UCD School of Chemical & Bioprocess Engineering

Pat McAdam Scholarship in Chemical & Bioprocess Engineering 2018

REPORT

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Introduction

Thanks to the Pat McAdam Scholarship I was lucky enough to spend 10 weeks during Summer 2018 working as a research assistant in the Colorado School of Mines in Golden. I had an amazing time, working as a member of the Wolden-Way research group and living in a house with another student, just a 15-minute walk away from the campus. She and I became very close friends and had a fantastic summer exploring the local area. The experience was truly a unique one. The highlight of my time in Colorado was a four-day camping trip deep into the Rocky Mountains. Travelling to the U.S. alone was both exciting and quite nerve-wracking, but probably the best thing I have ever done!

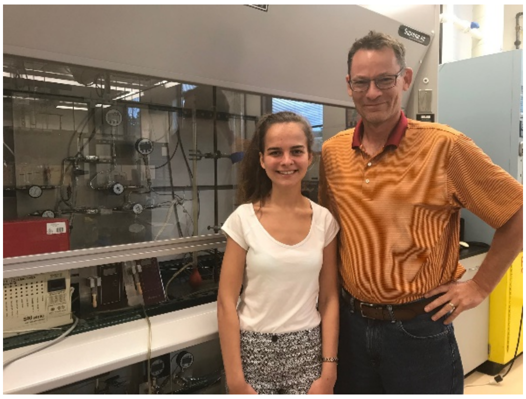
Research

Background

My research was based on a novel apparatus for small-scale ammonia production. Ammonia is a highly useful chemical. Currently, it is used primarily as a fertilizer for land. However, with the increasing interest in hydrogen as fuel, ammonia synthesis is becoming an even hotter topic for research.

The system which we were working to optimise is designed to operate at a much smaller scale than current ammonia plants, which typically produce >50,000 metric tonnes of ammonia per annum, via the Haber-Bosch process. Use of a novel, membrane-based system allows for the economically-viable production of ammonia, but at a much smaller scale. For example, using a system very similar to that under investigation at the Colorado School of Mines, individual farmers could produce ammonia for use on their own crops. A wind turbine could be employed to separate hydrogen from water via hydrolysis. This hydrogen would then be fed to the catalyst, along with nitrogen, to be converted to ammonia at a temperature 450°C. The gas is then condensed, via cooling, before being spread on crops.

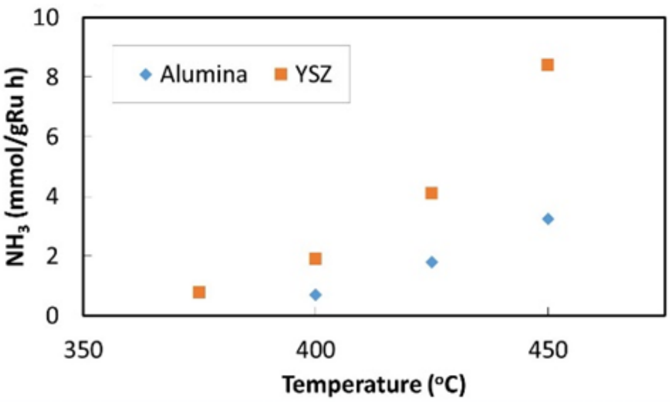
My work focused on optimizing the membrane, which consists of catalyst particles on a tubular support. Currently, the industry standard is alumina supports, which are cheap and readily available. However, much higher rates of ammonia synthesis have been achieved using other materials and I worked on yttria-stabilised zirconia (YSZ). The photo to the right shows Prof. Colin Wolden and myself, in front of some of the equipment which I employed for my research, in Lab 107 in the Department of Chemical & Biological Engineering, at the Colorado School of Mines.



