# Porous Carbon with Ultrahigh Surface Area for $CO_2$ Capture at Elevated Pressure and Developing Methods for Measuring $CO_2$ Adsorption Dynamics

**Investigators**

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**Abstract**

Natural gas is the cleanest fossil fuel source. However, natural gas wells typically contain considerable amounts of $CO_2$, with on-site $CO_2$ capture necessary. Solid sorbents are advantageous over traditional amine scrubbing due to their relatively low regeneration energies and non-corrosive nature. However, it remains a challenge to improve the sorbent's $CO_2$ capacity at elevated pressures relevant to natural gas purification. Here, we report the synthesis of porous carbons derived from a 3D hierarchical nanostructured polymer hydrogel, with simple and effective tunability over the pore size distribution. The optimized surface area reached 4196 $m^2$ $g^{-1}$, which is among the highest of carbon-based materials, with abundant micro- and narrow mesopores (2.03 $cm^3$ $g^{-1}$ with d < 4 nm). This carbon exhibits a record-high $CO_2$ capacity among reported carbons at elevated pressure (*i.e.*, 28.3 mmol $g^{-1}$ total adsorption at 25 °C and 30 bar). This carbon also showed good $CO_2/CH_4$ selectivity and excellent cyclability. Molecular simulations suggested increased $CO_2$ density in micro- and narrow mesopores at high pressures. This is consistent with the observation that these pores are mainly responsible for the material's high-pressure $CO_2$ capacity. This work provides insights into material design and further development for $CO_2$ capture from natural gas.

In addition, we discuss a quantitative thermodynamic analysis for a series of amine-functionalized SBA-15 materials using simultaneous thermal analysis (STA), a technique that combines differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in one simultaneous measurement. Values of $\Delta H°_{ads}^{avg}$ determined experimentally by STA are coupled to independent equilibrium adsorption isotherm measurements to provide $\Delta G°_{ads}^{avg}$ and $\Delta S°_{ads}^{avg}$ values using the well-known Langmuir adsorption model.

**Introduction**

Global annual energy-related $CO_2$ emission reached a record high of 31.2 gigatonnes (Gt) in 2012[1], and is expected to rise continuously given the growing energy demands and the remaining fossil fuel-dependent energy infrastructure. The mitigation of $CO_2$ emission has been recognized as a crucial necessity, as $CO_2$ is a major contributing greenhouse gas that gives rise to global warming and associated consequences, including

sea level rise, significant variation in weather patterns and threats to human health and wildlife habitats[2].

Natural gas has been viewed as the cleanest fossil fuel, as its combustion leads to the lowest carbon dioxide ($CO_2$) emission per unit of energy generated, as well as negligible emissions of sulfur oxides ($SO_x$), nitrogen oxides ($NO_x$) and mercury compounds[3]. In particular, for the equivalent energy, combusting natural gas produces ~30% and ~45% lower $CO_2$ emissions than combusting petroleum and coal, respectively[3]. However, natural gas wells contain considerable amounts of $CO_2$ (*i.e.*, typically 10-20 mol% and as high as 70 mol% in some locations)[4]. which require on-site $CO_2$ capture. Amine scrubbing has been used previously for $CO_2$ removal from natural gas, but its drawbacks are prominent, some of which include the corrosive nature of the amine solution, significant energy penalty associated with material regeneration, and difficulty in the implementation of off-shore capture units[5, 6].

**Background**
*High-Pressure $CO_2$ Capture*
The development of novel materials and technologies for $CO_2$ capture has attracted tremendous interest from the scientific community, while solid sorbent technologies have shown great promise[7, 8]. Among the broader class of solid sorbents, porous carbons are of particular interest due to their exceptional chemical and physical stability, high surface area and flexibility in terms of tunable pore structure and surface functionality[9-11]. However, it is still challenging to improve the $CO_2$ capacity at high pressures relevant to natural gas purification. An interesting strategy of heteroatom-induced $CO_2$ polymerization has been explored[12]; however, it has shown relatively low $CO_2$ capacity at elevated pressures compared to some commercial activated carbons[13]. Another attractive approach is to optimize the pore properties including surface area, pore volume and pore size[14]; however, the synthesis of these high-surface area carbons involves the use of sacrificial templates of metal-organic frameworks (MOFs), which adds complexity and increases material cost.

