

Supplementary file for ‘The required level of isosteric heat for the adsorptive storage/delivery of H₂ in the UiO series of MOFs’

K. Vasanth Kumar*, G. Charalambopoulou, M. Kainourgiakis, A. Stubos, Th. Steriotis

National Center for Scientific Research “Demokritos”, Agia Paraskevi Attikis, 15310, Athens, Greece

E-mail: vasanth_yit@yahoo.com

Experimental

In this study, Grand Canonical Monte Carlo (GCMC) simulations were used to study the adsorption of hydrogen in UiO type MOF structures. All the fluid-fluid and solid-fluid interactions were modelled using 12-6 Lennard-Jones potential. For each point on the isotherm, 5 million Monte Carlo steps were performed. Each step consisted of insertion of a new molecule, deletion of an existing molecule, or translation of an existing molecule. The first half of the run was used to ensure equilibration, and the last half was used to calculate the ensemble averages. The MOF structures were treated as rigid frameworks with their atoms frozen at their crystallographic positions during the simulations. The simulation box contains 8 unit cells (2 x 2 x 2) of the MOF structures studied. Fugacity is used in the simulations, and the component fugacity of bulk phase was transformed to the component bulk phase pressure using Peng-Robinson equation of state. Periodic boundary conditions are applied on all directions. All the simulations were performed using Multipurpose Simulation code, MUSIC 4.0¹

The crystallographic information files of UiO-66, UiO-67 and UiO-68 were obtained from the supporting information available from the work of Yang *et al.*². In this work, all the MOFs are represented atomistically. We chose the Lennard-Jones (LJ) parameters from the DREIDING forcefield³ to model the C, H and O atoms in the frameworks, and for Zr atom we used a UFF model⁴.

In the case of H₂, to study the adsorption at 298 K, we used the parameters of Michele *et al.*⁵ that were originally derived from experiments as this model successfully predicts the Virial coefficients over a temperature range from -175 to 150 °C. This model has been earlier used in several studies and accurately predicted the H₂ adsorption behavior at room temperature in different MOFs^{6,7}, zeolites⁸ and carbon structures⁹. Quantum effects and electrostatic interactions were not considered.

Lorentz-Berthelot rules were applied to calculate all cross interactions (including solid-fluid interactions). The usual periodic boundary conditions were applied in all three coordinate directions to mimic infinite size systems. Cutoff distances for the potentials were set at 14.8 Å and no long-range interactions were applied.

The simulation results in terms of H₂ adsorbed (via physisorption) per unit cell at 298 K in the UiO series MOFs are presented in Fig 1s, while some key calculated features of the respective structures are summarised in Table 1s.

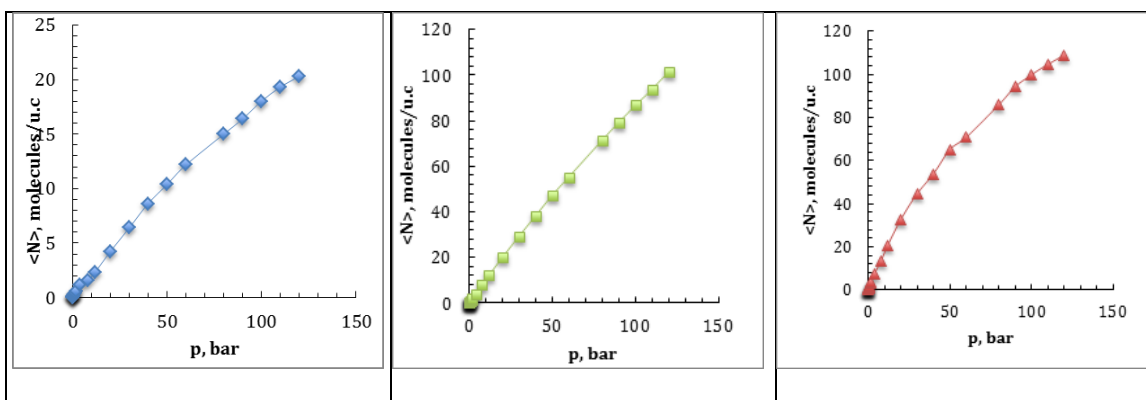


Fig 1s: Plot of H₂ adsorbed (number of molecules/unit cell) versus p (bar) in (a) UiO-66, (b) UiO-67 and (c) UiO-68

Table 1s: Details about the volume, total free volume and mass of the simulation cell for the studied UiO MOFs.

