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Optimizing carbon dioxide uptake and carbon dioxide-methane selectivity of oxygen-doped porous carbon prepared from oxygen containing polymer precursors

Saunab Ghosh,^[a] and Andrew R. Barron^{[b]*}

Abstract: We report the reproducible synthesis of oxygen containing porous carbons (OPC) by the KOH activation at 500-800 °C of two oxygen containing precursor polymers: polyfurfuryl alcohol (PFFA) and polyanisyl alcohol (PAA) yielding FFA-OPC and AA-OPC, respectively. Both OPCs exhibits thermal stability and reproducible gas uptake properties for multiple cycles. The surface area and pore volumes of the OPC are independent of the precursor identity, but controlled by the activation temperature. Similarly, the uptake of CO₂ is determined by the physical properties of the OPC: activation at 750 °C results in uptake that equals or out-performs existing PCs for high pressure uptake (30 bar) at 24.0 °C (FFA-OPC₇₅₀: 117 wt%; AA-OPC₇₅₀: 115 wt%). The high uptake is related to a high relative percentage of pores <2 nm. The uptake of CH₄ for both OPCs is greatest for samples activation at 750 °C, FFA-OPC₇₅₀ shows enhanced uptake compared to AA-OPC₇₅₀, 15.5 wt% versus 13.7 wt%, respectively. Uptake for CH₄ appears to relate to a high relative percentage of pores 1-2 nm, which is observed for AA-OPC₇₅₀. As a consequence, AA-OPC₇₅₀ demonstrates superior selectivity for CO₂ capture over CH₄ uptake (AA-OPC₇₅₀: $V_{\text{mass}}(\text{CO}_2/\text{CH}_4) = 8.37$ at 30 bar) as compared to reported PCs. A higher value for the isosteric heat of adsorption of CO₂ (33 kJ mol⁻¹) versus CH₄ (11 kJ mol⁻¹) suggests a new temperature dependent strategy for removing CO₂ from natural gas via selective adsorption and desorption cycles.

Introduction

The goal of the COP21 meeting in Paris in 2015, to limit the global temperature rise associated with climate change to 1.5 °C, has placed renewed interest in the topic of CO₂ sequestration due to it being one of the main manmade contributors to global climate change. The capture of CO₂ from the atmosphere or emissions source is the first step in any sequestration process. However, many sources of natural gas are high in CO₂ and cannot be distributed through utility natural gas pipelines unless it is cleaned up to less than 3% CO₂. One popular way to remove CO₂ by means of chemical adsorption is using chemical sorbents synthesized from different amine containing molecules.¹ Aminated sorbents suffer from many limitations including: cost, their corrosive nature, high temperature/energy

for regeneration, thermal stability, and toxicity. Additionally, aminated sorbents exhibit much lower gas uptakes at high pressure (>1 bar) compared to other sorbents. Thus, solid sorbents such as microporous zeolite,^{2,3} metal-organic-frameworks (MOFs),⁴⁻⁶ mesoporous silica⁷ and other hybrid solid materials have been being utilized instead. Among sorbents with mesoporous structures, activated porous carbons (PCs) are unique due to their high BET surface area, pore volumes, micro- and meso-porous structures with significant adsorption capacity. PC composites also demonstrate remarkable stability and repeatability for selective gas uptakes.

To date, a common approach is to synthesize PC via the KOH activation of carbon rich precursors such as polymers and bio-sourced materials.⁸⁻¹⁰ It has been traditional thought that the presence of nitrogen or sulfur enhanced the uptake,¹¹ however, recent work has shown that this is not true,¹²⁻¹⁵ and that the oxygen (or total heteroatom content) is more important.^{14,15} In fact, the carbon content may be used as a quick guide to uptake efficiency. As with other solid sorbents, the major parameters that contribute to CO₂ capture for PCs are the apparent surface area and the total pore volumes. Researchers have previously concentrated on improving CO₂ capturing capacity by attempting to fabrication materials with ever larger surface area with abundant micropores. Counter to this approach, we have shown that there is an upper limit of both surface area and pore size, above which no improved adsorption of CO₂ appears to be observed.¹⁵ We have suggested that it is unwarranted to further attempt to investigate materials with higher and higher surface areas and/or pore volumes. Instead, and based upon both our data and that of other researchers reports, we proposed that an ideal PC would have a surface area of >2800 m²g⁻¹, a pore volume >1.35 cm³g⁻¹, and a carbon content of between 80-95%.¹⁵ In this regard, we have concentrated our research efforts in developing routes to such materials that allow for low cost and reproducible synthesis. Furfuryl alcohol (FA) has previously been formed into a highly cross-linked precursor via acid catalysis that can be converted to a PC;^{16,17} however, the process results in only a modest surface area and adsorption not sufficient to reach the performance parameters listed above. Herein we report that through FeCl₃ catalyzed polymerization and activation of polyfurfuryl alcohol (PFFA) an oxygenated PC (OPC) sorbent may be prepared which demonstrated higher room temperature CO₂ uptake as compared to other PC materials.

In prior work,^{15,18} we have shown that process conditions (temperature and KOH:precursor ratio) control the formation of micro (<2 nm) versus meso (>2 nm) porosity that is responsible for the highest CO₂ uptake. Although there appeared to be no significant difference in the performance as a function of the precursor, in creating nitrogen-doped PCs (NPCs) it was noted that incorporation of nitrogen into 6 versus a 5-membered cyclic

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precursor made a difference in the performance.¹⁵ Thus, there is interest as to whether using identical process conditions the precursor makes any significant effect. We have therefore investigated a new OPC precursor polyanisyl alcohol (PAA) to compare with PFFA.

Finally, if OPC is to be scaled the cost of the catalyst used for PFFA, and similar polymeric precursors, is an issue to be addressed. Anisyl alcohol (4-methoxybenzyl alcohol), which is used as fragrance and flavorant and thus produced on a large scale, represents a low cost OPC precursor, while the formation of the polymer feedstock for OPC, polyanisyl alcohol (PAA), is synthesized by treating anisyl alcohol with concentrate H_2SO_4 in a single step.

Results and Discussion

The experimental procedures for the synthesis of the best PC sample using KOH activation with the highest CO_2 uptake property rely on the optimization of two major parameters: the KOH:PFFA ratio and the temperature of activation (T_a). Earlier reports suggest that the overall porosity and the surface area of a chemically activated PC material increase with KOH concentration,^{8,9} and initial results suggested that KOH:PFFA = 3 is best for developing nano-sized micropores (1-2 nm range).¹⁸ Thus, our procedures were carried out by keeping KOH:PFFA ratio fixed to 3 and by activating premixed.

A schematic outlining the synthetic protocol for OPC from FA is presented in Figure 1. In the first step, a solid powder-like polymer of FA was prepared from liquid FA by the reaction in the presence of a FeCl_3 catalyst in CH_3CN (see ESI). The synthesis of polyanisyl alcohol (PAA) is simpler and involves treating anisyl alcohol with concentrate H_2SO_4 in a single step (Scheme 2).

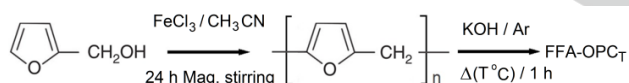


Figure 1. Synthetic reaction scheme for FFA-OPC, where FeCl_3 :FA = 10, KOH:PFFA = 3, and $T = 500\text{-}800\text{ }^\circ\text{C}$.

The PFFA and PAA are then chemically activated by mixing with pre-ground KOH followed by pyrolysis at a stable temperature in the $500\text{-}800\text{ }^\circ\text{C}$ range (see Experimental). A significant advantage of the use of the PFFA prepared in this manner, as compared to previous methods,^{16,17} is that it only releases a small amount of oily product during activation, unlike other PC precursors.

