Adsorption Characterization and Decomposition of Isotherm in UiO-66

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Abstract

Gas adsorption is one of the most important methods for characterizing nanoporous materials like Carbon, Silica, Zeolites, and MOFs. Paricular, metal-organic frameworks (MOFs) have drawn immense attention due to their high surface areas, high porosity, and overall stability. Traditional methods of measuring adsorption into such materials do not consider the pore geometry within the framework. Here, we study a popular MOF, UiO-66, by measuring Ar adsorption using the Grand Canonical Monte Carlo method. UIO-66 has 2 kinds of pores with tetrahedral and octahedral geometry with sizes 8 Å and 11 Å. We use a molecular simulation software called RASPA to simulate adsorption at several pressures from which we form an isotherm. We then decompose the simulated isotherm corresponding to individual pores to get detailed insight into the pore architecture. This method would help us predict the crystallinity, pore blockage, and degree of hydration of a sample.

Background

- Metal-organic frameworks(MOFs) are a relatively new and promising class of hybrid nanomaterials combining the versatility of organic compounds with orderly crystalline structure
- High surface area, adjustable topology, and various chemical properties
- Applications include gas storage and separation, reaction catalysis, and drug storage and delivery
- UiO-66 is unique because of its stability under extreme hydrothermal conditions, mechanical pressure, high temperatures, acidic and alkali conditions, and within a number of different solvents namely water and dimethylformamide

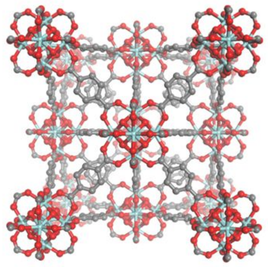

Fig 1: UiO-66 Framework Full

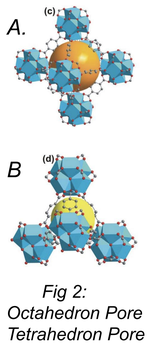

Fig 2:
A. Octahedron Pore
B. Tetrahedron Pore

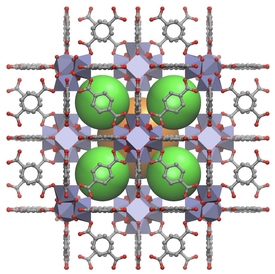

Fig 3: UiO-66 Framework With Pores Visualized

- Building units formed from inorganic $Zr_6O_4(OH)_4$ clusters connected by 12 1,4-benzenedicarboxylic acid(BDC) struts yielding a high coordination number of 12 and realization of two types of pores: an octahedron with pore size 11 Å and a tetrahedron with pore size 8 Å
- Purpose of Study: to decompose adsorption isotherms to obtain ideal data based on UiO-66's geometry that can be used to find sample quality from experimental data

Materials and Methods

- We studied the adsorption of Argon(Ar), Nitrogen gas(N2), and Carbon-Dioxide(CO2)
- We used the simulation package RASPA to run simulations for each adsorbate at various pressures
- The Grand Canonical Monte Carlo(GCMC) method:
  - Imposes a constant temperature and chemical potential on the simulation cell containing the adsorbent
  - The equilibrium between the simulation cell and the reservoir is achieved by Monte Carlo moves: particle insertion/deletion at/from random position, translation, and rotation
  - The acceptance criteria of the moves is based on the detailed balance of interactions between fluid-fluid and solid-fluid particles modelled using the Lennard-Jones potential and Ewald summation

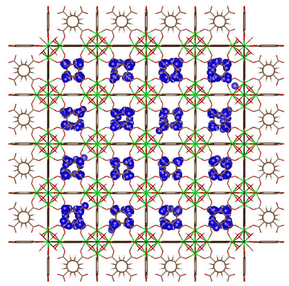

*Fig 4: Argon Adsorption at 2.195*e-4 kPa*

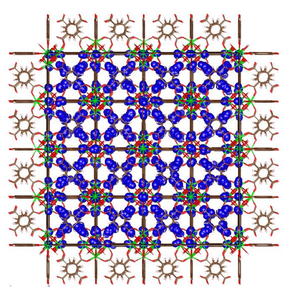

Fig 5: Argon Adsorption at 30 kPa

- MATLAB and visualization softwares VESTA and VMD used to study and triangulate the surfaces of the pores

