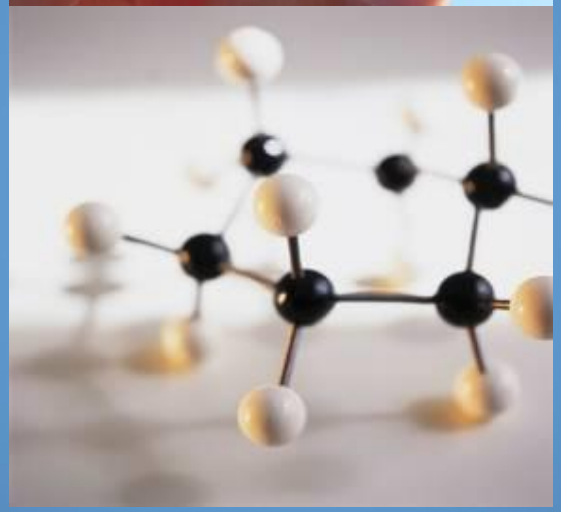


2013 DOE Bioenergy Technologies Office (BeTO) Project Peer Review: GASIFICATION

–Catalyst Characterization–

20 May 2013

Ted Krause, ANL
Jesse Hensley, NREL

Goal Statement

Project Goal – Develop catalysts and processes for cost-competitive production of hydrocarbon fuels from biomass-derived syngas

- Invent novel catalyst/reactor systems informed by the development of **structure-function relationships**
- **Provide data and validation** for IDL platform TEAs

Quad Chart Overview

Timeline

- Project start: 2012
- Project end: 2022
- 5% complete

Barriers

- Tt-G fuels catalyst development
  - Selectivity to hydrocarbon fuels
  - Impactful product yield
- Process and market-driven attributes (achieve MFSP ≤ $3/gal)
  - Compatibility with biomass syngas
  - Production of distillates/jet preferred to gasoline
  - Minimize fixed and variable costs
  - Product yield and purity

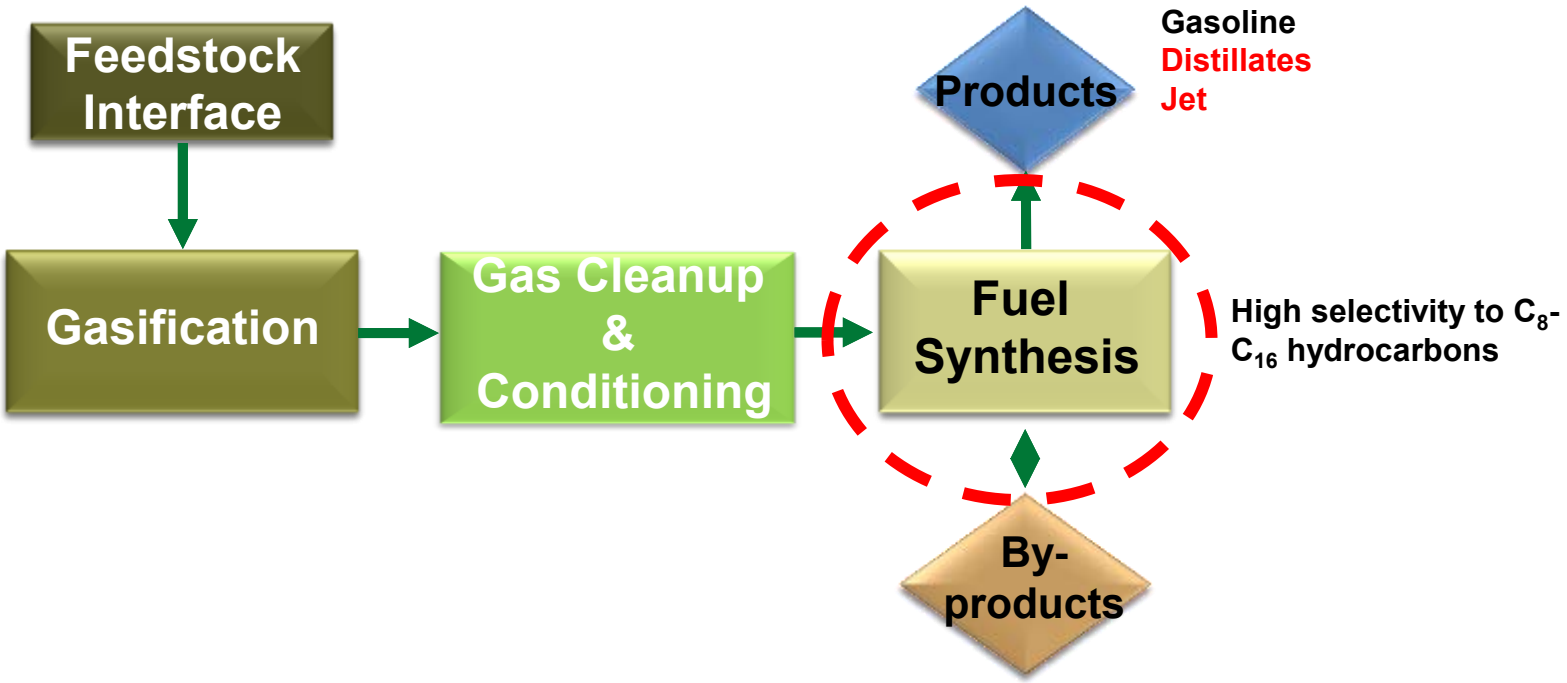
Budget

- Total project funding to date
  - $600k DOE
- FY13 funding
  - $200k ANL
  - $400k NREL

