

# A Novel Slurry-Based Biomass Reforming Process

Thomas Henry Vanderspurt, Sean Emerson,  
Ying She, Hongmei Wen, Susanne Opalka

United Technologies Research Center

May 24, 2005

Project ID #

**PD 14**

This presentation does not contain any proprietary or confidential information

# Overview

## Timeline

- 1 May 2005
- 31 Oct 2008
- 2%

## Budget

- Total project funding
  - \$2.9 million, DoE
  - \$737k, cost share
- \$0, FY04
- \$300K, FY05

## Barriers

- Barriers:
  - V. Feedstock Cost and Availability
  - W. Capital costs and efficiency of technology
- Barriers Addressed
  - Technology Energy Efficiency
  - Capital Cost
  - Feedstock Flexibility

## Partners

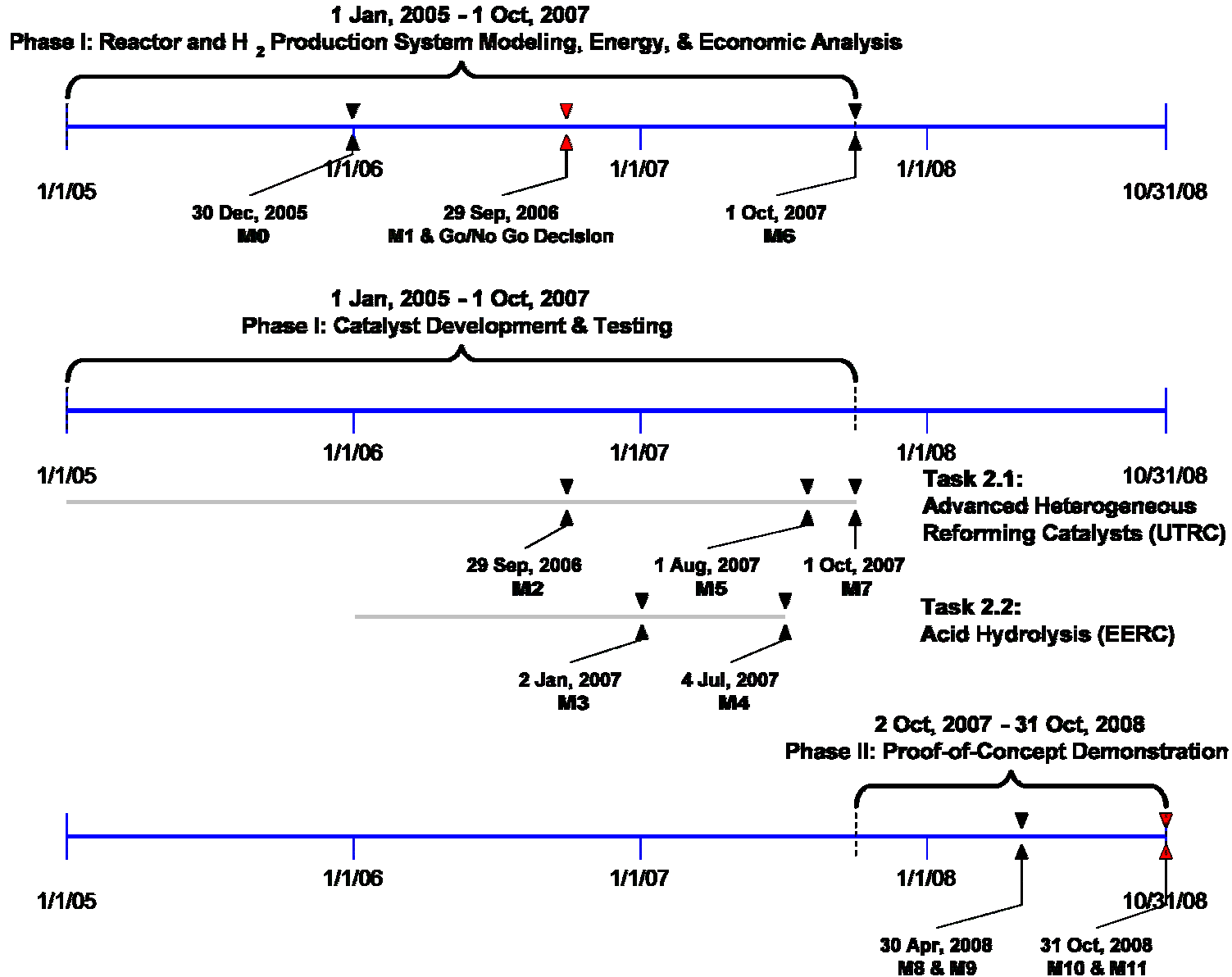
- University of North Dakota Environment Energy Research Center

# Biomass Slurry Reforming Objectives

DOE: \$1.75 kg 99.9+% H<sub>2</sub> with an LHV efficiency of 50%

1. Determine LHV Efficiency Using HYSYS
  - Major efficiency determinants and impact of catalyst efficiency/selectivity
  - Required hydrolysis rate per in unit input energy
  - Capital and energy cost of intermediate hydrogenation step
2. H<sub>2</sub> Cost via H2A Spreadsheet: Plant Cost, Rate of Return & Feedstock Costs
3. If DOE Cost and Efficiency Targets Can Be Met, Commence Next Phase
  - Optimum hydrolysis conditions: Energy and Capital Cost
  - Hydrolysis product chemical composition and physical properties
    - Sugar identification and concentrations
    - Identification and quantification of low molecular weight organics
    - Solubility, AMW and surfactant/foaming properties of lignin fraction
  - Catalysis discovery and testing
4. Micro-scale continuous operation of membrane reformer with batch hydrolysis
  - ~500 hr catalyst performance test
  - Collection of material and heat balance data important for plant design
5. Final Economic and Energy Analysis for Final Report

# Project Schedule



# Approach: Biomass Slurry to Hydrogen Concept

**Slurry of ~ 10 % Ground Biomass (Wood) in Dilute Acid**  
44% cellulose  
19% hemicellulose  
13% "other"  
23% lignin  
<1% "ash"  
<1% protein

→  
1 or more  
Hydrolysis  
Steps

**Reformer Feed**  
~41% soluble C<sub>6</sub> and (C<sub>6</sub>)<sub>n</sub> "sugars"  
~18% soluble "C<sub>5</sub>" sugars  
~10% "reformable others"  
~31% lignin+cellulose fragments etc.  
*Hydrolysis targets*

Preferential RCHO  
Hydrogenation Catalysts

## Optional Sugar Hydrogenation

~59% sugar alcohols  
~10% "reformable others"  
~31% lignin + cellulose fragments, etc.

