Spectroscopic Investigation into Oxidative Degradation of Silica-Supported Amine Sorbents for CO₂ Capture

Chakravartula S. Srikanth and Steven S. C. Chuang^{*,[a]}

Oxidative degradation characteristics of silica-supported amine sorbents with varying amounts of tetraethylenepentamine (TEPA) and polyethylene glycol (PEG; P₂₀₀ or P₆₀₀ represents PEG with molecular weights of 200 or 600) have been studied by IR and NMR spectroscopy. Thermal treatment of the sorbents and liquid TEPA at 100 °C for 12 h changed their color from white to yellow. The CO₂ capture capacity of the TEPA/SiO₂ sorbents (i.e., SiO₂-supported TEPA with a TEPA/SiO₂ ratio of 25:75) decreased by more than 60%. IR and NMR spectroscopy studies showed that the yellow color of the degraded sorbents resulted from the formation of imide species. The imide species, consisting of NH associated with two C=O functional groups, were produced from the oxidation of methylene

groups in TEPA. Imide species on the degraded sorbent are not capable of binding CO₂ due to its weak basicity. The addition of P₂₀₀ and P₆₀₀ to the supported amine sorbents improved both their CO₂ capture capacities and oxidative degradation resistance. IR spectroscopy results also showed that TEPA was immobilized on the SiO₂ surface through hydrogen bonding between amine groups and the silanol groups of SiO₂. The OH groups of PEG interact with NH₂/NH of TEPA through hydrogen bonding. Hydrogen bonds disperse TEPA on SiO₂ and block O₂ from accessing TEPA for oxidation. Oxidative degradation resistance and CO₂ capture capacity of the supported amine sorbents can be optimized through adjusting the ratio of hydroxyl to amine groups in the TEPA/PEG mixture.

Introduction

CO₂ emission from coal-fired power plants constituted more than 40% of anthropogenic CO₂ released into the atmosphere in 2010.^[1] CO₂ separation and sequestration from coal-fired power plant flue gas is an attractive option to control CO₂ emissions. The use of commercially available aqueous amine technology for capturing CO₂ from flue gas could result in more than an 85% increase in the cost of electricity.^[2] One approach to improve the aqueous amine process is to immobilize amine on porous solids, allowing surface amine sites for direct contact with CO₂ in the flue gas. The solid amine sorbents could potentially decrease the cost of CO₂ capture by 1) reducing the energy needed for sorbent regeneration, 2) avoiding equipment corrosion, and 3) increasing the rate of CO₂ adsorption/absorption and desorption.

Solid amine sorbents should possess a minimum CO₂ capture capacity of 2.0 mmol per gram of sorbent to provide a performance comparable to that of a large-scale liquid amine process.^[2a,3] Solid sorbents studied so far include supported amine sorbents,^[2a,3a,4] carbon-based amine sorbents,^[5] amines coated on glass fibers,^[3b,6] zeolites,^[7] SiO₂,^[7] SBA-15,^[3a,8] and MCM-41.^[9] The approaches to immobilize amines include 1) amine grafting,^{[3a,4c][3b,6]} using aminosilanes, and 2) physical adsorption of amines on the support surface.^[8a,9a,10] Recently, covalently tethered hyper-branched aminosilane (HAS) materials have been prepared on SBA-15, which has CO₂ adsorption sites that can be easily regenerated.^[11] The sorbents prepared from the above approaches, despite having high capture capacities, may have limited potential for large-scale operations due to the cost of either the amines (aminosilanes) or the supports (mesoporous supports) used.

The major concern associated with amine-based sorbents is that the amines gradually degrade during thermal regeneration.^[12] Solid amine sorbents could be more prone to oxidative degradation due to the accessibility of O₂ to the highly dispersed amines relative to limited access of O₂ in liquid amines.

Oxidative degradation products of liquid amines, such as ethanolamines and ethylenediamines, have been identified as aldehydes and carboxylic acids.^[12] Jones et al. recently showed that secondary amines were more prone to oxidation than primary and tertiary amines when exposed to 100% oxygen in temperature ranges of 25–135 °C.^[13] Sayari and Belmabkhout found that degradation of amine-grafted solid sorbent in the presence of CO₂ at 105 °C led to conversion of amine to form urea and the presence of moisture in the CO₂ gas stream slowed down the degradation.^[14] Our recent IR study showed that the addition of polyethylene glycol (PEG) to amine/SiO₂ slowed down the formation of a thermally degraded product—carboxylate species—during CO₂ adsorption in the presence of air and desorption in an argon gas environment.^[15] In

[a] C. S. Srikanth, Prof. S. S. C. Chuang
FirstEnergy Advanced Energy Research Center
Department of Polymer Science
The University of Akron
Akron, OH 44325-3909 (USA)
Fax: (+1) 330-972-5856
E-mail: chuang@uakron.edu

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Table 1. Composition of the silica-supported sorbents described herein.

