

Influence of Electric Field on Methane Adsorption in Metal-Organic Frameworks

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Introduction

Natural gas (methane) is seen as an ideal intermediate solution before developing the hydrogen storage technologies necessary for the development of a carbon free energy cycle. Methane is the cleanest fossil fuel, producing 40% less CO₂ than any other fossil fuel, while releasing 55MJ/kg energy [1]. Methane is also widely available as the reserves increased steadily with the development of better drilling technology. Currently, methane is 57% cheaper than oil and there are millions of kilometers of pipelines worldwide.

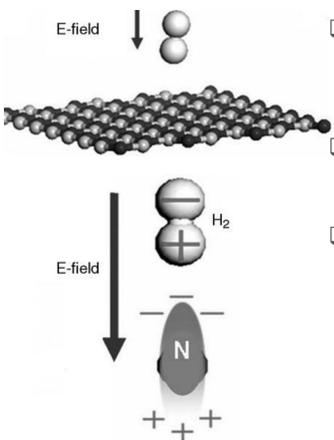
But, methane is a low density gas – 0.716g/L at standard pressure and temperatures (STP) conditions. A storage system usable onboard of vehicles must be able to insure a vehicle autonomy of at least 500km, so the US DOE recommended storage densities to be at least 350cm³_{STP}/cm³ volumetric density and 0.5g_{STP}/g gravimetric density [2]. At this point, it is clear that traditional solutions using liquefied or compressed methane are not feasible onboard of light vehicles, so alternative solutions are investigated.

Storage in metal organic frameworks (MOFs) by physisorption is a promising solution as storage densities, are in some cases within 30% of the DOE limits (e.g. HKUST-1 230cm³_{STP}/cm³ at 35 bar and 270cm³_{STP}/cm³ at 65bar) [3]. However, reaching DOE limits is problematic, because there aren't enough strong binding sites in the framework. The **strong binding sites** in MOFs are usually localized on the metallic atoms of the secondary inorganic building unit (SBU) and often have large enough binding energies (~15-20kJ/mol) to adsorb methane efficiently even at room temperature. The weak binding sites are usually localized on the organic linkers.

Recently it has been proposed to apply electric fields to polarize the adsorbent and the adsorbate (hydrogen) molecules, aiming to increase the adsorption enthalpies [4]. Starting from this idea investigate how the effect of applied electric fields on **weak binding sites** in MOFs with high methane uptake at room temperature and 35 bar (a pressure easily attained with standard compressors).

Electrically controlled adsorption

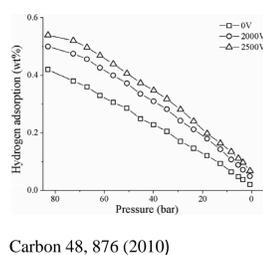
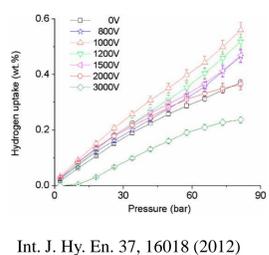
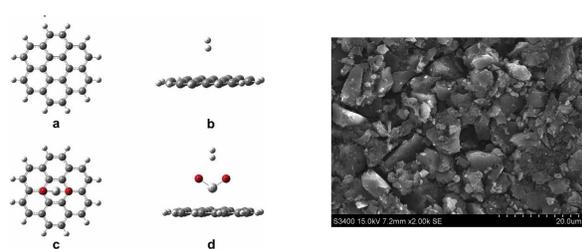
Adsorption of hydrogen on 2D sheets [4]



- The electric field induces a dipole-dipole interaction between the sorbate molecules and the adsorbent's atoms.
- For hydrogen, electric fields are of the order of 0.01=5GV/m – too large for applications.
- Graphene, graphene with Li impurities, AlN, BN sheets have been investigated, the heteroatomic sheets being more polarizable.

PNAS 107, 2801 (2010). Check also J. Nanopart. Res. 14, 1256 (2012), Int. J. Hy. En. 37, 11842 (2012), Int. J. Hy. En. 41, 10776 (2016).

Experiments: hydrogen adsorption in electric field



Int. J. Hy. En. 37, 16018 (2012)

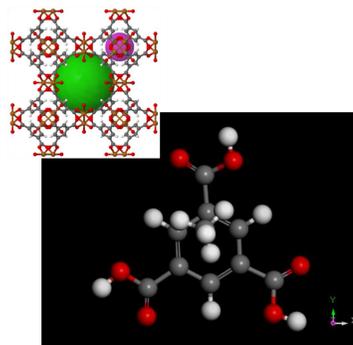
Carbon 48, 876 (2010)

- Uptake is usually improved by applied electric fields.
- The necessary voltages seem accessible experimentally.