*Only if advanced catalysts seem unlikely reach g H<sub>2</sub> / kg feed goals*

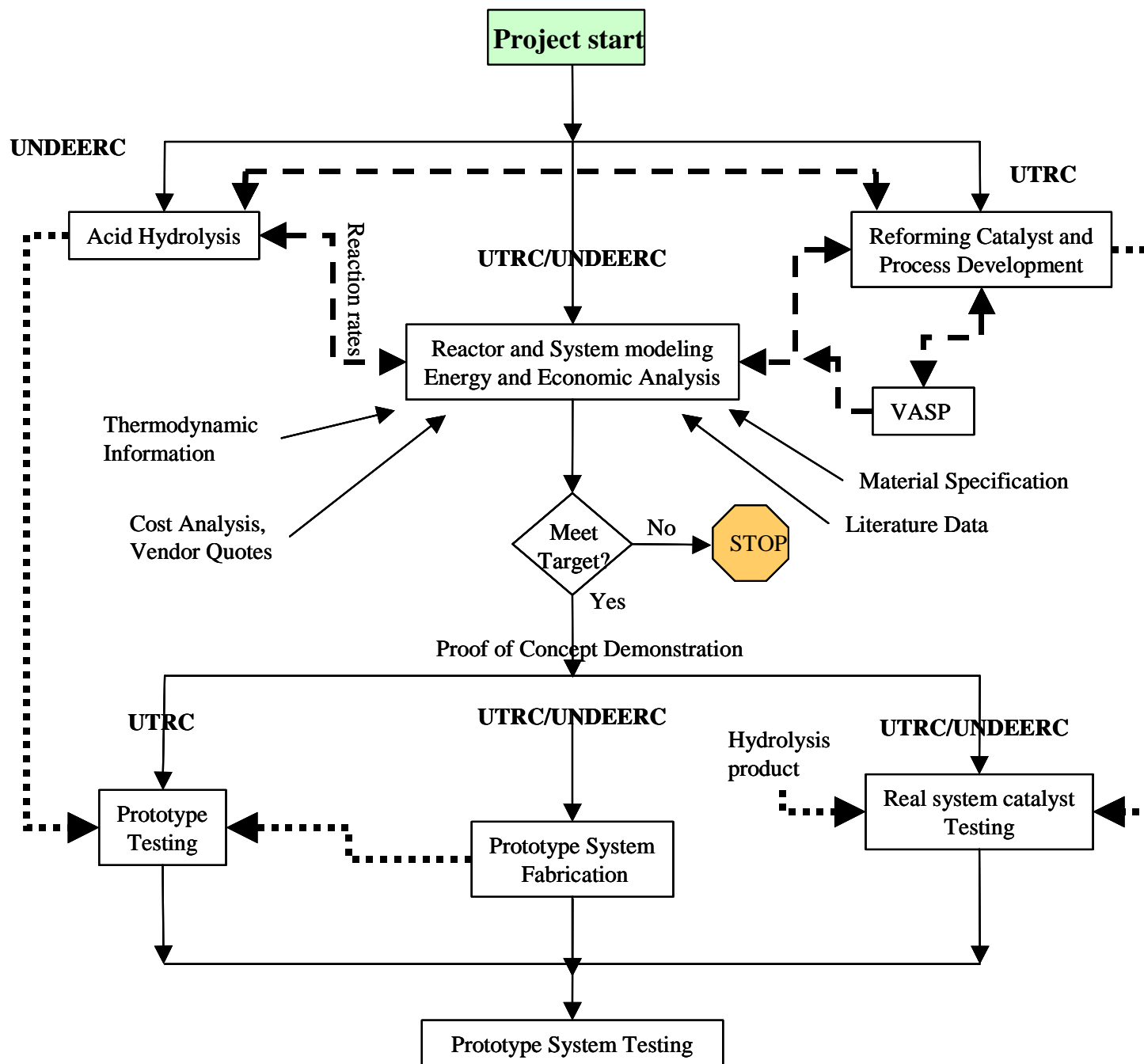
↓  
High Selectivity Pt-MM rafts on engineered nano-structured oxide like Ti<sub>[1-(x+y)]</sub>Dp<sub>1x</sub>Dp<sub>2y</sub>O<sub>2</sub>

**~83 g 99.9+ H<sub>2</sub> / kg dry Feed Recovered Through Membrane**

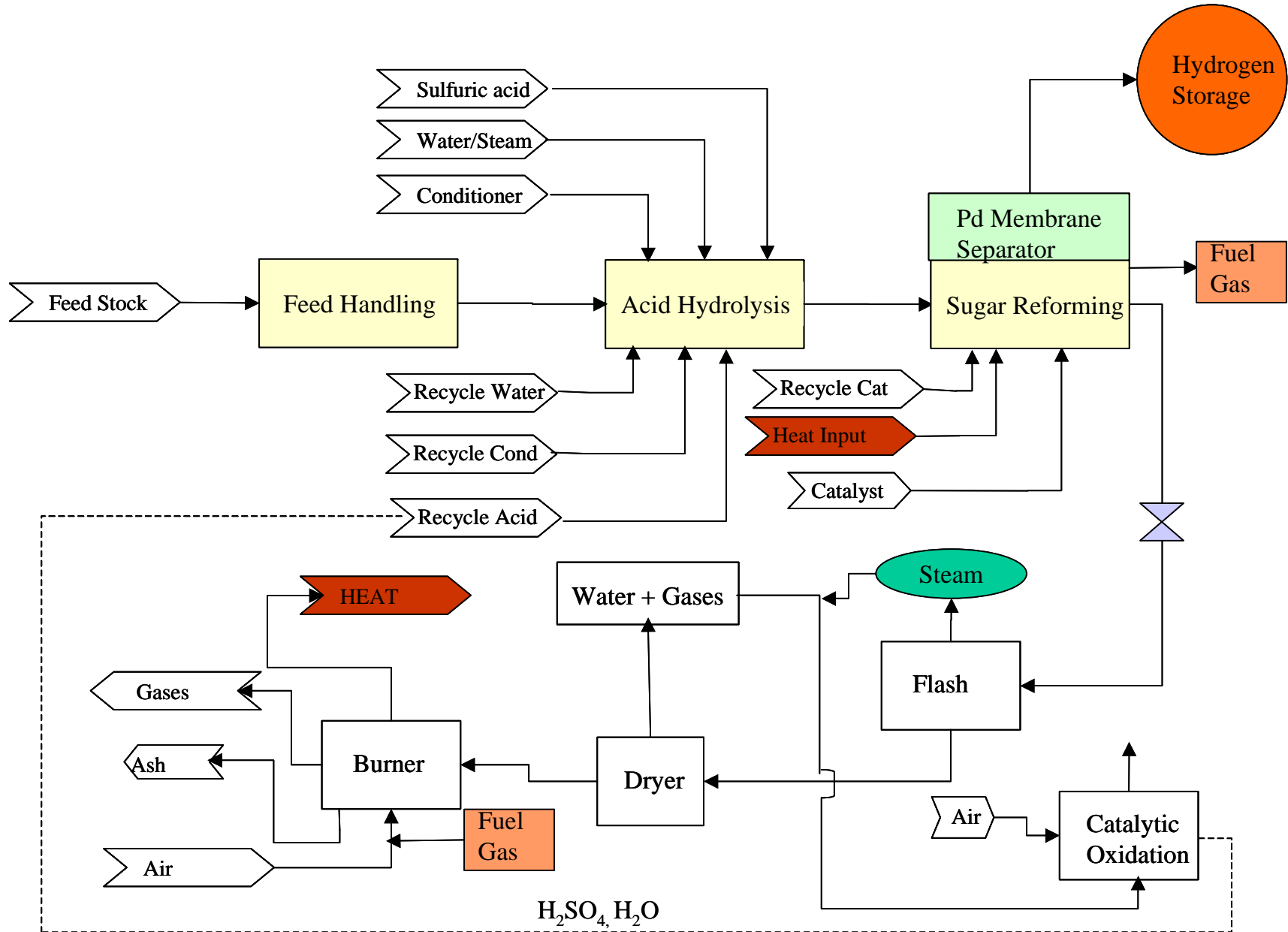
~9 g H<sub>2</sub> or Equivalent as fuel gas  
~300 g Lignin and other fuel  
~1 kg CO<sub>2</sub>

