PRF#: 55946-DNI5
Project Title: Designing Uniform Paired Copper Catalytic Sites for Conversion of Methane to Methanol
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Progress of the Research

The research has continued to progress with additional material synthesis and characterization. Initial work focused on the synthesis of a dimeric organosilane that had a propyl linker between the silicon atoms. This organosilane was characterized with ^{1}H and ^{13}C NMR before incorporating into the synthesis gel for SAPO-5. The SAPO-5 material was allowed to crystallize at high temperature before quenching and characterizing with XRD, nitrogen physisorption, and ^{13}C NMR. The XRD revealed that the desired crystalline structure had been successfully created and the nitrogen physisorption indicate that the material was highly porous. The key characterization to demonstrate that the silane dimer was incorporated into the material was ^{13}C NMR (**Figure 1**). The extra peaks in this material are consistent with the organosilane being successfully functionalized into the material. These promising results led us to seek additional characterization using a technique recently identified to characterized Bronsted acid sites in zeolite MFI and zeolite CHA involving the exchange with the protons with Co(II) nitrate. While this previous work could demonstrate a fraction of the sites are paired, our attempts to utilize this test produce a complex diffuse reflectance UV-Vis pattern that was difficult to deconvolute (**Figure 2**). This work continued throughout the duration of the grant. Interestingly, this work has evolved into a direction that is examining the synthesis of zeolites with paired Lewis acid sites that has been funded by a separate grant.

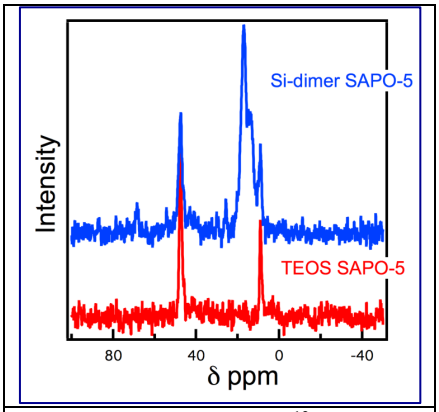

Figure 1. Comparison of ^{13}C NMR synthesized using tetraethyl ortho silicate (TOES) and the organosilane dimer.

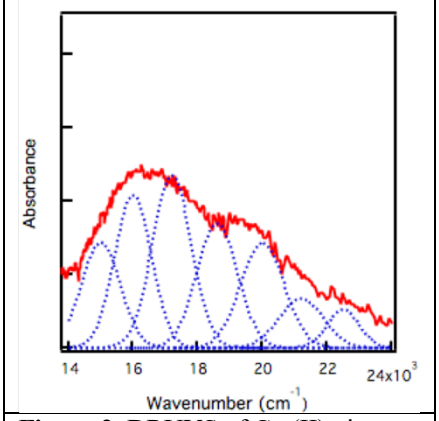

Figure 2. DRUVS of Co (II) nitrate exchanged SAPO materials.

During the course of the work, the student trained an undergraduate to synthesize organofunctionalized zeolites and mesoporous materials that contain different catalytic groups. The undergraduate became a Goldwater Scholar and has since matriculated to graduate school at MIT. The undergraduate students work was promising, but graduation prevented completing the manuscript. Therefore, the graduate student completed the work, becoming first author. During the course of finishing this work, the graduate student noticed an interesting behavior. The graduate student noticed that SBA-15 – typically a material considered only mesoporous - also contained a significant amount of micorpores. The graduate pursued this work and synthesized a silica material with limited to no micropores (NMP SBA-15). Interestingly, this material had twice the catalytic activity as the conventional synthesis of SBA-15 for the Aldol reaction and condensation (**Figure 3**). A similar increase in catalytic activity was found for the Knoevenagel condensation. Additional work is examining the molecular basis for the improved catalytic activity. Overall, this is an important discovery and could represent the key limitation for why grafting on mesoporous materials produces catalytic materials that are less active than the homogeneous counterparts. This work is currently being summarized in a manuscript that will be submitted in the near future.

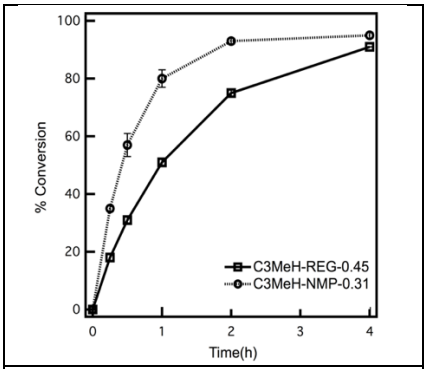

Figure 3. Comparison of catalytic activity for the aldol reaction and condensation for REG-SBA-15 and NMP-SBA-15.

