Development of Silica-Gel-Supported Polyethylenimine Sorbents for CO_2 Capture from Flue Gas

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In order to reduce the sorbent preparation cost and improve its volume-based sorption capacity, the use of an inexpensive and commercially available silica gel was explored as a support to prepare a solid polyethylenimine sorbent (PEI/SG) for CO_2 capture from flue gas. The effects of the pore volume and particle size of the silica gels, molecular weight of polyethylenimine and amount of polyethylenimine loaded, sorption temperature and moisture in the flue gas on the CO_2 sorption capacity of PEI/SG were examined. The sorption performance of the developed PEI/SG was evaluated by using a thermogravimetric analyzer and a fixed-bed flow sorption system in comparison with the SBA-15-supported polyethylenimine sorbent (PEI/SBA-15). The best PEI/SG sorbent showed a mass-based CO_2 sorption capacity of 138 mg-CO_2/g-sorbent, which is almost the same as that of PEI/SBA-15. In addition, the PEI/SG gave a high volume-based sorption capacity of 83 mg-CO_2/cm^3-sorbent, which is higher than that of PEI/SBA-15 by a factor of 2.6. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 2495–2502, 2012

Keywords: carbon dioxide, CO_2 capture, flue gas, polyethylenimine, silica gel, sorption

Introduction

The influence of greenhouse gases on global climate has attracted great attention with respect to developing strategies for the reduction of carbon dioxide (CO_2) emissions.[1] CO_2 capture and separation from the flue gas have been considered as a key option for greenhouse gas control.[2,3,4] Among various approaches reported for CO_2 capture, the amine scrubbing process is currently more favored technology for CO_2 capture on industrial scale.[5,6,7] However, this process has some problems, including high-energy consumption, low-absorption/desorption rate, degradation of amine solution in the process, and corrosion of the amine solution. In comparison with the liquid amine scrubbing technique, the solid-supported amine sorbents have shown some significant advantages, including high capacity, no or less corrosion, higher sorption/desorption rate and lower energy consumption.

Currently, there are two types of the solid-supported amine sorbents according to their preparation methods. The sorbents of type 1 are prepared through the formation of the covalent bonds between the amine-containing compounds and the surface of the solid support, such as SBA-12,[8] SBA-15,[9–13] SBA-16,[14,15] MCM-41,[16] and MCM-48.[17] A significant advantage of this type of the sorbents is less loss and migration of the amine-containing compounds from the surface in the sorption-desorption cycles due to the strong covalent bonds between the amine-containing compounds and the support surface. However, this kind of the sorbents usually shows relatively lower CO_2 adsorption capacity due to the limitation of the amine groups on the surface, although a significant progress has been made recently. The preparation method for these sorbents is also relatively complex, resulting in higher cost for the sorbent preparation. The sorbents of type 2 are prepared by loading the amine-containing polymer or oligomer, such as polyethylenimine (PEI) or oligoethylenimine, on the nanoporous materials, such as KIT-6,[18] SBA-15,[19–21] and MCM-41,[22–27] using a simple wet-impregnation method on the basis of the ''molecular basket'' sorbent (MBS) concept proposed first by Xu

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et al.[22–25] and further developed by others.[21,28,29] The significant advantages of these sorbents are that the sorbents can be prepared relatively easily by loading a large amount of CO_2-philic polymer/oligomer on various porous materials, and are able to offer a sorption capacity higher than 140 mg-CO_2/g-sorbent, as the method is easy to increase and control amount of the amines loaded. However, most porous materials, such as MCM-41, SBA-15 and KIT-6, reported currently in literature for preparation of these solid amine sorbents are expensive and commercially unavailable. For using MCM-41 and SBA-15 as supports, it was estimated that the expense of the support materials accounts for more than 90% of the total sorbent preparation cost, which results in a preparation cost higher than \$700/kg.[35] Therefore, using an inexpensive support material can significantly reduce the preparation cost of the sorbent. Furthermore, poor hydrothermal stability of the mesoporous silica molecular sieves[30] may cause the degradation of the sorbents within the sorption/desorption cycles. The volume-based sorption capacity of these sorbents is also lower due to low-packing density of the sorbents. All these limit the practical application of these solid amine sorbents in the large-scale CO_2 capture from flue gas. Currently, a great deal of attention has been paid to development of the inexpensive solid amine adsorbents/sorbents, such as amine-treated Zeolite 13X,[31] glass fiber,[32,33] and activated carbon.[34,35] It is highly desired to develop a solid amine sorbent with high performance and low cost for the large-scale CO_2 capture from the power station flue gas.

