Towards Data-Driven Structure-Property Relations for Predicting Adsorption Entropy in Siliceous Zeolites

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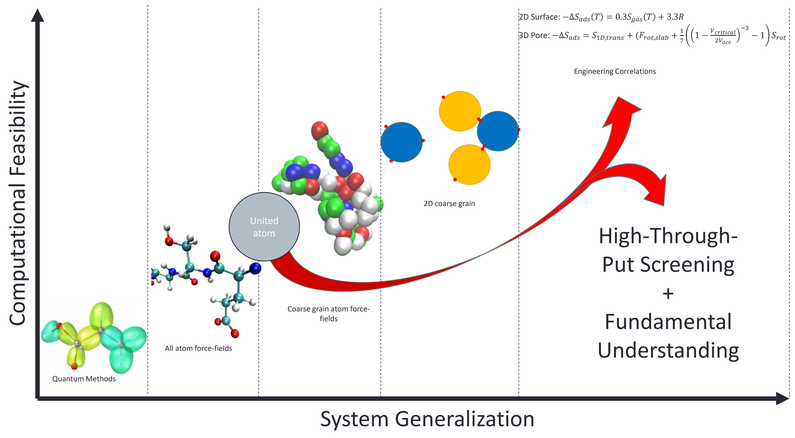
INTRODUCTION

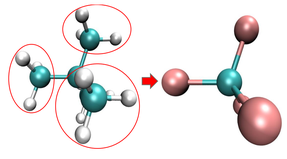
Adsorption is a critical step in carbon capture and separations technology; the ability to predict this free energy can supplement framework optimization through high-throughput screening[1]. A vital, yet difficult to measure contributor to the free energy is the entropy upon adsorption, which has been shown to follow linear trends for several heterogenous catalysts through the works of Campbell & Sellers[2] and Abdelrahman & Dauenhauer[3]. In this work we expand upon this idea by exploiting the versatility of molecular simulations. First, we demonstrate the competence of our model by reproducing linear trends for which experimental alkanes adsorb on siliceous zeolites. We expand this concept to fictious geometries, where variables such as attractive forces, pore geometry, and occupiable volume are configured. We conjecture that these trends are preserved across many systems, which allows for sensible prediction/estimation of adsorbate entropies.

METHODS

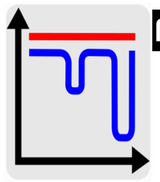


- We use **Canonical Ensemble Monte-Carlo** methods within the **low pressure regime** to quantify ΔS^o_{ads} across **real** and **fictitious** frameworks.

Transferable Potentials for Phase Equilibria



- Our goal is to find engineering correlations with **universal descriptors** that may be used in **High-Throughput Screening** of frameworks.
- We use the proven (TRAPPE)[4] United Atom forcefields within (FEASST)[5].



NIST

The Free Energy and Advanced Sampling Simulation Toolkit **(FEASST)**

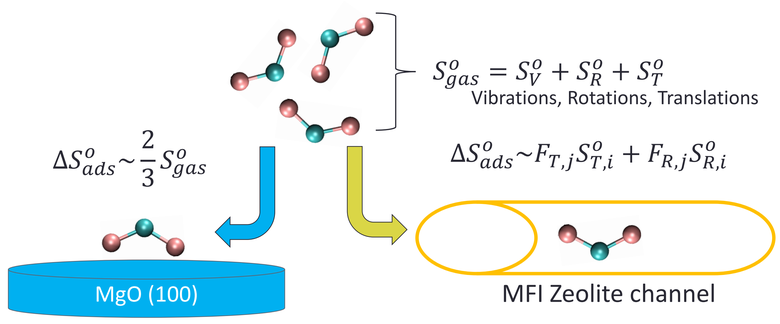
BACKGROUND

- Campbell & Sellers[2] have shown that an adsorbate on a 2D catalyst entropy follows the trend:

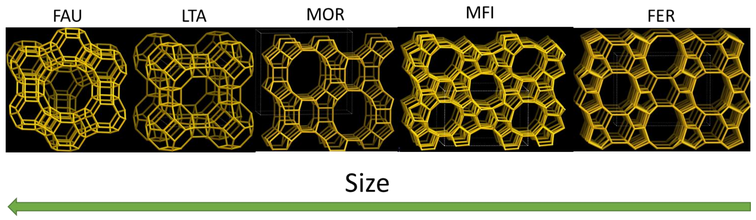
$$S^o_{ads}(T) = 0.7S^o_{gas}(T) - 3.3R$$

- Abdelrahman & Dauenhauer[3] have shown that an adsorbate on a 3D zeolite catalyst follows:

