Porous Aromatic Frameworks Impregnated with Lithiated Fullerenes for Natural Gas Purification

Afsana Ahmed,†,‡ Ravichandar Babarao,‡ Runhong Huang,§ Nikhil Medhekar,§ B. D. Todd,† Matthew R. Hill,‡ and Aaron W. Thornton*,‡

†Department of Mathematics, School of Science, Faculty of Science, Engineering and Technology and Centre for Molecular Simulation, Swinburne University of Technology, Melbourne, VIC 3122, Australia
‡CSIRO Manufacturing Flagship, Private Bag 10, Clayton South MDC, VIC 3169, Australia
§Department of Materials Engineering, Monash University, Clayton, VIC 3168, Australia

ABSTRACT: Natural gas, a lower emission alternative than its fossil fuel counterparts, requires the removal of carbon dioxide, known as "sweetening", prior to its use. In this study we computationally explore the separation of methane and carbon dioxide using a new adsorbent consisting of lithium-decorated fullerenes (Li6C60) impregnated within a series of porous aromatic frameworks (PAFs) of various pore sizes. The strong affinity of CO2 with the impregnated frameworks, confirmed by density functional theory, leads to selective adsorption over CH4. The impregnation can also double the CO2 adsorption capacity compared to the bare PAF and increase selectivity of CO2/CH4 up to 48 for an optimum amount of Li6C60, which is above the current industry benchmark. Overall, the study reveals physical insights and proposes impregnated PAFs to be promising candidates for CO2/CH4 separations for natural gas purification.

I. INTRODUCTION

Natural gas as a vehicular fuel has a number of advantages both economically and environmentally. Compared to other fossil fuels like gasoline or diesel, natural gas reduces the amount of byproduct of CO, CO2, and SO2 by 97, 24, and 90%, respectively.1,2 Natural gas contains a variable amount of methane (CH4) ranging from (27–95%), with a wide range of other components including CO2 depending on the source; see the world reservoir Table S1 (Supporting Information). The presence of CO2 reduces the energy content of natural gas, contributes to climate change and often leads to pipeline corrosion.1,4 To prevent this and also to increase the commercial value of natural gas, it should meet established purity specifications that are known as "pipeline-quality-methane". To meet this criteria, the maximum amount of CO2 concentration cannot exceed 2%.1 In addition, when natural gas is transported over great distances, the use of pipelines is too expensive and inefficient, and therefore liquefied natural gas (LNG) is a more efficient form of transport.5 To make LNG, the gas is cooled to cryogenic conditions. During this process, the CO2 present can freeze and block pipeline systems which will cause transportation issues.6

In locations such as Germany (Central European Pannonian basin) or South Australia (Cooper Eromanga basin)7 this CO2 contamination exceeds 10%. As a result, it is critical to remove CO2 from natural gas for economic, operational, safety, and environmental reasons.8,9

For the separation of CO2 from a CO2/CH4 mixture, various technologies are available, such as chemical absorption,10,11 thermal and pressure swing adsorption,12,13 cryogenic distillation,10 and membrane separation.14,15 Among these gas separation techniques, adsorption-based separation has become a major gas separation tool in industry due to its inherent simplicity, ease of control, and relatively low operating costs.3,16 However, with the growing global demand for natural gas, separations must become more efficient for natural gas to remain economically competitive above other harmful fuel alternatives.

Several families of microporous materials have been considered for the selective adsorption of CO2/CH4 mixtures such as zeolites, metal–organic frameworks, activated carbons, silica, nanotubes, and other inorganic structures.4,9,17–21 In industry, for example, the adsorption process has been successfully implemented across the USA for the recovery of CH4 from landfill gases using zeolites.3,22 To further improve the performance of these systems, adsorbents must adsorb...
more gas at higher selectivities while retaining chemical, physical, and thermal stability.

Porous aromatic frameworks (PAFs) were reported as a new family of ultraporous materials with surface areas above 5000 m²/g, 5 times above that for zeolites, and thus capable of adsorbing copious amounts of gas. To date, most studies of adsorption in PAFs have focused on gas storage applications, and it is known that capacities can be drastically enhanced when the PAF surface is chemically functionalized.25,26 We recently considered PAFs for enhancing volumetric hydrogen storage at low pressure.27 Our work showed that the recently considered PAFs for enhancing volumetric hydrogen storage at low pressure.

