Facilely Synthesized Meso-Macroporous Polymer as Support of Poly(ethyleneimine) for Highly Efficient and Selective Capture of CO₂

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ABSTRACT

Poly(ethyleneimine) (PEI) impregnated adsorbents are promising alternatives to amine-based liquid absorbents for post-combustion capture of CO₂. A current challenge is to identify meso- and/or macroporous supports with large pore volumes that can be facilely synthesized from a cost-effective approach as supports for PEI. In this work, hierarchically nanoporous poly(divinylbenzene) (PDVB) is synthesized through a one-step polymerization of readily available divinylbenzene (DVB) under solvothermal conditions without use of any template or catalyst. The synthesized PDVB is found to have abundant meso-macropores, as well as a large pore volume. Subsequently, a series of PEI-impregnated PDVB sorbents is prepared and their performance for the selective adsorption of CO₂ is investigated. The PEI-PDVB composites are found to exhibit promising CO₂ capacities and exceptionally high CO₂/N₂ selectivities. The strength of CO₂ adsorption is experimentally determined by direct calorimetric measurements. The PEI-PDVB composites show excellent stability under both dry and humidified sorption conditions during extended adsorption-desorption cycles. Based on the results obtained, these PEI-PDVB composites are identified as sorbents with significant potential for application in practical CO₂ capture from industrial gas streams.

KEYWORDS

Porous Polymer; Poly(divinylbenzene); Poly(ethyleneimine); Physical Impregnation; CO₂ Adsorption; Selectivity.

1. INTRODUCTION

The constant increase in the CO₂ concentration in the atmosphere over the past century is an issue of wide concern because it may cause various climatic and environmental problems, such as global warming and ocean acidification.[1] Emissions of CO₂ mainly stem from industrial activity, which relies greatly on the use of fossil fuels. However, fossil fuels will still be the major source of energy for industrial activity in the near future, and eliminating CO₂ from the tail gases of industrial processes is thus a direct solution to reducing CO₂ emissions. For this purpose, wet amine-scrubbing technology was developed and has been widely employed for capturing CO₂ from various gas streams industry.[2] It makes use of the chemical reactivity of amine compounds with CO₂, which results in the formation of carbamate or bicarbonate, to realize the effective removal of CO₂. However, the regeneration of amine-based absorbents is energy-intensive because of the high heat capacity of liquid aqueous solvents.[3] In addition, organic amines are highly volatile and corrosive; those characteristics contribute to a number of problems, for example, rapid consumption of absorbents and high operational costs for replacing corroded units.[3]

As substitutes for amine-based absorbents, various solid adsorbents—including porous silicas,[4] porous carbons,[5] zeolites,[6] metal-organic framework (MOFs)[7] and porous organic polymers (POPs)[8]—have been developed for CO₂ adsorption. Compared with the amine-scrubbing process, the solid-adsorption process features lower energy consumption and negligible volatility and corrosivity,[9] making solid

adsorbents promising candidates for CO₂ capture. Among those solid adsorbents, POPs are particularly attractive because of their versatility in building blocks and synthetic routes, which makes it easy to tune their structure and porosity.[10-13] POPs have a low skeleton density because they are composed of only light elements (e.g., C, H, N and O).[14] The covalent structure of POPs endows them with high thermal stability.[15] Furthermore, most POPs show good water-tolerance,[16-18] unlike many MOFs,[19] which is crucial for their application in the post-combustion capture of CO₂.

To enable them to compete with traditional amine-based absorbents, improvement of the CO₂ capacity and CO₂/N₂ selectivity of pristine POPs under industrial conditions (e.g., elevated temperature and low partial pressure) is needed, because the inherent surface inertness of pristine POPs results in weak interactions between CO₂ and pristine POPs. Inspired by the chemistry of the amine-scrubbing process, functionalizing the surface of nanoporous adsorbents with amine groups is a widely used strategy for enhancing the selective adsorption of CO₂ on them.[9,20] For example, Zhou et al.[21] tethered polyamines to the benzene ring of PPN-6. The resultant PPN-6-CH₂-DETA can adsorb 3.04 mmol/g of CO₂ at 22°C and 0.15 bar, with a CO₂/N₂ selectivity of 442. The same group[22] also developed a facile strategy to construct porous polymers with secondary amine groups embedded in the framework, using a nucleophilic substitution reaction between 2,4,6-tris(chloromethyl)mesitylene and ethylene diamine with triblock copolymer

P123 as the template. As-prepared PPN-81 can adsorb 1.93 mmol/g of CO₂ at 22°C and 1 bar, with a CO₂/N₂ selectivity of 4716.

Although relatively stable amine-POP composites can be obtained through the chemical grafting of amine groups to the surface of POPs, the physical impregnation of amine compounds, especially poly(ethyleneimine) (PEI), into the inner pores of POPs represents a potentially more attractive method of preparing amine-POP composites.[20,23] The synthetic route of physical impregnation is very simple and easy for large-scale production. To our knowledge, the study of POPs as supports for PEI for CO₂ adsorption is very limited[24-28], although many other porous materials have been extensively studied.[29-44] A representative work most recently published is from Suh et al.,[27] who reported the efficient and selective capture of CO₂ by PEI-PAF-5 composites. A PEI-PAF-5 composite containing 40 wt.% of PEI can adsorb 2.66 mmol/g of CO₂ at 25°C and 0.15 bar with a CO₂/N₂ selectivity of 1200. Another study is from Lively et al.,[28] who used PIM-1 as a solution-processable PEI support for CO₂ capture. The PEI-PIM-1 composite containing 21 wt.% of PEI can adsorb 1.15 mmol/g of CO₂ at 35°C from 10% CO₂ balanced in N₂.

However, the synthesis of PAF-5 and PIM-1 is relatively complicated and requires expensive monomers and/or catalysts. Actually, most reported PEI supports also are uneconomical to synthesize, hindering their industrial application. For example, the mesopores in SBA-15 are created by employing large amounts of a high-cost template.[29] Moreover, the microporous structures of PAF-5 and PIM-1 are not ideally suitable for good dispersion of PEI because of the large molecular size of

PEI. In addition, their relatively small pore volumes limit the amount of PEI that can be incorporated. As a consequence, a meso- and/or macroporous support with large pore volume that can be facilely synthesized via a cost-effective route is highly interesting for the impregnation of PEI. In this work, hierarchically nanoporous poly(divinylbenzene) (PDVB) was synthesized through the one-step polymerization of readily available divinylbenzene (DVB) under solvothermal conditions without use of any template and catalyst.[45,46] The resultant PDVB is found to have distinctive meso-macroporosity and a large pore volume. Considering the simple synthetic route and meso-macroporous structure of this PDVB, it is thought to be a promising PEI support for the selective capture of CO₂. With this in mind, different amounts of PEI were incorporated into the inner pores of PDVB via a physical impregnation method, giving a series of composite adsorbents. The performance of PEI-PDVB composites for the selective capture of CO₂ was investigated systematically.

2. EXPERIMENTAL

2.1 Chemicals

Divinylbenzene (DVB, technical grade, 80 wt.%), azobisisobutyronitrile (AIBN, 98 wt.%), poly(ethyleneimine) (PEI, branched type, average M_w =800 by LS) and tetrahydrofuran (THF) were supplied by Sigma Aldrich Co. Ltd., USA. CO₂ (research grade, 99.999mol%), CO₂ (research grade, 14.92 mol% in N₂), and N₂ (ultrahigh purity grade, 99.999mol%) were supplied by Airgas Co. Ltd., USA. All the reagents were used as received without further purification.