*Pt-Re/Ce<sub>[1-(x+y)]</sub>Zr<sub>x</sub>Dp<sub>y</sub>O<sub>2</sub> WGS Catalysts have high activity and very low CH<sub>4</sub> make*

# Original Project Plan Overview

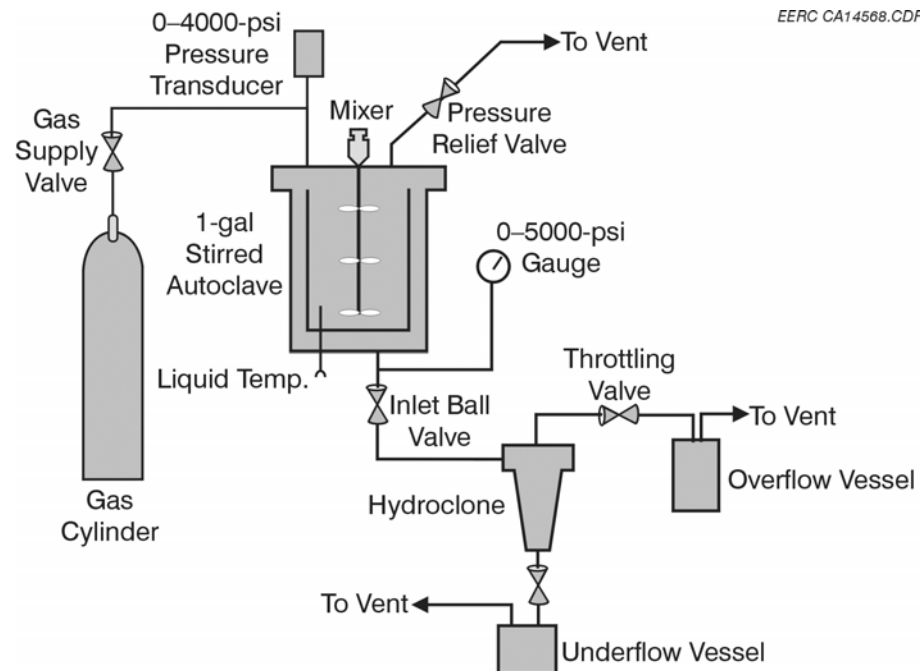


# Approach: Initial Process Inputs and Outputs



# Approach: Experimental Design to Optimize Hydrolysis

- Overall efficiency depends on optimizing hydrolysis energy / acid requirements
  - Lower acid concentration
    - + Less expensive alloys etc.
    - + Higher SA & activity reforming catalysts = smaller reforming reactors
    - + Less unnecessary chemical degradation = higher H<sub>2</sub> yield
  - Lower Temperature
    - + Increased residence time thus larger volumes and increased costs
    - + Lower autogenous steam pressures = lower capital costs
    - + Less expensive alloys etc.
    - + Less dehydrogenation etc. = higher H<sub>2</sub> yields
- Poplar assumed to be initial feed; grinding energy similar to mechanical pulping
- Input data for refined economic and efficiency model

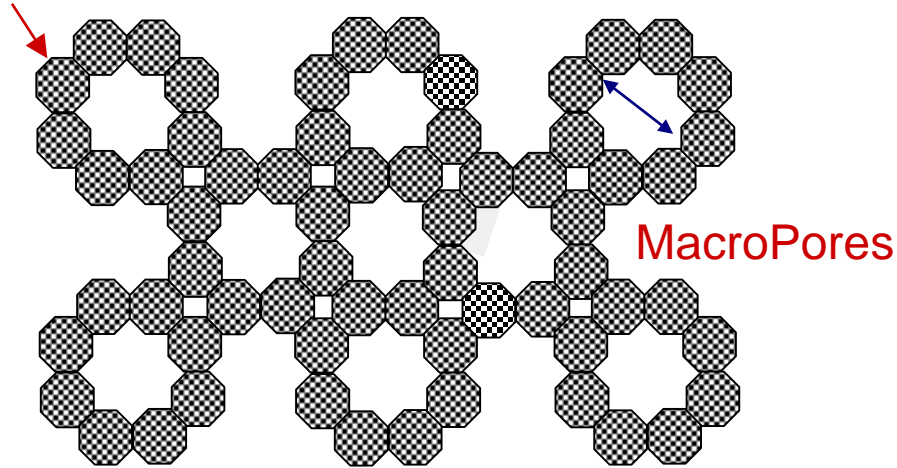




# Nano-Engineered Noble Metal / Doped Metal Oxide Catalyst

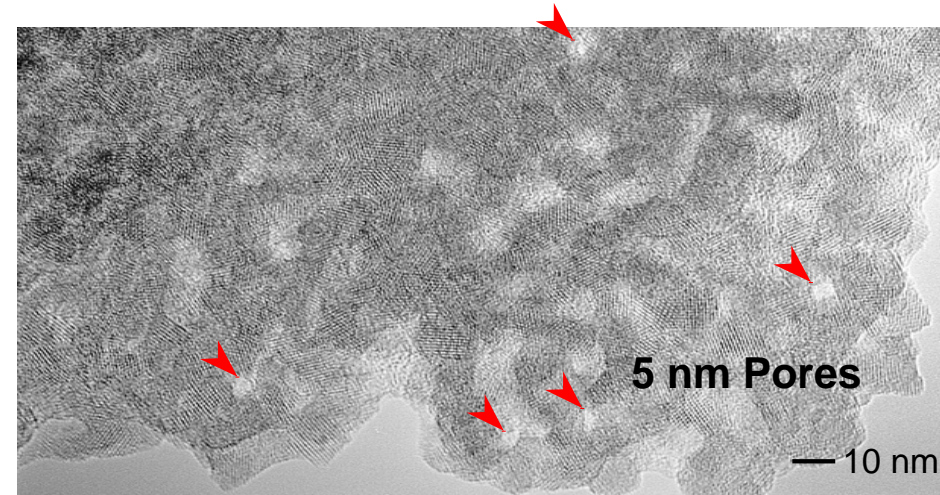
Design & synthesize active oxide structure to maximize accessible sites/vol.

Nanoparticle (< 3.5 nm) Micropore ( $\geq 5$  nm)



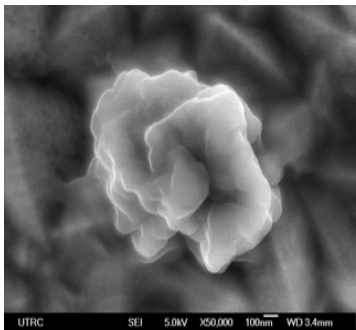
Conceptual Porous Metal-Oxide Framework Shown in 2D

Self assembly used to create high surface area, large pore thermally stable active oxide support with 100% dispersed 2 wt% Pt based mixed metal clusters

