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Support-Free Porous Polyamine Particles for CO_2 Capture

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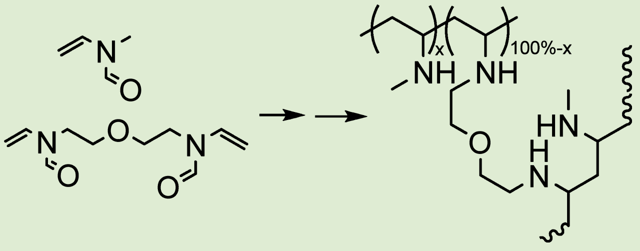
S *Supporting Information*

ABSTRACT: CO_2 emission from fossil fuel combustion is a major anthropogenic factor for global warming. Solid amine sorbents may be used to remove CO_2 from waste flue gases before their emission into the atmosphere. These particles are currently obtained by loading amine-containing compounds or polymers onto premade or commercially available porous supports. These supports play no active role in CO_2 uptake and increase the amount of heat or cost required to regenerate CO_2-sorbed particles by heating. Reported in this communication are the preparation, by precipitation polymerization, of support-free polyamine porous particles and the performance of these particles in CO_2 capture at room temperature and release at 100 °C.



CO_2 emission from fossil fuel combustion is a major anthropogenic factor for global warming. Power generation plants using fossil fuels constitute a major CO_2 emitting source. One strategy to reduce CO_2 emission from such plants and other sources is to capture the generated CO_2 with an adsorbent before it is emitted to the atmosphere. The captured CO_2 can then be released for sequestration under controlled changed conditions such as by heating the adsorbent.[1−4]

CO_2 capturing and sequestering technologies do exist. For example, aqueous alkanolamine solutions are used industrially to remove CO_2 and other acidic gases from natural gas at ambient temperature. Upon heating, CO_2 is released and alkanolamine solutions are regenerated.[5]

The aqueous-alkanolamine-based thermal swing process is not used for CO_2 removal from the waste flue gases of plants because of economical considerations. The alkanolamine solutions contain >70 wt % of high-heat-capacity water and cost much energy to heat for regeneration.[6] Furthermore, the facilities that are resistant to alkanolamine corrosion are expensive.

Many solids have specific heat capacities that are substantially less than that of water.[4,7−11] Also, they are easier to handle and free of corrosion problems. Because of these, porous solids such as silica and charcoal have been physically impregnated or chemically grafted with amines and polyamines and have been suggested as an alternative for aqueous alkanolamines for CO_2 capture.

The current solid CO_2 sorbents can be further improved if they are molecularly designed and tailor-made to eliminate the use of the inert porous support. Techniques exist for preparing macroporous polymer particles for chromatography packing materials and for ionic exchange resins.[12] They can also be used to prepare porous polyamine particles for CO_2 capture. Using this approach, the particles can be prepared to contain, in principle, scaffolds that also bear amines and actively uptake CO_2. Reported in this paper are our preliminary results for preparing support-free porous polyamine particles for CO_2 capture.

Primary amines, forming stable complexes with CO_2, capture CO_2 efficiently but are difficult to regenerate.[13] Tertiary amines do not capture CO_2 as efficiently but are regenerated readily at relatively low temperatures.[13−19] We chose in this study the preparation of particles bearing only secondary amines. This type of amine was targeted because it offered a compromise between the primary and tertiary amines.[9,13−22]

The monomer and cross-linker used to prepare the particles were *N*-methyl-*N*-vinylformamide (MVF) and di[2-(*N*-vinylformamido) ethyl] (DVFE). While the cross-linker was prepared using a modified literature method,[23] the new monomer was synthesized by recipes and procedures developed by us. The amine groups in the monomer and cross-linker were protected in the formamide form because the formyl group was shown to hydrolyze readily under either acidic or basic conditions to regenerate amine.[23] Monomers bearing primary and secondary amines are not directly polymerized by radical polymerization because the amine groups are known to undergo the Michael reaction with double bonds and interfere with polymerization.[24] Scheme 1 shows the structures of the monomer and cross-linker as well as the cross-linked polymer after amine deprotection. The preparation procedures for the monomer and cross-linker are detailed in the Supporting Information (SI).

