2008 DOE Annual Merit Review Meeting

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

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PD-5

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Overview

DOE Hydrogen Program

Timeline

- Start Date - May 1, 2005
- End Date - April 31, 2010
- 60% 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)

Barriers

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

Partners

- NexTech Materials, Ltd.
  - Catalyst manufacturing scale-up
- Chemistry Dept. at OSU (Prof. Hadad)
  - Molecular simulation
- Directed Technologies Inc.
  - Economic analysis and feasibility considerations

OSU HCRG

Project overview

- Catalytic H_2 production from bioethanol
  - Renewable sources;
  - Plant matter (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

- 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^oC)
    - High EtOH conversion
    - High selectivity and yield of hydrogen
    - High catalyst stability
    - Minimal byproducts such as acetaldehyde, methane, ethylene, and acetone
  - Enabling H_2 production from renewable sources at low cost

Tasks

- Setting up the experimental systems, establishing protocols, training personnel
- Catalyst synthesis and optimization
- In-situ, pre-, post-rxn catalyst characterization
- Activity tests, kinetic studies, deactivation, regeneration studies
- Economic and energy analysis
- Information dissemination
- Data analysis, reproducibility tests, literature awareness

Phase I Milestones

✓ Completion of a successful HAZOP review for the ethanol reforming reactor system. Modification to the design based on the HAZOP review will be implemented and standard operating procedures will be adopted prior to the construction and shakedown of the system.

✓ Acquisition and installation of equipment items.

✓ A minimum of 20 batches of catalysts that are synthesized in 10 gram batches. Commercial alumina, titania, and alumina supports will be evaluated as effective supports for cobalt. Other supports, such as zinc oxide and magnesia will be prepared in-house and evaluated. On the optimal support, the optimal cobalt loading will be determined.

✓ Completion of initial characterization studies using CO chemisorption, X-ray diffraction, temperature programmed reduction, and thermogravimetric analysis to benchmark the characteristics of cobalt catalysts as related to the preparation procedure and support used.

✓ Evaluation of 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}.

✓ Completion of optimized catalyst synthesis evaluating the effectiveness of nitrate salt, organometallic, and sol-gel cobalt precursors, the effect of mixed oxide supports, and metallic promoters. Reaction performance will be evaluated.

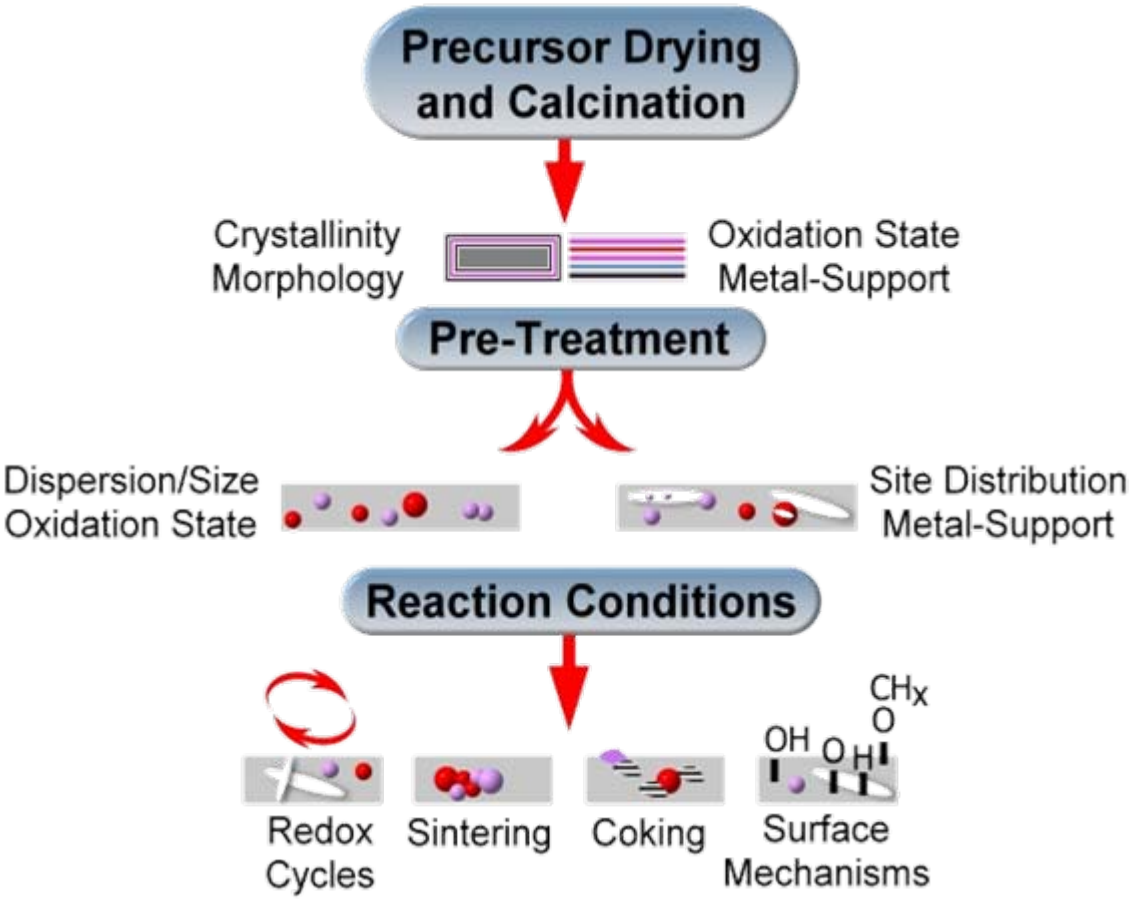
✓ Completion of advanced characterization studies evaluating the synthesis procedures for cobalt metal dispersion, pre- and post-reaction chemical state, and deactivation mechanisms.

