Nitrogen-functionalized porous carbons for enhanced CO2 capture

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Nitrogen-Functionalized Porous Carbons for Enhanced CO₂ Capture

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Mission Statement:

To design and understand trace metal and carbon dioxide transformation and/or capture on surfaces to prevent their release into the atmosphere.
Surface Functionalization

\[ \phi = \phi_D + \phi_R + \phi_P + \phi_\mu + \phi_Q + \phi_S \]

\[ \phi_Q = \frac{1}{2} Q \frac{\delta E}{\delta r} \]

\[ Q = \frac{1}{2} \int q(\rho, \theta)(3\cos^2\theta - 1)\rho^2 dV \]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Kinetic diameter (nm)</th>
<th>Dipole moment (Debye)</th>
<th>Quadrupole moment ((10^{-40}) Coulomb·m²)</th>
<th>Polarizability ((10^{-24}) cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.330</td>
<td>0</td>
<td>-13.71, -10.0</td>
<td>2.64, 2.91, 3.02</td>
</tr>
<tr>
<td>N₂</td>
<td>0.364</td>
<td>0</td>
<td>-4.91</td>
<td>0.78, 1.74</td>
</tr>
</tbody>
</table>

N-functionalization

Carbon, 1995, 33(11), pp 1641-1653
Carbonization and Activation Treatments

Carbonization = 350 °C; Activation = 500, 600, 800 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carb. temp</th>
<th>Act. Temp</th>
<th>C content</th>
<th>N content</th>
<th>N-5/N5′</th>
<th>N-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>deg C</td>
<td>deg C</td>
<td>wt%</td>
<td>wt%</td>
<td>wt%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350-500</td>
<td>350</td>
<td>500</td>
<td>56.8</td>
<td>5.77</td>
<td>5.01</td>
<td>0.76</td>
</tr>
<tr>
<td>350-600</td>
<td>350</td>
<td>600</td>
<td>57.0</td>
<td>4.0</td>
<td>3.69</td>
<td>0.31</td>
</tr>
<tr>
<td>350-800</td>
<td>350</td>
<td>800</td>
<td>65.4</td>
<td>3.19</td>
<td>2.66</td>
<td>0.54</td>
</tr>
</tbody>
</table>


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CO\textsubscript{2} Performance

Geometric Optimization and Surface Charge (Bader)

*VASP, 750ev, 6x6x1, PBE
GCMC Molecular Simulation

\[ E = E_{\text{LJ}} + E_{\text{coul}} \]

\[ e^{-\beta \Delta E} \]

\([0, 1]\)

\(\mu, V, T\)
Part I

N-Functionalized Carbon Sorbents for Post-Combustion Capture
Functional Effect

Psarras et al., *manuscript in preparation*
Charge/Loading Relationship

- Pure Graphene
- Monovacancy
- Quaternary Nitrogen
- Pyrrolic Nitrogen
- Pyridinic Nitrogen
- Oxidized Pyridinic
- 2-Hydroxypyridine
- 2-Pyridone

CO$_2$ Loading (mmol/g sorbent) vs Pressure (kPa)

Loading vs. $q_{H,O,N}$

$\rho_{\text{Bar}}$: 0.001, 0.01, 0.1, 1.0
N-Coverage Effect

<table>
<thead>
<tr>
<th>Pressure (kPa)</th>
<th>N wt %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>3.63</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.1740</td>
</tr>
<tr>
<td>N₂</td>
<td>0.0016</td>
</tr>
<tr>
<td>Selectivity</td>
<td>108.8</td>
</tr>
</tbody>
</table>
Pore Size Effect

PC

NGCC
Binary Loading

10:90 CO₂:N₂

[Graphs showing CO₂ and N₂ loading as a function of pressure for different samples.]

[Bar charts showing CO₂ and N₂ loading at different pressures for PG, NQ, N6, NO, NP, NT samples.]
CO$_2$:N$_2$ Selectivity

![Graph showing CO$_2$:N$_2$ selectivity and IAST HL values for different pore sizes.](image)

<table>
<thead>
<tr>
<th></th>
<th>IAST</th>
<th>HL</th>
<th>3.5</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG</td>
<td>21.70</td>
<td>30.12</td>
<td>61.81</td>
<td>26.29</td>
<td>10.00</td>
<td>6.84</td>
<td>3.89</td>
<td>3.58</td>
</tr>
<tr>
<td>NQ</td>
<td>37.67</td>
<td>87.84</td>
<td>225.69</td>
<td>97.13</td>
<td>18.63</td>
<td>11.15</td>
<td>10.81</td>
<td>6.69</td>
</tr>
<tr>
<td>N6</td>
<td>37.56</td>
<td>78.11</td>
<td>212.97</td>
<td>101.00</td>
<td>14.23</td>
<td>10.61</td>
<td>9.21</td>
<td>6.92</td>
</tr>
<tr>
<td>N5</td>
<td>24.11</td>
<td>31.13</td>
<td>73.66</td>
<td>29.12</td>
<td>13.07</td>
<td>7.80</td>
<td>4.31</td>
<td>1.92</td>
</tr>
<tr>
<td>NO</td>
<td>47.02</td>
<td>153.51</td>
<td>251.93</td>
<td>199.63</td>
<td>100.93</td>
<td>41.65</td>
<td>21.45</td>
<td>28.52</td>
</tr>
<tr>
<td>NP</td>
<td>28.45</td>
<td>72.74</td>
<td>119.65</td>
<td>40.85</td>
<td>18.17</td>
<td>7.71</td>
<td>11.36</td>
<td>1.34</td>
</tr>
<tr>
<td>NT</td>
<td>26.05</td>
<td>91.00</td>
<td>129.86</td>
<td>43.91</td>
<td>18.23</td>
<td>7.82</td>
<td>9.77</td>
<td>12.17</td>
</tr>
</tbody>
</table>
Part II

N-Functionalized Carbon Sorbents for Natural-Gas Sweetening
Conclusions

- Ultra-microporous volumes are crucial to the enhancement of CO$_2$ capacity and HL selectivity
- Oxidized pyridinic nitrogen was most influential to loading enhancement, followed by quaternary and pyridinic groups
- There appears to be an optimal coverage for N-moieties – increasing N coverage did not enhance CO$_2$ selectivity
- PC/NGCC PCC is particularly sensitive to ultra-microporous structure

Acknowledgements

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