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Large-Pore Mesoporous Silica Impregnated with Blended Amines for CO₂ Capture

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ABSTRACT: Mesoporous silica materials with different pore volumes were functionalized by wet impregnation with a variety of amines for the purpose of CO₂ adsorption. The effects of the concentration and composition of amine blends, silica supports, and adsorption temperature on CO₂ adsorption were investigated. The mechanism of an observed synergistic effect between blended amines is also discussed. The experimental results showed that in addition to the pore volume of the supports and the adsorption temperature the molecular functional groups of the blended amines play an important role and greatly affect the CO₂ adsorption capacity. The silica material with the largest pores (MSU-F) had the highest CO₂ adsorption capacity after impregnation with a mixture of 40 wt % tetraethylenepentamine and 30 wt % diethanolamine. For 100 kPa CO₂, the adsorption capacity at 50 °C was 5.91 mmol/g.

1. INTRODUCTION

The increase in atmospheric CO₂ from fuel combustion is a major global environmental problem. It is widely believed that CO₂ capture and storage (CCS) is a promising option for reducing CO₂ emissions.^{1,2} Various processes such as amine scrubbing,^{3,4} membrane separation,^{5,6} and pressure (and/or temperature) swing adsorption¹ have been proposed for the separation and recovery of CO₂ from industrial gas streams. Although liquid amine scrubbing is commercially available, the process is highly energy-intensive and expensive for CO₂ separation from flue gases. Apart from the high energy input required to regenerate the adsorbent, the mentioned techniques also have other drawbacks such as solvent evaporation and equipment corrosion.^{7–9} Therefore, the development of new energy-efficient techniques for CO₂ separation is necessary for CCS applications.

One of the most suitable techniques for improving the aqueous amine process is to introduce amines into the pores of a porous solid, allowing the surface amine sites to contact CO₂ directly in the gas phase.¹⁰ These solid amine sorbents integrate advantages of CO₂ separation from gas mixtures with low cost because (i) the energy required for sorbent regeneration is lower, (ii) equipment corrosion is avoided, (iii) the CO₂ adsorption–desorption rate increases,^{7,8,10–14} and (iv) the toxicity is lower because the amines are anchored to solid supports. The solid sorbents can be prepared by the wet impregnation of liquid organic amines into porous supports or the covalent grafting of amines to porous surfaces using silane coupling agents. The wet impregnation method is a simple preparation method, and a larger number of amines can be introduced into the pores of the support by wet impregnation, leading to a higher CO₂ adsorption capacity compared to that of grafting methods.¹⁵

To prepare sorbents with high CO₂ adsorption performance by wet impregnation, several amines such as tetraethylenepent-

amine (TEPA),^{8,9,12,13,15} pentaethylenetetramine (PEHA),¹³ diethylenetriamine (DETA),¹⁶ and polyethylenimine (PEI)^{7,11–13,17} have typically been used to load the supports. Structurally ordered materials with high surface areas and large pore sizes such as Y-zeolite¹⁸ and graphite oxide¹⁹ or silica materials such as SBA-12,²⁰ SBA-15,^{15,20} MCM-41,^{20–22} SBA-16,²³ MSU,²⁴ and MSF^{9,25} are often selected to load a larger number of amines into the pore channels and retain stability. Supports with large pore volumes, large pore sizes, and good pore interconnections tend to improve the CO₂ capture capacity of the sorbents.⁹ For this reason, silica mesoporous materials such as MSU²⁴ and MSF^{9,25} with large uniform pores make them promising candidates as supports of solid amine sorbents. Wang et al.²⁴ developed a highly efficient solid sorbent for CO₂ adsorption by the impregnation of TEPA into as-synthesized mesoporous silica MSU-1. The concentration of TEPA was 50 wt %. The sorbent showed a maximum CO₂ adsorption capacity of 3.87 mmol/g at 75 °C and at 11 kPa CO₂. Feng et al.⁹ reported the use of TEPA at a higher concentration (70 wt %) to modify MSF (pore volume of 2.04 cm³/g). They found that the sorbent exhibited high CO₂ adsorption performance with a maximum value of 4.57 mmol/g (determined by TG analysis) at 10% CO₂/N₂ and 10 mL/min at 75 °C.

The CO₂ adsorption capacity of adsorbents can be increased by mixing the amine with other organic compounds containing hydroxyl groups. Xu et al.¹¹ found that PEI (30 wt %) blended with poly(ethylene glycol) (PEG, 20 wt %) to modify MCM-41 improved the CO₂ adsorption performance of the sorbent and the adsorption capacity was about 1.75 mmol/g under a pure

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CO₂ atmosphere at a flow rate of 100 mL/min and at 75 °C. Recently, Yue et al.¹⁵ loaded a mixture of TEPA and diethanolamine (DEA) into the pores of as-synthesized SBA-15 (as-SBA-15) by wet impregnation and obtained a solid sorbent that showed improved CO₂ adsorption performance compared to that of a sorbent impregnated with TEPA or DEA. The CO₂ adsorption capacity of SBA-15 modified with a mixture of TEPA (30 wt %) and DEA (20 wt %) reached 3.7 mmol/g at 75 °C, which is larger than that for 50 wt % TEPA (3.3 mmol/g) or 50 wt % DEA (0.5 mmol/g). They also evaluated glycerol (Gly) instead of DEA and reported that the presence of hydroxyl groups in the guest can promote the formation of carbamate-type zwitterions. However, the mechanisms underlying the synergistic effect are still unclear.