Sorbent ^[a] [wt %]	Amine groups [10 ⁻³ mol g ⁻¹]	Hydroxyl groups [10 ⁻³ mol g ⁻¹]	Ratio hydroxyl/amine	Final color ^[b]
TS 25/75	13.20	0.00	0.00	intense yellow
P ₂₀₀ S 25/75	0.00	12.50	–	white
P ₆₀₀ S 25/75	0.00	4.13	–	white
TP ₂₀₀ S 5/5/90	2.64	2.50	0.95	white
TP ₂₀₀ S 10/10/80	5.38	5.00	0.95	pale yellow
TP ₂₀₀ S 15/15/70	7.92	7.50	0.95	white
TP ₂₀₀ S 20/20/60	10.56	10.00	0.95	yellow
TP ₂₀₀ S 25/25/50	13.20	12.50	0.95	pale yellow
TP ₆₀₀ S 5/5/90	2.64	0.83	0.31	white
TP ₆₀₀ S 10/10/80	5.38	1.65	0.31	pale yellow
TP ₆₀₀ S 15/15/70	7.92	2.48	0.31	yellow
TP ₆₀₀ S 20/20/60	10.56	3.30	0.31	intense yellow
TP ₆₀₀ S 25/25/50	13.20	4.13	0.31	intense yellow
TGS 25/25/50	13.20	16.20	1.22	brown
TES 25/25/50	13.20	16.21	1.22	intense yellow

[a] The sorbents are written with the following notation: T=TEPA, S=SiO₂, P₂₀₀ and P₆₀₀ refer to PEG with molecular weights of 200 and 600, respectively, G=glycerol, and E=ethylene glycol, and numbers to represent the ratio of the components. For example, TP₂₀₀S 5/5/90 refers to the sorbent with 5 wt% TEPA, 5 wt% PEG-200, and 90 wt% SiO₂. [b] The color of all of fresh sorbents was white.

other studies, PEG has also been used as an additive to improve the CO₂ capture capacity of the amine-based sorbents^[9a,16] and for SO₂ capture.^[17] The oxygen in a flue gas stream, which can be trapped in the porous structure of the supported-amine sorbent, could initiate oxidative degradation during thermal desorption of adsorbed CO₂ on the sorbent. A better understanding of the oxidative degradation process and the effect of PEG on the process could help in the development of more effective sorbents. In the present work, we used IR and NMR spectroscopy to study the structure of tetraethylenepentamine (TEPA) and PEG immobilized on SiO₂ and to determine the oxidative degradation products. TEPA, which is a small molecule with a well-defined structure, serves as an excellent model compound to study the interaction of amines with the OH (surface silanol) groups of silica, the OH groups of PEG, and O₂ in an oxidative environment. The results presented herein showed that oxidative degradation of the sorbent and liquid amines resulted from oxidation of methylene groups of TEPA to form imide/amide. The presence of PEG in the sorbents not only increased the CO₂ capture capacity, but also slowed down the degradation of SiO₂-supported amine sorbents in the oxidative (i.e., flue gas) environment. The results of this study show that the degradation of SiO₂-supported amine strongly depends on its environment. A degradation study should be carried out in an oxygen-containing environment to emulate the practical conditions of CO₂ capture processes.

Results and Discussion

Oxidative degradation study

An oxidative degradation study on silica-supported amine sorbents and TEPA/PEG liquid samples was carried out at 100 °C for 12 h. Table 1 shows the compositions of the sorb-

ents prepared, the number of moles of amines from TEPA (NH₂ and NH), the number of moles of hydroxyl groups from PEG present on each sorbent, and the sorbent color changes observed after the oxidative degradation studies. The extent of the color change may reflect the degree of degradation of the sorbent. All of the fresh sorbents were initially white. After oxidative degradation, the TEPA/SiO₂ (TS 25/75) sorbent became intense yellow, whereas the PEG/SiO₂ (P₂₀₀S 25/75 or P₆₀₀S 25/75) sorbents remained white. The change in the color of the TPS (TEPA/PEG/SiO₂) sorbents varied from white to intense yellow, as shown in Table 1. The sorbents with P₂₀₀ showed less color change than P₆₀₀. This observation could be attributed to the higher ratio of OH to amine on P₂₀₀ (i.e., TP₂₀₀S) than P₆₀₀ (i.e., TP₆₀₀S) sorbents. The sorbents with ethylene glycol (E) and glycerol (G) changed color to intense yellow and brown, respectively. Treating liquid TEPA, PEG, and TEPA/PEG at 100 °C for 12 h also resulted in color changes and followed the same trend as those observed on TP₂₀₀S and TP₆₀₀S sorbents. These results showed that the presence of PEG in TS sorbents and in liquid samples slowed down the color change.

