Progress Report
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Project Title: Use of Organic Monolayers to Tune the Surface Properties of Zeolites for Enhanced Separations
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The separation of mixtures to yield high purity components by distillation accounts for 10-15% of the world's energy consumption. Alkene/alkane separations are among the most difficult and energy intensive. Propylene, for example, is typically produced via thermal and fluid catalytic cracking, resulting in propylene/propane mixtures. Propylene/propane distillation is one of the most energy-intensive separations used on a commercial scale, with up to 0.3% of global energy consumption used to purify propylene and ethylene. With >70 million tonnes produced annually, propylene is one of the most important building blocks of everyday life, ending up in products like clothing, carbon fiber, or diapers. Propylene production is a rapidly growing industry, with the global demand for propylene expected to grow at an annual rate of 5%. More broadly, separations costs are high for many mixtures of light gases, including light hydrocarbons that are recovered in large amounts during shale gas extraction.

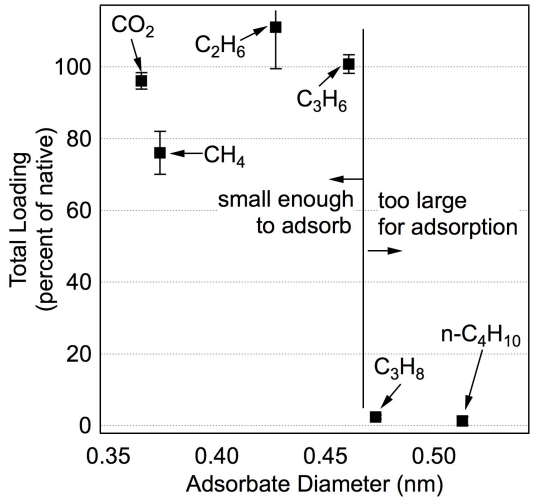

Figure 1: Normalized total loading as a percentage of native performance for zeolite 5A+MPA for carbon dioxide, methane, ethane, propylene, propane, and n-C4H10 as a function of the Chung Diameter of each adsorbate molecule. Error bars are standard error.

Zeolites are crystalline microporous materials that have received attention because of their uniform pores that approach molecular diameters, allowing size-based separations of small molecules. By forming a zeolite membrane or a pellet-based pressure swing adsorption system, the energy demands and cost associated with distillation can be significantly decreased. Though zeolites have a range of pore diameters, available zeolites do not have diameters that are continuous across the range of light gases, and substantial effort has been devoted to create materials with more tunable pore diameters or chemistries. One approach that has recently been used to improve the specificity of interactions between organic molecules and porous materials has been in the application of organic self-assembled monolayer (SAM) coatings to heterogeneous catalysts. In this project, for the first time we modified zeolite 5A via the deposition of phosphonic acids (PAs) on zeolites for separations applications.

To better control diffusion and adsorption in zeolites, we modified zeolite 5A with organic phosphonic acids having different alkyl tail lengths and measured how the diffusion rate and adsorption loading changed for the gases CO_2, CH_4, C_2H_6, C_3H_6, C_3H_8, and n-C_4H_{10}. All phosphonic acids, regardless of chain length, decreased the diffusion rate of n-C_4H_{10}, but generally had a smaller effect on the diffusion rate and loading of smaller molecules such as CO_2 and CH_4. However, methylphosphonic acid (MPA) decreased by >90% both the diffusion rates and equilibrium uptakes of n-C_4H_{10} and C_3H_8, as summarized in Figure 1. Surprisingly, the achievable loadings of C_3H_6, C_2H_6, CH_4, and CO_2 were affected much less by MPA modification, resulting in a C_3H_6/C_3H_8 ideal adsorption selectivity of 59±14. The unique effects of MPA on the selective uptake of gases appear to be due to its ability to enter the zeolite pores; in contrast, longer-chain phosphonates were confined to the external surface of 5A crystals. Our results suggest phosphonic acids or other organic modifiers could be an effective tool to tune total loadings and diffusion

rates for zeolites for applications such as C_3H_6/C_3H_8 separation. Moreover, the flexibility of this modification strategy suggests that it could be further optimized and applied to many separations applications.

This research appears to be opening up a new research direction for the career of the PI; his main area of research is in heterogeneous catalysis, and this represent a new direction for applications in separations. Multiple students and postdocs have participated in the research. One student, whose participation was funded by an external fellowship, recently completed his PhD requirements, with one chapter of his thesis describing work on this project. Work will accelerate on this project in the next year of the grant. We are preparing a manuscript for submission in the next month that is based on the thesis chapter.