Silica gel is a porous material, which has been produced on a large scale with a price less than \$40/kg, and used widely in industry. Recently, Zhu et al. reported their development of the solid amine sorbent by loading polyethylenimine onto silica gels, but the CO_2 sorption capacity was only 46.9 mg-CO_2/g-sorbent at a CO_2 partial pressure of 4.88 atm.[36] The objective of this study is to explore the use of inexpensive and commercially available silica gel as a support to prepare the silica-gel-supported polyethylenimine sorbent (PEI/SG) with high-sorption performance and low cost for CO_2 capture from flue gas. The effects of the silica gel pore volume, silica gel particle size, polyethylenimine molecular weight and loading amount on the CO_2 sorption capacity were examined to determine the best PEI/SG formulation. The PEI/SG was evaluated in a thermogravimetric analyzer (TGA) and a fixed-bed flow sorption system in comparison with the SBA-15-supported polyethylenimine sorbent (PEI/SBA-15) reported in our previous study.[21]

Experimental

Materials

Various silica gel samples with pore volume of 0.68, 0.75 and 1.15 cm^3/g, and particle size of 33–75, 75–150, and 250–425 μm, respectively, were purchased from Aldrich, and used as supports for preparation of the PEI/SG samples.

Polyethylenimine (PEI) with an average molecular weight (Mn) of 423, 25,000, and 50,000 g/mol, respectively, was purchased from Aldrich. Methanol with a purity of 99.8% was also purchased from Aldrich for using as a solvent in preparation of PEI/SG.

Preparation of PEI/SG samples

The PEI/SG samples were prepared by a wet-impregnation method.[17,18] In a typical preparation, about 1.0 g of PEI was dissolved in 20 cm^3 of methanol under stirring for $\sim$60 min to make a PEI/methanol solution, and then desired amount of the silica gel after vacuum drying at 108°C was added to the PEI/methanol solution. The slurry was continuously stirred at room temperature for about 5 h, allowing the methanol in the slurry to be evaporated. After methanol was mainly evaporated, the sample was further dried in a vacuum oven at 40°C, 1 kPa for 12 h, and then was sealed in a bottle before use. The PEI/SG samples with different PEI loading amount were denoted as PEI(x)/SG, where x is the weight percentage of PEI-loading amount in the sorbent.

Evaluation of CO_2 sorption/desorption performance

The CO_2 sorption/desorption performance of the prepared sorbents was evaluated by using TGA (TA Instruments). A typical analysis is described as below: About 15 mg of the sorbent was placed at the TGA sample pan. The sample was first heated from room temperature to 100°C at a rate of 10°C/min under a pure N_2 flow with a flow rate of 100 cm^3/min, and was kept at 100°C for 60 min to remove the remained solvent, the sorbed moisture and CO_2 from the sample. Then, the sample was cooled down to the desired sorption temperature and kept at this temperature for 20 min. The sorption was started by switching the flow gas from pure N_2 to pure CO_2 at the same flow rate and hold at the sorption temperature for 40 min for CO_2 sorption. After the sorption, the flow gas was switched back to the pure N_2 and the temperature was increased to 100°C for 50 min for desorption. The sorption capacity of the sorbent was calculated according to the mass change during sorption.

The CO_2 sorption performance of some samples was also evaluated in a fixed-bed flow sorption system. A schematic diagram of the system is shown in Figure 1. The sorbent was placed in a stainless column with 150 mm length and 7 mm inner dia. The column was set in a furnace with a temperature controller. The gas was controlled by a mass flow controller and flowed up through the column. The concentration of CO_2 was monitored by an on-line SRI 861°C gas chromatography (GC). A typical evaluation procedure is described below: About 5.8 cm^3 sorbent sample was packed into the column. The sorbent in the column was heated to 100°C and hold at this temperature overnight under an ultrahigh pure helium flow at a flow rate of 50 cm^3/min to remove the sorbed moisture and/or CO_2 in the sorbent. Then, the column was cooled to a desired sorption temperature, such as 75°C, under the same helium flow. The sorption was started by switching the helium gas to a simulated flue gas with 15 v% CO_2, 4.5 v% O_2 in N_2 at a flow rate of 20 cm^3/min. After saturation of the sorbent, the simulated flue gas was switched to the ultrahigh pure helium gas at a flow rate of 100 cm^3/min, and the sorbent bed temperature was increased to 100°C and kept at this temperature for 240 min for desorption. The CO_2 concentration in the effluent was measured by using the on-line GC with an interval of 2.5 min. The sorption capacity was calculated on the basis of the breakthrough curve, as described in our previous study.[29]

Design of orthogonal tests for optimization of PEI/SG formulation

Many factors, including pore volume and particle size of silica gel, molecular weight of PEI, and amount of PEI loaded, can affect the sorption capacity of PEI/SG. In order to optimize the PEI/SG formulation, a design of orthogonal tests was used to improve the experimental efficiency.

