FIRST YEAR’S HIGHLIGHTS

Presented by Dion Vlachos, Director
Lead Institution: University of Delaware
CCEI’s Partners

Consists of 22 faculty researchers from 9 academic institutions

UD team: 9 faculty
Non-UD team: 13 faculty from 8 affiliated institutions

3 NAE members, 1 NAS member, 11 named professors, 4 junior faculty

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CCEI’s Mission

**Develop** the enabling science leading to improved or radically new heterogeneous catalytic technologies for viable and economic operation of biorefineries from various lignocellulosic biomass feedstocks

**Educate** the workforce needed to further develop and implement these new technologies

**Pursue** technology transfer strategically via multi-institutional collaborations and joint ventures with industrial partners

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Major Research Goals

**Transform** biomass and/or its derivatives into valuable chemicals, fuels and electricity through a fundamental understanding of the chemistry and catalyst performance

**Design** novel hierarchical multiscale materials with nanoscale resolution suitable for processing derivatives from complex, multiphase media of biomass to ensure efficient, highly selective and benign processes

**Promote** catalyst design and technology advancement through novel theoretical and multiscale simulation platforms and cutting-edge characterization tools
Lignocellulosic biomass decomposition (e.g., pyrolysis) leads to coking and the process is slow

- Complex feedstock renders fundamental studies difficult
- Biomass and its derivatives are over-functionalized molecules
  - Selectivity is critical
  - Chemical transformations require fundamental understanding of chemistry and catalyst performance (currently lacking)

- Processing of biomass derivatives occurs in a complex environment
  - Low volatility and thermal stability require solution chemistry
    - Typical supports (e.g., Al₂O₃, SiO₂) dissolve in water
    - Acid-based chemistry (e.g., HCl) is environmentally harsh
    - Models do not exist
Research Thrusts

Crosscutting Research Thrust

Hierarchical Multiscale Materials

Multiscale Modeling

Characterization Techniques

Technological Platform

Reforming

Furans

Biomass Degradation/Oil Upgrade

Direct Carbon FCs

Science

Fuels

Electricity

Processing

Chemicals

CO+2H₂/FT

Reaction Pathways, Kinetics, Structure-Property Relationships

Process Innovation, Optimization

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CCEI First-Year Highlights

- Novel catalyst for the single pot conversion of glucose to HMF
- Computational engine for model-based bimetallic catalyst discovery applied to reforming technologies
- Defined surrogates of bio-oil
- Molten metal electrolyte-based fuel cells for the direct conversion of carbon to electricity
CCEI First-Year Highlights

- Novel catalyst for the single pot conversion of glucose to HMF
- Computational engine for model-based bimetallic catalyst discovery applied to reforming technologies
- Defined surrogates of bio-oil
- Molten metal electrolyte-based fuel cells for the direct conversion of carbon to electricity
Chemicals: Objectives

- Develop technologies for production of chemicals and hydrogen or syngas from biomass derivatives (e.g., sugars, glycerol, ethylene glycol, etc.)

- Understand the reaction mechanisms

- Design active, selective, stable, and inexpensive catalysts that will enable effective and selective transformation of oxygenates to desirable products
Chemicals: Sub-thrusts

- **Furans**: Selective transformation of sugars to value-added chemicals, while retaining or increasing the number of carbon atoms
  - e.g., isomerization of glucose to fructose; conversion of sugars to valuable chemicals, such as HMF, EMF, etc.
  - **Selective deoxygenation** (mainly C-O bond scission; e.g., dehydration) and possibly **hydrogenation**
  - **Acid and base** catalytic functional groups

- **Reforming**: H₂ and syngas production
  - **Selective C-C bond scission** (followed by dehydrogenation)
  - **Metal catalysis** for hydrogenation and reforming

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Biomass Contains a lot of Glucose

- Corn Grain
- Corn Stover
- Cane
- Cane Bagasse
- Pine
- Aspen

- Ash
- Uronic Acids
- Extractives
- Lignin
- Hemicellulose
- Cellulose / Algin

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Tin-Containing Zeolite Beta for Sugar Isomerizations in Water

by

Manuel Moliner, Yuriy Roman-Leshkov, Eranda Nikolla & Mark Davis

Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

Isomerization of Glucose to Fructose: Intermediate Step to Fuels and Chemicals

**Glucose isomerization is a crucial step** in the efficient **production** of valuable **chemical intermediates**, such as 5-hydroxymethylfurfural (HMF).

