Adsorptive Separation of CO₂ in Sulfur-doped Nanoporous Carbons: Selectivity and Breakthrough Simulation

Dipendu Saha^{1,*}, Gerassimos Orkoulas¹, Jihua Chen², Dale K. Hensley²

¹ Department of Chemical Engineering,
Widener University, One University Place, Chester, PA 19013

² Center for Nanophase Materials Sciences, Oak Ridge National Laboratory. Oak Ridge, TN
37831, USA

*Corresponding author's E-mail: dsaha@mail.widener.edu, Phone: +1 610 499 4056, Fax: 610 499 4059 (D. Saha)

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Abstract

Sulfur-doped nanoporous carbons were synthesized by post-synthesis modifications with a sulfur-bearing compound that simultaneously enhanced the surface area and introduced sulfur functionalities on carbon. The BET surface areas of these materials were within 837 to 2865 m²/g with total sulfur contents of 8.2 to 12.9 %. The heat of adsorption of CO₂ in low uptake was 60-65 kJ/mol, which is the highest for CO₂ adsorption in porous carbons. In order to investigate the adsorptive separation of CO₂, nitrogen (N₂) and methane (CH₄) adsorption isotherms were also measured at 298 K and 760 torr. The selectivity of separation for CO₂/N₂ and CO₂/CH₄ was calculated based on the Ideal Adsorbed Solution Theory (IAST) and all the results demonstrated the high CO₂ selectivity for the carbon with higher sulfur content. The adsorption isotherms were combined with mass balances to calculate the breakthrough behavior of the binary mixtures of CO₂/N₂ and CO₂/CH₄. The simulation results demonstrated that the dimensionless breakthrough time is a decreasing function of the mole fraction of CO₂ in the feed stream. In a comparative study with a commercial activated carbon (Maxsorb: BET~3300 m²/g), both selectivity and breakthrough time were higher for sulfur-doped carbons. The overall results suggest that these sulfur-doped carbons can be employed as potential adsorbents for CO₂ separation, natural gas sweetening and biogas upgrading purposes.

1. Introduction

In today's perspective, there is an overwhelming need for separation of CO₂ from flue or post-combustion gas mixtures. The primary source of post-combustion CO₂ emission can be attributed to the burning of coal, oil and natural gas that contribute to 80 % of CO₂ release worldwide [1]. Amongst these sources, coal powered electricity generation plants release maximum amount of CO₂, contributing to 41% and 60% of CO₂ in U.S. and world, respectively [2]. The anthropogenic CO₂ emission has increased 80% in 2004 compared to previously recorded values. Its concentration in atmosphere has exceeded the value of 390 ppm, which is higher than any value recorded in modern time [3]. According to International Panel on Climate Change (IPCC), the expected temperature rise [3] at the end of 21st century is within 1.8 to 6.4 °C and the major part of it is caused by the anthropogenic greenhouse gas emission including CO₂. Separation of CO₂ from the flue gas stream is part of the carbon capture and sequestration (CCS) process, in which the captured CO₂ is either injected into different geological formations for permanent sequestration or employed as feedstock for other chemicals. For separation of CO₂ from coal based power plants or for gas sweetening, alkanolamine is the current technology for post-combustion CO₂ capture. However, this process is quite expensive and associated with different types of hazards. For coal power plants that utilize alkanolamine technique, the total energy penalty rises to 30% of the total output [1] and 70% of the total cost of CCS is contributed by the CO₂ separation unit. The other separation need for CO₂ lies with the natural gas sweetening process. Methane in natural gas is often associated with sour gases including CO₂ and other sulfur bearing compounds. In order to lower carbon emission, prevent corrosion and meet pipeline quality, natural gas needs to be separated from sour gases including CO₂. Biogas upgrading is another need for CO₂ separation, where CO₂ needs to be separated from CH₄ increase the fuel value of biogas.

Adsorptive separation, especially pressure swing adsorption (PSA) is an alternative process for CO₂ separation. It provides the advantage of inexpensive and sustainable separation process compared to other chemical separations. The key challenge for utilizing adsorptive separation is to employ a suitable adsorbent with high selectivity for CO₂ compared to other gases that are mixed with it. For post-combustion CO₂ separation, the

most common impurity that is often associated with it is nitrogen (N_2) and therefore, a high selectivity of CO_2/N_2 is required. For natural gas sweetening or biogas upgrading, CO_2 needs to be selectively separated from methane. Different kinds of adsorbents, including nanoporous carbons [4,5] zeolites [6-9], silica [10-12] or Metal-Organic Frameworks (MOFs) [3,13] have successfully demonstrated their potential role in CO_2 separation from N_2 or CH_4 . The details of CO_2 capture by adsorbent materials have been described in several review articles [3,10,13-18]. In order to investigate the preferential CO_2 adsorption from the gas mixture and owing to the difficulty in performing mixed gas adsorption, the selectivity and breakthrough behavior need to be evaluated from pure-component adsorption data using simple thermodynamic models (such as Ideal Adsorbed Solution Theory-IAST) and mass balances.

