Stationary Mixed Metal-Oxide Acid Catalysts for Endothermic Fuel Decomposition and Enhanced Ignition/Flame Holding Characteristics

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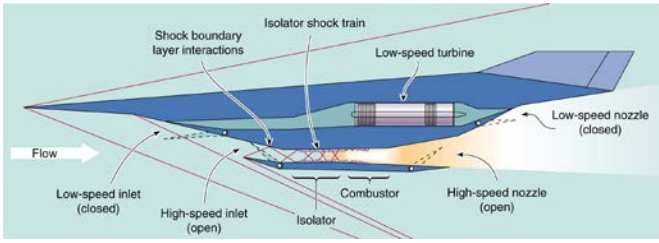
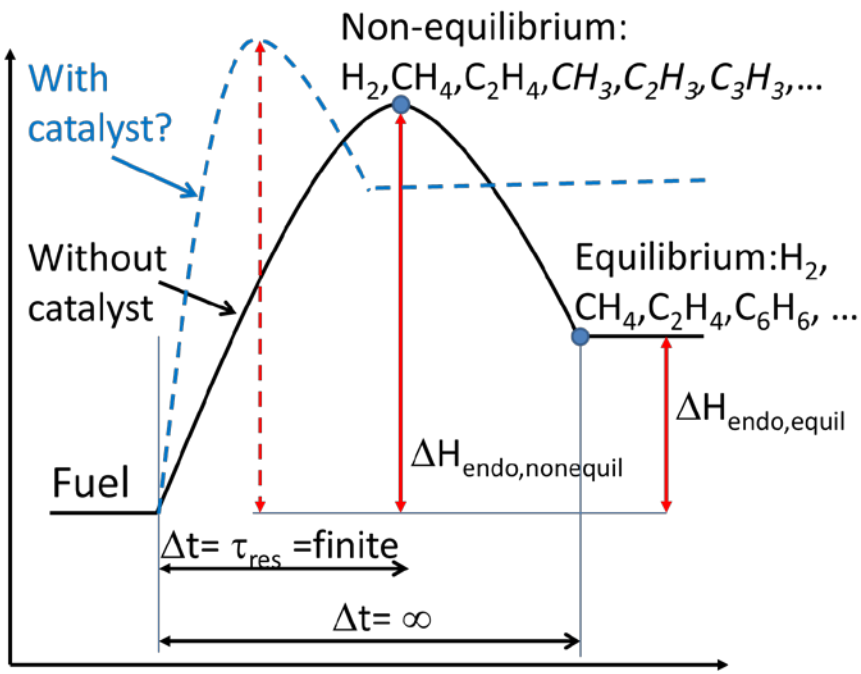
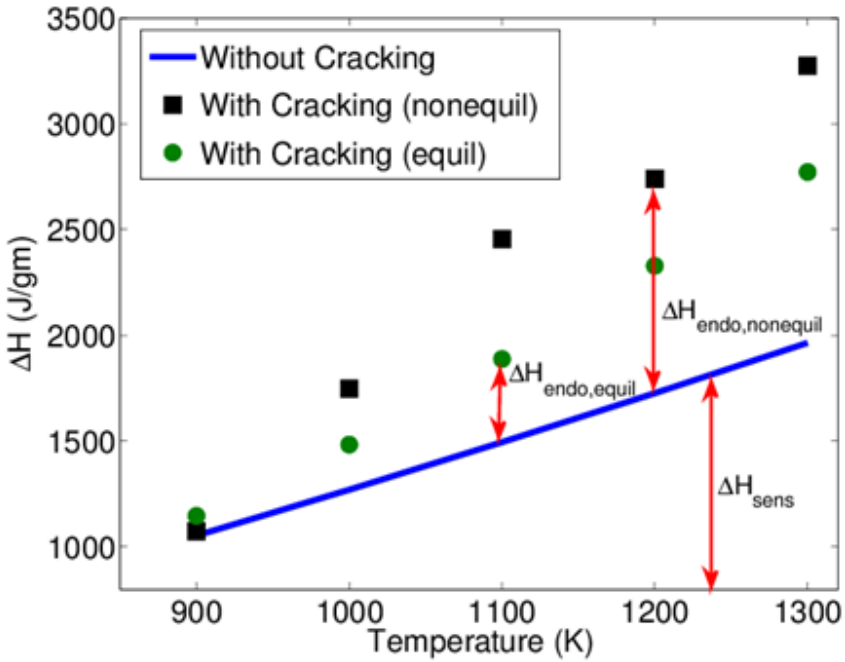
Background



- ***Enhanced cooling via endothermic cracking***
  - *Investigated since 1960's (UTRC and others)*
  - *Supercritical conditions for stable heat transfer*
  - *Limited understanding of catalytic effects, especially acid catalysts*
- ***Reduced ignition delay and enhanced operability***
  - *H2, C2H4, .. mixtures have much lower ignition delay*
  - *Limited knowledge about the role of radical species*
- **Challenges: coking /blockage of cooling channels**
  - Ni, Fe catalyzed coking – metal carbide formation
    - can be minimized by using silica coated surfaces
  - dehydrogenation promotes high PAH – instead promote C-C bond breaking