In our recent work, we reported a low-cost and template-free synthesis of a highly porous 3D carbon with superior performance for energy storage applications[9]. Herein, we extend the synthetic approach with efficient tunability on the surface area and pore size distribution. Our strategy is based upon the thermal annealing of a 3D hierarchical nanostructured polymer hydrogel (polyaniline, or PAni) without any sacrificial templates, followed by chemical activation. The surface area and pore size distribution can be tuned simply by varying the carbonization temperature. The final porous carbon (denoted as SU-AC) materials have ultrahigh surface areas up to 4196 $m^2$ $g^{-1}$ and total pore volume as large as 2.26 $cm^3$ $g^{-1}$. More importantly, the SU-AC materials have abundant micro- and narrow mesopores (d < 4 nm) up to 2.03 $cm^3$ $g^{-1}$ (~90% of the total pore volume), which are beneficial for $CO_2$ adsorption at elevated pressures. The maximum $CO_2$ capacity of the SU-AC materials (28.3 mmol $g^{-1}$ total adsorption at 25 °C and 30 bar) outperforms the highest reported value for porous carbon materials at identical conditions[14]. Furthermore, the hierarchical porous structures and highly interconnected pore networks of the SU-AC materials facilitate efficient gas diffusion. The SU-AC materials also show excellent $CO_2/CH_4$ selectivity, easy $CO_2$ regenerability and multicycle stability. In

addition, the precursors used for synthesis are commercially available and have relatively low cost. All these desired properties render the SU-AC materials promising candidates for high-pressure $CO_2$ capture from natural gas. We also performed molecular simulation investigations on the $CO_2$ capacity relationships, which provides insight into material design and further development for $CO_2$ capture from natural gas.

A diverse range of solid $CO_2$ sorbents have been studied in the literature, with emphasis placed typically on maximizing the equilibrium $CO_2$ capacities of materials. The fundamental thermochemistry of the adsorption/desorption reactions under conditions relevant to flue gas capture and, specifically, how the structure and surface distribution of immobilized sorbent molecules affect the free-energy of both adsorption and desorption reactions, is not well understood. The most common approach to assessing the strength of $CO_2$-sorbent interactions reported in the literature is to calculate isosteric heats of adsorption ($\Delta H°_{ads}$) from equilibrium adsorption isotherm data measured at multiple temperatures using empirical isotherm models[15-18]. Reports of directly measured calorimetric heats of adsorption are far less common[19].

## Results
### *High-Pressure $CO_2$ Capture*
The separation of $CO_2$ from natural gas typically occurs at elevated $CO_2$ partial pressures up to 30 bar[12]. It has been reported that the high-pressure $CO_2$ capacity largely correlates to the pore volumes of micro- and narrow mesopores[14, 20]. As was shown in the previous sections, the SU-AC materials possess large pore volumes in the pore size regime below 4 nm, which indicates their potential for high-pressure $CO_2$ capture applications. Figure 1a shows the $CO_2$ total adsorption isotherms of the SU-AC materials at 25 °C and 0 – 50 bar. SU-AC-400 exhibits the highest total $CO_2$ capacity, i.e., 28.3 mmol $g^{-1}$ (124.5 wt%) at 30 bar and 35.0 mmol $g^{-1}$ (154.2 wt%) at 50 bar. Due to its ultrahigh surface area and large pore volume, the $CO_2$ adsorption has not reached saturation even at 50 bar. The $CO_2$ capacity decreases as the carbonization temperature increases from 400 to 800 °C, i.e., from SU-AC-400 to SU-AC-800. This trend is in good agreement with that of surface area. For all samples tested, no hysteresis was observed between the adsorption and desorption data points, which suggests the reversible nature of $CO_2$ adsorption even up to 50 bar. To evaluate the recyclability of the sorbent, $CO_2$ adsorption was repeated for multiple cycles on SU-AC-400. The adsorption-desorption cycles were conducted as a pressure swing adsorption (PSA) process, with 30 bar and 1 bar as the adsorption and desorption pressure, respectively. No heat was applied to the system during the desorption process. The $CO_2$ capacity over 10 cycles is plotted in Figure 2. No reduction in the $CO_2$ capacity was observed, which indicates the stability and regenerability of the sorbent material.