In this work, silica mesostructured materials were impregnated with various amines such as TEPA, piperazine (PZ), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), monoethanolamine (MEA), DEA, triethanolamine (TEA), and 3-(diethylamino)-1,2-propanediol (DEAP), as shown in Figure 1. This was done

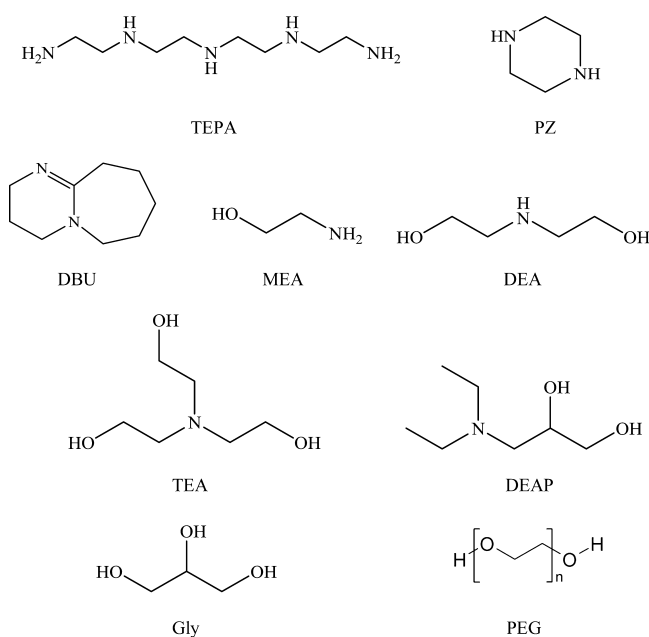


Figure 1. Chemicals used for the preparation of solid sorbents.

to shed light on the effect of blended amines toward CO₂ adsorption reactions. Furthermore, we investigated the effects of the support pore size, solvent for impregnation, and adsorption temperature with the aim of optimizing the adsorption capacity.

2. EXPERIMENTAL SECTION

2.1. Materials. TEPA (Sigma-Aldrich, St. Louis, MO, 98%), branched PEI (molecular weight of 600, Wako, Osaka, Japan), DEA (Wako, 99%), DEAP (Sigma-Aldrich, 98%), MEA (Wako, 99%), TEA (Wako, 98%), Gly (Wako, 97%), PEG (Wako, first grade), PZ (Wako, 97%), and DBU (Sigma-Aldrich, 98%) were purchased and used without further purification. Mesoporous silica materials from Sigma-Aldrich, including mesostructured cellular form silica (MSU-F), mesostructured cellular form aluminosilicate (Al-MSU-F), mesostructured hexagonal silica (MCM-41), and mesostructured large-pore 2D hexagonal silica (MSU-H) were used as supports for the solid sorbents. Methanol (MeOH, 99.8%) was supplied by Wako and used as a

solvent for wet impregnation. Helium (99.9999%), argon (99.9999%), and nitrogen (99.9999%) were purchased from Iwatani (Osaka, Japan). CO₂ (99.995%) and CO₂ (19.98%), with the balance being N₂, were supplied by Sumitomo Seika Chemicals (Osaka, Japan).

2.2. Preparation of Amine-Impregnated Mesoporous Silica Materials. Amine-functionalized mesoporous silica materials were prepared by wet impregnation. In the first step of a typical preparation procedure, a specific amount of silica material was added to the solvent (MeOH) and agitated by ultrasound for 3 min. For the preparation of 3 g of sorbent, 100 g of MeOH was used. The required amounts of amines were then added to the mixture and agitated for more than 3 min. To obtain the products the solvents were removed in a rotary evaporator. The prepared samples were denoted Ax-By/S, where *x* and *y* represent the mass fractions of components A and B, respectively, and S is the support. For example, TEPA60-DEA10/MSU-F represents the sample prepared using MSU-F (30 wt %) as a support loaded with TEPA (60 wt %) and DEA (10 wt %).

2.3. Characterization of Porous Materials. Nitrogen adsorption–desorption isotherms of the materials were obtained using a surface area and porosimetry measurement system (ASAP 2420, Micromeritics, Norcross, GA). To remove adsorbed water or CO₂ from the atmosphere, a degasification step was carried out before nitrogen adsorption–desorption analysis under nitrogen flow for 6 h. To improve the data integrity, all of the experiments including CO₂ adsorption isotherms were set up for enough equilibration intervals, and the filler rods were used to ensure accuracy in the samples by reducing the free-space volume. Equilibrium was reached when the pressure change per equilibration time interval was less than 0.01% of the average pressure during the interval. The specific surface areas of the materials were calculated using the Brunauer–Emmett–Teller (BET) method in the relative pressure (*P/P*₀) range of 0.03–0.1. The total pore volume was determined as the volume of liquid nitrogen adsorbed at a relative pressure of 0.97. The pore size was determined by the Barrett–Joyner–Halenda (BJH) method using the adsorption branch. Thermogravimetric (TG) curves were obtained with an analyzer (Thermo Plus TG-DTA 8120, Rigaku, Tokyo, Japan) in helium at a flow rate of 300 mL/min. The samples were heated from approximately 30 to 1000 °C at a constant rate of 5 °C/min.

