Doctoral Dissertation

Development of Amine-Impregnated Adsorbents for Carbon Dioxide Capture

二酸化炭素回収のためのアミン含浸吸着剤の開発

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Nara Institute of Science and Technology
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Development of Amine-Impregnated Adsorbents for Carbon Dioxide Capture

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By

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Abstract

The ever-increasing concentration of CO_2 in the atmosphere significantly has been contributing to global warming and climate change. Carbon capture and storage (CCS) has been proposed as a paramount option to significantly reduce CO_2 emission from industrial exhaust sources. Liquid amine scrubbing has been well-established for decades as a current benchmark CO_2 capture technology. However, this technology suffers from high cost because of high energy consumption for heating aqueous amine solution from absorption temperature to desorption temperature to release CO_2 in regeneration. Amine solid sorbents where amines are incorporated on solid carriers have emerged as promising candidates that can overcome this challenge. They can lower energy consumption for regeneration because solid sorbents do not use water as a solvent in the adsorption column. For industrial-scale applications in the field of capture and sequestration of CO_2, amine solid sorbents should possess high CO_2 adsorption performance and high thermal and oxidative stability. The improvement of CO_2 adsorption performance is a preferred way needed to lower the price of CO_2 capture technology. Stability of amine solid sorbents mainly depends on amine degradation which results in losses in CO_2 capture ability as well as lifetime of a sorbent. This dissertation focuses on the development of amine solid sorbents for CO_2 capture with the following issues: (1) improve CO_2 adsorption performance, (2) understanding degradation of amines, and (3) improve material stability.

With the goal of improving CO_2 adsorption performance, a mixture of imidazoles (Ims) and tetraethylenepentamine (TEPA) was impregnated to mesostructured cellular silica foam (MF). Blending TEPA with Ims with electron-donating groups were found to give advantages of CO_2 adsorption capacity, amine efficiency, working capacity, and heat of adsorption. MF modified with 30 wt% 4MIm and 40 wt% TEPA exhibited a high first-pass CO_2 adsorption capacity of 4.88 mmol/g at 100 kPa and 40 °C and a working capacity of 4.15 mmol/g following vacuum regeneration. Further insight into oxidative degradation of amine solid sorbents led that it is impossible to prevent such degradation even at ambient temperature. The stability of sorbents depended on the amine loading and its structure, oxidation duration, temperature, and O_2 concentration. With respect to improvement of material stability, sulfur-containing additives were found to owe effectiveness to inhibition of amine degradation, leading a longer lifetime of sorbents. Blending such additives into amine solid sorbents increased 1.5–4 times higher CO_2 adsorption capacity retention.

Preface

This dissertation focuses on the development of effective amine solid sorbents for CO_2 capture with high CO_2 adsorption performance and high oxidative stability. Amine and additives blending approaches are introduced to improve CO_2 adsorption performance and lifetime of amine solid sorbents, respectively.

This dissertation is divided into 5 chapters. Chapter 1 gives an overview of CO_2 emissions, global warming, and targets to mitigate the CO_2 emissions together with global warming problems. The following context states merits and demerits of promising capture technology using amine solid sorbents to cut down the greenhouse gas CO_2 emissions. Finally, the objectives of this dissertation are summarized.

Following the first general background chapter, chapter 2 focuses on the development of new binary amines impregnated systems for CO_2 removal from industrial exhaust streams. The mixtures of tetraethylenepentamine (TEPA) and imidazoles (Ims) are used to modify mesostructured cellular silica foam (MF) support to improve CO_2 adsorption performance of materials. CO_2 adsorption measurement, N_2 physisorption porosimetry, and thermogravimetry (TG) and differential scanning calorimeter (DSC) analyses are performed to characterize material properties. The impact of different amines and the adsorption temperature on CO_2 adsorption performance are investigated. The mechanism of the synergistic effect between blended binary mixtures of amines is discussed in detail. The degradation of such as-made adsorbents is also reported.

Chapter 3 investigates the stability of TEPA solid sorbents in the O_2-containing environment for CO_2 removal from industrial exhaust streams. To characterize the sorbents, CO_2 adsorption measurements, elemental analyses, N_2 physisorption porosimetry, TG analyses, diffuse reflectance Fourier-transform infrared spectroscopy, and gas chromatography are carried out. The strong dependence of the oxidative stability of sorbents on amine concentration and operating conditions of the oxidation is investigated and discussed. The changes in the composition of sorbents containing commercial TEPA during oxidative degradation and further insight into the oxidative degradation processes are also presented and discussed in this chapter.

Chapter 4 investigates oxidative degradation inhibition of amine-impregnated MF sorbents using various candidates including hydrogen-donating antioxidants and sulfur-containing compounds. The materials are characterized by CO_2 adsorption-desorption measurements, N_2 physisorption porosimetry, and elemental analyses. The effect of the hydrogen-donating antioxidants and sulfur-containing additives are presented and discussed. Further insight into the mechanism of the inhibition processes is also discussed in detail in this chapter.

Chapter 5 summaries findings in previous chapters, and provides perspectives for future work in this research.

List of Abbreviations

1BM	1-n-butylimidazole
4HMIm	4(5)-(hydroxymethyl)imidazole
4MIm	4(5)-methylimidazole
a.u.	Absorbance unit
BHT	Butylated hydroxytoluene
BET	Brunauer-Emmett-Telller
CCS	Carbon dioxide capture and storage
DBU	1,8-diazabicyclo(5.4.0)undec-7-ene
DBPD	*N,N′*-di-2-butyl-1,4-phenylenediamine
DCIm	4,5-dicyanoimidazole
DPPD	*N,N′*-diphenyl-1,4-phenylenediamine
DTDP	3,3′-dithiodipropionic acid
FT-IR	Fourier transform-infrared spectroscopy
GC	Gas chromatography
GISS	Goddard Institute for Space Studies
HEDS	2-hydroxyethyl disulfide
Im	Imidazole
IPCC	Intergovernmental Panel on Climate Change
MEA	Monoethanolamine
MF	Mesostructured cellular silica foam
NASA	National Aeronautics and Space Administration
NOAA	National Oceanic and Atmospheric Administration
PBR	Packed-bed reactor
PEG	Polyethylene glycol
PEI	Polyethyleneimine

PET	Pentaerythritol tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]
PZ	Piperazine
TBD	2,2′-thiodiethylene bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]
TDE	Thiodiethanol
TEPA	Tetraethylenepentamine
TG	Thermogravimetric
T-BRN	4-(2-aminoethyl)-N-(2-aminoethyl)-N´-[2-[(2-aminoethyl)amino]ethyl]-1,2-ethanediamine
T-EPZ	1-[2-[[2-[(2-aminoethyl)amino]ethyl]-amino]ethyl]piperazine
T-LIN	1,4,7,10,13-pentaazatridecane
T-IPZ	1-(2-aminoethyl)-4-[(2-aminoethyl)amino]ethyl]piperazine

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Chapter 1. General Introduction

This chapter briefly reviews the recent advances in the use of amine impregnated silicas for capturing CO_2 emissions from post-combustion. For application of these materials in commercial technologies, key parameters that need to be addressed are identified and discussed. The objectives of this dissertation are presented at the end of this chapter.

1.1. CO_2 Emissions and Global Warming

According to Goddard Institute for Space Studies (GISS) of National Aeronautics and Space Administration (NASA) report, the average global temperature of the planet has increased by about 1.1 °C compared to the end of the 19th.[1,2] Global warming can cause ecological, health impacts, and severe weather events such as floods, droughts, and sea-level rise. Hundreds of millions of people are already being damaged by climate change. One in five of the world's plants and animals assessed so far are threatened with extinction if the temperature increases more than 1.5–2.5 °C.[3] The predominant factor responsible for the warming of the earth is mainly ascribed to the increase in the concentration of the primary greenhouse gas CO_2 in the atmosphere. Figure 1.1 shows strong relationship between the change in global mean temperature[4] and CO_2 level[5] over the past 4 decades. The global mean temperature increase with the rapid increase of atmospheric CO_2 concentration.

The CO_2 concentration in the atmosphere has been persistently increasing since the industrial era and has now reached a dangerous level of 410.6 ppm in 2019[5] which has never seen in the last 3 million years. CO_2 can be emitted from many stationary sources such as the combustion of fossil fuels, carbonate decomposition, industrial process plants, and deforestation and other land-use changes. The use of fossil fuels for electricity production accounts for more than 65% of global CO_2 emissions[6,7] and has increased the concentration of the greenhouse gas emissions at an all-time high in 2019, putting us on track to reach a temperature increase of approximately 1.1 °C above pre-industrial levels. The atmospheric CO_2 concentration is expected to cross the permissible level of 450 ppm by 2050. According to the scenario of the Intergovernmental Panel on Climate Change,[8] the global average temperature is likely to rise by an additional 1.4 °C to 5.8 °C by 2100 in case of non-CO_2 emission reduction.

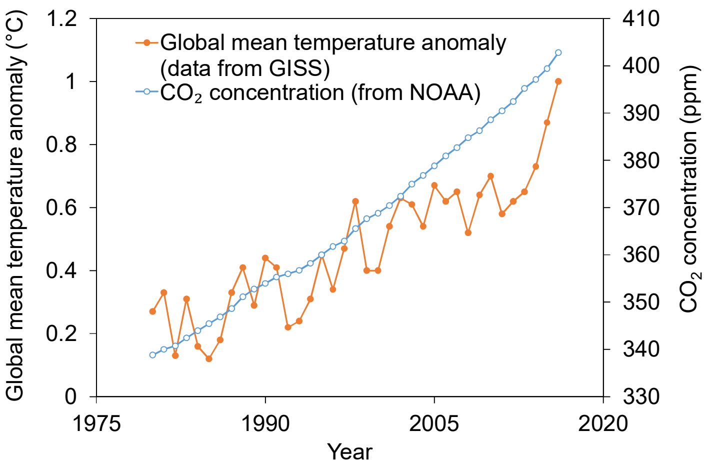

Figure 1.1. Annual atmospheric carbon dioxide (data from US National Oceanic and Atmospheric Administration (NOAA)) and annual global temperature anomaly (data from GISS) from 1980 to 2016.

As a result, the Kyoto Protocol[9] was adopted by many countries in 1997 that implements essential policies to support greenhouse emission reduction and sustainable development. Recently, the Paris Climate Change Agreement[10] replacing the Kyoto Protocol was signed in 2016 by 185 parties pursues a goal of controlling the average temperature of the global rise to below 2 °C above pre-industrial levels and undertakes ambitious efforts to limit the temperature increase to 1.5 °C. These missions have led the scientific community and industries to research and develop novel and effective technology to cut down the greenhouse gas CO_2 emissions.

1.2. Carbon Capture and Storage

As stated above that the emission of CO_2 is one of the most critical issues in the world. The ideal mitigation option to reduce the CO_2 emissions is to switch current fuels energy sources to nuclear power and/or to cleaner renewable energies such as wind, hydropower, biomass energy, photovoltaics, and solar powers. However, these alternatives suffer limitations compared with traditional energy. Nuclear insecurity is a challenge for nuclear power[11] while renewable energies suffer the limitations that they are still not large quantities of power, not cost-effective, and unreliable.[12,13] Unfortunately, fossil fuels have a combined share of 80% of world energy consumption in 2015 and will likely remain the main source of supply for enormous demand in the foreseeable future with 68% in 2050.[14,15]

In order to mitigate the CO_2 emissions from fossil fuel combustion, CO_2 capture and storage (CCS) technology have been proposed as a paramount option before a more environmentally sustainable energy infrastructure which can adapt the incremental energy requirement of the world is available. CCS is a portfolio process of separation of the CO_2 emissions from large point industrial sources, compression, and transportation to a storage site. This technology holds the promise of capturing up to 90% of the CO_2 emissions from large point emission sources, such as power stations, cement plants, and industrial sites.[16] The International Energy Agency has estimated the potential contribution of CCS in mitigation of climate change to achieve the 2 °C target to be about one-seventh of the total emissions in 2050.[17]

There are currently three primary CO_2 capture systems associated with how or where the carbon dioxide is removed. In the former, CO_2 is separated from H_2O (oxyfuel-combustion), H_2 (pre-combustion), and N_2 (post-combustion).[18–20]

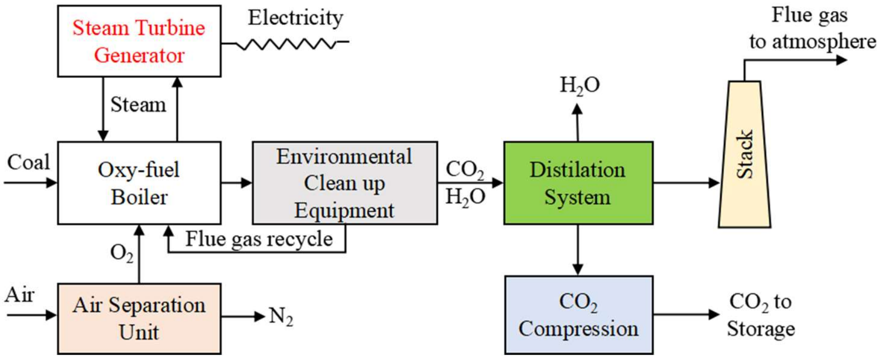

Figure 1.2. Diagram of oxy-combustion CO_2 capture from a coal-fired power plant.

In the oxyfuel combustion process, pure O_2 rather than air is used for the combustion of fuel (Figure 1.2). The major composition of the combustion is CO_2, water, particulates, and SO_2. Particulates and SO_2 can be removed by electrostatic precipitator and flue gas desulphurization methods, respectively, while H_2O is condensed using cryogenic distillation.

The incondensable CO_2 rich gas-stream (80–98%)[18] is obtained and can be compressed, transported, and stored.

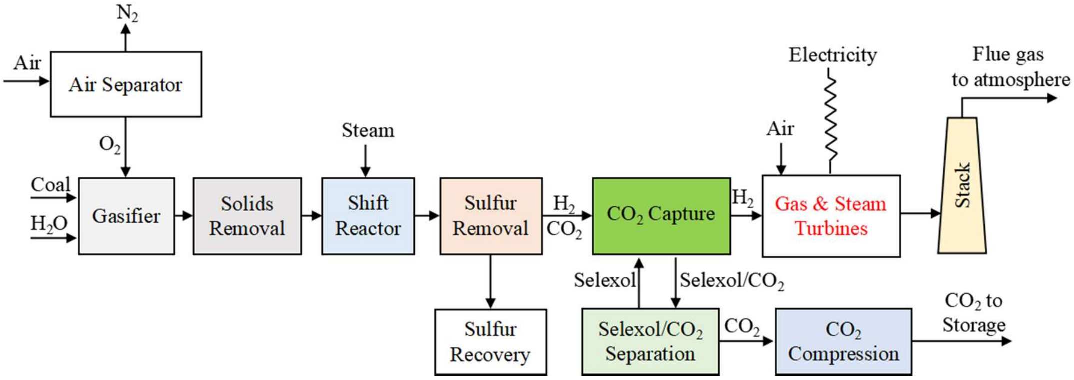

Figure 1.3. Diagram of pre-combustion CO_2 capture from an integrated gasification combined cycle power plant.

In pre-combustion capture, CO_2 is separated from fossil fuel (normally coal or natural gas) before combustion (Figure 1.3). It firstly converts the fossil fuel into synthesis gas ($CO+H_2$) then transforms CO to CO_2 via reaction with steam. The high CO_2 concentration (>20%) in the H_2/CO_2 fuel gas mixture can be captured and separated.[21] Subsequently, H_2 is sent to the turbine to be combusted producing mainly N_2 and water vapor.

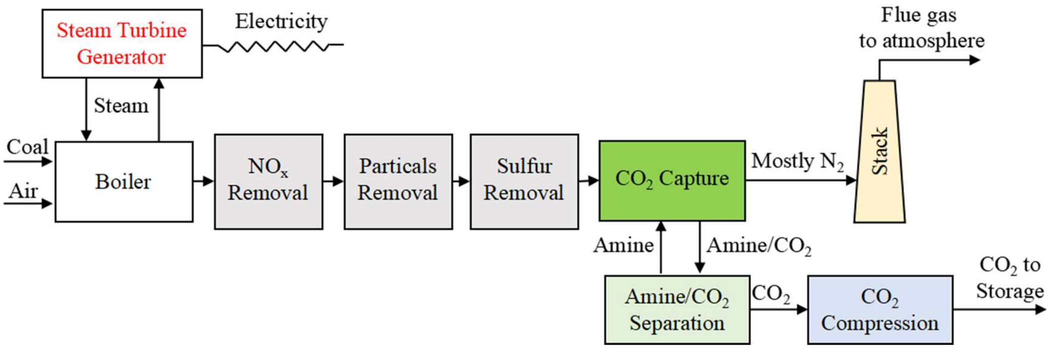

Figure 1.4. Diagram of post-combustion CO_2 capture in a coal-fired power plant using an amine scrubber system.

In post-combustion capture, CO_2 is separated from combustion exhaust gases using a liquid solvent or other separation methods. Figure 1.4 shows the schematic picture of post-combustion capture process using an aqueous amine as a chemical solvent which typically captures 85 to 90% of CO_2.[18] Flue gases are normally emitted at close to atmospheric pressure with 3–15% CO_2, N_2, NO_x, SO_2, and particulates.[20] After being captured, CO_2 can be released from the CO_2-laden solvent by heating to form a high purity CO_2 stream which is then compressed and piped to a storage site. Post-combustion capture is considered to be a preferred option for retrofitting existing power plants.

1.3. CO_2 Capture with Amine Impregnated Solid Sorbents

Amine scrubbing using aqueous amine solutions is the current state-of-the-art technology for post-combustion CO_2 capture from industrial exhaust gases.[22,23] In this approach, CO_2 can be captured by aqueous amine solutions to form chemical compounds in which primary and secondary amines react with CO_2 in a 2:1 ratio to form carbamates while tertiary amines interact with CO_2 in a 1:1 ratio to form bicarbonates (eq. 1.1 and 1.2): [24,25]

$$2R^1R^2NH + CO_2 \rightleftarrows R^1R^2NCOO^- + R^1R^2NH_2^+ \tag{1.1}$$

$$R^1R^2R^3N + CO_2 + H_2O \rightleftarrows HCOO^- + R^1R^2R^3NH^+ \tag{1.2}$$

where R^1, R^2, R^3 represent H or alkyl groups.

Despite the several decades of optimization, this mature technology suffers from high regeneration cost because the use of water as a solvent consumes considerable energy through sensible heat, vapor losses, and endothermic reactions during the CO_2 desorption process.[26–28] As well as the extensive energy expenditure of the separation, this method has inherent problems including amine loss and equipment corrosion.[27,29,30]

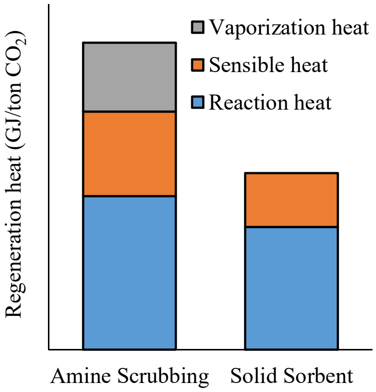

Figure 1.5. Comparison of regeneration energy the solid sorbent CO_2 capture system with the benchmark amine scrubbing system.

One approach to address these challenges is adsorptive separation by incorporating amine into porous solid support which merges the respective merits of both liquid and solid materials. Solid sorbents do not use water as a solvent in the adsorption column. Therefore, they can lower the energy consumption for regeneration.[29,31–34] The advantage in the regeneration energy of solid sorbents compared with amine scrubbing can be obviously seen in Figure 1.5.[34] Additionally, the volatilization of amines can be prevented by anchoring amines to porous support, thereby slowing the rate of equipment corrosion. Intensive research has developed solid sorbents using different types of porous support materials such as zeolite,[35] metal-organic frameworks (MOFs),[36] covalent organic frameworks (COFs),[37] porous carbon,[38] and silica-based supports.[39] Among such materials, amine impregnated mesoporous silicas (Figure 1.6) have especially fascinated as functional materials for CO_2 adsorption since such promising support has large pore volume and pore size that enable a high concentration of large molecule load into support.

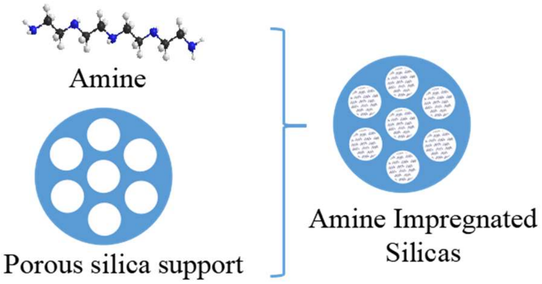

Figure 1.6. The concept of amine impregnated silicas.

Solid sorbents which are applicable in a large scale for CO_2 capture from coal-fired power plants should possess a minimum CO_2 adsorption capacity of 2.0 mmol per gram of sorbent to afford a performance comparable to the *benchmark* amine scrubbing.[40] As for a practical approach, with their relatively high boiling points, polyamines including polyethyleneimine (PEI) and tetraethylenepentamine (TEPA) are the most common commercial amines that have been impregnated into porous supports for CO_2 capture.[39,41–44] Ordered mesoporous silica materials with large-pore size such as MCM-41,[39] SAB-15,[45,46] KIT-6,[47] and mesostructured cellular silica foam MSU-F[48,49] are often designed as potential candidates for dispersing a higher number of amines into the pore channels.