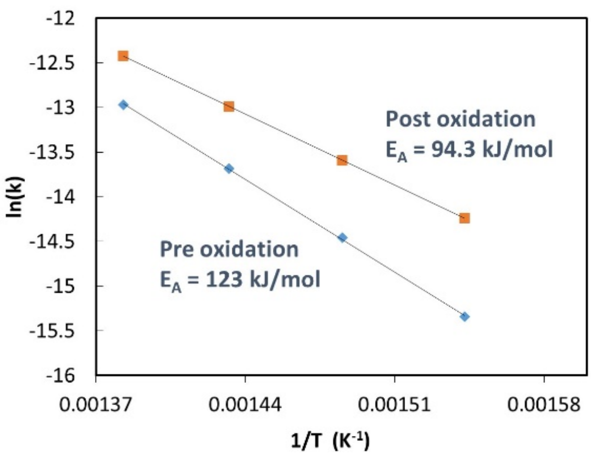
Experimental Work

A summary of my experimental work is presented in the poster provided with the report. This is the poster which I presented, along with many other summer research students, to members of the faculty from Colorado School of Mines, industry experts and other chemical engineering students at the end of my 10-week internship at the School of Mines.

My first week or so in the lab was spent familiarising myself with the equipment, materials and procedures. I learned to use a sonic heater, nondispersive infrared sensor (NDIR) and mass spectrometer. These are all pieces of equipment of which I had absolutely no prior experience, so it was excellent to have the opportunity to work with them. I perfected the liquid impregnation technique, which involves soaking the support (a YSZ tube) in a catalyst solution of a specifed concentration for a specified period of time, to achieve the desired uptake of catalyst (ruthenium oxide). I tested ammonia synthesis rates using both YSZ supports and traditional alumina supports. To the left is a plot comparing rates of ammonia synthesis using these different supports. As anticipated, over the synthesis temperature range investigated, YSZ consistently yielded higher ammonia synthesis rates than alumina.

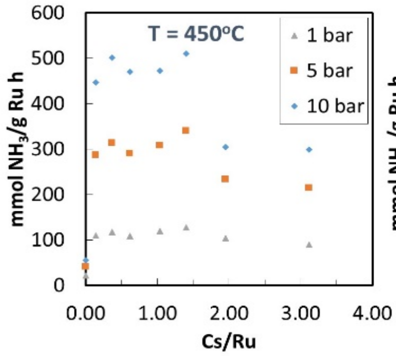


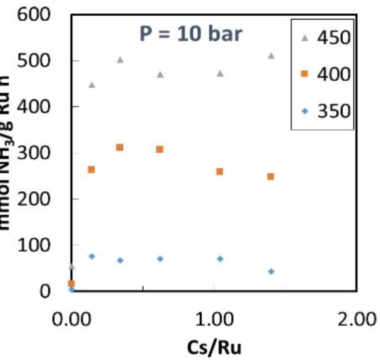
Once I felt comfortable with all of the relevant techniques I began to undertake my own experiments. The first experiment was based on some of my findings from my preliminary practice runs with the materials. While changing gas cylinders, I had inadvertently exposed the catalyst to oxygen. Under normal circumstances, oxygen would react negatively with the catalyst, rendering it completely inactive. However, I had observed a significant increase in ammonia synthesis rates using the oxygen-exposed catalyst. For two weeks I tested catalyst before and after oxidation, at different conditions of reaction temperature and pressure. As can be seen in the plot to the right, oxygen significantly reduced the activation energy (E_A) under the conditions investigated. This was a very significant finding, for which there was no prior reference in the literature, for any support. The Wolden-Way group hypothesized that the observed change was due to a change in morphology of the catalyst surface.



I then proceeded to explore the effects of oxygen on catalysts on an alumina support. As alumina supports are much cheaper, it would have been extremely beneficial to be able to achieve the same reduction in activation energy via oxygenation. However, it was observed that oxygen had a negative effect on the catalyst when using an alumina support, yielding significantly reduced ammonia synthesis rates.