2.2 Synthesis of Materials

Poly(divinylbenzene) (PDVB) was synthesized by a solvothermal and template-free method.[45,46] First, 0.065 g of AIBN was dissolved in 25 mL of THF/water (10/1 v/v), and 3 mL of DVB was added to the mixture under vigorous stirring for 3 h at room temperature. The solution was then transferred into an autoclave and heated at 120°C for 24 h. After the completion of the reaction, the solvent was evaporated at room temperature for 24 h and the product was dried under vacuum at 80°C for another 24 h. PDVB was obtained as a white, powdery solid. PEI-loaded PDVB samples were prepared by physical impregnation: 1.0 g of PDVB was mixed with 10 mL of a methanolic solution of PEI (containing 0.5, 1.0, 1.5, and 2.0 g of PEI, respectively) and stirred at room temperature for 24 h. The methanol was then removed by rotary evaporation at 60°C, followed by drying under vacuum at 80°C for 12 h. According to the measured PEI loadings (x , defined as the weight fraction of PEI in the composite), the final samples were denoted as $x\text{PEI@PDVB}$.

2.3 Characterization

Before characterization, the powdery samples were pretreated at 110°C under flowing N_2 for 2 h to remove adsorbed CO_2 and other residual solvents (e.g., water and methanol). The N_2 adsorption isotherms at -196°C were measured on a Micromeritics Gemini 2390a system to determine the textural properties. The total surface area was calculated from the N_2 adsorption isotherms using the BET equation in a relative pressure range of 0.05~0.30. The total pore volume was determined from the amount of N_2 adsorbed at a relative pressure of 0.97. The micropore volume was calculated from the N_2 adsorption isotherms using the carbon black STSA t -plot

equation within a thickness range of 0.45~0.60 nm. The pore size distribution was derived from the N₂ adsorption isotherms using the BJH model. The PEI loading was measured by elemental analysis on an Elementar vario EL II analyzer. Fourier transform infrared (FTIR) spectra were acquired on an Excalibur Series instrument with a MVP-Pro ATR accessory. The thermal stability was evaluated by a Seiko 6300 thermogravimetric analyzer (TGA) under flowing N₂ (150 mL/min) with a ramping rate of 10°C/min. Scanning electron microscope (SEM) images were collected on a Zeiss Auriga Crossbeam SEM at an acceleration voltage of 5 kV. Transmission electron microscope (TEM) images were collected on a Zeiss Libra200 TEM at an acceleration voltage of 200 kV.

2.4 Gas Adsorption Measurements

Before gas adsorption measurements, the powdery samples were pretreated at 110 °C under flowing N₂ for 2 h to remove adsorbed CO₂ and other residual solvents (e.g., water and methanol). The CO₂ adsorption capacity at atmospheric pressure and recycling of CO₂ adsorption under both dry and humidified conditions were measured gravimetrically on the same TGA instrument. Approximately 5 mg of the sample was placed in a ceramic crucible and transferred to the TGA chamber; after the sample was stabilized at the target temperature (25, 50, 75 or 100°C) under flowing N₂ (150 mL/min) for 0.5 h, the N₂ flow was switched to a CO₂ flow (99.999% or 14.7% in N₂, 50 mL/min); subsequently, both the temperature and CO₂ flow were maintained for 3 h, and the weight gain during this period of time was taken as the CO₂ adsorption capacity. For the cycling of CO₂ adsorption under dry conditions, after the sample

was stabilized at 25 °C under flowing N₂ (150 mL/min) for 0.5 h, the N₂ flow was switched to a CO₂ flow (99.999%, 50 mL/min); both the temperature and CO₂ flow were maintained for 3 h; subsequently, the CO₂ flow was switched back to the N₂ flow and the temperature was increased to 75°C; both the temperature and N₂ flow were maintained for 2 h; the sorbent cycling was performed 10 times. For the cycling of CO₂ adsorption under humidified conditions, after the sample was stabilized at 75 °C under flowing N₂ (150 mL/min) for 0.5 h, the N₂ flow was switched to a CO₂ flow with a relative humidity of 10% at 75 °C; both the temperature and CO₂ flow were maintained for 3 h; subsequently, the CO₂ flow was switched back to the N₂ flow, and the N₂ flow was maintained for 2 h; the sorbent cycling was performed 10 times. Additionally, the CO₂ and N₂ adsorption isotherms at 25°C were measured volumetrically on a Micromeritics Gemini 2390t system to calculate the ideal selectivity of CO₂/N₂.

2.5 Calorimetric Measurements

The isosteric heats of CO₂ adsorption at 30°C were measured using a customized Setaram Sensys Evo calorimeter, a conduction calorimeter which is also known as Tian-Calvet heat flux microcalorimeter. The detailed experimental procedure can be found in prior reports.[47,48] In brief, the sample was first pressed at 1000 psig and then crushed into pellets with particle size of 150~250 μm. Theoretically, the aggregation of samples for calorimetric measurements and CO₂ adsorption measurements should be the same for rational comparison. However, our previous work[49] has systematically investigated the effect of pelletization on the physical

and chemical properties of supported amine adsorbents, and found no change in chemical structure after pelletization at 1000 psig. Although the pelletized adsorbents had higher mass transfer resistance than powdery counterparts due to slight change in porosity, their equilibrium capacity are comparable. Since we mainly discussed the CO₂ adsorption on the basis of pseudo-equilibrium state, it does not matter to use pelletized or powdery samples for measurements. Subsequently, ~50 mg of the pellets was loaded into one side of sample cell that has two prongs. Another side of the cell was left empty as a reference. This cell is connected to the dosing manifold and encased in an aluminum block that contains highly sensitive thermometers. The sample was pretreated at 110°C for 3 h under 15 Pa of vacuum, and then the temperature was cooled down to 30°C. Two pressure transducers were connected to the reservoir and cell areas, which were maintained at 30°C with heating tape. The amount of adsorbed CO₂ after dosing was calculated by mole balance using initial and final pressure values from the cell and reservoir sides. Heats of CO₂ adsorption were simultaneously recorded while the dosed CO₂ was adsorbed by the adsorbents.

3. RESULTS AND DISCUSSION

3.1 Textural Properties

It is well established that the textural properties of the support have a significant impact on the dispersion of PEI in the inner pores of the support.[29,38,50] Since the PEI typically used has a large molecular size ($M_w=800$), a support with large pores is considered to be a good choice for PEI impregnation. Figure 1 shows the N₂ adsorption isotherms at -196°C and the pore size distributions of the PDVB support

and PEI-PDVB composites, and the calculated textural properties are summarized in Table 1. Notably, the PDVB support shows a type-IV isotherm with low N₂ uptake at low relative pressure and high N₂ uptake at high relative pressure. The N₂ uptake displays a steep increase at a relative pressure of 0.8~0.975. The pore size distribution of PDVB covers a wide range of 0~50 nm, with considerable dV/dlog(w) pore volume in the pore width range of 10~50 nm, indicating that abundant meso-macropores are present in the PDVB support. As a result, PDVB is found to exhibit a large total pore volume (2.05 cm³/g). The micropore volume (0.09 cm³/g) accounts for only 4.4% of the total pore volume, implying that most inner pores of PDVB are likely accessible to PEI.

