AFOSR BRI: Heterogeneously Catalyzed Endothermic Fuel Cracking

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Overview

Problem: Very high speed vehicles require additional cooling

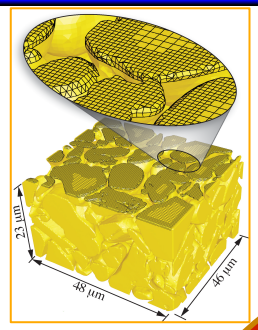
Potential Solution: Extract heat by heat transfer to incoming fuel and maximize heat transfer by promoting endothermic reaction

Technical Hurdles: Maximize ethylene production (desired endotherm) while minimizing coking

Project Objective: Develop and apply experimental and computational methodologies to develop fundamental understanding of coupled homogeneous–heterogeneous reactions and transport that can lead to improved design of fuel/catalyst/heat exchanger systems for cooling hypersonic vehicles

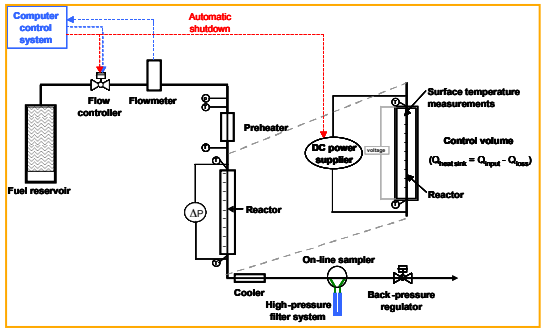
Impact: Potential to identify leads to system design required to operate hypersonic vehicles at Mach 6 or higher for repeated, extended missions

Integrated Iterative Approach

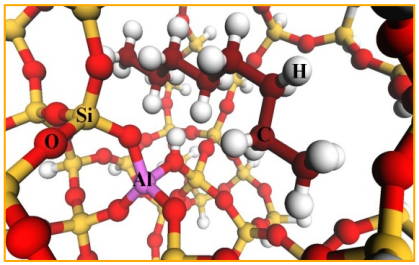


Microstructure measurement

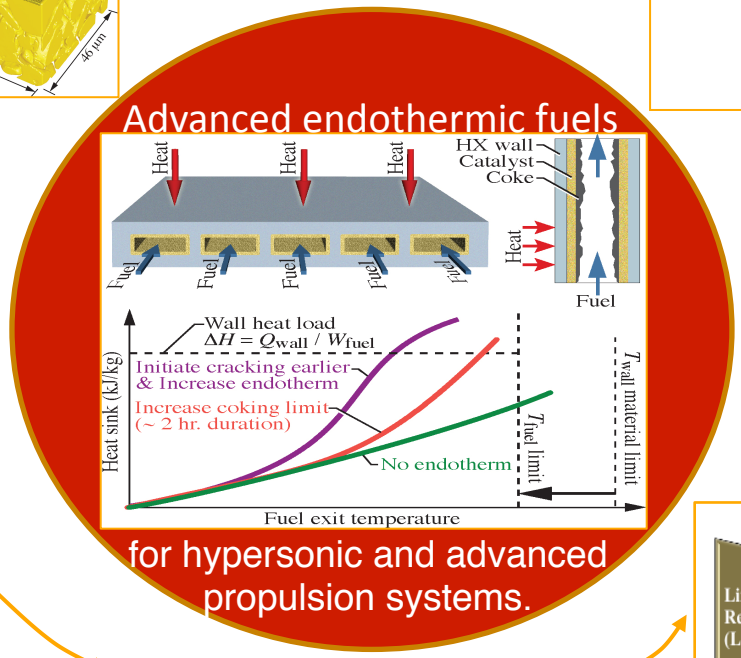
Fundamental knowledge and design criteria

