

PRF# 57504-UNI6

“Investigation of the Molecular-Level Interactions Which Control the Transition Metal Based Catalytic Conversion of CO₂”
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Results from Year 1

During our first year of funding, we worked in collaboration with Dr. Richard Mabbs and his group at Washington University in St. Louis to record photoelectron spectra of the copper difluoride anion (CuF₂⁻) at a variety of photon energies using the velocity map imaging technique. Figure 1 shows representative images, photoelectron spectra, and anisotropy parameters (β) describing the photoelectron angular distributions for each of the observed transitions.

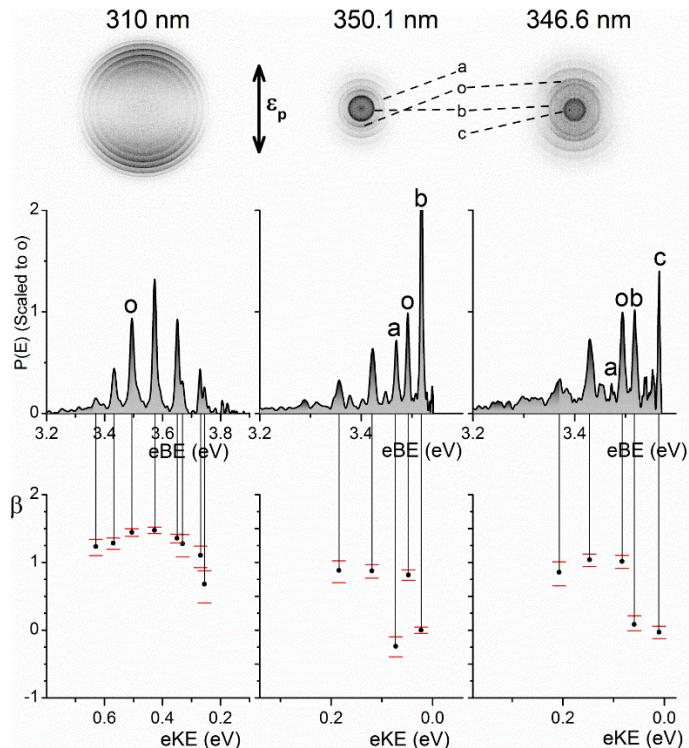


Figure 1. Photoelectron images (top row), spectra presented in the electron binding energy (eBE) domain (middle row), and anisotropy parameters of the indicated transitions presented in the electron kinetic energy (eKE) domain (bottom row). The results were obtained at wavelengths of 310 nm (photon energy of 3.999 eV), 350.1 nm (3.541 eV), and 346.6 nm (3.577 eV). The peak labeled o corresponds to the origin transition from the vibrational ground state of the anion to the vibrational ground state of the neutral.

Results from Year 2

In a continuation of our work, the undergraduate students working on this project were able to make multiple significant improvements to the time-of-flight mass spectrometer and photoelectron velocity map imaging apparatus. These improvements include design, construction, and installation of an “ion-buncher” in the mass spectrometer which will improve the signal-to-noise ratio and spectral resolution of photoelectron spectra and an improved, custom data acquisition program that allows real-time monitoring of photoelectron images that have been corrected for pixel saturation issues.

Our initial research proposal was based upon work by Bhaduri and Siller¹ that indicated that nickel nanoparticles

(NiNP) could effectively catalyze the hydration of carbon dioxide (CO_2) to form carbonic acid (H_2CO_3). In an attempt to replicate these results, Ramsden *et al.*² repeated the previous experiments, but they did not observe any catalytic activity. Based on these conflicting reports, we conducted a similar set of experiments by bubbling CO_2 into a mixture of ultrapure water that contained a suspension of NiNP. In order to monitor the kinetics of the hydration reaction, we measured the pH and conductivity of the solution. As part of our investigation, we explored what impacts, if any, the CO_2 flow rate and bubble size had on the catalytic activity of NiNP in the hydration of CO_2 . Figure 2 shows the results of measurements of the conductivity and pH as CO_2 was bubbled through nanopure water and aqueous NiNP suspensions. As can be seen, the rates at which the pH decreased and the conductivity increased was essentially the same for the nanopure water and the NiNP mixture, indicating that the NiNP did not catalyze the hydration reaction under our conditions.

