

Investigation of reaction networks and active sites in bio-ethanol steam reforming over Co-based catalysts

Acknowledgement
US DOE

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Overview

Timeline

- ❖ Start Date - May 1, 2005
- ❖ End Date - April 31, 2010
- ❖ 80% Complete

Budget

- ❖ Total project funding
 - \$1,145,625 (DOE)
 - \$299,715 (OSU cost share)
- ❖ Funding received in FY05
 - \$100,000(DOE)
 - \$10,458 (OSU Cost share)
- ❖ Funding received in FY06
 - \$185,000 (DOE)
 - \$147,987 (OSU cost share)
- ❖ Funding received in FY07
 - \$290,473 (DOE)
 - \$67,316 (OSU)
- ❖ Funding received in FY08
 - \$140,703 (DOE)
 - \$9,780 (OSU)
- ❖ Funding received in FY09
 - \$429,449 (DOE)
 - \$54,163 (OSU)

Barriers

- ❖ A. Fuel Processor Capital Costs
- ❖ C. Operation and Maintenance
- ❖ D. Feedstock Issues

Partners

- ❖ Chemistry Dept. at OSU (Prof. Hadad.)
 - Molecular simulation
- ❖ NexTech Materials, Ltd
 - Catalyst manufacturing scale-up
- ❖ Argonne National Laboratory
 - XAFS & NEXAFS
- ❖ Directed Technologies Inc.
 - Economic analysis and feasibility considerations
- ❖ PNNL
 - Sharing findings

Relevance

Project overview

- ❖ Catalytic H₂ production from bioethanol
 - Renewable sources;
 - Plant matter (natural CO₂ recycling);
 - Lends itself well to distributed H₂ production strategy;
- ❖ Non-precious metal catalysts, low-temperature operation
- ❖ A university program addressing many fundamental questions such as:
 - Catalytic active sites;
 - Reaction networks and mechanisms;
 - Surface species and intermediates;
 - Deactivation mechanisms;
 - Regeneration mechanisms.

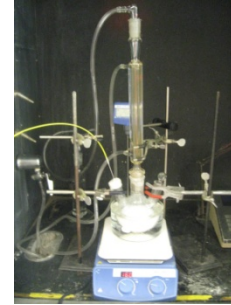
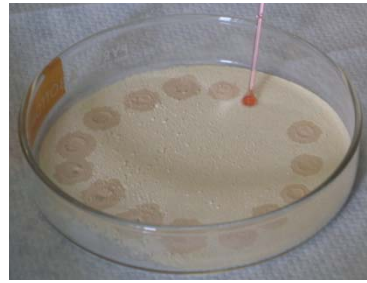
Objectives-Relevance

- ❖ To acquire a fundamental understanding of the reaction networks and active sites in bio-ethanol steam reforming over Co-based catalysts that would lead to
 - Development of a precious metal-free catalytic system which would enable
 - ❑ Low operation temperature (350-550°C)
 - ❑ High EtOH conversion
 - ❑ High selectivity and yield of hydrogen
 - ❑ High catalyst stability
 - ❑ Minimal byproducts such as acetaldehyde, methane, ethylene, and acetone
 - Addressing the barriers
 - ❑ Fuel Processor Capital Costs
 - ❑ Operation and Maintenance
 - ❑ Feedstock Issues

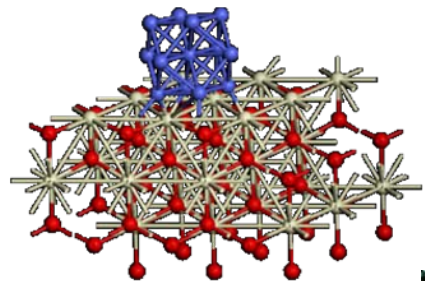
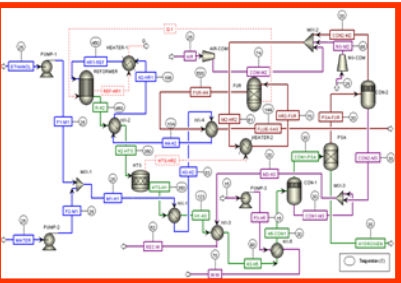
Milestones and Progress

	Tasks	Progress	% comp
1	Setting up the experimental systems, establishing protocols, training personnel	Built, installed a reactor system and established experimental protocols; Completed a HAZOP review for the ethanol reforming reactor system;	100%
2	Economic analysis	Completed an initial economic analysis based upon a 1,500 kg/day of hydrogen process using H2A model	80%
3	Catalyst synthesis and optimization	Prepared over 100 batches of catalysts; Investigated the effect of support, promoters, active metal loading, synthesis techniques and parameters on catalytic performance;	90%
4	In-situ, pre- and post-reaction characterization	Completed initial characterization studies using CO chemisorption, X-ray diffraction, temperature programmed reduction, oxidation, desorption, and thermogravimetric analysis; Combined characterization studies (XPS, DRIFTS, LRS, TGA) with mechanistic investigations to understand the pre- and post-reaction nature of the catalyst, reaction mechanisms and deactivation characteristics;	80%
5	Activity tests, kinetic studies, deactivation, regeneration studies	Established correlations between synthesis parameters, structure and activity; Evaluated synthesized catalysts for ethanol steam reforming in the temperature range 200-500°C and gas hourly space velocities from 5,000-300,000h ⁻¹ ; Conducted transient and steady-state experiments to understand the reaction network and mechanisms	80%
6	Information dissemination	Published three articles in refereed journals and gave 21 presentations, one key-note lecture and five invited lectures.	60%
7	Data analysis, reproducibility tests, literature awareness	Built a literature data base; Data analysis and reproducibility tests are performed in conjunction with the experiments.	70%

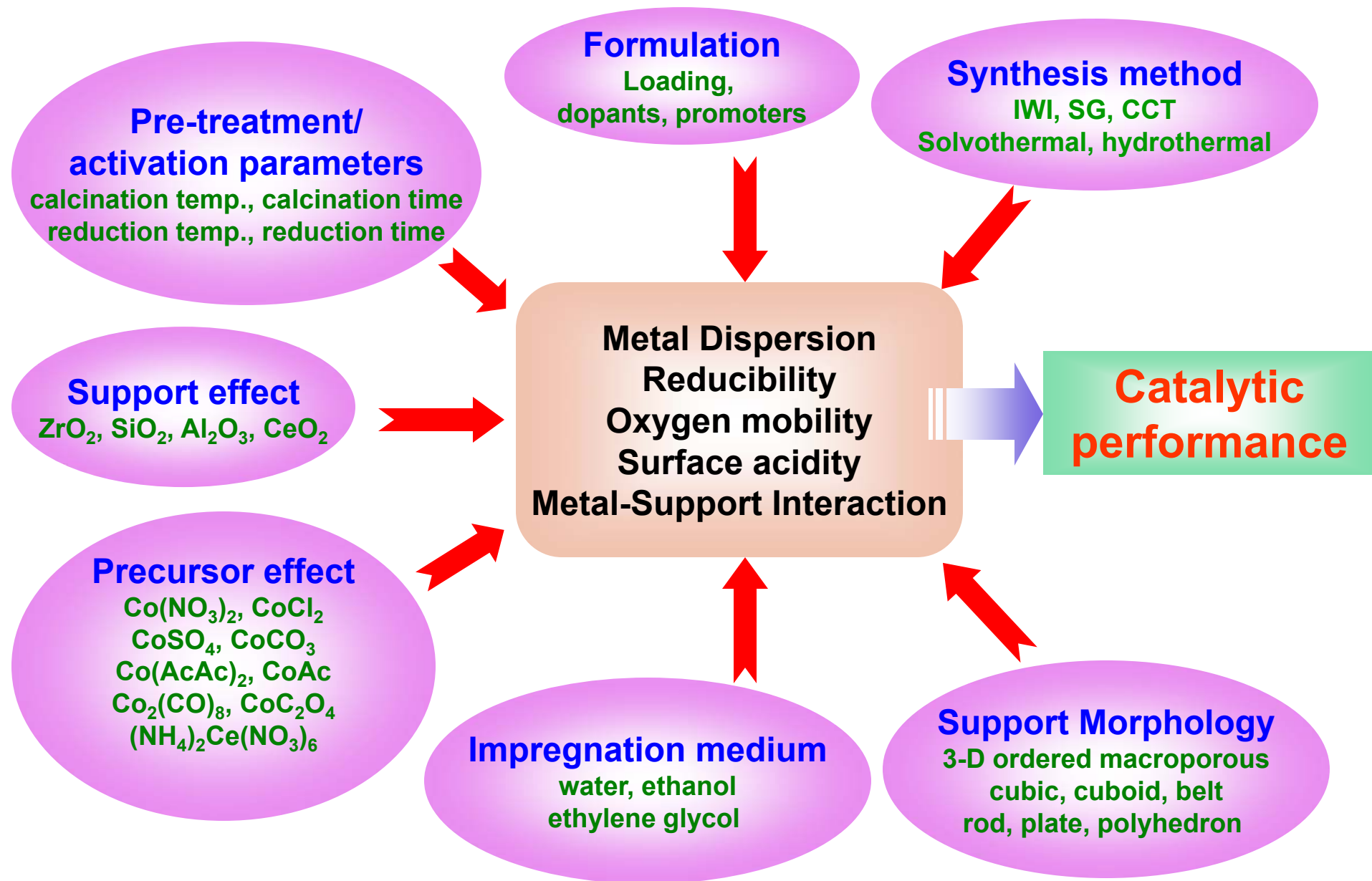
An integrative approach - Iterative with feed-back



Development of non-precious metal, low-temperature catalysts with:
high activity
high selectivity
high stability
economical feasibility



Systematic study of catalyst synthesis



Technical Approach

Catalyst characterization during its life history



BET

surface area
pore size & distribution



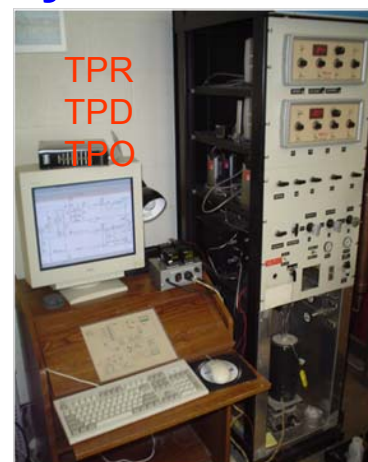
DRIFTS

surface intermediates
Molecular structure



Laser Raman

Molecular structure
surface intermediates



TPR
TPD
TPO

Adsorption/desorption
Reduction/oxidation
characteristics



XRD

particle size
crystalline phase

Understanding the structural and molecular nature of the catalyst and the surface sites

