

NORTHWESTERN UNIVERSITY FACILITY FOR CLEAN CATALYTIC PROCESS RESEARCH
Final Technical Report

T. J. Marks

Center for Catalysis and Surface Science, Northwestern University

Catalytic processes are today practiced on a vast scale to convert basic feedstocks (today largely petroleum, gas, and coal based) into fuels, plastics, agricultural chemicals, pharmaceuticals, foods, paints/coatings, and numerous other materials that underpin our economy and well-being. Catalysts are also used extensively to provide a cleaner environment by treating automotive and industrial (e.g., power plant) exhausts and water-borne effluents. Indeed, it has been estimated that more than 50% of the US GDP derives from catalytic processes. In the past several years, it has become apparent that the US energy supply and demand picture has shifted dramatically, and that a major scientific research and development effort must be mounted to maintain US economic leadership and our quality of life. The challenges are to use and convert more abundant, lower cost/lower quality, and more sustainable feedstocks into the products we need with unprecedented energy- and atom-efficiency. The need to develop more efficient, cleaner and greener catalytic processes is “grand challenge” of national import.

The Center for Catalysis and Surface Science at Northwestern University is a world-leader in catalytic research, spanning five university departments, allied with Argonne National Laboratory and a number of companies, and attacking problems as important as new energy-efficient feedstock production, new ways to treat automotive exhaust streams, hydrogen production and storage, catalysts for cleaner, greener plastics, catalysts activated by solar energy, and atom-efficient routes to specialty chemicals and pharmaceuticals. The center members are divided into teams that carrying out nationally-recognized, cutting-edge research in all of these areas. In the past decade, catalytic research worldwide has moved dramatically from an empirical trial-and-error approach to discovering new catalysts and catalytic processes, to “molecularly engineered catalysts by design” approaches. These approaches combine state-of-the-art computer modeling to define promising catalyst structures in advance, the rational synthesis of sophisticated catalyst precursor molecules, “self-assembly of” nanostructured catalytic systems, use of new activating modalities (e.g., sunlight), and use new catalytic reactor designs and alternative feedstocks.

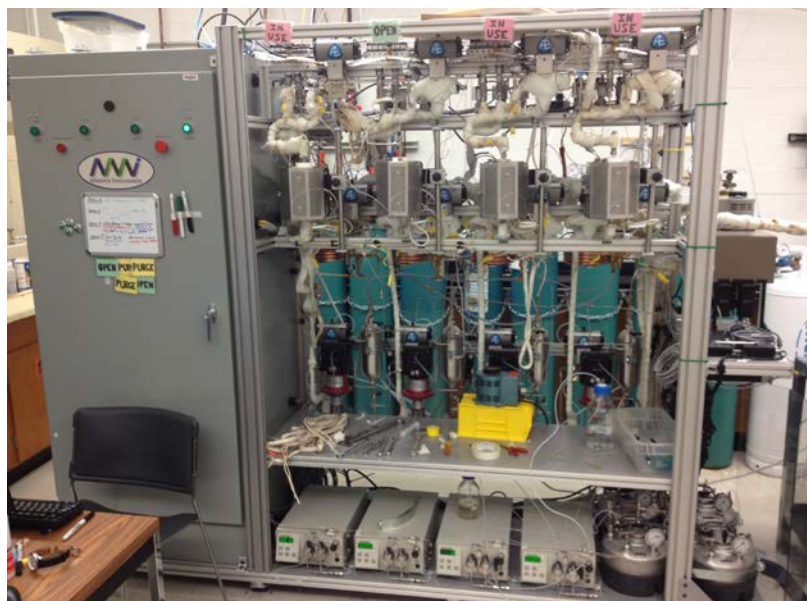
To respond to the National grand challenges described above, Northwestern University with DOE support created a Facility for Clean Catalytic Process Research. This facility is designed to further strengthen our already strong catalysis research capabilities and thus to address these National challenges. Thus, state-of-the art instrumentation and experimentation facility was commissioned to add far greater breadth, depth, and throughput to our ability to invent, test, and understand catalysts and catalytic processes, hence to improve them via knowledge-based design and evaluation approaches. The Northwestern Facility for Clean Catalytic Process Research is described below.

