Ultra-High Surface Area Activated Porous Asphalt for CO₂ Capture through Competitive Adsorption at High Pressures

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Here we report an improved method for activating asphalt to produce ultra-high surface area porous carbons. Pretreatment of asphalt (untreated Gilsonite, uGil) at 400 ºC for 3 h removes the more volatile organic compounds to form pretreated asphalt (uGil-P) material with a larger fraction of higher molecular weight π-conjugated asphaltenes. Subsequent activation of uGil-P at 900 ºC gives an ultra-high surface area (4200 m² g⁻¹) porous carbon material (uGil-900) with a mixed micro and mesoporous structure. uGil-900 shows enhanced room temperature CO₂ uptake capacity at 54 bar of 154 wt % (35 mmol g⁻¹). The CH₄ uptake capacity is 37.5 wt % (24 mmol g⁻¹) at 300 bar. These are relevant pressures in natural gas production. The room temperature working CO₂ uptake capacity for uGil-900 is 19.1 mmol g⁻¹ (84 wt %) at 20 bar and 32.6 mmol g⁻¹ (143 wt %) at 50 bar. In order to further assess the reliability of uGil-900 for CO₂ capture at elevated pressures, we studied competitive sorption of CO₂ and CH₄ on uGil-900 at pressures from 1 to 20 bar at 25 ºC. CO₂/CH₄ displacement constants were measured at 2 to 40 bar, and found to increase significantly with pressure and surface area.

1. Introduction

Climate change caused by the release of increased amounts of greenhouse gases into the atmosphere has resulted in growing demands for the development of alternative and environment friendly energy resources.[1-7] Despite many efforts made worldwide, fossil fuels remain the most economically viable source of energy.[8,9] Natural gas, however, often contains 2 to 10 % carbon dioxide (CO₂) as it comes from the well.[10,11] Thus, the separation of CO₂ from the hydrocarbon remains challenging since the typical aqueous amines such as ethanolamine only capture < 15 wt% CO₂, and their regeneration is energy intensive requiring ~125 ºC steam.[12,13] Physical sorption by solid sorbents such as porous carbons, nanoporous...
sieves, zeolites, porous polymers and metal-organic frameworks (MOFs) are among the promising separation alternatives for CO\textsubscript{2} capture, along with membrane technologies.\textsuperscript{[14-18]}

Particularly, high-pressure sorption has become increasingly attractive since there is no temperature swing required and it can also be considered for increased gas storage under pressure.\textsuperscript{[19]}

Carbonaceous materials, especially porous carbon materials, have been extensively used in gas separation processes.\textsuperscript{[14,20,21]} Differing types of porous materials could find specific practical applications depending on the employed separation system: gas-gas, gas-liquid, or liquid-liquid. The high thermal and electrical conductivity of porous carbon materials make them attractive for thermal swing adsorption (TSA)\textsuperscript{[22]} and electric swing adsorption (ESA)\textsuperscript{[23-25]} in addition to the pressure swing adsorption (PSA).\textsuperscript{[19,26]} Furthermore, the low cost, high specific surface area, high porosity, controlled narrow pore structures, surface functional groups, high mechanical strength and high apparent density (> 0.3 g/cm\textsuperscript{3}) are attractive features for porous carbons.\textsuperscript{[14]} Recently, we reported porous carbon material prepared from asphalt as an inexpensive carbon source.\textsuperscript{[27]} However, the highest CO\textsubscript{2} uptake performance was afforded by a specific type of the asphalt source that is rare and among the highest costing asphalts, and the surface area attained was 2800 m\textsuperscript{2} g\textsuperscript{-1} after activation.