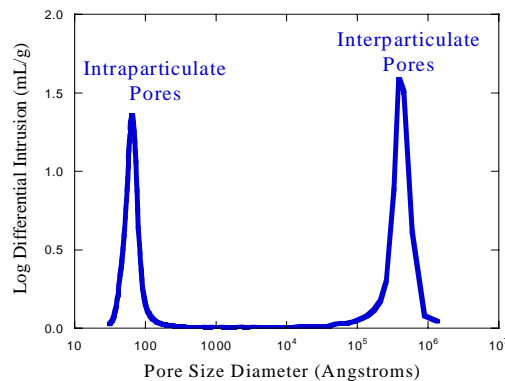


Conceptual Structure Realized

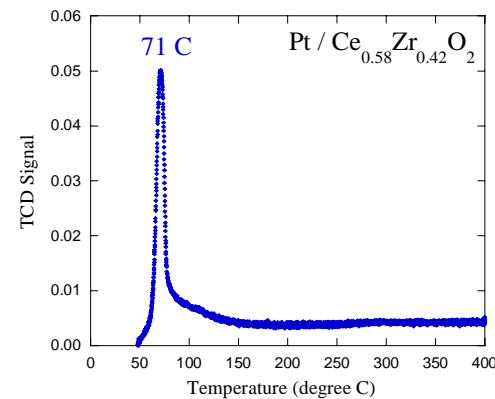
Fractal Morphology



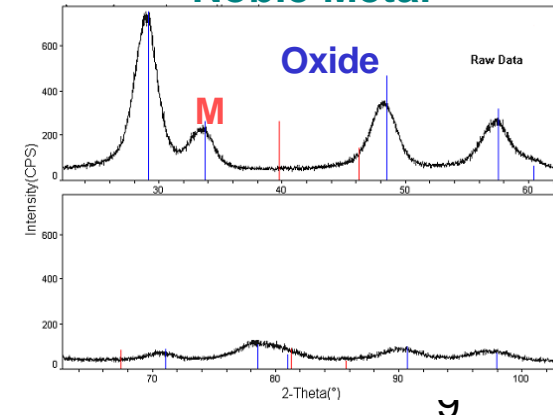
Large, Bimodal Pore Structure



Low Temperature Reducibility



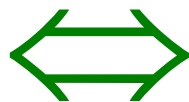
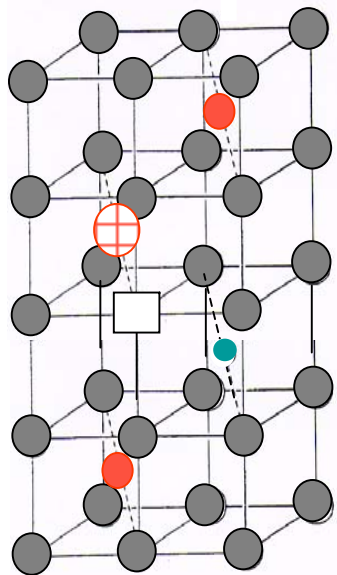
100% Dispersed Noble Metal



# UTRC Catalyst Discovery Approach

*Atomistic catalyst design, synthesis, characterization, reaction studies & kinetic analysis*

## Conceptual Catalyst Design



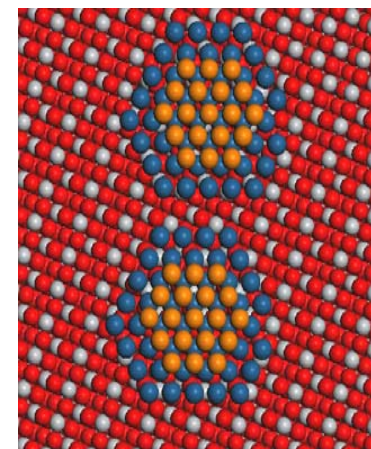
## Catalyst Synthesis



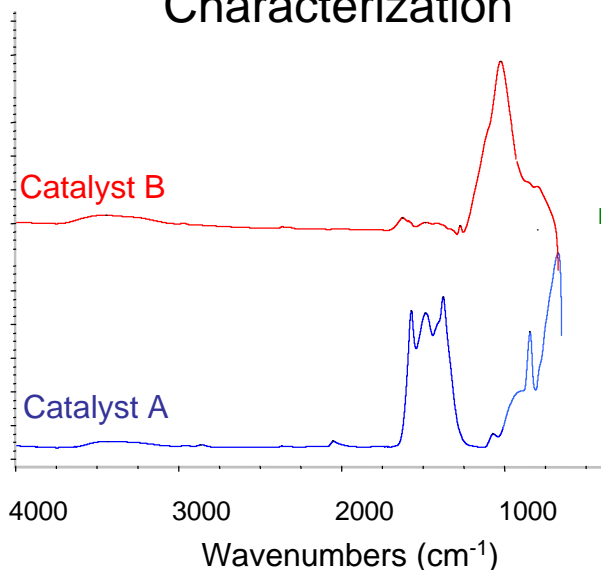
High active surface area  
Nanocrystalline structure  
~100% NM dispersion



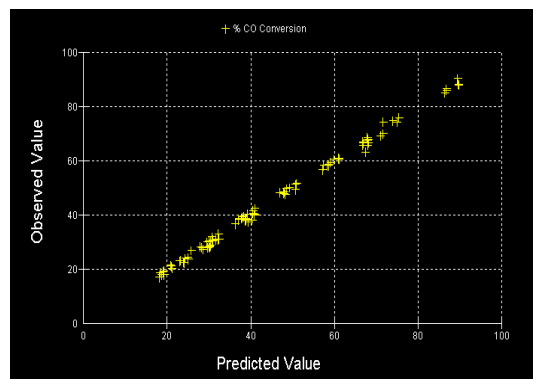
## Quantum Mechanical Atomistic Modeling for advanced catalyst design



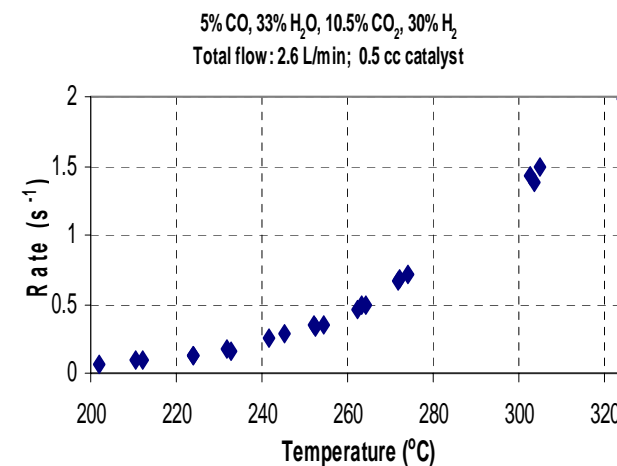
## Characterization



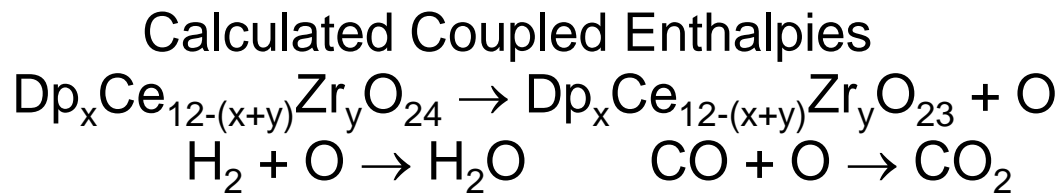
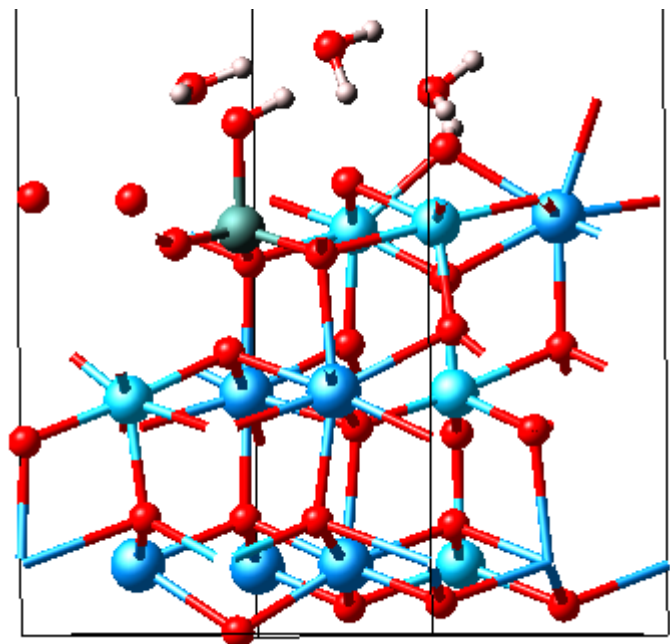
## Kinetic Expressions Derived From Reaction Data