The particles were prepared using a MVF/DVFE molar ratio of 0.25/0.75 by precipitation polymerization[25] in water/propanol mixtures at v/v = 37.5/62.5, where water and propanol were a good solvent and a precipitant for PMVF, respectively. Above this propanol content, the particles precipitated prematurely during the polymerization. If the

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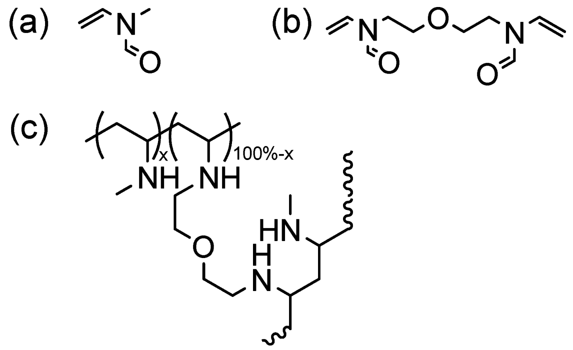
Scheme 1. Structures for Monomer *N*-Methyl-*N*-vinylformamide (a); Cross-Linker, Di[2-(*N*-vinylformamido) ethyl ether] (b); and the Cross-Linked Polyamine (c)



propanol content was too low, coagulum with poorly defined shapes were produced. The polymerization temperature was initially held at 60 °C for 12 h and then maintained for 1 h at 70, 80, and 90 °C, respectively. The initiator 2,2′-azobisisobutyronitrile (AIBN) was added in two batches with the second half added before the temperature was increased. This procedure was implemented because it facilitated the complete conversion of the double bonds and enabled the preparation of structurally stable particles. Polymerizing the mixture directly at 90 °C for 4 h with all AIBN added initially yielded particles that were not structurally stable and contained residual DVFE double bonds that were detected by FTIR spectroscopy (Figure S1). The latter procedures led to inferior particles, probably because of the high concentrations of radicals generated, and thus the efficient termination reactions and short lifetimes of the produced radicals.

The prepared particles were settled by centrifugation, rinsed repeatedly with water and methanol, and were finally cleaned by Soxhlet extraction with water. Scanning electron microscopy (SEM) images (Figure 1a) show that particles with sizes ranging between micrometers and tens of micrometers were formed from the fusion of nanometer-sized nodules.

The formyl protecting groups of MVF and DVFE were partially removed by heating the particles sequentially in aqueous HCl and then aqueous NaOH solutions, conditions used to quantitatively remove the formyl protecting groups of poly(*N*-vinyl formamide).[26] The generation of surface-accessible amine groups after the hydrolysis was confirmed by titration. Before the hydrolysis, the quantity of amine groups present, as determined via titration with aqueous HCl, was essentially zero (0.0013 mmol/g). The corresponding value measured after the hydrolysis was 6.9 mmol/g, which was ~50% of the theoretical amine groups present in the particles. Presumably the other half of the amine groups was not accessible by HCl or existed still in the formamide form. The titrated fraction was comparable to those reported by others for amine or carboxyl groups in macroporous polymer resins prepared from suspension polymerization.[27]

The particles before and after the hydrolysis treatment were also analyzed by Fourier transform infrared (FTIR) spectroscopy (Figure 2). The carbonyl absorbance at 1665 cm^{-1} decreased by 68% relative to those at 2953 and 2875 cm^{-1}, which corresponded to the C−H stretching of the methylene and methine groups of the polymerized vinyl units. This suggested that approximately 2/3 of the formyl groups were hydrolyzed. This was higher than the titrated amine fraction of ~50%, suggesting some of the deprotected amine groups were not accessible by HCl. Further evidence supporting amine formation after the hydrolysis was the emergence of the broad amine absorption peak at 3300 cm^{-1}.