CO₂ capture

The sorbents were pretreated in an oven at 100 °C for 7 min and saturated in a bath with pure CO₂ flowing at 50 cm³ min⁻¹ for 10 min over the sorbents at 25 °C. The CO₂ capture capacity of the sorbents was measured by determining the change in

Table 2. CO₂ capture capacities of fresh and degraded TS, TP₂₀₀S, TP₆₀₀S, TGS, and TES sorbents.

Sorbent	CO ₂ capture capacity [mmol g ⁻¹]			
	fresh	CO ₂ /amine	degraded	CO ₂ /amine
TS 25/75	1.234	0.18	0.454	0.07
TP ₂₀₀ S 5/5/90	0.631	0.47	0.346	0.26
TP ₂₀₀ S 10/10/80	1.107	0.41	0.582	0.22
TP ₂₀₀ S 15/15/70	1.585	0.39	0.868	0.21
TP ₂₀₀ S 20/20/60	2.093	0.39	0.832	0.15
TP ₂₀₀ S 25/25/50	2.436	0.37	1.011	0.15
TP ₆₀₀ S 5/5/90	0.455	0.34	0.253	0.19
TP ₆₀₀ S 10/10/80	0.842	0.32	0.448	0.16
TP ₆₀₀ S 15/15/70	1.234	0.31	0.529	0.13
TP ₆₀₀ S 20/20/60	1.448	0.27	0.585	0.11
TP ₆₀₀ S 25/25/50	1.807	0.27	0.667	0.10
TGS ^[a] 25/25/50	2.645	0.40	0.364	0.05
TES ^[b] 25/25/50	2.714	0.41	0.956	0.15

[a] G = glycerol. [b] E = ethylene glycol.

weight of the sorbents before and after saturation. Table 2 contains the CO₂ capture capacities and corresponding amine efficiencies (i.e., CO₂/amine) of the fresh and degraded TS 25/75, TP₂₀₀S, TP₆₀₀S, TGS, and TES sorbents; sorbents with E and G (TES and TGS are included for comparison. A comparison of TS 25/75 with TP₂₀₀S 25/25/50 showed that the addition of PEG

to the TEPA sorbents increased both the initial capture capacity and the amine efficiency. Increasing the TEPA and PEG loading on both TP₂₀₀S and TP₆₀₀S sorbents increased the CO₂ capture capacity, but decreased the amine efficiency. The decrease in the amine efficiency with TEPA and PEG loading can be attributed to the unavailability of amine sites due to agglomeration of TEPA, which causes diffusion limitations for CO₂ to access the amine sites. The sorbents with E and G with about 30% more hydroxyl groups than P₂₀₀ showed higher initial capture capacities than on P₂₀₀.

CO₂ is known to adsorb on the amine as carbamate and bicarbonate by the following reactions: in the absence of water, one mole of CO₂ reacts with two moles of amine to form carbamate [Eq. (1)], and in the presence of water one mole of CO₂ reacts with one mole of amine to form bicarbonate [Eq. (2)].^[8b,18]

Since CO₂ adsorption in this study was carried out in the absence of H₂O vapor, it is expected that CO₂ is adsorbed in the form of carbamate on two amine sites, as shown in Equation (1). The maximum achievable amine efficiency would be 0.5. Recent studies suggested that the presence of PEG in solid amine sorbents increased the CO₂ capture capacity by changing the rate of CO₂ adsorption/desorption.^[16,18] The CO₂ capture results reported herein showed that the addition of PEG increased the CO₂ capture capacities and the amine efficiencies of the sorbents; this is in good agreement with the literature.^[16,18] Assuming that TEPA and PEG are adsorbed on the SiO₂ surface by hydrogen bonding through primary amines and hydroxyl groups with the surface silanol groups, as shown in Scheme 1 below; TP₂₀₀S 5/5/90 would occupy 30% of the SiO₂ surface (specific surface area 160 m² g⁻¹) and TP₂₀₀S 15/15/70 would occupy 90%. Increasing the TEPA and PEG loading beyond this value resulted in 100% monolayer coverage and eliminated the isolated OH band at 3750 cm⁻¹ (Figure 2 below). This would lead to agglomeration of TEPA and decrease the amine efficiency. However, the results in Table 2 show that amine efficiencies decrease as the loading increases from TP₂₀₀S 5/5/90 to TP₂₀₀S 15/15/70, indicating the occurrence of significant agglomeration and close packing of the TEPA/PEG molecules.

