2009 DOE Annual Merit Review Meeting

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

Acknowledgement
US DOE

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OSU HCRG Heterogeneous Catalysis Research Group

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Overview

DOE Hydrogen Program

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

OSU HCRG Heterogeneous Catalysis Research Group

Relevance

Project overview

- Catalytic H_2 production from bioethanol
  - Renewable sources;
  - Plant matter (natural CO_2 recycling);
  - Lends itself well to distributed H_2 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^{o}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

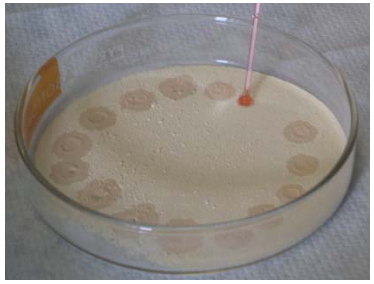
Approach

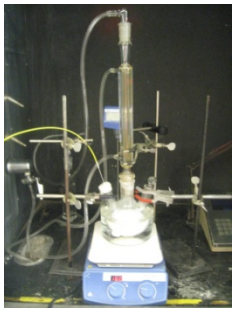
Milestones and Progress

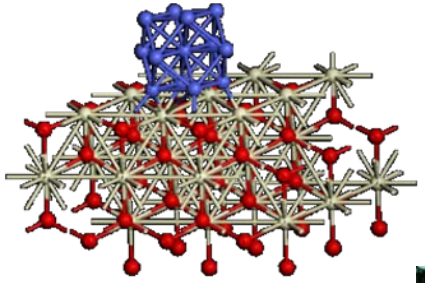
	Tasks	Progress	% comp
1	Setting up the experimental systems, establishing protocols, training personnel	Built, installed a reactor system and established experimental protocols; Completed a HAZOP review for the ethanol reforming reactor system;	100%
2	Economic analysis	Completed an initial economic analysis 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^{o}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%

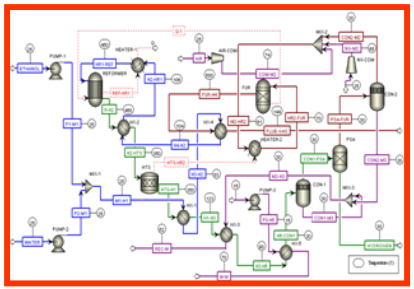
Technical Approach

An integrative approach - Iterative with feed-back







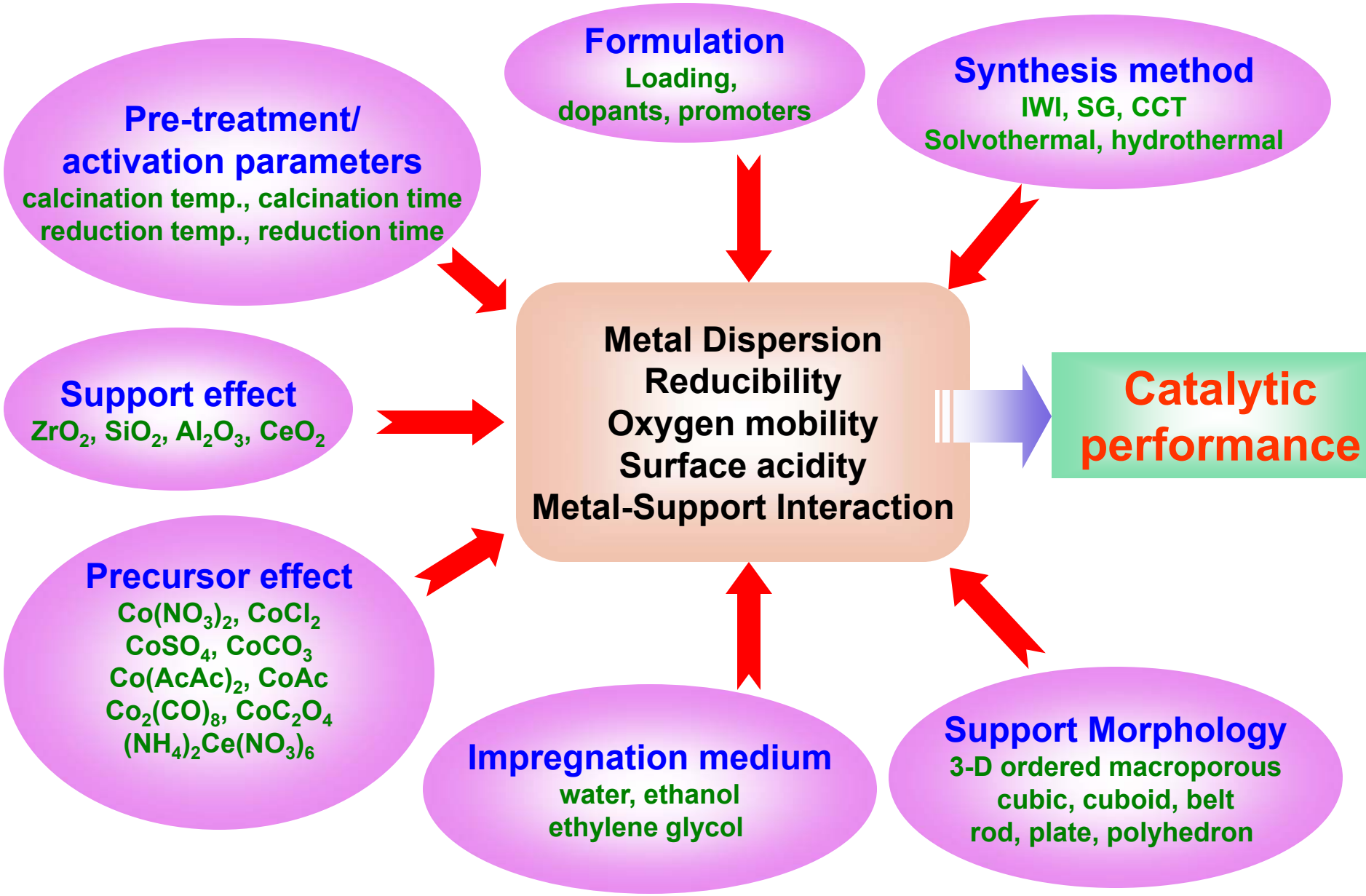


Development of non-precious metal, low-temperature catalysts with:
high activity
high selectivity
high stability
economical feasibility

DOE Hydrogen Program

Technical Approach

Systematic study of catalyst synthesis



Technical Approach

Catalyst characterization during its life history

surface area
pore size &distribution

surface intermediates
Molecular structure

Molecular structure
surface intermediates

Adsorption/desorption
Reduction/oxidation
characteristics

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

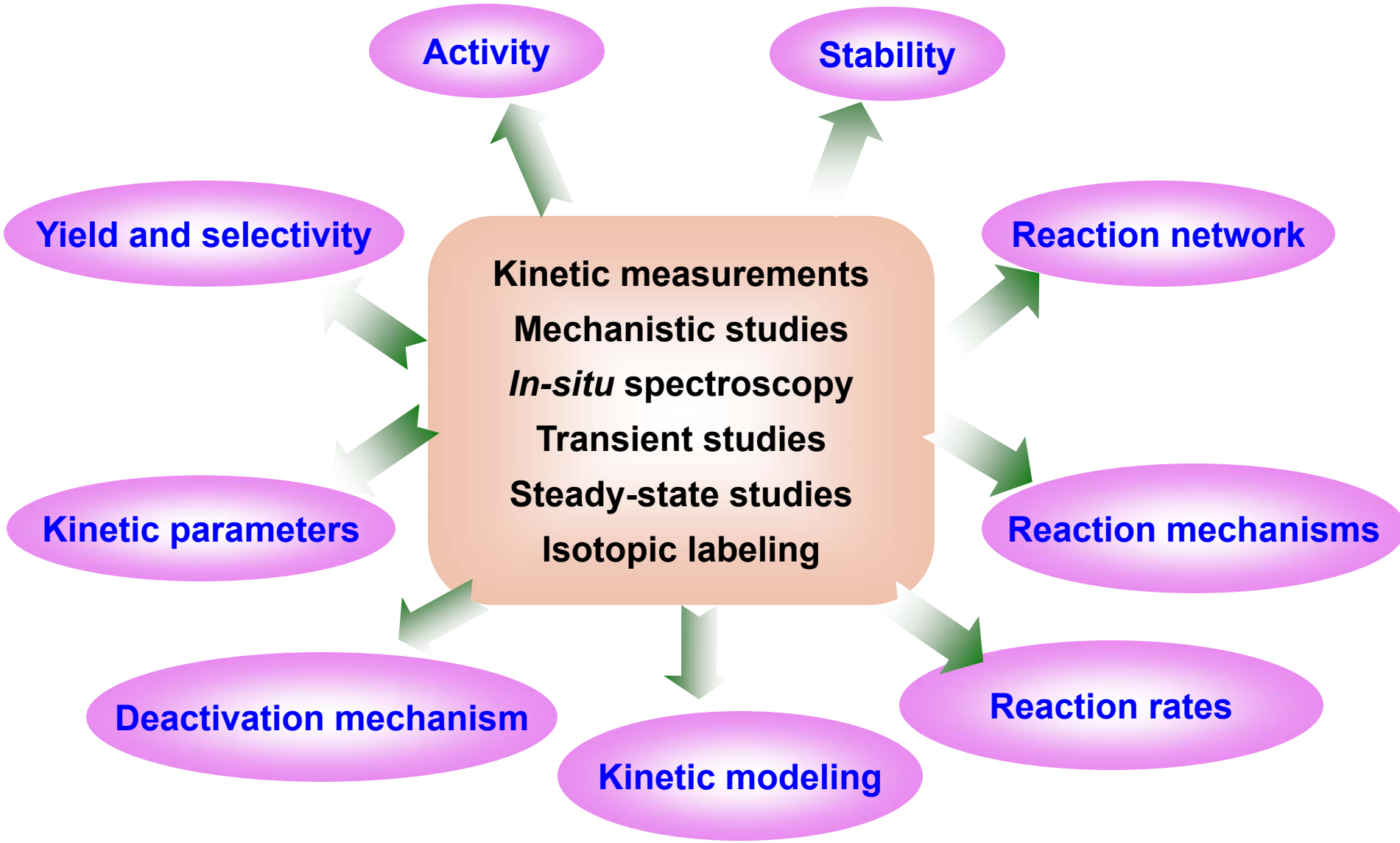
particle size
morphology
elemental analysis

