

# Asphalt-Derived High Surface Area Activated Porous Carbons for Carbon Dioxide Capture

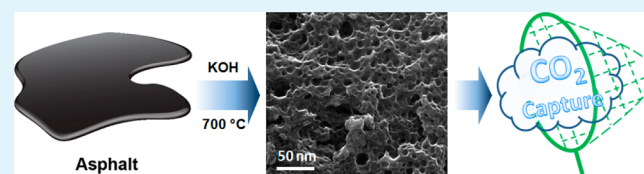
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## Supporting Information

**ABSTRACT:** Research activity toward the development of new sorbents for carbon dioxide (CO<sub>2</sub>) capture have been increasing quickly. Despite the variety of existing materials with high surface areas and high CO<sub>2</sub> uptake performances, the cost of the materials remains a dominant factor in slowing their industrial applications. Here we report preparation and CO<sub>2</sub> uptake performance of microporous carbon materials synthesized from asphalt, a very inexpensive carbon source. Carbonization of asphalt with potassium hydroxide (KOH) at high temperatures (>600 °C) yields porous carbon materials (A-PC) with high surface areas of up to 2780 m<sup>2</sup> g<sup>-1</sup> and high CO<sub>2</sub> uptake performance of 21 mmol g<sup>-1</sup> or 93 wt % at 30 bar and 25 °C. Furthermore, nitrogen doping and reduction with hydrogen yields active N-doped materials (A-NPC and A-rNPC) containing up to 9.3% nitrogen, making them nucleophilic porous carbons with further increase in the Brunauer–Emmett–Teller (BET) surface areas up to 2860 m<sup>2</sup> g<sup>-1</sup> for A-NPC and CO<sub>2</sub> uptake to 26 mmol g<sup>-1</sup> or 114 wt % at 30 bar and 25 °C for A-rNPC. This is the highest reported CO<sub>2</sub> uptake among the family of the activated porous carbonaceous materials. Thus, the porous carbon materials from asphalt have excellent properties for reversibly capturing CO<sub>2</sub> at the well-head during the extraction of natural gas, a naturally occurring high pressure source of CO<sub>2</sub>. Through a pressure swing sorption process, when the asphalt-derived material is returned to 1 bar, the CO<sub>2</sub> is released, thereby rendering a reversible capture medium that is highly efficient yet very inexpensive.

**KEYWORDS:** asphalt, CO<sub>2</sub> capture, porous carbonaceous materials, carbonization, nitrogen addition



## INTRODUCTION

Global climate change is the main environmental concern that might be directly affected by anthropogenic carbon dioxide (CO<sub>2</sub>) emission sources, which include industrial power plants, refineries, and natural gas wells, the last having CO<sub>2</sub> contents that can range from 1 to 70 mol % depending on the region of the world.<sup>1,2</sup> Therefore, efficient and reversible CO<sub>2</sub> capture from flue gas or from the higher pressure natural gas wells remains important in the use of carbon fuels if we are to maintain high standards of environmental stewardship, or the so-called “green carbon” approach.<sup>3–6</sup> In the sorption processes, in addition to the highly used aqueous amine solvents and membrane technologies, solid sorbents such as activated carbon, zeolites and, more recently, metal organic frameworks (MOFs) are promising alternative materials for capturing CO<sub>2</sub>.<sup>7–9</sup> Despite the many new solid sorbents developed in past years, cost remains a dominant factor when it comes to choosing the ultimate material.

Within CO<sub>2</sub> capture technologies, compression and separation of CO<sub>2</sub> at high pressures, high flow rates and low partial pressures of CO<sub>2</sub> remains a challenge for next-generation solid sorbents. Although aqueous amine solutions are among the most common industrial processes for CO<sub>2</sub> capture,<sup>10</sup> the process is corrosive and energy intensive due to the high energy requirements for regeneration of the amines, and their large

space requirements exclude off-shore use. Solid sorbents are promising alternative technologies for CO<sub>2</sub> capture,<sup>8</sup> and they project several advantages over conventional separation technologies. These include lower energy regeneration requirements, higher capacity and selectivity, and easier handling of the noncorrosive solids.<sup>8</sup> Generally, lower heat capacities, faster kinetics of sorption and desorption, and mechanical strength of solid sorbents are the primary advantages of solid sorbents for the use of pressure swing methods of CO<sub>2</sub> gas separation.<sup>11,12</sup>

An advantage of the meso- and microporous activated carbon materials over the other solid sorbents are the low cost of raw materials. The availability of a wide variety of carbon sources (e.g., coals, polymeric materials, coke pitch, wood, biomass, and industrial byproducts) makes activated carbons cost-effective at the industrial production stage. Recently, we reported porous carbon materials synthesized from sulfur and nitrogen containing polymers. These afforded sulfur and nitrogen-containing porous carbons, SPC and NPC, respectively, which showed superior CO<sub>2</sub> uptake at higher pressures and greater CO<sub>2</sub>/CH<sub>4</sub> gas separation selectivity relative to the most