Figure 1b shows the comparison of the $CO_2$ adsorption isotherm (25 °C) of our SU-AC-400 sample with the best-performing literature carbon materials with surface areas larger than 2000 $m^2$ $g^{-1}$. It can be seen that the total CO2 uptake of SU-AC-400 at 30 bar (28.3 mmol $g^{-1}$) is superior to those of the previously reported carbon materials[12-14, 20-22]. Table 1 lists the $CO_2$ and $CH_4$ adsorption uptakes and $CO_2/CH_4$ selectivities for the SU-AC samples. Table 5 summarizes the textual properties and high-pressure $CO_2$

capacities of SU-AC-400 in comparison with previously reported carbons. The promising $CO_2$ capacity along with high $CO_2/CH_4$ selectivity of the SU-AC materials makes them excellent candidates for high-pressure $CO_2$ capture from natural gas. In addition, the potential applicability of the SU-AC materials in precombustion $CO_2$ capture was also evaluated using the high-pressure $CO_2$ uptake at 50 °C. As shown in Figure 1c, the SU-AC-400 sample still exhibits a high total $CO_2$ capacity of 25.3 mmol g-1 (111.3 wt%), which far exceeds that of the best-performing literature carbon (20.4 mmol g-1) under identical conditions[14]. The adsorption-desorption of $CO_2$ is also fully reversible at 50 °C in a PSA process. The exceptional high-pressure $CO_2$ uptakes of the SU-AC materials can be attributed to the large amounts of micropores and narrow mesopores, i.e., d < 4 nm. This will be discussed in greater detail in later sections.