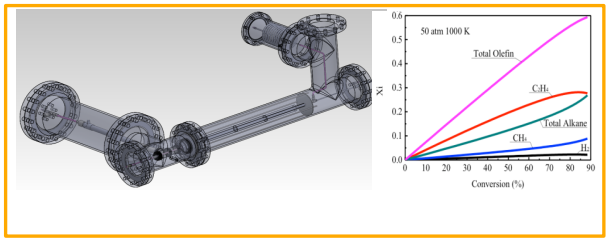


Heat exchanger simulation rig

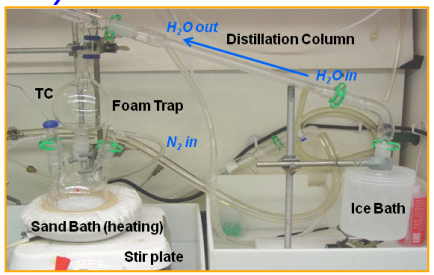


Atomic modeling of catalytic mechanisms

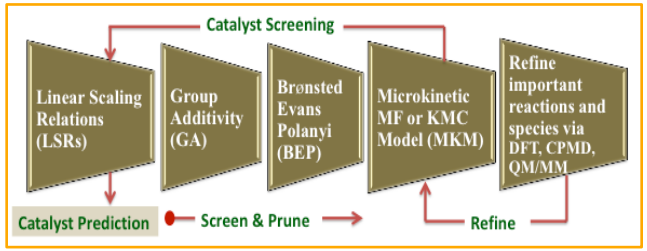




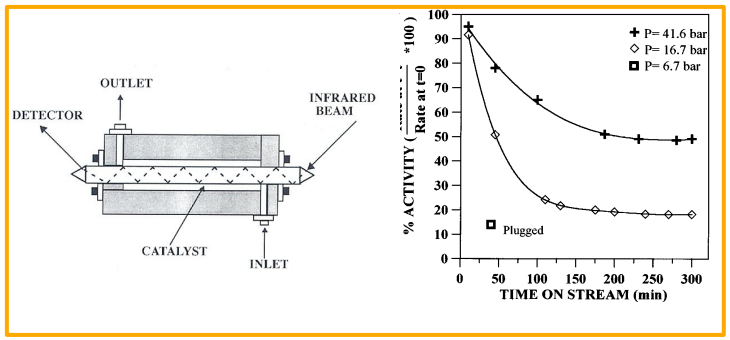
High pressure reactor kinetics



Catalyst synthesis and characterization



Hierarchical multiscale modeling framework



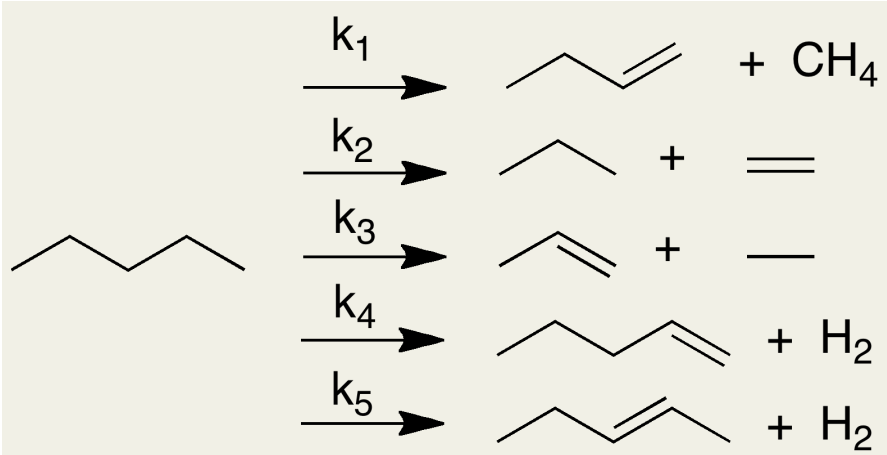
CIR-FTIR analysis of catalytic fuel cracking

Integrated Iterative Approach

Timeline	FY I		FY II	FY III
Phase Focus **Tasks**	**Phase I** Select fuel and catalyst	**Phase II** Mechanistic research on select fuel-catalyst system		**Phase III** Expand to other fuels and catalysts
MAKE and characterize select fuel-cracking catalysts	**UD/UTRC** Catalyst synthesis and treatment **UD** Catalyst structure and chemistry characterization **UTRC** Catalyst functionality characterization			
MODEL coupled interactions of gas and surface kinetics with transport processes	**UTRC** Catalyst mechanism DFT modeling **UD** Catalyst multiscale microkinetics modeling **CSM** Pyrolysis modeling **All** Coking simulation **CSM** Coupled gas-surface and microscale transport modeling			
MEASURE and characterize materials structure and kinetics behavior as related to catalyst performance	**CSM** Homogeneous reactor studies **UTRC** Catalyst mechanism supercritical CIR-FTIR/GC-MS **CSM** Microstructural characterization, FIB-SEM **UD** Catalyst differential isothermal reactor kinetics **CSM** Catalytic reactor studies			

Microreactor-Based Characterization of Kinetics of Model Catalyst Systems

- Reaction rate constants for simple molecules will be investigated using microreactors to determine rate constants and activation energies
- Supercritical reaction conditions similar to actual fuel channels
- Information to be fed to multi-scale models to verify model predictions
- Key catalysts variables will be explored
  - Particle size
  - Composition
  - Surface treatments to prevent coking



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Approaches to Minimize Catalytic Coke Formation

- Coke formation on catalyst particles is a major hurdle for the application of endothermic fuel cracking because coke reduces catalytic activity and decreases flow rates
- Coke formation will be investigated by aging catalyst samples at "accelerated" aging conditions (flow and temperature)
- Most likely coke grows out of catalytic sites on the exterior of the zeolite crystals
  - External catalyst sites (Al) can be removed by catalyst pretreatment with citric acid and other complexing agents
  - The activity of external sites can be decreased by silylation whereby siloxane moieties are deposited on external sites selectively