Xu et al.[39] fabricated as-synthesized MCM-41 with PEI, and reported the effects of PEI loading, temperature, and gas conditions on CO_2 adsorption capacity of the as-made sorbents. The CO_2 adsorption capacity increased together with a higher PEI loading. MCM-41 impregnated with 75 wt% PEI exhibited the highest CO_2 adsorption capacity of 3.02 mmol/g under pure CO_2 at 75°C. The CO_2 adsorption capacity increased with the CO_2 concentration in the CO_2/N_2 gas mixture. Heydari-Gorji[50] described the effect of the mesoporous silica pore length on the CO_2 adsorption performance of PEI modified silica materials. In their work, the SBA-15 platelets with very shorter pore channels are preferable for PEI impregnation regarding capacity and adsorption rate. Son et al.[51] investigated the effects of textural properties of silica support on the CO_2 adsorption performance of PEI supported materials by using a wide range of mesoporous silica materials with different pore sizes and arrangement of including KIT-6, SBA-16, SBA-15, MCM-48, and MCM-41 as supports. The authors demonstrated that CO_2 adsorption capacity depended on the pore size of supports and varied in the order of KIT-6 > SBA-16 ≈ SBA-15 > MCM-48 > MCM-41. The corresponding between adsorption performance of sorbents and pore size of supports found in this work is in good consonance with those reported by other groups.[48,52,53] Yan et al.[52] impregnated PEI into several SBA-15 silicas with different structural properties and concluded that CO_2 adsorption capacity depended on the adsorption temperature and increased with the total pore volume of the SBA-15 substrate. They found that 50 wt% PEI impregnated the largest pore volume SBA-15 (114 cm^3/g) displayed the highest CO_2 capture capacity of 2.39 mmol/g at 75 °C. Han et al.[53] compared several PEI-impregnated hierarchically porous silica beads and interconnected 3-D macro-pore structures and concluded that millimeter-sized spherical silica foams (SSFs) which have the highest total pore volume among as-tested supports exhibited the highest CO_2 capacity of 4.28 mmol/g at 75 °C. The advantages of the larger pore size of support on the CO_2 capture performance of amine impregnated sorbents were also reported in the Dao's work.[48] This work compared several silica types with different pore size, and this parameter increases as follows: MCM-41 (2.1 nm) < HMS (18.1 nm) < Al-MSU-F (20.2 nm) < MSU-F (28.0 nm). After impregnated with 70 wt% TEPA, the CO_2 adsorption capacities at 40 °C and at 100 kPa of these sorbents followed in the range of MCM-41 (2.53 mmol/g) < HMS (3.53 mmol/g) < Al-MSU-F (3.83 mmol/g) < MSU-F (4.17 mmol/g). Jiao et al.[54] synthesized a three-dimensional worm-hole framework structured mesoporous silica MSU-J that was then impregnated with TEPA, diethylenetriamine, and triethylenetetramine. The highest adsorption capacity of 3.73 mmol/g was achieved for the MSU-J material containing 50 wt% TEPA under 100 kPa of pure CO_2 at 25 °C. Liu et al.[47] studied CO_2 capture using KIT-6 type mesoporous silica impregnated with TEPA. The KIT-6 material containing 60 wt% TEPA displayed the highest CO_2 adsorption capacity of 3.10 mmol/g under 10% CO_2 in N_2 at 60 °C.

The improvement of CO_2 adsorption is considered as a preferred way needed to lower the price of CO_2 capture. In the literature, many studies have been made efforts to improve the CO_2 capture performance of amine-based sorbents.[48,49,55–57] Xu et al.[55] reported that the addition of polyethylene glycol (PEG) as an additive into the PEI impregnated MCM-41 adsorbent improved not only the CO_2 adsorption capacity but also the rates of CO_2 adsorption/desorption. MCM-41 containing a mixture of 30 wt% PEI and 20 wt% PEG displayed a CO_2 capture capacity of 1.75 mmol/g at 75 °C and 100 kPa CO_2 which is higher than that of MCM-41 containing 30 wt% PEI only (1.56 mmol/g). Chuang group[56] further investigated the role of PEG in the TEPA/SiO_2 systems. PEG was found to decrease the CO_2 adsorption capacity, yet improve the cyclic stability and the adsorption half-time relative to adsorption rate. Yogo group[48,49] devoted to improving the CO_2 adsorption capacity of amine-impregnated MSU-F by blending TEPA with other organic compounds. Compounds containing hydroxyl groups such as diethanolamine (DEA), 3-(diethylamino)-1,2-propanediol (DEAP), aminoethylethanolamine (AEEA), and triethanolamine (TEA) improved CO_2 adsorption, while those without hydroxyl groups—such as PEI, 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), and piperazine (PZ)—negatively influenced CO_2 adsorption performance. They stated two main reasons that may explain the positive effect of hydroxyl groups. First, hydroxyl groups can act as Brønsted bases that facilitate carbamate formation by accepting protons (eq. 1.3):

$$R^1R^2\mathrm{NH} + \mathrm{CO_2} + \mathrm{B} \rightleftarrows R^1R^2\mathrm{NCOO^-} + \mathrm{BH^+} \qquad (1.3)$$

Secondly, hydroxyl groups favor to stabilize the carbamate anion through hydrogen bonding (eq. 1.4):

$$R^1R^2\mathrm{NCOO^-} + \mathrm{HOR^3} \rightleftarrows R^1R^2\mathrm{NCOO^-}\cdots\cdots\mathrm{HOR^3} \qquad (1.4)$$

Wang et al.[57] reported the positive effect of 2-amino-2-methyl-L-propanol (AMP) on the CO_2 adsorption performance and amine efficiency of TEPA/MCM-41 composites. The literature amine-impregnated silica adsorbents using various amines and supports as described above are given in Table 1.1.

Table 1.1. The most common -related amine-impregnated silicas used for CO_2 adsorption from literature.

Amine	Amine loading (%)	Support	Adsorption capacity (mmol/g)	CO_2 (%)	Temperature (°C)	Method	Ref
PEI	75	MCM-41	3.02	100	75	TGA	[39]
PEI	50	MCM-41	2.52	100	75	TGA	[39]
PEI	55	SBA-15	3.09	10	75	TGA	[50]
PEI	50	MCM-41	2.52	100	75	TGA	[51]
PEI	50	MCM-48	2.70	100	75	TGA	[51]
PEI	50	SBA-15	2.89	100	75	TGA	[51]
PEI	50	SBA-16	2.93	100	75	TGA	[51]
PEI	50	KIT-6	3.07	100	75	TGA	[51]
PEI	50	SBA-15	2.39	15	75	GC-TCD	[52]
PEI	60	SSFs	4.28	100	60	TGA	[53]
TEPA	50	MSU-J	3.73	100	25	As made CO_2 adsorber	[54]
TEPA	30	KIT-6	2.20	10	60	GC	[47]
TEPA	50	KIT-6	2.90	10	60	GC	[47]
TEPA	60	KIT-6	3.10	10	60	GC	[47]

Table 1.1. Continued.

Amine	Amine loading (%)	Support	Adsorption capacity (mmol/g)	CO_2 (%)	Temperature (°C)	Method	Ref
TEPA	70	MCM-41	2.53	100	40	Volumetric method	48
TEPA	70	HMS	3.53	100	40	Volumetric method	48
TEPA	70	Al-MSU-F	3.83	100	40	Volumetric method	48
TEPA	70	MSU-F	4.17	100	40	Volumetric method	48
TEPA	40	MSU-F	3.13	100	40	Volumetric method	48
TEPA/DEA	40/30	MSU-F	5.62	100	40	Volumetric method	48
TEPA/DEAP	40/30	MSU-F	5.13	100	40	Volumetric method	48
TEPA/TEA	40/30	MSU-F	4.89	100	40	Volumetric method	48
TEPA/AEEA	40/30	MSU-F	5.93	100	60	Volumetric method	49
PEI/PEG	30/20	MCM-41	1.75	100	75	TGA	55
PEI	30	MCM-41	1.56	100	75	TGA	55
TEPA/AMP	30/30	MCM-41	3.01	15	70	GC	57
TEPA	60	MCM-41	2.45	15	70	GC	57

Amine functionalized materials benefit from high CO_2 adsorption capacity and selectivity because of the specific CO_2-amine chemistry and have many desirable properties for CO_2 capture such as low volatility and low specific heat.[29,31,33,39,48,49] However, amine degradation also becomes a challenge for such materials, resulting in losses in CO_2 capture ability as well as a lifetime of sorbents. Additionally, the products of degradation processes may relate to health and environmental impacts. Amine impregnated materials are widely known to degrade via three main types of degradation that shorten the lifetime of materials: thermal degradation (e.g., evaporation and decomposition),[44,58,59] CO_2-induced degradation,[58,60,61] and chemical degradation induced by impurities gas species such as O_2,[1,8,11] SO_2,[1,5] and NO_x[1] presence in the flue gas (Table 1.2). Among these species, O_2 is the most pervasive component in flue gas and has been identified as the driving force for the oxidative degradation of amine-containing sorbents, shortening the sorbents lifetime.[6,14,15] More and more attention in the literature has been paid to the CO_2-induced degradation as well as the oxidative degradation caused by O_2 in the flue gas of PEI and TEPA containing materials. Sayari group[60,62] evaluated the CO_2-induced stability and oxidative stability of silica SBA-15 containing branched PEI (BPEI, $M_n \sim 600$) with linear PEI (LPEI, $M_n \sim 2500$). These adsorbents rapidly deactivated in a CO_2-rich atmosphere via the formation of urea. After 30 temperature swing adsorption cycles at 50/130 °C, LPEI deactivated readily, showing 50% CO_2 adsorption capacity loss versus 76% for BPEI. They also reported that such materials underwent oxidative degradation processes in the pure dry air at 80-120 °C. However, LPEI was more resistant to O_2 than BPEI. The deactivated species contained C=O and -CH=N- species supported by ^{1}D and ^{2}D techniques of NMR such as ^{13}C, ^1H-^{15}N HMBC, ^1H-^{13}C HMQC and ^1H-^{13}C HMBC. Another report of Sayari group[58] showed oxidative degradation of the silica SBA-15 impregnated with BPEI ($M_n \sim 600$) in the carbon-free air, simulated flue gas, and in the different $CO_2/O_2/N_2$ mixture at 100 °C for 30 h. These materials exhibited fast degradation on carbon-free air even at moderate temperatures and high stability in the presence of humidified gases containing both CO_2 and O_2. The negative effect of carbon-free air was associated with the formation of an IR band at 1665-1680 cm^{-1} consistent with the occurrence of C=O species. Bali et al[63] evaluated the oxidative stability of BPEI ($M_n \sim 800$) and polyallylamine (PAA) modified γ-alumina in the presence of 5% and 21% dry O_2 at 70 and 110 °C using Fourier transform-infrared spectroscopy (FT-IR), FT-Ranman, and ^{13}C solid-state NMR spectroscopies. They found that secondary-amine free, a primary-amine-rich polymer like PAA is stable while PEI is sensitive to oxidation. The oxidative degradation of BPEI based sorbents was consistent with the formation of carbonyl species which may come from amide, acids, or imides. In the later work, Pang[64] et al. compared the stability of LPEI and linear polypropyleneimine (PPI)/SBA-15 composites after the exposure to 21% O_2, 110 °C for 24 h. The PPI/SBA-15 composite was found to be more resistant to oxidative degradation than PEI, as supported by FTIR studies. Chuang groups[56,65,66] investigated the degradation of TEPA and PEG supported on silicas using various techniques: diffuse reflectance FT-IR spectroscopy and mass spectrometry, and solid-state magic-angle spinning (MAS) ^{13}C NMR spectroscopy. The degradation of TEPA supported silicas after 30 cycles of adsorption/desorption of CO_2 in an inert environment was found to correlate with the development of carboxylate/carbamic species.[56] The oxidatively degraded TEPA silica composites contain amide and imide species.[65,66] They also found that the addition of PEG to the sorbent slowed down the degradation rate of the sorbents.

Table 1.2. Typical composition of flue gas.

Unit (%)	CO_2	N_2	O_2	H_2O	NO_x	SO_x	Ar
Coal-fired	12-16	75-80	2-4	10-15	400 ppm	150 ppm	0.82
Gas-fired	3-5	70-75	10-12	7-10	<50 ppm	<10 ppm	0.89

Despite these efforts, the stability of amine impregnated materials in the O_2-containing environment is still a vague concept. In the light of the oxidative degradation of polyamines containing materials, several questions arise: What would be the detailed picture of the oxidative degradation? Are there any tools to inhibit the oxidative stability of new amine? To develop an effective sorbent for the practical applications, therefore, it is crucial to understand and mitigate oxidative degradation of amine in CO_2 capture systems.

Oxidation of amines occurs by a radical chain mechanism that is similar to the proposed mechanism for hydrocarbon oxidation. The hydrocarbon oxidation process involves free radical initiation, propagation, and termination processes.[67–69] In the initiation stage, a free radical is formed from a hydrocarbon molecule by abstraction of a hydrogen atom in the presence of a reactive species ($X^\bullet$) (eq. 1.5), dissolved transition metal ions (eq. 1.6), or excitation sources such as ultraviolet (UV) light or heat (eq. 1.7).

$$RH + X^\bullet \rightarrow R^\bullet + XH \quad (1.5)$$

$$RH + M^{n+1} \rightarrow R^\bullet + H^+ + M^n \quad (1.6)$$

$$RH \xrightarrow{E} R^\bullet + H^\bullet \quad (1.7)$$

Further reactions include free radical propagation and formation of hydroperoxides, which also decompose to form free radicals (eq. 1.8–1.10):

$$R^\bullet + O_2 \rightarrow ROO^\bullet \quad (1.8)$$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet \quad (1.9)$$

$$ROOH \rightarrow RO^\bullet + OH^\bullet \quad (1.10)$$

A compound that prevents formation of radicals can be considered to be an oxidation inhibitor. Therefore, oxidative degradation of amines can probably be controlled by blending such compounds with sorbents. A radical scavenger can be added to a sorbent to react with free radicals in the above reaction mechanism. A chelating agent can also be used as an additive to bind with the dissolved transition metals and prevent them from participating in the reaction.[70] Another way of inhibiting oxidative degradation is to add peroxide decomposers that promote decomposition of organic hydroperoxide to form stable products. In addition, UV light absorbents can be used to prevent formation of radicals.

Based on the literature review discussion, CO_2 capture behavior and stability of sorbent are crucial parameters for the scale-up purpose to enable applications of CCS. CO_2 capture performance can be improved by blending amine with organic compounds which play as proton acceptors to facilitate carbamate formation. Oxidative stability of sorbent can probably be improved by blending additives that can prevent the formation of radicals into the sorbent. Therefore, understanding the mechanism of oxidative degradation as well as finding antioxidant additives play important roles in the development of effective adsorbents for CO_2 capture.

1.4. Research Objective

This dissertation has devoted to the development of novel amine solid sorbent to overcome the challenges stated above including CO_2 adsorption performance as well as oxidative degradation of amine. Blending amine with additives into porous support is used as an approach to improve the CO_2 adsorption performance and the stability of amine solid sorbents. The following tasks are set in this work:

- ➢ Preparation of high-performance CO_2 adsorbent using a wet impregnation method.
    - Synthesis of amine solid sorbents by blending the mixture of amines with imidazoles (Ims) into the mesoporous silica
    - Evaluation and clarification of the role of Ims agents on CO_2 adsorption performance
    - Characterization of produced materials using CO_2 adsorption measurement, N_2 physisorption porosimetry, and thermogravimetry (TG), and differential scanning calorimeter (DSC) analyses
- ➢ Investigation of the stability of amine solid sorbents in O_2-containing environments.
    - Designation of a suitable reactor for oxidative degradation experiments

  - Evaluation of the effect of amine concentration and operating oxidation conditions on degradation of amine solid sorbents
  - Clarification of the changes in the composition of sorbent during the oxidative degradation
  - Characterization of materials using CO_2 adsorption measurements, elemental analyses, N_2 physisorption porosimetry, TG analyses, diffuse reflectance Fourier-transform infrared spectroscopy, and gas chromatography

- Preparation of adsorbent with high oxidative stability
  - Synthesis of effective amine solid sorbents by blending the mixture of amines and various inhibitor-candidates including hydrogen-donating antioxidants and sulfur-containing compounds into the mesoporous silica
  - Evaluation and clarification of the role of inhibitor-candidates in the amine solid sorbent systems.
  - Characterization of materials using CO_2 adsorption-desorption measurements, N_2 physisorption porosimetry, and elemental analyses.

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Chapter 2. Improve the CO_2 Adsorption Performance of Amine Solid Sorbents for CO_2 Capture Using Tetraethylenepentamine/Imidazoles Binary

This chapter describes the development of new binary amines impregnated mesostructured cellular silica foam (MF) for CO_2 removal from industrial exhaust streams. The mixture of tetraethylenepentamine (TEPA) and imidazoles (Ims) are impregnated MF to improve the adsorption-desorption characteristics. The mechanism of the synergistic effect between blended binary mixtures of amines is investigated and discussed in detail. The sorbent developed by impregnating the mixture of TEPA and 4-methylimidazole (4MIm) shows an excellent CO_2 adsorption capacity, high working capacity, and low heat of adsorption.

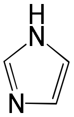
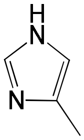
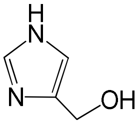
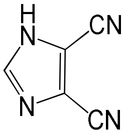
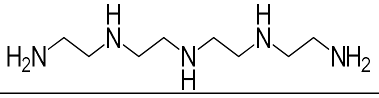
Parts of this chapter are reproduced from “Quyen T. Vu, Hidetaka Yamada, and Katsunori Yogo. Exploring the Role of Imidazoles in Amine-Impregnated Mesoporous Silica for CO_2 Capture. *Ind. Eng. Chem. Res.* 2018, 57, 2638–2644.”

2.1. Introduction

As described in Chapter 1, CO_2 adsorption using amine-impregnated materials has attracted great attention because of their simple preparation procedure, high CO_2 adsorption performance, carrying out fast CO_2 uptake/regeneration, and being tolerant to moisture.[1] MF material, with its large pore volume and pore size, has been reported as a promising support owing to its high amine-loading and CO_2 adsorption capacities.[2] TEPA has a high boiling point and shows good CO_2 adsorption performance and, therefore, is one of the most common commercial amines that has been impregnated into mesoporous silica.[2–6] Jiao et al.[3] reported that the MSU-J silica material containing 50 wt% TEPA showed the highest adsorption capacity of 3.73 mmol/g under 100 kPa of pure CO_2 at 25 °C. The impregnation of MF supports with 30–80 wt% TEPA was investigated by Dao et al.[2] There, MF with a pore volume of 1.54 cm^3/g was blended with 80 wt% TEPA yielding a CO_2 adsorption capacity of 4.36 mmol/g under conditions of 40 °C and 100 kPa. The same work also investigated the CO_2 adsorption capacity of amine-impregnated MF with TEPA blended with organic compounds. Compounds containing hydroxyl groups were found to improve CO_2 adsorption performance due to the accepting proton ability of hydroxyl groups and the structural interaction of blended amines.

Ims are basic aromatic ring compounds with high boiling points and good stability against oxidizing and reducing agents. Recently, Shannon et al.[7] reported that alkylimidazole was an efficient, low-volatility solvent for CO_2 separation that offered a high CO_2-absorption capacity. The same work also reported that 1-n-butylimidazole (1BIm) exhibited a synergistic effect with monoethanolamine (MEA) during CO_2 absorption. A mixture of neat MEA and neat 1BIm (of the approximate mass ratio of 1:4) showed a capacity of 0.73 mol CO_2/mol MEA, 45% higher than the theoretical CO_2-absorption capacity of MEA in a non-aqueous solvent, based on a MEA:CO_2 stoichiometry of 2:1. The authors proposed that 1BIm takes part in the CO_2-absorption reaction as a Brønsted base via a proton-transfer mechanism.

Table 2.1. The structures and p*Ka** values of the employed amines in this chapter.

Compound	Molecular structure	p*Ka*
Im		6.99[8]
4MIm		7.54[8]
4HMIm		6.54[9]
DCIm		5.2[10]
TEPA		9.64[11]

**Ka* is the acid dissociation constant of the protonated amine. The more positive the value of p*Ka* the higher the Bronsted basicity of amine.

This chapter describes how MF was impregnated with a series of amine-containing compounds to investigate the effects of Ims on the CO_2 adsorption performance of solid sorbents, also investigating blending ratios and adsorption temperature. The following commercial amines, which have high boiling points and low volatilities, were selected for this study: TEPA, Im, 4(5)-methylimidazole (4MIm), 4(5)-(hydroxymethyl)imidazole (4HMIm), and 4,5-dicyanoimidazole (DCIm). The structures and p*Ka*s of these amines are shown in Table 2.1. The materials are characterized by N_2 physisorption measurements, thermogravimetric analysis (TGA), CO_2 adsorption-desorption measurements, and Fourier-transform infrared (FT-IR) spectroscopy. The results show that Ims containing electron-donating groups showed a synergistic effect with TEPA regarding adsorption/desorption performance. Impregnating MF with such Ims and TEPA increased CO_2 adsorption performance and decreased the heat of adsorption compared with those obtained for MF impregnated only with TEPA. The mechanism of the synergistic effect between Ims and TEPA is discussed in detail. Further, the stability of adsorbents during a long time of storage is also investigated and discussed in this chapter.

2.2. Experimental Section

2.2.1. Materials.

MF (product name: silica, mesostructured, MSU-F (cellular foam); product number: 560979) was purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). TEPA (95%; Wako

Pure Chemical Industries Co., Tokyo, Japan), Im (98%; Wako), 4MIm (97%; Wako), 4HMIm (97%; Sigma–Aldrich), and DCIm (98%; Tokyo Chemical Industry Co., Tokyo, Japan) were purchased and used without any further purification. Methanol (99.8%; Wako) was used as the solvent for the preparation of the solid sorbents. He (99.9999%) and N_2 (99.9999%) gases were supplied by Iwatani Co. (Osaka, Japan). CO_2 (99.995%) gas was purchased from Sumitomo Seika Chemicals Co. (Osaka, Japan).

2.2.2. Preparation of solid sorbents.

Amine-modified sorbents were prepared by the wet impregnation method. This first involved adding a specific mixture of silica support and amine compounds to methanol. The solvent was then completely removed in a rotary evaporator. The as-made sorbents were denoted as Imx-TEPAy/MF where x and y represent the weight percentages of Im and TEPA loading, respectively.

2.2.3. Materials characterization.

N_2-physisorption isotherms were observed at −196.15 °C using an ASAP 2420 automatic adsorption system (Micromeritics Instrument Co., Norcross, GA, USA). The specific surface area (S_{BET}) and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda methods,[12,13] respectively. S_{BET} was evaluated from adsorption data in the relative pressure range of 0.05 to 0.3. The total pore volume was calculated from the amount of adsorbed N_2 at $P/P_o = 0.97$. Before the adsorption-desorption analysis, solid sorbents were degasified at 40 °C by flowing N_2 for 6 h to remove water and CO_2. Thermogravimetric (TG) curves were obtained using a Thermo Plus TG–DTA 8120 apparatus (Rigaku Co., Tokyo, Japan). The samples were heated to 1000 °C at a constant rate of 5 °C /min under a He atmosphere at a gas flow rate of 300 mL/min. The FT-IR spectra were collected using a Prestige-21FT-IR spectrometer (Shimadzu, Tokyo, Japan) with 4 cm^{-1} resolution at room temperature.