Here, we show a synthesis of an ultra-high surface area porous carbon material routinely reaching 4200 m\textsuperscript{2} g\textsuperscript{-1} from readily available asphalt sources that are among the least expensive asphalt types. Pretreatment of raw asphalts at 400 °C to first remove volatile lower molecular weight organics, provides enhanced asphaltene aggregates. These asphaltene aggregates primarily consist of nanosized conjugated heteroatom-containing aromatic domains covalently linked by short aliphatic side-chains.\textsuperscript{[28-31]} These serve as a template for carbonization to prepare ultra-high surface area porous carbon materials. The potential for CO\textsubscript{2}/CH\textsubscript{4} separation using competitive adsorption on these ultra-high surface area porous carbon materials is demonstrated through the kinetics of gas displacement.\textsuperscript{[32,33]}
2. Results and Discussion

2.1 Synthesis and characterization of porous carbon materials. Asphalt is the heaviest fraction of oil, which consists of a mixture of high boiling organic molecules.\textsuperscript{[34]} A relatively well-defined fraction of heavy oil is the asphaltenes; a porous network that resulted from the combination large polyaromatic and polyaliphatic cyclic systems interconnected via short alkyl chains and complexes of non-covalent interactions.\textsuperscript{[35,36]} The thermogravimetric analysis (TGA) of various asphalts from different sources reveals the similar weight loss profiles for most of the studied samples, as shown in Figure 1. Except for Asphasol Supreme, which primarily consist of various inorganic sulfate salts, all studied asphalts start to lose weight beginning at ~400 °C, and they lose from ~60 to 80 % of their original weight by 500 °C. The weight loss is mainly due to the evaporation of lower molecular weight volatile organic oil residues. These volatile organic oil residues are slower to carbonization during activation with KOH.

Direct activation of raw asphalts with KOH in a single step resulted in porous carbons with smaller surface areas and lower gas uptake performances,\textsuperscript{[27]} except for Versatrol HT, which is the specific expensive type of asphalt that has a low amount of volatile component. Therefore, unlike the previously reported method of direct one step activation of asphalts with KOH,\textsuperscript{[27]} this work reports improved method of synthesis of porous carbons using two-step process as shown in Scheme 1, which nearly doubles the surface area of the porous carbons and substantially increased the CO\textsubscript{2}/CH\textsubscript{4} displacement constants (\(D\)).

After the raw asphalt (untreated Gilsonite, uGil) was treated at 400 °C for 3 h under inert atmosphere and ambient pressure in a tube furnace, it afforded pretreated asphalt (uGil-P) in 40 % yield (Scheme 1). X-ray photoelectron spectroscopy (XPS) analysis reveals a decrease in the relative amounts of oxygen functionalities after this thermalization step (see
Tables S1, S2 and Figures S1, S2) due to evaporation of various lower molecular weight oxygen-containing organic species, such as esters, ethers, alcohols and carboxyls. This pretreatment step is essential to form higher boiling species containing primarily carbon-rich polycyclic aromatic hydrocarbons that are more accessible for carbonization. Subsequent activation of uGil-P with 4 equivalents of KOH at various temperatures (600, 700, 800 and 900 °C) for 20 min gives porous carbons uGil-600, uGil-700, uGil-800 and uGil-900, respectively. The uGil-900 was characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (PXRD) and XPS (Figure 2). SEM images of the uGil-900 show formation of the mesoporous carbon structure, a typical morphology for activated carbons (Figure 2a). While the HRTEM displays the dominant presence of amorphous carbon, the HRTEM reveals the formation of graphitic crystalline stacked layers at the edges with the average stacking distance of ~ 3.4 Å (Figure 2b). Raman spectroscopy shows higher intensities of G and D as well as 2D bands upon increasing the activation temperatures, further indicating formation of larger crystalline graphitic domains at higher activation temperatures (Figure S3).

The PXRD patterns of bulk uGil-900 shown in Figure 2c displays two weak and broad peaks at 2θ = 23° and 44°. The absence of sharp peaks reveals mainly amorphous nature of material. 2θ = 23° corresponds to the 002 crystalline region of the diffractions for layering of graphitic carbons, and 2θ = 44° corresponds to the 010 region indicating to the formation of smaller two-dimensional lattice, agreeing well with the HRTEM result that the carbon has small crystallinity at the edges. Porous carbons were further characterized by XPS. Surface analyses reveal the presence of oxygen functionalities, and the relative oxygen content decreases as the activation temperature increases (Table 1). The oxygen content was raised relative to uGil-P due to hydroxide treatment. Figure 2d shows the deconvoluted peaks of high resolution XPS spectra (C 1s) of the uGil-900. From the deconvoluted C 1s peaks (Table S1), it is apparent that the oxygen-containing groups are predominantly in the form of ether,
epoxy and hydroxyl (C─O, C─O─C, and C─OH, 286.2 eV) groups. There are also carbonyl
(C=O, 287.4 eV) groups in the form of ketones or quinones and carboxyl (HO─C=O, 289.0
eV) groups. Note that the spectra were centered at 284.8 eV for the graphitic carbon
(C─C/C=C). Relative contributions of each functional group are summarized in Table S1.