Hetero-atom doped nanoporous carbons, mostly, B, N, S or P-doped carbons have gained a lot of interest in today's perspective owing to their different applications in catalysis or energy storage [19,20]. Sulfur doping is one unique approach of heteroatom doping and provides several remarkable features to the host carbon. Unlike other heteroatoms, a sulfur atom is much larger compared to boron or nitrogen, so it protrudes out of the graphene plane, thereby creating an uneven surface with unique properties, such as superconductivity [21,22] as revealed in the theoretical studies. Other than structural defects, the lone pair of electrons in a sulfur atom induces polarizability and interactions with oxygen [20]. In the field of CO_2 adsorption, Xia et al. [23] reported an elevated CO_2 adsorption amount of 2.4 mmol/g at 25 °C on sulfur doped nanoporous carbons. The heat of adsorption was in the range of 59 kJ/mol near zero loading, which was one of the highest values ever reported for carbon-based materials. Seema et al.[24] reported an even higher CO_2 uptake amount of 4.5 mmol/g at 25 °C and ambient pressure in a reduced graphene oxide/polythiophene complex. Recently, Badosz et al. [25,26] reported the chemical interactions between sulfur doped carbons and CO_2 . Despite there are several reports on CO_2 adsorption on sulfur doped nanoporous carbons, the two drawbacks of the current works are (a) The sulfur doped nanoporous carbons were synthesized either from sulfur bearing polymers, some fine chemicals, or nanocarbons, which possesses an arduous task of scale-up to synthesize in bulk quantity, and (b) In the past studies, only CO_2 adsorption

isotherms were reported, but not the selectivity of separation of CO₂ from other gases or breakthrough plots. In this article, we reported a simple technique of synthesizing sulfur doped nanoporous carbons that are easy to scale-up and calculated the selectivity of CO₂ separation from N₂ and CH₄. Furthermore, we calculated the dimensionless breakthrough time associated with a pressure swing adsorption (PSA) process.

2. Experimental

2.1 Synthesis of sulfur-doped nanoporous carbons

To synthesize the sulfur doped carbon, we have modified the procedures reported by Liu and Antonietti [27]. The synthesis protocol requires two-steps, the synthesis of pure carbon and the simultaneous activation and sulfur doping. The synthesis of the pure nanoporous carbon is very similar to that of our previous publications [28-32]. Typically, 5 g of resorcinol and 4.3 g of Pluronic F127 were dissolved in solvent mixture composed of 20 mL water and 30 mL ethanol. After they are dissolved, 0.5 mL 36% HCl was added as catalyst and stirred for over an hour. Then, 4.8 mL of 36% formaldehyde solution was added as cross-linking agent and stirred for 3 days. The polymer layer is subsequently separated from the solvent and transferred to a Lindberg/Blue M™ tube furnace for carbonization. In the process of carbonization, the sample was heated to 100 °C at a ramp rate of 10 °C/min, then up to 400 °C at 2°C/min, and finally up to 1000 °C at 5°C/min. All the heating and cooling profiles were performed in nitrogen atmosphere.

In order to insert sulfur functionality and further activation of pure carbon, sodium thiosulfate (Na₂S₂O₃) was employed as the activating agent. Typically, solid sodium thiosulfate and carbons were mixed in 1:1, 2.5:1 and 4:1 ratio in a lab-scale blender and heated in a tube furnace up to 800 °C at 10°C/min in nitrogen atmosphere and cooled in the same fashion. The sample was removed from the furnace, washed with DI water for five times in 24 hours and then overnight. Throughout the manuscript, the sulfur doped carbons that were produced with 1:1, 2.5:1 and 4:1 ratios of sodium thiosulfate to carbons are termed as CS-1, CS-2 and CS-3, respectively.

2.2 Materials Characterization

All types of sulfur-doped carbons were characterized with x-ray photoelectron spectroscopy (XPS), pore textural properties and electron microscopy (SEM and TEM). XPS analyses were performed in a Thermo-Fisher K-alpha instrument operating at monochromatic Al-K α as an x-ray anode. The intensity of x-ray energy was 1486.6 eV and the resolution was 0.5 eV. The pore textural properties including BET surface area and pore size distributions were calculated from nitrogen adsorption-desorption experiments at 77 K and upto 760 torr in Quantachrome's Autosorb-iQ instrument. Pore size distribution data were obtained by using non-local density functional theory (NLDFT) in the instrument's built-in software. Scanning electron microscopic images were obtained in a Carl Zeiss Merlin SEM microscope operating at 30 kV. As a part of SEM imaging system, the energy dispersive X-ray (EDX) results were obtained with a system from Bruker Nano GmbH using an XFlash detector 5030. TEM images were captured in Carl Zeiss Libra 120 TEM operating at 120 kV. All the characterization results are best values.

2.3 Adsorption experiments

All the adsorption experiments were performed in volumetric mode in Quantachrome's Autosorb-iQ instrument up to ambient pressure (760 Torr) and varying temperature (278, 288 and 298 K). Before any adsorption experiment, all the samples were outgasses at 300 °C in the same instrument. Prior to measuring the adsorption isotherms, the free space volume was measured *in-situ* in the instrument automatically by helium expansion. An external Julabo temperature controller with a 1:1 mixture of propylene glycol and water as chilling fluid controlled the temperature for all the adsorption experiments except liquid nitrogen temperature (77 K). The preciseness of the temperature controller was within ± 0.02 °C of the set point. All the adsorbate gases were of ultra-high purity grade (UHP) and obtained from commercial source (Airgas, an Air Liquide company).