Partners

- ANL/NREL
- Project Management via AOP/PMP

Overview: Biomass Gasification for Fuels



Overview: Project Objectives & Timeline

Objectives

- Develop **novel and selective catalysts** to maximize conversion of syngas to distillate and gasoline-range hydrocarbon fuels
- **Improve understanding** of selectivity to different products through *in-situ* and *operando* catalyst characterization
- Design catalyst + process strategies to **meet MFSP goals**

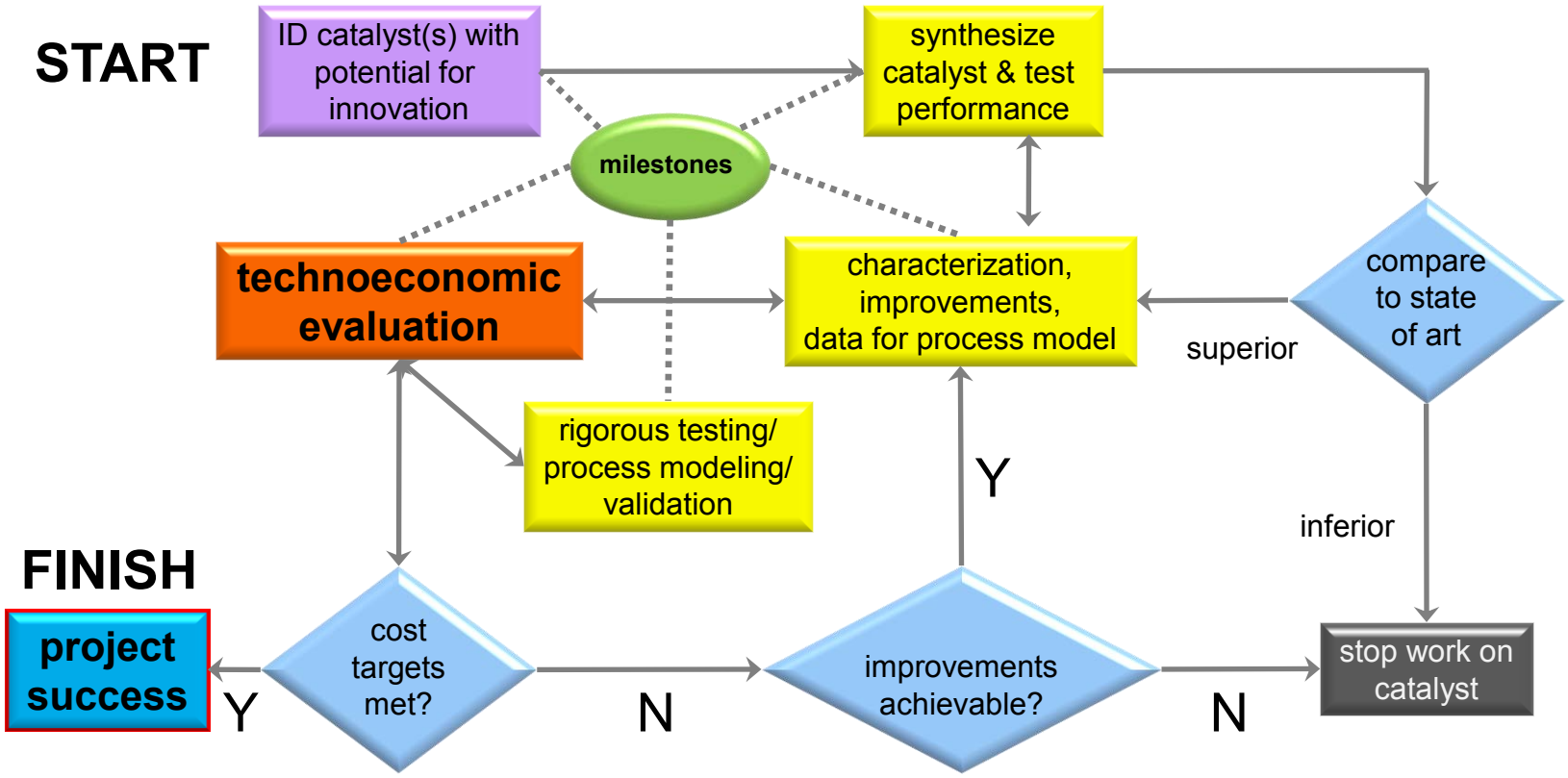
Timeline

- **FY13**: Identify structure-function relationships for an advanced alkylation catalyst
- **FY14**: Catalyst development for oligimerization, alkylation, and hydrogenation, generate SOT
- **FY15**: Data collection and validation for process models, catalyst refinement
- **FY16**: Scale-up of catalysts

Approach

Target: modeled and pilot-validated MFSP of $3/gal

Catalyst development informed by TEA and directed by progress, go/no-go decision points, etc.



