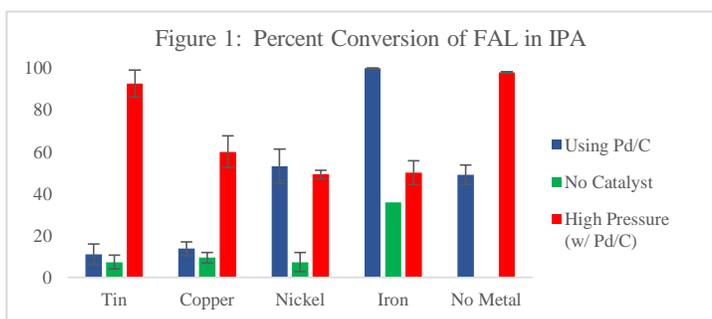


Progress of Research

Through the first year of this ACS PRF UNI funding, results have been collected for both the liquid phase hydrogenation of cinnamaldehyde and furfural using the methods described in the original proposal. So far, the reactions of cinnamaldehyde in isopropyl alcohol (IPA) with iron (III) chloride, tin (II) chloride, nickel (II) chloride, and copper (II) chloride as additives under atmospheric pressure of hydrogen at 75 °C with a 5wt% Pd/C commercial catalyst have been completed in duplicate. Additionally, these same reactions have been completed with alpha-methyl-trans-cinnamaldehyde and furfural (FAL) in IPA. Sample data are shown in Figure 1 for the effect of metal chloride salts (5mol%) on the conversion FAL in IPA with 1 atm H₂ and via transfer hydrogenation at 60 bar. Further work has begun by varying the solvent (e.g. toluene, cyclohexane, and acetonitrile), the metal salt (i.e. introducing acetate salts and other cations such as Al³⁺ and Co²⁺), and the amount of metal salt (5 mol% and 20 mol% with respect to the aldehyde) to begin identifying the role of these solvents and salts in the mechanism of hydrogenation. Preliminary results have also been collected for the liquid phase hydrogenation of a similar α,β -unsaturated aldehyde (citral) using these conditions.



Furthermore, additional commercial catalysts have been compared in reactions with cinnamaldehyde. In particular, cinnamaldehyde has been reacted with a 5wt% Pd/Al₂O₃ commercial catalyst (Sigma-Aldrich) which led to the most compelling results. As hypothesized in the initial proposal, the Lewis acid salts were expected to enhance the selectivity to the unsaturated alcohol product, cinnamyl alcohol (COH), via the electrostatic interaction between the carbonyl oxygen and the metal cation. The observed trend in these reactions in IPA solvent was that the selectivity of the reaction to the COH product corresponded to the trend in hard-soft acid base theory. In other words, the harder acids led to higher selectivity to COH with a concomitant decrease in selectivity to the saturated aldehyde, hydrocinnamaldehyde. This conclusion was further supported by using the corresponding metal acetate salt to corroborate the role of acid-base chemistry in this reaction. The result was that the presence of the basic acetate ion in place of the neutral chloride ion eliminated the enhanced selectivity observed with the chloride salts of the hard acids. Preliminary results are summarized in the table below.

Pd/Al ₂ O ₃	Absolute Hardness ¹ η	Conversion ²	Hydrocinnamaldehyde Selectivity	Cinnamyl Alcohol Selectivity
no additive	n/a	100%	94.7%	0.0%
FeCl ₃	12.08	100%	0.0%	21.1%
AlCl ₃	45.77	100%	0.0%	27.9%
NiCl ₂	8.50	100%	6.5%	31.6%
Ni(CH ₃ COO) ₂		56%	100.0%	0.0%
CuCl ₂	8.27	0%	0.0%	0.0%
Cu(CH ₃ COO) ₂		24%	42.6%	0.0%
CoCl ₂	8.22	100%	47.4%	29.9%
Co(CH ₃ COO) ₂		100%	90.2%	0.0%

¹Absolute hardness values (units of eV) are reported from Meissler and Tarr's 4th Ed. Inorganic Chemistry (Prentice Hall, 2010); ²Conversion is averaged over two trials.