2.4. CO₂ Adsorption Isotherms. Pure CO₂ adsorption isotherms at different temperatures were measured on an ASAP 2020 (Micromeritics) or a chemical adsorption analyzer (ChemiSorb HTP, Micromeritics) in the adsorption temperature range from 20 to 70 °C and under pressure ranging from 0.0024 to 120 kPa. Degassing was performed over 6 h under vacuum before the adsorption–desorption measurement to remove any preadsorbed moisture and gas. For the multiple adsorption–desorption test, the CO₂ adsorbed sorbent was degassed and analyzed under the same conditions as for the first run. The same adsorption–desorption procedures were conducted over five cycles to evaluate the cyclic stability of the sorbent.

For the adsorption of the CO₂ balance N₂ mixture at 40 °C, the CO₂ adsorption performance was determined using the breakthrough curve in a packed bed column that was operated under atmospheric pressure. The packed bed column apparatus is shown in Figure 2. For a typical adsorption process, a specific amount of adsorbent was placed in the middle of a stainless

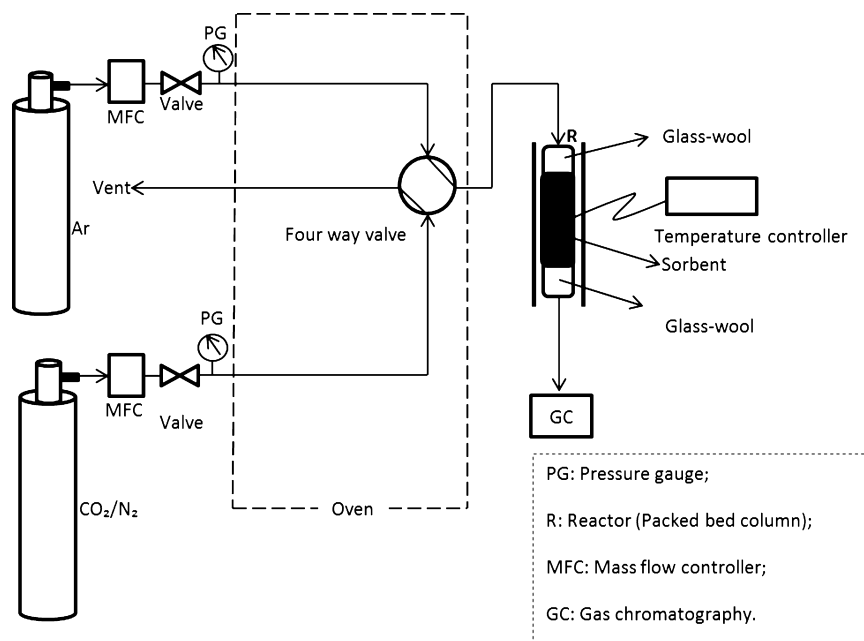


Figure 2. Apparatus for CO₂ adsorption measurements in a packed bed column.

steel column (inner diameter of 7.6 mm) that was supported by glass wool. Before each adsorption measurement, the sorbent was first degassed by holding the temperature at 50 °C for 6 h under a flow of argon. When the degassing step was complete, the sorbent was cooled to 40 °C and a mixture of dilute CO₂ at a flow rate of 30 mL/min was passed over the adsorbent until the adsorbent was saturated. During the adsorption time, the flow rate was determined using an electronic flow control instrument (ADM 1000, Agilent Technologies, Santa Clara, CA). Breakthrough curves for CO₂ were obtained by analyzing the effluent gases using a gas chromatograph (GC-323, GL Science, Tokyo, Japan) equipped with a thermal conductivity detector. The detector was connected via the adsorption column outlet. The CO₂ adsorption capacity was calculated from the area above the breakthrough curve, flow rate, and mass of sorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of Materials. The textural parameters of the mesoporous silica supports and all of the amine-loaded materials were analyzed by nitrogen physisorption. Typical results are summarized in Table 1. Among the mesostructured supports, MSU-F has the largest pore size, and this parameter decreased as follows: MSU-F (28.0 nm) > Al-MSU-F (20.2 nm) > MSU-H (8.0 nm) > MCM-41 (2.1 nm). After the amines were loaded onto the supports, both the BET surface area and the total pore volume of the samples decreased, indicating that the amines were loaded into the pores of the silica supports.^{11,15}

The thermal properties of the materials were measured by TG analysis. The silica supports had good thermal stabilities, and the sorbents started to lose mass at different temperatures, which depended on the boiling points of the amines used. For example, the TG curves of the four materials shown in Figure 3 indicate that the support (MSU-F) gave a loss of about 2 wt % below 100 °C because of moisture. All of the amines that were used for the preparation of the sorbents were loaded onto the supports because the weight of the solids was about 30% after

Table 1. Textural Parameters of Mesoporous Silica Materials and Amine-Impregnated Adsorbents

material	total pore volume (cm ³ /g)	BET surface area (m ² /g)	pore size (nm) ^a
MSU-F	1.54	272	28.0
Al-MSU-F	1.97	561	20.2
MSU-H	0.90	719	8.0
MCM-41	0.81	996	2.1
TEPA40/MSU-F	0.5239	79.5	
TEPA70/MSU-F	0.0108	4.26	
TEPA40-DEA30/MSU-F	0.0089	4.47	
TEPA40-DEA30/MSU-H	0.0038	2.82	
TEPA40-DEA30/Al-MSU-F	0.0100	4.71	
TEPA40-DEA30/MCM-41	0.0007	0.89	