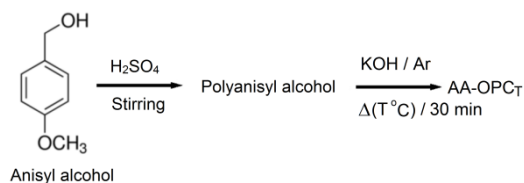


Figure 2. Synthetic reaction scheme for AA-OPC, where KOH:PAA = 3, and $T = 500\text{-}800\text{ }^\circ\text{C}$.

Figure 3a and b show representative images of the PFFA and the resulting FFA-OPC750. Both the as prepared OPC has a large pellet-like morphology. In comparison an image of sulfur containing porous carbon (SPC) sample¹¹ prepared under identical activation conditions is shown in Figure 3c. This important structural rigidity makes OPC sorbents more appropriate for practical applications as opposed to other powder like sorbents.

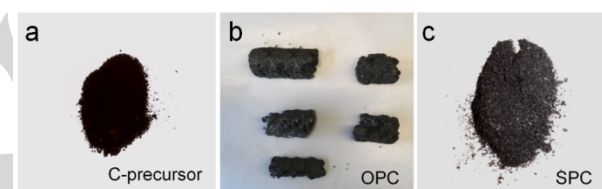


Figure 3. Photographs of (a) PFFA precursor, (b) as-synthesized OPC, and (c) as-synthesized SPC samples.

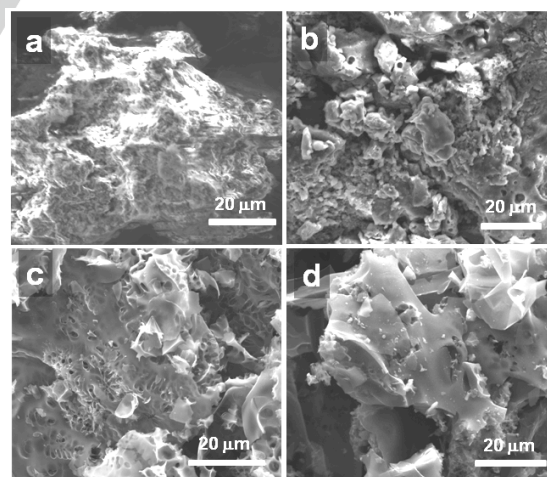


Figure 4. SEM images of the PFFA (a) and PAA (b) precursors and the associated OPCs: (c) FFA-OPC₇₅₀, and (d) AA-OPC₇₅₀.

The structural and textural morphology of the as-synthesized polymer and resulting activated OPC samples were determined by scanning electron microscopy (SEM) as represented by Figure 4. The PFFA precursor has a relatively dense morphology, but after activation by KOH, the resulting FFA-OPC

exhibits a texture full of multiple corners and edges that are absent in the precursor. The related energy dispersive X-ray spectroscopy (EDS) determined elemental composition confirms the OPCs are primarily composed of carbon and oxygen (Table 1).

Table 1. Elemental composition of OPC as determined by XPS and EDS.^[a]

Sample	XPS		EDS		Surface area S_{BET} [c] (m^2g^{-1})	Total pore Volume V_p [d] (cm^3g^{-1})
	C (wt%)	O (wt%)	C (wt%)	O (wt%)		
PFFA-precursor	69.91	30.09	68.64	31.36	48	0.02
FFA-OPC ₅₀₀	77.49	22.51	78.64	18.85	1143	0.78
FFA-OPC ₆₀₀	82.04	17.74	87.09	12.91	2116	1.19
FFA-OPC ₇₀₀	85.07	14.93	89.92	10.08	2610	1.46
FFA-OPC ₇₅₀	88.21	11.79	90.12	8.08	2856	1.77
FFA-OPC ₈₀₀	89.28	10.72	90.58	9.42	3005	1.92
PAA-precursor ^[b]	74.90	21.41	76.12	21.85	55	0.03
AA-OPC ₅₀₀	76.66	23.34	77.95	22.05	853	0.49
AA-OPC ₆₀₀	83.36	13.64	85.20	14.8	1980	1.13
AA-OPC ₇₀₀	89.37	10.63	91.57	8.43	2700	1.54
AA-OPC ₇₅₀	91.01	8.99	92.18	7.82	3310	1.87
AA-OPC ₈₀₀	91.27	8.73	93.05	6.95	3040	2.27
Act. Char. ^[e]	94.10	5.90	-	-	845	0.41
BPL ^[f]	91.30	8.70	-	-	951	0.53

[a] Contributions from elemental H were excluded. [b] PAA-precursor contained 3.7% S residue from the acid catalyst. [c] Apparent BET surface area estimated in P/P₀ range of 0.05-0.30. [d] Total pore volume measured at P/P₀ ~0.99. [e] Purchased from Mallinckrodt chemical works. [f] Purchased from Calgon carbon corp.

In order to image the microporous structure of activated OPCs, high-resolution transmission electron microscopy (HRTEM) was utilized. Figure 5a-c display a set of images demonstrating randomly distributed micropores with dimension in the range of 1-2 nm for FFA-OPC₆₀₀ and slightly larger but evenly distributed micropores for FFA-OPC₈₀₀ and AA-OPC₈₀₀ samples. These nano-sized micropores play key role in the ultra high CO₂ uptake at higher pressure.¹⁵

Further characterization to determine important structural parameters such as surface area, pore size distribution and the total pore volumes of C-precursor and different OPC specimens activated at a fixed temperature in the range of 500-800 °C with a fixed KOH/PFFA ratio of 3 was carried out by measurement of the N₂ adsorption isotherms (at 77 K) using a BET (Brunauer–

Emmett–Teller) surface area analyser. Figure 6 shows such set of isotherms for the OPCs activated at labelled temperature. Difference in the shape of these isotherms was noticed depending on the activation temperature; the isotherm for FFA-OPC₈₀₀ was much steeper than that of FFA-OPC₅₀₀ up to a relative pressure of 0.4 (Figure 6a), indicating the variation in microporosity and adsorption capacity. The isotherm for AA-OPC₈₀₀ was shallow than that of the other samples, suggesting meso pore generation (see below).

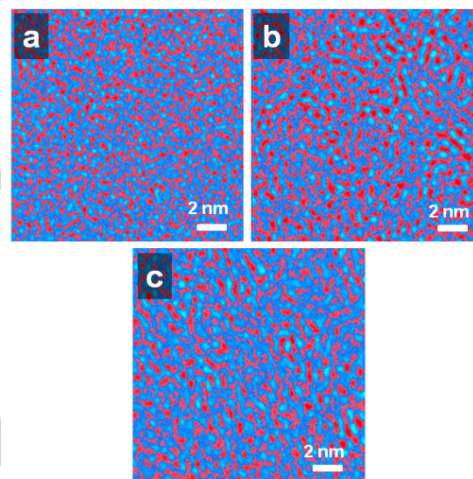


Figure 5. Representative high-resolution TEM images of (a) FFA-OPC₆₀₀, (b) FFA-OPC₈₀₀, and (c) AA-OPC₈₀₀ samples showing nm sized micro porous structures.

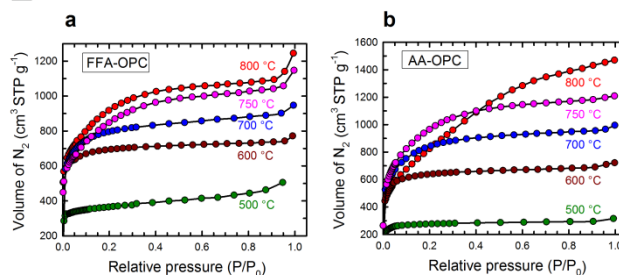


Figure 6. N₂ adsorption isotherms for (a) FFA-OPCs and (b) AA-OPCs measured at liquid N₂ temperature (77K).