2.2.4. CO_2 adsorption studies.

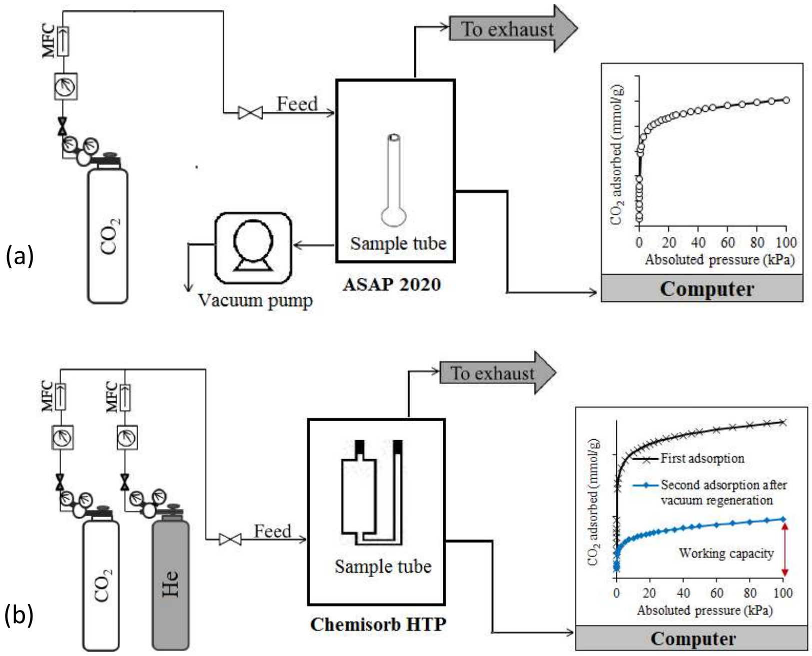


Figure 2.1. (a) ASAP 2020 and (b) Chemisorb systems used for the measurement of CO_2 adsorption isotherm.

CO_2 adsorption isotherms at temperatures in the range 20–80 °C were measured using an ASAP 2020 (Micromeritics Instrument Co.) or a ChemiSorb HTP chemical adsorption analyzer (Micromeritics Instrument Co.) for pressures ranging from 2.4 Pa to 100 kPa. These apparatus systems were shown in Figure 2.1. Prior to the CO_2 adsorption analysis, water and CO_2 were outgassed by flowing He or vacuuming for 6 h at the adsorption temperature. After the first adsorption process, the solid sorbents were regenerated by decreasing the pressure to

1.3 Pa for 20 min. The second adsorption process was then conducted under the same adsorption conditions to evaluate the working capacity following vacuum regeneration.

Cyclic adsorption test was conducted at 50 °C in 5 adsorption-desorption cycles by an integrated TG and differential scanning calorimeter (DSC) instrument STA 449 F5 Jupiter (Netzsch Co., Selb, Germany), as shown in Figure 2.2. About 20–50 mg of the sorbent was loaded into an aluminium pan, and pretreated at 80 °C for 6 h under N_2 at a flow of 50 cm^3/min for removing pre-adsorbed gases. The sample was then cooled to 50 °C, and CO_2 was passed over the sorbent for 2 h. Subsequently, the sorbent was regenerated for 2 h at 100 °C under N_2 flow, and then same adsorption-desorption procedures were repeated to evaluate the cyclic stability of the sorbent. A blank control measurement for baseline correction was performed using an empty aluminum crucible under the same conditions.

The heat of adsorption was monitored by a TG-DSC STA 449 F5 Jupiter (Netzsch). Here, approximately 20–50 mg of the amine-impregnated MF was pretreated at 80 °C for 6 h under N_2 at a flow rate of 50 cm^3/min. The material was then cooled to 40 °C before pure CO_2 was passed over the sample at 50 cm^3/min for 2 h under atmospheric pressure. A blank control measurement for baseline correction was performed using an empty aluminum crucible under the same conditions. The TGA–DSC curves resulted from the notable mass increase and heat release caused by CO_2 adsorption. The heat of adsorption was then determined based on the measured value of the heat released and the CO_2 adsorption capacity.

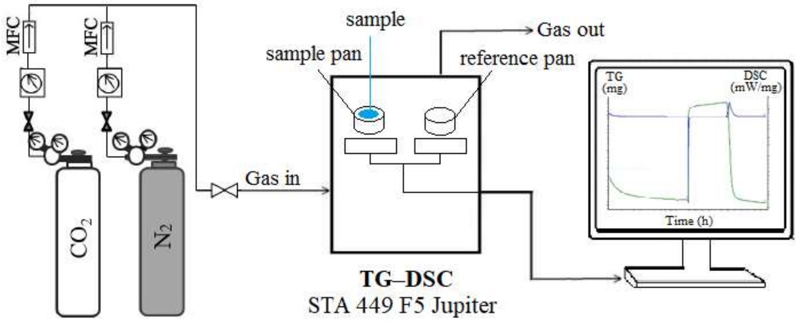


Figure 2.2. TG–DSC system used for the determination of heat of adsorption.

2.3. Results and Discussion

2.3.1. Materials characterization.

The textural parameters of the MF support and the as-made adsorbents were measured by N_2 adsorption-desorption analysis. Introducing 70 wt% amine into MF dramatically decreased the BET surface from 448.05 to 6.23 m^2/g and the pore volume from 1.95 to 0.01 cm^3/g, suggesting that the pores of the silica support were almost completely filled by amine. From the MF pore volume (1.95 cm^3/g) and the amine density (ca. 1 g/cm^3), the maximum amine loading per g of MF was estimated to be 1.95 g, which corresponded to nearly 70 wt% amine in the adsorbent.

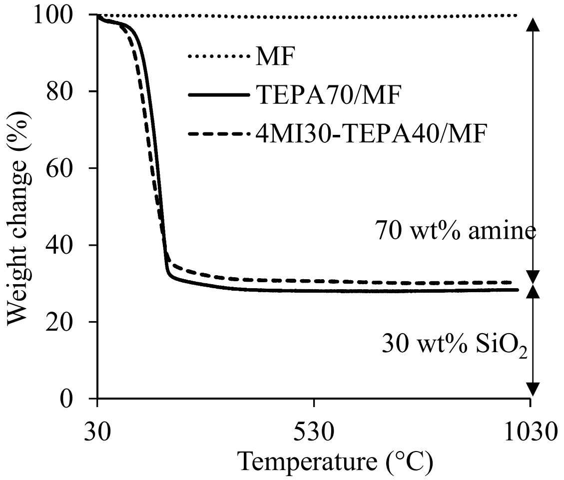


Figure 2.3. TG profiles of pure MF and MF impregnated with 70 wt% amine (TEPA70 and 4MIm30-TEPA40).

The thermal stability of the adsorbents was investigated by TG analysis. Figure 2.3 illustrates the relationship between temperature and mass loss for some typical samples. Between 25 and 1000 °C, the MF support exhibited excellent thermal stability with no obvious mass loss. Conversely, mass losses of 0.3%–4.7% were witnessed for amine-impregnated mesoporous silica below 100 °C, probably owing to losses associated with adsorbed water, CO_2, or residual methanol. The total-mass-loss results for MF, TEPA70/MF, and 4MIm30-TEPA40/MF were 0.2%, 71.7%, and 69.8%, respectively. These TG observations also provided clear evidence that the selected amines were successfully blended into the MF support.

2.3.2. Synergies between Ims and TEPA for CO_2 adsorption.

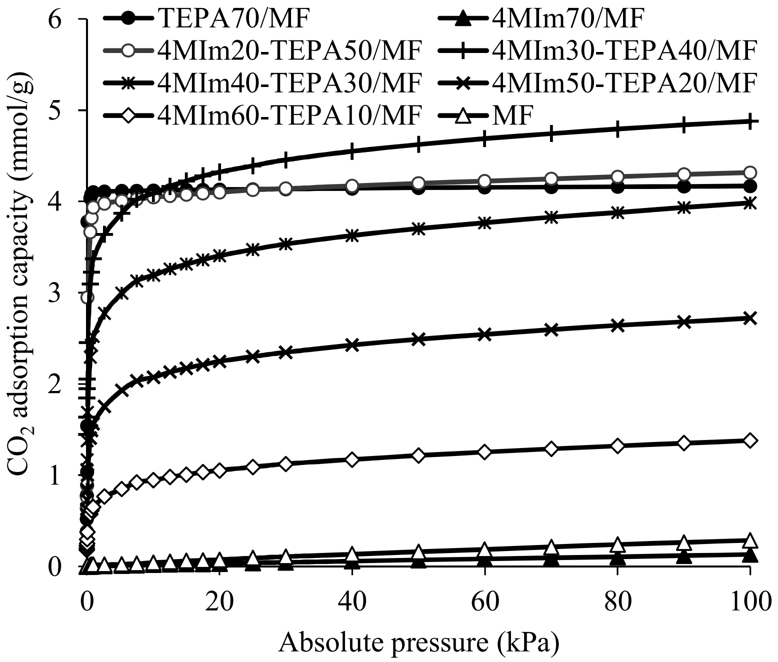


Figure 2.4. CO_2 adsorption isotherms for 4MIm*x*-TEPA*y*/MF adsorbents at 40 ºC.

CO_2 adsorption isotherms for 4MIm*x*-TEPA*y*/MF adsorbents at 40 ºC are shown in Figure 2.4. On the basis of the discussion in the previous section, the amount of 4MIm and TEPA in the adsorbents was maintained at 70 wt%. Under conditions of 40 °C and 100 kPa, CO_2 adsorption capacities of 1.38, 2.72, 3.98, 4.88, and 4.32 mmol/g were achieved for 4MIm60-TEPA10/MF, 4MIm50-TEPA20/MF, 4MIm40-TEPA30/MF, 4MIm30-TEPA40/MF, and 4MIm20-TEPA50/MF, respectively. At these conditions, the amount of CO_2 adsorbed by TEPA70/MF (4.17 mmol/g) was lower than those observed for 4MIm30-TEPA40/MF and 4MIm20-TEPA50/MF. The CO_2 adsorption capacity of 4MIm70/MF was 0.13 mmol/g at 100 kPa and 40 °C, which was slightly less than the CO_2 uptake on the mesoporous MF support, indicating that 4MIm exhibited no reactivity towards CO_2 at these conditions. This was similar to that found by Geoppert et al.[14] who reported that the silica support HI-SIL T-600 containing

50 wt% Im exhibited a low CO_2 uptake of approximately 0.2 mmol/g under ambient conditions. It is well known that primary and secondary amines react with CO_2[15–17] while tertiary amines are unable to absorb CO_2 without water also being present.[1,15] 4MIm, with low basicity (p*Ka* = 7.54),[8] was a poor scavenger of CO_2 despite possessing a secondary amine, which may be because of the delocalization of the nitrogen's unpaired electrons into the ring.

Figure 2.5 compares the CO_2 adsorption capacity of TEPA*y*/MF with that of 4MIm*x*-TEPA*y*/MF at 40 °C and 100 kPa. Although 4MIm is not a good CO_2 scavenger, the CO_2 adsorption capacities of 4MIm*x*-TEPA*y*/MF were consistently higher than those of TEPA*y*/MF, clearly demonstrating 4MIm's positive influence on the CO_2 adsorption performance. Here, the possibility of 4MIm-carbamate formation followed by the deprotonation from NH of 4MIm with the protonation of TEPA is considered because the anionic form of Ims is more reactive to CO_2.[18–20] However, compared with the p*Ka* value of 9.64[11] for TEPA, that for the deprotonation of 4MIm is substantially high (>14.4).[21] Thus, 4MIm hardly reacts with CO_2 to form carbamate even in the presence of TEPA.

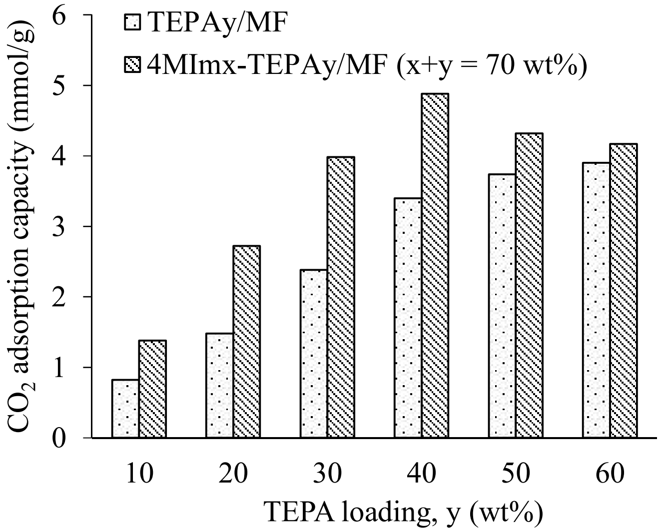


Figure 2.5. CO_2 adsorption capacity for TEPA*y*/MF and 4MIm*x*-TEPA*y*/MF at 40 °C and 100 kPa.

The inability of 4MIm to absorb CO_2 indicated that it contains no available amino group for CO_2 absorption. I, therefore, defined the amine efficiency of solid sorbents consisting of a mixture of TEPA and 4MIm as the molar ratio of adsorbed CO_2 per TEPA amino group. The change in the amine efficiency of the adsorbents can be easily seen in the results shown in Table 2.2.

Table 2.2. CO_2 adsorption capacity and amine efficiency of different adsorbents at 40 ºC and 100 kPa CO_2.

Material	CO_2 adsorption capacity (mmol/g)	amine efficiency[a] (mol CO_2/mol N of TEPA)
MF	0.29	-
TEPA10/MF	0.82	0.30
TEPA20/MF	1.48	0.29
TEPA30/MF	2.38	0.34
TEPA40/MF	3.40	0.32
TEPA50/MF	3.74	0.30
TEPA60/MF	3.90	0.25
TEPA70/MF	4.17	0.24
4MIm10-TEPA60/MF	4.17	0.26
4MIm20-TEPA50/MF	4.32	0.33
4MIm30-TEPA40/MF	4.88	0.46
4MIm40-TEPA30/MF	3.98	0.50
4MIm50-TEPA20/MF	2.72	0.51
4MIm60-TEPA10/MF	1.38	0.52
4MIm70/MF	0.13	-

[a] N content of TEPA was calculated based on the wt% of TEPA in the sorbent and assuming that TEPA's molecular weight was 189.3 g/mol.

The CO_2 adsorption capacity of MF impregnated with only TEPA at 40 °C and 100 kPa increased with TEPA loading. However, the amine efficiency of these adsorbents was less than or equal to 0.34. This is in agreement with work describing the amine efficiency of polyamines, including polyethyleneimine and TEPA.[2,11,14] Blending 4MIm with TEPA dramatically increased the amine efficiency, reaching more than 0.5 for 4MIm*x*-TEPA*y*/MF; the theoretical limit for formation of carbamate anions.[15–17] Such a high efficiency suggests a partial contribution from physical CO_2 capture, in addition to that from the chemical reaction between TEPA and CO_2.

To further my understanding, Im and Im derivatives with different functional groups (4MIm, 4HMIm, and DCIm) were selected to study their influence on the sorbents' CO_2 adsorption behavior. Similar to 4MIm, all the selected Ims70/MF exhibited a lower CO_2 adsorption capacity than MF support at 40 °C (Figure 2.6).

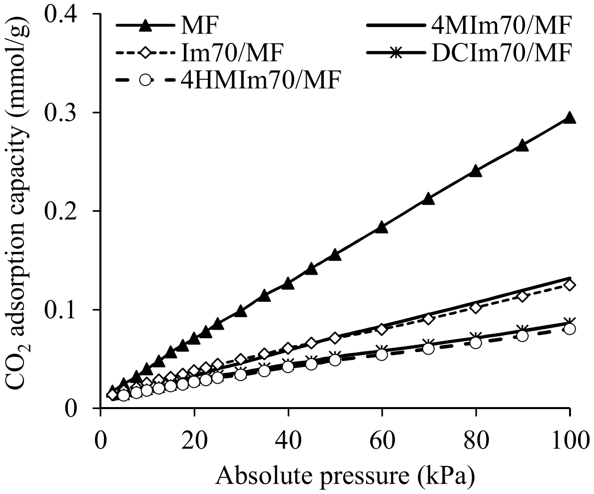


Figure 2.6. CO_2 adsorption capacity at 40 °C for Ims70/MF.

Figure 2.7 shows the CO_2 adsorption capacity at 40 °C for MF loaded with a mixture of 40 wt% TEPA and 30 wt% of the selected Im species. The results show that at 40 °C and 100 kPa the CO_2 adsorption capacities of Im30-TEPA40/MF and 4MIm30-TEPA40/MF were 4.90 and 4.88 mmol/g, respectively. These values were greater than the 3.40 and 4.17 mmol/g observed for TEPA40/MF and TEPA70/MF, respectively. Contrastingly, low CO_2 adsorption values were observed for DCIm30-TEPA40/MF and 4HMIm30-TEPA40/MF; 0.58 and 1.64 mmol/g, respectively. These results can be explained partly by the Brønsted basicity of Ims (see Table 2.1). In addition, the possibility of deprotonation from NH of Ims should be considered. The p*Ka* values for the deprotonation of Im is still high (14.4[21]) compared with the p*Ka* value for the protonation of TEPA. Thus, the deprotonation of Im in the presence of TEPA can be ignored as is the case with 4MIm. On the other hand, such acid-base reactions might occur in the DCIm–TEPA and/or 4HMIm–TEPA system. However, it still remains unclear in this work.

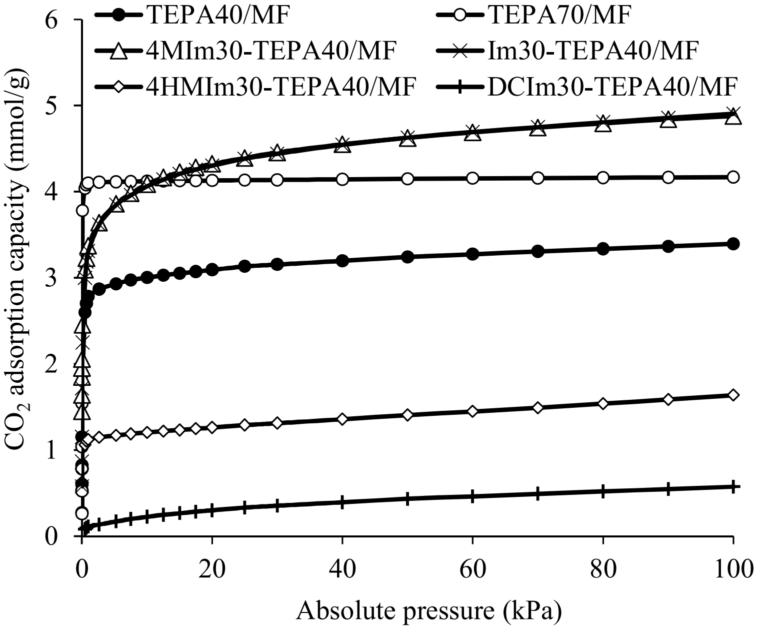


Figure 2.7. CO_2 adsorption capacity at 40 °C for Im species containing electron-donating and electron-withdrawing groups.

These results confirmed that adsorbents containing Im species with electron-withdrawing groups in combination with TEPA have a lower CO_2 adsorption capacity than those with electron-donating groups, which exhibit a synergistic effect with TEPA. The behavior of 4MIm in this study is coherent with that reported by Shannon et al.[7] who noted a synergistic effect between 1BIm and MEA for CO_2 absorption capacity.

2.3.3. Mechanism of the synergistic effect.

It is known that carbamates may be formed by a reaction between a primary/secondary amine and CO_2 in the absence of water.[15–17] The proposed reaction mechanism is as follows (eq. 2.1 and 2.2):

$$R^1R^2NH + CO_2 \rightleftarrows R^1R^2NH^+COO^- \quad (2.1)$$

$$R^1R^2NH^+COO^- + R^1R^2NH \rightleftarrows R^1R^2NCOO^- + R^1R^2NH_2^+ \quad (2.2)$$

where R^1 and R^2 represent H or alkyl groups. The overall reaction is represented by equation (2.3):

$$2R^1R^2NH + CO_2 \rightleftarrows R^1R^2NCOO^- + R^1R^2NH_2^+ \tag{2.3}$$

First, the amine reacts with CO_2 to form a zwitterion, which then reacts with another amine to form the carbamate. Overall, one CO_2 molecule reacts with two amino groups, hence a maximum amine efficiency of 0.5.

It is also well known that stable ion pairs of carbamate anions and protonated amino cations form as soon as CO_2 is loaded onto amine sorbents. The strong electrostatic interactions between these ions may prevent the diffusion of CO_2 to the inner amine layer,[22] resulting in a decrease the number of amino sites active in CO_2 uptake, and an amine efficiency of less than 0.5 for TEPA-modified systems. By adding the Ims with an electron-donating group into TEPA impregnated MF, both the CO_2 adsorption capacity and the amine efficiency were dramatically improved. This may be because some Ims can act as a proton acceptor in the amine-modified system. Similar to that proposed by Shannon et al.[7] for 1BIm and MEA in liquid amine systems, the mechanism is as follows (eq. 2.4):

$$R^1R^2NH + CO_2 + Ims \rightleftarrows R^1R^2NCOO^- + ImsH^+ \tag{2.4}$$

Here, only one amino group is consumed per CO_2 molecule. This improves the CO_2 adsorption capacity of the system and its amine efficiency.

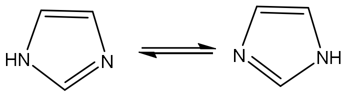
The above mechanism is based on Im compounds' ability to accept protons. Thus, this mechanism strongly depends on the basicity of these components: a component with a higher basicity is a better proton acceptor. Adding electron-donating groups to Im increased its basicity whereas electron-withdrawing groups decreased it. Therefore, unlike the positive effect observed for electron-donating groups, adding electron-withdrawing groups to Im, as observed for DCIm and 4HMIm experiments, caused a decrease in the CO_2 adsorption capacity, as shown in Figure 2.7.