^aPore size of the supports.

thermal analysis. For TEPA40-MEA30/MSU-F, about 30 wt % of the sorbent losses below 100 °C arose because the boiling point of MEA is relatively low (ca. 170 °C) and it evaporates easily. DEA and TEPA are less likely to evaporate than MEA because the boiling points of these are relatively high (ca. 217 and 340 °C, respectively). For TEPA40-DEA30/MSU-F and TEPA70/MSU-F, the samples began to lose about 6–10% of their weight below 100 °C, and this can be attributed to moisture and CO₂ adsorbed from the atmosphere^{11,16} as well as solvent that could not be completely removed during adsorbent preparation.⁹ Additionally, a portion of the amines that were not stable in the pores of the supports may also cause the above phenomena.

3.2. Effect of Amino and Hydroxyl Groups. The mesostructured silica material with the largest pores (MSU-F) was used as the support to investigate the effect of the dose of amino and hydroxyl groups on the CO₂ adsorption capacity and the molar ratio of CO₂/N (amine efficiency).

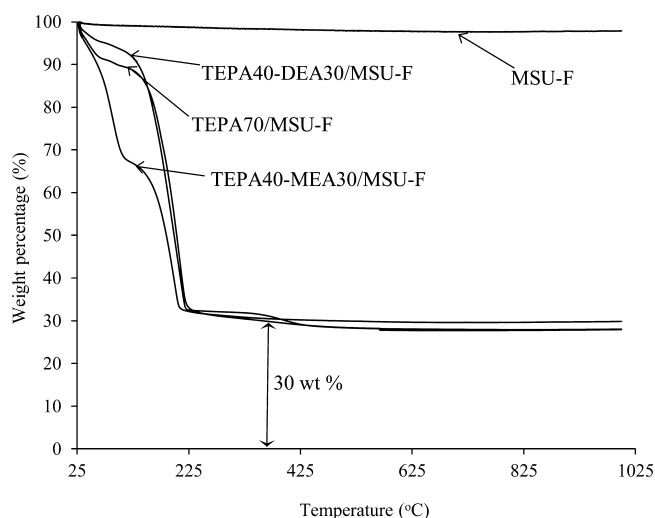


Figure 3. TG curves of MSU-F before and after loading with TEPA70, TEPA40-MEA30, and TEPA40-DEA30.

First, MSU-F was modified using only TEPA with a concentration increase from 30 to 80 wt %. The textural parameters of the TEPA-modified MSU-F sorbents (partially shown in Table 1) showed that the amines were loaded into the pores of the support. Figure 4 shows the effect of the amount of

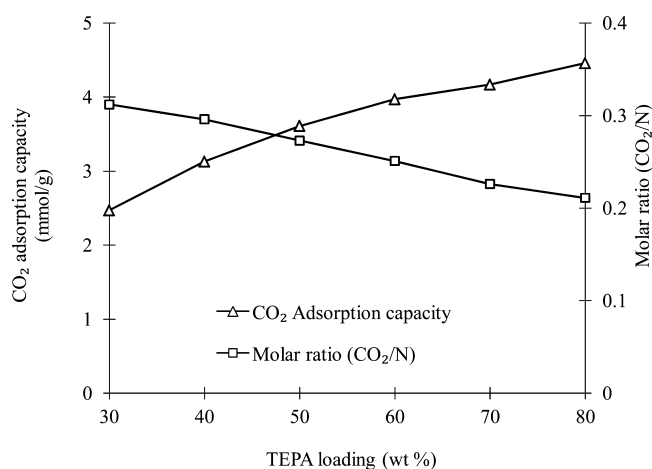


Figure 4. Effect of amount of loaded TEPA on amine efficiency and CO₂ adsorption capacity at 40 °C and at 100 kPa for MSU-F impregnated with TEPA.

loaded TEPA on the CO₂ adsorption capacity and the amine efficiency. Results of the CO₂ adsorption isotherms confirmed that the amount of CO₂ adsorption increased with the concentration of TEPA, as shown in Figure 4. On the contrary, the amine efficiency (mol CO₂/mol N), which is defined as the molar ratio of absorbed CO₂ to the amino group, decreased with the concentration of TEPA. Although a higher concentration of impregnated TEPA can supply more active sites, it can also block the pores.²⁵ Therefore, the reduction in amine efficiency shown in Figure 4 might be partially explained by the reduction in accessibility of the adsorption sites.

The effect of amine/amino alcohol composition on CO₂ adsorption was investigated using mixtures of TEPA and DEA. For this discussion, the total concentrations of TEPA and DEA were kept at a constant 70 wt %. The results shown in Figures 5 and 6 and summarized in Table 2 show that the CO₂

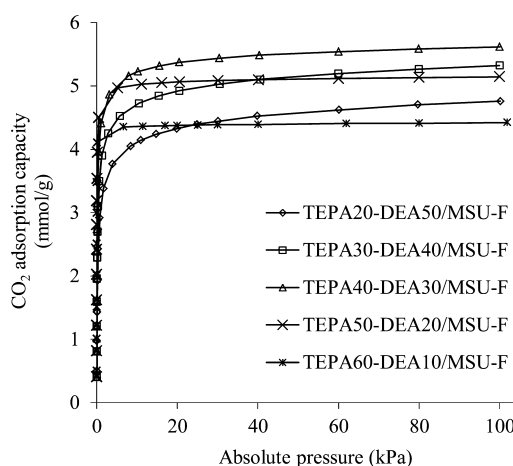


Figure 5. CO₂ adsorption isotherms for MSU-F silica impregnated with a mixture of TEPA and DEA at 40 °C.