The estimated surface area (S_{BET}) and the total pore volume (V_p) gradually increased with activation temperature (Figure 7) describing the incremental trend for mildly to strongly activated samples. Activation between 650 °C and 800 °C the surface area for FFA-OPCs varied smoothly than that for pore volumes (Figure 7a). In contrast, the surface area for AA-OPCs reaches an apparent maximum at 750 °C (Figure 7b). Irrespective of these differences, both parameters increase with increasing activation temperature, with activation above 750 °C giving

materials with surface area and pore volume above the threshold (i.e., $>2800 \text{ m}^2\text{g}^{-1}$ and $>1.35 \text{ cm}^3\text{g}^{-1}$, respectively) to enable maximum CO_2 uptake.¹⁵ Figure 8 provides a comparison with other reported carbon based activated sorbents such as activated charcoal, SPC, NPC¹¹ and asphalt derived PC¹⁹ specifically, explored for high pressure CO_2 uptakes. The values for AA-OPC₇₅₀ are amongst of the highest reported surface area and pore volume values for carbon based PC samples reported to date.

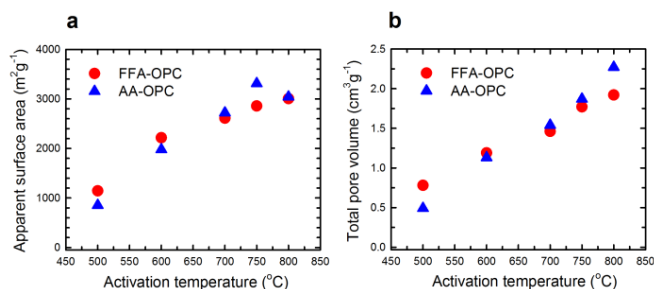


Figure 7. Estimated (a) apparent surface area and (b) total pore volumes versus activation temperature for FFA-OPC and AA-OPC.

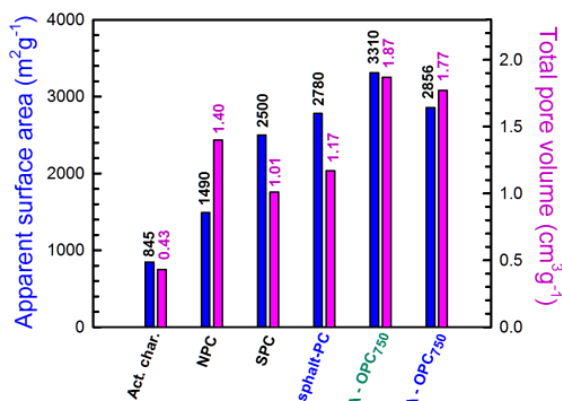


Figure 8. Apparent surface area (blue bars) and total pore volumes (purple) for activated charcoal and PC samples with high CO_2 uptake properties at 30 bar ($>12 \text{ mmol.g}^{-1}$).

Figure 9 depicts the distributions of pore sizes as a function of pore width for activation temperatures ($500 \text{ }^{\circ}\text{C} \leq T_a \leq 800 \text{ }^{\circ}\text{C}$) to strong ($T_a = 800 \text{ }^{\circ}\text{C}$) activation conditions. These plots show that samples activated at temperature between 500 and 700 $^{\circ}\text{C}$ mainly consisted of micropores in the range of 1-2 nm. In contrast, the distribution plot for FFA-OPC₈₀₀ indicates that chemical activation at temperature $\sim 800 \text{ }^{\circ}\text{C}$, created some additional mesopores in the 2.0-3.5 nm range, confirming the findings from HRTEM images discussed earlier (Figure 5b). Pores larger than 4 nm were practically absent in all samples,

except for AA-OTC₈₀₀ where the mesopore ($> 2 \text{ nm}$) contribution is dominant (Figure 9b).

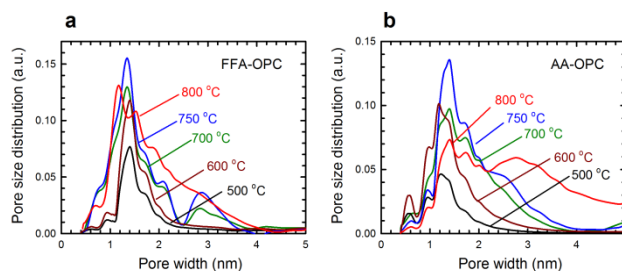


Figure 9. Distribution of pore sizes as a function of pore width for five activation temperatures as determined by the nonlocal DFT method for (a) FFA-OPC and (b) AA-OPC.

As noted above, the best CO_2 uptake of a PC is observed with a carbon content of 80-95 wt%.^{15,18} The chemical composition of polymer precursors and the subsequent OPCs was determined by X-ray photoelectron spectroscopy (XPS). The identity and wt% of the elements present on the sample surface were determined by XPS survey scans for core level electrons (Table 2 and Figure S1 and S2, see ESI). The XPS data further confirms that OPC samples primarily contained C and O (the H contents are not shown in XPS). As expected the C and O content varied from the polymers to the OPCs during chemical activation, and for the OPC samples the general trend was that the wt% of C increased and O decreased gradually with increasing activation temperature (Figure 10). Based upon the analysis, samples activated between 600 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$ fall within the range required for maximum CO_2 uptake.^{15,18}

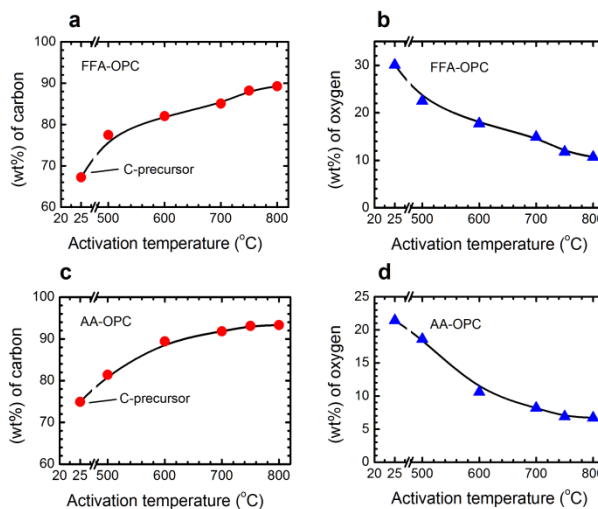


Figure 10. The wt% of elemental carbon (a and c) and oxygen (b and d) as determined by XPS versus activation temperature for FFA-OPC (a and b) and AA-OPC (c and d).

Table 2. CO₂ and CH₄ uptake properties (@ 24 °C) in comparison with commercial PC samples of OPC samples prepared from polyfurfuryl alcohol (FFA-OPC) and polyanisyl alcohol (AA-OPC).

