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Development of Carbon-Based "Molecular Basket" Sorbent for CO_2 Capture

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ABSTRACT: The objective of the present study is to develop a new type of "molecular basket" sorbent (MBS) by using inexpensive and commercially available carbon materials instead of mesoporous silica molecular sieves as supports for CO_2 capture from flue gas. Several commercial carbon materials, including activated carbons and carbon blacks, with different pore sizes and pore volumes have been used to prepare the carbon-based MBS (CB-MBS) by loading the CO_2-philic polyethylenimine (PEI) on them. The CO_2 sorption performance of the prepared CB-MBS was evaluated by using a thermogravimetric analyzer and a fixed-bed flow sorption system. Effects of the pore properties of the carbon supports, PEI loading amount, sorption temperature, and moisture on the sorption capacity were examined. A sorption capacity of 135 mg-CO_2/g-sorb was obtained by loading 50 wt % PEI on a carbon black, which is almost the same as that of PEI(50)/SBA-15 prepared by loading 50 wt % PEI on SBA-15. The higher CO_2 sorption capacity of 154 mg-CO_2/g-sorb was achieved when increasing the PEI loading on the carbon black to 65 wt %. Characterization of the porous structure of the carbon materials indicates that the high sorption capacity of the carbon-black-supported PEI sorbents can be ascribed to their high pore volume and large pore size. It was further found that the volume-based capacity of PEI(50)/C4 was even higher than that of PEI(50)/SBA-15 by 57% due to the higher packing density (0.35 g/mL) of the former than that (0.22 g/mL) of the latter. Because of its high CO_2 sorption performance and low preparation cost, the carbon-based MBS could be a promising sorbent for cost-efficient CO_2 capture from flue gas.

1. INTRODUCTION

CO_2 has been widely recognized as a major greenhouse gas, and the concentration of it in the atmosphere has been found to be significantly related to the global climate change. Meeting increasing energy demand while mitigating CO_2 emission has become a major global challenge.[1−3] Coal-fired power generation plants are one of the major stationary sources of CO_2 emission, which contribute to approximately one-third of the total CO_2 emission to the atmosphere.[4] In recent years, worldwide efforts have been devoted to developing new technologies for CO_2 capture from flue gas. The development of a CO_2 capture process based on solid amine sorbents has been considered as one of the promising, less-energy-intensive technologies for postcombustion CO_2 capture.[5,6]

In our previous studies on CO_2 capture, we have developed novel sorbents, called "molecular basket" sorbents (MBS), which are prepared by immobilizing CO_2-philic polyethylenimine (PEI) on the silica molecular sieves, such as PEI(50)/MCM-41 and PEI(50)/SBA-15.[7−10] Similar sorbents were also reported by others using MCM-48[11]or KIT[12] as a support. In comparison with commercial or state-of-the-art absorbents, adsorbents, and sorbents, MBS has shown many potential advantages, such as higher capacity (140 mg-CO_2/g-sorb at 15 kPa CO_2 partial pressure), high selectivity, a fast sorption/desorption rate, no or less corrosion problem, good regenerability and stability, and lower energy consumption during regeneration.[13] However, the support materials used for preparation of these sorbents were mesoporous silica molecular sieves (MCM-41, MCM-48, SBA-15, and KIT-6).[11,12] Most of these materials are commercially unavailable right now or are

costly to prepare. Consequently, it may be impractical to apply these materials to prepare the sorbents for mass CO_2 capture from flue gas. On the other hand, mesoporous silica molecular sieves usually show poor hydrothermal stability, even at 100 °C,[14] which may result in degradation of the sorbent within the sorption/desorption cycles. It is necessary to develop a new type of MBS with a low sorbent preparation cost, good hydrothermal stability, and excellent performance for CO_2 capture.

According to our preliminary estimation of the preparation cost of PEI(50)/MCM-41 and PEI(50)/SBA-15,[15] the cost for sorbent preparation is higher than $700/kg, in which the cost of the support materials accounts for more than 90% of the total sorbent preparation expense. Therefore, the preparation cost of MBS can be reduced significantly if a low-cost support material can be used to replace the expensive mesoporous silica molecular sieves. With this in mind, using carbon-based porous materials, including activated carbons and carbon blacks, as a support for preparation of MBS has attracted our attention because of their inexpensive price, well-developed pore structure, and wide availability. In general, the cost of the commercial coal-derived activated carbon and carbon black is less than $20/kg.[16] In addition, the porous structure and surface chemistry of the carbon materials can be easily tailored and modified.[17−19] Because of these advantages, porous carbon

Table 1. Pore Properties of Carbon Materials, MCM-41 and SBA-15

sample ID	source	S_{BET} (m²/g)	S_{micro} (m²/g)	$S_{meso+macro}$ (m²/g)	V_{total} (mL/g)	V_{micro} (mL/g)	$V_{meso+macro}$ (mL/g)	pore size (nm)
C1	AC from coal	1151	910	241	0.64	0.44	0.20	2.22
C2	AC from wood	1495	1000	495	1.21	0.55	0.66	2.91
C3	AC from wood	2320	1397	923	1.64	0.79	0.84	2.85
C4	CB from coal	1486	575	911	2.69	0.50	2.19	7.26
C5	CB from coal	1121	380	741	2.47	0.47	2.00	6.95
SBA-15[47]		950			1.31	0	1.31	6.59
MCM-41[47]		1229			1.15	0	1.15	2.74

materials should be economically attractive materials for MBS preparation.

Because many porous carbon materials have a high surface area and pore volume, it is no surprise that porous carbon materials have been studied for CO_2 separation;[1] however, due to their low adsorptive selectivity for CO_2, practical application of porous carbon materials for CO_2 capture from flue gas is limited.[20] To improve the selectivity of the porous carbon materials for CO_2 sorption, building a "chemical" interaction between CO_2 and the active sites on the porous carbon materials, such as introducing basic nitrogen functionalities on the surface, is necessary.[21,22] In general, there are many approaches for increasing the nitrogen functional groups on the surface of the carbon materials, including directly introducing nitrogen atoms to the carbon structure, grafting nitrogen-containing groups on the surface, and impregnating with amine polymer.[23,24] Nitrogen atoms can be incorporated into the carbon structure by preparation of activated carbon from nitrogen-containing polymers[25] or by adding nitrogen-containing compounds (such as ammonia,[26−28] monoethanol-amine,[27,29,30] and 3-aminopropyl-triethoxysilane[31,32]) into the carbon precursor. A problem in these methods is that only a smaller amount of the nitrogen-containing functional groups can be introduced to the structure of the carbon materials or to the surface of the carbon, which leads to a relatively low CO_2 sorption capacity of the adsorbents. Unlike these methods, the impregnation of PEI on carbon materials can incorporate a large amount of amine functional groups into the pore structure of carbon materials, resulting in a significant improvement of the CO_2 sorption capacity.