gas analysis
Isotopic labeling

oxidation state
coordination environment

weight variation
heat effects

Technical Approach
Reaction Studies

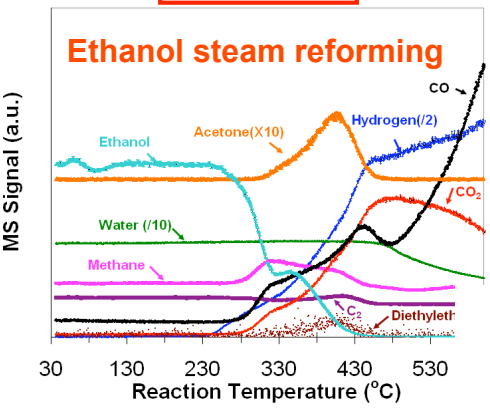


Technical Accomplishments and Progress

Understanding the Reaction Network

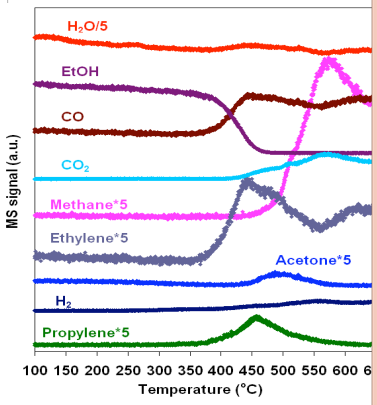
10%Co/ZrO_2

Ethanol steam reforming

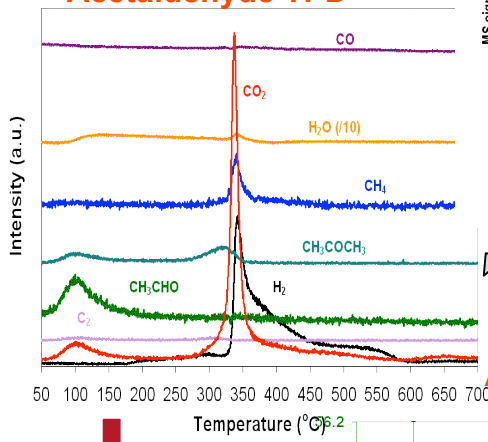


Acidic sites lead to formation of alkanes and olefins

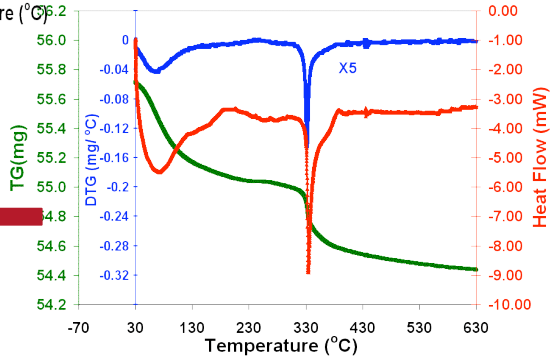
Acidic supports



Acetaldehyde TPD



TGA-DSC during Acetaldehyde SR



Acetaldehyde steam reforming and/or decomposition progress easily

A complex network of reactions catalyzed by different sites

Ethanol steam reforming:
$CH_3CH_2OH+H_2O \rightarrow 2\ CO+4H_2$

Ethanol dehydrogenation:
$CH_3CH_2OH \rightarrow CH_3CHO+H_2$

Acetic acid formation:
$C_2H_5OH+H_2O \rightarrow CH_3COOH+2\ H_2$

Ethanol decomposition:
$CH_3CH_2OH \rightarrow CH_4+CO+H_2$

Ethanol dehydration:
$CH_3CH_2OH \rightarrow C_2H_4+H_2O$

Acetaldehyde decomposition:
$CH_3CHO \rightarrow CH_4+CO$

Acetaldehyde steam reforming:
$CH_3CHO+3H_2O \rightarrow 2CO_2+5H_2$

Acetone formation:
$2\ CH_3CHO \rightarrow CH_3COCH_3+CO+H_2$

Water-gas shift:
$CO+H_2O \leftrightarrows CO_2+H_2$

Reverse water-gas shift:
$CO_2+H_2 \leftrightarrows CO+H_2O$

Methanation:
$CO+3\ H_2 \rightarrow CH_4+H_2O$

Methane steam reforming:
$CH_4+2\ H_2O \rightarrow CO_2+4\ H_2$

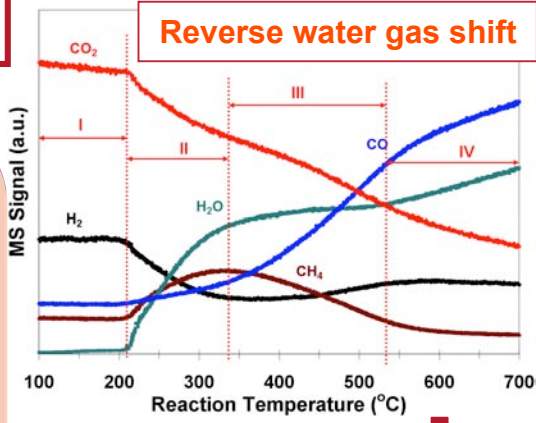
Ethylene decomposition:
$C_2H_4 \rightarrow coke$

Methane decomposition:
$CH_4 \rightarrow C+2\ H_2$

Boudouard reaction:
$2\ CO \rightarrow CO_2+C$

10%Co/ZrO_2

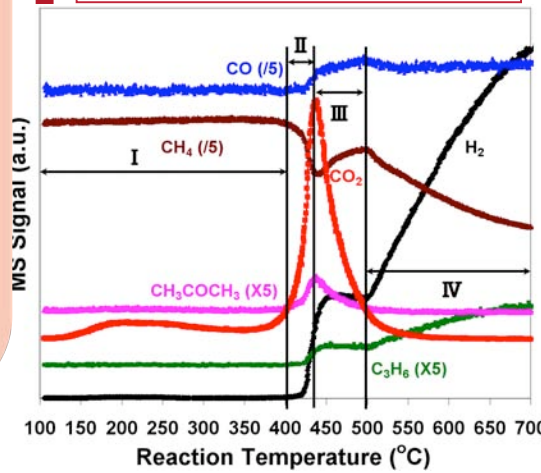
Reverse water gas shift



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

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

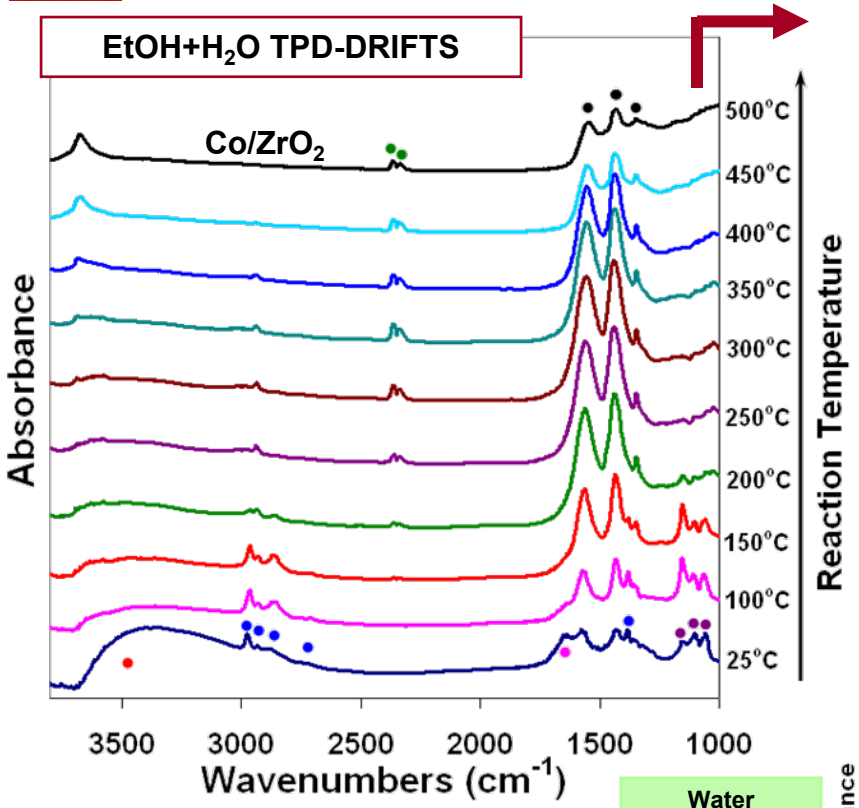
Methane steam reforming



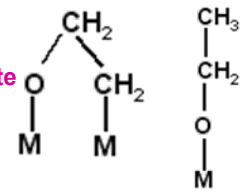
Technical Accomplishments and Progress

Understanding the surface species and surface mechanisms

EtOH+H_2O TPD-DRIFTS

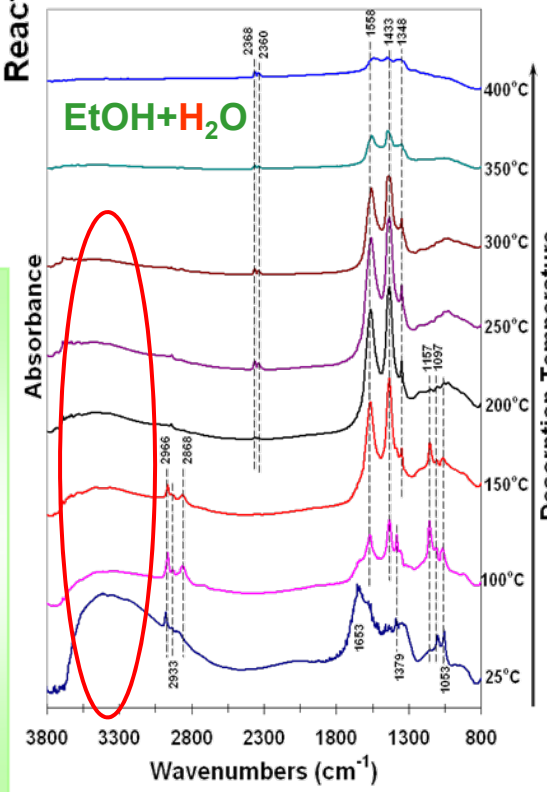


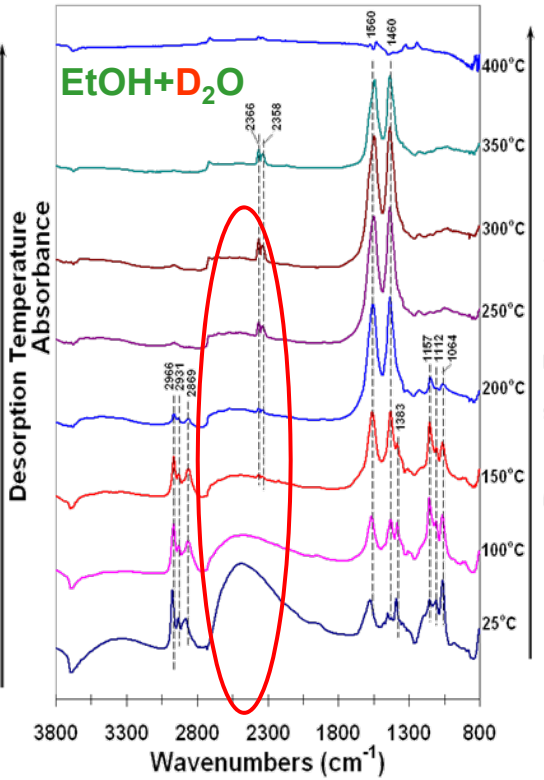
- **M-OH**
  3650~3150cm^{-1}, O-H stretching
- **CH_3- or CH_3CH_2-**
  2962, 2927, 2865 cm^{-1}:C-H stretching
  1385cm^{-1}: CH_3- bending
- **Monodentate and bidentate ethoxide**
  1169, 1106, 1063cm^{-1}
  CCO stretching

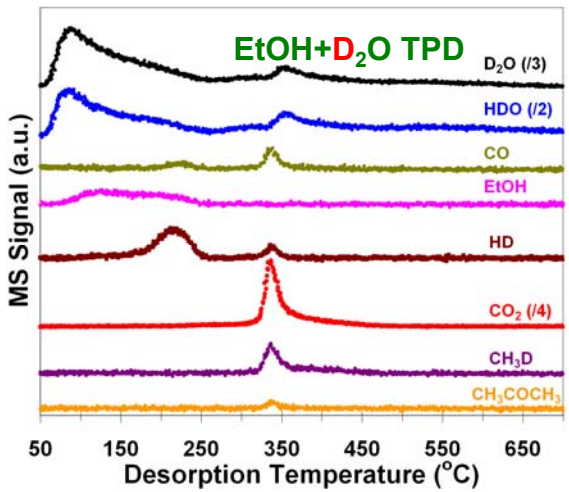


- **Acetates**
  CH_3COO
  1569, 1429, 1348cm^{-1}
- **Adsorbed CO_2**
  2361, 2336cm^{-1}: O=C=O stretching
- **Molecularly adsorbed H_2O**
  1654cm^{-1}

Role of Water: In-Situ DRIFTS with Isotopic Labeling of H_2O in EtOH+H_2O TPD







Water participates in ESR by providing the surface OH groups.