Sample ^[a]	Surface area S _{BET} (m ² ·g ⁻¹) ^[e]	Total pore volume V _P (cm ³ ·g ⁻¹) ^[f]	Uptake CO ₂ @ 10 bar		Uptake CO ₂ @30 bar		Uptake CH ₄ @30 bar		Molar ratio CO ₂ /CH ₄ @30 bar	Mass ratio CO ₂ /CH ₄ @30 bar
			(mmol·g ⁻¹)	(wt%)	(mmol·g ⁻¹)	(wt%)	(mmol·g ⁻¹)	(wt%)		
FFA-OPC ₅₀₀	1143	0.78	8.6	37.8	17.1	75.2	6.7	10.7	2.5	7.0
FFA-OPC ₆₀₀	2116	1.19	12.5	55.0	20.0	88.1	8.3	13.3	2.4	6.6
FFA-OPC ₇₀₀	2610	1.46	12.7	55.9	20.8	91.5	9.1	14.6	2.3	6.3
FFA-OPC ₇₅₀ ^[b]	2856	1.77	15.1 (18.5)	66.4 (81.5)	26.6 (42.9)	117.0 (188.9)	9.6 (14.6)	15.5 (23.4)	2.8 (2.9)	7.6 (8.0)
FFA-OPC ₈₀₀	3005	1.92	12.9	56.7	23.0	101.2	9.0	14.4	2.5	7.0
AA-OPC ₅₀₀	853	0.49	6.7	29.7	9.5	41.6	3.8	6.1	2.7	7.3
AA-OPC ₆₀₀	1980	1.13	11.6	50.9	17.6	77.3	6.8	10.9	2.6	7.1
AA-OPC ₇₀₀	2700	1.54	11.9	52.6	22.4	98.5	7.9	12.7	2.8	7.8
AA-OPC ₇₅₀ ^[b]	3310	1.87	13.9 (17.6)	61.0 (77.5)	26.0 (39.3)	114.5 (172.9)	8.5 (10.5)	13.7 (16.8)	3.0 (3.7)	8.4 (10.3)
AA-OPC ₈₀₀	3040	2.27	9.6	42.2	21.8	96.0	8.3	13.2	2.6	7.2
Act. Charcoal ^[c]	845	0.47	6.3	27.6	8.5	37.2	6.0	9.7	1.4	3.9
BPL ^[d]	951	0.53	6.3	27.7	8.7	38.1	6.2	9.9	1.4	3.8

[a] OPC activation temperature. [b] Values in parenthesis performed at 0.5 °C. [c] Purchased from Mallinckrodt chemical works. [d] Purchased from Calgon carbon corp. [e] Apparent BET surface area estimated in P/P0 range of 0.05-0.30. [f] Total pore volume measured at P/P0 ~0.99.

A set of high resolution XPS elemental scan data for C1s and O1s of PFFA and FFA-OTC samples (Figure 11), de-convoluted by appropriate basis peaks helped us identify the possible functional groups present in the precursor and numerous activated samples. For PFFA, the C1s band could be resolved into four main peaks and labelled according to probable functional groups as in polythiophene.⁹ Thus, these peaks were assigned to the following functional groups: sp² hybridized C=C (284.7 eV), C-C (286.1 eV), C-O-C (287.1 eV) and C=O (288.9 eV). An additional shoulder near 291.3 eV is attributed to π-π* shake-up peak. In contrast to PFFA, the activated sample exhibited much narrower C=C peak (FWHM: 1.3 eV versus 2.2 eV for PFFA). The resolved basis peaks under O1s spectra were attributable to two main functional groups: the C-O-C group at 533.2 eV (O within the furan ring) and the carbonyl group (C=O) at 531.8 eV. We believe that KOH induced oxidation during chemical activation at higher temperature resulted in formation of more carbonyl groups, though the absence of well resolved band for O1s made it difficult to extract the absolute proportion of these two functionalities.

The nature of carbon and oxygen functional groups present in the as-synthesized PFFA and activated FFA-OPCs were further explored via FTIR spectroscopy. The IR spectrum for PFFA (Figure 12) exhibited well defined but broad peaks originated

from various IR active vibrational stretches identified as: C-O-C asymmetric stretching vibration (1020 cm⁻¹), C-C stretching (1358 cm⁻¹),⁹ C=C symmetric and asymmetric stretching vibrations in the furan ring (1510 and 1585 cm⁻¹, respectively). The IR frequencies with possible assignments for a PFFA sample are listed in Table S1. The frequency shift and broadness of these bands may be attributed to the aggregated phase of the synthesized polymer. In contrast to PFFA, the activated samples exhibited multiple stretching vibrations with gradually decreasing intensity. The intensity of all these peaks decreased systematically with increasing activation temperature as evidenced by the spectra of FFA-OPC₅₀₀ and FFA-OPC₈₀₀. For FFA-OPC₅₀₀, in addition to C=C stretching frequencies another shoulder peak was identified near 1710 cm⁻¹ which could be assigned to C=O stretching vibrations.²⁰ Moreover, the C-O-C and O-H functional groups that were present in the C-precursor and mildly activated samples (T_a = 500 °C) slowly removed due to chemical activation at higher temperature.

The aromatic sp² hybridized C=C and amorphous sp³ hybridized C-C bonds present in PFFA and activated FFA-OPCs were further characterized by Raman spectroscopy. Figure 13a-c represents a set of three normalized spectra depicting spectral changes for two major bands; the sharp graphene (G) band (1590 cm⁻¹) and the broad disorder (D) band located (1360 cm⁻¹),

attributing to the aromatic sp^2 and amorphous sp^3 hybridized carbons respectively. A more direct dependence for the (D/G) intensity ratio on activation temperature is shown in Figure 13d, bottom panel. The D/G value varied from 0.56 for PFFA, to 0.75 for FFA-OPC₅₀₀ and 0.83 for FFA-OPC₈₀₀ signifying the gradual removal of sp^2 and addition of sp^3 carbons as a result of chemical activation under mild to strong activation conditions.

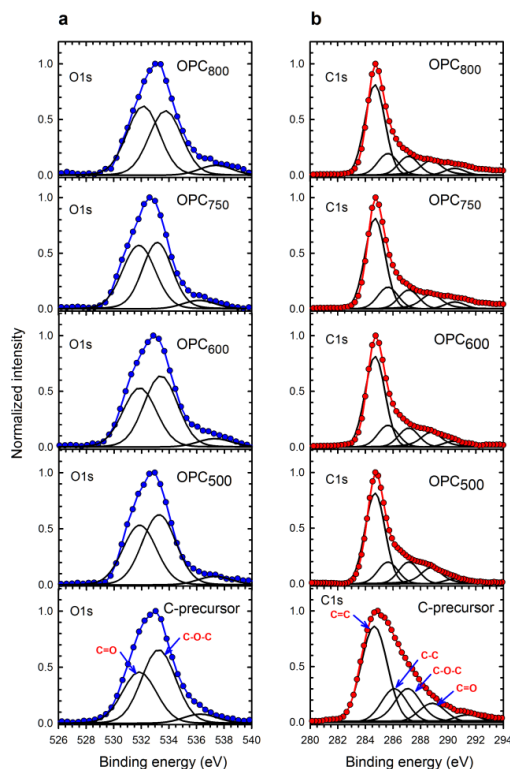


Figure 11. XPS elemental scanning for (a) oxygen O1s and (b) carbon C1s for PFFA precursor and FFA-OTC.

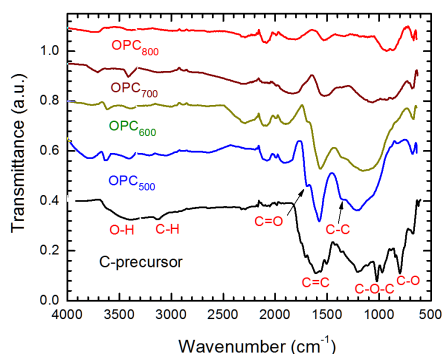


Figure 12. FTIR spectra of PFFA precursor and activated FFA-OPCs. Spectra are base line corrected and vertically offset for clarity. KOH:PFFA = 3 in all cases.

