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# Adsorption of Carbon Dioxide from Gas Streams via Mesoporous Spherical-Silica Particles

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## ABSTRACT

A relatively new mesoporous silica sorbent for environmental protection applications (i.e., mesoporous spherical-silica particles [MSPs]), was modified by *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (EDA) solution and was tested for its potential in the separation of carbon dioxide (CO<sub>2</sub>) from flue gas. The CO<sub>2</sub> adsorption capacity of MSP and MSP(EDA) increased with temperature from 20 to 60 °C but decreased with temperature from 60 to 100 °C. The mechanism of CO<sub>2</sub> adsorption on both samples is mainly attributed to physical interaction regardless of temperature change. The MSP(EDA) have good adsorption performance as compared with EDA-modified zeolite or granular activated carbon conducted in this study and many types of silica sorbents reported in the literature. The cyclic CO<sub>2</sub> adsorption showed that spent MSP(EDA) could be effectively regenerated at 120 °C for 25 min and CO<sub>2</sub> adsorption capacity of MSP(EDA) was preserved during

16 cycles of adsorption and thermal regeneration. These results suggest that MSP(EDA) are efficient CO<sub>2</sub> sorbents and can be stably used in the prolonged cyclic operation.

## INTRODUCTION

The carbon dioxide (CO<sub>2</sub>) capture and storage (CCS) technologies from flue gas are considered to be completely feasible means to lessen the global warming issue.<sup>1</sup> Various CO<sub>2</sub> capture technologies, including absorption, adsorption, cryogenics, membranes, and so forth, have been investigated.<sup>2</sup> Among them, the absorption-regeneration technology has been recognized as the most matured process so far, with the amine-based or ammonia-based absorption processes receiving the greatest interest.<sup>3–7</sup>

However, because the energy penalty to regenerate liquid amine or ammonia in the absorption process is high due to the high heat capacity of liquid amine/ammonia and large amount of water,<sup>2</sup> other technologies are being investigated throughout the world. The Intergovernmental Panel on Climate Change (IPCC) special report concluded that the design of a full-scale adsorption process might be feasible.<sup>8</sup> Possible CO<sub>2</sub> sorbents investigated in the literature include activated carbon,<sup>9–11</sup> X-type zeolites,<sup>12,13</sup> carbon nanotubes (CNTs),<sup>11,14,15</sup> SBA-15 mesoporous silica sorbents,<sup>16–19</sup> and mesoporous molecular sieve MCM-41.<sup>20–23</sup>

Mesoporous spherical-silica particles (MSPs), which were modified from the MCM-41 materials,<sup>24</sup> are a relatively new sorbent for environmental protection applications.<sup>25</sup> The MSPs possess advantages of much faster preparation time, higher packing density, and lower pressure drop than MCM-41 because of their well-defined spherical shape.<sup>26</sup> These advantages make MSPs more practical

## IMPLICATIONS

The adsorption process via amine-functionalized carbon or silica sorbents for CO<sub>2</sub> capture from flue gas has attracted much attention because of its low energy penalty to regenerate spent sorbents as compared with absorption process. This paper studies the physicochemical properties of raw and EDA-functionalized MSPs and their adsorption/desorption of CO<sub>2</sub> from gas streams. The test results showed that the MSP(EDA) are efficient sorbents for CO<sub>2</sub> capture and their adsorption performance can be maintained during 16 cycles of adsorption and thermal regeneration.

for gas cleaning or gas separation in terms of overall engineering considerations. Thus, the MSPs would also be expected to have a good affinity for CO<sub>2</sub>; however, such studies are still unattainable in the literature.

In this paper, the MSPs were fabricated and functionalized by *N*-[3-(trimethoxysilyl) propyl]ethylenediamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>) (EDA) to study their physicochemical properties and adsorption/desorption of CO<sub>2</sub> from gas streams. The effects of temperature and water vapor on the CO<sub>2</sub> adsorption are also investigated and discussed.

## MATERIALS AND METHODS

### Sorbents

MSP was synthesized via the evaporation-induced self-assembly (EISA) method.<sup>25</sup> Cetyltrimethyl ammonium bromide (CTAB) was used as the structure-directing template and tetraethyl orthosilicate (TEOS) was used as the silica precursor. The molar gel composition of the synthesized mixture was TEOS:0.18 CTAB: 10 ethanol:40 H<sub>2</sub>O: 0.008 HCl. Raw MSPs (2 g) were dispersed into flasks containing C<sub>9</sub>H<sub>23</sub>NO<sub>3</sub>Si (APTS; 50 mL of 97% APTS + 200 mL of 99.8% toluene), EDA (50 mL of 97% EDA + 200 mL of 99.8% toluene), or polyethylenimine (PEI; 200 mg 50% PEI + 800 mg methanol) solutions to determine the optimum modification method of MSPs to enhance CO<sub>2</sub> adsorption. Literature screening indicates that these grafting agents show good potential to modify carbon sorbents<sup>10</sup> or silica sorbents.<sup>16,17</sup> The APTS mixture and EDA mixture were refluxed at 100 °C for 10 and 2 hr, respectively, whereas the PEI mixture was stirred for 30 min. After cooling to room temperature, the mixture was filtered, dehydrated at 105 °C for 2 hr, and dried at 120 °C by passing pure nitrogen gas (N<sub>2</sub>) for 2 hr. The amount of APTS, EDA and PEI grafted on the final product was approximately 10 wt %.