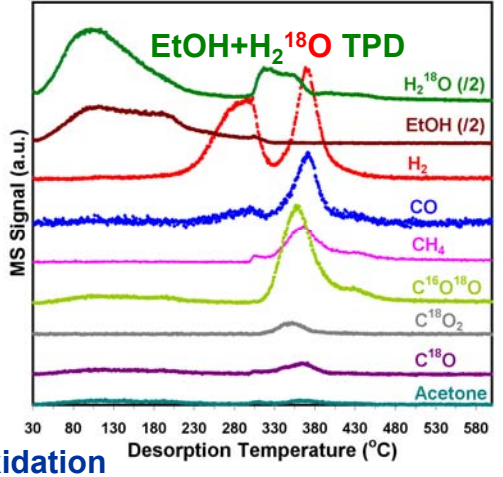
The H atoms simultaneously formed during the dissociative adsorption of water are involved in the final hydrogen and CH_4 formation.

Technical Accomplishments and Progress

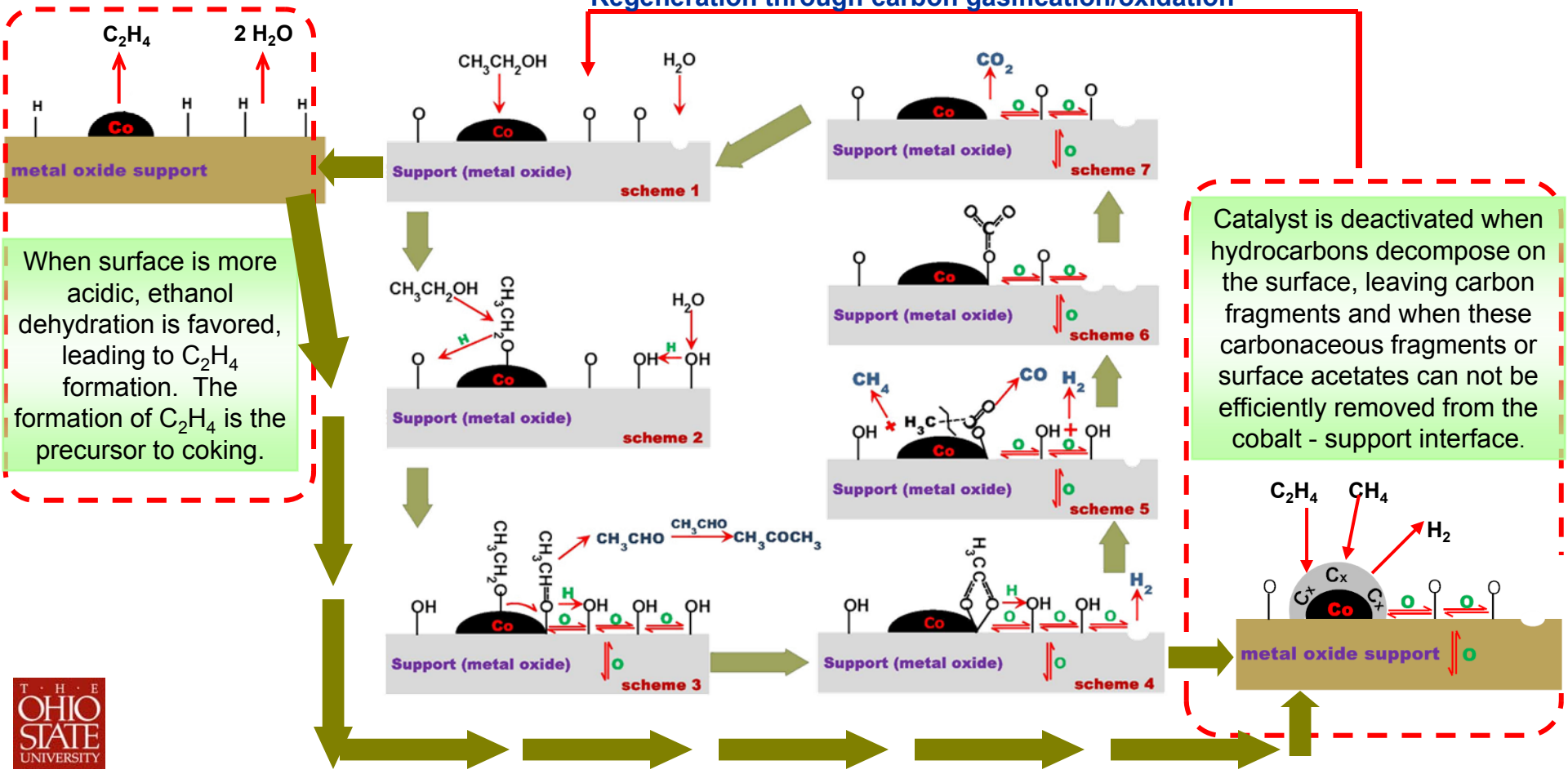
Understanding the surface species and surface mechanisms

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.



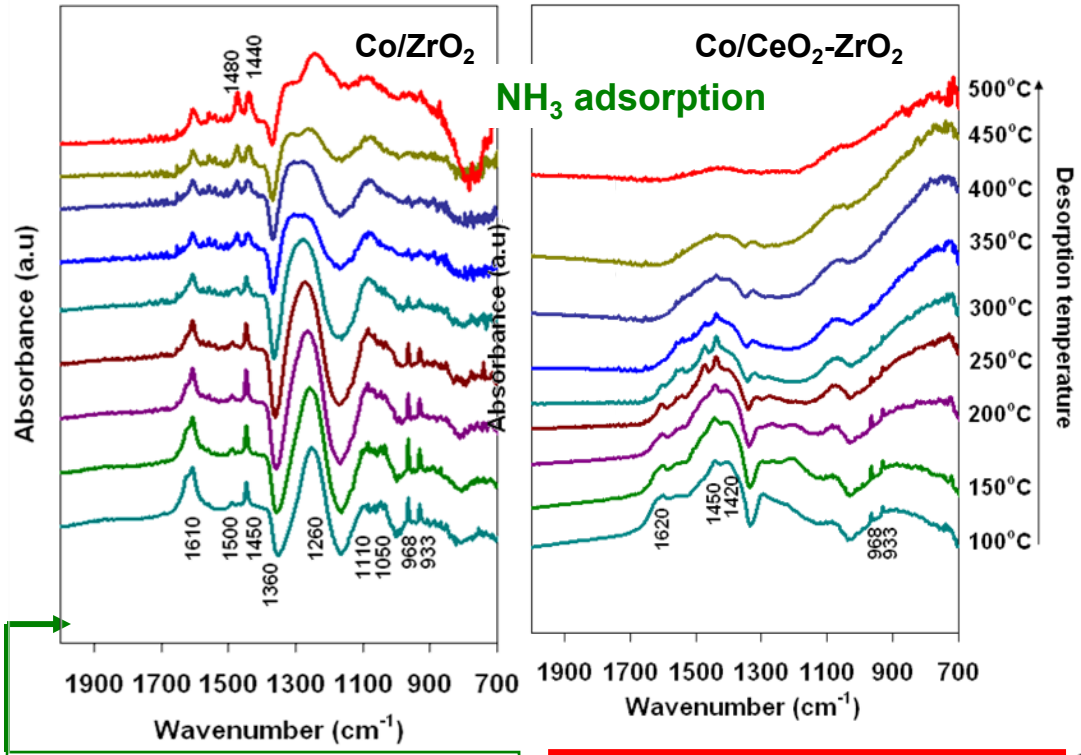
Regeneration through carbon gasification/oxidation



Technical Accomplishments and Progress

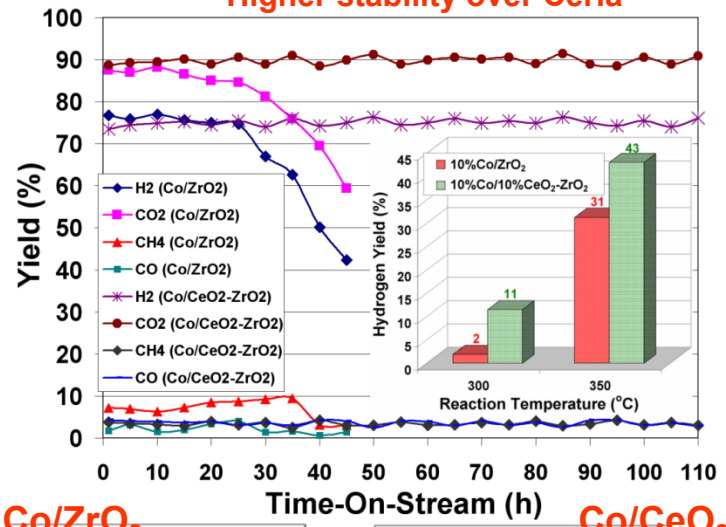
Decreasing surface acidity

Controlling Stability

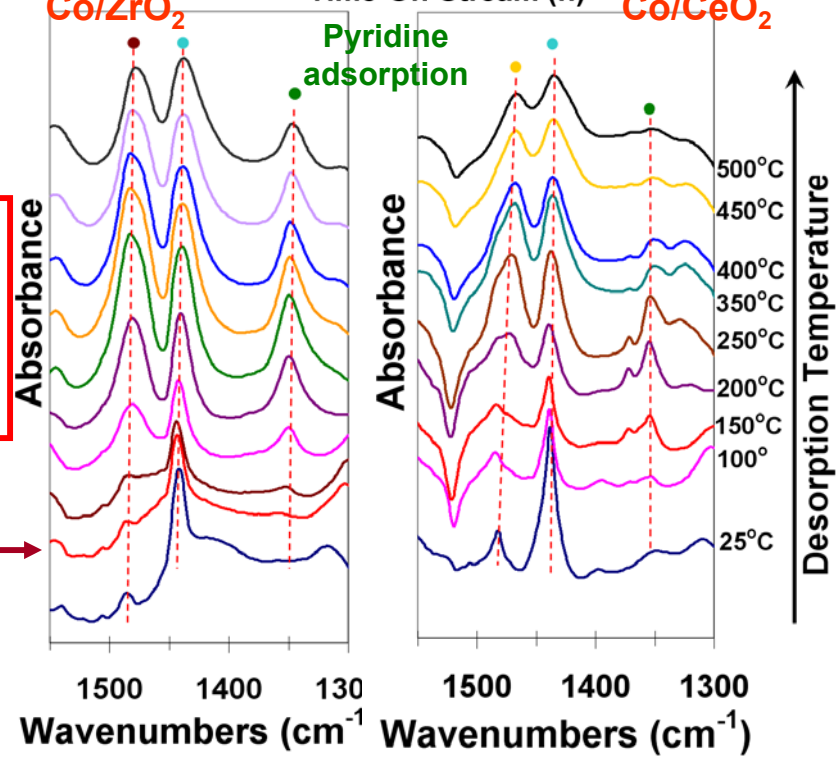


- NH_4^+: 1450, 1500cm^{-1} (asymmetric) 1610cm^{-1} (symmetric)
- NH_3: 1260cm^{-1} (co-ordinatively bonded) 1110, 1050cm^{-1} (molecularly)
- Brønsted acid sites: 1620, 1450, 1420cm^{-1}