Structural properties such as porosity, surface area, pore volume and pore size
distributions of porous carbons were characterized by means of nitrogen (N₂, 77 K) sorption
isotherms (Figure 3) and summarized in Table 1. These results are consistent with
morphologies revealed from the SEM and TEM analyses. The shape of the isotherms depends
on the carbonization temperature, and gradually transforms from Type-I, microporous
materials with a steep increase at low partial pressure, to mixed Type-I and Type-IV isotherms
with micro- and mesopores (Figure 3a). As a result, increase in carbonization temperature
from 600 ºC to 900 ºC gives substantial increase in Brunauer–Emmett–Teller (BET) specific
surface area (S_{BET}) from 2320 m² g⁻¹ to 4200 m² g⁻¹ and pore volumes from 1.31 cm³ g⁻¹ to
2.41 cm³ g⁻¹ (Figure S5). The average pore sizes also tend to increase with carbonization
temperature (Table 1). A dominant presence of microporous morphologies generated at lower
carbonization temperature is also noticeable from the higher apparent density for uGil-600
(Table 1). Collapsing of macro- and to some extent mesopores is common during the packing
of porous carbon materials under high pressure. It is noteworthy that the theoretical surface
area of a double sided separated graphene sheet is 2630 m² g⁻¹,[37] and such a high value for
surface area in the uGil-900 is explained by the stacking of the gas molecules within the pores.
The yield of the carbon material, from the uGil-P, decreased from 37 % to 13 % in increasing
the time from 10 to 60 min of KOH treatment at 900 ºC (Figure S6). Upon prolonged KOH
treatment at 900 ºC, the surface area also reduced to 2500 m² g⁻¹ (Figure S7), hence the short
activation time (15 to 20 min) at 900 ºC is the optimal condition for this ultra-high surface
area carbon.
The nitrogen adsorption-desorption isotherms exhibit hysteresis loops for **uGil-800** and **uGil-900**, reflecting the ink-bottle shaped mesopores. Further details of the pores are corroborated by the pore size distributions (PSDs) based on NLDFT models (Figure 3b). The results show that the porous carbons have narrow PSDs mainly centered in micro (~1.0 nm) and mesopore (~2 to 4 nm) regions. Mesoporosity expanded for **uGil-900** with the maximum at 2.0 nm (Figure 3b), which also resulted in larger average pore sizes (Table 1). It reveals that surface area gradually increases with the carbonization temperature as a result of the formation of mesopores. Further increase in the carbonization temperature or the heating time resulted in lowering of the surface area and the yield of the resultant porous material (Figure S6, S7).