The extent of the decrease in CO₂ capture capacities and amine efficiencies of the sorb-

ents followed the order TGS > TS 25/75 > TES > TP₆₀₀S > TP₂₀₀S after oxidative degradation. The sorbents with P₂₀₀ also showed higher capture capacities and amine efficiencies than the TS 25/75 and TP₆₀₀S sorbents before and after oxidative degradation. The higher capture capacities can be attributed to the presence of higher amounts of OH groups in P₂₀₀ compared with P₆₀₀ (Table 1). Even though the sorbents with E and G showed higher initial CO₂ capture capacities than P₂₀₀, they degraded more than those with P₂₀₀ during oxidative degradation. These results indicate that the presence of P₂₀₀ in the sorbents is more effective at slowing down the oxidative degradation of the sorbent than other additives.

Table 3 shows the CO₂ capture capacities and amine efficiencies of amine-based sorbents reported in the literature. A maximum CO₂ capture capacity of 4.5 mmol g⁻¹ was reported on TEPA/MSF sorbent with 35% amine efficiency.^[22] mesocellular silica foam (MSF) is a high surface area mesoporous material prepared from costly precursors. The sorbents in the present study were prepared from low-cost SiO₂ with a surface area of 160 m² g⁻¹; in contrast to 600–1000 m² g⁻¹ for MSF, MCM-41, or SBA-15. As expected, the low surface area of the SiO₂ support used in this study resulted in a lower CO₂ capture than those prepared from high-surface-area supports. However, these low-surface-area supported amine sorbents have CO₂/amine ratio (i.e., amine efficiency) values of 0.37 and 0.27 for TP₂₀₀S 25/25/50 and TP₆₀₀S 25/25/50, respectively (Table 2), which are comparable to the values reported in literature (Table 3). The CO₂ capture of our low-surface-area SiO₂ is more than 50% of the highest reported CO₂ capture capacity on support with more than four times the surface area of our support. These results suggest that the surface area may not be a dominating factor that governs CO₂ capture capacity. It is noteworthy that different methods are used to measure CO₂ capture capacity in the literature. A large number of CO₂ capture capacity data, listed in Table 3, were determined by using the TGA method for which the weight gain in the sorbent during adsorption was measured as a function of time. Each adsorption/desorption

Table 3. Comparison of CO₂ adsorption capacities on different amine-based sorbents reported in the literature.

Sorbent	Amine [wt %]	CO ₂ capture capacity [mmol g ⁻¹]	CO ₂ /NH ₂	Cycle time [min]	Adsorption/desorption technique ^[a]	T [°C]	Ref.
glass fiber	30-PEI ^[b]	4.12	0.36	70	GC-TPD	80/120	[3b]
fly ash	60-PEI ^[b,c]	1.10	0.08	90	TGA	75/75	[16]
SiO ₂	54-TEPA ^[c]	2.08	0.15	30–40 ^[d]	MS-TPD	30/120	[15]
SBA-15	50-PEI ^[b]	3.18	0.28	150	TGA	75/75	[19]
MCM-41	50-PEI ^[b,c]	2.50	0.22	150	TGA	75/75	[9a]
carbon	50-PEI ^[b]	3.06	0.27	150	TGA	75/75	[19]
SBA(P)	50-TEPA	3.93	0.30	150–180	fixed bed-TPD	75/100	[20]
Y60	50-TEPA	4.27	0.28	–	Ads.-vac.-TD	60/100	[21]
SBA-15	APTS	0.73	–	60 ^[a]	Ads.- TPD	30/120	[4a]
MSF	50-TEPA	4.50	0.35	120	TGA	75/75	[22]
HAS	30-aziridine	1.98	0.28	> 180	MS-TPD	75/130	[11]
SiO ₂	25-TEPA ^[c]	2.43	0.37	20	Ads.-TPD	30/100	this work

[a] GC-TPD = gas chromatography–temperature-programmed desorption, TGA = thermogravimetric analysis, MS-TPD = mass spectrometry–temperature-programmed desorption, Ads.-vac.-TD = Adsorption-vacuum desorption-thermal desorption, Ads.-TPD = Adsorption-Temperature Programmed Desorption. [b] PEI = polyethylenimine. [c] Sorbents with PEG as an additive. [d] Results from our previous work.

cycle in these studies takes more than one hour, providing equilibrium CO_2 adsorption data rather than working capacity data. These equilibrium values are expected to be significantly greater than the sorbent working capacity under practical operating conditions, where a short time period is used for adsorption/desorption. The equilibrium capture capacity of the sorbents in the present study, after keeping the sorbents in the CO_2 bath for 30 min, was 30% more than the values reported in Table 2. The TGA method could also overestimate the sorbent capture capacity due to the presence of H_2O or other adsorbing contaminants in the gas stream. Non-zero steady-state CO_2 capture capacities of TS 25/75 and TP_{200}S sorbents are determined by degrading the sorbents at 100°C and measuring the capture capacity every hour. The results (Figure S1 in the Supporting Information) showed that the degradation was fractional per cycle and TS 25/75 reached its steady state after 10 h, whereas TP_{200}S sorbents reached a steady state after 24 h of oxidative degradation. These results suggest that the presence of PEG in the sorbents prevent the degradation of amines on the sorbents.