Some studies on preparation of CO_2 sorbents by loading PEI on the carbon materials and evaluation of their CO_2 sorption capacity at 75 °C have been reported in the literature.[33−36] Arenillas et al. reported the preparation of a sorbent by loading 60 wt % of PEI on a fly ash-derived activated carbon, which showed a CO_2 capacity of 40 mg-CO_2/g-sorb.[33] Maroto-Valer et al. reported the preparation of the sorbents by loading 33.5 wt % of PEI on activated anthracites. The measured sorption capacity of the sorbent was 26.3 mg-CO_2/g-sorb.[1,34] Recently, Maroto-Valer et al. reported loading 39 wt % of PEI on a fly ash to prepare a CO_2 sorbent with a measured capacity of 49.8 mg-CO_2/g-sorb.[1,35] Zhang et al. reported the preparation of sorbents by loading PEI on fly ashes collected from a research boiler.[36] They obtained a CO_2 sorption capacity of 93.6 mg-CO_2/g-sorb, which is the highest CO_2 sorption capacity reported so far for the sorbents prepared by loading PEI on carbon materials. However, all the sorbents prepared by loading PEI on the carbon materials showed a much lower CO_2 capacity in comparison with those by loading PEI on mesoporous silica molecular sieves, which limits their practical application for CO_2 separation from flue gas.

Recently, an approach of using various carbon materials as a support to prepare carbon-based MBS (CB-MBS) for CO_2 capture has been conducted in our laboratory.[15] It was found that some commercial and inexpensive carbon black was an excellent support for preparing high-performance CB-MBS with a CO_2 sorption capacity as high as 135 mg-CO_2/g-sorb and good regenerability, which has been reported in a short communication.[15] However, why the CB-MBS samples prepared by using different carbon materials exhibited quite different sorption capacities, how the structure of the carbon materials influences the sorption capacity of CB-MBS, and whether it is able to improve further the sorption performance of the CB-MBS by modifying the support carbon materials were not addressed in the previous communication. The present paper will report our current approaches on (1) detailed examination of the effects of the carbon properties (including surface chemistry and pore structure), PEI loading amount, sorption temperature, and CO_2 partial pressure and coexisting moisture on the CO_2 sorption capacity of the developed CB-MBS; and (2) modification of the support carbon materials to improve the CO_2 sorption performance. The ultimate purpose of this study is to develop a new type of MBS using a commercially available and inexpensive carbon material as a support, which is expected to allow CO_2 capture from flue gas to be conducted more cost-efficiently.

2. EXPERIMENTAL SECTION

2.1. Carbon Samples. Some commercial carbon materials, including three activated carbons and two carbon blacks, with different pore structures were chosen to use as supports to prepare the carbon-based MBS. The porous properties of the carbon materials are listed in Table 1. Within these carbon samples, C1 is a coal-derived activated carbon, NORIT SA 4 PAH, from Norit; C2 is a wood-derived activated carbon, Nuchar SA 20, from Westvaco; C3 is a coconut-derived activated carbon, Nuchar 1500, from Westvaco; C4 is a coal-derived carbon black, BP 2000, from Cabot; and C5 is a coal-derived carbon black, EC 600JD, from Akzo Nobel.

2.2. Modification of Carbon Materials by Steam Treatment. To enlarge the pore size or develop the porosity of the activated carbon, a steam modification of the samples was performed in a vertical tubular furnace. Typically, ~3 g of the carbon sample was placed into a quartz reactor, and the temperature of the reactor bed was increased from room temperature to 600 °C at a rate of 10 °C/min under a pure N_2 flow with a flow rate of 20 mL/min. Then steam as an activation agent with a concentration of 89 vol % in N_2 was introduced into the reactor at a flow rate of 81 mL/min. The reactor temperature was increased to the desired temperatures (800, 900, or 1000 °C), and kept at the temperature for 1 or 2 h for steam modification. The activated carbon prepared by steam modification was denoted as Cx-Sy, where Cx is the ID

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of the carbon material (x = 1, 2, 3, and 4), and Sy represents the steam treatment at y °C.

2.3. Preparation of MBS Samples. CB-MBS samples were prepared by using the original carbon samples and the steam-modified carbon samples as support and using the wet impregnation method reported in our previous paper.[7,8] The desired amount of polyethylenimine (PEI), which was purchased from Aldrich with an average molecular weight (M_n) of 423 g/mol, was dissolved in 20 mL of methanol and stirred for ~30 min. Then, 2.5 g of carbon sample was added into the PEI solution under stirring. The methanol in the slurry was removed by evaporation in a hood under stirring. The solid sample was further dried in a vacuum oven at 45 °C for 12 h. The dried samples were ground into a fine powder and sealed in a vial before using. The prepared CB-MBS samples with different PEI loading were denoted as PEI(x)/y, where x is the weight percentage of the PEI loaded in the sorbent, and y indicates the support of the carbon material.

2.4. Evaluation of Sorption−Desorption Performance of CB-MBS. *Thermogravimetric Analysis (TGA).* The sorption−desorption performance of the prepared CB-MBS samples were evaluated by using a thermogravimetric analyzer (TA Q600-SDT TGA-DSC) on the basis of the weight gain and loss during the sorption and desorption process. A typical TGA temperature program and weight change profile for sorption and desorption are shown in Figure 1. The evaluation
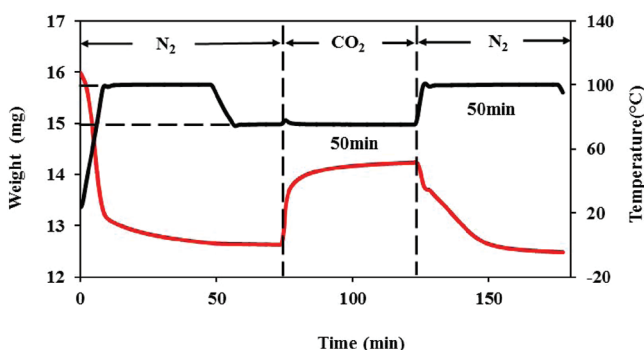

