

Single-Walled Zeolitic Nanotubes: Advantaged Supports for Poly(ethylenimine) in CO₂ Separation from Simulated Air and Flue Gas

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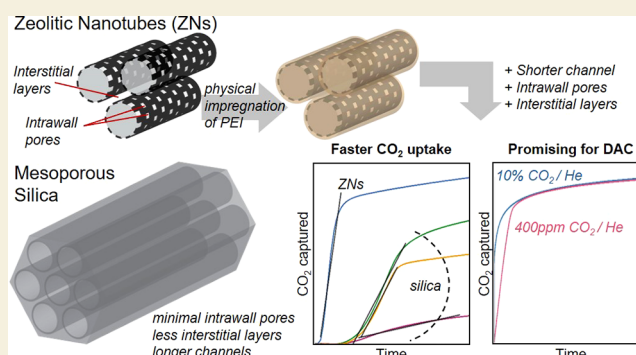
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ABSTRACT: Previous research has demonstrated that amine polymers rich in primary and secondary amines supported on mesoporous substrates are effective, selective sorbent materials for removal of CO₂ from simulated flue gas and air. Common substrates used include mesoporous alumina and silica (such as SBA-15 and MCM-41). Conventional microporous materials are generally less effective, since the pores are too small to support low volatility amines. Here, we deploy our newly discovered zeolite nanotubes, a first-of-their-kind quasi-1D hierarchical zeolite, as a substrate for poly(ethylenimine) (PEI) for CO₂ capture from dilute feeds. PEI is impregnated into the zeolite at specific organic loadings. Thermogravimetric analysis and porosity measurements are obtained to determine organic loading, pore filling, and surface area of the supported PEI prior to CO₂ capture studies. MCM-41 with comparable pore size and surface area is also impregnated with PEI to provide a benchmark material that allows for insight into the role of the zeolite nanotube intrawall micropores on CO₂ uptake rates and capacities. Over a range of PEI loadings, from 20 to 70 w/w%, the zeolite allows for increased CO₂ capture capacity over the mesoporous silica by ~25%. Additionally, uptake kinetics for nanotube-supported PEI are roughly 4 times faster than that of a comparable PEI impregnated in SBA-15. It is anticipated that this new zeolite will offer numerous opportunities for engineering additional advantaged reaction and separation processes.

KEYWORDS: 1D zeolite, nanotube, amine, direct air capture, DAC, flue gas, adsorption, porous materials



INTRODUCTION

As carbon dioxide (CO₂) levels continue to rise, the reduction of atmospheric CO₂ is necessary to limit the effects of climate change.¹ One promising way to lower these levels is through the capture of CO₂ from the air.^{2–4} Technologies for CO₂ capture from air have existed since the 1940s–1950s^{5,6} and have been commercially deployed in spacecraft and submarines. However, CO₂ removal from air was first connected with combatting climate change by Lackner in 1999,^{3,7} and at such large scales, the technical approach may need to differ from small-scale vehicular applications noted above. CO₂ capture from the air—or direct air capture (DAC), as it is now called—can allow for “negative emissions” when coupled with geological storage. Negative emissions technologies (NETs) produce a fundamentally different product from CO₂ removal from point sources, which is a more mature technology area that produces “avoided emissions”.⁸ In principle, DAC can be practiced at many locations, but in practice, it requires suitable land, water, and (ideally renewable) energy. Furthermore, as a technology to be implemented

outdoors and in all seasons, DAC must be compatible with varying weather conditions and is affected by many factors including temperature and humidity.^{9,10}

Carbon dioxide capture is often carried out utilizing aqueous amines¹¹ or solid-supported amines.¹² While effective, aqueous amine solutions for CO₂ capture require significant energy for regeneration and offer challenges of material corrosion and production of toxic byproducts.¹³ Solid-supported amines, which are less developed at the commercial scale, can potentially offer the advantage of lower energy costs and less equipment corrosion.^{14,15} The performance of solid amine sorbents can be affected by a range of factors such as the sorbent composition, including how the amine is loaded onto