EtOH+H2O at 450°C : Higher stability over Ceria



- Pyridinium ion: 1349cm^{-1};
- Lewis acidic sites: 1439cm^{-1};
- Both Brønsted and lewis acidic sites : 1479cm^{-1};
- Brønsted acidic sites: 1467cm^{-1};



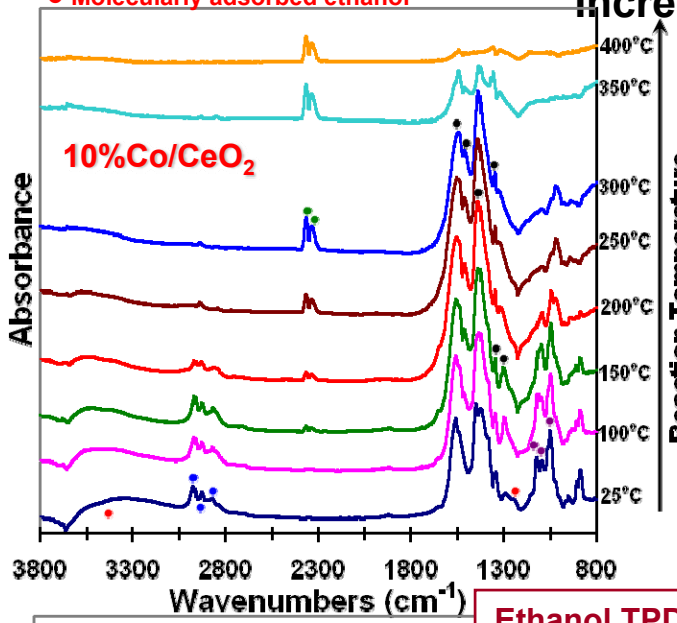
- Acidic surfaces catalyze the dehydration reaction, forming C1-C2 hydrocarbons, which lead to carbon deposition on the surface.
- CeO_2 support is less acidic than ZrO_2

Technical Accomplishments and Progress

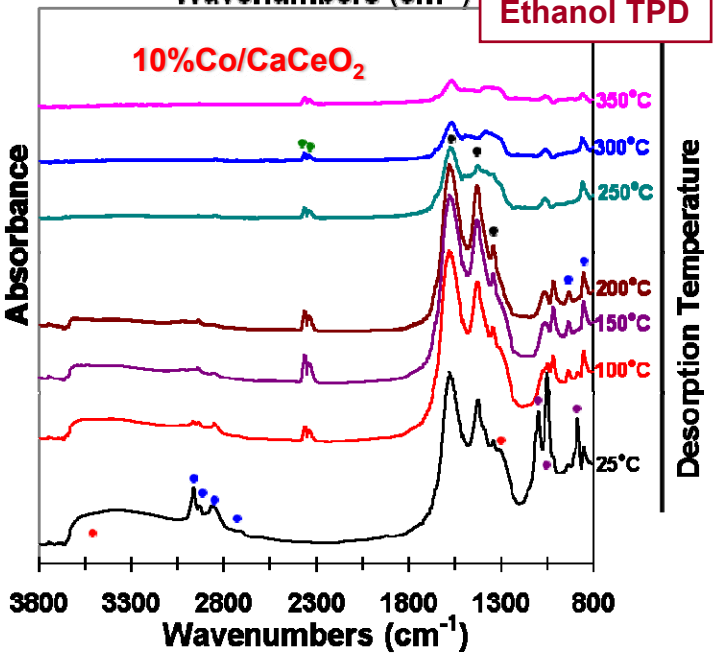
Controlling Stability

- CH_3- , -CH_2-
- Adsorbed CO_2
- Acetates, or carbonate at various adsorbed forms
- Ethoxide
- Molecularly adsorbed ethanol

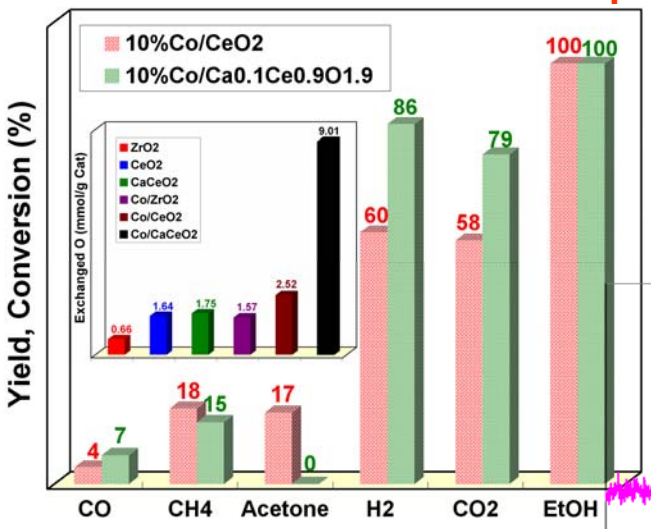
Increasing oxygen mobility of the catalyst



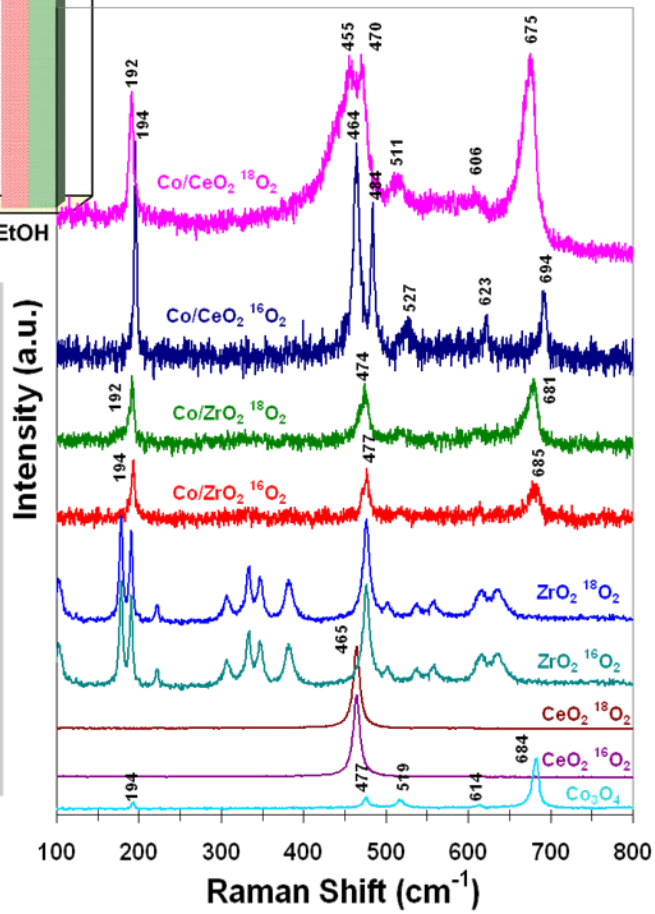
Ethanol TPD



T=400°C under neat conditions



Investigation of oxygen exchange using $^{18}O_2$ Isotopic Shift in Raman Spectra



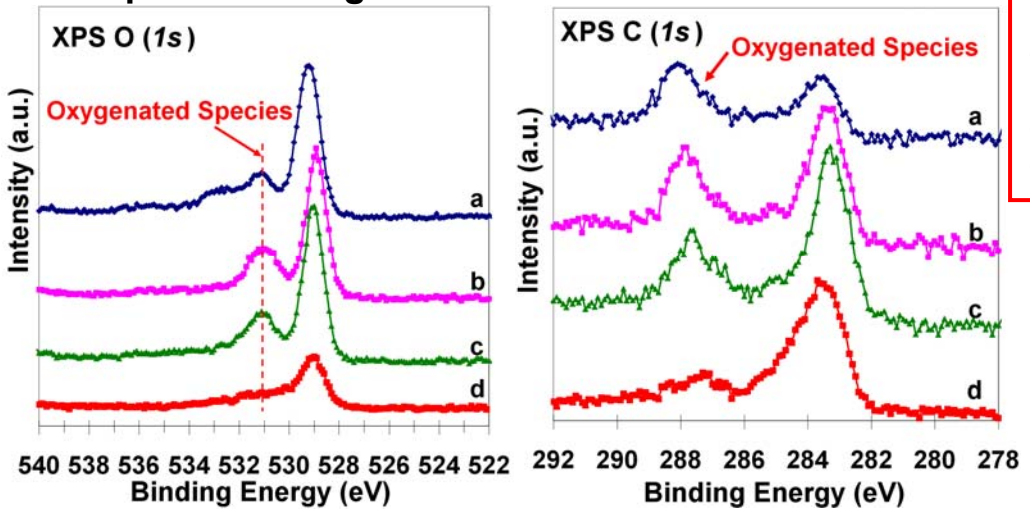
- Doping the support with a low-valance ion (e.g., Ca) will create oxygen vacancies, leading to higher oxygen mobility;
- Higher oxygen mobility will provide better stability by readily oxidizing the carbonaceous fragments on the surface.
- Ca doping also improved selectivity under neat conditions

Technical Accomplishments and Progress

Controlling Selectivity

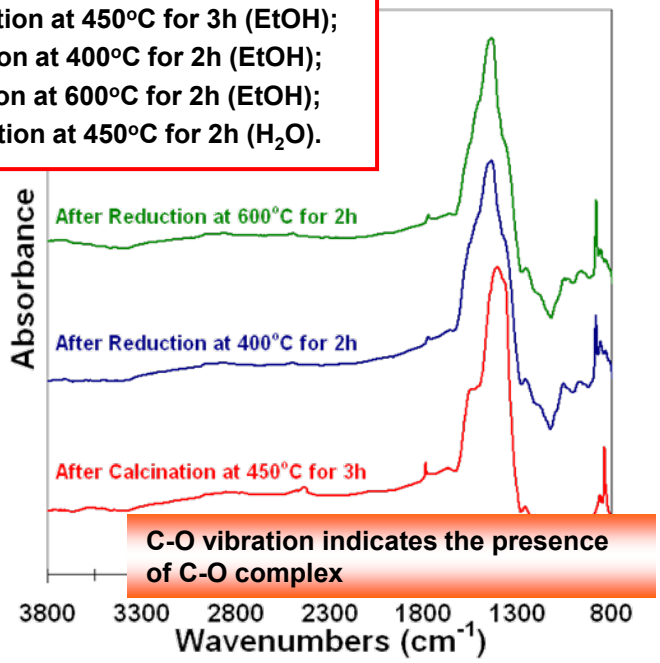
Effect of Impregnation medium

Aqueous vs organic media



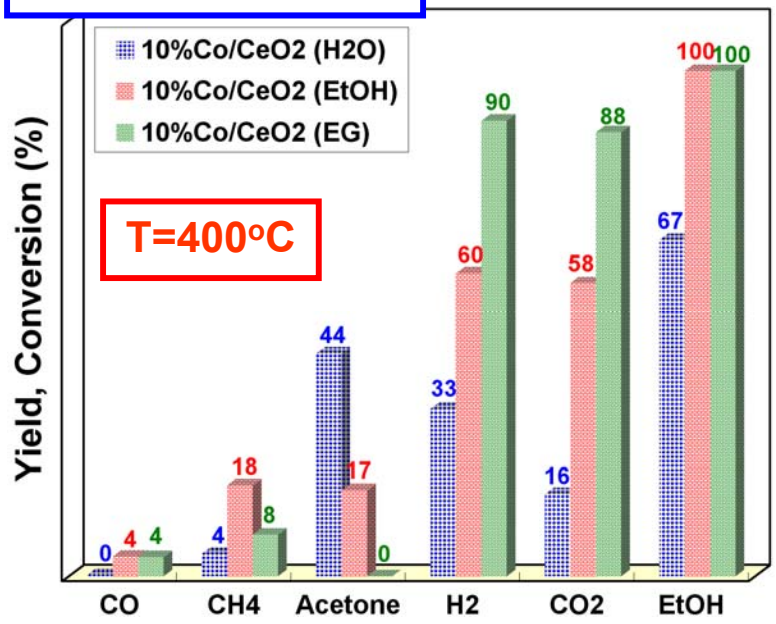
10%Co/CeO_2 :

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 (H_2O).