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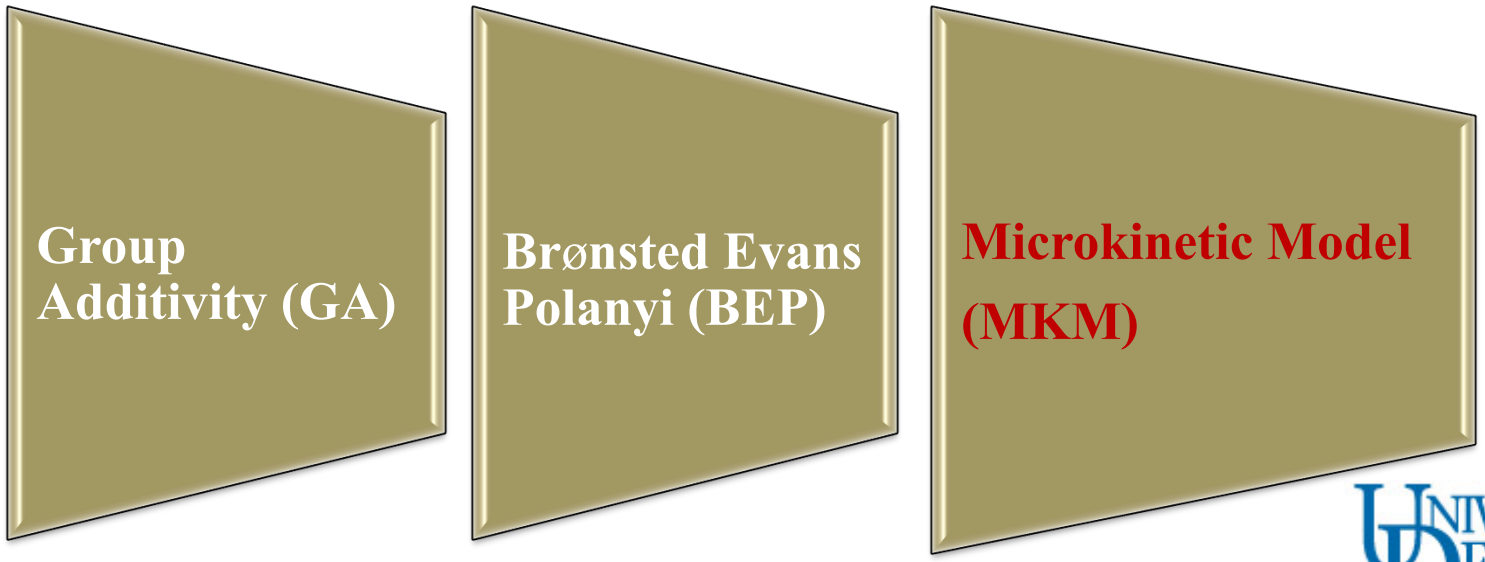
Overall Tasks of Surface Kinetics Modeling

- Develop microkinetic models for surface kinetics using hierarchical multiscale methodology
- Develop semi-empirical methods for zeolite catalysts:
  - Group additivity (GA) methods for the estimation of thermodynamically consistent thermochemistry based on a small group of DFT-based adsorbate free energies and entropies of formation on the active sites
  - Linear free-energy relations to predict reaction barriers of reactions in a homologous series from the thermochemistry



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Microkinetic Modeling Development

- Screen mechanism and eliminate energetically unfavorable adsorbates and reactions using semi-empirical (GA and BEP) methods
- Improve accuracy of estimates of the remaining (pruned) important thermochemistry and kinetics via DFT theory
- Include lateral adsorbate-adsorbate interactions for the dominant surface species
- Employ mean field microkinetic models but consider if necessary graph-theoretical kinetic Monte Carlo (KMC) simulations to account for spatial inhomogeneities
- Understand the effect of supercritical fluids on the interaction of hydrocarbons with the fluid and the active site of the zeolite
  - Employ Car-Parrinello MD (CPMD) or efficient quantum mechanics/molecular mechanics (QM/MM) MD frameworks and possibly classic MD (for understanding solvent effects)

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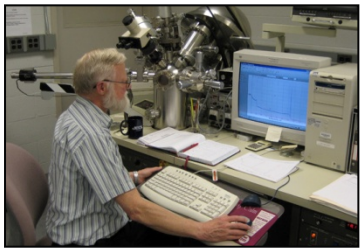
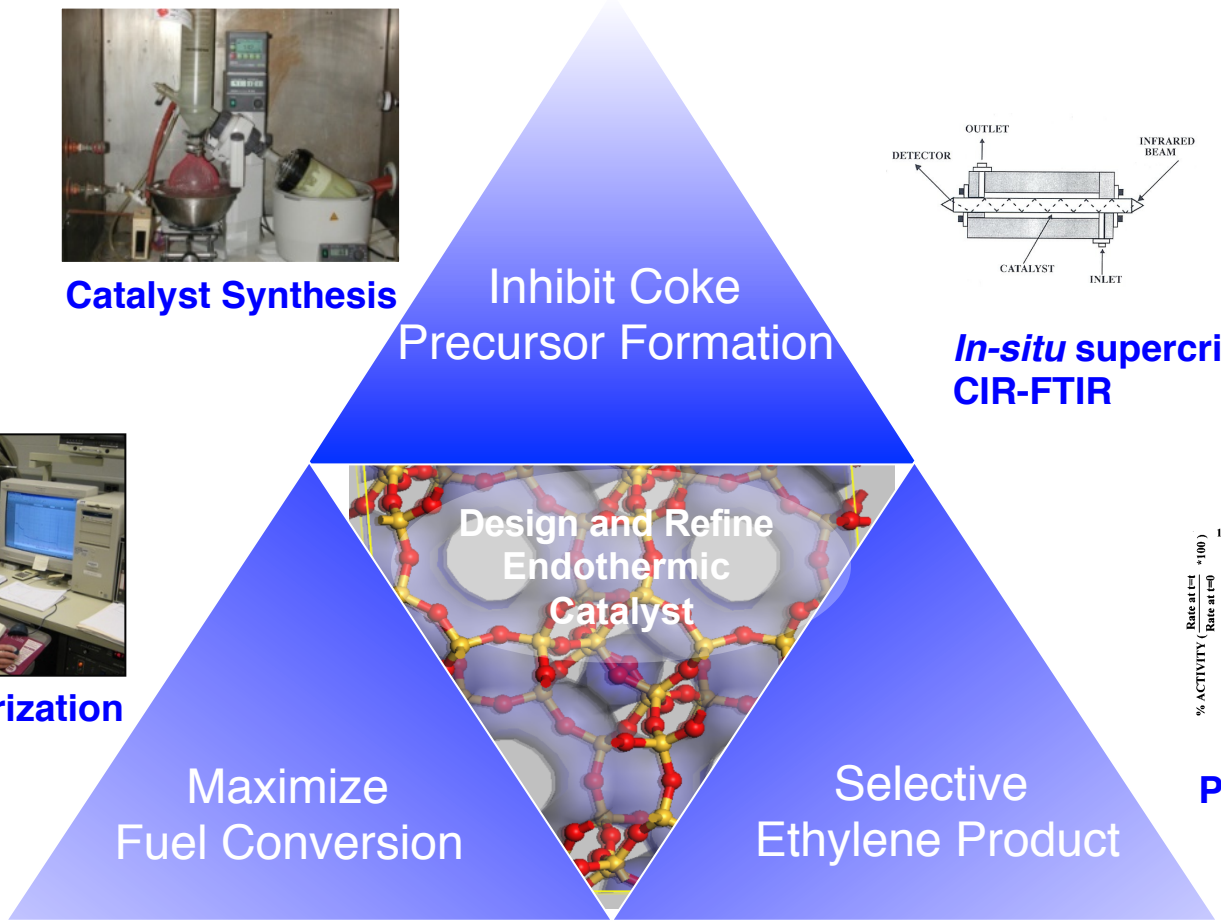
Cross-disciplinary UTRC Integrated Approach to Advanced Fuel Systems

