the adsorbed species at the bottom of the film which is near the surface of the ZnSe window.

Figure 6.7: Normalized DRIFTS and ATR absorbance intensity profiles of carbamate (COO⁻) during TPD. The time scales of the ATR profiles were offset by 0.7 min relative to those for DRIFTS to account for the different heating rates of the IR accessories.
Desorption of strongly adsorbed CO$_2$ from the thicker films likely occurred in two stages: (i) slow facilitate transport process via the formation and decomposition of primary ammonium-carbamate species, as shown by the ATR curves in Figure 6.7 followed by (ii) rapid surface desorption of primary and secondary ammonium-carbamate species at 100 °C, as shown by the DRIFTS profiles. At 100 °C, the surface network of ammonium-carbamate species was eliminated, which liberated bulk CO$_2$. The flat ATR and DRIFTS carbamate profiles for the 20 μm film up to 80 °C reveal the inability of adsorbed CO$_2$ to desorb from the thick, strongly bound surface network at a lower temperature.

6.5 Conclusions

The adsorption and desorption of CO$_2$ with different thicknesses of TEPA films were studied by in situ ATR and DRIFTS techniques under transient conditions. The IR results showed that CO$_2$ adsorbed onto the 4 μm film as ammonium-carbamate ion pairs and zwitterions, which rapidly diffused into the bulk. Increasing the film thickness to 20 μm resulted in a 10 μm thick, interconnected surface network of strongly adsorbed species. This network contained a high concentration of ammonium ions and slowed down CO$_2$ gas diffusion into and diminished access of the bulk amine groups, reducing the CO$_2$/N$_2$ efficiency by 65%. The corresponding ATR spectra of thick TEPA films confirmed the low concentration of adsorbed CO$_2$ within the bulk due to diffusion limitations. TPD studies showed that weakly adsorbed CO$_2$, of which the IR spectra exhibited low intensity of ammonium ions, were released from the 4 μm film beginning at 50 °C by decreasing the CO$_2$ partial pressure through flowing Ar. Desorption of adsorbed CO$_2$ from the thicker films could occur in two stages: (i) slow facilitated transport processes
via the formation and decomposition of primary ammonium-carbamate species followed by (ii) elimination of the ammonium-carbamate surface network at 100 °C for rapid desorption of CO₂. These results show that diffusion, as well as binding strength, play a key role for CO₂ adsorption/desorption onto/from thick amine films. Faster CO₂ mass transfer and higher amine efficiencies for sorbents can be achieved by using thinner layers of immobilized amines on the porous support.

6.6 Supporting Information

This section describes the procedures for determining the penetrations depths of the DRIFTS and ATR into the TEPA films.

6.6.1 Determining the Penetration of the DRIFTS into TEPA films

![DRIFTS absorbance spectra](image)

**Figure 6.8:** DRIFTS absorbance spectra (Absorbance=\log(1/I)), of a 4 μm polyvinyl alcohol (PVA) film coated with different thickness of TEPA.
Figure 6.8 shows the DRIFTS absorbance spectra of a 4 \( \mu \text{m} \) thick film of polyvinyl alcohol (PVA) deposited onto the metal disk (MW=75,000) and then coated with different thicknesses of TEPA. PVA exhibits two characteristic C-O stretching bands at 1144 and 1098 cm\(^{-1}\), a broad O-H stretching band between 3600 and 3000 cm\(^{-1}\), and C-H stretching and bending bands at 2929 and 1456 cm\(^{-1}\), respectively [103].

Increasing the amine film thickness enhanced the N-H/C-H stretching and bending band intensity ratios for TEPA and diminished the features of all PVA bands. For a 12 \( \mu \text{m} \) thickness of TEPA coated on PVA, the N-H/C-H ratios represented those of pure TEPA and the two distinct C-O bands were merged to a single broad band of reduced intensity. These results show that the IR features of the amine were primarily observed for 12 \( \mu \text{m} \) of TEPA coated on PVA, where 12 \( \mu \text{m} \) represents the penetration depth of the DRIFTS into the amine film.

6.6.2 Determining the Penetration of the ATR into TEPA films

The ATR spectra of all films in Figure 6.3 show similar intensities and shapes for nearly all bands because of the shallow penetration depth \( d_p \) of the IR beam into the film. The penetration depth can be calculated according to the following equation (1) [161], where \( \lambda \) is the penetrating wavelength, \( n_1 \) and \( n_2 \) are the refractive indices of ZnSe (2.4) and TEPA (1.5) respectively, and \( \theta \) is the angle of incidence of the IR beam (45\(^\circ\)).

\[
d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - (n_2/n_1)^2}}
\]

The maximum penetration of the IR into the film was calculated to be 1.9 \( \mu \text{m} \) at 1000 cm\(^{-1}\). However, this value is only approximate because anomalous dispersion and polarization of the IR beam are not considered. The overall shape of the ATR spectra
should be similar to those of DRIFTS for films with thicknesses less than or equal to 1.9 μm. This argument is supported by the similarity in the IR features of 4 μm TEPA film on DRIFTS and ATR.

6.6.3 Determining the Molar Absorption Coefficient of CO\textsubscript{2} Gas in Transmission Mode

The transmission IR cell (path length $l_{\text{Trans.}}=1.35$ cm) was purged with 150 cm\textsuperscript{3}/min of Ar at 40 °C to remove residual ambient gases. The Ar flow was then switched to 150 cm\textsuperscript{3}/min of 5, 10, or 20 vol% CO\textsubscript{2}/air for 5 min to allow equilibration of gas-phase CO\textsubscript{2} concentration inside of the IR cell. After gas-phase CO\textsubscript{2} was equilibrated, the IR cell was heated from 25 to 110 °C while flowing the CO\textsubscript{2}/air mixture and then while cooling down.

Figure 6.9(a) shows the integrated absorbance profile of gas-phase CO\textsubscript{2} and the IR transmission cell temperature profile during heating from 25 to 110 °C and Figure 6.9(b) shows the corresponding IR absorbance spectra of CO\textsubscript{2} at 50 °C. The absorbance spectra were obtained by Absorbance=$\log(I_0/I)$, where $I_0$ is the single beam spectrum at 25 °C while flowing Ar and I is the single beam spectrum at different times while flowing CO\textsubscript{2}/Ar. Increasing the CO\textsubscript{2} gas concentration from 5 to 20 vol% enhanced the integrated absorbance within the 2400 and 2250 cm\textsuperscript{-1} region due to more CO\textsubscript{2} molecules absorbing the infrared light. Increasing the IR cell and gas temperature decreased the integrated absorbance of CO\textsubscript{2} by less than 9%, suggesting that temperature would have a minimal effect on the molar absorption coefficient value.
Figure 6.9: (a) Integrated IR absorbance intensity profiles for 5, 10, and 20 vol% CO₂/air in transmission mode during heating and (b) IR absorbance spectra of gas-phase CO₂ at 50 °C.

Beer’s law, $\varepsilon_{\text{gas}}=A_{\text{gas}}/(l_{\text{Trans}}/c_{\text{gas}})$ [161], was used to calculate the molar absorption coefficient of CO₂ gas ($\varepsilon_{\text{gas}}$) at 50 °C, shown in Table 6.4, from the following values: (i)
the IR path length through the transmission cell ($l_{\text{trans.}}=1.35 \text{ cm}$) and (ii) the integrated absorbance of gas-phase CO$_2$ ($A_{\text{gas}}$) between 2400 and 2250 cm$^{-1}$ for a specific CO$_2$ concentration ($c_{\text{gas}}$). Table 6.4 shows that the $\varepsilon_{\text{gas}}$ values decreased from 12.9 L·mmol$^{-1}$·cm$^{-1}$ at 5 vol% (1.88 mmol/L) to 8.7 L·mmol$^{-1}$·cm$^{-1}$ at 20 vol% (7.54 mmol/L). This trend of declining $\varepsilon_{\text{gas}}$ with increasing CO$_2$ concentration is consistent with that reported for adsorbed CO on supported Ru and Pt catalyst surface, which showed a decreased molar adsorption coefficient with increased coverage [238].

Table 6.4: Molar absorption coefficients of CO$_2$ gas at 50 °C.

<table>
<thead>
<tr>
<th>CO$<em>2$ conc., $c</em>{\text{gas}}$ (vol%)</th>
<th>Molar absorption coefficient, $\varepsilon_{\text{gas}}^*$ (L·mmol$^{-1}$·cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>8.7</td>
</tr>
<tr>
<td>10</td>
<td>10.1</td>
</tr>
<tr>
<td>5</td>
<td>12.9</td>
</tr>
</tbody>
</table>

* $\varepsilon_{\text{gas}}=A_{\text{gas}}/(l_{\text{trans.}} \cdot c_{\text{gas}})$; $A=$CO$_2$ integ. abs., $l_{\text{trans.}}=$IR path length (1.35 cm), and $c_{\text{gas}}=$conc. (mmol/L).

Individual CO$_2$ rotational-vibrational bands were not observed due to the low resolution (4 cm$^{-1}$) of the FTIR relative to their band widths. These calculated molar absorption coefficients are further used to estimate the effective IR beam path through the DRIFTS cell.

6.6.4 Determining the Effective IR Beam Path Through the DRIFTS Cell

The DRIFTS cell was purged with 150 cm$^3$/min of Ar at 40 °C to remove residual ambient gases. After purging with Ar, the DRIFTS cell was set in batch mode by closing the inlet and outlet valves. Sequential injections of different volumes of 100% CO$_2$ were
introduced into the batch-mode DRIFTS cell via the septum, producing CO₂ gas concentrations between 0.06 and 28.4 mmol CO₂/L. Figure 6.10(a) shows that the integrated absorbance within the 2400 and 2250 cm⁻¹ region for the injected CO₂ increased almost linearly with concentration up to 1.42 mmol CO₂/L and then increased at a decreasing rate (i.e. absorbance vs. conc.) up to 28.43 mmol CO₂/L. This observed change resulted from the saturation of the IR detector, which was observed by the flattened IR intensities of CO₂ in Figure 6.10(b) at higher concentration. The inset of Figure 6.10(a) highlights the concentration range of the DRIFTS cell corresponding to that of the transmission cell used to determine $\varepsilon_{\text{gas}}$.

Figure 6.10: (a) Integrated absorbance of CO₂ for different concentrations and (b) the corresponding IR absorbance spectra.

Beer’s law, $l_{\text{DRIFTS}}=A_{\text{gas}}/(\varepsilon_{\text{gas}} c_{\text{gas}})$, was used to calculate effective IR path lengths through the DRIFTS cell from: (i) the $\varepsilon_{\text{gas}}$ values for each CO₂ concentration, shown in Table 6.5 and (ii) the integrated absorbances ($A_{\text{gas}}$) for each CO₂ concentration ($c_{\text{gas}}$).
Table 6.5: Estimation of the effective IR beam path through the DRIFTS cell.

<table>
<thead>
<tr>
<th>$c_{\text{gas}}$ (mmol/L)</th>
<th>$\varepsilon_{\text{gas}}^a$ (L·mmol⁻¹·cm⁻¹)</th>
<th>$l_{\text{DRIFTS}}^b$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.84</td>
<td>11.47</td>
<td>1.18</td>
</tr>
<tr>
<td>5.69</td>
<td>9.37</td>
<td>1.20</td>
</tr>
<tr>
<td>8.53</td>
<td>8.29</td>
<td>1.15</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>1.18</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td>2.14</td>
</tr>
<tr>
<td>(STD), $\sigma$ (%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Determined by interpolation of the values calculated for transmission mode at the same concentration.

b. Calculated by $l_{\text{DRIFTS}} = A_{\text{gas}} / (\varepsilon_{\text{gas}} c_{\text{gas}})$.

The $\varepsilon_{\text{gas}}$ values for the DRIFTS were determined by interpolating the values obtained from the transmission IR. Because the effective path length should be independent of $c_{\text{gas}}$ and $\varepsilon_{\text{gas}}$, an average value of 1.18 cm ($\sigma$=2.1%) was obtained. This effective path length, illustrated in Figure 6.11(a), represents the distance traveled by a single IR beam that enters the DRIFTS cell and is specularly reflected from the metal disk without diffuse reflectance. The calculated average $l_{\text{DRIFTS}}$=1.18 cm length is close to the measured length of $l_{\text{meas}}$=1.83 cm between the metal disk and the IR windows.
6.6.5 Determining the Effective IR Beam Paths Through the TEPA Films

Snell’s law of reflection, \(\frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{n_2}{n_1}\), was first used to calculate the diffraction angle \(\theta_2\) of the IR beam into the films, which is illustrated in Figure 6.11(b).

The single incident IR beam exits the CO\(_2\)/air mixture (index of refraction \(n_1\)) and enters the TEPA film with a different refractive index \(n_2\) at an angle \(\theta_1\), causing the IR beam to refract at an angle \(\theta_2\) (26.5°). The refracted IR beam strikes the metal disk or a TEPA layer and is reflected back up through the film.

Using the law of cosines, \(\cos(\theta_2) = \frac{x}{0.5 \cdot l_{\text{TEPA}}}\), we calculated the effective path length of the IR beam through each TEPA film, \(l_{\text{TEPA}}\), having thickness \(x\). Table 6.6 lists all of the parameters and independent variables used for calculating \(\theta_2\) and \(l_{\text{TEPA}}\).

Because of the limited penetration depth of the IR beam, a value of \(x = 12 \mu\text{m}\) was used to calculated the effective path length through the 20 \(\mu\text{m}\) film.

Figure 6.11: Schematics illustrating the effective IR beam path through (a) the DRIFTS cell and (b) the TEPA films.
Table 6.6: Parameters and variables used for calculating the effective DRIFTS IR path lengths through the TEPA films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index, air</td>
<td>$n_1$</td>
<td>1</td>
<td>NIST</td>
</tr>
<tr>
<td>Refractive index, TEPA</td>
<td>$n_2$</td>
<td>1.51</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>IR path length (est.)</td>
<td>$l_{\text{meas.}}$</td>
<td>1.35</td>
<td>Measured</td>
</tr>
</tbody>
</table>

**Independent variable**

- Incident angle $\theta_1$ (deg.) $42$ Calculated
- Film thickness $x$ (µm) 4, 10, 20 Calculated

**Dependent variable**

- Refraction angle $\theta_2$ (deg.) 26.5 Calculated
  4; 8.94
- Film thickness; effective $x$(µm); $l_{\text{TEPA}}$ 10; 22.34 Calculated
- Path length $b$ (µm)
  20 (12)$^c$; 26.8

  a. Calculated using Snell’s law of refraction: $\sin(\theta_1)/\sin(\theta_2)=n_2/n_1$.
  b. Calculated by the law of cosines: $\cos(\theta_2)=[x/(0.5 \cdot l_{\text{TEPA}}]$.
  c. An $x=12$ µm value was used in calculating $l_{\text{TEPA}}$ for the 20 µm film because of the limited penetration depth of the DRIFTS.

The refractive index of CO$_2$/air was assumed to be the same as that of pure air, and the refractive index of the TEPA films were assumed constant despite the formation of adsorbed species. The effective IR path lengths through the TEPA films will further be used calculate the molar absorption coefficients of adsorbed CO$_2$. 

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### 6.6.6 Determining the Molar Absorption Coefficients of Adsorbed CO$_2$

A calibration was first performed which correlated the IR absorbance intensity of carbamates and ammonium ions with the amount of adsorbed CO$_2$ on a TEPA film. A 4 μm TEPA film was prepared on the metal disk, which was set inside of the DRIFTS cell containing a septum, by injecting a TEPA/ethanol solution onto the disk and evaporating ethanol at 50 °C in 150 cm$^3$/min flowing Ar. After ethanol evaporation, the DRIFTS cell was set in batch mode and sequential injections of 100% CO$_2$ were introduced into the cell via the septum for adsorption by the amine film. The CO$_2$ injections were performed 5 min apart to allow equilibrium between gas-phase and adsorbed CO$_2$.

Figure 6.12(a) shows that the absorbance intensities of all species increased almost linearly with concentration up to 10.63 mmol CO$_2$/g-TEPA, and then increased at a slightly decreasing rate up to 17.71 mmol CO$_2$/g-TEPA.

![Figure 6.12](image)

Figure 6.12: (a) IR absorbance intensity of carbamates and ammonium ions at different concentrations of adsorbed CO$_2$ and (b) corresponding IR absorbance spectra of the adsorbed species.
The amount of adsorbed CO$_2$ was determined based upon Figure 6.12(b), which shows the absence of the gas-phase CO$_2$ band at 2349 cm$^{-1}$ up to a total of 100 μL of CO$_2$ injected. Absence of the 2349 cm$^{-1}$ band shows that all injected CO$_2$ was absorbed by the amine film. Incorporating the concentrations of adsorbed CO$_2$, $c_{ads}$, the absorbance intensities of individual bands for the adsorbed species, $A_{ads}$, and the effective path length through the 4 μm film ($l_{TEPA}=8.94$ μm) into Beer’s law allowed us to calculate the molar absorption coefficients for carbamates and ammonium ions, $\varepsilon_{ads}$, which are reported in Table 6.1.
CHAPTER VII

TUBULAR REACTOR STUDIES ON THE EFFECT OF OPERATING CONDITIONS ON THE CO\textsubscript{2} CAPTURE OF IMMOBILIZED AMINE PARTICLE AND PELLET SORBENTS

7.1 Summary

CO\textsubscript{2} adsorption-desorption studies of immobilized amine sorbent particles and pellets were performed in a tubular fixed bed reactor system under different operating conditions. Pulsing pure CO\textsubscript{2} after flowing dry 10\% CO\textsubscript{2} for adsorption onto the sorbent particles increases the partial pressure in the reactor and retains the weakly adsorbed species. High concentration of adsorbed and gas-phase CO\textsubscript{2} inside the reactor after CO\textsubscript{2} pulsing compared to air purging increases the purity of desorbed CO\textsubscript{2} from 41 to 85 vol\% during steam regeneration. Pulse adsorption of 226 cm\textsuperscript{3} of 10\% CO\textsubscript{2} at 30 psi over the sorbent particles revealed that strongly adsorbed species (1.3 mmol CO\textsubscript{2}/g-sorb.) are likely formed up to CO\textsubscript{2} breakthrough and are attributed to hydrogen bonding with the unreacted amine groups CO\textsubscript{2}. Weakly adsorbed species (0.3 mmol CO\textsubscript{2}/g-sorb.) formed after breakthrough experience less hydrogen bonding than the strongly adsorbed species because of fewer neighboring amine groups. Adsorption of CO\textsubscript{2} onto the pellet sorbent in the presence of H\textsubscript{2}O vapor enhances the total CO\textsubscript{2} capture capacity by 41\%, which could be attributed to the liberation of previously inaccessible amine groups by H\textsubscript{2}O.
7.2 Experimental Section

This section describes the procedures for preparing TPSENa particle and pellet sorbents, and for performing CO₂ adsorption-desorption under different conditions.

7.2.1 Sorbent Preparation

Sorbent particles were prepared by combining two solutions consisting of (i) 22.5 g of tetraethylenepentamine (TEPA tech 98%, Sigma-Aldrich); 4.3 g of PL (polymer linker); 40.0 g of ethanol; and 15.0 g of polyethylene glycol 200 (PEG, Sigma-Aldrich); and (ii) 0.62 g of AO (antioxidant) and 80.0 g H₂O, and then mixing with 40.0 g of silica (Tixosil 68B, Rhodia). The resultant wet mixture was dried at 100 °C for 90 min, producing sorbent particles with an average diameter of 15 μm as determined by scanning electron microscopy (SEM, Hitachi TM-3000). Spherical pellets were prepared by mixing 20.0 g of the sorbent particles with 20.0 g of a binder solution containing 10 wt% TEPA, 10 wt% of polymer binder, and 0.6 wt% PEG in water. The resultant wet dough was extruded into 1 mm diameter rods and dried at 130 °C for 5 min. After drying, the semi-wet rods were lightly coated with sorbent particles and broken into 10-20 mm lengths. The rods were then placed into an in-house spheronizer for 5 min and dried at 130 °C for 15 min, which produced 1 mm diameter spherical pellets (optical microscope).

7.2.2 Preventing Weakly Adsorbed CO₂ Removal

Figure 7.1 shows the experimental set-up used for the adsorption-desorption experiments, consisting of (i) a gas manifold with mass flow controllers, pressure vessel, water saturator maintained at 45-50 °C, 4-port valve, and 6-port valve; (ii) an aluminum tubular reactor filled with sorbent particles or pellets, a steam generator, and a condenser;
and (iii) a Pfeiffer QMS quadruple mass spectrometer (MS) and computer Labview software to monitor and control the reactor temperature.

Figure 7.1: Experimental set-up for performing the CO₂ adsorption-desorption studies.

Prior to adsorption-desorption studies, 15.0 g of sorbent particles were pretreated at 100-110 °C for 5 min in a 0.6 L/min air flow to remove water and CO₂ adsorbed from ambient. After pretreating, three adsorption-desorption cycles were performed by (i) flowing 0.6 L/min of 10 vol% CO₂/10 vol% CH₄/air through the sorbent bed at 55 °C for 12 min for CO₂ adsorption; (ii) (cycle 1 ) pulsing 226 cm³ air at 30 psig through the bed
for removal of weakly adsorbed CO₂, (cycle 2) pulsing 226 cm³ of 50% CO₂ at 30 psig for retention of weakly adsorbed CO₂, or (cycle 3) flowing 0.6 L/min air for 6 min for removal of weakly adsorbed CO₂; and (iii) performing steam regeneration to desorb the adsorbed CO₂. Steam regeneration was accomplished by stopping flow to the reactor and heating the sorbent bed to 100-110 °C by flowing steam through the reactor jacket, pulsing 6.5 g steam at 130 °C and 30 psig through the sorbent bed, and then flowing air until all desorbed CO₂ was removed from the system.

The concentrations (mol/L) of effluent CO₂ and CH₄ from the system were determined using the MS by flowing 0.6 L/min of known CO₂ or CH₄ concentrations and constructing a calibration curve, with MS intensity plotted against concentration. The concentrations of N₂ and O₂ were calculated using the ideal gas law and assuming a total gas concentration of 0.041 mol/L at STP.

7.2.3 CO₂ Pulse Adsorption onto Particles

A separate 15.0 g sample of sorbent particles was pretreated at 100-110 °C, and then CO₂ adsorption-desorption was performed by (i) pulsing 15, 226 cm³ volumes of the 10% CO₂/10% CH₄/air mixture at 30 psig through the sorbent bed for adsorption and allowing 3 min between each pulse for equilibration of the gas concentrations, (ii) pulsing 226 cm³ of 100% CO₂ at 30 psig through the bed to retain all adsorbed CO₂, and then (iii) performing steam regeneration to desorb adsorbed CO₂.

7.2.4 CO₂ Adsorption onto Sorbent Pellets in the Presence of H₂O Vapor

A 22.0 g sample of spherical sorbent pellets were first pretreated at 100-110 °C similarly as the sorbent particles prior to the adsorption-desorption cycles. Adsorption-desorption of CO₂ was performed by (i) flowing 4.2 L/min of the CO₂/CH₄/air mixture...
(a) through the pellet bed at 55 °C for 5 min for dry adsorption or (b) through an H₂O saturator maintained at 45-50 °C and then the bed for wet adsorption, (ii) pulsing 226 cm³ of 100% CO₂ at 30 psig through bed to retain weakly adsorbed CO₂, and (iii) performing steam regeneration to desorb CO₂.

7.2.5 Characterization

The nature of impregnated species on fresh sorbent particles and pellets was examined by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). A 30-50 mg sample of sorbent was placed into a DRIFTS cell (Harrick) and set inside of a Nicolet 6700 FTIR, and was heated to 100 °C in a 150 cm³/min Ar flow. After 5 min at 100 °C, single-beam spectra, I, from 32 co-added scans with a resolution of 4 cm⁻¹ were obtained for each sample.

The amine distributions on the particles and pellets were determined by energy-dispersive X-ray spectroscopy (EDS, Quantax 70).

7.3 Results and Discussion

Figure 7.1 shows the IR absorbance spectra (abs=(log(1/I)) and EDS nitrogen mapping of the sorbent particles and pellets. The IR spectra reveal characteristic features for impregnated TEPA on the particles and pellets by (i) asymmetric and symmetric N-H stretching bands at 3356 and 3306 cm⁻¹, respectively and an N-H deformation band at 1601 cm⁻¹, and (ii) asymmetric and symmetric C-H stretching bands at 2931 and 2819 cm⁻¹ and a C-H deformation band at 1461 cm⁻¹ [6]. Impregnated PEG produces C-H bands which overlap with those of TEPA, and produces a broad O-H stretching band between 3600 and 3000 cm⁻¹ [6, 67]. Increased N-H/C-H band intensity ratios for the
pellets compared to particles shows enhanced TEPA content contributed by the binder solution.

Figure 7.2: IR absorbance spectra and EDS mapping of nitrogen on sorbent particles and pellets.

The particles exhibited an EDS N/Si ratio of 0.22, which corresponded to an amine loading of 7.2 mmol N/g*sorb. shown in the inset table. The pellets exhibited a higher N/Si (0.94) than the particles, which corresponded to an amine loading of 8.2 mmol N/g*sorb. Enhanced TEPA content and the presence of the polymer binder within the pores of the particles decreased their ethanol uptake from 1.3 to 0.6 mL EtOH/g*sorb. for the pellets.

Figure 7.3 (a) shows the concentration profiles of effluent CO₂, CH₄, N₂, and O₂ gases from the system and temperatures profiles of the sorbent bed during all adsorption-desorption cycles. Step-switching from air to 10%CO₂/10%CH₄/air for adsorption during all cycles decreased the N₂ and O₂ concentrations as CH₄ and CO₂ were introduced. The
CO₂ breakthrough occurred 2-5 min after CH₄ reached 0.041 mol/L (10%) for all cycles, indicating high capture capacity.

Figure 7.3: (a) N₂, O₂, CH₄, and CO₂ gas profiles, and top and bottom sorbent bed temperature profiles during adsorption-desorption cycles. (b) Details of cycle segments and calculated weakly and strongly adsorbed CO₂ capture capacities.
The trailing of the CO$_2$ profile after breakthrough has been attributed to intraparticle diffusion limitations and the presence of no homogenous particle [14]. The bottom of the sorbent bed showed rapid temperature rises compared to the top, suggesting fast adsorption kinetics near the reactor inlet. The decreasing CO$_2$ concentration profile through the reactor resulted in delayed adsorption kinetics and temperature rise at the top. Temperature rises for both the bottom and top of the bed after total adsorption were about 25 °C, resulting from the highly exothermic reaction between CO$_2$ and the NH and NH$_2$ of TEPA.

Figure 7.3 (b) shows the details of the segments for removal/retention of weakly adsorbed CO$_2$ and steam regeneration of strongly adsorbed CO$_2$. Pulsing 226 cm$^3$ of air 30 psi in cycle 1 decreased the concentration of CH$_4$ and CO$_2$ gases, and caused the removal of weakly adsorbed CO$_2$ evidenced by the gradual decay in the CO$_2$ profile. Gradual decay of the CO$_2$ profile has been attributed to the removal of weakly adsorbed species from other immobilized amine sorbents [67, 164]. Steam regeneration of the sorbent by pulsing steam into the sorbent bed concentrated the desorbed CO$_2$ inside of the reactor. Opening the reactor and purging concentrated, desorbed CO$_2$ and steam with hot air produced the sharp increase in the CO$_2$ profile up to 0.020 mol/L (49 vol%), which gradually decayed as desorbed CO$_2$ was mixed with the air. Condensation of the steam also allowed desorbed CO$_2$ to be concentrated. The amount of CO$_2$ (strongly adsorbed, mmol) desorbed (1.5 mmol/g) was calculated by integrating the area beneath the CO$_2$ concentration profile with using the CH$_4$ tracer profile as a baseline, and multiplying by the total flow rate of 0.6 L/min. The mmol of CO$_2$ was divided by the sorbent weight to obtain mmol CO$_2$/g*sorb.
Pulsing 50 vol% CO\textsubscript{2} after adsorption in cycle 2 rapidly increased the CO\textsubscript{2} gas concentration within the system to 0.017 mol/L (41 vol%) and decreased the concentration of air by 50%. Steam regeneration revealed that the amount of desorbed CO\textsubscript{2} increased from 1.3 to 1.8 mmol/g at 85 vol%. These results indicate that increasing the CO\textsubscript{2} gas concentration/partial pressure throughout the sorbent bed after adsorption retains the weakly bound species. The temperature rise at the top of the bed associated with the CO\textsubscript{2} pulse indicates that some of the gas was adsorbed.