IR studies on solid amine sorbents

Figure 1 shows the IR absorbance spectra of pure SiO_2 , fresh and degraded TS 25/75 (i.e., TEPA/ SiO_2) sorbents, and urea obtained by DRIFTS at 100°C . Urea is included for comparison purposes. Pure SiO_2 exhibited isolated O–H stretching at 3750 cm^{-1} , hydrogen-bonded O–H at 3660 cm^{-1} , hydrogen-bonded water at $2700\text{--}3600\text{ cm}^{-1}$, and a water bending vibration at 1630 cm^{-1} .^[23] Impregnation of TEPA/ethanol onto SiO_2 followed by drying produced the IR spectra of TS 25/75, which showed symmetric and asymmetric NH_2 stretching vibrations at 3290 and 3360 cm^{-1} , NH_2 deformation of primary amines at 1601 cm^{-1} , CH_2 stretching vibrations at 2931 and 2810 cm^{-1} , and bending at 1458 cm^{-1} . The absence of the broad water band at $2700\text{--}3600\text{ cm}^{-1}$ indicates that the impregnation process displaced H_2O from the SiO_2 surface; the absence of the isolated O–H

band at 3750 cm^{-1} suggests that these surface OH groups are bound with N in NH/NH_2 functional groups. The IR band assignments in this study are presented in Table 4.

Degraded TS 25/75 sorbent showed 60% less capacity than that of the fresh sorbent. The spectra of these degraded sorbents exhibited bands that were significantly different from those of urea (Figure 1). Although urea has been identified as the degradation product of aminosilane/MCM-41 in the CO_2 stream,^[14] the absence of the IR absorbance features of urea indicated that urea was not formed in the oxidative degradation environment. The formation of urea due to reaction of CO_2 with amines was not only associated with production of C=O , observed at 1670 cm^{-1} , but should also give a peak at 1410 cm^{-1} for C–N , which was not observed in degraded sorbents of the present study. Oxidative degradation decreased the

Figure 1. IR absorbance spectra of pure SiO_2 , fresh and degraded TS 25/75 sorbents, and urea collected by using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) at 100°C . $\text{Abs} = \log(1/I)$, in which I is the single beam spectra of interest.

Table 4. IR band assignments.

Wavenumber [cm^{-1}]	Assignment	Species	Ref.
3750	free OH groups	SiO_2	[23]
3700–3000	hydrogen bonding	PEG, TEPA	[3a,b,6,23]
3660	OH-hydrogen bonded	SiO_2	[3a,b,6,23,27]
3500–3400	O–H stretching	PEG	[17b]
3360, 3290	N–H stretching	TEPA	[4c,7,8,9b,27,28]
3445, 3325			
2931	C–H stretching	TEPA, PEG	[4c,7,8,9b,23,28c]
2810, 2880	C–H stretching	TEPA, PEG	[4c,7,8,9b,23,28c]
1670	C=O stretching	amide	[14,29]
1670	N=O stretching	nitrite	[25]
1630	H–O–H	adsorbed water	[23]
1601	N–H deformation of primary amine	TEPA	[23,27,28b,c]
1458	CH_2 bending	TEPA, PEG	[23]
1410	C–N stretching	TEPA,	[30]

intensity of the CH_2 bands more than the NH_2 stretching bands. A decrease in the intensities of these bands was accompanied by the emergence of a prominent $\text{C}=\text{O}$ band at 1670 cm^{-1} and a broad $\text{N}-\text{H}$ band at 3290 cm^{-1} . These two bands coincide with the IR spectra of an imide species consisting of NH associated with two $\text{C}=\text{O}$ groups. Assignment of these IR bands for the yellowish degraded sorbents to imide is further supported by the yellow color of polyimide species.^[24] The yellow color could also result from oxidation of primary amines to form nitrites,^[25] which exhibit $\text{N}=\text{O}$ stretching at 1670 cm^{-1} , overlapping with the imide $\text{C}=\text{O}$ band.^[26] The distinct asymmetric and symmetric NH_2 bands at 3360 and 3290 cm^{-1} became a broad band centered at 3290 cm^{-1} , indicating the occurrence of oxidation of these primary amine species. The spectra of the degraded sorbent also showed an increase in the intensity of the isolated OH at 3750 cm^{-1} . The above IR observations suggested that TEPA on SiO_2 was degraded through 1) oxidation of both $\text{C}-\text{H}$ next to the secondary amines ($\text{N}-\text{H}$) and 2) oxidation of primary amines (NH_2) to nitrite species. The latter appears to occur at a lesser extent than the former because the decrease in NH intensity is significantly less than $\text{C}-\text{H}$ intensity. The NH group of the imide or amide and nitrite species is known to be a significantly weaker base than the primary amine functional group in TEPA. The weak basicity of these species prevents them from adsorbing CO_2 . These amide/imide species are not expected to interact with isolated OH at 3750 cm^{-1} .^[14] Thus, degradation of TS 25/75 sorbent would allow the isolated OH to return to its initial state, causing its IR intensity to increase.

