

SLATT UNDERGRADUATE RESEARCH FELLOWSHIP FINAL REPORT

SCHOLAR NAME:	Tomas Romero
FACULTY ADVISOR:	Adam Jaffe
PROJECT PERIOD:	Fall Semester 2022
PROJECT TITLE:	Generating Catalytic Sites Relevant for Cleaner Fuels in Solid-State Materials through Atom- Transfer Chemistry
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	<input type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input checked="" type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Learn to use IR and PXRD	Was able to successfully perform analyses using both methods.	100
Setting a foundation for next steps in reaching a catalytically relevant iron IV-oxo	Built out a system, with a lot of different variables controlled for in terms of working with metal-cyanides. The groundwork has been laid in order to reach the next steps.	85
Learn about research presentations and eventually present findings	Attended other research presentations and compiled data in order to present my progress towards the end of the fall semester.	100
Becoming comfortable handling hazardous materials and other processes in the lab as an individual	Eventually was able to go through chemical processes and experimentation without asking mentor for help. Was able to safely execute several experiments safely and without issue.	100

RESEARCH OUTPUT

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	n/a
EXTERNAL AWARDS RECEIVED	n/a
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	n/a
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	n/a
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	n/a
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	n/a
INTERNAL COLLABORATIONS FOSTERED	n/a
EXTERNAL COLLABORATIONS FOSTERED	n/a
WEBSITE(S) FEATURING RESEARCH PROJECT	n/a
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	n/a

RESEARCH EXPERIENCE

Overall, the lab experience was fulfilling and enlightening. There were never issues with members of my research group and I was able to learn several valuable lab practices such as using IR spectrometers, X-ray diffractometers, etc. In order to improve the experience, I believe getting to explore a wider variety of chemical reactions would be beneficial.

FINAL WRITTEN REPORT

OBJECTIVE:

The motivation behind this project lies in securing a cleaner energy future by developing methods to modify solid-state materials through previously unexplored means. This involved studying the use of molecular atom-transfer reagents in order to isolate and study catalytic sites within extended solids. More specifically, the research consisted of generating and analyzing metal-oxo and metal-sulfido intermediates relevant for alkane hydroxylation/oxidation and hydroprocessing—important processes for increasing sustainability of fossil fuels. This work also seeks to provide a solid foundation for future projects by developing new methods for material tuning, allowing us to improve existing catalysts and design next-generation materials.

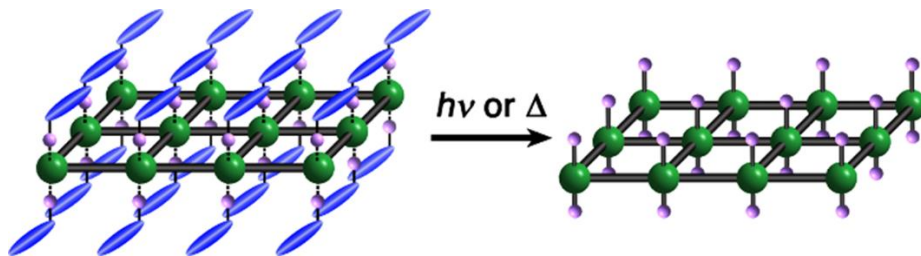


Figure 1. Schematic of the atom transfer process. Here, an inorganic sub-lattice (in black and green) is coordinated by atom-transfer ligands (blue carrier molecules with pink spheres representing atoms to transfer) to form a hybrid organic-inorganic material. With the application of a stimulus like light or heat, the atom-transfer process can occur.

Roles and Responsibilities:

My main role was to assist in the synthesis and characterization of inorganic materials as well as their subsequent modification by atom transfer reagents. To achieve intended objectives, I learned various solution and solid-state synthesis techniques on top of materials characterization techniques such as X-ray diffraction and infrared spectroscopy. Initially, I worked with a graduate student who was leading the project and I eventually developed a high degree of independence working on a subset of materials.

Personal Mission and Relevancy to Future:

My career goals as a Chemical and Biomolecular Engineer are focused on being a driving force in solving the world's clean energy crisis. The research performed by the Jaffe Lab group strives to provide a strong foundation for more sustainable energy production methods in the future, which perfectly fits into what I wish to achieve. In addition, the techniques and methodologies that I stated in previous sections have helped strengthen my understanding of energy sources and the process that goes into creating a cleaner energy future.