In light of the highly interesting meso-macroporous structure of PDVB, four PEI-PDVB composites with different PEI loadings were prepared in this work. The PEI loadings were calculated from the nitrogen contents determined by elemental analysis (see Table S1). The PEI loading ranges from 29 to 70 wt.%, representing low to high occupancy of the inner pores. It can be seen from Figure 1 that the N₂ uptake and dV/dlog(w) pore volume decrease dramatically with the increase in PEI loading. Accordingly, the BET surface area and total pore volume also decrease dramatically with the increase in loading, as presented in Table 1. The PEI loading can reach as high as 70 wt.% in PEI-PDVB composites, corresponding to the PEI/PDVB mass ratio of 2.33, which approaches the theoretical value calculated from the total pore volume of PDVB (2.05). Therefore, the inner pores of PDVB are almost completely filled by PEI in the highest loading sample. This is attributed to the large pore widths

of PDVB, which make the deep channels easily accessible to large PEI molecules. However, the highest PEI loading in PEI-PAF-5 composites reported in the literature was 40 wt.%,^[27] corresponding to a PEI/PAF-5 mass ratio of 0.80, much lower than the theoretical value calculated from the total pore volume of PAF-5 (1.43). The small pore width of PAF-5 (2.11 nm) makes the deep channels easily blocked by aggregated PEI. Based on this comparison, it can be concluded that meso-macroporous PDVB has great potential as a PEI support.

Note that the units of N₂ uptake and dV/dlog(w) pore volume in Figure 1 are based on the mass of PEI-PDVB composites (i.e., m²/g composite and cm³/g composite). To clearly demonstrate the changes in the porosity of PDVB after PEI impregnation, those units were transformed to be based on the mass of PDVB (i.e., m²/g PDVB and cm³/g PDVB), as shown in Figure S1. It can be seen that when a small amount of PEI (29 wt.%) is impregnated, the decrease in the dV/dlog(w) pore volume over a small pore-width range (0~10 nm) is much more pronounced than the decrease over a large pore-width range (10~50 nm). As more and more PEI (42~70 wt.%) is impregnated, the dV/dlog(w) pore volume over a small pore-width range (0~10 nm) further decreases to negligible values, while the volume over a large pore-width range (10~50 nm) starts to decrease gradually. From this phenomenon, it is deduced that PEI fills the small pores first and then fills the large pores stepwise, indicating that PEI is well dispersed in the inner pores of PDVB.

3.2 Morphology

The porous structure and surface morphology of PDVB and PEI-PDVB composites were further examined by electron microscopy. Figure 2 shows the TEM images of PDVB and SEM images of PDVB and PEI-PDVB composites. The hierarchical meso-macroporosity of PDVB can be clearly observed from the TEM and SEM images, which is consistent with the results calculated from the N₂ adsorption isotherms at −196°C. The porous structure of PDVB displays wormhole-like and disordered characteristics. The surface morphology of PEI-PDVB composites is somewhat similar to that of pristine PDVB, and obviously open pores can still be seen in the PEI-PDVB composites. Moreover, no stacking particles can be found in the SEM images of PEI-PDVB composites. These observations are consistent with the hypothesis that PEI resides in the inner pores of PDVB, not on the external surface.

3.3 FTIR Characterization

To ensure the presence of PEI in PEI-PDVB composites and probe the interaction of PEI with PDVB, the FTIR spectra of PEI, PDVB and PEI-PDVB composites were collected, as shown in Figure 3. The characteristic peaks of PEI can be clearly seen in PEI-PDVB composites. For example, the peak at 910 cm^{−1} is attributed to the out-of-plane deformation of −NH₂, the peak at 1045 cm^{−1} is attributed to the stretching vibration of the C-N bond, the peak at 1600 cm^{−1} is attributed to the deformation of the N-H bond, and the double peaks at around 3300 cm^{−1} are attributed to the symmetric and asymmetric stretching vibrations of the N-H bond. The strength of these peaks increases with the increase in PEI loading. Furthermore, no blue shift or red shift of the characteristic peaks of PEI can be observed, implying

that the interactions of PEI with PDVB are rather weak. This is reasonable, since there are only aromatic rings and alkyl chains in the skeleton of PDVB, neither of which can interact with PEI strongly.

3.4 Thermal Stability

The thermal stability of PEI-PDVB composites was examined by thermogravimetric analysis (TGA), as shown in Figure 4. From the TGA profiles, it can be seen that PEI-PDVB composites are stable up to 200°C. The thermal stability of the PEI-PDVB composites is sufficient for them to be used in the post-combustion capture of CO₂ from industrial streams.[51] Furthermore, there are two peaks in the derived TG (DTG) profiles of the PEI-PDVB composites, demonstrating bimodal behavior for the decomposition of the PEI-PDVB composites. The first DTG peak is centered at 390°C, which is attributed to the volatilization and decomposition of PEI. The second DTG peak is centered at 460°C, which is attributed to the decomposition of the PDVB network. It is interesting that the positions of the two peaks are the same as those appearing in the DTG profiles of pure PEI and pristine PDVB, further validating the rather weak interactions between PEI and PDVB.

3.5 CO₂ Capacities

The adsorption capacities of the PDVB and PEI-PDVB composites using pure CO₂ were determined by TGA. The CO₂ adsorption profiles at different temperatures can be found in the Supplementary Material (Figures S2~S5). The CO₂ capacities of the PEI-PDVB composites are much higher than those of pristine PDVB, and the difference is more pronounced at high temperatures. For example, the CO₂ capacities

of the PEI-PDVB composites at 25 and 75°C (2.08~3.70 and 1.59~3.83 mmol/g) are 4.6~8.2 and 9.4~22.5 times greater than those of PDVB (0.45 and 0.17 mmol/g), respectively. The significantly enhanced CO₂ adsorption on the PEI-PDVB composites is undoubtedly a result of the strong chemical reactivity of amine compounds with CO₂, whereas pristine PDVB exhibits only very weak physical interactions with CO₂ because of its surface inertness.

To demonstrate the structure-property relationship of the PEI-PDVB composites for CO₂ adsorption, the CO₂ capacities were plotted against the adsorption temperatures and PEI loadings in Figure 5. Figure 5A shows the variation of the CO₂ capacity with the adsorption temperature, which is somewhat complicated. The negative effect of temperature on the CO₂ capacity of pristine PDVB is not surprising because of the very weak physical interactions of CO₂ with PDVB. However, temperature has two contradictory effects on the CO₂ capacity of the PEI-PDVB composites: (1) CO₂ adsorption on PEI-PDVB composites is a diffusion-controlled process, and increasing the temperature enhances CO₂ diffusion into thick layers of PEI; (2) the reaction of CO₂ with amine compounds is exothermic, and increasing the temperature weakens the interaction of CO₂ with PEI. The first effect enhances CO₂ adsorption and the second does not. For 0.29PEI@PDVB and 0.42PEI@PDVB, the PEI loadings are relatively low (29.0 wt.% and 42.2 wt.%), and the materials still have considerable BET surface areas (227 and 77 m²/g) and total pore volumes (0.83 and 0.45 cm³/g). Additionally, the thickness of the PEI layers in the low PEI loading materials is relatively limited. Therefore, CO₂ can easily diffuse into the PEI layers of

these materials, and the CO₂ adsorption on the two samples is thermodynamically controlled. As a result, the CO₂ capacity of 0.29PEI@PDVB and 0.42PEI@PDVB decreases as temperature increases. In contrast, the PEI loadings for the 0.58PEI@PDVB and 0.70PEI@PDVB (57.7 wt.% and 70.0 wt.%) materials are markedly higher, and these samples have low BET surface areas (38 and 1 m²/g) and small total pore volumes (0.32 and 0.13 cm³/g). At 25~75°C, CO₂ can hardly diffuse into the deep layers of PEI, and the adsorption of CO₂ on the two samples is increasingly kinetically controlled by CO₂ diffusion through the PEI layers. Therefore, the CO₂ capacities of 0.58PEI@PDVB and 0.70PEI@PDVB at 75°C (3.76 and 3.83 mmol/g) were found to be even higher than those at 25°C (3.70 and 3.17 mmol/g). However, at 100°C diffusion is sufficiently fast and thermodynamics take over, and from that point, the adsorption of CO₂ is no longer kinetically controlled. Hence, the CO₂ capacities of 0.58PEI@PDVB and 0.70PEI@PDVB at 100°C (3.05 and 3.58 mmol/g) are lower than those at 75°C (3.76 and 3.83 mmol/g).