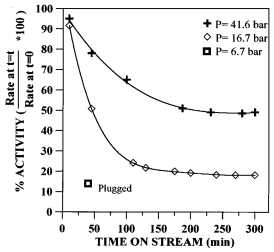
Catalyst Synthesis

In-situ supercritical CIR-FTIR

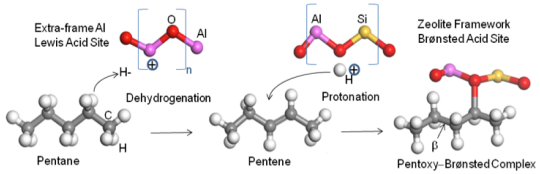


Catalyst Characterization





Product Analyses



DFT Atomic Modeling

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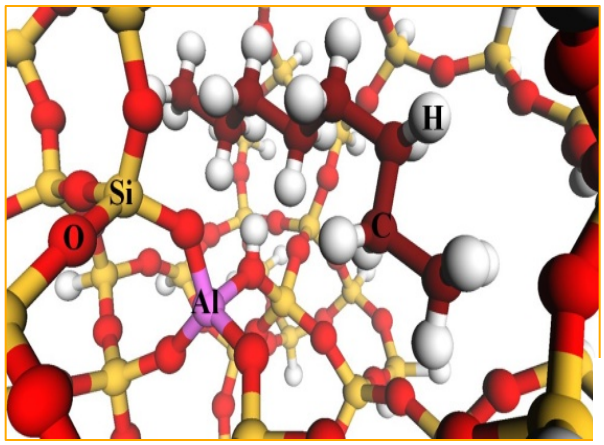
Atomic Modeling Insights to Guide Catalyst Design & Refinement

Hierarchical multiscale modeling iteratively coupled with experiments

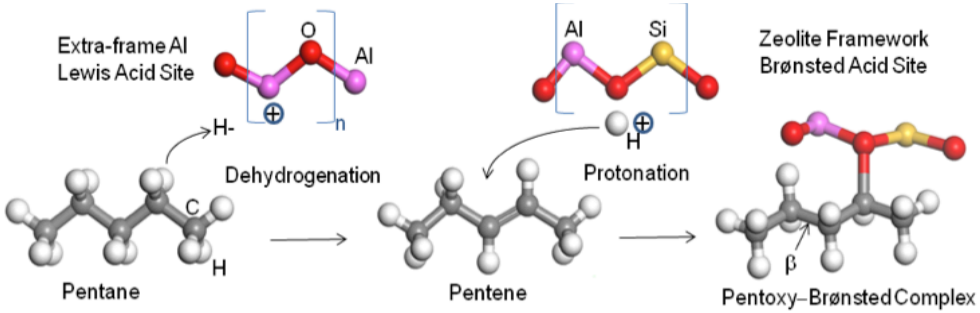


Fuel interacting with catalyst surface.

Two parallel modeling tasks:

a) Density functional theory (DFT) calculations: catalyst structures, functionalities, and reaction mechanisms (UTRC)

b) Develop accurate multiscale microkinetic models to describe heterolytic catalyzed fuel cracking behavior (UD)



Catalyzed hydrocarbon activation

UTRC DFT atomic modeling approach:

1) Survey adsorption and activation of fuels on catalysts with varying crystal-type, morphology, hydration, and reaction site compositions / functionalities.
2) Investigate influence of reaction site influence on fuel reactivity (isomerization, dehydrogenation, cracking, …)
3) Refine selected catalyst functionality to improve selectivity

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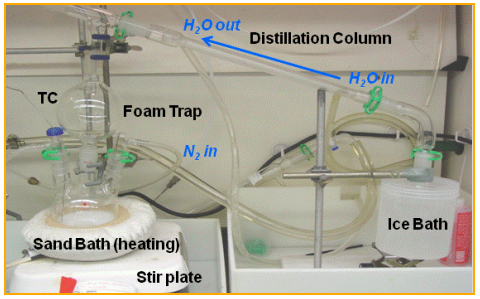
Develop Synthesis Methods to Enhance Catalyst Functionality

Coordinated UTRC-UD efforts will synthesize, mechanistically characterize, model, and design bifunctional catalysts for ethylene production:

1) identify optimum catalyst structure for high alkane cracking activity,
2) balance catalyst bifunctional reaction sites to increase light alkene yield,
3) explore catalyst functionality enhancements to minimize H^- transfer and coking.