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Table 1. Physical Characteristics of Four Support Materials Loaded with PEI and Corresponding CO₂ Uptake Performance

sorbent	PEI loading ^a (w/w%)	pore volume ^b (cm ³ /g)	pore filling ^c (%)	CO ₂ capture at 10% CO ₂ ^d (mmol CO ₂ /g sorbent)	amine efficiency (mol CO ₂ /mol N)
zeolite nanotubes	0	1.50	0	0.36	0.00
	20	0.98	37	0.61	0.13
	30	0.71	54	1.34	0.20
	40	0.56	64	1.64	0.18
	50	0.34	78	1.84	0.16
	60	0.12	92	1.94	0.14
	65	0.05	97	2.23	0.15
	70	0.00	100	2.09	0.13
SBA-15	0	0.97	0	0.10	0.00
	10	0.63	35	0.31	0.13
	30	0.24	75	0.49	0.07
	40	0.13	87	1.08	0.12
	50	0.03	97	1.30	0.12
	60	0.00	100	1.80	0.13
	0	0.90	0	0.01	0.00
MCM-41-2.9	10	0.56	38	0.24	0.11
	12	0.47	48	0.29	0.11
	15	0.31	65	0.40	0.12
	18	0.24	73	0.45	0.11
	20	0.21	77	0.54	0.12
	30	0.018	98	0.10	0.01
	40	0.00	100	0.03	0.00
MCM-41-5.8	0	2.23	0	0.05	0.00
	20	0.77	65	0.79	0.18
	40	0.39	83	1.74	0.19
	50	0.12	95	1.49	0.13
	60	0.01	100	1.52	0.11

^aOrganic loading calculated by burn off studies via thermogravimetric analysis (TGA) under inert conditions. ^bPore volume and width were obtained via N₂ physisorption experiments. Zeolite nanotubes have a pore volume of 1.54 cm³/g and a pore width of 6.2 nm. SBA-15 has a pore volume of 0.97 cm³/g and a pore size of 6.6 nm. MCM-41 small pore has a pore volume of 0.90 cm³/g and a pore size of 2.9 nm. MCM-41 large pore has a pore volume of 2.23 cm³/g and a pore size of 5.8 nm. ^cPore filling is obtained by comparing initial pore volume with pore volume after amine impregnation. ^dCO₂ capture pseudoequilibrium obtained via TGA with a gas flow of 10% CO₂ in He at 30 °C for 3 h.

the substrate.¹⁶ In this regard, amine containing sorbents have been previously categorized into three classes. Class 1 sorbents are solid supports physically impregnated with amines.¹⁴ Class 2 sorbents contain amines covalently bound to a substrate, typically via silane linkages.¹⁷ Lastly, class 3 sorbents are made by polymerizing *in situ* to covalently bond the aminopolymer to the support.¹⁸ Each class has its benefits, with class 1 materials allowing for the easiest access to a wide array of amines, higher amine loadings, and ease of scalability.^{3,19}

The design of the solid-supported amine sorbents significantly affects carbon capture efficiency.²⁰ The two primary constituents of sorbents for carbon capture are the amine(s) and the solid, which is typically a mesoporous, support. Poly(ethylenimine) (PEI) is the most commonly used amine and is a useful baseline oligomeric amine for use in any sorbent development project. PEI is made in a range of molecular weights and degrees of branching and is commercially available, and it yields high CO₂ sorption capacities while also being easily handled and stored.^{3,15,21–23} There are a number of different substrates that can be used for CO₂ capture including polymers, oxides, activated carbons, metal organic frameworks, and zeolites.^{15,24–28} Commonly used silica supports include highly ordered mesoporous substrates like SBA-15 and MCM-41.²⁹ These well-defined porous materials aid scientific investigation, while more disordered, amorphous mesoporous oxides are typically deployed in practical applications at larger scales. High pore

volume associated with ordered mesoporous materials allows for increased amine loading and thus greater CO₂ uptake capacities. In contrast, microporous materials such as zeolites are less frequently employed as supports for amines in carbon capture. Their microporous structure limits the size of the amine that can be used, with small amines being potentially too volatile for practical temperature swing adsorption cycles. Furthermore, the small micropores of zeolites can limit to loading of amines that can be achieved. Additionally, many zeolites are quite hydrophilic, limiting their utility for CO₂ capture at warm temperatures with high relative humidities, though low-temperature applications may facilitate their use.^{30–32}

However, there are attractive features of zeolites, including their ordered, crystalline structures and the ability to tune the particle size, shape, and morphology in many cases, with an array of lamellar or layered zeolites (2D) now complimenting their more well-known 3D counterparts. Recently, an example of a 1D zeolite, or zeolite nanotube, was discovered by Korde et al.³³ These zeolite nanotubes are composed of a central, mesoporous channel of 2.5 nm in diameter bounded by microporous, crystalline zeolitic walls. Like the conventional 1D mesoporous substrates mentioned above (MCM-41, SBA-15, etc.), bundles of zeolite nanotubes possess similar mesoporous structures, while offering the potential added advantage of gas sorption through the zeolitic nanotube walls instead of only in the mesopore openings at the end of each