The mechanism described in equation (2.4) is proposed not only for Ims, but for Brønsted bases, such as amino groups, that facilitate carbamate formation by accepting protons. [2,11,23] An amine with a higher basicity should be more likely to accept a proton, thus promoting CO_2 adsorption. However, although piperazine (PZ) and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) are more basic than Im (Table 2.3), their addition decreased the CO_2 adsorption capacity.[2] At 40 °C and 100 kPa, the CO_2 adsorption capacities of DBU30-TEPA40/MF, PZ30-TEPA40/MF, TEPA70, and Im30-TEPA40/MF were 3.61, 3.73, 4.17, and 4.90 respectively. Therefore, the basicity of components alone does not explain the synergistic effect between Ims and TEPA on CO_2 adsorption and another role of Ims in the amine-modified systems should be considered.

Table 2.3. p*Ka* value of various compounds (X) and the associated CO_2 adsorption capacity of X30-TEPA40/MF at 40 °C and 100 kPa.

Compound X	p*Ka*	CO_2 adsorption capacity (mmol/g)
TEPA	9.64[11]	4.17
Im	6.99[8]	4.90
PZ	9.73[24]	3.73
DBU	12[25]	3.61

As seen in equations (2.1)–(2.3), one CO_2 molecule consumes two amino groups with one acting as a proton acceptor and the other forming a carbamate anion. Therefore, the CO_2 adsorption capacity of amine-impregnated supports depends on the diffusion of CO_2 and protons to active amino sites. If protons can be transported to the inner amine layer, the outer amine layer will be more likely to react with CO_2 to form carbamate anions, as schematically illustrated in Figure 2.8. Such a process can occur because Ims tautomerize rapidly in solution, as shown in equation (2.5), and protonated Ims are stabilized by electron delocalization.[26]



(2.5)

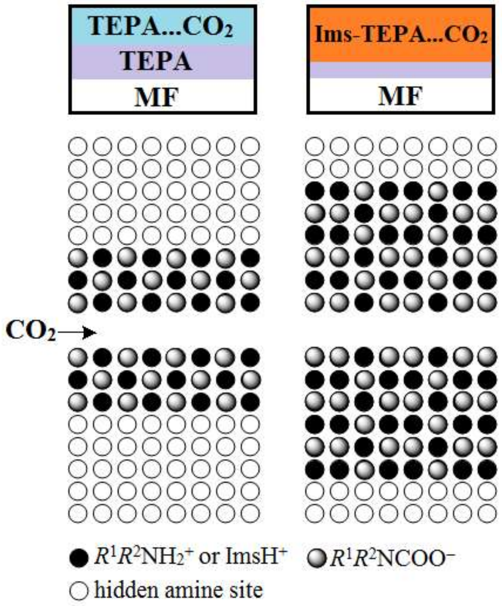


Figure 2.8. Schematic illustration of CO_2 adsorption on MF impregnated with TEPA, and with a mixture of Ims-TEPA.

These species form hydrogen-bond networks that provide a means for proton transfer.[27–29] The ability of Im species to act as a proton shuttle may promote proton diffusion and could have led to the higher CO_2 adsorption capacity in the amine-blended system.

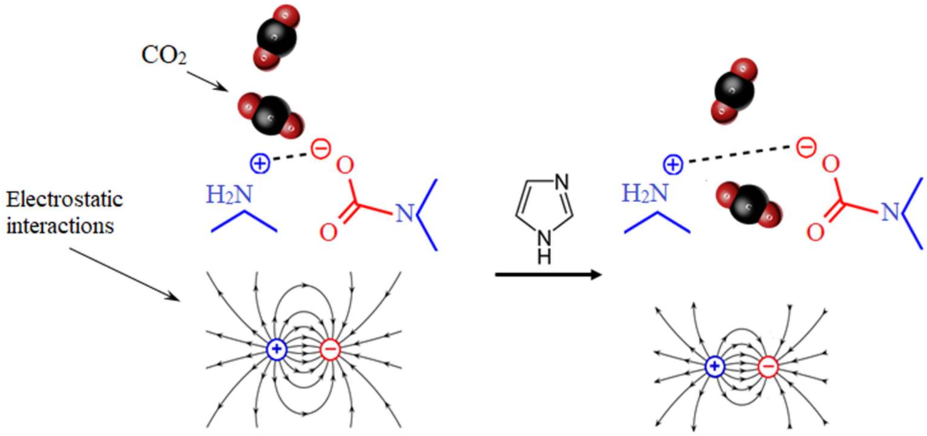


Figure 2.9. Scheme illustration of effect of Im on the electrostatic interactions between carbamate anions and protonated amino cations.

Moreover, as discussed above, the strong electrostatic interactions between carbamate anions and protonated amino cations prevent the diffusion of CO_2 to the inner amine layer. When Ims are introduced between the carbamate anions and the protonated amino cations, the electrostatic interactions will be weakened creating space for CO_2 diffusion to occur, as shown in Figure 2.9. This may partly explain the synergistic effect between Ims and TEPA on CO_2 adsorption.

2.3.4. Effect of adsorption temperature.

The adsorption temperature is a critical parameter for practical CO_2 adsorption applications. The relationship between the adsorption temperature and the CO_2 adsorption capacity of 4MIm30-TEPA40/MF was investigated across the temperature range of 20–80 °C, and is shown in Figure 2.10.

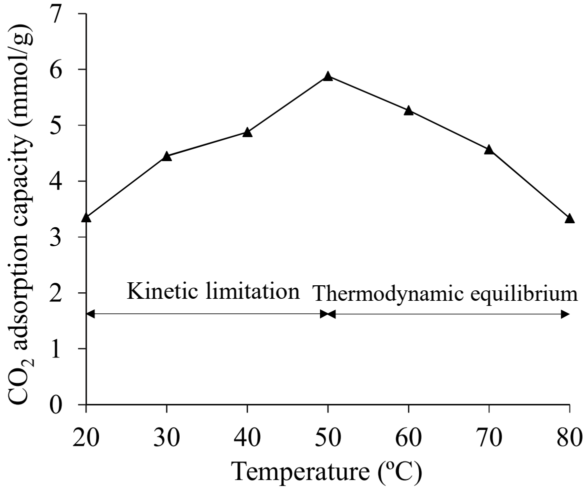


Figure 2.10. Influence of temperature on the CO_2 adsorption performance of 4MIm30-TEPA40/MF at 100 kPa.

CO_2 adsorption is an exothermic process[30] and is strongly affected by the adsorption temperature. Meanwhile, it is necessary to consider that CO_2 must diffuse from the surface into the inner channel of the mesoporous sorbents to encounter sub-surface reactive sites.[31] The influence of temperature, therefore, involves assessing its impact on both diffusion and thermodynamics. The impacts are illustrated in Figure 2.10 using 4MIm30-TEPA40/MF as an example. There, increasing the temperature from 20 to 50 °C caused the adsorption capacity to gradually increase from 3.35 to 5.88 mmol/g. In contrast, further increasing the temperature from 50 to 80 °C caused the adsorption capacity to steadily decline from 5.88 to 3.34 mmol/g.

At 100 kPa, the maximum CO_2 adsorption capacity for 4MIm30-TEPA40/MF was therefore observed to be 5.88 mmol/g at 50 °C. In the 20–50 °C region, diffusion was the rate-limiting step and increasing the temperature exposed more CO_2 to reactive sites, bringing about the improved adsorption capacity. However, increasing the temperature in the 50–80 °C region favored the reverse reaction and shifted the chemical equilibrium to yield a decline in capacity. This decline might also have been affected by the amines' volatility.

2.3.5. Regenerability.

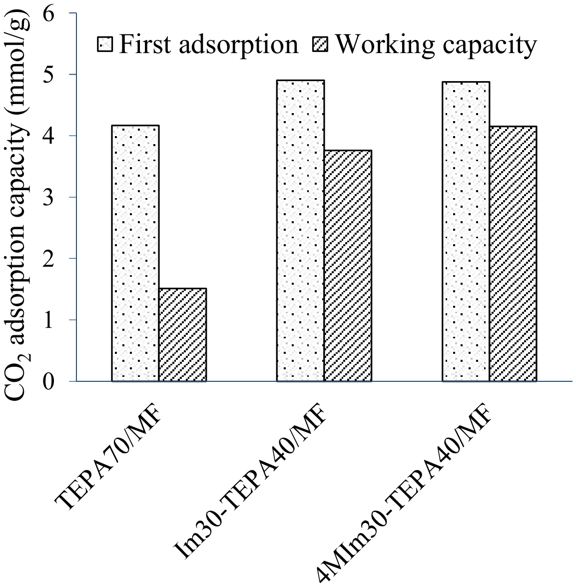


Figure 2.11. First-pass and working capacity of Ims30-TEPA40/MF and TEPA70/MF at 40 °C and 100 kPa.

Figure 2.11 shows the first-pass and working CO_2 adsorption capacities in pure CO_2 at 100 kPa and 40 °C for sorbents containing a mixture of Ims and TEPA. TEPA70/MF exhibited a lower working capacity than the solid sorbents that were modified with a mixture of Ims and TEPA. Despite TEPA70/MF exhibiting a relatively high CO_2 adsorption capacity of 4.17 mmol/g during the first adsorption cycle, this fell to 1.51 mmol/g (36% of the initial value) in the second adsorption cycle. This low regeneration capacity was ascribed to stable carbamate formation.[2,32] Following vacuum treatment, 4MIm30-TEPA40/MF and Im30-TEPA40/MF showed much higher regenerative capacities and achieved 93% and 77% of their initial uptakes, respectively, further confirming the benefit of adding Ims to TEPA for CO_2 adsorption performance.

Figure 2.12 shows the cyclic adsorption behavior of 4MIm30-TEPA40/MF in pure CO_2 at 50 °C and at atmospheric pressure in 5 cycles. The sorbent exhibited a very high stable adsorption performance. Particularly, the adsorption capacity of the sorbent lost 5% from 5.88 to 5.57 mmol/g, indicating that 4MIm30-TEPA40/MF possessed durable cyclic adsorption-desorption properties over 5 cycles. These results confirm that 4MIm30-TEPA40/MF is a promising candidate for practical applications.

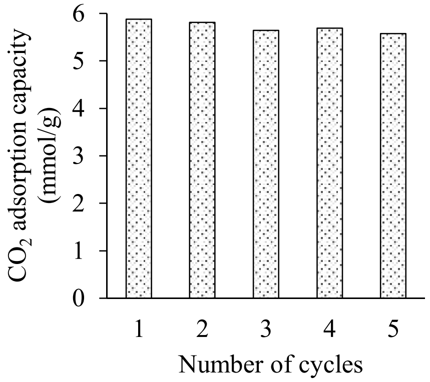


Figure 2.12. Adsorption-desorption cycles for 4MIm30-TEPA40/MF sorbent at 50 °C and atmospheric pressure.

The process' heat of adsorption is associated with the energy required for sorbent regeneration and CO_2 release. The heat of adsorption observed in this study was similar to those obtained for other amine sorbents.[31–33] Compared with TEPA70/MF, Im30-TEPA40/MF and 4MIm30-TEPA40 exhibited higher CO_2 adsorption capacities but lower heats of adsorption (71 and 69 kJ/mol, respectively, compared to 83 kJ/mol). This indicated that using Ims in amine-modified systems could benefit practical applications in terms of decreasing energy consumption during the regeneration step.

2.3.6. Stability.

Further experimental works were developed to investigate the stability of amine solid sorbents during long time storage. About 3 g of the adsorbents was stored in a Laboran screw vial capacity of 20 mL with the dimensions (mm) of 14.5 (inner caliber) × 27 (shell diameter) × 55 (high) in the dark at ambient temperature for 28 months. The stability of the adsorbents was assessed by the CO_2 capture ability. The CO_2 adsorption isotherms of typical sorbents after 7 and 28 months storage are shown in Figure 2.13. The CO_2 capture ability of sorbents continuously reduced with the time of storage. After 7 months of storage, 4MIm30-TEPA40/MF captured 4.31 mmol CO_2 per gram of sorbent at 100 kPa and 40 °C which corresponds with 88 % of the original one. The CO_2 capture ability of this sorbent reduced 2.5 times after 28 months storage with CO_2 adsorption capacity of 1.98 mmol/g at 100 kPa and 40 °C. The degradation of sorbents may be caused by O_2, NO_x, CO_2, SO_2, H_2O, and other impurities available in the sorbents when keeping sorbents in the Laboran Screw vials. It is recommended that the degradation of solid amine sorbents in the presence of flue gas contaminants at higher temperature should be further investigated.

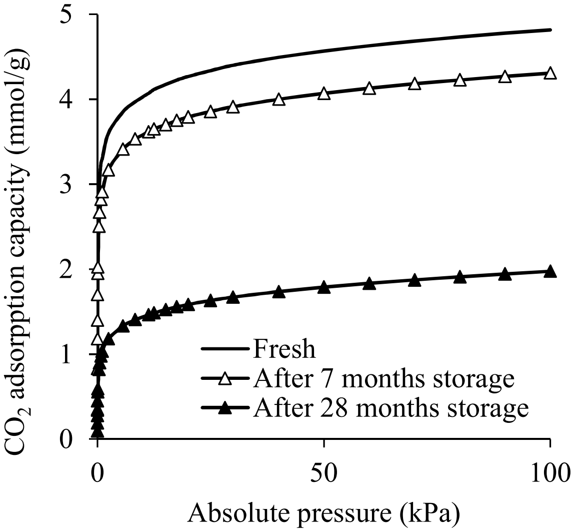


Figure 2.13. CO_2 adsorption isotherms for 4MIm30-TEPA40/MF before and after 7-28 months storage at room conditions.

The decrease in the CO_2 adsorption capacity of sorbents paralleled with the increase in absorbance intensity of a band at 1670 cm^{-1} which often be reported for induced amine solid sorbent (Figure 2.14).[36–42]

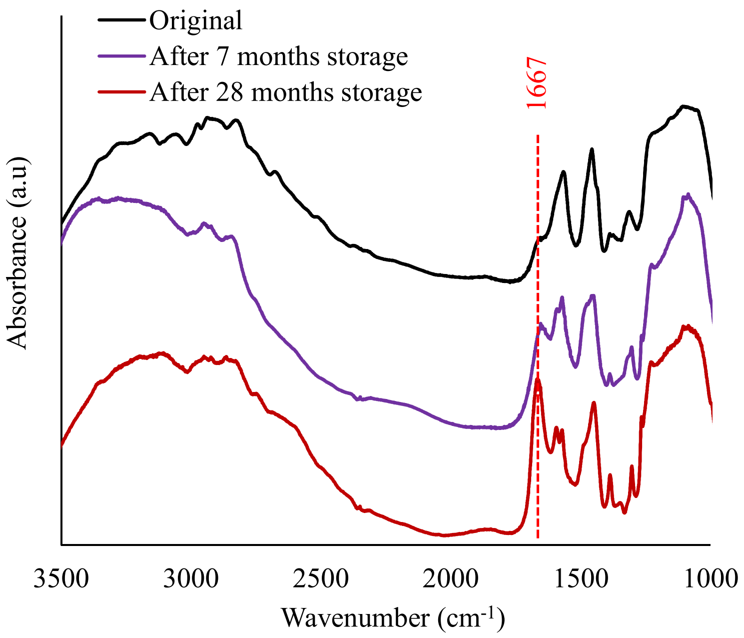


Figure 2.14. FI-IR spectra for 4MIm30-TEPA40/MF before and after 7-28 months storage at room conditions.

2.4. Conclusion

Adding Ims containing electron-donating groups to TEPA synergistically improved the CO_2 adsorption capacity, amine efficiency, working capacity, and regeneration energy requirement of sorbents. Positive interactions between Ims and the amino group may have been caused by Ims' proton-acceptor ability and improvements in the diffusion of protons and CO_2 to sub-surface reactive sites. A mesostructured cellular silica foam impregnated with 30% 4MIm and 40% TEPA was the best performing of the tested sorbents for CO_2 adsorption. This sorbent exhibited a high adsorption capacity (4.88 mmol/g) and working capacity (4.15 mmol/g) under conditions of 40 °C and 100 kPa CO_2, and low heat of adsorption (69 kJ/mol) under conditions of 40 °C and atmospheric pressure. A maximum CO_2 uptake of 5.88 mmol/g with this sorbent was observed under conditions of 50 °C and 100 kPa CO_2. However, after long time storage, the sorbents were degraded, resulting in a decrease in the CO_2 capture ability of sorbents. Degradation of amine solid sorbents will be further investigated and discussed in chapter 3.

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Chapter 3. Oxidative Degradation of Tetraethylenepentamine-Impregnated Silica Sorbents for CO_2 Capture

This chapter focused on the stability of amine impregnated solid sorbent in the O_2-containing environment for CO_2 removal from industrial exhaust streams. Effects of amine loading and operating condition of the oxidation are investigated. The changes in the composition of sorbents containing commercial tetraethylenepentamine during oxidative degradation and further insight into the oxidative degradation processes are also invesigated and discussed in detail.

Parts of this chapter are reproduced from: "Quyen T. Vu, Hidetaka Yamada, Katsunori Yogo. Oxidative Degradation of Tetraethylenepentamine-Impregnated Silica Sorbents for CO_2 Capture. *Energy Fuels* 2019 33, 3370–3379."

3.1. Introduction

As mentioned in Chapter 1, the durability of amine sites, which have to maintain their structure under practical operating conditions, is important for the development of an effective amine solid sorbent. With their relatively high boiling points, polyethyleneimine (PEI) and tetraethylenepentamine (TEPA) are the most common commercial amines that have been impregnated into porous supports for CO_2 capture.[1–5] The stability of amine solid materials can be affected by both physical and chemical conditions, leading to thermal degradation (e.g., evaporation and decomposition)[5–7] and chemical degradation induced by gas species such as O_2,[1,8,9] SO_2,[1,5] and NO_x.[1] The degradation mechanism also depends on the presence of CO_2.[6,10,11] Among these species, O_2 is the most pervasive component in flue gas and has been identified as the driving force for the oxidative degradation of amine-containing sorbents, shortening the lifetime of sorbents.[6,12,13] Calleja et al.[13] evaluated the exposure of amine-functionalized silicas to air at different temperatures and showed that the loss in CO_2 capture capacity of sorbent in atmospheric O_2 was accompanied by an increase in an infrared (IR) band at 1667 cm^{-1}. Jones group[9] studied the effect of O_2 (5% and 21%) on PEI and poly(allylamine) (PAA) supported materials at two temperatures using Fourier transform (FT)-IR, FT-Raman, and ^{13}C solid-state NMR spectroscopies. They found that secondary-amine free, a primary-amine-rich polymer like PAA is stable while PEI is sensitive to oxidation. Heydari-Gorji and Sayari[6] evaluated the behavior of PEI-impregnated SBA-15 silica in carbon-free air, simulated flue gas conditions, and different $CO_2/O_2/N_2$ mixtures at temperatures up to 120 °C. In their study, PEI-based materials degraded rapidly when exposed to carbon-free air at moderate temperatures. Furthermore, they noticed that the negative effect of carbon-free air was accompanied by the development of an infrared band at 1665–1680 cm^{-1}, which was associated with the formation of oxime and/or imine species. Tanthana et al.[14] investigated the degradation characteristics of silica-supported TEPA (TEPA/SiO_2) and polyethylene glycol (PEG)-

modified TEPA/SiO_2 (PEG/TEPA/SiO_2) using diffuse reflectance FT-IR spectroscopy and mass spectrometry. They reported that the degradation of TEPA/SiO_2 in 15 vol% CO_2, 4 vol% H_2O, and the balance air correlated with the accumulation of carboxylate/carbamic species. They also showed that the degradation rate of sorbent and the formation of carboxylate species were suppressed by addition of PEG to the sorbent. Srikanth et al.[15] studied the oxidative degradation of silica-supported amine sorbents with varying amounts of TEPA and PEG. They reported that TEPA generated a different type of amide under O_2 treatment. FT-IR and NMR spectroscopic studies showed that the yellowish color of degraded sorbents originated from the formation of imide species. They also found that the addition of PEG to the supported amine sorbents improved their oxidative degradation resistance and slowed down the color change. The hydrogen bonds between amine and hydroxyl (OH) groups could change the reactivity of the amines toward O_2 molecules and block O_2 from accessing TEPA to induce oxidation. The results in chapter 2 also show the degradation of sorbents which accompanied with an increase intensity of the absorbance band at 1667 cm^{-1} and a decrease in the CO_2 adsorption capacity.

However, the oxidative degradation of amine solid sorbents has still not been thoroughly investigated. Clearer understanding of the oxidative degradation process could contribute to the development of more effective sorbents. The effect of amine content on the oxidative degradation of amine solid sorbents and the changes in the amine composition of solid sorbents during oxidation have not been studied. To address this issue and to gain further insight into the oxidative degradation processes of amine solid sorbents, here the stability of mesostructured cellular silica foam (MF) impregnated with varying amounts of TEPA under a range of oxidation conditions including different oxidation durations, temperatures, and O_2 concentrations is comprehensively studied. To characterize the sorbents, CO_2 adsorption measurements, elemental analyses, N_2 physisorption measurements, diffuse reflectance FT-IR spectroscopy, and gas chromatography (GC) are carried out. The results demonstrate that the degradation of silica-supported amine sorbents strongly depends on the oxidative environment and amine content. The degradation of amine solid sorbents is related to the accumulation of C=O or C=N species. The OH groups of the MF support could contribute to the stability of sorbents in oxidative environments.

Further of this study is to investigate the change in the components of commercial TEPA-impregnated silica sorbents during the oxidative degradation. Commercial technical-grade TEPA is a mixture of four main ethyleneamine compounds with close boiling points including linear, branched, and two cyclic TEPA products (Figure 3.1): 1,4,7,10,13-pentaazatridecane (T-LIN), 4-(2-aminoethyl)-N-(2-aminoethyl)-N′-[2-[(2-aminoethyl)amino]ethyl]-1,2-ethanediamine (T-BRN), 1-(2-aminoethyl)-4-[(2-aminoethyl)amino]ethyl]piperazine (T-IPZ), and 1-[2-[[2-[(2-aminoethyl)amino]ethyl]-amino]ethyl]piperazine (T-EPZ). To the best of my knowledge, however, in almost all the literature on TEPA-containing materials for CO_2 capture, there is no mention about such components. Recently, Numaguchi et al.[16] first reported that these components were separated from crude TEPA by fractional distillation and then the molecular species of each fraction were identified. The experimental data reveals that the four main components of commercial TEPA show different stabilities depending on their molecular structure.