1. List of the equipment acquired

- Altamira BenchCAT4000
 - Dell Computer for BenchCAT 4000

- 2 Parr 4590 Series Bench-top Micro Reactor
- 3 Agilent 7890A Gas Chromatographs
- 2 Agilent 5975 Series Gas Chromatograph/Mass Selective Detectors
 - 2 HP Computers for Agilent analyticals
- Agilent 1200/1260 High Performance Liquid Chromatograph
 - Dell Computer for 1200/1260 HPLC

2. Photos of the facility



BenchCAT 4000 plug flow reactor unit with liquid pumps and vaporizer unit



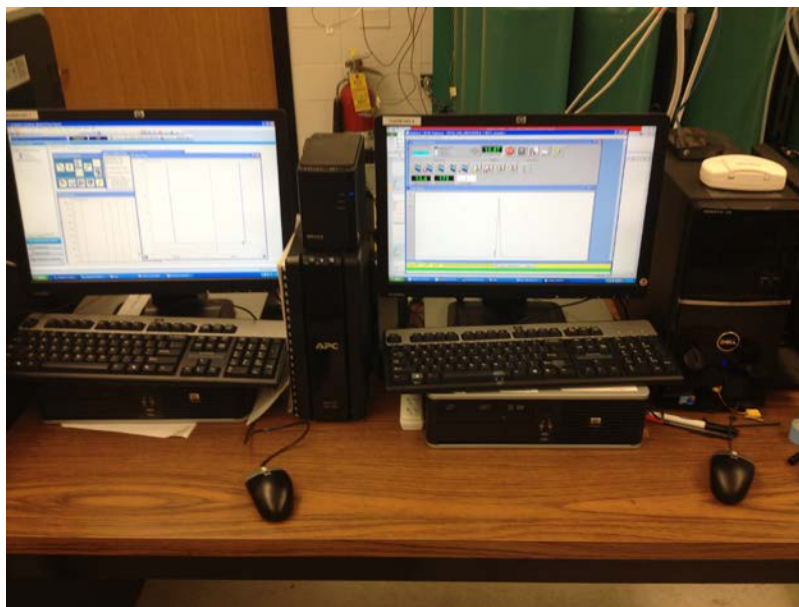
Analytical 1: Agilent 7890A GC with 5975C MSD



Analytical 2 (Agilent 7890A GC with 5975C MSD) and Analytical 3 (Agilent 7890A GC)



Agilent 1200/1260 HPLC and computer



HP Computers for Analytical 1-3 and Dell Computer for BenchCAT4000 unit

3. List of users

- C. Downing of the research group of Professor P. Stair
- N. Ray of the research groups of Professors P. Stair and R. Van Duyne
- C. Canlas of the research group of Professor J. Notestein
- S. Yacob of the research group of Professor J. Notestein
- M. Barach of the research groups of Professors J. Notestein and T. Marks
- A. Salazar of the research group of Professors H. Kung and M. Kung
- J. Galloway of the research group of Professors H. Kung and M. Kung
- X. L. Hou of the research group of Professors H. Kung and M. Kung
- J. She of the research group of Professors H. Kung and M. Kung
- A. Atesin of the research group of Professor T. Marks
- Z. Li of the research group of Professor T. Marks
- P. Young of the research group of Professor J. Notestein

4. Examples of Research Projects Using this Equipment

N. Ray, C. Downing, and C. Canlas

Reactor 3, a quartz plug-flow system, was set up for propylene hydrogenation. Using propylene hydrogenation, the activity of palladium nanoparticle nanobowls treated with long chain thiols was evaluated and compared. (Stair Group: Ray) The system was used to compare the effects of catalyst regeneration on catalytic rates for supported palladium and platinum nanoparticles with ultra-thin mesoporous silica shells. (Notestein Group: Canlas, manuscript in preparation). Coking

reactions, high temperatures with high propylene flow, were performed on high purity alumina, low purity alumina, and atomic layer deposition grown alumina to compare the acidity of the materials. (Stair Group: Ray, Downing)