![Chemical diagram](image)

**HYDROLYSIS**

Starch → Glucose

**ISOMERIZATION**

Glucose → Fructose

**DEHYDRATION**

Fructose → HMF

Combination of enzymes or acid treatment → Enzymes → Acid treatment

*Juben N. Chheda, George W. Huber, & James A. Dumesic, Angewandte Chemie Int. Ed., 46 2007*

**A heterogeneous isomerization catalyst** that can easily integrate glucose isomerization with the transformations of starting polymers of sugars and of fructose into fuels intermediates is **lacking**.
Isomerization of Glucose into Fructose by Immobilized Enzymes

- Isomerization of glucose into fructose is the largest immobilized biocatalytic process worldwide for the production of high-fructose corn syrup (HFCS, 8 × 10^6 tons/year).
- Reaction slightly endothermic (ΔH=3 kJ/mol) and reversible (Keq ~ 1 at 298 K).
- Equilibrium mixture of 42% (wt/wt) fructose, 50% (wt/wt) glucose, and 8% (wt/wt) other saccharides using xylose isomerase.

Starch-Starke. 2002.54, 75
Isomerization of Glucose into Fructose by Immobilized Enzymes

Drawbacks

1) Pre-reaction purification processes to remove impurities that inhibit enzyme activity

2) Use of buffered solutions to maintain pH~7-8 (Na$_2$CO$_3$) and to activate the enzyme (MgSO$_4$), requires post-reaction ion-exchange

3) Optimal operating temperature of 60ºC to maximize enzyme lifetime

4) Periodic replacement of the enzyme due to irreversible deactivation
Non-bio Glucose Isomerization

Current non-biological catalysts involve:

- Cr salts in ionic liquids (Zhao et al. Science, 316 (2007) 1597)
- SnCl$_4$ in ionic liquids (Hu et al., Green Chem., 11 (2009) 1746)
- Mixed base (glucose to fructose with hydrotalcite)-acid (fructose to HMF with Amberlyst-15) (Takagaki et al., Chem Commun., 2009, 6276)

No heterogeneous catalysts that can function in aqueous solutions and no catalysts that can function at acidic conditions that would allow for “one-pot” couplings to other reactions (like fructose to HMF)
Can Lewis Acid Centers in Zeolites Perform Sugar Isomerizations in Pure Water?

Corma et al. have shown that Sn-Beta zeolites are highly active in the Meerwein–Ponndorf–Verley (MPV) reaction, whereby a hydride transfer occurs from the hydroxyl group of an alcohol to the carbonyl group of a ketone.\(^{(1)}\)

We hypothesized Sn-Beta would also have strong interactions with the hydroxyl/carbonyl moieties that are present in aldoses, such as glucose, and thus be active in the isomerization reaction. If the zeolite structure could be sufficiently hydrophobic, the reaction may also be possible in aqueous solvent.

Screening Materials of Different Pore Size

**TS-1** (5.5-6 Å)

**Ti-Beta, Sn-Beta** (7.5-8 Å)

**Ti-MCM-41, Sn-MCM-41** (35 Å)

Reaction conditions:
10% (wt/wt) glucose in water, 413 K, 90 min, and 1/50 metal:glucose molar ratio.
Kinetic Studies at Different Temperatures with Sn-Beta

**REACTION CONDITIONS:**

10% (wt/wt) glucose in water, and 1/50 metal:glucose molar ratio

**RESULTS:**

46% (wt/wt) glucose
31% (wt/wt) fructose
9% (wt/wt) mannose

after 30 min and 12 min at 383 K and 413 K
### Results for the Isomerization of Glucose in Water

**Reaction conditions:**  
10% (wt/wt) glucose in water, and 1/50 metal : glucose molar ratio.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Temperature (K)</th>
<th>Time (min)</th>
<th>Glucose (wt%)</th>
<th>Fructose (wt%)</th>
<th>Mannose (wt%)</th>
<th>Total Saccharides (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>383</td>
<td>90</td>
<td>97</td>
<td>0</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>413</td>
<td>90</td>
<td>95</td>
<td>1</td>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>HCl (pH = 2)</td>
<td>383</td>
<td>90</td>
<td>98</td>
<td>0</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>Sn-Beta</td>
<td>383</td>
<td>30</td>
<td>45</td>
<td>32</td>
<td>9</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>Sn-Beta</td>
<td>413</td>
<td>12</td>
<td>46</td>
<td>30</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>Sn-Beta/HCl (pH = 2)</td>
<td>383</td>
<td>30</td>
<td>44</td>
<td>33</td>
<td>9</td>
<td>86</td>
</tr>
<tr>
<td>7</td>
<td>Ti-Beta</td>
<td>383</td>
<td>90</td>
<td>74</td>
<td>14</td>
<td>5'</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>SnO₂</td>
<td>383</td>
<td>60</td>
<td>96</td>
<td>0</td>
<td>0</td>
<td>96</td>
</tr>
<tr>
<td>9</td>
<td>SnCl₄ · 5H₂O</td>
<td>383</td>
<td>60</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>10*</td>
<td>Sn-Beta</td>
<td>383</td>
<td>60</td>
<td>46</td>
<td>29</td>
<td>8</td>
<td>83</td>
</tr>
</tbody>
</table>