### 2.2 High pressure CO$_2$ and CH$_4$ uptake

We recently reported asphalt-derived porous carbons (**A-PC**) prepared by a direct single step chemical carbonization method which possess high CO$_2$ and CH$_4$ uptake performances.$^{[27]}$ The pretreatment step disclosed here increased the surface area of the **A-PC** from 2800 m$^2$ g$^{-1}$ to 4200 m$^2$ g$^{-1}$ and permits us to use inexpensive asphalt sources. The highest surface area porous carbon, **uGil-900**, has uniform and narrow distribution of micro and mesoporocicity, exhibit exceptional room temperature CO$_2$ uptake capacity at 54 bar and CH$_4$ uptake capacity at 300 bar of 154 wt % (35 mmol g$^{-1}$) and 37.5 wt % (24 mmol g$^{-1}$), respectively. 54 bar is the critical point for CO$_2$ at 25 ºC. And 300 bar was chosen as a common working pressure of the natural gas wells. Excess CO$_2$ uptake isotherms were measured at 25 ºC, and as expected, **uGil-900** shows one of the highest CO$_2$ and CH$_4$ uptakes among the porous carbonaceous materials (Table 1 and Figures 4 and S8). The gas uptake performance of **uGil-900** is comparable with the ultra-high surface area MOFs used under similar conditions,$^{[38,39]}$ yet it is far less expensive to prepare. CO$_2$ uptake does not show any hysteresis, which suggests the reversible nature of CO$_2$ uptake of the materials. No degradation of the porous carbons is observed during the multiple CO$_2$ and CH$_4$
sorption-desorption processes from 0 to 54 bar and 0 to 300 bar, respectively (Figure S9). Excess CO\textsubscript{2} uptake isotherms reveal that at 54 bar \textit{uGil-900} still does not reach its saturation uptake. On the other hand, from the excess CH\textsubscript{4} uptake isotherm of \textit{uGil-900} (Figure 4b) it is clear that it reaches the saturation uptake at 90 bar (21.9 wt%).

We further estimated the absolute gas uptakes using the pore volume and the density of gases at 25 °C (Figure 4b).\textsuperscript{[27]} The room temperature absolute CO\textsubscript{2} and CH\textsubscript{4} uptake isotherms show higher uptakes than excess gas uptakes. For CH\textsubscript{4}, it reached the saturation uptake (37.5 wt%) and exhibits constant absolute uptake beyond 150 bar. However, the absolute CO\textsubscript{2} uptake isotherm still was not saturated, showing an increase in uptake with pressure, pointing to the exceedingly high absolute uptake of 154 wt% (Figure 4b), beyond the critical point of CO\textsubscript{2}. It is evident that \textit{uGil-900} has ultra-high surface area and reaches the ultimate CO\textsubscript{2} and CH\textsubscript{4} uptake capacity among the porous carbonaceous materials. The room temperature working CH\textsubscript{4} uptake capacity for \textit{uGil-900} is 11.6 mmol g\textsuperscript{-1} (18.5 wt %) at 30 bar and 16.1 mmol g\textsuperscript{-1} (257 wt %) at 60 bar, which can be calculated as the difference between the absolute uptake at low pressures (1 bar) and higher pressures (30 and 60 bar, respectively).

2.3 CO\textsubscript{2} versus CH\textsubscript{4} displacement measurements. The surface interactions of \textit{uGil-900} with CO\textsubscript{2} and CH\textsubscript{4} were investigated by analysis of isosteric heats of absorptions ($Q_{st}$) estimated using virial method (Figure 5). The isosteric heat of absorptions ($Q_{st}$) of CO\textsubscript{2} and CH\textsubscript{4} on the surface of \textit{uGil-900} was calculated using low pressure CO\textsubscript{2} and CH\textsubscript{4} sorption isotherms at 23 °C and 30 °C as shown in Figures S10 and S11. The $Q_{st}$ value of CH\textsubscript{4} was found to be 25 kJ mol\textsuperscript{-1} and gradually decreases to ~12 kJ mol\textsuperscript{-1} during the filling of the pores. This suggests the stronger affinity of CH\textsubscript{4} with the micropore surface of \textit{uGil-900} at low pressures, which is slowly dominated by CH\textsubscript{4}−CH\textsubscript{4} interactions at higher pressures as the pores begin to fill, ultimately reaching the liquefaction enthalpy of methane (8.2 kJ mol\textsuperscript{-1}).
The observed $Q_{st}$ value at initial loading (25 kJ mol$^{-1}$) for uGil-900 is slightly higher than the reported values for porous carbon materials, which could be ascribed to its narrow pore sizes and high micropore volume.$^{[40]}

For CO$_2$, which has a larger quadrupole moment (13.4 C m$^2$) than does the CH$_4$ (nonpolar), the $Q_{st}$ starts at much higher value, 50 kJ mol$^{-1}$ at initial gas loading and drops to 21 kJ mol$^{-1}$ as surface binding sites become less accessible and CO$_2$–CO$_2$ interactions become more important. The enthalpy of liquefaction of CO$_2$ is 17.2 kJ mol$^{-1}$. The higher $Q_{st}$ values for CO$_2$ than for CH$_4$ indicate overall stronger gas-surface and gas-gas interaction for CO$_2$ at low and high pressures.