S. Yacob

Station 4 and Analytical 2 of the Clean Catalysis Facilities Benchcat system was used to test the process stability of the system, especially for liquid feeds. Ethanol and ethanol mixtures were fed through the HPLC pump, vaporizer, and volumizer at various flow rates over an inert reactor bed and observed the peak stability using GC-FID detection. As a result, the feed system on Station 4 was modified to allow for an atmospheric pressure syringe pump injection upstream of the reactor bed. For low pressure, relatively low flow conditions, this dramatically improved stability with time on stream and decreased the lead/dead time from liquid injection to detection in the GC. Other operations included fully heat-tracing the system, recalibrating all gas delivery mass flow controllers, and installing additional traps to handle impurities gasses like CO. These upgrades will significantly enhance the utility of this system for other users with liquid feeds and high boiling products. The station has been subsequently used to understand carbonylation reactions before the Notestein group finishes construction of dedicated reactors for further study. Two manuscripts are in preparation.

M. Barach

Quinoline is a representative recalcitrant impurity in crude oils. With industrial catalysts like NiMo/Al₂O₃, quinoline hydrodenitrogenation (HDN) leads to a majority of the saturated denitrogenated product propylcyclohexane (PCH) and a minority of the aromatic product propylbenzene (PB). Saturation to PCH is undesirable as it leads to a H₂ consumption greater than stoichiometrically required to remove the N atom. We studied the use of Pd/Ta-Al₂O₃ catalysts which exhibit high selectivity toward PB. This work made use of the GC-MS (product identification), GC-FID (product quantification), and Parr autoclave reactors (catalytic reactions) in the Clean Catalysis facility. This work will be submitted shortly for publication with Energy & Environmental Science being the target journal.

A. Salazar

Preliminary evaluation of sodium tartrate oxidation products from visible light photoreduction of Cr(VI) to Cr(III) by Fe(III) nitrate were evaluated using the CleanCat HPLC facility fitted with a ICSep COREGEL-87H3 column (Transgenomic) and 5mM H₂SO₄(aq) mobile phase. Since tartrate and its oxidation products are high boiling point mono-, di- and tri- carboxylic acids, volatilization of the products is difficult making HPLC the best choice for their separation and identification. The refractive index detector was employed in conjunction with the diode array detector to identify products with known UV absorptions, which allowed for more efficient identification of the few oxidation products. Control kinetic experiments indicated that the tartrate was not appreciably consumed during the reaction and further study the oxidation products was discontinued.

P. Young

The Notestein group has developed hybrid amine base – Lewis acid solid catalysts, which were tested in the isomerization and dehydration of glucose and fructose. Current processing of sugars requires several steps at very different pH, leading to many process inefficiencies that could be avoided using a bifunctional acid-base catalyst. Products were analyzed using the CleanCat HPLC facility fitted with a CARBOSEP Coregel87C column (Transgenomics) and the refractive index detector. Data continue to be evaluated to identify several unknown products, but several unusually reactive catalyst formulations have been identified. This preliminary work will pave the way for further, more detailed, investigations, publication, and independently funded research.

A. Atesin and Z. Li

Biomass has a high oxygen content, much of which is found as ether linkages and alcohol functional units. As part of our effort to devise rational, mechanism/thermodynamics-based strategies for breaking down C-O linkages in biomass, we have developed using the equipment of the Facility for Clean Catalytic Process Research a tandem catalytic system consisting of recyclable lanthanide triflate Lewis acids, a robust ALD-derived Pd nanoparticle hydrogenation catalyst developed by Stair, and a “green”, recyclable imidazolium triflate ionic liquid solvent system.¹ At elevated hydrogen pressures, this system is effective in the hydrogenolysis of a great many linear and cyclic ethers, and detailed kinetic and mechanistic studies have been carried out. From these we find that C-O cleavage is turnover-limiting (the reverse of a hydroalkoxylation process), followed by rapid hydrogenation of the resulting unsaturated alcohol. Using deuterium-labeled substrates, we measure a kinetic isotope effect (KIE) of 2.7 for the retro-hydroalkoxylation.³ In a collaborative DFT theoretical study of this catalytic process, collaborators from Argonne National Laboratory find a transition state very similar to that proposed from the experimental studies; the computed activation energies as a function of trends in lanthanide ionic radius and KIE of 2.4, are in excellent agreement with experiment. Their work also suggests unusual lanthanide coordination numbers that will be explored in collaborative EXAFS studies with other collaborators from Argonne National Laboratory.