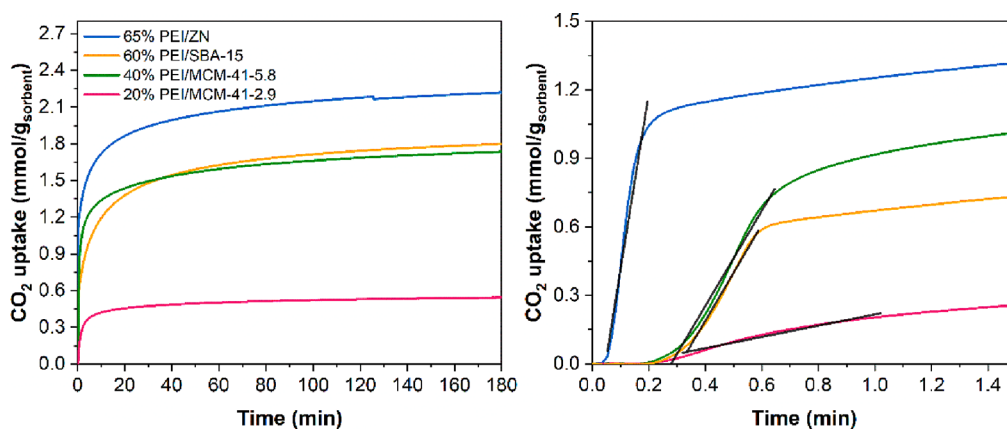


Figure 1. CO₂ uptake kinetics of PEI-loaded ZN, SBA-15, MCM-41-2.9, and MCM-41-5.8 with a flow of 10% CO₂/He at 30 °C, with each sorbent having the PEI loading that gives maximum CO₂ uptake (left) comparison for the rate of uptake on all four sorbents from 0–1.5 min (right).

tube (or mesoporous silica particle, in the case of MCM-41 and SBA-15). Zeolite nanotubes may offer unique properties for applications in catalysis or adsorption, though no applications of these newly discovered materials have been reported to date.

Here, we explore the use of these newly reported quasi-1D hierarchical zeolite nanotubes as a support for CO₂ capture after impregnation of the nanotubes³⁵ with PEI. The zeolite nanotubes (ZNs) are compared with common substrates for CO₂ capture that offer straight 1D mesopores, including SBA-15, MCM-41 with large pores (MCM-41-5.8), and MCM-41 with small pores (MCM-41-2.9). All supports were wet impregnated with PEI (800 *M_w*) in differing loadings until a decrease in CO₂ uptake efficiency was observed, normally at ~100% mesopore filling, as determined via N₂ physisorption data. The results demonstrate a noteworthy ~25% increase in CO₂ capture capacity by the PEI-impregnated ZNs over the mesoporous silicas. More importantly, uptake kinetics are over 4× faster than for PEI-impregnated mesoporous silica.

RESULTS AND DISCUSSION

Composites of porous silicates and amines were synthesized via wet impregnation of PEI utilizing four different substrates. All substrates were loaded with amines over a range of pore filling from 0 to 100% to evaluate the CO₂ sorption capacity, uptake rates, and amine efficiency (mol CO₂/mol N). The amine primarily used for this study was branched PEI with a molecular weight (*M_w*) of 800 g/mol. PEI was chosen due to its pervasive use in the literature as well as high CO₂ uptake. Three mesoporous substrates were chosen to compare CO₂ sorption performance against PEI-impregnated ZNs: SBA-15, MCM-41 with small mesopores, and MCM-41 with large mesopores. Of the three substrates, the most direct comparison to the ZN is small-pore MCM-41 (MCM-41-2.9) with a mesopore diameter of 2.9 nm. A comparison to the ZNs is closely comparable since the ZNs have an inner channel diameter of 2.5 nm but differ from MCM-41 in containing a microporous wall of ~5–6 Å pore openings.³³ The large-pore MCM-41 (MCM-41-5.8) with a pore size of 5.8 nm was chosen because this pore diameter is close to the pore size of the zeolite nanotubes as calculated from a nitrogen sorption isotherm using the Barrett–Joyner–Halenda (BJH) method. Crystallographically, this pore size is close to the outer diameter of ZNs. SBA-15 is one of the most widely used substrates for CO₂ capture with amines. SBA-15, which is

perhaps the most studied support for PEI in CO₂ capture experiments, was synthesized with a typical pore size of 6.6 nm, slightly larger than the observed ZN mesopore size. The surface areas of three of the four substrates are very similar: ZN at 1050 m²/g, MCM-41-2.9 at 1230 m²/g, and MCM-41-5.8 at 1280 m²/g, with only SBA-15 at a lower value of 620 m²/g. As bare substrates, free of amines, ZNs performed the best of all four materials in the physisorption of CO₂ at 30 °C in the absence of added amines, with uptakes over 3× higher than that for SBA-15 (Table 1), owing to the micropores of the ZNs.

