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Designing Structured Carbon Sorbents for CO₂ Capture through Experimental and Monte Carlo Simulation Insights

Erik C. Rupp^{1*}, Jiajun He¹, Beibei Wang¹, John To², Jianguo Mei², Zhenan Bao², and Jennifer Wilcox¹

¹Department of Energy Resources Engineering, Stanford University,
Stanford, California 94305, USA

²Department of Chemical Engineering, Stanford University,
Stanford, California 94305, USA

*Corresponding Author: ecrupp@stanford.edu

Adsorption of CO₂ on solid sorbents, both structured and not, is a concept that has a range of applications, from large point source emissions to CO₂ purification to atmospheric scrubbing. A primary benefit of solid sorbents is the ability to tune the structural parameters (such as microporosity and surface area) of the material, as well as perform chemical modifications (including surface functionalization and amine doping), to enhance CO₂ uptake for specific applications. In addition, materials such as carbon possess favorable heat conduction properties when compared to an aqueous amine solution. This work mainly focuses on CO₂ adsorption parameters of tuned carbon sorbents with high surface area and ordered pore structures. A comprehensive analytical evaluation of the carbon sorbents has been performed in order to determine the parameters that are most beneficial for low pressure CO₂ adsorption, and to help guide further research into the field of CO₂ capture.

Low-pressure adsorption isotherms (developed both gravimetrically and volumetrically) were used to analyse pore characteristics, using N₂, Ar and CO₂ as probe gases, to measure pore volume, distribution and surface area. The CO₂ adsorption performance of the porous carbons was evaluated under both static equilibrium and dynamic conditions, at relevant temperatures (0 to 50 °C) and pressures (0 to 1 bar).

Parallel to the experimental work, Grand canonical Monte Carlo (GCMC) simulations are used to study the adsorption behavior of CO₂ on carbon-based materials. A rigid, graphitic slit pores of varying width between 0.3 and 10 nm were used to simulate the adsorption density of CO₂, which is then combined with the experimentally determined pore distribution to yield CO₂ capacity predictions, which are compared to the experimental measurements. CO₂-CO₂ interactions, as well as CO₂-surface interactions were modeled with a combination of Lennard-Jones (LJ). The combined experimental and computational approach allows for feedback into both sorbent design and computational modeling accuracy.

Towards metal-organic framework adsorbents and membranes for gas separations: A combined computational-experimental approach

Sankar Nair*, David Sholl, Christopher Jones, and William Koros

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology,
Atlanta, Georgia 30332, USA

*Corresponding Author: sankar.nair@chbe.gatech.edu

This talk will describe our recent progress in the synthesis and properties of ZIF-type MOF materials for molecular separation applications, and their subsequent use in the scalable fabrication of molecular sieving membranes on polymeric hollow fibers. New separations technology is key to increased energy efficiency in the chemical sector, as well as the efficient production of clean and renewable fuels. It is hypothesized that ZIF materials may find successful applications in this area. Towards this goal, we will first discuss approaches to controlling the pore structure and separation properties of ZIF materials via mixed-linker synthesis. We then discuss the processing and use of these MOF materials in the fabrication of membranes for gas and hydrocarbon separations. The transport properties of such membranes are discussed. We will discuss some key scientific and engineering questions whose resolution (via combined experimental and computational methods) may enable the successful application of ZIF membranes in separations processes.

Adsorption in Flexible Structures: Experiment and Simulations

Peter I. Ravikovitch*

ExxonMobil Research and Engineering Company,
Annandale, New Jersey 08801, USA

*Corresponding Author: peter.ravikovitch@exxonmobil.com

It is customary in adsorption science to consider solid adsorbents as inert materials. The advent of novel metal-organic framework and related materials shows that this convenient simplification no longer works. Framework flexibility that arises from a generally softer nature of these materials often gives rise to complex equilibrium and kinetic behaviors, including structural phase transitions, and presents challenges for modeling adsorption and diffusion.

In this talk we will present an overview of our molecular simulations and experimental results for zeolitic Imidazolate frameworks (ZIF) that exhibit different degree of framework flexibility. Grand Canonical Monte Carlo simulations were used to predict equilibrium adsorption properties. To elucidate the extent of framework flexibility we performed classical and ab-initio Molecular Dynamics simulations. We will present experiment and modeling studies for ZIF materials that undergo structural transitions upon adsorption of guest molecules. Combination of modeling and experiment allowed us to elucidate the thermodynamics of this process. We show that accounting for the framework flexibility and possible structural transitions is important and often critical for accurate predictions of adsorption and diffusion.