Technical Approach: Integrate experimentation and technoeconomic evaluation to achieve cost targets

Management Approach: DOE-approved Project Management Plans detail schedules/milestones/risk abatement

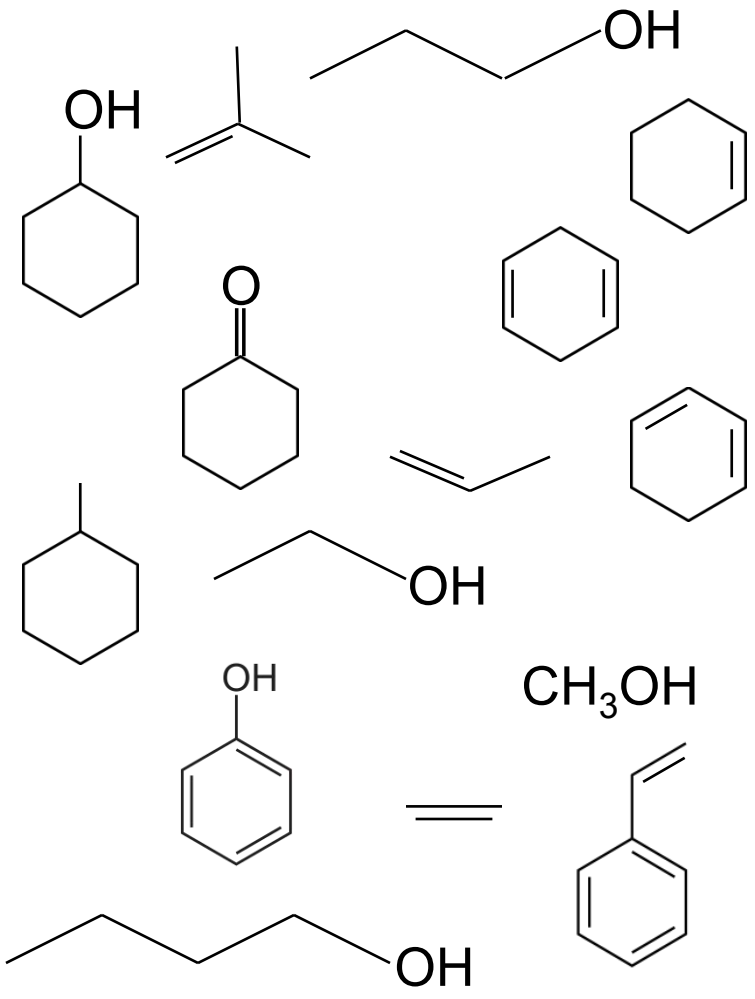
Hydrocarbon from Syngas or Biochemical Intermediates
Process and Catalyst Driven by Product Requirements

oxygen content, fuel components' incompatibilities

- **Aviation Fuels**
  - Jet A (most common commercial fuel)
  - Jet B (cold regions)
  - JP-X (military grades)
  - Requirements:
    - Essentially zero O, S
    - C_8-C_{16}
    - Very low freeze point = branching and unsaturation (≤ - 40°C)
    - High auto ignition temperature (≥ 210°C)
    - Aromatics ≤ 20%
- **Diesel**
  - Requirements:
    - high cetane (≥ 40 required) = minimal branching
    - High energy density = some aromatics (≤ 30% allowed)
    - Low cloud point = branching
    - C_8-C_{21}
    - Low S (≤ 15 ppm, may get lower with new fuel standards)
    - No O allowed for non-FAME blends without EPA register/waiver/E-tests (big $)
- **Gasoline**
  - Requirements:
    - High octane (≥ 87) = branching, low MW
    - C_4-C_{12}
    - High energy density = more aromatics
    - Aromatics ≤ 40% (Europe), similar regulations coming for US
    - Low O, S (≤ 3.7%, 80ppm, may get lower with new fuel standards)
    - Required ranges for boiling, vapor pressure
    - Stable, no crystallization (durene +) or phase separation in water

