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"Catalytic Liquid Phase Hydrogenation of Aromatic Aldehyde Compounds Using Pd/C Assisted by Metal Salt Additives"

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Narrative Report 2019

Progress of Research

Through the second year of this funding, experiments have been completed to explore the effect of solvent (polar/nonpolar, protic/aprotic), the effect of commercial catalyst, and the amount of metal salt additive in the liquid phase hydrogenation of furfural, cinnamaldehyde and one of its analogs, alpha-methyl-trans-cinnamaldehyde. Investigation of solvent effects led to determinations that alcohol solvents yielded to a larger variety of side products, and that no solvent in this study significantly enhanced selectivity toward the desired unsaturated alcohol. The effect of secondary alcohol solvents on the transfer hydrogenation of furfural at high pressure and temperature was investigated, but there was no significant difference determined due to the metal additives. At the mild conditions (1 atm hydrogen gas and 75°C) used in this project, the commercial catalyst with the highest conversion of cinnamaldehyde to hydrogenation products was 5wt% Pd/Al_2O_3. All catalysts used in this project were 5-10wt% Pd on either carbon or alumina supports, with the exception of 1wt% Ir/C, which showed no hydrogenation activity under these conditions.

Beyond wet chemistry experiments, surface analysis techniques were employed to connect the elemental composition of the catalysts before and after reactions. First, post-reaction catalyst samples were collected and dried for analysis at Rutgers University with ThermoScientific K Alpha X-ray photoelectron spectroscopy (XPS). Results from the analysis of Pd/Al_2O_3 commercial catalyst before reaction and after reactions in the presence of nickel (II) chloride $NiCl_2$ and nickel (II) acetate $Ni(OAc)_2$ with XPS are shown in Figure 1. The Pd *3d* signal with diminished after the liquid phase hydrogenation reactions with the nickel salts. The Ni 2*p* signal was much more intense for the catalyst which was reacted with $Ni(OAc)_2$, which could indicate a site-blocking effect from the additive.

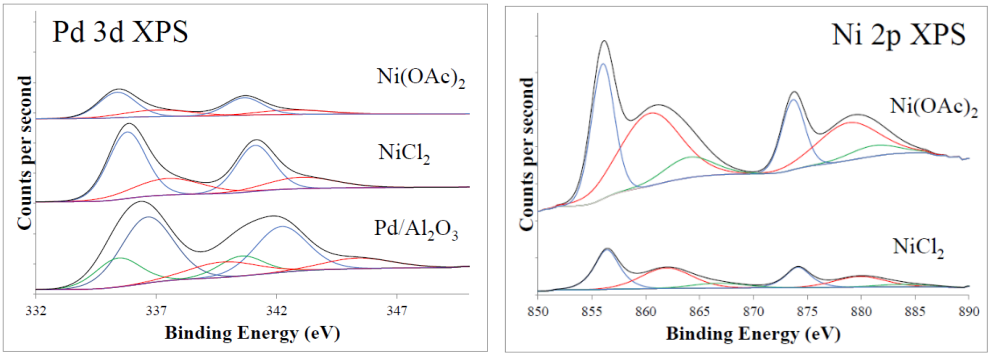

Figure 1: Pd 3*d* (left) and Ni 2*p* (right) XPS spectra for fresh Pd/Al_2O_3 catalyst and spent catalyst after reaction with $NiCl_2$ and $Ni(OAc)_2$

Further surface analysis with the use of low energy ion scattering (LEIS) spectroscopy at Lehigh University revealed the elemental composition of the catalyst surfaces post-reaction. The collection of surface analysis data has delayed the submission of a manuscript for publication, but has enhanced the understanding of the role of these metal additives in the surface chemistry and catalysis in this reaction system. These surface science studies will aid in the explanation of the results from the first year, which identified the role of the hard-soft acid base concept in the selective hydrogenation of cinnamaldehyde. While many questions have been explored during the past two years, further work can be continued to elucidate the connections between hydrogenation reactions of similar alpha, beta-unsaturated compounds. Remaining funds for this project were used to purchase additional catalysts for comparison with supported Pd to determine if metals such as Ru or Rh in the presence of metal salt additives may effectively catalyze hydrogenation of unsaturated aldehydes.