While the work with synthesis and characterization continued, the graduate student also pursued investigations using Lewis acidic zeolites for alcohol ring opening of epoxides. This work has been accepted for publication and has led to other work examining how pore size impacts catalytic activity. Specifically, this additional work has demonstrated that diffusion limitations associated with the formation of bulky products could be mitigated through the synthesis of nano-zeolites. One article has already been accepted for the nano-zeolite work and a second article is under review.

Overall, this work has enabled development of a strong skill set in the group that utilizes homogeneous synthesis methods to produce well-defined catalytic sites in heterogeneous catalytic materials. Additional work is still working to understand the characterization of paired Bronsted acid sites in SAPO materials.

Impact of the Research on My Career

This research grant has greatly impacted my overall research career, allowing me to pursue risky projects that have ultimately turned into several publications and additional grant funding. This research grant was the first grant that I received, making it possible for me to fully support a graduate student. While I was learning to be a better advisor, it was very helpful to have a student working full time in the research lab so that progress could be rapid and new ideas could quickly be tested.

From this grant support, I was able to work with my student to build a strong skillset in organic and inorganic that has been used to train additional graduate and undergraduate students. Indeed, all of the current students in my research group have benefitted by the training that they received from the student supported by this work. This skill set led me to receive two additional external grants, including the NSF Career award that focuses on the synthesis of Lewis acidic zeolites with paired catalytic sites. This was a meaningful award that was brought about by fruitful discussions involving the graduate student supported on this grant.

In addition to grant support, this work has produced sufficient data that will be incorporated into seven overall publications. These publications will serve as a significant portion of the work that will be included for my tenure case. The publications represent a broad range of work that we continue to add depth to as we continue to uncover new phenomena. I anticipate that the work will produce two additional manuscripts.

The publications associated with the grant funding have been increasingly recognized through recent awards. In 2018, I was included in the 2018 Class of Influential Researchers for ACS Industrial and Engineering Chemistry Research. This was followed up by additional awards that will be announced in 2019. Additionally, the intrigue in the work has garnered me several invited talks at international conferences including the American Chemical Society and the American Institute of Chemical Engineering (AIChE). Recently, the work has also been presented at departmental seminars in chemical engineering departments inside and outside the U.S. Indeed, the work has been well-received.

Overall, I would summarize that the ACS-PRF-DNI award has really allowed me to start my career successfully. It was a risky proposal that allowed me to develop the skill in the lab that will result in a productive research environment. This has allowed our lab to collect data that will allow us to continue our success.

Impact of the Research on Student

The research grant has had a profound impact on the students working on this project. The funding enabled the students to focus on research, which has enabled them to make some unique observations that will have a transformative impact. For one student, the research support made it possible to improve the synthetic ability for both organic and inorganic materials.

The skills gained enable the first student to author many publications. After recent submissions have been accepted, the first student will have four first author publications, two second author publications, and a third author publication for a total contribution of seven publications in total. All of the publications are relevant to catalysis and describe our work on catalytic material synthesis.

The student has been able to present the work in several different venues. During 2017 and 2018, the student traveled to the Annual Meeting of the American Institute of Chemical Engineers (AIChE) to deliver an oral presentation on the work. The travel funds helped the student attend both of these meetings. Additionally, the student has presented the work at the Graduate Research Symposium hosted in Chemical and Biomolecular Engineering at Ohio State and the Institute of Materials Research (IMR) Materials Week. I have encouraged the student to apply to present to the work at an additional conference in 2019.

Based on the skill set that the student acquired, the student was able to receive a job in a field relevant to the experience of the student. This opportunity was obtained through discussions of the work at the IMR Materials Week and Graduate Research Symposium. Overall, the training that we were able to provide the student through this grant will serve the student well in the next job.

For the second student, the funds were used to support the student after his first year over the summer to facilitate development of organic and inorganic synthetic methods. The student took advantage of this opportunity and has been very productive during the first year and a half. We anticipate a publication being submitted from this work in March. The successful completion of this work will also position him to be able to present at the Graduate Research Symposium in the Fall.

A third student was associated with this project, but the student was funded by a separate grant. The student has also been productive, authoring five first author publications. This student has also presented work at international conferences. Based on the work and interactions with this project, the student gained the necessary skill to secure a job as well. Overall, these students have had and will continue to have success because of this grant funding.