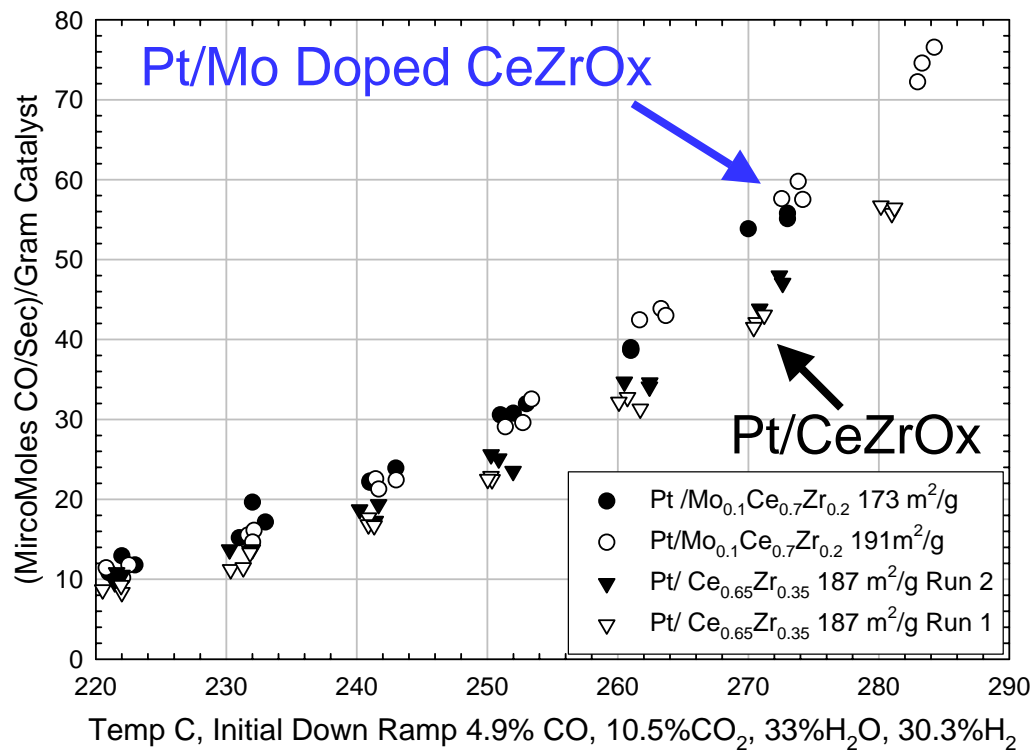
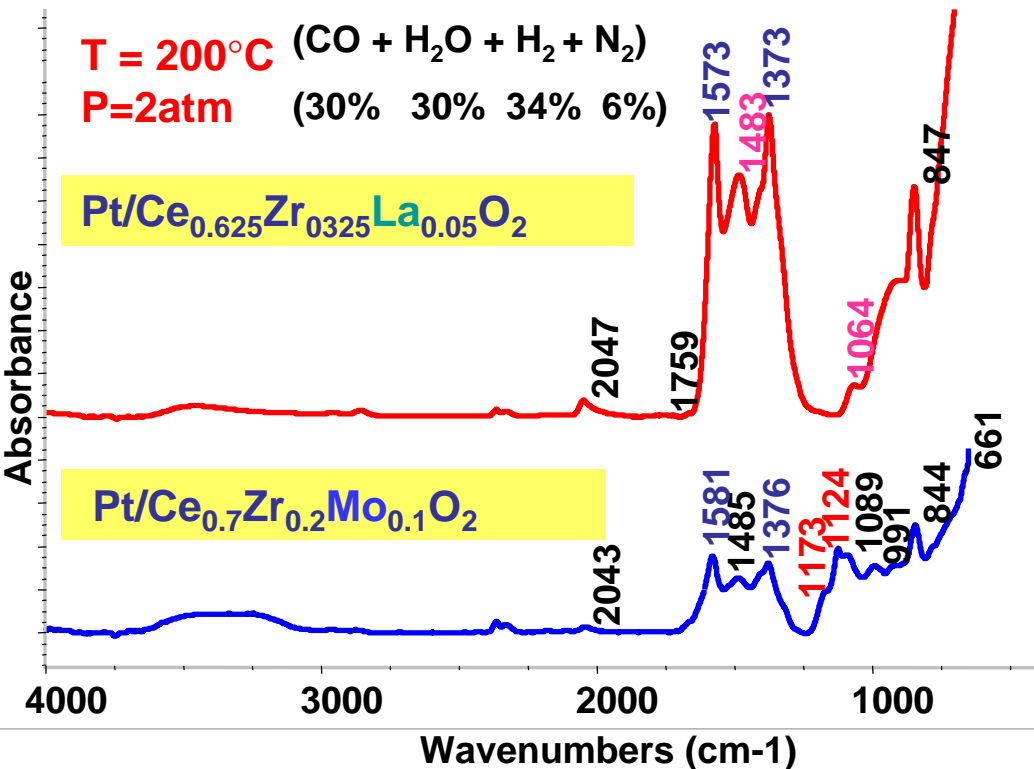
## Superior Performance



# VASP Modeling Insights Led To Better Catalysts



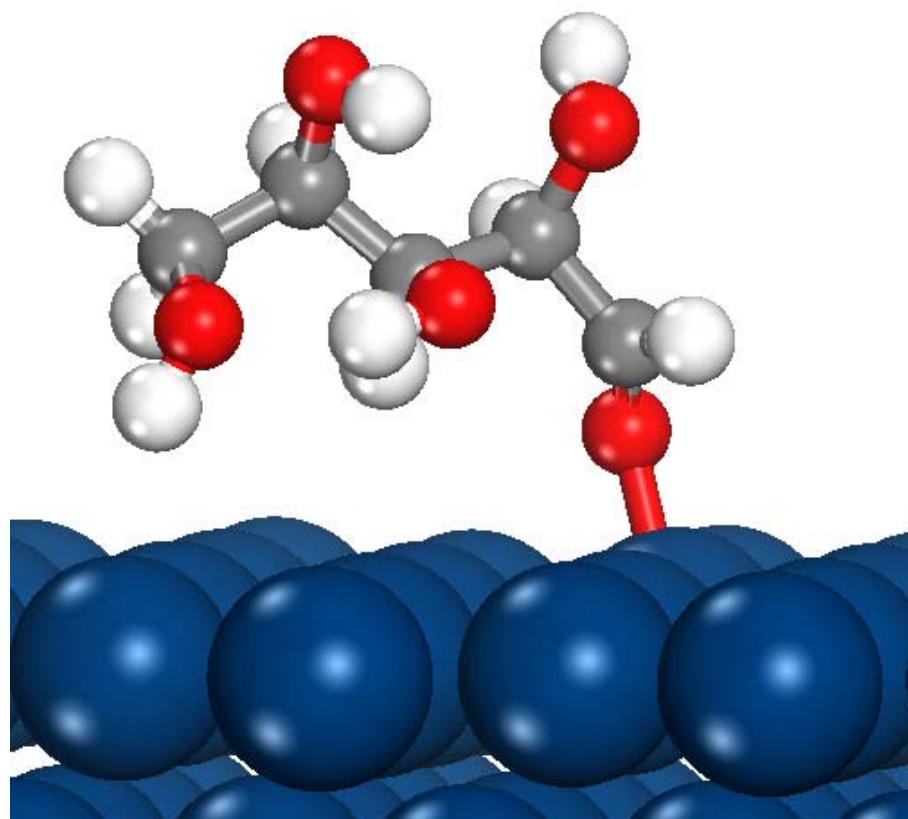
| Oxide Slab                 | $H_2 + O \rightarrow H_2O$ kJ/Mole | $CO + O \rightarrow CO_2$ kJ/Mole |
|----------------------------|------------------------------------|-----------------------------------|
| $Ce_{12}O_{24}$            | -154.5                             | -222.4                            |
| $Ce_7Zr_5O_{24}$           | -154.5                             | -222.1                            |
| <b>Ta</b> $Ce_6Zr_5O_{24}$ | 77.2                               | 9.6                               |
| <b>Mo</b> $Ce_6Zr_5O_{24}$ | 48.3                               | -19.3                             |