Figure 1. Typical TGA temperature program and weight change profile for evaluation of sorption/desorption performance of MBS.

procedure is described as the following: About 10 mg of the sample was loaded onto the sample pan, and the temperature was increased at a rate of 10 °C/min from 30 to 100 °C and kept at 100 °C for 40 min under N$_2$ (99.99%) with a flow rate of 100 mL/min to remove any possible moisture, solvent, or other adsorbates from the sample. After the temperature was reduced to the desired temperature (75 °C), the gas was switched from N$_2$ to pure CO$_2$ (99.99%) and held at this temperature for 50 min for CO$_2$ sorption. After 50 min of CO$_2$ sorption, the temperature was increased to 100 °C, and the gas flow was switched from CO$_2$ to N$_2$ for desorption. The mass-based CO$_2$ sorption capacity (mg-CO$_2$/g-sorb) was calculated according to the weight change of the sample recorded by the TGA analyzer in the sorption/desorption process. It needs to be pointed out that the sorption capacity measured by TGA in this study is not an equilibrium sorption capacity, because the weight of the sample still showed an increasing trend after 50 min sorption due to the low sorption rate, as observed in Figure 1.

Evaluation in a Fixed-Bed Flow Sorption System. A fixed-bed flow sorption system with gas flow controllers, sorption column, and an online gas chromatograph was built for evaluation of the sorbents. The sorption column consisted of a stainless steel tube 150 mm in length and 7.7 mm in i.d., corresponding to a bed volume of 7.0 mL. A K type thermocouple was put in the middle of the sorbent bed to monitor the bed temperature. In a typical test, about 2−3 g of dry sorbent was packed into the sorption column. Before starting CO$_2$ sorption, the sorbents were pretreated at 100 °C in a N$_2$ gas flow at a flow rate of 50 mL/min for 12 h to remove moisture, solvent, or other adsorbates from the sample. Then the sorption column was cooled down to 75 °C for the sorption test. After the temperature of the sorption bed was stable at 75 °C, a simulated flue gas was introduced into the sorption column at a flow rate of 20 mL/min. The composition of the simulated flue gas was 15 vol % CO$_2$ and 4.5 vol % O$_2$ in N$_2$, which was purchased from GT&S Inc. When the outlet CO$_2$ concentration reached the CO$_2$ concentration in the simulated flue gas, the gas was switched to pure N$_2$ (99.99 vol %) at a flow rate of 50 mL/min, and the sorbent bed temperature was increased to 100 °C for desorption. The outlet gas was monitored by an online SRI 8610C gas chromatograph (GC) equipped with a molecular sieve 5A column, silica-gel column and a thermal conductive detector.

CO$_2$ Sorption Isotherm Measurement. The CO$_2$ sorption isotherms were measured by using a modified Micromeritics ASAP 2020 Analyzer with CO$_2$ instead of N$_2$ at the desired temperatures. Before the measurement, the sample was dried in a vacuum oven and degassed at 50 °C under vacuum for 48 h. The CO$_2$ sorption isotherms were measured at 25, 75, and 100 °C for a range of pressures from 0.2 to 101 kPa. The sorbed CO$_2$ amount in mass was calculated on the basis of the measurement of the sorbed CO$_2$ standard volume.

2.5. Characterization of Textural Structure. Characterization of the textural structure of the carbon and CB-MBS samples was carried out by the physical adsorption of N$_2$ at −196 °C in a Micromeritics ASAP 2020 analyzer. The carbon samples were degassed at 200 °C under vacuum for 24 h. To avoid the degradation of PEI, CB-MBS samples were degassed at 50 °C under vacuum for 48 h.

The Brunauer−Emmett−Teller (BET) surface area (S_{BET}) was obtained from physical adsorption of N$_2$ using the BET equation. The total pore volume (V_t) was calculated on the basis of the absorbed N$_2$ after finishing pore condensation at a relative pressure of P/P_0 = 0.995. The t-plot method was used to estimate the micropore volume (V_{micro}). The meso- + macropore volume ($V_{meso+macro}$) is calculated by subtracting the micropore volume from the total pore volume. The pore size distribution was determined by the density functional theory (DFT) method, which can provide detailed information of the carbon porosity in the range from micropores to mesopores.

3. RESULTS AND DISCUSSION

3.1. Screening of Porous Carbon Materials for Preparation of CB-MBS. A series of CB-MBS samples were prepared by using different carbon materials with 50 wt % PEI loading. The CO$_2$ sorption capacity of the CB-MBS samples was evaluated by using TGA, and the results are shown in Table 2 in comparison with the first and secondary generations of MBS (PEI(50)/MCM-41 and PEI(50)/SBA-15) developed in our laboratory.[7−10] The measured CO$_2$ sorption capacities of the various CB-MB samples were quite different. PEI(50)/C1

Table 2. CO$_2$ Sorption Capacity of CB-MBS in Comparison with PEI(50)/SBA-15 and PEI(50)/MCM-41[a]

sample ID	packing density (g/mL)	mass-based CO$_2$ sorption capacity (mg-CO$_2$/g-sorb)	volume-based CO$_2$ sorption capacity (mg-CO$_2$/mL-sorb)
PEI(50)/C1		33	
PEI(50)/C2	0.52	63	33
PEI(50)/C3	0.61	59	36
PEI(50)/C4	0.35	135	47
PEI(50)/C5	0.22	126	28
PEI(50)/SBA-15	0.22	138	30
PEI(50)/MCM-41[7−9]	0.27	110	30

[a]Measured by TGA at 75 °C under a pure CO$_2$ flow at a flow rate of 100 mL/min

gave the least capacity of 33 mg-CO$_2$/g-sorb among all the tested samples. The PEI(50)/C1 sample also appeared to be a sticky slurry, unlike other PEI(50)/Cx samples that were a solid powder. It is probably because the volume of the loaded PEI (∼0.5 mL/g-sorb) was larger than the pore volume of C1 (0.32 mL of total pore volume per 0.5 g of C1). The excessive amount of PEI was coated on the external surface of the carbon particles, which allows the particles to stick to each other. Both PEI(50)/C2 and PEI(50)/C3 showed a higher CO$_2$ sorption capacity than that of PEI(50)/C1, but less than half that of PEI(50)/C4. In all tested CB-MBS samples, PEI(50)/C4 gave the highest CO$_2$ sorption capacity of 135 mg-CO$_2$/g-sorb, which is higher than that of the best carbon-based sorbent reported in the literature by 44% under comparable test conditions.[36] This capacity is also significantly higher than that of PEI(50)/MCM-41 (110 mg-CO$_2$/g-sorb)[7−10] and almost the same as that of PEI(50)/SBA-15 (138 mg-CO$_2$/g-sorb, measured under the same conditions).[15] The measured CO$_2$ sorption capacity of PEI(50)/C5 was 126 mg-CO$_2$/g-sorb, which is slightly lower than that of PEI(50)/C4, but considerably higher than other CB-MBS samples.