3. Results and Discussions

3.1 Materials characteristics

The qualitative and quantitative analyses of surface functionalities were obtained by the analysis of S-2*p* spectra of XPS ([figure 1](#)) and the results are shown in [table 1](#). The total sulfur contents vary from CS-1 to CS-3 in 8.2 to 12.9%, respectively. The key sulfur functionalities are C=S, C-S, -COS and SO_x, with the highest functional group being the C-S and SO_x groups in all the carbons. As per XPS results, the actual sulfur content may be slightly higher than reported value, as there are two overlapping regions between S-O and C-O groups, C-S-C/C-SH functionality and C-1*s* peaks. Therefore, three additional sulfur bearing functionalities, including S-O, C-S-C and C-SH may also be present in these samples, which were not possible to distinctively identify through XPS analysis. CS-1, CS-2 and CS-3 have 5.4, 6.3 and 8.6 % S-O/C-O groups, respectively. Besides that, CS-1, CS-2 and CS-3 have 8.9, 12.8 and 20.1% of oxygen, respectively, with approximately 1% or lower sodium in each sample that might have originated from sodium thiosulfate. From the XPS studies, it is evident that higher ratio of sodium thiosulfate in the synthesis stage resulted in higher sulfur content in the resultant carbons. The total sulfur contents in these two materials are higher than most of the sulfur-doped carbon materials synthesized from sulfur containing precursors, proteins or other sulfur bearing compounds, like thiophene or hydrogen sulfide [33]. However, this amount is lower than that of reported by Liu and Antoinette [27] (~30 %). The key reason for having a low sulfur content may be attributed to the fact that these authors [27] employed glucose as the carbon source unlike a porous carbon as in our study. At elevated temperature, glucose itself has a lower carbon or char yield compared to porous carbon and hence these numbers may not provide a one-to-one comparison with respect to the starting carbon materials. In order to provide a more light on the residual functionalities after adsorption experiments, we have selected the highest sulfur containing carbon, CS-3, for further analysis with XPS. The analysis confirmed that the sulfur content has decreased from 12.9 % to 9.6 %, whereas oxygen content decreased from 20.1 % to 14.8%. The detailed sulfur functionality was, C=S: 0.4%, C-S: 5.8%, -COS: 0.8 % and SO_x: 2.5%. A comparison from initial functionality suggests that the largest decrease belonged to the C-S (from 7.4 to 5.8 %) and SO_x (from 4.3 to 2.5%) that might have happened during repeated outgassing at elevated temperature and/or adsorption experiments [25,26]. However, a constant working capacity (mentioned in [fig 6\(d\)](#) later) suggests that lowering

of sulfur did not have a significant influence on CO₂ adsorption; may be the leaving functionalities, like C-S and SO_x has minimal interaction with CO₂.

The degree of burn off (B.O.) in CS-1, CS-2 and CS-3 are 55%, 35% and 24.5%, respectively, upon treating with sodium thiosulfate at elevated temperature. Interestingly, higher ratio of sodium thiosulfate resulted in lower degree of burn off, which is in contrary to the normal circumstances and the remarks made by Liu and Antonietti [27]. Such opposing trend may be attributed to the strong dependence of stoichiometric ratio of sodium thiosulfate in the mixture. Most likely, a higher ratio of sodium thiosulfate results in higher degree of functionalization of parent carbon with sulfur and oxygen compared to the actual burn-off. As mentioned earlier, a direct comparison with the results from Liu and Antonietti [27] is also difficult owing to the different natures of carbon precursors. Nitrogen adsorption-desorption isotherms at 77 K for all the sulfur-doped carbons including the pure carbon are shown in figure 2(a). All the isotherms are of Type IV according to IUPAC classifications with the hysteresis loop showing the capillary condensation in the mesopores. The pore textural properties of the carbons are shown in details in table 2. The BET specific surface area of parent carbon was 605 m²/g. Upon activating with sodium thiosulfate, the BET surface area of all the carbons increased; these are 2865, 1228 and 837 m²/g for CS-1, CS-2 and CS-3, respectively. It is clear that the BET surface area directly follows the trend in degree of burn off. Pore size distribution of both the samples are obtained by combining the NLDFT calculations from nitrogen adsorption at 77 K and CO₂ adsorption at 273 K, while employing CO₂ adsorption results for narrow micropore regions only. The pore size distribution results are shown in figure 2(b). All the carbons have micropore widths in the regions of 3.5, 4.8 and 15.4 Å, while the mesopore width lies within 40 to 45 Å. The total pore volume of the parent carbon was about 0.6 cm³/g; it was increased to 2.3, 1.1 and 0.71 cm³/g for CS-1, CS-2 and CS-3, respectively. To the best of our knowledge, the BET surface area of CS-1 (2865 m²/g) is probably higher than most of the sulfur-doped nanoporous carbons reported in literature, except that of reported by Liu and Antonietti [27]. The higher BET surface area possessed by most of the sulfur-doped carbons are in the range of 1100 m²/g [33]. CS-3 possessed the lower BET surface owing to its lower degree of burn off as mentioned earlier. However such BET

surface area is still higher than several other sulfur doped carbons produced from sulfur containing protein or polymeric materials [33]. In a pycnometer study, the helium or solid density of the materials were found to be 2.0-2.1 g/cm³.

