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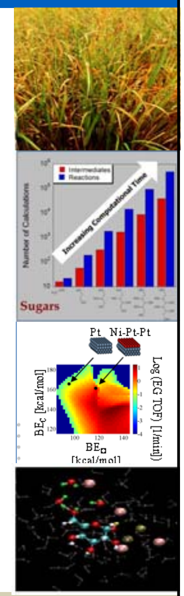
Process and Catalyst Intensification for Distributed Energy and Chemicals



Dion Vlachos September 30, 2014

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an Energy Frontier Research Center

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Concepts and Technologies for Energy and Chemicals

- **Environment: Capture and sequestration of CO_2**
  - ✓ Particulates, NOx from diesel engines
- **Efficiency**
  - ✓ Economics, atom economy, energy savings, reduced emissions
  - ✓ Improved selectivity, process intensification
- **Hydrogen [economy]**
  - ✓ Production, storage, utilization (PEM FCs, biomass upgrade)
- **Increase energy supply**
  - ✓ Renewables (wind, solar, biomass, water split, CO_2)
  - ✓ Underutilized resources (offshore NG, shale gas, light oils)
- Down-scaling: **An emerging frontier**
  - ✓ Reliability, expensive or impossible transportation, process intensification and efficiency, H_2 production
- Novel materials: **A cross-cutting theme**

Review: Vlachos & Caratzoulas, *Chem. Eng. Sci.* **65**, 18 (2010)

Concepts and Prototypes of Process Intensification

- **Microtechnology**
  - Offshore natural gas utilization
- **Reactive separation**
- **Cascade of chemical reactions**
- **Bifunctional catalysts and site cooperativity**
  - Sugar transformation to platform chemicals

Future Energy Will be Associated with Down-Scaling

- H_2 PEM fuel cells: ✓ Onboard ✓ Gas-stations

- Renewables' use localized
  - ✓ Solar/distributed need
  - ✓ Biomass/transportation cost

Vlachos and S. Caratzoulas, *Chem. Eng. Sci.* **65**, 18 (2010)

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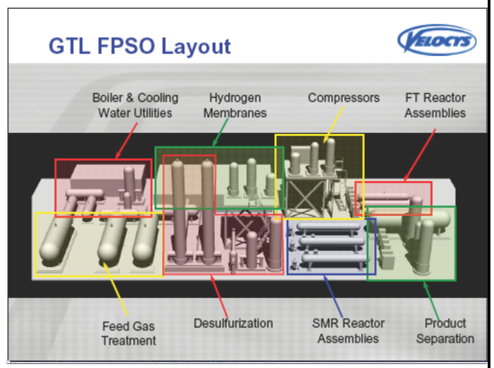
Down-Scaling: Untapped Reserves in Remote and Offshore Locations

- Offshore GTL
  - Large reservoirs of unutilized natural gas
  - Restrictions on flaring require stranded gas to be re-injected (costly)



Kaisare and Vlachos, *Prog. Energy Comb. Sci.* **38**, 321 (2012).
ExxonMobil report, www.exxonmobil.com

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Current Syngas Production Route

- Steam reforming: endothermic
  - Fixed bed catalytic reactors with Ni catalyst

SR: $CH_4 + H_2O = CO + 3H_2 + 206$ kJ/mol
WGS: $CO + H_2O = CO_2 + H_2 - 41$ kJ/mol

- Heat transfer controlled
  - Flames supply the heat to multitubular reformers
  - Half of NG is burned; NOx, particulates and CO_2 form
- Slow (τ~1s); bulky

Need for
more efficient,
less bulky processes
via better catalysts and
process intensification

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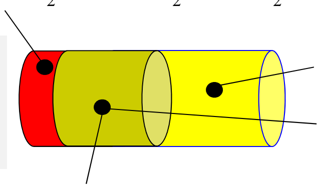
Stratified Partial Oxidation Reactor

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Short Contact Time Technology of L. Schmidt, 1993