Mapping reaction network steps to the catalytic surface sites

Understanding the deactivation mechanism



MS

gas analysis
Isotopic labeling



XPS

oxidation state
coordination environment



TGA-DSC

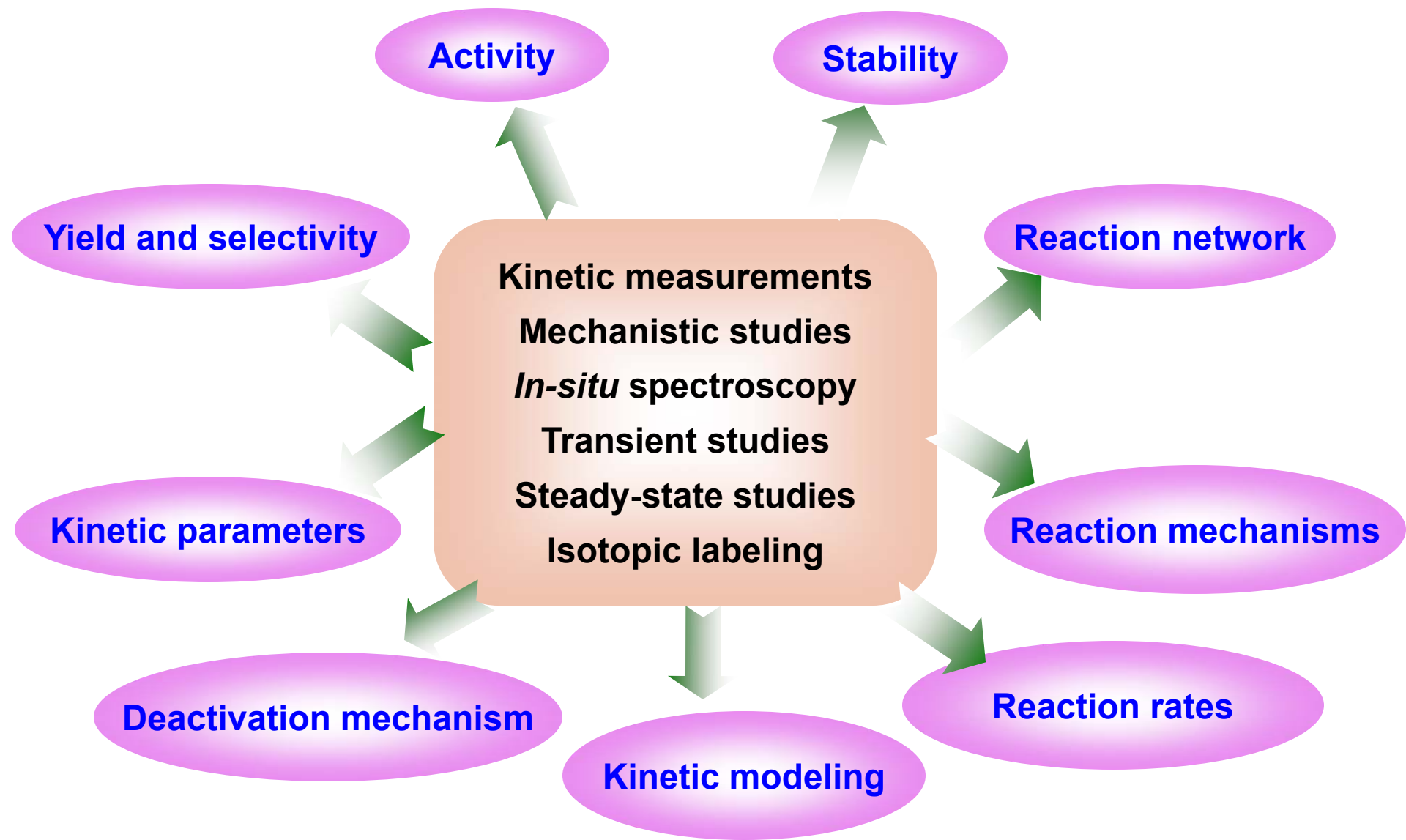
weight variation
heat effects



TEM-EDX

particle size
morphology
elemental analysis

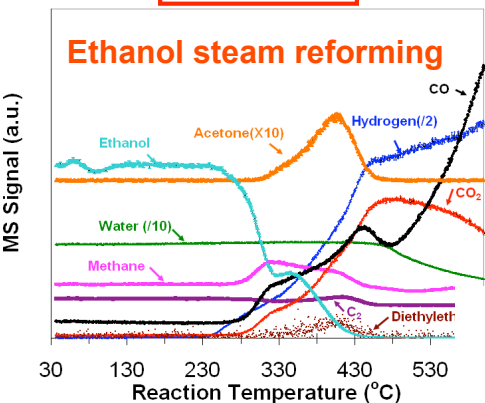
Technical Approach Reaction Studies



Technical Accomplishments and Progress

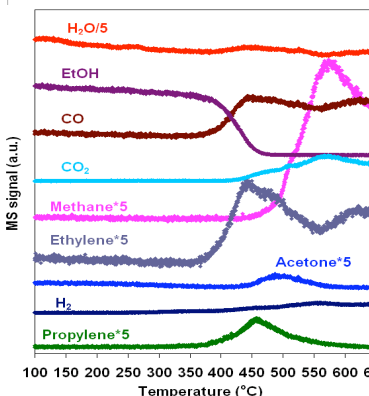
Understanding the Reaction Network

10%Co/ZrO₂



Acidic sites lead to formation of alkanes and olefins

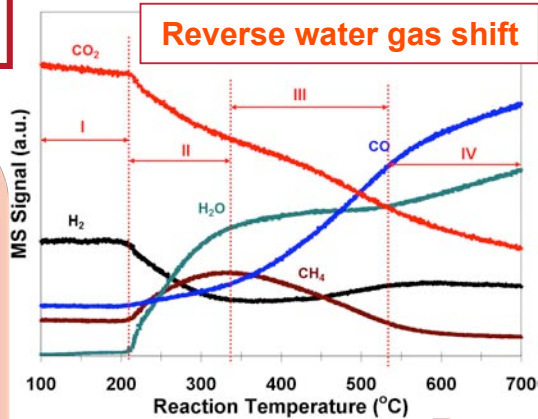
Acidic supports



A complex network of reactions catalyzed by different sites

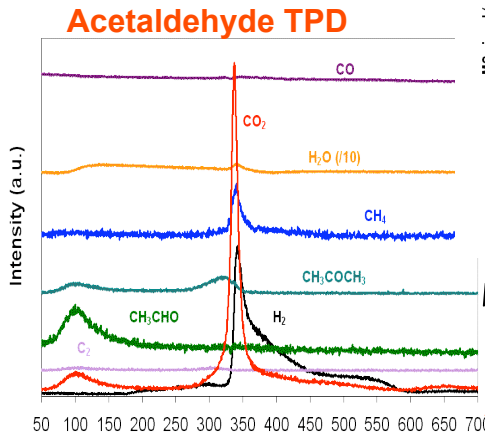
- Ethanol steam reforming: $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow 2 \text{CO} + 4\text{H}_2$
- Ethanol dehydrogenation: $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2$
- Acetic acid formation: $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2$
- Ethanol decomposition: $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2$
- Ethanol dehydration: $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$
- Acetaldehyde decomposition: $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$
- Acetaldehyde steam reforming: $\text{CH}_3\text{CHO} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 5\text{H}_2$
- Acetone formation: $2 \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO} + \text{H}_2$
- Water-gas shift: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
- Reverse water-gas shift: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$
- Methanation: $\text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$
- Methane steam reforming: $\text{CH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{H}_2$
- Ethylene decomposition: $\text{C}_2\text{H}_4 \rightarrow \text{coke}$
- Methane decomposition: $\text{CH}_4 \rightarrow \text{C} + 2 \text{H}_2$
- Boudouard reaction: $2 \text{CO} \rightarrow \text{CO}_2 + \text{C}$

10%Co/ZrO₂

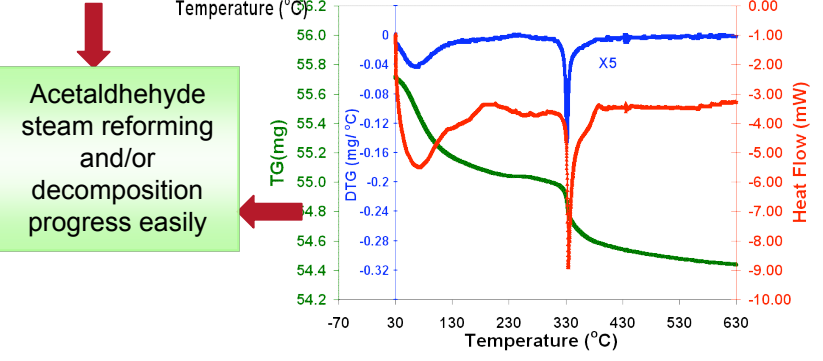


Methane SR takes place in a narrow T window. At higher temperatures coke formation dominates

Rev-WGS and methanation reactions become important above 200°C

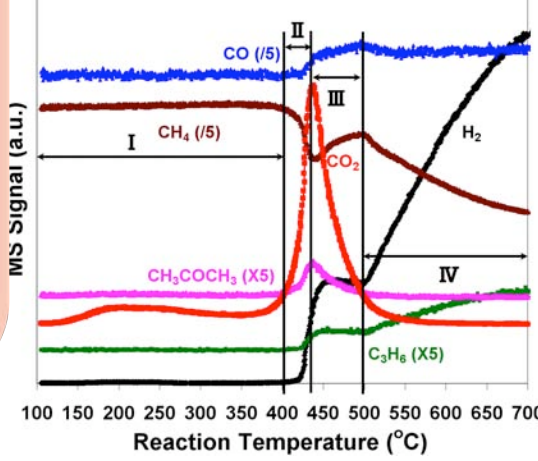


TGA-DSC during Acetaldehyde SR



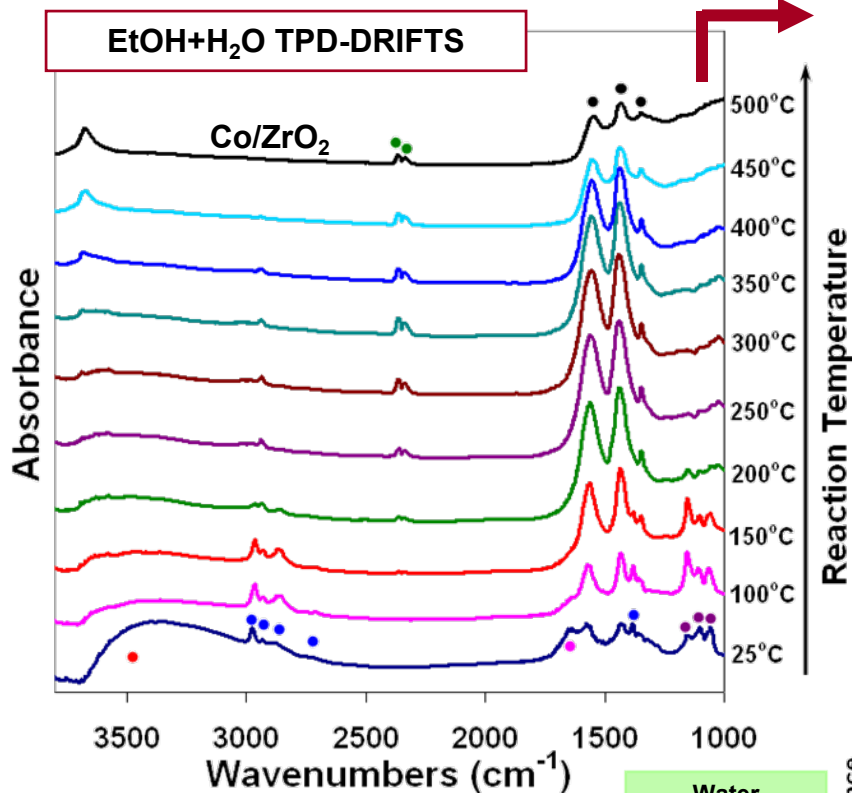
Acetaldehyde steam reforming and/or decomposition progress easily

Methane steam reforming



Technical Accomplishments and Progress

Understanding the surface species and surface mechanisms

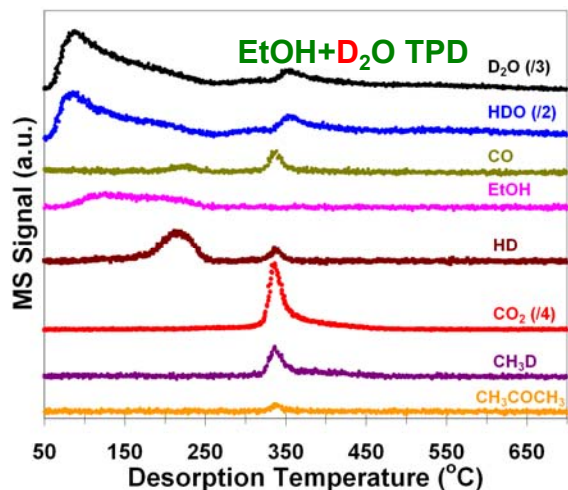


- **M-OH**
3650~3150cm⁻¹, O-H stretching
- **Acetates**
CH₃COO
1569, 1429, 1348cm⁻¹
- **CH₃- or CH₃CH₂-**
2962, 2927, 2865 cm⁻¹: C-H stretching
1385cm⁻¹: CH₃- bending
- **Adsorbed CO₂**
2361, 2336cm⁻¹: O=C=O stretching
- **Monodentate and bidentate ethoxide**
1169, 1106, 1063cm⁻¹
CCO stretching
- **Molecularly adsorbed H₂O**
1654cm⁻¹

CH2-CH2
 $\begin{matrix} \text{O} & \text{CH}_2 \\ | & / \\ \text{M} & \text{M} \end{matrix}$