In order to attain quantitative insight into the nature of gas-surface and gas-gas interactions within the pores of uGil-900 at higher pressures, we conducted dual (CO$_2$ and CH$_4$) absorption measurements at high pressures. Displacement of CH$_4$ by CO$_2$ from the CH$_4$ preadsorbed uGil-900 at various pressures was monitored as a function of time, enabling extraction of kinetic parameters. Figure 6 shows representative measurements describing multicomponent (CO$_2$ and CH$_4$) adsorptions on uGil-900 at 25 °C. In Figure 6a shown in red, preadsorbed uGil-900 with 20 bar CO$_2$ is subjected to the addition of another 20 bar CH$_4$ and the system is permitted to equilibrate, during which the relative weight change of the total gas mass is monitored (Figure 6b, in red). When an additional 30 bar of CH$_4$ added, the further gravimetric uptake on the carbon was minimal (Figure 6a), so the majority of the sorption sites on uGil-900 are already occupied by the CO$_2$. However, when on the preadsorbed uGil-900 with 20 bar CH$_4$ is subjected to another 20 bar of CO$_2$, and the system is permitted to equilibrate, rapid gravimetric uptake can be observed (Figure 6a, in blue and Figure 6b in black), suggesting that the initial CH$_4$ binding sites were replaced by the newly adsorbed CO$_2$.

Kinetics of the gas displacement were conducted in a Rubotherm magnetic suspension balance at 25 °C by sequential dosing of gases at various pressures and recording weight change over time (Figure 6b). The rate constant of the CH$_4$ displacement by coadsorbed CO$_2$
(k_{CO2}) was estimated from the positive slope of the kinetics curve, Figure 6b (black). And the rate constants of the CO2 displacement by CH4 (k_{CH4}) was estimated from the negative slopes of the kinetics curve, Figure 6b (red), since the displacement of CO2 by coadsorbed CH4 resulted in a decrease of the overall mass of the gas-adsorbed porous material. Scheme 2 illustrates the equilibrium of the competitive adsorption of CO2 and CH4. In the case of gas mixings (CO2 vs CH4), competitive adsorption proceeds at the same sites within the pores. However, as a result of differences in electronic structures, such as polarizability of CO2 vs CH4, CO2 can interact more efficiently with the polar surface functional groups such as C−OH, C=O, or C−O−C (Figure 2d) of the porous carbon. These measurements were repeated at pressure range of 2 to 40 bar (Figure S12-S14) and the rate constants for gas displacement were extracted (Table S3). The displacement constant (D_{CO2}) defined as the ratio of k_{CO2}/k_{CH4} was shown to increase with the total pressure. It is important to note that the displacement constant on molar basis (Table S3) is also increases with pressure from 2.2 (at 1 bar) to 22.8 (40 bar).

The effect of surface area on the D_{CO2} was analyzed by comparing the gas displacement measurements on porous carbons with different surface areas (Figure 7). Although there are small differences in D_{CO2} at lower pressures (<20 bar) between porous carbons with surface areas that range from 1500 to 4200 m^2 g^-1, uGil-900 shows the highest D_{CO2} at high pressure. Given a common pressure at natural gas extraction wells of ~ 300 bar, under kinetic conditions uGil-900 with the highest displacement constant, D_{CO2} can provide efficient selectivity of CO2 over CH4. While we investigated competitive adsorption of a 1:1 mixture of CO2:CH4, displacement constants also depend on the relative partial pressures of the components in the mixture, though further concentrations are not directly addressed here.