Catalyst Synthesis and Functionalization

High Temperature Conditioning

FTIR Analyses of Catalyst Site Density

TPD Analyses of Site Strength

Catalyst slurries formulated for application of coherent thin coatings on interior reactor tube walls to maximize fuel access to active sites

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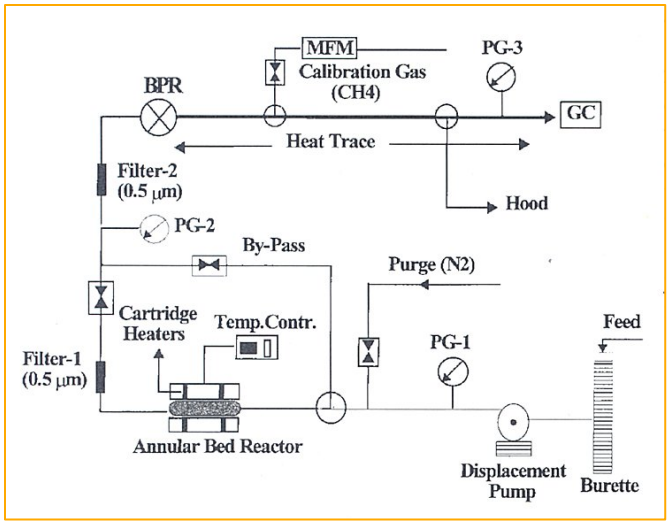
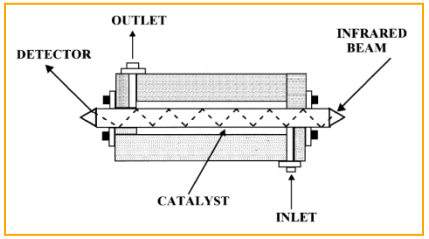
Real Time Observation of Catalyzed Fuel Cracking Intermediates

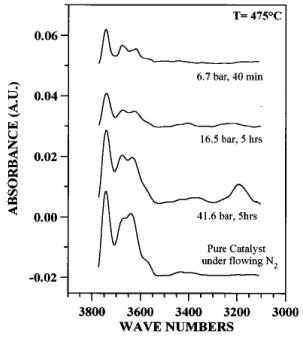
In-situ **cylindrical internal reflectance - Fourier transform infrared (CIR - FTIR) spectroscopy of surface reaction intermediates and product analysis by GC -MS**



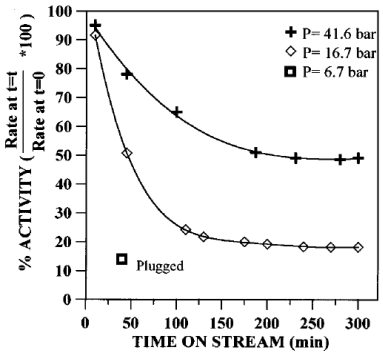
CIR - FTIR - GC Schematic



CIR - FTIR
Micro-reactor



CIR - FTIR Fuel
Intermediates



Catalytic Activity
from Conversion

- **Survey fuel reaction intermediates and analyze product selectivity to guide catalyst down-selection**
- **Characterize reactive intermediates in down-selected catalysts to develop insights into product selectivity and coking**

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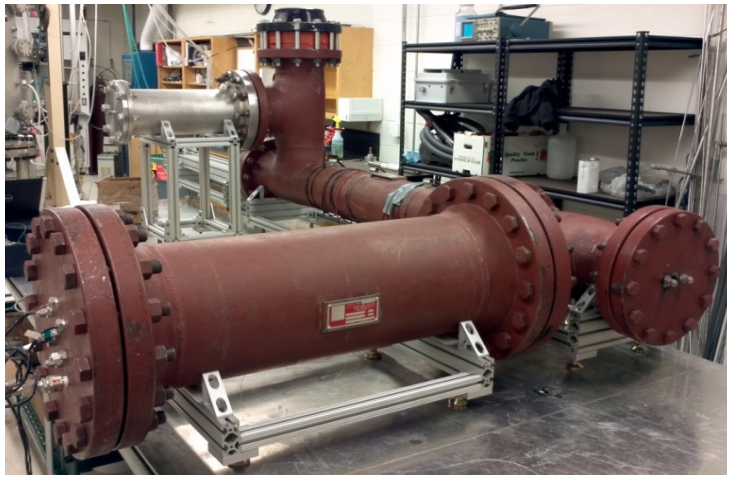
High Pressure Flow Reactor (HPFR)