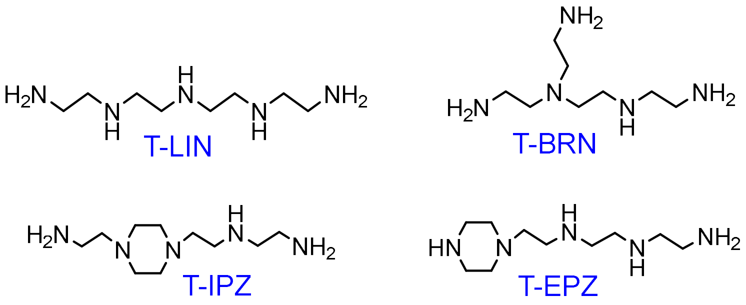


Figure 3.1. Structures of four main ethyleneamine compounds in the commercial technical-grade TEPA.

3.2. Experimental Section

3.2.1. Materials and synthesis.

MF powder was purchased from Sigma–Aldrich Co., St. Louis, MO, USA. TEPA and methanol were purchased from Wako Pure Chemical Industries Co., Tokyo, Japan and used without any further purification. He (99.9999%) and N_2 (99.9999%) were supplied by Iwatani Co. (Osaka, Japan). CO_2 (99.995%) and gas mixture (5% O_2/balance N_2) were purchased from Sumitomo Seika Chemicals Co., Osaka, Japan. O_2 (99.995%) and air (99.9%) were provided by Japan Fine Products Co., Tochigi, Japan.

The preparation of supported amines was described in previous chapter. A mixture of TEPA, methanol, and MF was agitated, and then the methanol was removed using a rotary evaporator. The resulting sorbents are denoted as TEPA*x*/MF, where *x* represents the weight percent of TEPA in the adsorbent. The TEPA loading used in this work was below 70 wt%, which is nearly the maximum allowable amine loading calculated from the density of TEPA (ca. 1 g/cm) and the pore volume of MF (1.95 cm^3/g).

3.2.2. Oxidative degradation of adsorbents.

The degradation of adsorbents was conducted in the packed bed reactor (PBR) illustrated in Figure 3.2.

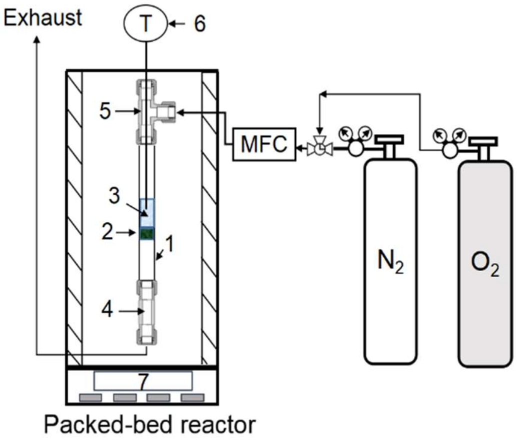


Figure 3.2. Schematic of the packed-bed reactor ((1) I-quartz tube; (2) silica wool; (3) adsorbent; (4) tube fitting union; (5) fitting tee union; (6) thermocouple; (7) oven with PID temperature controller).

In a typical experiment, a sorbent (0.3 g) was loaded into the PBR, which consisted of a quartz tube column with an inner diameter of 7.0 mm, outer diameter of 9.5 mm, and length of 14 cm. The temperature of the PBR was controlled by a proportional–integral–derivative (PID) temperature controller. N_2 was first flowed through the PBR (40 cm^3/min) at 100 °C for 1 h to remove the pre-adsorbed gases and moisture. Subsequently, the degradation step was performed at a temperature of 60 to 100 °C under flowing pure O_2/air/gas mixture (40 cm^3/min) for the time of interest (5 h, 18 h and 42 h). After exposing the sample to O_2 for the designated time, the sample was rapidly cooled to room temperature in flowing pure N_2 (40 cm^3/min). The degraded sample was then collected. To assess the thermal effect independently from that of O_2, the fresh sorbents were treated in N_2 (flow rate of 40 cm^3/min) at 100 °C for 19 h before being rapidly cooled to room temperature. The treated TEPA-impregnated MF samples are denoted as TEPA*x*/MF-gas (used in the degradation step)-temperature (°C)-time of oxidation (h). For example, TEPA50/MF-O_2-100-5 and TEPA50/MF-5%O_2-100-18 represent MF containing 50 wt% of TEPA exposed to pure O_2 at 100 °C for 5 h and MF containing 50 wt% of TEPA exposed to 5% O_2 at 100 °C for 18 h, respectively.

3.2.3. CO_2 adsorption studies.

Pure CO_2 adsorption isotherms for all fresh and degraded samples were monitored using a surface area and porosimetry measurement system (ASAP 2020, Micromeritics Instrument Co., Norcross, GA, USA) under pressures ranging from 2.4 Pa to 100 kPa. Prior to the measurements, samples (~100 mg) were pretreated to remove any moisture and pre-adsorbed gas under vacuum at 40 °C for 6 h. The degradation of each sample was evaluated by calculating its CO_2 adsorption capacity retention (%) from the adsorption isotherms measured before and after the degradation test.

3.2.4. Materials characterization.

All materials were characterized by N_2 physisorption isotherms measured at −196 °C on an ASAP 2420 automatic adsorption system (Micromeritics Instrument Co.). Before measurement, solid sorbents were degassed under vacuum at 40 °C for 6 h to remove water and pre-adsorbed gases. The specific surface area (S_{BET}) and pore size distribution of each sample were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda methods,[17,18] respectively. S_{BET} was evaluated from adsorption data in the relative pressure (P/P_o) range of 0.05 to 0.3. The total pore volume was determined from the amount of adsorbed N_2 at $P/P_o = 0.97$. The organic loading of each silica support was determined by TG analysis, which was conducted on a Thermo Plus TG-DTA 8120 analyzer (Rigaku, Tokyo, Japan). The samples were heated to 1000 °C at a rate of 5 °C/min under a He atmosphere.

3.2.5. Elemental analysis, FT-IR spectroscopy, and GC.

Elemental analyses were performed on a PerkinElmer 2400II CHNS/O instrument (Waltham, MA, USA).

The FT-IR spectra of original and degraded sorbents were collected using a Prestige-21 FT-IR spectrometer (Shimadzu, Tokyo, Japan) with 4 cm^{-1} resolution at room temperature.

For GC analyses, samples were extracted from solid sorbents by stirring them in ethanol (99.5%, 6 mL) for 18 h at room temperature. After filtration, the extracted samples were quantified by GC using a flame ionization detector (FID). Analyses were performed on a Shimadzu GC 2010 instrument with a split injector and FID. Compounds were separated on a Restek column Rtx-5-amine (30 m x 0.25 m i.d x 0.1 μm-thick film). The column temperature was 100 °C for 10 min, heated to 280 °C at a rate of 20 °C min^{-1}, and then held at 280 °C for 10 min. The total time was 29 min. The split injector was held at 250 °C with a split ratio of 50:1 at a flow rate of 3 mL/min. The FID temperature was maintained at 300 °C, and the injected volume was 1 μL. Ultrapure He (99.9999%, *Air Liquide Kogyo Gas* Ltd., Japan) was used as a carrier gas at a constant linear velocity of 30.0 cm/s. Samples were diluted with ultrapure ethanol depending on the amine content of the sorbent.

3.3. Results and Discussion

3.3.1. CO_2 adsorption behavior of adsorbents.

The stabilities of MF impregnated with varying amounts of TEPA from 10 to 70 wt% in the presence of pure O_2, air, or 5% O_2 for different times under different temperature conditions were assessed. To evaluate the stability of adsorbents against oxidative degradation, their CO_2 adsorption capacities were measured.

3.3.1.1. Effect of oxidation duration on sorbent performance.

The effect of oxidation duration on the stabilities of MF impregnated with varying amounts of TEPA is presented in Figure 3.3. Initial CO_2 adsorption capacities of 0.82, 2.38, 3.74, 3.99, and 4.17 mmol/g at 40 °C and 100 kPa were observed for MF impregnated with 10, 30, 50, 60, and 70 wt% of TEPA, respectively. The amine solid sorbents exhibited a dramatic decrease in CO_2 adsorption capacity under oxidative conditions and the degradation rate increased with oxidation duration. After 5 h of O_2 exposure, TEPA10/MF retained 95% of its original CO_2 adsorption capacity, whereas the adsorption capacities of TEPA30/MF, TEPA50/MF, TEPA60/MF, and TEPA70/MF decreased to 33%, 41%, 43%, and 32% of their initial values, respectively. After being treated in pure O_2 at 100 °C for 18 h, CO_2 adsorption capacities decreased by 13%, 88%, 95%, 95%, and 96% for TEPA10/MF, TEPA30/MF, TEPA50/MF, TEPA60/MF, and TEPA70/MF, respectively. Under these degradation conditions, MF loaded with 30–70 wt% TEPA exhibited CO_2 adsorption capacities of less than 0.28 mmol/g, which is the CO_2 adsorption capacity measured for the MF support (Table 3.1). This indicates that amino groups in these adsorbents were totally inactivated and could not capture CO_2. The degradation rate of amine solid sorbents depended on the amine loading. Among the sorbents, TEPA10/MF showed the highest stability toward O_2. After exposure to pure O_2 at 100 °C for

42 h, the CO_2 adsorption capacity of TEPA10/MF remained at 0.53 mmol/g (65% of its original capacity), whereas those of TEPA30–70/MF were less than 8% of their original capacities.

Table 3.1. Element contents and CO_2 uptakes of representative sorbents.

Sorbent	**C (%)**	**H (%)**	**N (%)**	**CO_2 adsorption capacity (mmol/g)**
MF	[a]	[a]	[a]	0.28
TEPA10/MF	6.25	1.50	3.81	0.82
TEPA10/MF-O_2-100-18	5.17	1.17	3.32	0.71
TEPA30/MF	15.12	3.74	9.90	2.38
TEPA30/MF-O_2-100-18	13.40	1.75	7.18	0.28
TEPA50/MF	26.55	6.47	17.55	3.74
TEPA50/MF-O_2-100-18	23.31	3.19	12.51	0.19
TEPA60/MF	30.48	7.30	22.22	3.99
TEPA60/MF-O_2-100-18	28.44	4.00	15.21	0.21
TEPA70/MF	35.53	8.51	25.91	4.17
TEPA70/MF-O_2-100-18	31.89	4.84	17.41	0.18

[a] Not measured.

Sanz-Pérez et al.[19] reported that the contribution of CO_2 physically adsorbed was significant in the adsorbent containing a low amount of amino groups. In the present results (Table 3.1), the CO_2 adsorption capacity of MF accounted for 34% of that of TEPA10/MF. This percentage dropped to 7–12% for TEPA30–70/MF. The high contribution of physisorption may partially explains why the TEPA10/MF showed the highest stability. However, assuming that the CO_2 physisorption of support remained in both fresh and degraded TEPA10/MF, a decrease in CO_2 chemisorption capacity can be calculated to be 20% after being treated in pure O_2 at 100 °C for 18 h, which is still the smallest among all the tested sorbents at the same conditions. The effect of amine concentration on the oxidative degradation of amine solid sorbents is discussed in detail later.

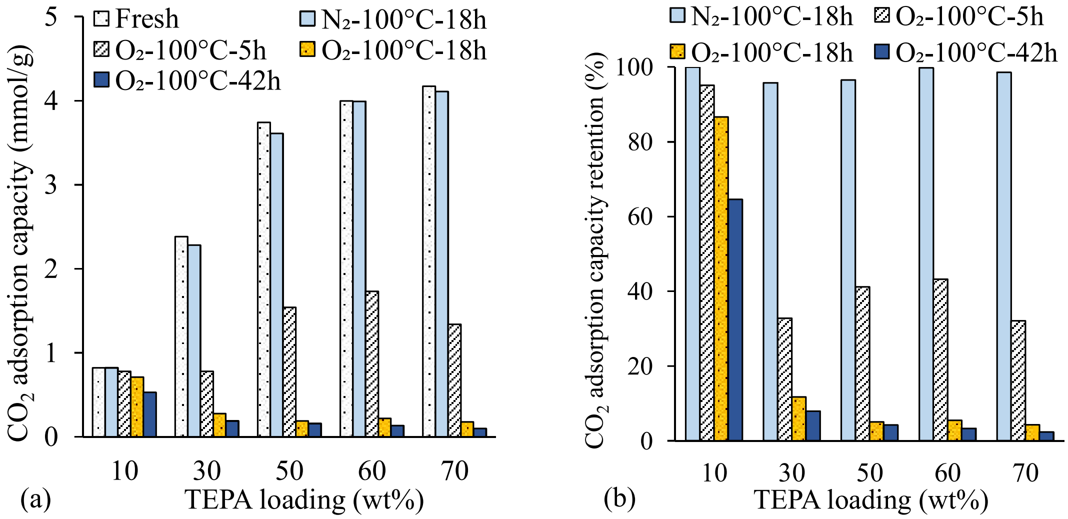


Figure 3.3. Effect of oxidation time on the CO_2 adsorption capacities of MF impregnated with 10 to 70 wt% of TEPA at 40 °C and 100 kPa: (a) absolute values and (b) capacity retention.

To evaluate the thermal effect independently from that of O_2, the sorbents were treated at 100 °C for 18 h in the presence of pure N_2. Figure 3.3 reveals that the CO_2 adsorption capacities of all sorbents remained above 96% of their original values when treated in pure N_2 at 100 °C for 18 h, indicating that these adsorbents displayed high thermal stability. Therefore, the decrease of the CO_2 uptake of sorbents caused by the thermal effect is negligible. This means that oxidative degradation was the main reason for the observed loss in CO_2 adsorption capacity of the amine solid sorbents under oxidizing conditions.

3.3.1.2. Effect of oxidation temperature on sorbent performance.

To investigate the effect of temperature on the oxidative degradation of amine solid sorbents, all sorbents were exposed to pure O_2 at a flow rate of 40 cc/min for 18 h in the temperature range from 60 to 100 °C. Figure 3.4 illustrates the temperature dependence of the CO_2 adsorption behavior of the sorbents during oxidation. The degree of deactivation of the amine solid sorbents increased with temperature. None of the amine solid sorbents were influenced by oxidative treatment at 60 °C, retaining above 98% of their original CO_2

adsorption capacities. However, with elevating temperature, the sorbents showed marked decreases in CO_2 adsorption capacities, which were caused by oxidative degradation rather than thermal degradation effects, as illustrated above. A small decrease of capacity during oxidative treatment was observed for TEPA10/MF. This sorbent retained 98% of its original CO_2 adsorption capacity after O_2 exposure at 80 °C for 18 h and 87% of its original uptake after O_2 exposure at 100 °C for 18 h. In contrast, TEPA30/MF, TEPA50/MF, TEPA60/MF, and TEPA70/MF decreased by 66%, 52%, 38%, and 43% of their initial CO_2 uptakes, respectively, after exposure to O_2 at 80 °C for 18 h. The CO_2 adsorption capacities of these samples decreased by more than 88% of their initial values after exposure to O_2 at 100 °C for 18 h.

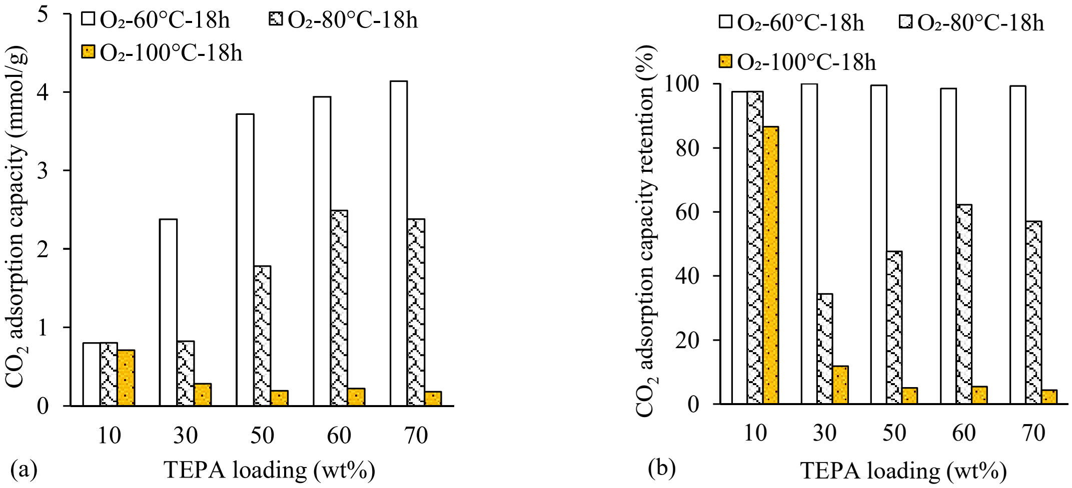


Figure 3.4. Effect of oxidation temperature on the CO_2 adsorption capacity of samples at 40 °C and 100 kPa: (a) absolute values and (b) capacity retention.

3.3.1.3. Effect of O_2 concentration on sorbent performance.

The effect of the O_2 concentration on the degradation rate of the sorbents was then investigated; the results are shown in Figure 3.5. 5% O_2, air, and pure O_2 exposure lowered the CO_2 capture ability of the sorbents. The decreases in the adsorption capacities of the adsorbents were associated with O_2 molecules inducing oxidation. As mentioned above, the CO_2 adsorption capacity of sorbents impregnated with 10, 30, 50, 60 and 70 wt% of TEPA in pure

O_2 at 100 °C for 18 h retained 87%, 12%, 5%, 5%, and 4% of their original CO_2 uptakes. The degradation proceeded slowly at the low concentrations of O_2. Treatment in air, which decreased the O_2 concentration by five times compared with that of O_2 treatment, lowered the degradation rate of these sorbents. Compared with treatment in pure O_2 under the same conditions, the degradation rates of samples containing 30–70 wt% of TEPA in air were decreased by 2–3 times. Specifically, TEPA10/MF, TEPA30/MF, TEPA50/MF, TEPA60/MF, and TEPA70/MF retained 87%, 21%, 15%, 15%, and 14% of their original adsorption capacities, respectively, after treatment in air. The corresponding values after treatment in 5% O_2 were even higher: 91%, 42%, 46%, 73%, and 61%, respectively. These results suggest that the oxidative degradation of TEPA-impregnated sorbents is difficult to avoid if O_2 is present in the feed gas.

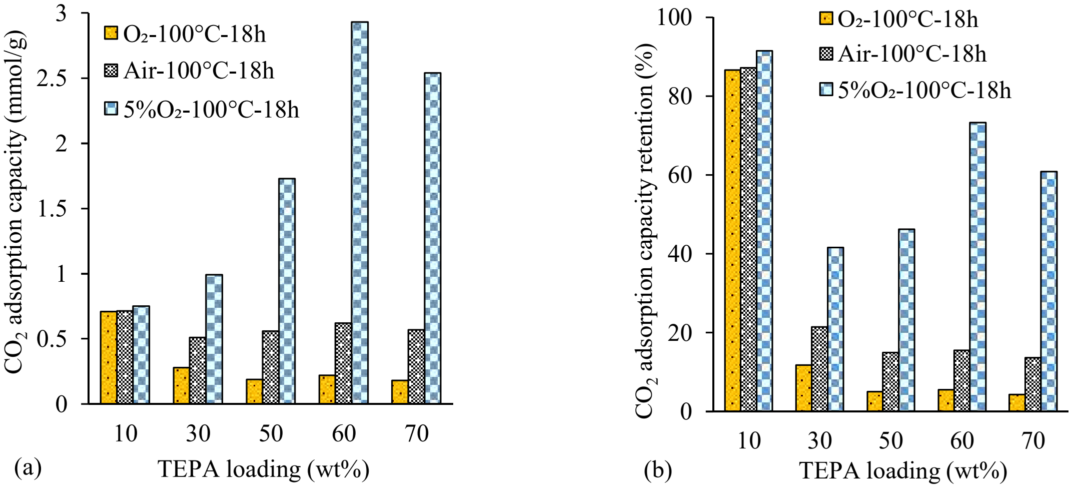


Figure 3.5. Effect of O_2 concentration on the CO_2 adsorption capacity of samples at 40 °C and 100 kPa: (a) absolute values and (b) capacity retention.

3.3.1.4. Effect of amine concentration on sorbent performance.

Comparison of Figure 3.3, 3.4, and 3.5 reveals that the oxidative stability of MF-supported TEPA depends on the amine loading of the support. Among the sorbents, TEPA10/MF exhibited the highest stability under oxidative degradation conditions. The stability of TEPA10/MF against oxidation suggests that amino groups on the silica surface resist oxidation more effectively than those of the amine bulk. This may be attributed to the hydrogen bonds formed between the OH groups of the MF support and amino groups of TEPA (Figure 3.6), which is consistent with previous results.[14,15,20,21] Chuang's group[14,15] reported that hydrogen-bonding interactions between OH groups of PEG and amino groups of TEPA suppressed the oxidative degradation of supported TEPA sorbents by blocking the amine sites from the approach of O_2, making them less sensitive to the oxidative conditions. The same group[20] also reported that the hydrogen bonding between OH groups of poly(vinyl alcohol) and secondary amines of branched PEI could protect PEI from oxidative degradation. Very recently, Min et al.[21] noted that the increased stability of macroporous silica impregnated with 1,2-epoxybutane-functionalized PEI was caused by the hydrogen bonds formed between the abundant OH groups generated after 1,2-epoxybutane functionalization and nearby amines.

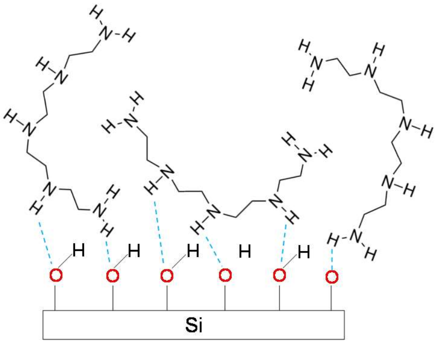


Figure 3.6. Illustration of hydrogen bonding interaction between amino groups of TEPA with surface silanol groups.

The rate of TEPA oxidation may depends on the concentrations of TEPA and O_2, which can be expressed as shown in equation (3.1). Amine oxidation requires the presence of dissolved O_2; therefore, it depends on the diffusion of O_2.

$$r = -k[O_2]^m[\mathrm{TEPA}]^n \qquad (3.1)$$

where k is the reaction rate constant, m and n are the reaction orders with respect to O_2 and TEPA, respectively. The m and n exponents should be determined experimentally. However, they have not been considered in this work.