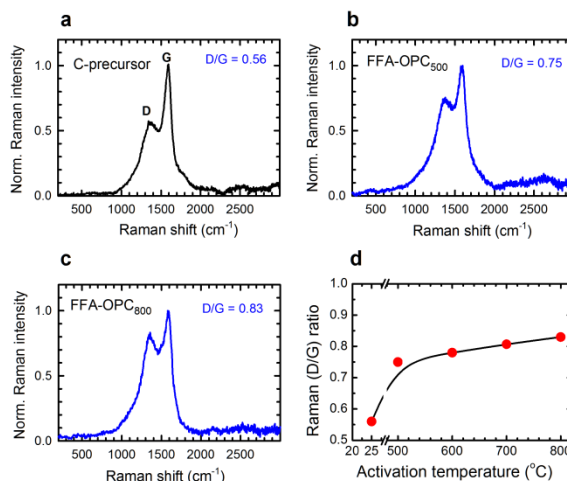


Figure 13. Raman spectra and Raman disorder (D) to graphene (G) band intensity ratio versus activation temperature. KOH:PFFA = 3 in all cases..

CO₂ uptake

Among the various types of solid porous materials that efficiently capture CO₂, MOFs (metal organic frameworks),^{5,6,21,22} zeolites, cross linked polyethylenimine,²³ and a variety of powder like activated PCs play critical roles over other sorbents and widely utilized for industrial application due to their high surface area, excellent thermal stability, low cost of synthesis, superior gas adsorption capacity with remarkable reproducibility. However, within the category of activated PC materials with high CO₂ uptake capacity, to date, most of the sorbents were investigated for CO₂ uptake performance up to a pressure limit of only 1 bar^{8,9} due to the limitation of available instruments. Though in industrial application higher pressures are needed. For example, removal of CO₂ from natural gas at the wellhead needs to be optimized between 15-30 bar. We have previously shown that the best PC materials show a maximum CO₂ uptake of 20-25 mmol.g⁻¹ at 30 bar and 24 °C.¹⁵ In this context, we have carried out careful volumetric CO₂ uptake experiments on the OPC sorbents as a function of gas pressure up to a limit of 30 bar and compared the results to previously reported PC samples measured under the same conditions.

In order to identify the OPC sorbent with the highest CO₂ uptake capacity, we measured pressure dependent CO₂ uptake for a set of OPC samples prepared with a fixed KOH:polymer = 3 and activated at a fixed temperature in the 500 - 800 °C range (Figure 14). Clear difference between the shapes of uptake isotherms indicates that uptake varies with activation temperature (T_a), i.e., more the value of T_a more the uptake value for a specific adsorption pressure. The C-precursors adsorbed negligible amount of CO₂ and the most mildly activated OPC; AA-OPC₅₀₀ showed an uptake similar to activated charcoal. The general trend was: OPC that was activated at higher temperature contained more micropores and with larger surface area performed better. Strikingly, both FFA-OPC₇₅₀ and AA-OPC₇₅₀ captured more CO₂ than their OPC₈₀₀ homologs; while in the case of FFA-OTC₈₀₀ it has a higher

surface area and pore volume (Table 1). Similar observation was reported by Sevilla and coworkers for low pressure (up to 1 bar) gas uptake of CO₂ by polypyrrole derived PCs.^{8,9} We believe that the reason for the higher uptake performance of OPC₇₅₀ was that OPC₈₀₀ contained more mesopores larger than 2 nm. In this context it is important to note that up to a pressure bar of 5 bar all OPC samples capture similar amount of CO₂ (except the OPC₅₀₀ samples).

Figure 14c displays a set of equilibrium volumetric CO₂ uptakes at room temperature as a function of adsorbate pressure for various PC specimens such as activated charcoal, NPC, SPC and the best of our samples FFA-OPC₇₅₀ and AA-OPC₇₅₀. We noticed that among the all activated OPCs, though all of them captured more CO₂ than previous reported SPC or NPC samples, both FFA-OPC₇₅₀ and AA-OPC₇₅₀, demonstrated the highest CO₂ capture capability, thus, we subsequently carried out repeated uptake experiments on different batches of both OPC₇₅₀. The CO₂ uptake result for FFA-OPC₇₅₀ was further verified by another gravimetric uptake experiment carried out in a Rubotherm magnetic suspension balance instrument (Figure 14c, open circles). These uptake plots further established that at a pressure of 30 bar, FFA-OPC₇₅₀ exhibited an ultrahigh CO₂ capture capacity of 26.6 mmol.g⁻¹ (117 wt%), outperforming other doped PCs by a large margin. Moreover, OPC₇₅₀ adsorbed slightly, but repeatedly, more CO₂ than the recently reported activated PCs made from asphalt Versatrol-HT (26.6 versus 26 mmol.g⁻¹).¹⁹ It should be noted that the latter material required multiple activation steps, pretreatment, N-addition and reduction by H₂ to be capable of adsorbing such quantity of CO₂, which is in contrast with the far simpler process described herein.

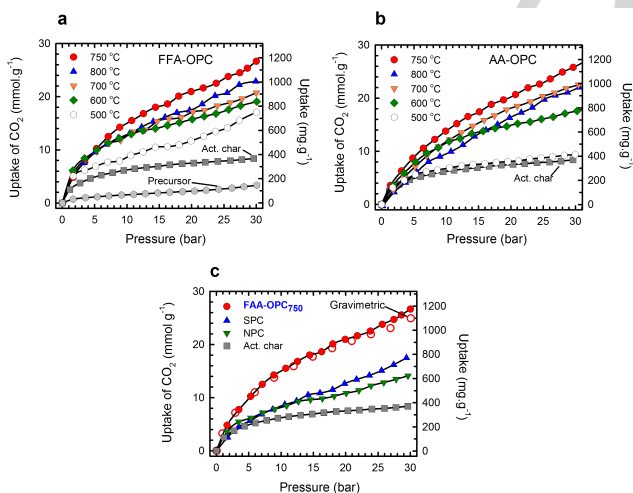


Figure 14. CO₂ uptake isotherms of (a) FFA-OPC and (b) AA-OPC samples activated at different temperatures. (c) Volumetric CO₂ uptakes of FFA-OPC₇₅₀, NPC, SPC, and activated charcoal up to a pressure limit of 30 bar. Measurements were performed in a PCTPro instrument at 24 °C.

In contrast, OPC₇₅₀ is prepared from a simple precursor in a single activation step without N-addition or H₂ reduction. To the best of our knowledge, among the category of high CO₂ uptake

PC materials FFA-OPC₇₅₀ exhibits remarkable CO₂ capture properties comparable to expensive MOFs with similar apparent surface area.^{24,25} For example, IRMOF-1 with surface area 2833 m².g⁻¹ captures ~21 mmol.g⁻¹ of CO₂ at 30 bar. IRMOF-6 with surface area 2516 m².g⁻¹ captures ~19 mmol.g⁻¹ at 30 bar.²⁶ The CO₂ uptake values at intermediate pressures are listed in Table S2, (see Supporting Information). The overall volumetric CO₂ uptake results at 30 and 10 bar, for various sorbents are compared in Table 1, while the maximum amounts of gas uptakes at 30 bar for different PC samples with corresponding surface area is represented by Figure 15.

For large scale gas uptake applications, such as removing CO₂ from natural gas, it is essential for a solid sorbent to exhibit both reproducible gas uptake capability and batch to batch reproducibility. This important requirement was examined via two experiments as shown in Figure 16a and b, which displays a set of pressure dependent CO₂ uptake plots for different OPC₇₅₀ batches synthesized and activated same way. Almost identical gas adsorption characteristics, up to an upper pressure limit of 30 bar, confirmed the applicability of both OPC materials as cheap but very effective sorbent for industrial application. The other necessity for practical usage was further established by four complete cycles of gas adsorption-desorption measurements recorded for 30 h that showed negligible or no hysteresis (Figure 16c). Our multiple cycle measurements and prolonged exposure to CO₂ on the same OPC sample satisfied two major requirements for practical application: no degradation in quality and no drop in gas uptake capacity.