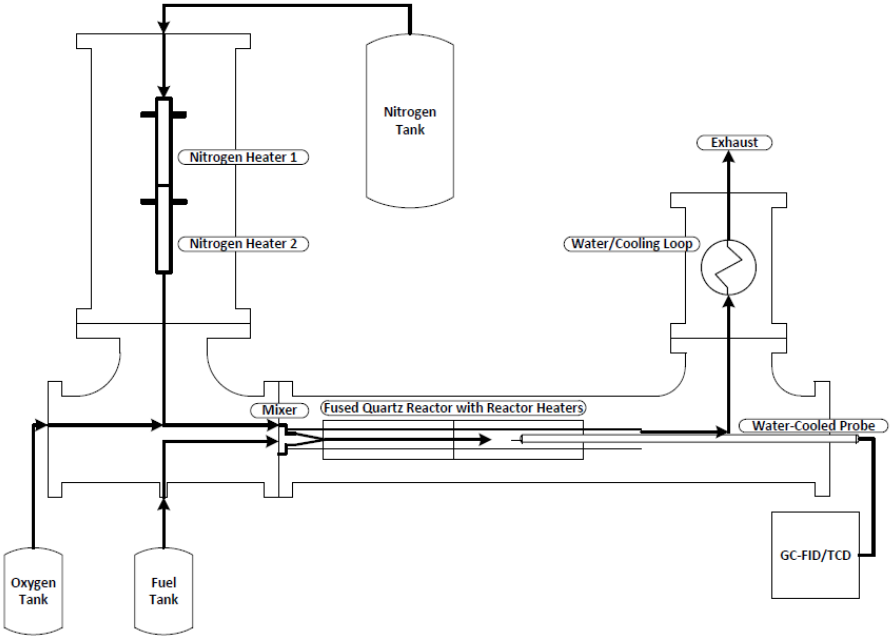
Capabilities:

- Fast residence times (~ 30 ms)
- Elevated pressures (~ 20 atm)
- Elevated temperatures (~ 1100°C)
- High flow rates (500 LPM at 850°C)
- Low volatility fuels (e.g. hexadecane)
- Water-cooled gas sampling probe



Gas Chromatography analysis:

- HP6890 dual injection chromatograph
- Thermal Conductivity Detector (TCD)
  - N_2, CO, CH_4, H_2, and CO_2
- Flame Ionization Detection (FID)
  - higher hydrocarbons (≥ C2)



Characterization of Gas-Phase and Coupled Gas-Phase/Catalytic Kinetics

HPFR experimental objectives:

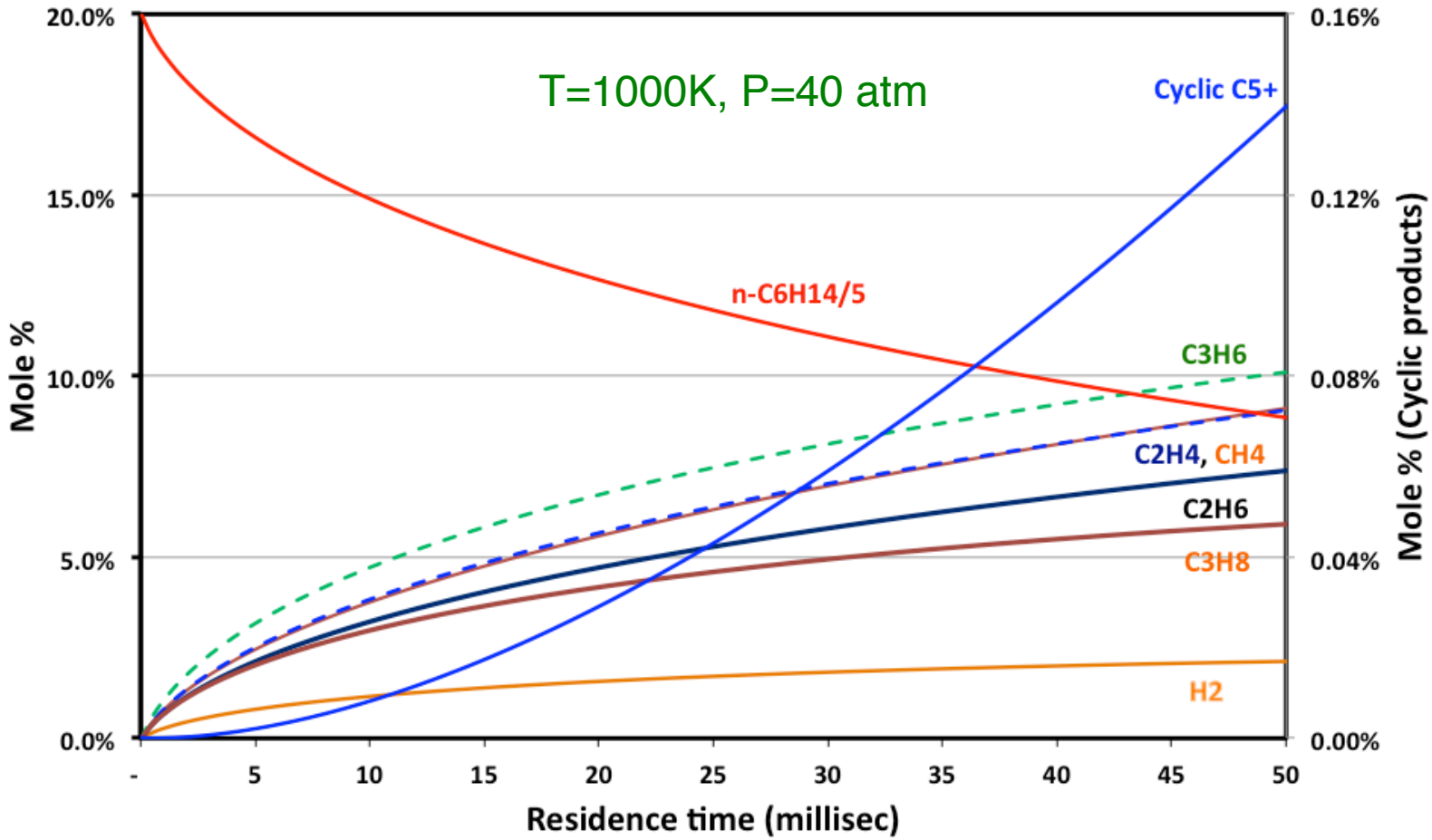
Gas-phase (quartz reactor)