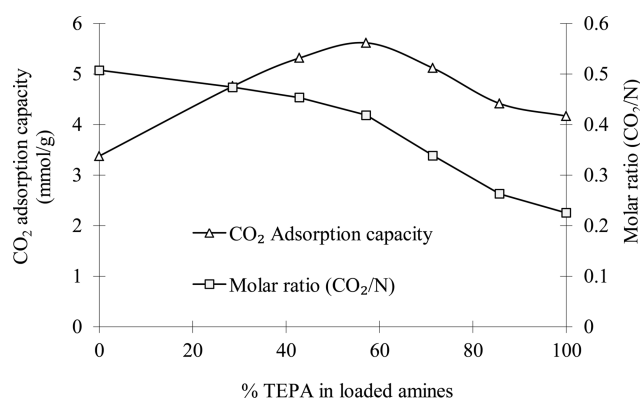


Figure 6. Effect of the amine/amino alcohol ratio on the CO₂ adsorption capacity of TEPA_x-DEA_y/MSU-F and the amine efficiency at 40 °C and at 100 kPa CO₂.

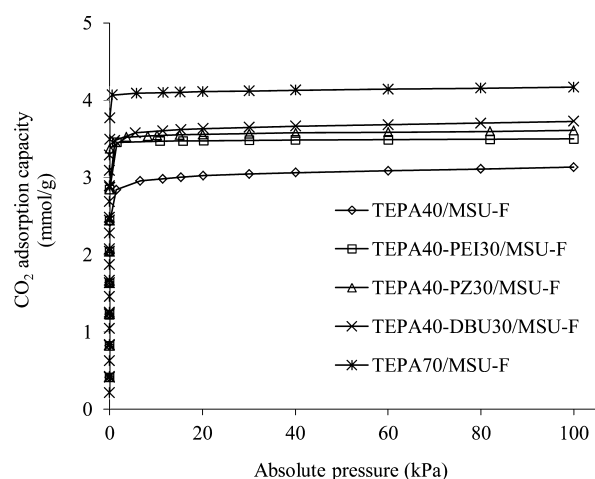
adsorption capacity at 40 °C and at 100 kPa increased as follows: TEPA70/MSU-F (4.17 mmol/g) < TEPA60-DEA10/MSU-F (4.42 mmol/g) < TEPA50-DEA20/MSU-F (5.12 mmol/g) < TEPA40-DEA30/MSU-F (5.62 mmol/g). However, this parameter decreased as follows when the amount of loaded DEA was more than 40 wt %: TEPA30-DEA40/MSU-F (5.32 mmol/g) > TEPA20-DEA50/MSU-F (4.76 mmol/g) > DEA70/MSU-F (3.38 mmol/g). These results confirm the existence of a synergistic effect between TEPA and DEA with regard to the adsorption capacity, and this is in agreement with the results of Yue et al.¹⁵

To examine the effects of hydroxyl groups, Gly and PEG (Figure 1) were selected, and mixtures of TEPA with each of these alcohols instead of DEA were evaluated and the results are shown in Table 2. When the amount of loaded TEPA was kept constant, the CO₂ adsorption capacity at 40 °C and at 100 kPa increased with the density of hydroxyl groups as follows: TEPA40/MSU-F (3.13 mmol/g) < TEPA40-PEG30/MSU-F (3.32 mmol/g) < TEPA40-Gly30/MSU-F (3.70 mmol/g). This result confirms that hydroxyl groups have a positive effect on CO₂ adsorption as reported by others.^{11,15} However, by comparison with the combination of TEPA and DEA the effect on the adsorption capacity is not very large. This is because the amino group of DEA also plays a functional role.

Figure 7 shows CO₂ adsorption isotherms for MSU-F silica impregnated with a mixture of TEPA and amine without

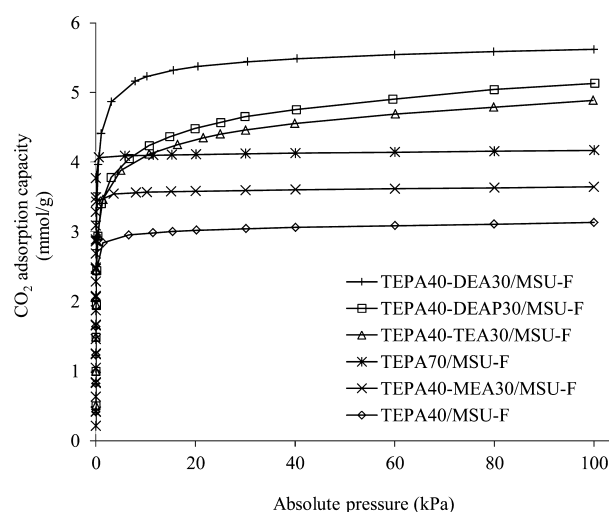
Table 2. Nitrogen and Hydroxyl Content, CO₂ Adsorption Uptake, and Amine Efficiency