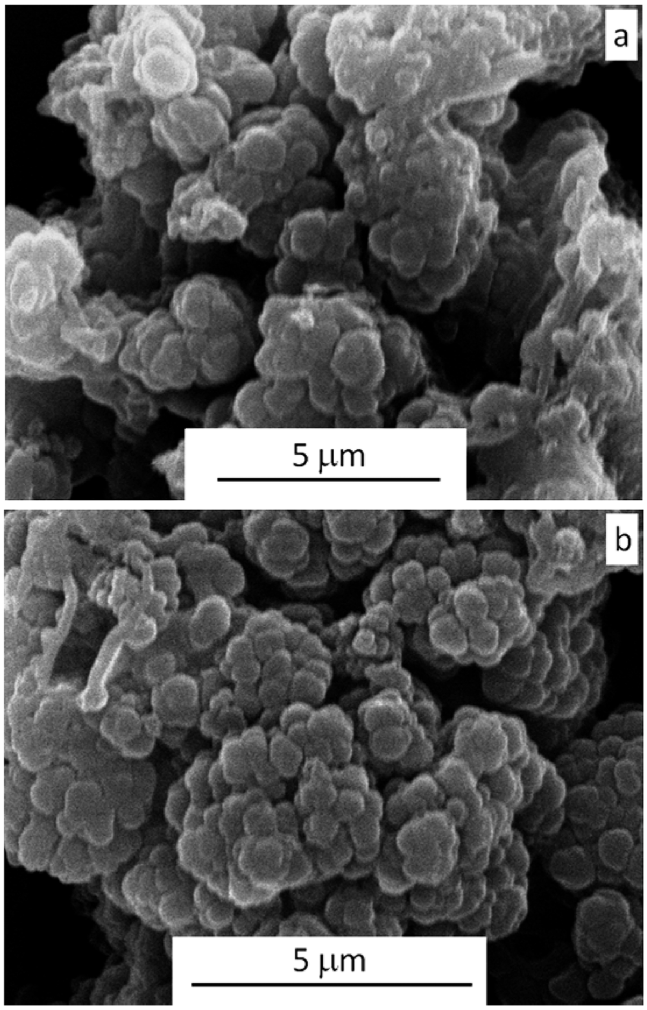


Figure 1. SEM images of poly(MVF-*co*-DVFE) particles before (a) and after (b) formyl group removal.

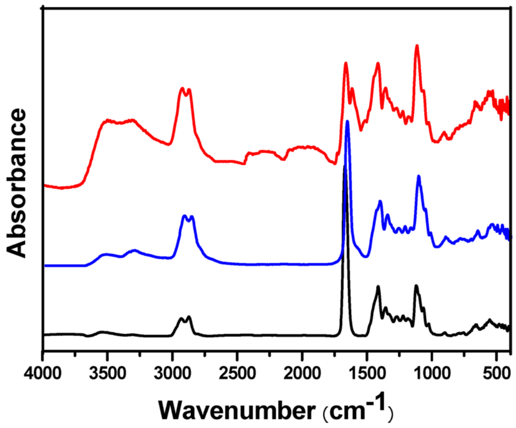


Figure 2. FTIR spectra of poly(MVF-*co*-DVFE) particles (black, bottom), polyamine particles (blue, middle), and polyamine particles exposed to CO_2 (red, top).

Figure 1b shows a SEM image of the particles after formyl group removal. While the nodular structure of the particles was retained, the creases between the different nodules became sharper, possibly because of the removal of the formyl groups and the shrinkage of the nodules. The specific surface area of the particles at this stage was determined at 77 K to be 246 m^2/g using the Brunauer−Emmett−Teller (BET) method (SI). Thermogravimetric analysis (TGA) showed that significant weight loss did not occur until ~300 °C. Thus, the particles were quite stable thermally.

To measure the CO_2 uptake, the porous polyamine particles were topped with sand in a small vial that was sealed with a rubber septum. Sand addition should not be essential in a properly designed reactor, but was employed here mainly as a safeguard against particle loss under gas flow. After equilibrating a vial in a bath at a given temperature, the rubber septum was punctured by two syringe needles to allow CO_2 in and out of the vial. The weight gain of the particles after their exposure to dry pure CO_2 at atmospheric pressure for a predesignated time was measured using an analytical balance. This weight gain should be due to CO_2 sorption by the particles, because no weight gain was observed in two control experiments. In one experiment, the vial was exposed to N_2 rather than CO_2 flow. In the other, the vial contained sand and no polyamine particles. Successful CO_2 uptake by our particles was further supported by the FTIR spectra shown in Figure 2. After particle exposure to CO_2, one new peak characteristic of the carbamate C═O stretch emerged at 1580 cm^{-1}, alluding to chemical sorption of CO_2.[28] In addition, the N−H stretch band at 3300 cm^{-1} has increased due to conversion of some of the R_2NH groups to $[R_2NH_2]^+$ groups.[29]

Figure 3a shows how the CO_2 uptake amount q (mmol of CO_2 sorbed per gram of particles) changed with the equilibration time t between the polyamine particles and pure CO_2 flowing at 30 mL/min, 1.00 atm, and 25 °C. The q value increased rapidly within the first 8 min to 2.2 mmol/g or 97 mg/g and then increased only slightly during the remaining 22 min. This kinetic behavior was comparable to that shown by silica-supported polyamine particles.[30] The slower uptake at longer times could be due to pore blocking by the carbamate formed.

The equilibrium sorbed CO_2 amounts at different temperatures T were measured after equilibrating the particles with pure CO_2 flowing at 30 mL/min and 1.00 atm for 15 min, and the capacity values q_m were plotted as a function of T in Figure 3b. q_m initially increased with T, reached a peak value of 2.3 mmol/g at 30 °C, and then decreased with T. Thermodynamically, the CO_2 capture capacity should decrease with increasing temperature because the interaction between a sorbent and a sorbate is weakened as T increases. The observed temperature dependence could have resulted from an interplay between sorption kinetics and thermodynamics. While a higher temperature reduced the CO_2 bindning constant, it increased the accessibility of the amine groups.