The third set of experiments involved the addition of cesium. Caesium is a promoter which has been reported, in the literature, to significantly increase ammonia synthesis rates when used with ruthenium as a catalyst. I was tasked by the research team to find the optimal caesium-to-ruthenium ratio. Previous experience with caesium, which is a relatively expensive substance, suggested that a Cs/Ru ration of about 1 would be appropriate. My objective was to determine if the increase in synthesis rate provided by the use of caesium was sufficient to justify the associated increase in cost. The results (shown above) indicated that, for the conditions of temperature and pressure investigated, a significant increase in ammonia synthesis rate could be achieved; most interestingly, optimal results were achieved with a caesium-to-ruthenium ratio of just 0.3, representing a significant cost saving relative to earlier estimates.

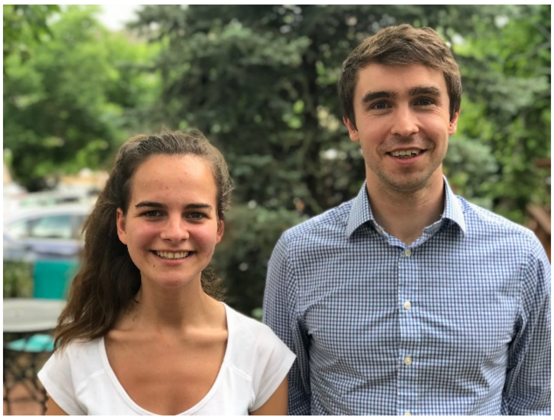




Outside the lab

Unlike the Pat McAdam Scholars of previous years, I was not involved in an organised programme with American students, as the Department of Chemical & Biological Engineering is no longer hosting an NSF-funded Summer Research Programme. I independently found accommodation in a house just a 10-minute walk from campus, across Clear Creek. I lived with Danielle, a chemical engineering student from Mines who has become a very close friend of mine; we shared the apartment with 2 geckos and 5 goldfish. We got on fantastically. After work, we played tennis on the public courts close to our house, skateboarded along Clear Creek and hiked the many trails surrounding the University. At weekends, we visited the nearby towns of Boulder and the ski town of Breckenridge. We spent time in Danielle's family home in Littleton, just half an hour from Golden, and took Danielle's family's boat out on the Chatfield Dam, where we wakeboarded. I also went to a few parties with Danielle and her friends from the School of Mines and I can confirm that they were just as good as the American college parties in the movies! We went to Denver on a few occasions, once for a concert, for which it rained consistently for 5 hours; and again, for the Denver BBQ festival and a trip to the aquarium. I also went to Coors Field to watch the Colorado Rockies play the Oakland A's. A truly unique experience for any avid sportsperson.

I was also lucky enough to have a visitor from home in Golden. Prof. Kieran visited the School of Mines while travelling in the United States. It was very nice to be able to show her around the campus



and also the work that I was doing. Prof. Kieran organised for me to meet Dr. Donal Finnegan, a former winner of the Pat McAdam Scholarship. Dr. Finnegan has since gone on to complete his Ph.D. in University College London and has now returned to US, working between the National Renewable Energy Laboratory in Golden and NASA in Houston. It was inspiring to meet someone who came from a background similar to my own and who is now working in such an iconic association.

My personal highlight from the 10 weeks I spent in Colorado was the unforgettable camping trip to the Gunnison National Park. Prof. Wolden was kind enough to give me 2 days off work to allow us to

stay in the forest for 4 days. On Thursday, June 14th, at 9 am, we left Golden in 3 4X4s to begin our adventures. We drove for 4 hours into the mountains, before heading off-road for 2 hours where we negotiated dust tracks, large boulders, shallow streams and chipmunks and we were even lucky enough to see a moose in the wild!! We eventually parked the trucks and unloaded before hiking for 2 miles with all our gear. Finally, we reached the small cabin shown in the picture. The cabin had been built in the 1950s by the grandfather (and his friends) of one of the boys with whom we were camping. It was a really sweet cabin, all built by hand, with scores of engravings dating back over 50 years. Including one from a helicopter pilot from the 1970s who crash-landed outside it and sheltered there for a week in the winter. Unfortunately, it was also infested with mice, which is why we had to camp *outside* it. While there, we spent our days hiking in the nearby mountains, swimming in the stream, reading books and simply enjoying the fine weather. The cold nights were spent around a small fire inside the cabin where we played card games and cooked our hot dogs.