To compare the CO<sub>2</sub> adsorption capacity of MSPs with other commercially available sorbents, granular activated carbon (GAC; F400, Calgon Carbon Co.) and Y-type zeolite with a Si/Al molar ratio of 5.1 (CBV100, Zeolyst International) were chosen because of their wide use for the removal of volatile organic compounds from waste gases. The surface area, pore volume, and average pore diameter, respectively, are 954 m<sup>2</sup>/g, 0.48 cm<sup>3</sup>/g, and 2 nm for GAC and 788 m<sup>2</sup>/g, 0.35 cm<sup>3</sup>/g, and 1.89 nm for zeolite. They were grafted with the EDA mixture under the same modification procedure.

### Adsorption Experiments

The CO<sub>2</sub> adsorption experiments were conducted in a cylindrical Pyrex glass column with a length of 20 cm and an internal diameter of 1.5 cm. The adsorption column was packed with 1 g of sorbents (packing height ~3.5 cm) and placed within a temperature-controlled oven. Because the best location for CO<sub>2</sub> adsorption to take place in a coal-fired power plant is after the flue gas desulfurization and before the stack,<sup>2</sup> the tested temperature was selected from 20 to 100 °C (in 20 °C increments), which covers the typical temperature range of 45–55 °C in post-flue gas desulfurization. The water vapor of the gas stream was kept at 0%, with the exception of during the moisture effect study in which the water vapor range of 0–17.5%

was evaluated at 60 °C. The selection of this water vapor range covers the typical water vapor range of 8–12% in flue gas.<sup>27</sup> In this case, moisture was introduced into the gas stream by dispersing the 15% of CO<sub>2</sub> gas through a water bath.

Compressed air was passed first through a silica gel air dryer to remove moisture and oil and then was passed through a high-efficiency particulate air (HEPA) filter (Gelman Science) to remove particulates. Two mass flow controllers (MKS Instruments, Inc.) were used to control the influent CO<sub>2</sub> concentration by regulating flow rates of clean air (diluting gas) and pure CO<sub>2</sub> gas (99.95%) entering the mixing chamber. The system flow rate was controlled at 80 cm<sup>3</sup>/min, equivalent to an empty-bed retention time of 4.6 sec. The influent and effluent gas streams were flowed into a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) for real-time measurement. All of the experiments are repeated two times and only the mean values were reported.

The influent CO<sub>2</sub> concentration was in the range of 5–50%, which was selected to be representative of different CO<sub>2</sub> levels in combustion gases from many kinds of industrial activities such as cement plants (14–33%), coal-fired power plants (12–14%),<sup>28</sup> or coal gasification systems (30–35%).<sup>29</sup> The variation in the influent CO<sub>2</sub> level was below 0.2%. Blank tests (without sorbents) were conducted with various influent CO<sub>2</sub> concentrations. The adsorption capacities of blanks were eliminated from the adsorption capacities of MSP and MSP(EDA).

### Physisorption and Chemisorption

Most adsorption processes are a combination of physical interaction (physisorption) and chemical interaction (chemisorption). A distinction of these two interactions is very useful in understanding the factors that influence the rate of the adsorption process. The equilibrium capacities of CO<sub>2</sub> due to physisorption ( $q_{ep}$ ) and chemisorption ( $q_{ec}$ ) were estimated as follows.<sup>30,31</sup>

As the adsorption reached equilibrium, the weight of adsorbed CO<sub>2</sub> was measured, and then the influent gas was changed from 15% CO<sub>2</sub> to N<sub>2</sub> and controlled at a Q of 0.1 L/min. The outlet of the adsorption column was connected to a vacuum pump that was operated at 0.145 bars. After the CO<sub>2</sub> level in the effluent gas stream was undetectable (~30 min), which reflects the completion of desorption process, the remaining weight of spent sorbents was measured. The weight loss after vacuum desorption is attributed to  $q_{ep}$ , whereas the weight remaining after vacuum desorption is attributed to  $q_{ec}$ .

### Adsorption/Desorption Experiments

The adsorption process was controlled at 60 °C and with a C<sub>in</sub> of 15%. As the CO<sub>2</sub> adsorption on MSP(EDA) reached equilibrium, the adsorption capacity of CO<sub>2</sub> was measured. Thermal desorption of CO<sub>2</sub> was tested by changing influent gas to purified air, which was operated at 120 °C for 25 min and controlled at the same flow rate as in the adsorption experiment. The cyclic CO<sub>2</sub> adsorption on MSP(EDA) was conducted for 16 cycles of adsorption and regeneration.