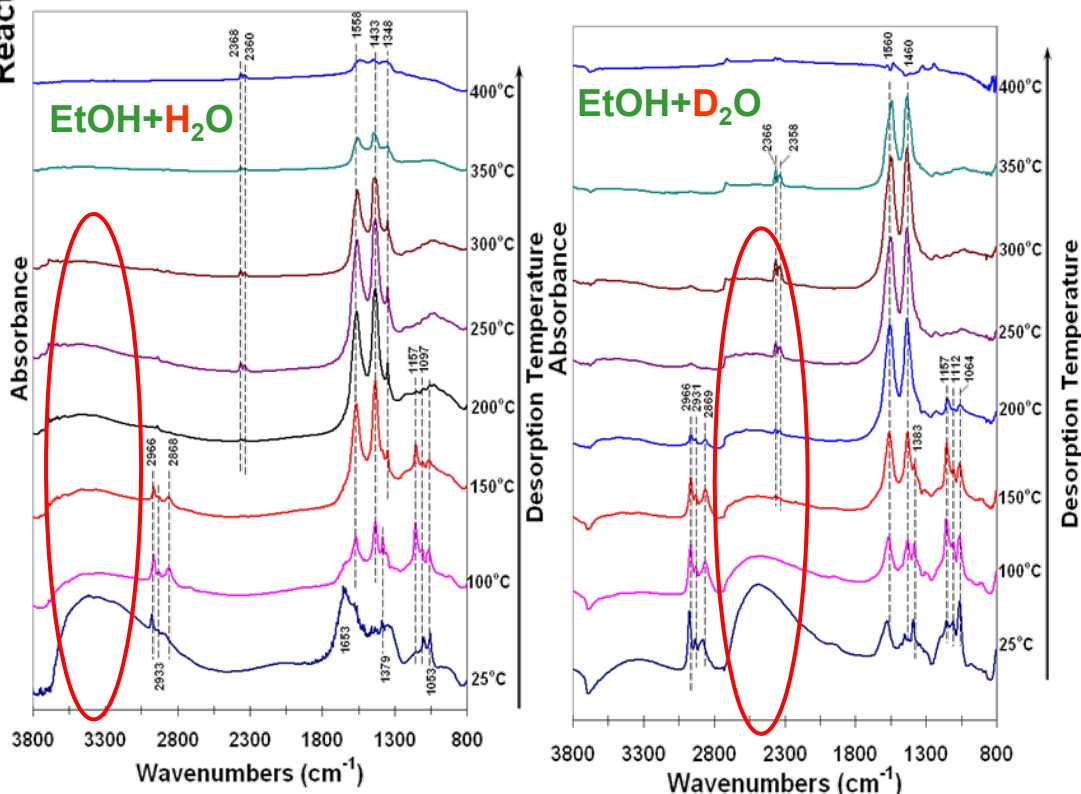
CH3-CH2
 $\begin{matrix} \text{CH}_3 \\ | \\ \text{CH}_2 \\ | \\ \text{O} \\ | \\ \text{M} \end{matrix}$

Role of Water: In-Situ DRIFTS with Isotopic Labeling of H₂O in EtOH+H₂O TPD



Water participates in ESR by providing the surface OH groups.

The H atoms simultaneously formed during the dissociative adsorption of water are involved in the final hydrogen and CH₄ formation.

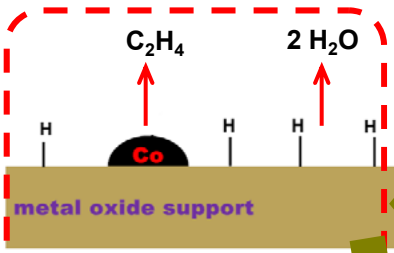
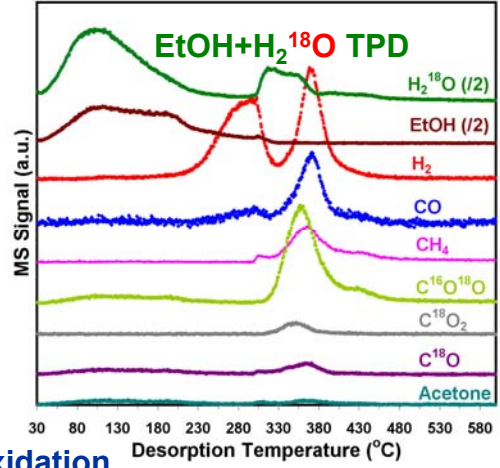


Technical Accomplishments and Progress

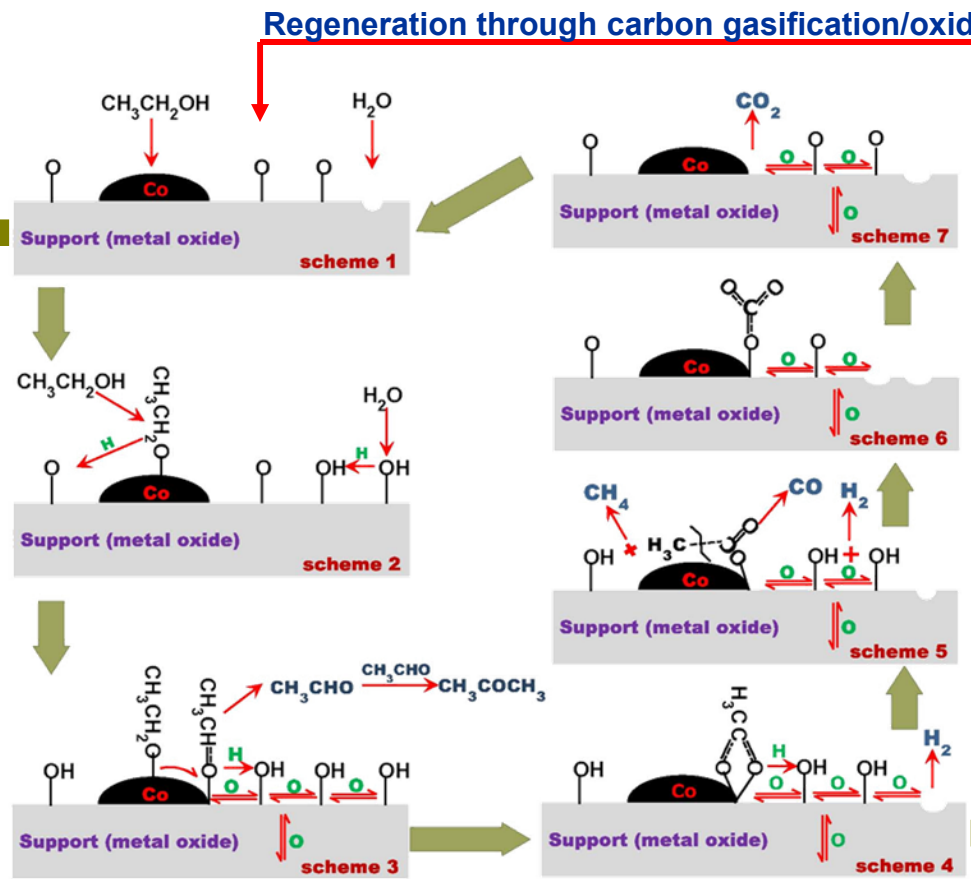
Understanding the surface species and surface mechanisms

Proposed Reaction Mechanism

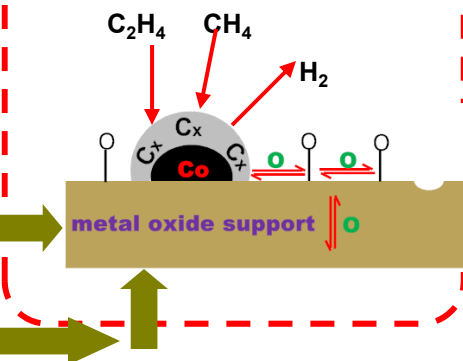
Ethanol steam reforming is a redox reaction during which carbon contained in ethanol is oxidized to CO_2 by oxygen in water (facilitated by surface and lattice oxygen mobility) and hydrogen formation is achieved by simultaneous reduction.



When surface is more acidic, ethanol dehydration is favored, leading to C_2H_4 formation. The formation of C_2H_4 is the precursor to coking.



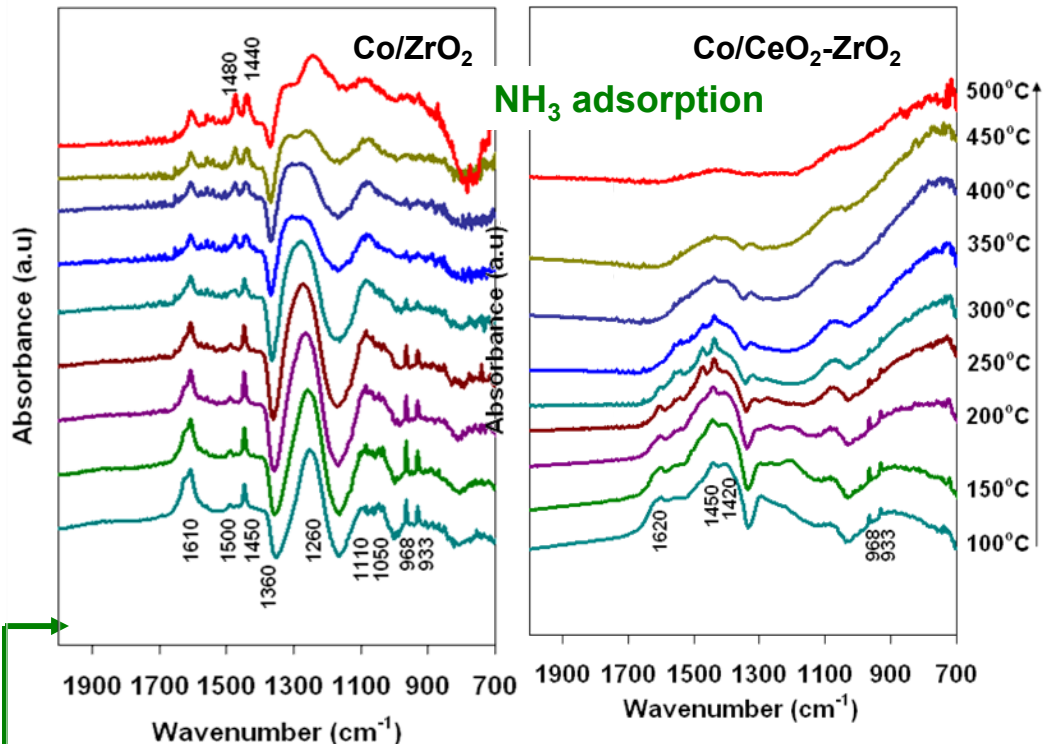
Catalyst is deactivated when hydrocarbons decompose on the surface, leaving carbon fragments and when these carbonaceous fragments or surface acetates can not be efficiently removed from the cobalt - support interface.



Technical Accomplishments and Progress

Decreasing surface acidity

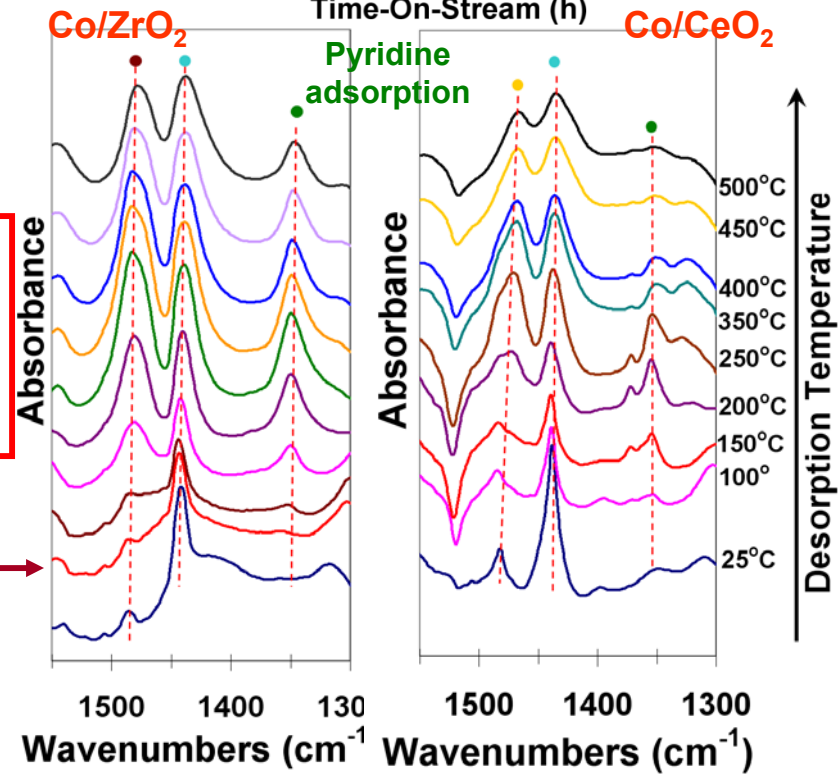
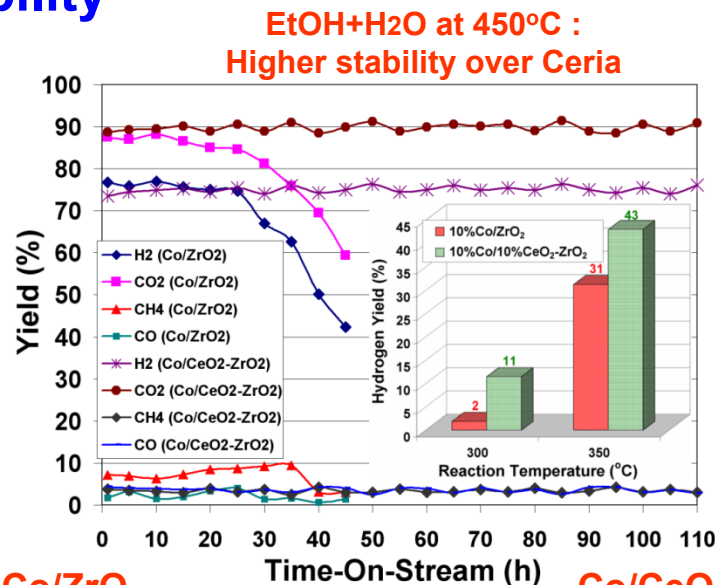
Controlling Stability