Flowing air after adsorption in cycle 3 removed weakly adsorbed CO\textsubscript{2} similarly as the air pulse in cycle 1, evidenced by the gradual decay in the profile. Because constant air flow was used, the amount of weakly adsorbed CO\textsubscript{2} removed was calculated to be 0.3 mmol/g. Steam regeneration revealed that the amount of strongly adsorbed CO\textsubscript{2} was 1.5 mmol/g (37 vol%), and showed the total amount weakly+strongly adsorbed CO\textsubscript{2} was 1.8 mmol/g. Importantly, the total amount of weakly+strongly adsorbed species produced by CO\textsubscript{2} pulse/steam regeneration in cycle 2 was equal to the total amount produced by air flow/steam regeneration in cycle 2, confirming that increasing the partial pressure inside of the reactor system prior to desorption retains weakly adsorbed CO\textsubscript{2}.

Because strongly and weakly adsorbed CO\textsubscript{2} should be associated with different binding strengths to the amines, i.e. temperature rises, it was worthwhile to further investigate CO\textsubscript{2} capture using pulse adsorption. Pulse adsorption could elucidate the incremental effect of pre-adsorbed CO\textsubscript{2} on further capture by all of the remaining amine groups.
Figure 7.4: The CO\(_2\) and CH\(_4\) gas concentration profiles, and bed temperature profiles during pulse adsorption over sorbent particles.

Figure 7.4 shows the CO\(_2\) and CH\(_4\) gas, and bed temperature profiles during pulse adsorption with the 10%CO\(_2\)/10%CH\(_4\)/air mixture. Complete adsorption of CO\(_2\) with increasing pulse number (P) was observed until breakthrough occurred at P10, which corresponded to a total capture capacity of 1.3 mmol/g. Temperature rises at the bottom of the bed were associated with each pulse, where the rises gradually decreased from about 31 °C at P1 to 1°C at P10, i.e. breakthrough. Negligible temperature rises were observed beyond breakthrough of the CO\(_2\) gas concentration, and coincided with the incrementally decreasing amount of adsorbed CO\(_2\) up to P15. These results are summarized in Figure 7.5, and suggest that the highly exothermic adsorption of 1.3
mmol/g of CO$_2$ prior to breakthrough is associated with the formation of strongly bound species, where 1.3 is close to the 1.5 mmol/g of strongly bound CO$_2$ desorbed at 110 °C during steam regeneration shown in Figure 7.3(b).

![Graph showing CO$_2$ gas concentration, amount of adsorbed CO$_2$, and temperature rises for the incrementally adsorbed CO$_2$ pulse.](image)

Figure 7.5: CO$_2$ gas concentration, amount of adsorbed CO$_2$, and temperature rises for the incrementally adsorbed CO$_2$ pulse.

Additionally, the 0.3 mmol/g of CO$_2$ adsorbed after breakthrough with negligible temperature rises corresponds to the amount of weakly bound species desorbed by flowing air at 55 °C (Figure 7.3(b)). Weakly adsorbed species could be formed after significant adsorption has already occurred because of limited hydrogen bonding of newly adsorbed CO$_2$ with few available, i.e. unreacted, neighboring amine groups.
Figure 7.6: The CO₂ and CH₄ gas concentration profiles, and bed temperature profiles during pulse dry and wet adsorption onto spherical sorbent pellets.
Figure 7.6(a) shows the overall gas concentration and temperature profiles for the two dry and two wet (RH=100% at 45 °C) CO₂ adsorption-desorption cycles performed on the sorbent pellets. Similar to adsorption-desorption cycling of the particles, (i) step-switching from air to 10%CO₂/10%CH₄/air for adsorption increased the CO₂ and CH₄ concentrations with CO₂ break through for all cycles occurring after about 12 s; (ii) pulsing with 100% CO₂ increased the CO₂ gas concentration in the system to near 0.041 mol/L (+99 vol%); and (iii) steam regenerating the sorbent concentrated desorbed CO₂ to +99 vol%.

Figure 7.6(b) compares the gas concentration and temperature profiles during the first cycles of dry and wet adsorption and desorption/steam regeneration for the pellets. Adsorption under dry and wet conditions produced (i) identical breakthrough times for the gas phase CO₂ profile relative to the CH₄ profiles, followed by a more gradual increase in the wet CO₂ profile than the dry profile and (ii) a higher temperature rise at the bottom of the bed for wet adsorption. Overall, these results indicate slightly enhanced CO₂ adsorption in the presence of H₂O vapor. The gradual increase of the wet CO₂ profile suggests diffusion-limited adsorption, likely resulting from the blockage of the sorbent pores by adsorbed H₂O. Identical CO₂ breakthrough times for dry and wet cycles are in contrast to those observed for 50 wt% TEPA/mesoporous ethane-silica nanotube (E-SNT) [51] and 65 wt% polyethyleneimine (PEI)/mesoporous carbon [239] sorbents, which exhibited longer breakthrough time (11-32% higher CO₂ capture capacity) and shorter profile trailing in the presence of H₂O. The authors attribute these observations to enhanced amine efficiency resulting from the formation of bicarbonate species. Importantly, one study used transmission FTIR to show that CO₂ adsorption onto (3-
aminopropyl)triethoxysilane (APTES) MCM-48 (3.47 mmol NH$_2$/g) in the presence of H$_2$O slightly enhanced the adsorbed species by liberating amine groups, not by forming bicarbonates [44]. Therefore, it is suggested that the CO$_2$ capture of our pellets could be enhanced by the liberation of many TEPA molecules which are blocked by the polymer binder.

During desorption/steam regeneration, higher CO$_2$ capture of the pellets for the wet (2.7 mmol/g) than for the dry (1.7 mmol/g) cycle was confirmed by the larger integrated area beneath the wet CO$_2$ profile. Initially slow decay of the wet CO$_2$ profile suggests gradual diffusion of desorbed CO$_2$ through the H$_2$O filled pores, where the presence of H$_2$O could also be contributed by partial condensation of the steam pulse at cold spots within the sorbent bed.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>CO$_2$ capture (mmol/g-sorb/.)</th>
<th>ΔT, top (°C)</th>
<th>ΔT, bot. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Each</td>
<td>Avg.</td>
<td>Each</td>
<td>Avg.</td>
</tr>
<tr>
<td>1 (D1)</td>
<td>1.7</td>
<td>1.9</td>
<td>21.7</td>
</tr>
<tr>
<td>2 (D2)</td>
<td>2.0</td>
<td>26.5</td>
<td>26.5</td>
</tr>
<tr>
<td>3 (W1)</td>
<td>2.7</td>
<td>30.5</td>
<td>37.6</td>
</tr>
<tr>
<td>4 (W2)</td>
<td>2.7</td>
<td>26.5</td>
<td>28.5</td>
</tr>
</tbody>
</table>

Table 7.1 summarizes the CO$_2$ capture capacities and temperature rises for each cycle, and shows enhanced CO$_2$ capture capacity of the pellets in the presence of H$_2$O for both wet cycles.
7.4 Conclusions

Adsorption-desorption of CO$_2$ on sorbent particles and pellets under dry and wet conditions, and using different techniques to retain and concentrate desorbed CO$_2$ was performed in a tubular reactor system. Pulsing with 100% CO$_2$ after adsorption onto particles retains weakly adsorbed species, allowing the desorbed CO$_2$ to be concentrated between 85 and +99 vol% during steam regeneration. Results for pulse adsorption of 10 vol% CO$_2$ onto the particles suggest that strongly adsorbed species are formed up to CO$_2$ breakthrough, followed by formation of weakly adsorbed species. Weakly adsorbed species likely result from limited hydrogen bonded with few unreacted, neighboring NH and NH$_2$ sites.

Adsorbing CO$_2$ onto the pellets in the presence of 100% RH of H$_2$O at 45 ºC enhances the total amount of adsorbed species by 42% compared to dry adsorption, likely attributed to the liberation of previously inaccessible amine groups of TEPA by H$_2$O.
CHAPTER VIII

SYNTHESIS OF NOVEL POLYVINYL ALCOHOL (PVA)-IMMOBILIZED AMINE SORBENTS FOR CO\textsubscript{2} CAPTURE

8.1 Summary

Novel immobilized amine sorbents for CO\textsubscript{2} capture were prepared by impregnation of tetraethylenepentamine (TEPA, T), polyethylene glycol 200 (PEG, P), and other additives into cross-linked porous polyvinyl alcohol (PPc) particles. PPc particles cross-linked with 1 wt% glutaraldehyde solution (PPc\textsubscript{1}) exhibited a similar BET surface area (202 m\textsuperscript{2}/g) and BJH pore volume (0.42 cm\textsuperscript{3}/g) as amorphous silica particles. CO\textsubscript{2} adsorption determined by the weight change of PPc\textsubscript{1} sorbents, labeled as TP(PPc\textsubscript{1})ENa\textsubscript{T}/P\textsubscript{Y}, revealed increased capture capacity from 0.9 mmol CO\textsubscript{2}/g-sorb. at a TEPA/PEG weight ratio of Y=6 to 2.46 mmol CO\textsubscript{2}/g-sorb. at Y=1, which is 82% of the silica-based TPSENa capture capacity. Enhanced capture capacity of the PPc\textsubscript{1} sorbents at lower TEPA/PEG ratios, i.e. higher PEG-OH/N molar ratios, is attributed to better access of CO\textsubscript{2} to the dispersed amines groups. In situ infrared studies reveal that CO\textsubscript{2} adsorption onto the PVA-immobilized sorbents produces more weakly adsorbed CO\textsubscript{2} compared to the silica-immobilized sorbent, which is attributed to weaker binding strength of CO\textsubscript{2} to TEPA in the presence of PVA-OH than silica-OH. Thermal stability testing of PPc\textsubscript{1} and the immobilized amine sorbents reveal further improvement is needed for their industrial application.
8.2 Experimental

This experimental section describes the process for synthesizing porous polyvinyl alcohol (PVA) and PVA-immobilized amine sorbents, and also the procedure for performing in situ CO$_2$ adsorption-desorption studies of the prepared sorbents.

8.2.1 Chemicals

The polymer solutions consisted of polyvinyl alcohol (Elvanol 71-30 fully hydrolyzed (PVA), est. Mw=75,000) purchased from The Chemistry Store which served as the polymer structure, and polyethylene glycol (Mw=200, PEG 200) served as the pore template. The cross-linking solutions consisted of glutaraldehyde (25 wt% aqueous; Aldrich) which served as the cross-linker to covalently attach the PVA chains, concentrated H$_2$SO$_4$ (VWR) which was used as a cross-linking catalyst, and Na$_2$SO$_4$ (Fisher) which prevented porous PVA materials from dissolving in the cross-linking solution. Chemicals used for preparing the immobilized amine sorbents include tetraethylenepentamine (TEPA tech. 98%, Sigma-Aldrich), PEG 200, E epoxy polymeric linker (E), antioxidant (Na), and silica (Tixosil 68B, Rhodia).

8.2.2 Synthesis of Porous Polyvinyl Alcohol (PP) Particles

A 7.5 g amount of PVA was dissolved in 42.5 g of DI H$_2$O at 130 °C, obtaining a 15 wt% PVA solution. A 97.0 g of amount of PEG was mixed with the PVA solution slowly at 130 °C under stirring, producing a templated PVA gel. Excess liquid was decanted from the templated gel and the gel was pulverized, producing templated particles. The templated particles were mixed with 0.5 L of acetone for phase inversion of H$_2$O and removal of PEG 200, and then the resulting particles were vacuum filtered.
Acetone rinsing and vacuum filtering was repeated four times followed by drying at 70 °C for 30 min, producing porous PVA particles.

8.2.3 Porous PVA Particle Cross-linking

The 7.5 g of porous PVA (PP) particles were cross-linked by mixing with 112.5 g of a solution containing different 0.5-7 wt% of glutaraldehyde (GA), 5.0 wt% H₂SO₄, and 25 wt% Na₂SO₄ at 50 °C for 60 min. Cross-linking enhances the mechanical properties of the PP particles and prevents them from dissolving in H₂O. The resulting cross-linked particles rinsed with 1.0 L of DI H₂O (X3), rinsed with 100 mL of acetone, vacuum filtered, and then dried at 70 °C for 30 min, producing cross-linked porous PVA particles (PPc_X, x=concentration of glutaraldehyde solution).

8.2.4 Immobilized Amine Sorbent Preparation

Herein, the immobilized amine sorbents are denoted as, TP(X)ENa_T/P_Y sorbents, where X=S (silica) PVA, PP, or PPc and Y=weight ratio of TEPA(T)/PEG 200 (P). TP(PVA, PP, PPc)ENa sorbents were prepared by impregnating 1.0 g of the PVA supports with 9.0 g of a solution containing different amounts of TEPA, PEG 200, E, and Na in EtOH and DI H₂O. The impregnation solutions were prepared by combining solutions (1) and (2), which consisted of: (1) TEPA, PEG 200, E, and ethanol mixed at 80 °C for 5 min and (2) Na and DI H₂O mixed at 25 °C. The impregnated particles were dried at 100°C for 60 min to evaporate EtOH and H₂O, which produced white sorbent particles. The final amine loadings on the sorbents were 20-39 wt%, with TEPA/PEG ratios of 0.5 to 6.0. An additional T(PPc) sorbent with a 32 wt% TEPA loading, labeled as T/PPc_1-32/68 was prepared by impregnating 1.0 g of PPc with 6.5 g of a 7 wt% TEPA/ethanol solution and then drying.
TPSENa was prepared by mixing 1.0 g of SiO$_2$ with 5.1 g of the impregnation solution, consisting of 11.1 wt% TEPA, 7.4 wt% PEG 200, 2.1 wt% E, and 0.3 wt% Na in ethanol and H$_2$O. The resulting mixture was dried at 100 °C for 75 min, producing a white powder sorbent with a 27 wt% TEPA loading.

8.2.5 Ex situ CO$_2$ Adsorption-Desorption and Steam Degradation Cycles

Three initial CO$_2$ adsorption-desorption cycles were performed to determine the CO$_2$ capture performance of the sorbents by (i) heating at 100 °C for 10 min for pretreatment, (ii) placing in a sealed CO$_2$ bath and flowing 1.5 L/min of 100% CO$_2$ for 10 min for adsorption, and (iii) placing the sorbents with CO$_2$ into the oven at 100 °C for 10 min for desorption. The samples were weighed before and after adsorption, where the weight increase after adsorption was the amount of CO$_2$ adsorbed. After 3 initial cycles, steam degradation was performed by placing the sorbents inside of a sealed bag in an oven at 130 °C and flowing a mixture of 97.9 %CO$_2$/2.1% H$_2$O vapor over the sorbents for 60 min. A total of 12 CO$_2$ adsorption-desorption cycles were performed after each successive steam degradation.

8.2.6 In situ CO$_2$ Adsorption-Desorption

In situ CO$_2$ adsorption/desorption was performed on 30-50 mg of TPSENa and TP(PPc$_{1\%}$)ENa set inside of a diffuse reflectance infrared Fourier transform infrared spectroscopy (DRIFTS) cell by (i) pretreating at 110 °C in 150 cm$^3$/min Ar flow for 5 min to remove CO$_2$ and H$_2$O adsorbed from the ambient environment, (ii) switching to 150 cm$^3$/min of 15% CO$_2$/air or 100% CO$_2$ air for 5 min for adsorption, (iii) switching back to Ar for 10 min to remove gas phase and weakly adsorbed CO$_2$, and (iv) performing temperature programmed desorption (TPD) of strongly adsorbed CO$_2$ by
heating at 10ºC/min to 110 ºC in Ar flow and holding for 5 min. CO₂ calibration was performed at 110 ºC by pulsing three, 5 cm³ volumes of 100% CO₂ through the sorbent bed and to the MS. The area beneath the CO₂ MS profile during TPD was divided by the area beneath the calibration pulses to determine the amount of strongly adsorbed CO₂. A calibration factor was generated by dividing the amount of strongly adsorbed CO₂ (mmol CO₂/g-sorb. calculated from the MS) by integrated area beneath the IR spectra of the strongly adsorbed species. This calibration factor was multiplied by the integrated area beneath the IR absorbance spectra after 5 min of CO₂ adsorption to determine the total amount of CO₂ adsorbed by the sorbents.

8.2.7 Characterization

The chemical structure of porous PVA materials and immobilized amine sorbents was examined by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). A 30-50 mg sample of PVA materials or sorbents was placed into a DRIFTS cell (Harrick) and set inside of a Nicolet 6700 FTIR, and was heated to 100 ºC in a 150 cm³/min Ar flow. After 5 min at 100 ºC, single-beam spectra, I, from 32 co-added scans with a resolution of 4 cm⁻¹ were obtained for each sample.

The BET surface area of silica and the PVA materials were calculated from nitrogen adsorption isotherms in the region of P/P₀=0.10-0.50 (Micromeritics ASAP 2020). Pore volumes and pore size distributions were calculated using the BJH method. Ethanol and H₂O uptake values were used as a method for rapid comparison of the pore volumes. Uptake was performed by saturating 0.5 g samples of PVA and the sorbents with ethanol or H₂O (24 h soaking), and then removing any excess.
The physical structure of porous PVA and the sorbents was determined from scanning electron microscope (SEM, Hitachi TM-3000) and optical microscope (OM) images.

8.3 Results and Discussion

Figure 8.1: (a) SEM images and (b) N\textsubscript{2} adsorption/desorption isotherms of porous PVA materials and silica.
Figure 8.1 shows the (a) SEM images and (b) N₂ adsorption/desorption isotherms for PVA materials and silica, which reveals their porous structure. The images in Figure 8.1 (a) reveal that the structure of untreated PVA particles (avg. size=116 μm, OM) consists of a network of non-porous agglomerated regions and semi-porous regions composed of interconnected spherical particles about 1 μm in diameter. Images of porous PVA (PPc) (avg. diameter=285 μm, OM) and cross-linked porous PVA (PPc_1) (avg. diameter=240 μm, OM) reveal a predominance of the interconnected spherical particle regions which are separated by large voids (macropores) up to about 25 μm, compared to nonporous agglomerates for untreated PVA. The structure of our porous PVA is similar to that observed elsewhere, in which a porous PVA monolith was synthesize using a thermally impacted non-solvent-induced phase separation (TINIPS) method [96]. Images of silica reveal a wide distribution of particles sizes from about <300 nm to 19 μm.

The N₂ adsorption isotherm for PP in Figure 8.1 (b) revealed increased adsorption compared to untreated PVA, corresponding to both higher surface area and pore volume for PP, \( S_{BET}=377 \text{ m}^2/\text{g} \) and \( V_{pore,BJH}=0.41 \text{ cm}^3 \) respectively, than for PVA with \( S_{BET}=78 \text{ m}^2/\text{g} \) and \( V_{pore,BJH}=0.08 \text{ cm}^3 \). The N₂ adsorption/desorption results for all samples are summarized in Table 8.1. The N₂ adsorption isotherm for PPc_1% resembles that for the PVA monolith prepared using the TINIPS method [96], which was described as type IV that indicated the presence of mesopores.

PPc_1% exhibited an \( S_{BET}=203 \text{ m}^2/\text{g} \) and \( V_{pore,BJH}=0.42 \text{ cm}^2 \), which is among the higher reported values for porous PVA-based materials [69, 81, 95-97, 113]. Monolayer
adsorption was observed up to about $P/P_0=0.7$, followed by capillary condensation inside of the mesopores.

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Pure PVA (untreated)</th>
<th>Porous PVA (PP)</th>
<th>PPc_1%</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{part.}, \text{avg.}}$ ($\mu$m)</td>
<td>116</td>
<td>285</td>
<td>240</td>
<td>15</td>
</tr>
<tr>
<td>$\rho_{\text{bulk}}$ (g/mL)</td>
<td>0.46</td>
<td>0.14</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>EtOH uptake (mL EtOH/g)</td>
<td>1.8</td>
<td>9.4</td>
<td>9.4</td>
<td>5.3</td>
</tr>
<tr>
<td>$S_{\text{BET}}$ ($m^2/g$)</td>
<td>78</td>
<td>377</td>
<td>203</td>
<td>202</td>
</tr>
<tr>
<td>$V_{\text{BJH}}$ ($cm^3/g$)</td>
<td>0.08</td>
<td>0.41</td>
<td>0.42</td>
<td>0.53</td>
</tr>
<tr>
<td>$D_{\text{pore avg.}, \text{BJH}}$ (nm)</td>
<td>5</td>
<td>5</td>
<td>7.3</td>
<td>16.7</td>
</tr>
</tbody>
</table>

Overall, these results confirm that highly porous PVA and cross-linked porous particles were synthesized by phase inversion of a PEG-templated PVA gel. The pore size distribution of all PVA materials revealed pore diameters between 1.5 and 45 nm. The adsorption isotherm for silica also reveals mesoporosity with diameters between 2 and 25 nm, and also macroporosity with pores between 70 and 106 nm. Interestingly the surface area and pore volume of silica were similar to those of synthesized PPc_1%, indicating that a porous PVA support could replace silica for preparing immobilized amine sorbents.

Figure 8.2(a) shows the IR absorbance spectra of PP and PPc_X, where X represents the different concentrations of glutaraldehyde used for cross-linking.
Figure 8.2: (a) IR absorbance spectra of porous PVA (PP) and PP cross-linked with glutaraldehyde (PPc).

(b)
Expectedly the spectra of PP exhibits nearly identical features to that of PVA, with an O-H stretching band for PVA-OH between 3700 and 3000 cm\(^{-1}\), a C-H stretching band for CH\(_2\) at 2942 cm\(^{-1}\), a C-H bending band for CH\(_2\) at 1451 cm\(^{-1}\), and C-O stretching bands at 1144 and 1103 cm\(^{-1}\). The C-O stretching band has been attributed to crystalline regions of PVA. The 1724 cm\(^{-1}\) band has been attributed to the C=O stretching of unhydrolyzed acetate groups during PVA synthesis \cite{103}, and is overlapped with the C=O band of unreacted or hydrogen bonded HC=O groups of glutaraldehyde on PPc.

The spectra of PPc show an increase in the 1143/1103 intensity ratio and a decrease of the 3404/2942 intensity ratio, confirming the formation of C-O-C acetal linkages resulting from cross-linking of the PVA-OH groups with glutaraldehyde.\cite{93, 103, 124} The reduced 3404/2942 intensity ratio was accompanied by a blue 3414 cm\(^{-1}\), indicating reduced hydrogen bonding with neighboring OH groups.

The 3404/2942 intensity ratio was used as an index to estimate the degree of cross-linking, i.e. reaction of PVA-OH with the aldehydes, and was calculated by Eq. 8.1

\begin{equation}
\text{Degree of cross-linking (\% OH) = } \frac{(I_{3404}/I_{2942})_{PP} - (I_{3404}/I_{2942})_{PPc}}{(I_{3404}/I_{2942})_{PP}}
\end{equation}

where the degree of cross-linking represents the percentage of OH groups reacted with the aldehyde groups. Figure 8.2(b) shows that the degree of cross-linking increased from 10.2\% to 22.1\% at 0.5 and 7.0 wt\% glutaraldehyde, respectively. Enhanced 1724 cm\(^{-1}\) band intensity with increased glutaraldehyde concentration shows either incomplete
reaction of the aldehyde groups with or hydrogen bonding of the groups to PVA-OH at high concentration.

Figure 8.3: (a) Initial CO$_2$ capture capacities of TP(PPc)ENa sorbents and (b) IR absorbance spectra of different TP(PPc)ENa sorbents.
Figure 8.3(a) shows the IR absorbance spectra of different sorbents prepared from PPc, TP(PPc_X)ENa, where all TEPA loadings are 27.2 wt% and the TEPA/PEG ratios are 1.5. The spectra of all sorbents show the characteristic features of impregnated TEPA on the surface of PVA; with asymmetric and symmetric N-H stretching bands of NH$_2$ at 3366 and 3302 cm$^{-1}$ respectively; an asymmetric CH stretching band of CH$_2$ at 2937 cm$^{-1}$; an N-H bending of NH$_2$ at 1605 cm$^{-1}$, and a C-H bending band of CH$_2$ at 1457 cm$^{-1}$.[6, 51, 67, 191] The OH and CH$_2$ IR bands for PEG hydroxyls are overlapped with those for PVA and TEPA. The spectrum of TP(PPc_7)ENa shows the presence of a C=N stretching band at 1666 cm$^{-1}$ along with a decreased band intensity of HC=O groups at 1724 cm$^{-1}$ for compared to their intensity for PPc_7, indicating that some of the unreacted or hydrogen bonded aldehyde groups reacted with the primary amines of TEPA to produce imine species. The formation of imine species were observed for the reaction of glutaraldehyde with the NH$_2$ of chitosan and polyethyleneimine (PEI) by the formation of the C=N IR band between 1650 and 1670 cm$^{-1}$ [142, 240-243].

The camera images of the sorbents reveal an agglomerated structure for TP(PP)ENa, resulting from partial dissolving of PVA in the impregnation solution during drying at high temperature. The agglomerated structure suggests that the TEPA filled pores collapsed. The images of TP(PPc_1)ENa and TP(PPc_7)ENa reveal that small particles were formed (avg. diameter=319 μm), indicating their ability to capture CO$_2$.

Figure 8.3(b) shows the average CO$_2$ capture capacities of the TP(PPc_X)ENa sorbents. Non cross-linked TP(PP)ENa exhibited a low CO$_2$ capture capacity of only about 0.19 mmol CO$_2$/g-sorb, resulting from the inability of CO$_2$ to access TEPA inside of the collapsed pores. The CO$_2$ capture capacity of the sorbents increased up to 2.10
mmol CO$_2$/g-sorb. for TP(PPc\_1)ENa, and then gradually decreased to 1.39 mmol CO$_2$/g-sorb. for TP(PPc\_7)ENa. Decreased CO$_2$ capture resulted from excessive cross-linking of the NH$_2$ groups of TEPA with glutaraldehyde, which eliminated these active sites to adsorb CO$_2$. These results show that cross-linked porous PVA, PPc\_1\%, could serve as a support for immobilized amine sorbents.

In order to optimize the CO$_2$ capture capacity of the sorbents, the TEPA/PEG ratio was varied from 6.0 down to 0.5, producing molar ratios of PEG-OH/ N from 0 up to 0.38. It is believed that the presence of PEG-OH groups could disperse the TEPA molecules, enabling CO$_2$ to better access the amine sites. Figure 8.4 shows the CO$_2$ capture capacities and amine efficiencies (CO$_2$/N) of the sorbents with varying mol PEG-OH/mol N.

![Figure 8.4: CO$_2$ capture capacity of different TP(PPc\_1)ENa-based sorbents with varying TEPA](image)
The CO$_2$ capture capacity increased with the molar ratio up to a maximum of 2.46 mmol CO$_2$/g-sorb. for 0.19 mol PEG-OH/mol N, i.e. TP(PPc$_{1}$)ENa$_{+}$T/P 1, and then decreased. The amine efficiency also rose to 0.37 mol CO$_2$/mol N, and was further enhanced with increased PEG-OH/N molar ratios.

Overall increasing of the amine efficiency with the PEG-OH molar ratio strongly indicates that the TEPA molecules were effectively dispersed on the PPc$_{1}$ surface, reducing the diffusion limitations of CO$_2$ to the amine sites. It has been show that the both the CO$_2$ capture capacity and amine efficiency (%) of 45 wt%PEI/X wt%PEG 400/SBA-15 increased from about 1.97 mmol CO$_2$/g and 37% at X=0 to 3.2 mmol CO$_2$/g and 63% at X=10 [11]. Importantly, the CO$_2$ capture capacity and amine efficiency of our optimum porous PVA based sorbent, TP(PPc$_{1}$)ENa$_{+}$T/P 1, were comparable to those for the silica based TPSENa (3.0 mmol CO$_2$/g-sorb. and CO$_2$/N=0.40). These results indicate that porous PVA based immobilized amine sorbents are a viable alternative to the silica based sorbents.

To compare the nature of chemisorbed CO$_2$ on TPSENa and TP(PPc$_{1}$)ENa, in-situ CO$_2$ adsorption-desorption was performed. Figure 8.5(a) shows that after 5 min of adsorption, total adsorbed CO$_2$ on TPSENa exhibited characteristic (i) COO$^-$ stretching bands at 1496 and 1560 cm$^{-1}$, a C-N stretching band at 1414 cm$^{-1}$, and a NCOO$^-$ skeletal vibration at 1327 cm$^{-1}$ for carbamate species; (ii) C=O stretching at 1696 cm$^{-1}$ for carbamic acid; (iii) NH$_3^+$ stretching bands at 2995 and 1630 cm$^{-1}$ for primary ammonium ions; and (iv) N-H vibrations for hydrogen bonded ammonium-carbamate ion pairs and zwitterions [13, 44, 233, 234].
Figure 8.5: (a) IR absorbance of adsorbed CO\textsubscript{2} on TPSENa and TP(PPc\textsubscript{1})ENa and (b) normalized IR intensity profiles of gas-phase adsorbed CO\textsubscript{2} species.
The total amount of adsorbed CO$_2$ was calculated to be 2.1 mmol CO$_2$/g-sorb. After 10 min of Ar purge, 38% of the ammonium-carbamate ion pairs and carbamic were removed as weakly adsorbed CO$_2$, leaving 1.3 mmol CO$_2$/g-sorb. as strongly adsorbed CO$_2$. Because the absorbance spectra of strongly and weakly adsorbed CO$_2$ are nearly identical, it is suggested that hydrogen bonding of the strongly bound ammonium-carbamate ions pairs and carbamic acid with neighboring amine groups of TEPA could result in their high binding strength compared to that of the weakly bound species.