cost of production and sale value

Hydrocarbon from Syngas or Biochemical Intermediates
Thesis Statement



— H_2O
H^+ Brønsted

Alkylates

M
+ H_2

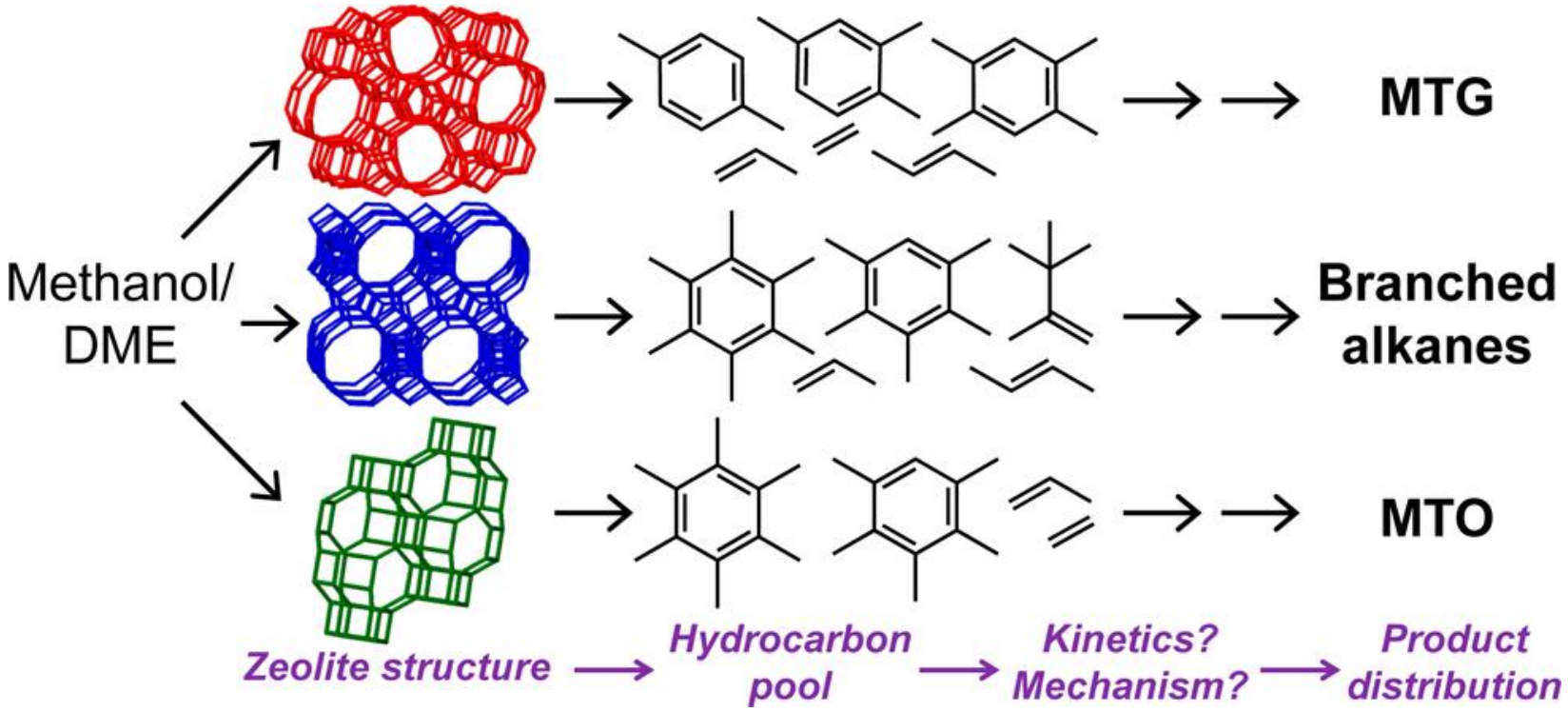
Aliphatics

H^+ Lewis
+ H_2

Oligimers

Reactive intermediate 'building blocks' can be used to selectively produce fuel-range hydrocarbons using novel acid and hydrogenation catalysts

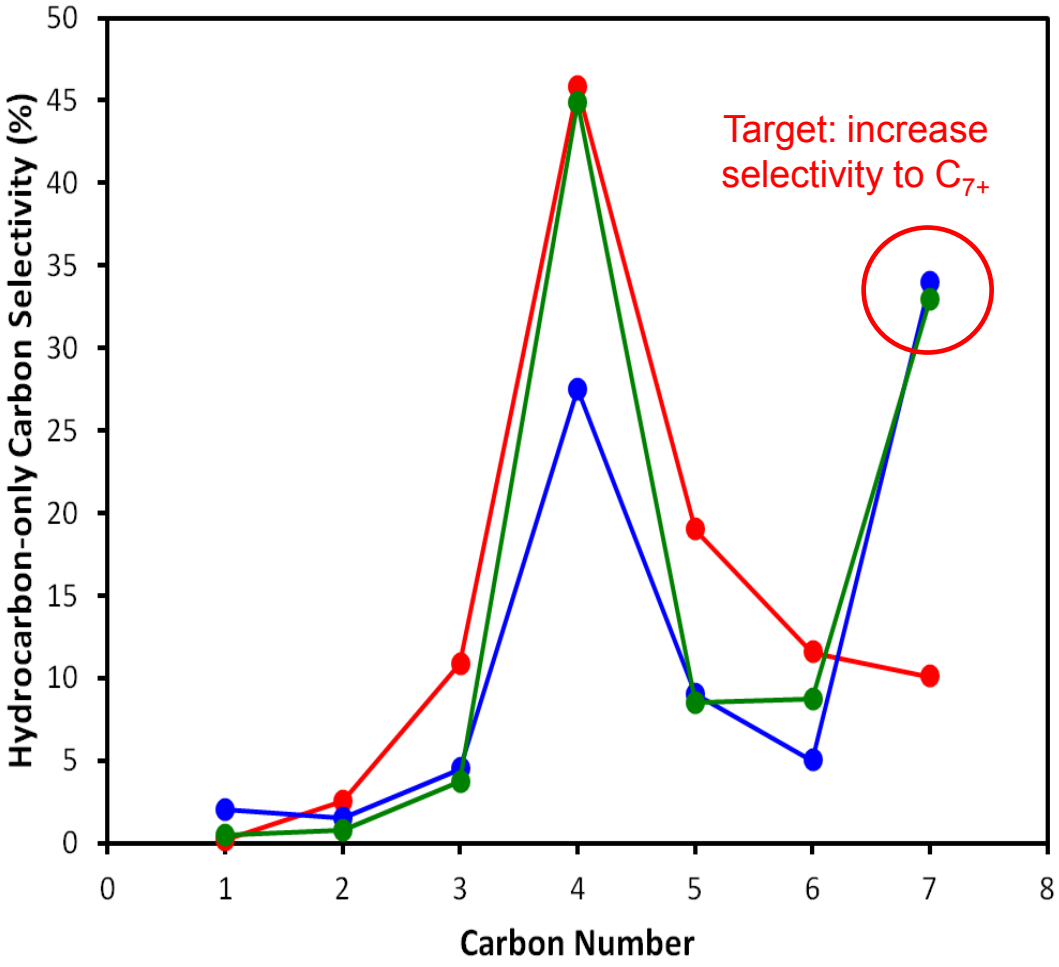
Example of Hydrocarbons from Syngas Intermediates
Hydrocarbons from Methanol



- Acidic zeolites produce aromatics, olefins and paraffins
- Product selectivity is controlled by process conditions
- Catalyst deactivation occurs by coke formation (short term) and dealumination (long term)
- *Other alcohols and ethers can also be used as reactants*

