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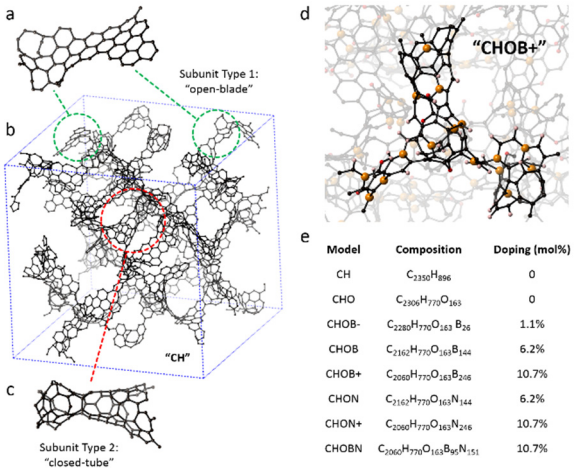
Tuning the Thermodynamics of Adsorbed Natural Gas via Heteroatom Doping

Nicholas P. Stadie (Department of Chemistry and Biochemistry, Montana State University)

Introduction. The objective of this work is to determine the effect of boron and nitrogen substitutional doping within ordered microporous carbon frameworks on the thermodynamics of adsorption of methane and ethane, the primary components of natural gas. We are carrying out this work in two parallel efforts: synthesis/characterization of novel B- and/or N-doped zeolite-templated carbon materials complemented by computational guidance using a wide range of theoretical methods. Synthetic efforts and subsequent characterization depend greatly on the construction and commissioning of custom apparatus for this purpose, especially a high-pressure, high-temperature reactor suited to handling diborane and ammonia, the precursors of relevance to this work. Computational efforts, on the other hand, rely on the convergence of simulations across several levels of theory, from full *ab initio* methods to molecular mechanics based on generic force fields. In the first year of this project, we have focused on improving the design of the reactor as well as the development of new structural models of boron- and nitrogen-containing porous carbons.

Structural Models of Zeolite-Templated Carbon. Several atomic-scale structural models of faujasite-templated carbon (**FAU**-ZTC) exist; the Roussel Model (2006, 2007), Nishihara Model I (2009), Nueangnoraj Model (2013), Kim Model (2016), Braun Model (2018), Nishihara Model II (2018), and Tanaka Model IV (2018). These models are categorized in our work into two distinct structure types based on the primary subunit type: "open-blade" or "closed-tube" connectors (the framework "struts"). The amount of hydrogen or other edge-site functional groups required to complete the carbon framework, the surface area, and the carbon packing number (per volume of strut) depend greatly on the type of framework; we find the open-blade networks are all closer to actual ZTCs synthesized in the laboratory. Nevertheless, some closed-tube character is also likely to persist, given the distribution of carbon packing density measured within laboratory-synthesized **FAU**-ZTC. In this work, we have developed a new model of **FAU**-ZTC based on Nishihara Model II that incorporates heteroatom dopants. The original Model II was first structurally relaxed using density functional tight binding (DFTB+) semi-empirical methods, using the "matsci" parameter set. Oxygen was incorporated according to the experimentally-determined oxygen-bearing functional groups native to **FAU**-ZTC. Boron and nitrogen inclusion were carried out by random substitution of carbon framework sites using the following rules: boron is only a BC_3 type "mid-strut" species while nitrogen is either of NC_3 "mid-strut" type, pyridinic NC_2 type, or pyrrolic NC_2H type, consistent with spectroscopic observations of experimental ZTCs. A total of eight models have been constructed, as shown in **Figure 1**. Compositions were selected to represent "low-doping," "mid-doping," and "high-doping" concentrations as well as pure and mixed scenarios to deduce the role of each heteroatom species in a controlled way. These structures are currently continuing to optimize using DFTB+ methods (reducing total electronic energy and lattice forces) and represent accurate, real-world materials as well as future, synthetically viable materials to be experimentally targeted within this project.



Model	Composition	Doping (mol%)
CH	$C_{2350}H_{896}$	0
CHO	$C_{2306}H_{770}O_{163}$	0
CHOB-	$C_{2280}H_{770}O_{163}B_{26}$	1.1%
CHOB	$C_{2162}H_{770}O_{163}B_{144}$	6.2%
CHOB+	$C_{2060}H_{770}O_{163}B_{246}$	10.7%
CHON	$C_{2162}H_{770}O_{163}N_{144}$	6.2%
CHON+	$C_{2060}H_{770}O_{163}N_{246}$	10.7%
CHOBN	$C_{2060}H_{770}O_{163}B_{95}N_{151}$	10.7%

Figure 1. Eight newly developed quantum-optimized structural models of **FAU**-ZTC based on Nishihara Model II with both (a-b) open-blade and (b-c) closed-tube type struts (H is omitted for clarity). (d) Close-up view of "CHOB+." (e) Model names and details.

Methane Interactions. Simulations of methane-ZTC interactions are being carried out at three levels of theory to determine an effective compromise between complexity and accuracy. The "CHO" model was selected as the starting point for this work, the closest structural model to archetypical experimental **FAU**-ZTC. High-pressure CH_4 adsorption isotherms were calculated at 238 and 298 K (see **Figure 2**) using molecular mechanical Lennard-Jones type pairwise interactions (TraPPE model/Peng Robinson EOS for CH_4, Dreiding model for ZTC, 14 Å cutoff radius) and the results are consistent with experiment. However, a lack of reliable forcefield parameters for CH_4-B and CH_4-N motivates further work at a higher level of theory. High-level, *ab initio* wave function methods (CCSD(T)) are now being employed on a computationally manageable subunit of ZTC: 1-methylidenephenalene (MPh). This trefoil-based aromatic molecule is chosen for its aromaticity, central atom (X) that can be easily changed, and the capability to add a variety of functional groups involving oxygen (for example, "MPhO" shown in **Figure 3d**).