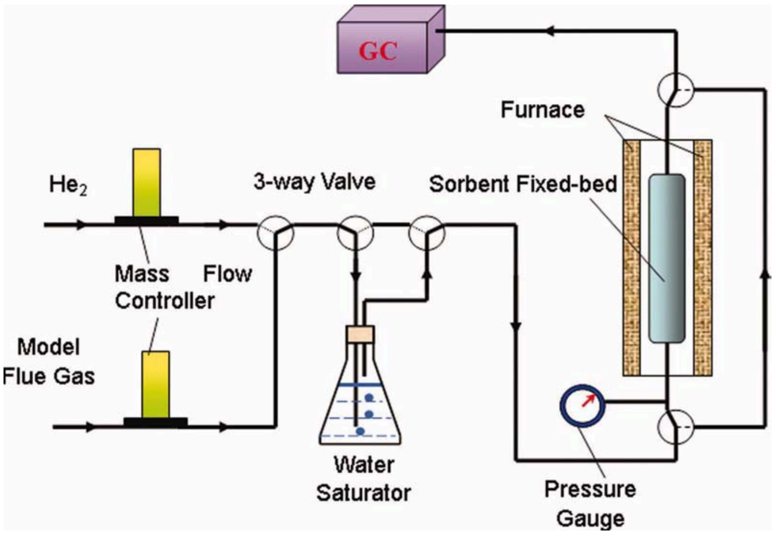

Figure 1. Schematic diagram of the fixed-bed flow system for evaluating CO_2 sorption-desorption performance.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The factors and levels for the orthogonal tests are listed in Table 1. There were four factors with three levels for each factor: pore volume of silica gel (0.68, 0.75, and 1.15 cm^3/g), particle size of silica gel (33–75, 75–150, 250–425 μm), PEI loading percentage (40, 50, and 60 wt %), and molecular weight of PEI (423, 25,000, and 50,000 g/mol).

Characterization of Silica Gel and PEI/SG

The Brunauer-Emmett-Teller surface area (S_{BET}), pore volume and pore size of the samples were measured by the N_2 adsorption-desorption at 77 K using the Micromeritics ASAP 2020 surface area and porosity analyzer. The pore volume of the materials was calculated on the basis of the adsorption amount of nitrogen at the relative pressure of $P/P_0 = 0.995$. The pore size was estimated according to the BJH pore size distribution curve. Thermal stability of PEI, silica gel and PEI(x)/SG samples was evaluated by using a TA Q600-SDT TGA-DSC thermal gravimeter. About 15 mg of the sample was heated at a ramp rate of 10 °C/min from room temperature to 600°C under an N_2 flow at 100 cm^3/min. The scanning electron microscopy (SEM) images were obtained on a FEI Quanta 200 environmental scanning electron microscope operating at 20 kV.

Results and Discussion

Optimization of PEI/SG formulation

Many factors may affect the sorption capacity of PEI/SG, including the pore volume and particle size of silica gel, molecular weight and loading amount of PEI. In order to optimize the PEI/SG formulation, the orthogonal test design was used for improving the efficiency of experiments. The orthogonal test design with a $L_9(3^4)$ array is shown in Table 2, which reduces the total test number from 3^4 (i.e., 81) to 9. The CO_2 sorption capacity of the prepared sorbents was measured using TGA at 75°C. The results of the test and the extreme difference analysis are also listed in Table 2, in which K_{ij} is the average CO_2 sorption capacity under the level i for investigating variable j, and $\mathrm{R}j$ is the difference between the $\max\{\mathrm{K}j\}$ and $\min\{\mathrm{K}j\}$. Comparison of $\mathrm{K}ij$ values for each factor indicates that in the variant ranges examined in this study increase of the pore volume, decrease of the particle size and reduction of the molecular weight benefit the increase of the CO_2 capacity significantly, while the change in the PEI loading in a range from 40 to 60 wt % has only a little effect on the CO_2 capacity. According to the K_{ij} values, the best combination of the parameters for preparation of PEI/SG are 1.15 cm^3/g pore volume; 33–75 μm particle size; 423 g/mol PEI molecular weight and 50 wt % PEI loading. A PEI/SG sample was prepared on the basis of the suggested parameters, and the measured CO_2 sorption capacity of this sample (PEI(50)/SG) was 131.1 mg-CO_2/g-sorbent, which is close to the capacity of PEI(50)/SBA-15 reported in our previous study.[21]

Table 1. Factors and Levels for Orthogonal Test

Factor	Level		
	1	2	3
Pore volume, cm^3/g	0.68	0.75	1.15
Particle size, μm	33–75	75–150	250–425
PEI loading, wt %	40	50	60
Molecular weight (Mn), g/mol	423	25000	50000

Table 2. Orthogonal Design of Experiments and Results

	Factor (j)				Cap.*
No.	Pore vol. (cm^3/g)	Particle Size (μm)	PEI Loading (%)	Mw (g/mol)	mg/g
1	0.68	250~425	40	423	5.6
2	0.68	75~150	50	25000	12.0
3	0.68	33~75	60	50000	8.2
4	1.15	250~425	50	50000	22.5
5	1.15	75~150	60	423	76.0
6	1.15	33~75	40	25000	77.5
7	0.75	250~425	60	25000	7.8
8	0.75	75~150	40	50000	11.4
9	0.75	33~75	50	423	60.6
K_{1j}	8.6	12.0	31.5	47.4	Best design
K_{2j}	58.7	33.1	31.7	32.4	1.15cm^3/g
K_{3j}	26.6	48.8	30.6	14.0	33–75 μm
$\mathrm{R}j$	50.1	36.8	1.1	33.4	50%, 423

*CO_2 sorption capacity of sorbents (unit is mg-CO_2/g-sorbent).