Figure 5B shows the variation of CO₂ capacity with PEI loading. Similar to adsorption temperature, PEI loading also has two contrary effects on CO₂ capacity: (1) increasing the PEI loading provides more active sites for the reaction with CO₂ and enhances the interaction of CO₂ with adsorbents; (2) increasing the PEI loading decreases the porosity of PEI-PDVB composites, thickens the PEI layers and hinders the diffusion of CO₂ into the depth of the PEI. In the relatively low PEI loading range of 0~57.7 wt.%, the first effect dominates CO₂ adsorption. Therefore, the CO₂ capacity increases with as increase in PEI loading in this range. However, when the

PEI loading is further increased to as high as 70.0 wt.%, two different trends for the variation in CO₂ capacity with PEI loading are observed. At 75 and 100°C, the first effect still dominates the adsorption of CO₂ because of the elimination of the diffusion barrier. Therefore, the CO₂ capacities of 0.70PEI@PDVB are higher than those of 0.58PEI@PDVB at the two temperatures. In contrast, the second effect dominates the adsorption of CO₂ at 25 and 50°C. As a result, the CO₂ capacities of 0.70PEI@PDVB are even lower than those of 0.58PEI@PDVB at the two temperatures. This kind of trend relating the CO₂ capacity and PEI loading has also been observed by others in the literature.[32,52]

Based on CO₂ capacities and PEI loadings, the amine efficiencies (defined as the ratio of adsorbed CO₂/amine group) of the PEI-PDVB composites were calculated, and the results are presented in Figure 6. Since the ratio of primary/secondary/tertiary amine groups in branched PEI is 0.44:0.33:0.23,[53] the maximum amine efficiency is 0.38, assuming that tertiary amine is unable to chemically react with CO₂ and the formation of ammonium carbamate consumes two primary/secondary amine groups. Owing to the good dispersion of PEI in the inner pores of PDVB, the amine efficiency of the PEI-PDVB composites can reach as high as 0.18~0.29 at 25°C and 0.22~0.27 at 75°C, implying an efficient utilization of PEI for CO₂ capture.

Considering the low CO₂ concentrations in industrial streams, the adsorption capacities of dilute CO₂ (typically 15v/v%) are more meaningful for practical assessments. Therefore, the adsorption capacities using 15% CO₂ on PDVB and the PEI-PDVB composites were also determined by TGA. The CO₂ adsorption profiles

can be found in the Supplementary Material (Figures S6~S9). The adsorption capacities of 15% CO₂ on PEI-PDVB composites at 25 and 75°C are 1.71~3.04 and 1.13~2.93 mmol/g, respectively. However, PDVB can adsorb only traces of CO₂ under the same conditions. The adsorption capacities using 15% CO₂ on the PEI-PDVB composites are comparable to or even higher than those on many other PEI-impregnated adsorbents, for example, 0.40PEI@PAF-5 (2.45 mmol/g, 15% CO₂ at 40°C),[27] 0.25PEI@PIM-1 (0.97 mmol/g, 10% CO₂ at 35°C),[28] 0.31PEI@SBA-15 (0.65 mmol/g, 10% CO₂ at 35°C),[31] 0.33PEI@Zr7-SBA-15 (1.56 mmol/g, 10% CO₂ at 25°C),[31] 0.40PEI@SBA-15 (1.61 mmol/g, 10% CO₂ at 25°C),[30] 0.50PEI@Al₂O₃ (1.95 mmol/g, 10% CO₂ at 25°C),[30] 0.70PEI@SBA-15 (2.00 mmol/g, 1 bar of pure CO₂ at 45°C),[23] 0.30PEI@PME (2.04 mmol/g, 10% CO₂ at 25°C)[43] and 0.40PEI@silica (2.16 mmol/g, 15% CO₂ at 70°C).[44] This comparison demonstrates the capability of PEI-PDVB composites to capture CO₂ at high efficiencies.

In Figure 7, the adsorption capacities using 15% CO₂ were plotted against the adsorption temperatures and PEI loadings. Using 15% CO₂, the variations in the adsorption capacity with temperature and PEI loading also suggest contributions of kinetic and thermodynamic factors, which are similar to those demonstrated in Figure 5. Based on the adsorption capacities using 15% CO₂ at various PEI loadings, the amine efficiencies of the PEI-PDVB composites for the adsorption of dilute CO₂ were also calculated, and the results are presented in Figure 8. The amine efficiency of the PEI-PDVB composites for the adsorption of 15% CO₂ can reach as high as 0.13~0.27

at 25°C and 0.17~0.22 at 75°C. The amine efficiencies of PEI-PDVB composites for the adsorption of dilute CO₂ are comparable to or even higher than those of many other PEI-impregnated adsorbents, for example, 0.40PEI@PAF-5 (0.25, 15% CO₂ at 40°C),[27] 0.25PEI@PIM-1 (0.16, 10% CO₂ at 35°C),[28] 0.31PEI@SBA-15 (0.09, 10% CO₂ at 35°C),[31] 0.33PEI@Zr7-SBA-15 (0.19, 10% CO₂ at 25°C),[31] 0.40PEI@SBA-15 (0.16, 10% CO₂ at 25°C),[30] and 0.50PEI@Al₂O₃ (0.16, 10% CO₂ at 25°C).[30] implying the efficient utilization of PEI for the capture of dilute CO₂ by PEI-PDVB composites.