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common solid sorbents such as activated carbon, zeolites and MOFs.<sup>13</sup>

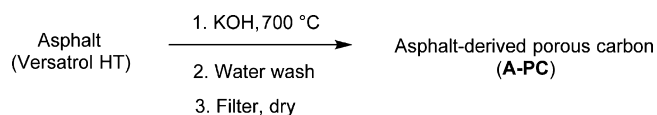
Here we report template free<sup>14,15</sup> synthesis and characterization of activated porous carbons from asphalt, which serves as a very inexpensive carbon source, and the synthesis is done in one step. In general, the structure of asphalt is complex, which mainly consists of asphaltenes, the toluene or benzene soluble portion of crude asphalt.<sup>16,17</sup> Asphaltenes contains nanosized conjugated aromatic domains that are linked by small aliphatic side chains with heteroatom containing-polar functional groups, which induces van der Waals, hydrogen bonding and charge-transfer interactions to form porous asphaltene aggregates.<sup>18,19</sup> Therefore, activation of crude asphalt formed micro- and mesoporous carbon materials that have high surface areas, which could be further activated by nitrogen impregnation, to yield activated porous carbons with even higher CO<sub>2</sub> uptake performances than SPC and NPC.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Porous Materials.

Porous carbons were prepared by carbonization of mixtures of asphalt and potassium hydroxide (KOH) at elevated temperatures under inert atmosphere (Ar). The treatment of asphalt with KOH was performed at various temperatures (200–800 °C) and different asphalt:KOH weight ratios (varied from 1:1 to 1:4). The CO<sub>2</sub> uptake performance of the final porous carbon materials (Figures S1 and S2, Supporting Information) was evaluated based upon the parameter changes in the synthesis. The asphalt-derived porous carbon is designated as A-PC. The highest surface area A-PC was synthesized at 700 °C (Scheme 1) with a weight ratio of asphalt:KOH = 1:4 (Figure S1, Supporting Information).

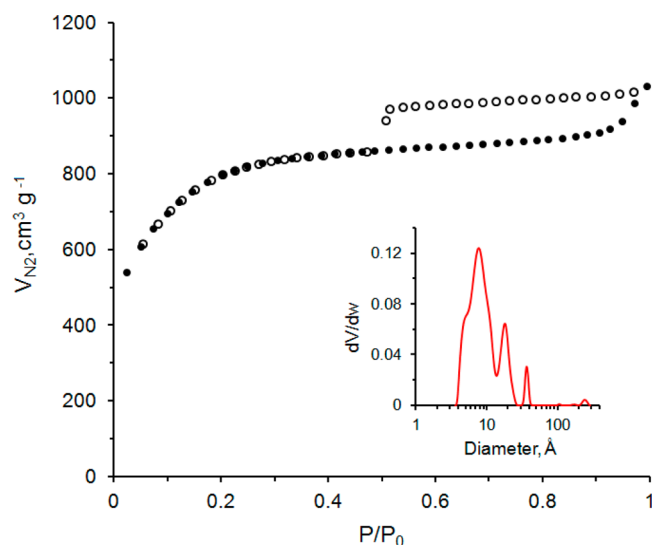
#### Scheme 1. Synthesis of Highest Surface Area A-PC



As shown in Figure 1, A-PC has a steep nitrogen uptake at low pressures (0–0.3  $P/P_0$ ), and has a typical type IV sorption isotherm, indicating meso-porosity of the material (Figure 1, inset). The Brunauer–Emmett–Teller (BET) surface area (2780 m<sup>2</sup> g<sup>-1</sup>) and the pore volume (1.17 cm<sup>3</sup> g<sup>-1</sup>) were calculated from the nitrogen isotherms (Table 1). X-ray photoelectron spectroscopy (XPS) of the A-PC showed C 1s and O 1s signals, with ~10% oxygen content, assigned to C–O and C=O functional groups (Figure S3, Supporting Information).

Scanning electron microscopy (SEM) images of the A-PC show porous material with a uniform distribution of the pores, as shown in Figure 2. Uniform distribution of the pores is further indicated by the transmission electron microscopy (TEM) image (Figure 2b) with pore diameters >2 nm. This is close to the values determined from the nitrogen absorption isotherms.