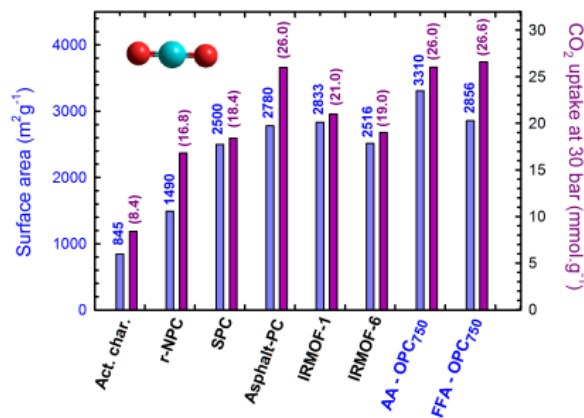


Figure 15. Graphical representation of surface areas and maximum CO₂ uptake capacities at 30 bar for activated charcoal and different sorbent samples with high CO₂ uptake properties at 30 bar (>12 mmol.g⁻¹).

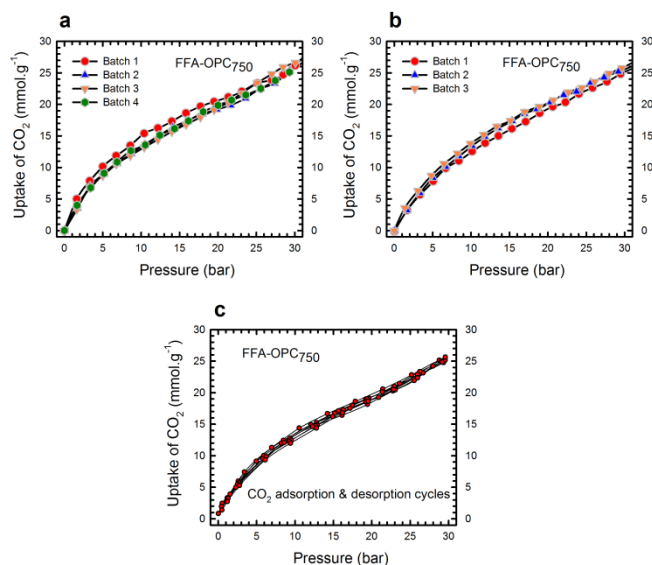


Figure 16. Demonstration of reproducibility of sample preparation and gas uptake properties. Volumetric CO_2 uptake measurements on different batches of (a) FFA-OPC₇₅₀ and (b) AA-OPC₇₅₀ synthesized and activated same way, and (c) four successive CO_2 adsorption and desorption cycle measurements on an individual FFA-OPC₇₅₀ sample.

For most of the solid sorbents the gas uptake capacity increases with decreasing capture temperature. At 0.5 °C and a pressure of 30 bar, FFA-OPC₇₅₀ demonstrated an ultrahigh CO_2 uptake capacity that maxed to 189 wt% (43 mmol.g^{-1}) that is 60% higher than room temperature uptake (Figure 17a). For any solid porous sorbents with high surface area, the trend of gas uptake is: higher the gas pressure the higher the CO_2 uptake and the uptake is both pressure and temperature dependent. This result is further established by a set of plots describing the gas uptake capacity at four different uptake pressures as a function of experiment temperature (Figure 17b). At a pressure of 5 bar, the CO_2 uptake varied from 5.2 to 12.6 mmol.g^{-1} (increased by 142%) for a temperature change of 60 to 0.5 °C; whereas, at 30 bar, the change was significantly high, uptake varied from 12.6 to 42.9 mmol.g^{-1} (increased by 240%). This important result signifies the possibility of selective CO_2 removal by exploiting the pressure-temperature dependent adsorption and desorption from a CO_2 rich gas mixture.

CO_2/CH_4 selectivity

The selective removal of CO_2 from natural gas, which essentially contains CH_4 and higher hydrocarbons along with other gases (CO_2 , H_2S , and N_2), is one of the important research goals, because these contaminant gases decrease power efficiency of the natural gas. The capture of CO_2 from natural gas primarily relies on purification strategies that allow the gas mixture to pass through a column packed with solid porous materials that captures CO_2 from the CH_4 -rich environment with minimal CH_4 uptake. We have previously shown that unlike total CO_2 adsorption, the best $\text{CH}_4:\text{CO}_2$ adsorption ratio requires a PC with a surface area $>2000 \text{ m}^2\text{g}^{-1}$,

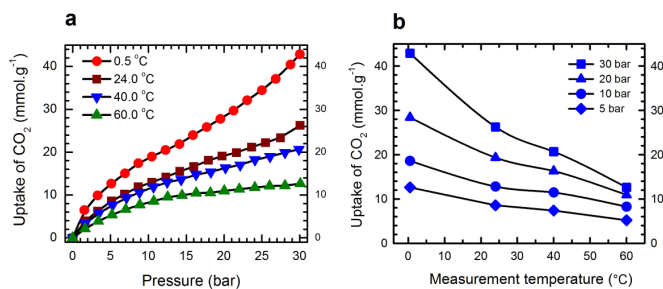


Figure 17. Demonstration of ultrahigh CO_2 uptake capability of an FFA-OPC₇₅₀ sample at low temperature. (a) Volumetric CO_2 uptake measurements on an FFA-OPC₇₅₀ sample at four different temperatures. At 0.5 °C and 30 bar pressure, sorbent adsorbed an ultrahigh amount of CO_2 that maxed to 43 mmol.g^{-1} (189 wt%). (b) CO_2 uptakes at four different (labelled) pressures as a function of experiment temperatures.

a total pore volume $>1.0 \text{ cm}^3\text{g}^{-1}$ and a carbon content of $<90 \text{ wt}\%$.¹⁵ Based upon the forgoing both OPC₇₅₀ materials meet these requirements. The absolute $\text{CO}_2:\text{CH}_4$ selectivity test was carried out by measuring volumetric CO_2 and CH_4 uptake isotherms up to a high pressure limit of 30 bar at 0.5 and 24.0 °C. Our study focused on the selectivity of FFA-OPC₇₅₀ and AA-OPC₇₅₀, though additional data for other activated OPCs are presented in ESI. Two sets of volumetric CO_2 and CH_4 adsorption uptake measurements performed on each OPC₇₅₀ sorbent, at 0.5 and 24.0 °C (Figure 18a and b) respectively. A similar set of room temperature uptake result for activated charcoal are presented in Figure 18c. Here, the molar uptake selectivity ($\eta_{\text{CO}_2/\text{CH}_4}$) is defined by the molar ratio of adsorbed CO_2 and CH_4 at a certain pressure, i.e., at 30 bar.

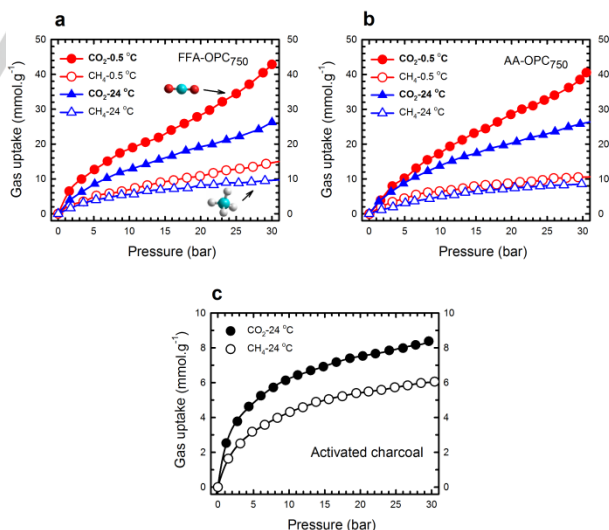


Figure 18. CO_2 and CH_4 uptakes measurements on (a) FFA-OPC₇₅₀ and (b) AA-OPC₇₅₀ sorbents up to a pressure range of 30 bar at 0.5 and 24 °C. (c) Volumetric CO_2 and CH_4 uptake measurements on commercial activated charcoal.

