A molecular simulation study of water adsorption in pristine and functionalized silica templated CMK-1, CMK-3 and CMK-5 carbon models
**Templated mesoporous carbons**

Experimental procedure

- Impregnation of carbon precursor
- Carbonization
- Carbon – silica
- Template removal


- These materials offer high mechanical and thermal stability, high pore volume and useful surface properties
- Application include adsorption of large molecules, catalysts in fuel cells and capacitor electrodes etc.
**Modeling methodology : an atomistic approach**

We start with a model of the MCM-41 pore and do carbon adsorption in the pore from a fictitious monoatomic ideal gas of carbon. Grand Canonical Monte Carlo simulation is used to do the carbon adsorption.

Pore surface is rough

at the local level

Model MCM-41 pore (contains Si, O and H)

[Coasne et al., *Langmuir*, 2006.]
Carbon adsorption in MCM-41 pore

Volume templated

Surface templated
Carbon structures obtained at different $T$ and $\mu$
**Proposed model for CMK-1**

The carbon rods are placed side by side horizontally in a *cubical lattice* to obtain model for CMK-1. The carbon rods are not smooth and have surface roughness and corrugation.

**Control Parameters**:
- a) rod diameter
- b) distance between the rods

(Unit cell)
Proposed model for CMK-3

- The carbon rods are placed in a *hexagonal order* in the two dimensions.
- The carbon rods are not smooth and have surface roughness and corrugation.

Control Parameters:
- a) rod diameter
- b) distance between the rods

Unit cell
Molecular model for CMK-5

- The carbon pipes are placed in a **hexagonal order** in the two dimensions.
- The carbon pipes are not smooth and have surface roughness and corrugation (both in the inner and outer tube surface).

**Control Parameters**:
- a) inner and outer tube diameters
- b) distance between the tubes

**Unit cell**
CMK-3 and CMK-5 models

- CMK-3 models made up of carbon rods arranged in hexagonal lattice. Carbon rods are connected via interconnections.
- CMK-5 models made up of carbon pipes arranged in hexagonal lattice. Carbon rods are connected via interconnections.
Adsorption of water in CMK-3 model at 300 K

- Adsorption isotherm of water at 300 K in CMK-3 models obtained from GCMC simulations (left). There is negligible water uptake at lower chemical potential and sudden pore filling occurs, when a threshold chemical potential is reached.
- Snapshot of water molecules in CMK-3 model at chemical potential (-6.0 Kcal/mol) (right)
Hydrogen bond statistics of water molecules confined in CMK-3 models

- The fraction of water molecules with two hydrogen bonds is more in bulk as compared to in pores.
- The fraction of water molecules with three and four hydrogen bonds is more in pore as compared to bulk.
- Water molecules tend to form more hydrogen bonds in confinement as compared to bulk.
There is negligible uptake of water at low chemical potentials. There is a small jump from $u=-10.0$ kcal/mol to $u=-9.9$ kcal/mol and also from $u=-9.9$ kcal/mol to $u=-9.8$ kcal/mol.

There are two kinds of porosity: inner porosity (inside the tubes) and outer porosity (between the tubes). Thus, the two small jumps relate to the filling of the inner porosity of the central pipe and the filling of the inner pores of the four corner pipes.
Pore filling mechanism of water in CMK-5 model

Snapshot of water molecules in CMK5-14A model at different chemical potentials, in kcal/mol.
(a) $u=-10.0$
(b) $u=-9.9$
(c) $u=-9.8$
(d) $u=-9.7$
(e) $u=-9.0$
(f)snapshot of water desorption in CMK5-10A model at $u=-10.0$.

In (d) we show water molecules as bonds to show the CMK5-14A structure also

- Water first fill the inner porosity and then fills the outer porosity, as seen in the figure.
Hydrogen bond statistics of water molecules confined in CMK-5 models

- The fraction of water molecules with two hydrogen bonds is more (for outer porosity) and less (for inner porosity) in bulk as compared to in pores.
- The fraction of water molecules with three and four hydrogen bonds is more (for outer porosity) and less (for inner porosity) in pore as compared to bulk.
CMK-1 (left), CMK-3 (middle) and CMK-5 (right) models with attached -COOH and -OH functional groups

Functional groups attached in 2 and 4 cylindrical shells

Color code: blue and orange reflects oxygen atoms of -COOH group. Green reflects oxygen atoms of -OH group and white reflects hydrogen atoms of both -COOH and -OH groups.
Adsorption of water in functionalized CMK-1 models at 300 K

- Adsorption isotherm (left) and Isosteric heat of adsorption (right).
- Adsorption phenomena starts at lower chemical potential
- Pore filling occurs at lower chemical potential for 4 shells as compared to 2 shells
- Fluid-wall contribution to isosteric heat dominates at lower chemical potential and fluid-fluid contribution dominates for higher chemical potential
Pore filling mechanism in CMK-1 models (2 cylindrical shells)

Snapshot of water adsorption in CMK-1 models with functional groups in 2 cylindrical shells. At chemical potential:

- (a) -11.2 kcal/mol (side view)
- (b) -11.2 kcal/mol (top view)
- (c) -10.9 kcal/mol
- (d) -10.7 kcal/mol
- (e) -10.6 kcal/mol
- (f) -10.4 kcal/mol

- 2 water clusters are formed near the functional groups at 2 cylindrical shells.
- These clusters grow on increasing chemical potential and merge to completely fill the pores.
Pore filling mechanism in CMK-1 models (4 cylindrical shells)

Snapshot of water adsorption in CMK-1 models with functional groups in 4 cylindrica shells. At chemical potential: (a) -11.2 kcal/mol (b) -11.0 kcal/mol (c) -10.9 kcal/mol and (d) -10.6 kcal/mol

- 4 water clusters are formed near the functional groups at 4 cylindrical shells.
- These clusters grow on increasing chemical potential and merge to completely fill the pores.
The fraction of water molecules having 2 hydrogen bonds is large in bulk as compared to confined water.