Treatment of A-PCs with NH<sub>3</sub> at elevated temperatures resulted in asphalt-derived N-impregnated porous carbon materials (A-NPC). The nitrogen content (3–9% from 0%) and the surface area 2860 m<sup>2</sup> g<sup>-1</sup> increased after treatment of A-PCs with NH<sub>3</sub> at higher temperatures (Figure S4, Supporting Information), as shown in Tables 1 and 2. This leads to the

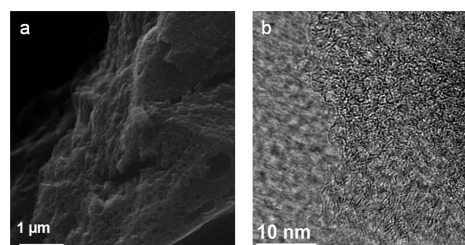


**Figure 1.** Nitrogen sorption isotherms for A-PC at 77 K. Absorption (filled symbols) and desorption (empty symbols). Inset: differential nonlocal density functional theory (NLDFT) pore size distributions curve.

**Table 1. Properties and CO<sub>2</sub> Uptake Performances of Activated Porous Carbons**

| samples           | $S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup> | pore volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup> | density (g cm <sup>-3</sup> ) | CO <sub>2</sub> uptake capacity at 30 bar <sup>b</sup> |      |
|-------------------|---|---|-------------------------------|--|------|
|                   |   |   |                               | mmol g <sup>-1</sup>                                   | wt % |
| A-PC              | 2780  | 1.17  | 1.78                          | 21.1   | 93   |
| A-NPC             | 2860  | 1.20  | 2.00                          | 23.8   | 104  |
| A-rNPC            | 2580  | 1.09  | 2.10                          | 26.0   | 114  |
| SPC               | 2500  | 1.01  | 2.21                          | 18.4   | 81   |
| NPC               | 1490  | 1.40  | 1.8                           | 14.7   | 65   |
| rNPC <sup>c</sup> | 1450  | 1.43  | 1.8                           | 16.8   | 74   |

<sup>a</sup>Estimated from N<sub>2</sub> absorption isotherms at 77 K; samples dried at 200 °C for 20 h prior to the measurements. <sup>b</sup>CO<sub>2</sub> uptake at 23 °C. <sup>c</sup>Prepared by H<sub>2</sub> reduction of NPC at 600 °C.<sup>13</sup>



**Figure 2.** (a) SEM and (b) TEM images of the A-PC.

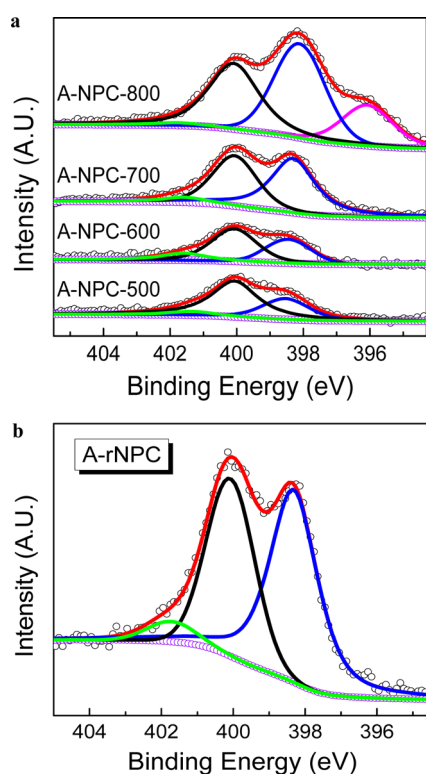
modified porous material of up to 9.3% N concentration obtained at 800 °C. At lower NH<sub>3</sub> treatment temperatures, the content of nitrogen decreased proportionally, reaching 2.7% at 500 °C (Table 2).

The surface N-bonding configurations reveal three main nitrogen functional groups in the surface of the carbon framework. As shown in Figure 3, the XPS N 1s spectra at variable doping temperatures deconvoluted into three peaks with binding energies at 399.0, 400.7, and 401.7 eV. These are in the range of typical binding energies corresponding to pyridinic N, pyrrolic N, and graphitic N, respectively. While

**Table 2. Elemental Composition and CO<sub>2</sub> Uptake Performances of Activated Porous Carbons That Were Aminated with NH<sub>3</sub> at 500–800 °C**

| samples <sup>a</sup> | XPS  |     |     |              |             |              | CO <sub>2</sub> uptake capacity at 30 bar <sup>b</sup> |      |
|----------------------|------|-----|-----|--------------|-------------|--------------|--|------|
|                      | C%   | O%  | N%  | pyridinic N% | pyrrolic N% | graphitic N% | mmol g <sup>-1</sup>                                   | wt % |
| A-NPC(500)           | 91.1 | 6.1 | 2.7 | 29.7         | 63.3        | 7.0          | 23.2   | 102  |
| A-NPC(600)           | 90.6 | 6.4 | 3.0 | 33.1         | 52.6        | 14.3         | 23.2   | 102  |
| A-NPC(700)           | 91.1 | 4.2 | 4.7 | 53.2         | 41.4        | 5.4          | 23.8   | 104  |
| A-NPC(800)           | 81.0 | 9.7 | 9.3 | 52.3         | 45.4        | 2.3          | 20.9   | 92   |
| A-rNPC               | 88.0 | 7.5 | 4.5 | 55.1         | 40.3        | 4.6          | 26.0   | 114  |

