Supporting Information

Computational Study of the Effect of Functional Groups on Water Adsorption in Mesoporous Carbons: Implications for Gas Adsorption

Xuan Penga,*, Jose Manuel Vicent-Luna, Surendra Kumar Jain, Qibing Jina, Jayant Kumar Singh
aCollege of Information Science and Technology, Beijing University of Chemical Technology, Beijing 100029, PR China
bDepartment of Physical, Chemical and Natural Systems, Universidad Pablo de Olavide, Ctra. Utrera Km 1, ES-41013 Seville, Spain
cDepartment of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

This supporting information provides the pore size distribution of CMK models (Figure S1), the experimental adsorption isotherms of water in CMK-1, CMK-3, and CMK-5 taken from the literature (Figure S2), the snapshots of water adsorption in CMK models (Figures S3-S6), the pair correlation functions for O-O and O-H in CMK models for 4 cylindrical shells (Figures S7-S9), the self-diffusion coefficients of water in CMK models without and with functional groups at low coverage (Figure S10), the potential parameters of water, functional groups and carbon materials (Table S1), the average number of molecules and energy with their corresponding error (Table S2), the O-H and O-O minimum and maximum distance for 1st and 2nd hydrogen bonded shells for water molecules for CMK models with 2 and 4 cylindrical shells (Tables S3-S10), and the cluster statistics for CMK models (Tables S11-S13).

* Corresponding author.

E-mail address: pengxuan@mail.buct.edu.cn (X. P.).
Figure S1. Pore size distribution of CMK-1, CMK-3 and CMK-5 models
Figure S2. Experimental adsorption isotherms (fractional filling in the top and gravimetric uptake in the bottom) of water in CMK-1, CMK-3, and CMK-5 taken from references [40] and [41] in the manuscript.
**Figure S3.** Snapshot of water adsorption in CMK-1 models with functional groups in 4 cylindrical shells.

**Figure S4.** Snapshot of water adsorption in CMK-3 models with functional groups in 4 cylindrical shells. At chemical potential ($\mu$) : (a) -11.2 kcal/mol (b) -11.0 kcal/mol (c) -10.8 kcal/mol and (d) -10.6 kcal/mol.
Figure S5. Snapshots of water adsorption in CMK-5 models (2 cylindrical shells) at different chemical potentials.
Figure S6. Snapshots of CMK-5 models (4 cylindrical shells) at different chemical potential: (a) -11.2 kcal/mol (b) -10.8 kcal/mol (c) -10.7 kcal/mol and (d) -10.5 kcal/mol
Figure S7. Pair correlation function for O-O (left) and O-H (right) in CMK-1 model at different chemical potentials for 4 cylindrical shells.

Figure S8. Pair correlation function for O-O (left) and O-H (right) in CMK-3 model at different chemical potentials for 4 cylindrical shells.
Figure S9. Pair correlation function for O-O (left) and O-H (right) in CMK-5 model at different chemical potentials for 4 cylindrical shells.

Figure S10. Self-diffusion coefficients of water in CMK-1, CMK-3, and CMK-5 models without and with functional groups as a function of the temperature from MD simulations at low coverage.
Table S1. Potential parameters for OH and -COOH groups

<table>
<thead>
<tr>
<th>Group</th>
<th>Site</th>
<th>σ (Å)</th>
<th>ε (kcal/mol)</th>
<th>q (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydroxyl</td>
<td>C&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.07</td>
<td>0.1554</td>
<td>-0.64</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.2</td>
<td>0.1554</td>
<td>-0.64</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.44</td>
<td>0.1554</td>
<td>-0.64</td>
</tr>
<tr>
<td>carboxyl</td>
<td>C&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.75</td>
<td>0.1033</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>2.96</td>
<td>0.21</td>
<td>-0.5</td>
</tr>
<tr>
<td></td>
<td>O(=C)</td>
<td>3.0</td>
<td>0.1701</td>
<td>-0.58</td>
</tr>
<tr>
<td></td>
<td>O(-H)</td>
<td>3.0</td>
<td>0.1701</td>
<td>-0.58</td>
</tr>
<tr>
<td></td>
<td>H(-O)</td>
<td>0.45</td>
<td>0.1701</td>
<td>-0.58</td>
</tr>
</tbody>
</table>

<sup>a</sup> carbon atom located in plane of nanopipe surface

Table S2. Average number of molecules and energy with their corresponding error at chemical potential of -11 kcal/mol