$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

$$CH_4 + CO_2 \longrightarrow 2CO + 3H_2$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

$$CH_4 + 0.5O_2 \xrightarrow[Rh]{} CO + 2H_2$$

- Up to three reaction zones
- The extent of combustion vs. mixed mode zone depends on mass transfer
  - No diffusion limitations eliminate the second zone
  - Strong diffusion limitations eliminate the combustion zone
- One can control/eliminate hot spot formation

Maestri et al., *J. Cat.* **259**, 211 (2008), *Topics Catal.* **52**, 1983 (2009)

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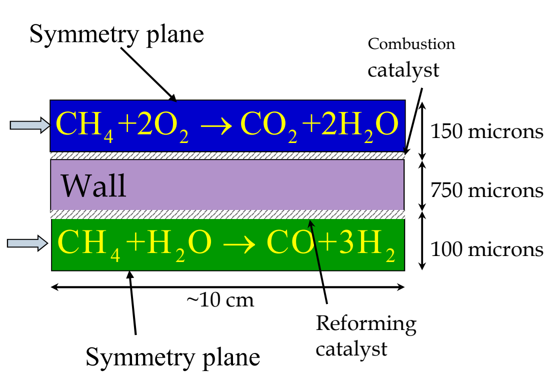
Multifunctional Microdevices

Spatially segregated coupling
(combustion and reforming in alternate channels)



- Heat exchange and chemical reaction
- Intimate coupling – compact devices
- Fast heat transfer
- Fast responses
- Flexibility: Different catalysts, fuels and flow configurations

Stefanidis and Vlachos, *Chem. Eng. Sci.* **65**, 398 (2010)

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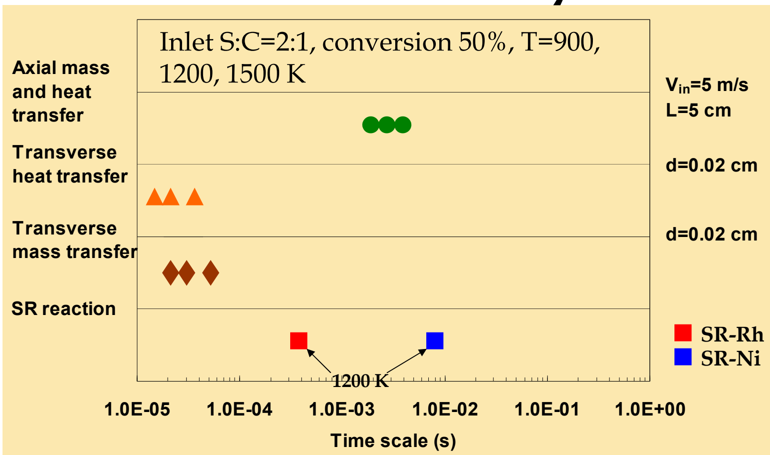
Time Scale Analysis



- Catalyst is rate controlling
- Rh order of magnitude faster than Ni (commercial catalyst). Further loss of throughput due to high temperatures (inability of Ni to remove heat)

Stefanidis and Vlachos, *Chem. Eng. Sci.* **65**, 398 (2010)

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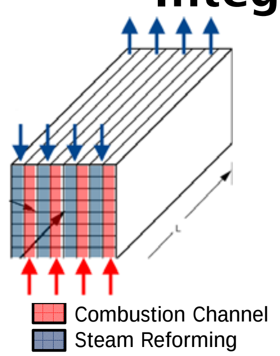
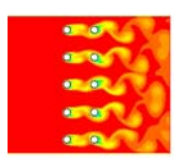
Integrated Devices



Internals



Tacchinno et al., in preparation
Norton et al., US Patent 60/691,990 , "Microcombustors For Compact Power or Heat Generation"