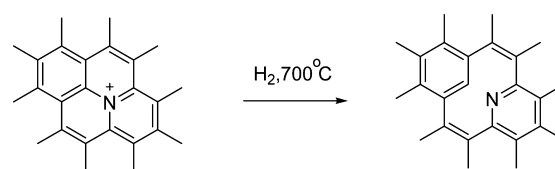
<sup>a</sup>The temperature of amination is shown in parentheses. <sup>b</sup>CO<sub>2</sub> uptake at 23 °C.



**Figure 3.** High-resolution XPS N 1s spectra of the (a) A-NPC formed at various NH<sub>3</sub> treatment temperatures, and (b) A-rNPC formed after reduction with H<sub>2</sub> at 700 °C. Experimental data are the open circles and the fitted curves are the solid lines.

lower temperature (500 °C) NH<sub>3</sub> treatment primarily leads to pyrrolic type functional groups, treatment at higher temperatures (800 °C) results in pyridinic and graphitic nitrogens.<sup>20</sup> The new peak at a binding energy of 396.0 was observed at 800 °C, which is assigned to the N–Si binding energy. It is likely that at higher pyrolysis temperatures, silica-doping from the quartz tube occurs, which also results in lower CO<sub>2</sub> uptake (Table 2). Further H<sub>2</sub> treatment of A-NPC at 700 °C with the intent of reducing the amines resulted in the reduced porous carbon material (A-rNPC). The elemental composition and the surface area of the A-rNPC were investigated using XPS (Figure 3b and Table 2). There is noticeable change in the graphitic nitrogen signal after the H<sub>2</sub> reduction of A-NPC, which decreased from 5.4% to 4.6% and an increase in the concentration of the pyridinic nitrogen signal from 53.2% to 55.1% (Table 2). This suggests the H<sub>2</sub>-induced transformation of graphitic nitrogen to the pyridinic nitrogen (Scheme 2). The proposed mechanistic pathway for H<sub>2</sub> reductive N–C bond cleavage is shown in Figure S5, eq 1 (Supporting Information).

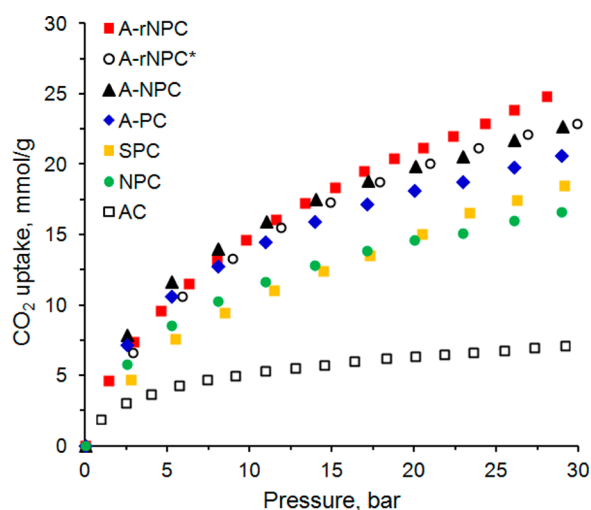
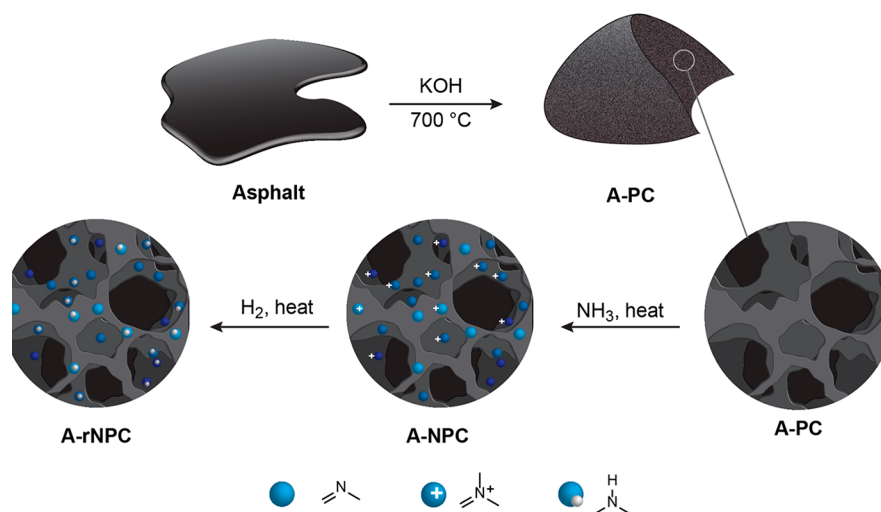
### Scheme 2. Conversion of Graphitic Nitrogen into Pyridinic Nitrogen during the Reduction with H<sub>2</sub>