### Characterizations of Sorbents

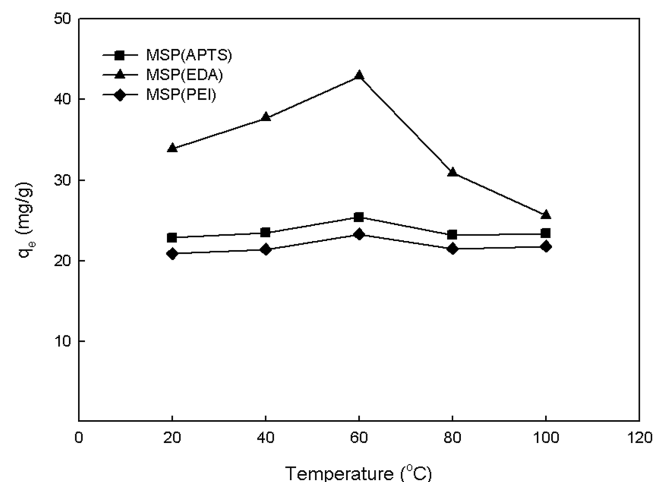
The porosity characteristics of sorbents were determined by  $N_2$  adsorption/desorption at 77 K using a Micromeritics ASAP 2020 volumetric sorption analyzer.  $N_2$  adsorption/desorption isotherms were measured at a relative pressure ( $P/P_0$ ) range of 0.0001–0.99 and then used to determine surface area, pore volume, and average pore diameter via the Barrett, Johner, and Halenda (BJH) equation. The crystal phase of sorbents was characterized by a powder X-ray diffractometer (XRD; Mac Science) using  $Cu K\alpha$  radiation (40 kV, 30 mA). The thermal stability of sorbents in air was determined by a thermogravimetric analyzer (Pyris 1 TGA, PerkinElmer) at a heating rate of 10 °C/min. The water vapor was measured by a temperature/relative humidity sensor (hygromer M130 d, ROTRONIC Co.).

The surface functional groups of sorbents were evaluated by a Fourier transform infrared (FTIR) spectrometer (Spectrum One, PerkinElmer) and the Boehm titration method.<sup>32</sup> The titration was conducted by adding 100 mg of sorbents into four 100-mL flasks having 50 mL of the following 0.1-M solutions: sodium bicarbonate ( $NaHCO_3$ ), sodium carbonate ( $Na_2CO_3$ ), sodium hydroxide (NaOH), and hydrochloric acid (HCl), which were sealed and shaken at 25 °C for 48 hr and then filtered through a 0.45- $\mu$ m fiber filter. The filtrate (10 mL) was pipetted and mixed with 15 mL of 0.1 M HCl or NaOH. The excess of acid and base was titrated with 0.1 M NaOH and HCl, respectively. The quantities of acidity of various types were determined from the assumption that  $NaHCO_3$  reacts with carboxylic ( $-COOH$ ) groups,  $Na_2CO_3$  reacts with  $-COOH$  and lactonic ( $-COO$ ) groups, and NaOH reacts with  $-COOH$ ,  $-COO$ , and phenolic groups ( $-OH$ ). The quantities of total basicity were determined from the amount of HCl reacted with the sorbents.

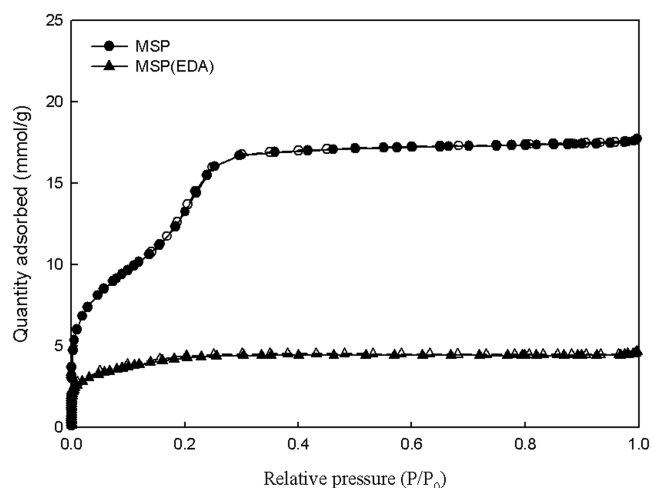
## RESULTS AND DISCUSSION

### $CO_2$ Adsorption via Various Amine-Functionalized MSPs

Figure 1 shows the  $q_e$  of 15%  $CO_2$  adsorption on various amine-functionalized MSPs at multiple temperatures. It is



**Figure 1.** Equilibrium amounts of 15%  $CO_2$  adsorption on various amine-functionalized MSP at multiple temperatures.



**Figure 2.**  $N_2$  adsorption (solid symbols) and desorption (open symbols) isotherms of MSP and MSP(EDA).

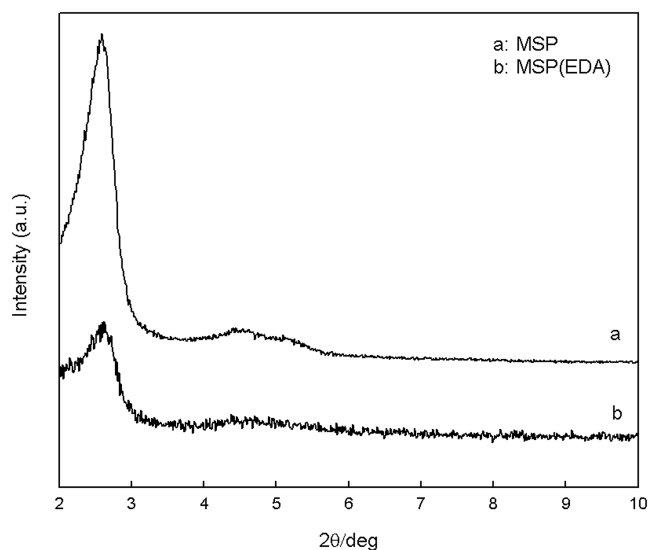
clear that all tested sorbents have the maximum  $q_e$  at 60 °C. The temperature dependence of  $q_e$  is more significant for MSP(EDA) than for MSP(APTS) and MSP(PEI). The MSP(EDA) show the best performance of  $CO_2$  adsorption at all tested temperatures, followed by the MSP(APTS) and then the MSP(PEI), showing that EDA is a potential modification of MSP for  $CO_2$  adsorption. Thus, the MSP(EDA) were selected to further study their physicochemical properties and adsorption/desorption of  $CO_2$  in gas streams.