The absorbance spectrum of total adsorbed CO$_2$ on TP(PPc$_1$)ENa exhibits similar features as those for TPSENa with the following exceptions: (i) a blue shift in the NH$_3^+$ stretching band from 1630 to 1637 cm$^{-1}$ along with an increase in its intensity, and a narrowing of the 1637 and 2995 cm$^{-1}$ band shapes; (ii) reduced broad features between 2750 and 2250 for less hydrogen bonding of the ion pairs and zwitterions; and (iii) red shifts in the 1560, 1414, and 1327 cm$^{-1}$ stretching bands of carbamate to 1543, 1404 cm$^{-1}$, and 1281 cm$^{-1}$, respectively. After purging with Ar, an 86% loss in the total amount of adsorbed CO$_2$ as weakly adsorbed carbamates, ammonium ions, and carbamic acid was observed by the reduction in their band intensities. The greater reduction in the IR band intensities of adsorbed CO$_2$ on TP(PPc$_1$)ENa than TPSENa after Ar purge was correlated with (i) the narrowed and shifted NH$_3^+$ ion bands, (ii) the less broadened features between 2750 and 2250 cm$^{-1}$, and (iii) the red shift in the carbamate bands for the total adsorbed CO$_2$. These results suggest that weakly adsorbed CO$_2$ could result from less hydrogen bonding between carbamates and ammonium ions with neighboring amines groups on the PPc$_1$ supported sorbent that silica supported sorbent. The average surface coverage of OH groups on silica is about 4.8 OH/nm$^2$ (avg. surface area=206
m²/g) compared to a calculated OH coverage of on PPc_1 of about 68 OH/nm² (surface area=203 m²/g). The high surface coverage of OH on PPc_1 could result in more hydrogen bonding between the amine groups and hydroxyl groups than between amine groups and adsorbed of TP(PPc_1)ENa. The opposite would be observed for TPSENa, with more hydrogen bonding between amines and adsorbed CO₂.

Figure 8.5(b) shows the IR intensity profiles for carbamates and ammonium ions during adsorption and desorption. A slightly faster increase in the adsorbed species’ profiles of TP(PPc_1)ENa than TPSENa could result from the higher concentration of CO₂ gas, which is evidenced by the stronger band intensities for the CO₂ overtone bands between 4000 an 3500 cm⁻¹. Importantly, faster decay in the carbamate and ammonium ion profiles for TP(PPc_1)ENa than TPSENa indicates the species are more weakly bound to the PPC_1 supported sorbent than the silica supported sorbent. Chuang et.al previously used the 1570 cm⁻¹ COO⁻ decay profiles to qualitatively describe the binding strength of CO₂ adsorbed on fresh and oxidatively degraded sorbents [45]. They stated that faster decay profiles for the degraded sorbents than the fresh sorbents indicated weaker binding strength to the degraded amines.

The thermal stability of organic polymers, especially PVA, is a significant concern in their use as supports for immobilized amines sorbents compared to that of inorganic supports, such as silica and activated carbon, because of the polymers’ susceptibility to oxidative degradation, their low melting points, and their solubility in H₂O. Because the melting and degradation temperatures of PVA (Mw=28,000 [244]: Tₘₑₐ₅=223 °C, Tₜₐₘₑₐₜ₇ₐₜ.₅ₐₜ.₅(D.(ₐ.)₅)=247 °C, and Tₜₐₘₑₐₜ₇ₐₜ.₅ₐ₅.(ₐ.)₅=378 °C; Mw=89,000 [245]: Tₘₑₐ₅=230 °C, Tₜₐₘₑₐₜ₇ₐₜ.₅ₐ₅.(ₐ.)₅=260-290 °C) exceed the maximum temperatures reached in
the CO₂ capture process (110-130 °C), we investigated the solubility of PPC_1 in pH=1 (HCl), pH=7 (H₂O) and pH=12 (KOH) solutions at 90 °C for 16 h.

Figure 8.6 shows the SEM images and ethanol uptake results for PPC_1 after the pH treatments.

![SEM images and ethanol uptake results for PPC_1 soaked in different pH solutions at 90 °C for 16 h.](image)

The images of pH=7 and 12 treated PPC_1 reveal slight agglomeration of the spherical network, resulting from partially dissolved PVA in the solution that resolidified into nonporous regions during drying. Agglomeration of the network was accompanied by an 18.1% and 12.8% reduction in the ethanol uptake values, respectively, confirming the loss of porosity. More significantly, the structure for pH=1 treated PPC_1 exhibited
significant formation of nonporous regions, which reduced the ethanol uptake value by 83.0% relative to the control. These results show that further modification of PPc_1 may be needed to produce a sorbent which is stable during extensive cycling in the presence of H_2O vapor.

To compare the performance of the PPc_1 and silica based sorbents, 12 cycles of CO_2 adsorption/desorption-steam degradation were performed on TPSENa, TP(PPc_1)ENa, and the optimized TP(PPc_1)ENA_T/P 1.

Figure 8.7: CO_2 adsorption-desorption/steam degradation cycling of PPc_1 and silica based immobilized amine sorbents.
The results of steam degradation cycling are presented in Figure 8.7. All sorbents exhibited a similar sharp drop in CO$_2$ capture capacity for the first adsorption-desorption cycle (4) after steam degradation, likely resulting from evaporation or agglomeration of the amines. However, the loss of the capture capacity by the sorbents could result from the oxidative degradation of TEPA because of air leakage from the ambient environment into the system. After 13 steam degradation cycles, the capture capacities of TP(PPc$_{1}$)ENa and TP(PPc$_{1}$)ENa$_{T/P}$ 1 decreased by 73 and 83%, respectively, compared to 54% for TPSENa. These results confirm that further improvement of porous PVA immobilized amine sorbents is needed regarding long term stability for industrial application.

8.4 Conclusions

A novel, cross-linked porous PVA support with similar surface area and greater pore volume than silica was synthesized by (i) phase inversion of a PEG-templated PVA gel in acetone, and then (ii) cross-linking the resulting porous PVA (PP) particles with varying concentrations, X wt%, of glutaraldehyde. Immobilized amine sorbents were prepared from cross-linked porous PVA (PPc$_{X}$) and silica by impregnation of TEPA, PEG 200, an epoxy linker, and an antioxidant into the porous supports.

The TP(PPc$_{1}$)ENa sorbent displayed the highest CO$_2$ capture capacity of the PPc$_{X}$-based sorbents with 2.1 mmol CO$_2$/g-sorb, compared to 3.0 mmol CO$_2$/g-sorb for TPSENa. A separate in situ IR adsorption-desorption revealed a higher fraction of weakly adsorbed ammonium-carbamate pairs and carbamic acid on TP(PPc$_{1}$)ENa than
TPSENa, which could be attributed to less hydrogen bonding of the adsorbed species with neighboring amines of the PVA support.

Increasing the PEG-OH/N molar ratio to 0.19 for the TP(PPc_1)ENa_T/P 1 sorbent enhanced the CO₂ capture capacity to 2.46 mmol CO₂/g-sorb (82% of the capacity for silica-based TPSENa) and amine efficiency to 0.37 mol CO₂/mol N, showing that PVA-based sorbents are a viable option to remove CO₂ emissions. Thermal stability testing of PPc_1 and the corresponding immobilized amine sorbents revealed that further improvement of the support and sorbent formulation are needed for industrial application.
CHAPTER IX

CONCLUSIONS

9.1 Probing the Adsorption/Desorption of CO₂ on Amine Sorbents with Benzene at Different Temperatures

Chapter IV presents the in situ benzene and CO₂/benzene adsorption-desorption studies of TEPA/silica sorbents performed at 40 ºC with a novel DRIFTS technique, using benzene as a surrogate CO₂ probe molecule. Because of the stronger interaction of benzene with the free Si-OH groups of silica that the amines of TEPA, the 3743 cm⁻¹ Si-OH and 3725 cm⁻¹ IR profile was used as an index to monitor benzene diffusion. The results showed that impregnated TEPA blocked the sorbent pores and inhibited the diffusion of benzene within the sorbent. More importantly, comparing the IR profiles for Si-OH and adsorbed CO₂ revealed that ammonium-carbamate ions pairs and carbamic acid formed an interconnected network which further inhibited the diffusion of benzene (CO₂ gas). Slower removal of adsorbed benzene (diffusion) than adsorbed CO₂ during desorption indicated that CO₂ readsobered along the pore wall and also on the external particle surface to reform the network.

Chapter V presents further DRIFTS and MS studies of the TEPA/Silica sorbents in Chapter V, where the effect of temperature on the adsorption-desorption of benzene at 40, 70, and 120 ºC was determined.
A Fickian slab equation was used to model the diffusion of benzene down through the sorbent bed by fitting the equation to the free Si-OH profiles of silica and the sorbents. Results showed a 48% reduction in the diffusion coefficient D for 37 wt% TEPA silica compared to silica at 40 °C, confirming that TEPA inhibits benzene diffusion. Increasing the temperature from 40 to 120 °C decreased the amount of adsorbed benzene on all samples, evidenced by their weaker IR band intensities and by the decreased amounts calculated from the 1/Ar tracer and C₆H₆ MS profiles. Increased D values with temperature for silica and the sorbents show enhanced transport of benzene through the pores, resulting from the rapid velocity of benzene gas molecules and likely improved surface transport across the Si-OH sites.

9.2 In situ ATR and DRIFTS Studies for CO₂ Capture by TEPA Films

Chapter VI presents the in situ CO₂ adsorption-desorption studies of different thicknesses of TEPA films performed with ATR and DRIFTS. Because DRIFTS and ATR allow observation of the surface and bulk regions of the film, respectively, we could observe their different CO₂ diffusion and adsorption/desorption processes. Rapid adsorption on a thinner 4 μm film at 50 °C occurred by reaction of CO₂ with primary amines throughout the film, producing weakly bound ammonium-carbamate ion species that were removed by Ar purge at 50 °C. Slower adsorption onto the thickest 20 μm film occurred first at the surface by reaction of CO₂ with primary and secondary amines to produce strongly bound species, which formed an interconnected network. Further adsorption occurred by slow CO₂ gas diffusion through the network and then reaction with the bulk primary amines. Desorption of the strongly bound CO₂ could occur first
with the dissociation of ionic hydrogen bonding between ammonium ions and neighboring amines followed by decomposition of carbamate species.

9.3 Tubular Reactor Studies for CO$_2$ Capture by Immobilized Particle and Pellet Sorbents

Chapter VI presents the adsorption-desorption studies of immobilized amine particles and pellets performed in a tubular reactor and MS set-up using different operating conditions. Flow calibration of CO$_2$ and benzene allowed the quantification of all gas concentrations and the CO$_2$ capture capacities of the sorbents. The result showed that pulsing pure CO$_2$ after adsorption with a 10% CO$_2$/10% C$_6$H$_6$/air mixture at 50 °C increased the partial pressure inside the reactor and allowed the retention of 0.3 mmol CO$_2$/g-sorb. as weakly adsorbed species (17% of total adsorbed), which would be lost by flowing air instead of pulsing CO$_2$. Pulse adsorption of the mixture indicated that the weakly adsorbed species were formed after breakthrough, resulting from reduced hydrogen bonding with amines. CO$_2$ adsorption on pellets in the presence of H$_2$O vapor followed increased the capture capacity by 42%, which could be attributed to the liberation of previously blocked amine sites. Pulsing with pure CO$_2$ followed by steam regeneration of the pellets after adsorption concentrated the desorbed CO$_2$ to 99+%, which is required for sequestration underground.

9.4 Synthesis of PPc-Immobilized Amine Sorbents for CO$_2$ Capture

Chapter VII presents the synthesis and characterization of novel, cross-linked polyvinyl alcohol-supported (PPc) immobilized amine sorbents for CO$_2$ capture. Because of the attrition of silica-supported amine pellet sorbents, the development of a
stable polymer-supported sorbent, which can be pelletized, is desired. Porous PVA was synthesized by templating/gelling a PVA solution with 66 wt% PEG 200, and phase inversion of the pulverized gel with acetone into particles. The particles were cross-linked with 1 wt% glutaraldehyde, and the resulting PPc particles exhibited a similar surface area (203 m$^2$/g) and pore volume (0.42 cm$^3$/g) as those for silica. Immobilized amine sorbents were prepared by impregnation of PPc with different amounts of TEPA, PEG, and other additives. It was found that increasing the PEG/TEPA ratio increased the capture capacity and amine efficiency of the sorbents, resulting from the dispersion of amine sites. The best performing sorbent achieved 82% of the capture capacity and 93% amine efficiency of the silica-supported sorbent. However, the PPc-supported sorbent was less stable during ex situ cycling with steam degradation. In situ DRIFTS results showed more weakly adsorbed species formed on the PPc than silica sorbent, showing that its use could reduce the overall cost to desorb CO$_2$ for in practical application.

9.5 Future Studies

CO$_2$/benzene adsorption-desorption studies should be performed on SBA-15, MCM-41, and other supported immobilized amine sorbents to determine the effect of sorbent geometries on CO$_2$ mass transfer. It is expected that the mass transfer of CO$_2$ will be faster through less tortuous pores of the more crystalline silica materials. Other supports, such as activated carbon and different polymers, should be tested for their ability to adsorb benzene.

CO$_2$ adsorption-desorption studies should be performed on PEI films, and other amine films containing PEG or other additives in DRIFTS and ATR to further examine
the effect of viscosity and film chemistry on CO$_2$ mass transfer and reaction kinetics. It is expected that CO$_2$ diffusion through PEI films will be slower compared to through TEPA, resulting in thinner surface network. The addition of PEG to PEI should disperse the amines, facilitating more rapid diffusion of CO$_2$ through the PEI/PEG film.

CO$_2$ adsorption-desorption studies of the immobilized amine particle sorbents should be performed in DRIFTS using a low flow rate (about 20 cm$^3$/min) in order to observe CO$_2$ breakthrough. Correlating the nature of adsorbed CO$_2$ observed from IR before and after breakthrough could provide more information regarding the nature of weakly and strongly adsorbed species. It is expected that strongly adsorbed species are formed before breakthrough because many amine sites will be available to hydrogen bond with and stabilize the ammonium-carbamate ions pairs and zwitterions.

Porous PVA should be synthesized using different molecular weights of PVA. It is hypothesized that the shorter PVA chains could create a more defined, and narrower pore structure compared to the longer chains. A ternary solubility diagram of PVA-H$_2$O-PEG 200 should be constructed in order describe the thermodynamics for synthesizing the templated porous PVA. The diagram may also be used to predict the porosity of the porous PVA particles.
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APPENDICES
APPENDIX A

THE EFFECT OF H₂O ON THE CO₂ ADSORPTION OF TPSENA PELLETS

A.1 Objective

To determine the effect of H₂O on the amount of weakly and strongly adsorbed CO₂ species.

A.2 Key Findings

1. The average CO₂ capture capacity of TPSENa pellets at 55 ºC under dry conditions was 2.1 mmolCO₂/g-sorb., where 50% of the adsorbed species were weakly adsorbed and 50% were strongly adsorbed.

2. CO₂ adsorption in presence of 9-11 vol% H₂O (wet adsorption) enhanced the average total CO₂ capture capacity by 10% to 2.4 mmolCO₂/g-sorb. However, the fraction of weakly adsorbed species decreased by 23% to 0.8 mmolCO₂/g-sorb relative to dry adsorption, and strongly adsorbed species increased by 43% to 1.6 mmolCO₂/g-sorb.

3. The average temperature rises at the bottom and top of the pellet bed for dry adsorption were 30.2 and 26.9 ºC respectively, and increased to 32.3 and 30.7 ºC for wet adsorption. The increase in temperature rises for wet adsorption is attributed to the enhancement of strongly adsorbed species.
4. IR spectra of pellets removed from the reactor after dry and wet CO\textsubscript{2} adsorption confirm the presence of adsorbed species as ammonia ions and carbamates. These spectra do not show clear differences in the adsorbed species between dry and wet adsorption.

A.3 Experimental

A.3.1 Sorbent Preparation

TPSE\textsubscript{Na} sorbent was prepared by mixing two solutions, (i) 22.5 g tetraethylenepentamine (TEPA) (Aldrich), 4.3 polymer binder (E), 40.0 g ethanol (Pharamaco), and 15.0 polyethylene glycol 200 (PEG) (Aldrich), and (ii) 0.62 g antioxidant (A) (Aldrich) and 80.0 g DI water. The resultant solution was added to 40.0 g Tixosil 68B, amorphous silica, and the wet mixture was dried at 100 °C for 90 min. TPSE\textsubscript{Na} cylindrical pellets were prepared by mixing 20.0 g TPSE\textsubscript{Na} sorbent with 20.0 g of a solution containing 10 wt\% TEPA, 10 wt\% polyvinyl alcohol Mw=75,000 (DuPont), and 0.6% PEG in water. The resultant mixture was extruded into 1 mm diameter cylindrical rods of varying lengths, lightly coated with sorbent, and dried at 130 °C for 30 min. After drying, the resulting cylindrical rods were broken by hand into small cylindrical pellets.

A.3.2 CO\textsubscript{2} Adsorption and Desorption

The experimental apparatus used for the adsorption and desorption study consists of a (i) gas manifold with mass flow controllers, water saturator, 4-port valve, and 6-port valve, (ii) tubular reactor (ID=0.5\”, L=9.6\”) filled with 22.0 g of TPSE\textsubscript{Na} cylindrical pellets, steam generator, and condenser, and (iii) Pfeiffer QMS quadruple mass spectrometer (MS) and computer interface software to monitor MS and temperature.
responses. Dry CO₂ adsorption and desorption was performed by (i) pretreating at 100 °C in a 4.5 L/min air flow for 5 min to remove water and CO₂ adsorbed from ambient, (ii) step-switching from air to 4.5 L/min of 10% CO₂/10%CH₄/air flow for 5 min for adsorption, (iii) switching back to air for 8 min to purge gas phase CO₂ and desorb weakly adsorbed CO₂ (pressure swing desorption), (iv) heating to 110 °C using jacket steam, opening the inlet and pulsing saturated steam at 75 psig and 153 °C into the reactor for 5 s, and opening the outlet and flowing air for 4-5 min to remove strongly adsorbed CO₂. The CH₄ was used as a tracer to represent the flow pattern of a non-adsorbing gas through the system. Wet CO₂ adsorption was performed by a similar procedure, where the CO₂/CH₄/air flow was passed through the H₂O saturator maintained at about 45 °C. Samples of the pellets (0.1 g) were removed from the reactor (i) before adsorption, (ii) after adsorption, and (ii) after air purge for DRIFTS analysis.

A.4 Results

Table A.1: CO₂ capture capacities for dry and wet cycles of CO₂ adsorption and desorption.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Weakly (mmol/g)</th>
<th>Avg (1, 2)</th>
<th>Strongly (mmol/g)</th>
<th>Avg. (1, 2)</th>
<th>Total (mmol/g)</th>
<th>Avg (1, 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.1</td>
<td>2.0</td>
<td>2.1</td>
</tr>
<tr>
<td>D2</td>
<td>1.1</td>
<td></td>
<td>1.1</td>
<td>1.1</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>1.0</td>
<td>1.8</td>
<td></td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W1</td>
<td>0.9</td>
<td>0.8</td>
<td>1.5</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W2</td>
<td>0.7</td>
<td></td>
<td>1.6</td>
<td>2.3</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>W3</td>
<td>1.2</td>
<td></td>
<td>1.6</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% change</td>
<td>-23.1</td>
<td></td>
<td>43.0</td>
<td>10.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure A.1: Concentration profiles for CO$_2$ and CH$_4$ and temperature profiles for the top and bottom of the pellet bed during cycle 1 of (a) dry CO$_2$ adsorption and (b) wet CO$_2$ adsorption.
Table A.2: Temperature rises at the top and bottom of the pellet bed during dry and wet (10 vol% H₂O) CO₂ adsorption over TPSENa pellets. Average values were calculated from cycles 1 and 2 only because the system was disturbed during cycle 3.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>ΔT_{top}</th>
<th>Avg (1, 2)</th>
<th>ΔT_{bot}</th>
<th>Avg (1, 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>28.0</td>
<td>30.2</td>
<td>23.3</td>
<td>26.9</td>
</tr>
<tr>
<td>D2</td>
<td>32.5</td>
<td></td>
<td>30.6</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>38.8</td>
<td></td>
<td>27.6</td>
<td></td>
</tr>
<tr>
<td>W1</td>
<td>32.7</td>
<td>32.3</td>
<td>31.2</td>
<td>30.7</td>
</tr>
<tr>
<td>W2</td>
<td>31.8</td>
<td></td>
<td>30.2</td>
<td></td>
</tr>
<tr>
<td>W3</td>
<td>13.8</td>
<td></td>
<td>31.8</td>
<td></td>
</tr>
</tbody>
</table>

% change | 6.7 | 14.0 |

1. CO₂ adsorption in the presence of H₂O enhances the total CO₂ adsorbed, where the amount of weakly adsorbed decreases and the amount of strongly adsorbed increases.

2. Enhancement in the total amount of adsorbed CO₂ in the presence of H₂O is also observed by the longer breakthrough time for the CO₂ MS profile. Enhancement in the amount of total adsorbed CO₂ could result from the liberation of entangled amine groups within the polymer binder by H₂O.

3. Enhancement of strongly adsorbed CO₂ was accompanied by an increase in the temperature rise at the bottom and top of the bed. Greater temperature rise for wet adsorption indicates more heat released by further adsorbed CO₂ molecules compared to those of dry adsorption. The additional release of heat could result from adsorption of H₂O to silanol or amine groups.
Figure A.2: Concentration profiles for CO₂ and CH₄ and temperature profiles for the top and bottom of the pellet bed during cycle 2 of (a) dry CO₂ adsorption and (b) wet CO₂ adsorption.
1. The spectra of the all pellets show the characteristic features of TEPA at 3360 and 3300 cm\(^{-1}\) for N-H stretching, 2931 and 2810 cm\(^{-1}\) for C-H stretching, and 1605 cm\(^{-1}\) for N-H deformation.

2. Adsorbed species on the CO\(_2\) adsorbed and air purged sorbents were evidenced by the (i) broadened features between 1750-1200 cm\(^{-1}\) due to the formation of bands at 1635 cm\(^{-1}\) for N-H deformation of NH\(_3^+\) ion, 1575 cm\(^{-1}\) for O=C=O stretching and 1410 cm\(^{-1}\) for NCOO of carbamates, (ii) enhanced intensity between 2750-1750 cm\(^{-1}\) for Zwitterions vibrations, and (iii) reduced N-H stretching band intensities as these groups were consumed by adsorption.
3. The spectrum for wet CO$_2$ adsorption shows enhanced broadening on the high
wavenumber side of the 3500-3000 region compared to dry adsorption, indicating
the presence of adsorbed H$_2$O.

Figure A.4: Concentration profiles for CO$_2$ and CH$_4$, temperature profiles for the top and
bottom of the pellet bed, and temperature profile of the H$_2$O saturator during dry and wet
CO$_2$ adsorption and desorption cycles.
Figure A.5: MS intensity profiles for CO\textsubscript{2}, CH\textsubscript{4}, and air; temperature profiles for the top and bottom of the pellet bed; and temperature profile of the H\textsubscript{2}O saturator during dry and wet CO\textsubscript{2} adsorption and desorption cycles.
APPENDIX B

THE EFFECT OF Na₂CO₃ ON THE DEGRADATION OF TEPA/SILICA SORBENTS

B.1 Summary

TEPA/silica sorbents with 29 and 50 wt% amine and different 0-5 wt% Na₂CO₃ were degraded in air at 130 °C for 70 min. For both amine loadings, TEPA/silica with no Na₂CO₃ exhibited severe degradation and changed color from white to dark brown. IR results confirmed that the change in color resulted from oxidation of amine and alkyl groups into C=O amide species. The severely degraded sorbents exhibited up to 78% reduction in CO₂ capture capacity compared to the fresh sorbents. Increasing the Na₂CO₃ loading from 0 to 4.9 wt% reduced the oxidative degradation of the sorbent, preserving the amine groups and allowing only 2.8% reduction in CO₂ capture capacity. IR results also revealed no significant interaction between TEPA and Na₂CO₃, indicating Na₂CO₃ functioned only as a reactive oxygen species (ROS) scavenger.

B.2 Objectives

The objective of this study was to determine the effect of Na₂CO₃ loading on the oxidative degradation of TEPA/silica sorbents.
B.3 Key Findings

1. IR results showed that increasing the Na$_2$CO$_3$ loading from 0 to 4.9 wt% on both 29 and 50 wt% TEPA/silica inhibited the formation of C=O amide species (brown color), the products of TEPA oxidation.

2. The CO$_2$ capture capacity of the 29 wt% TEPA/silica sorbent decreased by 78% in the absence of Na$_2$CO$_3$ and decreased only 2.8% for 4.9 wt% Na$_2$CO$_3$ loading. The CO$_2$ capture capacity for 50 wt% TEPA/silica decreased 77% in the absence of Na$_2$CO$_3$, however increased for all Na$_2$CO$_3$ loadings. This increase was not expected.

3. IR results of 12 and 30 wt% TEPA depositied onto Na$_2$CO$_3$ did not show shifting of the N-H stretching vibrations or broadening of the same, indicating no significant interaction between the species. The Na$_2$CO$_3$ inhibited degradation by primarily functioning as a reactive oxygen specie scavenger.

B.4 Experimental

A total of 8 samples were prepared. Four, 3.0 g samples of Tixosil 68B silica (Rhodia) were impregnated with 10.8 g of a 30 wt% tetaethylenpentamine, TEPA, (tech. 98% Sigma-Aldrich) in H$_2$O solution containing 0, 0.5, 1.0, and 3.0 wt% Na$_2$CO$_3$. Four additional 3.0 g samples of silica were impregnated with 12 wt% TEPA/H$_2$O containing Na$_2$CO$_3$. The resulting mixtures were dried at 100 °C for 60 min to evaporate H$_2$O. The dried mixtures were white granular sorbents containing 29 and 50 wt% TEPA, and 0, 0.9, 1.7, and 4.9 wt% Na$_2$CO$_3$. 
The sorbents were degraded in the oven at 130 °C for 70 min. CO$_2$ adsorption/desorption was performed on the fresh and degraded samples by (i) pretreating at 100 °C for 10 min, (ii) placing in the sealed CO$_2$ bath and flowing 1.5 L/min of 100% CO$_2$ for 10 min for adsorption, and (iii) placing the sorbents with CO$_2$ into the oven at 100 °C for 10 min for desorption. The samples were weighted before and after adsorption, and the weight change was calculated as the amount of CO$_2$ adsorbed.

IR scans of the fresh and degraded sorbents were taken by placing the samples into the DRIFTS cell maintained at 105 °C and holding for 5 min. This method of scanning allowed rapid collection of IR data of many samples without having to heat/cool, which saved considerable time.

B.5 Needed Experiments

1. Determine why the capture capacities of 50 wt% TEPA silica sorbents behaved strangely.

2. Prepare and test sorbents with K$_2$CO$_3$ and another antioxidant for a more complete study of antioxidants.

3. Perform in-situ degradation of sorbents in the DRIFTS.

4. Take nmr of fresh and degraded sorbents, with and without Na$_2$CO$_3$.

5. Perform in-situ CO$_2$ ads on a couple of fresh and degraded sorbents.
B.6 Results

Figure B.1: IR absorbance spectra of 29 wt% TEPA/silica with different amounts of Na$_2$CO$_3$, fresh and degraded in the oven at 130 °C for 70 min. The spectra were collected in DRIFTS after 5 min at 105 °C.

1. The fresh sorbents exhibited the characteristic bands of TEPA, which are N-H stretching at 3360 and 3300 cm$^{-1}$, N-H bending at 1604 cm$^{-1}$, C-H stretching at 2934-2814 cm$^{-1}$, and C- bending at 1456 cm$^{-1}$.