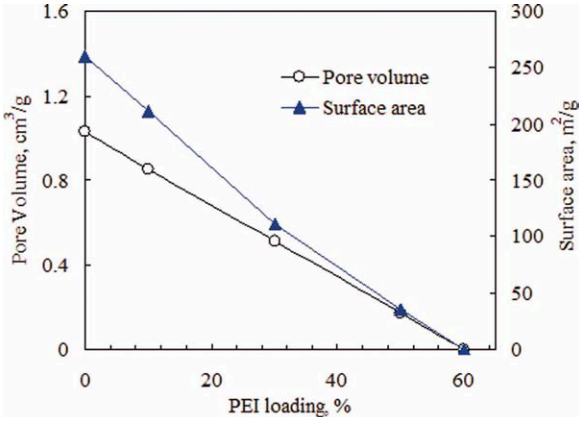

Figure 2. Effect of different PEI loading on pore volume and BET surface area of PEI/SG samples.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of PEI loading

In order to further examine the effect of PEI loading, a series of PEI/SG samples were prepared by using a silica gel with 1.15 cm^3/g pore volume and 33–75 μm particle size, and PEI with an average molecular weight of 423 g/mol at different PEI loading of 10, 30, 50, and 60 wt %, respectively. The surface area, pore volume and pore-size distribution of the prepared PEI/SG samples were measured by the nitrogen adsorption/desorption. Figure 2 shows the pore volume and surface area of the PEI/SG samples as a function of PEI loading amount. The pore volume and the surface area of the silica gel support were 1.03 cm^3/g and 260 m^2/g, respectively. With increase of the PEI loading, both the pore volume and the surface area of PEI/SG decreased continuously. The pore volume and surface area of PEI(50)/SG were 0.17 cm^3/g and 35 m^2/g, respectively. When the PEI loading amount increased to 60 wt %, almost no pore volume and surface area were measurable. Since the pore volume of the silica gel is 1.03 cm^3/g and the density of the PEI liquid is about 1.0 g/cm^3, the theoretical maximum PEI loading amount in the pores of the silica gel is about 50.7 wt %, if assuming that all loaded PEI is put into the pores of the silica gel, and the PEI density does not change after loading the PEI into pores of the silica gel. When PEI loading is over 50 wt %, for example PEI(60)/SG, the pores in the silica gel are completely filled by PEI, resulting in almost no measurable pore volume and no measurable surface area, as shown in Figure 2. The excessive PEI may be coated on the external surface of the silica gel particles, leading to the agglomeration of the silica gel particles. Figure 3 showed the pore-size distribution of PEI/SG samples with different PEI loading, which clearly indicates that the loaded PEI was filled into the pores and resulted in the significant reduction of the pore volume and surface area. Interestingly, it was found that the increase of the PEI loading amount reduced the pore volume, but not significantly changed the pore size. The similar phenomenon was also found in our previous study of PEI/SBA-15.[21]

SEM images of silica gel, PEI(10)/SG, PEI(50)/SG, and PEI(60)/SG are shown in Figure 4. The images clearly show that almost no PEI or very little of PEI was observed on the external surface of the particles in PEI(10)/SG, PEI(50)/SG, while some PEI coated on the external surface of PEI(60)/SG particles was observed, leading to the partial agglomeration of the particles. The SEM results further confirm that the most of PEI was filled into the silica gel pores in PEI(50)/SG sample. The effect of PEI loading amount on the CO_2 sorption capacity at 75°C was further examined by TGA and the results are shown in Figure 5. The silica gel alone gave a CO_2 adsorption capacity of 5.1 mg-CO_2/g-sorbent, indicating that there is also a weaker interaction between CO_2 and the silica gel at 75°C. When PEI loading amount increased from zero to 50 wt %, the CO_2 sorption capacity increased to the maximum of 131.1 mg-CO_2/g-sorbent. After this point, the CO_2 sorption capacity decreased with increase of the PEI loading amount. This trend is similar to the result observed in our previous study of the PEI/SBA-15 samples.[22] It is clearly shown that loading of PEI on the silica gel increases the CO_2 sorption capacity significantly. This is because PEI contains a great number of the potential CO_2-philic sites and the silica gel makes these sites accessible through improving the dispersion of PEI. When the PEI loading is higher than 50 wt %, the excessive PEI is coated on the external surface of the silica gel particles, resulting in the agglomeration of the particles, as shown in Figure 4d, and, thus, the number of the accessible sorption sites is reduced.

