



CHANGING WHAT'S POSSIBLE

Electrochemical Approaches to Modular Power Generation

C-H Bond Activation Breakout Session

June 6, 2013



Question on piece of paper before breakout starts



How did I get here?

Draw 2 different mechanistic pathways.

You may use any catalysts you wish, and there is no limit to the number or types of mechanistic steps you can use.

List any necessary assumptions.

Brainstorming responses to Warm-Up Question

- ▶ High temp steam reforming reaction
 - Microchannel reactors, bimetallic catalysts, built-in combustor to create high temp steam
- ▶ This is an endothermic process: requires energy input. Scaling up is an issue.
- ▶ Functional ceramics/ graded ceramic surface to help spillover.
- ▶ Sulfur cycle: $\text{CH}_4 + \text{SO}_3 \rightarrow \text{CH}_3\text{OH} + \text{SO}_2$
- ▶ Halogenation followed by oxidation, hydrolysis, regenerate X_2
- ▶ Chemical looping: Combustion with metal oxide, regenerated with oxygen.
- ▶ Mixed metal oxide, spillover– MO and MH created on a surface.
- ▶ MOFs
- ▶ High voltage discharge to catalyze/lower activation energy.
- ▶ Electrophilic, oxidative addition, metallo-radical reactions, concerted metallation-deprotonation (metal + base).
- ▶ Organometallic catalysts: 200-500C lowers the activation energy, but lower selectivity compared to @ room temp.
- ▶ Flow reactor
- ▶ Photocatalyzed– solar or LED to excite a certain wavelength
- ▶ Enzyme + membrane separator, electron-transfer through a redox couple.
- ▶ Bio-organisms
 - Anaerobic enzymes, methane \rightarrow protons and methyl anion.
 - Methane monooxygenase the energy goes downhill.

Brainstorming Rules

- ▶ Withhold criticism
- ▶ Welcome unusual ideas
- ▶ Combine and improve ideas
- ▶ Liu Rule: Don't invite Box to house
- ▶ ARPA-E Rule: Consensus not necessary

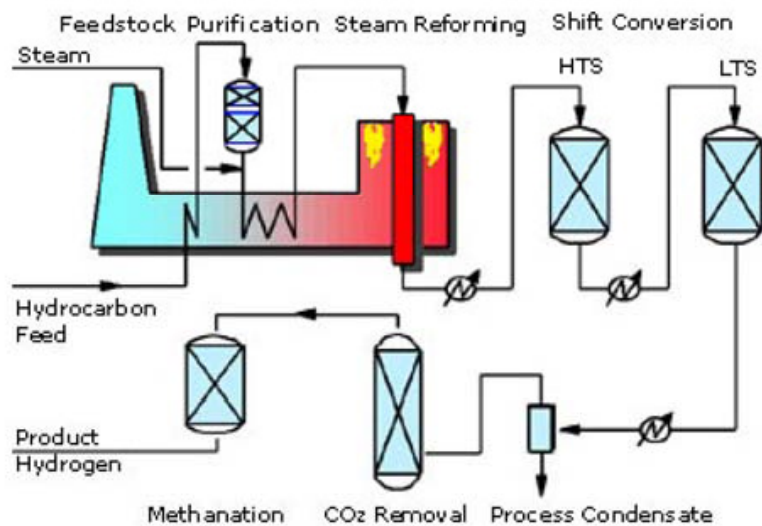
Topics for Discussion

- ▶ What are the thermodynamic and kinetic barriers to C-H bond activation?
- ▶ What are some different ways of dehydrogenating a hydrocarbon at temperatures <500 C?
- ▶ What recent advances can we leverage?
- ▶ Anecdotal/past examples of reforming in the intermediate temperature range
- ▶ What key breakthroughs are needed?

Thermodynamics and Kinetics

- ▶ What are the thermodynamic and kinetic barriers to C-H bond activation?
- ▶ Methane reforming thermodynamics are shown on the following slide.
 - At intermediate temperatures, the balance of reaction products changes rapidly. Temperature gradients across the cell may cause problems.
- ▶ Thermodynamic limits for methanol:
 - Above 300C, CH_3OH disintegrates to CO_2 and H_2 . This reaction can be runaway to 550C to get CH_4 .
 - Cool the reaction to get higher selectivity, and you lose the kinetics!
 - Need to separate out the methanol to keep the reaction going.
- ▶ Kinetics and thermodynamics cross-compete.
- ▶ For higher hydrocarbons, requires higher temps and pressures.
- ▶ Carbon formation / coking
- ▶ Sulfur tolerance

Cheating Thermodynamics



The thermodynamics require high temperatures for complete conversion.

One possibility: Cheat using kinetics.

Chemical looping,
Electrochemical separation,
Sorbents,
Surface modifications.