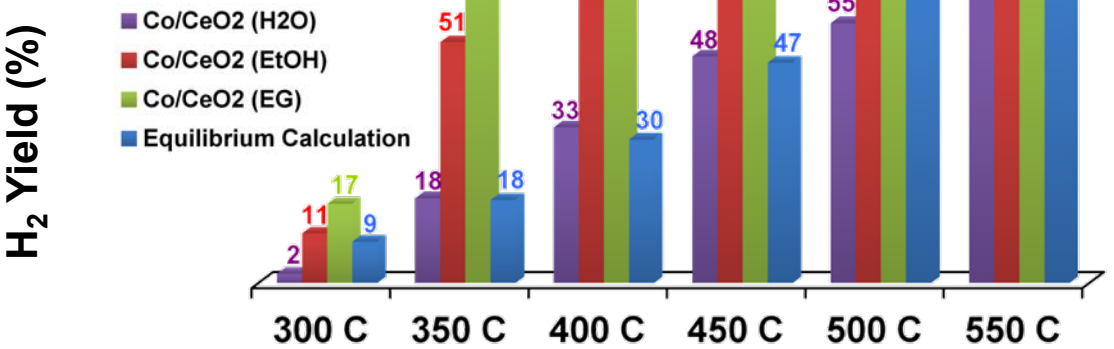


C-O vibration indicates the presence of C-O complex

EtOH:H_2O=1:10 (molar ratio);
C_{EtOH}=7.5vol.%;
WHSV=~0.54gEtOH/gCat/h;



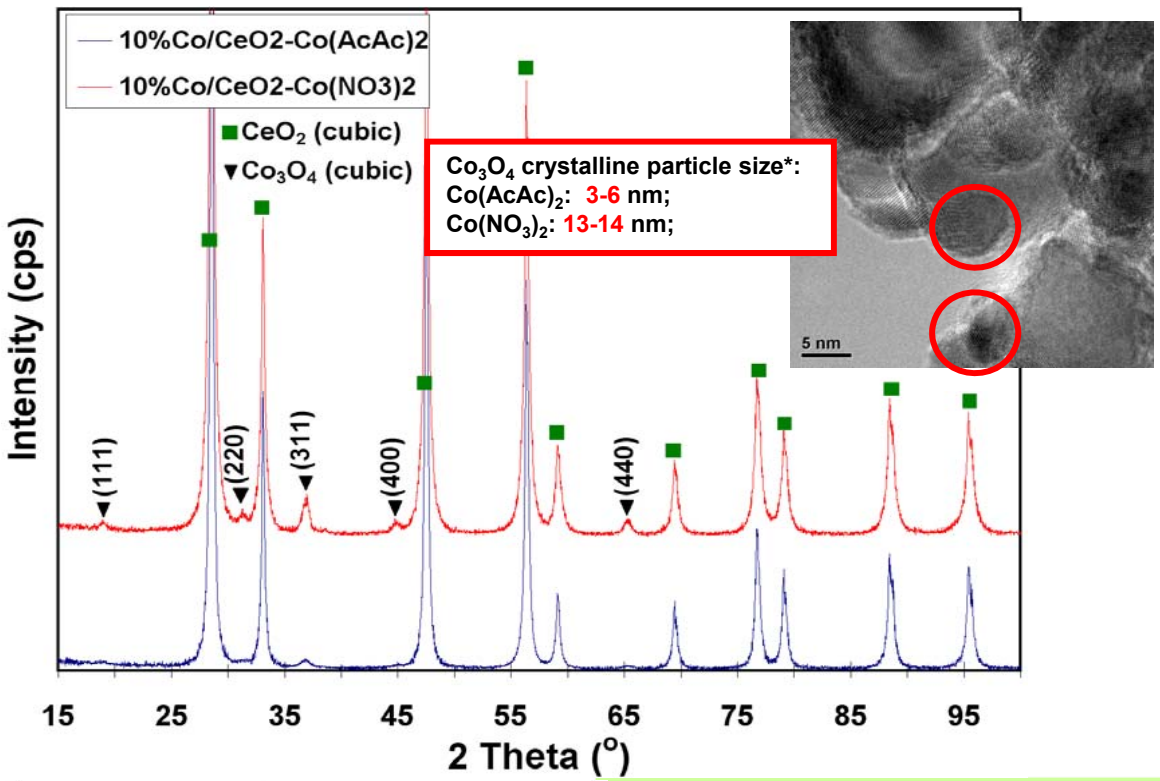
Organic impregnation media lead to more selective and active catalysts, due to the presence of the presence of C-O complexes on the surface, possibly providing segregation of the Co sites.



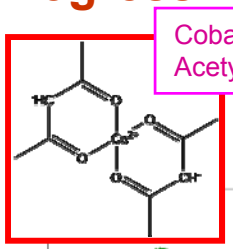
Technical Accomplishments and Progress

Choice of precursor

Controlling dispersion



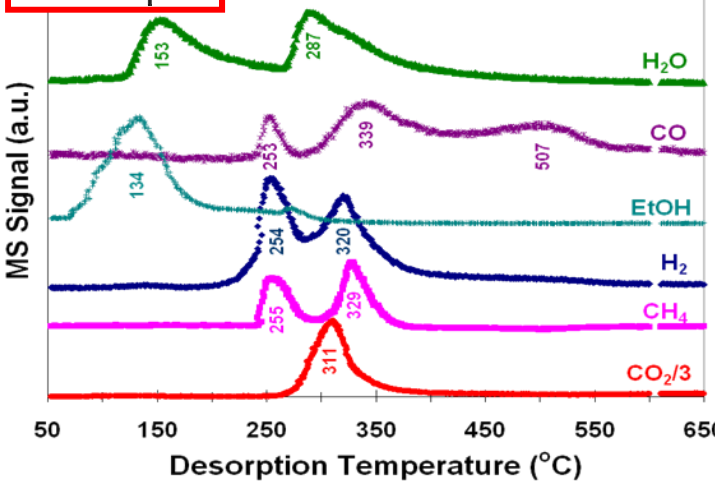
Co_3O_4 crystalline particle size*:
$Co(AcAc)_2$: 3-6 nm;
$Co(NO_3)_2$: 13-14 nm;



Cobalt (II) Acetyl acetonate

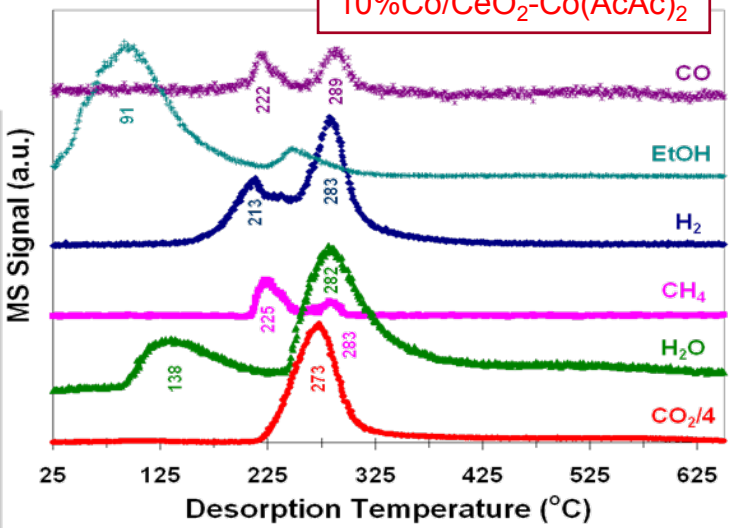
EtOH TPD

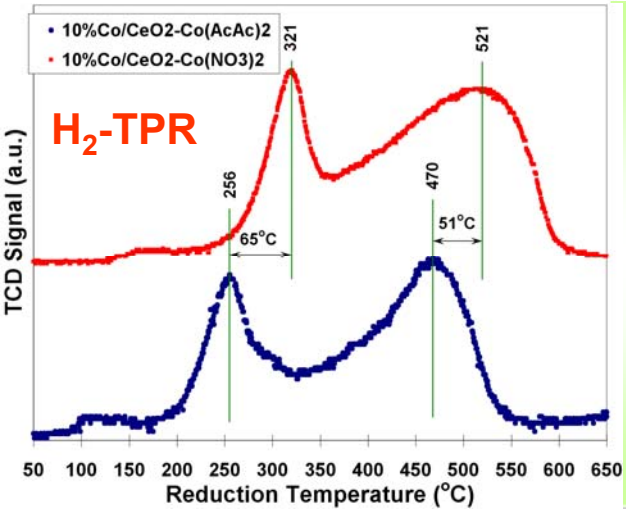
$10\%Co/CeO_2\text{-}Co(NO_3)_2$



EtOH TPD

$10\%Co/CeO_2\text{-}Co(AcAc)_2$



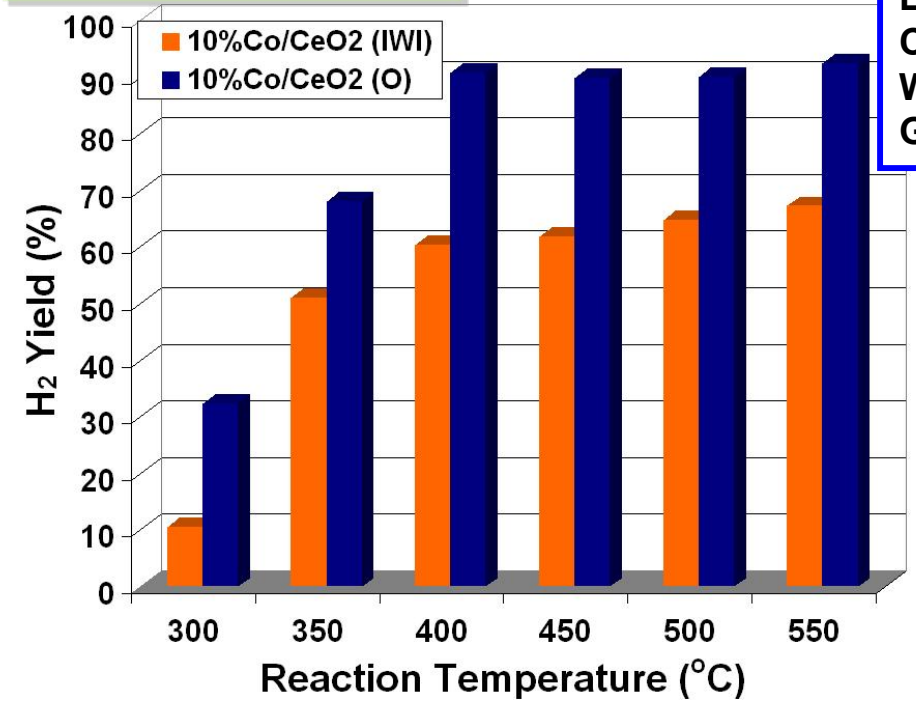


- Co precursor affects the particle size and dispersion as seen in XRD and TEM results.
- Use of $Co(AcAc)_2$ leads to much smaller particle size and better dispersion.
- Dispersion affects reducibility and activity, as seen in TPD and TPR experiments.