- NH₄⁺: 1450, 1500cm⁻¹ (asymmetric)
1610cm⁻¹ (symmetric)
- NH₃: 1260cm⁻¹ (co-ordinatively bonded)
1110, 1050cm⁻¹ (molecularly)
- Brønsted acid sites: 1620, 1450, 1420cm⁻¹

- Pyridinium ion: 1349cm⁻¹;
- Lewis acidic sites: 1439cm⁻¹;
- Both Brønsted and Lewis acidic sites: 1479cm⁻¹;
- Brønsted acidic sites: 1467cm⁻¹;

- ❖ Acidic surfaces catalyze the dehydration reaction, forming C1-C2 hydrocarbons, which lead to carbon deposition on the surface.
- ❖ CeO₂ support is less acidic than ZrO₂

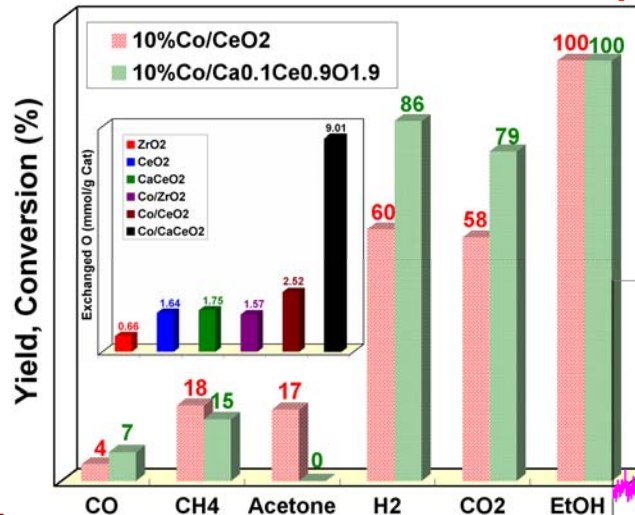
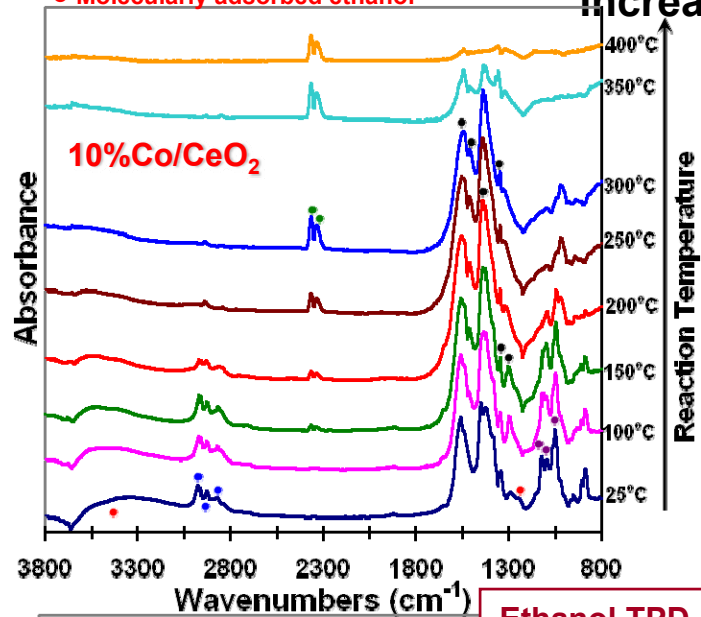


Technical Accomplishments and Progress

Controlling Stability

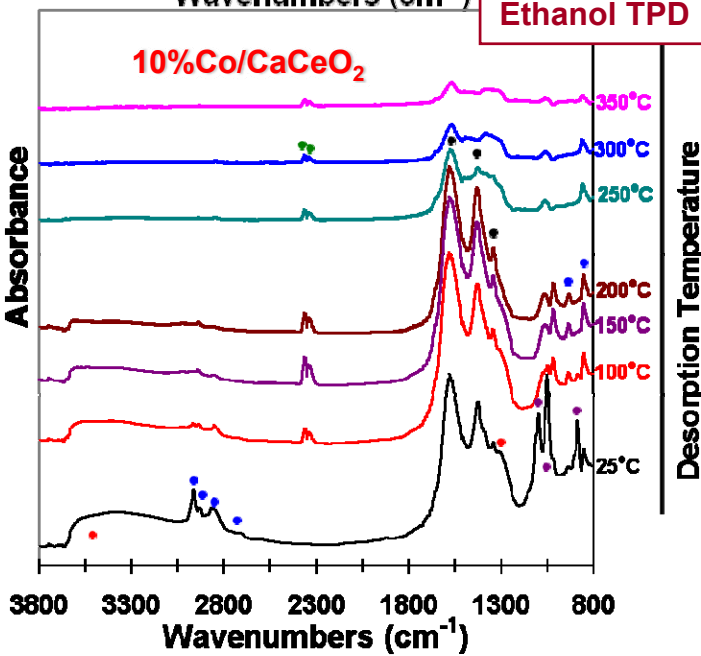
- CH_3^- , $-\text{CH}_2^-$
- Adsorbed CO_2
- Acetates, or carbonate at various adsorbed forms
- Ethoxide
- Molecularly adsorbed ethanol

Increasing oxygen mobility of the catalyst

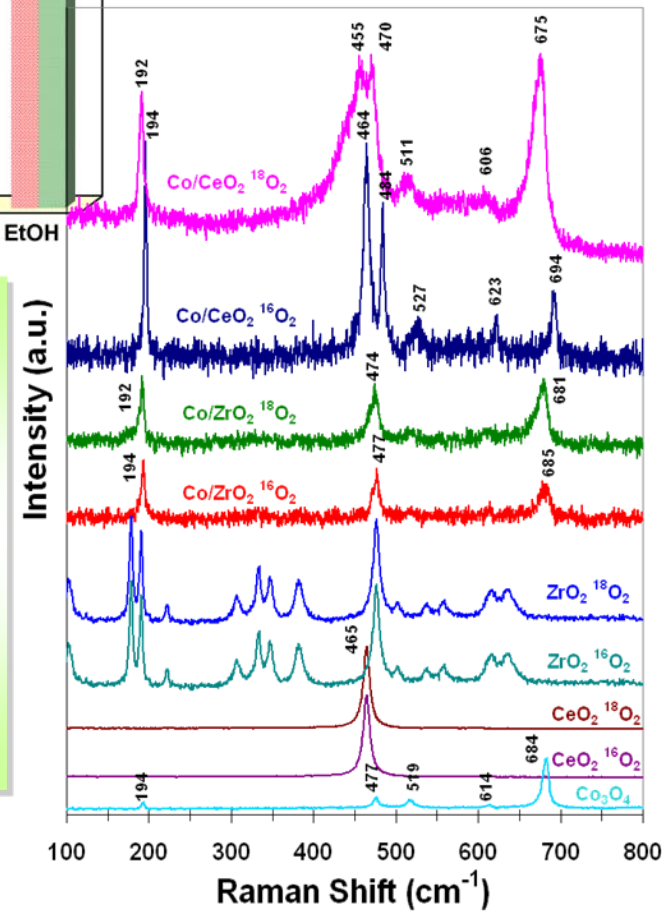


T=400°C under neat conditions

Investigation of oxygen exchange using ¹⁸O₂ Isotopic Shift in Raman Spectra



- ❖ Doping the support with a low-valence ion (e.g., Ca) will create oxygen vacancies, leading to higher oxygen mobility;
- ❖ Higher oxygen mobility will provide better stability by readily oxidizing the carbonaceous fragments on the surface.
- ❖ Ca doping also improved selectivity under neat conditions

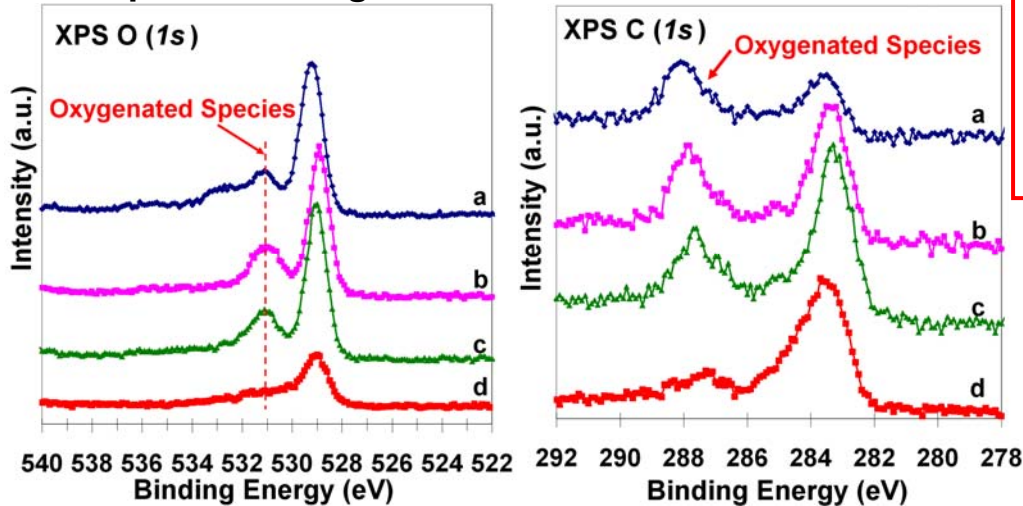


Technical Accomplishments and Progress

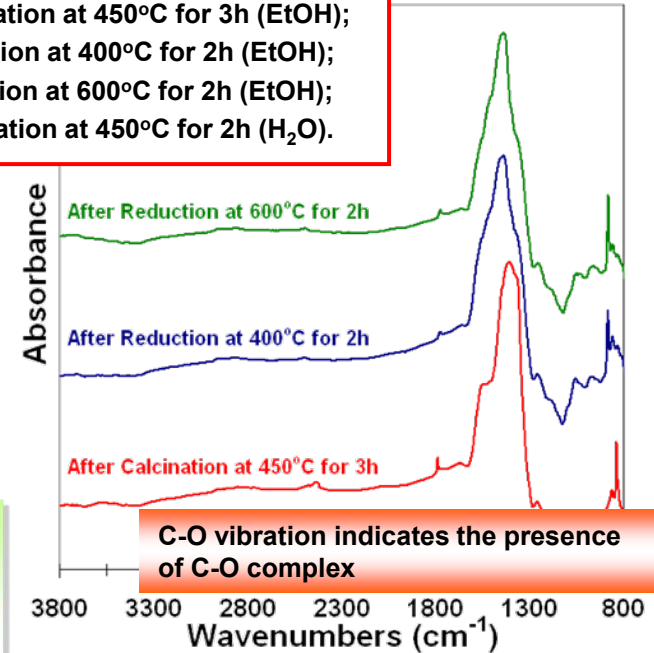
Controlling Selectivity



Effect of Impregnation medium Aqueous vs organic media

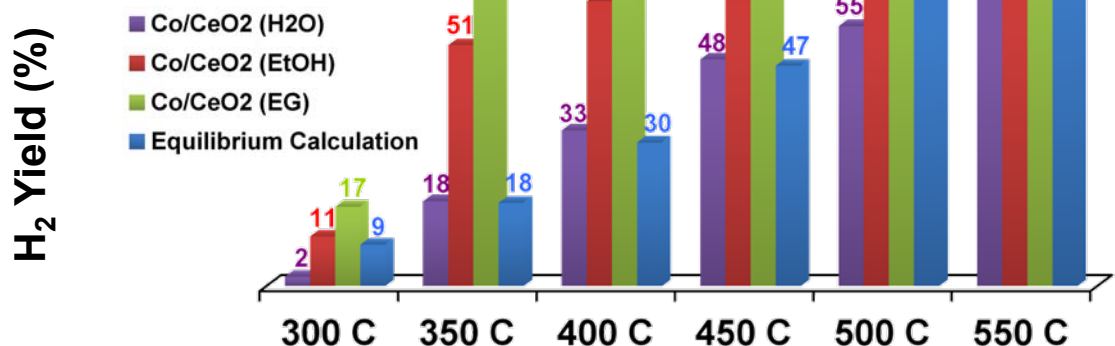
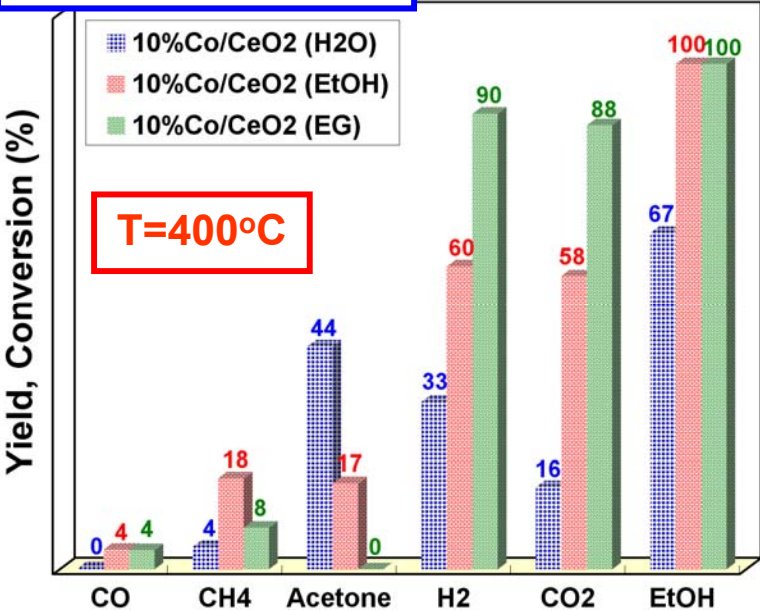