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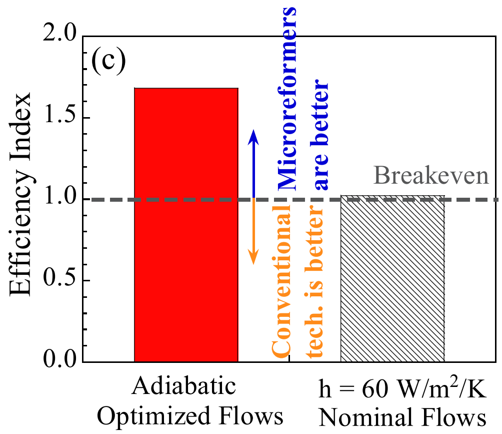
Efficiency of Microreformers vs. Conventional Reformers



$$\eta = \frac{F_{CO,out} LHV_{CO} + F_{H_2,out} LHV_{H_2}}{F_{Me,in} LHV_{Me}}$$

$$\mathrm{EI} = \frac{\eta_{\mu}}{\eta_{c}}$$

Kaisare and Vlachos, *Prog. Energy Comb. Sci.* **38**, 321 (2012).
Mettler et al., *Chem. Eng. Sci.* **66**, 1051 (2011)

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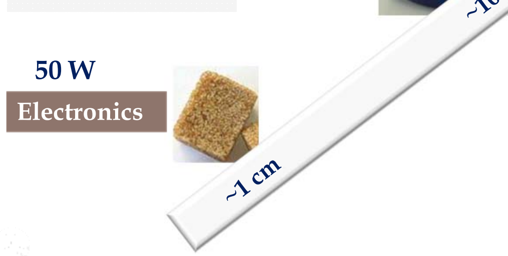
Scale-out for Different Powers

- Reforming scaled-out to produce power for various applications



Challenges
- Heat management
- Water management
- Catalyst

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Concepts and Prototypes of Process Intensification

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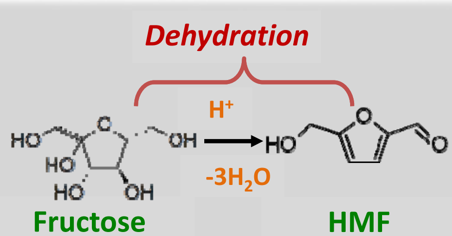
Production of HMF

- 5-hydroxymethylfurfural (HMF) is a key platform for fuels and chemicals
- HMF is being produced by dehydration of fructose typically via homogeneous acid catalysis
- **Side reactions** consume a significant fraction of reactants and products and lead to reactor shut down
- **Minimize side reactions via reactive extraction**

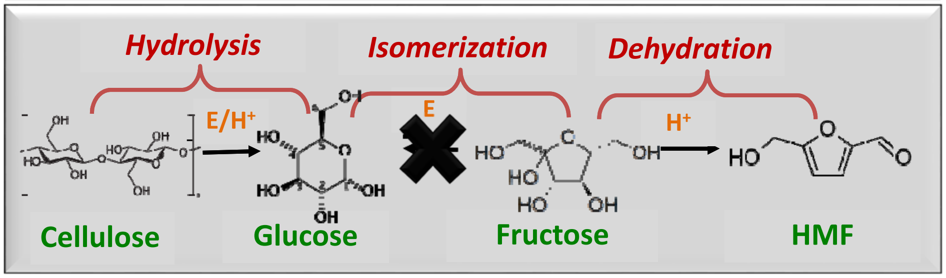


Chheda et al., *Green Chem.* 9, 342, (2007)

Lowering Production Cost of HMF

- Fructose has been *the* compound for fundamental studies
- Glucose is the building block of cellulose
- Glucose to fructose isomerization is practiced with *enzymes* *but this is a costly and equilibrium limited process*
- Selective conversion of glucose to fructose and other platforms can have a profound impact on future biorefineries

Review on Sugar Chemistry: Caratzoulas et al., *J. Phys. Chem. C*, (2014).



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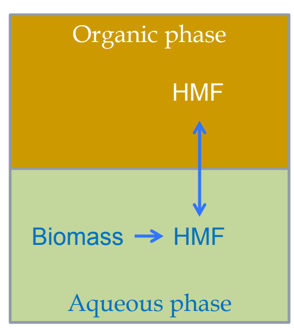
From Carbohydrates to High HMF Yield in Biphasic Systems