SEM and TEM images of CS-1, CS-2 and CS-3 are shown in figure 3. TEM images did not reveal an ordered structure or porosity. SEM image of CS-3 revealed an ordered porosity in the structure as observed in figure 3(f). The top arrow on the left side of the figure 3(f) shows the network of channel-like structures, which are the side view of the mesopore passages. Similar arrow on the right hand side of the figure shows the opening or mouth of the mesopores that are arranged in an orderly fashion. Such ordering of mesopore networks were not observed for CS-1 or CS-2, most likely higher degree of burn off destroyed the ordered mesoporosity. The inset views of the SEM images (fig 3b, 3d and 3f) represent the EDX mapping for sulfur. According to EDX results, sulfur percent in CS-1, CS-2 and CS-3 and 7.55 to 9.53%, 9.8 to 11.1% and 12.52 to 13.9% respectively, which are very close to that of obtained in XPS results.

3.2 Adsorption results

Figure 4(a) through (d) show the CO₂ adsorption uptake for pure carbon, CS-1, CS-2 and CS-3, respectively, at the three different temperatures of 278, 288 and 298 K and pressure up to 760 Torr. It is clear that all the adsorbents demonstrated a higher adsorption of CO₂ from the parent carbon at all the three temperatures and as a consequence, the overall uptake of CO₂ is always higher for CS-1 at all conditions. At ambient temperature (298 K), the CO₂ uptakes were 2.06, 1.87, 1.81 and 1.63 mmol/g at 760 torr for CS-1, CS-2, CS-3 and parent carbon, respectively. The adsorption of CO₂ onto these sulfur-doped carbons may be attributed to both physisorption and a stronger reactive interaction between CO₂ and sulfur functionality as suggested by Seredych et al. [26] In the nanosized pores, the sulfur embedded onto the aromatic rings enhances the CO₂ adsorption by acid-base interactions. Additionally, sulfonate and sulfoxide groups can attract CO₂ by polar interactions. Hydrogen bonding between acidic groups on carbon surface and CO₂ may also influence CO₂ adsorption [26]. The highest CO₂ uptake in our work is slightly lower than that of reported by Xia et al. [23], (maximum 2.4 mmol/g) and

almost of half of that of reported by Seema et al [24] (maximum 4.5 mmol/g). The lower pure component CO₂ adsorption compared to that of previously published sulfur-doped carbons might be attributed to the lower micropore area in our carbons. From figure 2(b), it is evident that these carbons have a very significant amount of mesopore volume. It is also well known that narrow micropores are most optimal for CO₂ adsorption. It is possible that the larger mesopore volume did not take part in the adsorbing CO₂ and therefore, overall CO₂ uptake remained lower compared to the purely microporous carbons.

In order to further analyze the CO₂ adsorption in these carbons, we have selected two carbons, CS-1 and CS-3, as they possess the highest and lowest amount of sulfur functionalities. Figure 4(e) and (f) show the kinetics of CO₂ adsorption at the same temperatures of 278, 288 and 298 K for CS-1 and CS-3, respectively. In these figures, m_t is the mass adsorbed at time t and m_{∞} is the saturation mass. It is evident that the adsorption kinetics in CS-1 is slightly sluggish compared to CS-3. It took about 100 to 120 seconds to reach the reached saturation level in CS-1 unlike CS-3 that reached the saturation within 50 to 60 seconds. The slow kinetics in CS-1 may be attributed to its higher microporosity. It is also observed that the kinetics became slightly more sluggish with the decrease in temperature that suggests the adsorption is an energetically activated process. In order to model the kinetics, we have employed pseudosecond order equation that fit well with the experimental kinetics plot with 99% of regression fit. The pseudosecond order equation is given by [34]

$$\frac{dq_t}{dt} = k_2(q_{e,2} - q_t)^2 \quad (1)$$

where, q_t , $q_{e,2}$ and k_2 are uptake amount at time t , equilibrium uptake and pseudosecond order equilibrium constant, respectively. Integration of above equation yields to

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_{e,2}} \quad (2)$$

The pseudosecond order equilibrium constant (k_2) can be calculated from the linear plot of t versus $\frac{t}{q_t}$. The equilibrium constant can be related to temperature through an Arrhenius type of equation given by

$$k_2 = k_{2o} \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where E_a is the activation energy. The pseudosecond order model constants (k_2) are shown in [table 3](#) for CS-1 and CS-3 in three different temperatures of 298, 288 and 278 K. The activation energies (E_a) for CS-1 and CS-3 are 8.3 and 15.4 kJ/mol, respectively. For the micropore diffusion, the kinetic model involving the diffusivity can be calculated by the equation [[35,36](#)]

$$1 - \left(\frac{m_t}{m_\infty}\right) = \frac{6}{\rho^2} \exp\left(\frac{-\rho^2 D_c t}{r_c^2}\right) \quad (5)$$

where, D_c is the intracrystalline diffusivity and r_c is the intracrystalline radius. D_c / r_c^2 is referred to as diffusive time constant. The diffusive time constant (D_c / r_c^2) can be calculated by the linear regression of t versus $\ln\left(1 - \frac{m_t}{m_\infty}\right)$ plot within 70% to 99% of the value. In this study, the diffusive time constants were shown in [table 3](#) for CS-1 and CS-3 in three temperatures of 298, 288 and 278 K. The higher diffusive time constants of CS-3 support its faster kinetics.