2. Degrading the sorbents at 130 °C for 70 min produced the 1676 band cm$^{-1}$, showing the formation of C=O amide species from oxidized TEPA. Formation of the C=O species corresponded to the reduction of all N-H and C-H vibrations. The sorbent without Na$_2$CO$_3$ showed significant degradation; reduction and transformation of N-H stretching doublet into a single broad band around 3330
cm\(^{-1}\), reduction of C-H vibrations at 2934-2814 cm\(^{-1}\) with the disappearance of 2814 cm\(^{-1}\), and significant reduction of N-H and C-H bending vibrations. The highly degraded sorbent exhibited a dark brown color typical of polyamides.

3. Increasing the Na\(_2\)CO\(_3\) loading to 0.9 wt% reduced the oxidative degradation of TEPA; less reduction of N-H vibrations with the stretching doublet present and C-H vibrations, and less formation of amide species. Less degradation corresponded to the pale yellow color.

4. Further increasing the Na\(_2\)CO\(_3\) loading to 1.7 and 4.9 wt% further reduced the oxidative degradation of TEPA, evidenced by the IR spectra and color of the sorbent.

Figure B.2: IR absorbance spectra of 50 wt% TEPA/silica with different amounts of Na\(_2\)CO\(_3\), fresh and degraded in the oven at 130 °C for 70 min. The spectra were collected in DRIFTS after 5 min at 105 °C.
1. Increasing the Na$_2$CO$_3$ loading of the 50 wt% TEPA/silica sorbent reduced the oxidative degradation of TEPA similar to the 29 wt% TEPA/silica sorbent.

2. The 50 wt% TEPA/silica sorbents showed more degradation than the 29 wt% TEPA/silica sorbents, resulting from the higher amine loading.

3. The % decrease in CO$_2$ capture capacity for the sorbents was not determined since the values increased after degradation, which was not expected.

![Figure B.3: IR absorbance intensity profile of 1676/806 (C=O of amide/Si-O-Si of silica) at different loadings of Na$_2$CO$_3$ on 29 and 50 wt% TEPA/silica sorbents.](image-url)
1. Increasing the Na$_2$CO$_3$ loading on both 29 and 50 wt% TEPA/silica sorbents decreased the oxidative degradation of TEPA, evidenced by the reduction in the 1676/806 IR ratio.

![Figure B.4: IR absorbance spectra of Na$_2$CO$_3$ pretreated at 150 °C for 5 min under Ar to remove adsorbed H$_2$O then cooled, and different loadings of TEPA on Na$_2$CO$_3$ pretreated at 105 °C for 5 min under Ar then cooled. The spectra were collected at 55 °C to compare with the spectra of TEPA, which was taken from another study.](image)

1. The spectrum of Na$_2$CO$_3$ used in this study is significantly different from that found in the OMNIC library, with strong bands around 2750-2300 cm$^{-1}$ and 2000-1000 cm$^{-1}$. These bands for our Na$_2$CO$_3$ may indicate contamination by other species. The characteristic bands for Na$_2$CO$_3$ appear at 1457 and 881 cm$^{-1}$. 


2. Depositing TEPA onto Na₂CO₃ produced the N-H stretching vibrations, in which the band positions were identical to that of a pure TEPA layer. The lack of shifting of the N-H positions for deposited TEPA indicates (i) no significant interaction between N-H and CO₃⁻ species or (ii) a thick layer of TEPA was deposited on the surface, in which the IR beam wasn’t able to penetrate to the TEPA-Na₂CO₃ interface where there may be observable interaction. The N-H bending vibration was not observed, resulting from overlap with Na₂CO₃ bands.

Table B.1: CO₂ capture capacities and amine efficiencies of 30 and 50 wt% TEPA/silica with different amounts of Na₂CO₃. The amine efficiencies of the degraded sorbents were calculated according to the initial amount of TEPA on the fresh sorbents.

<table>
<thead>
<tr>
<th>% TEPA</th>
<th>% Na₂CO₃</th>
<th>CO₂ capture (mmol/g)</th>
<th>mol CO₂/mol N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Deg.</td>
<td>% change</td>
</tr>
<tr>
<td>50 wt%</td>
<td>0</td>
<td>1.48</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>1.35</td>
<td>1.61</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>1.10</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>4.9</td>
<td>0.98</td>
<td>1.50</td>
</tr>
<tr>
<td>29 wt%</td>
<td>0</td>
<td>1.31</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>1.43</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>1.58</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>4.9</td>
<td>1.19</td>
<td>1.16</td>
</tr>
</tbody>
</table>

1. The CO₂ capture capacities and amine efficiencies of all fresh sorbents were significantly lower than expected; the 50 wt% sorbents should capture around 3.0-3.5 mmol/g. Performing CO₂ capture cycles of the TPSENa standard the day after this experiment was run showed no problem with the weighing system. One possible explanation for the unexpected sorbent behavior results from the sorbent preparation. There may have been insufficient solution impregnated onto silica for effective dispersion of amine sites. Ineffective dispersion would lead to more
agglomeration and deposition of TEPA at the pore mouth, which would inhibit diffusion of CO$_2$ to agglomerated amine sites.

2. The CO$_2$ capture capacities of the degraded 50 wt% TEPA/silica sorbents significantly increased after degradation, which was contrary to the IR results and was not expected. The increased capture capacity may result from evaporation of agglomerated TEPA at the pore mouth, as well as dispersion of remaining TEPA. The evaporation and dispersion would allow more efficient diffusion and adsorption of CO$_2$ on the amine sites.

3. Increasing the Na$_2$CO$_3$ content of the 29 wt% TEPA silica sorbents stabilized their CO$_2$ capture capacities after degradation.
APPENDIX C

THE EFFECT OF PH ON THE LIQUID-PHASE CROSS-LINKING OF PVA WITH GLUTARALDEHYDE

C.1 Summary

The effect of pH on the liquid phase cross-linking reaction between polyvinyl alcohol (PVA) and glutaraldehyde was investigated at 60 °C, with pH values of 2-11 and HC=O/OH molar ratios of 0.05-0.51. Cross-linking was not observed above a pH of 4 regardless of the HC=O/OH molar ratio, resulting from insufficient H$_3$O$^+$ to catalyze the reaction. Cross-linking at pH=4 at high molar ratios produced a malleable gel, consisting of a semi-ordered network of linked PVA chains with entrapped H$_2$O molecules. FTIR results showed that the semi-ordered network was created through C-O-C linkages between PVA and glutaraldehyde. Further decreasing the pH to 2 enhanced the cross-linking reaction and produced rigid white gels. FTIR showed the extent of cross-linking of the gels increased from 2.8% for 0.05 molar ratio to 11.8% for 0.51 molar ratio. Crush tests showed that the nominal crush pressure of the gels increased from 2.4 to 48.7 psi. Enhancement of the mechanical strength of the gels resulted from the high degree of covalent bonding and crystallinity within the cross-linked PVA network. The cross-linking PVA particles were nearly insoluble in H$_2$O.
C.2 Summary

C.2.1 Objectives

1. Determine the effect of pH on the extent of cross-linking between polyvinyl alcohol and glutaraldehyde.

2. Estimate the extent of cross-linking with FTIR spectroscopy.

3. Correlate the mechanical properties of cross-linked PVA gels with the extent of cross-linking.

C.2.2 Key Findings

1. FTIR results showed that no cross-linking occurred above pH=4

2. Cross-linking at pH=4 was observed for samples with 0.32 and 0.51 HC=O/OH molar ratios, resulting from C-O-C linkages in the presence of the acid catalyst. The extent of cross-linking was not estimated due to the difference in the IR backgrounds of the samples and the powder PVA control.

3. Rapid cross-linking at pH=2 produced rigid gels with varying extents of cross-linking, estimated by FTIR as; 2.8, 6.8, 9.5, and 11.8% for 0.05, 0.14, 0.32, and 0.51 HC=O/OH molar ratios respectively.

4. Nominal crush pressures of pH=2 cross-linked gels increased with % of cross-linking and followed as; 2.4, 6.8, 22.7, and 48.1 for 0.05, 0.14, 0.32, and 0.51 HC=O/OH molar ratios respectively
C.2.3 Experiments needed

1. Perform crush tests with more samples for a statistical analysis; run a sample or two using ASTM standard method.

2. Improve technical content, provide description for XRD (need spectra of precipitated PVA film), and provide description for wash solution IR films.

3. Take IR of gels before processing

C.3 Experimental

C.3.1 Chemicals

Polyvinyl alcohol (PVA, 100% hydrolyzed, mw=75,000) from thechemistrystore.com was the polymeric network and 25 wt% aqueous glutaraldehyde from Alfa Aesar was the polymer cross-linking agent. Potassium hydroxide solid pellets (KOH) from Fisher and HCl (36.5-38% assay) from EMD were the catalysts for the cross-linking reaction.

C.3.2 Preparation of Stock Solutions

A 5 wt% PVA stock solution was prepared by dissolving 10.0g PVA in 190.0 g of de-ionized H₂O at 110 °C for 60 min then cooling down to 25 °C. Basic solutions of 0.2, 0.5, and 1.0 M KOH and acidic solutions of 0.1, 0.2, and 0.5 M HCl were prepared by mixing the appropriate amount of KOH solid pellets and HCl respectively with de-ionized H₂O.
C.3.3 Cross-linking

Five sets of 40.0 g of PVA stock solution were mixed with 0.48, 1.28, 2.88, and 4.65 g of glutaraldehyde solution, yielding HC=O/OH molar ratios of 0.05, 0.14, 0.32, and 0.51. Four, 10.0 g samples from each set were placed into 20 mL vials and pH adjusted with different KOH and HCl solutions to 2, 4, 7, 9, and 11(±0.5). The ±0.5 pH variation resulted from possible error in reading the color of the pH paper. The vials with pH adjusted solutions were placed into an oven at 60 °C for 2 h for cross-linking between PVA and glutaraldehyde. The structures of cross-linked samples ranged from liquids to solid gels, and were processed in different ways for FTIR analysis. Table C.1 shows the composition of each sample.

C.3.4 Preparation of Thin Membranes from Liquids

Membranes were prepared using the phase inversion method. A 1.0-2.0 g amount of each cross-linked liquid was placed onto a hydrophilic mylar sheet attached to the stage of an automated tape-caster. A moveable arm passed a 200 µm doctor blade over the liquid at 0.37 cm/s to cast the membrane. The membranes were immediately submerged into an acetone bath for 5 min to remove H₂O then allowed to dry in ambient at 25 °C for 18 h. The membrane thicknesses determined by micro-calipers were 25-102 µm.

C.3.5 Preparation of Powders from Solid Gels

The residual 1-2 ml of liquid remaining in the vials was decanted off and the gels were crushed in the vials with a stainless steel spatula. The crushed gels were (i) washed with 20 mL of acetone, (ii) vacuum filtered, and (iii) ground with a mortar and pestle. Washing and grinding the gels removed much of the liquid from the cross-linked PVA.
and reduced their particle size. Steps 1-3 were repeated, followed by drying the ground cross-linked PVA at 80 °C for 20 min.

C.3.6 FTIR

Prior to characterization, all samples were pretreated at 90 °C for 15 min to desorb H2O adsorbed from the ambient atmosphere. All samples were characterized with a Nicolet 6700 FTIR equipped with an MCT detector. Membranes were prepared for reflection mode FTIR by taping LxW=1.0x1.0 cm sections onto reflective aluminum foil sheets and placing onto a moveable stage inside of the FTIR. The powders were characterized in DRIFTS. All spectra were collected with 10 co-added scans at a resolution of 4 cm⁻¹, optical velocity of 3.164 cm/s, and aperture of 150.

C.3.7 Crush Test

Figure C.1 shows the set-ups for determining the crush strength of the cross-linked PVA gels. Set-up (a) consisted of a (i) steel platform with a stage to hold the gel and an attached stand with a clamp, (ii) aluminum, vertical guide tube held by the clamp, (iii) plastic weight vessel to hold steel weights, and (iv) steel press rod with a flat base attached to the weight vessel. Each cylindrical gel was cut to a length of 11-12 mm and placed vertically onto the stage. The base of the press rod was gently lowered until contacting the gels. Steel weights were loaded into the weight vessel until the gels became crushed. The heights of the gels were recorded at different added weights to determine their compressibilities. Set-up (b) was capable of producing stronger crush force than set-up (a) and consisted of (i) a steel frame mounted to a table, (ii) turn rod used to drive a press rod downward, (iii) spacer with a flat bottom to provide a smooth contact surface with the gel, and (iv) an OHAUS, 6 kg capacity scale. A strong gel was
placed onto the scale and the spacer was placed onto the gel. The turn rod was rotated to
drive the press rod and spacer onto the gel until the gel became crushed. The height of
the gel was recorded at different applied forces.

Table C.1: Initial compositions of the solutions for cross-linking.

<table>
<thead>
<tr>
<th>pH (±0.5)</th>
<th>mol HC=O/mol OH</th>
<th>% Theoretical Cross-link</th>
<th>5 wt% PVA soln. (g)</th>
<th>25 wt% glut. soln. (g)</th>
<th>Catalyst (g)/Conc. (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.05</td>
<td>10.6</td>
<td>9.88</td>
<td>0.12</td>
<td>0.387/0.2 M HCl</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>28.2</td>
<td>9.69</td>
<td>0.31</td>
<td>0.200/0.5 M HCl</td>
</tr>
<tr>
<td>2</td>
<td>0.32</td>
<td>63.3</td>
<td>9.33</td>
<td>0.67</td>
<td>0.192/0.5 M HCl</td>
</tr>
<tr>
<td>2</td>
<td>0.51</td>
<td>102.0</td>
<td>8.96</td>
<td>1.04</td>
<td>0.192/0.5 M HCl</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>10.6</td>
<td>9.88</td>
<td>0.12</td>
<td>0.048/0.1 M HCl</td>
</tr>
<tr>
<td>4</td>
<td>0.14</td>
<td>28.2</td>
<td>9.69</td>
<td>0.31</td>
<td>0.129/0.1 M HCl</td>
</tr>
<tr>
<td>4</td>
<td>0.32</td>
<td>63.3</td>
<td>9.33</td>
<td>0.67</td>
<td>0.192/0.1 M HCl</td>
</tr>
<tr>
<td>4</td>
<td>0.51</td>
<td>102.0</td>
<td>8.96</td>
<td>1.04</td>
<td>0.110/0.2 M HCl</td>
</tr>
<tr>
<td>7</td>
<td>0.05</td>
<td>10.6</td>
<td>9.88</td>
<td>0.12</td>
<td>0.142/0.2 M KOH</td>
</tr>
<tr>
<td>7</td>
<td>0.14</td>
<td>28.2</td>
<td>9.69</td>
<td>0.31</td>
<td>0.148/ 0.2 M KOH</td>
</tr>
<tr>
<td>7</td>
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<td>63.3</td>
<td>9.33</td>
<td>0.67</td>
<td>0.155/ 0.5 M KOH</td>
</tr>
<tr>
<td>7</td>
<td>0.51</td>
<td>102.0</td>
<td>8.96</td>
<td>1.04</td>
<td>0.299/ 0.5 M KOH</td>
</tr>
</tbody>
</table>
Table C.1 continued.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>9</td>
<td>0.05</td>
<td>10.6</td>
<td>9.88</td>
<td>0.12</td>
</tr>
<tr>
<td>9</td>
<td>0.14</td>
<td>28.2</td>
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<td>0.31</td>
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<td>9</td>
<td>0.32</td>
<td>63.3</td>
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<td>0.67</td>
</tr>
<tr>
<td>9</td>
<td>0.51</td>
<td>102.0</td>
<td>8.96</td>
<td>1.04</td>
</tr>
<tr>
<td>11</td>
<td>0.05</td>
<td>10.6</td>
<td>9.88</td>
<td>0.12</td>
</tr>
<tr>
<td>11</td>
<td>0.14</td>
<td>28.2</td>
<td>9.69</td>
<td>0.31</td>
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<tr>
<td>11</td>
<td>0.32</td>
<td>63.3</td>
<td>9.33</td>
<td>0.67</td>
</tr>
<tr>
<td>11</td>
<td>0.51</td>
<td>102.0</td>
<td>8.96</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Figure C.1: Set-ups for determining the crush strength and compressibility of the gels.
C.4 Results

C.4.1 Pictures

Figure C.2 shows pictures of the gels formed from cross-linking PVA with glutaraldehyde at different HC=O/OH molar ratios and pH’s=2 and 4.

Cross-linking at pH=2 with a 0.05 HC=O/OH molar ratio produced a white translucent, weak gel with only 73.5% of the initial solution volume. The covalent bonding of PVA with glutaraldehyde created a cross-linked, porous network with entrapped H$_2$O.

Reduction of the gel volume compared to the initial solution resulted from the limited porosity of the gel. Increasing the HC=O/OH molar ratio from 0.05 to 0.14 enhanced the opacity of the white gel and reduced the volume to 43.3% of the initial solution. The change in physical characteristic of the gel resulted from enhanced cross-linking, which produced a dense network of PVA+glutaraldehyde+PVA chains. Subsequent increases in
the HC=O/OH molar ratio enhanced the mechanical strength and opacity of the gels due to further cross-linking. Visual observation showed that a white powder with semi-uniform particle size was obtained after processing the gels. Cross-linking at pH=4 with HC=O/OH molar ratios of 0.32 and 0.51 produced highly viscous, self-cohesive gels with no specific shape. Irregular chunks were obtained after processing the self-cohesive gels, resulting from their inability to create a thin layer or particle during phase inversion in acetone.

Cross-linking at pH=4 with 0.05 and 0.14 HC=O/OH molar ratios did not produce gels due to insufficient formation of the covalently bound network. Cross-linking at all other pH values with all HC=O/OH molar ratios did not produce gels due to insufficient linkage of PVA chains. Figure C.3 shows the thin membranes prepared by casting the cross-linked liquid solutions onto the hydrophilic mylar sheet then drying overnight. The white appearance of the membranes shows successful removal of H₂O from the weakly bound PVA networks. Cross-linking with 0.05 and 0.14 molar ratios produced membranes with somewhat consistent white appearance compared to those produced from other ratios. The consistent appearance shows uniform casting of the membranes due to slightly high concentration of PVA in the solutions. The slightly high concentration increased the viscosities of the solutions, preventing their migration during casting. The thicknesses of the membranes determined by the micro-caliper were between 25 and 102 µm. However, the precision of the caliper was only 25 um so the reported values are only estimates.
Figure C.3: Pictures of dried thin membranes on the hydrophilic mylar sheet.

C.4.2 FTIR-Reflection

Figure C.4 shows the IR absorbance spectra of PVA reacted with glutaraldehyde at 0.32 and 0.51 HC=O/OH molar ratios and pH values of 2-11. The spectrum of pure PVA powder was included as a reference. Absorbance was obtained by the equation, Absorbance=log(1/I), where I was the single beam spectrum of interest. Pure PVA powder produced characteristic bands of O-H stretching at 3500-3000 cm\(^{-1}\) centered at 3386 cm\(^{-1}\), symmetric and asymmetric methyl C-H stretching at 2941 and 2907 cm\(^{-1}\) respectively, methyl C-H bending at 1454 cm\(^{-1}\), and C-O-C stretching of crystalline and
amorphous regions at 1146 and 1105 cm$^{-1}$ respectively. The presence of hydrogen bonded H$_2$O on the OH groups of PVA is evidenced by the H-O-H bending at 1661 cm$^{-1}$. The adsorbed H$_2$O also contributes a small portion of the O-H stretching band.

Figure C.4: IR absorbance spectra of PVA cross-linked with 0.32 and 0.51 HC=O/OH molar ratios and various pH’s at 60 °C for 2 h. The spectrum of pure PVA powder was included as a reference. Absorbance = -log (I/I$_o$), where I$_o$ was the single beam spectrum of the cross-linked sample. The pictures show the cross-linked gel (left) and processed powder (right). The spectrum of a thin glutaraldehyde film was included as reference.

A weak shoulder is observed at 1712 cm$^{-1}$ for un-hydrolyzed acetate groups of polyvinyl acetate, which served as the precursor to PVA. Reacting PVA at pH=11 and 0.32 HC=O/OH molar ratio did not produce significant changes in the spectrum compared to pure PVA powder, with the exception of flattening of the 3386 cm$^{-1}$ band.
The cause of flattening is unclear. However, the flattening was not due to cross-linking since the corresponding increase in C-O-C stretching at 1146 cm\(^{-1}\) was not observed. The spectrum of PVA reacted with glutaraldehyde at 0.52 molar ratio also shows similar features to pure powder PVA, but with a decrease in the I\(_{1146/1105}\) intensity ratio. The decreased ratio indicates a significant loss of crystallinity in the membrane compared to pure PVA powder due to the phase inversion process. Phase inversion with acetone removes H\(_2\)O from the reacted PVA solution, causing PVA chains to reorganize into a more amorphous structure.

The spectra of PVA reacted at pH=9 and 7 and all molar ratios do not show an increase in the 1146 cm\(^{-1}\) band due to the absence of cross-linking. Reacting PVA at pH=4 with 0.32 and 0.51 molar ratios formed covalent acetal linkages between PVA chains and glutaraldehyde (cross-linking), evidenced by the increase in the 1146 cm\(^{-1}\) band. The enhanced crystallinity of the cross-linked samples is clearly shown in Table C.2, in which the I\(_{1146/1105}\) intensity ratio increased from 1.10 for pure PVA powder to 1.45 and 1.64 for the 0.32 and 0.51 molar ratio samples respectively. The accompanying blue shift of 1146 to 1149 cm\(^{-1}\) showed enhanced strength of the C-O-C bond due to formation of the crystalline structure. Reduction in the PVA OH groups of the cross-linked samples was not observed due to differences in the spectral background of the samples compared to pure PVA powder. However, blue shifting of OH stretching from 3386 to 3475 cm\(^{-1}\) showed enhanced strength of the PVA OH bond due to isolation from neighboring OH groups. The presence of un-reacted HC=O groups of glutaraldehyde produced the strong C=O stretching band at 1712 cm\(^{-1}\).
Table C.2: IR intensity ratios for crystalline PVA and unreacted aldehyde groups.

<table>
<thead>
<tr>
<th>pH_Molar ratio</th>
<th>$I_{1146/1105}$</th>
<th>$I_{1712/1454}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PVA powder</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>4_0.32</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>4_0.51</td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td>2_0.05</td>
<td>1.27</td>
<td>0.55</td>
</tr>
<tr>
<td>2_0.14</td>
<td>1.32</td>
<td>0.93</td>
</tr>
<tr>
<td>2_0.32</td>
<td>1.63</td>
<td>1.12</td>
</tr>
<tr>
<td>2_0.51</td>
<td>1.54</td>
<td>1.04</td>
</tr>
</tbody>
</table>

The un-reacted groups indicated that a portion of the glutaraldehyde molecules did not link PVA chains together. Alternatively, the C=O stretching may result from un-reacted glutaraldehyde molecules trapped inside pores surrounded by the solid, crystalline PVA structure. Trapped glutaraldehyde would not be washed away from the gels by acetone during phase inversion. The alky chain of glutaraldehyde produced methylene C-H stretching vibrations at 2861, 2731, and 2627 cm$^{-1}$

Cross-linking at pH=2 further enhanced the formation of crystalline regions of PVA through C-O-C linkages compared to pH=4, evidenced by the increase in the 1146 cm$^{-1}$ band. Clear reduction in the 3386 cm$^{-1}$ band showed consumption of PVA OH groups by glutaraldehyde HC=O groups to form the C-O-C linkages. Blue shifting of 3386 to 3476 cm$^{-1}$ accompanied the decrease in band intensity. A large amount of un-reacted or trapped glutaraldehyde was also observed by the strong C=O stretching intensity.
Figure C.5 shows the IR absorbance spectra of pure PVA powder and PVA cross-linked with all HC=O/OH molar ratios at pH=2.

Figure C.5: IR absorbance spectra of PVA cross-linked with different HC=O/OH molar ratios at pH=2 and 60 °C for 2 h. The spectrum of pure PVA powder was included as a reference. Absorbance=\log (I/I_0), where I was the single beam spectrum of the cross-linked sample. The pictures show the cross-linked gel (left) and processed powder (right).

Increasing the molar ratio from 0 (pure PVA powder) to 0.51 enhanced the crystalline C-O-C linkages and CH₂ methylene groups, and decreased the amount of PVA OH groups due to cross-linking. The 1146 cm⁻¹ band blue shifted to 1151 cm⁻¹ for the 0.14 molar ratio and to 1156 cm⁻¹ for the 0.32 and 0.51 molar ratios due to enhanced strength of the crystalline bonds. Table C.2 shows that the I₁₇₁₂/I₁₄₅₄ intensity ratio increased from 0.55 to
1.04 for the 0.05 and 0.51 molar ratios respectively. The increased ratio suggested incomplete linkage of PVA chains with glutaraldehyde or a high amount of trapped glutaraldehyde.

Figure C.6 shows the $I_{3476/2841}$ and $I_{1146/1454}$ absorbance intensity ratio profiles for PVA cross-linked at pH=2.

![Graph showing IR absorbance intensity ratio plots of 3386/2841 and 1146/1454 for PVA cross-linked with different HC=O/OH molar ratios at pH=2. The percentage values represent the % decrease in the 3386/2841 intensity ratio compared to pure PVA powder. The % decrease is the estimated % of cross-linking between PVA and glutaraldehyde.](image)

Figure C.6: IR absorbance intensity ratio plots of 3386/2841 and 1146/1454 for PVA cross-linked with different HC=O/OH molar ratios at pH=2. The percentage values represent the % decrease in the 3386/2841 intensity ratio compared to pure PVA powder. The % decrease is the estimated % of cross-linking between PVA and glutaraldehyde.

The decrease in the $I_{3476/2841}$ ratio with the increase in the $I_{1146/1454}$ ratio confirms that the reaction of PVA OH groups with glutaraldehyde formed crystalline C-O-C linkages. The extent of cross-linking of PVA OH groups was estimated according to Eq. C.1.
Eq. C.1: Calculating the extent of PVA cross-linking.

\[
\% \text{ cross-link} = \left( \frac{I,_{PVA_{3476}/2841} - I,_{x_{3476}/2841}}{I,_{PVA_{3476}/2841}} \right) \times 100\%
\]

The “x” notation represents the HC=O/OH molar ratio. It can be seen that the % cross-link increased from 2.8% at 0.05 molar ratio to a maximum of 11.8% at 0.51 molar ratio. The % cross-link of PVA OH groups was significantly lower than the theoretical values listed in Table C.2, confirming that a significant portion of glutaraldehyde was un-reacted.

Figure C.7: Nominal crush pressures of pH=2 cross-linked PVA+glutaraldehyde gels for different degrees of cross-linking. Nominal crush pressure was obtained by dividing the crush force by the initial cross-sectional area of the gel.
Figure C.7 shows the results of the crush tests performed on the pH=2 gels with different % cross-linking. The nominal crush pressure was determined by dividing the crush weight by the initial cross-sectional area of the gel. The nominal crush pressure of the gels increased from 2.4 psi at 2.8% cross-link to 48.1 psi at 11.8% cross-link due to extensive covalent bonding within the crystalline PVA network. Crystalline structures typically have high compressive strengths due to the ordered lattice structure, which evenly distributes the applied crush force within the molecular network.

