Department Events:

- **CCST Seminar**
  Dr. Zhongwei Chen, University of Waterloo
  Friday, May 17, 2013
  1:30pm in 366CLB
  "Advanced Non-precious Oxygen Catalysts for Metal-Air Batteries"

- **Colburn Club Happy Hour**
  Friday, May 17, 2013
  starting 4:00 pm at Kildare’s
  Come join us for numerous specials on drinks and appetizers!

- **You are cordially invited to Stefan Gaida’s thesis defense**
  Thursday, May 16, 2013
  11:00am in 102 DBI
  "Development of genomic and genetic systems to expand the searchable genomic space for engineering complex bacterial phenotypes."
  Light refreshments will be served.

- **You are cordially invited to Scott Crown’s thesis defense**
  Friday, May 17, 2013
  10:00 am in 366 CLB
  "Novel methodologies for isotopic tracer and experiment design: Applications to 13C-metabolic flux analysis and isotopic studies."
  Light refreshments and snacks will be served
  Please see attached for dissertation abstract

In the News:

- **Germany Bound**
  [http://www.udel.edu/udaily/2013/may/kelley-lindau-nobel-051413.html](http://www.udel.edu/udaily/2013/may/kelley-lindau-nobel-051413.html)

- **Stellar Subjects**
  [http://www.udel.edu/udaily/2013/may/qs-world-rankings-051013.html](http://www.udel.edu/udaily/2013/may/qs-world-rankings-051013.html)

- **University Faculty Senate elects new officers**
  [http://www.udel.edu/udaily/2013/may/faculty-senate-051013.html](http://www.udel.edu/udaily/2013/may/faculty-senate-051013.html)

- **Faculty Promotions**
  [http://www.udel.edu/udaily/2013/may/faculty-promotions-051013.html](http://www.udel.edu/udaily/2013/may/faculty-promotions-051013.html)

- **Senior Thesis Symposium**

- **DOE’s Office of Science Announces 61 Scientists to Receive Early Career Research Program Funding**

- **Five from MIT win Early Career Awards**

Future Department Events:

- **CMET Seminar**
  Seth Fraden, Brandeis University
  “Materials Morphogenesis”
  Thursday, May 23, 2013
  2:30 pm – 366 CLB
• **COE Invited Guest Lecture**
  David A. Pensak
  Thursday, May 23, 2013
  9:30am in 116 Gore Hall
  “A Logical Structure For Technological Innovation”

• **Save the Date:**
  What: Annual Softball Picnic
  Where: Lums Pond State Park
  When: Saturday, June 8

• **You are cordially invited to Weitng Yu’s thesis defense**
  Monday, May 20, 2013
  9:30 am in 106 CCM
  "Catalytically Controlling the Reaction Pathways of Biomass-derived Oxygenate Molecules"
  Light refreshments will be served
  Abstract attached.

**Jobs/Recruiting:**

Available positions can be found on the Chemical & Biomolecular Engineering opportunity website ([http://www.che.udel.edu/biz/Oppindex.html](http://www.che.udel.edu/biz/Oppindex.html)), so be sure to check it regularly.
Catalytically Controlling the Reaction Pathways of Biomass-derived Oxygenate Molecules

Weiting Yu

The declining supply of petroleum resources, combining with the increasing energy demand by the rapidly developing economies, as well as the political and environmental concerns about fossil fuels lead to the imperative development of sustainable energy. Biomass, because of its advantages of being widely available, renewable and potentially CO₂-neutral, is regarded as an alternative energy source to fossil fuels. Briefly, plants can make use of solar energy to combine carbon dioxide and water to form oxygen and carbohydrates. The carbohydrates in the plant can be broken down to smaller oxygenates, such as glucose, sorbitol, ethylene glycol, and others. Small oxygenates from non-food competing biomass feedstock such as trees and grasses, are chosen to be studied in this work.

The objective of this work is to utilize biomass-derived molecules to produce hydrogen, syngas (H₂ and CO) or other valuable chemicals. Controlling the activity and selectivity of biomass-derivative conversion is critical for the utilization of biomass feedstocks as renewable sources for fuels and chemicals. The key chemistry in the conversion is the selective bond scission of the -OH, C=O and furan ring functionalities, which are present in many biomass-derivatives such as glucose, fructose and furfural.

In this study, glycolaldehyde (HOCH₂CH=O), the smallest molecule that contains both the C-OH and C=O functional groups, as well as the same C/O ratio as C6 sugars, is used as a probe molecule of biomass-derivatives such as glucose and fructose. Identifying a good catalyst is very important for the highly efficient and selective conversion of biomass-derivatives. In this work, Ni/Pt(111) bimetallic system is chosen for glycolaldehyde reaction theoretically using density functional theory (DFT) calculations and experimentally using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) measurements. The combination of theoretical and experimental results indicate that the reaction
pathway of glycolaldehyde to produce syngas can be enhanced by supporting monolayer (ML) Ni on a Pt(111) substrate, which shows higher activity than either of the parent metals\(^2\).

