

### Progress Report

Research activities in the first year of this grant focused on measuring adsorption energies of ethane, ethylene, and acetylene on the dehydroxylated UiO-66(Zr) metal-organic framework (MOF) having none,  $-\text{NH}_2$ , and  $-\text{NO}_2$  functional groups on the organic linker. To complete the work, the MOFs were synthesized, washed, and activated followed by structural characterization and then testing with adsorption calorimetry at 293 K and 195 K. A unique feature of this research was the direct measurement of adsorption energies at low temperature, 195 K, which is needed to better define the energies of different adsorption sites than can be done at 293K due to a more strongly separated partition function. Calorimetry is needed for this work because indirect calculation of adsorption energies using isotherms is difficult to resolve at low temperature.

Successful synthesis of the three UiO-66(Zr) MOFs was confirmed with x-ray diffraction. Successful functionalization and dehydroxylation was confirmed with fourier-transform infrared spectroscopy (FTIR). Brunauer-Emmett-Teller (BET) surface area, Langmuir surface area, and pore volume was calculated with nitrogen physical adsorption measurements at 77 K. Finally, adsorption calorimetry measurements were completed at 293 K for UiO-66(Zr) having none,  $-\text{NH}_2$ , and  $-\text{NO}_2$  functional groups and at 195 K for UiO-66(Zr)- $\text{NO}_2$ .

Figure 1 shows differential adsorption energy as a function of coverage for ethane, ethylene, and acetylene for each UiO-66(Zr) MOF. The order of adsorption energies for the three MOFs was  $\text{UiO-66} < \text{UiO-66-NH}_2 < \text{UiO-66-NO}_2$  for all three adsorbates. UiO-66 and UiO-66- $\text{NH}_2$  were within 2 kJ/mol of each other over the entire coverage range; however, UiO-66- $\text{NO}_2$  was consistently 4-6 kJ/mol higher. In comparing the adsorbates, the differential energies from highest to lowest were acetylene > ethane > ethylene. Ethane was consistently 1-2 kJ/mol higher than ethylene, and acetylene was ~4 kJ/mol higher than ethylene. Finally, the adsorption energies at 293K steadily decreased with increasing coverage suggesting the presence of multiple types of adsorption sites.

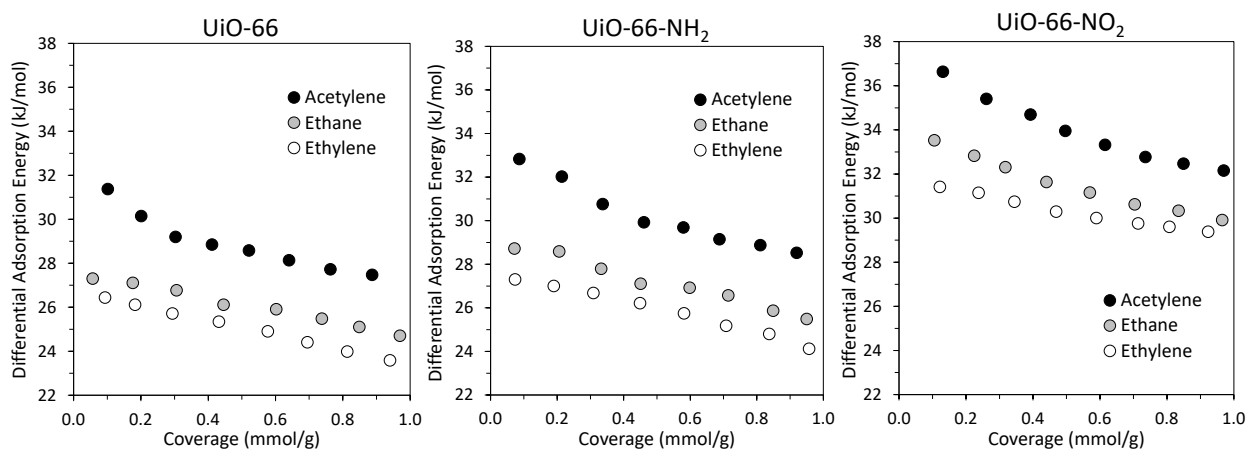


Figure 1. Differential adsorption energy as a function of coverage at 293K.