Ab initio modeling of adsorption and reaction of CO₂ and H₂ in Lewis Pair Functionalized Metal Organic Frameworks

J. Karl Johnson^{1,2*} Jingyun Ye¹

¹Department of Chemical & Petroleum Engineering, University of Pittsburgh,
Pittsburgh, Pennsylvania, 15261, USA

²National Energy Technology Laboratory, 626 Cochrans Mill Road, Pittsburgh,
Pennsylvania 15236, USA

*Corresponding Author: karlj@pitt.edu

Metal organic frameworks (MOFs) are highly versatile nanoporous materials because of their structural and functional tailorability. We use density functional theory (DFT) methods to design functionalized MOFs that are capable of chemically binding and hydrogenating CO₂. We employ UiO-66 as our starting base material because it is a MOF that has high chemical and thermal stability, is highly selective toward CO₂ and can be post-synthetically functionalized. We design functional moieties for CO₂ hydrogenation based on frustrated Lewis pairs (FLPs) because these have been shown to be very active for chemisorption of CO₂ and the heterolytic dissociation of H₂. One candidate FLP is 1-[bis(pentafluorophenyl)boryl]-3,5-di-*tert*-butyl-1H-pyrazole. We have developed a family of functional groups based on a modified version of this FLP, having both Lewis acid and base sites embedded within the molecule. We have examined the properties of UiO-66 functionalized with derivatives of the FLP. We computed the electronic structure, charge distribution, and CO₂/H₂ binding energies and found that chemisorption of CO₂ and dissociation of H₂ are both energetically favorable with many of the functional groups. We have identified possible scenarios for CO₂ hydrogenation through either binding CO₂ to the functional group and then supplying H₂ or cleaving H₂ on the modified FLP and then supplying CO₂.

Carbon Capture Properties of Nanoporous Solid Materials

Lan Li*, Izaak Williamson, and Eric Nelson

Department of Materials Science and Engineering, Boise State University,
Boise, Idaho 83725, USA

*Corresponding Author: lanli@boisestate.edu

Developing solid adsorbents is of great research interest for CO₂ capture applications. Experiments exhibit the phenomenon of sorption hysteresis, whereby the path to adsorb CO₂ molecules by the solid materials differs from that of desorption. Through first-principles quantum simulations, based on van der Waals density functional theory, we found that the types, charges and concentrations of cations doped in the solid adsorbents significantly affect the structural features, sorption hysteresis, and CO₂ capture properties of the adsorbents. Our presentation will focus on manganese dioxide OMS-2 (Octahedral Molecular Sieve), which is a one-dimensional nanoporous solid structurally stabilized in the presence of cations, e.g. K⁺, Na⁺ and Ba²⁺. The cations behave as a "gate keeper", disturbing CO₂ adsorption and diffusion in OMS-2 and resulting in the CO₂ sorption hysteresis. These effects are tunable by varying the types and charges of the cations and the cation/manganese ratios. In the presentation, we will also discuss the CO₂ sorption mechanism in details.

Development of a piezoelectric molecular dynamics model for boron nitride nanotubes

Vesselin Yamakov^{1*}, Cheol Park², Jin Ho Kang¹, Kristopher Wise², Catharine Fay²

¹National Institute of Aerospace, Hampton, Virginia 23666, USA

²NASA Langley Research Center, Hampton, Virginia 23681, USA

*Corresponding Author: yamakov@nianet.org

A classical molecular dynamics model with an incorporated strain dependent dipole potential energy term is introduced to represent the piezoelectric properties of boron nitride nanotubes (BNNTs). The model allows for an analytical expression of the piezoelectric tensor for a hexagonal boron nitride monolayer through the properties of the interatomic potential and two fitting parameters. The deformation-induced polarization predicted by this model is verified against the results of previously published electronic structure (ab-initio and tight-binding) calculations. The model works well for BNNTs over the full range of chiral angles from $\theta = 0^\circ$ (zig-zag tubes) to $\theta = 30^\circ$ (armchair tubes) and under loading in both tensile and twist modes. The presented atomistic model can be a foundation for atomic- and continuum-level modeling of the electroactive properties of large systems of BNNTs and BNNT composites, as well as a basis for analytical studies. Additionally, this atomistic model can contribute towards better understanding of inter-wall and intermolecular interactions in these materials, as well as tube functionalization and gas absorption properties.

Large-scale screening for adsorption behavior of complex molecules in zeolites

J. Ilja Siepmann^{*1}, Peng Bai¹, Chris Knight², Michael W. Deem³, and Michael Tsapatsis¹

¹Departments of Chemistry and of Chemical Engineering and Materials Science and Chemical Theory Center, University of Minnesota – Twin Cities, Minneapolis, Minnesota 55455 USA

²Leadership Computing Facility, Argonne National Laboratory, Argonne, Illinois 60439 USA

³Departments of Bioengineering and of Physics and Astronomy, Rice University, Houston, Texas 77005 USA

*Corresponding Author: siepmann@umn.edu

Zeolites play numerous important roles in modern petroleum refineries and have the potential to advance the production of fuels and chemical feedstocks from renewable resources. The performance of a zeolite as separation medium and catalyst depends on its framework structure and the type or location of active sites. To date, 213 framework types have been synthesized and > 330,000 thermodynamically accessible zeolite structures have been predicted. Hence, identification of optimal zeolites for a given application from the large number of candidate structures is attractive for accelerating the pace of materials discovery. Here we identify, through a large-scale, multi-step computational screening process, promising zeolite structures for two energy-related applications: ethanol/water separation and hydrocarbon isodewaxing. These results demonstrate that predictive modeling and data-driven science can now be applied to solve some of the most challenging separation problems involving highly non-ideal mixtures and highly articulated compounds.