It should be noted that a significant drawback associated with PEI-PDVB composites is the slow kinetics, which should arise from the blocking of diffusion channels and significant increase in the viscosity of impregnated PEI after complexed with CO₂. As shown in Figures S2~S9, the adsorption of CO₂ on PEI-PDVB composites still does not reach equilibrium even at 180 min, therefore, the CO₂ capacities mentioned above are pseudo-equilibrium capacities. Furthermore, the rate of CO₂ adsorption decreases with the increase of PEI loading, which is similar to the variation trend of porosity with PEI loading (see Table 1). These observations are consistent with the adsorption of CO₂ on most other PEI-impregnated adsorbents.[24-44]

3.6 CO₂/N₂ Selectivities

In addition to CO₂ capacity, CO₂/N₂ selectivity is also an important factor that should be taken into account in evaluating the performance of solid adsorbents for CO₂ capture. Since the adsorption of N₂ on PDVB and the PEI-PDVB composites is

hardly detectable by TGA, the CO₂ and N₂ adsorption isotherms at 25°C for PDVB and the PEI-PDVB composites were measured by the volumetric method to calculate the ideal adsorption solution theory (IAST)[54] selectivity of CO₂/N₂ (0.15/0.85) at 1 bar (see Figure 9). The CO₂ capacities at 1 and 0.15 bar determined by the volumetric method are similar to those determined by the TGA method, validating the accuracy of the data reported in this work. The CO₂ adsorption isotherm of PDVB displays a typical physical profile, with the CO₂ capacity increasing almost linearly with the CO₂ pressure. This is consistent with the surface inertness of PDVB, which results in weak interactions of CO₂ with PDVB. In contrast, the CO₂ adsorption isotherms of the PEI-PDVB composites display typical chemical profiles, with the CO₂ capacity increasing significantly with the CO₂ pressure in the low-pressure range. However, the increasing trend gradually fades in the high-pressure range. This is consistent with the strong chemical reactivity of amine compounds with CO₂. Moreover, the N₂ adsorption isotherms of PDVB and the PEI-PDVB composites display typical physical profiles, with the N₂ capacity increasing almost linearly with the N₂ pressure. This is within expectations, considering the inertness of N₂. Significantly, the N₂ capacities of PEI-PDVB composites are 2~3 magnitudes lower than their CO₂ capacities.

The IAST selectivity of CO₂/N₂ can be calculated by the equation $S=(q_1/p_1)/(q_2/p_2)$, where q_1 is the capacity of CO₂ at the partial pressure of p_1 , and q_2 is the capacity of N₂ at the partial pressure of p_2 . For the calculation of CO₂/N₂ selectivity in full CO₂ concentration range (0~1), the CO₂ and N₂ adsorption

isotherms should be fitted with an adsorption model, for example dual-site Langmuir model or dual-site Langmuir-Freundlich model. However, only the single point CO₂/N₂ selectivity (CO₂:N₂=0.15:0.85 at 1 bar) was calculated in this work, where the CO₂ concentration is typical for flue gas. The capacity of CO₂ at 0.15 bar and the capacity of N₂ at 0.85 bar could be directly read from the isotherms, therefore, the calculated CO₂/N₂ selectivity is independent on the adsorption model applied. Even though, it should be noted that the calculated CO₂/N₂ selectivity is very sensitive to the accuracy of N₂ capacity, since the N₂ uptake was very low at the pressure range of testing (0~1 bar). According to the calculated IAST CO₂/N₂ selectivities, PDVB has poor capability for the selective capture of CO₂, with an IAST CO₂/N₂ selectivity of 19. However, impregnating PEI into the inner pores of PDVB not only enhances CO₂ adsorption but also reduces N₂ adsorption for the composite materials, thus providing exceptionally high IAST CO₂/N₂ selectivities of 721~3274. Obviously, the IAST CO₂/N₂ selectivity of the PEI-PDVB composites increased as the PEI loading increased, and 0.70PEI@PDVB was found to exhibit the highest IAST CO₂/N₂ selectivity, 3274, among the four PEI-PDVB composites prepared in this work. This value is also higher than many other PEI-impregnated adsorbents, 0.40PEI@PAF-5 (1200),[27] 0.56PEI@MIL-101 (730),[33] and 0.50PEI@MIL-101(Cr) (1030),[36] demonstrating the capability of the PEI-PDVB composites for highly selective CO₂ capture.

3.7 Heats of Adsorption

The heat of CO₂ adsorption is an important parameter that reflects the strength of interaction between CO₂ and adsorbent, and can be used for the preliminary evaluation of the energy penalty for the desorption of CO₂. The Clausius-Clapeyron equation is a widely used tool for the calculation of isosteric heats of CO₂ adsorption on porous materials from isotherm data obtained at multiple temperatures.[22,35] However, the Clausius-Clapeyron equation is not a good choice for the calculation of isosteric heats of CO₂ adsorption on PEI-impregnated adsorbents, because the adsorption of CO₂ on PEI-impregnated adsorbents can be a diffusion-controlled process, and the observed variation trend between CO₂ pressure and temperature at a specific CO₂ uptake may be flawed. To quantitatively and directly assess the interaction of CO₂ with the PEI-PDVB composites, the isosteric heats of CO₂ adsorption on the PEI-PDVB composites were experimentally measured as a function of CO₂ uptake at 30°C by calorimetry, with the results shown in Figure 10. Since CO₂ is preferably bonded to stronger sites, the CO₂ adsorption heat displays a typical decreasing trend with the CO₂ uptake. The initial CO₂ adsorption heats of the four PEI-PDVB composites at a low CO₂ uptake of ~0.1 mmol/g are 57~87 kJ/mol, corresponding the chemical reaction of CO₂ with PEI. Generally, the initial CO₂ adsorption heat increases with an increase of PEI loading, which can be ascribed to the increase of amine density.[48] As the CO₂ uptake increases to ~2 mmol/g, the difference in CO₂ adsorption heats of the four PEI-PDVB composites diminishes and the CO₂ adsorption heat decreases to 20~30 kJ/mol. At this stage, the accessible

chemical sites are saturated and the adsorption of CO₂ is dominated by physical adsorption on the surface of the PEI-PDVB composites.

3.8 Sorbent Cycling

The stability of the PEI-PDVB composites for CO₂ adsorption under dry conditions was tested by applying a combination of temperature swing and concentration swing cycling, and the results are shown in Figure 11. The adsorbed CO₂ can be totally released under an N₂ purge for 120 min at 75°C, indicating the easy desorption of CO₂ from the PEI-PDVB composites. A slight decrease in the baselines of the TGA profiles suggests the minor loss of PEI during cycling. However, many other reports did not investigate the possibility of regenerating their adsorbents at a relatively low temperature of 75°C, for example PEI-G-silica (120°C),[35] PEI-Al₂O₃ (110°C),[30] PEI-SBA-15 (110°C),[31] PEI-Zr7-SBA-15 (110°C),[31] PEI-MIL-101 (110°C),[33] PEI-MIL-101(Cr) (110°C),[36] PEI-silica (120°C)[39] and PEI-MDCM (100°C).[38] Maybe those PEI-impregnated adsorbents can also be recycled under similar conditions. Even though, the easy desorption of CO₂ for the PEI-PDVB composites demonstrated here clearly shows the easy cyclability of these new composite materials. As evidenced by the FTIR spectra and TGA results, the interactions of PEI with PDVB are rather weak, and this may offer good PEI mobility that allows for straightforward cycling. Considering the inert surface of PDVB, the main possible interaction of PEI with PDVB is a N-H--- π interaction, the strength of which is located in the range of the van der Waals interactions. However, many other supports (e.g., SBA-15 and Al₂O₃) have abundant hydroxyl groups or Lewis acidic

sites,[20] which can interact with the amine group in PEI strongly through a complex hydrogen bonding network or Lewis acid-base interactions, thus constraining the mobility of PEI. Furthermore, the CO₂ capacities of the PEI-PDVB composites remain almost unchanged (the loss in CO₂ capacities is less than 5%) even after 10 cycles of adsorption/desorption. This can be explained by the relatively low temperature required for CO₂ desorption, i.e., 75°C. At such a temperature, the volatilization and degradation of PEI can be more efficiently avoided than when cycling at higher temperatures. In previous work, it has been elucidated that a high desorption temperature (e.g., 110°C) is likely to induce the transformation of carbamate to urea under concentrated CO₂ conditions,[55] which can be a major cause of the capacity loss during the regeneration of PEI-impregnated adsorbents. For example, the CO₂ capacity of a PEI-SBA-15 composite decreased by 34% after four cycles if the desorption was performed at 110°C for 3 h,[31] indicating that a conventional PEI/SBA-15 composite can have limited stability during higher temperature regeneration. In contrast, the PEI-PDVB composites prepared in this work demonstrate comparably high stability for CO₂ capture.