An increase in the basic character of the nitrogen functional groups would be anticipated due to the H<sub>2</sub> reduction of the pyridinic nitrogens to aliphatic nitrogens (Figure S5, eq 2, Supporting Information); however, we were not able to detect an increase in the pyrrolic nitrogen content during the H<sub>2</sub> reduction. Instead, the H<sub>2</sub> reduction could be contributing to the changes in the pore structures, which leads to the decrease in the BET surface area. Because the nitrogen sorption isotherms did change considerably during both the N-impregnation and reduction processes (Figure S6, Supporting Information), we conclude that such activation has substantial effect on the morphological parameters of the porous carbons. Similar behavior was observed during the activation of porous carbons with NH<sub>3</sub>, where the authors of that study explained the observed increase in the surface area by the reaction between the carbon lattice and NH<sub>3</sub> to afford an evolution of methane. The gaseous evolution can increase the surface area.<sup>21</sup> Schematic representation of the synthetic route for the A-rNPC is shown in Scheme 3.

**CO<sub>2</sub> Uptake.** Activated carbons with a wide variety of surface parameters including surface area, pore structure and active sites on the surface, have been widely used as gas sorbents. SPC and NPC were prepared from the carbonization of poly[(2-hydroxymethyl)thiophene] and poly(acrylonitrile), respectively.<sup>13</sup> SPC and NPC showed high CO<sub>2</sub> uptake 18.4 mmol g<sup>-1</sup> (82 wt %) and 14.7 mmol g<sup>-1</sup> (65 wt %) (Table 1), respectively; comparable or better than conventional solid sorbents such as activated carbons, zeolites and MOFs.<sup>13</sup> Shown in Figure 4 are the CO<sub>2</sub> uptake of the activated porous carbons from asphalt (A-PC, A-NPC, and A-rNPC) along with the SPC, NPC, and commercial activated carbon (AC), measured by the volumetric method at room temperature over the pressure range 0 to 30 bar. 30 bar was chosen as the upper pressure limit from the approximation that a 300 bar natural gas well-head pressure containing ~10% CO<sub>2</sub> has 30 bar partial pressure of CO<sub>2</sub>. Volumetric CO<sub>2</sub> uptakes show little hysteresis, which suggests the reversible nature of CO<sub>2</sub> uptake of the materials. No degradation of the porous carbons is observed during the CO<sub>2</sub> sorption–desorption process from 0 to 30 bar (Figure S7, Supporting Information) or over 8 cycles (Figure S8, Supporting Information). CO<sub>2</sub> uptake at a pressure

Scheme 3. Schematic Illustration of the Preparation of A-NPC and A-rNPC



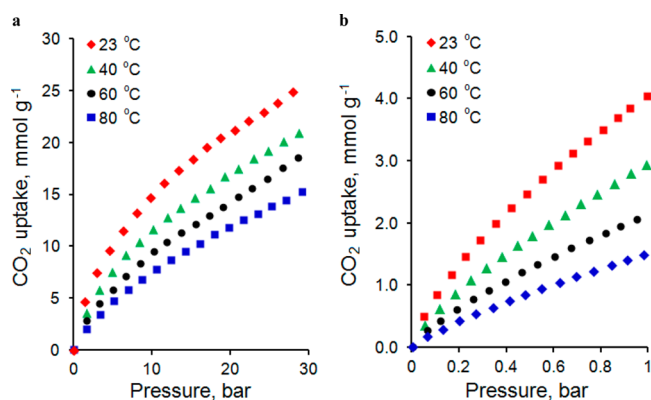
**Figure 4.** Comparison of volumetric and gravimetric  $\text{CO}_2$  uptake of A-PC, A-NPC and A-rNPC with the other porous carbon sorbents at 23 °C. An asterisk indicates gravimetrically performed absolute  $\text{CO}_2$  uptake of A-rNPC at 25 °C (Figures S9–S11, Supporting Information).

of 30 bar are given in Tables 1 and 2, and the uptake capacities are up to 26  $\text{mmol g}^{-1}$  (114 wt %), which are not only the highest reported among the activated carbons<sup>22–24</sup> but also comparable with MOFs used under similar conditions.<sup>25–28</sup> Unlike MOFs, these can be prepared at a much lower cost and in one or two thermalization steps from asphalt.