### Characterizations of MSP

Figure 2 presents the  $N_2$  adsorption/desorption isotherm curves of MSP and MSP(EDA). It is seen that the  $N_2$  adsorption capacity is larger for MSP, indicating a greater amount of porosity in MSP. The isotherm curve of MSP shows a type IV shape<sup>33</sup> displaying a rapid rise in  $N_2$  adsorption capacity up to a  $P/P_0$  of 0.23, which is evidence of capillary condensation of  $N_2$  molecules in the primary mesopores. This is typical for mesoporous solid particles. The isotherm curve of MSP(EDA) is approximately type I, which is classified as Langmuir-type adsorption and is characterized by the formation of a complete monolayer. After an increase up to a  $P/P_0$  of 0.02, the isotherm curve exhibits a very small increment with  $P/P_0$ , reflecting a very narrow pore size distribution. The adsorption and desorption curves coincide with each other, implying the absence of adsorption hysteresis.<sup>34</sup>

Surface area, pore volume, and average pore diameter are, respectively, 1129  $m^2/g$ , 0.765  $cm^3/g$ , and 2.42 nm for MSP and 345  $m^2/g$ , 0.155  $cm^3/g$ , and 2.56 nm for MSP(EDA). It is clear that the surface area and the pore volume are smaller for MSP(EDA), likely because of the partial blockage of pore entrance by the formation of functional groups on the external and internal surface of MSP(EDA). Similar findings have been reported in the literature for various amine-functionalized silica sorbents.<sup>35</sup>

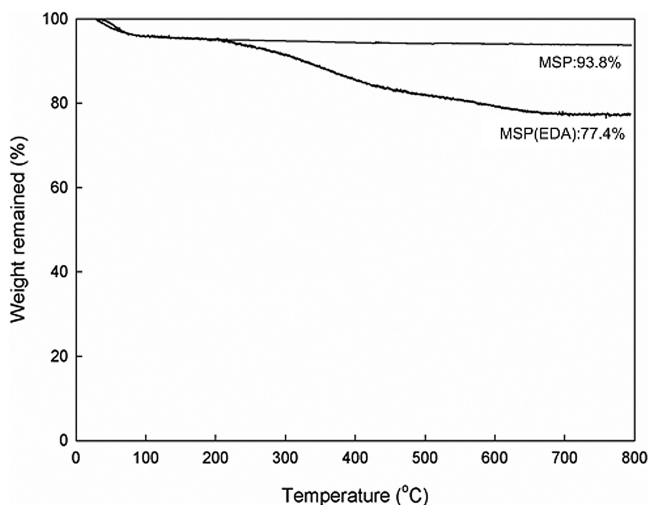
The XRD patterns of MSP and MSP(EDA) are displayed in Figure 3. The(100) diffraction peaks located at



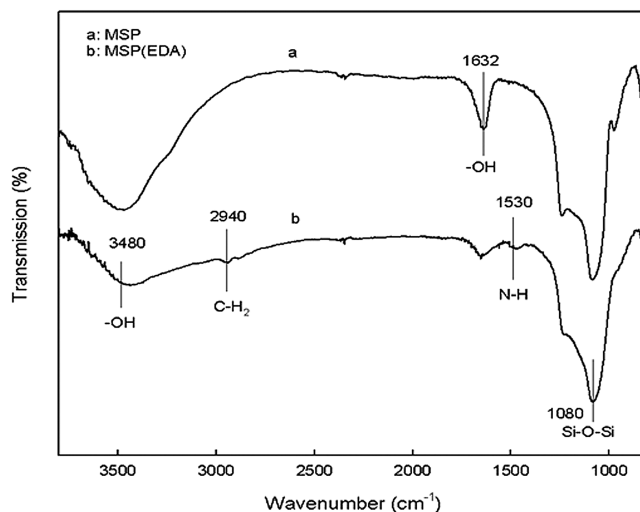
**Figure 3.** XRD patterns (0.01°, 2θ step size, and 1-sec step time) of MSP and MSP(EDA).

$2\theta = 2.3\text{--}2.7^\circ$  are clearly observed for both samples, indicating the evidence of well-ordered two-dimensional hexagonal structure.<sup>25</sup> The intensity of the diffraction peak became weak after the modification, which could be due to grafting of EDA on the surface of MSP(EDA).

Figure 4 shows the TGA profiles of MSP and MSP(EDA). It is obvious that the TGA profile of MSP shows a weight loss close to 5% below 110 °C because of the evaporation of adsorbed water. After the temperature exceeds 110 °C, the weight loss becomes insignificant and a remaining weight of 93.8% was found at 790 °C. The MSP(EDA) have a broader temperature range for weight loss and exhibit three main weight loss regions. The first weight loss region (<210 °C) is very similar to the weight loss of MSP. The second weight loss region (in 210–650 °C) appears relatively remarkable and can be attributed to the loss of surface functional groups. The third weight loss region only shows a very little weight loss, in which a remaining weight of 77.4% was observed at



**Figure 4.** TGA profiles (temperature ramp rate = 10 °C/min, gas flow rate = 65 cm<sup>3</sup>/min) of MSP and MSP(EDA).