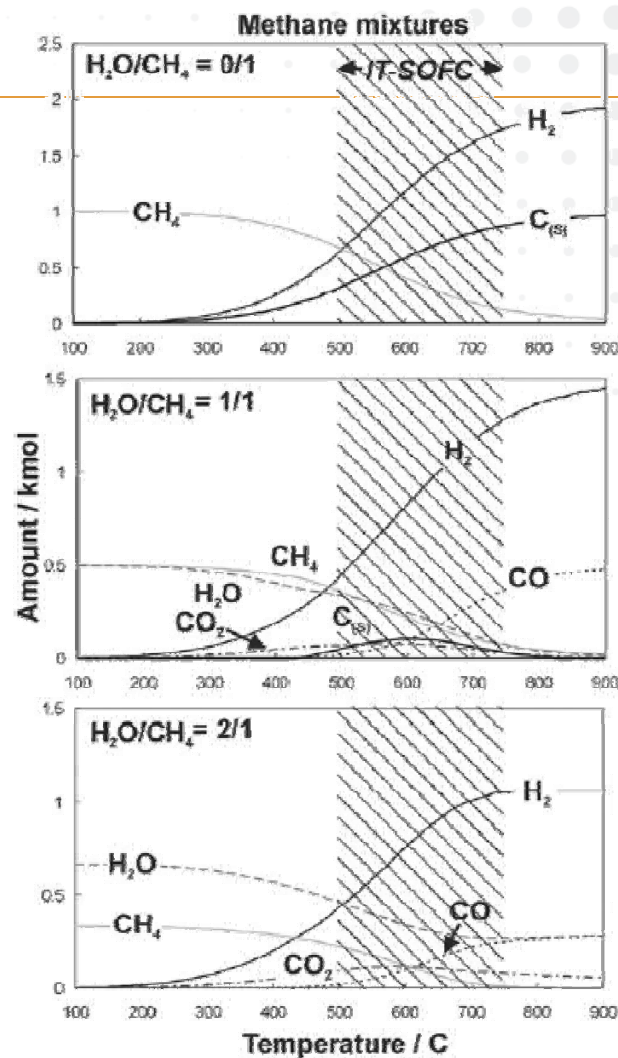
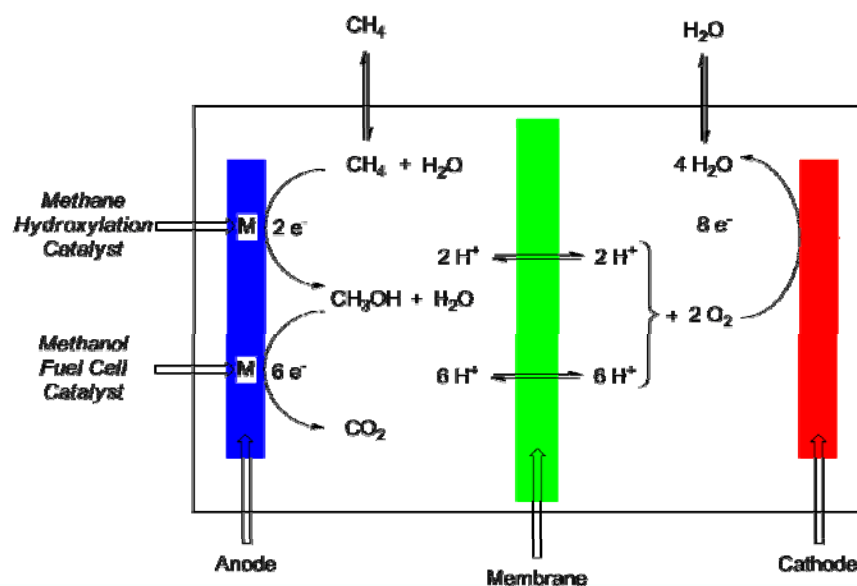


Fig. 7 Thermodynamic predictions of the equilibrium composition for methane fed at different temperatures and steam-to-carbon ratios. The combined $\text{CH}_4 + \text{H}_2\text{O}$ input amount is 1 kmol in each case.

Chem. Soc. Rev., 2008, 37, 1568–1578

C-H bond activation under 500C

- ▶ Brainstorm different mechanisms for C-H bond activation
- ▶ How could these be coupled to an electrochemical power generation device?
- ▶ One example:



From U Va. Center for Catalytic Hydrocarbon Functionalization

Brainstorming C-H bond activation methods

- ▶ CO₂ adsorbent to drive the rxn @ lower temps
- ▶ New oxidants– activating the CH bond, then regenerated using oxygen.
- ▶ Ex: I₂ to methyl iodide to make methanol, product is HI, regenerate using energy input.
- ▶ Sulfate to sulfuric acid
- ▶ Knowledge gap here regarding temperature.
- ▶ Methanol works @ lower/intermediate temps: make methanol at a lower temp, use it in a device?
- ▶ Methanol can be incorporated into IT-FC with internal reforming on CuZnO catalyst. Staged conversion.

Insights: advances, experience with C-H

- ▶ What recent advances can we leverage?
- ▶ Anecdotal/past examples of reforming in the intermediate temperature range
 - In high temp SOFCs, you can see a 100C temp difference across the stack. In intermediate temp stacks, you will still have a temp gradient.
 - For IT-FCs, the balance of equations is changing rapidly. Temp gradients will cause chemical gradients.
 - Common oxidants are O₂ and H₂O, due to cost.
 - Other oxidants haven't been investigated @ this temp.
 - Grading the material composition
 - Integrating steam from the reformer to control temperature and chemical balance
 - Chemical looping to pull out the CO₂ separately.
 - Electrochemical separation
 - Sorbents
 - Sulfur / other impurities must be separated.

Key breakthroughs needed

- ▶ What key breakthroughs would be needed to enable the use of a hydrocarbon fuel such as gasoline, diesel, or natural gas
 - Directly in a fuel cell
 - In a simplified fuel reformer?
 - Manage Sulfur:
 - separate it out
 - use it as part of the cycle?
 - Manage C deposition.
 - Ceramic electrode, graded composition and functionality
 - New ways to cheat thermodynamics. Separation methods. Selective catalysis. Recyclable oxidant / chemical looping
 - Materials problems if it's a direct fuel device
 - Methane to another fuel/ methanol
 - Corrosion of BOP due to S
 - More system integration
 - Ceramic oxides and titanates might be able to oxidize sulfur, other hydrocarbons above 800C.
 - Fluorocarbon to hydrocarbon