**A)** The active sites for the isomerization reaction in Sn-Beta are Sn atoms incorporated into the framework of the zeolite. Neither SnCl₄ nor SnO₂ showed isomerization activity.
Results for the Isomerization of Glucose in Water

*Reaction conditions:
45% (wt/wt) glucose in water, and 1/225 metal : glucose molar ratio.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Temperature (K)</th>
<th>Time (min)</th>
<th>Glucose (wt/wt%)</th>
<th>Fructose (wt/wt%)</th>
<th>Mannose (wt/wt%)</th>
<th>Total saccharides (wt/wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>383</td>
<td>90</td>
<td>97</td>
<td>0</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>413</td>
<td>90</td>
<td>95</td>
<td>1</td>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>HCl (pH = 2)</td>
<td>383</td>
<td>90</td>
<td>98</td>
<td>0</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>Sn-Beta</td>
<td>383</td>
<td>30</td>
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<td>9</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>Sn-Beta</td>
<td>413</td>
<td>12</td>
<td>46</td>
<td>30</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>Sn-Beta/HCl (pH = 2)</td>
<td>383</td>
<td>30</td>
<td>44</td>
<td>33</td>
<td>9</td>
<td>86</td>
</tr>
<tr>
<td>7</td>
<td>Ti-Beta</td>
<td>383</td>
<td>90</td>
<td>74</td>
<td>14</td>
<td>5^t</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>SnO₂</td>
<td>383</td>
<td>60</td>
<td>96</td>
<td>0</td>
<td>0</td>
<td>96</td>
</tr>
<tr>
<td>9</td>
<td>SnCl₂ · 5H₂O</td>
<td>383</td>
<td>60</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>10⁺</td>
<td>Sn-Beta</td>
<td>383</td>
<td>60</td>
<td>46</td>
<td>29</td>
<td>8</td>
<td>83</td>
</tr>
</tbody>
</table>

B) Sn-Beta catalyst can be used with more concentrated glucose solutions like those employed in large-scale conversion processes. A product distribution of **46% (wt/wt) glucose, 29% (wt/wt) fructose, and 8% (wt/wt) mannose** was obtained after reacting a **45 wt% glucose solution**.

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Results for the Isomerization of Glucose in Water

Reaction conditions:
10% (wt/wt) glucose in water, and 1/50 metal:glucose molar ratio.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Temperature (K)</th>
<th>Time (min)</th>
<th>Glucose</th>
<th>Fructose</th>
<th>Mannose</th>
<th>Total saccharides</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>383</td>
<td>90</td>
<td>97</td>
<td>0</td>
<td>0</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>413</td>
<td>90</td>
<td>95</td>
<td>1</td>
<td>0</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>HCl (pH = 2)</td>
<td>383</td>
<td>90</td>
<td>98</td>
<td>0</td>
<td>0</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>Sn-Beta</td>
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<td>30</td>
<td>45</td>
<td>32</td>
<td>9</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>Sn-Beta</td>
<td>413</td>
<td>12</td>
<td>46</td>
<td>30</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>Sn-Beta/HCl (pH = 2)</td>
<td>383</td>
<td>30</td>
<td>44</td>
<td>33</td>
<td>9</td>
<td>86</td>
</tr>
<tr>
<td>7</td>
<td>Ti-Beta</td>
<td>383</td>
<td>90</td>
<td>74</td>
<td>14</td>
<td>5</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>SnO₂</td>
<td>383</td>
<td>60</td>
<td>96</td>
<td>0</td>
<td>0</td>
<td>96</td>
</tr>
<tr>
<td>9</td>
<td>SnCl₄ · 5H₂O</td>
<td>383</td>
<td>60</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>10*</td>
<td>Sn-Beta</td>
<td>383</td>
<td>60</td>
<td>46</td>
<td>29</td>
<td>8</td>
<td>83</td>
</tr>
</tbody>
</table>

C) Remarkably, Sn-Beta is able to perform the isomerization reaction in a highly acidic environment. No differences in activity or product distribution were observed for reactions using Sn-Beta in an acidic 10% (wt/wt) glucose solution (pH=2, HCl), when compared to the reaction performed without HCl.
Catalyst Stability Studies:
Catalyst is Stable for Reuse Without Regeneration