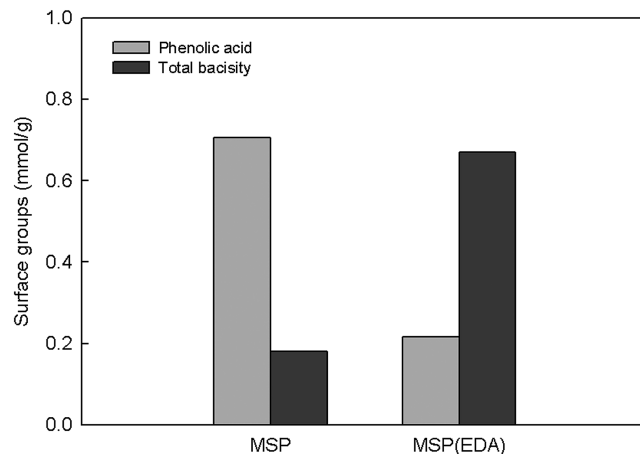


**Figure 5.** IR spectra of MSP and MSP(EDA).

790 °C. Both samples show high thermal stability in air up to 210 °C.

Figure 5 displays the infrared (IR) spectra of MSP and MSP(EDA). It is observed that the IR spectrum of MSP shows remarkable bands at 3480, 1632, and 1081 cm<sup>-1</sup> that are related to -OH stretching vibrations of the hydrogen-bonded silanol groups, adsorbed water molecules, and Si-O-Si asymmetric stretching vibrations, respectively.<sup>36</sup> The IR spectrum of MSP(EDA) shows significant bands at 3480, 2940, 1632, 1530, and 1081 cm<sup>-1</sup>. The bands at 2940 and 1530 cm<sup>-1</sup> can be assigned to C-H stretching from CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-NH<sub>2</sub> groups and N-H vibration, respectively.<sup>37,38</sup> The presence of the C-H stretching band at 2940 cm<sup>-1</sup> and the N-H vibration band at 1530 cm<sup>-1</sup> as well as the decrease in the -OH intensity at 3480 and 1632 cm<sup>-1</sup> after the modification reflect the grafting of EDA on the surface of MSP. The impregnation of amine functional groups to the MSP surface provides chemical sites for CO<sub>2</sub> adsorption.

Figure 6 exhibits the Boehm titration results of MSP and MSP(EDA). It is seen that the amounts of -OH groups decreased from 0.71 to 0.22 mmol/g, but the amount of total basicity increased from 0.18 to 0.67 mmol/g after the modification, both of which are consistent with the FTIR



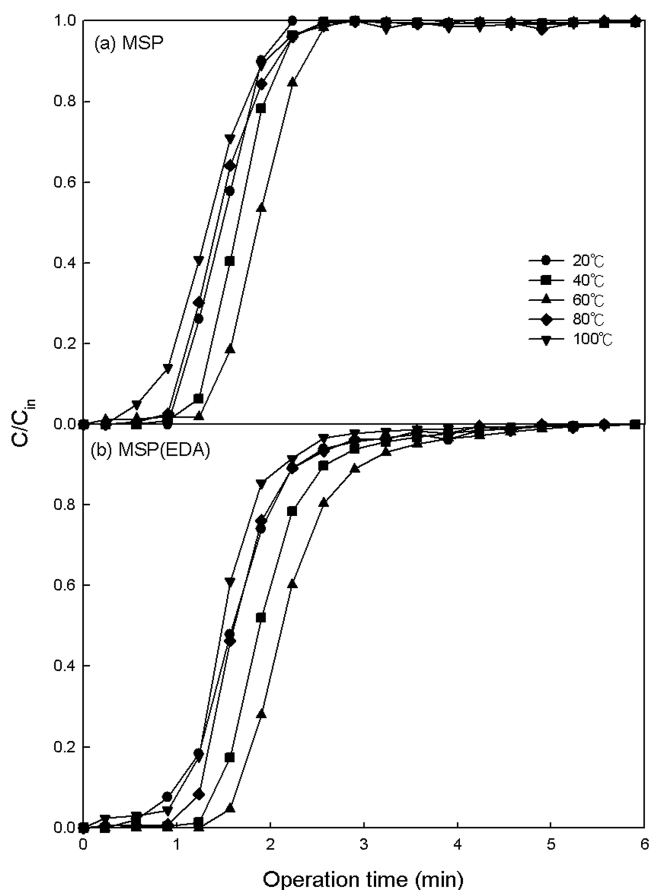
**Figure 6.** Boehm titration results of MSP and MSP(EDA).

results. The decrease in  $-OH$  groups could be explained by the reaction between EDA and  $-OH$  groups on silica during the modification. Similar findings have been reported in the literature.<sup>36</sup> The increase in total basicity, which is directly related to chemical sites for  $CO_2$  adsorption, could be due to the grafting of amine groups on the MSP surface after the modification.