CO₂ sorption experiments were performed on a thermogravimetric analyzer (TGA) under a flow of 10% CO₂ in He at 30 °C. Samples were dried under inert gas for 1 h at 100 °C prior to an exposure to CO₂ for 3 h. Uptake is calculated in mmol of CO₂ per dry mass of the sorbent (mmol CO₂/g sorbent). As shown in Table 1 and Figure S1, the CO₂ uptake capacity does not scale with pore filling. Perhaps, for the composites having a limited amount of PEI (i.e., lower pore filling), the PEI chains were strongly bound to the pore walls, limiting the availability of amines for CO₂ sorption. Increasing PEI loadings and thus pore filling can augment the number of accessible amine sites, leading to higher CO₂ uptake capacities. However, filling too much pore volume may limit mass transfer of CO₂, as shown in MCM-41-2.9 and MCM-41-5.8, causing a decrease in uptake capacities during the limited time of exposure to CO₂ gas (Table 1). Such trends of uptake capacities versus pore fill fraction can be better understood by analyzing trends of amine efficiencies (mol CO₂/mol N). Sorbents studied in this paper generally showed volcano-shaped curves of amine efficiencies versus PEI loadings (Figure S2). Such a volcano-type relationship can be understood when considering that CO₂ capture happens through diffusion and reaction of CO₂ along the amine-packed phase, and excess PEI limits access to all amine sites in the period of sorption.^{34–38}

Comparing the CO₂ uptake capacities, zeolite nanotubes at 65% PEI loading captured 2.23 mmol CO₂/g sorbent, with the next best sorbent, SBA-15, at 60% PEI loading, capturing 1.8 mmol CO₂/g sorbent. Higher amine loadings were attempted for SBA-15, as no capacity decrease was observed as pore filling approached 100%; however, above 60% PEI loading, samples were too viscous and sticky to handle efficiently as they were well over 100% pore filling. Indeed, some TEM images show evidence of thick PEI layers on the outer surfaces of SBA-15 after complete pore filling is achieved. The two MCM-41

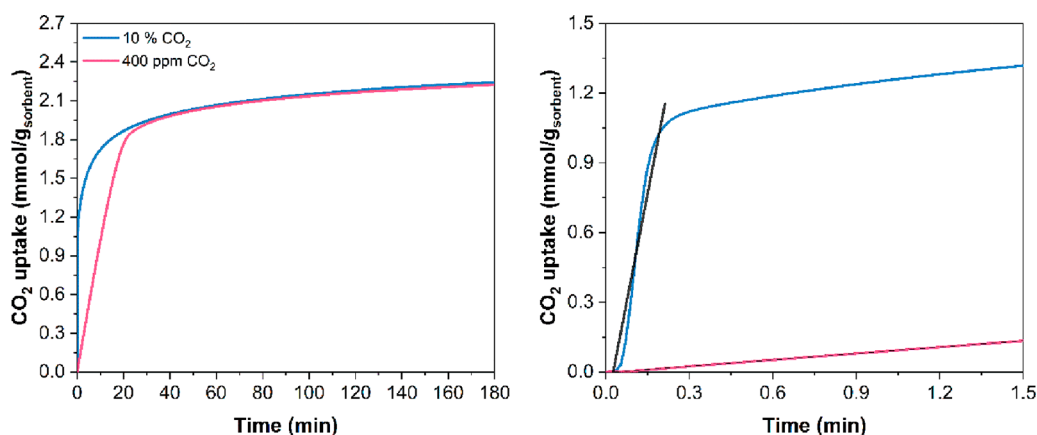


Figure 2. CO₂ sorption dynamics comparison between PEI loaded ZN with flow of 10% CO₂/He and 400 ppm of CO₂ at 30 °C (left) and comparison of the rate of uptake from 0–1.5 min (right).