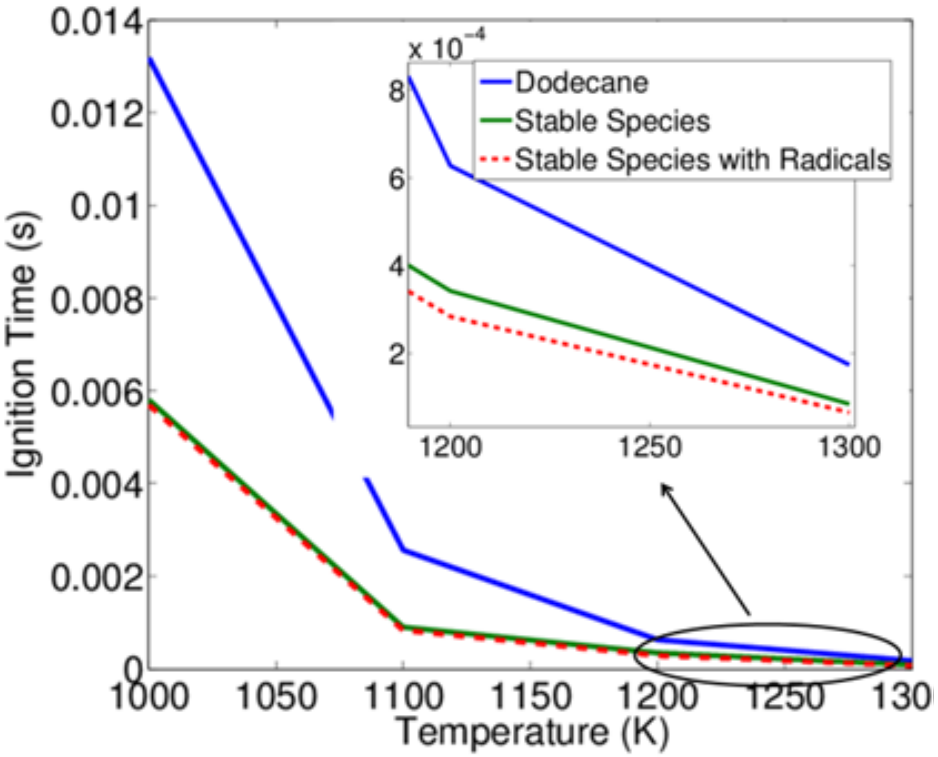
Our Hypothesis I

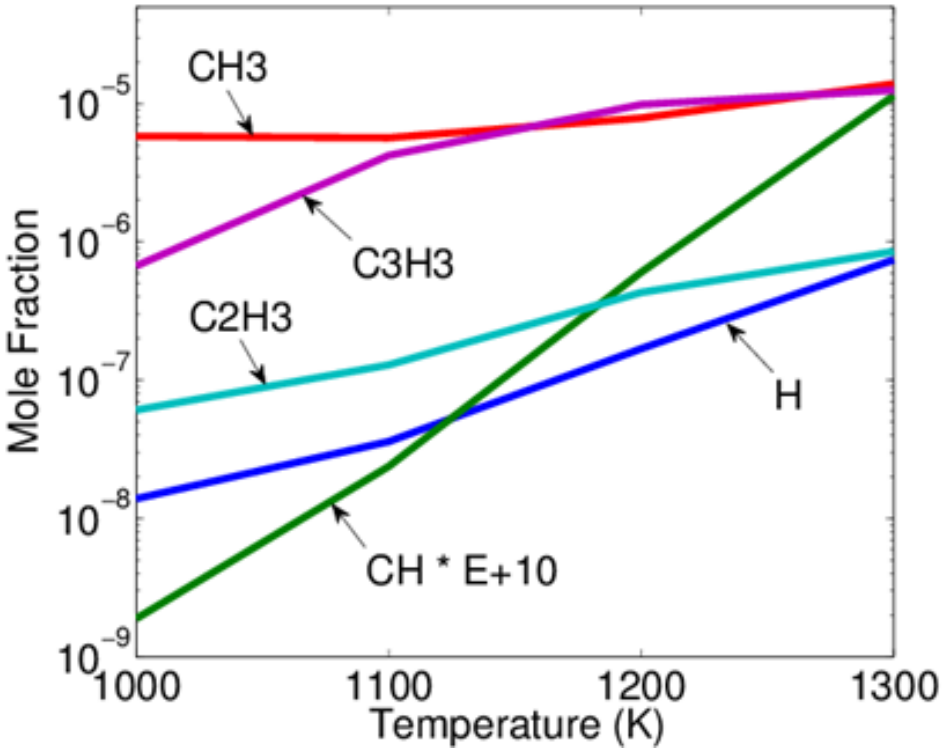




- Enhanced cooling capacity, especially when cracked species are in non-equilibrium state (i.e. short residence times in the cooling channels)
- Identify best **mixed metal-oxide** catalyst/fuel pairings?

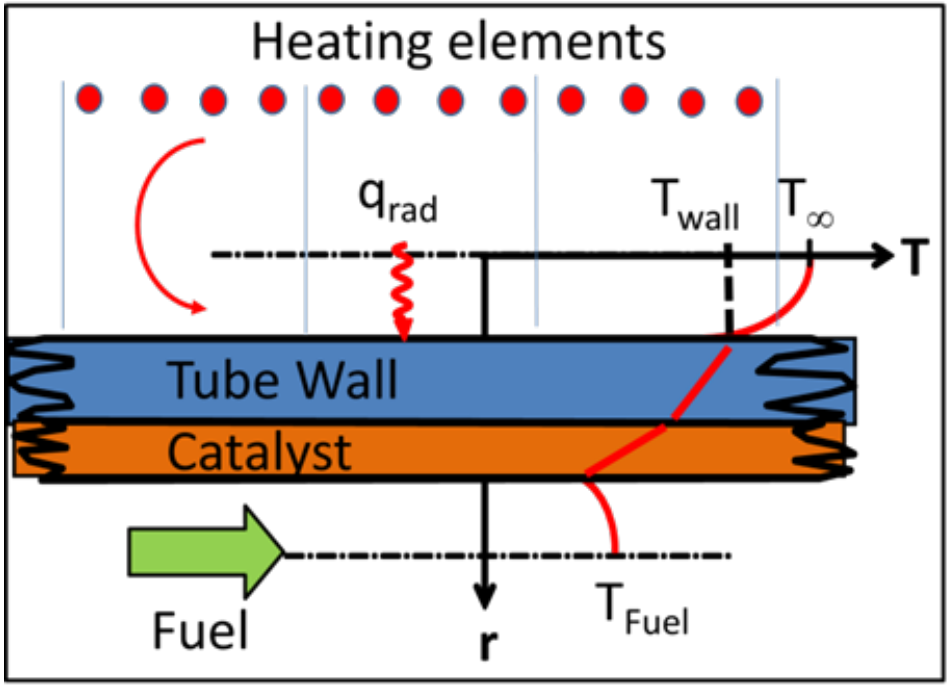
Our Hypothesis II

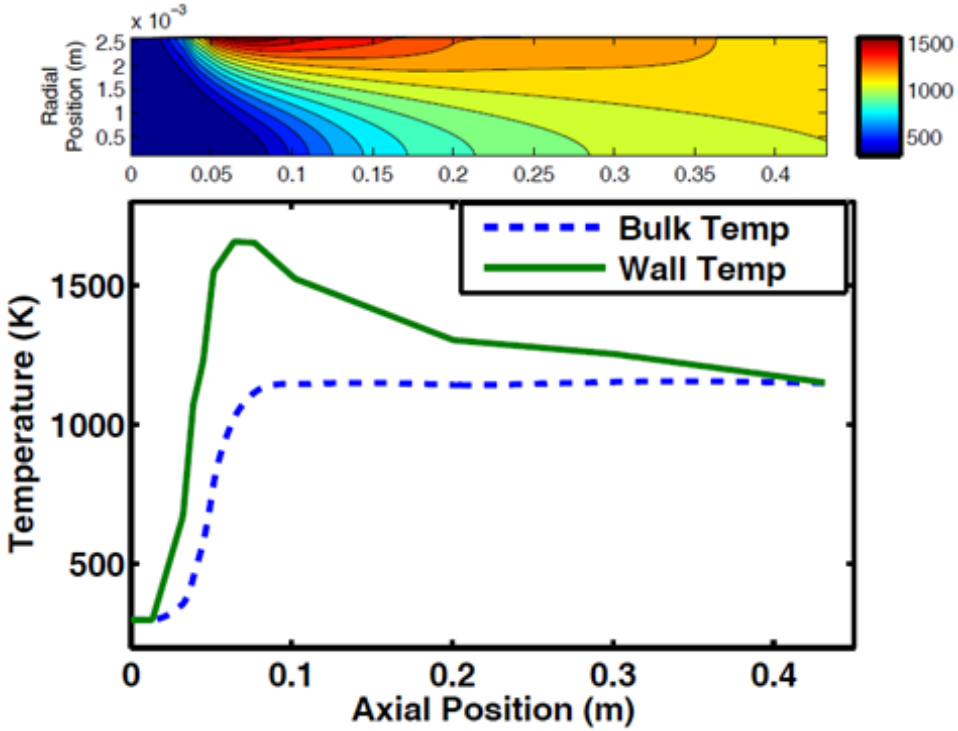




- Significant reduction in induction time with cracked fuel composition
- Radical species have non-negligible effect
- Experimental quantification, with and without catalysts