Figure C.8: XRD of pure PVA and cross-linked PVA particles.
Figure C.9: IR absorbance spectra of pure PVA film on a metal disk, and films prepared by evaporating the H$_2$O from 10 uL of solubility test wash solution. Intensities were magnified 10 times to show clear features of the film. Absorbance=-\log(I_{\text{film}}/I_{\text{blank cup}}).
APPENDIX D

DEVELOPMENT OF LOOP SEALS FOR A 200 G CAPACITY CO₂ CAPTURE CIRCULATING FLUIDIZED BED UNIT

D.1 Summary

Two loop seal valves were designed and installed into a 200 g circulating fluidized bed adsorption/desorption system. Loop seal 1 below the adsorber consisted of an inlet tube, cylindrical chamber with dimensions of W x H=2.5”x2.5”, and an outlet tube with H=10.5”. The total pellet capacity of the seal is 130 g, and the pressure drop across the 13.5” pellet bed length ranged from 0.07 psi at 7.6 L/min air flow to 0.66 psi at 44.1 L/min air flow. Loop seal 2 above of the desorber consisted of an inlet tube, L-shaped reservoir plus chamber with dimensions of WxH=3.5”x6.5”, and an outlet tube with H=9”. The total pellet capacity of the seal is 430 g, and the pressure drop across the 22” pellet bed length ranged from 0.08 psi at 8.5 L/min air flow to 0.67 psi at 41 L/min air flow. The presence of leaks in seal 2 caused the pressure drop across the 22” bed to be similar to the pressure drop across the 13.5” bed for seal 1. Both seals prevented back flow of the adsorber and desorber gases. The designs of the 200 g system loop seals will be used as a basis to develop loop seals for a10 kg system.
D.2 Introduction

Chemical looping combustion (CLC) and circulating fluidized bed (CFB) adsorption/desorption are commonly studied techniques for mitigating the world’s CO\textsubscript{2} emissions. CLC combines fuel combustion and CO\textsubscript{2} production into a single process, making it a cost effective method of CO\textsubscript{2} remediation. CLC utilizes circulating fluidized bed technology to transport a metal, such as Cu, Ni, and Co, across two reactors, oxidizer (fuel) and reducer (air). The oxidizer facilitates the reaction between the metal and O\textsubscript{2} to produce a metal oxide. The reducer facilitates the reaction between the metal oxide and fuel, such as methane or natural gas, to produce large amounts of heat along with CO\textsubscript{2} and H\textsubscript{2}O. The CO\textsubscript{2} and H\textsubscript{2}O mixture is then cooled to condense H\textsubscript{2}O, producing essentially pure CO\textsubscript{2} [246]. CFB adsorption/desorption consists of an adsorber filled with amine-based solid sorbent maintained at 40-60 °C, in which combustion flue gas fluidizes the sorbent for adsorption. The sorbent with CO\textsubscript{2} is sent to the desorber maintained at 70-110 °C, where CO\textsubscript{2} is released at high temperature. Pure CO\textsubscript{2} is used to fluidize the desorber to concentrate and flush out the desorbed CO\textsubscript{2} [16].

Both CLC and CFB adsorption/desorption processes incorporate non-mechanical loop seal valves between the reactors to control the flow rate of solids and prevent the mixing of gases [16, 246, 247]. The basic design of the loop seal consists of a (i) stand pipe which collects the solid particulates from the fluidized bed reactor, (ii) a supply chamber which houses the collected solids, and (iii) a recycle chamber with fluidizing air, which transports the solids over a weir and into a recycle tube. The recycle tube then sends the solids into the second fluidized reactor. A steady flow of solids through the system must be maintained by adjusting the rate of fluidization air in the loop seal and
both reactors to achieve a proper pressure balance. Specifically, the proper air flow in the loop seal ensures constant volume and residence time of the pellets to create the seal. Currently, a number of studies have been conducted regarding the design and operation of loop seals for the CLC and CFB adsorption/desorption continuous process [16, 246, 247]. However, no research has been done to address the design of loop seals for a semi-batch CFB adsorption/desorption process. The objective of this study was to design two loop seals for a 200g semi-batch CFB adsorption/desorption unit. The loop seals will be located below the adsorber and above the desorber. The results of our final designs shows that the two loop seals allowed for effective transport of pellets through the system with an effective gas seal between the adsorber and desorber. The loop seals designed here will be used as the basis for scale up to a 10 kg system.

D.3 Experimental

D.3.1 Sorbent and pellet preparation

A 1 kg batch of TPSENa sorbent was prepared by wet impregnation method. Solution 1, containing 314 g tetraethylenepentamine tech. 98%, (TEPA), 51 g polymer linker (E), 171 g polyethylene glycol 200 (PEG 200), and 913 g ethanol, was mixed with solution 2, containing 7 g antioxidant (A) and 913 g DI water. The resulting mixture was impregnated into 456 g Tixosil 68B amorphous silica, and was dried at 100 °C for 2 h. The final dried product was a white powder, which was sieved with a 500 um mesh to achieve particle uniformity.

A 1 kg batch of pellet binder solution was prepared by slowly mixing solution 3, containing 819 g DI water, 43 g PVA, and 8.6 g of 25 wt% glutaraldehyde, with solution
4, containing 86 g of 50 wt% branched PEI and 43 g of NaHCO₃. The resulting binder solution was allowed to cross-link for 30 min at 75°C under stirring. The 1 kg of TPSENa was mixed with 1 kg of cross-linked binder solution, which produced a wet dough. The wet dough was extruded into 1mm diameter rods of varying lengths using a manual screw extruder. The rods were lightly dusted with TPSENa sorbent and divided into 50 g batches. The batches were placed into a spin-disk spheronizer for 1 min at 1500 rpm, which caused the rods to become spheres with 1-2 mm diameter. The spheres were dried at 130 °C for 20 min to produce strong pellets.

D.3.2 Loop Seal Development

The initial design of the loop seal was based upon the design currently used for continuous processes, and was then modified to accommodate the semi-batch process. [16, 246-250]. Figure D.1 shows the schematic of the semi-batch CFB adsorption/desorption system for which the loop seals were designed, consisting of a (i) 100 g capacity adsorber with gas inlet for 15% CO₂/air, loop seal 1 at the base, and CO₂ gas sensor, (ii) 100 g capacity desorber with 100% CO₂ and steam inlets, blower, and loop seal 2 at the top, (iii) recycle pump, condenser, vacuum pump, and CO₂ gas sensor, and (iv) computer controlled automation with Labview software. The system allows for simultaneous adsorption and desorption, which is followed by circulating the pellets through the loop seals and into the next reactor.

The initial criteria used to determine the effectiveness of the seals was their ability to transport pellets between the adsorber and desorber. Basic trial and error procedures were used to determine the optimum geometries and sizes of the seals to allow for good pellet flowability. Observations regarding the pellet flow pattern inside the seal and the
nature of pellet transport from the valves were used to improve each design. The pellet flowability of each seal design was determined by attaching a pellet reservoir to each seal and pneumatically transporting the pellets to a collection vessel.

Figure D.1: Schematic of the 200g CFB adsorption/desorption system for which loop seals 1 and 2 were designed. The optimized loop seal designs are shown in the figure, and are to scale relative to the adsorber and desorber. The blue (→) and black (→) arrows represent gas flows, and the red (←) arrow represents pellet flow. Loop seal 2 is connected to the desorber and adsorber as indicated by the pellet flow, and is located in front at the same height.
D.3.3  Pellet and Transporting Air Flow Rates

Once the optimum designs for seals 1 and 2 were achieved, the actual flow rate of pellets exiting the seals and the corresponding transporting air flow rates were determined using the set-up in Figure D.2. The flow rate of the pellets from seal 1 shown in Figure D.2b was determined by filling the adsorber and seal with pellets, sending the transporting air through the seal, and measuring the amount of pellets accumulated in a collection vessel after 1 min. Filling the adsorber with pellets created the back pressure needed to direct the transporting air to the outlet of the seal. The flow rate of transporting air was determined by connecting the outlet of the seal to a large flow meter. The flow rate of pellets from seal 2 shown in Figure D.2a was determine by filling the desorber with pellets, sending the transporting air, and measuring the amount of pellets collected after 1 min. The transporting air flow rate was determined by connecting the seal outlet to the flow meter.

Figure D.2: Schematic for testing the pellet and transporting air flow rates out of loop seals, and performing the back flow tests in loop seal (a) 2 and (b) 1. The adsorber and desorber were filled with pellets to create back pressure, which directed the flow of air.
out of the loop seals to push the pellets. Transporting air was not used during back flow testing.

D.3.4 Back Flow Testing

The set-up for the back flow testing of seals 1 and 2 are shown in Figure D.2b and Figure D.2a respectively. The effectiveness of loop seal 1 to create a gas seal was determined by filling the adsorber and seal with pellets, flowing 5.0 L/min air through the adsorber gas inlet, and submerging the seal outlet into a beaker of water. The formation of bubbles would indicate gas which by-passed the seal. The effectiveness of seal 2 to create the seal was determined by filling the desorber and seal with pellets, flowing 5.0 L/min air through the inlet and turning on the vacuum pump, and submerging the seal outlet into water. The transporting air was not used and pellets were not moved when testing each seal.

D.3.5 Pressure Drop

Figure D.3: Schematic of the set-up for determining the pressure drop across loop seals (a) 2 and (b) 1 with a U-tube H₂O manometer. The transporting air inlet and the vents were closed.
Figure D.3 shows the set-up to determine the pressure drops across the optimized loop seals. The pressure drop at different gas flow rates was determined using a homemade U-tube H$_2$O manometer, with the ends inserted into the seals at the beginning and end of the seal beds. The difference in the height of water was recorded while flowing 5-45 L/min air through the seals. An extender tube was added to loop seal 1 to simulate the height of pellets that would remain in the adsorber once the adsorber bed was drained into the desorber. The height of pellets remaining in the drained adsorber is used as part of the seal.

D.4 Results

D.4.1 Loop Seal Development

Figure D.4 through Figure D.10 show the design stages which represent the key modifications and observations made to develop loop seals 1 below the adsorber and loop seal 2 above the desorber. The primary materials of construction were the following: “Loctite” super glue, “Gorilla” adhesive tape, polyethylene tubing, acrylic sheets, “J.B. Kwik” epoxy resin binder, cardboard, and various other plastics. Efficient transport of the pellets through the seals required appropriately sized tubing to prevent plugging. Therefore, it was necessary to use ID=1” tubing. The diameter of the tubing affected the volume of the seals, resulting in a somewhat large pellet capacity compared to the adsorber and desorber.
Figure D.4: Stage 1 evolution design of the loop seal for the circulating bed unit.

- **Stage 1 Specifications**
  1. Chamber diameter: 3”
  2. Chamber height: 3”
  3. Total pellet capacity: 200 g
  4. Transporting air flow rate: 120 L/min

- **Stage 1 Observations**
  1. The first design of the loop seal showed that the flow of pellets proceeded from (i) the chamber to the outlet and (ii) from the inlet into the chamber as the chamber was emptied. The pellets easily transported 2 ft above the seal into the collection vessel.
  2. The ramp was needed to efficiently direct the flow of pellets toward the outlet.
3. There was little backflow of the transporting air from the blower up into the inlet.

4. The fluidizing air was not necessary to mobilize the pellets due to the high flow rate of the blower.

5. This initial design provided insight into the transport of pellets through the loop seal.

Figure D.5: Stage 2 evolution design of the loop seal following for the circulating bed unit. The inlet/outlet connections may be adapted for positioning below the adsorber or above the desorber.

- **Stage 2 Specifications**

1. Chamber diameter: 3”

2. Chamber height: 4”
3. Total pellet capacity: 250 g

4. Transporting air flow rate: 55 L/min

- **Stage 2 Observations**

1. The transporting air moved the pellets from the chamber to the outlet, causing the chamber to empty at a constant rate. The outflow of pellets reduced the level inside the chamber, causing the pellets at the inlet to flow in.

2. The fluidizing air was not needed to mobilize the pellets.

3. The divider directed the transporting air primarily towards the outlet, reducing back flow up into the inlet.

4. Once the level of pellets at the inlet side of the chamber was equal to the level on the outlet side, there was significant backflow into the inlet.

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**Figure D.6:** Stage 3 evolution design of the loop seal for circulating bed unit. The inlet/outlet connections may be adapted for positioning below the adsorber or above the desorber.

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• **Stage 3 Specifications**

1. Chamber diameter: 3”

2. Chamber height: 3.5”

3. Total pellet capacity: 300 g

4. Transporting air flow rate: 55 L/min

• **Stage 3 Observations**

1. The flow of pellets was from the chamber to the outlet, and from the inlet into the chamber.

2. The addition of the ramp caused the pellets to flow more smoothly from the inlet to the outlet by guiding them to the transporting air.

3. The funnel replaced the divider and collected the pellets being blown out by the transporting air.

4. Once the level of pellets at the inlet dropped about half way into the chamber, there was significant back flow.

5. Rotating the seal towards the outlet caused the pellets to accumulate above the transporting air. The accumulation resulted in rapid flow of the pellets out of the chamber.

6. The large diameter of the chamber caused a significant pressure drop for the transporting air, reducing the flow rate of pellets through the seal compared to the stage 2 design.
Figure D.7: Stage 4 evolution design of the loop seal above the desorber of the circulating bed unit.

- **Stage 4 Specifications**

  1. Chamber diameter: 2”

  2. Chamber height: 2.5”

  3. Total pellet capacity: 130 g

  4. Transporting air flow rate: 55 L/min

- **Stage 4 Observations**

  1. The size of the chamber was reduced in order to minimize the amount of pellets needed to create the seal.
2. The addition of the reservoir was to hold some of the pellets from the desorber. A larger reservoir was later added to accommodate all of the pellets.

3. A vent covered with a mesh was added to the inlet to reduce the pressure drop between the desorber and the seal. The reduced pressure drop allowed rapid transport of the pellets from the desorber into the seal.

4. Once the level of pellets at the seal inlet was below 3-4”, there was significant back flow of the transporting air into the adsorber.

5. The effectiveness of the seal to prevent leaking of the desorber process gas into the adsorber was evaluated. Air was flowed through the ¼” desorber gas inlet, which exited from a ¼” outlet, and the outlet of the loop seal above the desorber was placed in a beaker of water. Bubbles were observed, indicating the seal was ineffective. However, when the gas outlet was switched to ¾”, no bubbles were observed, showing that increasing the size of the gas outlet allows the seal to prevent the gas from flowing to the adsorber.
Figure D.8: Stage 5 evolution design of the loop seal below the adsorber of the circulating bed unit.

- **Stage 5 Specifications**
  
  1. Chamber diameter: 2”
  
  2. Chamber height: 2.5”
  
  3. Total pellet capacity: 100 g
  
  4. Transporting air flow rate: 55 L/min

- **Stage 5 Observations**
  
  1. The low volume of the chamber was to minimize the amount of pellets needed to create the seal.
  
  2. Transporting air was used to move the pellets from the seal to the desorber, which was located below the adsorber.
3. The rapid flow of pellets from the seal caused the bed height in the adsorber to decrease.

4. The effectiveness of the seal to prevent leaking of the adsorber process gas into the desorber was evaluated. Air was flowed through the ¼” adsorber gas inlet, which exited from a ¼” outlet, and the outlet of the loop seal below the adsorber was placed in a beaker of water. Bubbles were observed, indicating the seal was ineffective. However, when the gas outlet was switched to ¾”, no bubbles were observed. This observation showed that increasing the size of the gas outlet reduces the pressure drop of the process gas, allowing the seal to prevent the gas from flowing to the desorber.

Figure D.9: Stage 6 final evolution design of the loop seal below the adsorber of the circulating bed unit.
• **Stage 6 Specifications**

1. Chamber diameter: 2.5”

2. Chamber height: 2.5”

3. Total pellet capacity: 130 g

4. Transporting air flow rate: 55 L/min

• **Stage 6 Observations**

1. Flowing the transporting air produced a low pressure vortex below the seal outlet, causing pellets to be drawn into the chamber from the inlet. As pellets were drawn into the chamber they accumulated below the seal outlet, allowing a slug to be formed. The slug was then pushed out by the transporting air.

2. The flow of pellets from the seal proceeded continuously in slugging fashion until the level of the pellets at the inlet dropped below about 3-4”. Once below 4”, pulsing of the transporting air was necessary to move the pellets from the seal.
Figure D.10: Stage 6 final evolution design of the loop seal above the desorber of the circulating bed unit.

- **Stage 6 Specifications**
  1. Chamber+reservoir diameter: 3.5”
  2. Chamber+reservoir height: 6.5”
  3. Separation of left and right side chamber with a 0.5” gap
  4. Total pellet capacity: 430 g
  5. Transporting air flow rate: 50 L/min

- **Stage 6 Observations**
  1. Multiple vents were needed to relieve the pressure from the blower as pellets were sent over from the desorber.
  2. A large reservoir was needed to store the pellets from the desorber to allow the pellets from the adsorber to be sent over.
3. The large L-shape of the seal and 0.5” chamber separation allowed efficient flow of transporting air to exit from the outlet, allowing for a high pellet flow rate.

4. The flow of pellets from the seal was continuous and in slugging fashion.

D.4.2 Flow rates, gas sealing, and pressure drop

Table D.1 summarizes the specifications for the optimized design of the loop seals, which include results from the flow rate tests. Different amounts of pellets were loaded into each seal, producing varying path lengths for gas to travel.

Table D.1: Summary of the specifications for the optimized loop seals.

<table>
<thead>
<tr>
<th>Seal</th>
<th>Pellet capacity (g)</th>
<th>Seal length (in)</th>
<th>Transporting air flow rate (L/min)</th>
<th>Transporting air velocity (m/s)</th>
<th>Pellet flow rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-below ads.</td>
<td>130</td>
<td>13.5</td>
<td>56.8</td>
<td>1.9</td>
<td>88.5</td>
</tr>
<tr>
<td>2-after des.</td>
<td>430</td>
<td>22.0</td>
<td>50.8</td>
<td>1.7</td>
<td>156.7</td>
</tr>
</tbody>
</table>
The total pellet capacity of loop seal 1 below the adsorber was 130 g, which corresponded to a bed length of 13.5”. Results of the flow tests showed that 56.8 L/min of transporting air produced a pellet flow rate of 88.5 g/min. The velocity of air through the outlet was 1.9 m/s, which was apparently higher than the minimum fluidization velocity. The total time to empty the adsorber bed was 90 s. The total pellet capacity of seal 2 above the desorber was 430 g, with a corresponding 22.0” bed length. The high capacity of seal 2 compared to seal 1 was due to the reservoir. A 50.8 L/min, 1.7 m/s, flow of transporting air produced a pellet flow of 156.7 g/min. The total time to empty an amount of pellets equivalent to that in the desorber was 78 s. Results of the back flow test showed that no bubbles were observed in the water filled beakers at the seal outlets, indicating no gas was escaping through the seals. However, it was observed that loop seal 2 had leaks which may affect the results of the test.
Figure D.11 shows the results of the pressure drop across the optimized seals at different flow rates. Both seals exhibited a low pressure drop of around 0.08 psi for 7-9 L/min of air flow, which increased linearly up to 0.66 psi at a high flow rate of 41-44 L/min. The high flow rate produced a small amount of pellet fluidization at the seal outlet. The similar pressure drop for the seals was not expected due to the difference in bed length of the pellets. The longer bed length for seal 2 should produce a large pressure drop compared to seal 1 due to increased resistance of the bed. However, the presence of leaks in the seal reduced the pressure drop by providing a vent for the air to escape. It is important to note that pressure data needs to be obtained at multiple locations of the CFB adsorption/desorption unit during full cycling since it is a semi-batch process. Electronic pressure transducers must be installed to continuously monitor pressure changes during different steps of cycling. This data will provide the complete pressure profile of the system.

D.5 Conclusions

Loop seals were successfully developed for a circulating fluidized bed (CFB) adsorption/desorption unit, located below the adsorber and above the desorber. The seals showed good flowability of the pellets through the system, and also prevented or reduced back flowing of reactor gas through the seals. The seal below the adsorber, seal 1, consisted of an 80 g pellet capacity polyethylene chamber equipped with transporting air inlet, and ID=1” polyethylene tube inlet and outlet. Flowing 56.8 L/min through the seal produced an outlet gas velocity of 1.9 m/s, causing pellets to exit the seal at 88.5 g/min. The pressure drop across the 13.5 cm bed length ranged from 0.08 to 0.66 psi for gas flows of 5-45 L/min. The seal below the desorber, seal 2, consisted of a 350 g capacity
plastic chamber+reservoir equipped with transporting air inlet, and ID=1” inlet and outlet. Flowing 50.8 L/min produced a gas velocity of 1.8 m/s, causing pellets to exit the seal at 156.7 g/min. The pressure drop across the 22 cm bed length was within a range similar to seal 1 due to the presence of leaks in the seal. The success of these loop seals provides the basis for designing seals installed into a 10 kg system.

D.6 Additional Work

1. Install electronic pressure transducers into the 200 g system and perform CO\textsubscript{2} adsorption/desorption cycles.

2. Use the loop seal designs here to develop seals for a 20 kg unit. Install the valves and test the pellet flowability and seal effectiveness, as well as pressure drop and flow rate data (in progress).
APPENDIX E

200 G CIRCULATING FLUIDIZED BED SYSTEM: TROUBLESHOOTING REPORT

E.1 Summary

A troubleshooting guide is presented to help solve cycling problems of the 200 g circulating fluidized bed system. The guide is organized by cycle segment and includes problems, possible causes, and solutions. The most significant problem is failing to achieve 99% pure CO\textsubscript{2} in the desorption segment, which is likely caused by leaks in the desorber, pumps, condenser, sensor, valves, or line fittings. Leaks from cracks in the equipment may be patched with adhesive sealant. Leaks from loose line fittings may be eliminated by tightening. Importantly, leaks may occur anywhere in the system and should be checked before cycling. Ensuring proper valve position in each segment is also important for smooth pellet flow through the system and rapid cycling. Electrical problems cause most failures of automated equipment, and result from loose or broken connections or broken relays. Only qualified personnel should attempt to re-wire connections or replace defective electrical components.

E.2 Introduction

Circulating fluidized bed technology with solid-amine sorbent has gained recent attention in removing CO\textsubscript{2} from post-combusted flue gas.
Advantages of circulating fluidized beds (CFB) over fixed fluidized beds for CO₂ removal are (i) reduced cycling time due to simultaneous adsorption and desorption, (ii) reduced energy for desorption due to a separate desorber unit maintained at constant temperature, and (iii) longevity of construction materials due to the absence of thermal shocking.

The set-up of a typical circulating fluidized bed system operated in continuous mode for CO₂ removal consists of an (i) adsorber filled with amine-based solid sorbent maintained at 40-60 °C and fluidized with post-combustion gas for CO₂ adsorption, (ii) loop seal filled with regenerated sorbent to prevent backflow of adsorber and desorber gases, (iii) vortex to separate CO₂-containing sorbent from effluent adsorber gas, and (iv) desorber filled with CO₂-containing sorbent maintained at 70-110 °C and fluidized with pure CO₂ for desorbing and purging CO₂. The effluent CO₂ from the desorber was 90% pure. [16] Inherently, two drawbacks of the continuous process are the high flow rate of pure CO₂ needed to fluidize the sorbent during desorption, and the inability to concentrate CO₂ beyond 90%.

The advantages of our 200 g semi-batch CFB system over the continuous process include no fluidization during desorption, reduced energy for desorption by the absence of fluidization gas, and ability to concentrate CO₂ to high purity. Cycling results of the semi-batch CFB system with amine-based pellets, 2.2 CO₂ mmol/g pellet capture capacity, showed the desorbed CO₂ was concentrated to 99% purity. Achieving high purity CO₂ required efficient operation of the semi-batch CFB system. Cycling presented numerous problems that affected the operation and required careful insight to solve. This report presents the troubleshooting strategies to solve the problems encountered when
cycling and problems that are likely to occur. The strategies combined a firm
understanding of basic engineering concepts with trial-and-error procedures.

E.3 Experimental

E.3.1 Sorbent and Pellet Preparation

A 1 kg batch of TPSENa sorbent was prepared by wet impregnation method.

Solution 1, containing 314 g tetraethylenepentamine tech. 98%, (TEPA), 51 g
POLYMER LINKER (e), 171 g polyethylene glycol 200 (PEG 200), and 913 g ethanol,
was mixed with solution 2, containing 7 g antioxidant (a) and 913 g DI water. The
resulting mixture was impregnated into 456 g Tixosil 68B amorphous silica, and was
dried at 100 °C for 2 h. The final dried product was a white powder, which was sieved
with a 500 um mesh to achieve particle uniformity.

A 1 kg batch of pellet binder solution was prepared by slowly mixing solution 3,
containing 819 g DI water, 43 g PVA, and 8.6 g of 25 wt% glutaraldehyde, with solution
4, containing 86 g of 50 wt% branched PEI and 43 g of NaHCO₃. The resulting binder
solution was allowed to cross-link for 30 min at 75°C under stirring. The 1 kg of
TPSENa was mixed with 1 kg of cross-linked binder solution, which produced a wet
dough. The wet dough was extruded into 1 mm diameter rods of varying lengths using a
manual screw extruder. The rods were lightly dusted with TPSENa sorbent and divided
into 50 g batches. The batches were placed into a spin-disk spheronizer for 1 min at 1500
rpm, which caused the rods to become spheres with 1-2 mm diameter. The spheres were
dried at 130 °C for 20 min to produce strong pellets. A more detailed description of
pellet preparation can be found here in the.
E.3.2 Adsorption/Desorption Cycling

Figure E.1 shows the schematic of the semi-batch CFB adsorption/desorption system consisting of a (i) 100 g capacity adsorber with gas inlet for 15% CO₂/air, loop seal 1 at the base, and 0-100% CO₂ gas IR sensor, (ii) 100 g capacity desorber with 100% CO₂ and steam inlets, blower, and loop seal 2 at the top, and (iii) recycle pump, condenser, vacuum pump, and 0-100% CO₂ gas IR sensor. Automated ball valves were used to open and close the adsorber and desorber vents, transporting air inlet, and steam jacket inlets. Manual valves were used in the rest of the system.

CO₂ adsorption was performed in the adsorber at 25 °C by flowing 10 L/min of 15% CO₂/air over 100 g of fresh pellets for 10 min. The effluent CO₂ concentration was monitored with the downstream CO₂ sensor. Simultaneous desorption was performed in the desorber at 110 °C by (i) flowing 6 L/min of 100% CO₂ over 100 g of CO₂-containing pellets for 30 s to purge air, (ii) setting the desorber in batch mode and flowing medium pressure steam through the jacket to heat the pellets to 110 °C, (iii) turning on the recycle pump to re-circulate the desorber gas to maintain a uniform temperature distribution, (iv) pulsing copper-free steam at 30 psi and 130 °C over the pellets for 10 s for CO₂ desorption, and (v) setting the desorber in flow mode and turning on the vacuum pump to remove steam and CO₂. The effluent CO₂/steam mixture was drawn through the condenser, where steam was removed and 99% CO₂ was sent to the CO₂ sensor. A 130 g loading of fresh pellets was present in loop seal 1 and 200 g was present in loop seal 2 to prevent back flowing of gases between the adsorber and desorber. After adsorption/desorption, (i) desorber pellets were pneumatically transported to the loop seal 2 reservoir with the blower by opening the loop seal 2 vents and blower valve and
flowing 60 l/min of air for 15 s, (ii) adsorber pellets were pneumatically transported through loop seal 1 to the desorber by flowing/pulsing 56.8 l/min of transporting air for 90 s, and (iii) 100 g of loop seal 2 pellets were pneumatically transported to the adsorber by flowing/pulsing 50.8 l/min of transporting air for 78 s. Once the desorber and adsorber were re-loaded, one full cycle was completed. Table E.1 provides the positions of all valves at each cycling segment.

Figure E.1: Schematic of the 200 g semi-batch CFB system. The blue (---) and black (→) arrows represent gas flows, and the red (←→) arrow represents pellet flow. Loop seal 2 is connected to the desorber and adsorber as indicated by the pellet flow, and is located in front at the same height.
E.4 Troubleshooting

Table E.2 shows the troubleshooting log for CO₂ adsorption/desorption cycling of the 200 g semi-batch CFB system. Solutions to encountered problems and potential problem are presented in the log. The log is divided into three sections, (i) cycle segment, (ii) problem, and (iii) solution. The cycle segment defines the segment in the adsorption/desorption cycle where the malfunction was encountered, or was possible. The problem specifies the malfunction in the cycle segment. The solution describes the actions taken to fix the malfunction.

Failure to flow the CO₂ mix gas is the easiest problem to fix during adsorption because it requires only correcting the valve positions. In contrast the most difficult problem is the lack of a temperature rise, which may be caused by incorrect gas flow, bad thermocouple connections, or low pellet capacity of loop seal 1. Desorption presents significant problems when cycling due to the strict requirement to concentrate CO₂ to 99%. Leaks in the desorber, pumps, valves, and line fittings result in low purity of desorbed CO₂. Large leaks may allow complete removal of desorbed CO₂ from the system. Less severe problems include temperature distribution inside the desorber and failure to flow CO₂ for purging, which are fixed by turning on the recycle pump and opening valve V11 respectively. Emptying the desorber, adsorber, and loop seal 2 do not pose significant problems because correcting the valves positions will usually fix them.

Electrical problems cause most equipment failures, and pose a high physical risk to the operator because they can result in electric shock if he or she is not familiar with wiring procedures. Before investigating electrical problems the operator must be trained, or be supervised by qualified personnel.
Table E.1: Valve positions at each segment of CO₂ adsorption/desorption cycling. “C” represents closed and “O” represents open valve positions.