3. Conclusion

In summary, we have demonstrated the preparation ultra-high surface area porous carbon
materials from readily available asphalt. This provides an inexpensive carbon source that
rivals some MOFs in surface area and selectivity. The essential pretreatment step removes
more volatile compounds, providing higher molecular weight asphaltene aggregates that serve
as templates for further carbonization. The uGil-900, with its surface area of 4200 m² g⁻¹, has
attained among the highest surface areas of the porous carbonaceous materials recorded to
date, yet it is made directly from an inexpensive asphalt carbon source.⁴¹⁻⁴³ Competitive
adsorptions of CO₂ and CH₄ on the synthesized porous materials were tested by analysis of
the kinetics measurements of the successive gas displacement steps. Investigations of kinetics
of the gas displacement show the increase in D_CO₂ with pressure. D_CO₂ reaches to 65 at 40 bar.
These observations indicate the porous materials from asphalt are promising inexpensive
sorbents for industrial applications where CO₂ needs to be removed from natural gas streams.
We also expect that this generalized method of preparation of porous carbons from asphalt
will be useful for other applications of carbon materials.

4. Experimental

4.1 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 were provided by Prince Energy. Activated carbon Darco G-60
and all other chemicals were purchased from Sigma-Aldrich and used without further
purification unless otherwise stated.

4.2 Synthesis of asphalt derived porous carbon (uGil-T). 1.50 g of asphalt (untreated
Gilsonite) was heated on a ceramic boat inserted within a quartz tube furnace at 400 °C for 2
h with Ar flow at 500 sccm, 1 atm, before being permitted to cool to room temperature to
form 0.50 g of pretreated untreated Gilsonite (uGil-P). 0.25 g of uGil-P and 1.00 g (17.9
mmol) of KOH were ground well in a mortar. The mixture was heated on a quartz boat
inserted within a quartz tube furnace at 600 °C, 700 °C, 800 °C or 900 °C for 20 min with Ar flow at 500 sccm, 1 atm, before being permitted to cool to room temperature. The product was washed thoroughly with DI water and acetone until the filtrate attained pH 7 to yield uGil-600, uGil-700, uGil-800 and uGil-900, respectively. The uGil-T powder was dried in an oven at 100 °C until a constant weight was achieved to afford 0.10-0.15 g of porous carbon materials. Under comparable conditions, different types of asphalt were screened: natural asphalt from Chile, Versatrol M, Asphasol Supreme, untreated Gilsonite and untreated Gilsonite Substitute.

4.3 Volumetric gas sorption. Volumetric sorption measurements of CO$_2$ or CH$_4$, or premixed gas were carried out in an automated Sievert instrument [27] (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.

4.4 Gravimetric gas sorption. Gravimetric sorption measurements of CO$_2$ were carried out in a Rubotherm magnetic suspension balance [27] (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. Kinetics of the gas displacement were conducted at 25 °C by subsequent dosing of gases at various pressures and recording the weight change over time.

4.5 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 take-off 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, and 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. TGA were performed on a TGA Q50 instrument (TA Instruments) at a heating rate of 10 °C/min under argon atmosphere, from room temperature to 800 °C. The experiments were carried out under an air atmosphere at a flow rate of 50 mL/min. SEM images were taken at 20 KeV in a FEI Quanta 400 high resolution field emission scanning electron microscope. HRTEM 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). Xray diffractograms of powder samples mounted on a grooved zero background holder were acquired with a Rigaku D/Max Ultima II Powder X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5418 Å) and JADE 2009 software. Raman spectral plots of powder samples placed on a glass slide were acquired with a Renishaw inVia Raman microscope equipped with 514 nm Ar ion laser and WiRe software.

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Disclosure. Several of the authors are co-inventors on the patents related to the work described here. The patents are owned by Rice University and licensed to Apache Corp. Conflicts are managed by the Rice University Office of Sponsored Projects and Research Compliance.

Supporting Information. Supporting Information is available from the Wiley Online Library or from the author.

References


2013, 7, 326.


**Figure 1.** TGA curves for various commercial asphalts.

**Scheme 1.** Schematic illustration of the preparation porous carbons from asphalt.

**Figure 2.** (a) SEM and (b) HRTEM images of the uGil-900. (c) PXRD pattern of the uGil-900, (d) high-resolution XPS C 1s spectrum of uGil-900.

**Figure 3.** (a) Nitrogen sorption isotherms at 77 K; (b) differential nonlocal density functional theory (NLDFT) pore size distributions curves.

**Figure 4.** (a) Excess CO₂ uptake isotherms of uGil-600, uGil-700, uGil-800 and uGil-900 at 25 °C. (b) Absolute and excess CO₂ and CH₄ uptake isotherms of uGil-900 at 25 °C. These measurements were performed using a gravimetric gas uptake apparatus.