Considering the inevitable presence of steam in industrial streams, it is more meaningful to investigate the recyclability of PEI-PDVB composites for CO₂ adsorption under humidified conditions. Therefore, 0.58PEI@PDVB was selected as a representative material for such testing, where it was evaluated in 10 consecutive concentration swing cycles, with result shown in Figure 12. The results clearly demonstrate that 0.58PEI@PDVB exhibits excellent steam-stability during CO₂

adsorption-desorption cycles under conditions with low water activity, with the uptake of humidified CO₂ remaining almost unchanged after 10 cycles. The observed stability of 0.58PEI@PDVB in this modestly humid stream might be attributed to the super hydrophobic and water-tolerant nature of PDVB,[45,46] which can preserve the porous structure of PDVB well. However, many other supports such as SBA-15 are vulnerable to steam-induced structural degradation under humidified conditions, which results the significant losses of CO₂ capacity after recycling.[30,56] This comparison further supports the potential of PDVB as a useful support for PEI for CO₂ adsorption applications.

It should be noted that N₂ can not be used as the regenerant in real process for capturing CO₂ from flue gas, since pure CO₂ can not be obtained with N₂ purge. However, concentration swing with N₂ purge is widely used and accepted in the preliminary investigation of the long-term recyclability of PEI-impregnated adsorbents.[24-44] In this work, we were aiming to investigate the possibility of using PEI-PDVB composites as recyclable adsorbents for CO₂ capture. It was found that no matter for the capture of dry CO₂ or humidified CO₂, PEI-PDVB composites can be facilely regenerated with N₂ purge at 75°C and maintains the capacity of CO₂ very well throughout consecutive cycles. As a preliminary work, we were not aiming to find a way to collect CO₂ as a pure product. To obtain CO₂ with high purity, steam regeneration is required. Steam regeneration is a technology recently developed for the effective recycling of CO₂ adsorbents.[57-60] Steam with high temperature is a waste source of heat, and widely available in power plants. It provides the thermal

driving force along with the concentration gradient for CO₂ desorption. After condensing out the moisture and compressing CO₂, concentrated CO₂ product can be obtained. This technology was traditionally used for volatile organic compound separation,[61] but only a few studies have focused on its application in CO₂ capture. Therefore, investigating the stability of PEI-PDVB composites after several cycles of CO₂ adsorption and steam regeneration is very meaningful, and this will be the task of our future work.

4. CONCLUSIONS

A porous polymer, poly(divinylbenzene) (PDVB), was synthesized through the solvothermal polymerization of readily available divinylbenzene (DVB) under template-free and catalyst-free conditions. The synthesized PDVB is found to be a highly effective support for poly(ethyleneimine) (PEI) owing to its abundant meso-macropores and large pore volume, which enables the good dispersion of PEI in the inner pores of PDVB. The CO₂ and N₂ adsorption experiments demonstrate that PEI-PDVB composites exhibit fascinating performance for the selective capture of CO₂. The adsorption capacity of CO₂ and IAST selectivity of CO₂/N₂ on PEI-PDVB composites are comparable or superior to those of many other reported PEI-impregnated adsorbents. With the assistance of calorimetric method, the strength of interaction between CO₂ and PEI-PDVB composites was quantitatively disclosed to provide a better understand about the behavior of CO₂ adsorption on PEI-PDVB composites. The inert surface of PDVB results in the weak interaction of PEI with PDVB, contributing to the good mobility of impregnated PEI and the easy desorption

of CO₂ from PEI-PDVB composites. Furthermore, PEI-PDVB composites display high stability in CO₂ adsorption/desorption cycles under both dry and humidified conditions. All these features suggest that PEI-PDVB composites are a class of promising materials with potential application in the post-combustion capture of CO₂. Future work will focus on the stability of PEI-PDVB composites in steam regeneration, which is a promising technology to obtain CO₂ product with high purity.

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NOTES

The authors declare no competing financial interest.

REFERENCES

- [1] J.D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava, Advances in CO₂ capture technology—The U.S. Department of Energy's Carbon Sequestration Program, *Int. J. Greenh. Gas Con.* 2 (2008) 9-20.
- [2] G.T. Rochelle, Amine scrubbing for CO₂ capture, *Science* 325 (2009) 1652-1654.
- [3] A.B. Rao, E.S. Rubin, A technical, economic, and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control, *Environ. Sci. Technol.* 36 (2002) 4467-4475.

- [4] Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, Adsorption of CO₂ from dry gases on MCM-41 silica at ambient temperature and high pressure. 1: Pure CO₂ adsorption, Chem. Eng. Sci. 64 (2009) 3721-3728.
- [5] A.H. Lu, G.P. Hao, X. Q. Zhang, Porous carbons for carbon dioxide capture, in: A.H. Lu, S. Dai (Eds.), Porous Materials for Carbon Dioxide Capture, Springer-Verlag, Berlin, 2014, pp. 15-77.
- [6] M.R. Hudson, W.L. Queen, J.A. Mason, D.W. Fickel, R.F. Lobo, C.M. Brown, Unconventional, highly selective CO₂ adsorption in zeolite SSZ-13, J. Am. Chem. Soc. 134 (2012) 1970-1973.
- [7] J. Liu, P.K. Thallapally, B.P. McGrail, D.R. Brown, J. Liu, Progress in adsorption-based CO₂ capture by metal-organic frameworks, Chem. Soc. Rev. 41 (2012) 2308-2322.
- [8] R. Dawson, E. Stöckel, J.R. Holst, D. J. Adams, A.I. Cooper, Microporous organic polymers for carbon dioxide capture, Energy Environ. Sci. 4 (2011) 4239-4245.
- [9] S. Choi, J.H. Drese, C.W. Jones, Adsorbent materials for carbon dioxide capture from large anthropogenic point sources, ChemSusChem 2 (2009) 796-854.
- [10] Q.Q. Dang, Y.F. Zhan, X.M. Wang, X.M. Zhang, Heptazine-based porous framework for selective CO₂ sorption and organocatalytic performances, ACS Appl. Mater. Interfaces 7 (2015) 28452-28458.

- [11] Y. Luo, B. Li, W. Wang, K. Wu, B. Tan, Hypercrosslinked aromatic heterocyclic microporous polymers: a new class of highly selective CO₂ capturing materials, *Adv. Mater.* 24 (2012) 5703-5707.
- [12] H. Gao, L. Ding, W. Li, G. Ma, H. Bai, L. Li, Hyper-cross-linked organic microporous polymers based on alternating copolymerization of bismaleimide, *ACS Macro. Lett.* 5 (2016) 377-381.
- [13] V.M. Suresh, S. Bonakala, H.S. Atreya, S. Balasubramanian, T.K. Maji, Amide functionalized microporous organic polymer (Am-MOP) for selective CO₂ sorption and catalysis, *ACS Appl. Mater. Interfaces* 6 (2014) 4630-4637.
- [14] M.G. Rabbani, H.M. El-Kaderi, Synthesis and characterization of porous benzimidazole-linked polymers and their performance in small gas storage and selective uptake, *Chem. Mater.* 24 (2012) 1511-1517.
- [15] S.Y. Ding, W. Wang, Covalent organic frameworks (COFs): from design to applications, *Chem. Soc. Rev.* 42 (2013) 548-568.
- [16] H.A. Patel, F. Karadas, J. Byun, J. Park, E. Deniz, A. Canlier, Y. Jung, M. Atilhan, C.T. Yavuz, Highly stable nanoporous sulfur-bridged covalent organic polymers for carbon dioxide removal, *Adv. Funct. Mater.* 23 (2013) 2270-2276.
- [17] D. Yuan, W. Lu, D. Zhao, H.C. Zhou, Highly stable porous polymer networks with exceptionally high gas-uptake capacities, *Adv. Mater.* 23 (2011) 3723-3725.
- [18] C. Xu, E. Dinka, N. Hedin, Hydrophobic porous polyketimines for the capture of CO₂, *ChemPlusChem* 81 (2016) 58-63.