The efficiency of the amine groups in the loaded PEI, which is defined as a molar ratio of the sorbed CO_2 to the amine groups in the sorbent, for each PEI/SG sample was calculated, and the results are also shown in Figure 5. This figure shows the maximum value of 0.28 mol-CO_2/mol-amine at 40 wt % PEI loading (PEI(40)/SG). Below 40 wt % PEI loading, the amine efficiency increases with increasing PEI loading. This is probably because the interaction of the amine groups in PEI with silanol groups on the silica gel surface, resulting in the consumption of a part of the amine groups. When the PEI loading is higher than 40 wt %, increase of the PEI loading results in reduction of the percentage of the accessible amine sites due to increase of the diffusion resistance of CO_2 into the bulk of PEI in the pores, especially in the case when the agglomeration is formed, as shown in Figure 4d.

Effect of temperature on the CO_2 sorption capacity

Effect of the sorption temperature on the sorption capacity of PEI(50)/SG was examined using TGA with pure CO_2 gas

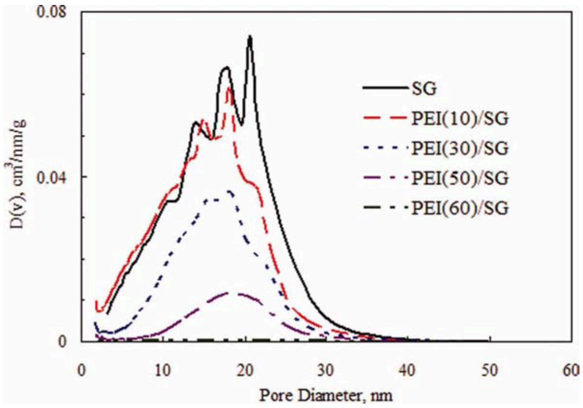

Figure 3. The pore-size distributions of silica gel before and after PEI loading.

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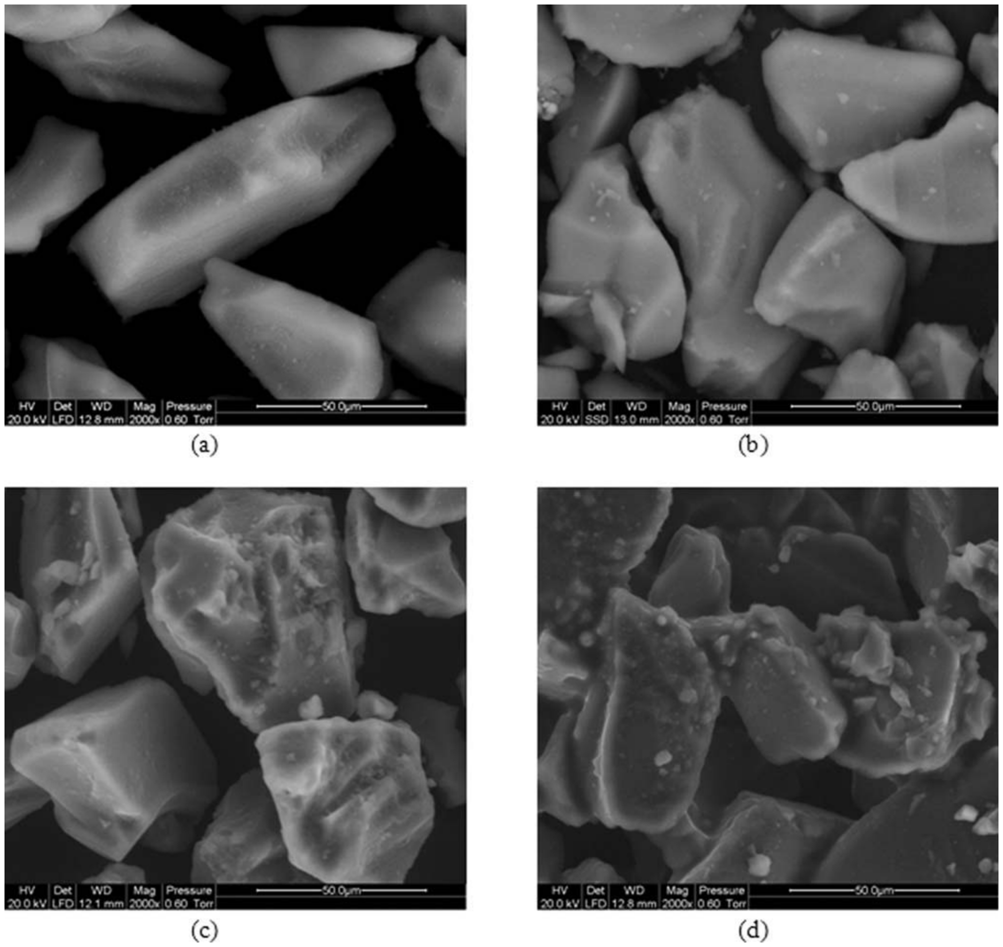

(a) (b)