Oxidative degradation of an amine can proceed via free radical formation through the reaction of O_2 and the amine at elevated temperature.[22–25] This type of free radical chain reaction is initiated by a trigger such as thermal fluctuation (eq. 3.2), resulting in abstraction of a hydrogen atom to form a free radical. Further reactions involve free radical propagation and formation of hydroperoxides, which also decompose to produce free radicals (eq. 3.3–3.7). The chain reaction is terminated when two radicals combine to produce an inactive species (eq. 3.8).

Initiation:

$$\mathrm{RH} \rightarrow \mathrm{R}^{\bullet} + \mathrm{H}^{\bullet} \tag{3.2}$$

Propagation:

$$\mathrm{R}^{\bullet} + \mathrm{O}_2 \rightarrow \mathrm{ROO}^{\bullet} \tag{3.3}$$

$$\mathrm{ROO}^{\bullet} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\bullet} \tag{3.4}$$

$$\mathrm{ROOH} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{OH}^{\bullet} \tag{3.5}$$

$$\mathrm{ROOH} + \mathrm{ROOH} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{ROO}^{\bullet} + \mathrm{H_2O} \tag{3.6}$$

$$\mathrm{RH} + \ \mathrm{RO}^{\bullet} \rightarrow \mathrm{ROH} + \mathrm{R}^{\bullet} \tag{3.7}$$

Termination:

$$\mathrm{R}^{\bullet}, \mathrm{RO}^{\bullet}, \mathrm{ROO}^{\bullet}, \mathrm{etc} + \mathrm{R}^{\bullet}, \mathrm{RO}^{\bullet}, \mathrm{ROO}^{\bullet}, \mathrm{etc} \rightarrow \mathrm{Non} - \mathrm{radical\ products} \tag{3.8}$$

The oxidation rate is slow in the induction period. However, the reaction accelerates until almost all reactants have been consumed. Many types of compounds that exhibit different CO_2 capture abilities can be formed by TEPA oxidation.

Except for TEPA10/MF, TEPA60/MF is the most stable of the samples in pure O_2 at 80 °C for 18 h. Under these conditions, the oxidation rate may mainly depend on the rate of O_2 diffusion to amine molecules. The pores and surfaces of the sorbent could influence the O_2 diffusion, regulating the oxidation rate. The diffusion rate of O_2 to amines decreased with increasing amine content because of the agglomeration of amine molecules in the pores of the support (Figure 3.7). Degradation of supported amine sorbents was directly proportional to the diffusion rate of O_2; therefore, the oxidation rate decreased as the amine content increased. For this reason, the degree of oxidative degradation of samples increased from TEPA30/MF to TEPA60/MF. As for TEPA70/MF, the surface of the support was almost completely covered by amine molecules. Thus, the diffusion rate of O_2 into the pores was low. However, O_2 could easily react with amines on the surface of the support, leading to an increase in the level of free radicals that promoted amine degradation. Therefore, TEPA70/MF was more sensitive to oxidative conditions than TEPA60/MF.

When the temperature was raised to 100 °C, the reaction rate increased and the O_2 diffusion was enhanced compared with those at lower temperature. Consequently, the degree of degradation of TEPA was affected depending on oxidation time, amine concentration, O_2 concentration, and the number of free radicals. The oxidation of TEPA possibly released many types of compounds that exhibited different CO_2 adsorption capacities. The behaviors of newly formed species also contributed to the stability of sorbents. The changes in the composition of sorbents during oxidation affected their adsorption capacities as well as their stability.

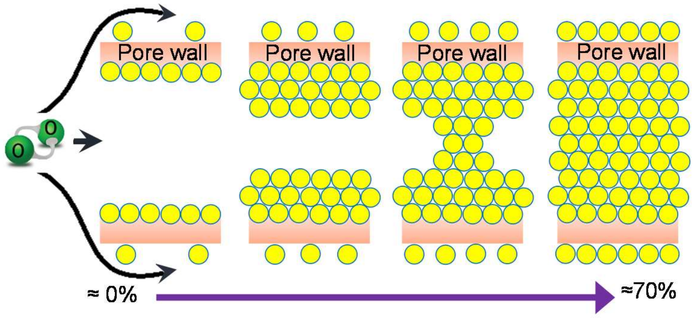


Figure 3.7. Illustration of the agglomeration of amine molecules in the pores and on the surface of silica with amine loadings from 10 wt% to 70 wt%.

After treatment in pure O_2 at 100 °C for 18–42 h, the stability of sorbents was as follows: TEPA30/MF>TEPA50/MF≈TEPA60/MF≈TEPA70/MF. The sorbents retained less than 12% of their original CO_2 adsorption capacities and lower CO_2 adsorption capacities than that of the support without TEPA, suggesting that the oxidation of TEPA in the sorbents was in the termination stages. Almost all of the TEPA was consumed to form new products that were incapable of capturing CO_2, therefore decreasing the ability of the sorbents to adsorb CO_2. Moreover, the agglomeration of these new inactive products on the surfaces and in the pores of the support may decrease the CO_2 adsorption capacity of the amine-supported sorbents below that of the support without TEPA.

3.3.2. Characterization of sorbents before and after oxidative degradation.

All the initial sorbents were white. After heating in O_2 at 80 °C for 18 h, all the sorbents remained white. After oxidation under more severe conditions, TEPA10/MF remained white, whereas the other sorbents varied from pale to intense yellow. The extent of the color changes of the sorbents was proportional to their degree of degradation.

The decrease in the CO_2 adsorption capacity of the amine-impregnated sorbents in an oxidative environment can be caused by three factors. First, the amine content may be decreased during oxidation because of thermal evaporation. To analyze this, TG and GC analyses were carried out. Second, new products may accumulate in the pores and on the surfaces of the support, probably leading to blocked pores in the degraded sorbents, which has a negative effect on the CO_2 uptake. To investigate this, the surface area and pore volume of the sorbents were measured. Third and most importantly, the amino functional group is modified by oxidation into new species that have no ability to capture CO_2. Some of the newly formed species may evaporate during the oxidation. FT-IR spectroscopic analysis was conducted to examine the changes in the functional groups and changes in the composition of sorbents were observed by GC. Elemental analysis was also performed to confirm the change in the composition of sorbents.

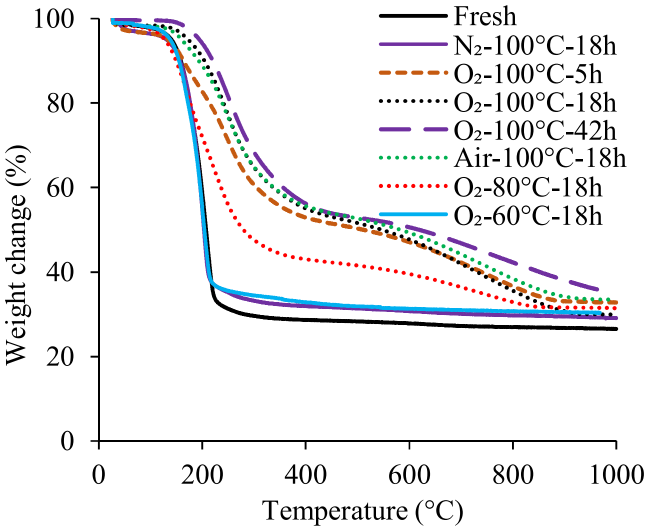


Figure 3.8. TG curves for TEPA70/MF before and after exposure to different oxidation treatments.

TG analysis was carried out on representative samples; the results are shown in Figure 3.8. The TG results indicated that after oxidative degradation, TEPA70/MF still retained at least 64 wt% of its total organic content. Compared with the original sorbent, the loss in total organic content was about 9 wt%. After being treated in N_2 at 100 °C for 18 h or in pure O_2 at 60 °C for 18 h, treated TEPA70/MF retained the same TG profile as that of the original sorbent. The sorbents lost almost all of their organic compounds (>94 wt%) when heated to 300 °C. Comparison with the TG data for the original sorbent revealed that the sorbent lost just 2 wt% of TEPA after thermal treatment in N_2, ruling out the possibility that thermal evaporation of the amine is the main reason for the decrease in CO_2 uptake. In contrast, when the oxidation temperature was raised to 80 and 100 °C, the TG profiles for the oxidatively degraded sorbents differed from that of the original sorbent, indicating that the degraded sorbents contain degradation products with a higher boiling point than that of TEPA. Heating to 300 ºC only removed part of the organic content (49–77 wt%) from the supports. The organic content remaining in the support was directly related to the degree of degradation. Almost all of the organic compounds were removed when the temperature was raised to 900 ºC. The changes in the TG profiles of the sorbents reflected the decrease in the CO_2 adsorption capacities of the sorbents during oxidation. The TEPA70/MF sorbent after exposure to N_2 at 100 °C for 18 h or O_2 at 60 °C for 18 h, which exhibited the same TG profiles as that of the fresh one, retained above 99% of their initial CO_2 uptakes. By contrast, under the other oxidation conditions used in this work, the treated TEPA70/MF sorbents displayed changes in their TG profiles and decreases in CO_2 uptake of at least 43% (Figure 3.3–3.5).

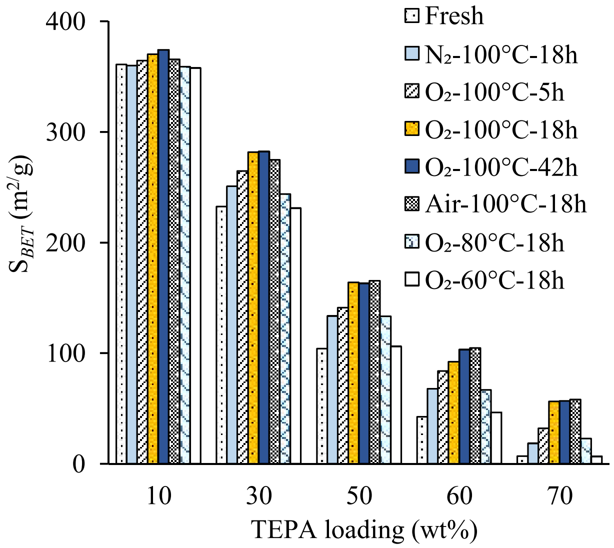


Figure 3.9. Surface areas (S_{BET}) of original and degraded sorbents.

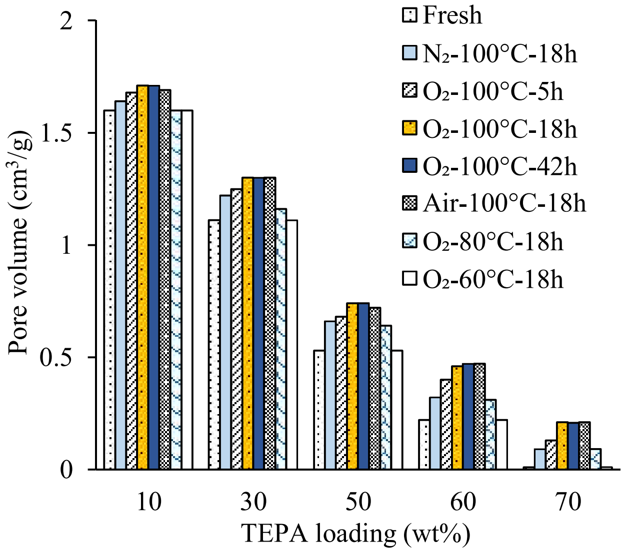


Figure 3.10. Pore volumes of original and degraded sorbents.

The residues of impregnated amines in the mesopores of the MF support were confirmed by N_2 physisorption experiments. The results are presented in Figure 3.9 and 3.10. Gradual decreases in the surface area and pore volume of the MF support were accompanied with a gradual increase in the amount of TEPA loading on/in the support. The surface area and pore volume of MF were 448 m^2/g and 1.95 cm^3/g, respectively. When MF was loaded with 70 wt% of TEPA, the surface area of the support decreased to 7 m^2/g and its pore volume fell to 0.01 cm^3/g, indicating that the surface and mesopores of MF were nearly completely covered and filled by amines, respectively. This result supported the agglomeration of amine molecules in/on the amine solid sorbents (see Figure 3.7), which can affect the diffusion rate of O_2 as well as that of CO_2. After thermal treatment in pure N_2 at 100 °C for 18 h, the surface area and pore volume of sorbents increased slightly, suggesting that a small amount of amine evaporated from the sorbents. This result is consistent with the change in the total amount of organic compounds determined by TG analysis. Both the pore volume and surface area of sorbents increased after oxidation under severe conditions, suggesting that the accumulation of new products in the pores and on the surfaces of the support did not block the pores in the oxidized sorbents. These changes can be explained by both the slight evaporation of TEPA and the release of degradation products with low molar mass during oxidation.

The evaporation of products with low molar mass during the degradation of amino functional groups corresponds to the change in the element content of the sorbents. The composition and CO_2 adsorption capacities of representative sorbents before and after oxidative degradation at 40 °C and 100 kPa are shown in Table 3.1 and Figure 3.11. The contents of C, H, and N of the sorbents decreased after oxidative degradation, supporting the evaporation of organic compounds. However, the decreases of the contents of N and other elements cannot fully explain the marked suppression of the CO_2 adsorption capacity of the sorbents. A typical example is TEPA60/MF: after degradation in pure O_2 at 100 °C for 18 h, its C, H, and N contents decreased by 93%, 55%, and 68%, respectively, yet its CO_2 adsorption capacity decreased by 95%. Therefore, the evaporation of amine-containing compounds is not the main reason for the observed decrease in CO_2 uptake after oxidation. The loss in CO_2 uptake of oxidized supported amine sorbents is mainly caused by the change of amino functional groups. The minor decrease of C content and the marked drops of N and H contents suggest that water and new volatile amine-containing compounds, such as ammonia and urea, form during the oxidative degradation of the sorbent.

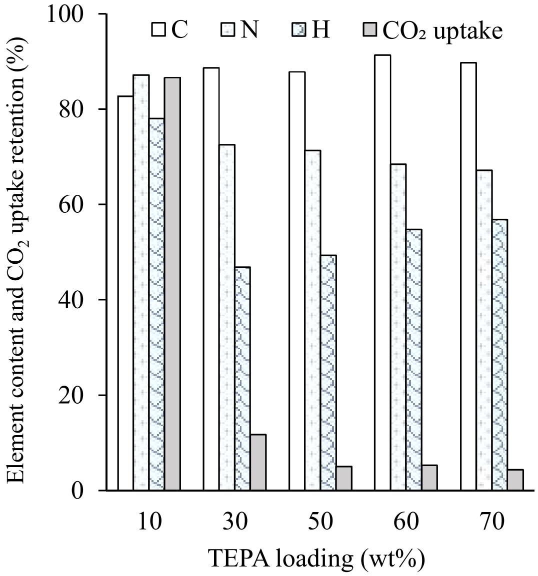


Figure 3.11. Element content and CO_2 uptake retentions of sorbents after degradation in pure O_2 at 100 °C for 18 h.

In this work, to examine the change in the composition of sorbents in an O_2-containing environment, a solvent extraction method was used to extract organic compounds from the silica support. GC analysis was performed on the extracted solutions of representative samples; the results are shown in Figure 3.12. The total amount of the four main compounds in TEPA60/MF was 92.7 area %, in which T-BRN, T-LIN, T-IPZ, and T-EPZ contributed 13.6, 47.8, 24.7, and 6.6 area %, respectively. The total amount of such compounds remained 90.24 area % after thermal treatment in pure N_2 at 100 °C for 18 h, suggesting the evaporation of a small amount of amine from the sorbent. This result is consistent with the changes in the total amount of organic compounds measured by TG analysis as discussed above. The total amount of these compounds in the sorbent decreased to 59.9 and 6.8 area % after exposure to O_2 at 80 °C for 18 h and 100 °C for 18 h, respectively. These results suggest that the rapid decrease in the organic content during the oxidation contributed to the sharp decline in the CO_2 capacity of the TEPA-supported materials. The GC results also revealed that during the oxidation, TEPA was modified to form new species, some of which had a low molar mass and were easily evaporated from the oxidized sorbents. However, the newly formed species were not identified in this study. Additionally, there were considerable changes in the contents of the four main compounds in commercial TEPA after oxidation. Figure 3.12 reveals that the intensities of peaks from T-BRN, T-LIN, T-IPZ, and T-EPZ in GC traces decreased after oxidation. The intensities of peaks from T-LIN, T-BRN, and T-EPZ decreased rapidly, whereas the decrease in the intensity of the peak from T-IPZ was the slowest of the four main TEPA components. These results suggest that T-IPZ exhibited the highest O_2 resistance among the four main components of TEPA.

The low stability of T-LIN, T-BRN, and T-EPZ can be explained by the formation of a six-membered ring through radical mechanism which was proposed for 1,1,4,7,7-pentamethyldiethylenetriamine by Lepaumier et al.[26] This mechanism is illustrated for T-LIN in Scheme 3.1. First, the amino group is activated into an aminium radical cation through an electron abstraction from a secondary amine. Then, an intramolecular rearrangement leads the [1,7] H migration in the ionized system. Subsequently, a capture of a hydrogen radical leads to the formation of aminium cation with $-NH_3^+$, a very good leaving group, which is followed by the formation of an ammonia and a six-membered ring compound. While T-IPZ cannot follow this scheme because of its structure, T-LIN, T-BRN, and T-EPZ can degrade to form ammonia, which is coherent with the losses in N and H contents measured by elemental analysis as mentioned above. The six-membered ring compound in Scheme 1 still contains amino groups reactive with CO_2. However, CO_2 adsorption capacities after degradation are not higher than those of bare silica, indicating that the six-membered ring compound is not a final product, but may be an intermediate. Because it has not been identified in this work, further studies are needed to support the proposed scheme.

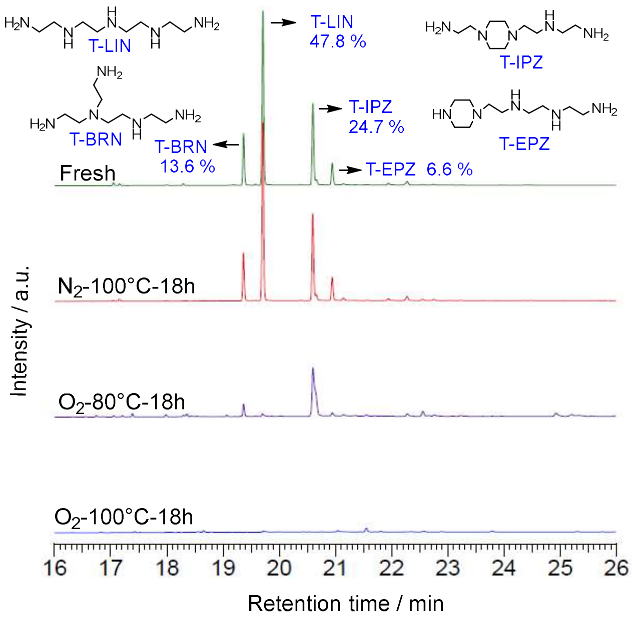
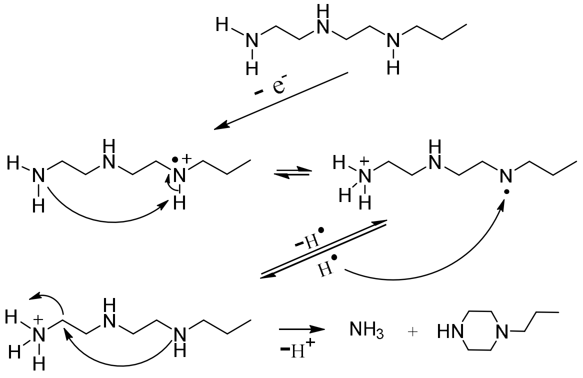


Figure 3.12. GC charts of TEPA60/MF before and after oxidative degradation.



Scheme 3.1. Radical mechanism of six-membered ring formation for the oxidative degradation of T-LIN.

It is well known that primary and secondary amines react with CO_2 whereas tertiary amines cannot react with CO_2 in the absence of water.[27–29] The proposed reaction mechanism is as follows (eq. 3.9):

$$2R^1R^2NH + CO_2 \leftrightarrow R^1R^2NCOO^- + R^1R^2NH_2^+ \qquad (3.9)$$

Among the four main compounds in commercial TEPA, T-LIN and T-BRN contain more primary and secondary amino groups than T-IPZ and T-EPZ. Therefore, T-LIN and T-BRN may have more potential to capture CO_2 than T-IPZ and T-EPZ. However, Numaguchi et al.[16] previously reported that T-LIN and T-BRN exhibited lower amine efficiencies, defined as moles of adsorbed CO_2 per mole of amino groups in an amine solid sorbent, and lower cyclic capacities than those of T-IPZ and T-EPZ. Moreover, T-LIN and T-BRN displayed higher adsorption heats than those of T-IPZ and T-EPZ. Considering the results in this work, an increase in the T-IPZ content of commercial TEPA should improve the CO_2 adsorption performance and stability of sorbents containing TEPA.

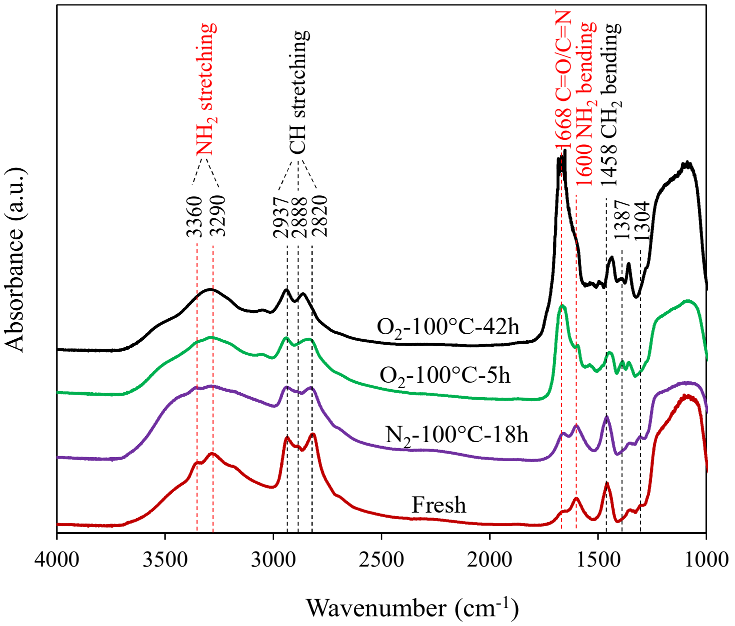


Figure 3.13. FT-IR single-beam spectra of TEPA70/MF before and after exposure to O_2/N_2 at 100 °C for different durations.