Background:

Atom transfer (or exchange) allows for precise control over molecular complexes. However, the methodology also holds the potential to be the foundation for new methods of material synthesis and control over solid-state properties. Its relevancy lies in the realms of energy storage, catalysis, and magnetism. Atom transfer has been primarily used for organometallics and molecular chemistry in general but has not been used for solid-state materials until now. A diagram of atom transfer can be seen below in Figure 1.

In this research term, metal cyanides were the primary substrates for the atom transfer process. Specifically, 2D metal cyanides called Hoffman Clathrates. These clathrates have the capability of keeping molecules or substances enclathrated, which means they are “trapped” in between the layers of the material. Metal cyanides have several advantageous features such as: porous layers which allow for more surface area for catalysis, tunability of electronic properties, different coordination geometries (provide more ways to coordinate with metallic centers), and there have been several reports of electrocatalysis (water splitting). For this experiment, iron and nickel were the primary metals used, with iron being the main focus. A visual for the synthetic process can be found below in Figure 2.

In reference to the figure above, DMSO was used as means to replace water through several washes and centrifugation steps. The miscibility of DMSO and water

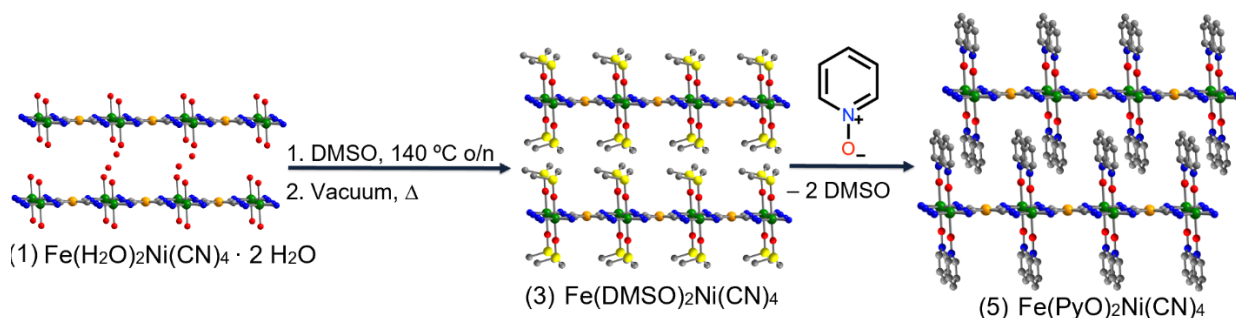


Figure 2. Synthetic process for forming a hybrid metal-cyanide material with atom-transfer ligands. Gold, green, gray, blue, and yellow spheres represent Ni, Fe, C, N, and S atoms, respectively.

makes DMSO effective as the primary wash that exchanges with the water within the compound. Later, pyridine-*N*-oxide can replace DMSO in the compound, using toluene as a solvent. Pyridine-*N*-oxide is a better ligand due to its better electron donating qualities when compared to DMSO. In order to calculate quantities required for the experiment, and application called ChemDraw was used. ChemDraw allows for compounds to be drawn and for stoichiometry for reactions to be calculated in real time. Items (1), (2), and (3) are also referred to as precursors to create the hybrid material containing the atom transfer reagent (pyridine-*N*-oxide).

Experimental:

In order to initiate the metal cyanide reactions and isolate item (1) in Figure 2, $\text{Na}_2[\text{Ni}(\text{CN})_4]$ was required. 3.185 grams of NaCN (sodium cyanide) were dissolved in 4 mL of water, using a stir bar and a magnetic stirrer. In a separate beaker, a solution of NiCl_2 was prepared in 4 mL of water. After being completely dissolved, the sodium cyanide solution was slowly added dropwise into the stirring, heated NiCl_2 solution. The final product went through a color change of green to orange, indicating the reaction process had taken its course. The solution was left in a fridge overnight to crystallize. The following day, the product was then washed with water in order to wash away unreacted starting materials and filtered. The initial attempt led to no leftover crystals due to their high solubility, so the solution was concentrated further to produce the desired product. After the second filtration, the reaction yielded large and higher quality crystals at the cost of quantity. This can be seen in Figure 3 below.