Example of System with Potential for Improvement

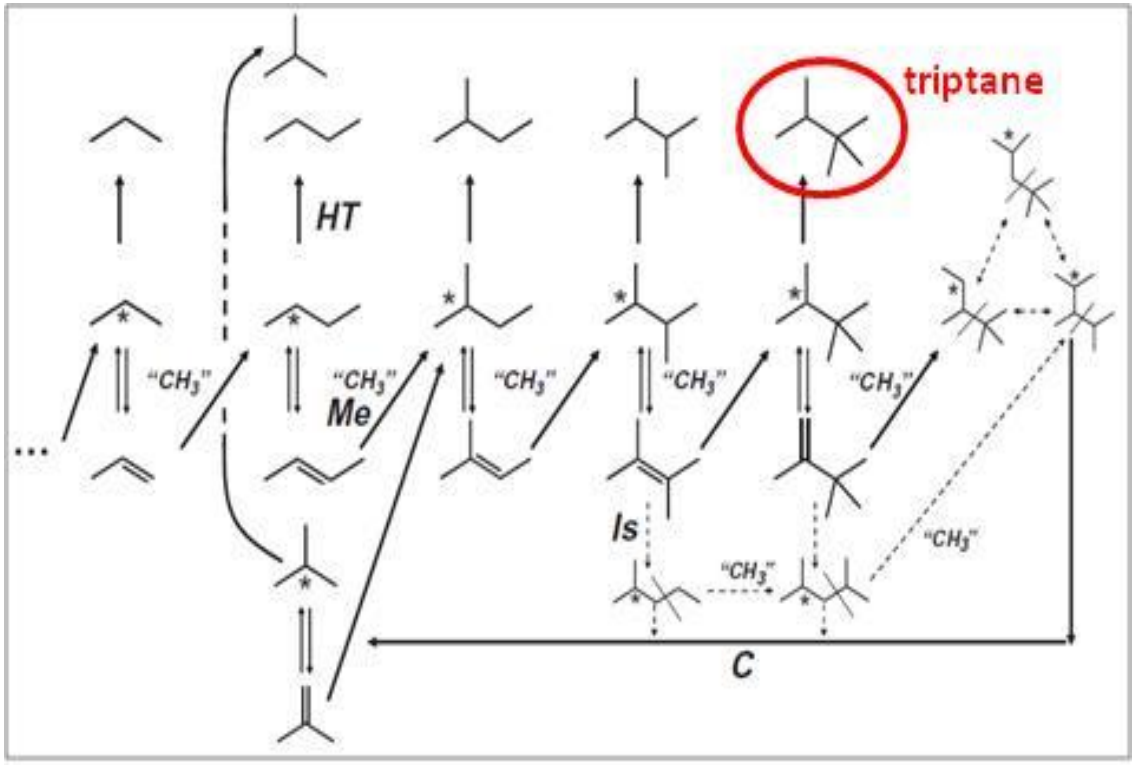
Increase Selectivity to C_7 Over Zeolite Catalysts



- Evaluating reaction pathway and surface chemistry to reduce cracking products (C_4)
- Investigating process intensification strategies to improve yield of C_7 and to reduce number of steps in reaction sequence

Example of Selective Hydrocarbon Synthesis

Reaction Pathway to Triptanes (C_7)



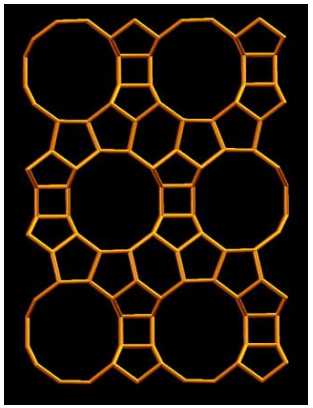
Scheme 1: Triptane synthesis mechanism;[3] '*' represents a reactive carbo-cation site where methylation or hydrogenation occur

D. A. Simonetti, R. T. Carr, E. Iglesia, *J Catal*, **285** (2012), 19-30

<u>Selectivity Control</u>

- Increase the methyl transfer to olefins vs. MTO
- Balance hydrogen transfer reactions
- Better catalysts by tuning of the active site, e.g. metal exchange and substitution