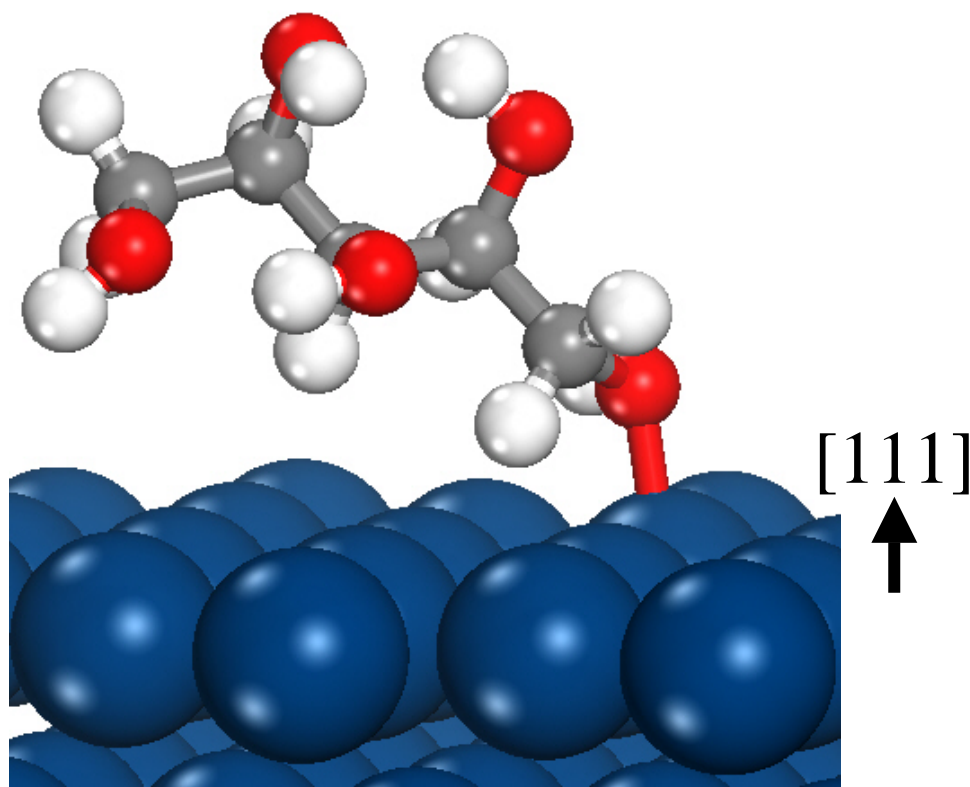
Higher Activity Catalyst w Similar Pt & SA

# Xylose Adsorbs More Strongly Than Xylitol on Pt(111)

Aldehyde O forms stronger bond than terminal alcohol O



Xylose/Pt(111)



Xylitol/Pt(111)

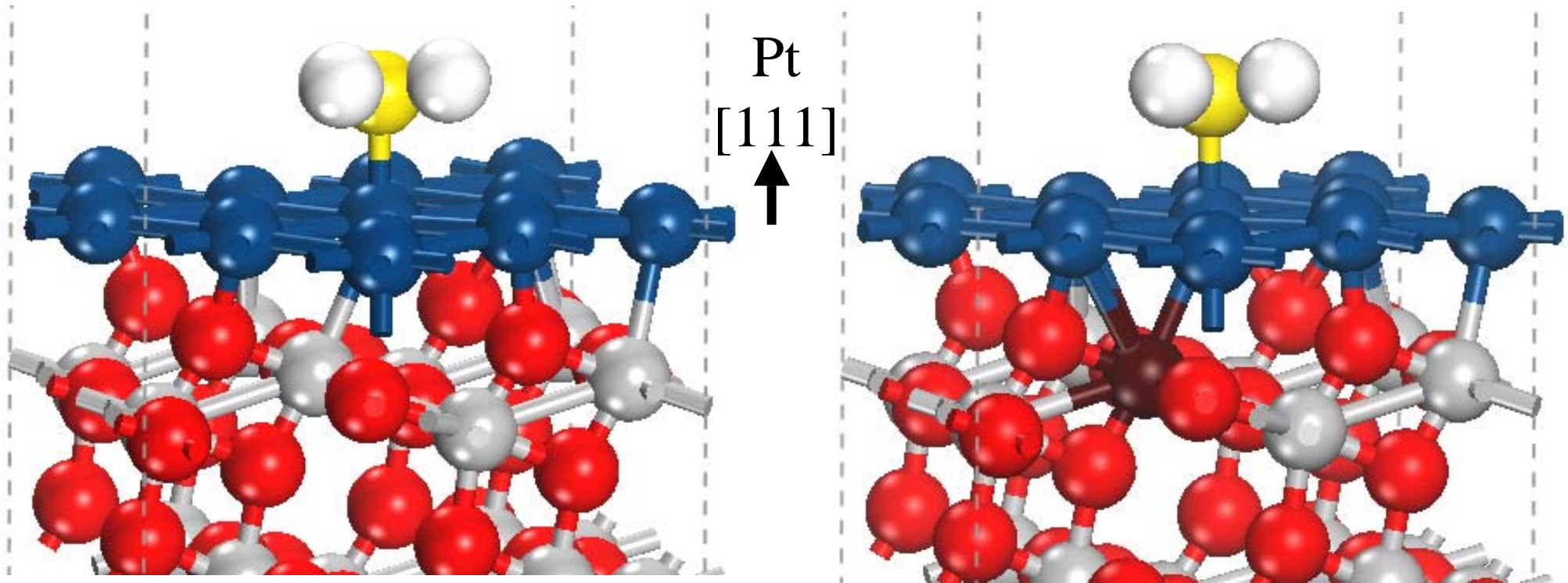
O C H Pt

Binding Energy = -92 kJ/mole    Binding Energy = -65 kJ/mole

Negative binding energy indicates exothermic process

# Ce Dopant in TiO<sub>2</sub> Decreases H<sub>2</sub>S-Pt Binding 16%

- Early results for Pt raft system, before full relaxation
- Anatase (101) TiO<sub>2</sub> with and without Ce



Pt(111)<sub>1ML</sub>/AnataseTiO<sub>2</sub>(101)