From the isotherms at these three temperatures, we have calculated the heat of adsorption by using the Van't Hoff equation, given by,

$$\frac{DH}{RT^2} = -\left(\frac{\partial \ln P}{\partial T}\right)_a \quad (6)$$

where DH is the enthalpy or heat of adsorption, P is pressure and T is temperature and a is the adsorption amount. Integration of Van't Hoff equation yields to

$$\frac{DH}{RT} = \ln P + C \quad (7)$$

where C is constant of integration. From the set of isotherms at three different temperatures, a series of isosteres are generated, and from the slope of isosteres the heat of adsorption is calculated. Heat of adsorption values are shown in [figure 5](#). It is observed that the heats of adsorption of the both the carbons are in similar range. In the higher uptake or higher-pressure range, the heat of adsorption lies within 20-30 kJ/mol. In the region of very low adsorption, these carbons demonstrate very high heat of adsorption values of 60-65 kJ/mol. Probably, these values are higher than that of all other porous carbons and very similar to that of sulfur-doped carbons reported by Xia et al [\[23\]](#).

In order to compare the CO₂ adsorption with other gases, we have employed two most common gases that need to be separated from CO₂, and these are methane (CH₄) and nitrogen (N₂). The pure component adsorption isotherms of CO₂, CH₄ and N₂ at 298 K are shown in [figure 6\(a\)](#) and [\(b\)](#) for CS-1 and CS-3, respectively. As observed for most of the porous materials including carbons, CO₂ adsorption amount was always highest followed by CH₄ and N₂. The CH₄ uptake amounts were in the range of 0.93 to 0.74 mmol/g and nitrogen demonstrated the lowest uptake of 0.29 to 0.25 mmol/g. It is clear that, similar to that of CO₂ uptake, CH₄ and N₂ uptake amounts were also the direct functions of BET surface area and micropore volume. In order to compare the performance of gas adsorption capacities, we included the CO₂, CH₄ and N₂ adsorption isotherms at 298 for a commercial activated carbon, often termed as Maxsorb or AX-21. It has a high surface area (BET: 3300 m²/g) with predominantly microporous structure. It was observed that CO₂ and CH₄ adsorption amounts of Maxsorb are lower than that of sulfur-doped carbons at low-pressure region but increase monotonically with the increase in pressure. The nitrogen adsorption of Maxsorb is similar to that of our carbons. The other key observation is that all the isotherms of Maxsorb are linear within the ambient pressure of these measurements. Complete scan of CO₂ adsorption-desorption at 298 K for CS-1 and CS-3 are shown in [figure 6\(c\)](#) and it demonstrates a negligible hysteresis. [Figure 6\(d\)](#) shows the working capacity for CO₂ adsorption-desorption at 298 K for 10 cycles in CS-1 and CS-3. It shows a constant CO₂ capacity without any loss in the cycles.

The equilibrium selectivity ($a_{1/2}$) of component 1 (stronger adsorbate, CO₂) over component 2 (weaker adsorbate, CH₄ or N₂) is defined as [37]:

$$a_{1/2} = \frac{x_1/y_1}{x_2/y_2} \quad (8)$$

where x and y are the mole fractions of adsorbate in adsorbed phase and bulk gas phase, respectively. The most common and popular way of calculating selectivity from adsorption isotherms is the Ideal Adsorbed Solution Theory (IAST), originally proposed by Myers and Prausnitz [38]. Figure 7(a) and (b) show the selectivity for CO₂/N₂ and CO₂/CH₄, respectively as a function of total pressure at a mole fraction of CO₂ of 0.15. The selectivity of CO₂/N₂ is within 110 to 190 in the low-pressure range and decreases with pressure. The selectivity for CO₂/CH₄ is much lower, within 23 to 13 in the low-pressure range. It is also noteworthy to mention that CS-3 possesses a greater CO₂ selectivity compared to that of CS-1 for the both the gas pairs of CO₂/N₂ and CO₂/CH₄, despite the fact that pure component adsorption amount of each of the three gases including BET surface area were higher for CS-1. For comparison purposes, we have also included the selectivity values for Maxsorb in the same sets of plots. It is observed that the selectivity values of Maxsorb for both CO₂/N₂ and CO₂/CH₄ are lower than that of sulfur-doped carbons.

For pressure swing adsorption (PSA), it is also useful to calculate adsorption selection parameter ($S_{1/2}$) given by [6,37]

$$S_{1/2} = \frac{Dq_1}{Dq_2} a_{1/2} \quad (9)$$

where Dq_1 and Dq_2 are the differences in adsorption capacity (working capacity) at the adsorption and desorption pressure for component 1 and 2, respectively. In order to calculate adsorption selection parameter ($S_{1/2}$), we set the adsorption and desorption capacity at 760 torr (1 bar) and 76 torr (0.1 bar), respectively, at a CO₂ mole fraction of 0.15. Adsorption selection parameter as a function of pressure of CO₂ (at a mole fraction of 0.15) is shown in the secondary axes of figure 7(a) and (b). It is obvious that selection parameters are also higher for CS-3 compared to CS-1.