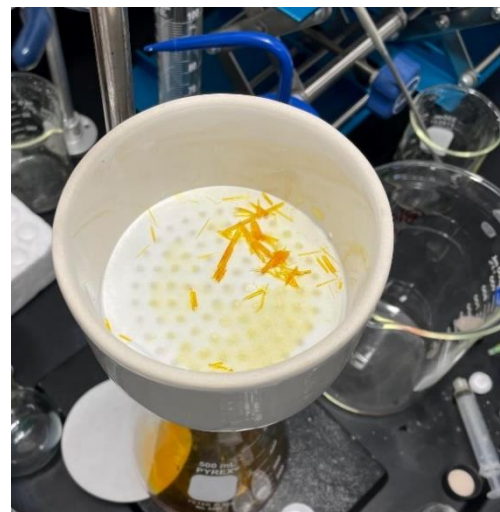


Figure 3. Crystallized $\text{Na}_2[\text{Ni}(\text{CN})_4]$ product.

The next step was synthesis of item (1) from Figure 2: $\text{Fe}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$. The reaction and respective stoichiometry can be seen in Figure 4. Using the values from Figure 4 as a reference, stoichiometry was used in order to calculate the

Notes					
1 mmol scale	$\text{Na}_2[\text{Ni}(\text{CN})_4] + (\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} \xrightarrow{\text{C}_4\text{H}_8\text{O}_2} \text{Fe}(\text{H}_2\text{O})_2[\text{Ni}(\text{CN})_4] \cdot 2\text{C}_4\text{H}_8\text{O}_2$				
JM1-3					
Compound	$\text{Na}_2[\text{Ni}(\text{CN})_4]$	Mohr's Salt		Chaltrate	
mass/mg	208.74	392.13		254.64	
MM/mg/mmol	208.74	392.13		254.64	
Equivalents	1	1		1	
mol/mmol	1	1		1	
Volume/mL	4	4			

Figure 4. Chemical equation and reactant stoichiometry for the synthesis of $\text{Fe}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$.

amount of Mohr's salt and water needed given the quantity of $\text{Na}_2[\text{Ni}(\text{CN})_4]$ crystals produced in the prior part of the experiment. 1.672 grams of Mohr's salt was measured out and dissolved into 43 mL of water. This solution was then mixed over the weekend along with the crystallized cyanide solution. After the weekend, fine solid precipitate was isolated via multiple centrifugation and water wash steps. The resulting samples were then dried through use of vacuum overnight in order to eliminate excess moisture.

To continue the reaction described in Figure 2, the bound water in the previous product now needed to be swapped with DMSO. To exchange these compounds, we used a large (40×) excess of DMSO relative to the solid $\text{Ni}(\text{H}_2\text{O})_2\text{Ni}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$. The weighed product was 0.6910 grams, so 16.5 mL of DMSO was used. The combination of solid and DMSO was placed in a sand bath at 140 °C overnight with stirring. The following day, the same centrifuge process stated earlier was repeated 3 times with DMSO washes, and then once with acetone to remove excess DMSO. Afterwards, vacuum was used once again to get rid of unwanted moisture and the solids were prepared for the next part of the experiment: exchange of DMSO with the pyridine-*N*-oxide ligand.

To test different effectiveness of pyridine-*N*-oxide ligands, three different types were used in the experiments. These were cyanopyridine oxide (A), pyridine-*N*-oxide (B), and nitro-pyridine oxide (C). For reaction A, the solid was 0.053 grams with 0.586 grams of the ligand. For solution B, 0.051 grams of DMSO solid was reacted with 0.4173 grams of the ligand. The final solution, C, was made with 0.0565 grams of the DMSO solid and 0.675 grams of its respective ligand.