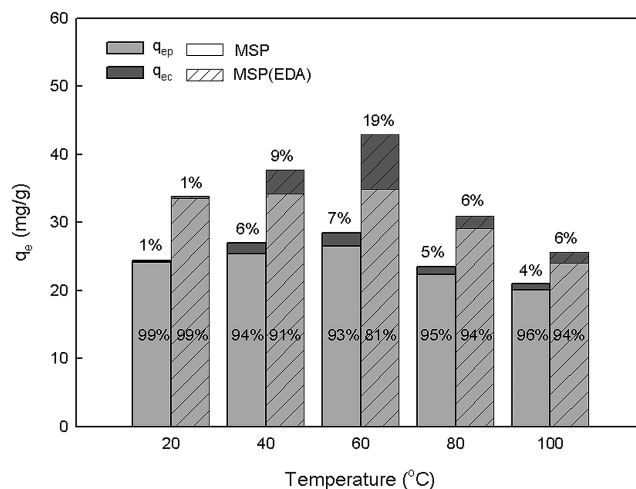
### Adsorption Behaviors

Figure 7 shows the breakthrough curves of 10%  $CO_2$  adsorption on MSP and MSP(EDA) at multiple temperatures. It is seen that initially the  $CO_2$  gas can be efficiently adsorbed on both samples with capture efficiencies greater than 98%. The breakthrough time (the time at which effluent  $CO_2$  concentration reaches 5% allowable breakthrough concentration), which represents the capacity of sorbents to adsorb  $CO_2$ , appears longer and shows more sensitivity to temperature change after the modification.

Figure 8 displays the  $q_{ec}$  and  $q_{ep}$  of 15%  $CO_2$  via MSP and MSP(EDA) at multiple temperatures. Percentage ratios of  $q_{ec}$  and  $q_{ep}$  to  $q_e$  also indicated in the top of each bar graph. It is clear that  $q_{ec}$  and  $q_{ep}$  increased after the modification, likely because of the increase in surface functional groups as shown in IR spectra (Figure 4) and affinity between  $CO_2$  molecules and sorbent surface. The  $q_{ec}$  and  $q_{ep}$  of both samples increased with temperature from 20 to 60 °C but decreased with temperature from 60 to 100 °C.



**Figure 7.** Breakthrough curves of 10%  $CO_2$  adsorption on (a) MSP and (b) MSP(EDA) at multiple temperatures.

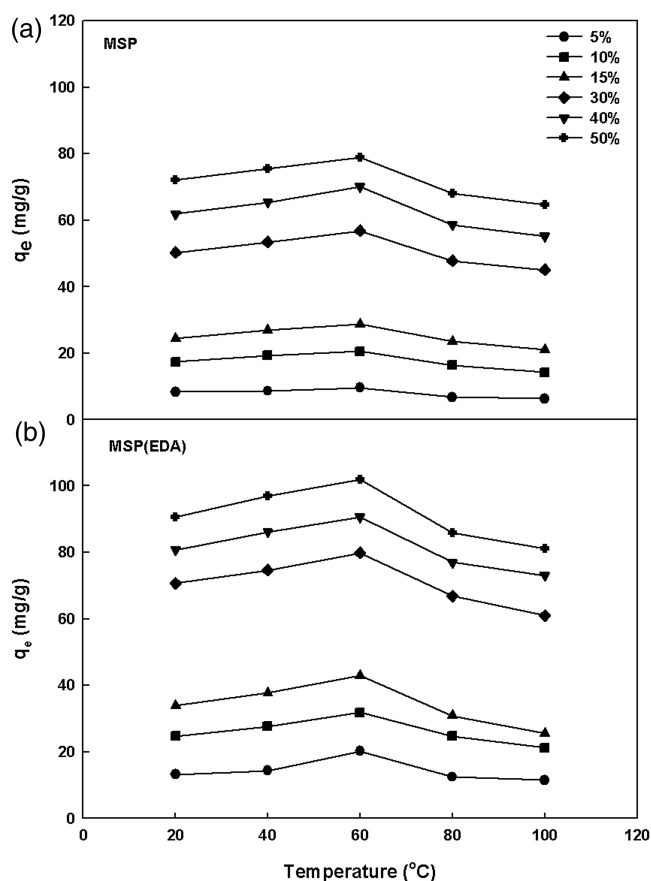


**Figure 8.** Physisorption and chemisorption capacities of 15%  $CO_2$  on MSP and MSP(EDA).

100 °C. Both samples have the greatest  $q_{ec}$  and  $q_{ep}$  at 60 °C. The increase in  $q_{ec}$  and  $q_{ep}$  with temperature from 20 to 60 °C could be explained by the decreased in adsorbed water on the surface of sorbents with temperature as indicated in TGA profiles (Figure 4), where near 2.72 and 2.22% weight loss were obtained at 60 °C for MSP and MSP(EDA), respectively, because of the evaporation of adsorbed water, resulting in the increase in chemical and physical sites. Furthermore, the swelling of amine polymer within the porous support at higher temperatures may also increase in  $q_{ec}$  and  $q_{ep}$ .<sup>39</sup> The decrease in  $q_{ec}$  and  $q_{ep}$  with temperature from 60 to 100 °C could be attributed to the decrease in chemical interaction and van der Waals force between  $CO_2$  molecules and the sorbent surface. The MSP(EDA) possess higher  $q_e$  and show more sensitivity to temperature change than the MSP and thus were used in the cyclic adsorption.

Percentage ratios of  $q_{ec}$  and  $q_{ep}$ , respectively, are in the range of 1–7% and 93–99% for the MSP and 1–19% and 81–99% for the MSP(EDA), reflecting that the major mechanism of  $CO_2$  adsorption on both samples is attributed to physical interaction from 20 to 100 °C.