The weekend after my final presentation, I said my goodbyes, packed up and travelled to Vancouver. Here, I spent 2 weeks with 16 people from my UCD Chemical Engineering class and, like many other Irish students. I got to experience the "J1 lifestyle": I slept on a yoga mat in a 1-bedroom apartment with 8 other girls. 2 weeks was enough!

While in Vancouver I visited the famous Granville Island market, where many of my friends had been working all summer. It's a wonderful indoor food market, very similar to Cork's English Market. We also climbed Grouse Grind, a long and steep hike just outside the city. One day was spent on the sea as we rented a speedboat and travelled along the coast to see a small seal colony. I also got the chance to visit my dad's first cousins who live in Nanaimo, on the east coast of Vancouver Island. It is a truly stunning area and one I would recommend everyone to see, after Colorado of course!

Conclusion

The past summer that I spent in Colorado was simply excellent. I made friendships which, I have no doubt, will last a lifetime and I have already begun planning my return for a week or two in August 2019. The experience has changed me as a person. I have developed hugely on a professional level, but even more so a personal level. I'm very happy to say that I made the very most of every opportunity I got while travelling.

To conclude, I would like to express my extreme gratitude to several people who helped to make my experience so rewarding. Firstly, Prof. Patricia Kieran, for organising so much, including the presentations from previous winners, the applications and the interviews. To Prof. Colin Wolden for so kindly accommodating me in his research group for the summer. His tutoring and guidance were invaluable, and I am sure they will stand to me for the rest of my chemical engineering career. Finally, to Martin and Kate McAdam, without whom none of this would have been possible. I can't thank you enough for the amazing opportunity you gave to me and to so many students before me. I am so grateful that I was able to meet you and thank you in person at the ceremony.

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Development of Catalysts for Membrane Synthesis of Ammonia

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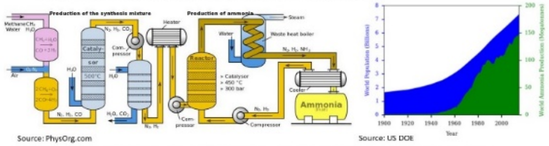
Motivation: Feed the World

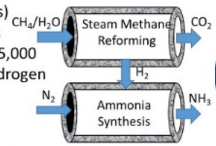
Ammonia Production

- High pressure (200 bar) Haber-Bosch, 2% of global energy consumption
- As fertilizer it supports roughly ½ of the world's population
- Use could dramatically increase if NH_3 used as a fuel; H_2 carrier
- Opportunities for process intensification/integration
- Limited by competition for catalyst sites by N_2, H_2



Innovation: Advanced Membrane Reactor Technology

- Dense H_2-Permeable Composite Metal Membranes
  - BCC metal foils or thin films (V, Nb, alloys)
  - Electroless deposition of Pd-based alloys
  - H_2 flux up to ~1 mol/m²*s; Selectivity > 5,000
  - Harness chemical potential of atomic hydrogen



- Advanced Catalysts and Reactor Design
  - Decouples H_2/N_2 Dissociation
  - Impregnated in support: efficient transport
  - Lower temperature and operating pressure

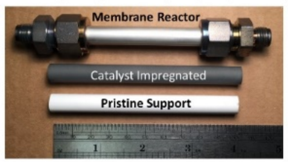
Project Goals / Approach

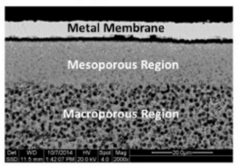
Develop Catalysts for Membrane Synthesis of NH_3