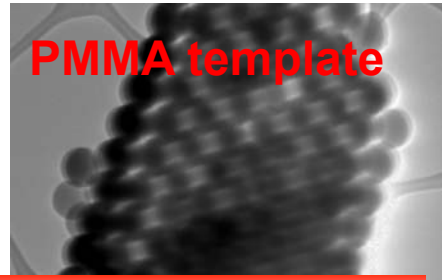
Technical Accomplishments and Progress

Controlling Support Morphology

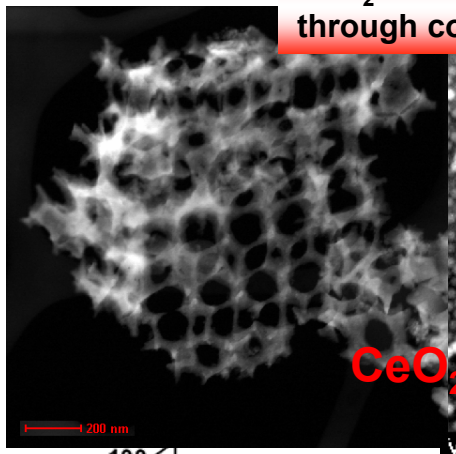
Novel colloidal synthesis techniques allow close control of morphology.

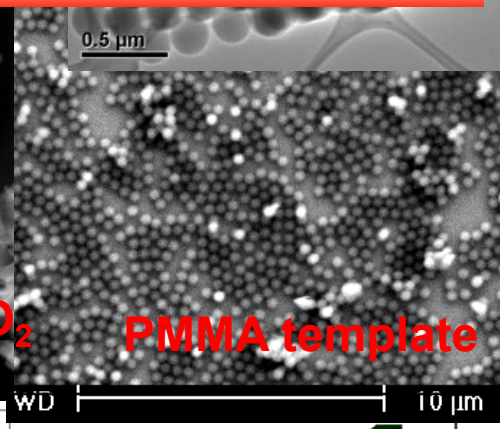


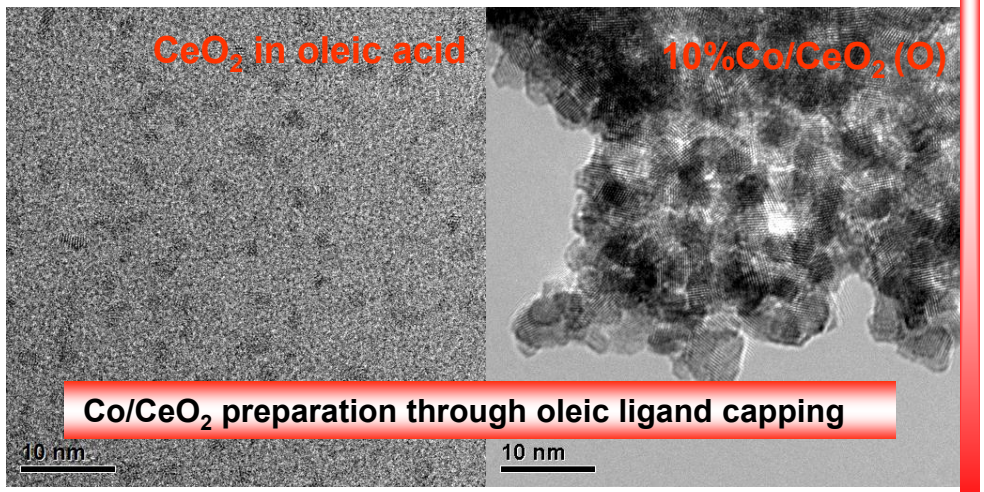
EtOH:H_2O=1:10 (molar ratio);
C_{EtOH}=7.5vol.%;
WHSV=~0.54gEtOH/gCat/h;
GHSV=~5,000h^{-1}



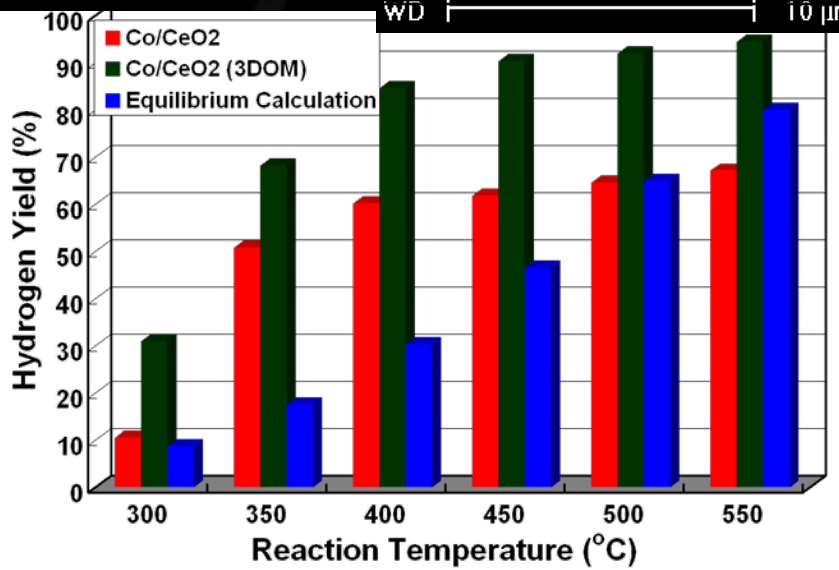
CeO_2 with 3DOM structure synthesized through colloidal crystal templating





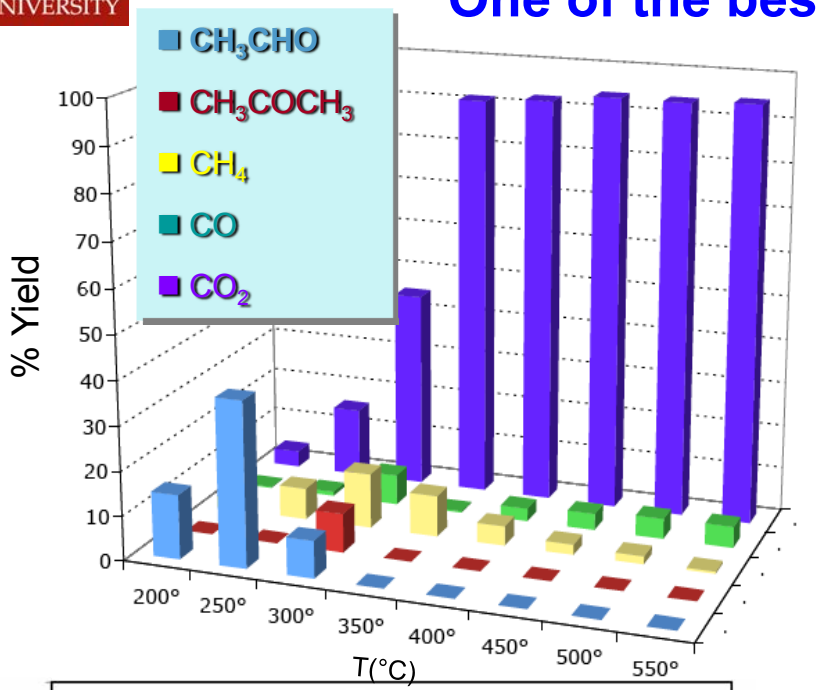


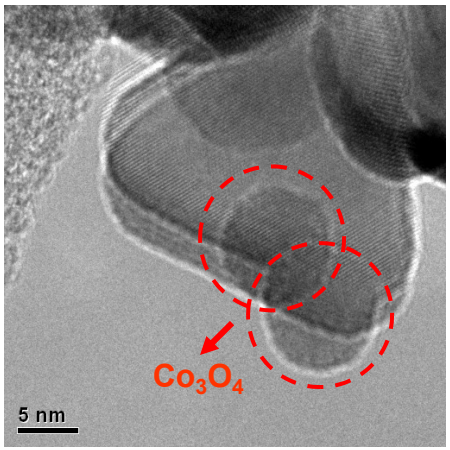
Co/CeO_2 preparation through oleic ligand capping

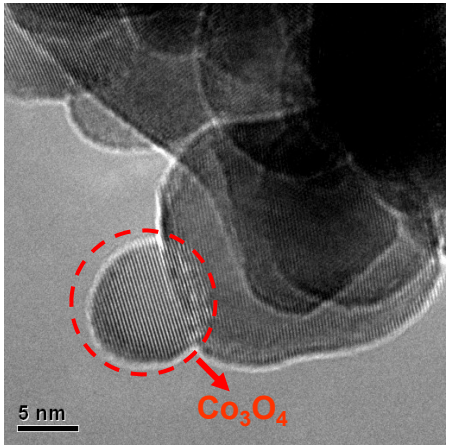


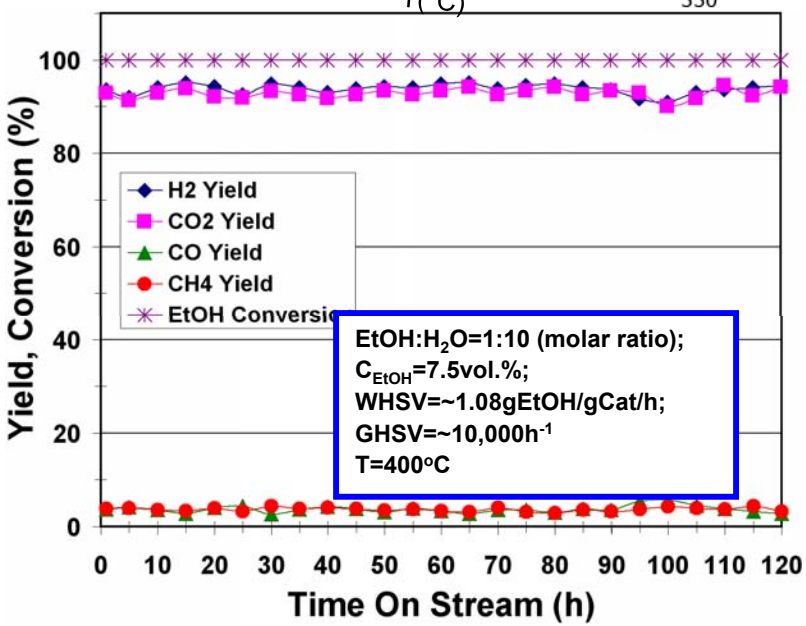
Technical Accomplishments and Progress

One of the best performing catalysts





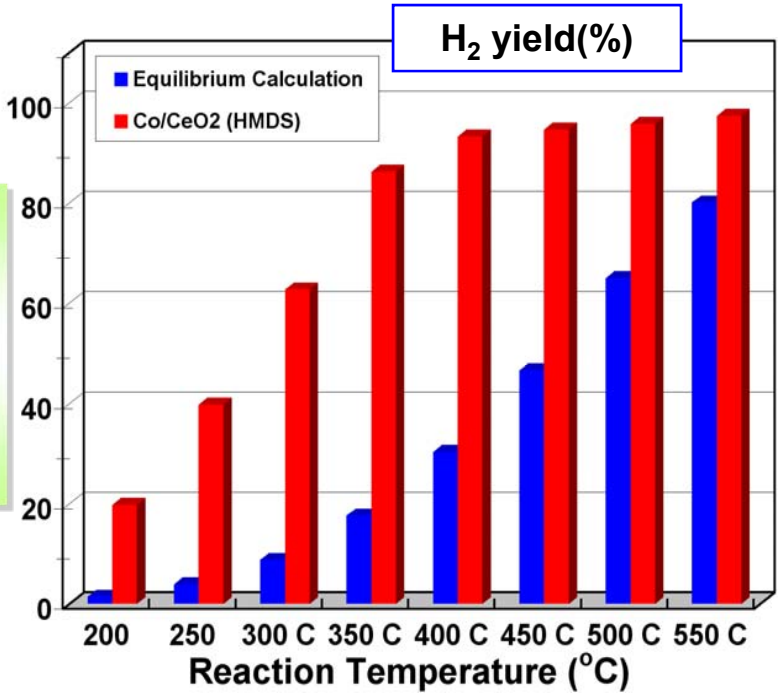




Above 300° C, no liquid products.