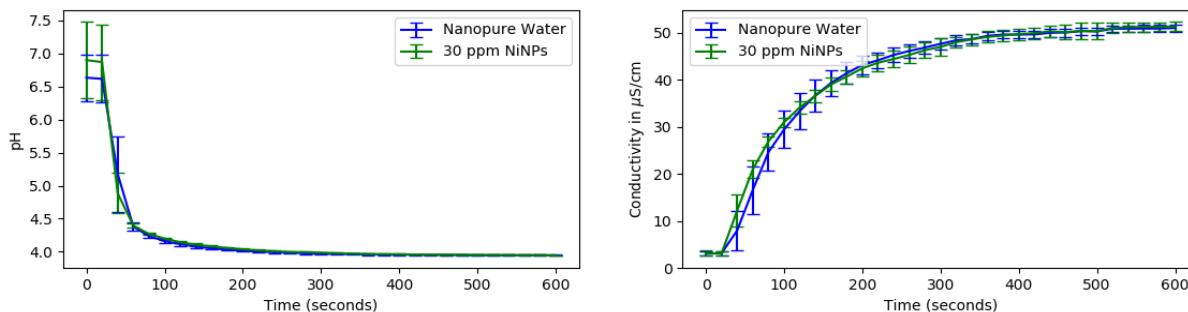


Figure 2. pH (left panel) and conductivity (right panel) plotted as a function of time as CO_2 was bubbled through nanopure water (blue) and a 30 ppm NiNP aqueous mixture (green) at a flow rate of $100 \text{ cm}^3/\text{min}$ using a Type E fritted glass disk. Similar results were observed with a Type A frit and a range of flow rates.

Impact

Washington University in St. Louis is approximately 120 miles from Millikin University in Decatur, IL. The funding provided by the ACS-PRF grant allowed the PI and undergraduate students working on the project to acquire temporary housing in St. Louis. Thus, this research would not be possible with ACS support. Additionally, this grant has allowed my group to purchase the computational software Gaussian 16 and WebMO Pro, as well as a multicore workstation to perform calculations on. This suite of hardware and software was used not only by the undergraduate students working on this research, but also on undergraduate students throughout the chemistry curriculum. Overall, the grant provided support for two students to conduct research during the summers of 2017, 2018, and 2019. As a result of this grant, the students were able to gain significant research experience, which has allowed them to develop their problem solving skills, improve their scientific communication skills, and work in a collaborative team environment. Additionally, the students have been provided with access to instrumentation that would not be readily available to most undergraduate students including a Wiley-McLaren time-of-flight mass spectrometer that is equipped with a photoelectron imager and multiple microchannel plate detectors, a pulsed Nd:YAG laser, a tunable dye laser, and a multichannel digital oscilloscope. The students gained familiarity with the simulation software SIMION, 3-D modeling software for instrument design and construction, and the computational software Gaussian. One of the students who worked on this project is currently in his first year as graduate student pursuing a PhD in environmental engineering at Washington University in St. Louis, a career trajectory that he had not envisioned before engaging in this project. He presented his research at the National ACS Meeting in Orlando, FL in 2019. The other student is currently interviewing at medical schools with the ultimate goal of entering an MD/PhD program starting in Fall 2020. Another student, not funded directly by the grant, also presented his research at the National ACS Meeting in Orlando, FL. The research has thus far resulted in a publication in the *Journal of Chemical Physics*, the two presentations at national ACS meetings already mentioned, and numerous poster presentations on campus. Another manuscript is currently in preparation. These scholarly outputs played a major role in my successful application for tenure and promotion to Associate Professor. I hope to use these results to provide the foundation for an NSF Research Opportunity Award application or a future ACS-PRF-UR application, either of which would be used to provide the support necessary to continue our collaboration with the Mabbs group.