Interestingly, it was also found that PEI(50)/C2, PEI(50)/C3, and PEI(50)/C4 had a much higher packing density—0.52, 0.61, and 0.35 g/mL, respectively—in comparison with those of PEI(50)/MCM-41 (0.27 g/mL) and PEI(50)/SBA-15 (0.22 g/mL). According to their packing densities, the CO$_2$ sorption capacity based on the sorbent bed volume for each sorbent was also estimated, and the results are also shown in Table 2. PEI(50)/C2, PEI(50)/C3, and PEI(50)/C5 have a volume-based sorption capacity similar to those of PEI(50)/MCM-41 and PEI(50)/SBA-15, and PEI(50)/C4 even has a volume-based sorption capacity as high as 47 mg-CO$_2$/mL-sorb, which is higher than that of PEI(50)/SBA-15 by 57%. It indicates that for capturing the same amount of CO$_2$, the required sorbent bed volume for PEI(50)/C4 is only about 64% of that for PEI(50)/SBA-15. For a large scale CO$_2$ sorption process, higher volume-based CO$_2$ sorption capacity is very important because it will reduce the sorbent bed size and, thus, reduce the infrastructure investment for mass CO$_2$ capture. Therefore, the high volume-based sorption capacity is another significant advantage of PEI(50)/C4 over mesopore-silica−molecular-sieve-based MBS.

3.2. Modification of Carbon Supports for Improvement of CO$_2$ Sorption Capacity. Both C4 and C5 are commercial carbon blacks. As is well-known, carbon black is virtually pure elemental carbon in the form of colloidal particles. Interestingly, although the porous structure of C4 and C5 is quite different from that of SBA-15 with a well-ordered mesoporous structure, the measured sorption capacity of PEI(50)/C4 and PEI(50)/C5 is similar to that of PEI(50)/SBA-15, indicating that a material with a structure of colloidal particles can also be used as a good support for preparing MBS with a high CO$_2$ sorption capacity. It was also found that the sorption capacities of the PEI(50)/C1, PEI(50)/C2, and PEI(50)/C3 were much poorer than those of PEI(50)/C4 and PEI(50)/C5.

C1, C2, and C3 are commercial activated carbons that consist of a random number of graphite platelets with various kinds of porosity. Possible reasons for the low sorption capacity of the activated-carbon-supported MBS might be the following: (1) The activated carbon may contain more oxygen-containing functional groups on the surface, which may interact with the amine groups in PEI, resulting in consumption of the sorption sites. (2) In comparison of the pore parameters of the three activated carbon samples with those of the two carbon blacks and SBA-15, in addition to the different pore structure, it is clear that the pore size and the mesopore plus macropore volume of the activated carbon samples are much less than those of the two carbon blacks and SBA-15, although the surface area of the activated carbon samples is in the same range as, or even higher than, that of the carbon blacks and SBA-15 (see Table 1). To clarify which property of the activated carbon samples is more critical in determining the sorption capacity of the activated-carbon-supported PEI(PEI/AC), it is necessary to examine the effects of the surface functional groups and textural properties of the activated carbon on the CO$_2$ sorption capacity of PEI/AC.

3.2.1. Modification of Carbon Surface Functional Groups and Its Effect on the CO$_2$ Sorption Capacity of PEI/AC. There are many oxygen-containing functional groups on the surface of carbon materials, such as carboxylic groups, phenolic hydroxyl groups, etc. These acidic groups might consume some amine groups in PEI through an acid−base interaction. To examine the effect of the surface oxygen-containing functional groups on the sorption capacity of PEI/AC, heat treatment of the activated carbons under a N$_2$ flow at 700 °C was applied to tailor the oxygen-containing functional groups on the surface. A temperature programmed desorption method, which was reported in our previous paper,[37] was used to characterize the surface oxygen-containing functional groups. The results indicate that more than 75% of the oxygen-containing functional groups on the surface of C3 were removed after the heat treatment at 700 °C for 2 h. However, the CO$_2$ sorption capacities of PEI(50)/heat-treated-C3 increased by only 5% in comparison with that of PEI(50)/C3, indicating that the oxygen-containing functional groups on the surface of carbon materials may have some effect, but they are not a key factor in determining the sorption performance of the activated-carbon-supported PEI sorbent.

3.2.2. Modification of Textural Properties of Carbon Supports and Its Effect on CO$_2$ Sorption Capacity of CB-MBS. Comparison of the textural properties of C4 and C5 with those of C1, C2, and C3 indicates that the larger pore size and higher pore volume of the carbon blacks may be beneficial for holding a greater amount of PEI in the pores and improving the

accessibility (efficiency) of the amine groups for CO_2, which might result in the higher sorption capacity of PEI(50)/C4 and PEI(50)/C5. To confirm it, steam modification of the activated carbons was conducted to increase the pore size and pore volume of the activated carbons because steam activation has been reported to be an effective method for enlarging the pore size and the pore volume of the activated carbon. The steam modifications of C1, C2, and C3 at a temperature range of 800−1000 °C, ambient pressure under a flow with 81 mL/min of steam and 10 mL/min of N_2 for 1 or 2 h was carried out in a fixed-bed reactor system. The product yield of the modified C3 decreased from 58 wt % to 33 wt % when the modification temperature increased from 800 to 900 °C for 2 h. Further increase of the temperature to 1000 °C for 2 h resulted in a product yield of only 8.5 wt %, indicating that most of the activated carbon reacted with steam at these conditions. Thus, 1 h of the modification time was selected for steam modification at 1000 °C.