Our Hypothesis III



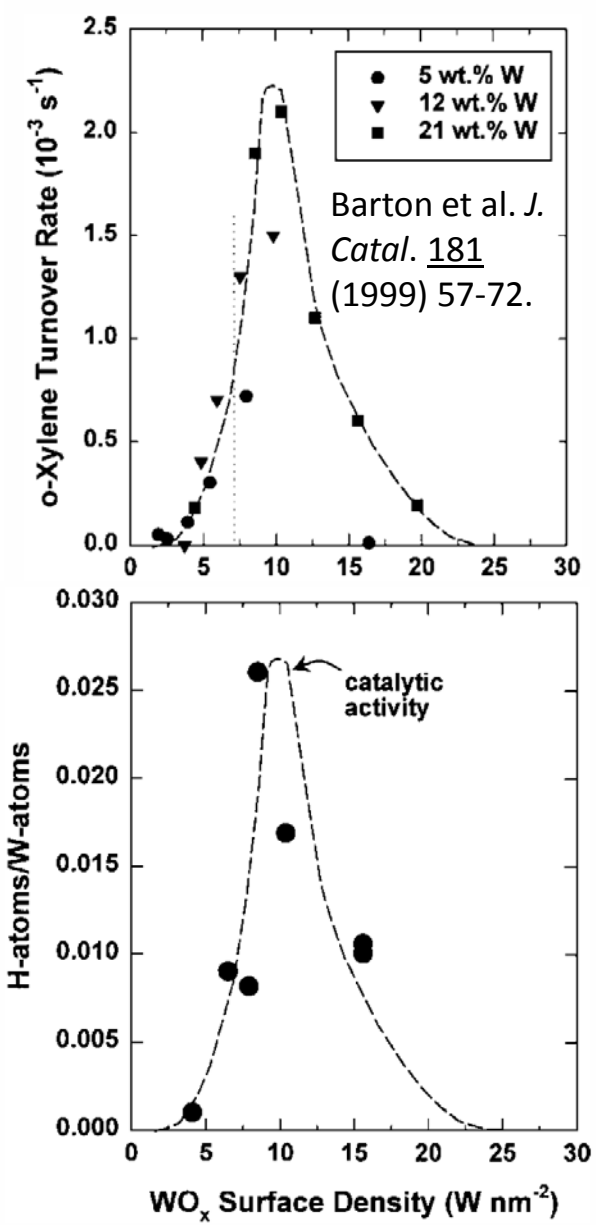


- Conjugate heat transfer can have a significant effect, especially in low residence time channels
- Depends on Peclet number for mass and heat transfer
- Need for multi-dimensional modeling?

Objectives

- **Explore mixed metal-oxide acid catalysts - synthesis/analysis/coating**
  - Withstand high temperatures
  - Pairing/tuning with specific fuels
  - Fixed bed/tube reactor experiments and first-principles chemistry
- **Characterize stable and unstable species on fundamental combustion properties**
  - For various pure fuels, temperature, pressure, residence times
  - Measurements at tube reactor exit as well as in-situ, with and without catalysts
- **Analyze conjugate heat transfer effects**
  - Analytical and computational investigations
  - Parameterization of heat transfer effects on cracking process

Mixed Metal-Oxide Acid Catalysts

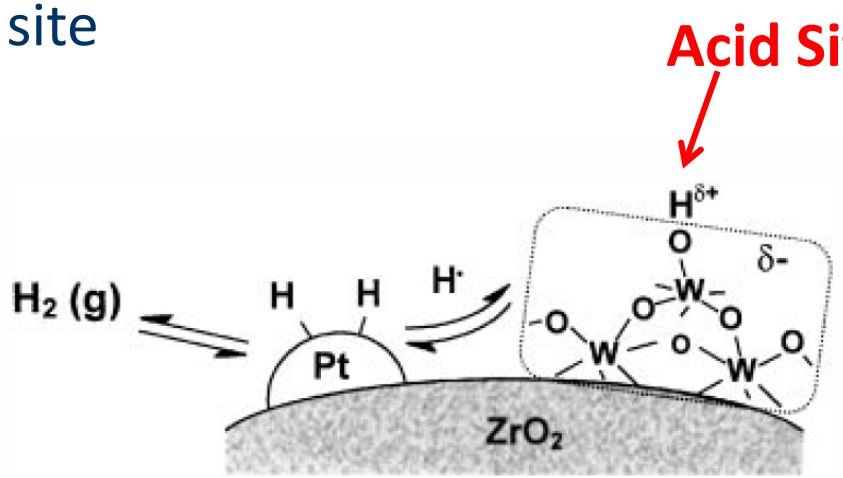


SUPPORTING EXAMPLE

Observed Behavior of WO_x/ZrO_2

(promoted with Pt)

Correlation of reversible H_2 uptake to catalytic activity of WO_x/ZrO_2 suggests the following model for the catalytically-active acid site



Partial reduction (eg. WO_3 to $WO_{2.9}$) and delocalization of negative charge in WO_x domains

Specific Goals on Catalysts

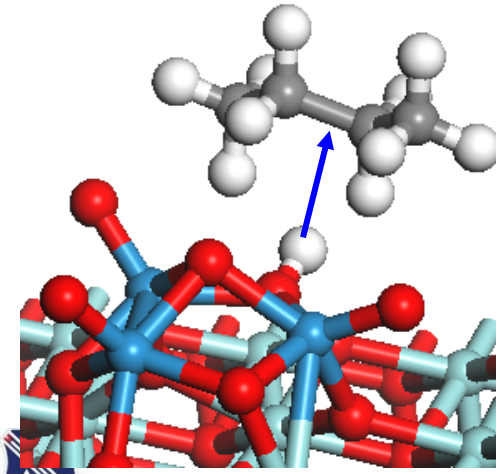
- **Synthesize high surface area catalyst powders**
  - WO_3 and Nb_2O_5 nanoclusters on ZrO_2, SiO_2, TiO_2, and Al_2O_3
- **Characterize acid catalysts to elucidate structure-property relationships that will enable catalyst design**
  - Spectroscopy (X-ray, UV-Vis, and IR)
  - Adsorption
- **Evaluate catalytic activity**
  - Catalytic cracking of jet fuel surrogate molecules under supercritical conditions in a fixed bed reactor
  - Deposition of carbonaceous residues
- **Use Density Functional Theory to Explore Catalytic Function**
  - Mechanistic understanding of acid site generation
  - Reaction path analysis of cracking and deactivation
  - Prediction of new <u>mixed</u> metal oxide clusters as solid acid catalysts

Close coupling between theory and experiment will facilitate discovery of new catalysts

Mechanism for Catalytic Cracking of Alkanes on WO_x Clusters Supported on ZrO_2

Preliminary Results

Reactant State



Proton Transfer from the acid site at WO_x/ZrO_2 interface

Energy is dictated by the release of the proton (Deprotonation Energy (DPE))