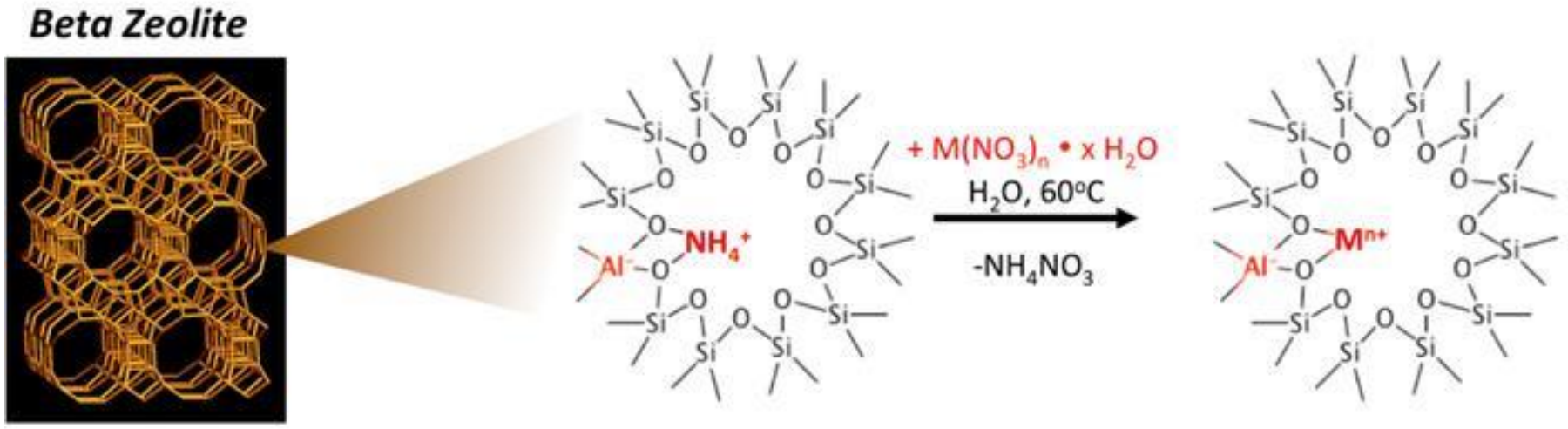
Zeolite BEA



Database of Zeolite Structures

Pathway to Selective Hydrocarbon Synthesis

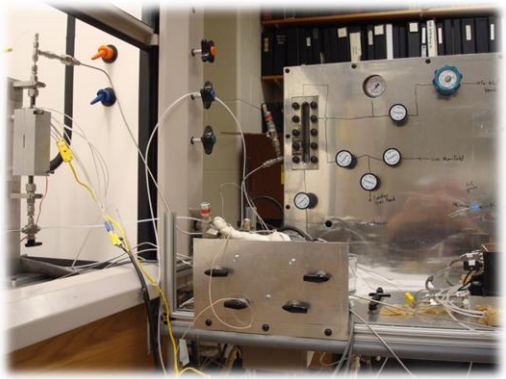
Novel Catalyst Synthesis

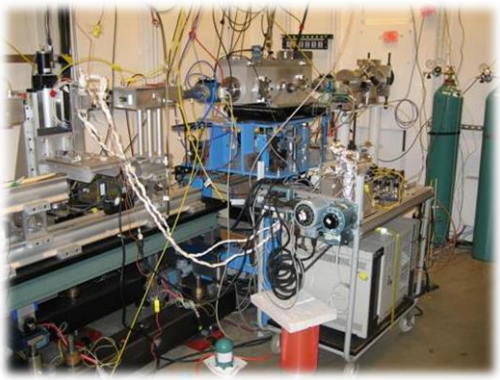


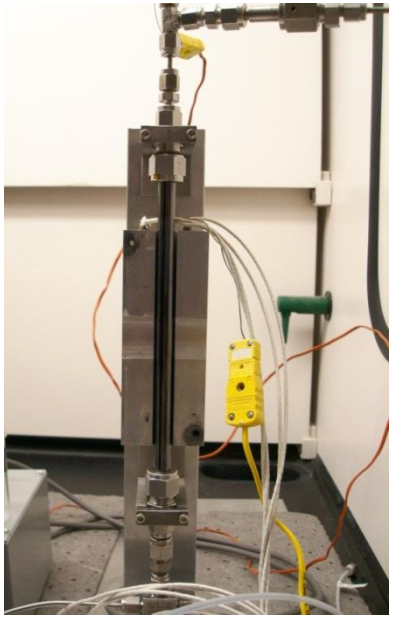
Scientific questions to address:

- What is the best method of metals addition, e.g., impregnation, ion exchange, other?
- What is the most effective metal ion?
- What is the structure of the metal ion under reaction conditions?
- What is the catalytic function of the metal ion, e.g., acidity, hydrogen transfer, MeOH activation, other?

Operando X-ray Absorption Spectroscopy is Used to Determine Catalyst Structure





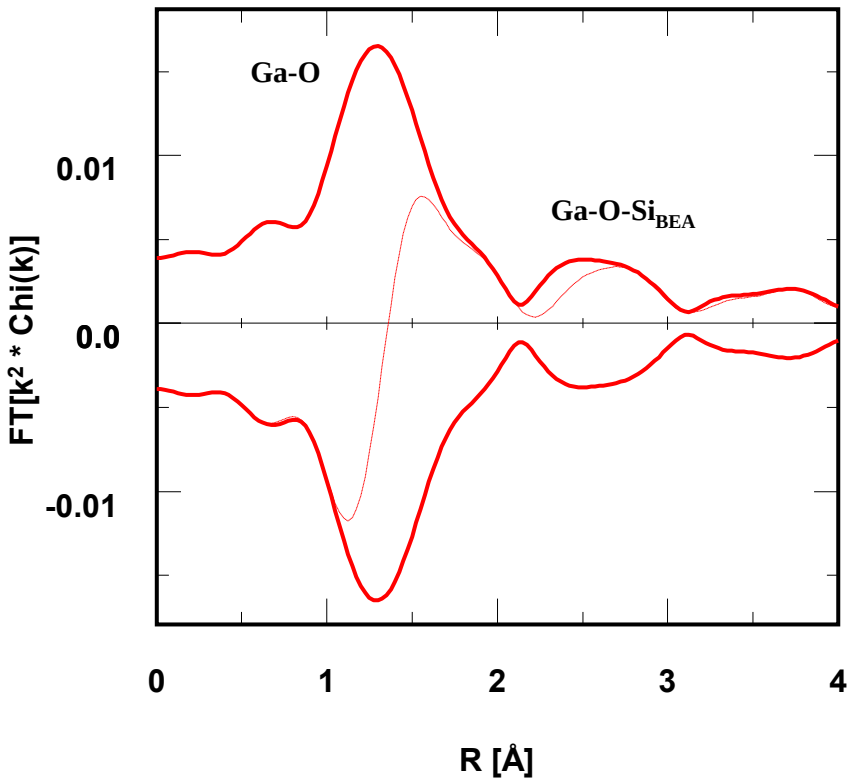


- Extended X-ray Absorption Fine Structure (EXAFS)
  - Types of neighbors, number of neighbors, bond distances
- X-ray Absorption Near-Edge Spectroscopy (XANES)
  - Oxidation states, information regarding adsorbates and surface coverage