The activated carbons obtained by steam modification at 800, 900, and 1000 °C were used to prepare CB-MBS samples with the same PEI loading of 50 wt %. The prepared CB-MBS samples were evaluated by using TGA for their CO_2 sorption capacity, and the results are shown in Figure 2 in comparison
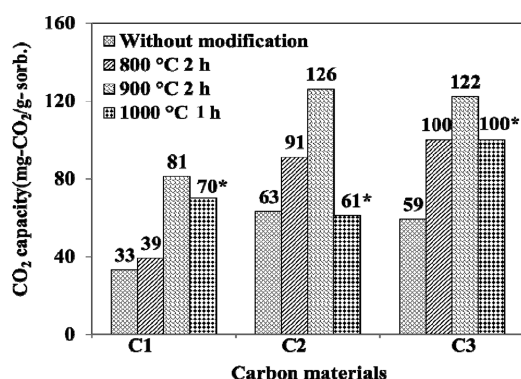

Figure 2. CO_2 sorption capacity of CB-MBS samples prepared by using the steam-modified carbon materials. The results were obtained by TGA at 75 °C and ambient pressure under a pure CO_2 flow at a flow rate of 100 mL/min. An asterisk (*) indicates steam modification at 1000 °C for 1 h.

with the CB-MBS prepared directly by activated carbons without the steam modification. It is clearly shown that steam modification could significantly improve the CO_2 sorption performance of the CB-MBS samples, especially for C2 and C3. The CO_2 sorption capacity of the PEI(50)/C2 increased from 63 mg-CO_2/g-sorb for the C2 without the modification to 91 mg-CO_2/g-sorb for the C2 modified at 800 °C and to 126 mg-CO_2/g-sorb for the C2 modified at 900 °C. The CO_2 sorption

capacity of the PEI(50)/C3 increased from 59 mg-CO_2/g-sorb for the C3 without the modification to 100 mg-CO_2/g-sorb for the C3 modified at 800 °C and to 122 mg-CO_2/g-sorb for the C3 modified at 900 °C. Even for PEI(50)/C1 with the C1 modified at 900 °C, a sorption capacity of 81 mg-CO_2/g-sorb was achieved. However, a further increase in the modification temperature to 1000 °C led to a decrease in the CO_2 sorption capacity of CB-MBS samples. It is evident that steam modification has a significant influence on the improvement of CO_2 sorption capacity of CB-MBS, and a maximum CO_2 sorption capacity was observed for the CB-MBS samples with the activated carbon modified at 900 °C for 2 h.

3.2.3. Relationship between Textural Structure of Carbon Supports and Sorption Capacity of CB-MBS. To further understand the reason for improving sorption capacity of CB-MBS through changing the textural properties of the carbon samples, the textural properties of the activated carbons modified by steam treatment at 900 °C were characterized by N_2 physical adsorption. Table 3 shows the pore properties of the steam-modified activated carbons in comparison with their parent samples. The surface area of C1−S900 and C2−S900 increased slightly, but C3−S900 did not. The major differences in pore properties between the steam-modified activated carbons and their parent samples are the significant increase in the total pore volume, especially the increase in their meso- + macropore volume, and the average pore size.

To elucidate the relationship between the CO_2 sorption capacity and the pore properties of the carbon supports, the CO_2 sorption capacity of CB-MBS samples as a function of total surface area, microporous surface area, and meso- + macroporous surface area, respectively, is shown in Figure 3. It
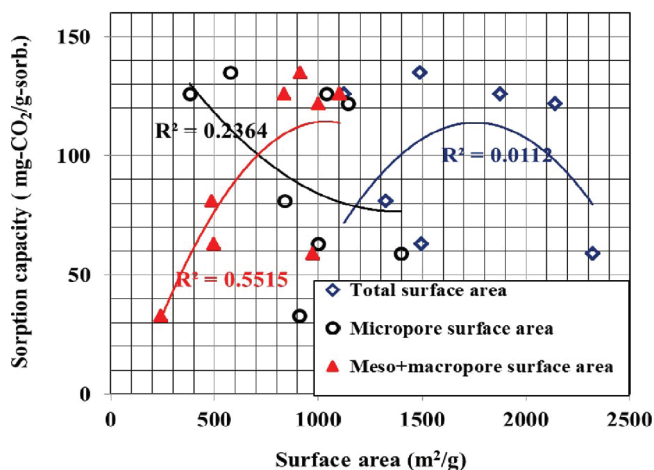

Figure 3. CO_2 sorption capacity of PEI(50)/Cx as a function of surface area of Cx. The capacity was measured by TGA at 75 °C and ambient pressure under a pure CO_2 flow at a flow rate of 100 mL/min.

Table 3. Textural Structure of the Steam-Modified Carbon Samples and Their Parent Carbon Samples[a]

sample ID	S_{BET} (m²/g)	S_{micro} (m²/g)	$S_{meso+macro}$ (m²/g)	V_{total} (mL/g)	V_{micro} (mL/g)	$V_{meso+macro}$ (mL/g)	pore size (nm)
C1	1151	910	241	0.64	0.44	0.20	2.22
C1−S900	1323	837	486	0.90	0.45	0.45	2.63
C2	1495	1000	495	1.21	0.55	0.66	2.91
C2−S900	1872	1039	833	1.57	0.56	1.01	3.45
C3	2320	1397	972	1.64	0.79	0.84	2.85
C3−S900	2140	1141	999	1.72	0.63	1.09	3.27

[a]Steam modification conditions: steam flow rate, 81 mL/min; N_2 flow rate, 10 mL/min; pressure, ambient; temperature, 900 °C; time, 2 h.

is clear that the correlation between the CO_2 sorption capacity of the PEI(50)/CB samples and the surface areas of their carbon supports is poor. It indicates that neither total surface area ($R^2 = 0.0112$), nor microporous surface area ($R^2 = 0.2364$), nor meso- + macroporous surface area ($R^2 = 0.5515$) is a significant factor in determining the CO_2 sorption performance of the CB-MBS samples.