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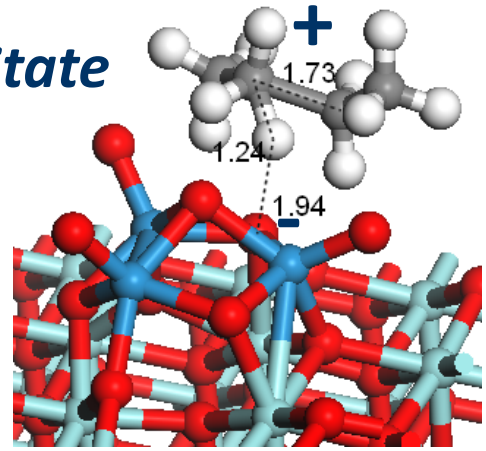
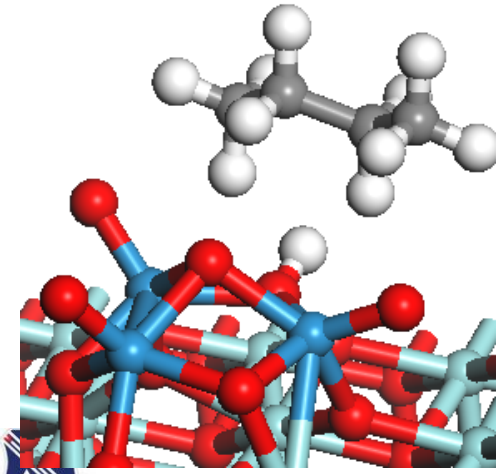
Transition State



Activation Energy
88 kJ/mol

$(\Delta E_{act} = DPE + \Delta H_{gas\ phase\ rxn} - \Delta E_{int} + \Delta H_{ads})$



Insertion of Proton Into C-C bond.

Formation of an ion pair
(Carbeniun Ion + $WO_x/ZrO_2(-)$)

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Mechanism for Catalytic Cracking of Alkanes on WO_x Clusters Supported on ZrO_2

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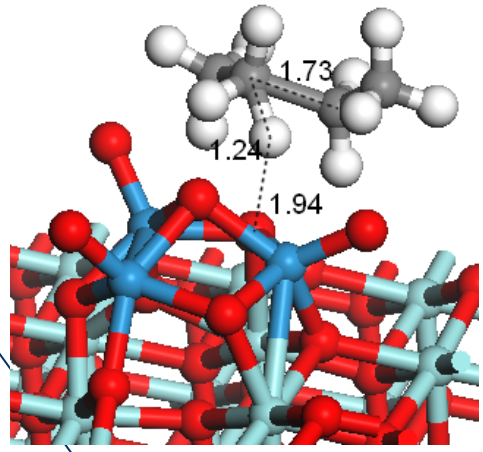

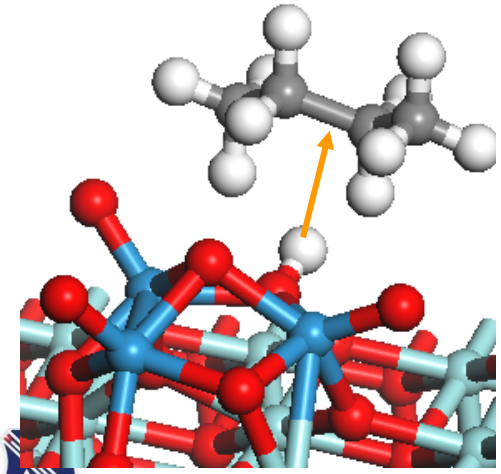

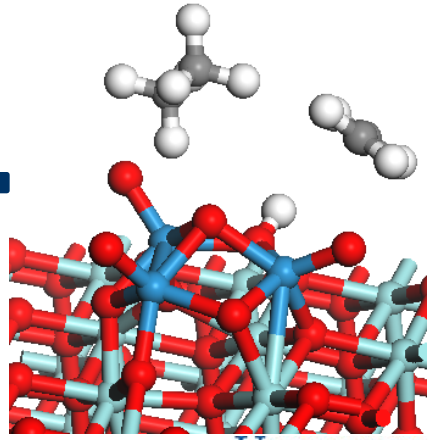

Deprotonation of the resulting alkoxide to form alkane and olefin products.

Overall reaction energy (53 kJ/mol)

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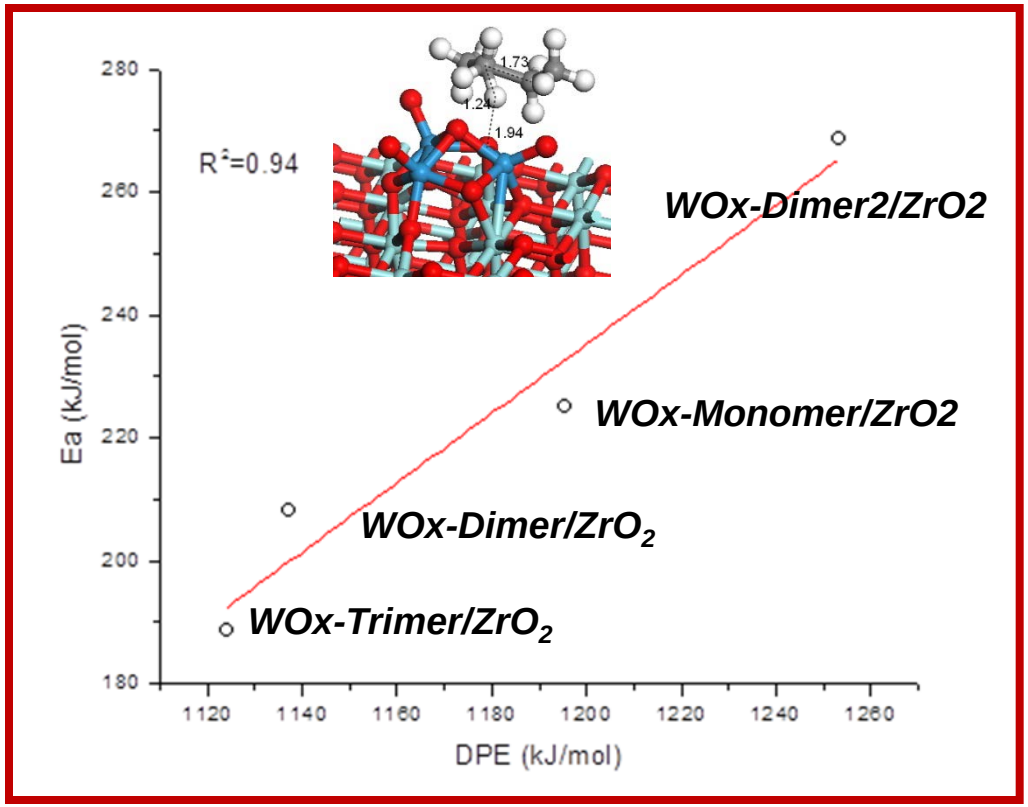
Cracking Activity is Related to the Energy Required to Deprotonate the Acid