High-Throughput Computational Screening of Metal-Organic Frameworks for Gas Separation Applications

Randall Q. Snurr*

Department of Chemical and Biological Engineering
Northwestern University, Evanston, Illinois 60208 USA

*Corresponding Author: snurr@northwestern.edu

There are an almost unlimited number of metal-organic frameworks (MOFs). This creates exciting opportunities but also poses a problem: How do we quickly find the best MOFs for a given application? Molecular simulations have advanced sufficiently that many MOF properties – especially structural and gas adsorption properties – can be predicted computationally, and molecular modeling techniques are now used increasingly to guide the synthesis of new MOFs. With increasing computational power and improved simulation algorithms, it has become possible to conduct high-throughput computational screening to identify promising MOF structures and uncover structure/property relations. We present some recent work from our group aimed at using high-throughput computational screening to identify promising MOFs for gas separation applications.

Usability and Reproducibility: Proper Programming Practices in Science

Patrick Fuller*,

NuMat Technologies, Skokie, Illinois 60077 USA

*Corresponding Author: pat@numat-tech.com

In academic settings, molecular modeling has proven itself as a useful tool for guiding experimental research. However, industrial adoption of these practices has been limited. Despite the promise of atomistic simulations to improve the efficiency of R&D projects, the costs and risks of implementation often outweigh the perceived benefit. While simulation accuracy is a constant concern, NuMat has found that the bulk of adoption challenges are rooted in the less technical areas of usability and reproducibility. By employing best practices espoused by organizations such as Software Carpentry, the economics of industrial collaboration in this space would be favorably altered.

Greg Wilson, D. A. Aruliah, C. Titus Brown, Neil P. Chue Hong, Matt Davis, Richard T. Guy, Steven H. D. Haddock, Katy Huff, Ian M. Mitchell, Mark Plumbley, Ben Waugh, Ethan P. White, and Paul Wilson: "Best Practices for Scientific Computing." arXiv preprint, submitted November 29, 2012. <http://arxiv.org/pdf/1210.0530v4.pdf>

Interrogating Simple Pore Models using Flat-Histogram Sampling Methods to Understand the Effect of Sorbent Flexibility on Fluid Adsorption

Vincent K. Shen* and [Daniel W. Siderius](#)

Chemical Sciences Division, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899, USA

*Corresponding Author: vincent.shen@nist.gov

While it is well known that sorbent flexibility can affect observed adsorption behavior, rigid sorbents are still commonly used in the study of adsorption via molecular simulation for both simplicity and practicality. Past attempts at incorporating sorbent flexibility in simulation have largely relied on computationally demanding atomistic descriptions of the sorbent framework. In this work, we present two simple pore models for flexible sorbents. The first model accounts for internal sorbent flexibility in a grand canonical ensemble formulation. The second model accounts for volume fluctuations via an osmotic ensemble formulation. In both cases, we use flat-histogram sampling methods to calculate precisely the relevant multi-dimensional probability distributions, which we will show are directly related to specific thermodynamic potentials and the deformation properties of the sorbent. Using a square-well fluid as the adsorbate, we are able to reproduce experimentally observed adsorption behavior, such as adsorption-induced deformation and breathing phase transitions. More importantly, we are able to identify the physically relevant features (or properties) of the sorbent that lead to these interesting and exploitable sorbent properties.

NIST Facility for Adsorbent Characterization and Testing

Laura Espinal^{1*}, Brad Boyerinas¹, Martin L. Green¹, and Roger D. van Zee²

¹Material Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

²Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

*Corresponding Author: laura.espinal@nist.gov

Sorbent materials are candidates for many commercial and industrial applications, including hydrogen and natural gas fuel storage, CO₂ gas separation, catalysis, environmental remediation, and gas purification. However, reproducible sorption properties are difficult to attain. There is a national need to develop universally accepted standards and testing procedures that are precise and accurate for adsorbent testing and characterization. Consistent characterization results of sorbent material properties are complicated by slight variations in sample preparation and handling due to changes in material properties after even brief exposures to ambient atmospheres and elevated temperatures. Compounded by inconsistent measurement protocols, these challenges have led to a general distrust of published material sorption properties. To address these technological challenges, the National Institute of Standards and Technology (NIST) with support from the U.S. Department of Energy's Advanced Research Projects Agency–Energy (ARPA-E) will construct a state-of-the-art Facility for Adsorbent Characterization and Testing (FACT). FACT will serve the sorbent materials research community by providing impartial testing and characterization of material sorption properties; establishing reference materials and testing procedures; and disseminating sorbent material property data and measurement “best-practices”. In this poster, we present an overview of FACT's planned measurement capabilities and current status to engage and inform the sorbent materials research community of our programmatic plans.