Adsorption calorimetry results at 195 K are compared to the 293 K results in Figure 2 for UiO-66(Zr)- $\text{NO}_2$ . For ethane and ethylene, there are differential energy plateaus in the low coverage (0-1 mmol/g) and high coverage (6-7 mmol/g) ranges. In between the plateaus, the differential energy of adsorption steadily decreases. The difference in energies between the plateaus are similar for both adsorbates; 8.5 kJ/mol for ethane and 9 kJ/mol for ethylene. The low coverage differential energies for acetylene behave differently than ethane and ethylene. The low coverage

energy starts at a very high value of 44 kJ/mol, 30% higher than ethane and ethylene, and then sharply decreases in the coverage range of 0-1 mmol/g.

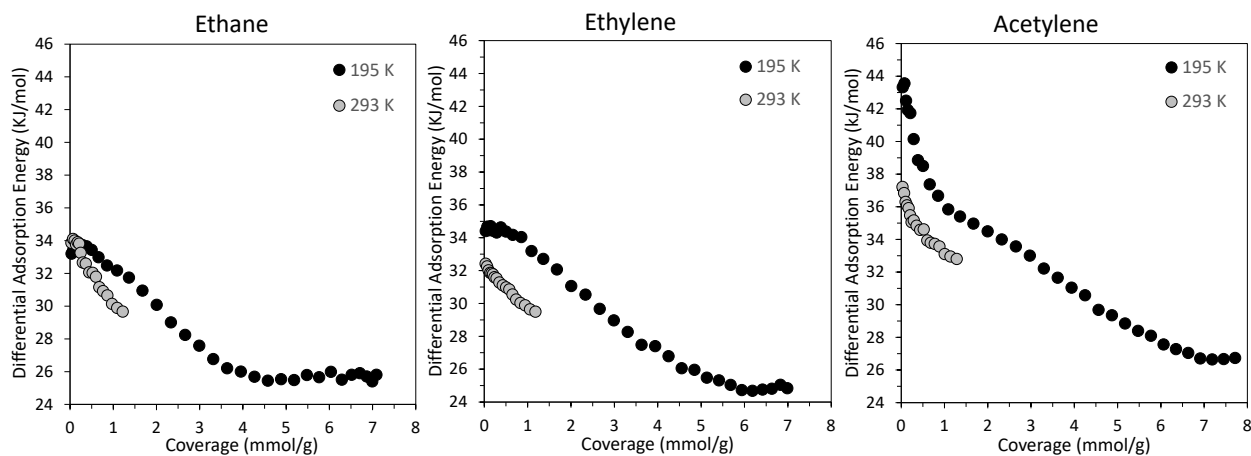


Figure 2. Differential adsorption energy as a function of coverage at 195K for UiO-66(Zr)-NO<sub>2</sub>.

We did not anticipate such a stark difference in the differential energies of acetylene compared to ethane and ethylene at low coverage. This suggests there is a minority (low concentration) type of adsorption site in the UiO-66(Zr)-NO<sub>2</sub> that adsorbs acetylene much more strongly than ethane or ethylene. This is an intriguing result in the context of industrial difficulties in separating ethylene and acetylene. We hypothesize that the strong adsorption site observed with acetylene is due to uncoordinated Zr metal sites, which have been shown to occur as a result of missing linker defects in the UiO-66 structure. We also hypothesize that the low coverage differential energy plateaus for ethane and ethylene represent the adsorption energy at the uncoordinated Zr metal sites. We are currently trying to follow synthesis procedures in the literature to prepare UiO-66(Zr)-NO<sub>2</sub> MOFs with varying concentrations of missing linker defect, and, in turn, varying concentrations of uncoordinated Zr metal sites. We have also initiated a collaboration at Wake Forest with a computational research group to explain the unique adsorption behavior we observed experimentally.

### **Impact on Career and Students**

This New Directions grant has already made a significant impact on my career. The adsorption calorimetry work was indeed a brand new direction of scholarly work for me. With the support of this grant, I was able to establish a home-built experimental technique that is only available to a handful of research groups in the country. In the first year, we have observed intriguing results that have allowed us to establish a foundation for future research, which includes a new collaboration with a computational modeling research group. The approach to collaboration is to close the feedback loop between computational modeling, synthesis, and experimental characterization. With this three-pronged approach, there is a high likelihood for success. The grant has supported a graduate student on a full time basis. The graduate student is scheduled to present their work at SERMACs in the spring of 2019. The data already collected is of publishable quality, and the work will ultimately be published in a scientific journal. In addition to the graduate student support, three undergraduate students gained research experience over the summer. The undergraduate students worked alongside the PI and the graduate student learning about the theory and instrumentation as well as conducting all facets of the experimental work, including synthesis, activation, and characterization.