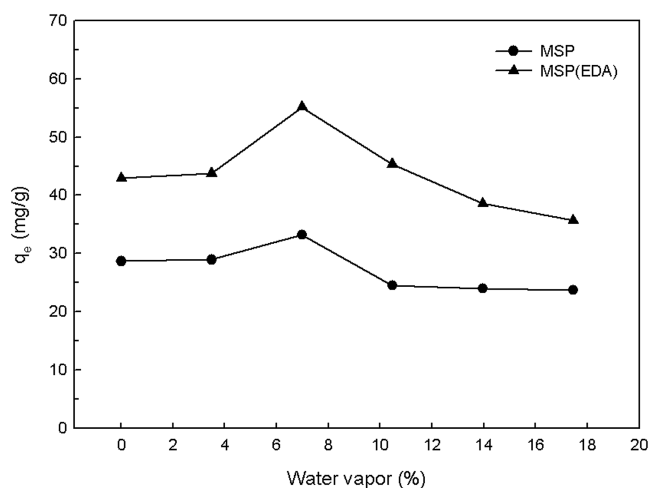
Figure 9 shows the effects of influent  $CO_2$  concentration ( $C_{in}$ ) and temperature on  $CO_2$  adsorption on MSP and MSP(EDA). It is apparent that the  $q_e$  of both samples significantly increased with  $C_{in}$ . At a temperature of 60 °C, the  $q_e$  increased from 28.7 to 78.9 mg/g for MSP and from 42.9 to 102.2 mg/g for MSP(EDA) as the  $C_{in}$  increased from 15 to 50%. This suggests that  $CO_2$  adsorption on both samples becomes more efficient and practical with a higher  $C_{in}$  such as from cement plants (14–34%) and coal gasification systems (30–35%). The  $q_e$  of both samples increased with temperature from 20 to 60 °C but decreased with temperature from 60 to 100 °C and have the maximum  $q_e$  at 60 °C. Similar observations on the correlation of  $q_e$  with temperature had been reported in other studies of silica sorbents,<sup>21,40</sup> where the maximum  $q_e$  was found at 75 °C. This may be because of the nature of silica sorbents. The  $q_e$  of MSP increased after the modification and the improvement was enhanced with  $C_{in}$ . The temperature dependence of  $q_e$  is more significant for MSP(EDA).



**Figure 9.** Effects of influent CO<sub>2</sub> concentration and temperature on CO<sub>2</sub> adsorption on (a) MSP and (b) MSP(EDA).

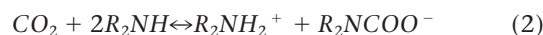
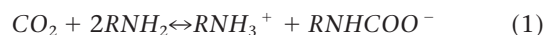
Figure 10 shows the effects of water vapor on 15% CO<sub>2</sub> adsorption on MSP and MSP(EDA) at 60 °C. It is apparent that the CO<sub>2</sub> adsorption performance of both samples showed no significant changes with water vapor below 3.64%. As the water vapor increased from 3.64 to 7%, the  $q_e$  of MSP and MSP(EDA), respectively, increased from 28.7 to 33.2 mg/g and 42.9 to 55.2 mg/g.

In the literature, the CO<sub>2</sub> adsorption capacity in moist stream may decrease if a hydrophilic material such

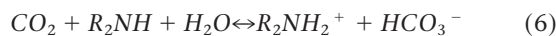


**Figure 10.** Effects of water vapor on 15% CO<sub>2</sub> adsorption on MSP and MSP(EDA) at 60 °C.

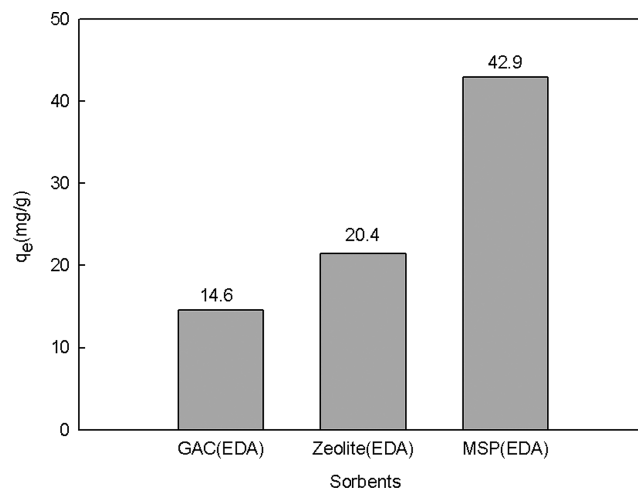
as 13X zeolite is being used,<sup>41</sup> or it may increase if a hydrophobic material such as CNTs are being used.<sup>15</sup> The MSP(EDA) used is a highly hydrophobic material as compared with the 13X zeolite; however, it still contains some –OH groups as indicated in IR spectrum (Figure 5), which make it slightly hydrophilic as compared with the CNTs. Thus, there are two possible reasons to explain the increase in  $q_e$  in the presence of some amount of moisture. First, the MSP(EDA) contain primary amine (RNH<sub>2</sub>) and secondary amines (R<sub>2</sub>NH), both of which can react with CO<sub>2</sub> and lead to the formation of carbamate by reactions 1 and 2. The presence of water then regenerates amine molecules by reactions 3 and 4.<sup>42</sup>