sorbents performed more poorly, with the MCM-41-2.9 at 20% PEI loading only capturing 0.54 mmol CO₂/g sorbent and the MCM-41-5.8 at 40% PEI loading capturing 1.74 mmol CO₂/g sorbent. Chosen as the direct comparison based on mesopore size, MCM-41-2.9 had significantly lower CO₂ uptake than the ZN-65% PEI, with 76% less CO₂ captured. Upon examining the uptake curves of these four sorbents with optimal PEI loadings for each support, not only is the total amount of CO₂ captured higher for the zeolite nanotubes, but the rate of uptake is faster as well. Uptake curves shown in Figure 1 allow for a more direct comparison between different supports with their corresponding best PEI loadings (from a sorption capacity perspective) for each sorbent. ZN-65% PEI has the fastest uptake rate, followed by SBA-15, MCM-41-5.8, and MCM-41-2.9, in order.

Figure 1 also highlights the initial uptake rates during the first 1.5 min; taking the slope of these initial curves gives the rate of uptake. ZN-65% PEI has a rate of uptake significantly faster than that of either of the other three sorbents at 6.2 mmol CO₂ g⁻¹_{sorbent} min⁻¹ compared to SBA-15 at 1.66, MCM-41-2.9 at 0.26, and MCM-41-5.8 at 1.9 (same units: mmol CO₂ g⁻¹_{sorbent} min⁻¹). ZN-65% PEI has a 24× faster uptake rate than its direct comparison, MCM-41-2.9, and over 3× faster uptake rate than SBA-15. These faster uptake rates can directly result in shorter CO₂ capture cycles, therefore allowing for more CO₂ capture per day if applied on a larger scale. The three PEI-impregnated mesoporous silica sorbents, MCM-41-2.9, MCM-41-5.8, and SBA-15, show a short latency or induction period before CO₂ starts being captured that is not present in the zeolite nanotube sorbent. We hypothesize that the lack of such an induction period for nanotubes can be ascribed to the small apertures (micropores) along the channels of the nanotubes,³³ promoting mass transfer of CO₂. This becomes more obvious when we compare amine efficiencies of the sorbents having similar pore fill fraction (thus similar extent of free volume), where ZN-based sorbents generally showed higher amine efficiencies than other sorbents. In addition to the presence of small apertures, referring to Figures S3–S6, the ZNs have a shorter average diffusion path lengths (or particle length) compared to other sorbents, which can promote rates of mass transfer and CO₂ sorption, mitigating the latency during uptake and promoting sorption. Indeed, trends in the uptake rates can also be reconciled considering channel lengths of the supports, as shorter channels may reduce diffusion resistance which leads to faster

CO₂ uptake rates.³⁹ As shown in Figure S6, ZNs showed shorter lengths (~85 nm), while MCM-41-2.9 (tubular shape, as shown in Figures S4 and S5) and SBA-15 (pill shape, Figures S4 and S5), which contain regular arrays of mesopores, had much longer channel lengths (MCM-41-2.9: 1.2 μm, SBA-15: 0.8 μm). MCM-41-5.8, as shown in Figures S4 and S5, lost its spherical morphology likely due to the addition of decane, which was as a swelling agent used to increase the pore size. The average length of many particles appeared shorter than MCM-41-2.9 and SBA-15 (Figure S6) but still longer than that of the ZNs. One interesting comparison can be made by comparing 65% PEI/ZN and 40% PEI/MCM-41-5.8, whose BJH pore sizes and average particle lengths were comparable (Figure S6). The 40% PEI/MCM-41-5.8 material showed much higher remaining pore volume compared to that of 65% PEI/ZN (Table 1), which should facilitate more rapid CO₂ uptake. However, 65% PEI/ZN showed much faster uptake compared to the 40% PEI/MCM-41-5.8. We hypothesize that the faster CO₂ uptake rates of the PEI/ZN materials are derived from (i) the straight crystalline mesopore (vs the more tortuous channels in PEI/MCM-41-5.8 (Figure S3 vs Figure S6)), (ii) the existence of micropores distributed along the walls of the nanotubes, and (iii) the marginally shorter average channel length.