material	nitrogen content (mmol N/g)	ratio of hydroxyl group (mol OH/mol N)	adsorption capacity (mmol CO ₂ /g) ^a	amine efficiency (mol CO ₂ /mol N)
TEPA40/MSU-F	10.6	0	3.13	0.30
TEPA70/MSU-F	18.5	0	4.17	0.23
PEI70/MSU-F	16.3	0	2.82	0.17
DEA70/MSU-F	6.66	2	3.38	0.51
TEPA20-DEA50/MSU-F	10.0	0.95	4.76	0.47
TEPA30-DEA40/MSU-F	11.7	0.65	5.32	0.45
TEPA40-DEA30/MSU-F	13.4	0.43	5.62	0.42
TEPA50-DEA20/MSU-F	15.1	0.25	5.12	0.34
TEPA60-DEA10/MSU-F	16.8	0.11	4.42	0.26
TEPA40-Gly30/MSU-F	10.6	0.93	3.70	0.35
TEPA40-PEG30/MSU-F	10.6	0.05	3.32	0.31
TEPA40-DEAP30/MSU-F	12.6	0.32	5.13	0.41
TEPA40-MEA30/MSU-F	15.5	0.32	3.64	0.24
TEPA40-TEA30/MSU-F	12.6	0.39	4.89	0.39
TEPA40-DEA30/MSU-H	13.4	0.43	5.21	0.39
TEPA40-DEA30/Al-MSU-F	13.4	0.43	5.47	0.41
TEPA40-DEA30/MCM-41	13.4	0.43	3.38	0.25

^aAdsorption capacity measured at 40 °C and at 100 kPa.Figure 7. CO₂ adsorption isotherms of MSU-F silica impregnated with a mixture of TEPA and amine without a hydroxyl group at 40 °C.

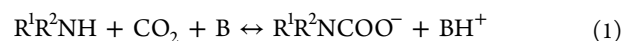
hydroxyl groups. DBU,²⁶ PZ,²⁷ and PEI^{7,11,17} are known to be highly efficient absorbents for CO₂, and the amine molecules do not contain hydroxyl groups. We found that unlike DEA these amines showed negative effects compared to TEPA and that their CO₂ adsorption capacities at 40 °C and at 100 kPa decreased as follows: TEPA70/MSU-F (4.17 mmol/g) > TEPA40-DBU30/MSU-F (3.73 mmol/g) > TEPA40-PZ30/MSU-F (3.61 mmol/g) > TEPA40-PEI30/MSU-F (3.50 mmol/g) > TEPA40/MSU-F (3.13 mmol/g).

Figure 8 shows CO₂ adsorption isotherms for MSU-F silica impregnated with a mixture of TEPA and alkanolamines DEA, DEAP, TEA, and MEA. The experimental results show that DEAP and TEA act synergistically, as was the case for DEA. For the TEPA70/MSU-F, TEPA40-TEA30/MSU-F, TEPA40-DEAP30/MSU-F, and TEPA40-DEA30/MSU-F sorbents, the CO₂ adsorption capacity at 40 °C and at 100 kPa was 4.17, 4.89 to 5.13, and 5.62 mmol/g whereas the amine efficiency was 0.30, 0.39, 0.41, and 0.42, respectively. It should be noted that the amine blending ratio ($x/y = 40/30$) was optimized for the

Figure 8. CO₂ adsorption isotherms of MSU-F silica impregnated with a mixture of TEPA and amino alcohol at 40 °C.

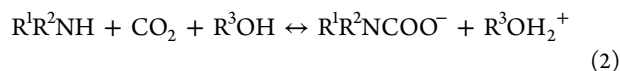
combination of TEPA and DEA. For the TEPA and MEA mixture used for the impregnation of MSU-F, the CO₂ adsorption capacity of the obtained sorbent was only about 3.64 mmol/g. This is because a significant amount of MEA evaporates during degassing and the adsorption is affected because of the lower thermal stability as described above.

3.3. Mechanism of the Synergistic Effect of Blended Amines. In the absence of water, primary and secondary amines absorb CO₂ by the formation of carbamates as follows^{28–32}

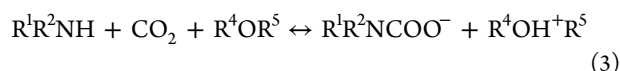


where R¹ and R² represent amino substituents. B represents Brønsted bases such as amino groups and hydroxyl groups that facilitate carbamate formation by accepting protons. Normally, one amine captures one CO₂ and another amine molecule functions as a proton acceptor in reaction 1, which limits the amine efficiency to less than 0.5.

The positive effect of hydroxyl groups on the CO₂ adsorption capacity might be explained as previously proposed by Yue et al.¹⁵ They suggested that the hydroxyl groups in DEA change the chemical adsorption mechanism of the TEPA-DEA-modified as-SBA-15, and the formation of carbamate might be promoted in the presence of hydroxyl groups as follows:



Recently, Yan et al.²⁵ obtained a novel sorbent with a high CO₂ adsorption capacity of up to 4.5 mmol/g by the impregnation of PEI into silica mesocellular foam with the template being retained. They explained the reaction mechanism by the following reaction



where the ether groups in the retained template act as proton receptors beside the amine functional groups.