Preliminary Results

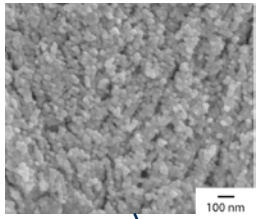
$$\Delta E_{act} = DPE - \Delta E_{int} = const. \times DPE$$

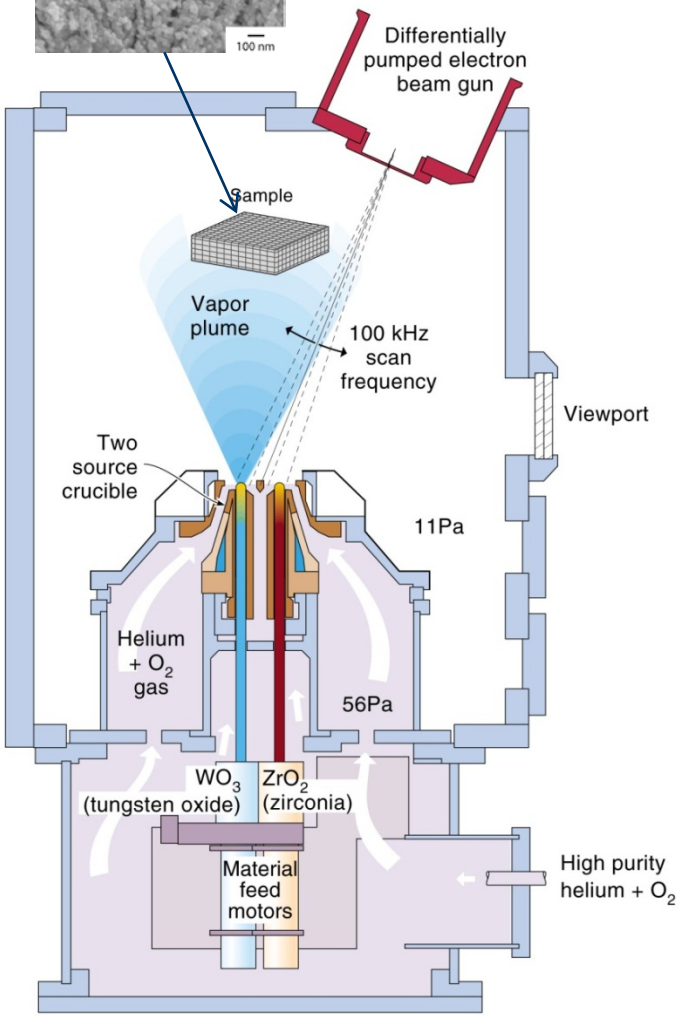


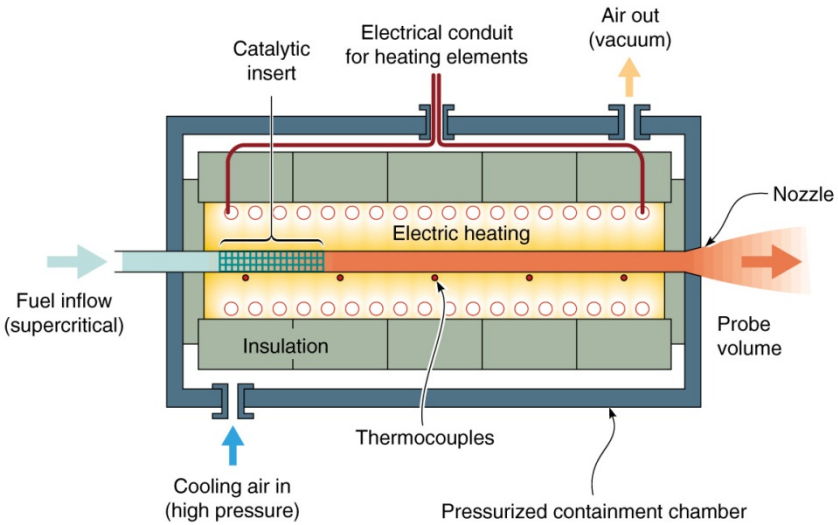
- Catalytic reactivity is linearly related to how strong the acid proton is bound for different tungstated clusters on zirconia
- Deprotonation Energy provides a direct probe of catalytic activity
- DPE will be used to rapidly screen many different catalysts to identify the most active materials

Directed Vapor Deposition Approach

- Better control of the catalyst stoichiometry and clustering (eg. WO_x density on ZrO_2)
- Key features of the device:
  - 60 kV Electron beam gun
  - Multiple metal-oxide sources (up to 6)
  - Variable dwell time to control the stoichiometry
  - Vapor carried in a supersonic jet of inert
  - Sample can be manipulated for uniform or non-uniform coating