- Characterize pyrolysis kinetics of model fuels at various pressures
- Specific focus on the kinetics of gas-phase molecular weight growth

Coupled gas-phase/catalysis (catalyst-coated reactor)

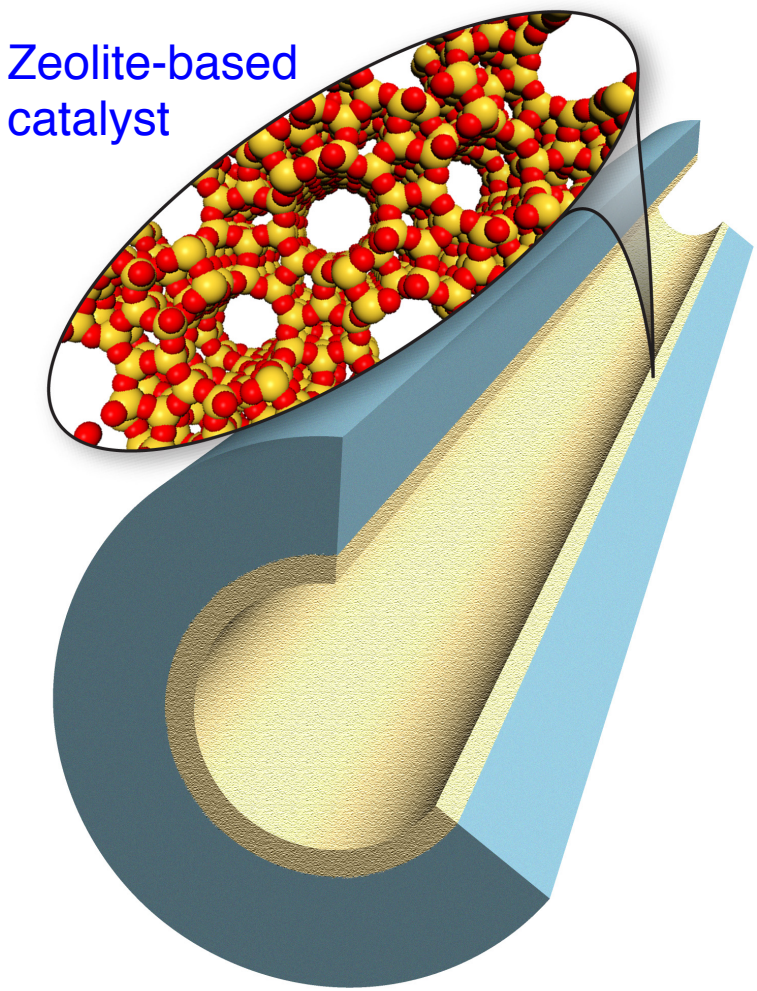
- Measured product distributions provide critical validation data for model development
- Explicit verification of ability to suppress coking
- Post-mortem of reactor cross section important to assess impact of reactions on affecting porous media transport

Gas-phase Chemistry Important At Supercritical Conditions



- Comparable production rate of olefins (desired) and alkanes (undesired)
- Potential for formation of gas-phase deposit precursors

Heterogeneous Catalytic Chemistry Is Intimately Coupled With Gas-phase Chemistry and Transport



Models assist fundamental understanding
- **Interpret laboratory measurements**

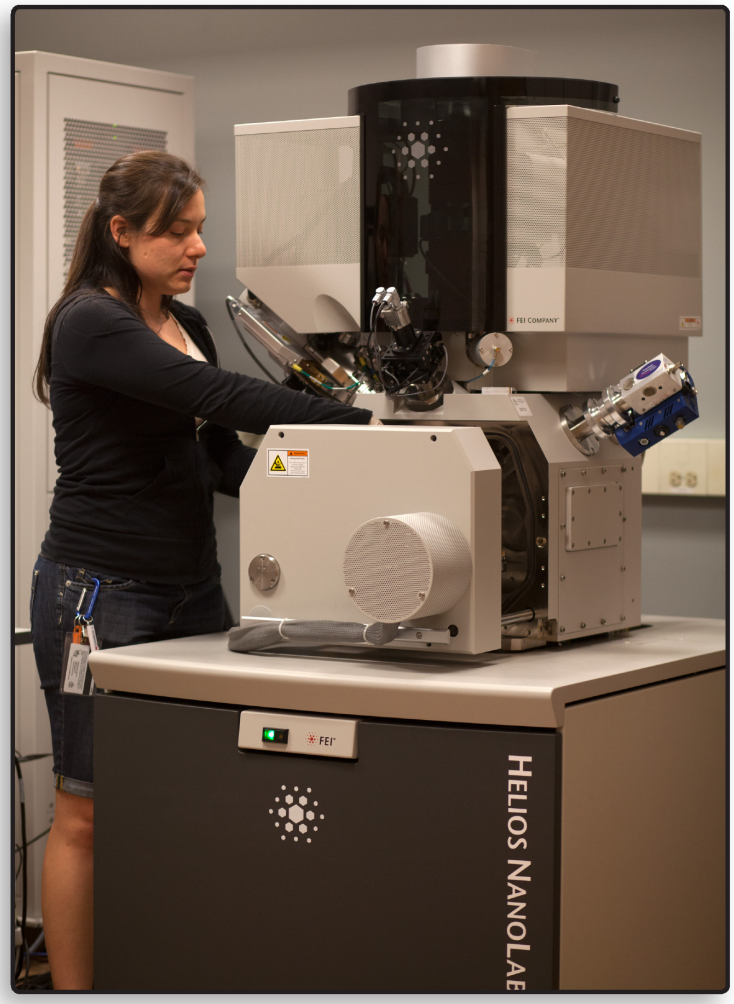
All models handle complex chemistry
- **Detailed gas-phase mechanisms**
- **Detailed surface mechanisms**
- **Multicomponent diffusion**