Figure 2a shows the IR absorbance spectra of fresh and degraded TP_{200}S sorbents, exhibiting the characteristic bands of TEPA and TP_{200} on SiO_2 . A comparison of the IR spectra of TS 25/75 and TP_{200}S sorbents shows that the addition of P_{200} broadens the bands in the $3000\text{--}3600\text{ cm}^{-1}$ region. The amine stretching bands on TP_{200}S sorbents are not as distinct as those observed on TS 25/75 sorbents. The emergence of a small hump at 3160 cm^{-1} for TP_{200}S 20/20/60 suggests the formation of hydrogen bonding between the amines and OH groups of PEG.

This vague band on the SiO_2 -supported sorbent became prominent in the mixture of TEPA and PEG (Figure 3 below). Figure 2 also shows that increasing the TP_{200} loading on the SiO_2 support increased the intensities of the NH_2 and CH_2 bands and decreased the intensity of the shoulder at 3660 cm^{-1} . This observation suggests that both TEPA and PEG displaced surface H_2O on the SiO_2 . The decrease in the isolated OH intensity with increasing TP_{200} loading on SiO_2 further supports the proposed interaction between isolated OH groups of silica with amines of TEPA and hydroxyl groups of PEG. Figure 2b shows the IR absorbance spectra of fresh and degraded TP_{600}S , TES, and TGS sorbents, exhibiting similar features to those observed in Figure 2a.

The increased intensity of the 1670 cm^{-1} band for degraded sorbents is approximately proportional to the TP_{200} loading on SiO_2 and the decrease in the intensity of $\text{N}-\text{H}$ deformation of the primary amine at 1601 cm^{-1} , CH_2 stretchings at 2880 and 2931 cm^{-1} , and the CH_2 bending mode at 1458 cm^{-1} . This ob-

Figure 2. IR absorbance spectra of fresh and degraded a) TP_{200}S sorbents and b) TP_{600}S , TES, and TGS sorbents collected by using DRIFTS at 100°C .

servation supports our proposition that degradation occurred through oxidation of C–H bonds in TEPA to form imide species and further indicates that the extent of oxidation is proportional to the TEPA loading. The imide and nitrite species have a significantly lower basicity than the original amine and are not able to interact with CO₂ at room temperature. These species could disrupt hydrogen bonding between those amines remaining intact and PEG OH groups on the degraded sorbents. The disruption of hydrogen bonding would allow the amines and PEG to return to hydrogen-bonding-free conditions, causing a higher intensity band of the hydroxyl groups of PEG at 3500 cm⁻¹ and amine stretching bands at 3360 and 3290 cm⁻¹ on the degraded sorbent relative to those on the fresh sorbents. Degradation also allows the isolated OH groups to return to their initial state, causing the IR intensity to increase, as observed in Figure 2a (insets). However, the increase in the intensity of the band at 3750 cm⁻¹ was observed more at lower loadings than those at higher loadings due to agglomeration of TEPA/PEG on the SiO₂ surface. Sorbents with E and G (Figure 2b) show a stronger degradation peak at 1670 cm⁻¹ and loss in the hydrogen bonding band at 3160 cm⁻¹ due to evaporation of the species owing to their smaller molecular size.

IR studies on TEPA/PEG liquid samples

Figure 3 shows changes in the ATR-IR spectra of the TEPA and PEG mixture as a result of hydrogen bonding in the absence of the effect of SiO₂. Significant broadening of the NH₂ and OH stretching bands was observed in the 3000–3250 cm⁻¹ region. Hydrogen bonding between NH₂ groups of TEPA and OH groups of PEG produced a shoulder at around 3160 cm⁻¹. The spectrum in TP₂₀₀ 70/30 resulted from a significant fraction of PEG molecules surrounded by TEPA molecules; the spectrum in TP₂₀₀ 30/70 resulted from TEPA molecules surrounded by PEG molecules.