Reaction conditions:
10% (wt/wt) glucose in water, 383 K, and 1/50 metal:glucose molar ratio.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Glucose (wt/wt%)</th>
<th>Fructose (wt/wt%)</th>
<th>Mannose (wt/wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sn-Beta Cycle 1</td>
<td>30</td>
<td>41</td>
<td>32</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Sn-Beta Cycle 2</td>
<td>30</td>
<td>45</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Sn-Beta Cycle 3</td>
<td>30</td>
<td>47</td>
<td>29</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>Sn Beta Cycle 4 (calcination)</td>
<td>30</td>
<td>46</td>
<td>30</td>
<td>8</td>
</tr>
<tr>
<td>5a</td>
<td>Sn-Beta</td>
<td>12</td>
<td>57</td>
<td>27</td>
<td>6</td>
</tr>
<tr>
<td>5b</td>
<td>None (catalyst removed by filtration)</td>
<td>30</td>
<td>57</td>
<td>27</td>
<td>6</td>
</tr>
</tbody>
</table>

Filtration of solid performed at reaction temperature
Schematics of the Glucose Isomerization Mechanisms

Standard base catalyzed mechanism

Glucose (α-pyranose form)
Fructose (α-furanose form)

Proposed Lewis acid mechanism
Reaction Mechanism: An Intramolecular Hydride Shift True Lewis Acid Catalysis in Water!

13C NMR

Fructose-D1

Glucose-D2

Nonamer

Base (B)

Sn-Beta

Fructose

glucose-D2_NaOH

glucose-D2_Sn-Beta

fructose_D1_Sn-Beta

fructose_NaOH

glucose-D2 feed

fructose-D1_Sn-Beta

glucose std.

fructose std.
Reaction Mechanism: An Intramolecular Hydride True Lewis Acid Catalysis in Water!

NMR studies on labeled glucose unequivocally demonstrate that, when Sn-Beta catalyzes the reaction, the deuterium atom remains in the fructose molecule, thus confirming an intramolecular hydride shift mechanism.
Proof-of-Concept Experiments Using Sn-Beta in an Acidic Environment

Working at low pH values opens up exciting opportunities to couple upstream and downstream acid-catalyzed reactions, e.g., hydrolysis or dehydration, with the glucose isomerization reaction without the need to use additional unit operations.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Feed solution</th>
<th>Catalyst</th>
<th>Time (min)</th>
<th>Yield (wt/wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Starch</td>
</tr>
<tr>
<td>1a</td>
<td>10 wt% Starch</td>
<td>HCl (pH = 1)</td>
<td>90</td>
<td>13</td>
</tr>
<tr>
<td>1b</td>
<td>Postreaction mixture of entry 1a</td>
<td>Sn Beta+HCl (pH = 1)</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>10 wt% Glucose</td>
<td>HCl (pH = 1)</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>10 wt% Fructose</td>
<td>HCl (pH = 1)</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>10 wt% Glucose</td>
<td>Sn-Beta+HCl (pH = 1)</td>
<td>120</td>
<td>-</td>
</tr>
</tbody>
</table>

Davis and co-workers, in preparation
Conversion of Glucose to HMF in “One-Pot”

**Reaction Conditions:**
1:3 water to organic phase volume ratio, pH of 1 in HCl, $T=180^\circ C$, 35g of NaCl in 100g of water.
Computations Complement Experimental Work

- Rational materials design requires a fundamental understanding of the reaction mechanism, the effect of solvent, and the catalyst.
- Computations can play an indispensable role in design.
- Multiscale modeling-methodology:
  - Pick a reaction coordinate for each step in the mechanism.
  - Scan the reaction coordinate while averaging over configurations of the system.
  - Configurations generated by QM/MM Molecular Dynamics:
    - Fructose is treated quantum mechanically (QM).
    - For solvent, we use Molecular Mechanics force field (MM).
  - Umbrella sampling to account for rare events (i.e., high barriers and infrequent transitions).
  - Calculate free energy change along the reaction coordinate.

www.efrc.udel.edu Caratzoulas and Vlachos, in preparation
Dehydration Mechanism

- Initialization by O2 protonation
- O3 or O4 protonation for 1st step are likely, but subsequent dehydration either improbable (O3 case) or lead to by-products (O4 case)
- Rate limiting step is hydride transfer (7 $\rightarrow$ 8)
Conclusions

- A large-pore zeolite that contains tin (Sn-Beta) is able to isomerize glucose to fructose in aqueous media with high activity and selectivity.

- The same reactivity is achieved also when a high-concentrated glucose solution is used (45 wt% glucose).

- Sn-Beta can be used for multiple cycles without regeneration.

- Sn-Beta is able to perform the isomerization reaction in highly acidic, aqueous environments with equivalent activity and product distribution as in media without added acid.

- Sn-Beta is able to perform Lewis Acid mediated isomerization of glucose in pure water solvent or saturated NaCl solutions – unprecedented for zeolite catalysis.

- “One-pot” synthesis of HMF from glucose with high yield is possible using Sn-Beta at low pH in a two phase system (second phase – THF).