Although the surface area and pore volumes and the CO₂ uptake of the two different OPC samples appear to be essentially independent of the choice of precursor (see Figure 7 and Table 1), the same is not true of CH₄ uptake. As may be seen from Table 1 the CH₄ uptake for FFA-OPC is greater than that for AA-OPC for any given activation temperature. Given the relationship observed in Figure 7 this trend is also true for surface area and pore volume (Figure 19). Thus, even with similar physical parameters (surface area and pore volume) OPC prepared from PFFA shows greater CH₄ uptake than materials prepared from PAA. Although the differences are ca. 10% this results in a comparable difference in CO₂/CH₄ selectivity, with AA-OPC samples providing better selectivity than FFA-OPC samples across the range of activation temperatures (Table 2).

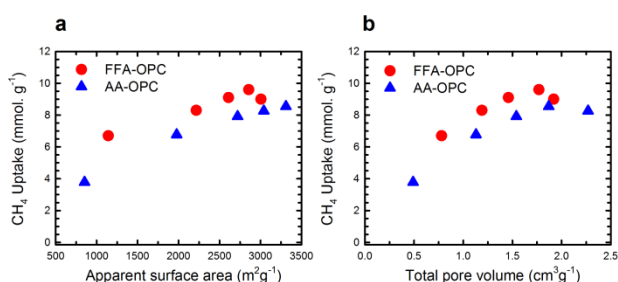


Figure 19. Plot of CH₄ uptake at 30 bar as a function of (a) surface area and (b) total pore volume for FFA-OPC and AA-OPC.

Another important parameter that can be determined from Figure 20 is the corresponding isosteric heat of adsorption of CO₂ and CH₄ for OPC₇₅₀ using the thermodynamic equations described elsewhere.²⁷ In thermodynamic point of view, isosteric heat of adsorption of a gas determines the temperature change in a sorbent as a result of adsorption of adsorbate molecules to the sorbent surface and thus, it is one of the key thermodynamic parameters that can be utilized to separate this gas from a mixture of gases. The higher the difference between isosteric heats of adsorption for two gases the better will be the separation. For instance, as shown by Figure 20 there is a higher value for the isosteric heat of adsorption of CO₂ as compared CH₄ (Table 3) allow us to propose a temperature dependent strategy for removing CO₂ from natural gas *via* selective adsorption and desorption of CH₄ and CO₂. It also suggest that understanding the factors controlling the difference between the values will offer a guide to the design of future adsorbents. However, we note that the difference appears to be more a function of the CO₂ adsorption, even though the observed difference in uptake is greater for CH₄.

We have previously reported that with regard CO₂ uptake the relative distribution of pores within defined ranges defined performance. The micro- and meso-porosity analysis of these samples was determined by the *t-plot method*²⁶ and revealed interesting pore volume dependencies on KOH amounts (Table 4). The absolute volumes and percentage of total pore volume

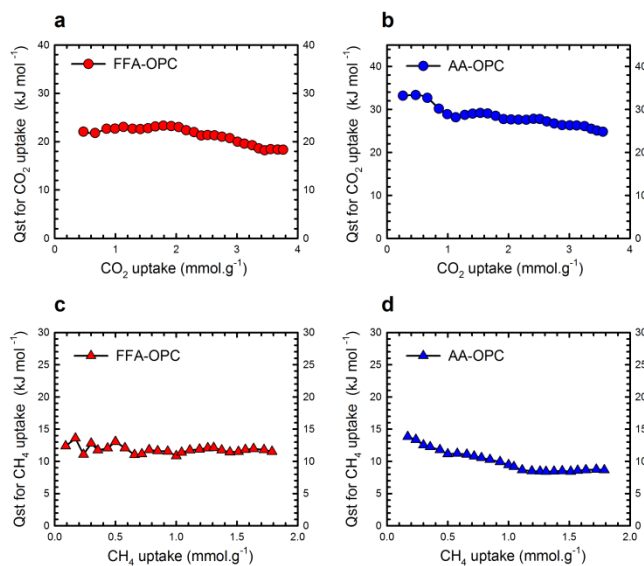


Figure 20. Isosteric heat of gas adsorption of (a and b) CO₂ and (c and d) CH₄ as a function molar gas uptake for FFA-OPC₇₅₀ (a and c) and AA-OPC₇₅₀ (b and d).

Table 3. Isosteric heat of adsorption for CO₂ and CH₄

Sample	CO ₂ (kJ mol ⁻¹)	CH ₄ (kJ mol ⁻¹)
FFA-OPC ₇₅₀	22	13
AA-OPC ₇₅₀	33	11
Act. Char.	16	8

for OPC₇₅₀ samples as a function of the CO₂/CH₄ selectivity suggest that our previous proposal is correct.¹⁸ The greater the relative percentage of pores <2 nm the greater the CO₂ uptake is in line with previous suggestions; however, the comparison of FFA-OPC₇₅₀ and AA-OPC₇₅₀ provides further insight into our previous proposal that it was pores in the range 1-2 nm that are most important in defining CO₂/CH₄ selectivity.

Table 4. Summary of meso (>2 nm), micro (<2 nm), and narrower micropore (<1 nm) volume (V) for OPC₇₅₀ samples.

Sample [a]	V _{MICRO} (0-2 nm) (cm ³ g ⁻¹)	V _{NARROW} (0-1 nm) (cm ³ g ⁻¹)	V _i (1-2 nm) (m ² g ⁻¹)	V _{MESO} (2-50 nm) (cm ³ g ⁻¹)	V _{MACRO} (>50 nm) (m ² g ⁻¹)
FFA-OPC ₇₅₀	1.10	0.23 (13%)	0.87 (49%)	0.57 (32%)	0.10 (6%)
AA-OPC ₇₅₀	1.24	0.12 (6%)	1.12 (60%)	0.58 (31%)	0.05 (3%)

[a] Micropore volumes determined by the t-plot method. Within parentheses, % of the total pore volume is shown.

In order to recognize the PC sorbent with the highest CO₂/CH₄ selectivity, we surveyed molar selectivity (at 30 bar) of recently explored PC sorbents such as SPC, NPC and activated charcoal

and AA-OPC₇₅₀. The absolute molar (CO₂/CH₄) uptake selectivity of OPC₇₅₀ (3.05) is greater than values for SPC (2.6), reduced-NPC (2.2) and activated charcoal (1.4) and slightly higher than the recently reported asphalt Versatrol-HT derived PC (3.0).¹⁹ These results clearly established that among the category of activated PC materials for selective CO₂ capture from natural gas, AA-OPC₇₅₀ is one of the best adsorbents reported so far and much lower cost relative to SPC and NPC prepared from analogous polymers.

Conclusions

Based upon prior work it is known that the best CO₂ uptake and CO₂/CH₄ differentiation is obtained with a defined set of parameters involving surface area, pore volume, and carbon content.¹⁵ The latter has been related to the relative percentage of pores <2 nm.¹⁸ These results suggested that the way to prepare an ideal PC adsorbent is to use a pre-formed O-containing precursor, and the formation of both PFFA and PAA meets these needs. Thus, the use of a designed precursor allows for the reproducible formation of an OPC material with the required physical attributes. Furthermore, unlike NPC and SPC materials, the OPC reported herein lends to pellet formation as required for scalable processes.