- *In situ* plug flow reactor (up to 50 atm, 600°C, gas- or liquid-phase reactions)
  - Types of neighbors, number of neighbors, bond distances
- Developed by Argonne's Institute for Atom-efficient Chemical Transformations (IACT)
  - Office of Science-funded Energy Frontier Research Center (EFRC)

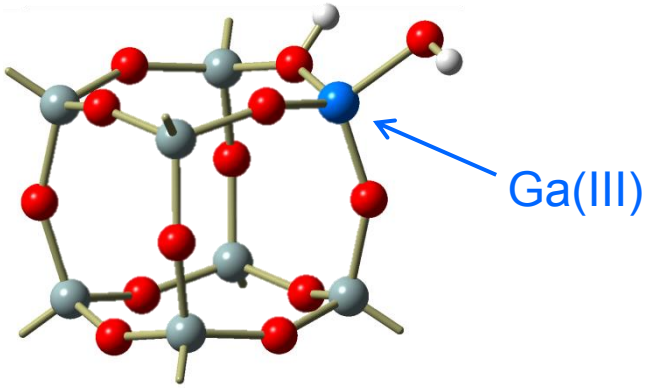
Example of Catalyst Characterization

Addition of Ga to Zeolite H-BEA

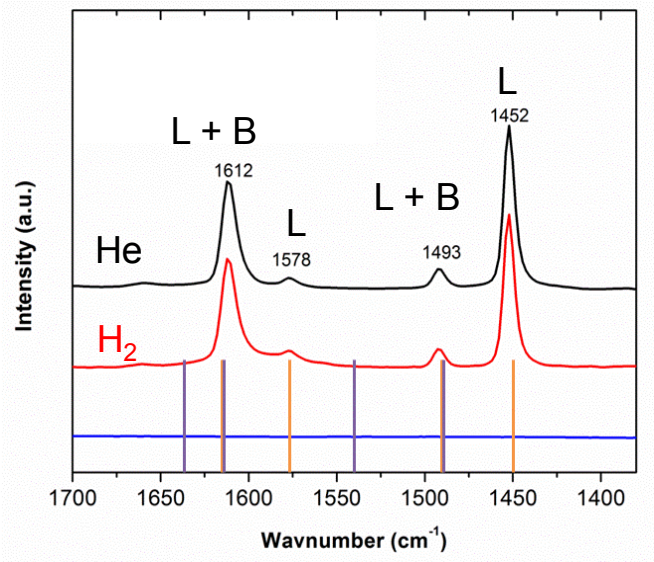


- Catalysts prepared by ion exchange and impregnation
- *In situ* X-ray absorption shows:
  - **Same metal oxidation state**
    - Tetrahedral coordination (low CN)
    - Short metal-oxygen bond length
  - Stable: does not form bulk oxides in He or O_2 and does not reduce in H_2 up to 500°C
- Adsorbs 2 equivalents of NH_3, showing that the material is a Lewis acid

Example of Structure-Function Relationships
Role of Ga on SiO_2



Infrared Spectra of Adsorbed Pyridine



Ga(III)/SiO_2
SiO_2
Lewis
Bronsted

- EXAFS of Ga on SiO_2 is identical to Ga-BEA, i.e. single site, Td Ga(III), Lewis acid
  - Thus, SiO_2 work is transferrable knowledge to other systems
- Catalytically active for hydrogenation
  - Increases hydrogen transfer activity
- Coordinates selectively to MeOH
- Doesn't oligomerize or crack olefins like H^+
  - Critical to tuning selectivity for molecule building instead of cracking

Relevance

- Addresses Thermochemical Conversion R&D Strategic Goal:
  *"Develop technologies for converting feedstocks into **cost-competitive** commodity liquid fuels such as renewable **gasoline, jet fuel, and diesel**."*
  - **Fundamental + applied approach** for efficient production of hydrocarbons at biomass scale
  - Research and development **guided by technoeconomic feedback**
  - **Combines core competencies at two premier DOE labs**: catalyst development (NREL) and molecular-level catalyst characterization (ANL)
- Project addresses two pathways:
  - M 6.13.1: Produce non-ethanol fuel from biomass syngas
  - M 6.13.3: Validate integrated process at pilot scale
- Contributes to BeTO portfolio of biomass conversion pathways:
  - Hydrocarbon synthesis from biomass via indirect liquefaction
  - Leverages significant investment in prior years (equipment, expertise, facilities)
  - **Combined with direct liquefaction platform, lowers the overall risk of meeting MFSP goals by 2022**

Success Factors

- Catalyst Characterization:
  - **Identify physical properties that influence selectivity**
  - Develop testable hypotheses for methods of selectivity adjustment
- Catalyst Development
  - **Leverage data from characterization** to design catalysts with improved selectivity
  - Minimize catalyst cost and complexity
- Process Design:
  - Integrate catalytic reactors within existing gasification/tar reforming designs and models
  - Combine unit operations and optimize heat flows to minimize capital and operating costs
  - **Configurations that maximize product yield** (gal/ton biomass)

