R & D facts

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Carbon Sequestration

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Development of Metal Organic Framework Materials for CO_2 Separation

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Summary

There are at least three different applications where separation of CO_2 from other gases is of interest. These are: 1. Separation of CO_2 from fuel gas (output from gasification, water gas shift reactors, etc.); 2. Separation of CO_2 from sour natural gas wells (natural gas containing large fractions of CO_2); and 3. Separation of CO_2 from flue gas. These separations must each be accomplished very cost effectively if sequestration is to be a viable technology, yet each has distinct requirements. For example, the CO_2 partial pressure and concentration is relatively low for the last application and therefore chemical-strength binding may be required to capture CO_2 from flue gas. To examine the potential of metal organic framework (MOF) materials for the ability to act as highly selective membranes for separation of CO_2 is proposed. This is a multi-scale problem that will require collaborations with researchers at NETL doing experimental work on synthesis and testing of MOFs and with university teams doing various levels of modeling, from detailed quantum mechanics to continuum-level approaches.

Problem:

Metal organic frameworks are crystalline materials that can be tailored to specific applications through varying the metals, ligands, and linkers making up the MOF. They can be synthesized inexpensively, relatively easily, in high purity, and in a highly crystalline form. The number of potential MOFs is virtually limitless, as changes in the ligands, secondary building blocks, or the linkers will produce novel MOF with distinct properties. Experimental characterization of a large number of different MOFs is a very expensive and time-consuming procedure. Therefore, significant progress could be made if computational methods could be applied to help screen candidate materials. In the best case scenario, computer simulations would be used to design new MOFs based on required performance of the material. This project is a first step toward computational design of functional MOFs. The main goals of the research are: (1) develop a detailed characterization of the interaction between CO_2 and a number of existing MOFs; (2) compute adsorption isotherms and transport diffusivities of pure and mixed gases in various MOF from atomic-scale simulations; (3) develop a macroscopic model for transport of gas mixtures through a model MOF membrane; and (4) identify candidate structures that increase the selective permeability of CO_2 through MOF membranes.

Methodology:

The most important aspect for numeric prediction of MOF behavior is the interaction potential model used in the simulations. Validation will occur with the potential models (Lennard-Jones parameters, point charges, etc.) to be used in the calculations and refinement of the potentials where needed by using highly-accurate ab initio molecular orbital and density functional theory methods. Potentials are needed

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for the framework atoms interacting with a number of adsorbates, including CO_2, N_2, O_2, H_2, CO, H_2O, and CH_4. Particular attention will be paid to the electrostatic interactions between the MOF and the adsorbate molecules. The electrostatic interactions are expected to be especially important for accurate modeling of CO_2 adsorption and transport. Once accurate potentials are in hand, Monte Carlo and molecular dynamics simulation techniques will be used to compute the adsorption of gas mixtures in and diffusion through MOF crystals. The initial work will focus on existing MOFs, such as MOF5 and Cu-BTC. Adsorption isotherms will be compared with experimental data for pure gases measured at NETL. Equilibrium molecular dynamics will be used to compute the self- and corrected diffusion coefficients, similar to methods used in previous work. Transport diffusivities will be computed from corrected diffusivities using adsorption isotherm information, computed from MC simulations. As an example the transport diffusivities calculated are shown in Figure 1 for H_2 in a novel zinc-based MOF (Zn[bdc][ted]) synthesized by Jing Li's group at Rutgers. It is critical to use molecular simulations to test assumptions that will be used to develop the continuum-scale model. The continuum-scale Maxwell model will be used for computing selective permeance through hypothetical MOF membranes. This continuum-level model will link the atomic-level simulations to experimental data, allowing us to assess how well various MOFs will perform under ideal conditions. It is critical to compare with experimental data as we generate simulation data on adsorption isotherms and diffusivities. Our recent work indicates that MOFs must be very carefully synthesized and activated (removal of solvent molecules) in order to achieve good agreement between simulations and experiments for adsorption isotherms. Moreover, electrostatic interactions between the framework and the adsorbate molecules can, in some cases, be very important. Therefore, development of potentials will be carried out in conjunction with experimental work measuring adsorption isotherms.

Once potential models have been developed, atomic and continuum-level computational techniques will be used to screen many existing materials for use as membranes that selectively transport CO_2. The ultimate goal of this work is to use computational methods to suggest new structures or chemical modifications to existing structures that will enhance the capability of MOFs to selectively transport CO_2. Design of new materials will require ab initio calculations and may involve use of software such as COSMO-RS, which can be used to relate the properties calculated from ab initio to thermodynamic properties such as Henry's law constants. Work will be confined to the physisorption regime. Chemisorption, as may be required for flue gas separation, will not be considered in this initial proposal.

Expected Outcomes

- An atomic-level picture of the potential for MOFs to separate CO_2 from various gas mixtures.
- A detailed characterization of the interactions between CO_2 and MOF and how that interaction might be controlled.
- Increased information from experiments due to modeling/experimental collaboration.
- The first detailed predictions of the performance of MOFs as gas separation materials.
- Quantitative comparisons of multiple MOF materials to guide experimental studies of MOF thin films.
- Quantitative study of the impact of lattice flexibility on gas solubility and diffusion in MOFs.
- Examination of possible applications of MOFs as components in polymer/MOF.

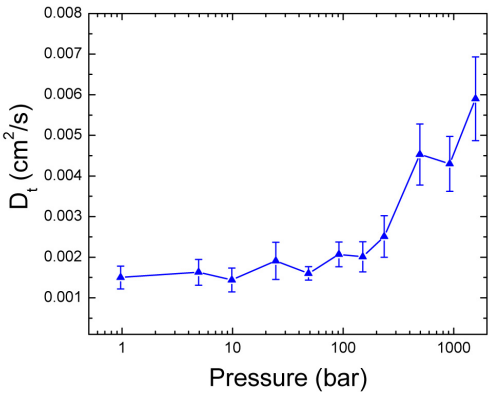

Figure 1: Transport diffusivities of H_2 in MOF Zn[bdc][ted] as a function of bulk gas pressure.