The amounts adsorbed in the porous material (in mmole/g), q_1 and q_2 , can be calculated from IAST as $q_1 = x_1 q$ and $q_2 = x_2 q$ where the total amount adsorbed, q , is found from the ideal solution formula

$$\frac{1}{q} = \frac{x_1}{q_1^*} + \frac{x_2}{q_2^*} \quad . \quad (10)$$

In Eq. (10), the terms q_1^* and q_2^* correspond to the adsorbed amounts of the pure species at the same temperature and spreading pressure (surface potential) as the binary system. The amounts adsorbed for CO₂/N₂ and CO₂/CH₄ in CS-1 and CS-3 in terms of the total pressure of the gas phase are shown in Figure 8. As is evident in figure 8, the equilibrium amount of CO₂ adsorbed at atmospheric pressure (760 torr) is in the range of 0.6 to 0.8 mmol/g.

In order to further investigate the efficiency of the materials as potential adsorbents for CO₂ separation, we have also developed a simple methodology that can be used to determine the breakthrough behavior of all binary mixtures studied. Consider flow of a binary gaseous mixture of species 1 and 2 through a column which is packed with adsorbent material. It is assumed that species 1 is the strong adsorbate (CO₂) compared to 2 (N₂ or CH₄). Furthermore, it is assumed that flow through the column resembles that of plug flow, the column is kept at isothermal conditions, and the pressure drop is negligible. Diffusion and mass transfer effects from the gas phase to the adsorber surface are also neglected. Thus, the gas phase, which is assumed to be an ideal gas, is always at thermodynamic equilibrium with the adsorbed phase. For the case for which the more selectively adsorbed component is present at low concentrations and or/the heats of adsorption are not large, the assumption of isothermal operation is satisfactory. Otherwise, an energy balance must also be considered. Although there have been some modeling approaches that considered diffusion and mass and heat transfer effects [39-42], most previous works [43-47] employed the same simplifying approximations as in this work, mainly due to difficulties in obtaining accurate estimates of the diffusion constants, the thermophysical properties of the system, and the relevant mass transfer parameters. Under these simplifying approximations, the adsorption process through the column can be

described by a set of two first-order partial differential equations [43-47], namely a mass balance for species 1

$$\frac{\partial C_1}{\partial t} + \frac{\partial(uC_1)}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \rho \frac{\partial q_1}{\partial t} = 0 \quad (11)$$

as well as a total mass balance

$$C \frac{\partial u}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \rho \frac{\partial q}{\partial t} = 0 \quad (12)$$

where C_j is the concentration of species j , $C = C_1 + C_2 = p/RT$ is the total concentration, u is the gas-phase velocity, ε is the column porosity, and ρ is the skeletal density of the solid material. The moles of species j adsorbed per unit adsorber volume, q_j , and the total moles, $q = q_1 + q_2$, are found from thermodynamic equilibrium relations (such as IAST). At fixed temperature T , and pressure p , the amounts adsorbed are functions of C_1 i.e., $q_1 = q_1(C_1)$ and $q = q(C_1)$. Solution of the system of equations (11) and (12) yields the concentration at position z within the column at time t . As material is deposited through the column the composition of the gas-phase changes and the gas-phase velocity u is, therefore, different from that at the inlet, u_0 .

Straightforward manipulation of (11) and (12) yields the following expression for the gas-phase velocity

$$\ln\left(\frac{u}{u_0}\right) = \int_{C_1(0,t)}^{C_1(z,t)} \frac{\frac{1-\varepsilon}{\varepsilon} \rho q'}{1 + \frac{1-\varepsilon}{\varepsilon} \rho \left(q'_1 - q' \frac{C_1}{C}\right)} dC_1 \quad (13)$$

where the prime signifies derivative with respect to C_1 . Using the previous expression for u , the mass balance (10) can be cast in the following form

$$\frac{\partial C_1}{\partial t} + u_c \frac{\partial C_1}{\partial z} = 0 \quad (14)$$

with

$$u_c = \frac{u}{1 + \frac{1-\varepsilon}{\varepsilon} \rho \left(q_1' - q' \frac{C_1}{C} \right)} \quad (15)$$

If an inlet condition $C_1(0,t) = f(t)$ is specified, the solution of (14) is of the form [37, 43] $C_1(z,t) = f(t - z/u_c)$. The inlet condition usually corresponds to a step function input (i.e., $f(t) = C_{10}H(t)$ where $H(t)$ is the unit step function). In that case, the outlet concentration, $C_1(L,t)$, will also be a step function characterized by a time lag t_{break} , given by

$$\frac{u_0 t_{\text{break}}}{L} = 1 + \frac{1-e}{e} r \left(q_1' - q' \frac{C_{10}}{C} \right) \quad (16)$$

which provides an estimate of the “breakthrough” time required to achieve separation of the binary mixture. For the case for which the pure-component isotherms are linear functions and the binary adsorption equilibrium can be described by IAST, the derivatives q_1' and q' are constants. For all other cases the derivatives must be evaluated numerically. In this work, the dimensionless breakthrough time defined as [44-47] $\tau = u_0 t_{\text{break}} / \varepsilon L$ has been calculated for all the binary systems under consideration.