Entry	Feed	System	Catalyst	Conv. [%]	HMF Selec. [%]	Time [min]	Temp [°C]
1	Glucose	Single phase (H_2O)	Sn-Beta, HCl	45	6	90	160
2	Glucose	Biphasic (H_2O/1-butanol)	Sn-Beta, HCl	77	26	90	160
3	Glucose	Biphasic (H_2O/1-butanol/NaCl)	Sn-Beta	75	18	90	160
4	Glucose	Biphasic (H_2O/1-butanol/NaCl)	HCl	26	40	90	160
5	Glucose	Biphasic (H_2O/1-butanol/NaCl)	Sn-Beta, HCl	75	55	90	160
6	Glucose	Biphasic (H_2O/THF/NaCl)	Sn-Beta, HCl	79	72	70	180
7	Glucose	Biphasic (H_2O/THF/NaCl)	Ti-Beta, HCl	76	70	105	180
8	Cellobiose	Biphasic (H_2O/THF/NaCl)	Sn-Beta, HCl	73	86	40,60	180
9	Starch	Biphasic (H_2O/THF/NaCl)	Sn-Beta, HCl	75	69	40,60	180



Nikolla, Roman-Leshkov, Moliner, Davis, *ACS Catal.* **1**, 408 (2011)

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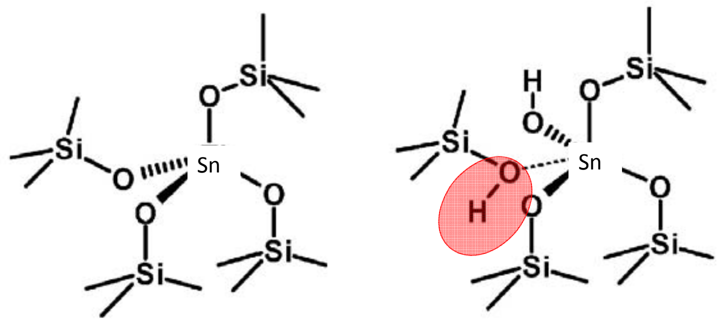
Active Site: Sn-Beta



closed site   open site

Question:
If the open site is the active site, does the silanol group participate in the reaction mechanism like with Ti in TS-1 and like other –OH groups within the enzyme?

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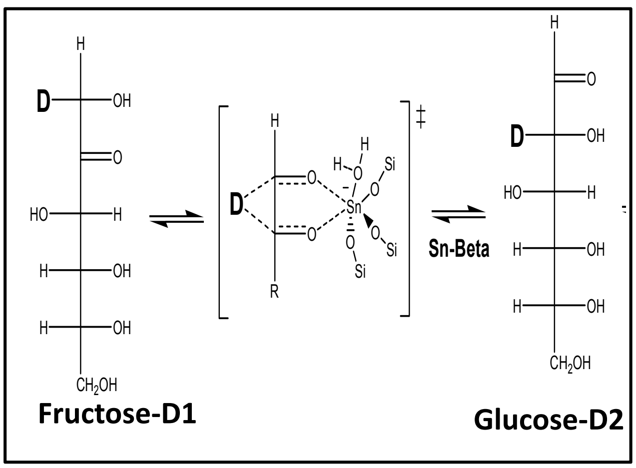
Mechanistic Insights Reveal Site Cooperativity



- Two possible rate-determining steps
- **OH acts as a basis** to remove H from OH
- **Sn acts as a Lewis acid** center to carry out intrahydride transfer

Exps: Roman-Leshkov, Moliner, Labinger, Davis, *Angew. Chem. Int. Ed.* **49**, 8954 (2010)
Model: Choudhary, Caratzoulas, and Vlachos, *Carbohyd. Res.* **368**, 89 (2013)