In addition, we performed high-pressure $CH_4$ adsorption experiments on the SU-AC samples at 25 °C (Figure 1d). Similar to the $CO_2$ uptake at identical conditions, the $CH_4$ adsorption uptake decreases from SU-AC-400 to SU-AC-800, with no hysteresis observed for all of the samples. It can be seen that the $CH_4$ uptake is significantly lower than the $CO_2$ uptake for all of the SU-AC samples. Among all the SU-AC samples tested, SU-AC-700 shows the highest $CO_2/CH_4$ selectivity, i.e., 6.5 and 14.3 at total pressures of 50 and 300 bar, respectively, assuming a gas mixture composed of 10% $CO_2$ and 90% $CH_4$. These selectivities are considerably higher than those of commercial activated carbon and ZIF-8 (Table 2). Also note that the SU-AC-400 sample with the highest $CO_2$ capacity has a lower $CO_2/CH_4$ selectivity (i.e., 11.2) compared to the rest of the SU-AC samples. As both capacity and selectivity are important factors, to evaluate the true potential of an adsorbent in a realistic $CO_2$ capture process, the adsorption data of the material needs to be coupled with rigorous process modeling and optimization. We will include this in our future studies.
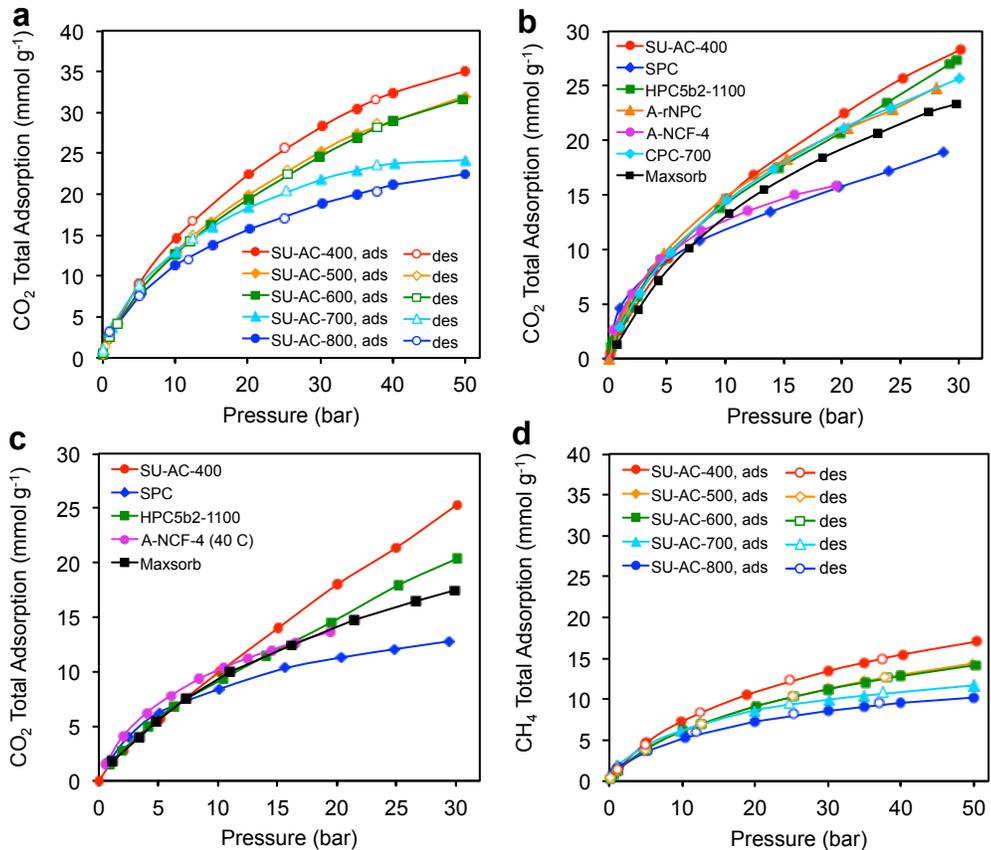
**Figure 1**: a) $CO_2$ total adsorption (solid symbols) and desorption (open symbols) isotherms of the SU-AC materials at 25 °C and pressures up to 50 bar. b) and c) comparison of $CO_2$ adsorption capacity of SU-AC-400 with literature-reported porous carbon materials at (b) 25 °C and (c) 50 °C[12-14, 20-22]. d) $CH_4$ total adsorption (solid symbols) and desorption (open symbols) isotherms of the SU-AC materials at 25 °C and pressures up to 50 bar.
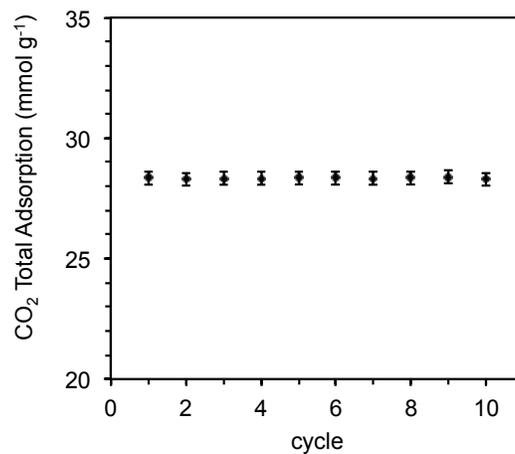


**Figure 2:** Cyclic capacities of SU-AC-400 at 25 °C and 30 bar, where desorption was perform by reducing the pressure to 1 bar while maintaining the temperature at 25 °C.