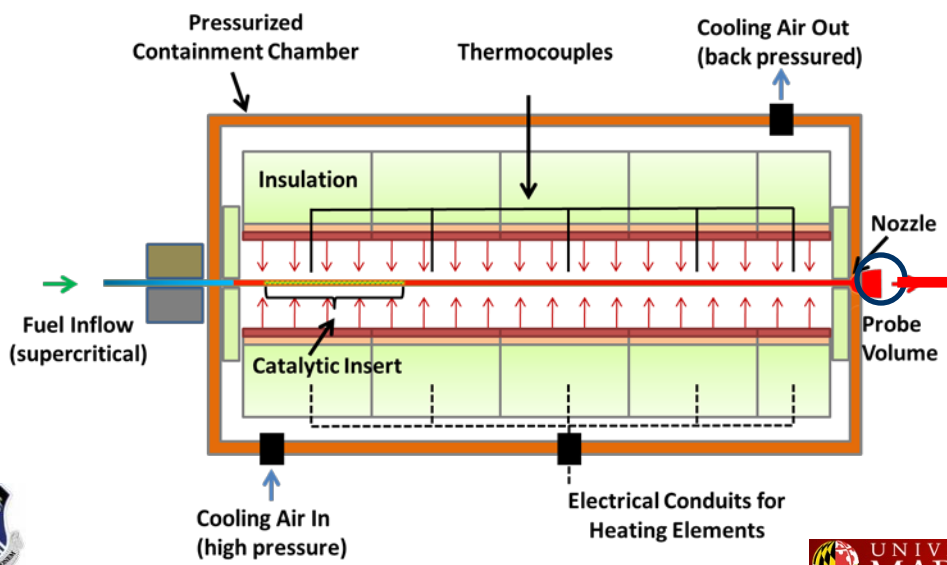


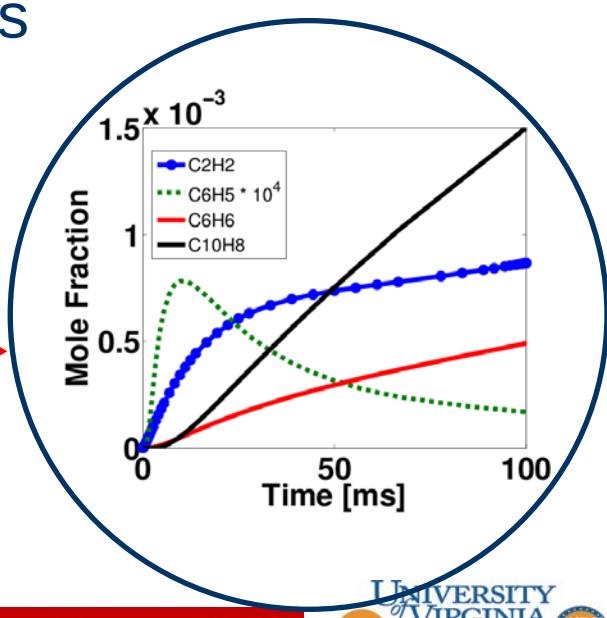




Measurement of Cracked Species Composition and Modeling

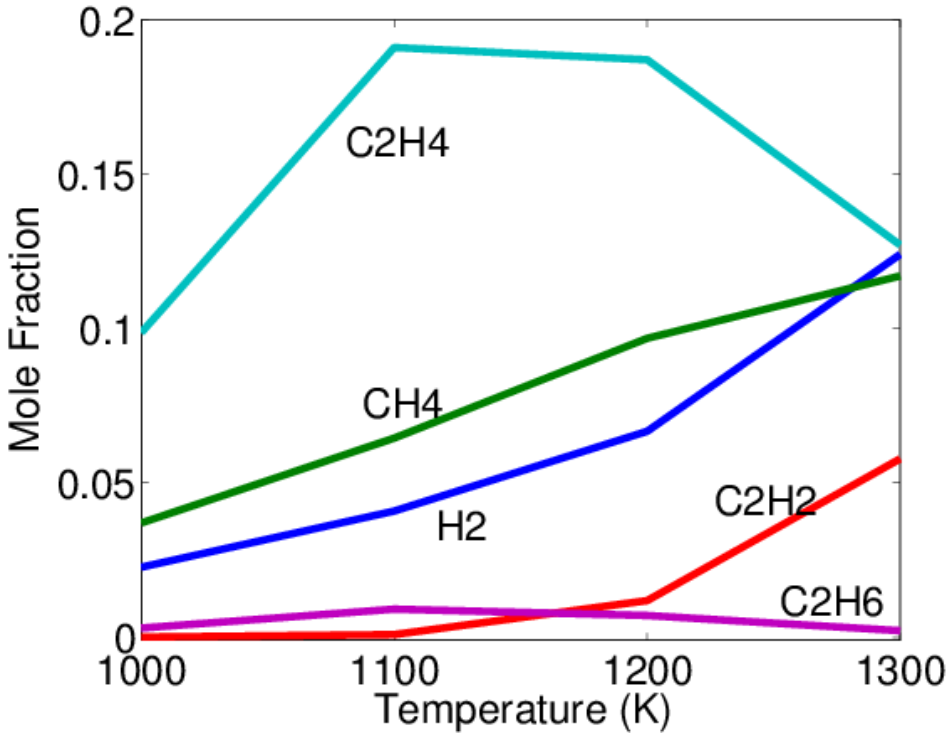
- Two types of reactors:
  - long residence time fixed-bed reactors (~ sec-mins)
  - short residence time microflow tube reactors(~100 msec)
  - Control residence time around above values by varying the mass flow rates
- Measurements are performed at the exit:
  - Stable species via standard GC/MS systems
  - Radical species using MBMS systems

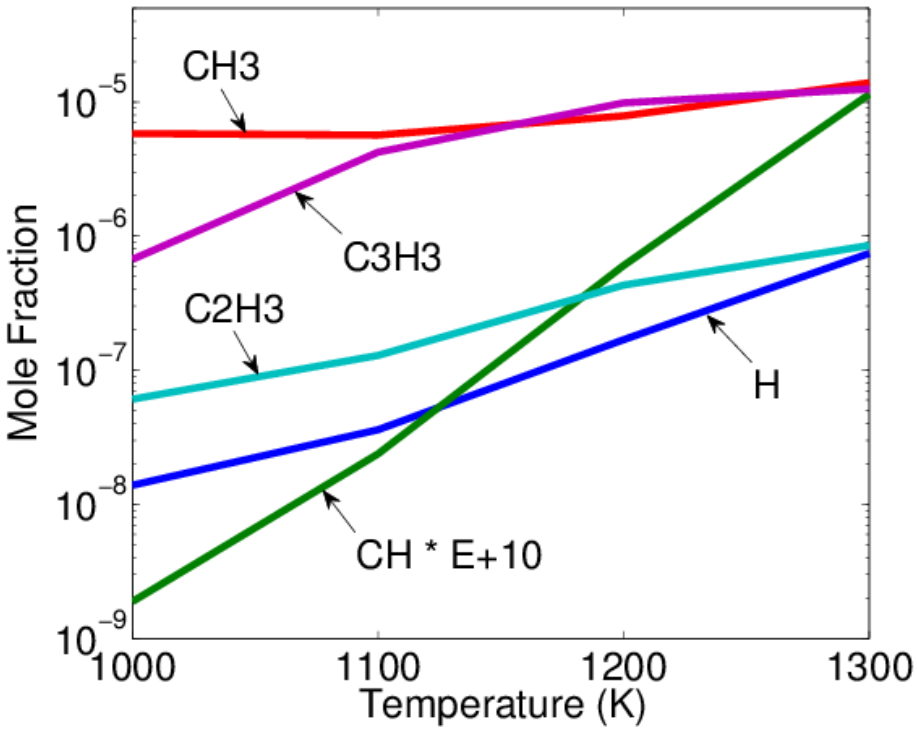




Supporting Examples …

- Dodecane decomposition without catalysts (predicted using JetSurf)



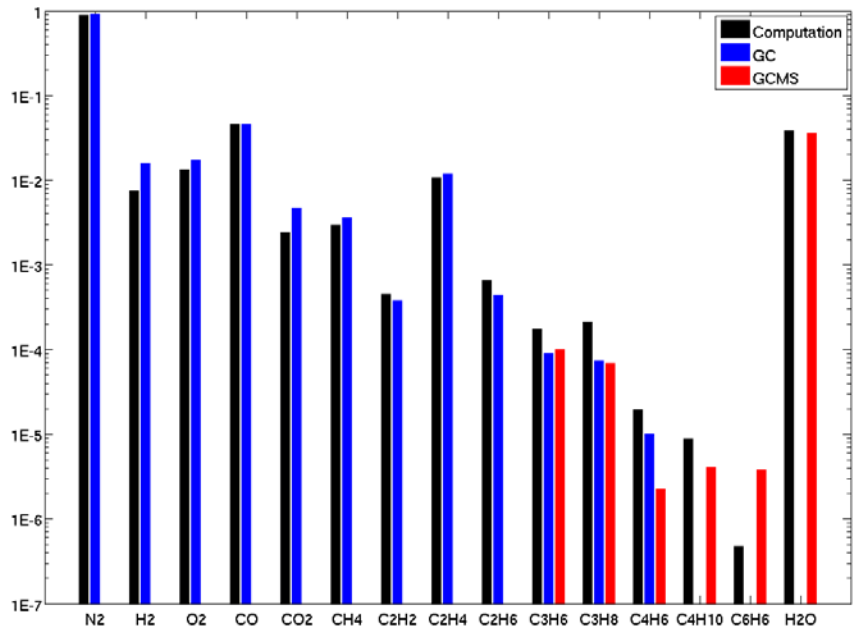


- Recent AFRL experiments have shown that **models and experiments can differ by two-orders** at super-critical conditions!!! (Sanders et al. 2012 based on hexane decomposition)