<table>
<thead>
<tr>
<th>2-shells</th>
<th>average number of molecules</th>
<th>root-mean-square error on the average</th>
<th>average energy</th>
<th>root-mean-square error on the average</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMK-1</td>
<td>1152.2385</td>
<td>0.1040</td>
<td>-13001.665</td>
<td>1.0338</td>
</tr>
<tr>
<td>CMK-3</td>
<td>1855.7213</td>
<td>0.1394</td>
<td>-20425.643</td>
<td>1.4776</td>
</tr>
<tr>
<td>CMK-5</td>
<td>1124.0615</td>
<td>0.1094</td>
<td>-12924.108</td>
<td>1.2190</td>
</tr>
</tbody>
</table>

Table S3. O-O minimum and maximum distance for 1<sup>st</sup> and 2<sup>nd</sup> hydrogen bonded shells for water molecules for CMK-1 models (2 shells and 4 shells)

<table>
<thead>
<tr>
<th>CMK-1</th>
<th>μ (kcal/mol)</th>
<th>O-O (max) 1&lt;sup&gt;st&lt;/sup&gt; hydrogen shell</th>
<th>O-O (min) 1&lt;sup&gt;st&lt;/sup&gt; hydrogen shell</th>
<th>O-O (max) 2&lt;sup&gt;nd&lt;/sup&gt; hydrogen shell</th>
<th>O-O (min) 2&lt;sup&gt;nd&lt;/sup&gt; hydrogen shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 shells</td>
<td>-11.0</td>
<td>3.44</td>
<td>2.49</td>
<td>6.40</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>-10.7</td>
<td>3.41</td>
<td>2.47</td>
<td>6.55</td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>3.45</td>
<td>2.43</td>
<td>6.39</td>
<td>2.54</td>
</tr>
<tr>
<td>4 shells</td>
<td>-11.0</td>
<td>3.43</td>
<td>2.51</td>
<td>6.28</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>-10.7</td>
<td>3.44</td>
<td>2.46</td>
<td>6.61</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>3.44</td>
<td>2.42</td>
<td>6.35</td>
<td>2.49</td>
</tr>
</tbody>
</table>
**Table S4.** O-H minimum and maximum distance for 1\textsuperscript{st} and 2\textsuperscript{nd} hydrogen bonded shells for water molecules for CMK-1 models (2 shells and 4 shells)

<table>
<thead>
<tr>
<th>CMK-1</th>
<th>μ (kcal/mol)</th>
<th>O-H (max) 1\textsuperscript{st} hydrogen shell</th>
<th>O-H (min) 1\textsuperscript{st} hydrogen shell</th>
<th>O-H (max) 2\textsuperscript{nd} hydrogen shell</th>
<th>O-H (min) 2\textsuperscript{nd} hydrogen shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 shells</td>
<td>-11.0</td>
<td>1.85</td>
<td>1.25</td>
<td>2.53</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>-10.7</td>
<td>1.84</td>
<td>1.25</td>
<td>2.55</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>1.86</td>
<td>1.25</td>
<td>2.52</td>
<td>1.26</td>
</tr>
<tr>
<td>4 shells</td>
<td>-11.0</td>
<td>1.85</td>
<td>1.25</td>
<td>2.50</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>-10.7</td>
<td>1.85</td>
<td>1.25</td>
<td>2.56</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>1.85</td>
<td>1.24</td>
<td>2.52</td>
<td>1.25</td>
</tr>
</tbody>
</table>

**Table S5.** O-O minimum and maximum distance for 1\textsuperscript{st} and 2\textsuperscript{nd} hydrogen bonded shells for water molecules for CMK-3 models (2 shells and 4 shells)

<table>
<thead>
<tr>
<th>CMK-3</th>
<th>μ (kcal/mol)</th>
<th>O-O (max) 1\textsuperscript{st} hydrogen shell</th>
<th>O-O (min) 1\textsuperscript{st} hydrogen shell</th>
<th>O-O (max) 2\textsuperscript{nd} hydrogen shell</th>
<th>O-O (min) 2\textsuperscript{nd} hydrogen shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 shells</td>
<td>-11.2</td>
<td>3.41</td>
<td>2.50</td>
<td>6.649</td>
<td>2.63</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>3.43</td>
<td>2.48</td>
<td>6.41</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>3.44</td>
<td>2.48</td>
<td>6.4</td>
<td>2.50</td>
</tr>
<tr>
<td>4 shells</td>
<td>-11.2</td>
<td>3.43</td>
<td>2.52</td>
<td>6.54</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>3.43</td>
<td>2.38</td>
<td>6.5</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>3.43</td>
<td>2.45</td>
<td>6.48</td>
<td>2.46</td>
</tr>
</tbody>
</table>