(c) (d)

Figure 4. SEM images of (a) silica gel, (b) PEI(10)/SG, (c) PEI(50)/SG, and (d) PEI(60)/SG.

at 25, 50, 65, 75, 85 and 100°C, respectively. The results are shown in Figure 6. At 25°C, the CO_2 sorption capacity of PEI(50)/SG was 85.6 mg-CO_2/g-sorbent. With increasing temperature, the CO_2 sorption capacity became higher and reached the highest capacity of 131.1 mg-CO_2/g-sorbent at 75°C. Continuously increasing temperature from 75 to 100°C, the sorption capacity decreased to 124.5 mg-CO_2/g-sorbent. The best capacity was obtained at 75°C, similar to the results observed for PEI(50)/MCM-41[22] and PEI(50)/SBA-15.[21] The results indicate that at the temperature range from 25 to 75°C, the diffusion of CO_2 in the PEI may be a sorption rate-control step. Consequently, elevating temperature results in increase of the number of accessible amine sites in the sorbent, and, thus, increases the CO_2 sorption capacity. When the temperature is higher than 75°C, the thermodynamics may play a more important role, thus, resulting in decrease of the sorption capacity with increasing temperature.

Effect of moisture on CO_2 sorption capacity

Effect of moisture on the CO_2 sorption capacity of PEI(50)/SG was examined in the fixed-bed flow system using a simulated flue gas with 15 v% CO_2, 4.5 v% O_2 in N_2. About 3.0 v% of H_2O was added to the simulated flue gas by bubbling the gas through water, as shown in Figure 1. The sorption breakthrough curves of PEI(50)/SG in the absence/presence of moisture are shown in Figure 7. The breakthrough capacity of PEI(50)/SG was 138 mg-CO_2/g-sorbent in the absence of moisture, while in the presence of moisture in the flue gas the breakthrough capacity of PEI(50)/SG increased to 185 mg-CO_2/g-sorbent, which is corresponding to an amine efficiency of 0.36 mol-CO_2/mol-amine. This result confirms that the presence of moisture improves the sorption capacity of the supported PEI

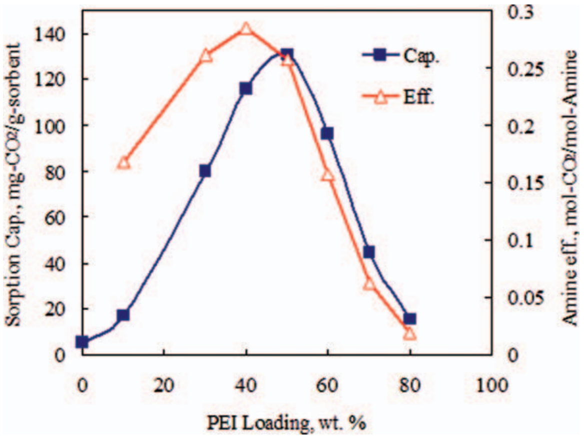

Figure 5. Effect of different PEI loading on the CO_2 sorption capacity and amine efficiency.

The data were from TGA at 75°C with pure CO_2 gas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

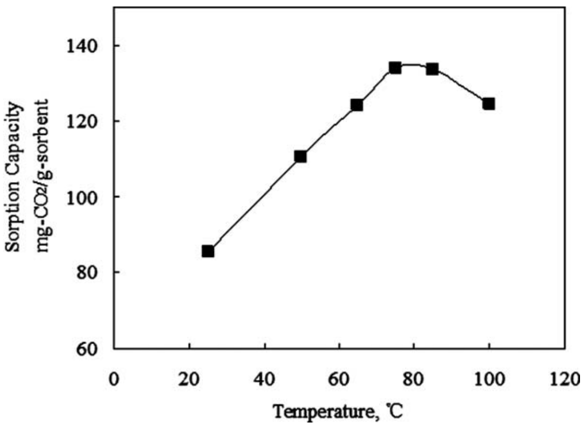

Figure 6. Effect of sorption temperatures on CO_2 sorption capacity.

The data were from TGA with pure CO_2 gas.

sorbents, which was first found in our previous study for CO_2 sorption on PEI(50)/MCM-41.[23]