<table>
<thead>
<tr>
<th>Valve</th>
<th>Description</th>
<th>CO₂ ads.</th>
<th>CO₂ desorption</th>
<th>Empty Des.</th>
<th>Empty Ads.</th>
<th>Empty loop seal 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ads. vent</td>
<td>O</td>
<td>O O O O</td>
<td>C</td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>2</td>
<td>Des. vent 1</td>
<td>C</td>
<td>C C C C</td>
<td>O</td>
<td>O</td>
<td>C</td>
</tr>
<tr>
<td>3</td>
<td>Des. vent 2</td>
<td>C</td>
<td>C C C C</td>
<td>O</td>
<td>O</td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td>Air, loop seal 2</td>
<td>C</td>
<td>C C C C</td>
<td>C</td>
<td>O</td>
<td>C</td>
</tr>
<tr>
<td>5</td>
<td>Air, loop seal 1</td>
<td>C</td>
<td>C C C C</td>
<td>C</td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>6</td>
<td>15% CO₂/air</td>
<td>O</td>
<td>C/O C/O C/O</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>7</td>
<td>Steam jacket inlet</td>
<td>O</td>
<td>O O O O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>8</td>
<td>Steam jacket outlet</td>
<td>O</td>
<td>O O O O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>9</td>
<td>Cu free steam inlet</td>
<td>C/O</td>
<td>C C C C</td>
<td>O</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>10</td>
<td>Blower outlet</td>
<td>C</td>
<td>C C C C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>11</td>
<td>CO₂ purge inlet</td>
<td>C/O</td>
<td>O C O O</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>12</td>
<td>Desorber outlet</td>
<td>C/O</td>
<td>O C C C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>13</td>
<td>Cooling water inlet</td>
<td>C/O</td>
<td>C C C C</td>
<td>O O</td>
<td>C</td>
<td>C</td>
</tr>
</tbody>
</table>

Ensuring that electrical wires and data cables are well insulated and tightly connected typically fixes the problems. The solid state relays should also be checked. A green light will be displayed when power is sent from the relay to the equipment. The
relays or equipment are replaced in rare cases. Overall, leaks require the most effort to fix when cycling because they can occur anywhere in the system.

Table E.2: Troubleshooting log for CO$_2$ adsorption/desorption cycling.

<table>
<thead>
<tr>
<th>Cycle segment</th>
<th>Problem</th>
<th>Possible cause</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>CO$_2$/air mix gas is not flowing</td>
<td>V6 closed</td>
<td>Open V6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electronic flow meter or channel shut off</td>
<td>Turn on flow meter or channel</td>
</tr>
<tr>
<td></td>
<td>CO$_2$ sensor does not shown an increase in % CO$_2$</td>
<td>Sensor is not powered</td>
<td>Plug in sensor</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sensor is contaminated with H$_2$O</td>
<td>Connect air purge line and flush sensor for 30 min.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Insufficient adsorption time for breakthrough to occur</td>
<td>Extend adsorption time until sensor reads 15% CO$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sensor gas sampling line is not connected to the adsorber outlet</td>
<td>Connect the sampling line</td>
</tr>
<tr>
<td></td>
<td>Thermocouples do not show temperature rise</td>
<td>Gas flow rate is too high, and absorbs heat of adsorption</td>
<td>Ensure flow rate is correct</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Concentration of CO$_2$ is too low and does not produce significant heat of adsorption</td>
<td>Ensure CO$_2$ flow rate and concentration are correct</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermocouples are not plugged in; show a reading of &gt;1000 °C</td>
<td>Connect thermocouples</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermocouple connections are loose, or bare wires are touching</td>
<td>Ensure all connections are tight and all exposed wires are well insulated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Significant back flow of gas through loop seal 1</td>
<td>Ensure loop seal 1 is filled with pellets</td>
</tr>
<tr>
<td>Desorption</td>
<td>Thermocouples do not show the temperature is at least 100 °C</td>
<td>Desorber is not heating because steam is not flowing to the jacket</td>
<td>Open valves 7 and 8</td>
</tr>
</tbody>
</table>
Table E.2 continued.

<table>
<thead>
<tr>
<th></th>
<th>Thermocouples are not plugged in, have loose connections, or have bare wires</th>
<th>Ensure thermocouples are plugged in, connections are tight, and bare wires are insulated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The pellets were transported from the adsorber and reduced the temperature</td>
<td>NO PROBLEM - allow sufficient time for the pellets to heat up</td>
</tr>
<tr>
<td></td>
<td>The system is set in flow mode and the desorber is being evacuated, removing the heat</td>
<td>Close valves 9, 10, 11, and 12 and turn off the vacuum pump</td>
</tr>
<tr>
<td><strong>CO\textsubscript{2}</strong> does not flow during purge</td>
<td>Valve 11 is closed or is malfunctioning</td>
<td>Ensure all electrical connections are tight and insulated and open valve 11</td>
</tr>
<tr>
<td></td>
<td>CO\textsubscript{2} cylinder is empty</td>
<td>Check cylinder's pressure and replace it if necessary</td>
</tr>
<tr>
<td></td>
<td>Electronic flow meter or channel is shut off</td>
<td>Turn flow meter on or channel</td>
</tr>
<tr>
<td><strong>The temperature distribution varies more than 15\textdegree C</strong></td>
<td>Non-uniform heating of the bed</td>
<td>Turn on the recycle pump for 30 s to re-circulate CO\textsubscript{2} and redistribute the heat</td>
</tr>
<tr>
<td></td>
<td>Thermocouples are not plugged in, have loose connections, or have bare wires</td>
<td>Ensure thermocouples are plugged in, connection are tight, and bare wires are insulated</td>
</tr>
<tr>
<td><strong>Steam does not flow during steam purging</strong></td>
<td>Valve 9 is closed</td>
<td>Open valve 9</td>
</tr>
<tr>
<td></td>
<td>The steam vessel is not filled with water</td>
<td>Ensure the vessel is filled with at least 100 mL of water</td>
</tr>
<tr>
<td></td>
<td>The steam vessel is not properly sealed and heated</td>
<td>Ensure the heating tapes are turned on to 45% power, the temperature is at least 130 \textdegree C, and the pressure is 30 psi</td>
</tr>
<tr>
<td><strong>The concentration of CO\textsubscript{2} does not increase to 99% during evacuation</strong></td>
<td>Desorbed CO\textsubscript{2} back flowed through the loop seals during heating and allowed air to enter the desorber</td>
<td>Ensure loop seal 1 and 2 are filled with pellets, and valves 1, 2, and 3 are closed</td>
</tr>
<tr>
<td></td>
<td>Valve 9 was open, allowing CO\textsubscript{2} to escape and air to enter the desorber</td>
<td>Close valve 9</td>
</tr>
</tbody>
</table>
Table E.2 continued.

<table>
<thead>
<tr>
<th>Emptying desorber</th>
<th>There are leaks present in the desorber, vacuum pump, condenser, sensor, valves, or line fittings</th>
<th>Perform a leak check and tighten loose fittings, or repair cracks with J.B Weld epoxy/resin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>The system is still set in batch mode or the pump is turned off</td>
<td>Open valve 12 and turn the vacuum pump on</td>
</tr>
<tr>
<td></td>
<td>The sensor is not working properly</td>
<td>Ensure sensors are powered and dry, disconnect the sensor and flow pure CO\textsubscript{2} to make sure it reads 100%</td>
</tr>
<tr>
<td></td>
<td>Steam is present in the gas stream</td>
<td>Ensure that V13 is open to allow cooling water flow</td>
</tr>
<tr>
<td></td>
<td>CO\textsubscript{2} was not adsorbed in the adsorber, so no CO\textsubscript{2} was desorbed</td>
<td>Refer to the troubleshooting for the adsorption category</td>
</tr>
</tbody>
</table>

| Steam is not fully removed in the condenser and flows to the sensor | Cooling water is not flowing to the condenser, or there is insufficient water flow | Ensure that V13 is open to allow cooling water flow; add a desiccant after the condenser if the maximum cooling water flow is still insufficient |

| The recirculation pump does not turn on | Electrical connections are loose or the pump is not powered | Ensure the pump is powered, all electrical connections are tight and there are no bare wires |

| The vacuum pump does not turn on | Electrical connections are loose or the pump is not powered | Ensure the pump is powered, all electrical connections are tight and there are no bare wires |

| Pellets do not flow from the desorber | The blower is turned off or V10 is closed | Turn on the blower and open valve 10 |

| Very slow flow of pellets from the desorber | Closed loop seal vent valves 2 and 3 | Open loop seal vent valves 2 and 3 |

| Not all of the pellets leave the desorber | The loop seal reservoir is full or insufficient time was allowed for transfer | Ensure the reservoir is empty enough to accommodate the pellets before transferring, and allow sufficient transfer time |
Table E.2 continued.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Some of the pellets backflow into loop seal 1</td>
<td>Loop seal 1 does not create an adequate seal or the blower air flow rate is too high</td>
<td>Ensure loop seal 1 has sufficient pellets, and the variac voltage for the blower is not set above 40%.</td>
</tr>
<tr>
<td>Some of the pellets in the loop seal 2 reservoir empty into the adsorber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emptying adsorber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The pellets do not flow from loop seal 1</td>
<td>The transporting air is turned off or the pellets do not flow down from the adsorber into the loop seal</td>
<td>Open V5 for pulsing the air, and gently shake the adsorber to allow the pellets to flow past the CO₂/air inlet line</td>
</tr>
<tr>
<td></td>
<td>Innsufficient pellets in the loop seal chamber to allow slugging to occur in the outlet tube</td>
<td>Close V5 to stop the air flow and allow the chamber to fill with adsorber pellets, then open V5 and pulse the air</td>
</tr>
<tr>
<td></td>
<td>The V1 adsorber vent is open, allowing transporting air to escape</td>
<td>Close V1 to allow back pressure to build up and force the pellets out</td>
</tr>
<tr>
<td></td>
<td>The V2 and V3 vents are closed, hindering the flow of air</td>
<td>Open V2 and V3</td>
</tr>
<tr>
<td>Emptying loop seal 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Very slow pellet flow, or no flow from the seal</td>
<td>The desorber is full of pellets</td>
<td>Empty the desorber</td>
</tr>
<tr>
<td></td>
<td>The V4 transporting air valve is closed</td>
<td>Open V4</td>
</tr>
<tr>
<td></td>
<td>The adsorber vent V1 is closed</td>
<td>Open V1</td>
</tr>
<tr>
<td></td>
<td>The loop seal 2 vents V2 and V3 are open, allowing the transporting air to escape</td>
<td>Close V2 and V3</td>
</tr>
<tr>
<td></td>
<td>The adsorber is full of pellets</td>
<td>Empty the adsorber</td>
</tr>
<tr>
<td>All-Electrical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labview software shows &quot;no longer connected&quot; error when starting the program.</td>
<td>There is no power to the DAQ or the DAQ is turned off</td>
<td>Turn on the main power to the system and the DAQ</td>
</tr>
<tr>
<td>Electrical equipment does not turn on</td>
<td>Electrical connections are loose or solid state relays don't work</td>
<td>Tighten all connections and ensure the green light on the relay is on when power is being sent to the equipment</td>
</tr>
</tbody>
</table>
Table E.2

<table>
<thead>
<tr>
<th>All-Leaks</th>
<th>CO₂/air, air, or CO₂ is leaking from the system</th>
<th>Fittings are loose, or there are cracks in the polyethylene tubing connections or process equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam is leaking from the steam lines or desorber jacket</td>
<td>There are loose connections in the metal-reinforced rubber tubing, line fittings, or cracks in the jacket</td>
<td>Tighten all gas line connections, and repair cracks with super glue, silicone tape, or J.B. Weld epoxy/resin</td>
</tr>
</tbody>
</table>

E.5 Conclusions

The troubleshooting guide presents strategies for solving cycling problems of the 200 g semi-batch CFB system. The solutions address potential problems in each segment of cycling which are adsorption, desorption, emptying desorber, emptying adsorber, and emptying loop seal 2. Overall, desorption may present the most critical problems due to the 99% pure CO₂ required. Failing to achieve high purity of desorbed CO₂ commonly results from back flow of desorbed CO₂ through the loop seals, improper valve positions, and leaks. Leaks may be present in the desorber, pumps, condenser, sensor, valves, or line fittings and cause desorbed CO₂ to escape from the system. Overall, leaks may occur anywhere in the system and require patching with an adhesive sealant or re-design of the equipment with more durable materials. A thorough leak check should be performed before cycling the system. Electrical problems are the most common cause of automated equipment failure, which may occur in any segment. Loose connections and broken relays prevent power from reaching the equipment.
APPENDIX F

CALIBRATION OF DESORBED CO\textsubscript{2} BY BATCH AND FLOW MODES WITH TWO IR’S AND MS

F.1 Objectives

1. Determine calibration curve for 100% CO\textsubscript{2} pulses injected into DRIFTS in batch mode at 110 °C.

2. Determine amount of CO\textsubscript{2} adsorbed on TPSENa using IR batch mode, and continuous flowing conditions through a second IR and MS.

F.2 Key Findings

1. CO\textsubscript{2} IR batch calibration over TPSENa at 110 °C produced a linear relationship between amount of CO\textsubscript{2} injected and absorbance intensity of 2350 and 3714 cm\textsuperscript{-1}.

2. CO\textsubscript{2} capture capacity determined by batch calibration was 0.4 mmol/g, which was verified by MS using flow calibration pulses. Typical capture capacity of this sorbent was 0.6-1.0 mmol/g in previous experiments with MS calibration only.

3. CO\textsubscript{2} capture capacity determined by IR 2 (gas phase monitoring) using calibration pulses was 40-45% higher than IR batch and MS results.
F.3  Experimental

IR batch calibration of TPSENa sorbent was performed by, (i) heating at 110°C for 5 min under 150 cc/min Ar for pretreating, (ii) closing the inlet and outlet for batch mode and successively injecting CO₂ calibration pulses, and (iii) flowing Ar for 10 min to purge CO₂ then cool down to 55 °C. IR and MS flow calibration was performed by sending three, 1 cc 100% CO₂ pulses through the sorbent bed at 110 °C using the 6-port valve. CO₂ adsorption/desorption was performed by, (i) flowing 150 cc/min of 15 vol% CO₂ in air over the sorbent for 5 min for CO₂ adsorption, (ii) switching the gas back to Ar for 10 min to purge gas phase CO₂ and CO₂ weakly adsorbed species, (iii) setting in batch mode and performing temperature programmed desorption with a heating rate of 10 °C/min up to 110 °C and holding for 5 min, and (iv) opening the inlet and outlet and flowing Ar for 10 min to purge desorbed CO₂ then cool down.

F.4  Results

Table F.1: Amount of CO₂ adsorbed/desorbed on/from 46 mg TPSENa determined by calibrations using (i) IR batch mode and continuous flowing conditions through (ii) IR 2 and (iii) MS. Batch mode calibration was determined using 2 different baselines, absolute and relative.

<table>
<thead>
<tr>
<th>Calibration Method</th>
<th>CO₂ adsorbed (cc)</th>
<th></th>
<th>CO₂ adsorbed (mmol/g)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1</td>
<td>Cycle 2</td>
<td>Cycle 1</td>
<td>Cycle 2</td>
</tr>
<tr>
<td>IR, batch-abs. baseline</td>
<td>0.42</td>
<td>0.34</td>
<td>0.41</td>
<td>0.33</td>
</tr>
<tr>
<td>IR, batch-rel. baseline</td>
<td>0.35</td>
<td>0.30</td>
<td>0.34</td>
<td>0.29</td>
</tr>
<tr>
<td>IR, flow</td>
<td>0.60</td>
<td>0.49</td>
<td>0.59</td>
<td>0.47</td>
</tr>
<tr>
<td>MS, flow</td>
<td>0.44</td>
<td>0.36</td>
<td><strong>0.43</strong></td>
<td><strong>0.35</strong></td>
</tr>
</tbody>
</table>
Figure F.1: IR absorbance spectra during CO$_2$ pulse injection calibration in DRIFTS at 110 °C set in batch mode. Abs=−log(I/Io), where Io was the single beam spectrum at 110 °C before injections and I was the single beam spectrum 5 min after each injection. Formation of bands for ammonium ion and carbamate species showed some adsorption of the injections even at high temperature.
Figure F.2: IR absorbance intensity plot for 2350/1566 and 2350/1410 based upon intensities from Figure F.1. Total CO$_2$ injected represents the amount of CO$_2$ in the DRIFTS cell after each successive injection. Increasing ratio for both plots with increasing amount of CO$_2$ injected indicates high CO$_2$ gas phase content compared to adsorbed species. Adsorbed species are believed to be only at the surface, which produced strong IR intensities for the bands in Figure F.1.
Figure F.3: IR absorbance intensity calibration plot for 2350, 3714 cm\(^{-1}\), and 3714/2350 based upon intensities from Figure F.1. Absolute baseline refers to the line which is drawn straight across from 4000 to 600 cm\(^{-1}\) and relative baseline refers to the line drawn which spans 2350 cm\(^{-1}\) centered vibration at the point where it is overlapped by ammonium ion.
Figure F.4: IR absorbance spectra during cycling of TPSENa after 5 min CO$_2$ adsorption, 10 min Ar purge, and 5 min at 110 °C for TPD in batch mode. Abs= log (I/Io), where Io was the single beam spectrum (i) at 55 °C before CO$_2$ adsorption or (ii) at 110 °C before pulse injection calibration and I was the single beam spectrum of interest. The notation in the figure of (i) or (ii) denotes the baseline used.
Figure F.5: 2350 cm$^{-1}$ IR absorbance intensity profile and m/e=44 MS intensity profile during CO$_2$ adsorption cycles and calibration
APPENDIX G

INHIBITING THE OXIDATIVE DEGRADATION OF AMINE SORBENTS WITH PVA

G.1 Objectives

The objectives of these experiments were to determine if PVA can replace PEG in the TPSENa sorbents.

G.2 Key Findings

1. Replacing PEG with PVA in TPSENa sorbent, T(PVA)SENa sorbents, reduced degradation due to low amide formation, but also reduced the CO$_2$ capture capacity.

2. Preparing TPSENa with PEG/PVA, T(PVA)SENa+PEG, increased the capture capacity compared to T(PVA)SENa while maintaining low degradation. T(PVA)SENa-.5+PEG showed the best performance of all PVA sorbents with 2.3 mmol/g average initial capture capacity and only 0.8 mmol/g*h degradation.

3. Preparing T(PVA)SENa and T(PVA)SENa+PEG sorbents with high MW PVA=96,000 and low MW PVA=9,500 showed similar capture capacities and degradations.
G.3 Experimental

G.3.1 Sorbent Preparation

TPSENa sorbent was prepared by dry impregnation method using two solutions. Solution 1 was prepared by dissolving 4.2 g polymer linker (E) into 22.5 g tetraethylenepentamine (TEPA) (Aldrich) at 70°C. After dissolving, 15.0 g polyethylene glycol MW=200 (PEG) (Aldrich) and 80.0 g ethanol (Phrmaco-Aaper) were added to the TEPA/E. Solution 2 was prepared by dissolving 0.625 g antioxidant (A) into 80.0 g DI water. The solutions were mixed together and impregnated onto 40.0 g Tixosil 68B silica (Rhodia), and the resultant mixture was dried at 100°C for 2 h.

T(PVA)SENa sorbents were prepared in two steps. For step 1, a solution of 4.2 g polymer linker, 22.5 g TEPA, and 80.0 g ethanol was impregnated onto 40.0 g silica and the resultant mixture was dried at 100 °C for 1.5 h. For step 2, a solution of 0.625 g antioxidant (A), 80.0 g water, and different amounts of polyvinyl alcohol (PVA) (Sigma-Aldrich) with varying molecular weights was prepared by mixing at 100 °C for 30 min. The resulting PVA solution was impregnated onto the TEPA/EPON/silica mixture from step 1 and dried at 100 °C for 1.5 hr.

T(PVA)SENa+PEG sorbents were prepared similarly as T(PVA)SENa sorbents. Different amounts of PEG were included in step 1 such that the weight of PEG+PVA in the sorbents was equal to the weight of PEG in TPSENa.

TPSENa+PEG sorbents were prepared by impregnating 5.0 g TPSENa sorbent with 5.0 g of PVA solutions with varying PVA concentrations and drying at 100 °C for 1.5 h.
G.3.2 CO₂ Adsorption

CO₂ adsorption was performed via the rapid screening CO₂ capture apparatus. The 1.0-1.2 g samples of the sorbents were first pretreated by heating at 100 °C for 7 min. After pretreatment, the sorbents were placed into the CO₂ bath, where 100% CO₂ at 5.0 L/min flowed for 10 min. After CO₂ adsorption, if initial capture was being performed the sorbents were placed into the oven at 100 °C for 10 min to desorb CO₂. If steam degradation was performed, the sorbents were placed into the steam chamber at 130 °C with 50 cc/min of 100% CO₂ flowing through a water saturator at 25 °C and over the sorbents for 60 min. Cycles 1-3 were performed with initial capture and the remaining cycles were performed with steam degradation.

G.4 Results

Table G.1 shows the average initial CO₂ capture capacities average degradation of the sorbents. Results of experiment 1 showed degradation of T(PVA)SENa sorbents decreased with increasing PVA content, suggesting PVA stabilized the sorbent. T(PVA)SENa-0.1, T(PVA)SENa-0.3, T(PVA)SENa-0.5 sorbents showed low degradation, 0.03-0.05 mmol/g*h, compared to TPSENa, 0.08 mmol/g*h. However, the average initial capture capacities of the sorbents also decreased due to presence of PVA; T(PVA)SENa-0.1, T(PVA)SENa-0.3, and T(PVA)SENa-0.5 showed capture capacities of 1.1-1.4 mmol/g compared to 2.2 mmol/g for TPSENa.

Table G.2 shows the ethanol uptake of TPSENa and some of the T(PVA)SENa sorbents. Results showed ethanol uptake did not follow a specific trend for the sorbents,
suggesting the low capture capacity of T(PVA)SENa sorbents was not due to plugging of the silica pores by PVA. The low capture capacities likely resulted from a different mechanism of CO$_2$ adsorption in the presence of PVA compared to PEG. Results of experiment 2 showed adding PEG to T(PVA)SENa, T(PVA)SENa+PEG sorbents, increased the capture capacities. T(PVA)SENa-.5+PEG prepared with MW=96,000 showed (i) a 15% increase in capture capacity from 2.0 to 2.3 mmol/g, and (ii) retention of low degradation of 0.08 mmol/g*h. The results also showed both decreasing degradation and capture capacity with increasing PVA content for sorbents prepared with PVA MW=9,500 similar to those prepared with MW=96,000, suggesting MW had little effect on the sorbent performance. T(PVA)SENa-.5+PEG prepared with MW=9,500 showed a 20% increase in capture capacity from 2.0 to 2.4 mmol/g and a slight increase in average degradation from 0.07 to 0.10 mmol/g*h. The differences in the performance of PVA MW=96,000 sorbents reproduced in experiment 2 compared to study 1 reflected variations in the (i) sorbent preparation and (ii) CO$_2$ adsorption procedures due to human error. Results of experiment 3 showed addition of PVA to TPSENa, TPSENa+PVA sorbents, (i) increased the degradation or (ii) decreased the capture capacity, showing these sorbents underperformed TPSENa.

Table G.1: Performance of TPSENa and all PVA sorbents prepared with PVA MW=96,000 or 9,500.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>PVA, MW</th>
<th>Sorbent</th>
<th>Avg. initial (mmol/g)</th>
<th>Avg deg (mmol/g*h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Effect of PVA on stability and capture of TPSENa/22 cycles</td>
<td>96,000</td>
<td>TPSENa</td>
<td>2.2</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T(PVA)SENa-0.001</td>
<td>1.4</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T(PVA)SENa-0.003</td>
<td>1.6</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T(PVA)SENa-0.005</td>
<td>1.4</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Table G.1 continued.

| T(PVA)SENa-0.007 | 1.5 | 0.13 |
| T(PVA)SENa-0.01  | 1.4 | 0.02 |
| T(PVA)SENa-0.05  | 1.3 | 0.03 |
| T(PVA)SENa-0.1   | 1.4 | 0.05 |
| T(PVA)SENa-0.3   | 1.3 | 0.03 |
| T(PVA)SENa-0.5   | 1.1 | 0.03 |

2. Effect of PVA/PEG on stability and capture of TPSENa using different MW PVA/PEG cycles

| 9,500  | TPSENa   | 2.8 | 0.14 |
| T(PVA)SENa-.5+PEG | 2.4 | 0.10 |
| T(PVA)SENa-.3+PEG | 2.8 | 0.11 |
| T(PVA)SENa-.1+PEG | 3.2 | 0.13 |
| T(PVA)SENa-.5     | 2   | 0.07 |
| T(PVA)SENa-.3     | 2.3 | 0.08 |
| T(PVA)SENa-.1     | 2.5 | 0.08 |

| 96,000 | TPSENa   | 2.8 | 0.14 |
| T(PVA)SENa-.5+PEG | 2.3 | 0.08 |
| T(PVA)SENa-.3+PEG | 2.8 | 0.13 |
| T(PVA)SENa-.1+PEG | 3.1 | 0.15 |
| T(PVA)SENa-.5     | 2   | 0.08 |
| T(PVA)SENa-.3     | 2.3 | 0.08 |
| T(PVA)SENa-.1     | 2.6 | 0.10 |
### Table G.1 continued.

3. Effect of adding PVA to TPSENa on stability and capture of same/13 cycles

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Ethanol uptake (g EtOH/g sorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPSENa</td>
<td>2.5</td>
</tr>
<tr>
<td>TPSENa+0.5% PVA sln</td>
<td>2.7</td>
</tr>
<tr>
<td>TPSENa+1.0% PVA sln</td>
<td>2.6</td>
</tr>
<tr>
<td>TPSENa+5.0% PVA sln</td>
<td>2.5</td>
</tr>
<tr>
<td>TPSENa+10.0% PVA sln</td>
<td>2.2</td>
</tr>
<tr>
<td>TPSENa+15.0% PVA sln</td>
<td>2.2</td>
</tr>
</tbody>
</table>

### Table G.2: Ethanol uptake of TPSENa and some T(PVA)SENa sorbents. Ethanol uptake was determined as the amount of ethanol needed to completely saturate 1.0 g of the sorbent.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Ethanol uptake (g EtOH/g sorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPSENa</td>
<td>1.0</td>
</tr>
<tr>
<td>T(PVA)SENa-.005</td>
<td>1.3</td>
</tr>
<tr>
<td>T(PVA)SENa-.01</td>
<td>1.4</td>
</tr>
<tr>
<td>T(PVA)SENa-.05</td>
<td>1.3</td>
</tr>
<tr>
<td>T(PVA)SENa-.1</td>
<td>1.2</td>
</tr>
<tr>
<td>T(PVA)SENa-.3</td>
<td>1.1</td>
</tr>
<tr>
<td>T(PVA)SENa-.5</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Figure G.1: IR absorbance spectra of (a) fresh TPSENa and T(PVA)SENa sorbents in experiment 1 (PVA MW=96,000) and (b) after 19 h steam degradation at 130 °C with 50 cc/min CO₂ flowing through a water saturator at 25 °C and over the sorbents. 
Abs=log(1/I), where I was the single beam spectrum of interest.
Table G.3: Comparing PVA content, hydrogen bonding, and OH/NH ratio of the fresh sorbents to sorbent degradation. The sorbents shown here provide the best representation of the data from all sorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>PVA content</th>
<th>OH/NH ratio</th>
<th>3700-3000 FWHM, fresh sorb. (cm(^{-1}))</th>
<th>(I_{1671}/I_{1605}), deg. sorb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPSENa</td>
<td>0</td>
<td>0.13</td>
<td>369</td>
<td>15.7</td>
</tr>
<tr>
<td>T(PVA)SENa-.005</td>
<td>0.005</td>
<td>0.003</td>
<td>223</td>
<td>11.8</td>
</tr>
<tr>
<td>T(PVA)SENa-.01</td>
<td>0.01</td>
<td>0.006</td>
<td>242</td>
<td>6.1</td>
</tr>
<tr>
<td>T(PVA)SENa-.05</td>
<td>0.05</td>
<td>0.03</td>
<td>262</td>
<td>6.1</td>
</tr>
<tr>
<td>T(PVA)SENa-.1</td>
<td>0.1</td>
<td>0.06</td>
<td>278</td>
<td>7.5</td>
</tr>
<tr>
<td>T(PVA)SENa-.3</td>
<td>0.3</td>
<td>0.17</td>
<td>339</td>
<td>6.4</td>
</tr>
<tr>
<td>T(PVA)SENa-.5</td>
<td>0.5</td>
<td>0.29</td>
<td>362</td>
<td>5.2</td>
</tr>
</tbody>
</table>

* FWHM, full width at half maximum, refers to the full peak width at half of the maximum peak intensity. This is commonly used to measure the peak width.