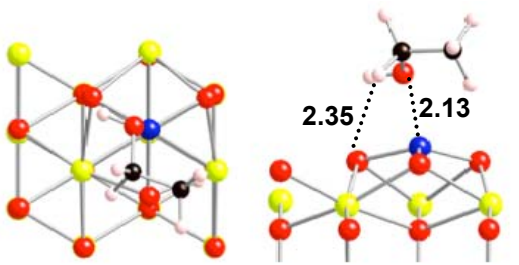
Over 90% H_2 yield

Stable in a 120-hr TOS experiment

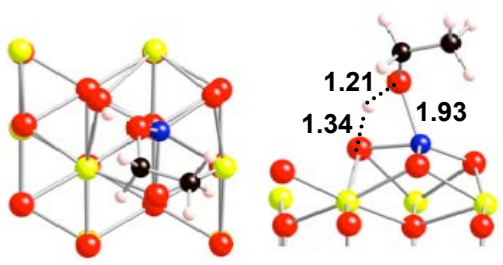


EtOH adsorption on Co/CeO_2 (111)

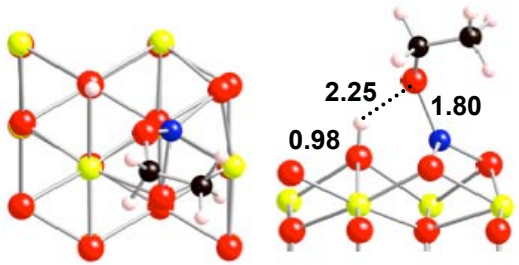
Technical Accomplishments and Progress
Combining Experimental Work with Molecular Simulation



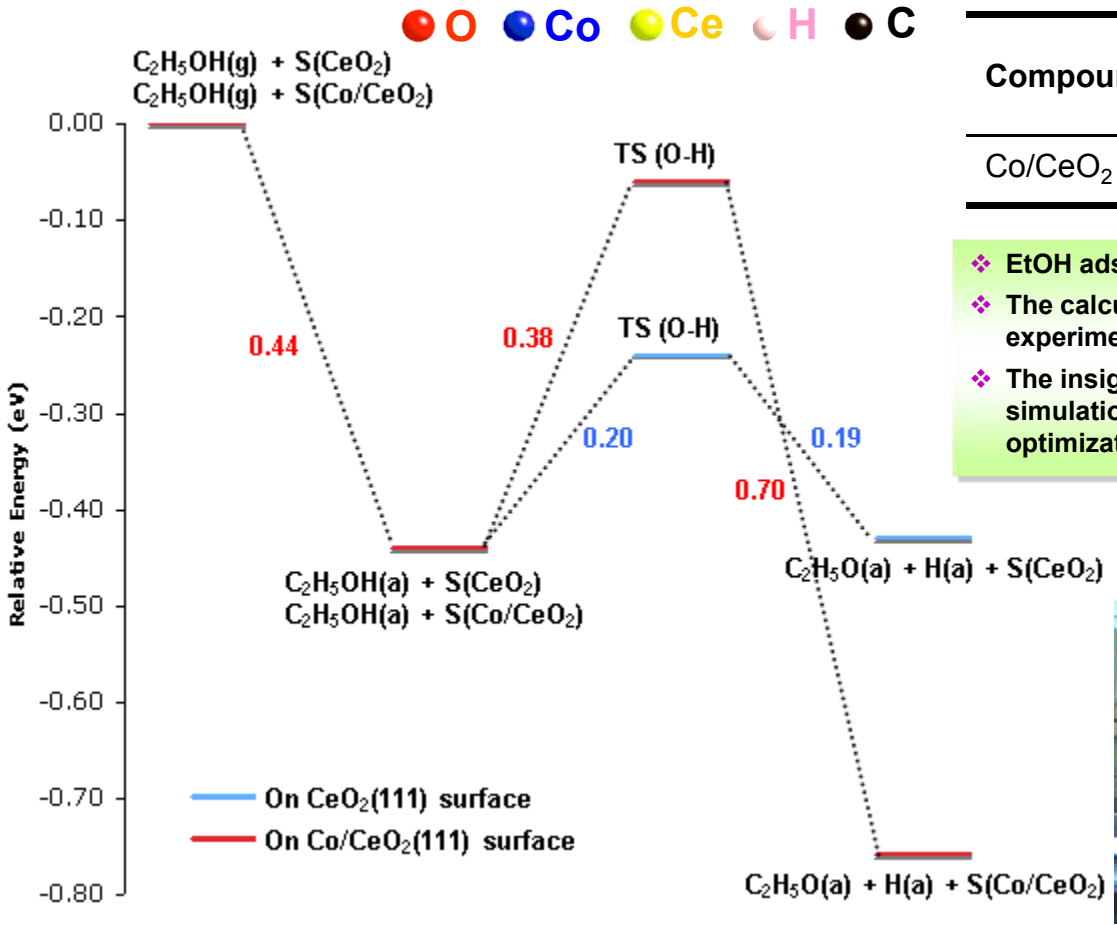
Initial Structure



$TS(O_e–H_e)$



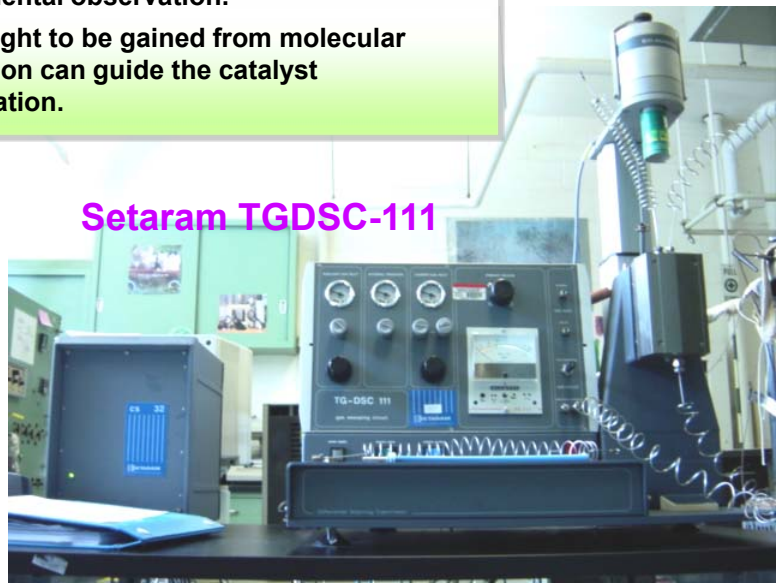
Product



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.

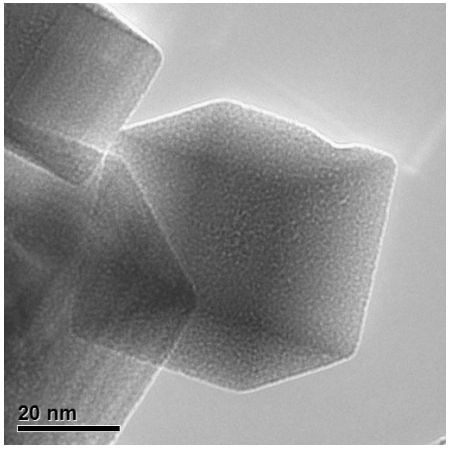
Setaram TGDSC-111



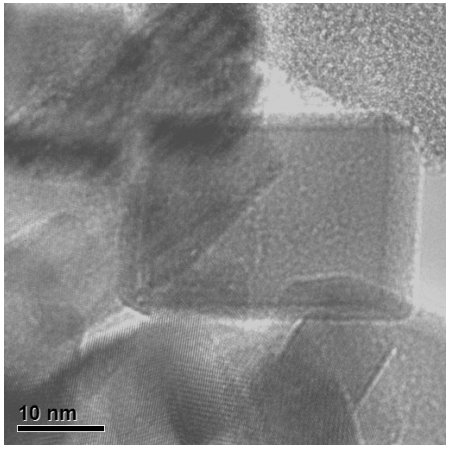
Technical Accomplishments and Progress

Control of support nano-structure

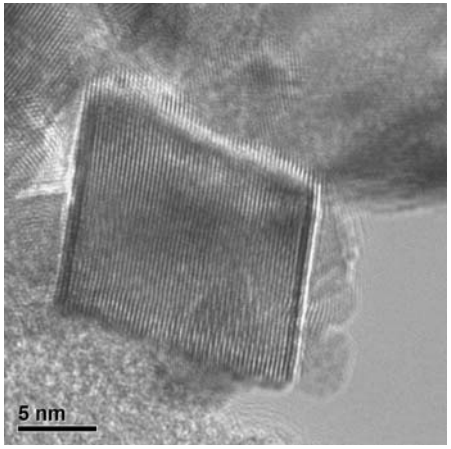
CeO_2



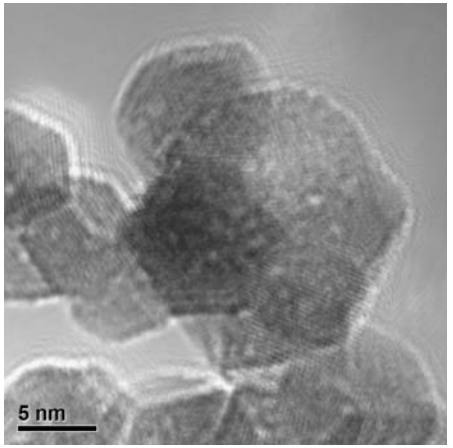
Nanocube



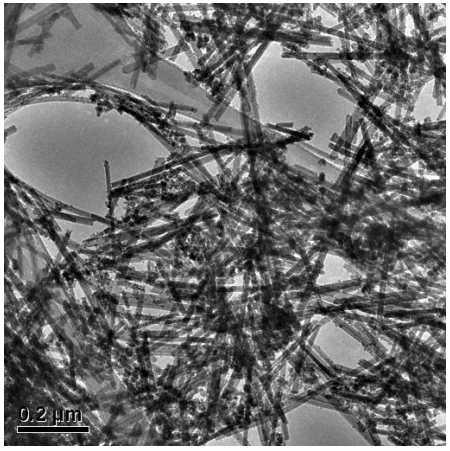
Nanocuboid



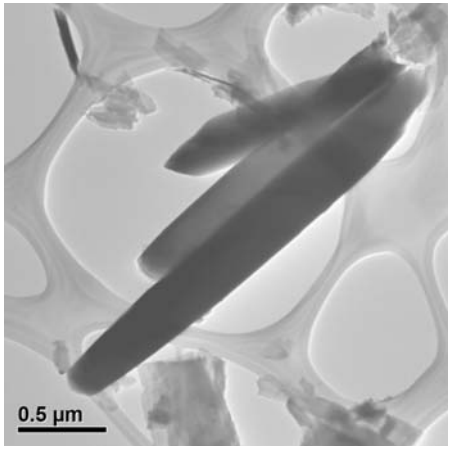
Nanoplate



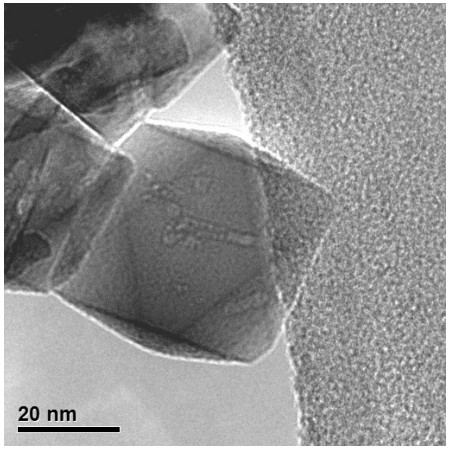
Nanopolyhedron



Nanorod



Nanobelt



Nano-octahedron

- It is possible to grow nano-structures with contolled 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 $Co/CeO_2(111)$: 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 H_2 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