**Table 1:** Summary of $CO_2$ capture properties of the SU-AC materials at 25 °C and 30 bar in comparison to commercial activated charcoal and ZIF-8.

| Material | $CO_2$ Adsorption [mmol g$^{-1}$] | | $CH_4$ Adsorption [mmol g$^{-1}$] | | $CO_2/CH_4$ Selectivity[a] |
|---|---|---|---|---|---|
| | Total | Excess | Total | Excess | |
| SU-AC-400 | 28.3 | 24.5 | 13.5 | 10.6 | 11.2 |
| SU-AC-500 | 25.2 | 21.9 | 11.3 | 8.4 | 12.1 |
| SU-AC-600 | 24.6 | 21.8 | 11.2 | 8.8 | 12.6 |
| SU-AC-700 | 21.8 | 19.4 | 10.0 | 7.9 | 14.4 |
| SU-AC-800 | 18.9 | 17.5 | 8.6 | 7.4 | 14.3 |
| Activated Charcoal | 9.1 | 8.2 | 6.4 | 4.9 | 10.2 |
| ZIF-8 | 9.1 | 8.2 | 5.0 | 4.1 | 9.5 |

[a]The $CO_2/CH_4$ selectivity was calculated using the Ideal Adsorption Solution Theory (IAST) assuming an ideal mixture of 10% $CO_2$ and 90% $CH_4$ at a total pressure of 300 bar).

**Table 2:** Summary of textual properties and high-pressure $CO_2$ capacities of SU-AC materials in comparison to literature reported porous carbons. The entries are organized according to increased capacity at 25 °C.

| Material | $S_{BET}$ [m$^2$ g$^{-1}$] | Total PV [cm$^3$ g$^{-1}$] | $CO_2$ Capacity at 30 bar [mmol g$^{-1}$] | | Reference |
|---|---|---|---|---|---|
| | | | 25 °C | 50 °C | |
| AC3-36 | 1367 | 0.71 | 7.9 | - | Marco-Lozar, et al.[23] |
| PFCLA | 1211 | - | 9.9 | - | Martin, et al.[24] |
| AC3000 | 3172 | 1.82 | 11.3 | - | Drage, et al.[25] |
| A-NCF-4 | 2309 | 1.03 | 15.9 (20 bar) | 13.7 (40 °C, 20 bar) | Li, et al.[22] |
| SPC | 2500 | 1.01 | 18.9 | 12.8 | Hwang, et al.[12] |
| ACB-5 | 3537 | 2.56 | 20.8 (18 bar) | - | Shao, et al.[26] |
| ZYC-1000 | 3010 | 1.84 | 21.2 | - | Youn, et al.[27] |
| Maxsorb | 3250 | 1.79 | 23.3 | 17.5 | Himeno, et al.[13] |
| AC1 | 3120 | 1.25 | 24.3 | - | Marco-Lozar, et al.[28] |
| FAU-ZTC | 3420 | 1.69 | 25.2 (30 °C) | - | Builes, et al.[29] |
| A-rNPC | 2580 | 1.09 | 25.2 | 21.1 (40 °C) | Jalilov, et al.[21] |
| CPC-700 | 3242 | 1.51 | 25.7 | - | Ashourirad, et al.[20] |
| HPC5b2-1100 | 2734 | 5.23 | 27.4 | 20.4 | Srinivas, et al.[14] |
| SU-AC-400 | 4196 | 2.26 | 28.3 | 25.3 | This work |

*Developing Methods for Measuring CO₂ Adsorption Dynamics*

Amine-functionalized SBA-15 materials were dried at elevated temperatures under N2 in order to desorb any adventitiously adsorbed water and $CO_2$. $CO_2$ adsorption/desorption was measured at 0.15 atm of $CO_2$ and 40 °C using STA (Figure 3). A sharp mass increase is observed in the TGA trace for all materials upon introduction of $CO_2$ at t = 0, accompanied by a sharp exothermic heat flow signal, consistent with $CO_2$ adsorption and the expected formation of an ammonium carbamate species[30]. Integration of the exothermic DSC peak over the initial 5 minutes of adsorption provides a quantitative assessment of $\Delta H°_{ads}^{avg}$ for each material under $CO_2$ concentrations similar to flue gas.
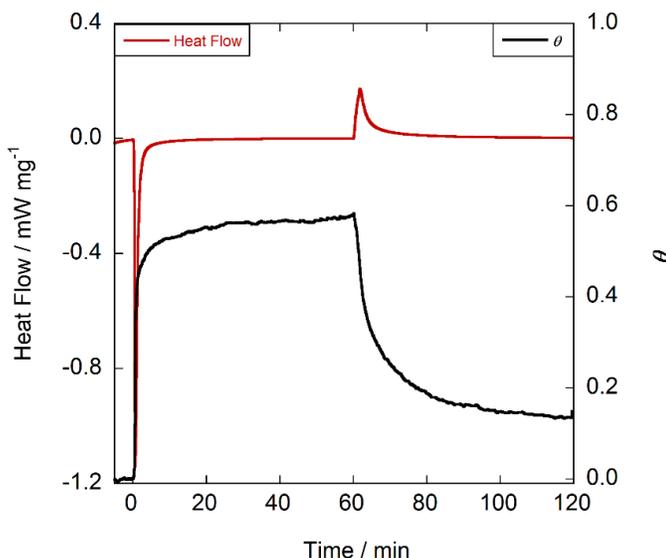