Here we considered PAFs impregnated with Li₆C₆₀ by enhancing volumetric surface area and tuning the porosity for the separation of CO₂ over CH₄ and calculated a selectivity of 8. We expect that capacities can be drastically enhanced when the PAF surface is chemically functionalized.25,26 The metal sites on Li₆C₆₀ will increase the polarization of CO₂ and it is known that capacities can be drastically enhanced.

Lithiated fullerenes were randomly inserted within the PAF and a unit cell was constructed using the Forcite module of the Materials Studio package with cubic periodic boundaries.32 The prediction of CO₂ and CH₄ uptake inside the nLi₆C₆₀@PAF structures were calculated by the Grand Canonical Monte Carlo (GCMC) routine. GCMC has been used widely for the simulated separation of CO₂/CH₄ mixtures.17,21,37-40 CO₂ was represented as a three-site rigid molecule, and its intrinsic quadrupole moment was described by a partial charge model. Each site contains a carbon atom and is represented as a three-site rigid molecule, and its intrinsic quadrupole moment was described by a partial charge model. The four partial charges calculated from DFT calculations were evaluated by fitting to the electrostatic potential function using the Merz–Kollman (MK) scheme.35,36

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Table 1. Lennard-Jones and and Coulombic Parameters<sup>a</sup>

<table>
<thead>
<tr>
<th>species</th>
<th>site</th>
<th>σ (Å)</th>
<th>ε/σ&lt;sub&gt;0&lt;/sub&gt;</th>
<th>q(e)</th>
<th>ref</th>
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<td>CO₂</td>
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<td>2.799</td>
<td>29.66</td>
<td>+0.576</td>
<td>51</td>
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<tr>
<td>CH₄</td>
<td>O</td>
<td>3.011</td>
<td>82.96</td>
<td>-0.288</td>
<td>51</td>
</tr>
<tr>
<td>CH₄−C₆₀</td>
<td>C</td>
<td>3.73</td>
<td>148</td>
<td>0</td>
<td>51</td>
</tr>
<tr>
<td>CO₂−C₆₀</td>
<td>C</td>
<td>3.11</td>
<td>32.33</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>OₐCH₄−C₆₀</td>
<td>C</td>
<td>3.16</td>
<td>54.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄−PAF</td>
<td>C</td>
<td>3.36</td>
<td>225.44</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>CO₂−PAF</td>
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<td>80.52</td>
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<tr>
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<td>59.88</td>
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<tr>
<td>Li−CO₂</td>
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<td>19.32</td>
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<tr>
<td>Li−OₐCO₂</td>
<td>Li</td>
<td>2.5975</td>
<td>32.31</td>
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</tr>
</tbody>
</table>

<sup>a</sup>Here, C<sub>S</sub> and C<sub>SP</sub> represent sp<sup>3</sup> and sp<sup>2</sup> carbon atoms in all PAFs, respectively.
DFT calculations were performed with the Vienna Ab Initio simulation package (VASP)\(^47\) to calculate the \(\text{CO}_2\)−PAF and \(\text{CO}_2\)−\(\text{Li}_6\text{C}_{60}\) binding energies. The projector augmented wave (PAW) methods\(^48\) were used to describe the core and valence electrons. The Perdew−Burke−Ernzerhof (PBE)\(^49\) was used to describe the electron exchange and correlations. The DFT-D2 method\(^50\) was applied for the long-term van der Waals dispersion corrections. The Brillouin zone was sampled centered \(\gamma\) centered \(k\)-point mesh. The binding energy was calculated according to the formula:

\[
E_{\text{binding}} = E_{\text{substrate+gas}} - E_{\text{substrate}} - E_{\text{gas}}
\]  

GCMC simulations were carried out for the adsorption of single components within the range of frameworks. As a widely used technique to simulate adsorption, GCMC allows the comparison of adsorbate chemical potentials in both adsorbed and bulk phases. In this method, the adsorbent structures were treated as a rigid body. A total of \(10^7\) trial moves were used for equilibration and another \(10^7\) moves for the production steps to calculate the average amount of adsorbed gas molecules. To verify the force field, comparisons were made to experimental single component \(\text{CO}_2\) isotherms\(^24\) (Figure 2).