10%Co/CeO₂ :
 a: After calcination at 450°C for 3h (EtOH);
 b: After reduction at 400°C for 2h (EtOH);
 c: After reduction at 600°C for 2h (EtOH);
 d: After calcination at 450°C for 2h (H₂O).



EtOH:H₂O=1:10 (molar ratio);
 C_{EtOH}=7.5vol.%;
 WHSV~0.54gEtOH/gCat/h;

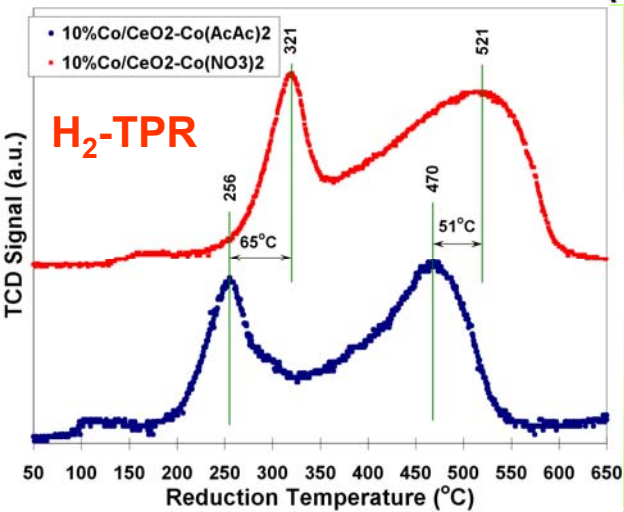
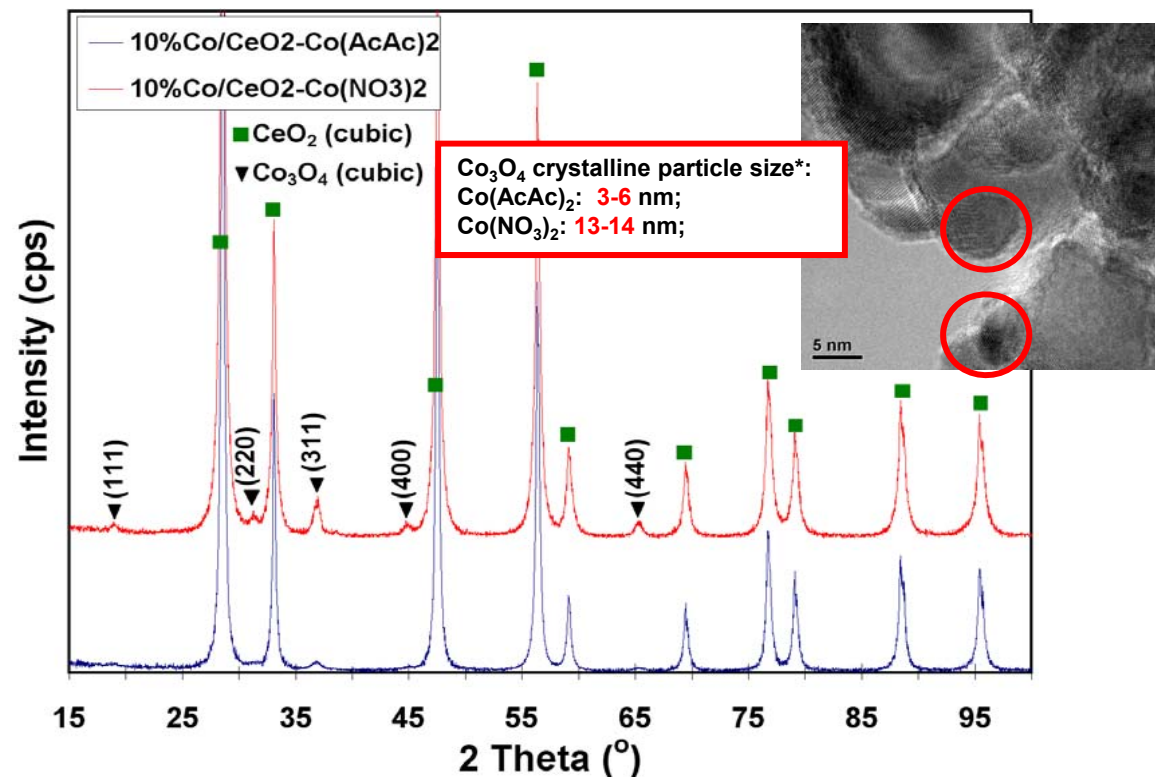
Organic impregnation media lead to more selective and active catalysts, due to the presence of the presence of C-O complexes on the surface, possibly providing segregation of the Co sites.



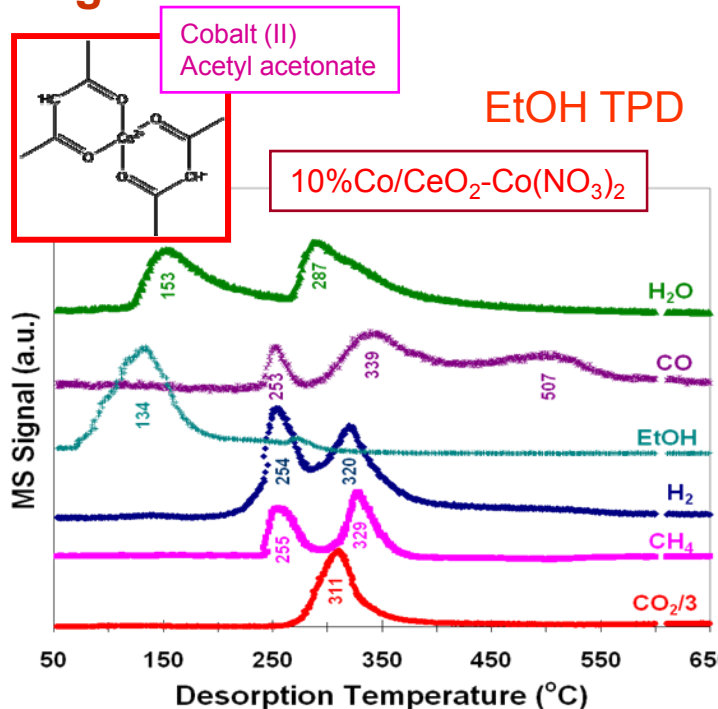
Technical Accomplishments and Progress

Controlling dispersion

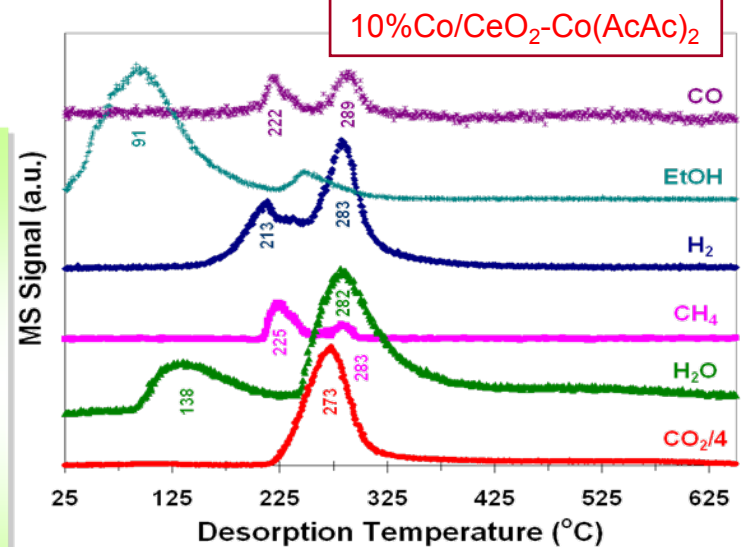
Choice of precursor



- ❖ Co precursor affects the particle size and dispersion as seen in XRD and TEM results.
- ❖ Use of Co(AcAc)₂ leads to much smaller particle size and better dispersion.
- ❖ Dispersion affects reducibility and activity, as seen in TPD and TPR experiments.