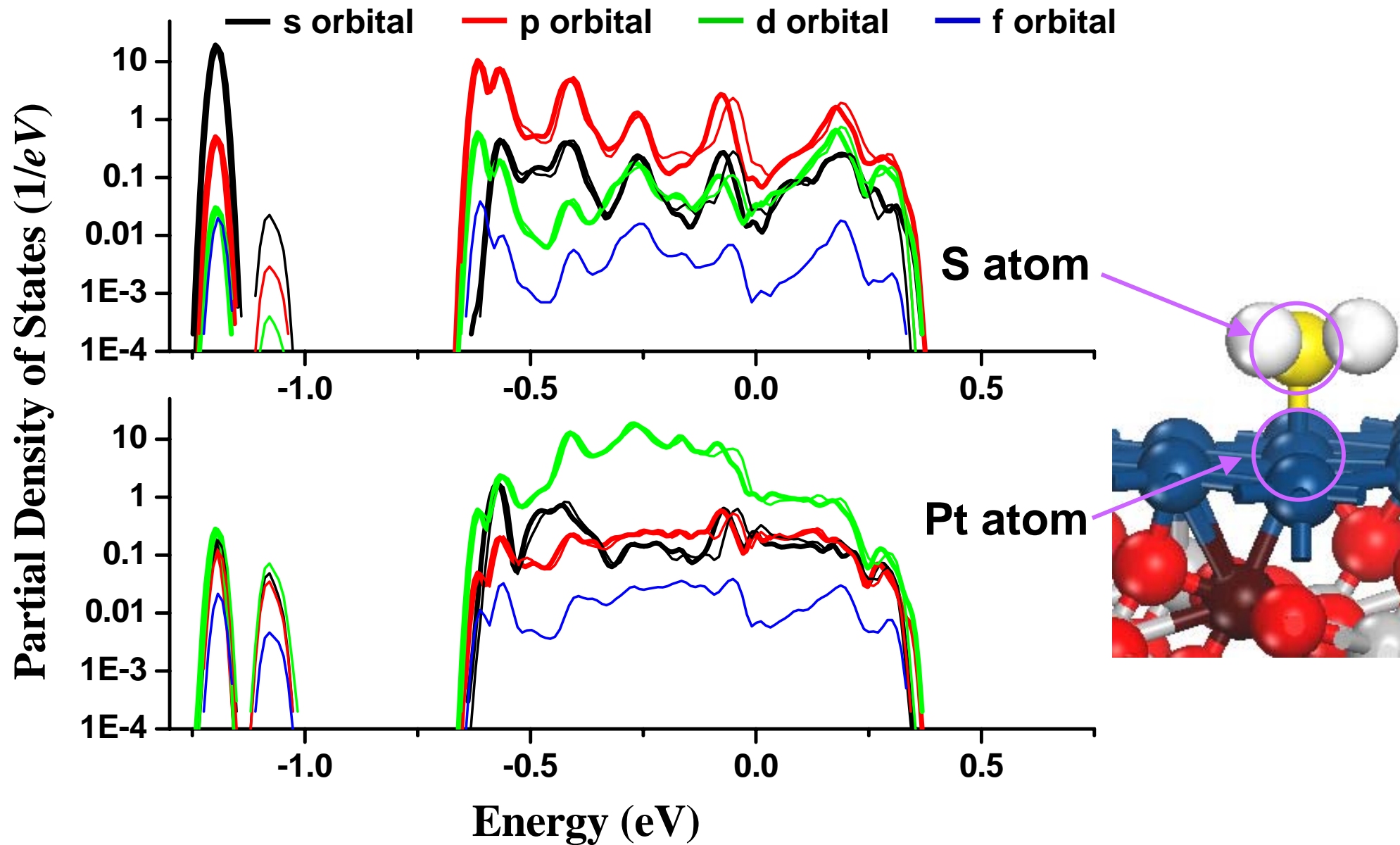
Binding Energy -106.53 kJ/mole

Pt(111)<sub>1ML</sub>/4.2a% Ce\_Anatase\_TiO<sub>2</sub>(101)