Figure 4 shows the ATR-IR absorbance spectra of fresh and degraded TEPA, TP₂₀₀ 50/50, TP₆₀₀ 50/50, and PEG liquid samples. Degradation of TEPA produced the C=O band at 1670 cm⁻¹ with a decrease in the CH₂ bands, suggesting that the mechanism of TEPA degradation is the same in the presence and absence of the SiO₂ support. The significantly more intense C=O band on TEPA/SiO₂ than that in liquid TEPA is a result of the direct exposure of TEPA to air. Oxidation in pure TEPA would require O₂ to be dissolved in the viscous TEPA liquid. In contrast to TEPA, PEG exhibited excellent thermal stability and oxidation resistance. The fresh TP₂₀₀ and TP₆₀₀ solutions exhibited similar characteristic bands. Due to the low OH/amine ratio in TP₆₀₀S sorbents, these sorbents showed less hydrogen bonding and greater degradation than TP₂₀₀S. Less hydrogen bonding and more degradation were also observed on sorbents with G and E (i.e., TGS and TES) due to evaporation. The presence of hydrogen bonding between amine and hydroxyl groups could change the reactivity of the amines toward oxygen molecules. In addition, PEG served as an oxygen-barrier enhancer, reflecting its

Figure 3. IR absorbance spectra of fresh TEPA, TP₂₀₀, and P₂₀₀ liquid samples with varying compositions collected by attenuated total reflectance (ATR) spectroscopy.

Figure 4. IR absorbance spectra of fresh and degraded TEPA, TP₂₀₀ (50/50), TP₆₀₀ (50/50), and P₂₀₀ liquid samples collected by ATR spectroscopy. Abs = $-\log(I/I_0)$, in which I_0 is the single beam spectrum of blank ATR and I is the single beam spectrum of interest.

low permeability to O₂.^[31] Thus, PEG enhances oxidative degradation resistance.

¹³C NMR spectroscopy results

Figure 5 shows the ¹³C NMR spectra of fresh and degraded TS 25/75 and TP₂₀₀S sorbents. All of the sorbents exhibited a signal at $\delta = 111.9$ ppm due to the background of the system and does not represent any functional group in the sample. Carbon bonded to a primary or secondary amine appeared at

Figure 5. Solid-state ^{13}C NMR spectra of fresh and degraded sorbents.

$\delta = 46.6$ and 39.7 ppm,^[32] CH_2O in PEG resulted in the signals at $\delta = 74.7$ and 71.0 ppm.^[33] Carbon attached to the hydroxyl groups of PEG was observed at $\delta = 61.8$ ppm in the TP_{200} sorbents. The spectra of the fresh sorbents did not show any signals of carbamate,^[14] since the sorbents were pretreated at 100°C in flowing argon (50 ccmin^{-1} for 30 min) prior to NMR spectroscopy analysis to remove CO_2 and water adsorbed from the atmosphere. Both degraded sorbents of TS and TP_{200}S showed an increase in the intensity of the signals at $\delta = 164.6$ and 160 ppm assigned to the formation of $\text{C}=\text{O}$ imides/amides due to the degradation of amines. These $\text{C}=\text{O}$ signals are not likely to be associated with urea,^[14] but associated with imide/amide species. The IR spectra of the sorbents (not shown herein) after NMR spectroscopy analysis showed peaks at 1670 cm^{-1} due to prolonged scanning to get a better signal-to-noise ratio. The increase in the intensities of CH_2NH at $\delta = 44.6$ and 39.7 ppm in the degraded sorbents needs further investigation. The carbon signal associated with nitrite was not observed in the NMR spectra. The ^{13}C NMR spectroscopy results confirm those of the DRIFT and ATR studies, which supported the proposal that amines were degraded by oxidation of CH_2 groups in TEPA to form imide/amide $\text{C}=\text{O}$ groups at 100°C in air.

Oxidative degradation mechanism

Oxidative degradation of liquid monoethanolamine and ethylenediamines at 140°C produced dealkylation products and small amounts of carboxylic acids.^[12] In contrast, the results described herein showed that the imide/amide species were the major degradation products formed during oxidative degradation of amines.

Scheme 1. Interactions of TEPA with SiO_2 and the formation of amide, imide, and nitrite groups by oxidative degradation.

