Computational Modelling of Bulk ZIF-8 for Carbon Capture Applications

Hari P. Paudel*, Wei Shi, Dan C. Sorescu, David Hopkinson, Yuhua Duan*
National Energy Technology Laboratory, U. S. Department of Energy, Pittsburgh, PA 15236, USA

Research & Innovation Center

NATIONAL ENERGY TECHNOLOGY LABORATORY

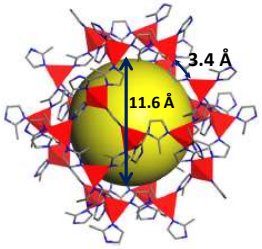
Motivation

- Metal-organic framework (MOF) materials and zeolite imidazolate frameworks (ZIFs) have selective adsorption properties and are useful for hydrogen and carbon dioxide separation. When compared to traditional chemical sorbents (mostly amines), ZIFs have (a) high CO_2 loading capacity, (2) lower-energy consumption, (3) high thermal and chemical stability, (4) fewer mechanical requirements and lower corrosion rates.

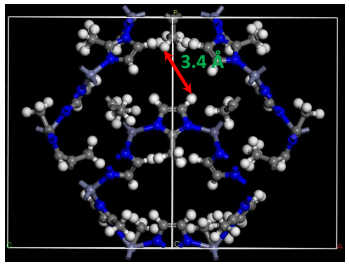
- ZIF-8 in particular has been studied extensively as its microcrystalline state is both chemically and thermally stable up to 500 °C. It has potential functional applications in gas storage (CO_2, H_2, and acetylene), catalysis, and gas separation applications. Several theoretical and experimental studies reveal that due to their hybrid metal/linker type structure, ZIF-8 materials is highly responsive to changes of the external physical and chemical environments. Here we present results of the computational modelling of bulk ZIF-8 for carbon capture applications in pre-combustion design. In particular, here, we present some preliminary results on the electronic properties of ZIF-8 material and the adsorption and diffusion properties of CO_2 and CH_4 in ZIF-8 using first principles density functional theory calculations.

Material Structures

- ZIF-8 is a zeolitic imidazolate framework having a sodalite geometry with space group I43m. It contains cages of diameter 11.6 Å which are connected through 6-ring windows of 3.4 Å in size.
- Small apertures of 3.4 Å is comparable to the kinetic diameters of the CO_2 and CH_4 molecules (3.3 Å and 3.8 Å). This enables ZIF-8 to capture gas molecules selectively where Van der Waals interaction plays a significant role.

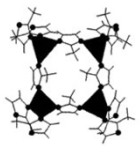


Pore sizes

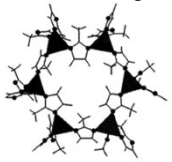


Unit cell of ZIF-8

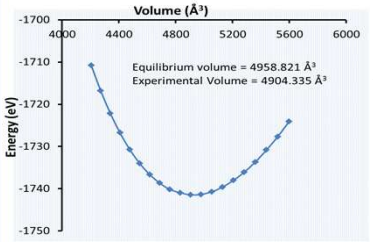
4 membered ring



6 membered ring

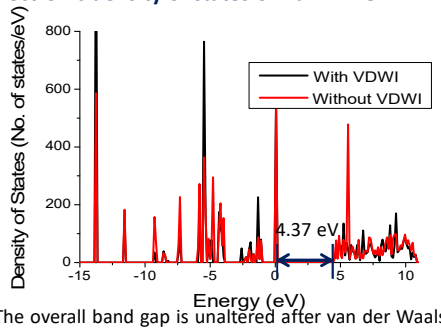


Electronic structure



- Variation of the energy per unit cell as function of volume and fitted using Murnaghan equation of state. The volume of the unit cell corresponding to minimum energy is 4958.821 Å³ which is overestimated by 1.1 % relative to experimental value.

Electronic density of states of Bulk ZIF-8

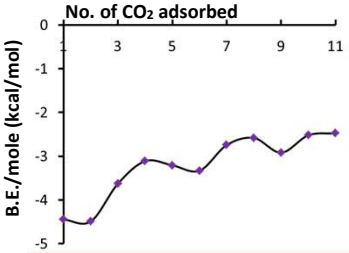


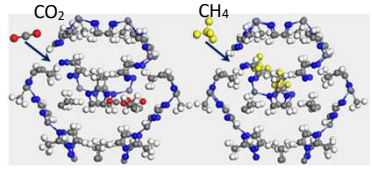
- The overall band gap is unaltered after van der Waals interactions are switched on. The energy gap is found to be 4.37 eV which is within 11 % of the experimental bandgap.