- Wet impregnation / reduction $RuCl_3$
- Compare Al_2O_3 and yittria-stabilized zirconia (YSZ) supports
- Sensitivity to oxygen (typically harmful)
- Role of Cs promoters, optimize ratio

Experimental System & Analysis

- Supply N_2 and H_2 at 1:3 ratio and GHSV = 10,000 h^{-1}
- Measure NH_3 synthesis (Mass spectrometry, NDIR detection)
- Vary temperature (350, 400, 450 °C) and pressure: 1, 5, 10 bar

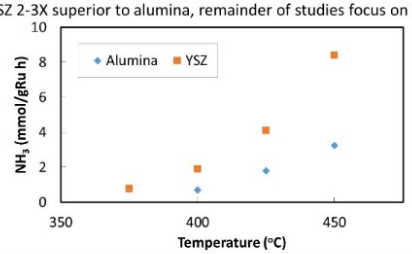




Role of the Supports

YSZ Superior to Alumina

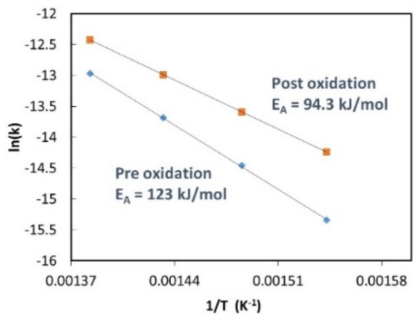
- Ammonia synthesis sensitive to catalyst-support interactions
- Alumina (Al_2O_3) most commonly studied support
- Yittria-stabilized zirconia (ZrO_2-Y) support not investigated
- YSZ 2-3X superior to alumina, remainder of studies focus on YSZ



Sensitivity to Oxygen

Sensitivity to Oxygen

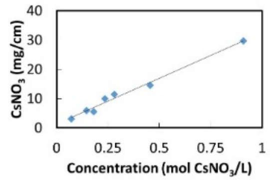
- Ammonia synthesis catalysts intolerant of oxygen
- Makes N_2 purification costly (cryogenic)
- YSZ/Ru catalyst "inadvertently" exposed to oxygen
- Performance improved! Reduced activation energy
- Systematic Treatment:
  - 94 % H2 and 6 % air
  - 450°C, 1 bar and 500 h^{-1}
  - 6 hours



Impact of Cs Promoter

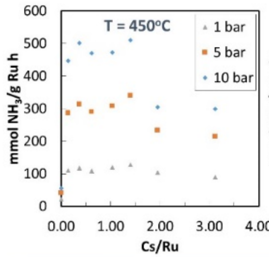
Application of Cs

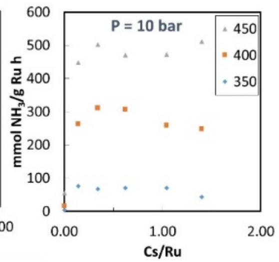
- Impregnation using $CsNO_3$
- Followed by reduction
- Loading scales w/concentration
- Cs/Ru ratio varied from 0 - 3

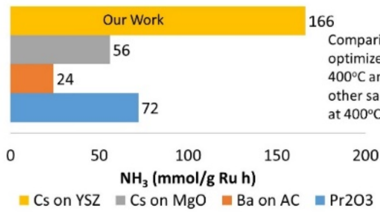


Impact on Rate

- Dramatic increase, followed by plateau and slow decline
- Optimum insensitive to exact Cs/Ru ratio
- Rate proportional to operating pressure
- Activation energy further reduced to ~75 kJ/mol
- Superior to recent literature reports
- Plan to extend to iron as a low cost alternative







Comparison between optimized YSZ based catalyst at 400°C and 1 bar gauge and other samples from literature at 400°C and 1 bar absolute

Sato, K., et al., A low-crystalline ruthenium nano-layer supported on praseodymium oxide as an active catalyst for ammonia synthesis. Chemical Science, 2017. 8(1): p. 674-679

Acknowledgments

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