Simulation cell volume, \AA^3	Free pore volume (\AA^3)	Mass $\times 10^{20}$ (g)
9085	5242	1.10466
19890	13938	1.4075
37029	29190	1.71034

Adsorption Excess

GCMC simulations give the measure of total adsorption or gas uptake, N_{tot} (mg), inside the pore structure. In the manuscript we expressed our results in terms of adsorption excess rather than total gas uptake, as the earlier is a more relevant quantity for practical applications as it measures the amount of H₂ that can be practically stored and delivered from a porous material and further it can be obtained directly from experiments. The absolute adsorption isotherms that were obtained from GCMC simulations were converted to adsorption excess, N_{ex} (mg) using the expression ¹⁰:

$N_{\text{tot}} = N_{\text{ex}} + \rho_g V_g$, where ρ_g (mg/cm³) is the density of the bulk gas obtained from an appropriate equation of state and V_g (cm³) is the total free pore volume of the adsorbent, which is determined based on a geometric method as will be discussed below.

Computational structure characterization

The surface area calculation was based on a Monte Carlo integration technique where a spherical probe molecule is “rolled” over the framework surface. This technique involves random insertion of probe molecules around each of the framework atoms and a check for overlap with other framework atoms. The fraction of the probe molecules that do not overlap with framework atoms is then used to calculate the accessible surface area. To

obtain surface area, we used in our calculations a probe sphere of diameter equivalent to the kinetic diameter of N₂ (3.68 Å), since surface area is routinely deduced from N₂ adsorption isotherms. To calculate the total pore volume (also referred as free pore volume), V_{tot} , we used similar trial insertions within the entire volume of the unit cell with a probe sphere of 0 Å. V_{tot} was subsequently used to convert our total (calculated) adsorption isotherms to excess values or vice-versa.

Pore size distribution

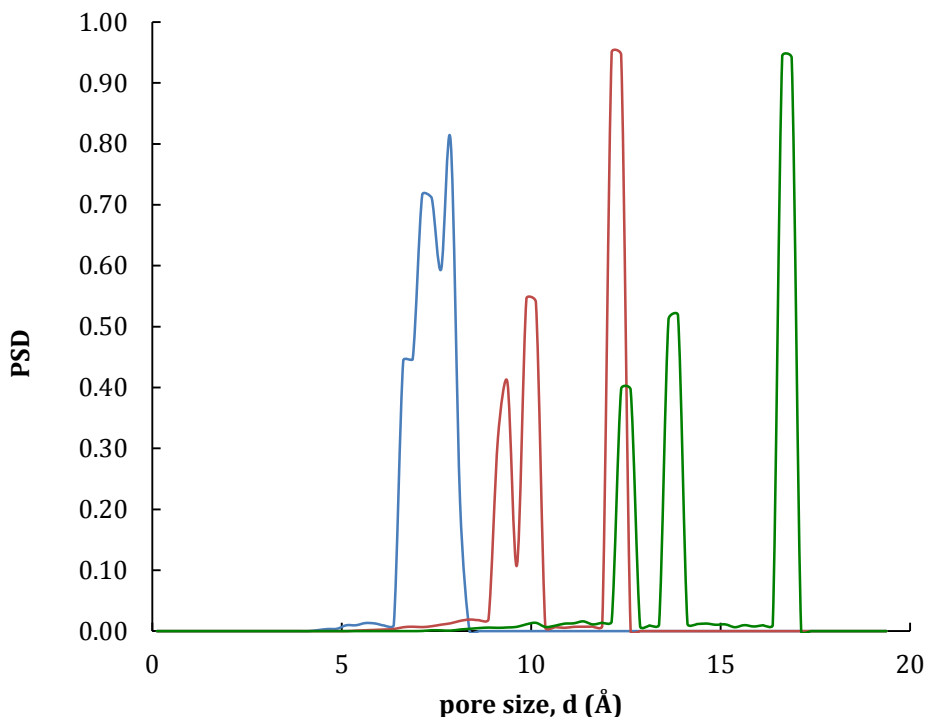


Fig 2s: Pore size distribution (PSD) as a function of pore size d (Å) of UiO-66 (blue line), UiO-67 (red line) and UiO-68 (green line) estimated via a geometric method ¹¹

Isosteric heat

The Q_{st} was obtained from the ensemble average fluctuations ¹²:

$$Q_{\text{st}} = RT - \frac{\langle UN \rangle - \langle U \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2}$$

where $\langle U \rangle$ is the average potential energy of the adsorbed phase and $\langle N \rangle$ is the average number of molecules in the simulation system.

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