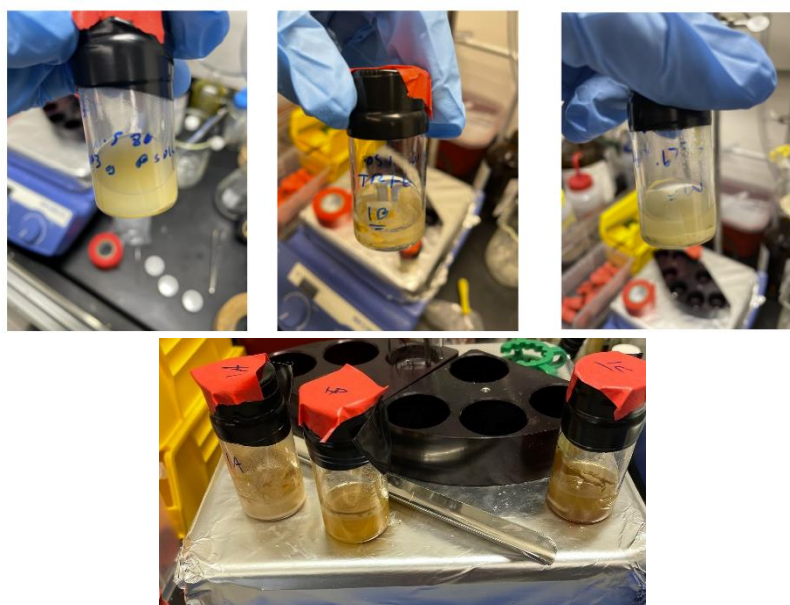


Figure 5. Images comparing ligand-exchange products.

Reactions with samples A, B, and C were placed into small glass vials with 5 mL of toluene as a solvent. All solutions were then placed over a magnetic stirrer and stirred slowly along with heat at 60 °C and left overnight. This process took two iterations, one over 3 days and the second happening over 9 days. After both trials were rinsed 5 times with toluene, centrifuged, and then left under vacuum overnight to secure a solid for IR and powder X-ray diffraction (PXRD) analyses. A comparison between the two trials can be found below in Figure 6, with the first trial on the upper row and the second trial on the bottom row.

Results and Discussion:

To determine whether the reactions had been completed, IR spectroscopy and PXRD analysis was performed. Data sets from the experimental products were compared with prior precursors, the ligands used in the reaction, as well as data pulled from attempts of the same experiment in glovebox conditions. The glovebox allows for an environment devoid of any moisture and for certain compounds to react with less interference. The IR data was analyzed by comparing the peaks of the products with their respective reactants or other experimental data. TR1-6 refers to data from the first trial, with “A” being the cyanopyridine oxide sample and “B” being the pyridine-*N*-oxide sample.

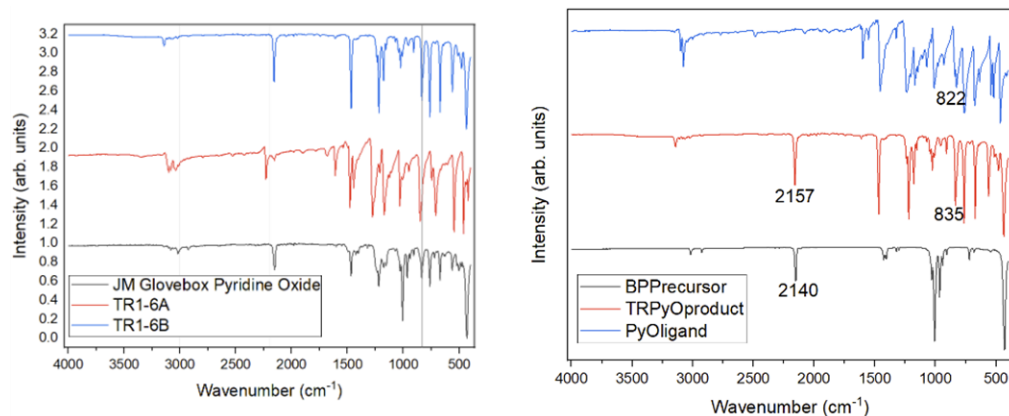


Figure 7. IR spectra for a comparison of cyanopyridine and pyridine-*N*-oxide to a glovebox sample (left) and pyridine-*N*-oxide compared to a ligand and prior experiment data (right).