The CO_2 sorption capacity of the CB-MBS samples with 50 wt % PEI loading as a function of pore volume, including total pore volume, meso- + macropore volume, and micropore volume, respectively, is shown in Figure 4. It is clear that the
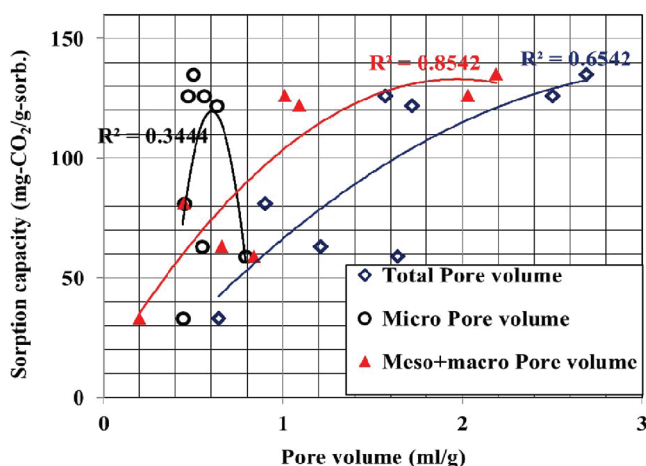

Figure 4. CO_2 sorption capacity of PEI(50)/Cx as a function of pore volume of Cx. The capacity was measured by TGA at 75 °C and ambient pressure under a pure CO_2 flow at a flow rate of 100 mL/min.

micropore volume has a poor correlation ($R^2 = 0.3444$) with the CO_2 sorption capacity; however, the total pore volume ($R^2 = 0.6542$), especially the meso- + macropore volume ($R^2 = 0.8542$), has a good correlation with the CO_2 sorption capacity of the CB-MBS samples. With increase in the meso- + macropore volume, the CO_2 sorption capacity of the CB-MBS samples increases. This result strongly indicates that the total pore volume, especially the meso- + macropore volume, plays a crucial role in determining the CO_2 sorption capacity of the CB-MBS samples. It can be explained that the large meso- + macropore volume could increase the total number of the accessible sorption sites of PEI in the sorbent for CO_2 sorption, resulting in the improved CO_2 sorption capacity of CB-MBS.

This result also answers the question why PEI(50)/C4 and PEI(50)/C5 exhibited better CO_2 sorption capacity than other carbon materials and further confirms the positive effect of pore volume on the CO_2 sorption capacity. Interestingly, the effect of pore volume on the CO_2 sorption capacity of the carbon-supported PEI sorbents found in the present study is in agreement with that of the mesoporous-silica-supported PEI sorbents reported in the literature,[38−40] although the pore structure and shape of the former are quite different from those

of the latter. Thus, it is clear that the pore volume, especially the meso-plus-macro-pore volume, but neither the surface area nor pore shape of the support materials, is crucial in determining the CO_2 sorption capacity of the supported amine sorbents.

3.3. Effect of PEI Loading on CO_2 Sorption Capacity of PEI/C4. As discussed in our previous studies,[13] the sorption of CO_2 on the supported PEI is through an interaction of CO_2 with the accessible amine groups in PEI. The amount of loaded PEI might play an important role in determining the CO_2 sorption capacity of CB-MBS. Since the C4 has the highest pore size and pore volume among all carbon materials tested in the present study, a series of PEI/C4 samples with different PEI loading amounts were prepared, and their textural structures were characterized by N_2 physical adsorption. Table 4 lists the surface area and pore volume of the parent C4 and PEI/C4 with different PEI loading. A significant reduction in the surface area and total pore volume with increasing amine loading was observed. For instance, the surface area and the total pore volume of C4 were 1486 m^2/g and 2.69 mL/g, respectively. With 30 wt % PEI loading, the surface area and the total pore volume decreased to 321 m^2/g and 1.31 mL/g. When the PEI loading was 50 wt %, the surface area and total pore volume further decreased to 37 m^2/g and 0.33 mL/g, respectively. Continuous increase in the PEI loading to 65 wt % caused the further decrease in the surface area and the total pore volume to 27 m^2/g and 0.29 mL/g, respectively. The decrease in the BET surface area and pore volume of PEI/C4 samples with increasing PEI loading suggests that the loaded PEI was filled into the pores of the carbon support, as also indicated by the pore size distribution (see Figure 5) measured by the N_2 adsorption with DFT method.
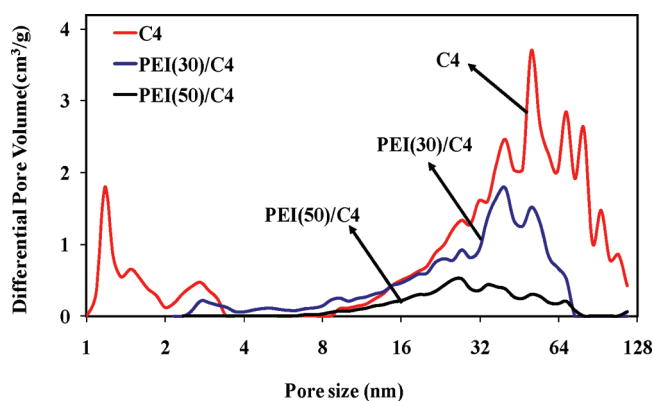

Figure 5. Pore size distribution of C4 and PEI/C4 samples with different PEI loadings.

The CO_2 sorption capacity of the PEI/C4 samples with different PEI loadings was evaluated by using TGA, and the results are shown in Figure 6. It was found that the CO_2 sorption capacity increased with increasing PEI loading amount

Table 4. BET Surface Area and Pore Volume of C4 and PEI/C4 with Different PEI Loading

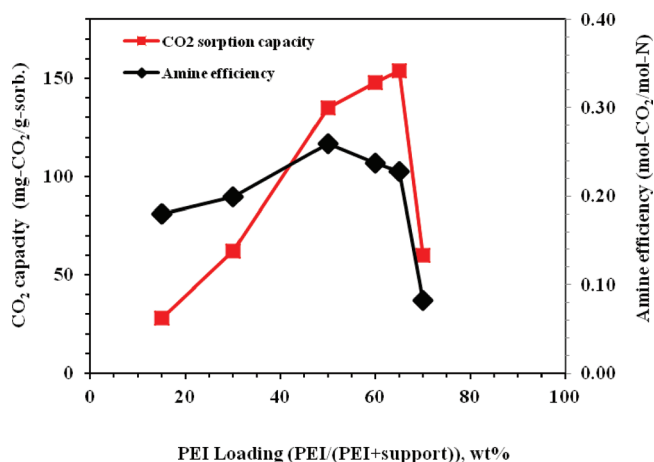| sample ID	S_{BET} (m^2/g)	S_{micro} (m^2/g)	$S_{meso+macro}$ (m^2/g)	V_{total} (mL/g)	V_{micro} (mL/g)	$V_{meso+macro}$ (mL/g)
C4	1486	575	911	2.69	0.50	2.19
PEI(30)/C4	321	5.40	315	1.31	0.14	1.17
PEI(50)/C4	37	0.60	36	0.33	0.02	0.31
PEI(65)/C4	27	0.45	26	0.29	0.01	0.28