Future Work

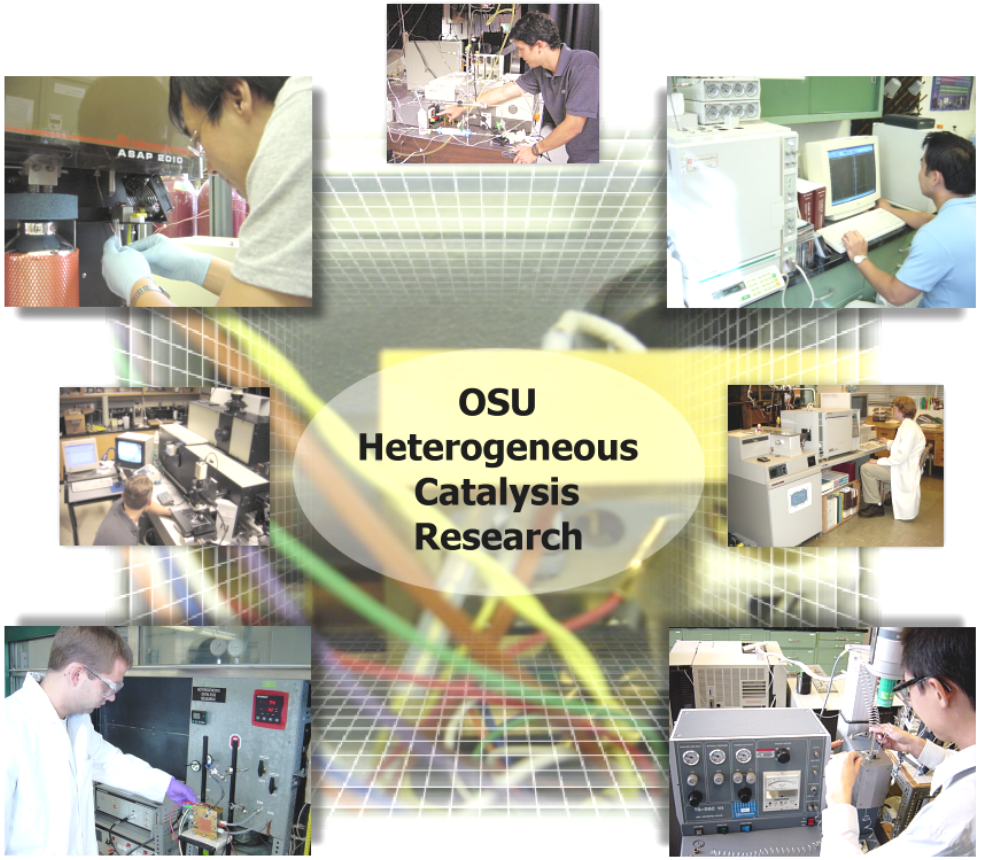
- Kinetic and mechanistic studies will be coupled with catalyst characterization under reaction conditions to obtain kinetic parameters. Rate expressions will be developed for kinetic modeling.
- Long term time-on-stream experiments will be performed (e.g., >100hrs under neat reaction conditions).
- 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.
- I*n-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

OSU HCRG Heterogeneous Catalysis Research Group

Department of Energy



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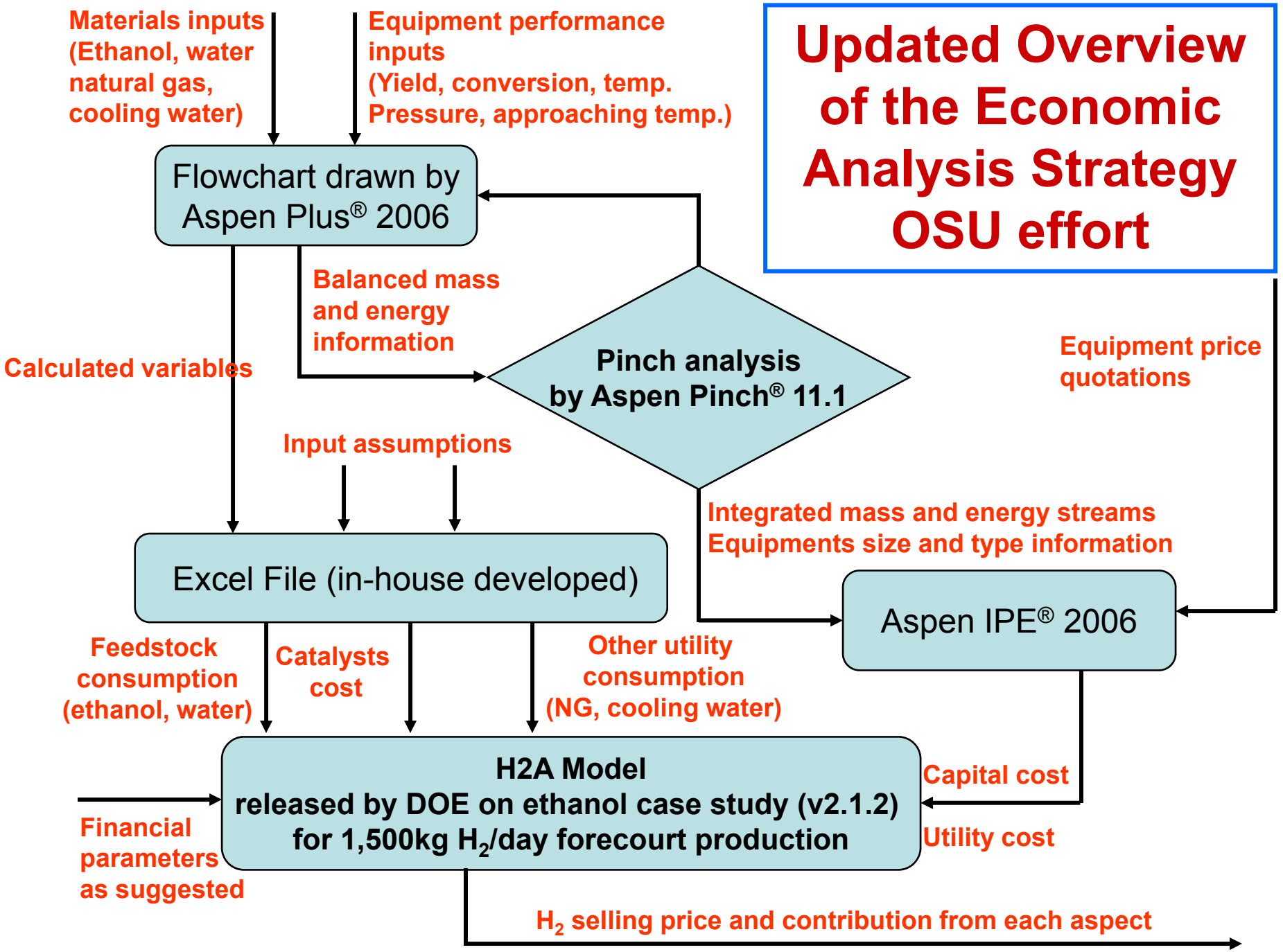
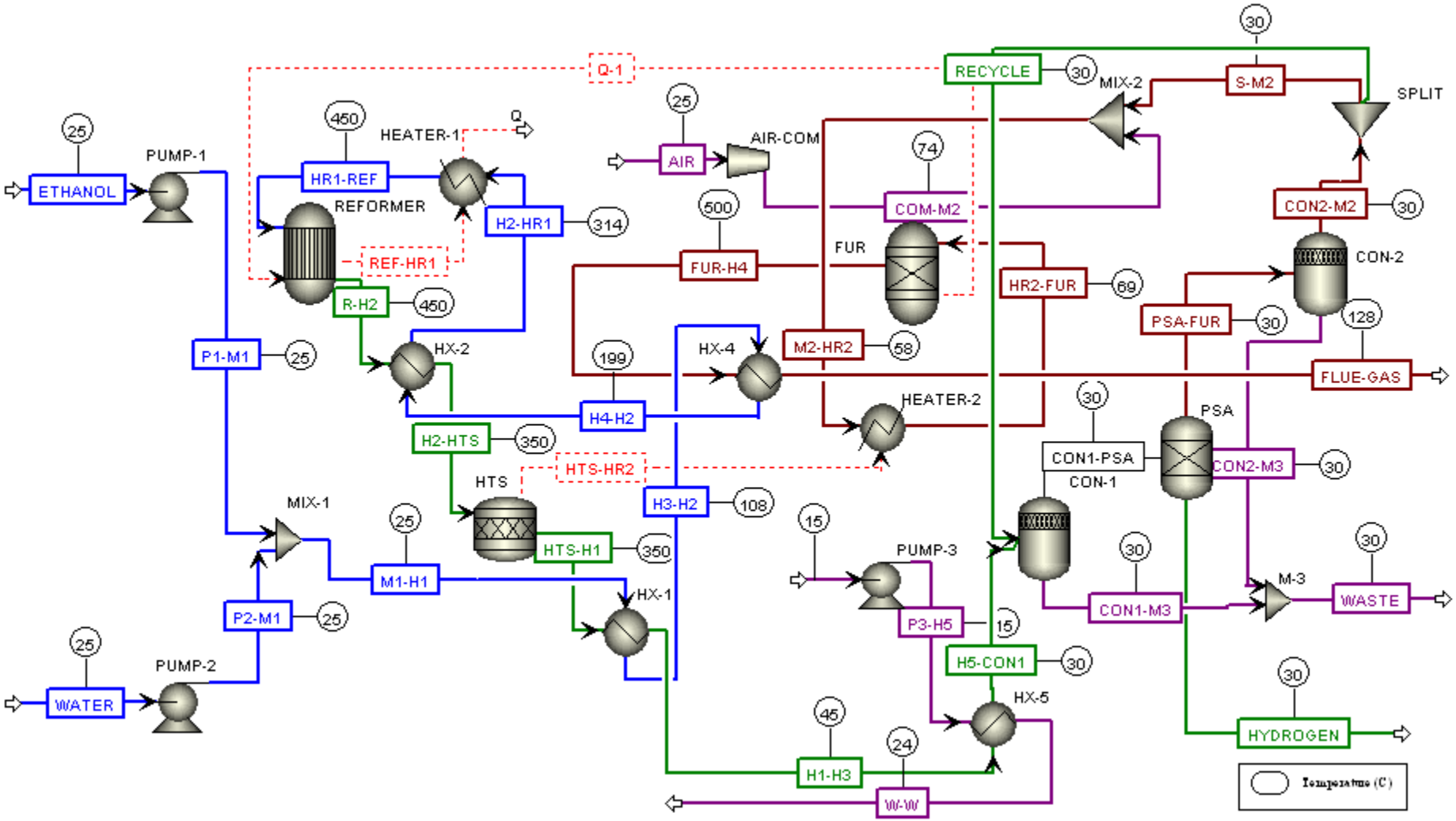
Additional slides

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^{o}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 H_2/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 H_2 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 H_2 cost is mainly attributed to the re-evaluation of the H_2 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 H_2 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% H_2 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.