IAST has proven an effective method for predicting gas mixtures within a wide variety of porous materials, such as zeolites,\(^17,56\) MOFs\(^9,57\) and ZIFs\(^21,38,58\). The method considers the spreading pressure of each gas upon a uniform surface. Perez-Carbajo et al.\(^59\) recently demonstrated that IAST could reasonably describe the mixed adsorption of a five component mixture (\(\text{CO}_2\), \(\text{CH}_4\), \(\text{CO}\), \(\text{N}_2\), and \(\text{H}_2\)) within a range of zeolites (FAU, MFI, MOR, and DDR) up to 100 bar. Here the method was utilized to calculate the selectivity across a range of feed composition ratios.

### III. RESULTS AND DISCUSSION

The effect of \(\text{Li}_6\text{C}_{60}\) impregnation upon adsorption up to 2 bar and 298 K is shown in Figure 2a–c for \(\text{CO}_2\) and for \(\text{CH}_4\) in Figure 3a–c for PAF-302, PAF-303, and PAF-304, respectively. The trends are highlighted with arrows. \(\text{CO}_2\) uptake reaches a maximum at a particular amount of \(\text{Li}_6\text{C}_{60}\) whereas the \(\text{CH}_4\) uptake continually decreases with impregnation.

The maximum uptake of \(\text{CO}_2\) at 2 bar was found to be 15.6 mmol/g in PAF-302 impregnated with one \(\text{Li}_6\text{C}_{60}\) molecule, which is approximately a 100% increase in adsorption capacity compared to that of the bare PAF. The maximum \(\text{CO}_2\) uptakes for PAF-303 and PAF-304 were 12 and 11.5 mmol/g with 10 \(\text{Li}_6\text{C}_{60}\) and 27 \(\text{Li}_6\text{C}_{60}\), respectively, which are approximately a 98% and 47% increases compared to uptakes of bare PAF-303 and PAF-304. Moreover, the maximum numbers of impregnated \(\text{Li}_6\text{C}_{60}\) that can fit within the PAF unit cells are 6, 17, and 40 for PAF-302, PAF-303, and PAF-304, respectively.

There are two reasons for the maximum \(\text{CO}_2\) uptake at a particular loading. One reason is that the highest \(\text{N}_2\) accessible volumetric surface area (m\(^2\)/cm\(^3\)) was reached at that particular loading, shown in Figure 4. The second reason is that the interactions between \(\text{CO}_2\) and \(\text{Li}_6\text{C}_{60}\) are strong whereas for \(\text{CH}_4\) these interactions are negligible, shown in Figure 5. Therefore, the \(\text{CO}_2\) uptake increases with the increased surface area whereas \(\text{CH}_4\) uptake does not benefit from the increased surface area and rather is inhibited by the loss in pore volume.

The volumetric surface area was found to correlate with the \(\text{CO}_2\) uptake (Figure 4). Upon impregnation of \(\text{Li}_6\text{C}_{60}\) in all three PAFs, the surface area and the \(\text{CO}_2\) uptake both increase up to a maximum level followed by a decrease with further \(\text{Li}_6\text{C}_{60}\) loading. The maximum volumetric surface areas of 2096, 2140, and 2109 m\(^2\)/cm\(^3\) were achieved for PAF-302, PAF-303, and PAF-304, respectively, with corresponding numbers of \(\text{Li}_6\text{C}_{60}\) molecules of 1, 10, and 27. Therefore, the maximum \(\text{CO}_2\) uptake is a result of maximizing the volumetric surface area with impregnation. Frost et al.\(^60\) also observed structure—

![Figure 2](image-url)
property relationships that were pressure-dependent. These trends are confirmed here within the medium to low range of pressures where impregnation and ligand extension allows the control of both the surface area and pore volume.