In an interesting observation, the pseudoequilibrium CO₂ capacity does not change when comparing the uptake of the zeolite nanotubes at 65% PEI loading at two different CO₂ concentrations, 10% and 400 ppm (0.04%). Normally, CO₂ capacities are strongly influenced by the driving force for adsorption, with smaller sorption capacities at lower CO₂ concentrations. The observation of equivalent CO₂ uptakes at 0.04 and 10% CO₂ has only been previously observed once before to the best of our knowledge.³⁷ Figure 2 shows a comparison between the uptake of the zeolite nanotubes at the two different CO₂ concentrations over a normal 3 h period of CO₂ sorption. At 400 ppm of CO₂, the rate of uptake is an order of magnitude lower, with the uptake rate using 10% CO₂ of ZN-65% PEI at 6.2 mmol CO₂ g⁻¹_{sorbent}/min, while the uptake in 400 ppm of CO₂ is only 0.1 mmol CO₂ g⁻¹_{sorbent} min⁻¹. Even with this slower sorption rate, the final CO₂ capture in both CO₂ concentrations remains the same at ~2.2 mmol CO₂/g sorbent. Previously when such behavior was observed, it was hypothesized that rapid CO₂ sorption at 10% CO₂ conditions led to rapid cross-linking of PEI chains and lowered the free volume around the easily accessible amines,

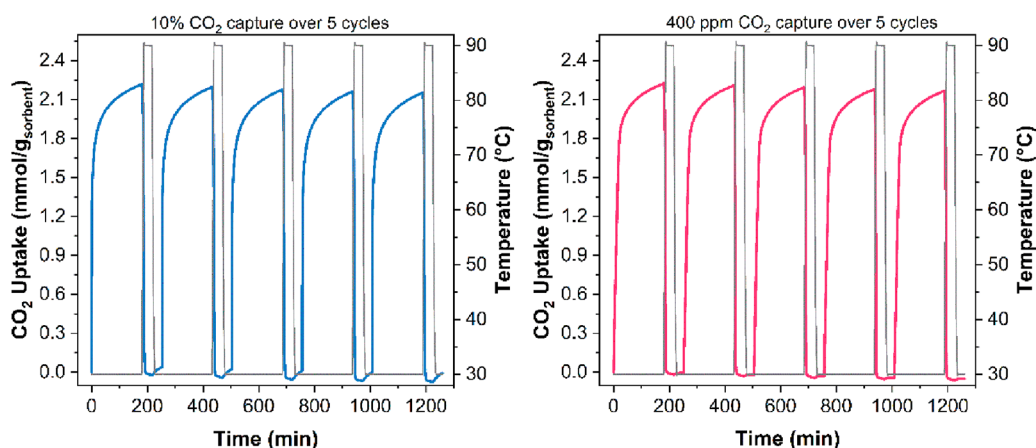


Figure 3. Normalized CO₂ sorption cycles using 10% CO₂ (left) and 400 ppm of CO₂ (right) for zeolite nanotubes loaded with 65 wt % PEI.

erecting a diffusive barrier for further sorption.³⁷ On the other hand, for 400 ppm of CO₂, slower CO₂ sorption may prevent rapid polymer cross-linking, keeping more of the amines accessible for CO₂ capture, eventually leading to comparable amine efficiencies at the pseudoequilibrium conditions. The high uptake rate here for the zeolite nanotube sorbent may lead to a similar observation, though further work is needed to fully probe this hypothesis.

Multiple temperature swing sorption cycles were run using both 400 ppm and 10% CO₂ to determine the retained capture efficiency of the amine-impregnated zeolite nanotubes over multiple uses. Cycles were run similarly to previous experiments after an initial pretreatment (100 °C). Samples were exposed to 3 h CO₂ capture, followed by desorption at 90 °C in flowing inert gas, 30 min isothermal at 30 °C in inert, and the cycle was repeated five times. The capture period in the TGA is longer than expected under optimized conditions in a practical contactor such as a fiber⁴⁰ or monolith^{41,42} due to the unique, nonideal flow patterns in the TGA. Figure 3 shows the normalized traces of the ZN-65% PEI at both 400 ppm of CO₂ and 10% CO₂. At both concentrations of CO₂, the sample preserves similar sorption performance over all five cycles. Both samples show a slight decrease in their baseline as some volatiles such as water or low molecular weight amines are removed during the desorption steps.