Using the maximum capture capacity of 2.3 mmol/g and the accessible amine amount of 6.9 mmol/g from the HCl titration experiment, we calculated a CO_2/N sorption stoichiometric ratio of 0.33. Theoretically, 1 mole of CO_2 reacts with 2 moles of amine groups, in the absence of water, to produce 1 mole of carbamate.[6] Thus, the theoretical reaction stoichiometry should be 0.50. The lower experimental sorption stoichiometry might be due to the inaccessibility of some of the amine groups by CO_2 at 1.00 atm.

We obtained the sorbed CO_2 amounts at 25 and 60 °C for particles that were equilibrated for 100 min with CO_2/N_2 mixtures flowing at a total rate of 300 mL/min and a total pressure of 1.00 atm. Plotted in Figure 4a was the variation of

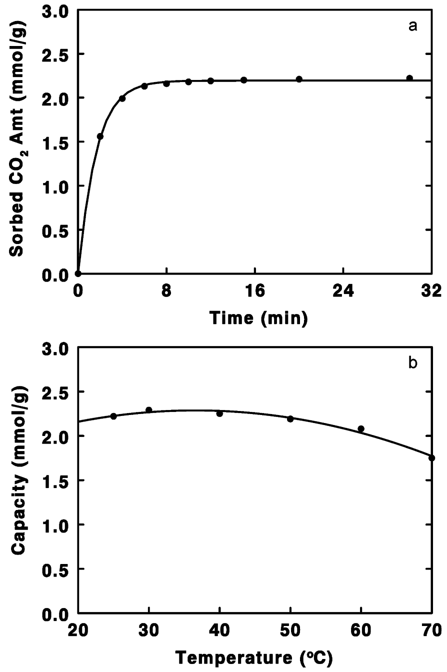


Figure 3. (a) Kinetic plot of CO_2 sorption by the polyamine particles in equilibrium with pure flowing CO_2 at 1.00 atm and 25 °C and (b) variation in the saturated sorbed CO_2 amount as a function of temperature under flowing 1.00 atm CO_2.

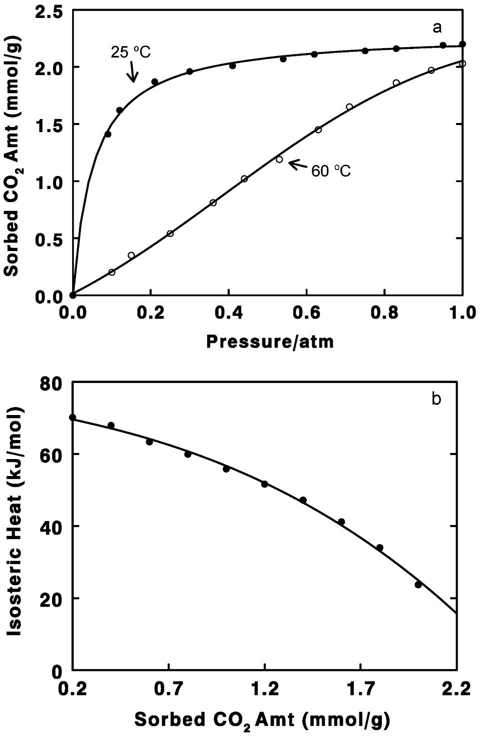


Figure 4. (a) CO_2 sorption isotherms at 25 and 60 °C and (b) variation of isosteric heat vs CO_2 uptake.

the sorbed CO_2 amount as a function of CO_2 partial pressure p_{CO_2}. These should be the equilibrium sorbed CO_2 amounts because the sorption equilibrium was shown to establish at 25 °C within 7 min between the particles and pure CO_2 flowing at 1.00 atm and 30 mL/min. In that case, the total volume of CO_2 that entered the sorption vial during 7 min was 210 mL. The amount of CO_2 that entered the sorption vial during 100 min for the experiments with results reported in Figure 4a increased as p_{CO_2} increased. At the lowest used p_{CO_2} of 0.10 atm, 3000 mL of CO_2 entered the sorption vial in 100 min. This was much higher than 210 mL and also the CO_2 was introduced over a much longer time span. Both of these should have facilitated sorption equilibrium establishment. Further evidence supporting this assessment was that the measured sorbed CO_2 amounts at all p_{CO_2}s did not increase when the particle/CO_2 equilibration time was increased from 100 to 240 min with other experimental parameters fixed.

