Supplementary Information

Is Catenation Beneficial for Hydrogen Storage in Metal-Organic Frameworks?

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GCMC Simulations

Translation, insertion, and deletion moves were used during each simulation.[1] $1x10^6$ moves were used for equilibration, and $4x10^6$ moves were used to calculate ensemble averages. The hydrogen molecule was modeled as a single Lennard-Jones sphere.[2] Framework atoms were considered rigid at their crystallographic coordinates.[3] Simulations were performed for one unit cell. Framework atoms were modeled with Lennard-Jones parameters from the DREIDING force field.[4] Lorentz-Berthelot mixing rules were used for the hydrogen/framework interactions. A Lennard-Jones cutoff of 12.8 Å was used. Fugacities of hydrogen were calculated using the Peng-Robinson equation of state. No electrostatic charge interactions were considered.

Classical force fields were used for both their computational efficiency and their ability to correctly predict adsorption behavior of hydrogen in IRMOF materials. While density functional theory (DFT) may be considered more "advanced" than classical force fields, it is well known that DFT does not handle van der Waals interactions well. Since van der Waals forces dominate hydrogen adsorption in the MOFs of interest here, classical models are very well suited to this task.

Isosteric heats of adsorption were calculated from the ensemble average fluctuations, as described by Snurr et al.[5] Liu et al.[6] have reported that quantum effects reduce the amount of hydrogen adsorbed by approximately 15-20% at 77 K and are negligible at room temperature. This investigation is mostly concerned with comparing isotherms in catenated versus non-catenated frameworks, and thus only classical interactions were considered for simplicity.

Table S1. Lennard-Jones Parameters

Atom or Molecule	Sigma (Å)	Epsilon/k_B (K)
C	3.47	47.86
O	3.03	48.19
Zn	4.04	27.7
H (MOF)	2.85	7.65
H_2	2.958	36.7

All results are reported as absolute adsorption rather than excess quantities. Note that experiments measure excess adsorption. The absolute values are relevant for storage applications and are more easily understood from a physical point of view. It is possible to convert between absolute and excess adsorption at a specified temperature and pressure for crystalline materials.[7]

Comparison with Experiment

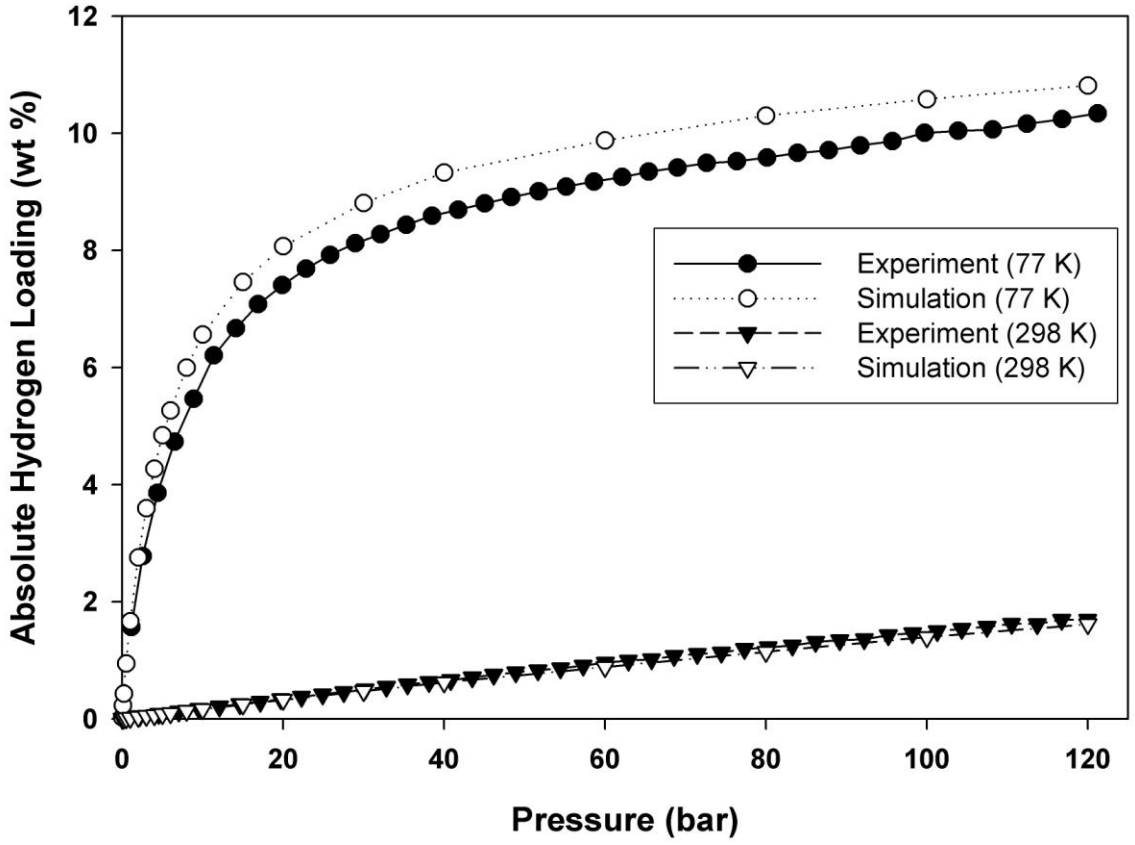

Figure S1. Simulated isotherms for IRMOF-1 compared with experimental isotherms from Kaye et al.[8]