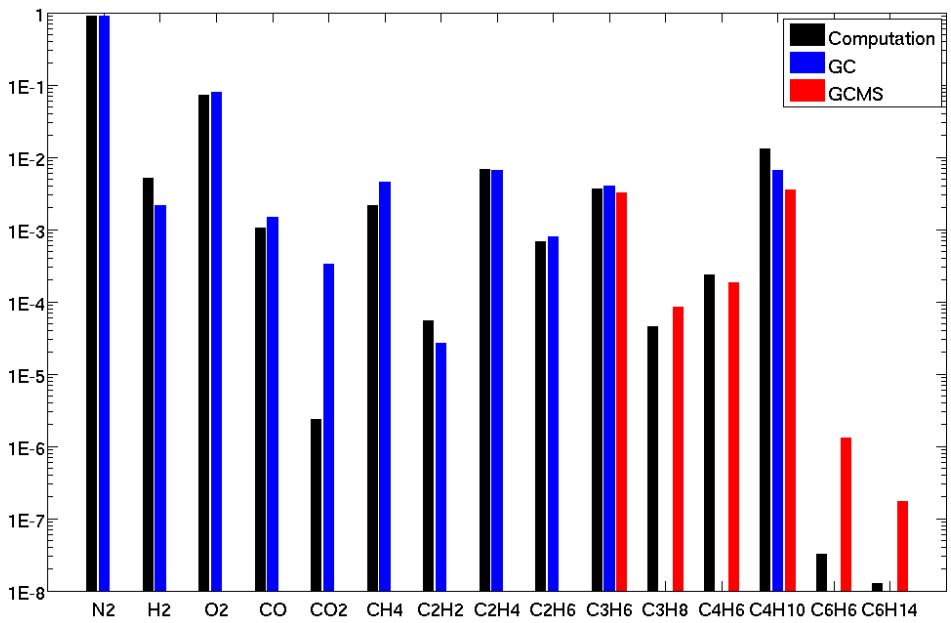
Supporting Examples …

- Tube reactor exit measurements vs. JetSurf 2.0 predictions

diluted ethylene-air
(p=1atm, T=1050K, ϕ=2.0, t=50 ms?)

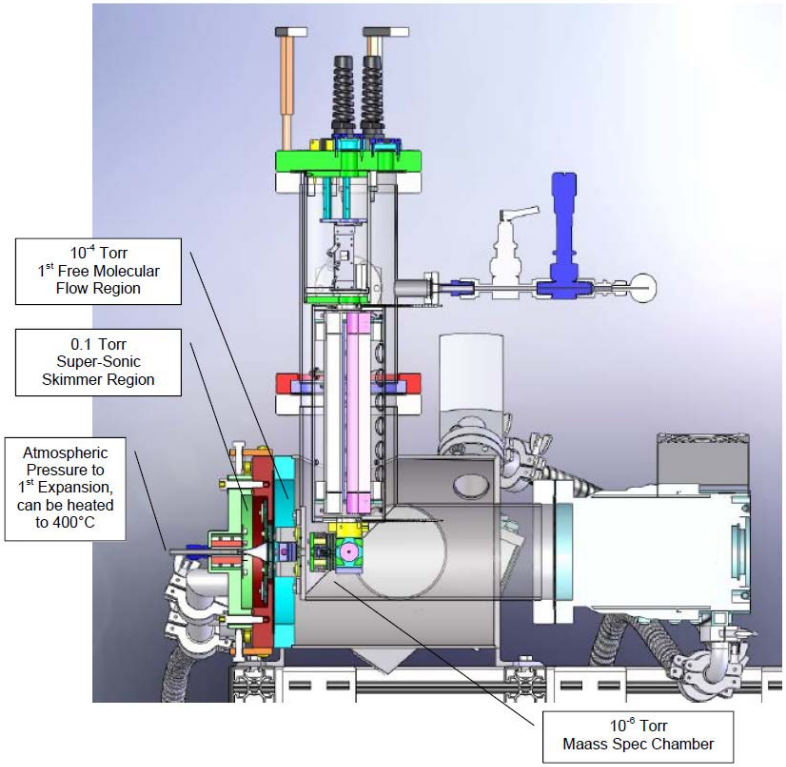


diluted butane-air
(p=1atm, T=1050K, ϕ=2.0, t=50 ms?)