Benchmarking simulations of interactions with standard small molecules (H_2, He, N_2, and Ar) are currently being carried out prior to simulations with CH_4, C_2H_6, and natural gas mixtures (**Figure 3e-g**).

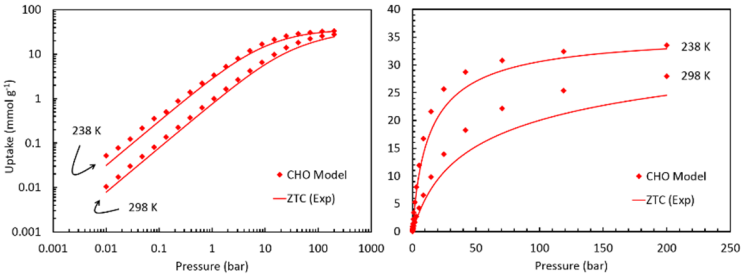


Figure 2. Comparison of CH_4 uptake on experimental (lines) and simulated (points) **FAU**-ZTC (using the "CHO" model).

Synthesis of ZTBC$_x$ and ZTNC$_x$. The novel synthetic methods to achieving **FAU**-ZTC with a wide tunable heteroatom content (of B and/or N) proposed in this work present a unique challenge in the evolution of large quantities of H_2 at 800 °C; the design of the reactor has had to be modified to account for the reaction between H_2 and the originally proposed graphite gasket. A new design incorporating a diamond shaped nickel 200 gasket has now been implemented; construction and commissioning are complete as of September 2019 (the current apparatus is shown in **Figure 4**). During commissioning, bulk graphitic samples of composition up to BC_5 (measured by energy dispersive X-ray spectroscopy using a sensitive low-energy XFlash 610 detector) have been obtained, ensuring reliability of the new design.

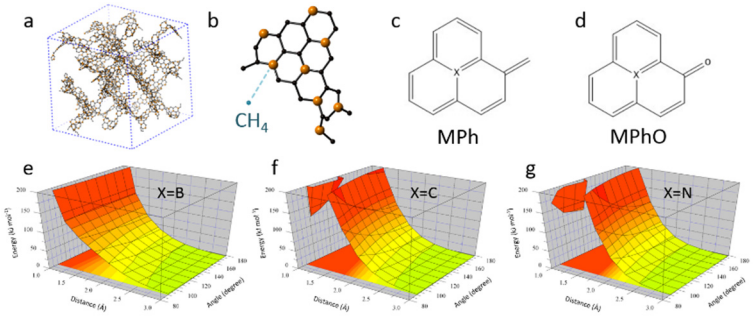


Figure 3. Benchmarking simulations of adsorbate-heteroatom interactions at several levels of theory: (a) molecular mechanics simulations of adsorption isotherms in full-scale, periodic ZTC structures, (b) DFTB+ simulations of adsorbate-strut interactions on large ZTC subunits, and (c-g) ab initio simulations of adsorbate-heteroatom interaction energy in aromatic MPh/MPhO as a function of approach angle, distance, and central atom (X) type.

Methane Adsorption Isotherms. A new Sieverts apparatus is fully constructed and commissioned for measurements up to 150 bar. Measured excess adsorption isotherms are routinely fitted and analyzed to deduce absolute uptake (as shown in **Figure 4**).

Summary. Phase I of this project has seen the development of several computational tools to determine the effect of boron- and nitrogen-inclusion within ordered porous carbon framework materials, namely ZTCs, and new results are forthcoming. Likewise, the synthesis of high boron-content ZTCs is imminent in the second-generation reactor recently developed.

Impact. This seed grant has had a massive impact on the principal investigator as well as the six students involved. Early results have been leveraged to secure a larger source of funding (DOE EERE, to begin in late 2019) and several startup allocations on high-performance computers, both locally and nationally (NSF XSEDE startup award and ORNL Director's Discretionary Fund). The primary graduate student, Devin McGlamery, is preparing the first manuscript, describing benchmarking synthetic experiments relating the structural features of graphitic materials to Raman spectroscopic and XRD observations, an important step to understanding the role of boron and nitrogen defects in the carbon lattice. The primary undergraduate student, Rylan Rowsey, is preparing a new parameter set to accurately describe CH_4-B and CH_4-N interactions in ZTC and similar materials (e.g., MOFs/COFs) and is expected to begin preparing a manuscript shortly. Four additional undergraduate students contribute to this work, all of whom remain involved in Phase II. Katrina Sandoval, for example, has been recognized as a MSU Presidential Emerging Scholar, and Seth Putnam has been recognized by receiving a Swager summer research fellowship. Our efforts have culminated in the start of several new collaborations: with Caltech (B. Fultz and C. Ahn), Tohoku University (H. Nishihara and A. Gabe), Shinshu University (H. Tanaka), Oregon State University (C. Simon), as well as at MSU (R. Szilagyi).

Figure 4. High-temperature (800 °C), high-pressure (34 bar) reactor compatible with H_2 evolution and air-sensitive gaseous precursors. Version 2.0 (with metal-metal seal) is commissioned as of Sep. 2019.