To some extent, reactions 2 and 3 might act to promote CO₂ adsorption. However, it should be pointed out that in the relevant molecular systems all of the amino groups have higher basicities than both the hydroxyl groups and the ether groups. In this study, none of the mixtures of TEPA and amines without a hydroxyl group showed a synergistic effect with regard to the CO₂ adsorption capacity. However, the mixtures of TEPA and alkanolamines such as DEA, TEA, and DEAP synergistically increased the CO₂ capacity, particularly in the high CO₂ partial pressure range. These facts suggest that the effect of hydroxyl groups cannot be explained solely by reaction 2.

As will be discussed, a synergistic effect on the CO₂ adsorption capacity of TEPA40-DEA30/MSU-F was observed at 40 °C in the diffusion-limited regime. Therefore, in addition to the absorption reaction the mobility of amine molecules is important for an increase in the CO₂ adsorption capacity. The ionic species produced by the CO₂ adsorption will reduce the molecular mobility because of the cation–anion interaction and will lower the accessibility. However, the hydroxyl group is considered to mitigate this problem. Additionally, the hydroxyl group tends to stabilize the carbamate anion through hydrogen bonding ($R^1R^2NCOO^- \cdots HOR^3$).³³ This stabilization further explains the increase in amine efficiency and the CO₂ adsorption capacity. Table 2 shows that DEA70/MSU-F gave the highest amine efficiency of 0.5 because of the stability of the DEA carbamate whereas TEPA70/MSU-F had the highest nitrogen content. As a result of these two factors, TEPA40-DEA30/MSU-F was found to have the largest CO₂ adsorption capacity (Figure 6).

3.4. Effects of Support Materials and Adsorption Temperature. The support materials were compared using a mixture of TEPA (40 wt %) and DEA (30 wt %) as shown in Table 1 (MSU-F, Al-MSU-F, MSU-H, and MCM-41). The CO₂ adsorption capacities of the TEPA40-DEA30-loaded mesoporous silica adsorbents at 40 °C and at 100 kPa CO₂ fall within the range of 3.38–5.62 mmol/g and increase as follows: MCM-41 (3.38) < MSU-H (5.21) < Al-MSU-F (5.47) < MSU-F (5.62). This data indicates that the adsorption capacity sequence corresponds to pore size as shown in Table 1. This result is in good agreement with that reported by others.^{8,14,17} With a larger pore diameter or pore volume, more amine molecules can be loaded, and they disperse better. CO₂

mass transfer is easier with lower diffusion resistance, resulting in a larger sorption capacity.⁸

The adsorption temperature is one of the most important factors in the adsorption technique because it strongly affects the adsorption performance. Figure 9 shows the influence of

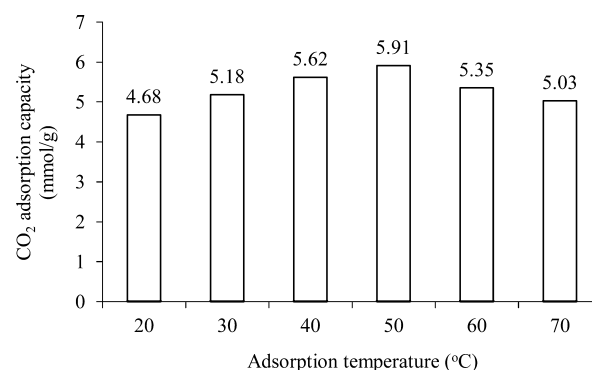


Figure 9. Effects of adsorption temperature on the CO₂ adsorption capacity at 100 kPa.

the adsorption temperature on the amounts of CO₂ adsorbed by TEPA40-DEA30/MSU-F. When the temperature is increased in the range of 20–50 °C, the adsorption capacity increases and has a maximum of 5.91 mmol/g at 50 °C. However, when the temperature is increased to 70 °C the adsorption decreases to 5.03 mmol/g. According to earlier reports,^{7,11,17} when the adsorption temperature is increased, the amines become more flexible and more CO₂-affinity sites will be exposed to CO₂. Therefore, the available pore space for CO₂ also increases to some extent and the CO₂ adsorption capacity thus increases, and this corresponds to the 20–50 °C region in Figure 9. Although the reaction between CO₂ and amino groups is exothermic, the observed temperature dependence in the 20–50 °C region suggests that the sorption of CO₂ is predominantly determined by the kinetics of diffusion rather than thermodynamic factors.^{7,8} Once efficient contact between CO₂ and an adsorption site is established, the adsorption process is accordingly dominated by thermodynamics: too high a temperature will reverse the equilibrium and desorption will be favored, leading to a decrease in the adsorption capacity. Therefore, the adsorption capacity will decrease at an adsorption temperature of 60 °C or higher. A small number of amines may evaporate at higher temperature, which will also contribute to the capacity reduction.⁷ The adsorption capacity for TEPA40-DEA30/MSU-F at 70 °C in this work is still high compared to the highest result of Yue et al.¹⁵ for TEPA30-DEA20/as-SBA-15 (3.7 mmol/g at 75 °C). This is mainly due to the difference in pore size between MSU-F (28 nm) and as-SBA-15 (8.9 nm).