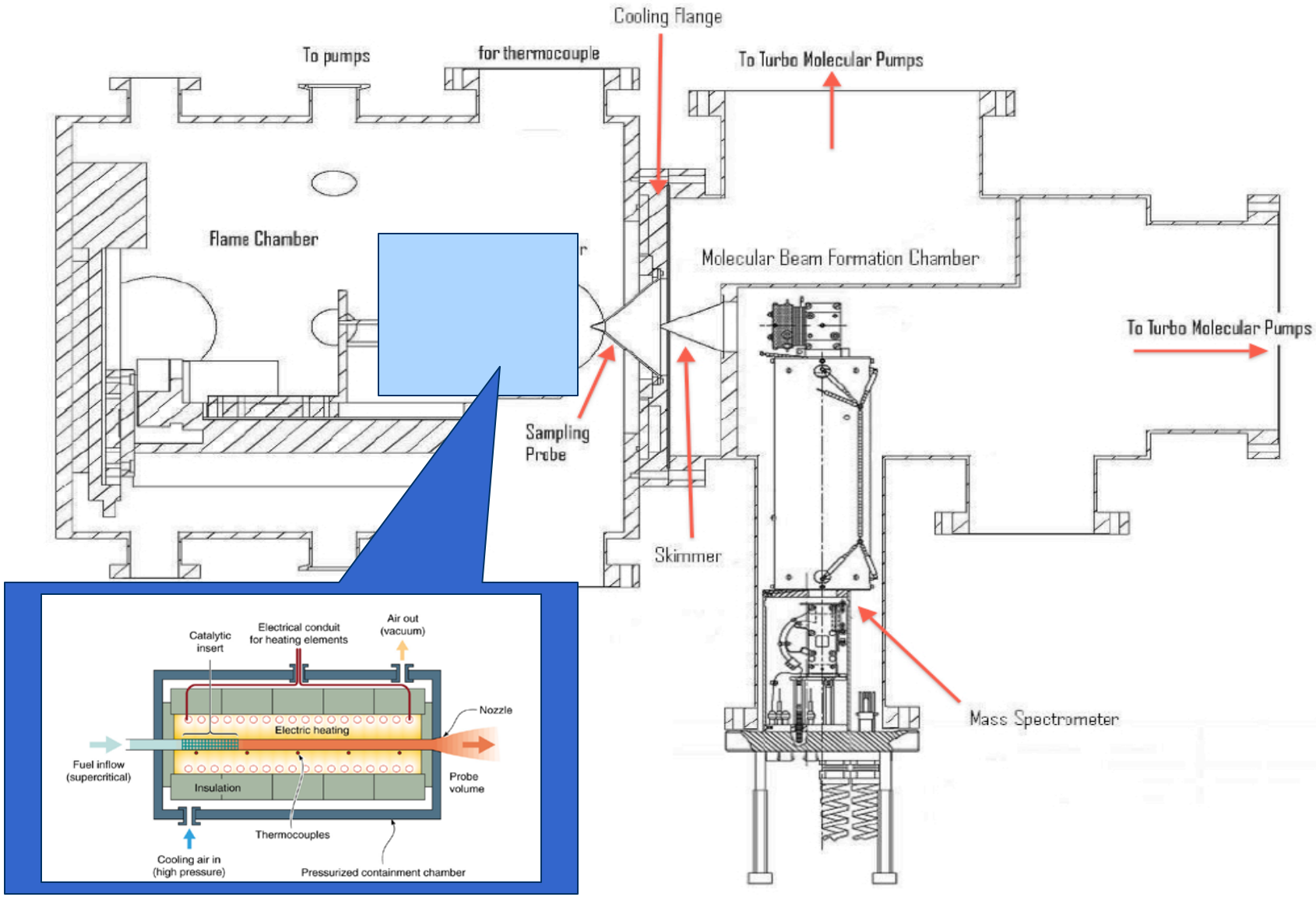


Radical Species Measurements

- MBMS (molecular-beam mass spectrometry) is near-general, measuring radicals and reactive species with mole fractions > ~10^{-6}.
  - Sample and quench wall-lessly to form a beam.
  - Tune electron-ionization source to just above ionization threshold, avoiding fragmentation.
  - Quadrupole MS separates species, including isomers if >2 eV difference in thresholds.

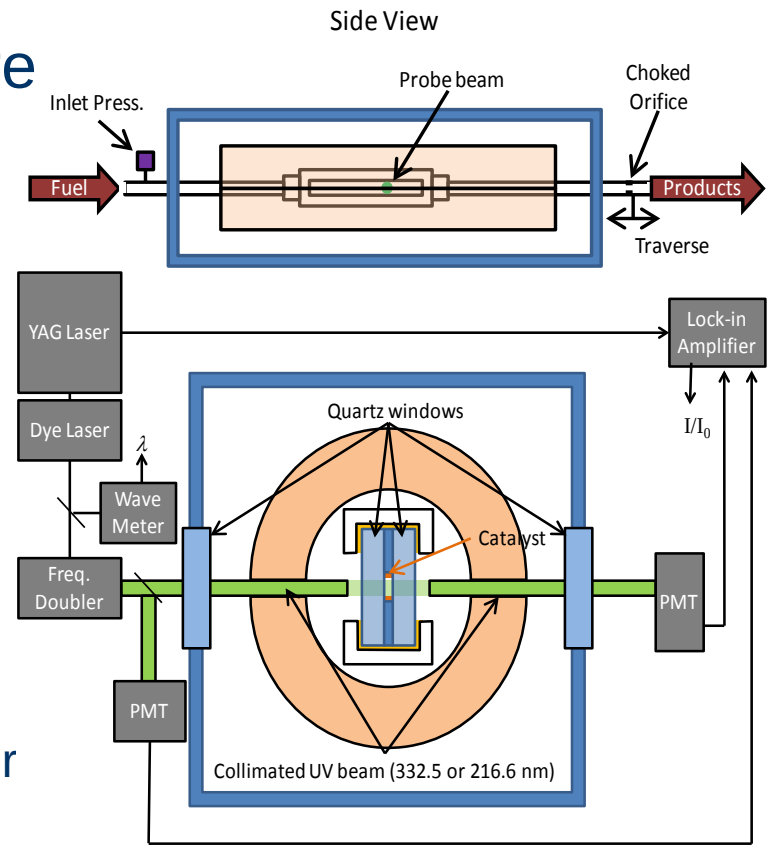


Interfacing of MBMS with Reactors



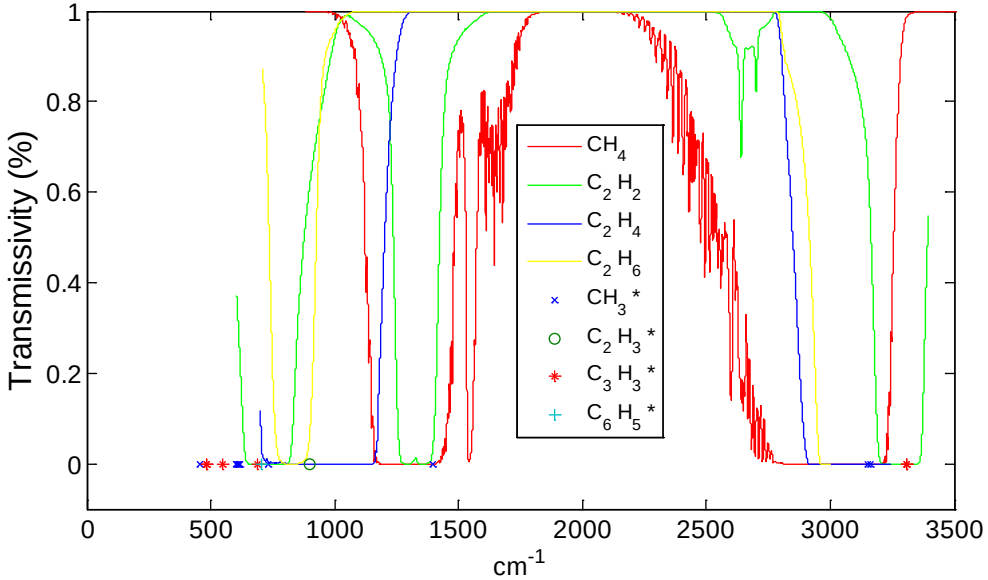
In-situ Micro-channel Diagnostics

- Measure decomposition products inside a micro-channel reactor where conjugate heat transfer effects are important
  - Support model validation efforts
- Use absorption spectroscopy in an optically accessible micro-channel reactor.
  - Infrared CH_4, C_2H_2, C_2H_4, C_2H_6 (major species)
    - Fourier Transform Infrared Spectrometer (FTIR)
  - Ultraviolet CH_3^*, $C_3H_3^*$ (radical species)
    - Tunable laser



Challenges of In-Situ Measurements

- Achieving optical access
  - Form channel walls with optical materials
  - Use water-cooled optical fiber beam guides.
- Pressure broadening of major species spectra obscures IR spectra of radical species at high pressures, eg.50 atm



  - Both FTIR and UV absorption measurements are necessary.

Goals of the Proposed Work

- Understand the mechanisms for the catalytic cracking of surrogate fuels over a range of mixed metal-oxide catalysts
- Identify the catalytic features that control catalytic cracking over WO_3 and Nb_2O_5 clusters supported on ZrO_2, Al_2O_3 and SiO_2
- Computationally screen a range of binary and ternary metal oxides to identify active catalytic materials with minimized coke formation tendencies and to guide experiments
- Coating of selected mixed metal-oxide catalysts using DVD in cooling channels
- Probe reactor exits for stable and unstable species with and without catalysts using GC/MS/MBMS
- In-situ species measurements using FTIR/UV absorption
- Model validation/combustion property predictions/ tuning of catalysts and fuel pairing

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