- [19] N.C. Burtch, H. Jasuja, K.S. Walton, Water stability and adsorption in metal-organic frameworks, *Chem. Rev.* 114 (2014) 10575-10612.
- [20] S.A. Didas, S. Choi, W. Chaikittisilp, C.W. Jones, Amine-oxide hybrid materials for CO₂ capture from ambient air, *Acc. Chem. Res.* 48 (2015) 2680-2687.
- [21] W. Lu, J.P. Sculley, D. Yuan, R. Krishna, Z. Wei, H.C. Zhou, Polyamine-tethered porous polymer networks for carbon dioxide capture from flue gas, *Angew. Chem. Int. Ed.* 51 (2012) 7480-7484.
- [22] L.B. Sun, A.G. Li, X.D. Liu, X.Q. Liu, D. Feng, W. Lu, D. Yuan, H.C. Zhou, Facile fabrication of cost-effective porous polymer networks for highly selective CO₂ capture, *J. Mater. Chem. A* 3 (2015) 3252-3256.
- [23] R. Sanz, G. Calleja, A. Arencibia, E.S. Sanz-Perez, CO₂ adsorption on branched polyethyleneimine-impregnated mesoporous silica SBA-15, *Appl. Surf. Sci.* 256 (2010) 5323-5328.
- [24] S. Lee, T.P. Filburn, M. Gray, J.W. Park, H.J. Song, Screening test of solid amine sorbents for CO₂ capture, *Ind. Eng. Chem. Res.* 47 (2008) 7419-7423.
- [25] M.L. Gray, J.S. Hoffman, D.C. Hreha, D.J. Fauth, S.W. Hedges, K.J. Champagne, H.W. Pennline, Parametric study of solid amine sorbents for the capture of carbon dioxide, *Energy Fuels* 23 (2009) 4840-4844.
- [26] Z. Chen, S. Deng, H. Wei, B. Wang, J. Huang, G. Yu, Polyethylenimine-impregnated resin for high CO₂ adsorption: an efficient adsorbent for CO₂ capture from simulated flue gas and ambient air, *ACS Appl. Mater. Interfaces* 5 (2013) 6937-6945.

- [27]S. Sung, M.P. Suh, Highly efficient carbon dioxide capture with a porous organic polymer impregnated with polyethylenimine, *J. Mater. Chem. A* 2 (2014) 13245-13249.
- [28]S.H. Pang, M.L. Jue, J. Leisen, C.W. Jones, R.P. Lively, PIM-1 as a solution-processable “molecular basket” for CO₂ capture from dilute sources, *ACS. Macro. Lett.* 4 (2015) 1415-1419.
- [29]W.J. Son, J.S. Choi, W.S Ahn, Adsorptive removal of carbon dioxide using polyethyleneimine-loaded mesoporous silica materials, *Micro. Meso. Mater.* 113 (2008) 31-40.
- [30]W. Chaikittisilp, H.J. Kim, C.W. Jones, Mesoporous alumina-supported amines as potential steam-stable adsorbents for capturing CO₂ from simulated flue gas and ambient air, *Energy Fuels* 25 (2011) 5528-5537.
- [31]Y. Kuwahara, D.Y. Kang, J.R. Copeland, N.A. Brunelli, S.A. Didas, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita, C.W. Jones, Dramatic enhancement of CO₂ uptake by poly(ethyleneimine) using zirconsilicate supports, *J. Am. Chem. Soc.* 134 (2012) 10757-10760.
- [32]D.X. Wang, X.L. Ma, C. Sentorun-Shalaby, C.S. Song, Development of carbon-based "molecular basket" sorbent for CO₂ capture, *Ind. Eng. Chem. Res.* 51 (2012) 3048-3057.
- [33]Y. Lin, Q. Yan, C. Kong, L. Chen, Polyethyleneimine incorporated metal-organic frameworks adsorbent for highly selective CO₂ capture, *Sci. Rep.* 3 (2013) 1859-1863.

- [34]Z.Y. Sui, Y. Cui, J.H. Zhu, B.H. Han, Preparation of three-dimensional graphene oxide–polyethylenimine porous materials as dye and gas adsorbents, *ACS Appl. Mater. Interfaces* 5 (2013) 9172-9179.
- [35]S. Yang, L. Zhan, X. Xu, Y. Wang, L. Ling, X. Feng, Graphene-based porous silica sheets impregnated with polyethyleneimine for superior CO₂ capture, *Adv. Mater.* 25 (2013) 2130-2134.
- [36]Y.C. Lin, H. Lin, H.M. Wang, Y.G. Suo, B.H. Li, C.L. Kong, L. Chen, Enhanced selective CO₂ adsorption on polyamine/MIL-101(Cr) composites, *J. Mater. Chem. A* 2 (2014) 14658-14665.
- [37]C. Chen, S.S. Kim, W.S. Cho, W.S. Ahn, Polyethylenimine-incorporated zeolite 13X with mesoporosity for post-combustion CO₂ capture, *Appl. Surf. Sci.* 332 (2015) 167-171.
- [38]S. Gadipelli, H.A. Patel, Z. Guo, An ultrahigh pore volume drives up the amine stability and cyclic CO₂ capacity of a solid-amine@carbon sorbent, *Adv. Mater.* 27 (2015) 4903-4909.
- [39]K. Li, J. Jiang, S. Tian, F. Yan, X. Chen, Polyethyleneimine–nano silica composites: a low-cost and promising adsorbent for CO₂ capture, *J. Mater. Chem. A* 3 (2015) 2166-2175.
- [40]M.A. Sakwa-Novak, S. Tan, C.W. Jones, Role of additives in composite PEI/oxide CO₂ adsorbents: enhancement in the amine efficiency of supported PEI by PEG in CO₂ capture from simulated ambient air, *ACS. Appl. Mater. Interfaces* 7 (2015) 24748-24759.