EtOH TPD

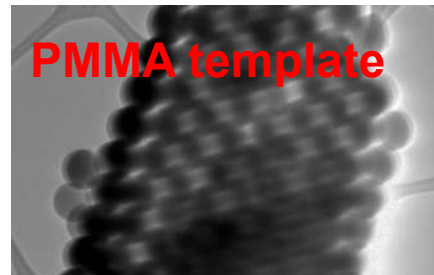


Technical Accomplishments and Progress

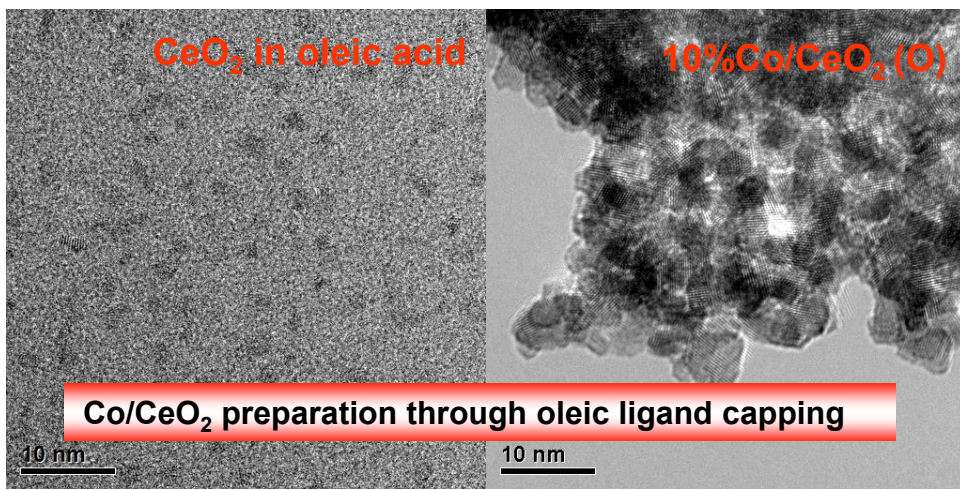
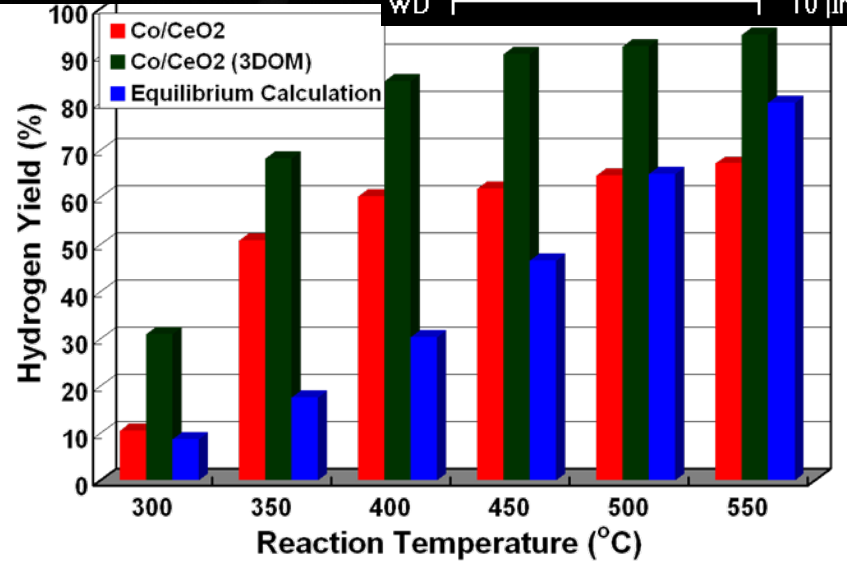
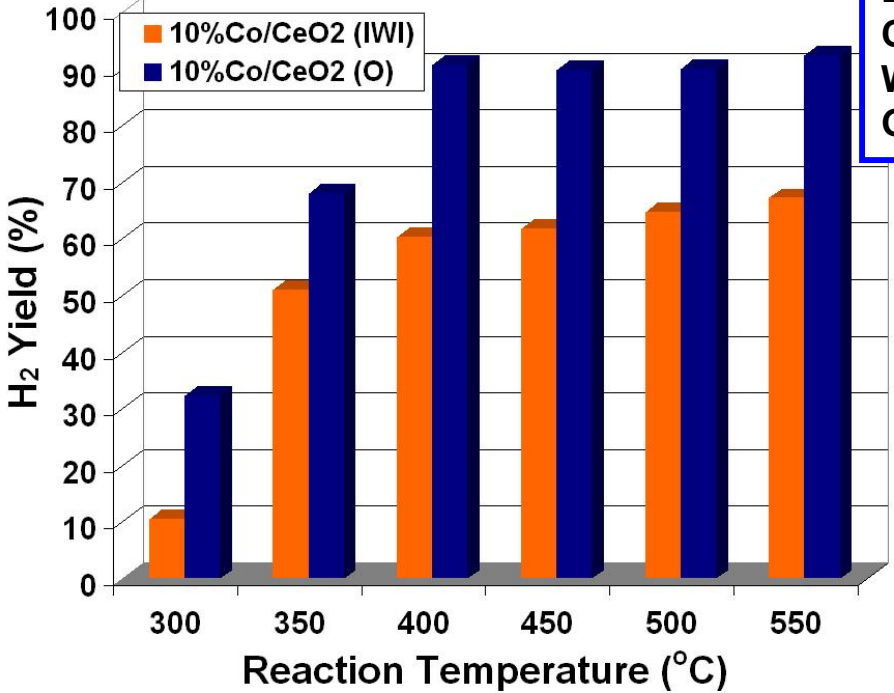
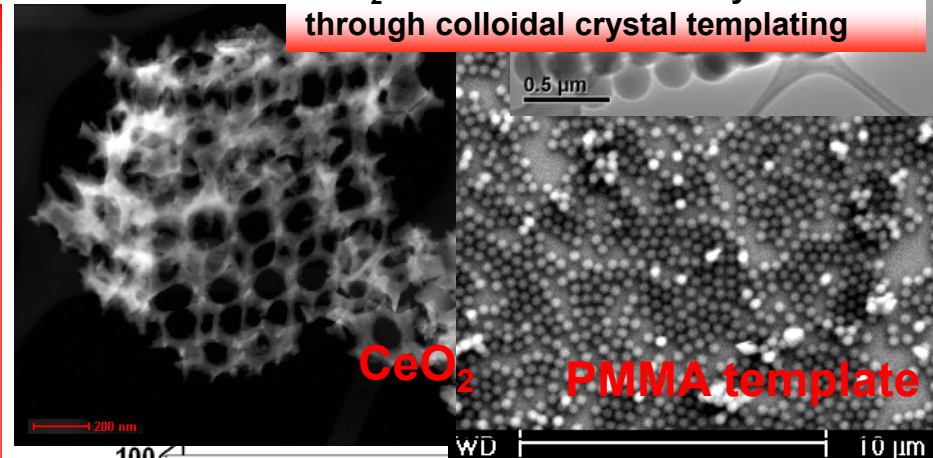
Controlling Support Morphology

Novel colloidal synthesis techniques allow close control of morphology.

EtOH:H₂O=1:10 (molar ratio);
 C_{EtOH}=7.5vol.%;
 WHSV~0.54gEtOH/gCat/h;
 GHSV~5,000h⁻¹



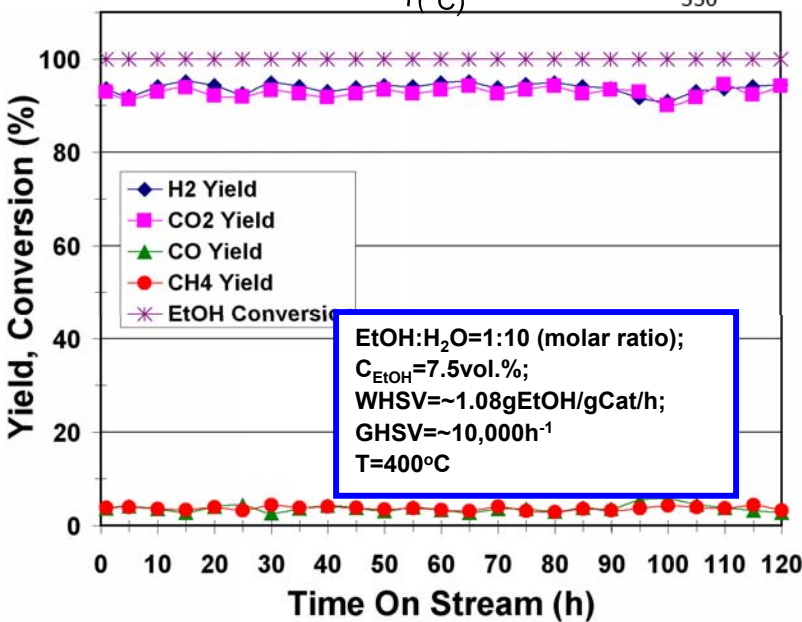
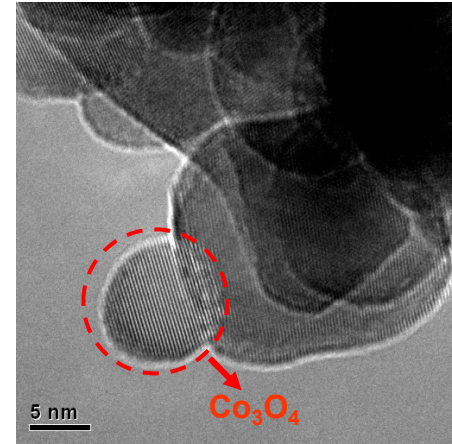
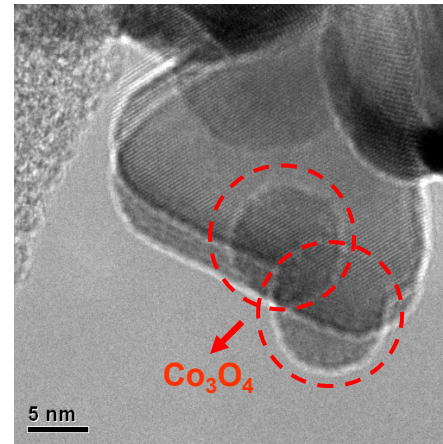
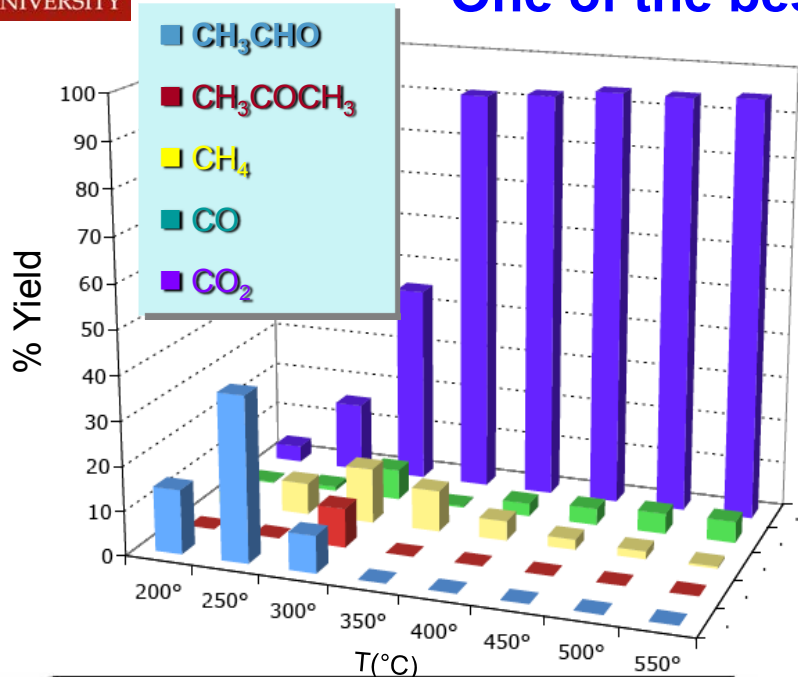
CeO₂ with 3DOM structure synthesized through colloidal crystal templating



Co/CeO₂ preparation through oleic ligand capping

Technical Accomplishments and Progress

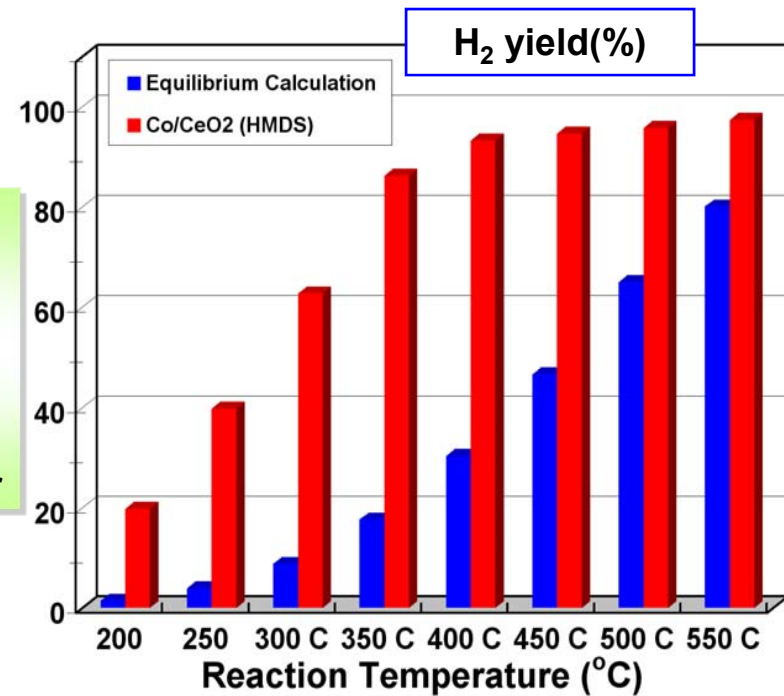
One of the best performing catalysts



Above 300° C,
no liquid
products.