Challenges

- Product selectivity
  - Avoid formation of oxygenated final products
  - **Produce molecules that are suitable as diesel and jet**
  - Minimize light gas formation
- Catalyst cost
  - Use of non-precious metals
  - **Robust and/or regenerable materials**
  - Straightforward and scalable synthesis
- Product yield
  - Minimize number of process steps, tail gas streams
  - **Minimize carbon loss to light gases and CO_2**
  - Minimize parasitic losses (compression, high temperatures, etc)

Future Work

- Characterize modified alkylation catalyst
  - Identify possible options to reduce byproduct formation
  - Develop improved activation protocols
  - Test improved activation procedures in a synthesis reactor
- Develop oligimerization catalysts
  - Target oligimerization of light olefins
  - Investigate mixed oxygenate intermediates
- Process intensification
  - Combine syngas intermediate and hydrocarbon syntheses in single reactor
  - Cascade reactions: hot→cool, high-pressure→low-pressure, etc.
- Rigorous characterization of novel synthesis catalysts
  - Leverage tools at the APS
  - Develop structure-function relationships

Detailed Milestones for FY13 and FY14

Due Date	Milestone Type	Milestone Title	Comments
12/21/12	E	Evaluate mixed alcohol catalyst performance with complete byproduct recycle	Complete, submitted for peer review
3/29/13	D	Process intensification for triptane synthesis	Complete
6/28/13	D	Extended operation of fuel synthesis catalyst	In-progress
9/27/13	D	Catalyst characterization at ANL	In- progress
12/20/13	D	Demonstrate alkylation of mixed alcohols using acid catalysis	Preliminary
3/31/14	D	Production of mixed olefins	Preliminary
6/30/14	D	Oligimerization of mixed olefins	Preliminary
9/19/14	E	Pilot reactor reconfiguration	Preliminary/in-progress
9/30/14	D	Catalyst characterization at ANL	Preliminary

Summary

- New project to develop catalysts and processes for cost-competitive production of hydrocarbon fuels from biomass-derived syngas
- Catalyst development focuses on
  - Using reactive intermediates as ‘building blocks’ for producing fuel-range hydrocarbons with high selectivity
  - Applying *operando* X-ray absorption spectroscopy to develop catalyst structure-function relationships
- Process development focuses on process intensification to reduce capital costs
- Leverages NREL expertise and capabilities in biomass gasification and related syn-gas chemistry with ANL expertise in catalyst characterization

Acknowledgements

ANL

Jeff Miller

Guanghui Zhang

Ted Krause

Seth Snyder

NREL

Adam Bratis

Mark Davis

Josh Schaidle

Jack Ferrell

Dan Ruddy

Susan Habas

Ming Pan

Jason Thibodeaux

Marc Pomeroy

Mike Sprague

Earl Christensen

Abhijit Dutta

Mike Talmadge

DOE Contracts:
DE-AC36-08-GO28308 (NREL)
DE-AC02-06CH11357 (ANL)

Additional Required Slides for Peer Evaluation

Responses to Previous Reviewers' Comments

New Project – Not Applicable

Recent Publications and Presentations

Publications

- Hensley, JE; Ferrell, JR, **2013** "Impacts of oxygenate recycle on product composition from a K-CoMoS$_x$ Catalyst" *Applied Catalysis A*, submitted for review.

Presentations

- Ferrell, JR; Hensley, JE, "Mixed Alcohol Synthesis on K-CoMoSx Catalysts: Recycle Studies." Presented by JR Ferrell at *Western States Catalysis Club annual meeting*, **April 19, 2013**, Provo UT.

Reports

- Hensley, JE, *2013* "Process Intensification for Triptane Synthesis," *NBC-11153*, National Renewable Energy Laboratory, Golden, CO.
- Hensley, JE, **2012** "Evaluation of Mixed Alcohol Catalyst Performance with Complete Byproduct Recycle," *NBC-11138*, National Renewable Energy Laboratory, Golden, CO.

Additional Slides

Glossary of Terms

ANL	Argonne National Laboratory
AOP	Annual Operating Plan
APS	Advanced Photon Source
BEA	Beta Zeolite
C_{x+}	Indicates molecules containing 2 or more carbon atoms. For example, ethanol is a C_2 alcohol, propane is a C_3 hydrocarbon, etc.
CN	Coordination Number
DOE	Department of Energy
EXAFS	Extended X-ray Absorption Fine Structure
Ga	Gallium
IACT	Institute for Atom-efficient Chemical Transformation (Argonne-led Energy Research Frontier Center)
He	Helium
IACT	Institute for Atom-efficient Chemical Transformation (Argonne-led Energy Research Frontier Center)
IDL	Indirect Liquefaction
MeOH	Methanol (CH_3OH)
MFSP	Minimum Fuel Selling Price
MTG	ExxonMobil's Methanol-to-Gasoline process
MTO	ExxonMobil's Methanol-to-Olefin process
MW	Molecular weight
NREL	National Renewable Energy Laboratory
O	Oxygen
P	Pressure
PMP	Project Management Plan
S	Sulfur
SOT	State of Technology
T	Temperature
TEA	Techno-Economic Analysis - includes mechanical process design, cost and revenue estimates, and sensitivity analysis
XANES	X-ray Absorption Near-Edge Spectroscopy

Future Work – Pilot Scale Testing