Finally, FT-IR spectroscopic analysis was carried out on representative sorbents to identify the newly formed species in the degraded sorbents. Figure 3.13 reveals that exposure to O_2 was accompanied by the development of a band at 1668 cm^{-1} that was correlated with the observed decrease in CO_2 capacity. The new intense peak at 1668 cm^{-1} was assigned to C=O or C=N stretching of urea, amide, nitrite, acid, imine or imide groups, consistent with the oxidation of polyamines.[6,9,12,15,30,31] The FT-IR spectra of TEPA-impregnated sorbents after oxidative treatment showed decreases in the intensities of NH vibration (3300–3600 cm^{-1}), CH stretching (2800–3000 cm^{-1}), and CH bending (1304 and 1458 cm^{-1}). The other characteristics of the TEPA60/MF FT-IR spectrum compared with that of oxidized TEPA60/MF were a decrease in the intensity of the vibration at 1600 cm^{-1}, which was the characteristic band of the N-H bending vibration of primary/secondary amines, and a shift of the CH bending vibration from 1458 to 1446 cm^{-1}. The changes in the formation of C=O/C=N species and the decreased intensity of bands from N-H and C-H species indicated that TEPA was oxidized to form nitrogen-containing groups with lower basicity and therefore lower affinity for CO_2, causing the CO_2 adsorption capacity to decrease. Furthermore, the appearance of additional bands at 1545, 1493, and 1387 cm^{-1} in the FT-IR spectrum of the oxidized sample provided evidence for urea formation,[12] supporting its exponential decay.

3.4. Conclusions

It is impossible to avoid the oxidative degradation of TEPA-impregnated silica sorbents if O_2 is present at moderate temperature. The oxidative stability of TEPA-supported sorbents depends on the amine loading, oxidation duration, temperature, and O_2 concentration. The marked loss in the CO_2 adsorption capacity of the sorbents was mainly caused by the conversion of basic amines into non-basic compounds and the formation of ammonia. Most importantly, the changes in the composition of commercial TEPA during oxidative degradation were first investigated. The deactivation of amine solid sorbents in O_2-containing environments depended on the amine structure. T-IPZ exhibited the highest oxidative stability of common TEPA components. The CO_2 adsorption behavior and stability of sorbents containing TEPA could be improved by increasing the T-IPZ content of commercial TEPA. Amines which are unfavorable to form six-membered rings may be advantages for the development of effective sorbents for CO_2 capture.

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Chapter 4. Inhibitors of Oxidative Degradation of Polyamine-Modified Silica Sorbents for CO_2 Capture

This chapter evaluates inhibition of oxidative degradation of polyamine-impregnated solid sorbents using various inhibitor-candidates including hydrogen-donating antioxidants and sulfur-containing compounds. The experimental results show that sulfur-containing compounds are a promising choice for inhibiting oxidative degradation of amine solid sorbents. Further insight into mechanism of the inhibition processes is also discussed.

Parts of this chapter are reproduced from "Quyen T. Vu, Hidetaka Yamada, Katsunori Yogo. Inhibitors of Oxidative Degradation of Polyamine-Modified Silica Sorbents for CO_2 Capture *Ind. Eng. Chem. Res.* 2019, 58, 15598–15605".

4.1. Introduction

As mentioned in previous chapters, a well-known problem of amine impregnated solid sorbents is that they are prone to degradation in the presence of O_2 species, resulting in losses in CO_2 capture ability as well as sorbent lifetimes. In addition, degraded products may cause health and environmental impacts.[1] The results in Chapter 3 also point out that it is impossible to avoid degradation of amine solid sorbents in O_2-containing environment even at moderate temperature. Additionally, Chapter 2 (and Chapter 3) also presents that amine solid sorbents even degraded after several-month storage in the dark at ambient temperature.

For commercial applications, adsorbents should be stable under practical operating conditions. Several groups have made effort to discover new supports and amines for amine solid sorbents with high durability against oxidation.[2–5] Pang et al.[2,3] designed a silica material supporting polypropyleneimine to help improve the stability against oxidative degradation compared with traditional polyethyleneimine (PEI)-based silicas. Zhai et al.[4] used cross-linked poly(vinyl alcohol) as a support for immobilizing PEI. This support provides OH groups for hydrogen-bonding interactions with the amino groups of PEI, which may enhance the resistance of PEI against degradation. To improve the long-term stability against oxidative degradation over repeated temperature swing adsorption cycles, Choi et al.[5] functionalized PEI with 1,2-epoxybutane to prepare an amino polymer immobilizing silica adsorbent. Besides development of new materials with high oxidative durability to prevent adsorbent degradation, additives can also minimize oxidative degradation of amine solid sorbents. However, no additives that can inhibit oxidative degradation of amine solid sorbents have been reported.

As mentioned in Chapter 1, radical pathway is believed to occur as for oxidative degradation.[6–8] The presence of reactive species ($X^\bullet$), dissolved transition metal ions,[9] or excitation sources such as ultraviolet (UV) light or heat has been known as the initial factors cause the formation of free radical (eq. 4.1–4.3):

$$RH + X^{\bullet} \rightarrow R^{\bullet} + XH \quad (4.1)$$

$$RH + M^{n+1} \rightarrow R^{\bullet} + H^{+} + M^{n} \quad (4.2)$$

$$RH \xrightarrow{E} R^{\bullet} + H^{\bullet} \quad (4.3)$$

Hydroperoxides which also decompose to form free radicals are formed in further reactions (eq. 4.4–4.6):

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad (4.4)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad (4.5)$$

$$ROOH \rightarrow RO^{\bullet} + OH^{\bullet} \quad (4.6)$$

Therefore, radical scavengers, chelating agents, peroxide decomposers, UV light absorbents can prevent formation of radicals and slow down oxidative degradation of amines.

This chapter focuses on effect of some additives on oxidative degradation of silica supported polyamines. Tetraethylenepentamine (TEPA) which is a commonly studied polyamine for CO_2 capture was impregnated into mesostructured cellular silica foam (MF). Transition metals including Cu, Fe, Cr, Ni, and V have been reported to be potent catalysts for oxidative degradation of aqueous amine solution.[10–13] These metal contaminants were found to be negligible in the commercial TEPA used in this study (less than 30 ppb) by inductively coupled plasma (ICP) analysis. Therefore, we ignored their catalytic effects on amine degradation for simplicity in this study, although a contribution of contaminants in MF cannot be ruled out. The specific additives with high boiling points used in this study were selected from the above oxidation inhibitor categories excluding chelating agents and UV light absorbers. The additives are sulfur-containing compounds such as 2,2-thiodiethanol (TDE), 2-hydroxyethyl disulfide (HEDS), and 3,3′-dithiodipropionic acid (DTDP), and hydrogen-donating antioxidants that are often used in the food and rubber industries such as butylated hydroxytoluene (BHT), *N,N′*-di-2-butyl-1,4-phenylenediamine (DBPD), *N,N′*-diphenyl-1,4-phenylenediamine (DPPD), 2,2′-thiodiethylene bis[3-(3,5-di-*tert*-butyl-4-

hydroxyphenyl)propionate] (TBD), and pentaerythritol tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] (PET). The structures of these compounds are shown in Figure 4.1.

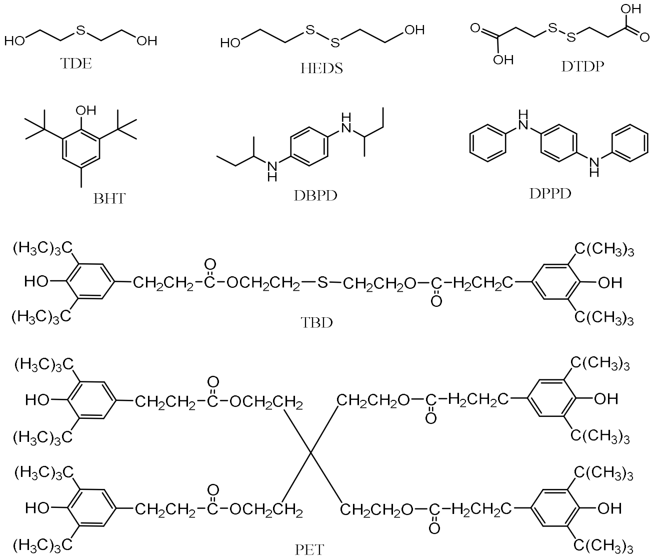

Figure 4.1. Molecular structures of the additives used in this study.

To assess the inhibition ability of the additives for the oxidative degradation, CO_2 adsorption measurements were performed. The results indicate that these selected hydrogen-donating antioxidants did not act as preventive antioxidants, and they even accelerated degradation of amine solid sorbents. In contrast, the selected sulfur-containing compounds inhibited degradation of the amine solid sorbents. The positive effect of these sulfur-containing inhibitors was confirmed for oxidative degradation of another polyamine (PEI) and for the binary amines developed in chapter 2 (4-methylimidazole (4MIm)/TEPA). Furthermore, the stability of the amine solid sorbents was investigated during long time storage with/without these additives. The sulfur-containing compounds consistently delayed oxidation of the amines and prolonged the lifetime of the amine solid sorbents.

4.2. Experimental Section

4.2.1. Materials.

MF powder (Sigma-Aldrich Co., St. Louis, MO, USA), TDE (99%, Sigma-Aldrich), DTDP (99%, Sigma-Aldrich), TEPA (95%, Wako Pure Chemical Industries Co., Tokyo, Japan), 4MIm (97%; Wako), PEI (M_n~1200, 98%, Junsei Chemical Co., Tokyo, Japan), HEDS (98%, TCI Tokyo Chemical Industry Co., Tokyo, Japan), BHT (99%, TCI), DPPD (95%, TCI) , DBPD 98%, TCI), TBD (98%, TCI), and PET (95%, TCI) were used without further purification. He (99.9999%) and N_2 (99.9999%) were supplied by Iwatani Co. (Osaka, Japan). CO_2 (99.995%) was purchased from Sumitomo Seika Chemicals Co. (Osaka, Japan). O_2 (99.995%) was provided by Japan Fine Products Co. (Tochigi, Japan).

4.2.2. Sorbent preparation.

The sorbents were prepared by the impregnation method.[14–16] A mixture of polyamine (TEPA or PEI), additives, MF, and methanol was agitated for 2 h, and then methanol was removed using a rotary evaporator. The obtained sorbents were stored in a Laboran screw vial with dimensions (mm) of 10 (inner caliber) × 21 (shell diameter) × 45 (height) at room temperature before further analysis. The mass fractions of the polyamine and additive in the sorbent were 30 and 5 wt %, respectively. The sorbents are denoted as the name of the additive in the sorbent. The control sample containing 30 wt % of the polyamine and no additives is called the non-additive sorbent.

4.2.3. Oxidative degradation test.

Degradation of adsorbents was performed in the packed-bed reactor (PBR) which has been shown in chapter 2. In a typical experiment, 0.3 g of the sorbent was loaded into the PBR, which was composed of a quartz tube column with an inner diameter of 7.0 mm, an outer diameter of 9.5 mm, and a length of 14 cm. The temperature of the PBR was controlled by a proportional-integral-derivative temperature controller. First, the sorbents were pretreated in N_2 with a flow rate of 40 cm^3/min at 100 °C for 1 h to remove the pre-adsorbed gases and moisture. Subsequently, the degradation step was performed at a temperature of 80 °C under flowing pure O_2 (40 cm^3/min) for 18–42 h. After the exposure of the sample to O_2 flow for the designated time, the sample was cooled to room temperature with flowing pure N_2 (40

cm^3/min) and then collected. The oxidation conditions are denoted gas (used in the degradation step)-temperature-oxidation time. For example, O_2-80°C-18h represents sorbents exposed to O_2 at 80 °C for 18 h.

4.2.4. Long-term stability.

After removing methanol used in sorbent preparation, the obtained dry sorbents were stored in a Laboran screw vial with dimensions (mm) of 10 (inner caliber) × 21 (shell diameter) × 45 (height) sealed with a scew cap in the dark at ambient temperature for 15 months. Volume ratio of a sorbent and atmospheric air in a bottle was about 9:1.

4.2.5. Materials characterization.

The thermogravimetric measurements were performed in a He atmosphere at a gas flow rate of 100 cm^3/min (Thermo Plus TG-DTA 8120, Rigaku Co., Tokyo, Japan). The samples were heated to 1000 °C at a constant rate of 10 °C/min.

The N_2 physisorption isotherms were obtained with an ASAP 2420 accelerated surface area and porosimetry measurement system (Micromeritics Instruments Co., Norcross, GA, USA). Before the measurements, the solid sorbents were degassed under vacuum at 40 °C for 6 h to remove water and pre-adsorbed gases. The specific surface area (S_{BET}) and pore size distribution of each sample were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda methods,[17,18] respectively. S_{BET} was determined from the adsorption data in the relative pressure (P/P_0) range 0.05–0.3. The total pore volume was determined from the adsorption data as the volume of liquid N_2 adsorbed at $P/P_0 = 0.97$.

To determine the N contents in the sorbents, elemental analysis was performed with a Perkin Elmer 2400II CHNS/O elemental analyzer (Waltham Co.) at 980 °C for the combustion zone temperature and 640 °C for the reduction zone temperature with He as the carrier gas. An about 2 mg sample was accurately weighed into a small tin capsule and pyrolyzed in the presence of O_2. The N_xO_y combustion products were reduced to N_2 by fine copper in a reduction tube for quantitative analysis of the N content.

4.2.6. CO_2 adsorption test.

The pure CO_2 adsorption isotherms of all of the samples were monitored using an ASAP surface area and a porosimetry analyzer 2020 (Micromeritics Instruments Co.) under pressures ranging from 2.4 Pa to 100 kPa. Before the measurements an about 100 mg sample was pretreated to remove any moisture and pre-adsorbed gases under vacuum at 40 °C for 6 h. The degradation of each sample was evaluated by calculating its CO_2 adsorption capacity retention (%) from the adsorption isotherms measured before and after the degradation test.

The pure CO_2 adsorption-desorption kinetics was evaluated at 40 °C and atmospheric pressure by thermogravimetric analysis differential scanning calorimetry (TGA-DSC, NETZSCH STA 449 F5 Jupiter, Bavaria, Germany). Before the analysis, about 10 mg of the sorbent was loaded into an aluminium pan, and heated to 80 °C for 6 h under N_2 flow at 50 cm^3/min for the pretreatment. The sample was then cooled to 40 °C before pure CO_2 was passed over the sample at 50 cm^3/min for 2 h. Subsequently, the sorbent was regenerated for 2 h at 80 °C under N_2 flow at a flow rate of 50 cm^3/min. A blank control measurement for baseline correction was performed using an empty aluminum crucible under the same conditions. The TGA curves resulted from the notable mass increase and decrease caused by CO_2 adsorption and desorption.

The amine efficiency is defined as the molar ratio of adsorbed CO_2 to amino groups in the sorbent. The amount of amino groups in the sorbent was calculated from the N content, which was determined by elemental analysis.

4.3. Results and Discussion

In this work, 5 wt% of additives was introduced in the adsorbents. The initial CO_2 adsorption capacities of all of the sorbents were measured. Compared with the non-additive adsorbent, the sorbent containing additives exhibited similar CO_2 adsorption capacities: the non-additive adsorbent adsorbed 2.4 mmol CO_2 /g adsorbent at 40 °C and 100 kPa, while the sorbents with additives adsorbed 2.2–2.6 mmol CO_2 /g adsorbent. Therefore, the effect of additives on the CO_2 saturated adsorption capacities of the sorbents is ignored. The results in chapter 3 indicate that TEPA impregnated silica sorbents have high thermal stability in a pure N_2 atmosphere at 100 °C. Therefore, the thermal degradation of sorbents in the absence of O_2 can be ignored.

4.3.1. Impregnated amount.

The typical TG curves of the prepared sorbents are illustrated in Figure 4.2. The total weight loss of the non-additive sorbent and sorbent containing a mixture of 30 wt% TEPA and 5 wt% DTDP additive were approximately 30 and 35 wt%, respectively, indicating that the amine and additive were successfully impregnated into the support.

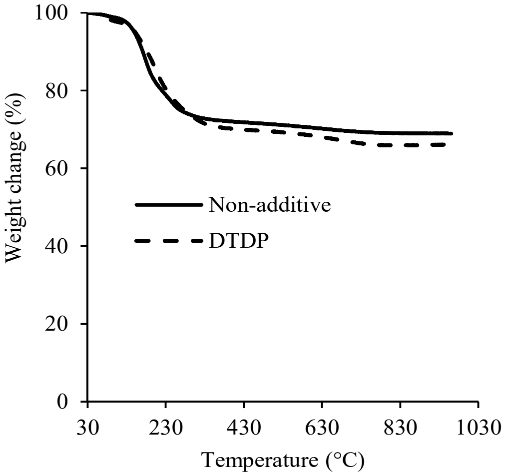

Figure 4.2. TG curves of prepared solid sorbents.

The N_2 physisorption isotherms of the MF support and amine impregnated MF materials are shown in Figure 4.3. The isotherm of support is a Type IV isotherm, which is a typical characteristic of mesoporous silica, indicating its uniform mesoporous structure. The surface area and total pore volume of MF were 479 m^2/g and 2.00 cm^3/g, respectively. Both the surface area and pore volume of mesoporous silica decreased after loading the amine and additive onto the MF support. For the non-additive sorbent containing 30 wt% TEPA, the surface area and total pore volume were 226 cm^2/g and 1.14 cm^3/g, respectively. After blending 5 wt% more of the DTDP additive, the surface area and total pore volume of support decreased to 182 m^2/g and 0.93 cm^3/g. These results confirm that the amines and additives were successfully loaded onto MF.

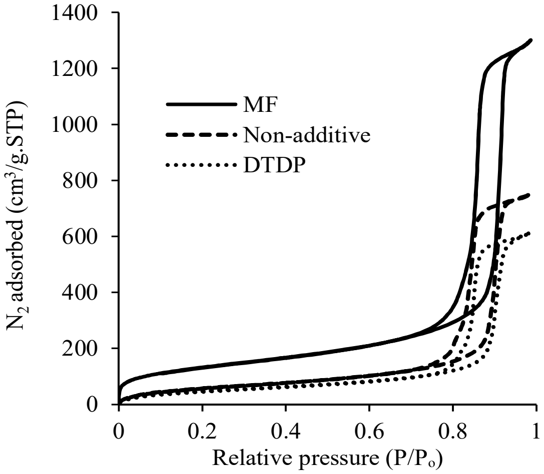

Figure 4.3. N_2 adsorption-desorption isotherms of MF, MF impregnated with 30 wt% TEPA, and MF impregnated with a mixture of 30 wt% TEPA and 5 wt% DTDP recorded at −196 °C.

4.3.2. CO_2 adsorption-desorption properties.

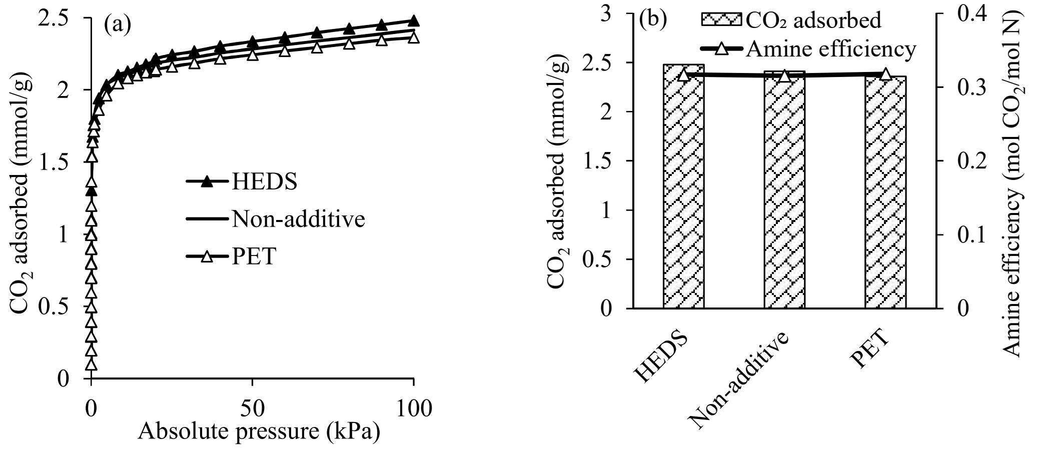

Figure 4.4. (a) Effect of additives on CO_2 adsorption isotherms of TEPA sorbents at 40 °C and (b) amine efficiency and CO_2 adsorption capacity at 40 °C and 100 kPa.

All of the adsorbents showed similar CO_2 adsorption isotherms, CO_2 adsorption capacities, and amine efficiencies. Examples of the CO_2 adsorption isotherms and the calculated amine efficiencies are shown in Figure 4.4. Additionally, similar CO_2 adsorption-desorption kinetics were observed for both non-additive and additive sorbents (Figure 4.5). These results indicate that the effect of additives on the diffusion parameter of the CO_2 adsorption behavior of the sorbents can be ignored.

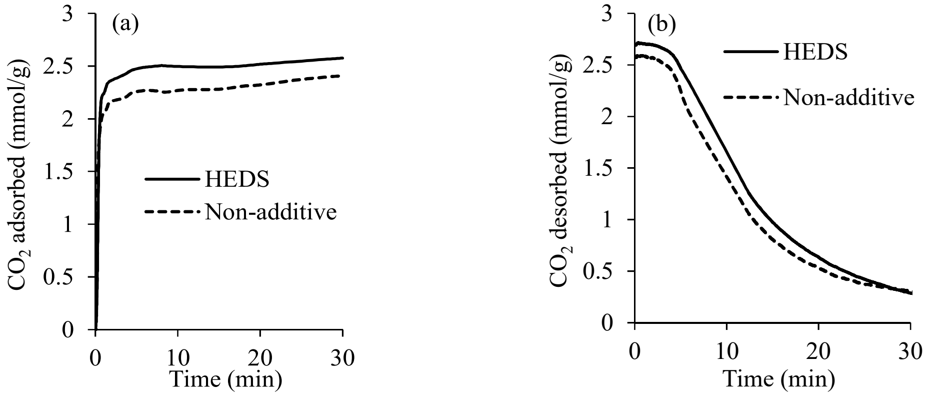

Figure 4.5. (a) CO_2 adsorption and (b) desorption kinetics for TEPA sorbents at 40 °C and atmospheric pressure.