Regenerability and stability of PEI(50)/SG

In addition of the high CO_2 capacity and selectivity, regeneration and stability of sorbent in cycles are crucial for practical application of the sorbent, as they are directly related to the cost of the sorption/desorption process. In this study, desorption was performed by switching the flue gas to pure N_2 gas. The 10 sorption-desorption cycles of PEI(50)/SG were conducted by using TGA. The sorption was at 75°C and the desorption was at 75 and 100°C, respectively, for comparison. The measured sorption capacities as a function of the cycle number are shown in Figure 8. For desorption at 100°C, a slight decrease of the sorption capacity with increasing cycle number was observed. The sorption capacity decreased from 131 mg-CO_2/g-sorb for the fresh sorbent to 116 mg-CO_2/g-sorb for the regenerated sorbent after 10 cycles. The sorption capacity was reduced by about 11.6% after 10 cycles. For desorption at 75°C, a less decrease of the sorption capacity with increasing cycle number was observed. The sorption capacity of the regenerated sorbent after 10 cycles was 125 mg-CO_2/g-sorb, indicating that 95.4% of the sorption capacity was recovered after 10 cycles. The results suggest that desorption at 75°C is better than that at 100°C for keeping the sorption capacity in the cycles. The detailed analysis of the sorption capacity as a function of the cycle number further shows that the degradation of the sorbent became insignificant with increasing cycle number. For example in the case of desorption at 75°C, almost no change in the capacity was observed at the last 5 cycles. The loss of the CO_2 sorption capacity in the first couple of cycles may be due to the evaporation of ethylenimine oligomers with lower molecular weight. Further investigation on it is necessary to clarify the degradation reason.

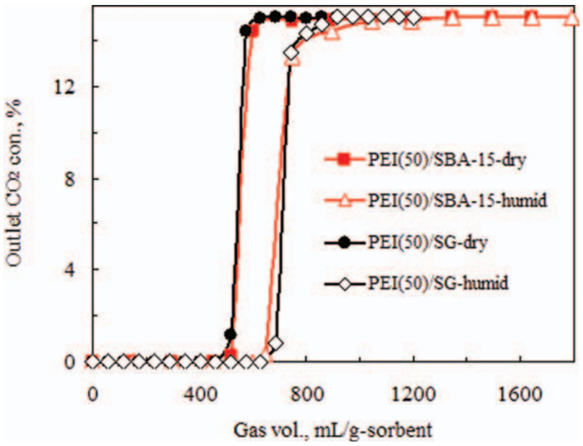

Figure 7. Breakthrough curves of PEI(50)/SBA-15 and PEI(50)/SG for CO_2 capture from the simulated flue gas (15 v% CO_2, 4.5 v% O_2 in N_2) in presence/absence of moisture at 75 °C and 207 h^{-1} GHSV in the fixed-bed flow sorption system.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

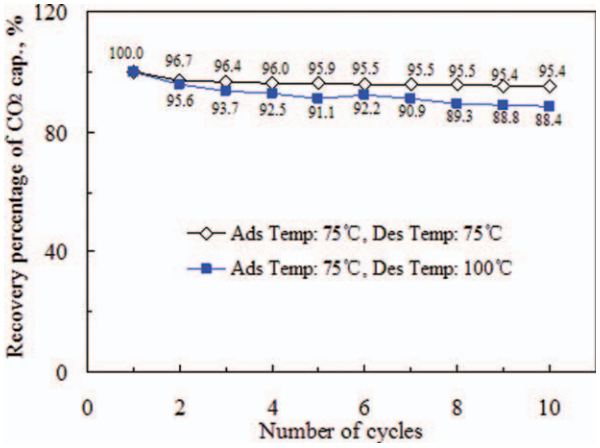

Figure 8. Recovery percentage of the CO_2 capacity as a function of sorption-desorption cycle number.

Data were from TGA at 75°C with pure CO_2 gas for sorption and desorption at 75 and 100°C, respectively, with pure N_2 gas for desorption. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The thermal stability of the silica gel, PEI and PEI/SG with different PEI loading were also examined by using TGA. Figure 9 shows the weight loss of the samples as a function of temperature in N_2. The silica gel was stable at

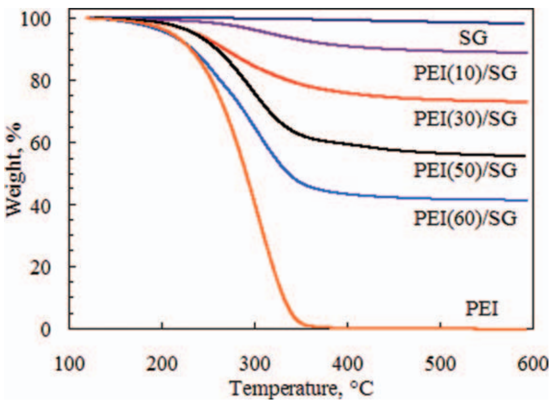

Figure 9. Stability of PEI and PEI/SG with different PEI loading.