Impact of Research on PI

The impact of this grant has been profound, in that the timing of the acquisition of funding provided the ability to collect research results in the last eighteen months before the submission of my application for tenure and promotion to associate professor. As an assistant professor at a predominantly undergraduate institution (PUI), the requirements for professional development and scholarly activities are not as rigorous as Research-1 institutions, but nonetheless are crucial to merit tenure and promotion. The acquisition of this ACS PRF UNI Award was the first significant successful submission of an extramural grant in my career, and it demonstrates to the senior faculty and

administrators of my institution that I am progressing forward with my scholarly endeavors toward the submission of successful peer-reviewed publications. In the past, I had noted in my annual self-evaluations that the absence of start-up funding as well as limited departmental budgets have hindered the progress of my scholarly research. Due to the gradual nature of undergraduate research progress, the ability to fund four students enabled me to collect a significant amount of results which are currently leading to the preparation of a manuscript based on the results from cinnamaldehyde reacting with Pd/Al₂O₃.

My application for tenure and promotion to associate professor was submitted on Sept. 15, 2018 and will be under review through the end of the Fall 2018 semester. The grant acquisition as well as my subsequent oral presentations of unpublished results at the 254th National ACS Meeting in Washington D.C., the 255th National ACS Meeting in New Orleans, LA, and the 94th Annual Meeting of the Pennsylvania Academy of Science all provided evidence of my dedication to pursuing scholarly activities. Additionally, the College recognizes professional service through the reviewing of grant proposals and submitted journal manuscripts, both of which I have completed as a result of being involved with the PRF program. I am hopeful that the forthcoming publications from this grant will springboard the progression of my career post-tenure as I pursue additional extramural research funding to support women in the chemical and physical sciences.

Impact of Research on Students

The impact of this grant has significantly benefitted the students who were funded in the first year of the grant cycle. The student population at Cedar Crest College is traditionally all female with approximately one-third of the students representing racial or ethnic minorities in the sciences. In addition, there is a significant number of first-generation students and students who exhibit financial need. By offering a funded summer research opportunity to this population of students, we can enhance the persistence of students from underrepresented groups in the sciences. Additionally, these students are gaining important hands on experience with instrumentation such as GC/MS, GC/IR, and other lab techniques which will prepare them for future careers in science.

Two of the students who were funded for summer research in 2017 have graduated and begun graduate (Ph.D.) programs in chemistry at competitive universities. These are the first students to graduate from my research group and enter doctoral programs. One student is attending the University of Delaware and the other is attending the Pennsylvania State University; both have teaching assistantships with full tuition remission. The experience with a funded summer undergraduate research program undoubtedly contributed to their ability to be accepted into these graduate programs. Another student funded by this grant in the summer of 2017 is continuing her studies as an undergraduate. She began this research with alpha-methyl trans-cinnamaldehyde, which is a substituted version of the model compound in the original proposal. Her work in the summer of 2017 followed the completion of only her freshman year. The fourth student funded in this first cycle of the grant has graduated with a degree in neuroscience and is working for the Academy of Natural Sciences Museum in Philadelphia, PA. In a letter she wrote on my behalf for my application for promotion and tenure, she stated that it was her experience researching with this project that led to her successful interview and hiring at this museum. She now works in their environmental science research team and as a public educator for the museum.

Beyond successful appointments following graduation, these students were also able to present their results at various venues. Specifically, students presented posters at the 2017 Mid-Atlantic Regional Meeting of the American Chemical Society in Hershey, PA, the 254th National Meeting of ACS in Washington, D.C., the 2017 Eastern Analytical Symposium in Plainsboro, NJ, the 94th Annual Meeting of the Pennsylvania Academy of Science (PAS) in Indiana, PA, and the Lehigh Valley ACS Local Section's 2018 Undergraduate Research Poster Session at DeSales University in Center Valley, PA. These five venues for presentations of research results included local, regional and national meetings, and provided students with important experiences in delivering scientific information for the purpose of disseminating findings and receiving constructive feedback. The presentation at the PAS meeting resulted in an Honorable Mention accolade for the student. In traveling to the national ACS meeting in Washington D.C. in 2017, the four students funded in the first year benefitted from networking and exposure to exciting technical program content.

Future work in the final year of this ACS PRF UNI award will involve the organization of results so far so that a manuscript with the cinnamaldehyde results will be submitted for publication by the end of 2018. Additionally, transfer hydrogenation studies have begun by examining the role of various secondary alcohol solvents as hydrogen donors in the reaction of furfural at high pressure. Other promising work which may lead to a publication is in the selection of solvents which lead to the selective hydrogenation of alpha-methyl trans-cinnamaldehyde its unsaturated alcohol product. We still anticipate using the 500 MHz NMR spectrometer in the characterization of our products.