Additional Results

Gravimetric and Volumetric Results at 77 K

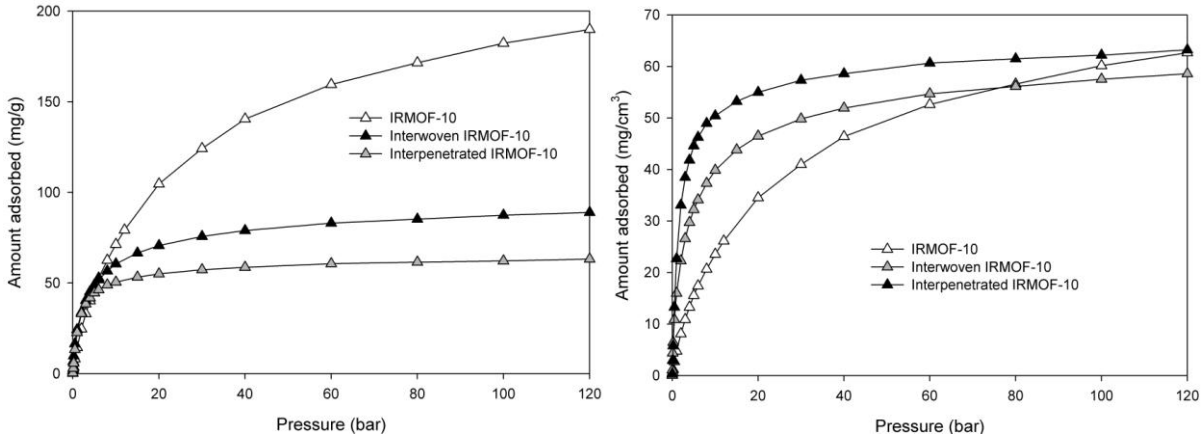

Figure S2. Hydrogen adsorption isotherms for IRMOF-10 structures at 77 K (left) on a gravimetric basis and (right) on a volumetric basis.

Gravimetric and Volumetric Results at 298 K

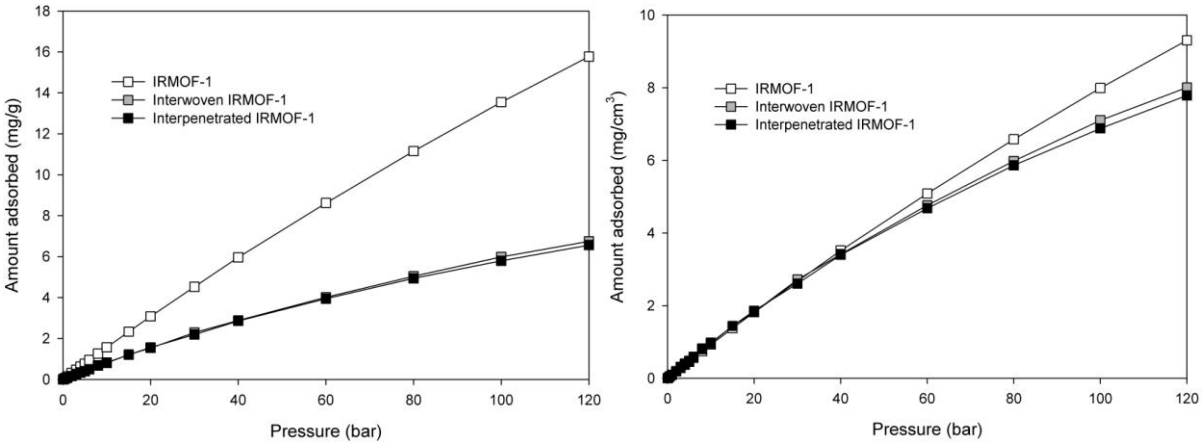

Figure S3. Hydrogen adsorption isotherms for IRMOF-1 structures at 298 K (left) on a gravimetric basis and (right) on a volumetric basis.

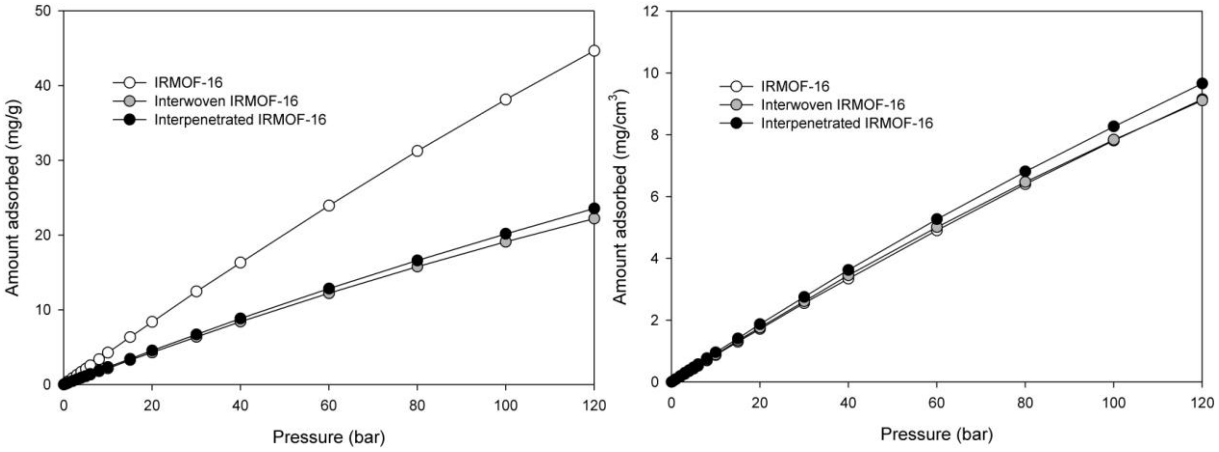

Figure S4. Hydrogen adsorption isotherms for IRMOF-16 structures at 298 K (left) on a gravimetric basis and (right) on a volumetric basis.

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