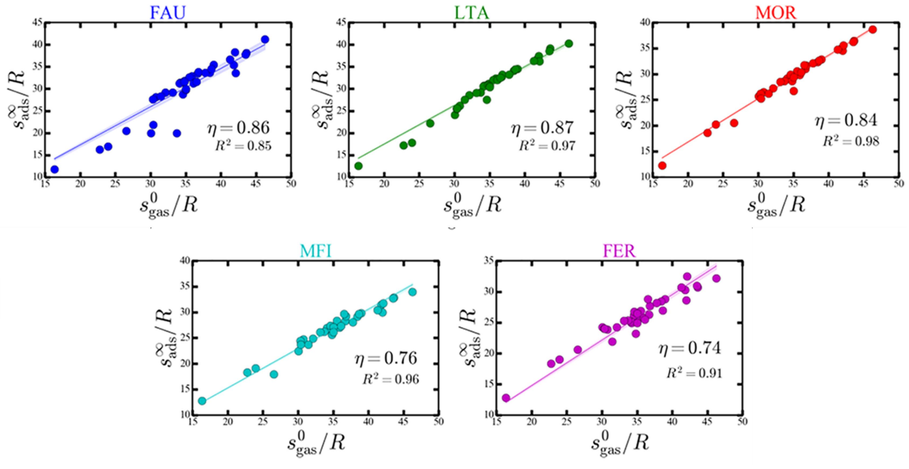
$$-\Delta S_{ads} = S_{1D,trans} + (F_{rot,slab} + \frac{1}{7}\left(\left(1 - \frac{V_{critical}}{2V_{occ}}\right)^{-3} - 1\right)S_{rot}$$



ZEOLITE COMPARISON



PRELIMINARY RESULTS



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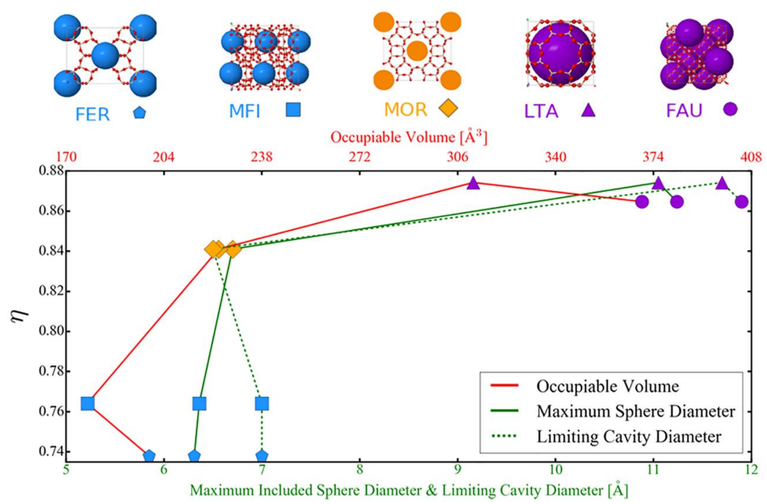

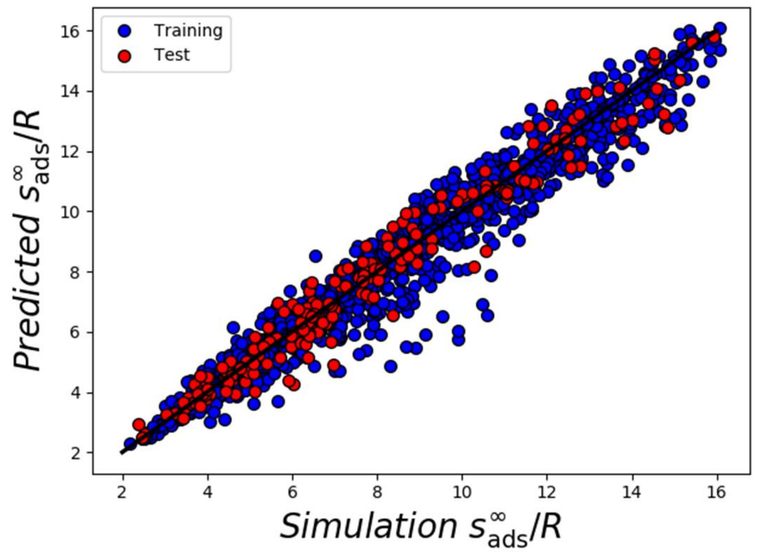

REFERENCES

1. Y. Lee, S. D. Barthel, P. Dłotko, S. M. Moosavi, K. Hess, B. Smit, J. Chemical Theory and Computation 2018 14 (8), 4427-4437
2. Campbell, C. T.; Sellers, J. R. V. The entropies of adsorbed molecules. J. Am. Chem. Soc. 2012, 134 (43), 18109−18115.
3. P. J. Dauenhauer, O. A. Abdelrahman, ACS Central Science 2018 4 (9), 1235-1243
4. M. G. Martin and; J. Ilja Siepmann, J. Physical Chemistry B 1998 102 (14), 2569-2577
5. Hatch HW, Mahynksi NA, Shen VK (2018) FEASST: Free Energy and Advanced Sampling Simulation Toolkit J Res Natl Inst Stan 123:123004
6. Zeolite Images: Ch. Baerlocher and L.B. McCusker, Database of Zeolite Structures, http://www.iza-structure.org/databases/