The IR data is missing reaction C (nitro-pyridine oxide) due to an issue with the IR spectrometer at the time the data collection was done. The notable peaks were the cyanide peak at 2200 cm⁻¹, the 3000 cm⁻¹ peak corresponding to the C(sp²)-H bonds from the rings of the ligand, and the N-O bond peak at around 830 cm⁻¹. These were the main peaks used to compare whether the reactions went to completion. The shifting of the peaks, in particular the N-O peak, signifies a reaction took place and that the new ligands are bound to the Fe center. Further comparisons and conclusions came from the PXRD data (Figure 8). Despite shifts from the IR for some of the products, the PXRD patterns for the reaction products revealed similar peaks to starting materials (Fe(DMSO)₂Ni(CN)₄), potentially indicating that no reaction occurred. Reactions performed outside of the glovebox appeared to produce more miscellaneous peaks when comparing them side to side. Although pyridine-*N*-oxide (B) seemed to have no reaction following this procedure, attempts within the glovebox produced the desired results. For trial 2, on the day when data was ready to be taken from the finished products, the IR device was unavailable. However, PXRD patterns were still able to be taken for trial 2 and charts with comparisons were made accordingly. Similar to the IR data, labels with 1-6 indicate products from the first trial, 1-7 indicates a second attempt at first trial data, and 1-8 indicates results from the second trial. The PXRD patterns for these comparisons can be found in Figure 8 below.

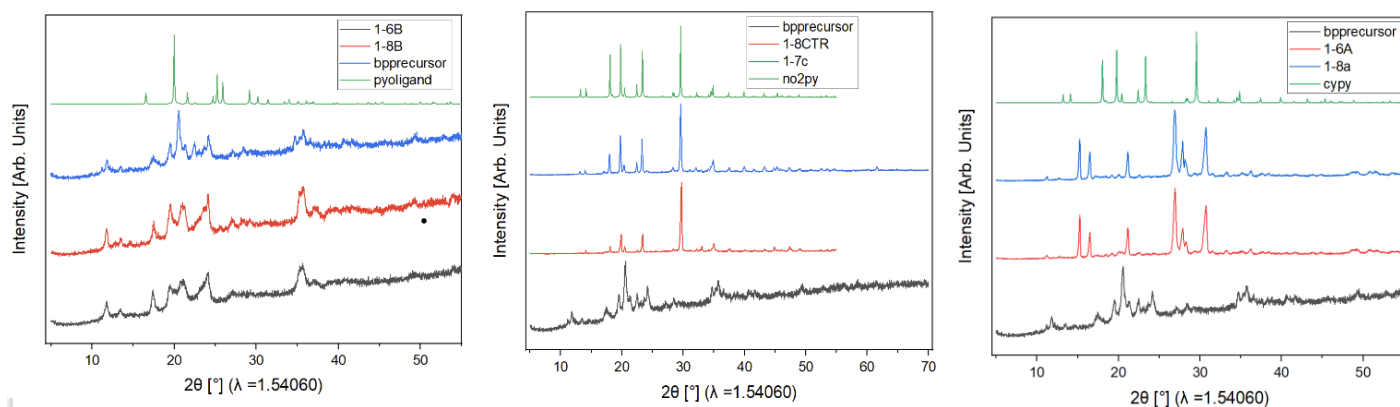


Figure 8. PXRD comparisons of experimental data between trials from pyridine-*N*-oxide (left), Nitro-pyridine-oxide (middle), and cyanopyridine-oxide (right)

Although it may be hard to see on this scale, the second trial produced higher quality PXRD data. This is due to a better signal/noise ratio. The theory behind this is that with more time for stirring and with constant heat, the conditions allowed for more time for the layers to stick together, leading to a more crystalline structure and producing better results. Referring to Figure 5, one is able to see a noticeable color change, as the products trial 2 are much darker, indicating a difference in the reaction. However, given that some of the peaks are missing or incomplete based on the results, a pure final product for the metal cyanides was not achieved.

Concluding Remarks

Although a pure product was unable to be produced for the precursors, a means of increasing their crystallinity was discovered through an increase in time. A further means of testing the products could be the use of fluorescence in order to get a more complex data analysis. The semester's research was fulfilling and enlightening in many aspects. I learned several important means of analyzing data, handling hazardous chemicals and complex reactions, as well as collaborating with fellow researchers in pursuit of a common goal.