Figure 9 shows the breakthrough plots for CO₂ in the mixture of CO₂/N₂ and CO₂/CH₄ in CS-1 and CS-3. The inlet mole fraction of CO₂ is 0.15 [44-47], the total pressure is 760 torr and the temperature is 300 K in all cases. The variation of the outlet velocity in terms of composition (mole fraction CO₂) is shown in Figure 10. As is evident in Figure 10, the outlet velocity varies at most 10% of the inlet. Based on the analysis, it is evident that the actual breakthrough time (t_{break}) for CO₂ in both CO₂/N₂ and CO₂/CH₄ mixture would be higher for CS-1 under the same condition of bed length, inlet velocity and bed porosity. Such longer breakthrough time in CS-1 may be attributed to the higher working capacity or essentially the higher adsorption uptake of CO₂ as observed in figure 6. In order to compare, we have also included the breakthrough time of Maxsorb for CO₂/N₂ and CO₂/CH₄ and it was observed that those time intervals were shorter than CS-1 and CS-3. Nonetheless, the breakthrough times shown in Figure 9 are roughly similar because the amounts of CO₂ adsorbed for all cases are also roughly similar and in the range of 0.6-0.8 mmol/g as is evident in figure 8. The dependency of the breakthrough time on the inlet

mole fraction and total pressure of CO₂ is shown in [figure 11\(a\)](#) and [\(b\)](#). The overall trend suggests that the breakthrough time decreases with the increase in mole fraction of CO₂ or total pressure as the bed becomes saturated quickly with the elevated level of CO₂ in the feed stream. For both the binary mixtures of CO₂/N₂ and CO₂/CH₄ and as a function of mole fraction, the difference in breakthrough time between CS-1 and CS-3 remains similar except for CO₂/N₂ when the CO₂ mole fraction is very low ($<10^{-3}$). The other distinct feature that can be observed from these plots is that the breakthrough time of CO₂ in CO₂/N₂ system decreases more sharply compared to that of CO₂/CH₄. Such difference may be attributed to the dissimilar interference in adsorption between N₂ and CH₄ in presence of CO₂ and difference in shapes of N₂ and CH₄ isotherms. For the breakthrough times with respect to pressure, all the patterns remained similar, i.e., breakthrough time decreases monotonically with the increase in pressure.

4. Conclusions

In this work, three sulfur-doped nanoporous carbons were synthesized by activating the resorcinol formaldehyde derived porous carbons with sodium thiosulfate in different ratios. The activation resulted in the dual results of incorporation of sulfur bearing functional groups onto the nanoporous carbons and enhancement of pore textural properties. The sulfur contents in the carbons were 8.2, 10.5 and 12.9%, where the major sulfur containing groups were C-S, C=S, -COS and SO_x. Volumetric CO₂ adsorption at the three temperatures of 298, 288 and 278 K confirmed the dependence of CO₂ adsorption on BET surface area. The kinetics of CO₂ adsorption fitted well with pseudosecond order model where the greater activation energy (calculated based on temperature dependent pseudosecond order rate constant) for higher sulfur bearing carbon demonstrated its stronger dependence with temperature for CO₂ adsorption. The heat of adsorption of CO₂ in low adsorption amount was 60-65 kJ/mol, which was highest for the porous carbons and is in the range of other sulfur-doped carbons reported in literature. In order to investigate the separation of CO₂ from other gases and to calculate the selectivity of separation, CH₄ and N₂ adsorption isotherms were also reported at 298 K. For both the materials, CO₂ adsorption was always higher followed by CH₄ and N₂. The selectivity of separation for

CO₂/N₂ and CO₂/CH₄ was calculated based on Ideal Adsorbed Solution Theory (IAST). The breakthrough plots for the gas pairs of CO₂/N₂ and CO₂/CH₄ were simulated by using mass balance and selectivity of separation. It was found that breakthrough time for CO₂ decreases with the increase in both its mole fraction and total pressure in the feed stream. In a comparative study with a commercial carbon (Maxsorb), the sulfur-doped carbons demonstrated both higher selectivity and longer breakthrough time. The overall results suggest that these sulfur-doped carbons can be employed as potential adsorbents for CO₂ separation and natural gas sweetening purposes. Although not economically verified, the overall results suggest that these sulfur-doped carbons as potential adsorbents for CO₂ capture and natural gas sweetening.

Due to reasons of simplicity, the modeling used in this work only considered local equilibrium and ignored mass and heat transfer effects. Future modeling efforts will be focusing on stochastic descriptions of the adsorption processes of the species in the porous materials using molecular dynamics [46, 47] and kinetic Monte Carlo simulations [48]. Furthermore, the macroscopic behavior of an adsorption column is determined by processes occurring at two different length and time scales: (a) those in the flowing gas phase that can be described by continuum equations such as Eqs. (11) and (12), and (b) those in the interior of the porous material that can be represented with mesoscopic/microscopic simulations. Future work on breakthrough modeling will be focusing on developing multiscale type of models [49, 50], in which one exchanges information between a fine and a coarse scale.