The isosteric heat of adsorption ($q_{st}$) for CO$_2$ and CH$_4$ is shown in Figure 5a,c, respectively, and is directly related to the gas–framework interaction strength. The $q_{st}$ in bare PAF-303 and PAF-304 for CO$_2$ is in the ranges 16–18 and 17–19 kJ/mol, respectively, whereas, for 10 Li$_6$C$_60$ PAF-303 and 27 Li$_6$C$_60$ PAF-304 this value reaches maximum ranges of 39–41 and 41–43 kJ/mol, respectively. These values are in agreement with DFT-based calculations that predict a binding energy of 19 and 45 kJ/mol for CO$_2$ on PAF and Li$_6$C$_60$, respectively, Figure 5b. These $q_{st}$ values of CO$_2$ in impregnated PAFs are much higher than CH$_4$ $q_{st}$ values, which are 17 and 18 kJ/mol for 10 Li$_6$C$_60$ PAF-303 and 27 Li$_6$C$_60$ PAF-304, respectively. These high differences in $q_{st}$ values also indicate the promise for high selectivity of CO$_2$ over CH$_4$.

The radial distribution function (RDF) between Li$_6$C$_60$ in PAF-304 and the guest molecules is shown in Figure S2 of Supporting Information. A peak in $g(r)$ for CO$_2$ is observed at $r = 4$ Å, indicating a high density of CO$_2$ close to charged Li$_6$C$_60$, whereas no significant peaks exist for CH$_4$, indicating bulk-like gas behavior. This confirms that CO$_2$ interacts strongly with the Li$_6$C$_60$ surface within the PAF, forming an adsorbed layer, whereas CH$_4$ molecules interact weakly. Considering this, an adsorbed layer that is denser than the bulk gas phase will enhance the overall uptake and will correlate directly with the available surface area. For CH$_4$, on the contrary, there is only bulk gas phase present, which correlates with the accessible pore volume that continually decreases with impregnation.

The adsorption separation factor is defined by $S_{ij} = \frac{x_i}{x_j}\frac{y_j}{y_i}$, where $x_i$ and $y_i$ are the mole fraction of component $i$ in the adsorbed phase and the bulk feed, respectively. For ideal selectivity $y_j/y_i = 1$, and therefore, $S_{ij} = x_i/x_j$. Here, the ideal gas selectivity for CO$_2$/CH$_4$ was plotted against CO$_2$ uptake in Figure 6a–c and Figure S2 (in Supporting Information) for pressures up to 2 bar. This can be defined as a trade-off plot where a maximum selectivity along with a maximum uptake is desired. The highest selectivities were observed for 27 Li$_6$C$_60$ PAF-304, 10 Li$_6$C$_60$ PAF-303, and 1 Li$_6$C$_60$ PAF-302. Both selectivity and uptake increased up to an optimum number of Li$_6$C$_60$ loading and then decreased with further impregnation.

For industrial application, the mixed selectivity is of interest. Here we predict the mixed selectivity using IAST for different ratios of CO$_2$/CH$_4$ (Figure 7 and Figure S3, Supporting Information). The feed composition is assumed to be 20:80. From the IAST predictions we observe a reduced CO$_2$ uptake and an increased selectivity. This is because the CO$_2$ will...
dominate available adsorption sites over CH$_4$ but at a loss of capacity. For a higher selectivity, fewer separation stages are required and for higher CO$_2$ uptake less material is required. For all gas mixture ratios, the selectivity of the impregnated PAFs followed the following order: 27 Li$_6$C$_{60}$ PAF-304 > 10 Li$_6$C$_{60}$ PAF-303. The IAST mixture adsorption also indicated that Li$_6$C$_{60}$ impregnation within PAFs enhanced the separation efficiency of an adsorbed based system. The separation of CO$_2$ from the 20:80 CO$_2$:CH$_4$ mixture is 47 and 31 for 27 Li$_6$C$_{60}$ PAF-304 and 10 Li$_6$C$_{60}$ PAF-303, respectively, which are larger than other promising adsorbents such as covalent organic frameworks, zeolitic imidazolate frameworks and IRMOF-1.\textsuperscript{51,62} The selectivities are also above the zeolite SA currently used within industry.\textsuperscript{63}

Figure 5. (a) CO$_2$ isosteric heats of adsorption with DFT-based binding energy values (solid black symbols). (b) Strongest binding sites for CO$_2$ on PAF and Li$_6$C$_{60}$ from DFT calculations with binding energies. (c) Isosteric heats of adsorption of CH$_4$ in bare PAFs and impregnated PAFs.