Data were from TGA with pure N_2 gas at a flow rate of 100 cm^3/min and a ramp rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

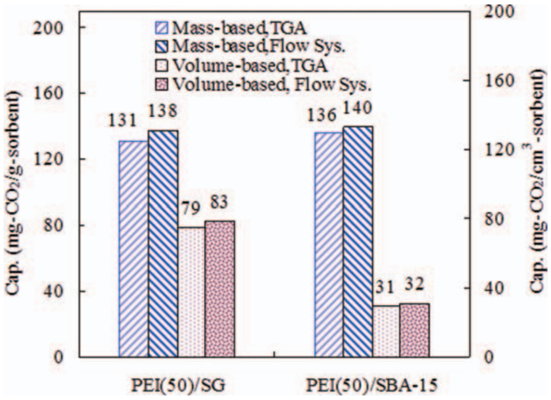

Figure 10. The CO_2 mass-based and volume-based sorption capacities of PEI(50)/SBA-15 and PEI(50)/SG measured in TGA with pure CO_2 gas and the fixed-bed flow system with the simulated gas (15 v% CO_2, 4.5 v% O_2 in N_2) both at 75°C.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the temperature less than 600°C with only mass loss of 3.9 wt %. The PEI lost about 1.0 wt % at 100°C, which is probably due to the moisture and other low-boiling compounds in PEI. PEI began to lose the weight significantly at above 120°C, and a sharp weight loss was observed at 300°C for decomposition of PEI. When the temperature increased to above 375°C, the weight of PEI sample became zero, indicating that PEI decomposed and/or evaporated completely. PEI/SG samples began to lose the weight around 120°C and ended the loss of the weight around 375°C with the sharp weight loss at 300°C, similar to the pure PEI. It indicates that there is almost no change in the thermal stability of PEI after loading PEI on the silica gel, and PEI(50)/SG should be stable at a temperature less than 120°C.

Comparison of PEI(50)/SG with PEI(50)/SBA-15

PEI(50)/SBA-15, which was prepared by loading 50 wt % PEI on a mesoporous molecular sieve of SBA-15, has been developed in our previous study.[21,29] In order to compare the sorption capacity of PEI(50)/SG with PEI(50)/SBA-15, both were evaluated at the same conditions by using both the TGA and the fixed-bed flow sorption system. The breakthrough curves of PEI(50)/SBA-15 at 75°C with the simulated flue gas (15 v% CO_2, 4.5 v% O_2 in N_2) in the presence/absence of moisture are also shown in Figure 7. The sorption capacities measured for the two sorbents in different tested systems are shown in Figure 10 for comparison. On the basis of the TGA results, the mass-based CO_2 sorption capacity of PEI(50)/SG is 131 mg-CO_2/g-sorbent, which is less than, but very close to that (136 mg-CO_2/g-sorbent) of PEI(50)/SBA-15. The mass-based CO_2 sorption capacity of PEI(50)/SG measured in the fixed-bed flow system is 138 mg-CO_2/g-sorbent, which is almost the same as that 140 mg-CO_2/g-sorbent of PEI(50)/SBA-15. It indicates that the mass-based sorption capacity of PEI(50)/SG is comparable with that of PEI(50)/SBA-15. In addition, the volume-based sorption capacity of PEI(50)/SG and PEI(50)/SBA-15 is 83 and 32 mg-CO_2/cm^3-sorbent, respectively, on the basis of the tests in the fixed-bed flow system. The higher volume-based capacity of PEI(50)/SG is due to its higher packing density (0.60 g/cm^3) than that (0.23 g/cm^3) of PEI(50)/SBA-15 by 173%. This difference in the packing density results in the greater volume-based sorption capacity of PEI(50)/SG than that of PEI(50)/SBA-15 by a factor of 2.6.

In comparison with the result from Zhu et al.,[36] the CO_2 capacity (86 mg-CO_2/g-sorbent) of PEI(50)/SG developed in this study is higher than that (46 mg-CO_2/g-sorbent) of the best PEI-modified silica gel sorbent prepared by Zhu et al. by more than 85% at the same sorption temperature (25°C). The significantly higher capacity of PEI(50)/SG can be attributed to the optimization of PEI/SG formulation in this study.

Summary and Conclusions

A new type of MBS with high capacity and low cost has been developed by loading PEI on a commercial silica gel. The effects of the silica gel pore volume, silica gel particle size, PEI molecular weight and PEI loading amount on the CO_2 sorption capacity were examined for optimizing the PEI/SG formulation. It was found that in the parameter range examined in this study the large pore volume and small particle size of silica gel, low-molecular-weight of PEI and 50 wt % PEI loading are better for preparation of high performance PEI/SG sorbent. The best PEI/SG sorbent, PEI(50)/SG, was obtained by loading 50 wt % PEI with an average molecular weight of 423 g/mol on a silica gel with a pore volume of 1.15 cm^3/g and a particle size of 33–75 μm, which gave a mass-based CO_2 sorption capacity of 138 mg-CO_2/g-sorbent, almost the same as that of PEI(50)/SBA-15. In addition, PEI(50)/SG gave a high volume-based sorption capacity of 83 mg/cm^3, which is higher than that of PEI(50)/SBA-15 by a factor of 2.6 due to the former has a higher packing density than the latter. The result indicates that the silica-gel-based MBS is promising for large-scale CO_2 capture from flue gas due to its high sorption capacity, especially the high volume-based capacity, low-preparation cost and commercial availability of the silica gel. However, there are still challenges for the practical application of this sorbent for CO_2 capture from flue gas, including the stability, regeneration method and the mass and heat transfers in the scale up of the process.

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