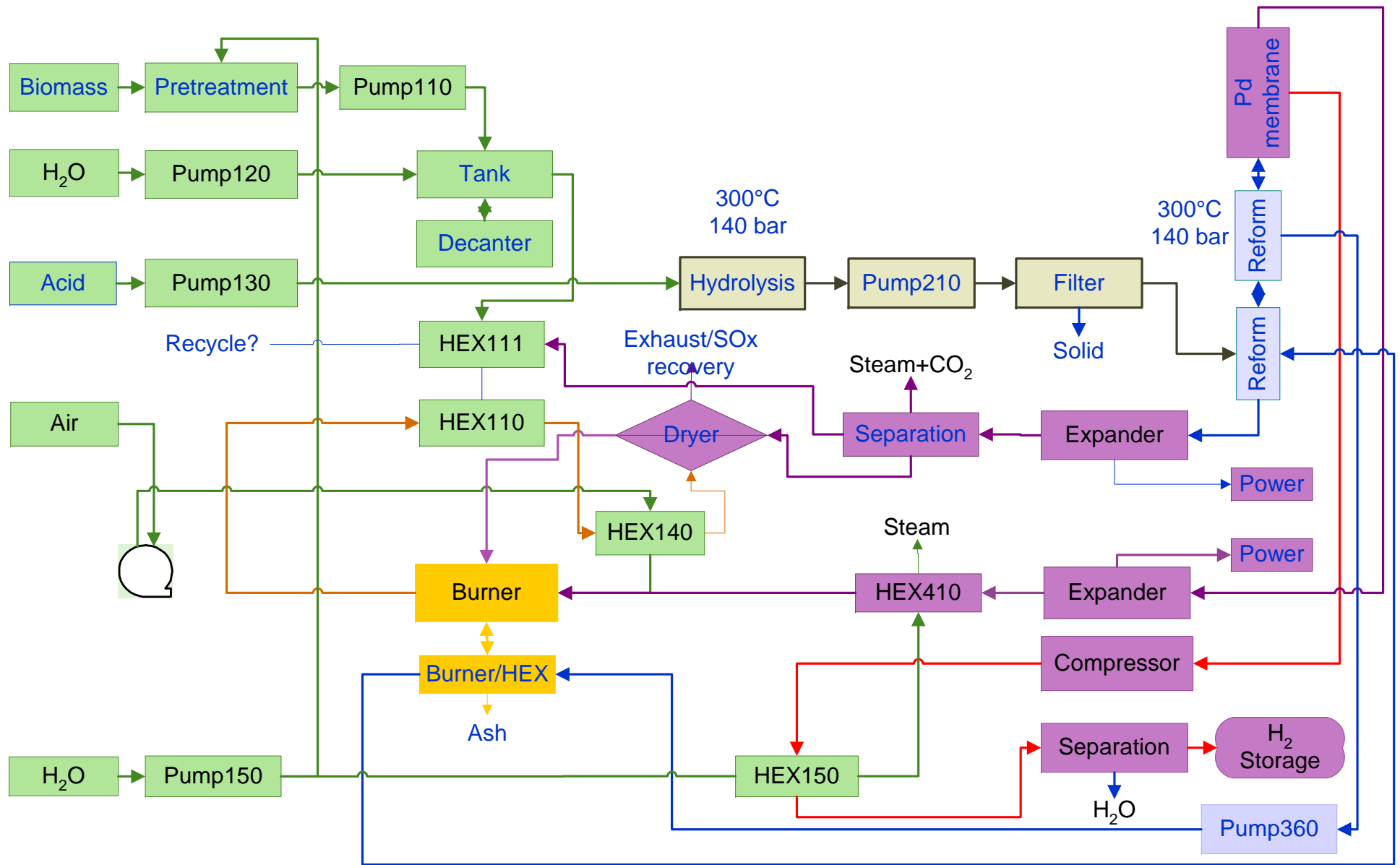
Binding Energy -89.50 kJ/mole

○ Ti H S Pt Ce

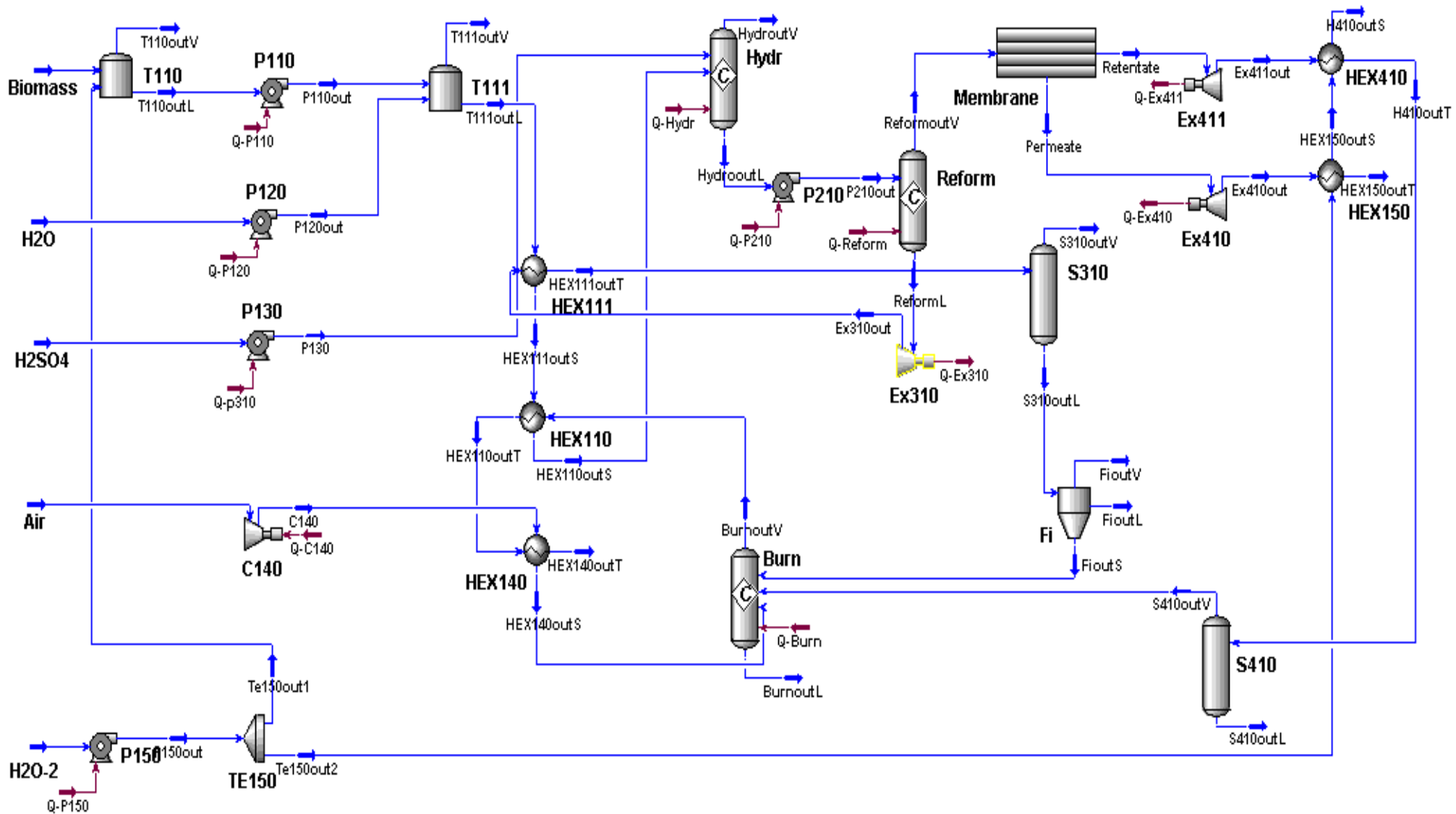
# Oxide Dopant Shifts Pt & S DOS to Higher Energy



# Progress: Conceptual Process Flow Diagram



# Progress: Current HYSYS Process Flow Diagram





# Future Work

- FY 2005:
  - Initial feasibility analysis of a 2000 ton/day (dry) plant design showing a viable path towards the DOE's 2010 efficiency (50% LHV) and cost (\$1.75/kg H<sub>2</sub>) targets.
  - Low-level construction of catalyst synthesis & testing infrastructure
- FY 2006:
  - Is there a preliminary 2000 ton/day (dry) biomass plant design that could reach the DOE's 2010 efficiency (50% LHV) and cost (\$1.75/kg H<sub>2</sub>) targets?
  - **GO/NO GO decision.**
  - Demonstrate an acid tolerant, model sugar solution reforming catalyst
    - + Promising kinetics and selectivity
    - + Path for cost-effective scale up (mass production) exists
  - Identify preliminary hydrolysis conditions at UND-EERC and hydrolyzed product chemical composition and physical properties

# Future Work

- FY 2007:
  - Demonstrate effective hydrolysis conditions for actual biomass system and a path to scale-up for a viable plant design
  - Demonstrate in the lab a potentially long lived, cost effective liquid phase biomass slurry reforming catalyst giving  $\sim 0.1$  moles  $H_2$ /Total Pt equivalent-second
  - Demonstrate that a plant designed with experimentally determined hydrolysis and reforming rates and conditions meets 50% LHV efficiency and \$1.75 /kg  $H_2$
  - Demonstrate wash coating of active catalyst on to selected support
- FY 2008:
  - Identify optimum hydrolysis conditions
  - Demonstrate wash-coated reforming catalyst with actual hydrolyzed biomass
  - Design, build, test and deliver proto-type continuous micro-scale reforming reactor to UND-EERC
  - Complete 500 hrs of reformer operation and collect data important to full scale pilot unit design
  - Estimate  $H_2$ /kg cost and LHV efficiency using 2000 T/day plant design finalized with actual batch hydrolysis and continuous micro-scale reforming reactor data.

# Hydrogen Safety

The most significant hydrogen hazard associated with this concept is the 10% H<sub>2</sub> content of the up to 2000 psig process gas.

# Hydrogen Safety

Our Approach to deal with the hazard in the laboratory is:

- H<sub>2</sub>/Flammable gas detectors and ventilation interlock
  - System alarms if > 10% LFL (0.4% H<sub>2</sub>) detected
  - All heater power and flammable gas flows shut off if either >25% of lower flammable limit (1% H<sub>2</sub>) detected, or drop in ventilation rate
  - System design limits flammable gas flows to <10% of lower flammable limit based on measured ventilation rate

# Hydrogen Safety

Our Approach to deal with the hazard in the proposed micro-scale demonstration unit is:

- Multiple H<sub>2</sub>/Flammable gas detectors
- System alarms if >10% LFL (0.4% H<sub>2</sub>) detected
- All heater power and flammable gas flows shut off if >25% of lower flammable limit (1.0% H<sub>2</sub>) detected at unit.
- N<sub>2</sub> purging of all potential sources of ignition