Figure G.1(a) shows the IR absorbance spectra for fresh TPSENa and all T(PVA)SENa sorbents prepared in experiment 1. The spectra show characteristic bands for (i) silica at 3732 cm\(^{-1}\) for free Si-OH stretching, 3676 cm\(^{-1}\) for H-bonded Si-OH, (ii) TEPA at 3363, 3304 cm\(^{-1}\), and 1605 for N-H vibrations, and 2931, 2871, 2814 cm\(^{-1}\), and 1456 cm\(^{-1}\) for C-H vibrations, (iii) PEG and PVA at 3700-3000 cm\(^{-1}\) for O-H stretching, (iv) EPON at 1508 cm\(^{-1}\) for C-C stretching, and other bands at 1577 and 1360 cm\(^{-1}\). The sorbents also showed a band at 1671 cm\(^{-1}\) for C-O stretching, indicating the presence of a small amount of amide species likely formed during sorbent preparation as a result of drying. Table G.3 shows that the T(PVA)SENa sorbents exhibited increased broadening, FWHM, at 3700-3000 cm\(^{-1}\) with increasing (i) PVA content and (ii) OH/NH ratio due to hydrogen bonding. Although the FWHM for TPSENa did not strictly follow into the trend for OH/NH ratio, it was among the highest observed. The position of the N-H
bands for the T(PVA)SENa sorbents were similar to those of TPSENa, suggesting similar interactions between TEPA/PVA and TEPA/PEG. Figure G.1b shows the IR absorbance spectra of the sorbents after 19 h steam degradation at 130 °C. The spectra for all degraded sorbents showed a (i) decrease in intensity for N-H vibrations and C-H vibrations and (ii) increase in intensity for C-O vibration compared to fresh sorbents indicating TEPA degraded to form amide species. The 3363 and 3304 cm⁻¹ bands for TPSENa were converted into a single broad band and the 2814 cm⁻¹ band was no longer observed, which corresponded to formation of the strong band at 1671 cm⁻¹. The spectra for T(PVA)SENa sorbents showed increased intensities for TEPA bands at high PVA content compared to TPSENa, suggesting the presence of un-oxidized TEPA. Table G.3 shows decreasing $I_{1671}/I_{1605}$ ratios for T(PVA)SENa sorbents with increasing PVA content compared to TPSENa, indicating the presence of PVA reduced degradation of TEPA to amides. The intensity ratios did not follow a specific trend regarding OH/NH ratio, suggesting PVA did not behave similarly as PEG. The small PEG molecules likely migrated from the pores away from TEPA during steam degradation. and the absence of PEG interacting with TEPA likely caused the degradation. The large, rigid structure of PVA prevented migration, allowing PVA to interact with TEPA. T(PVA)SENa-.5 exhibited the lowest intensity ratio, 5.2, which corresponded to the lowest degradation in CO₂ capture capacity, 0.08 mmol/g*cycle.

G.5 Conclusions

The CO₂ capture results from experiments 1 and 2 showed that replacing PEG in TPSENa with PVA, T(PVA)SENa sorbents, reduced degradation and significantly reduced the capture capacity up to 50% compared to TPSENa. Adding PEG to the
T(PVA)SENa, T(PVA)SENa+PEG sorbents, increased the capture capacity by 15-30% while retaining low degradation. Sorbents prepared with PVA MW=96,000 and MW=9,500 showed similar results. Experiment 3 showed adding PVA to TPSENa, TPSENa+PVA sorbents, decreased the capture capacity and increased degradation compared to TPSENa. Importantly, the CO₂ capture results showed T(PVA)SENa-.5+PEG exhibited the best performance of all PVA-based sorbents with 2.3 mmol/g capture capacity and 0.08 mmol/g*h degradation over 19 h steam degradation.

IR results of degraded sorbents from experiment 1 showed rapid degradation in CO₂ capture capacity corresponded to high formation of amide species. IR results of fresh PVA sorbents showed large FWHM for hydrogen bonded species corresponded to low I₁₆₇₁/I₁₆₀₅ intensity ratio of degraded sorbents, suggesting PVA stabilized TEPA through hydrogen bonding between O-H and N-H groups.

The high stability of T(PVA)SENa-.5+PEG corresponded to the (i) low I₁₆₇₁/I₁₆₀₅ intensity ratio of the degraded sorbent and (ii) high FWHM for hydrogen bonded species of the fresh sorbents. TPSENa showed high degradation despite the high FWHM of the fresh sorbent, suggesting PEG migrated away from TEPA during steam degradation due to its high mobility. The large structure of PVA prevents migration of TEPA, allowing OH groups to remain in intimate contact with N-H groups of TEPA. Future in situ studies would involve examining the oxidative degradation and mass transfer characteristics of the sorbents, using benzene.
Figure G.2: CO₂ capture cycles for T(PVA)SENa sorbents in experiment 1 prepared with PVA MW=96,000.
Figure G.3: CO$_2$ capture cycles for T(PVA)SENa and T(PVA)SENa+PEG sorbents in experiment 2 prepared with PVA MW=96,000 and MW=9,500.
APPENDIX H

SYNTHESIS OF POROUS PVA PELLETS

H.1 Objective

To synthesize amine-functionalized porous PVA pellets for use in CO₂ capture processes.

H.2 Key Findings

1. Coating all PVA and PEI/PVA liquid beads with Aerogel and phase inverting with 100% acetone under 800 rpm of mixing is required to produce the spherical pellets.

2. Templating PVA with PEG 200 or Na₂SiO₃ solution doesn’t produce pellets with uniform pore structure. A solid SiO₂ template is required because it does not leach out during phase inversion.

3. Phase inverting PEI/PVA liquid beads in acetone likely degrades the amine, turning the final pellets brown.

4. All PEI/PVA pellets capture <0.5 mmol CO₂/g-pellet at 25 °C, which wasn’t enhanced by acid/base treatment. Pellets with PEI/PVA ratios>1 are soft and sticky.
5. The best pellet involving phase inversion was the SiO₂-templated pure PVA pellet, named “PVA (16.7 wt% SiO₂); SiO2/PVA-2”: (I) Conditions: (a) precursor solution: PVA=10 wt% and SiO₂ (Tixosil 68B)=16.7 wt%; (b) phase inv.=100% acetone, 25 °C, 30 min; (c) cross-link=1 wt% glut. (25 wt% stock), 70 °C, 30 min; (d) SiO₂ removal=14 wt% KOH, 50 °C, 20 min. (II) Pellet properties: (a) EtOH uptake=2.8 g-EtOH/g-pellet; (b) diameter=2-3 mm, (c) 52 wt% TEPA/PVA pellet=1.5 mmol CO₂/g-pellet.

6. The first initial batches of emulsion-prepared PVA and TEPA/PVA beads are poly-dispersed in size (500-1400 um), exhibit low porosity (avg. H₂O swelling=70 vol%), and do not capture CO₂. The following need optimized: (i) aqueous solution formulation, (ii) aqueous/organic soln. ratio, (iii) amount of glutaraldehyde (cross-linking), and (iv) mixing speed and configuration.

H.3 Experimental: Pellet and Bead Preparation

The general procedures for the phase inversion and emulsion pellets are shown in Figure H.1 and Figure H.2, respectively. Phase inversion pellets are prepared by (i) coating PVA, template/PVA, or PEI/PVA liquid beads with Aerogel, (ii) phase inverting in acetone, and if necessary (iii) cross-linking with glutaraldehyde then removing the template. Emulsion beads are prepared by (i) adding acidic aqueous PVA or TEPA/PVA solution to an organic solution containing surfactant (Span 80) under vigorous mixing, then (ii) adding glutaraldehyde to the resulting emulsion and cross-linking.
Figure H.1: General preparation procedure of Group 1 porous PVA, templated-PVA, and amine/PVA pellets by phase inversion.
Figure H.2: General procedure for preparing Group 4 PVA and TEPA/PVA beads by emulsion.

H.4 Results

Table H.1 shows a summary of the precursor solution compositions and preparation conditions of the different pellets and bead presented along with their overall analysis. The pellets and beads were separated into four groups according to precursor solution composition and preparation method: Group 1-PVA and no template, with phase inversion; Group 2-PVA and liquid or solid template, with phase inversion; Group 3-PEI/PVA with phase inversion; and Group 4-emulsion.
Table H.1: Summary of the preparation of porous PVA pellets.

<table>
<thead>
<tr>
<th>Precursor solns.</th>
<th>Conditions</th>
<th>Results</th>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(Group 1)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous: PVA</td>
<td>1. Phase inv.: 100-50 wt% Ace./EtOH and Ace./H₂O. 2. Coated and not coated with Aerogel 3. Mixing: 200-1000 rpm</td>
<td>1. Macro-voids, swell in H₂O. 2. &gt;600 rpm to prevent liquid bead sticking. 3. Pellet diameter=2-2.7 mm</td>
<td>1. Acetone for rapid phase inv. 2. Aerogel coating for spherical shape. 3. Swelling/cross-linking does not preserve swollen size.</td>
</tr>
<tr>
<td>(Mw=75,000)=10 wt%</td>
<td></td>
<td>PVA fibers</td>
<td></td>
</tr>
<tr>
<td>Aqueous: PVA</td>
<td>1. Phase inv.: 100% EtOH 2. Aerogel coated 3. 800 rpm</td>
<td>* PVA fibers</td>
<td></td>
</tr>
<tr>
<td>(Mw=75,000)=10 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous: PVA</td>
<td>* Phase inv.: 100% Ace., Aerogel coated</td>
<td>* PVA fibers</td>
<td>* In-sufficient strength of low Mw to form pellets.</td>
</tr>
<tr>
<td>(Mw=9,500)=10-40 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>1. Phase inv.: 100% Ace. 2. Aerogel coated 3. 800 rpm</td>
<td>1. Pellet diameter (2-3 mm). 2. Low swelling in H₂O. 3. 5 wt% doesn't form pellet</td>
<td>* High Mw too rigid for effective swelling.</td>
</tr>
<tr>
<td>(Mw=145,000)=5-10 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous: (a) PVA</td>
<td>1. Phase inv.: 100% Ace. 2. Aerogel coated 3. 800 rpm</td>
<td>1. Macro-voids, swell in H₂O. 2. &gt;30% PEG causes gelling. 3. Pellet diameter=2-3 mm.</td>
<td>1. PEG removed during phase inv. 2. Swelling/cross-linking does not preserve swollen size.</td>
</tr>
<tr>
<td>(Mw=75,000)=10 wt%; (b)PEG 200=5-30 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aqueous: (a) PVA</td>
<td>1. Phase inv.: 100% Ace. 2. Coated and not coated with Aerogel 3. 800 rpm</td>
<td>1. Uniform internal porosity. 2. SiO₂/PVA=2 for optimum EtOH uptake. 3. Spheronize ratio &gt;= 3. 4. Pellet diameter=2-4 mm.</td>
<td>1. SiO₂ for uniform internal porosity. 2. Swelling/cross-linking does not preserve swollen size. 3. 52 wt% TEPA/PVA (SiO₂/PVA=2); 1.5 mmol/g</td>
</tr>
<tr>
<td>(Mw=75,000)=5-10 wt%; SiO₂=4-28 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mw=75,000)=10 wt%; (b) Na₂SiO₃ soln (26% SiO₂)=5-50 wt%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table H.1 continued.

(Group 3)

Aqueous: (a) PVA (Mw=75,000)=5-15 wt%; (b) PEI (50,000, 50 wt%)=1-27 wt% (Also includes template)

1. Phase inv: 100-50 wt% Ace./EtOH.
2. Aerogel coated
3. Mixing: 200-1000 rpm

1. Macro-voids and H2O swells.
2. >800 rpm mixing to reduce sticking.
3. CO2 capture <0.5 mmol/g at 25°C
4. Phase inversion turns pellets brown.
5. Swelling/cross-linking may enhance pellet size.
6. Pure PEI/PVA ratio>1 makes pellet soft and sticky

1. PEI/PVA captures insignificant CO2 and 25°C.
2. Impregnate PEI into PVA after phase inversion to avoid deg.

(Group 4)

1. Aqueous: PVA=8-10 wt%; TEPA=0-7 wt%; pH=2 (HCl)
2. Organic: 75-100 wt% toluene; 0-25 wt% benzene; <5% Span 80
3. Cross-linker: Glut (50 wt%)=2 wt% of aqueous + organic

1. Addition order: organic to aqueous; mixing=600-800 rpm
2. T=60 °C, 30 min

1. Partial precipitation of Span 80 for all conditions.
2. Final product is a mixture of poly-dispersed beads (low porosity) and PVA films/flakes.
3. Significant cross-linking of PVA and TEPA with glut.
4. Bead size=500-1400 um.

1. Emulsion is not fully stable.
2. In-sufficient mixing for bead uniformity; poor shear stress distrib. and mixing config.
3. Excessive cross-linking and absence of template decreases porosity.

Analysis of group 1 shows that pure PVA pellets should be prepared by coating 10 wt% PVA (Mw=75,000) with Aerogel and phase inverting in 100% acetone under 800 rpm of mixing. Although possessing an excellent H2O swelling of 300-500%, pellets prepared by this method are limited to having non-uniform porosity and large voids. Despite phase inversion in a less vigorous acetone/EtOH solution and swelling/cross-linking with glutaraldehyde solution, uniform porosity was not achieved. Pellets could not be prepared with low Mw PVA (Mw=9,500) even at 40 wt%. These mixtures

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produced only PVA fibers because of the inability of the short length polymer chain to entangle as a pellet.

Analysis of group-2 pellets revealed that templating with PEG 200 did not eliminate voids or enhance porosity, likely because PEG 200 was removed during phase inversion. Templating with Na₂SiO₃ also failed to produce uniform porosity due to excessively low concentration, or inability of SiO₂ to precipitate out and template the pore. Only the Tixosil 68B silica template produced pellets with uniform porosity because silica remained after phase inversion. The optimum ratio of SiO₂/PVA was 2.0; deviating from the ratio either higher or lower reduces the EtOH uptake. A sorbent based on this pellet with 52 wt% impregnated TEPA captures 1.5 mmol CO₂/g-pellet

Group 3 pellets showed that incorporating PEI and PVA together in the precursor solution caused agglomeration of the pellets, and sticking of the pellets to the beaker walls during phase inversion. It was necessary to coat a thin layer of vacuum grease to the beaker to prevent sticking. Phase inversion in acetone likely degraded the amines, and turned the pellets brown. Similar to pure PVA and template-PVA pellets, non-uniform porosity of PEI/PVA was observed. Keeping the PEI/PVA ratio at 1 or below is necessary to avoid forming a soft, sticky pellet. The CO₂ capture capacity of all pellets at 25 °C was below 0.5 mmol CO₂/g-pellet. Increasing the adsorption temperature to 75 °C would enhance the capture capacity of the pellets. Swelling/cross-linking the pellets in glutaraldehyde solution did not enhance the CO₂ capture capacity. PEI should be impregnated on pure PVA pellets rather than directly incorporated into the PVA solution to avoid degradation during phase inversion.
Group 4 shows that micron-size beads can be prepared using an emulsion process by mixing PVA and TEPA/PVA solutions with a toluene/benzene/surfactant solution. Only two experiments were performed in which pure PVA and TEPA/PVA beads were prepared. The surfactant (Span 80) partially precipitated in both experiments, showing that the emulsion was not fully stable; a new surfactant should be tried. The lack of a template in the PVA and TEPA/PVA solutions, along with excessive cross-linking by glutaraldehyde, produced beads with low porosity and insignificant CO$_2$ capture capacity. A template primarily soluble in aqueous compared to organic solution should be used, and the amount of glutaraldehyde should be decreased. Additionally, the poly-dispersity of the bead diameter likely resulted from insufficient shear stress throughout the system because of the mixing configuration; single stir bar in the beaker. In other words, a mixer with blades along the entire z-axis of the beaker would cause more collisions between the suspended liquid PVA beads and blades than the single stir bar. The higher collision frequency would break apart the PVA beads into a more narrowly distributed size range. The overall size of the beads may be largely controlled by the mixing speed.

Table H.2 and Table H.3 show the detailed preparation procedures for and the physical properties of all porous PVA beads, respectively. Templating PVA with silica solid particles, followed by cross-linking with glutaraldehyde and removing silica produced a highly porous and durable pellet. This pellet could be impregnated with amine and other additives and used for CO$_2$ capture.
Table H.2: preparation procedures for porous PVA pellets. The remaining weight percentage of the pellet precursor solutions is for H$_2$O.

<table>
<thead>
<tr>
<th>Pellet name Name:</th>
<th>Group</th>
<th>Preparation procedure</th>
<th>Pellet precursor aqueous solution (wt%)</th>
</tr>
</thead>
</table>
| "Amine/PVA_nominal wt%
Amine/wt% PVA (wt% precursor template)_post treatment; comment" |       |                       |                                        |
| PEI/PVA_4.8/95.4 | 3     |                       | 10.0 1.0                               |
| PEI/PVA_9.1/90.9 | 3     |                       | 10.0 2.0                               |
| PEI/PVA_16.7/83.3 | 3     | (1) Precursor solution: (a) Dissolve PVA (Mw=75,0000, %hyd=99+) in H2O at 100-120 C and let cool to 25-50 C. (b) Mix PEI (Mn=60,000, 50 wt% in H2O) (and PEG 200 where appropriate) with PVA solution. | 10.0 4.0 |
| PEI/PVA_23.1/76.9 | 3     |                       | 10.0 6.0                               |
| PEI/PVA_28.6/71.4 | 3     |                       | 10.0 8.0                               |
| PEI/PVA_33.3/66.7 | 3     | (2) : Aerogel-coated beads: Syringe-extrude PEI/PVA (PEG) drops onto hydrophobic mylar covered with Aerogel and coat drop surface. | 10.0 10.0 10.0 |
| PEI/PVA_50/50 (10 PEG 200) | 2     |                       | 10.0 10.0 10.0 |
| PEI/PVA_50/50 (20 PEG 200) | 2     |                       | 10.0 10.0 20.0 |
| PEI/PVA_50/50 (30 PEG 200) | 2     |                       | 10.0 10.0 30.0 |
| PEI/PVA_75/25; 16 wt% pure PEI+PVA precursor | 3     |                       | 6.0 19.0 |
| PEI/PVA_75/25; 18 wt% pure PEI+PVA precursor | 3     |                       | 7.0 22.0 |
| PEI/PVA_75/25; 20 wt% PEI+PVA/H2O precursor | 3     |                       | 8.0 24.0 |
Table H.2 continued.

<table>
<thead>
<tr>
<th>PEI/PVA</th>
<th>n</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI/PVA_33/67</td>
<td>3</td>
<td>(1) Precursor solution: (a) Dissolve PVA (Mw=75,0000, %hyd=99+) in H2O at 100-120 C and let cool to 25-50 C. (b) Mix PEI (Mn=1,300, 50 wt% in H2O) (and PEG 200 where appropriate) with PVA solution.</td>
</tr>
<tr>
<td>PEI/PVA_50/50</td>
<td>3</td>
<td>Syringe-extrude PEI/PVA (PEG) drops onto hydrophobic mylar covered with Aerogel and coat drop surface.</td>
</tr>
<tr>
<td>PEI/PVA_60/40</td>
<td>3</td>
<td>(2): Aerogel-coated beads: Syringe-extrude PEI/PVA (PEG) drops onto hydrophobic mylar covered with Aerogel and coat drop surface.</td>
</tr>
<tr>
<td>PEI/PVA_67/33</td>
<td>3</td>
<td>(3): Porous pellet: (a) Add Aerogel-covered drops to a 500 mL grease-coated beaker containing 300 mL acetone while stirring at 60-100 rpm for phase inversion for 0.5 hr for phase inversion. (b) Remove phase inverted wet pellets and dry at 70 C for 40 min, producing dry porous pellets.</td>
</tr>
<tr>
<td>PEI/PVA_33/67 (10 PEG 200)</td>
<td>2</td>
<td>pH treatment (pH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets into 50.0 g of pH=12 KOH solution for 30 s. (b) Dry pH-treated beads at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_50/50 (8.3 PEG 200)</td>
<td>2</td>
<td>pH treatment (pH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets into 50.0 g of pH=12 KOH solution for 30 s. (b) Dry pH-treated beads at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_50/50 (5.7 PEG 200)</td>
<td>2</td>
<td>pH treatment (pH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets into 50.0 g of pH=12 KOH solution for 30 s. (b) Dry pH-treated beads at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_60/40 (7.2 PEG 200)</td>
<td>2</td>
<td>pH treatment (pH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets into 50.0 g of pH=12 KOH solution for 30 s. (b) Dry pH-treated beads at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_60/40 (4.9 PEG 200)</td>
<td>2</td>
<td>pH treatment (pH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets into 50.0 g of pH=12 KOH solution for 30 s. (b) Dry pH-treated beads at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_33/67 (10 PEG 200)_pH=12</td>
<td>2</td>
<td>pH treatment (pH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets into 50.0 g of pH=12 KOH solution for 30 s. (b) Dry pH-treated beads at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_50/50_pH=12</td>
<td>3</td>
<td>Rapid heating treatment (RH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets in 100 mL of boiling H2O for 10 s, then into 100 mL cold H2O for 30 s, and finally acetone for 30 s. (b) Dry at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_67/33_pH=12</td>
<td>3</td>
<td>Rapid heating treatment (RH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets in 100 mL of boiling H2O for 10 s, then into 100 mL cold H2O for 30 s, and finally acetone for 30 s. (b) Dry at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_75/25 _pH=12; 20 wt% PEI+PVA/H2O precursor</td>
<td>3</td>
<td>Rapid heating treatment (RH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets in 100 mL of boiling H2O for 10 s, then into 100 mL cold H2O for 30 s, and finally acetone for 30 s. (b) Dry at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_60/40_RH</td>
<td>3</td>
<td>Rapid heating treatment (RH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets in 100 mL of boiling H2O for 10 s, then into 100 mL cold H2O for 30 s, and finally acetone for 30 s. (b) Dry at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_33/67 _RH</td>
<td>3</td>
<td>Rapid heating treatment (RH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets in 100 mL of boiling H2O for 10 s, then into 100 mL cold H2O for 30 s, and finally acetone for 30 s. (b) Dry at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_16.7/83.3 _RH</td>
<td>3</td>
<td>Rapid heating treatment (RH): (a) Submerge 1.0 g of PEI/PVA and PEI/PVA (PEG) (Mn PEI=1,300) pellets in 100 mL of boiling H2O for 10 s, then into 100 mL cold H2O for 30 s, and finally acetone for 30 s. (b) Dry at 80 C for 40 min.</td>
</tr>
<tr>
<td>PEI/PVA_50/50 (8.3 PEG 200)_RH</td>
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<td>8.3</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---</td>
<td>-----</td>
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<tr>
<td>PEI/PVA_60/40 (4.9 PEG 200)_RH</td>
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<td>4.9</td>
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(1) Precursor solution: Dissolve PVA (Mw=75,0000, %hyd=99+) in H2O at 100-120 C and let cool to 25-50 C.  
(2) : Aerogel-coated beads: Syringe-extrude PVA drops onto hydrophobic mylar covered with Aerogel and coat drop surface.  
(3) Porous PVA pellet: (a) Add Aerogel-covered drops to a 500 mL grease-coated beaker containing 300 mL acetone/H2O mixture while stirring at 60-100 rpm 0.5-1 hr for phase inversion. The amount of acetone and H2O is listed in the pellet name. (b) Remove phase inverted wet pellets and dry at 70C for 1 hr, producing dry porous pellets.

<table>
<thead>
<tr>
<th>PVA; 100% acetone</th>
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<th>10.0</th>
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<tr>
<td>PVA; 90 wt%acetone/10 wt%H2O</td>
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<td>10.0</td>
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<tr>
<td>PVA; 80 wt%acetone/20 wt%H2O</td>
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<tr>
<td>PVA; 70 wt%acetone/30 wt%H2O</td>
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<tr>
<td>PVA; 60 wt% acetone/40 wt% H2O</td>
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<td>10.0</td>
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</table>

(1) Precursor solution: Dissolve PVA (Mw=75,0000, %hyd=99+) in H2O at 100-120 C and let cool to 25-50 C.  
(2) : Aerogel-coated beads: Syringe-extrude PVA drops onto hydrophobic mylar covered with Aerogel and coat drop surface.  
(3) Pellet: (a) Add Aerogel-covered drops to a 500 mL grease-coated beaker containing 300 mL acetone/EtOH mixture while stirring at 60-100 rpm 0.5-1 hr for phase inversion. The amount of acetone and H2O is listed in the pellet name. (b) Remove phase inverted wet pellets and dry at 70C for 1 hr, producing dry porous pellets.

<p>| PVA; 82 wt% acetone/18 wt% EtOH | 1 | 10.0 |
| PVA; 65 wt% acetone/35 wt% EtOH | 1 | 10.0 |
| PVA; 50 wt%acetone/50 wt% EtOH | 1 | 10.0 |</p>
<table>
<thead>
<tr>
<th>Material</th>
<th>Weight % SiO2</th>
<th>Crosslinker</th>
<th>Precursor Solution</th>
<th>SiO2/PVA</th>
<th>H2O</th>
<th>EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA (5 wt% PEG 200)</td>
<td>10.0</td>
<td>5.0</td>
<td>(1) Precursor solution: (a) Dissolve PVA (Mw=75,000, %hyd=99+) in H2O at 100-120 C and let cool to 25-50 C. (b) Mix PEG 200 or 400 with PVA solution. The type of PEG is listed in the pellet name.</td>
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<tr>
<td>PVA (10 wt% PEG 200)</td>
<td>10.0</td>
<td>10.0</td>
<td>(2) : Aerogel-coated beads: Syringe-extrude PVA drops onto hydrophobic mylar covered with Aerogel and coat drop surface.</td>
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<tr>
<td>PVA (15 wt% PEG 200)</td>
<td>10.0</td>
<td>15.0</td>
<td>(3) Porous PVA pellet: (a) Add Aerogel-covered drops to a 500 mL grease-coated beaker containing 300 mL acetone/H2O mixture while stirring at 60-100 rpm for 0.5-1 hr for phase inversion. The amount of acetone and H2O is listed in the pellet name. (b) Remove phase inverted wet pellets and dry at 70C for 1 hr, producing dry porous pellets.</td>
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<tr>
<td>PVA (10 wt% PEG 400)</td>
<td>10.0</td>
<td>10.0</td>
<td>(1) Precursor solution: (a) Dissolve PVA (Mw=75,000, %hyd=99+) in H2O at 100-120 C and let cool to 25-50 C. (b) Mix Tix. 68B with PVA sol.</td>
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<tr>
<td>PVA (9.1 wt% SiO2); SiO2/PVA-1</td>
<td>9.1</td>
<td>9.1</td>
<td>(2) : SiO2/PVA beads: Prepare Aerogel-coated beads, then perform phase inversion in acetone or acetone/EtOH and dry at 70 C for 40 min. (3) Cross-linked SiO2/PVA wet pellets:(a) Mix 0.5 g of SiO2/PVA beads with 7.5 g of cross-linking solution (1 wt% GA (25% stock soln), 5 wt% H2SO4, 20 wt% Na2SO4) and react at 70C for 30 min. (b) Rise beads with 1000 mL H2O (4). Porous PVA pellet: Mix 1.0 g wet cross-linked pellets with 7.5 g of 14 wt% KOH at 50 oC for 20 min to dissolve SiO2 template. (b) H2O rinse pellet, dry at 70C for 45min.</td>
<td></td>
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</table>

PVA (16.7 wt% SiO2); SiO2/PVA-2 8.3 16.7
PVA (4.8 wt% SiO2); SiO2/PVA=0.5 9.5 4.8
PVA (75 wt% SiO2); SiO2/PVA=3 7.7 23.1
PVA (16.7 wt% SiO2); 65% acetone/35% EtOH 2
PVA (16.7 wt% SiO2); 100% EtOH 2
| PVA (4.8 wt% SiO2); SiO2/PVA=0.5 | 2 | (1) Precursor solution: (a) Dissolve PVA (Mw=75,000, %hyd=99+) in H2O at 100-120 C and let cool to 25-50 C. (b) Mix Tixosil 68B with PVA solution. | 9.5 | 4.8 |
| PVA (13 wt% SiO2); SiO2/PVA=1.5 | 2 | (2) : SiO2/PVA beads: Prepare Aerogel-coated beads, then perform phase inversion in acetone and dry at 70 C for 40 min. | 8.7 | 13.0 |
| PVA (20% SiO2); SiO2/PVA=2.5 | 2 | (3) Cross-linked SiO2/PVA wet pellets:(a) Mix 0.5 g of SiO2/PVA beads with 7.5 g of cross-linking solution (1 wt% GA (25% stock soln), 5 wt% H2SO4, 20 wt% Na2SO4) and react at 70C for 30 min. (b) Remove cross-linked beads and rinse with 500 mL H2Ox2. | 8.0 | 20.0 |
| PVA (23.1% SiO2); SiO2/PVA=3 | 2 | (4). Porous PVA pellet (SiO2 removed): Mix 1.0 g wet cross-linked pellets with 7.5 g of 14 wt% KOH at 70 oC for 30 min to dissolve SiO2 template. (b) Remove pure PVA pellet and rinse with 500 mL H2O x2, then dry at 70 for 45 min. | 7.1 | 28.6 |
| PVA (28.6% SiO2); SiO2/PVA=4 | 2 | | | |
| PVA (28.6% SiO2); SiO2/PVA=5 | 2 | (1) Precursor solution: (a) Dissolve PVA (Mw=75,000, %hyd=99+) in H2O at 100-120 C and let cool to 25-50 C. (b) Mix Na2SiO3 (27 wt% SiO2 in H2O) with PVA soln. | 10.0 | 5.4 |
| PVA [5.4 wt% Na2SiO3 (27% SiO2)] | 2 | (2) : Aerogel-coated beads: Syringe-extrude PEI/PVA (PEG) drops onto hydrophobic mylar covered with Aerogel and coat drop surface. | 10.0 | 9.7 |
| PVA [9.7 wt% Na2SiO3 (27% SiO2)] | 2 | (3) Porous pellet: (a) Add Aerogel-covered drops to a 500 mL grease-coated beaker containing 300 mL acetone while stirring at 60-100 rpm for phase inversion for 0.5 hr for phase inversion. (b) Remove wet pellets and dry at 70C for 40 min. | 10.0 | 15.2 |
| PVA [15.2 wt% Na2SiO3 (27% SiO2)] | 2 | | | |
| PVA [16.6 wt% Na2SiO3 (27% SiO2)] | 2 | | | |
Table H.2 continued.