Figure 6. Ideal selectivity CO$_2$/CH$_4$ vs CO$_2$ uptake at 298 K in Li$_6$C$_{60}$ impregnated (a) PAF-302, (b) PAF-303, and (c) PAF-304. Arrows emphasize the trends with the increasing amount of impregnation.
Finally, comparisons with simulated performances for other materials were made (Figure 8). Here, the ideal selectivity and the working capacity (or delta loading) were used. The working capacity is defined as the difference between uptakes at desorption (1 bar) and adsorption (10 bar) pressures. Twenty-seven Li$_6$C$_{60}$ PAF-304 and 10 Li$_6$C$_{60}$ PAF-303 showed moderate selectivities with relatively high working capacities compared to those of the other adsorbents. Higher selectivities were found at 2 bar, which means that the separation could be performed at lower pressures, assuming that the materials is completely evacuated of gas. This could possible reduce the energy requirements for separation.

There is an apparent upper bound trade-off between selectivity and capacity that the impregnated PAFs cannot overcome. Overall, the impregnated PAFs have tunable surface areas and porosity to customize separation requirements.

IV. CONCLUSION

The adsorption of CO$_2$/CH$_4$ mixtures has been investigated using molecular simulation for Li$_6$C$_{60}$ impregnated PAF structures. The simulation isotherms for pure components of CO$_2$ and CH$_4$ are in good agreement with the literature. The highest adsorption selectivity for CO$_2$ over CH$_4$ is predicted as 47–48 for 27 Li$_6$C$_{60}$ PAF-304 and 30–31 for 10 Li$_6$C$_{60}$ PAF-303. The highest volumetric surface area correlated with the highest CO$_2$/CH$_4$ selectivity and the highest CO$_2$ uptake at the optimal Li$_6$C$_{60}$ loading. The results show that the available surface area within 27 Li$_6$C$_{60}$ PAF-304 and 10 Li$_6$C$_{60}$ PAF-303 offer stronger adsorption sites for CO$_2$ than for CH$_4$. The high CO$_2$ adsorption selectivity at 2 bar suggests that Li$_6$C$_{60}$@ PAF could be successfully used for natural gas (CH$_4$) purification.

In comparison with other adsorbents, the impregnated PAFs showed moderate selectivities with relatively high working capacities at standard operating conditions cycling between 1 and 10 bar. There is an apparent upper bound trade-off between selectivity and capacity that the impregnated PAFs cannot overcome. Overall, the impregnated PAFs have tunable surface areas and porosity to customize separation requirements.

ASSOCIATED CONTENT

Supporting Information

Table S1 shows the composition of natural gas reservoirs across the world. Figure S1 shows the charge assignment within the frameworks for (a) PAF-302 (four types of carbon and one type of hydrogen atom), (b) PAF-303 (eight types of carbon and two types of hydrogen atom), (c) PAF-304 (eight types of carbon and two types of hydrogen atom), and (d) Li$_6$C$_{60}$ (three types of carbon and one type of lithium atom). Figure S2 shows the radial distribution function $g(r)$ between the Li$_6$C$_{60}$ and the center of mass for CO$_2$ and CH$_4$ molecules. Figure S3 shows the ideal selectivity of CO$_2$/CH$_4$ at 298 K and 2 bar. Figure S4 shows the selectivity vs CO$_2$ uptake at 298 K in (a) 27 Li$_6$C$_{60}$ PAF-304 and (b) 10 Li$_6$C$_{60}$ PAF-303 for different ratios of CO$_2$:CH$_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* A. W. Thornton. Tel: +61418438423. E-mail: aaron.thornton@csiro.au.

Notes

The authors declare no competing financial interest.

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