Figure 6. Effect of PEI loading on the CO_2 sorption capacity and the amine efficiency of PEI/C4. The capacity was measured by TGA at 75 °C and ambient pressure under a pure CO_2 flow at a flow rate of 100 mL/min.

when the PEI loading was <65 wt %. PEI/C4 with 65 wt % PEI loading (PEI(65)/C4) gave the highest CO_2 sorption capacity of 154 mg-CO_2/g-sorb. Upon further increasing the PEI loading amount, a significant decrease of the CO_2 sorption capacity was observed. The CO_2 sorption capacity of PEI(70)/C4 was reduced to only about 60 mg-CO_2/g-sorb. This is because the 70 wt % PEI loading is beyond the saturation pore volume of C4, and the extra PEI was coated on the external surface of the C4 particles, which results in the agglomeration of the particles, as also visibly observed. The agglomeration of the particles could reduce the total number of accessible amine sites as a result of an increase in the diffusion resistance of CO_2 into the bulk of the PEI in the pores. Therefore, the maximum CO_2 sorption capacity of 154 mg-CO_2/g-sorb was obtained for the PEI/C4 sorbent with 65 wt % PEI loading (PEI(65)/C4). It needs to be mentioned that the best PEI loading (65 wt %) on C4 is higher than the best PEI loading (50 wt %) on MCM-41 and SBA-15. This can be ascribed to the higher pore volume of C4 than that of MCM-41 and SBA-15.

The efficiency of the amine groups in the sorbent, which is defined as a molar ratio of the sorbed CO_2 to the amine groups in the sorbent for each PEI/C4 sample, was calculated, and the results are shown in Figure 6. The amine efficiency for the PEI/C4 increased initially with increase of PEI loading amount and reached the maximum of 0.26 mol-CO_2/mol-amine at 50 wt % of PEI loading. This value is lower than the stoichiometric ratio of 0.5 mol-CO_2/mol-amine. A decrease in the amine efficiency was observed when the PEI loading was higher than 50 wt %, especially when the PEI loading was higher than 65 wt %. The lower amine efficiency of PEI(65)/C4 than that of PEI(50)/C4 indicated that a higher percentage of amine sites in the PEI were not accessible to CO_2 molecules, although the former contained more amine groups per gram of sorbent than that of the latter. The lower amine efficiency at higher amine loading can be ascribed to the agglomeration of the particles being caused by the higher PEI loading, which results in a decrease in the accessibility of the amine sites due to higher diffusion resistance of CO_2 into the bulk of PEI in the pores.

3.4. Sorption Isotherms and Effect of Temperature on CO_2 Sorption Capacity of PEI(50)/C4. As is well-known, in a sorption process, the temperature is an important factor that influences directly the sorption capacity of the sorbent. In our

previous study,[7,13] we found that the best temperature for the maximum apparent CO_2 capacity on both PEI(50)/MCM-41 and PEI(50)/SBA-15 was around 75 °C. In the present study, the temperature effect on the CO_2 capacity of PEI(50)/C4 was examined by using the modified Micromeritics ASAP 2020 analyzer. The measured sorption isotherms at 25, 75, and 100 °C are shown in Figure 7. The curves appear to be typical type I isotherms according to the classification by Brunauer et al.[41,42]
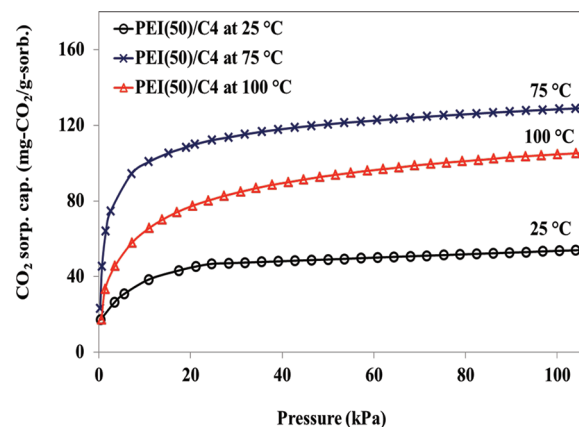

Figure 7. CO_2 sorption isotherms of PEI (50)/C4 measured at 25, 75, and 100 °C. The CO_2 sorption isotherm at 25 °C may be not a true sorption isotherm because of a very slow sorption rate. The CO_2 sorption isotherms measured at 75 and 100 °C may be closer to the true ones.

The PEI(50)/C4 exhibited a CO_2 sorption capacity of 64 mg-CO_2/g-sorb at 25 °C and 100 kPa. With increasing sorption temperature to 75 °C, the measured CO_2 sorption capacity of PEI(50)/C4 became higher and reached a CO_2 sorption capacity of 129 mg-CO_2/g-sorb at 75 °C. Upon further increasing the temperature to 100 °C, the measured CO_2 sorption capacity of PEI(50)/C4 decreased to 106 mg-CO_2/g-sorb. This result is in agreement with that observed in the fixed-bed flow system test. The lower CO_2 sorption capacity at 25 °C can be attributed to the higher kinetic barrier for the diffusion of CO_2 from the surface into the bulk of PEI at the low temperature, which reduces significantly the total number of accessible sorption sites. Thus, the measured sorption isotherm, especially at 25 °C, may be an apparent sorption isotherm, but not a true equilibrium sorption isotherm. An increase in temperature may facilitate the diffusion of the CO_2 molecules from the surface into the bulk of PEI by overcoming the kinetic barrier and allow more CO_2-affinity amine sites to be accessible to CO_2, which results in the increase in the CO_2 sorption capacity of PEI(50)/C4 at 75 °C. However, if the temperature is higher than 75 °C, the sorption may change from a kinetically determined region to a thermodynamically determined region, in which the sorption capacity decreases with rising temperature according to the van't Hoff equation. Consequently, the CO_2 sorption capacity of PEI(50)/C4 at 100 °C is lower than that at 75 °C. Therefore, an apparently optimal CO_2 sorption temperature was observed at about 75 °C, which resulted from a compromise between kinetic and thermodynamic factors.