**Table S6.** O-H minimum and maximum distance for 1\textsuperscript{st} and 2\textsuperscript{nd} hydrogen bonded shells for water molecules for CMK-3 models (2 shells and 4 shells)

<table>
<thead>
<tr>
<th>CMK-3</th>
<th>μ (kcal/mol)</th>
<th>O-H (max) 1\textsuperscript{st} hydrogen shell</th>
<th>O-H (min) 1\textsuperscript{st} hydrogen shell</th>
<th>O-H (max) 2\textsuperscript{nd} hydrogen shell</th>
<th>O-H (min) 2\textsuperscript{nd} hydrogen shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 shells</td>
<td>-11.2</td>
<td>1.84</td>
<td>1.25</td>
<td>2.57</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>1.85</td>
<td>1.255</td>
<td>2.53</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>1.85</td>
<td>1.25</td>
<td>2.53</td>
<td>1.258</td>
</tr>
<tr>
<td>4 shells</td>
<td>-11.2</td>
<td>1.85</td>
<td>1.26</td>
<td>2.55</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>1.85</td>
<td>1.24</td>
<td>2.55</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>1.85</td>
<td>1.25</td>
<td>2.54</td>
<td>1.25</td>
</tr>
</tbody>
</table>
### Table S7. O-O minimum and maximum distance for 1\textsuperscript{st} and 2\textsuperscript{nd} hydrogen bonded shells for water molecules for CMK-5 models with 2 cylindrical shells (inner and outer porosity)

<table>
<thead>
<tr>
<th>CMK-5 (2 shells)</th>
<th>(\mu) (kcal/mol)</th>
<th>O-O (max) 1\textsuperscript{st} hydrogen shell</th>
<th>O-O (min) 1\textsuperscript{st} hydrogen shell</th>
<th>O-O (max) 2\textsuperscript{nd} hydrogen shell</th>
<th>O-O (min) 2\textsuperscript{nd} hydrogen shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner porosity</td>
<td>-11.0</td>
<td>3.43</td>
<td>2.55</td>
<td>6.21</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>3.42</td>
<td>2.42</td>
<td>6.26</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>3.41</td>
<td>2.44</td>
<td>6.58</td>
<td>2.55</td>
</tr>
<tr>
<td>Outer porosity</td>
<td>-11.0</td>
<td>3.37</td>
<td>2.55</td>
<td>6.14</td>
<td>2.63</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>3.41</td>
<td>2.45</td>
<td>6.4</td>
<td>2.53</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>3.42</td>
<td>2.42</td>
<td>6.49</td>
<td>2.50</td>
</tr>
</tbody>
</table>

### Table S8. O-O minimum and maximum distance for 1\textsuperscript{st} and 2\textsuperscript{nd} hydrogen bonded shells for water molecules for CMK-5 models with 4 cylindrical shells (inner and outer porosity)

<table>
<thead>
<tr>
<th>CMK-5 (4 shells)</th>
<th>(\mu) (kcal/mol)</th>
<th>O-O (max) 1\textsuperscript{st} hydrogen shell</th>
<th>O-O (min) 1\textsuperscript{st} hydrogen shell</th>
<th>O-O (max) 2\textsuperscript{nd} hydrogen shell</th>
<th>O-O (min) 2\textsuperscript{nd} hydrogen shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner porosity</td>
<td>-11.0</td>
<td>3.41</td>
<td>2.48</td>
<td>6.33</td>
<td>2.59</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>3.39</td>
<td>2.46</td>
<td>6.26</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>3.4</td>
<td>2.49</td>
<td>6.41</td>
<td>2.52</td>
</tr>
<tr>
<td>Outer porosity</td>
<td>-11.0</td>
<td>3.39</td>
<td>2.45</td>
<td>6.3</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>3.43</td>
<td>2.47</td>
<td>6.41</td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>3.44</td>
<td>2.41</td>
<td>6.51</td>
<td>2.52</td>
</tr>
</tbody>
</table>

### Table S9. O-H minimum and maximum distance for 1\textsuperscript{st} and 2\textsuperscript{nd} hydrogen bonded shells for water molecules for CMK-5 models with 2 cylindrical shells (inner and outer porosity)