The working temperature is important for a CO₂ sorbent to be robust. With the average temperature of the planet being under 30 °C, subambient (below room temperature) CO₂ sorption testing is necessary to determine the effectiveness of new sorbents over a range of temperatures if the sorbent is to be considered for DAC applications.^{9,43} ZN-65% PEI was tested at temperatures between 0 and 30 °C with 400 ppm of CO₂ to determine its efficacy under subambient conditions. CO₂ sorption at lower temperatures should lead to a decrease in sorption rate but could lead either to an increase or decrease in CO₂ uptake.⁴³ If mass transfer is a dominant factor, for example through polymer-filled pores, one may expect reduced uptake at low temperatures at a fixed uptake time. In contrast, if sorption equilibria can be approached quickly enough, CO₂ uptake should increase due to thermodynamics. CO₂ uptake capacity increased from 30 to 15 °C (~1.25 to 1.6 mmol/g_{sorbent}) and then decreased as temperature was reduced, reaching ~0.8 mmol/g_{sorbent} at 0 °C. We hypothesize that PEI chains retained their mobilities at 15 °C so that the rate of CO₂ diffusion appeared sufficiently fast to take advantage of the

thermodynamic advantage of lower temperature conditions. However, further decreasing the uptake temperatures yielded lower uptake capacities, likely due to significantly lowered PEI mobilities and thus slower CO₂ diffusion. More detailed low-temperature characterization can be explored in a future, full paper describing these materials.

Along with temperature, humidity can also play a large role in CO₂ sorption. In dry conditions, to achieve high uptakes,^{12,44,45} two amines are needed to form carbamate linkages, as one amine reacts with CO₂ and a second amine is necessary to stabilize the charge generated. Amine sorbents often show increased efficiency in the presence of humidity, as a new sorption pathway becomes available where only one amine reacts with water and CO₂ to form bicarbonate species.⁴⁶ Using TGA capable of applying a humid stream, CO₂ capture with ZN-65% PEI was studied at 400 ppm in relative humidities between 0 and 37.5% at 30 °C.

As shown in Figure 4, under the humidity range we explored (0–37.4%), the sorbents showed enhanced uptake capacities up to a certain level of humidity but decay in uptake at the higher limit (37.5%), while the H₂O uptake steadily increased with increasing humidity. The dry CO₂ capacity measured using the humid TGA gave an uptake of 1.95 mmol CO₂/g sorbent, which is about 13% lower than what was measured

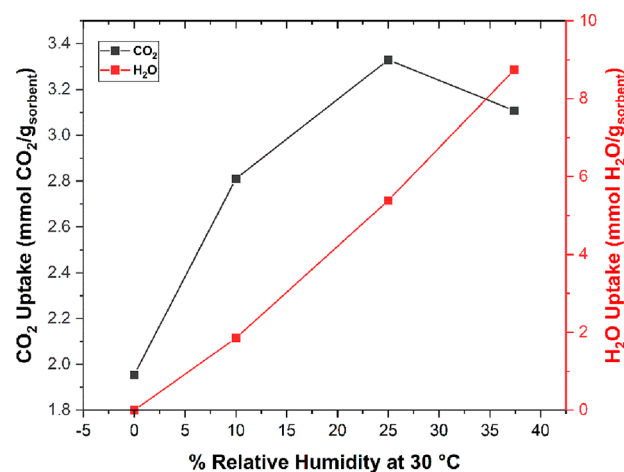


Figure 4. CO₂ uptake (400 ppm of CO₂) under humid conditions from 0 to 37.4% relative humidity at 30 °C in a gravimetric system equipped with CO₂ stream with varied humidity.

with the TGA without a humid stream (2.23 mmol CO₂/g sorbent, as shown in Figure 1). We suspect that this difference comes from a slightly lower concentration of CO₂ in the inlet gas in this second TGA instrument. Exposed to a humid gas flow, the sorbent exhibited an initial increase in uptake (up to 25% relative humidity) followed by a drop as the relative humidity further increased (37.4%). At 10 and 25% relative humidity, we observed uptakes of 2.81 and 3.33 mmol CO₂/g sorbent, which accounted for an increase of 44 and 71% over the dry sample, respectively. When raising the relative humidity to 37.4%, there was a 28% decrease in efficiency when compared to the dry sample.

We expect that having adsorbed H₂O can lubricate chain motions of PEI^{47,48} while promoting formation of bicarbonate species.⁴⁶ However, sorption of too much water may leave too little free volume, reducing the uptake performance by slower diffusion of CO₂. This hypothesis can be supported by analyzing the uptake rates. Interestingly, the dry CO₂ case showed a surge of uptake followed by a shallow increase, while the humid CO₂ cases showed short induction times followed by consistent mass gain (Figure S7, inset). For the dry CO₂ case, the first rapid increase (up to ~1.5 min) shown in the dry CO₂ case can be attributed to CO₂ sorption to highly accessible amines within relatively large free volume, and the following gradual increase (up to ~70 min) can be ascribed to penetration of CO₂ through a mobile PEI phase. Lastly, the very slow mass gain (~70 min and thereafter) can be related to slow CO₂ diffusion along relatively less mobile PEI domains. Interestingly, the wet CO₂ cases lack the first stage where rapid mass gain was observed in the case of dry conditions. Perhaps the absence of such a rapid mass gain for the wet CO₂ cases comes from occluded free volume from adsorbed water. However, except for the early stage of CO₂ uptake, the wet CO₂ cases showed consistently higher uptake rates over extended times (Figure S7, inset) compared to the dry CO₂ case. We analyzed the uptake rates in the time range from 2 to 5 min and confirmed that the wet streams yielded faster uptake rates (Table S1). Moreover, as shown in Figure S7, higher humidity levels (e.g., 25, 37.4%) resulted in extended times for the second uptake regime (i.e., CO₂ diffusion through mobile PEI phase), as shown in Figure S7. All humid CO₂ uptake curves are given in Figure S8.