The high CO_2 capacity at 75 °C is another significant advantage of PEI(50)/C4 in comparison with other carbon-based CO_2 adsorbents reported in the literature. In most cases, the CO_2 sorption capacity of adsorbents/sorbents decreases rapidly with increasing temperature because the low temper-

ature is thermodynamically favorable for adsorption. Plaza et al. found an ~50−60% decrease in the CO_2 sorption capacity of a nitrogen-enriched carbon material when the temperature increased from 25 to 100 °C.[43] In contrast to the nitrogen-enriched carbon materials, PEI(50)/C4 exhibited a higher CO_2 sorption performance in the temperature range from 60 to 80 °C. This special property of the supported PEI sorbent is favorable for CO_2 capture from flue gas because the typical temperature of flue gas from the fossil fuel power plant is in the range of 60−120 °C, depending on the operation conditions.[44]

On the other hand, the observed sorption isotherms of PEI(50)/C4 at different temperatures also provide another important message: For regeneration of the spent MBS, using the thermal-swing adsorption (TSA) alone is insufficient because an increase in the temperature from 75 to 100 °C can desorb only ~18% of the sorbed CO_2, and the regeneration of the spent PEI(50)/C4 at higher temperature may cause decomposition or degradation of the PEI. Thus, for the regeneration of the spent sorbent, a combination of TSP and pressure-swing adsorption or using steam as a carrier gas is necessary. More investigation in regeneration of CB-MBS is required for practical application.

3.5. Effect of Moisture on CO_2 Sorption Capacity of PEI(50)/C4. For practical application, it is important to clarify the effect of moisture on the CO_2 sorption capacity because moisture is one of the key components in flue gas that may compete with CO_2 for the sorption sites. Since the TGA analysis cannot distinguish the take-up of CO_2 or H_2O, the influence of moisture on the CO_2 sorption capacity of PEI(50)/C4 was examined in a fixed-bed flue system by passing the simulated flue gas, which contain 15 vol % CO_2 and 4.5 vol % O_2 in N_2, with and without moisture. The moisture concentration in the simulated flue gas was about 2.5 vol %, which is the saturation H_2O concentration at room temperature.

The breakthrough curves for CO_2 sorption on PEI(50)/C4 with the simulated gases are shown in Figure 8. In the absence
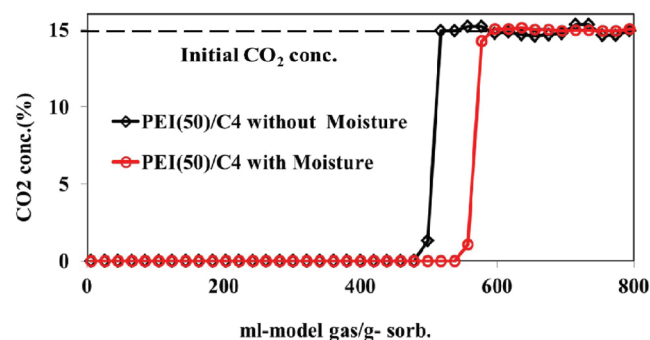

Figure 8. Effect of moisture in the simulated flue gas on the CO_2 sorption capacity of PEI(50)/C4. Measured in a fixed-bed flow sorption system at 75 °C and ambient pressure with the simulated flue gas at a flow rate of 20 mL/min. Composition of the simulated flue gas: 15 vol % CO_2 and 4.5 vol % O_2 in N_2. Composition of the simulated flue gas with moisture: 2.5 vol % H_2O (gas), 14.6 vol % CO_2, and 4.4 vol % O_2 in N_2.

of H_2O, PEI(50)/C4 was saturated by CO_2 at 459 mL-gas/g-sorb, corresponding to a saturation sorption capacity of 137 mg-CO_2/g-sorb. In the presence of 2.5 vol % H_2O, PEI(50)/C4 was saturated by CO_2 at 518 mL-gas/g-sorb, with a saturation sorption capacity of 147 mg-CO_2/g-sorb. The results

clearly indicate that the presence of 2.5 vol % H_2O has a promoting effect on the CO_2 sorption capacity of PEI(50)/C4. The higher amine efficiency (CO_2/N molar ratio) of 0.28 was observed for (PEI)/C4 in the presence of moisture. The increase in the CO_2 sorption capacity in the presence of moisture could be explained by the different chemical reaction between CO_2 and amine under dry and humid conditions. Under dry conditions, two amine groups may be required to capture one CO_2 molecule to form a carbamate compound, whereas under humid conditions, only one amine group may be needed to capture one CO_2 molecule to form a bicarbamate compound, as reported in the literature.[45,46] Khatri et al. has provided direct evidence for the formation of bicarbonate species using IR analysis of humid CO_2 sorption on a supported PEI sorbent.[47]

4. CONCLUSIONS

Several commercial carbon materials, including three activated carbons and two carbon blacks, with different pore properties have been used to prepare carbon-based MBS by loading PEI on them. Among all carbon-based supports tested in this study, the carbon black C4 was found to be the best support for preparation of CB-MBS for CO_2 capture. The CO_2 sorption capacity of 135 mg-CO_2/g-sorb was obtained for PEI(50)/C4 prepared by loading 50 wt % PEI on the carbon black C4, which is almost as high as that of PEI(50)/SBA-15. The higher CO_2 sorption capacity of 154 mg-CO_2/g-sorb was achieved for PEI(65)/C4 with 65 wt % PEI loading. Furthermore, it was found that the volume-based sorption capacity of PEI(50)/C4 is as high as 47 mg-CO_2/mL-sorb, which is higher than that of PEI(50)/SBA-15 by 57% because of the higher packing density (0.35 g/mL) of the former than that of the latter.

The correlation between the CO_2 sorption capacity and the pore properties of the carbon supports indicates that the total pore volume, especially the meso-plus-macro-pore volume, of the carbon supports plays a crucial role in determining the CO_2 sorption capacity of the CB-MBS, which was further confirmed by the significant improvement of the CO_2 sorption capacity of the CB-MBS prepared by using the steam-modified activated carbons. The highest capacity of PEI(50)/C4 can be ascribed to the highest pore volume and pore size of the carbon black C4 among all the tested carbon-based supports.

The high CO_2 sorption capacity, especially the volume-based capacity, positive effect of moisture, and low preparation cost of CB-MBS indicate that CB-MBS could be a promising sorbent for cost-efficient CO_2 capture from flue gas.

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■ ACKNOWLEDGMENTS

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