**Figure 3**: Example of STA data of $CO_2$ adsorption/desorption with amine-functionalized SBA-15. (black) TGA, (red) heat flow. Conditions: 0.15 bar $CO_2$, 0.85 bar $N_2$, 40 °C, dry, 100 mL min-1. $\theta$ = # of sites occupied/ # of sites in total.

To quantify $\Delta G°_{ads}^{avg}$, pure gas adsorption isotherms were measured at 40 °C in the pressure range 0.01 – 1.0 atm of CO2 for the series of material under dry conditions. A duel-site Langmuir adsorption model provides excellent fits for the series of adsorption data, and gives estimates of $\Delta G°_{ads}^{avg}$ in the range of – (2.9 – 3.5) kcal mol$^{-1}$. A $\Delta S°_{ads}^{avg}$ value of -58 ± 3 cal mol$^{-1}$ K$^{-1}$ was calculated using the well-known Gibbs free energy equation (($\Delta G°_{ads}^{avg} = \Delta H°_{ads}^{avg} - T\Delta S°_{ads}^{avg}$).

Developing a more generalized model for $CO_2$ capture using thermodynamic and thermogravimetric data is desirable for gaining fundamental understanding of $CO_2$-amine interactions on functionalized surfaces, as well as predicting the behavior of new materials. Development of a generalized adsorption model has been centered around the capture behavior of SBA-15 that has been hydrosilylated with N-[3-(trimethoxysilyl)propyl]ethylenediamine (ED-SBA-15), surface diamine loading of 1.6 mmol g$^{-1}$ determined by elemental analysis).
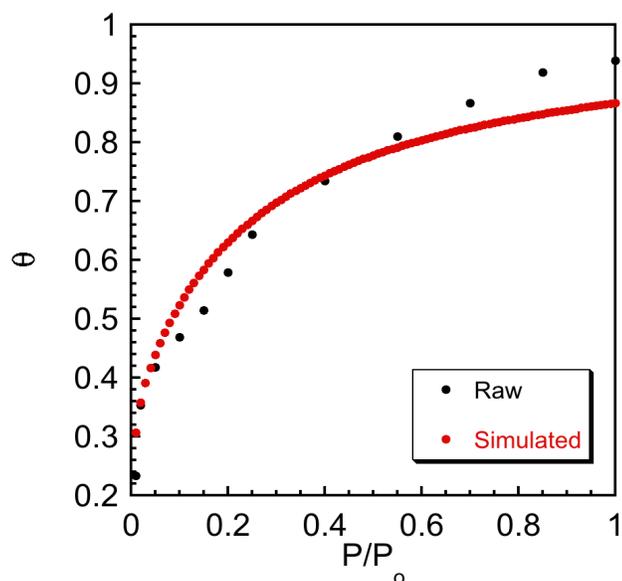
**Figure 4**: Pressure dependence of $CO_2$ adsorption on ED-SBA-15 at 25 °C for experimental (black) and simulated (red) data.

Properties of ED-SBA-15 were probed using STA at various temperatures and pressures in the range of 25 – 100 °C and 0.01 – 1.0 atm, respectively. The use of a dynamic temperature range allows for the generalization of the adsorption model developed previously for a single temperature and $CO_2$ pressure (i.e. 40 °C and 0.15 atm).