A-rNPC has the highest  $\text{CO}_2$  uptake performance at 30 bar, although the highest surface area is obtained for A-NPC. The volumetric uptake measurements correlate with the gravimetric uptake measurements (Figures 4, S9–S11, Supporting Information). As we increase the N-impregnation temperature (from 100 to 800 °C, Figure S4, Supporting Information), the nitrogen content starts to increase gradually, which affects the  $\text{CO}_2$  uptake performance of the A-NPCs (Table 2). Thus, we conclude that the basic nitrogen functional groups (pyridinic and pyrrolic) are essential for the enhanced  $\text{CO}_2$  uptake performance of the porous carbon material. At lower  $\text{NH}_3$  treatment temperatures, the concentration of the pyrrolic nitrogens increases while pyridinic nitrogens decrease (Table 2). These results indicated that the pyrolysis temperature

during the  $\text{NH}_3$  treatment is one of the critical factors in determining the  $\text{CO}_2$  uptake performance.

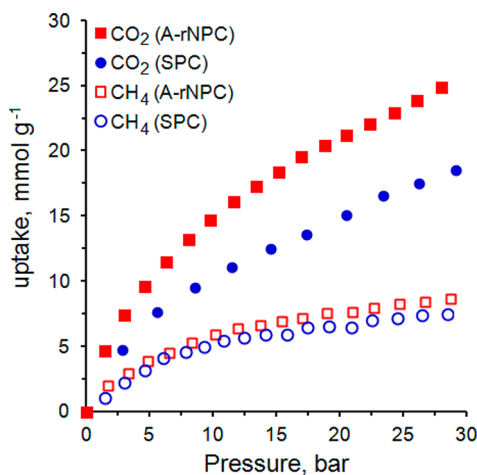
Figure 5 shows the high and low pressure  $\text{CO}_2$  uptake of A-rNPC as the temperature increases. As in other solid sorbents



**Figure 5.** Volumetric uptake of  $\text{CO}_2$  on A-rNPC as a function of temperature. (a) Higher pressure range of 0 to 30 bar; (b) lower pressure range of 0 to 1 bar.

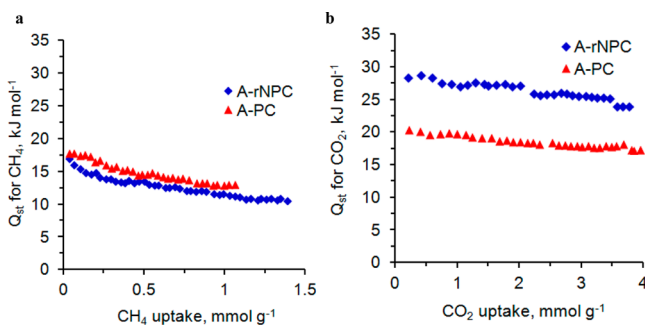
such as activated carbons, zeolites and MOFs, the capacity decreases with increasing temperature. However, when compared with commercial activated carbon and SPC, the A-rNPC has a greater  $\text{CO}_2$  uptake at higher temperatures.

One of the key properties of the solid sorbents is their  $\text{CO}_2/\text{CH}_4$  selectivity.  $\text{CO}_2:\text{CH}_4$  selectivity in this paper is defined as the molar ratios of sorbed  $\text{CO}_2$  and  $\text{CH}_4$  ( $\nu_{\text{CO}_2}/\nu_{\text{CH}_4}$ ). In order to evaluate the  $\text{CO}_2:\text{CH}_4$  selectivity of A-PC, A-NPC and A-rNPCs, we compared  $\text{CH}_4$  uptake performances with SPC, activated carbon and ZIF-8 sorbents at 23 °C. Figure 6 shows the comparison of the  $\text{CO}_2$  and  $\text{CH}_4$  sorption capacities of A-rNPC and SPC. A-rNPC has higher  $\text{CH}_4$  (8.6  $\text{mmol g}^{-1}$ ) uptake relative to SPC (7.7  $\text{mmol g}^{-1}$ ) at 30 bar, although both A-rNPC and SPC have similar apparent surface areas of 2580  $\text{m}^2 \text{g}^{-1}$  and 2500  $\text{m}^2 \text{g}^{-1}$ , respectively. The molar ratios of sorbed  $\text{CO}_2$  and  $\text{CH}_4$  ( $\nu_{\text{CO}_2}/\nu_{\text{CH}_4}$ ) were estimated by the ratios of the amount of the absorbed gases at 30 bar, which was highest for A-rNPC (3.0), as compared to values for SPC (2.6), activated carbon (1.5) and ZIF-8 (1.9).<sup>13</sup>



**Figure 6.** Volumetric CO<sub>2</sub> (filled symbols) and CH<sub>4</sub> (empty symbols) uptake of A-rNPC (red) and SPC (blue) at 23 °C.