Second, the amine groups can also directly react with CO<sub>2</sub> and water to form bicarbonate (HCO<sub>3</sub><sup>-</sup>), as shown in reactions 5 and 6.<sup>21</sup>



However, further increases in the moisture content lead to decreases in the CO<sub>2</sub> adsorption capacity. The  $q_e$  of MSP and MSP(EDA), respectively, decreased from 33.2 to 23.7 mg/g and 55.2 to 35.7 mg/g as the water vapor further increased from 7 to 17.5%. This might be explained by the competitive adsorption between CO<sub>2</sub> and water at the same adsorption sites. It was indicated in the literature for amine-functionalized MCM-41 materials that when preexposed to moisture, the water molecule



**Figure 11.** Comparisons of 15% CO<sub>2</sub> adsorption on EDA-modified MSP, GAC, and zeolite at 60 °C.

**Table 1.** Comparisons of  $q_e$  via various raw and amine-functionalized silica sorbents.

Sorbents	Modification Chemicals	$q_e$ (mg/g)	Conditions	References
MSP	EDA	43.3, 114.0	$C_{in} = 15\%$ , $T = 60^\circ\text{C}$ , $C_{in} = 50\%$ , $T = 60^\circ\text{C}$	This work
SBA-15	APTS	88.5	$C_{in} = 10\%$ , $T = 25^\circ\text{C}$	16
SBA-15	APTS	2.2, <sup>a</sup> 6.6	$C_{in} = 15\%$ , $T = 60^\circ\text{C}$	17
SBA-15	EDA	20	$C_{in} = 15\%$ , $T = 25^\circ\text{C}$	36
SBA-15	APTS	9.9	$C_{in} = 4\%$ , $T = 25^\circ\text{C}$	37
Silica xerogel	APTS	25	$C_{in} = 5\%$ , $T = 25^\circ\text{C}$	38
Amorphous silica gel	TA	46	$C_{in} = 90\%$ , $T = 20^\circ\text{C}$	35
MCM-41	PEI	8.6, <sup>a</sup> 112	$C_{in} = 99\%$ , $T = 75^\circ\text{C}$	40

Notes: TA = *N*-[3-(trimethoxysilyl)propyl]diethylenetriamine. <sup>a</sup>Without modification.

will be absorbed and thus the CO<sub>2</sub> adsorption capacity could not be enhanced.<sup>43</sup>

Figure 11 presents the  $q_e$  of 15% CO<sub>2</sub> adsorption on MSP(EDA), GAC(EDA), and zeolite(EDA) at 60 °C. It is seen that MSP(EDA) have approximately double the  $q_e$  of zeolite(EDA) and triple the  $q_e$  of GAC(EDA), reflecting that MSP(EDA) are efficient sorbents for CO<sub>2</sub> capture.

The comparisons of  $q_e$  with various raw and modified silica sorbents are given in Table 1. It is noted that the  $q_e$  of these sorbents can usually be enhanced after modification by various kinds of grafting agents. Under similar conditions, MSP(EDA) have good performance of CO<sub>2</sub> adsorption at 60 °C as compared with many types of silica sorbents documented in the literature.

### Cyclic CO<sub>2</sub> Adsorption

Evaluating the reversibility of CO<sub>2</sub> adsorption on MSP(EDA) is required to reduce their replacement cost. The test results indicated that the CO<sub>2</sub> could be effectively desorbed from the surface of MSP(EDA) at 120 °C for 25 min and the  $q_e$  under 0, 4, 8, 12, and 16 cycles of adsorption and thermal regeneration are 42.90, 42.40, 42.76, 43.33, and 41.27 mg/g, respectively. The attrition of CO<sub>2</sub> adsorption on regenerated MSP(EDA) is below 4% after 16 cycles of operation.

It is clear from above results that MSP(EDA) not only displayed good performance of CO<sub>2</sub> adsorption but also proved thermally stable in the cyclic adsorption operation. These advantages suggest that MSP(EDA) are promising for practical applications of CO<sub>2</sub> capture in the field.

### CONCLUSIONS

The MSP and MSP(EDA) were selected as sorbents to study their physicochemical properties and adsorption/desorption of CO<sub>2</sub> in gas streams. The surface nature of MSP was changed after the modification, including the increase in affinity between CO<sub>2</sub> molecules and the MSP(EDA) surface and the increase in surface amine groups and surface total basicity, which enable MSP to adsorb more CO<sub>2</sub> gas. The CO<sub>2</sub> adsorption capacities of both samples significantly increased with influent CO<sub>2</sub> concentration, reflecting that CO<sub>2</sub> adsorption becomes more efficient and practical with a higher influent concentration such as from cement plants or from coal gasification systems. The mechanism of CO<sub>2</sub> adsorption on both samples appears mainly attributable to physical interaction regardless of

temperature change. The MSP(EDA) have better performance of 15% CO<sub>2</sub> adsorption at 60 °C as compared with EDA-modified GAC and zeolite conducted in this study. The cyclic CO<sub>2</sub> adsorption on MSP(EDA) showed that the adsorbed CO<sub>2</sub> can be effectively desorbed at 120 °C for 25 min, and their performance can be preserved during 16 cycles of adsorption and regeneration. These results suggest that the MSP(EDA) are efficient sorbents for CO<sub>2</sub> capture and can be used in prolonged cyclic operation.

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