The fraction of water molecules having 3 and 4 hydrogen bonds is smaller in bulk as compared to pore.
Adsorption of water in functionalized CMK-3 models at 300 K

- Adsorption isotherm (left) and Isosteric heat of adsorption (right).
- Adsorption phenomena starts at lower chemical potential
- Pore filling occurs at lower chemical potential for 4 shells as compared to 2 shells
- Fluid-wall contribution to isosteric heat dominates at lower chemical potential and fluid-fluid contribution dominates for higher chemical potential
Pore filling mechanism in CMK-3 models (2 cylindrical shells)

Snapshot of water adsorption in CMK-3 models with functional groups in 2 cylindrical shells. At chemical potential ($\mu$): (a) -11.2 kcal/mol (b) -10.9 kcal/mol (c) -10.6 kcal/mol and (d) -10.4 kcal/mol

- Small water clusters are formed near the functional groups at 2 cylindrical shells of each rod.
- These clusters grow on increasing chemical potential and merge to completely fill the pores.
Pore filling mechanism in CMK-3 models (4 cylindrical shells)

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

- Small water clusters are formed near the functional groups at 4 cylindrical shells of each rod.
- These clusters grow on increasing chemical potential and merge to completely fill the pores.
Hydrogen bond statistics of water molecules confined in functionalized CMK-3 models

The fraction of water molecules having 2 hydrogen bonds is slightly larger in bulk as compared to confined water. The number of water molecules having 3 hydrogen bonds larger in pore as compared to bulk. However, the number of water molecules having 4 hydrogen bonds is almost same in bulk and in pore.
Adsorption of water in functionalized CMK-5 models at 300 K

- Adsorption isotherm (left) and Isoenergetic heat of adsorption (right).
- Pore filling for inner porosity occurs at lower chemical potential as compared to outer porosity.
- Pore filling occurs at lower chemical potential for 4 shells as compared to 2 shells.
- Fluid-wall contribution to isosteric heat dominates at lower chemical potential and fluid-fluid contribution dominates for higher chemical potential.
Pore filling mechanism in CMK-5 models (2 cylindrical shells)

Snapshots of CMK-5 models (2 cylindrical shells) at different chemical potential: (a) -11.2 kcal/mol (b) -10.9 kcal/mol (c) front view at -10.7 kcal/mol (d) -10.5 kcal/mol and (e) -10.4 kcal/mol

- Small water clusters are formed near the functional groups at 2 cylindrical shells, of each pipe, at both inside (intra pipe) and outside porosity (inter pipe).
- These clusters grow on increasing chemical potential and merge to completely fill the pores.
Pore filling mechanism in CMK-5 models (4 cylindrical shells)

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

- Small water clusters are formed near the functional groups at 4 cylindrical shells, of each pipe, at both inside (intra pipe) and outside porosity (inter pipe).
- These clusters grow on increasing chemical potential and merge to completely fill the pores.
Hydrogen bond statistics of water molecules confined in functionalized CMK-5 models

For inner porosity, the number of water molecules with 2 hydrogen bonds is higher in pore than in bulk. The number of water molecules with 3 hydrogen bonds is similar in bulk and in pore. However, the number of water molecules with 4 hydrogen bonds is higher in bulk than in pore.
Hydrogen bond statistics of water molecules confined in functionalized CMK-5 models

For outer porosity, the number of water molecules with 2 hydrogen bonds is higher in bulk than in pore. However, the number of water molecules with 3 and 4 hydrogen bonds is higher in pore than in bulk. This is due to the space available in the outer porosity for water molecules to form 3 dimensional clusters.
Conclusions

- For pristine CMK-3 and CMK-5 models, there was negligible water adsorption at lower chemical Potential and complete pore filling occurs when a threshold chemical potential is reached.

- Water adsorption occurs via clustering mechanism in hydrophobic carbons, where water molecules form hydrogen bonds with each other and fill the pore. This is in stark contrast with adsorption of non-polar molecules like nitrogen, where adsorption phenomena occurs via wetting and layer formation mechanism.

- Addition of functional groups result in water adsorption occurring at lower chemical potential. Water forms clusters around functional groups and these clusters grow on increasing chemical potential and fill the pores. No wetting or layering of water molecules on CMK pore surface was found. Water adsorbs via clustering mechanism.

- Increase in the concentration of functional groups and decreasing the distance between functional groups result in formation of bigger water clusters (due to merging of nearby clusters) and pore filling occurs at lower chemical potential.
Future work

- We conducted water adsorption in one pore size for functionalized CMK models. It will be interesting to study water adsorption as a function of pore size. At bigger pore size it will be interesting to see if water molecules form bridges between carbon rods and pipes, as is observed in our work.

- To conduct GCMC simulations of water at different temperatures. It will be nice to study the effect of temperature on water cluster size formation.

- To study the diffusion and transport properties of water confined in pristine and functionalized CMK-1, CMK-3 and CMK-5 models using MD simulations.

- It will be interesting to see if water moves as a single molecule or as a cluster during MD simulations. It will be nice to also study the diffusion of center of mass of each water cluster present in CMK models.

- For CMK-5 models, that has both inner and outer porosity, it will be nice to label the water molecules as present in inner or outer porosity and then study diffusion properties of these inner and outer water molecules separately.