As expected, adsorption isotherms maintain the same overall shape with increasing temperature. However, θ values decrease while $\Delta H°_{ads}$ values become more negative, suggesting that a distribution of $CO_2$ binding sites exists on the surface of ED-SBA-15, and that entropic balancing ($T\Delta S°_{ads}$) of the enthalpy of adsorption at elevated temperatures disfavors $CO_2$ binding events for diamine sites associated with less exothermic heats of adsorption.

With these results in mind, a Langmuirian adsorption model was developed with the assumption that $\Delta S°_{ads}$ is relatively constant across the distribution of $CO_2$ binding sites. Using these variables and assumptions, we sought to minimize residual error in our calculated θ and $\Delta H°_{ads}$ values when fitting the experimental data. Preliminary results are shown for $CO_2$ adsorption with ED-SAB-15 at 25 °C in Figure 4. Further work to determine the optimal number of binding sites needed to best model the data, as well as their percent contribution to the overall experimental binding isotherm at the different temperatures tested, is currently underway.

**Progress**

We have demonstrated the synthesis of a class of highly porous carbon-based sorbents for applications of high-pressure $CO_2$ capture from natural gas. The carbon sorbents were prepared through a two-step carbonization and activation process based upon a polyaniline crosslinked polymer network. The pore size distribution can be tuned by simply varying the carbonization temperature. These porous carbons, exhibiting a

maximum surface area of 4196 m$^2$ g$^{-1}$, achieved a record-high $CO_2$ capacity at ambient temperature and elevated pressures (28.3 mmol g$^{-1}$ total adsorption at 25 °C and 30 bar) as compared to previously reported carbon sorbents. Furthermore, these porous carbons show good $CO_2/CH_4$ selectivity under conditions relevant to $CO_2$ separation from natural gas mixtures. In addition, they can be fully regenerated by a conventional pressure swing adsorption (PSA) process, showing excellent stability during multiple cycles at elevated adsorption pressures. Moreover, this work has investigated the relationship between $CO_2$ uptake and pore size. It was found that pores with diameters smaller than 4 nm are mainly responsible for the $CO_2$ uptake at 25 °C and 30 bar. Finally, the impact of pore size and nitrogen functionality were investigated based on grand canonical Monte Carlo (GCMC) simulations. Quantitative predictions of the pore-confined $CO_2$ fluid densities were obtained and validated based upon the reasonable match of the simulation results with the experimental measurements. This work provides useful insights into the development of sorbent materials tailored for a specific $CO_2$ capture application, in particular, high-pressure $CO_2$ capture from natural gas.

**Future Plans**

Gas diffusion and adsorption kinetics is one of the key factors in practical separation, as it governs the separation efficiency and productivity. The carbon sorbents developed in this work should be carefully characterized on their gas uptake kinetics. There are a number of possible approaches towards this end, including thermogravimetric analysis (TGA) and magnetic suspension balance, etc. In addition, to evaluate the true potential of an adsorbent, rigorous simulation and optimization of the cyclic adsorption processes are required, which should be carried out in the future. Typical sorbent-based gas separation processes alternate between the adsorption and desorption steps. Depending on the adsorption and desorption conditions, the processes can be categorized as temperature swing adsorption (TSA), pressure swing adsorption (PSA), and pressure-vacuum swing adsorption (PVSA).

Natural gas, with methane as a major component, has been widely used as fuel for vehicles. It is advantageous over gasoline in that it provides more efficient combustion with higher energy per unit mass; and it is cheaper and cleaner. However, the main obstacle of natural gas involves its low energy density per unit volume. To overcome this challenge, high-pressure storage at ambient temperature or storage in liquid form at low temperatures is often required, which would impose potential safety hazard and/or increased cost. Methane storage in porous materials has been considered as a promising alternative, which operates at relatively less demanding temperatures and pressures. The polyaniline-derived carbon (SU-AC) can be a promising candidate for methane storage, given its ultra-high surface area and large pore volume.

**Publications and Patents**
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