CO_2 Binding Energy in Bulk ZIF-8

Binding energy per molecule:

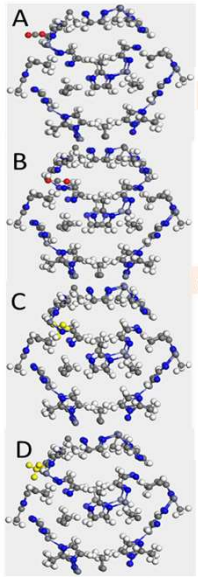
$$B.E/mole = \Delta E = E(nCO_2 + ZIF) - \{E(nCO_2) + E(ZIF)\}$$



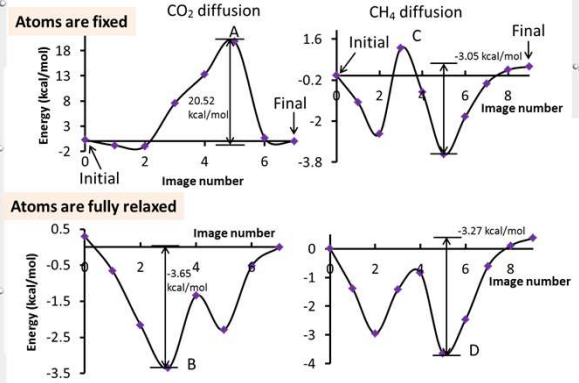


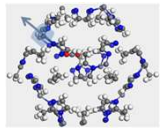
Two CO_2 are in the cage | Two CH_4 are in the cage

The smallest binding energy per molecule for CO_2 is found for configurations close to the center of the cage whereas the largest binding energy is found to be near the pore walls.

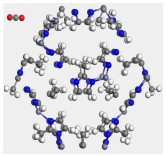


CO_2 and CH_4 Diffusion Barriers in Bulk ZIF-8





Initial image



Final image

- Diffusion barrier for CO_2 is reduced by 16.8 kcal/mol when atoms are relaxed as compared to the case when the atoms are fixed.
- Diffusion barrier for CH_4 is less sensitive to atom relaxation; it has variations of less than 0.30 kcal/mol when atoms are relaxed as compared to the case when the atoms are fixed.

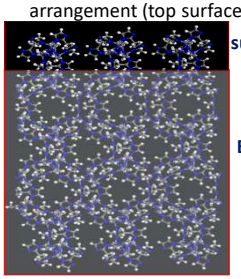
Conclusions

- First principles density functional theory calculations were used to evaluate the structural and electronic properties of bulk ZIF-8 and to determine the adsorption and diffusion properties of CO_2 and CH_4 in ZIF-8 materials. Calculations included long-range dispersion interactions.
- Diffusion barriers for CO_2 and CH_4 were determined for both surface to subsurface as well as for bulk diffusion in ZIF-8. We analyzed both the case of relaxed and fixed atoms optimizations to study the diffusivity, and obtained that important variations take place when relaxing the atoms in the framework. For relaxed system the diffusion barriers were found to be less than 3.2 kcal/mol.

Future Work

- Using the optimized bulk geometry of ZIF-8, we will create different surface terminations (as guided by a recent experiments[a]) and calculate the corresponding surface energies.
- In the next step, we will investigate the surface electronic and diffusion properties for most stable surface with & without ligand molecules attached. We will also explore the charge distribution across the surface/interface.
- We will investigate how diffusivity and selectivity are modified after different ligand molecules become attached on the surface.
- Calculations of CO_2 and CH_4 diffusion properties will be performed using CPMD code at realistic working conditions.

(110) surface in armchair arrangement (top surface)



Top few layers of surface is relaxed while the rest of the slab of thickness about 6 nm is kept fixed as a bulk . The surface properties should not be affected by freezing the bulk atoms.

References

- *Cravillon, et al., Chem. 2011, **123,** 8217–8221*
- *Wang, et al., Energy Environ. Sci. 2014, **7,** 2831–2867*
- *[a]Zhu et al., Nature Mat. 2017, **16**, 532-537*
- *Chizallet et al., J. Phys. Chem. Letts. 2010, **1**, 349–353*
- *Chapman et al., J. Am. Chem. Soc. 2009, **131**, 17546–17547*

*Contact information: email: hari.paudel@netl.doe.gov, yuhua.duan@netl.doe.gov

U.S. DEPARTMENT OF ENERGY

Science & Engineering To Power Our Future