3.5. Cyclic CO₂ Adsorption Tests and Dilute CO₂ Adsorption Capacity. For practical applications, the sorbents should have a high adsorption capacity and stable sorption performance over a wide CO₂ concentration range under prolonged operations.¹⁵ Figure 10 shows the cyclic adsorption behavior of the TEPA40-DEA30/MSU-F sorbent using pure CO₂. The sorbent exhibits very stable adsorption performance, and its CO₂ adsorption capacities in the first cycle and the fifth cycle were 5.62 and 5.58 mmol/g, respectively. These results confirm that the TEPA40-DEA30/MSU-F sorbent is a potential candidate for practical application.

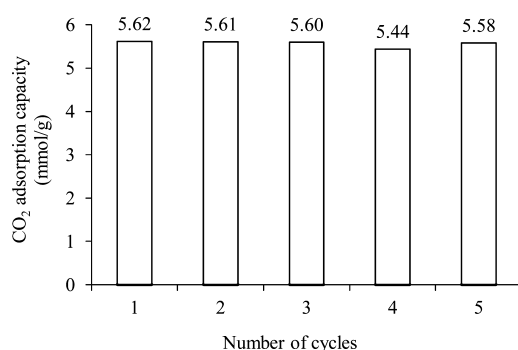


Figure 10. Cyclic adsorption of CO₂ by the TEPA40-DEA30/MSU-F sorbent in pure CO₂ at 40 °C.

For the dilute CO₂ balance N₂, experiments were carried out under dry conditions and atmospheric pressure in a packed-bed column (Figure 2). From the breakthrough curve shown in Figure 11, the CO₂ adsorption capacity of TEPA40-DEA30/

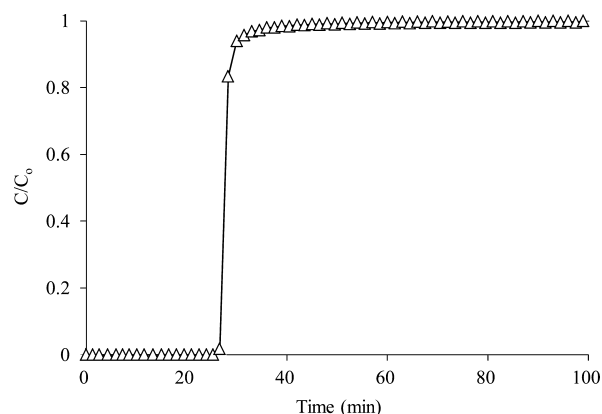


Figure 11. Breakthrough curve for CO₂ over TEPA40-DEA30/MSU-F under a total pressure of 100 kPa for 20% CO₂ balance N₂ at 40 °C.

MSU-F at 40 °C and at 20 kPa CO₂ under dry conditions was 5.53 mmol/g, which agrees well with the results from the adsorption isotherms. We compared the CO₂ adsorption results in this work with those of different amine-modified sorbents reported in the literature in Table 3. We found that TEPA40-DEA30/MSU-F had excellent performance in terms of the CO₂ adsorption capacity.

4. CONCLUSIONS

Several new sorbents with high performance for CO₂ adsorption were developed by the impregnation of TEPA and amino alcohols into mesostructured silica materials. The pore size of the supports, the molecular structures of the blended amines, the amine composition, and the adsorption temperature were found to play important roles and greatly affect the CO₂ adsorption performance. The CO₂ adsorption capacity of amine-impregnated silica can be improved by blending organic compounds containing hydroxyl groups. Detailed experimental investigations revealed that the effect of hydroxyl groups cannot be explained solely by a simple reaction. The prepared TEPA40-DEA30/MSU-F sorbent, which is based on the largest pore silica (MSU-F), was impregnated with TEPA (40 wt %) and DEA (30 wt %) and it had the largest CO₂ adsorption capacities of 5.62 and 5.91 mmol/g under a pressure of 100 kPa at 40 and 50 °C, respectively. After repeated adsorption–

Table 3. Comparison of CO₂ Adsorption Capacities on Different Amine-Modified Sorbents as Reported in the Literature

material	temperature (°C)	gas (N ₂ balance)	adsorption capacity (mmol/g)	ref
TEPA30-DEA20/SBA-15	75	pure CO ₂	3.70	15
PEI30-PEG20/MCM-41	75	pure CO ₂	1.75	11
TEPA70/MSF ^a	75	10% CO ₂	4.57	9
PEI65/MC ^b	75	15% CO ₂	4.82	7
PEI60/MCF ^c	70	66% CO ₂	4.5	25
TEPA60/MCM-41	35	pure CO ₂	5.02	34
TEPA40-DEA30/MSU-F	70	pure CO ₂	5.03	this study
TEPA40-DEA30/MSU-F	50	pure CO ₂	5.91	this study
TEPA40-DEA30/MSU-F	40	pure CO ₂	5.62	this study
TEPA40-DEA30/MSU-F	40	20% CO ₂	5.53	this study

^aMSF: mesocellular silica foam. ^bMC: mesoporous carbon. ^cMCF: siliceous mesocellular foam.

desorption cycles, the sorbent retained its high performance. This sorbent also showed a high CO₂ adsorption capacity for dilute CO₂ adsorption, and its adsorption capacity was 5.53 mmol/g at 20 kPa CO₂ balance N₂ and at 40 °C.

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Notes

The authors declare no competing financial interest.

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