To explore the scope of this unique tandem C-O hydrogenolysis process, three exploratory synthetic/mechanistic thrusts are currently underway using model etheric substrates:

1) Screening alternative triflate Lewis acids. We find that, of the ~15 metal triflates and Brønsted acids screened to date, $\text{Hf}(\text{OTf})_4$ and $\text{Zr}(\text{OTf})_4$ are the most active by a wide margin. Collaborative theoretical work is focusing on issues such as charge: ionic radius ratio and how this affects the reaction coordinates and activation energies for C-O cleavage.

2) Screening alternative hydrogenation catalysts and solvents. With these more active tetravalent Lewis acids, more conventional hydrogenation catalysts are also found to be effective. These reactions proceed both in water and when only neat substrate is used,

eliminating the need for ionic liquids as the solvent in many cases. Thus, for a model dialkyl ether, the turnover frequency for the catalyst system consisting of $\text{Hf}(\text{OTf})_4 + \text{Pd}/\text{BaSO}_4 + \text{neat}$ substrate is found to be 650x greater than for a $\text{Yb}(\text{OTf})_3 + \text{Pd@ALD} + \text{imidazolium}$ ionic liquid catalyst. Currently in progress are experimental and theoretical mechanistic studies of these transformations to understand how they differ from our first-generation catalysts and to guide the synthesis of even more active/selective catalysts. We will also be examining other ALD-derived hydrogenation catalysts prepared by the Stair group, as well as solid Lewis acid catalysts and hydrogenation catalysts.

3) All-heterogeneous catalytic systems. The goal here is to further simplify the processing of low molecular weight feedstocks by heterogenizing both the triflate Lewis acid and hydrogenation catalysts. In preliminary work we prepared a support consisting of Nafion coated high surface area silica, and have impregnated it with $\text{Hf}(\text{OTf})_4$ and Pd nanoparticle precursors. We find that this system is also effective at C-O bond hydrogenolysis. Currently we are exploring the substrate scope and mechanism of these $\text{Hf}(\text{OTf})_4$ -mediated reactions, and characterizing the Nafion-based supported catalyst system in terms of morphology and microstructure. We anticipate collaborating with other collaborators from Argonne National Laboratory on these latter issues.

Importantly, almost none of these experiments would have been possible without the equipment provided by the Facility for Clean Catalytic Process Research.

5. References to any publications using the equipment, either in print, in press, submitted, or in preparation.

1. Atesin, A.C.; Ray, N.; Stair, P.C.; Marks, T.J. Etheric C—O Bond Hydrogenolysis Using a Tandem Lanthanide Triflate/Supported Palladium Nanoparticle Catalyst System, *J. Am. Chem. Soc.* **2012**, *134*, 14682–14685.
2. Assary, R.S.; Atesin, A.C.; Curtiss, L.A.; Marks, T.J. Reaction Pathways and Energetics of Etheric C-O Bond Cleavage Catalyzed by Lanthanide Triflates, submitted for publication.
3. Bachrach, M.; Morlanes-Sanchez, N.; Canlas, C.P.; Miller, J.T.; Marks, T.J.; Notestein, J.M. Enhanced Hydrodenitrogenation Selectivity with Pd/Ta-Alumina Catalysts, submitted for publication.
4. Christian P. Canlas, Natalie Ray, Sara Yacob, Brandon O'neil, Cem Akatay, Richard van Duynes, James Dumesic, Eric Stach, Fabio Ribeiro, Peter Stair and Justin M. Notestein Sinter-proofing Catalytic Metal Nanoparticles with Ultra-thin Silica Overcoats, in preparation.
5. Li, Z.; Atesin, A.C.; Marks, T.J. Highly Efficient Tandem Catalysts for Etheric C—O Bond Hydrogenolysis to Alcohols and Alkanes. Substrate and Catalyst Scope, in preparation.