Interactions depend on flow conditions
- **Pressure, temperature, flow rates**
- **Fuel composition**

Alternative representations of fuel flow
- **Plug-flow produces efficient models**
- **Boundary-layer improves fidelity**

Catalyst and support structure is important
- **Initial models use effective area**
- **Microscale models improve empiricism**

FIB-SEM Capability for Nanoscale Measurements Provide Data for 3D Microscale Modeling



New FEI Helios NanoLab 600i

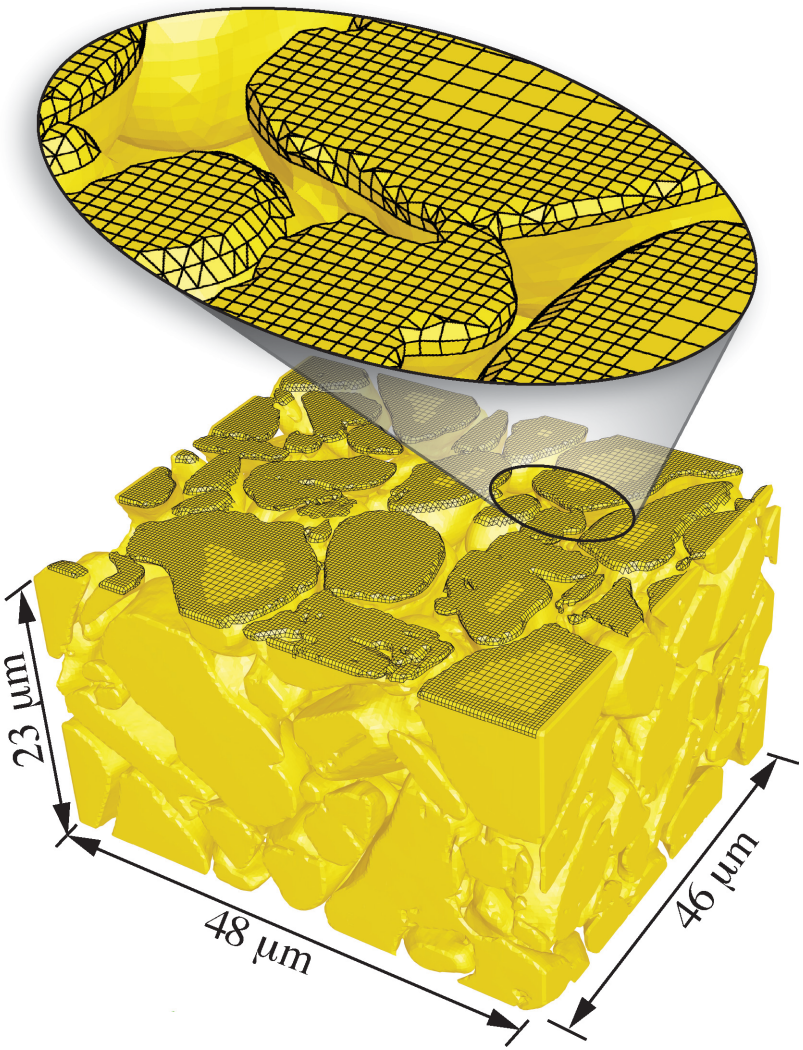
FIB-SEM reveals critical microstructures

3D microstructural models are possible
- Model exact pore structure
- Model diffusion within washcoat pores
- Understand catalysis at the microscale
- Understand carbon formation
- Improve performance predictions

3D microstructure reconstruction
- Typically 50 X 50 X 25 micron sample
- Typically 50 nm voxel resolution
- Clearly identify ceramic pore structures

Spatially resolved composition (EDS) and structure (EBSD)

Reconstructed Structure Is Discretized as the Basis For Detailed Computational Analysis



1M polyhedra cells, 4.3M faces, 2.9M nodes

Actual 3D geometry is discretized
- Solid phase and pore phase
- Robust algorithms developed

Model transport and chemistry
- Multicomponent diffusion in pores
- Heterogeneous catalysis on surfaces

Important questions to be addressed
- How does microstructure affect gas transport?
- Where does coke formation begin?
- How do deposits affect pore closure?
- What is the effective catalyst area?

Proposed Deliverables

- Integrated modeling methodologies for endothermic catalyst design
- Fundamental insights on impact of zeolite functionality on cracking and coking
- Experimental validation of kinetic models for gas-phase/surface-reaction interactions
- Impact of supercritical conditions on reaction kinetics and transport
- Measurement of catalyst microstructure
- Explicit account for impact of microstructure on transport and reaction
- Identification of path forward for effective fuel/catalyst/heat exchanger system for cooling hypersonic vehicles