<table>
<thead>
<tr>
<th>Pellet name</th>
<th>Group</th>
<th>Nominal pellet composition (wt%)</th>
<th>Avg. CO₂ capture (2-3 cycles)</th>
<th>Avg. size (mm)</th>
<th>Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEPA/PVA_42/58</td>
<td>2-impreg.</td>
<td>9.1 wt% SiO₂; SiO₂/PVA-1</td>
<td>25 wt% TEPA/EtOH.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEPA/PVA_53/47</td>
<td>2-impreg.</td>
<td>16.7 wt% SiO₂; SiO₂/PVA-2</td>
<td>Dissolve TEPA in EtOH; 25 wt% TEPA/EtOH.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Impregnation solution: Dissolve TEPA in EtOH; 25 wt% TEPA/EtOH.
(2) Sorbent: (a) Submerge 0.3 g of PVA (9.1% SiO₂); SiO₂/PVA-1 beads in 10.0 g of 25 wt% TEPA/EtOH for 30 min. (b) Remove TEPA-impregnated wet pellets and dry at 70°C for 45 min.

(1) Aqueous solution: Dissolve 2.6 g of PVA (Mw=75,0000, %hyd=99+) in 17.4 g of H₂O at 100-120°C and let cool to 25-50, then add 1.3 g TEPA. pH adjust to 2 with 12.1 M HCl (2-3 mL)
(2) Organic solution: Mix 1.5 g of Span 80 with 20 g of toluene/benzene (1/4 wt ratio)
(3) Emulsion cross-linking: Vigorously stir/mix 20 mL aqueous and 21.5 mL organic solutions on a hotplate at 80°C, then add 1.8 g of glutaraldehyde (50 wt% stock) and react for 30 min to produce cross-linked beads.
(4) Wash cross-linked beads with toluene or benzene, ethanol, and H₂O. Dry washed beads at 70-100 for 30-60 min.

Table H.3: Physical properties and CO₂ capture of porous PVA pellets.

<table>
<thead>
<tr>
<th>Pellet name</th>
<th>Group</th>
<th>Nominal pellet composition (wt%)</th>
<th>Avg. CO₂ capture (2-3 cycles)</th>
<th>Avg. size (mm)</th>
<th>Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI/PVA_4.8/95.4</td>
<td>3</td>
<td>4.8</td>
<td>95.4</td>
<td>0.42</td>
<td>0.38</td>
</tr>
<tr>
<td>PEI/PVA_9.1/90.9</td>
<td>3</td>
<td>9.1</td>
<td>90.8</td>
<td>0.48</td>
<td>0.23</td>
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</tbody>
</table>
Table H.3 continued.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample</th>
<th>PEI</th>
<th>PVA</th>
<th>PEI%</th>
<th>PVA%</th>
<th>PEI Weight</th>
<th>PVA Weight</th>
<th>Result</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI/PVA_16.7/83.3</td>
<td>3</td>
<td>16.7</td>
<td>83.3</td>
<td>0.45</td>
<td>0.11</td>
<td>2.25</td>
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<tr>
<td>PEI/PVA_23.1/76.9</td>
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<td>23.1</td>
<td>76.9</td>
<td>0.21</td>
<td>0.04</td>
<td>2.38</td>
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<tr>
<td>PEI/PVA_28.6/71.4</td>
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<td>28.6</td>
<td>71.4</td>
<td>0.32</td>
<td>0.05</td>
<td>2.33</td>
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<tr>
<td>PEI/PVA_33.3/66.7</td>
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<td>33.3</td>
<td>66.7</td>
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<td>2.49</td>
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<tr>
<td>PEI/PVA_50/50 (10 PEG 200)</td>
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<td>PEI/PVA_50/50 (20 PEG 200)</td>
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<tr>
<td>PEI/PVA_75/25; 16 wt% pure PEI+PVA precursor</td>
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<td>75.0</td>
<td>25.0</td>
<td>0.12</td>
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<tr>
<td>PEI/PVA_75/25; 18 wt% pure PEI+PVA precursor</td>
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<td>25.0</td>
<td>1.10</td>
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<tr>
<td>PEI/PVA_75/25; 20 wt% PEI+PVA/H2O precurs.</td>
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<td>25.0</td>
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<td>67.0</td>
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<tr>
<td>PEI/PVA_67/33</td>
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<td>67.0</td>
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<tr>
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Table H.3 continued.

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<th>% PEI</th>
<th>% PVA</th>
<th>% H2O</th>
<th>% PEG</th>
<th>% RH</th>
<th>% Acetone</th>
<th>% Acetone</th>
<th>% H2O</th>
<th>% Ethanol</th>
<th>% PEG 200</th>
<th>% Ethanol</th>
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<tr>
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<td>40.0</td>
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</tr>
<tr>
<td>PEI/PVA_33/67_RH</td>
<td>3</td>
<td>33.0</td>
<td>67.0</td>
<td>0.07</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI/PVA_16.7/83.3_RH</td>
<td>3</td>
<td>16.7</td>
<td>83.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI/PVA_50/50 (8.3 PEG 200)_RH</td>
<td>3</td>
<td>50.0</td>
<td>50.0</td>
<td>0.20</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>PEI/PVA_60/40 (4.9 PEG 200)_RH</td>
<td>3</td>
<td>60.0</td>
<td>40.0</td>
<td>0.16</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA: 100% acetone</td>
<td>1</td>
<td>100</td>
<td></td>
<td>2.26</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA: 90 wt% acetone/10 wt% H2O</td>
<td>1</td>
<td>100</td>
<td></td>
<td>2.26</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA: 80 wt% acetone/20 wt% H2O</td>
<td>1</td>
<td>100</td>
<td></td>
<td>2.26</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA: 70 wt% acetone/30 wt% H2O</td>
<td>1</td>
<td>100</td>
<td></td>
<td>2.26</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA: 60 wt% acetone/40 wt% H2O</td>
<td>1</td>
<td>100</td>
<td></td>
<td>2.26</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA: 82 wt% acetone/18 wt% EtOH</td>
<td>1</td>
<td>100</td>
<td></td>
<td>2.59</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA: 65 wt% acetone/35 wt% EtOH</td>
<td>1</td>
<td>100</td>
<td></td>
<td>2.13</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA: 50 wt% acetone/50 wt% EtOH</td>
<td>1</td>
<td>100</td>
<td></td>
<td>2.34</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA (5 wt% PEG 200)</td>
<td>2</td>
<td>100</td>
<td></td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA (10 wt% PEG 200)</td>
<td>2</td>
<td>100</td>
<td></td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA (15 wt% PEG 200)</td>
<td>2</td>
<td>100</td>
<td></td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Note:**
- PVA (10 wt% PEG 400): SA(BET)=56 m2/g
- Vpore (BJH)=0.09 cm3/g
- Davg, pore (BJH)=4.6
Table H.3 continued.

| PVA (9.1 wt% SiO2); SiO2/PVA=1 | 2  | 100  | 1.2 |
| PVA (16.7 wt% SiO2); SiO2/PVA=2 |

| SA(BET)=165 m2/g | Vpore (BJH)=0.18 cm3/g | 4.1 |
| Davg, pore(BJH)=5.3 |
| 2  | 100  | 2.8 |

PVA (4.8 wt% SiO2); SiO2/PVA=0.5 2 100 0.4
PVA (75 wt% SiO2); SiO2/PVA=3 2 100 1.0
PVA (16.7 wt% SiO2); 65% acetone/35% EtOH 2
PVA (16.7 wt% SiO2); 100% EtOH 2

| PVA (4.8 wt% SiO2); SiO2/PVA=0.5 | 2  | 100  | 0.5 | 1.5 |
| PVA (13 wt% SiO2); SiO2/PVA=1.5 | 2  | 100  | 1.6 | 3.1 |
| PVA (20% SiO2); SiO2/PVA=2.5 | 2  | 100  | 1.0 | 4.9 |
| PVA (23.1% SiO2); SiO2/PVA=3 | 2  | 100  | 1.0 | 3.9 |
| PVA (28.6% SiO2); SiO2/PVA=4 | 2  | 100  | 0.3 | 1.2 |
| PVA (28.6% SiO2); SiO2/PVA=5 | 2  | 100  | 0.8 | 2.2 |
| PVA [5.4 wt% Na2SiO3 (27% SiO2)] | 2 |
| PVA [9.7 wt% Na2SiO3 (27% SiO2)] | 22 |
| PVA [15.2 wt% Na2SiO3 (27% SiO2)] | 2 |
| PVA [16.6 wt% Na2SiO3 (27% SiO2)] | 2 |
Table H.3 continued.

<table>
<thead>
<tr>
<th>Composition</th>
<th>2-impregn.</th>
<th>42.0</th>
<th>58.0</th>
<th>1.45</th>
<th>0.13</th>
<th>3.14</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEPA/PVA_42/58 (9.1 wt% SiO2); SiO2/PVA-1</td>
<td>impregn .</td>
<td>42.0</td>
<td>58.0</td>
<td>1.45</td>
<td>0.13</td>
<td>3.14</td>
</tr>
<tr>
<td>TEPA/PVA_53/47 (16.7 wt% SiO2); SiO2/PVA-2</td>
<td>impregn .</td>
<td>53.0</td>
<td>47.0</td>
<td>1.43</td>
<td>0.10</td>
<td>3.48</td>
</tr>
<tr>
<td>TEPA/PVA_33/67; emulsion</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVA; emulsion</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX I

PROGRESS FOR THE RAPID DRYING OF WET SORBENT MIXTURES

I.1 Objectives

The objectives of the trials and modifications to the rapid drying system were (i) reduce drying time and (ii) increase sorbent drying capacity.

I.2 Key Accomplishments

1. Previous accomplishment: 300 g wet TPSENa dried in 19 min with mixer-dryer.

2. Current accomplishment: (1) 800 g wet TPSENa was 85-95% dry in 40 min and (2) 450 g wet TPSENa was 88-95% dry in 25 min using the mixer-dryer with high air flow and sequential injections.

I.3 Experimental

I.3.1 Sorbent Preparation

A 1 kg batch of wet TPSENa sorbent was prepared by mixing two solutions. Solution 1 was prepared by dissolving 185.7 g tetraethylenepentamine (Aldrich) in 34.7 g polymer linker (e) at 80 °C, and adding 123.8 g polyethylene glycol 200 (Aldrich) and 660.3 g ethanol (Pharmaco-AAPER). Solution 2 was prepared by dissolving 5.2 g antioxidant (A) in 660.3 g deionized water. Solutions 1 and 2 were mixed and added to 330.1 g Tixosil 68B, amorphous silica (Rhodia).
I.3.2 Trials

Table I.1 shows a summary of the recent trials and modifications made to the rapid drying system to decrease drying time or increase drying capacity. Each trial is explained in detail below.

I.3.3 Trial 1

Figure I.1 shows the schematic of the mixer-dryer (MD) system used in trial 1, consisting of a (i) gas manifold with air valve, rotameter, and two insulated in-line heaters, (ii) MD with inlet manifold, drying chamber, lid with syringe injection port, and mechanical mixer, and (iii) vortex separator with a cone to vortex the air flow and sorbent collector to catch dried sorbent. The MD inlet manifold was filled with foil balls to diffuse the air flow and prevent channeling. A steel mesh insert with mixer stop supported the wet TPSENa sorbent, and four thermocouples, T1, T2, T3, and T4 inside the chamber monitored temperature profiles during drying. A glass jar, not shown, was located after the vortex separator to catch escaping sorbent. The MD was heated to 110 °C under 70.0 L/min air, then 490 g wet TPSENa sorbent was loaded into chamber and the mechanical mixer was set to est. 2 rev/s. The sorbent was checked after all temperatures reached 100 °C and was allowed to further dry. The dried TPSENa sorbent was collected from the chamber, sorbent collector, and glass jar and dried in an oven at 100 °C for 60 min. The oven drying removed remaining ethanol and water.

I.3.4 Trial 2

The drying system used for trial 2 was similar to the system in trial 1, with the exception that the mixer had only one level of blades. Thermocouple 5 was also added to monitor the temperature inside the sorbent collector.
Table I.1: Summary of the recent trials and modifications made to the rapid drying system to decrease drying time or increase drying capacity.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Current problem</th>
<th>Current design</th>
<th>Soln./Mod.</th>
<th>Test conditions</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1. Not enough sorbent dried</td>
<td>Mixer-dryer, 2X in-line heaters</td>
<td>Use more sorbent</td>
<td>T=110 °C, Air=70 L/min 490 g wet TPSENa</td>
<td>Dried in 40 min Long dry time</td>
</tr>
<tr>
<td>2</td>
<td>2. Long drying time</td>
<td>Mixer-dryer, 2X in-line heaters</td>
<td>Add injection port, increase air flow</td>
<td>T=110 °C, Air=90 L/min 450 g wet TPSENa</td>
<td>Dried in 25 min</td>
</tr>
<tr>
<td>3</td>
<td>3. Long drying time</td>
<td>Mixer-dryer config.</td>
<td>Spray-dryer config. with injections</td>
<td>T=110 °C, Air=90 L/min 300 g wet TPSENa</td>
<td>Wet after 15 min Agglomerated in cone</td>
</tr>
<tr>
<td>4</td>
<td>4. Long drying time</td>
<td>Spray-dryer config. with injections</td>
<td>Spray-dryer config. with hand dryer not in-line heaters</td>
<td>T=110 °C, Air=140 L/min 250 g wet TPSENa</td>
<td>Wet after 15 min Dryer heating elements broke</td>
</tr>
<tr>
<td>5</td>
<td>5. Long drying time</td>
<td>Spray-dryer config. with hand dryer</td>
<td>Replace dryer with 2X in-line heaters and heating coil</td>
<td>T=110 °C, Air=150 L/min 150 g wet TPSENa</td>
<td>Dried after 10 min Most sorbent in cone</td>
</tr>
<tr>
<td>6</td>
<td>5. Not enough sorbent dried</td>
<td>Mixer-dryer config, 2 in-line heaters and heat coil</td>
<td>Dry more sorbent using sequential injections</td>
<td>T=110 °C, Air=150 L/min 800 g wet TPSENa</td>
<td>Dried after 40 min Needed to open and break chunks</td>
</tr>
</tbody>
</table>
The MD was heated to 110 °C under 90 L/min air and the vortex separator was heated to 51 °C. Initially, 300 g wet TPSENa was syringe injected into the chamber and the remaining 150 g was injected after 10 and 20 min drying using two, 75 g injections. The sorbent was checked after 20 min and allowed to further dry. The dried TPSENa was collected and further dried in the oven.

I.3.5 Trial 3

Figure I.2A shows the schematic of the spray-dryer system used in trial 3, consisting of a (i) gas manifold with air valve, rotameter, and two insulated in-line heaters and (ii) vortex separator, which served as the drying vessel, with thermocouples 5 and 6 in the sorbent collector and cone respectively. The cone was heated to 115 °C and the sorbent collector was heated to 70 °C under 90 L/min air. The 300 g wet TPSENa was introduced with four, 75 g injections after 0, 4, 8, 11 min drying. Once dried, the sorbent was collected and further dried in the oven.

I.3.6 Trial 4

Figure I.2B shows the schematic of the spray-dryer system used in trial 4, consisting of (ii) an Xlerator hand dryer with a compressor and heating element, and (ii) the vortex separator with temperature profile monitoring. The hand dryer was first tested for (i) maximum flow rate and (ii) minimum flow rate needed to achieve an outlet temperature of 120 °C. The maximum flow rate was 204 L/min, and was decreased to 140 L/min to achieve 120 °C. During drying 250 g wet sorbent, the heating element of the hand dryer burned out and did not dry the sorbent and was not successful.
I.3.7 Trial 5

Figure I.2C shows that the set-up of the spray-dryer system used in trial 5 was similar to trial 4 with the addition of a heating coil to sufficiently heat high air flow. A 150 g batch wet TPSENa was dried under 150 L/min air using 3 injections, (i) 70 g after 0 min, 70 g after 4 min, and (iii) 10 g after 8 min. The sorbent was checked after 10 min. This was the last test of the spray-dryer configuration.

I.3.8 Trial 6

Trial 6 used the same set-up as trial 2. The MD was heated to 110 °C under 150 L/min air and 300 g wet TPSENa was initially injected into the drying chamber followed
by three, 167 g injections after 6, 12, and 18 min. The sorbent was checked after 28 min, then allowed to further dry until all thermocouples reached 100°C. Once dried, the sorbent was collected and further dried in the oven.

Figure I.2: Schematic of the spray-dryer systems used in trials 3, 4, and 5 consisting of (i) different gas manifolds or Xlerator hand dryer, (ii) vortex separator, and glass jar, not shown, located after the vortex separator to catch escaping sorbent.

I.4 Results

The detailed results from trials 1-6 are presented in Table I.2. The results of each trial were used to make modifications to the dryer for improved performance in the proceeding trials.
Table I.2: Summary of the testing results during development of the drying system.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Mass (g)</th>
<th>Dry time (min)</th>
<th>Recovered (g)</th>
<th>% Dry</th>
<th>Full dry (g)</th>
<th>Actual dry (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>490</td>
<td>40</td>
<td>Total=161</td>
<td>Dry chamber=8.5</td>
<td>Total=152.4</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dry chamber=99</td>
<td>Sorb collector=95</td>
<td>Dry chamber=8.4</td>
<td>Sorb collector=144</td>
</tr>
<tr>
<td>2</td>
<td>450</td>
<td>25</td>
<td>Total=138 est.</td>
<td>Dry chamber=42 est.</td>
<td>Dry chamber=94</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sorb collector=96 est.</td>
<td>Sorb collector=88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>&gt;15</td>
<td>Total=19</td>
<td>Cone=83</td>
<td>Total=16</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cone=14</td>
<td>Sorb collector=77</td>
<td>Cone=12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sorb collector=5</td>
<td></td>
<td>Sorb collector=4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>250</td>
<td>&gt;15</td>
<td>-</td>
<td>-</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>10</td>
<td>Total=54</td>
<td>Cone=47</td>
<td>-</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cone=47</td>
<td>Sorb collector=2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Jar=4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>800</td>
<td>40</td>
<td>Total=288</td>
<td>Dry chamber=95</td>
<td>Total=258</td>
<td>272</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dry chamber=72</td>
<td>Sorb collector=85</td>
<td>Dry chamber=71</td>
<td>Sorb collector=187</td>
</tr>
</tbody>
</table>

The drying times were determined as the time at which all thermocouples reached 100 °C unless otherwise stated.

Figure I.3 shows the drying profile during trial 1. The initial heating rates were 6-9 °C/min and temperatures reached 95-120 °C. Adding wet TPSENa sorbent reduced the temperatures to 40-75°C due to heat absorption. The T1 showed low temperature after the addition because it was submerged in the wet sorbent. The temperatures sharply increased after 20 min as the sorbent dried. Although all temperatures read 100 °C after 28 min, checking the sorbent revealed it was partially wet due to limited heat transfer.
between the hot air and the sorbent; the temperature of sorbent was not yet 100 °C. The 490 g wet sorbent dried in 40 min, and recovered total sorbent was 161 g. The sorbent collector contained 95% of the total compared to 5% found in the drying chamber due to sorbent escaping from the chamber. Further oven drying showed that sorbent recovered in the chamber and collector was greater than 95% dry, suggesting the mixer-dryer system was efficient. Based upon the % dry, 91% of the theoretical total dry sorbent mass was recovered. The remaining 9% was loss due to sticking to the walls and escaping from the jar. The estimated drying time using the standard oven is about 90 min.

![Mixer-dryer temperature profiles of T1-T4 during trial 1 drying; 490 g wet TPSENa, 70 L/min air flow, 40 min dry time.](image)

Figure I.3: Mixer-dryer temperature profiles of T1-T4 during trial 1 drying; 490 g wet TPSENa, 70 L/min air flow, 40 min dry time.
Figure I.4 shows the drying profile during trial 2. The initial heating rates inside the drying chamber were 8.5 °C/min, and inside the sorbent collector the rate was 2.7 °C/min.

The slow heating rate for the collector was due to low flow rate of heated air into it. Adding wet sorbent reduced the temperatures inside the chamber to 40 °C. The wet sorbent quickly dried in 25 min compared to trial 1 due to (i) less amount present with each injection and (ii) increased energy input from the heated air. The low amount of...
sorbent and high air flow facilitated high heat and mass transfer. An estimated 153 g sorbent was recovered, with 30% in the chamber and 70% in the collector. The sorbent from the chamber and collector was 94% and 88% dry respectively. A total of 90% of the theoretical dry mass was recovered. The estimated drying time using the standard oven is about 90 min.

The results of trial 3 shown in Figure I.5 that the spray-dryer configuration was not able to fully dry 300 g wet TPSENa.

Figure I.5: Spray-dryer temperature profiles of the cone and sorbent collector during trial 3 drying; 300 g wet TPSENa introduced with four 75 g injections, 90 L/min air, >15 min dry time because not completely dry.
Drying was stopped after 15 min and the sorbent was collected. A total of 19 g was recovered, with 14 g, 83% dry, removed from the cone and 5 g, 77% dry, removed from the sorbent collector. Only 16% of the theoretical total dry mass was recovered, and the remaining sorbent was wet and remained inside the cone. Although the thermocouple inside the cone read 100 ºC the sorbent was not dry. The small size of the cone caused the injected wet sorbent to agglomerate and stick to the walls. The agglomeration prevented efficient heat and mass transfer resulting in incomplete drying.

Figure I.6: Spray-dryer temperature profiles of the cone and sorbent collector during trial 4 drying; 250 g wet TPSENa introduced with four 75 g injections, 140 L/min air flow produced by Xlerator hand dryer, >15 min dry time.
The results for trial 4 shown in Figure I.6 were not significant because the heating elements for the Xlerator hand dryer failed during drying and the run was stopped after 15 min. The sorbent was wet and agglomerated inside the injection port and the cone of the vortex separator.

Figure I.7 shows the drying profile during trial 5. The cone was initially heated at 11.2 °C/min, and the sorbent collector was slowly heated at 4.8 °C/min due to low flow rate of heated air into it.

![Graph showing drying profiles](image)

Figure I.7: Spray-dryer temperature profiles of the cone and sorbent collector during trial 5 drying: 150 g wet TPSENa introduced with two 70 g and one 10 g injections, 150 L/min, >15 min dry time.
The first injection of wet sorbent decreased the cone temperature to 50 °C as heat was absorbed, and the temperature quickly increased as wet sorbent dried. The sorbent collector temperature did not increase because no wet TPSENa present. The system leaked at the injection port after 8 min drying and the experiment was stopped. The 150 g wet sorbent was dried in 10 min due to the high flow rate of heated air. A total of 54 g sorbent was recovered after drying, with 87% found in the cone. The sorbent in the cone was not significantly agglomerated, but still needed to be physically removed using a metal rod. Since the spray-dryer configuration was no longer considered as a viable design, the % dry of the sorbent was not determined.
Figure I.8: Mixer-dryer temperature profiles of T1 and T3 during trial 6 drying; 800 g wet TPSENa introduced with 300 g initially injected followed by three 167 g injections after 6, 12, and 18 min, 150 L/min air flow, 40 min dry time.

Figure I.8 shows the drying profile during trial 6. Similar to trial 2, the temperatures decreased after injecting the wet TPSENa, and rapidly increased as the sorbent dried. The sorbent was not fully dry after all temperatures reached 100 °C due to limited heat transfer and agglomeration of the sorbent. The 800 g wet sorbent dried in 40 min using high air flow and sequential injections, and the total recovered sorbent was 258 g. The sorbent collector contained 72% of the total compared to 28% found in the drying chamber. The sorbent from the collector and chamber was 85% and 95% dry.
respectively. A total of 95% of the theoretical dry mass was recovered. The estimated drying time using the standard oven is about 120 min.

I.5 Conclusions

Six key trials and modifications to reduce drying time or increase drying capacity of the rapid drying system were presented. Results of trial 2 with the mixer-dryer showed that using sequential injections and high air flow to dry 450 g wet TPSENa decreased the drying time from 40 min in trial 1 to 25 min. Trial 6 showed that increasing the sorbent mass to 800 g yielded a 40 min drying time and a % dry similar to that of the 450 g dried in trial 2. During drying 800 g, the sorbent caked above the blades due to the large amount and was manually broken up, which suggested this as the maximum capacity of the mixer-dryer. Also, additional levels of blades may be needed to dry >500 g. Over all trials with the mixer-dryer, the dried sorbent recovered from the collector was 85-95% dry compared to 94-99% dry for the sorbent from the chamber. The low % dry for the collector was due to low flow of heated air into it.

Therefore, it is necessary to maintain high temperature, 80-90 °C, in the sorbent collector via external heating to prevent condensation of water and ethanol and further dry the sorbent as it is stored. The collector temperature must be closely monitored and the storage time of the sorbent in the collector must be minimized to prevent burning. The amount of sorbent recovered from the jar was insignificant compared to the sorbent recovered from the chamber and collector.

The results of the spray-dryer trials showed that it was not useful to dry sorbent and will not be tested further.
I.6  Suggested Experiments and Procedures

1. A total of 800 g wet TPSENa will be dried using a semi-batch approach with eight, 100 g injections. Each injection will be introduced after the previous one dries; the chamber temperatures reach 100 °C \(\rightarrow\) COMPLETED and data being processed.

2. The injected sorbent will be optimized to allow minimal drying time \(\rightarrow\) DATA BEING PROCESSED FROM LATEST TEST

3. Re-circulation of the heated inlet air should be considered and designs should be proposed \(\rightarrow\) PROPOSED

4. The current mixer-dryer design should be tested as a vessel to prepare the sorbent and then dry it \(\rightarrow\) PROPOSED

5. The system may be automated to operate a long term, semi-batch process \(\rightarrow\) PROPOSED

6. The sorbent may be re-designed to allow removal of the dried sorbent during long term, semi-batch drying \(\rightarrow\) PROPOSED

I.6.1 Appendix
Figure I.9: Picture of the mixer-dryer system used in trial 6 consisting of a (i) gas manifold with two in-line heaters and heating coil to increase in-let air temperature, (ii) mixer-dryer with inlet manifold, drying chamber, lid with wet sorbent injection port, and mechanical mixer, and (iii) vortex separator with a cone and sorbent collector to remove dried sorbent, and glass jar to catch escaping sorbent. The system used in trials 1 and 2 was similar, but did not have the coil.
Figure I.10: Picture of the spray-dryer system used in trials 3 and 4 consisting of a (i) gas manifold with two in-line heaters and heating coil to increase in-let air temperature and injection port to introduce wet sorbent, and (ii) spray-dryer with thermocouples in the cone and sorbent collector to monitor temperature profiles during drying and glass jar to catch escaping sorbent. The spray-dryer set-up used in trial 2 was similar, but did not have the coil.
Figure I.11: Picture of the spray-dryer system used in trial 5 consisting of (i) Xlerator hand dryer with re-wired controls to adjust the air flow and injection port to introduce wet sorbent, and (ii) spray-dryer with thermocouples in the cone and sorbent collector to monitor temperature profiles during drying and glass jar to catch escaping sorbent.