4.3.3. Effect of hydrogen-donating antioxidants

Figure 4.6 shows a comparison of the CO_2 adsorption retention at 40 °C and 100 kPa for the non-additive TEPA sorbent and those containing hydrogen-donating antioxidants after exposure to O_2. All of the sorbents underwent dramatic deactivation in the O_2-containing environment and exhibited a significant decrease in CO_2 adsorption capacity. After 18 h of O_2 exposure at 80 °C, the non-additive sorbent retained 46% of its original CO_2 adsorption capacity, whereas the adsorption capacities of sorbents containing DPPD, TBD, DBPD, BHT, and PET decreased to 55%, 22%, 10%, 48%, and 18% of their original CO_2 adsorption capacities, respectively. The degree of deactivation increased with the oxidation duration. After degradation in an O_2-containing environment at 80 °C for 42 h, the non-additive sorbent retained 21% of its original adsorption capacity, and the sorbents containing the hydrogen-donating additives exhibited lower CO_2 adsorption retention than the non-additive sorbent. The CO_2 adsorption capacity retention values were 16%, 8%, 10%, 16%, and 9% for the sorbents containing DPPD, TBD, DBPD, BHT, and PET, respectively. The results indicate that hydrogen-donating antioxidants did not prevent amine-containing sorbents from oxidation, and they even accelerated oxidative degradation of amine.

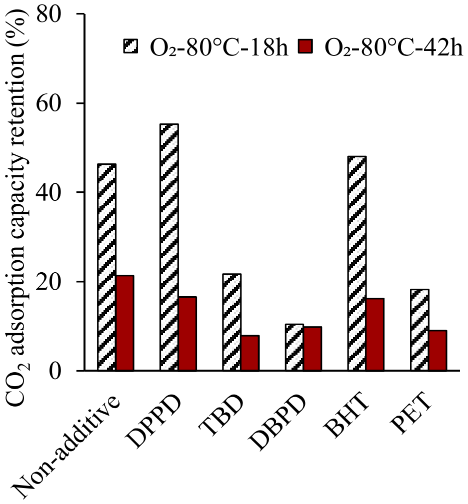

Figure 4.6. Effect of hydrogen-donating antioxidants on CO_2 adsorption capacity retention of TEPA sorbents at 40 °C and 100 kPa.

In general, hydrogen-donating antioxidants neutralize free radicals by donating an active hydrogen atom to the free radical and interrupting the free radical chain reaction.[19,20] Antioxidant molecule becomes a free radical in the process of neutralizing a free radical molecule to a non-free-radical molecule. These hydrogen-donating antioxidants are characterized by phenols, secondary amines and quinones.[19,20] They are considered to work in the following way (eq. 4.7):

$$X^\bullet + AH \rightarrow XH + A^\bullet \qquad (4.7)$$

The antioxidant effectiveness depends on several important factors: oxidation-reduction potential, activation energy, molecular stability, and solubility, which are closely related to the antioxidant molecular structure. TBD, BHT, and PET are phenolics, while DPPD and DBPD are categorized as secondary amines. In oxidative degradation of TEPA, which is recognized as a mixture of primary, secondary and tertiary amines,[21] such antioxidants may be less reactive to free radicals than TEPA. In this case, the “antioxidant” does not act as a radical scavenger and it instead catalyzes degradation of TEPA. In other words, TEPA can act as an antioxidant in the oxidation of such hydrogen-donating antioxidants, resulting in an increase in oxidative degradation of TEPA. The negative effect of several hydrogen-donating antioxidants on preventing oxidative degradation of aqueous amine methanolamine (MEA) has been reported.[12,22] Goff et al.[12] reported that both ascorbic acid and hydroquinone, two hydrogen-donating antioxidants, act as pro-oxidants in the degradation of MEA from ammonia production, which is known to be the product of degradation of MEA. Delfort et al[22] also observed such a pro-oxidative effect for ascorbic acid, hydroquinone, and other substituted benzene antioxidants. These additives showed an increase in organic acid production from MEA in the presence of O_2.

4.3.4. Effect of sulfur-containing compounds.

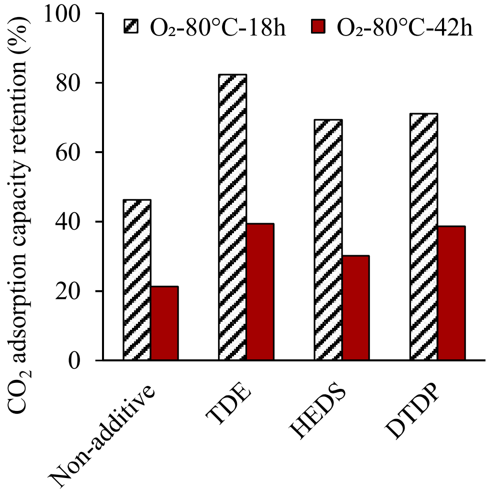

Figure 4.7. Effect of sulfur-containing compounds on the CO_2 adsorption capacity retention of the TEPA sorbents at 40 °C and 100 kPa.

The stability of the non-additive sorbent is compared with those of the sulfur-containing sorbents in an O_2-containing environment in Figure 4.7. The results show that TDE, HEDS, and DTDP can prevent TEPA oxidation. After oxidation, sorbents containing such additives exhibited higher CO_2 capture abilities than the non-additive sorbent. The CO_2 adsorption capacity retention values of the sorbents containing such additives were 1.5–2 times higher than that of the non-additive sorbent after exposure to an O_2-containing environment. In particular, after O_2 exposure at 80 °C for 18 h, the sorbents containing TDE, HEDS, and DTDP retained 82%, 69%, and 71% of their original adsorption capacities, respectively. After oxidation for 42 h, the CO_2 adsorption capacity retention values of the sorbents containing TDE, HEDS, and DTDP were 39%, 30%, and 39%, respectively, which were still higher than that of the non-additive sorbent.

Sulfur-containing compounds can delay oxidative degradation of amines for several reasons. Compounds containing organic sulfur are active hydroperoxide decomposers.[20,23,24] Oxidative degradation of amines can possibly occur by a free radical chain reaction,[11–13,25] and hydroperoxides are known to be the main products of such oxidation reactions. Sulfur-containing antioxidants can decompose hydroperoxides to alcohols (non-radical products), which will be described below, so the rate of the oxidation reaction can be decreased.

Thiols react with hydroperoxides to give disulfides (eq. 4.8):

$$\mathrm{ROOH + 2R^1{-}SH \rightarrow ROH + R^1{-}S{-}S{-}R^1 + H_2O} \qquad (4.8)$$

Sulfides and 3,3'-thiodipropionic acid, are oxidized to sulfoxides (eq. 4.9 and 4.10):

$$\mathrm{ROOH + R^1{-}S{-}CH_3 \rightarrow ROH + R^1{-}SO{-}CH_3} \qquad (4.9)$$

$$\mathrm{ROOH + HOCOR^1{-}S{-}R^1COOH \rightarrow ROH + HOCOR^1SO{-}\ R^1COOH} \qquad (4.10)$$

Disulfides can be further oxidized to thiosulfinate (eq. 4.11):

$$\mathrm{ROOH + R^1{-}S{-}S{-}R^2 \rightarrow ROH + R^1{-}S{-}SO{-}R^2} \qquad (4.11)$$

Sulfoxides can react with other hydroperoxide molecules to give sulfones (eq. 4.12):

$$\mathrm{ROOH + R^1{-}SO{-}R^2 \rightarrow ROH + R^1{-}SO_2{-}R^2} \qquad (4.12)$$

The intermediates of the transformation of sulfides and disulfides can also terminate chains by reacting with peroxyl radicals during the chain oxidation,[22,26,27] thereby decreasing the oxidation rate (eq. 4.13–4.15):

$$\mathrm{R^1{-}SO{-}CH_2{-}CH_2{-}R^2 \rightarrow R^1{-}SOH + CH_2{=}CH{-}R^2} \qquad (4.13)$$

$$\mathrm{R^1{-}SOH + RO_2^\bullet \rightarrow R^1{-}SO^\bullet + ROOH} \qquad (4.14)$$

$R^1–SO^\bullet + RO_2^\bullet \rightarrow R^1–SO_2OR$ (4.15)

Because organic sulfur-containing compounds can react multiple times with reactive free radicals or peroxides, these compounds are a promising option for inhibiting oxidative degradation of amine.

4.3.5. Long-term stability.

The CO_2 adsorption capacity retention values of the sorbents after 15 months storage at room temperature varied, as shown in Figure 4.8. The non-additive sample containing 30 wt% TEPA retained 52% of its initial adsorption capacity. The ability of the fresh sample to capture CO_2 decreased, indicating that TEPA was slowly but steadily oxidized even at room temperature. In accordance with the above results for degradation by pure O_2 at 80 °C, the presence of thiols in the sorbents decreased oxidative degradation, whereas the presence of hydrogen-donating antioxidants enhanced oxidative degradation. After 15 months storage at room temperature, the CO_2 adsorption capacity retention values of the amine solid sorbents containing TDE, DTDP, and HEDS were 69%, 76%, and 83%, while they were 5%, 34%, 36%, 37%, and 48% for the sorbents containing DBPD, TBD, DPPD, PET, and BHT, respectively.

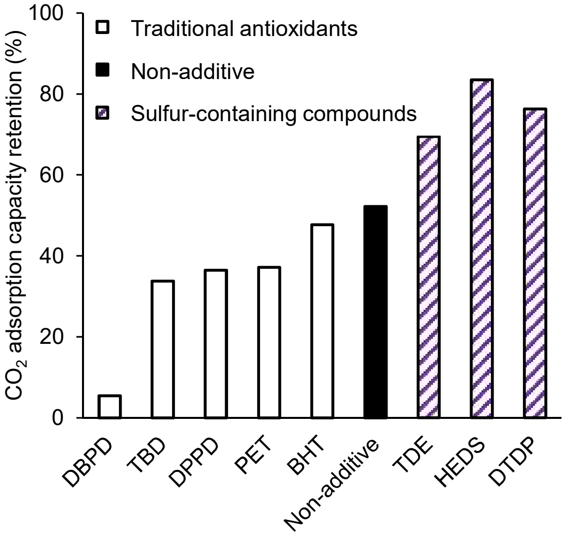

Figure 4.8. CO_2 adsorption capacity retention values of the TEPA sorbent compounds at 40 °C and 100 kPa after 15 months storage at room temperature.

4.3.6. Other amine system.

In addition to TEPA, PEI is also one of the most widely used polyamines for solid sorbents for CO_2 capture. The sulfur-containing compounds that worked well as inhibitors of oxidative degradation of TEPA were used as additives for PEI sorbents. Oxidative degradation experiments were performed in the same way as for the TEPA sorbents. The oxidation conditions were 80 °C for 42 h in pure O_2. The CO_2 adsorption retention values for the PEI sorbents with and without additives are compared in Figure 4.9. The results show that TDE, HEDS, and DTDP effectively inhibit oxidative degradation of PEI. The CO_2 adsorption capacity retention values of the sorbents containing these additives were about 1.5 times higher than that of the non-additive sorbent. In particular, the CO_2 adsorption capacity of the PEI sorbent without additives retained 42% of its original value, whereas those of the PEI sorbents containing HEDS, DTDP, and TDE were 62%, 66% and 74%, respectively.

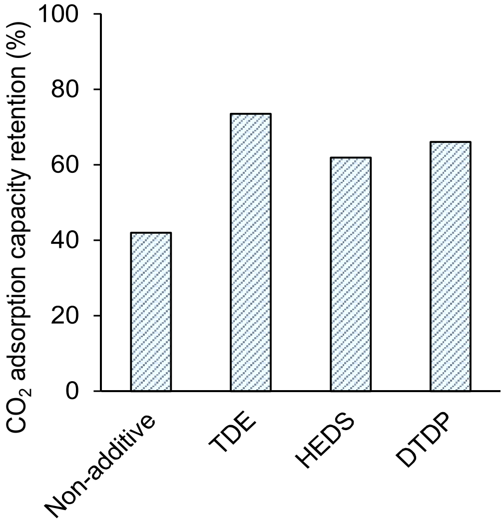

Figure 4.9. CO_2 adsorption capacity retention values of the PEI sorbents at 40 °C and 100 kPa.

In chapter 2, the new binary amines (4MIm/TEPA) composites have been developed as promising candidates for practical CO_2 separation. The mixture of 4Im and TEPA synergistically improved the CO_2 adsorption capacity, amine efficiency, working capacity, and regeneration energy requirement of sorbents. However, such materials degraded during storage. Therefore, further experiments were performed in the same way as for the TEPA sorbents to investigate effect of sulfur-containing compounds for 4MIm/TEPA sorbents. 5wt % of each TDE, HEDS, and DTDP was added into MF containing 20 wt% 4MIm and 30 wt% TEPA. The CO_2 adsorption capacity values of the sorbents after the exposure to pure O_2 at 80 °C and 18 h are shown in Figure 4.10. The results show that the sulfur-containing compounds effectively inhibit oxidative degradation of not only single polyamine but also binary amine mixture. The non-additive 4MIm/TEPA sorbent dramatically deactivated in the presence of O_2 species. After the oxidation, this sorbent retained 14 % its original value. Those values for the sorbents containing TDE, HEDS, and DTDP corresponded to 55, 41, and 42 % which were ca. 3–4 times higher than that of the non-additive sorbent.

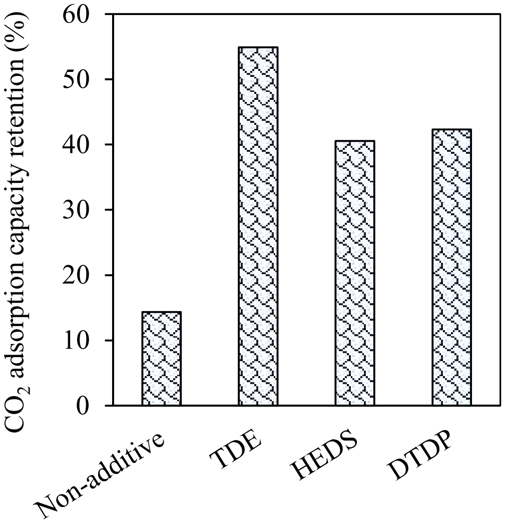

Figure 4.10. CO_2 adsorption capacity retention values of the 4MIm/TEPA sorbents at 40 °C and 100 kPa.

4.4. Conclusion

A laboratory-scale evaluation study of oxidative degradation inhibitors for sorbents containing single and binary amines has been performed under accelerated oxidation and room temperature conditions. Several well-known hydrogen-donating antioxidants, such as butylated hydroxytoluene, *N*,*N*′-diphenyl-1,4-phenylenediamine, *N*,*N*′-di-2-butyl-1,4-phenylenediamine, 2,2′-thiodiethylene bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], and pentaerythritol tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], do not inhibit oxidative degradation of amine solid sorbents, and they even accelerate the oxidation rate. It was found that oxidative degradation of polyamines can be delayed by blending them with organic sulfur-containing compounds such as 2,2-thiodiethanol, 2-hydroxyethyl disulfide, and 3,3′-dithiodipropionic acid. Such sulfur-containing compounds may react multiple times with reactive free radicals or peroxides, decreasing the oxidation rate, thereby, increasing lifetime of adsorbents. Therefore, sulfur-containing compounds are a promising choice for inhibiting oxidative degradation of amine solid sorbents for CO_2 capture.

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Chapter 5. Summary and Perspectives for Future Works

This chapter reviews major findings of chapters 2–4 and presents perspectives for possible future work of this research.

5.1. Summary

This dissertation introduces approaches to improve CO_2 adsorption performance and oxidative stability of amine solid sorbents for CO_2 capture. The synergistic effect of the binary amines IMs/TEPA significantly improved CO_2 adsorption capacity, working capacity, and reduced heat of adsorption. Blending amines with sulfur-containing compounds led to significant enhancements in lifetime of amine solid sorbents. Additionally, insight into the oxidative degradation of amine solid sorbents investigated in this work could contribute to the development of new amine with high O_2-resistance for CO_2 capture. Therefore, the results from this dissertation play important roles for the development of cost-effective amine adsorbents relevance to post-combustion CO_2 capture applications.

In Chapter 2, MF was selected as support and impregnated with a mixture of TEPA and Ims to improve the initial and working CO_2 adsorption capacity. Ims with electron-donating groups showed a synergistic effect with TEPA regarding adsorption/desorption performance. Impregnating MF with such Ims and TEPA improve the CO_2 adsorption capacity, amine efficiency, working capacity, and decreased the heat of adsorption compared with those obtained for MF impregnated only with TEPA. Positive interactions between Ims and the amino group may have been caused by Ims' proton-acceptor ability and improvements in the diffusion of protons and CO_2 to sub-surface reactive sites. MF modified with 30 wt% 4MIm and 40 wt% TEPA exhibited a high first-pass CO_2 adsorption capacity of 4.88 mmol/g at 100 kPa and 40 °C and a working capacity of 4.15 mmol/g following vacuum regeneration. CO_2 adsorption performance of sorbents was strongly affected by adsorption temperature. A maximum CO_2 uptake of 5.88 mmol/g with this sorbent was observed under conditions of 50 °C and 100 kPa CO_2.

In chapter 3, the stability of silica impregnated with commercial TEPA under accelerated oxidizing conditions was evaluated and the changes in the composition of sorbents during oxidative degradation were reported. The oxidative stability of sorbents depended on the TEPA loading, oxidation duration, temperature, and O_2 concentration. The marked loss of the CO_2 adsorption capacity of the sorbents in O_2-containing environments was mainly caused by changes in the functional groups of TEPA and the sorbent composition, as supported by thermogravimetric, elemental, infrared spectroscopic, and gas chromatography analyses. The results suggested that the hydroxyl groups of silica help to protect TEPA from oxidation. The pore and surface characteristics of sorbent have a significant influence on the O_2 diffusion, regulating the oxidation rate. Among isolated components in commercial TEPA, 1,4,7,10,13-pentaazatridecane, 1-(2-aminoethyl)-4-[(2-aminoethyl)amino]ethyl]piperazine displayed strong O_2 resistance whereas 1-[2-[[2-[(2-aminoethyl)amino]ethyl]-amino]ethyl]piperazine and 4-(2-aminoethyl)-N-(2-aminoethyl)-N′-[2-[(2-aminoethyl)amino]ethyl]-1,2-ethanediamine were revealed to be sensitive to O_2. Amines which are unfavorable to form six-membered rings may be advantages for the development of effective sorbents for CO_2 capture.

In chapter 4, the effect of different oxidation inhibitors on degradation of MF impregnated with typical amines including TEPA, PEI, and 4MIm/TEPA binary system was investigated. Sulfur-containing compounds and hydrogen-donating antioxidants were selected as additives. Oxidative degradation tests of the amine solid sorbents were performed in a designed packed-bed reactor equipped with a temperature controller. The results showed that hydrogen-donating antioxidants, such as butylated hydroxytoluene, *N*,*N*′-diphenyl-1,4-phenylenediamine, *N*,*N*′-di-2-butyl-1,4-phenylenediamine, 2,2′-thiodiethylene bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], and pentaerythritol tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], catalyzed oxidative degradation. In contrast, sulfur-containing additives, which owe their effectiveness to free-radical scavenging and peroxide decomposition actions, decreased the oxidation rate. Amine solid sorbents containing such additives had 1.5–4 times higher CO_2 adsorption capacity retention values than the non-additive sorbents under accelerated oxidation conditions. Furthermore, the long term stability of the amine solid sorbents over 15 months storage was demonstrated. These sulfur-containing additives also delayed sorbent degradation.

5.2. Perspectives for Future Work

As discussed, flue gas carries not only CO_2, N_2, O_2 but also several trace impurities such as SO_x, NO_x, moisture, and particulates which probably reduce CO_2 adsorption performance, selectivity, and stability of amine solid sorbents. However, effect of such impurities toward amine solid sorbents has not been completed in this work. Degradation of amines releases degradation compounds related to health and environment impacts. Understanding formation of degradation products contributes to fundamental concepts for degradation mechanism of amines. Therefore, it is necessary to identify and understand toxicity of degradation products of amine solid sorbents used CO_2 capture. The results of this study point out that sulfur-containing compounds can prevent oxidative degradation of amine solid sorbent, yet the optimum ratio of such compounds and amines in sorbents has not been investigated. Although this study reveals that degradation of amines in O_2-containing environments depended on structures of amines, their oxidative stability is still a vague concept.

Therefore, further researches should be conducted as the following purposes:

(1) Investigation of optimum ratios of amines, sulfur-containing additives, and support for preparing effective sorbents for CO_2 capture,

(2) Investigation of adsorption performance of amine solid sorbents in real flue gas conditions and their degradation in the presence of impurities including NO_x, SO_x, and metal particulates

(3) Identification of degradation products and understand their formation,

(4) Investigation of effect of amine structures including molecular weight, homogenous series, and alkyl linker between amine functions on the degradation of amines, and

(5) Design of new amines with high CO_2 capture ability and high stability.

Publications & presentations

Publications

1. **Quyen T. Vu**, Hidetaka Yamada, and Katsunori Yogo. Exploring the Role of Imidazoles in Amine-Impregnated Mesoporous Silica for CO_2 Capture. *Ind. Eng. Chem. Res.* 2018, 57, 2638–2644.

2. **Quyen T. Vu**, Hidetaka Yamada, Katsunori Yogo. Oxidative Degradation of Tetraethylenepentamine-Impregnated Silica Sorbents for CO_2 Capture. *Energy Fuels* 2019, 33, 3370–3379.

3. **Quyen T. Vu**, Hidetaka Yamada, Katsunori Yogo. Inhibitors of Oxidative Degradation of Polyamine-Modified Silica Sorbents for CO_2 Capture. *Ind. Eng. Chem. Res.* 2019, 58, 15598–15605.

Presentations

1. **Quyen T. Vu**, Hidetaka Yamada, Katsunori Yogo. Impregnation of Tetraethylenepentamine and Imidazoles in Mesoporous Cellular Foam Silica for CO_2 Capture. 11th International Conference on Separation Science and Technology, 9–11th November, 2017 Busan, Korea (Oral presentation).

2. **Quyen T. Vu**, Hidetaka Yamada, Katsunori Yogo. Oxidative Degradation of Polyamine-Containing CO_2 Adsorbents. 5th Post Combustion Capture Conference, 17–20th September, Kyoto, Japan (Oral presentation).