To obtain CO_2/N_2 mixtures at different p_{CO_2}, CO_2 and N_2 at controlled flow rates were mixed, and p_{CO_2} in the mixture was equated to the ratio between the flow rate of CO_2 and the total flow rate for CO_2 and N_2. This assumption was validated in the SI by comparing the times required to reduce the pH of 200 mL of a 0.104 M NaOH solution to 8.30 using different mixed gases flowing at a constant total rate of 150 mL/min. At this pH, NaOH should have reacted with CO_2 to yield $NaHCO_3$.

The q values increased at both temperatures as p_{CO_2} increased, as expected. The q data increased more quickly with p_{CO_2} at 25 than 60 °C, suggesting the particles sorbed CO_2 more efficiently at the lower temperature. The isotherms measured at the two temperatures were used to calculate the isosteric heat Q_I at a given q using

$$\ln(p_2/p_1) = Q_I/R(1/T_2 - 1/T_1) \quad (1)$$

where p_2 and p_1 are the p_{CO_2} values read from the fitting curves for the experimental data; T_2 and T_1 are 333 and 298 K, respectively; and R is the gas constant.[31] Plotted in Figure 4b was the variation in Q_I with q. Q_I being the negative of or equal to the absolute value of the partial or differential molar heat of adsorption denotes the heat released upon the sorption of 1 mol of CO_2 by an infinite amount of particles that have presorbed CO_2 to a capacity of q.[32,33] Q_I decreased as q increased (Figure 4b) because the more readily accessible sites were used for CO_2 sorption first. The Q_I value at lower q determined by us was ~70 kJ/mol. This was comparable with that reported by others for CO_2 sorption by secondary amine, confirming the validity of our experimental results.[34] With increasing CO_2 uptake, the isosteric heat decreased and reached values typical of physical adsorption (~20 kJ/mol) at higher CO_2 uptake.

CO_2 was fully stripped, within our tested time of 30 min, from our particles at 100 °C under N_2 flow. This should not be surprising because data of Figure 3a and 4a showed that the CO_2 sorption capacity of our particles decreased both with increasing temperature and with decreasing CO_2 partial pressure. Evidently, N_2 flow helped dilute CO_2 and reduce CO_2 partial pressure.

The regenerated particles were cooled to room temperature and then used again as a CO_2 scavenger. Figure 5 shows how the amount of captured CO_2 oscillated with the temperature swings. The particle capacities barely changed with the temperature swings, demonstrating the stability of these particles for repeated CO_2 capture and release applications.

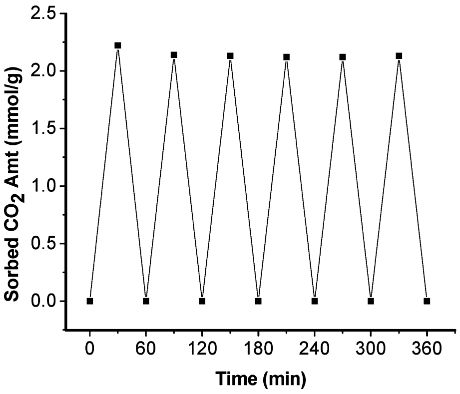


Figure 5. Oscillation in captured CO_2 amount with temperature swing. Each cycle consisted of flowing CO_2 at 1.00 atm at 25 °C for 30 min and then flowing N_2 at 1.00 atm at 100 °C for 30 min.

In conclusion, support-free porous polyamine particles were designed and tailor-made by precipitation polymerization for CO_2 capture and release. The particles had a high specific surface area of 246 m^2/g and contained 6.9 mmol/g of amines that were accessible to HCl. When they were tested under dry conditions and at a CO_2 pressure of 1.00 atm and 30 °C, the particles displayed a moderate CO_2 capture capacity of 2.3 mmol/g. This solid sorbent is very easy to regenerate, requiring heating to only 100 °C under N_2 flow. Furthermore, the particles were stable and survived repeated CO_2 sorption/desorption cycles. While the capacities of our particles were not exceptional, they were higher than those of some silica-supported sorbents.[21,22] It is noted that capture capacities could be enhanced in the presence of water.[35] In these cases, the reaction stoichiometric ratio between CO_2 and amine should be 1 instead of 0.5. We further anticipate increases in the capacities of future porous tailor-made polyamine particles by increasing their specific surface areas and by tailoring the structure and thus the Q_I values for CO_2 capture.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

All the experimental details, additional discussion, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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