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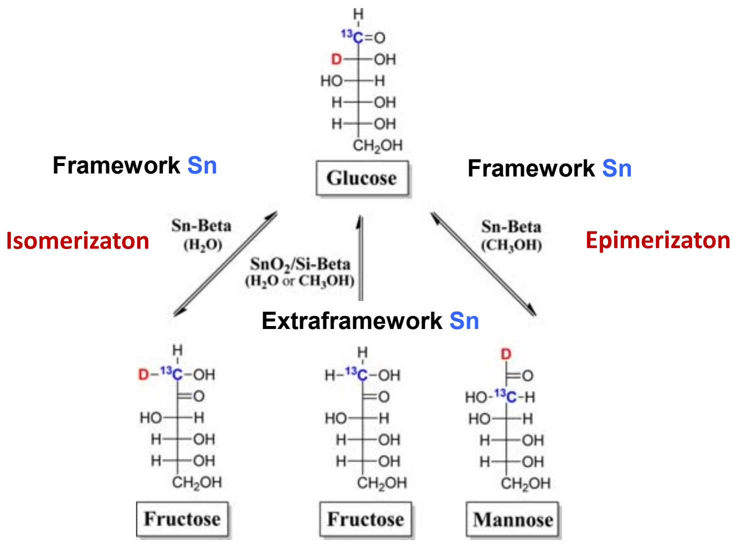
Solvent-Induced Tuning of Chemistry in Sn-BEA



Ricardo Bermejo-Deval; Rajamani Gounder; Mark E. Davis; *ACS Catal.* **2**, 2705 (2012)

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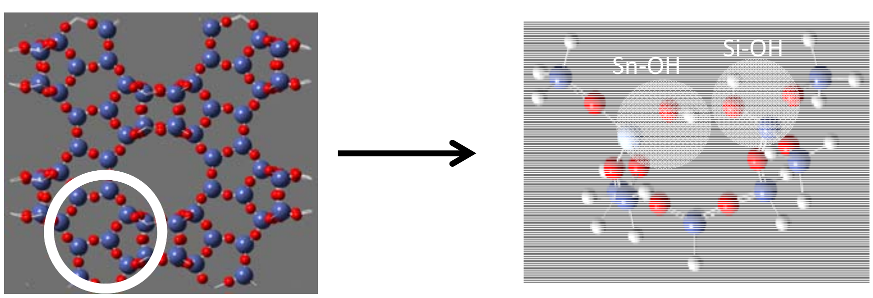
Multiple Active Sites at Work!



Sn-Beta crystal **Cluster calculation**

Two alternate mechanisms explored:

A) Hydride transfer or “Bilik” facilitated by SiOH
B) Hydride transfer or “Bilik” with SiOH as spectator

Reaction steps:

(1) Proton transfer (to the active SnOH); (2) Hydride transfer; Bilik

Rai, Caratzoulas, and Vlachos, *ACS Catal.* **3**, 2294 (2013)

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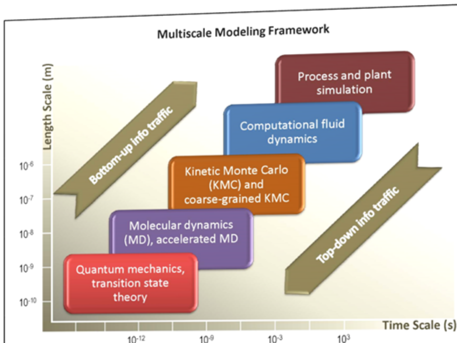
Bottom-up and Top-down Modeling: Process Design and Catalyst Screening

- Mathematical and computational methods developed
  - Bottom-up modeling
    - ✓ **Process design**
  - Coarse-graining
  - **Top-down modeling**
    - ✓ **Catalyst design**



Multiscale modeling framework for catalytic processes that exhibit strong coupling between scales. Adapted from Vlachos, *Adv. Chem. Eng.* 30, 1-61 (2005)

Reviews: *Chem. Eng. J.* **90**, 3 (2002); *Chem. Eng. Sci.* **59**, 5559 (2004); *Adv. Chem. Eng.* **30**, 1 (2005)

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Outlook

- Microdevices provide process intensification, modularity, portability, and potentially higher efficiency
- Reactive separation has been an important pillar for PI but new separations for biomass are needed
- Tandem reactions offer opportunities: lower capital, drive equilibrium
  - Design principles for integrating multiple catalysts are lacking
- Process intensification may need to be accompanied by catalyst intensification
- Novel materials can play a crucial role
  - Multifunctional catalysts offer untapped opportunities for PI
- Multiscale modeling can be an enabler for PI

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  - NSF (Microreformers)