However, the ML Ni-Pt(111) structure favorable for the reforming reaction is not stable at high temperatures and the base metal Pt is scarce and expensive. It is therefore very important to identify other materials to replace Pt as the bulk to support ML Ni. Tungsten monocarbide (WC)\(^3\) has been reported to possess similar electronic properties to Pt, and therefore the reaction of glycoaldehyde is also studied on the Ni/WC surfaces. On the ML NiWC surface glycolaldehyde undergoes C-C bond cleavage to produce syngas with similar activity as the ML Ni-Pt(111) surface\(^2\), which indicates that ML NiWC may be preferable to ML Ni-Pt(111) as active and selective catalyst for biomass reforming with higher stability and lower cost. In addition, on the clean WC surface, glycolaldehyde reacts via the deoxygenation pathway to produce ethylene, resulting from the C-O bond scission with the C-C bond remaining intact\(^2\). The results found on clean WC and ML NiWC surface from the study of glycolaldehyde can also be extended to other C2 oxygenates with different functional groups such as ethylene glycol, acetaldehyde and acetic acid\(^6\).

Moreover, another carbide, molybdenum carbide (Mo\(_2\)C), and different metal (Ni, Au, Cu and Pt) modified Mo\(_2\)C surfaces have also been studied for the reaction of ethylene glycol. A methodology for catalyst design is established in this work by the combination of a microkinetic model and parallel TPD and HREELS measurements. This methodology for catalyst design based on the oxygen and carbon affinity provides guidelines for future catalyst discovery.

Furthermore, precious-metal free bimetallic Fe/Ni(111) surfaces are studied in this work for the conversion of biomass-derivatives. Three molecules, furfural, glycolaldehyde and acetaldehyde, are compared on Fe/Ni(111) surfaces to study the effect of the furan ring, -OH and C=O functional groups on the reaction pathways. This work confirms the feasibility of using precious-metal free Fe/Ni(111) surfaces for biomass conversion.
References:


ABSTRACT

Over the past 20 years, $^{13}$C-metabolic flux analysis ($^{13}$C-MFA) has emerged as the leading technology for accurate quantification of intracellular fluxes in microbial, mammalian and plant systems. Despite major advances in experimental, analytical and computational techniques, isotopic experiment design is often neglected for $^{13}$C-MFA. Optimal design of isotopic experiments is of central importance as it determines the resolving power of $^{13}$C-MFA, i.e. the precision with which fluxes can be estimated. Three experimental variables directly influence flux precision: (1) metabolite measurements, i.e. $^{13}$C-enrichments and concentrations; (2) isotopic tracers; and (3) experiment layout, i.e. single vs. parallel labeling experiments. Here, we present methodologies and metrics for optimal isotopic tracer selection, with emphasis on determining the optimal tracer for a single isotopic experiment or the best combination of tracers for multiple isotopic experiments conducted in parallel.

First, we describe the development of a novel framework for rational tracer selection based on the Elementary Metabolite Unit (EMU). The strength of this approach is the decoupling of substrate labeling, i.e. the EMU basis vectors, from the dependence on free fluxes, i.e. the coefficients. We also demonstrate that flux observability inherently depends on the number of independent EMU basis vectors and the sensitivities of coefficients with respect to free fluxes. Furthermore, we apply this framework to a realistic network model of mammalian metabolism and determine two novel tracers that have not been previously considered for $^{13}$C-MFA of mammalian cells, i.e. $[2,3,4,5,6-{^{13}}C]glucose$ and $[3,4-{^{13}}C]glucose$.

Second, we describe the development of scoring metrics for global analysis of a network’s flux precision. Specifically, we develop a precision score, which accounts for the nonlinear confidence intervals for fluxes and does not introduce biasing due to normalization by the flux value. In addition, we propose a synergy score to estimate the flux information gain.
associated with conducting parallel labeling experiments as opposed to a single tracer experiment. Then, we utilize the scoring metrics to systematically evaluate in silico isotopic tracer designs for $^{13}$C-MFA in *E. coli*. In particular, we focus on tracer selection for two experiment layouts: (1) single tracer experiment, and (2) two parallel tracer experiments. We demonstrate the major improvement in flux precision that can result from careful selection of isotopic tracers for parallel labeling experiments.

Lastly, we present an application of innovative tracer selection and parallel labeling experiments to probe biological questions. Specifically, parallel $^{13}$C-tracer experiments were performed in 3T3-L1 adipocytes to quantify the contributions of amino acids to fatty acid synthesis. Through isotopomer spectral analysis, we demonstrate that branched chain amino acid catabolism plays an important role in fatty acid synthesis. Also, we systematically determined the synthetic route of odd-chain fatty acids using novel GC-MS techniques. Furthermore, we provide evidence that suggests a methylmalonic acid shunt, which challenges the current understanding of propionate metabolism.