<table>
<thead>
<tr>
<th>CMK-5 (2 shells)</th>
<th>(\mu) (kcal/mol)</th>
<th>O-H (max) 1\textsuperscript{st} hydrogen shell</th>
<th>O-H (min) 1\textsuperscript{st} hydrogen shell</th>
<th>O-H (max) 2\textsuperscript{nd} hydrogen shell</th>
<th>O-H (min) 2\textsuperscript{nd} hydrogen shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner porosity</td>
<td>-11.0</td>
<td>1.85</td>
<td>1.264</td>
<td>2.49</td>
<td>1.266</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>1.85</td>
<td>1.24</td>
<td>2.5</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>1.84</td>
<td>1.25</td>
<td>2.51</td>
<td>1.26</td>
</tr>
<tr>
<td>Outer porosity</td>
<td>-11.0</td>
<td>1.83</td>
<td>1.26</td>
<td>2.46</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>1.846</td>
<td>1.25</td>
<td>2.51</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>1.85</td>
<td>1.24</td>
<td>2.54</td>
<td>1.258</td>
</tr>
</tbody>
</table>
Table S10. O-H minimum and maximum distance for 1\textsuperscript{st} and 2\textsuperscript{nd} hydrogen bonded shells for water molecules for CMK-5 models with 4 cylindrical shells (inner and outer porosity)

<table>
<thead>
<tr>
<th>CMK-5 (4 shells)</th>
<th>$\mu$ (kcal/mol)</th>
<th>O-H (max) 1\textsuperscript{st} hydrogen shell</th>
<th>O-H (min) 1\textsuperscript{st} hydrogen shell</th>
<th>O-H (max) 2\textsuperscript{nd} hydrogen shell</th>
<th>O-H (min) 2\textsuperscript{nd} hydrogen shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner porosity</td>
<td>-11.0</td>
<td>1.84</td>
<td>1.25</td>
<td>2.51</td>
<td>1.268</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>1.84</td>
<td>1.25</td>
<td>2.50</td>
<td>1.265</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>1.84</td>
<td>1.25</td>
<td>2.53</td>
<td>1.26</td>
</tr>
<tr>
<td>Outer porosity</td>
<td>-11.0</td>
<td>1.84</td>
<td>1.25</td>
<td>2.51</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>1.85</td>
<td>1.25</td>
<td>2.53</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>1.85</td>
<td>1.24</td>
<td>2.55</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Table S11. Cluster statistics for CMK-3 model (2 shells and 4 shells)

<table>
<thead>
<tr>
<th>CMK-3</th>
<th>$\mu$ (kcal/mol)</th>
<th>Size of #1 cluster</th>
<th>Size of #2 cluster</th>
<th>Size of #3 cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 shells</td>
<td>-11.2</td>
<td>257</td>
<td>126</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>1771</td>
<td>1672</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>5461</td>
<td>43</td>
<td>12</td>
</tr>
<tr>
<td>4 shells</td>
<td>-11.2</td>
<td>113</td>
<td>32</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>4180</td>
<td>15</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>5250</td>
<td>17</td>
<td>17</td>
</tr>
</tbody>
</table>

Table S12. Cluster statistics for CMK-5 model with 2 cylindrical shells (inner and outer porosity)

<table>
<thead>
<tr>
<th>CMK-5 (2 shells)</th>
<th>$\mu$ (kcal/mol)</th>
<th>Size of #1 cluster</th>
<th>Size of #2 cluster</th>
<th>Size of #3 cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner</td>
<td>-11.0</td>
<td>51</td>
<td>29</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>194</td>
<td>97</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>341</td>
<td>167</td>
<td>163</td>
</tr>
<tr>
<td>Outer</td>
<td>-11.0</td>
<td>230</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>1508</td>
<td>1339</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>6590</td>
<td>17</td>
<td>15</td>
</tr>
</tbody>
</table>
Table S13. Cluster statistics for CMK-5 model with 4 cylindrical shells (inner and outer porosity)

<table>
<thead>
<tr>
<th>CMK-5 (4 shells)</th>
<th>μ (kcal/mol)</th>
<th>Size of #1 cluster</th>
<th>Size of #2 cluster</th>
<th>Size of #3 cluster</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner</td>
<td>-11.0</td>
<td>108</td>
<td>99</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>136</td>
<td>103</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>473</td>
<td>211</td>
<td>52</td>
</tr>
<tr>
<td>Outer</td>
<td>-11.0</td>
<td>73</td>
<td>52</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>-10.6</td>
<td>3940</td>
<td>42</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>-8.0</td>
<td>6543</td>
<td>30</td>
<td>17</td>
</tr>
</tbody>
</table>