The isosteric heat of absorption ( $Q_{st}$ ) of CO<sub>2</sub> and CH<sub>4</sub> on the surfaces of A-PC and A-rNPC were calculated using low pressure CO<sub>2</sub> sorption isotherms at 0 and 23 °C, as shown in Figure 7. The values for absorption of CH<sub>4</sub> were found to be



**Figure 7.** Isothermic heat of absorption ( $Q_{st}$ ) using (a) CH<sub>4</sub> and (b) CO<sub>2</sub> on A-PC and A-rNPC at 0 and 23 °C.

comparable for A-PC and A-rNPC at 17 to 20 kJ mol<sup>-1</sup> (Figure 7a), and they have relatively constant values during the filling of the pores. This points to the nucleophilic sites that can interact with CO<sub>2</sub> but that do not have strong interactions with sorbed CH<sub>4</sub> molecules.<sup>13</sup> The observed values of 17 to 20 kJ mol<sup>-1</sup> are close to the reported values for the absorption of methane on MOFs (MIL-53, 17.0 kJ mol<sup>-1</sup>)<sup>29</sup> and zeolites (NaY, 17–17.8 kJ mol<sup>-1</sup>)<sup>30</sup> and are all above the liquefaction enthalpy of methane (8.2 kJ mol<sup>-1</sup>). Contrarily, the absorption energies of CO<sub>2</sub> changes considerably between A-PC (20 kJ mol<sup>-1</sup>) and A-rNPC (29 kJ mol<sup>-1</sup>), as seen in Figure 7b, which is indicative of the stronger interactions between nitrogen containing nucleophilic sites of the pores in A-rNPC with the CO<sub>2</sub> molecules. During the increase in the filling of the pores, the CO<sub>2</sub> absorption enthalpy of A-PC starts to decrease and eventually reaches the enthalpy of liquefaction of CO<sub>2</sub> (17.2 kJ mol<sup>-1</sup>) (Figure 7b), while A-rNPC reaches its lowest value at 24 kJ mol<sup>-1</sup> (Figure 7b). Relatively weak enthalpy for A-PC, in contrast to the previously reported SPC (57 kJ mol<sup>-1</sup>), suggests a better reversible CO<sub>2</sub> uptake performance of undoped A-PC for the more efficient removal of CO<sub>2</sub> at low pressures, in comparison to the nitrogen doped A-rNPC and sulfur containing SPC. Higher sorption enthalpy for the sulfur containing SPC than A-rNPC points to the stronger

interactions of nucleophilic sulfur-containing sites of the pores with CO<sub>2</sub> molecules. It is also worthy to mention that the SPC and A-rNPC have smaller CH<sub>4</sub> sorption selectivity in comparison to the CO<sub>2</sub> sorption selectivity (Figure 6). This points to a weak interaction of CH<sub>4</sub> with the sulfur and nitrogen functional groups in the pores. CO<sub>2</sub> has a larger quadrupole moment (13.4 C m<sup>2</sup>) than does the CH<sub>4</sub> (nonpolar).

## CONCLUSION

In summary, we have demonstrated the successful synthesis of microporous active carbon from asphalt with uniform distribution of pore sizes and the subsequent activation with nitrogen functional groups. Changing the preparation conditions, the porous materials possess variable surface areas and nitrogen contents. Activated porous carbons from asphalt have been shown to have CO<sub>2</sub> uptake of 26 mmol g<sup>-1</sup> (114 wt %), which is the highest for any porous carbons and also one of the highest among all the porous materials. Additionally, nitrogen functionalized microporous carbon materials exhibit greater CO<sub>2</sub>:CH<sub>4</sub> than the nucleophilic porous materials prepared from the heteroatom-containing organic polymers. These observations indicate the porous materials from asphalt are promising and very inexpensive sorbents for industrial applications where CO<sub>2</sub> is removed from natural gas streams.

## EXPERIMENTAL SECTION

**Materials.** Versatrol HT, Versatrol M, Asphasol Supreme and Natural asphalt from Chile were kindly provided by MI SWACO, a Schlumberger Company. Untreated Gilsonite and Untreated Gilsonite Substitute are both provide by Prince Energy. Activated carbon Darco G-60 and KOH were used as received from Sigma-Aldrich.