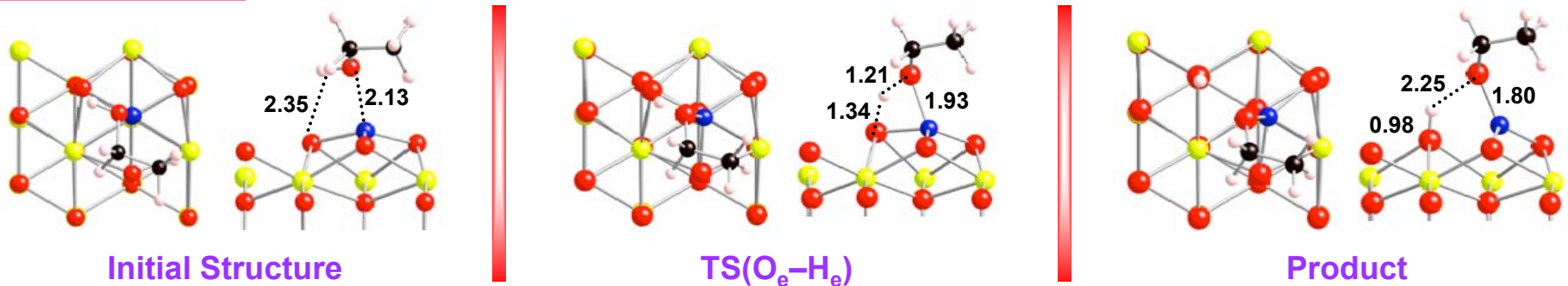
Over 90% H₂
yield

Stable in a 120-hr
TOS experiment

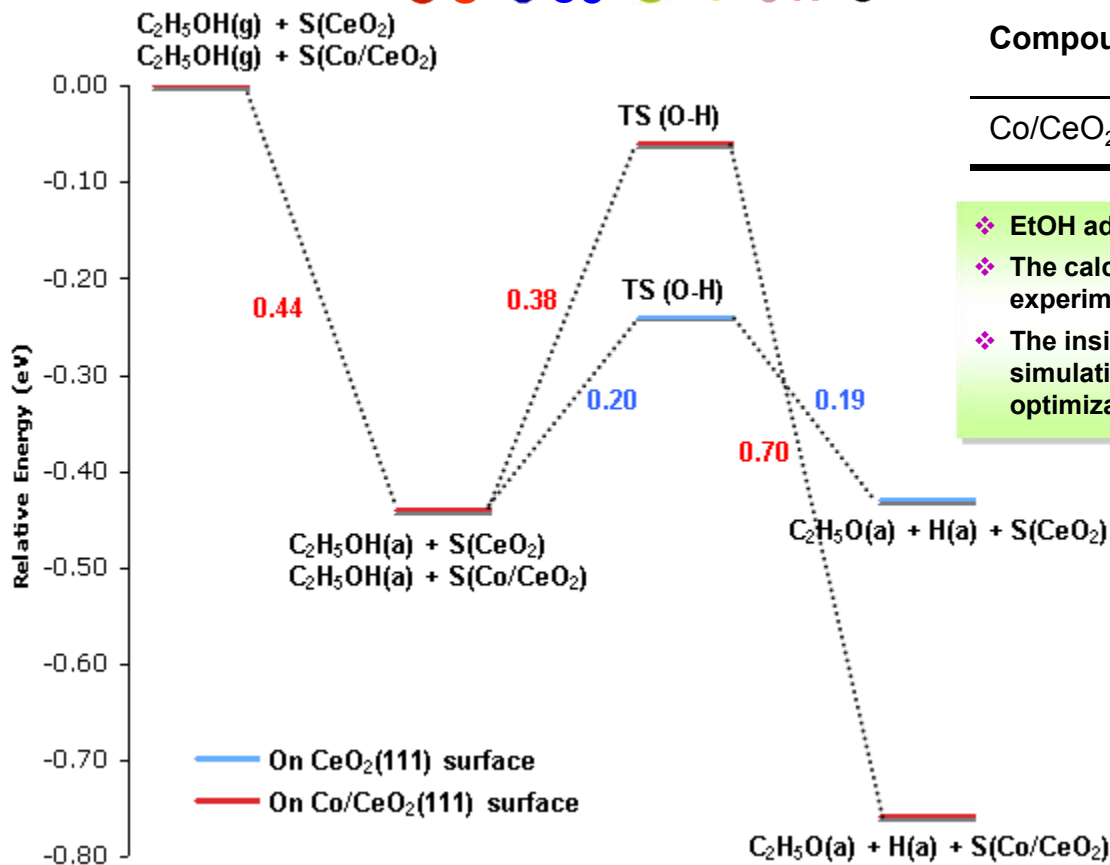


**EtOH
adsorption on
Co/CeO₂ (111)**

Technical Accomplishments and Progress Combining Experimental Work with Molecular Simulation

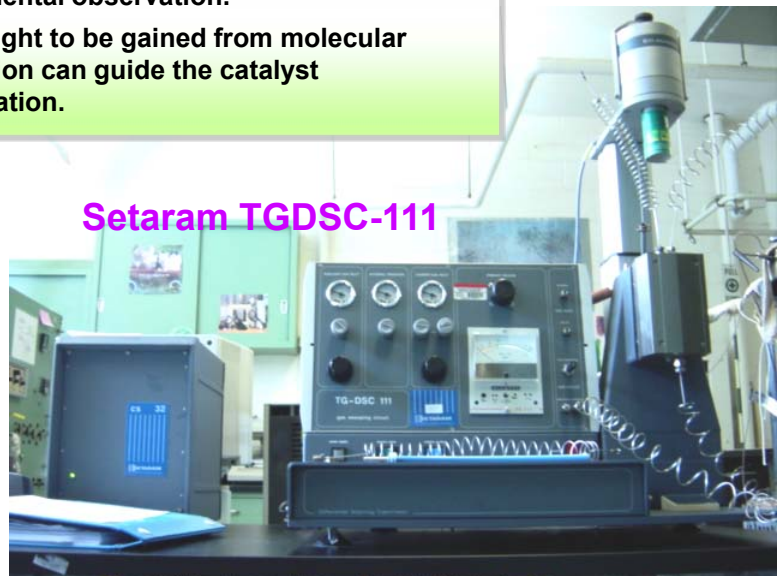


● O ● Co ● Ce ● H ● C

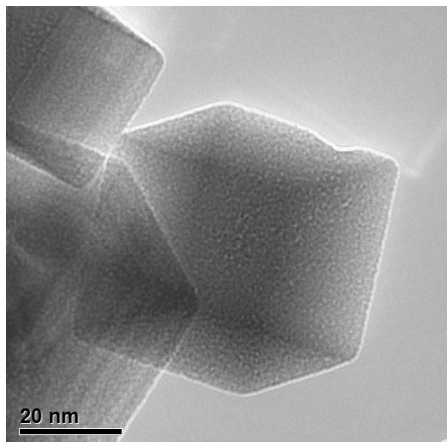


Compound	Adsorption Energy		
	Experimental	Calculation	Difference
Co/CeO ₂	16.63kcal/mol	17.52kcal/mol	5.3%

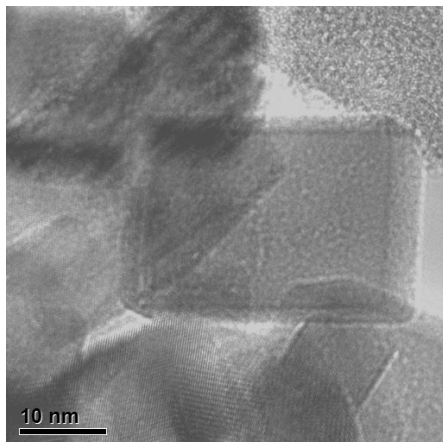
- ❖ EtOH adsorption on Co is favored.
- ❖ The calculation result is consistent with experimental observation.
- ❖ The insight to be gained from molecular simulation can guide the catalyst optimization.



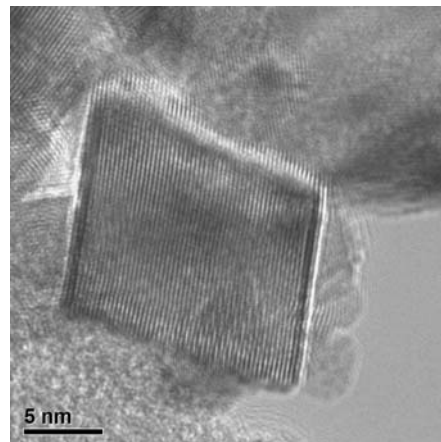
Control of support nano-structure



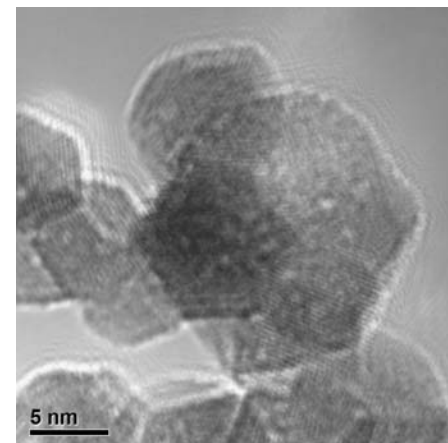
Nanocube



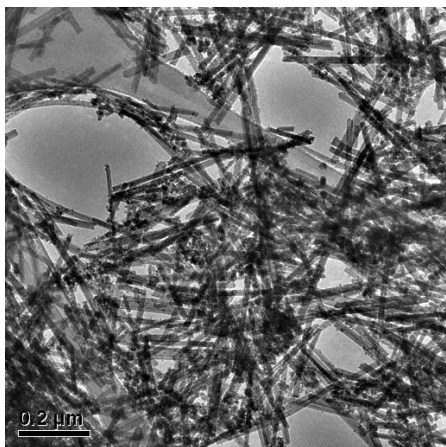
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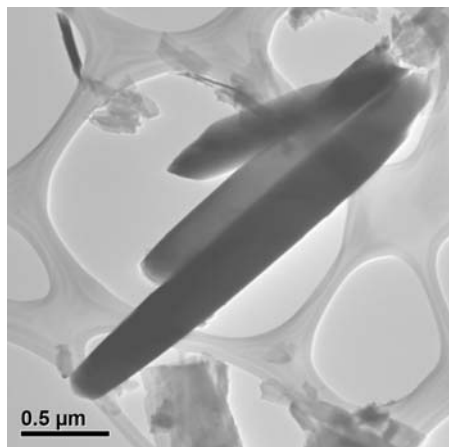
Nanoplate



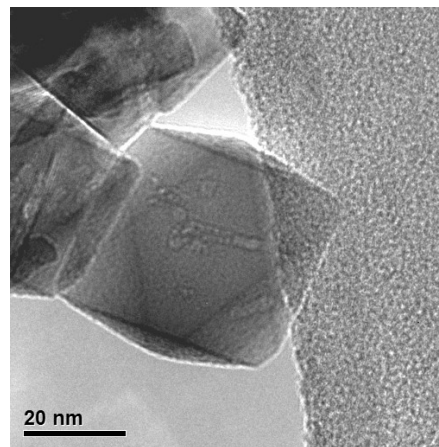
Nanopolyhedron



Nanorod



Nanobelt



Nano-octahedron

- ❖ It is possible to grow nano-structures with controlled architectures.
- ❖ Based on the results of molecular simulation, different support nano-structures can be used.

Collaborations

- ❖ Collaboration with Chemistry Department (Prof. Hadad) on combining experimental work with molecular simulation has progressed. A paper, that resulted from this collaboration “Computational Study of the Ethanol Steam Reforming Reaction over Co/CeO₂(111): from Ethanol to Acetate” has already been submitted to ACS for presentation at the ACS National Meeting in August 2009. A post-doctoral researcher and a graduate student are being jointly advised by the P.I. and Dr. Hadad.
- ❖ A new collaboration with Argonne National Lab (Dr. Christopher Marshall’s team) has been initiated to incorporate XAFS studies in the project. A proposal titled “In-situ XAFS Characterization of cobalt-based catalysts for steam reforming of bio-derived liquids” has been submitted to Argonne National laboratory to request beam time at the synchrotron facilities. Five members of the P.I.’s team have registered as facility users at Argonne National Lab.
- ❖ Collaboration with Nextech Materials, Inc. for scale-up of the catalyst manufacturing process is in place.
- ❖ Collaboration with PNNL. Sharing findings

Summary



Relevance:

A fundamental study aimed at developing precious-metal free catalysts for hydrogen production from bio-ethanol

Approach:

An integrative approach that combines catalyst synthesis, characterization and kinetic studies in an iterative manner to develop a fundamental understanding of the nature of active sites, reaction networks and reaction mechanisms involved in ethanol steam reforming over Co-based catalysts

Technical accomplishments and progress:

Developed an understanding of the reaction networks and surface mechanisms that allow correlating specific sites with specific reaction steps and deactivation mechanisms

Developed techniques for tailoring the catalytic properties to meet the needs of the reaction

Developed promising catalyst formulations that can achieve high H₂ yields and selectivities at low temperatures

Collaborations:

Active partnership with Chemistry Department on molecular simulation

New partnership with Argonne National Lab for XAFS studies

Partnership with NexTech for catalyst manufacturing

Proposed Future work:

Long term stability tests, accelerated deactivation tests, kinetic measurements to obtain kinetic parameters and allow kinetic modeling, *in-situ* XAFS studies

- ❖ Kinetic and mechanistic studies will be coupled with catalyst characterization under reaction conditions to obtain kinetic parameters. Rate expressions will be developed for kinetic modeling.
- ❖ Long term time-on-stream experiments will be performed (e.g., >100hrs under neat reaction conditions).
- ❖ Accelerated deactivation and regeneration studies (e.g., higher C/S ratio and GHSV) will be performed.
- ❖ Economic analysis will be fine-tuned based on updated catalyst system knowledge database and the new H2A model.
- ❖ Molecular simulation work using DFT calculations will be continued and used to guide rational catalyst design. This is a collaborative activity.
- ❖ *In-situ* XAFS experiments will be performed at Argonne National Lab to elucidate the oxidation state and coordination environment of cobalt sites during reaction. This will be a collaborative activity.
- ❖ Catalyst synthesis for best performing catalysts will be scaled-up through industrial partnership.
- ❖ Several publications are in preparation and will be submitted within the next 6 months.