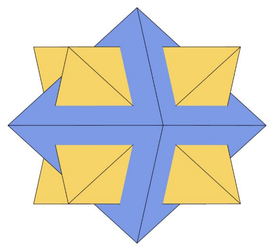

Fig 6: Visualizing Pore Geometry
Orange - Tetrahedrons
Blue - Octahedrons

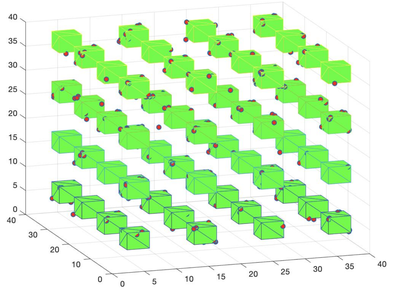

Fig 7: Isometric View of Ar Adsorption with cubes representing tetrahedral pores

- To distinguish adsorption in different pore compartments, we developed a special procedure of assigning adsorption molecules
- To ensure high quality data we compare the obtained isotherms with experimental data and calculated sample quality of experimental data

Results

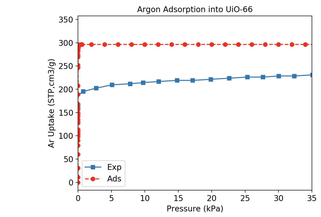

Fig 8: Ar Adsorption at 87.3 K with experimental data (Linear)

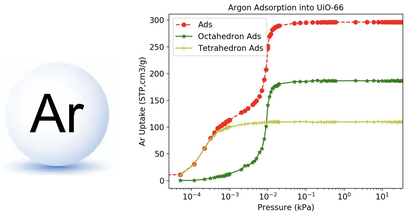

Fig 9: Decomposed Ar Adsorption at 87.3 K (Semi-log)

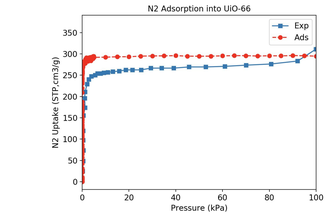

Fig 10: N_2 Adsorption at 77 K with experimental data (Linear)

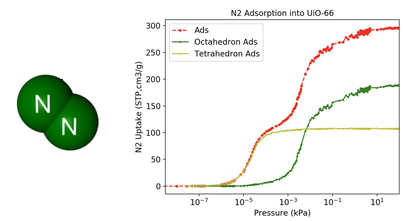

Fig 11: Decomposed N_2 Adsorption at 77 K (Semi-log)

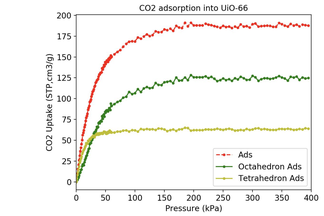

Fig 12: CO_2 Adsorption at 194.7 K

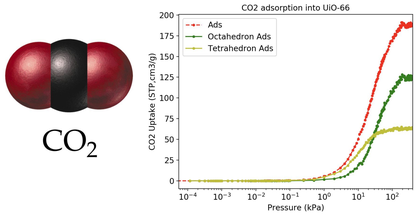

Fig 13: Decomposed CO_2 Adsorption at 194.7 K (Semi-log)

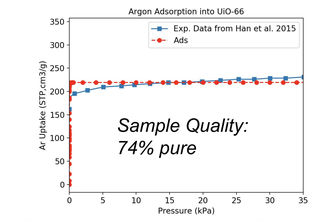

Fig 14: Adjusted Ar Adsorption to Determine Sample Quality

Sample Quality

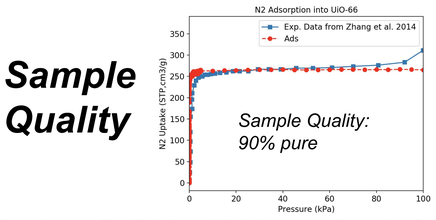

Fig 15: Adjusted N2 Adsorption to Determine Sample Quality

Conclusion

- Particles first adsorb and saturate the tetrahedral pores before filling the octahedral pores
- We measured the sample purity of two different samples for Argon and Nitrogen adsorption and found them to be 74% and 90% respectively
- We decomposed the total isotherm of Ar, N_2, and CO_2, into fingerprint isotherms of individual pores to unveil information at the pore level

Acknowledgments

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