Managing competitive H₂O and CO₂ sorption in PEI/ZN sorbents will be critical to their potential practical use for CO₂ capture. Sayari and co-workers^{49,50} reported that pore-expanded MCM-41 supports lined with hydrophobic alkyl chains were robust CO₂ sorbents when impregnated with PEI. Such materials exhibited significantly higher CO₂ uptake, consistently high uptake under a broad range of humidity, and maintained their performance after multiple CO₂ sorption–desorption cycles compared to similar materials with hydrophobic additives. This points toward potentially leaving some of the zeolite structure-directing agents within the nanotube materials prior to PEI impregnation or using other hydrophobic additives to tune the hydrophilic/hydrophobic balance of the materials, broadening the range of conditions for practical CO₂ capture.

CONCLUSIONS

In the work, newly discovered ZNs were used as a substrate for oligomeric PEI to create sorbents for CO₂ sorption from simulated flue gas or air. The ZNs provided both elevated CO₂ capacities and faster uptake kinetics when compared against

commonly used mesoporous silica substrates, including mesoporous MCM-41-2.9, with similar mesopore size to the ZNs. Under simulated DAC conditions, in comparison with MCM-41-2.9, ZN-65% PEI captured four times more CO₂ with an uptake rate an order of magnitude faster. When compared to SBA-15-60% PEI, a benchmark material that is well-studied in the literature, ZN-65% PEI captured ~25% more carbon with 4-fold faster uptake. The improved uptake capacity and kinetics can be ascribed to the improved access to the mesopores through the zeolitic, microporous walls of the nanotube as well as the short nanotube lengths relative to the size of the mesoporous silica particles. Interestingly, the maximum CO₂ uptake for ZN-65% PEI is identical (~2.2 mmol CO₂/g sorbent) under two different CO₂ concentrations, 400 ppm and 10% CO₂, showing promise for use under ambient DAC conditions. Over multiple temperature swing cycles, the performance of ZN-65% PEI did not decrease using either concentration of CO₂; however, uptake rates at 10% CO₂ were 60 times faster than at 400 ppm of CO₂. The CO₂ uptake of ZN-65% PEI increases up to intermediate relative humidity (in this paper, up to 25%) and then decreases as humidity goes higher. Competitive binding to water, less free pore volume due to adsorbed water, and changes in zeolite structure/stability under humid conditions may contribute to this trend.

In this preliminary communication, only a narrow range of conditions could be explored (temperature, humidity, P_{CO₂}, etc.), and future work should explore a broader array of conditions. However, these preliminary results show that ZN-65% PEI outperforms common, benchmark PEI-loaded mesoporous silica sorbents, exhibits stability over multiple cycles under both 10% and 400 ppm of CO₂ concentrations, and performs well in moderate humidities up to 35%, the maximum tested in this work. Additional temperature and humidity conditions should be explored in future work, alongside use of additives to modulate the hydrophilicity of the composite materials.

This work represents the first application of newly discovered zeolite nanotubes, and the work demonstrates that advantaged sorption and diffusion might be obtained relative to more traditional supports, such as noncrystalline mesoporous silicas and crystalline 2D or 3D zeolites. Additional exploration of the potentially unique properties of zeolite nanotubes is warranted.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.2c00553>.

Detailed description of experimental methods and material synthesis, characterization data (SEM, STEM, and average length of support particles), effects of pore filling on CO₂ uptake, humid CO₂ adsorption behavior of ZN-65% PEI under varied relative humidity (10–37.4%) at 30 °C (PDF)

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Notes

The authors declare the following competing financial interest(s): C.W.J. has a financial interest in Global Thermostat Operations, LLC. Georgia Tech has a conflict of interest management plan in place for C.W.J.

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