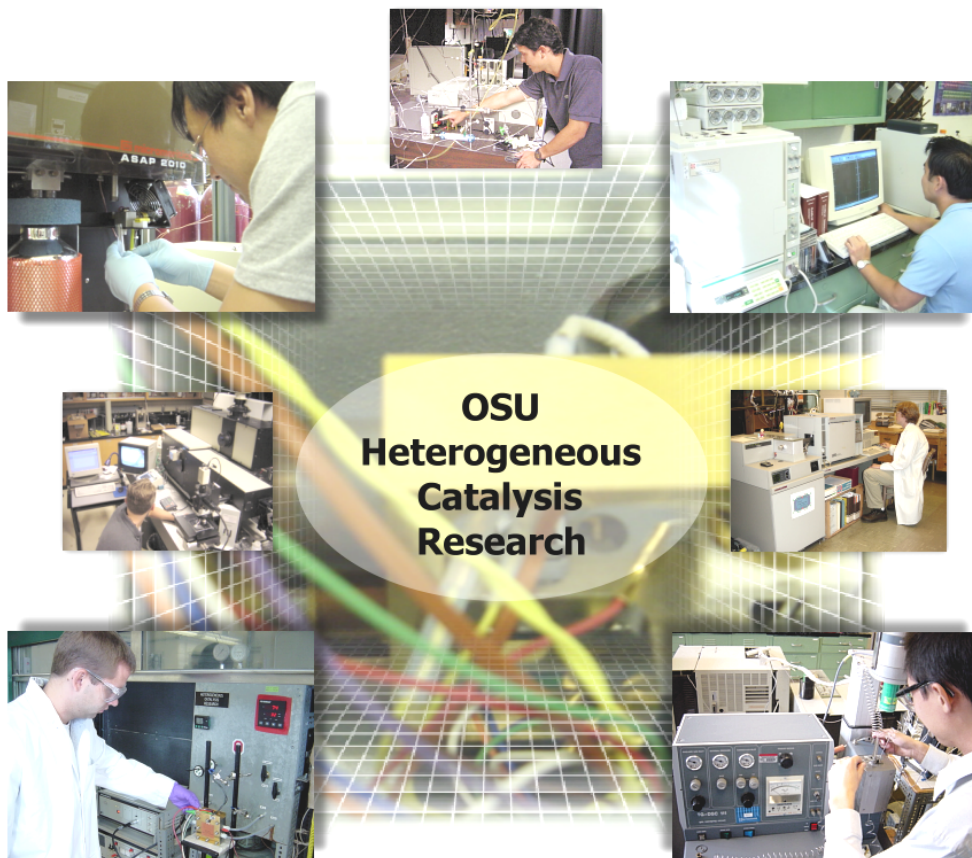


DOE Hydrogen Program

Acknowledgement



Department of Energy

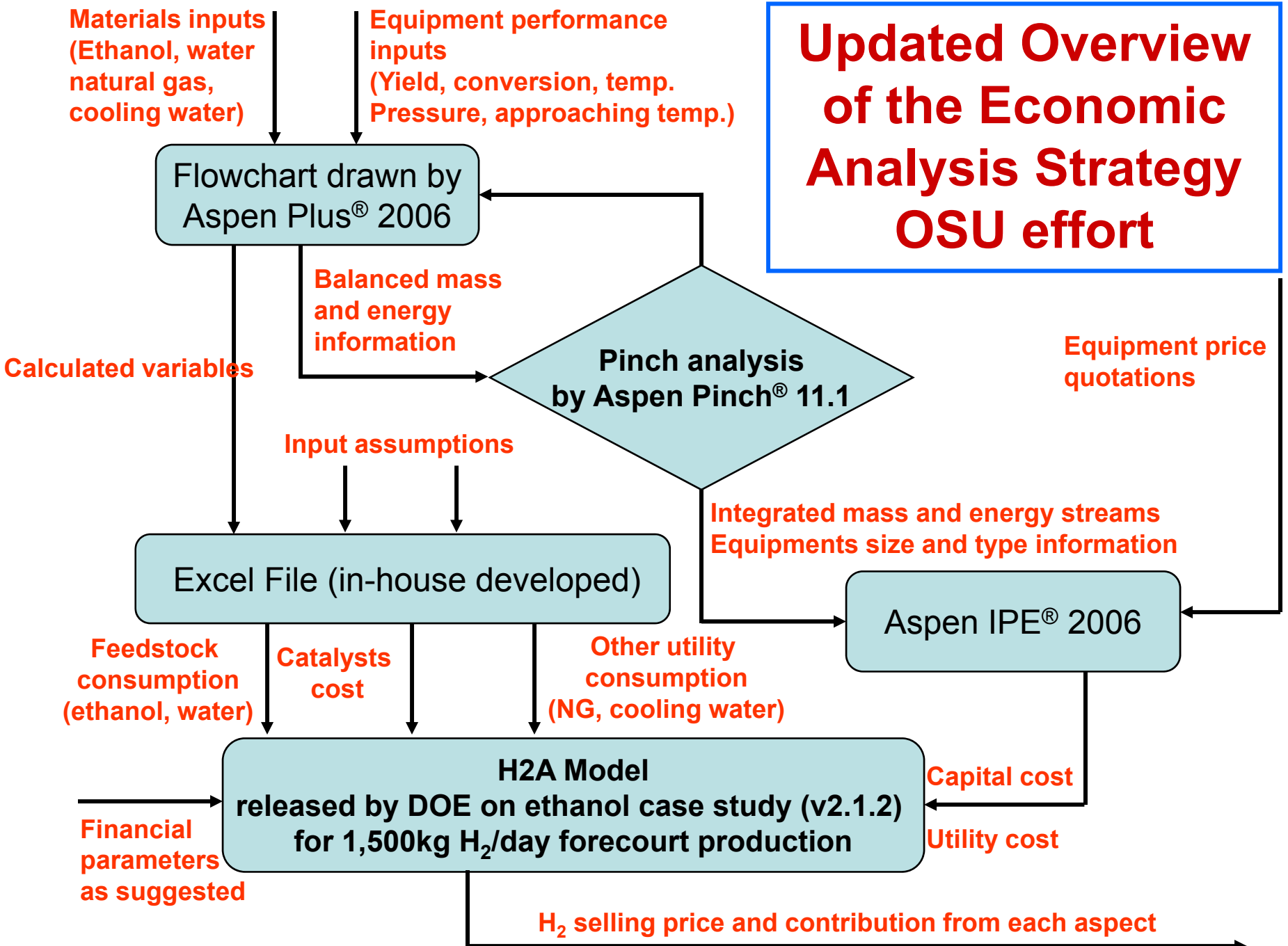


**OSU
Heterogeneous
Catalysis
Research**

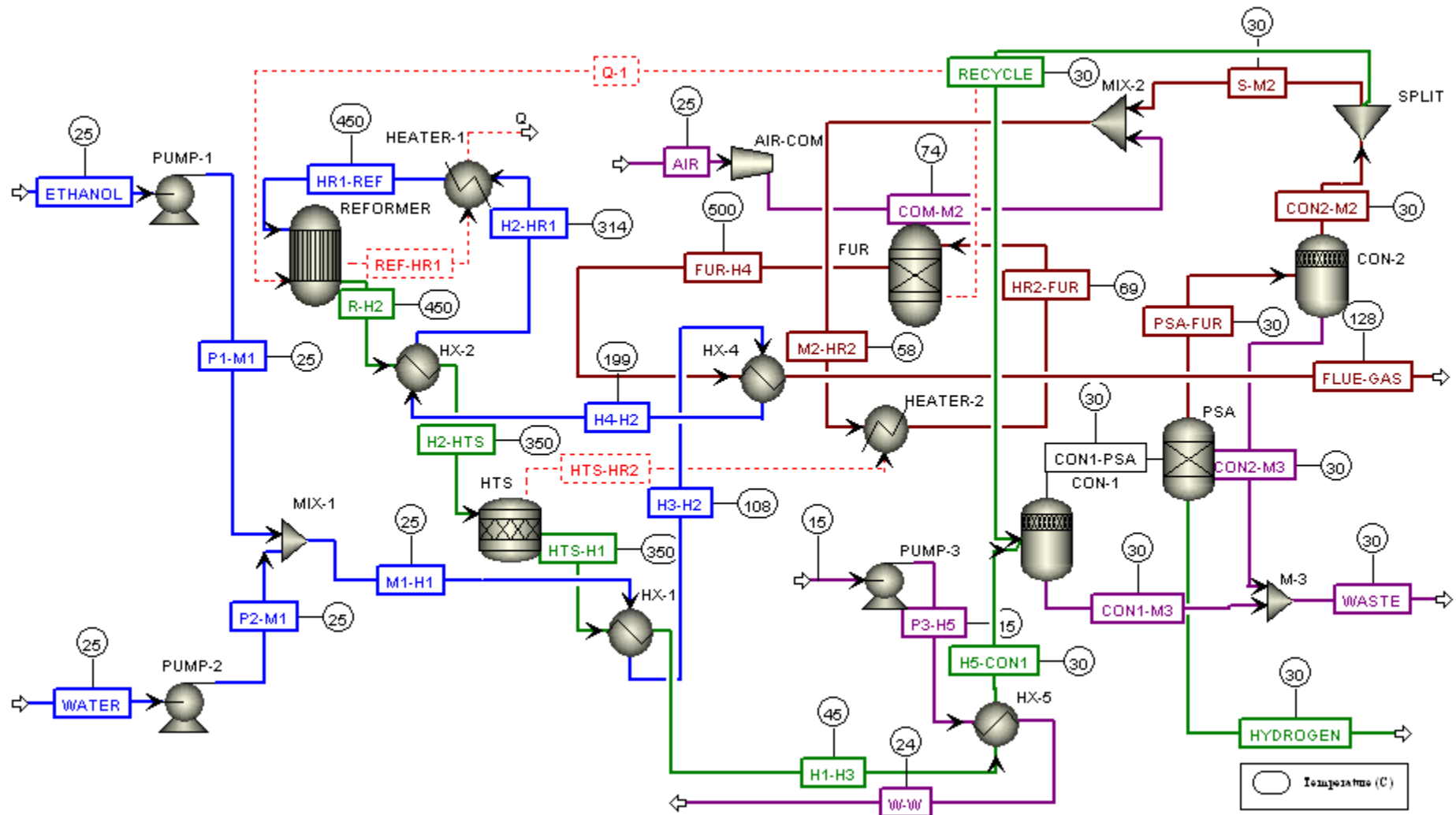


Additional slides

Updated Overview of the Economic Analysis Strategy OSU effort



Updated Economic Analysis – Simulation Flowchart (OSU effort)



- ❖ 75% hydrogen recovery on PSA. Part of the flue gas exiting from PSA was recycled back into PSA to improve H_2 recovery;
- ❖ Reformer is simulated as RYield with temperature at 450°C and furnace is simulated as RGibbs model;
- ❖ HTS reactor is simulated as RStoic model with conversion of CO as 90%;
- ❖ 1:10 molar ratio of EtOH-to- water is used for simulation (except when the effect of this ratio is examined).

Updated Economic Analysis at Forecourt Production Scale - (1,500 kg H₂/day)



Estimation Case	Production Cost \$/kg	Total Cost (Production/Storage/Disp.) \$/kg
Old OSU Efforts	3.59	4.27
OSU & Directed Tech. Collaborative Efforts	2.95	4.97
H2A Ethanol Case Study (v2.1.2)	3.18	5.07
New OSU Efforts*	2.75	4.63

- ❖ The reduction of H₂ production cost is due to the employment of higher operating capacity factor and longer lifetime and slightly higher GHSV of the OSU developed catalyst;
- ❖ The increase of final H₂ cost is mainly attributed to the re-evaluation of the H₂ compression /storage / dispensing cost in the latest released H2A model, which is not related with the contribution from production part.

- ❖ *75% hydrogen recovery on PSA. Part of the flue gas exiting from PSA was recycled back into PSA to improve H₂ recovery;
- ❖ *85.2% is employed as the standard operating capacity factor for forecourt production;
- ❖ 1:10 molar ratio of EtOH-to- water is used for simulation (except when the effect of this ratio is examined).
- ❖ *New version (v2.1.2) of H2A model is used for the updated cost estimation;
- ❖ 90% H₂ yield with ethanol to water of 1 to 10 and 70% capacity factor are assumed;
- ❖ *"OSU" catalyst is used for bioethanol steam reforming with 5,000h⁻¹ GHSV and 1 year lifetime;
- ❖ Commercial catalyst is used for HTS reaction with 3000h⁻¹ GHSV and 5 years lifetime at \$4.67/lb;
- ❖ Same financial parameters and capital cost for forecourt station compression and storage are used.