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Table 1. Characteristics of sulfur content

Content/functionality (%)	CS-1	CS-2	CS-3
Total sulfur (excluding S-O, C-O, C-S-C, C-SH)	8.2	10.5	12.9
C=S	0.2	0.22	0.3
C-S	5.1	6.7	7.4
-COS	0.9	0.8	0.9
SO _x	1.9	2.7	4.3
S-O/C-O	5.4	6.3	8.6
Total carbon content	82.9	76.5	67
Total oxygen content	8.9	12.8	20.1

Table 2. Pore textural properties of the carbons

Carbon type	BET SSA (m²/g)	Total pore volume (cm³/g)	Micropore volume (cm³/g)
Pure carbon	605	0.6	0.18
CS-1	2865	2.3	0.82
CS-2	1228	1.1	0.38
CS-3	837	0.71	0.23
Maxsorb (commercial, for Comparative study only)	3300	1.5	1.3

Table 3. Pseudosecond order rate constant (k_2) and diffusive time constants (D_c/r_c^2) for CS-1 and CS-3

Adsorbent	Parameters	T=298 K	T=288 K	T=278 K
CS-1	k_2 (mmol ⁻¹ s ⁻¹)	1.70	1.40	1.33
	D_c/r_c^2 (s ⁻¹)	4.19x10 ⁻³	3.21x10 ⁻³	2.81x10 ⁻³
CS-3	k_2 (mmol ⁻¹ s ⁻¹)	3.97	3.82	2.56
	D_c/r_c^2 (s ⁻¹)	9.02x10 ⁻³	8.79x10 ⁻³	5.79x10 ⁻³

Figure 1. XPS spectra of CS-1 (a) and CS-2 (b) and CS-3 (c)

Figure 2. Nitrogen adsorption-desorption plot at 77 K (a), Pore size distribution (PSD) obtained by non-local density function (NLDFT) theory calculations (b). The PSD was calculated by CO_2 adsorption at 273 K (left-side arrow, filled symbol) and N_2 adsorption at 77 K (right-side arrow, open symbol).

Figure 3. TEM images of CS-1, CS-2 and CS-3 (a, b, c) and SEM images of CS-1, CS-2 and CS-3 (d, e, f) and. The inset images of fig (d) through (f) show the EDX mapping for sulfur. The arrows in fig (f) indicate the ordered porosity in CS-3. The left arrow show the channel (side-view) of the mesopore while the right arrow shows the opening of the mesopore.

Figure 4. CO₂ adsorption isotherms in three temperatures of 298 K, 288 K and 278 K in pure carbon (a), CS-1 (b), CS-2 (c) and CS-3 (d). CO₂ adsorption kinetics in CS-1 (e) and CS-3 (f)

Figure 5. Heat of CO₂ adsorption in CS-1 and CS-3

Figure 6. Adsorption isotherms of CO₂, CH₄ and N₂ at 298 K in CS-1 (a) and CS-3 (b). For comparison, CO₂, CH₄ and N₂ isotherms on commercial activated carbons (Maxsorb) are also provided in the same plots. CO₂ adsorption-desorption in CS-1 and CS-3 at 298 K (c) and working capacity of CO₂ at 298 K for 10 cycles in CS-1 and CS-3.

Figure 7. Selectivity (α) and adsorption selection parameter (S) for CO₂/CH₄ (a) and CO₂/N₂ (b) as a function of total pressure of CO₂ (at $Y_{\text{CO}_2} = 0.15$) for CS-1 and CS-3. For comparison, selectivity values were also shown for Maxsorb.

Figure 8. Binary gas adsorption amounts (mmol/g) in CS-1 and CS-3 at 298 K as predicted by IAST. CO₂ and N₂ in CS-1 (a), CO₂ and CH₄ in CS-1 (b), CO₂ and N₂ in CS-3 (c), CO₂ and CH₄ in CS-3 (d)

Figure 9. Breakthrough plots for CO₂/N₂ and CO₂/CH₄ in CS-1 and CS-3. Breakthrough time (τ) is represented as, $t = u_0 t_{break} / \epsilon L$ (u_0 =feed velocity, t_{break} = actual breakthrough time, ϵ = bed porosity, L = bed length). All the plots were made with the mole fraction of CO₂ as 0.15 in the feed stream, a total pressure of 760 torr [44-47], and ambient temperature (300 K). For comparison, breakthrough plots for Maxsorb are also provided.

Figure 10. Outlet velocity u/u_0 in terms of mole fraction of CO_2 at the outlet for CO_2/N_2 and CO_2/CH_4 in CS-1 and CS-3. The inlet conditions are the same as those of figure 9.

Figure 11. Dimensionless breakthrough time ($t = u_0 t_{\text{break}} / eL$) of CO_2 as a function of: (a) its mole fraction in the feed stream (at a total pressure of 760 torr and temperature 300 K), and (b) the total pressure (at 300 K and 15% mole fraction of CO_2 at the inlet).