Impact of Research on PI

The acquisition of this funding from ACS PRF was a key factor in my successful application for tenure and promotion in this past grant cycle. In September 2018, I submitted my application for promotion to associate professor with

tenure, which was unanimously approved by the Tenure & Promotion Committee, Provost, President, and finally the Board of Trustees at Cedar Crest College. In February 2019, the final vote by the Board of Trustees validated my promotion to associate professor with tenure. By acquiring this external funding, I was able to develop a strong research program by permitting undergraduate students to be funded over two summers. In the absence of start-up funding, it was difficult to make significant progress toward building a research program as an assistant professor. The acquisition of this funding both helped attract students to my group as well as provided dedicated summer time toward the collection of data for the project. This progress has also aided in the development of valued collaborations with other scientists at regional institutions. One of these collaborations has provided our lab with an additional Parr reactor to be used in the collection of additional high pressure hydrogenation data. With the submission of results from this project to yield a peer-reviewed journal publication, my future progress toward subsequent research success and extramural grant applications will be fruitful.

The data collected during these years was presented at multiple conferences. In this past year, results from this project were presented by me at the New York Metropolitan Catalysis Society's Spring Symposium at Princeton University and the 26th North American Meeting of the North American Catalysis Society in Chicago, IL. This work was also shared as a part of a presentation delivered as a guest speaker at Lewis University (Romeoville, IL) in their Leonard T. Weisenthal Colloquium Series. These oral presentations represent scholarly activities which are required for faculty in pursuit of promotion at Cedar Crest College. The chemicals purchased by this funding remain in the department so that future students can continue to benefit from research experience through additional experiments stemming from this original project.

Impact of Research on Students

Four students were funded for summer research during the second year of this grant funding. These students shared the lab space while investigating various aspects of the project. All four of these students were female undergraduates who were pursuing degrees in chemistry or biochemistry at Cedar Crest College. One of those students graduated in May 2019 and is using her acquired experience and skills (e.g. GC/MS instrumentation and data analysis) as she is interviewing for various regional laboratory positions. Two of the other students are seniors preparing to graduate this year; one of the seniors is planning to apply to graduate programs in the coming months. The ability to offer paid research positions in the summer months is particularly advantageous for our institution because it is a predominantly undergraduate institution (PUI) for women. Furthermore, our institution is the most racially diverse private four-year institution in the region with a large population of first-generation students. Of the four students funded in this cycle, one student was African American and one student was a non-traditional aged, first generation college student. The students funded through this grant were given the opportunity to live on campus to be immersed in the college experience over the summer while conducting research in the laboratory because the College offered free housing to students in this program.

Students who contributed to this project were supported to travel to a national meeting of the American Chemical Society where they were able to experience the diversity of fields of chemistry and network with other students and scientists in the field. Two of the students also traveled to the 2018 Eastern Analytical Symposium in Princeton, NJ, where they presented their results in an electronic poster session. One of these students then presented her poster at the 2019 Pennsylvania Academy of Science meeting, which was hosted at Cedar Crest College this year. One student submitted an abstract for her work to be presented at the 26th North American Meeting of the North American Catalysis Society, but although her abstract was accepted for a poster session, she was unable to travel to the conference, and it was subsequently withdrawn. Two of the students funded in the first year of this grant have successfully completed their first year in doctoral programs in chemistry and passed Ph.D. candidacy exams.

Cedar Crest College has demonstrated its impact on women in the STEM fields by ranking in the top 100 colleges sending women into doctoral programs in the sciences, according to a 2019 study completed by The Council for Independent Colleges. A statistic of note is that Cedar Crest College ranked 16th in the nation for yielding women who go on to complete doctoral degrees in chemistry. The funding received from ACS PRF will aid in the continued progress of our institution to foster an environment to educate women in the chemical and physical sciences and feed the pipeline of strong female students into graduate programs in STEM fields.