- [41] M. Irani, M. Fan, H. Ismail, A. Tuwati, B. Dutcher, A. G. Russell, Modified nanosepiolite as an inexpensive support of tetraethylenepentamine for CO₂ sorption, *Nano Energy* 11 (2015) 235-246.
- [42] L. Guo, J. Yang, G. Hu, X. Hu, H. DaCosta, M. Fan, CO₂ removal from flue gas with amine-impregnated titanate nanotubes, *Nano Energy* 25 (2016) 1-8.
- [43] A. Heydari-Gorji, Y. Belmabkhout, A. Sayari, Polyethylenimine-impregnated mesoporous silica: effect of amine loading and surface alkyl chains on CO₂ adsorption, *Langmuir* 27 (2011) 12411-12416.
- [44] W. Zhang, H. Liu, C. Sun, T. C. Drage, C.E. Snape, Performance of polyethyleneimine-silica adsorbent for post-combustion CO₂ capture in a bubbling fluidized bed, *Chem. Eng. J.* 251 (2014) 293-303.
- [45] Y.L. Zhang, J. N. Wang, Y. He, Y. He, B.B. Xu, S. Wei, F.S. Xiao, Solvothermal synthesis of nanoporous polymer chalk for painting superhydrophobic surfaces, *Langmuir* 27 (2011) 12585-12590.
- [46] Y.L. Zhang, S. Wei, F. Liu, Y. Du, S. Liu, Y. Ji, T. Yokoi, T. Tatsumi, F.S. Xiao, Superhydrophobic nanoporous polymers as efficient adsorbents for organic compounds, *Nano Today* 4 (2009) 135-142.
- [47] M.A. Alkhabbaz, P. Bollini, G.S. Foo, C. Sievers, C.W. Jones, Important roles of enthalpic and entropic contributions to CO₂ capture from simulated flue gas and ambient air using mesoporous silica grafted amines, *J. Am. Chem. Soc.* 136 (2014) 13170-13173.

- [48] C.J. Yoo, L.C. Lee, C.W. Jones, Probing intramolecular versus intermolecular CO₂ adsorption on amine-grafted SBA-15, *Langmuir* 31 (2015) 13350-13360.
- [49] F. Rezaei, M.A. Sakwa-Novak, S. Bali, D.M. Duncanson, C.W. Jones, Shaping amine-based solid CO₂ adsorbents: effects of pelletization pressure on the physical and chemical properties, *Micro. Meso. Mater.* 204 (2015) 34-42.
- [50] C.F. Cogswell, H. Jiang, J. Ramberger, D. Accetta, R.J. Willey, S. Choi, Effect of pore structure on CO₂ adsorption characteristics of aminopolymer impregnated MCM-36, *Langmuir* 31 (2015) 4534-4541.
- [51] D. Ko, H.A. Patel, C.T. Yavuz, Synthesis of nanoporous 1,2,4-oxadiazole networks with high CO₂ capture capacity, *Chem. Commun.* 51 (2015) 2915-2917.
- [52] X. Xu, C. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO₂ capture, *Energy Fuels* 16 (2002) 1463-1469.
- [53] J.C. Hicks, J.H. Drese, D.J. Fauth, M.L. Gray, G. Qi, C.W. Jones, Designing adsorbents for CO₂ capture from flue gas-hyperbranched aminosilicas capable of capturing CO₂ reversibly, *J. Am. Chem. Soc.* 130 (2008) 2902-2903.
- [54] A.L. Myers, J.M. Prausnitz, Thermodynamics of mixed-gas adsorption, *AIChE J.* 11 (1965) 121-127.
- [55] A. Sayari, A. Heydari-Gorji, Y. Yang, CO₂-induced degradation of amine-containing adsorbents: reaction products and pathways, *J. Am. Chem. Soc.* 134 (2012) 13834-13842.

- [56] W. Li, P. Bollini, S.A. Didas, S. Choi, J.H. Drese, C.W. Jones, Structural changes of silica mesocellular foam supported amine-functionalized CO₂ adsorbents upon exposure to steam, *ACS Appl. Mater. Interfaces* 2 (2010) 3363-3372.
- [57] W. Li, S. Choi, J. Drese, M. Hornbostel, G. Krishnan, P. Eisenberger, C. Jones, Steam stripping for regeneration of supported amine-based CO₂ adsorbents, *ChemSusChem* 3 (2010) 899-903.
- [58] B. Dutcher, H. Adidharma, M. Radosz, Carbon filter process for flue-gas carbon capture on carbonaceous sorbents: steam-aided vacuum swing adsorption option, *Ind. Eng. Chem. Res.* 50 (2011) 9696-9703.
- [59] B. Dutcher, K. Krutkramelis, H. adidharma, M. Radosz, Carbon filter process for flue-gas carbon capture on carbonaceous sorbents: field tests of steam-aided vacuum swing adsorption, *Energy Fuels* 26 (2012) 2539-2545.
- [60] N.K. Sandhu, D. Pudasainee, P. Sarkar, R. Gupta, Steam regeneration of polyethylenimine-impregnated silica sorbent for postcombustion CO₂ capture: a multicyclic study, *Ind. Eng. Chem. Res.* 55 (2016) 2210-2220.
- [61] R. Suri, J. Crittenden, D. Hand, Removal and destruction of organic compounds in water using adsorption, steam regeneration, and photocatalytic oxidation processes, *J. Environ. Eng.* 125 (1999) 897-905.

Table 1. Textual properties of PDVB and PEI-PDVB composites

Samples	PEI loading (wt.%)	S _{BET} (m ² /g) ^[a]	V _t (cm ³ /g) ^[b]	V _m (cm ³ /g) ^[c]
PDVB	0	897	2.05	0.09
0.29PEI@PDVB	29.0	227	0.83	0
0.42PEI@PDVB	42.4	77	0.45	0
0.58PEI@PDVB	57.7	38	0.32	0
0.70PEI@PDVB	70.0	1	0.13	0

[a] BET surface area; [b] total pore volume; [c] micropore volume.

Figure 1. N_2 adsorption isotherms at -196°C (A) and pore size distributions (B) of PDVB and PEI-PDVB composites.

Figure 2. TEM images of PDVB (A, B) and SEM images of PDVB (C, D), 0.29PEI@PDVB (E, F), 0.42PEI@PDVB (G, H), 0.58PEI@PDVB (I, J) and 0.70PEI@PDVB (K, L).

Figure 3. FTIR spectra of PEI, PDVB and PEI@PDVB composites.

Figure 4. TGA (A) and DTG (B) profiles of PEI, PDVB and PEI-PDVB composites.

Figure 5. Variation in CO₂ capacity with adsorption temperature (A) and PEI loading (B) (adsorption conditions: pure CO₂, 50 mL/min, 3 h).

Figure 6. Amine efficiencies of PEI-PDVB composites (adsorption conditions: pure CO₂, 50 mL/min, 3 h).

Figure 7. Variation in CO₂ capacity with adsorption temperature (A) and PEI loading (B) (adsorption conditions: 15% CO₂, 50 mL/min, 3 h).

Figure 8. Amine efficiencies of PEI-PDVB composites (adsorption conditions: 15% CO₂, 50 mL/min, 3 h).

Figure 9. CO₂ and N₂ adsorption isotherms at 25°C (A) and IAST selectivities of CO₂/N₂ (0.15/0.85) at 1 bar (B) of PDVB and PEI-PDVB composites.

Figure 10. Isosteric heats of CO₂ adsorption on PEI-PDVB composites as a function of CO₂ uptake measured by the calorimetric method.

Figure 11. Cycling of CO₂ adsorption on PEI-PDVB composites under dry conditions (adsorption conditions: pure CO₂, 25°C, 50 mL/min, 180 min; desorption conditions: pure N₂, 75°C, 150 mL/min, 120 min).

Figure 12. Cycling of CO₂ adsorption on PEI-PDVB composites under humidified conditions (adsorption conditions: CO₂ with 10% relative humidity, 75°C, 50 mL/min, 180 min; desorption conditions: pure N₂, 75°C, 150 mL/min, 120 min).