**Figure 5.** Isostreric heat of absorption (Qₛₐ) for CH₄ and CO₂ on uGil-900 estimated from the data at 25 and 30 °C. These measurements were performed using a volumetric gas uptake apparatus.

**Figure 6.** (a) Adsorption isotherms of gas mixing (CO₂ and CH₄) on the uGil-900 at total of 40 bar (20 bar CO₂ + 20 bar CH₄) at 25 °C. Each data point is recorded for 2 h. (b) Kinetics of relative weight change of the CH₄ (black) and CO₂ (red) pressurized uGil-900 at 20 bar during the mixing with additional CO₂ (black) and CH₄ (red) at 20 bar (red) at 25 °C. Graph shows total mixing pressures. These measurements were performed using a gravimetric gas
uptake apparatus.

**Scheme 2.** Schematic illustration of CO$_2$ versus CH$_4$ displacement.

**Figure 7.** Three-dimensional CO$_2$/CH$_4$ displacement surface of the various porous carbons (commercial activated carbon Darco G-60 $S_{\text{BET}} = 1445$ m$^2$ g$^{-1}$, and biochar derived activated carbons B-PC-1995 $S_{\text{BET}} = 1955$ m$^2$ g$^{-1}$ and B-PC-3130 $S_{\text{BET}} = 3130$ m$^2$ g$^{-1}$ both prepared here, and uGil-900). These measurements were performed using a gravimetric gas uptake apparatus.

**Table 1.** Properties and CO$_2$ and CH$_4$ uptake performances of porous carbons made from asphalt.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)$^a$</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)$^b$</th>
<th>$D_{\text{pore}}$ (nm)$^c$</th>
<th>Density (g cm$^{-3}$)</th>
<th>XPS</th>
<th>CO$_2$ uptake capacity at 54 bar$^d$</th>
<th>CH$_4$ uptake capacity at 60 bar$^d$</th>
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<td>0.37</td>
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$^a$Surface area estimated from N$_2$ absorption isotherms at 77 K and was determined using the data in the relative pressure range of 0.05 to 0.25 bar (Figure S5); samples dried at 240 °C for 20 h prior to the measurements. $^b$Total (micro- and meso-) pore volume obtained at P/P$_0 =$ 0.994. $^c$Average pore diameter ($D_{\text{pore}}$). $^d$Absolute CO$_2$ and CH$_4$ uptake at 25 °C. $^e$From Ref [27].
Pretreatment of asphalt (untreated Gilsonite, uGil) at 400 °C for 3 h removes the more volatile organic compounds to form pretreated asphalt (uGil-P) material with a larger fraction of higher molecular weight π-conjugated asphaltenes. Subsequent activation of uGil-P at 900 °C gives an ultra-high surface area (4200 m² g⁻¹) porous carbon material (uGil-900) with a mixed micro and mesoporous structure. uGil-900 shows enhanced room temperature CO₂ uptake capacity at 54 bar of 154 wt % (35 mmol g⁻¹).

**Keywords** asphalt, carbon dioxide capture, porous carbon, natural gas, competitive adsorption

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**Ultra-High Surface Area Activated Porous Asphalt for CO₂ Capture through Competitive Adsorption at High Pressures**

![Figure 1](attachment:image.png)

**Scheme 1**
Figure 2

Untreated Gilsonite → 400 °C → uGil-P

KOH → 900 °C → uGil-900

Figure 3

a) SEM image of uGil-P at 100 nm scale.
b) High-resolution SEM image of uGil-P at 10 nm scale.

c) X-ray diffraction (XRD) pattern showing peaks at 002 and 010.
d) X-ray photoelectron spectroscopy (XPS) showing C-C/C=C, C=O, and O-C=O.
Figure 4

Figure 5
Figure 6

Scheme 2
\[
\text{CH}_4 + \text{CO}_2 \xrightleftharpoons[k(\text{CO}_2)]{k(\text{CH}_4)} \text{CO}_2 + \text{CH}_4
\]

Figure 7
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