Methane binding energies on typical carboxylate linkers

BTC (tricarboxylic acid)

HKUST-1 230cm³_{STP}/cm³ 35 bar

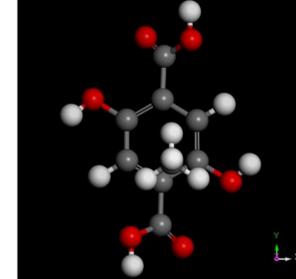


$$E_b(E_z = 0) = 8.76\text{kJ/mol}$$

$$E_b(E_z = 0.01) = 10.13\text{kJ/mol}$$

DOBDC (dioxo-benzene dicarboxylate)

Co-, Mg-, Mn-MOF-74 221, 200, 176cm³_{STP}/cm³ 35 bar

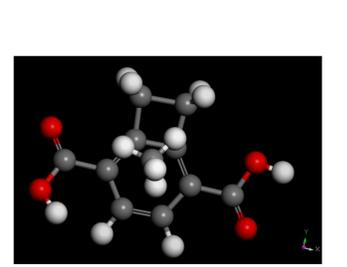


$$E_b(E_z = 0) = 9.06\text{kJ/mol}$$

$$E_b(E_z = 0.01) = 10.21\text{kJ/mol}$$

Cyclobutylbenzene dicarboxylate

IRMOF-6 177cm³_{STP}/cm³ 35 bar



$$E_b(E_z = 0) = 9.89\text{kJ/mol}$$

$$E_b(E_z = 0.01) = 22.04\text{kJ/mol}$$

BPTC (biphenyl tetracarboxylic acid)

NOTT-100 194cm³_{STP}/cm³ 35 bar

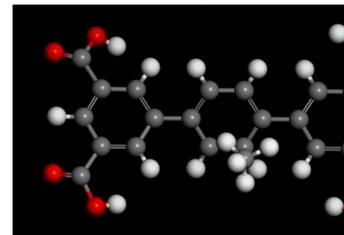


$$E_b(E_z = 0) = \text{kJ/mol}$$

$$E_b(E_z = 0.01) = 17.24\text{kJ/mol}$$

TPTC (Terphenyl tetracarboxylic acid)

NOTT-101 196cm³_{STP}/cm³ 35 bar

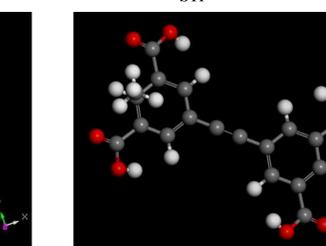


$$E_b^{\text{left}}(E_z = 0) = 10.57\text{kJ/mol}$$

$$E_b(E_z = 0.01) = 17.7\text{kJ/mol}$$

EBDC (ethynediyl-bis-benzenedicarboxylic acid)

PCN-16 192cm³_{STP}/cm³ 35 bar

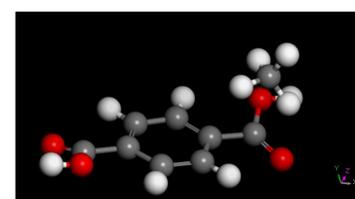
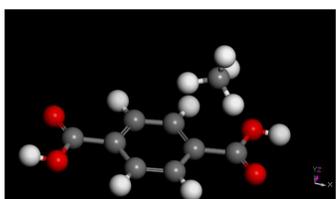


$$E_b(E_z = 0) = 9.16\text{kJ/mol}$$

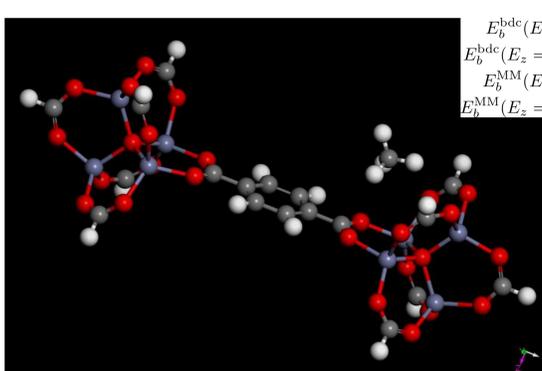
$$E_b(E_z = 0.01) = 17.94\text{kJ/mol}$$

Methane binding on IRMOF-1

BDC (benzene dicarboxylic acid) linker



Molecular model (MM) of IRMOF-1



$$E_b^{\text{bdc}}(E_z = 0) = 8.27\text{kJ/mol}$$

$$E_b^{\text{bdc}}(E_z = 0.01) = 9.68\text{kJ/mol}$$

$$E_b^{\text{MM}}(E_z = 0) = 17.04$$

$$E_b^{\text{MM}}(E_z = 0.01) = 16.72$$

Discussion

- The binding energies for methane adsorbed on weaker sites are ~9-10kJ/mol, almost independent of linker → they most likely don't contribute much to room temperature adsorption. Most likely the main contribution comes from the strong binding sites on the secondary building units of MOF.
- In zero electric field, the linkers are be useful as molecular models for the MOFs, because the weak binding sites represent dips in the potential of interaction of MOF with the adsorbed CH₄ molecules.
- But, in non-zero electric field, the longer linkers tend to buckle, which sends CH₄ to the carboxyl group that is connected to the inorganic SBU in MOFs → more realistic molecular models (MMs) are needed that contain the SBUs.
- For large enough fields, the interaction with the linkers can increase by ~10%. However, these fields E=0.01a.u.=5GV/m are impractical for applications. Nonetheless, we can expect **internal** fields of this size in polarizable MOFs.
- In the case of IRMOF-1, we see that the electric field moves the methane towards the SBU. In this case, the electric field can actually slightly lower the binding energy between CH₄ and the strong site on SBU.

Technical details

The DFT calculations were performed with TURBOMOLE [5], using the def2-TZVP basis set, PBE functional with dispersion [Grimme 2011] corrections.

Acknowledgements

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References

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