The interesting issue is that structural features of the precursor appear to be irrelevant to the OPC that is formed when considering CO₂ adsorption. However, this is not true for CH₄ adsorption and hence CO₂/CH₄ selectivity. Based upon the results herein we suggest that the identity of the precursor and the subsequent control over the pore structure is important for CH₄ adsorption and hence CO₂/CH₄ selectivity and should be subject to further study. In conclusion, we propose that while CO₂ uptake is optimized by maximization of pores <2 nm, the CO₂/CH₄ selectivity requires optimization of pores in the 1-2 nm range. This, therefore, should be the goal of future synthetic strategies.

Experimental Section

Materials and methods

FeCl₃, furfuryl alcohol (Sigma Aldrich, 98% purity), anisyl alcohol (Sigma Aldrich, 98% purity), CH₃CN, powdered KOH, distilled water, acetone, HCl, Ar (99.9% pure), CO₂ (99.99% pure, Matheson TRIGAS) and CH₄ (99.9% pure) were used as supplied. The SPC and NPC samples used as comparison were synthesized from 2-thiophenemethanol and polyacrylonitrile (Sigma Aldrich) respectively following the protocol previously described.¹⁵ Chemical composition of the polymer and porous carbon materials were determined by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The XPS measurements were carried out in a PHI Quantera scanning XPS microprobe. The wt% of chemical elements was determined by XPS survey scans with pass energy of 140 eV. For detailed elemental analysis high-resolution multi-cycle elemental scans with pass energy 26 eV was performed. Each spectrum was then deconvoluted by appropriate basis functions. Before spectral fitting, each spectrum was corrected for reference binding energy for C1s to 284.8 eV.

FTIR spectral measurements were performed in a Nicolet FTIR Infrared Microscope equipped with a liquid N₂ cooled detector. Raman spectra of solid samples were measured in a Renishaw Raman microscope equipped with a 514 nm excitation laser. Scanning electron microscopic images were obtained by a FEI Quanta 400 ESEM FEG high-resolution field emission scanning electron microscope. The high-resolution TEM images of activated OPCs were obtained by a JEOL 2100 field emission gun transmission electron microscope. The textural properties: surface areas, distributions of pore volumes and total pore volume of carbonaceous materials were obtained by analysing N₂ sorption isotherms (measured at 77 K), measured in a Quantachrome Autosorb-3b BET Surface Analyser. The surface area (S_{BET}) was calculated by the multipoint BET (Brunauer–Emmett–Teller) method. Before measurements samples were dried at 140 °C for 12 h under high vacuum system equipped with a liquid N₂ cold trap. The apparent BET surface area (S_{BET}) of the activated PC samples was calculated from the N₂ adsorption isotherm in the partial pressure (P/P₀) range of 0.05-0.30 and the total pore volume (V_P) was estimated from the amount of N₂ adsorbed at P/P₀ = 0.99. The distributions of pore volumes were determined by analysing the data via non-local density functional theory. Selected results are given in Table 1. Micropore and narrow pore volumes were determined by the *t*-plot method. Micropores include pores between 0.4 to 2 nm using Autosorb 6 software. The isosteric heat of adsorption for CO₂ and CH₄ capture was estimated at an uptake of 0.5 mmol.g⁻¹.

Synthesis of polyfurfuryl alcohol (PFFA)

In a typical synthesis, a solution was prepared by dissolving FeCl₃ (50 g) in CH₃CN (200 mL). To this a solution of furfuryl alcohol (5 g, Sigma Aldrich, 98%) mixed with CH₃CN 50 (mL) was slowly added. The mixture was stirred for 24 h under continuous argon purging. The polymerized product, brown colored polyfurfuryl alcohol (PFFA) was separated by filtration, washed thoroughly with DI water (ca. 4 L) and acetone (500 mL), before being dried at 40 °C for 12 h under vacuum (Yield = 98%).

Synthesis of polyanisyl alcohol (PAA)

In a typical synthesis, concentrated H₂SO₄ (~6 mL) was slowly added dropwise to a glass beaker containing anisyl alcohol (10 g) in three steps. In each step, H₂SO₄ (2 mL) was added in drops to the glass beaker, stirred with a glass stirrer and a purple coloured solid polymer of polyanisyl alcohol was formed. The synthesized polymer was separated from the mixture. To avoid over heating of reactants the glass beaker was kept surrounded by water/ice mixture. The reaction process continued until all the anisyl alcohol was converted into solid polymer. The synthesized polymer was washed with DI water (4 x 50 mL) to remove excess acid and then with acetone (200 mL). The solid polymer was then crushed into powder, transferred to a glass beaker and quickly washed with acetone (100 mL) and dried at room temperature for 12 h.

Conversion of polymer precursors to oxygenated porous carbon (OPC)

In a typical activation process, either PFFA or PAA (500 mg) was thoroughly mixed with KOH powder (1.5 g, crushed previously) in a mortar for 10 min. The mixture was then placed inside a quartz tube/tube furnace, dried for 20 min and then heated for 1 h (30 min for AA-OPC) at 500, 600, 700, 800 or 750 °C, under a flow of Ar (99.9%, flow rate 600 sccm). The activated samples were then washed with HCl (100 mL, 1.4 M) and DI water until the filtrate attained pH= 7. The product was dried at 70 °C for 12 h under vacuum. The yield of activated PC materials depended on the activation temperature, e.g., FFA-OPC₅₀₀ = 55%, FFA-

OPC₆₀₀ = 40%, FFA-OPC₇₀₀ = 30%, FFA-OPC₇₅₀ = 25-27%, and FFA-OPC₈₀₀ = 15%.

CO₂ and CH₄ uptake measurements

The volumetric uptake measurements (pressure dependent excess isotherms) of CO₂ and CH₄ were performed in an automated Sievert instrument (Setaram PCTPro).¹⁵ Various OPC samples were first crushed into powders and packed in a stainless steel autoclave sample cell. Initial sample pre-treatment was carried out at 130 °C for 1.5 h under high vacuum. The free volume inside the sample cell was determined by a series of calibration procedures done under helium. Gas uptake experiments were carried out with high purity research grade CO₂ (99.99% purity, Matheson TRIGAS) and CH₄ (99.9% purity). The gravimetric uptake measurements were performed in a Rubotherm magnetic suspension balance instrument (Rubotherm, Germany). A summary of selected results is given in Table 2.

Acknowledgements

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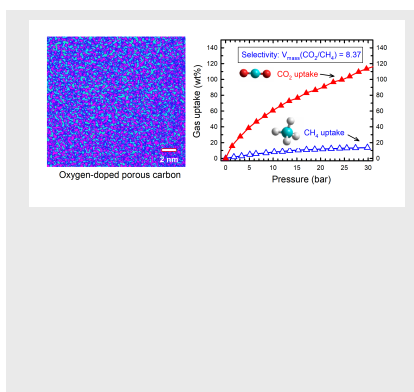
Keywords: CO₂ capture • Gas uptake • Surface area • Pore volume • Uptake selectivity

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Entry for the Table of Contents

FULL PAPER

We report the reproducible synthesis of oxygen containing porous carbon (OPC) by the KOH activation at 500-800 °C of two oxygen containing precursor polymers: polyfurfuryl alcohol (PFFA) and polyanisyl alcohol (PAA) yielding FFA-OPC and AA-OPC, respectively. Both OPC exhibits remarkable thermal stability and reproducible CO₂ capture properties for multiple cycles. The AA-OPC₇₅₀ demonstrates superior selectivity for CO₂ capture over CH₄ uptake.



Saunab Ghosh, Andrew R. Barron*

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Optimising carbon dioxide uptake and carbon dioxide-methane selectivity of oxygen-doped porous carbon prepared from oxygen containing polymer precursors