Conclusions

The results of this study summarize in Scheme 1 show that amine functional groups of tetraethylenepentamine (TEPA) interact with surface hydroxyl groups of SiO_2 . Hydroxyl groups of polyethylene glycol (PEG) are also expected to interact with the surface hydroxyl groups. These interactions are evidenced by the decrease in the intensity of isolated OH groups with increasing TEPA/PEG loading. Oxidative degradation of TEPA in liquids and on SiO_2 supports occurs through oxidation of methylene groups in TEPA to $\text{C}=\text{O}$, converting an amine species into imide/amide species, which leads to a color change to yellow. The weak basicity of the $\text{N}-\text{H}$ group in imide/amide species prevents them from interacting with CO_2 and lowers the CO_2 capture capacities. The addition of PEG improved the CO_2 capture capacity and oxidative resistance. The positive effect of PEG was attributed to the formation of hydrogen bonds between NH_2 groups of TEPA and OH groups of PEG. These hydrogen-bonding interactions between amines and OH groups increased the dispersion of TEPA and slowed down the oxidation of the amine to imide species by blocking the amine sites from access to oxygen. P_{200} was more effective at slowing down the oxidative degradation of the amines than P_{600} due to more OH groups. The extent of degradation, color change, and decrease in the CO_2 capture capacity of the sorbents are in agreement with each other.

Experimental Section

Preparation of TPS sorbents: The specific chemicals used in the present study are tetraethylenepentamine (TEPA: T), poly(ethylene glycol) (PEG) with molecular weights 200 (P_{200}) and 600 (P_{600}), ethylene glycol (E), and glycerol (G), obtained from Aldrich Chemicals, USA. Silica (Brunauer–Emmett–Teller surface area $160\text{ m}^2\text{g}^{-1}$) was used as a support. Sorbents with varying weight ratios of TEPA/PEG/ SiO_2 (TPS) were prepared by impregnating 10 cm^3 of TEPA/ethanol solution onto SiO_2 followed by impregnating 10 cm^3 of PEG/ethanol solution onto TEPA/ SiO_2 . For example, the TP_{200}S 5/5/90 sorbent was prepared by dissolving TEPA (0.25 g) or P_{200} (0.25 g) in ethanol to make a 10 cm^3 solution for impregnation over SiO_2 (4.5 g). The sorbents were heated at 100°C for 15–20 min to evaporate the excess ethanol after each impregnation. TEPA/PEG liquid

samples with varying compositions were prepared by mixing pure TEPA and PEG. For example, the compositions of the liquid sample TP₂₀₀ 30/70 was obtained by mixing TEPA (0.3 g) and P₂₀₀ (0.7 g).

CO₂ capture and oxidative degradation: CO₂ capture measurements for the solid sorbents were measured as follows: 1) pretreatment: sorbents were heated at 100 °C for 7 min to remove CO₂ and H₂O pre-adsorbed from the atmosphere; 2) CO₂ adsorption: CO₂ (50 cm³ min⁻¹) was flowed for 10 min over the sorbents at 25 °C for CO₂ adsorption; and 3) regeneration: sorbents were heated at 100 °C for 10 min for the removal of adsorbed CO₂. The CO₂ capture capacity of the sorbent was determined by the weight change before and after CO₂ saturation. Short adsorption and desorption periods were used to determine the working capacity of the sorbent. The working capacity determined herein reflects the amount of captured CO₂ in a 20 min thermal swing cycle. After regeneration the sorbents were subjected to oxidative degradation by heating the sorbent at 100 °C for 12 h in air. After oxidative degradation treatments the sorbents were described as degraded samples. The CO₂ capture capacity of the degraded sorbents was measured in a similar way to the fresh sorbents. The liquid samples were also subjected to the same treatment to produce degraded liquid samples.

IR and NMR spectral analysis: The IR study of the fresh and degraded solid sorbents was performed ex situ by placing 50 mg of the sorbent in a DRIFT (Harrick) cell on a Nicolet-6700 FTIR spectrometer. The IR spectra of the sorbents were collected after pretreatment in flowing argon (150 ccmin⁻¹) at 100 °C for 10 min to remove preadsorbed water and CO₂ from the atmosphere. The IR study of the fresh and degraded liquid samples (TEPA, P₂₀₀, P₆₀₀, TP₂₀₀, and TP₆₀₀) was performed using ATR by coating a 0.1 mm liquid layer on the ZnSe (length = 4.35 cm; width = 0.63 cm) window. The single beam spectra of both solid and liquid samples were collected by 32 co-added scans and a resolution of 4 cm⁻¹. The absorbance spectrum was obtained by the equation $\text{Abs} = \log(1/I)$, in which I is the single beam spectrum of interest. Solid-state magic-angle spinning (MAS) ¹³C NMR spectra of the fresh and degraded sorbents were collected by using multiple-pulse direct polarization (DP) experiments at 400 MHz (Innova-400, Varian). Sorbents (~50 mg) were packed in a Zirconia pencil rotor and spun at magic angle at 10 kHz. A relaxation time of 8 s was applied for single-pulse experiments to allow thermal equilibrium and at least 1536 scans were utilized to achieve a proper signal-to-noise ratio. Prior to NMR spectroscopy analysis the sorbents were degassed at 100 °C to remove any adsorbed CO₂ or water from the atmosphere.

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