**Synthesis of Asphalt Derived Porous Carbon (A-PC).** 0.50 g of asphalt (Versatrol HT) and 1.50 g (26.7 mmol) of KOH were mixed well in a mortar.<sup>13</sup> The mixture was heated on a quartz boat inserted within a quartz tube furnace at 700 °C for 1 h with Ar flow at 500 sccm, 1 atm, before being permitted to cool to room temperature. Then the product was washed thoroughly with DI water and acetone until the filtrate attained pH 7. The A-PC powder was dried in an oven at 100 °C until a constant weight was achieved to afford 0.22 g of A-PC. Under comparable conditions different types of asphalt were screened: natural asphalt from Chile, Versatrol M, Asphasol Supreme, Untreated Gilsonite and Untreated Gilsonite Substitute; Figure S12 (Supporting Information) shows the comparative CO<sub>2</sub> uptake data. Moreover, higher CO<sub>2</sub> uptake was reached by preliminary pretreatment of Versatrol M for 2 h at 400 °C and then activating at 800 °C for 1 h (Figure S13, Supporting Information). Also, increasing the asphalt:KOH ratio to 1:5 and the temperature of the pretreatment to 750 °C for Natural asphalt, increased CO<sub>2</sub> uptake (Figure S14, Supporting Information).

**Synthesis of Nitrogen Doped Asphalt Derived Porous Carbon (A-NPC) and Reduced Nitrogen Doped Asphalt Derived Porous Carbon (A-rNPC).** 0.20 g of A-PC powder was placed in a quartz boat and transferred into to a quartz tube furnace. The powder was heated at 700 °C for 1 h with NH<sub>3</sub> flow at 100 sccm, 1 atm, before cooling to room temperature to afford 0.17 g of A-NPC. To synthesize A-rNPC, 0.20 g of A-NPC powder was heated at 700 °C for 1 h with H<sub>2</sub> flow at 100 sccm and Ar flow at 200 sccm at 1 atm to afford 0.18 g of A-rNPC.

**Volumetric Sorption.** Volumetric sorption measurements of CO<sub>2</sub> or CH<sub>4</sub>, or premixed gas were carried out in an automated Sievert instrument<sup>13</sup> (Setaram PCTPro). Typically, ~120 mg of sorbent was placed in a stainless steel sample cell and pretreated at 150 °C for 2 h under vacuum (~20 mTorr). The sample volume was calibrated by helium before the sorption measurement.

**Gravimetric Sorption.** Gravimetric sorption measurements of CO<sub>2</sub> were carried out in a Rubotherm magnetic suspension balance<sup>31</sup>

(Rubotherm, Germany). A blank test without sample was used to measure the weight and volume of the empty sample holder. For a typical measurement, ~120 mg of sorbent was placed in the sample holder and pretreated at 150 °C for 2 h under vacuum (~20 mTorr). A buoyancy test with helium was then used to measure the sample weight and sample volume before the sorption measurement.

**Characterization.** The XPS were obtained on a PHI Quantera SXM scanning X-ray microprobe system using a 100 μm X-ray beam of which the takeoff angle was 45° and pass energy was 140 eV for the survey and 26 eV for the high resolution elemental analysis. The surface areas, pore volumes and pore size distributions (Barrett–Joyner–Halenda, BJH) of different samples were obtained using an automated BET surface analyzer (Quantachrome Autosorb-3b). The samples were heated at 150 °C for 15 h under vacuum (20 mTorr) before each measurement. Scanning electron microscopy (SEM) images were taken at 20 keV in a FEI Quanta 400 high resolution field emission scanning electron microscope. High resolution transmission electron microscopy (TEM) images were obtained in a 2100F field emission gun transmission electron microscope. The porous carbon samples were transferred to a C-flat TEM grid (Protochips).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Optimization of the asphalt:KOH ratio during the carbonization process, optimization of the temperature during the carbonization process, XPS of A-PC, optimization of the NH<sub>3</sub> treatment temperature during N-impregnation of A-PC, proposed mechanisms for high temperature H<sub>2</sub> reduction of A-NPC, nitrogen sorption isotherms for A-PC, A-NPC, and A-rNPC, CO<sub>2</sub> sorption–desorption cycle on the A-NPC over a pressure range from 0 to 30 bar at 23 °C, eight consecutive CO<sub>2</sub> sorption–desorption cycles on the A-NPC over a pressure range from 0 to 30 bar at 23 °C, gravimetric CO<sub>2</sub> uptake on A-PC, comparison of the volumetric and gravimetric CO<sub>2</sub> uptake for A-PC at 23 and 25 °C, gravimetric CO<sub>2</sub> uptake on the A-rNPC, volumetric CO<sub>2</sub> uptake of porous carbons derived from different asphalt sources over a pressure range from 0 to 30 bar at 23 °C, volumetric CO<sub>2</sub> uptake of porous carbons derived from Versatrol M under different activation conditions over a pressure range from 0 to 30 bar at 23 °C, and volumetric CO<sub>2</sub> uptake of porous carbons derived from natural asphalt under different activation conditions over a pressure range from 0 to 30 bar at 23 °C. 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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