✓ Completion of an economic analysis based upon a 100-1,500 kg/day of hydrogen process and the purity requirements of the DOE Distributed Hydrogen Production Technologies. The most complete data available from the reaction studies will be used with additional information needed from outside sources highlighted.

✓ Using the research results, at least one presentation will be given at a national or international conference and at least one publication will be submitted to a refereed journal.

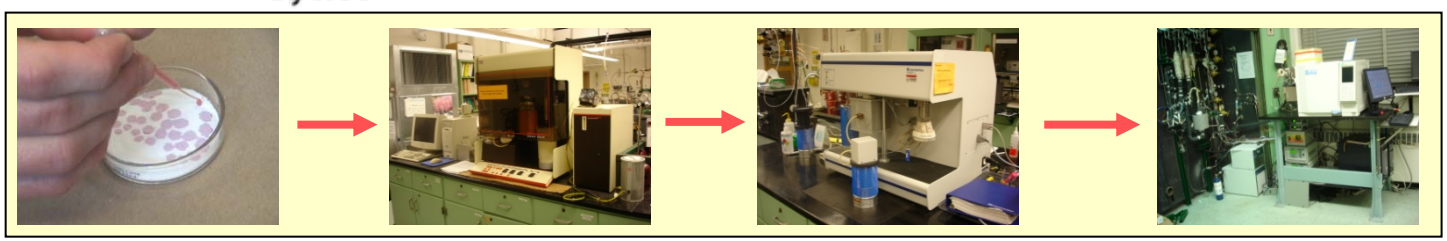
Technical Approach

Development of non-precious metal catalysts to operate at lower temperatures



Supported Co-catalysts

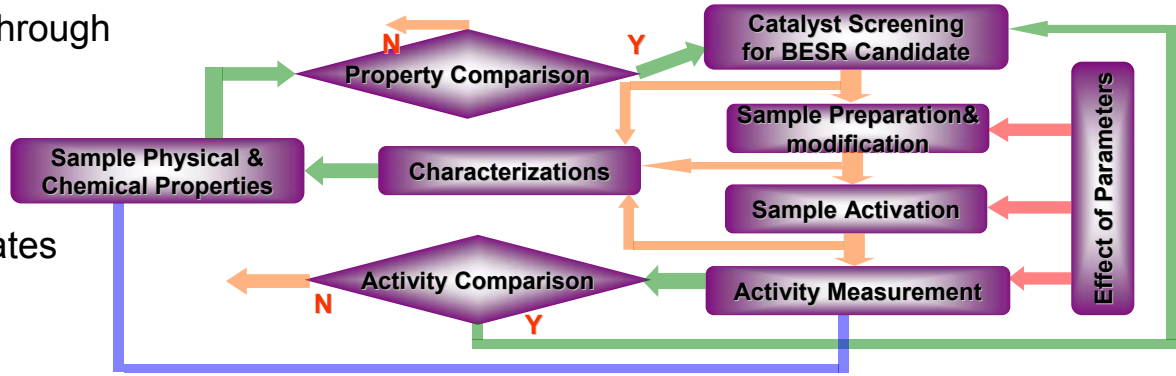
- **Preparation**
  - IWI, SG
  - Precursor
  - Precursor solution
  - Promoter
  - Support
  - Cobalt loading
- **Calcination**
  - Temperature
- **Reduction**
  - Temperature
  - Time
- **Reaction**
  - GHSV
  - EtOH:Water ratio
  - Temperature
  - Oxygen addition
  - Deactivation
- **Deactivation/Regeneration**

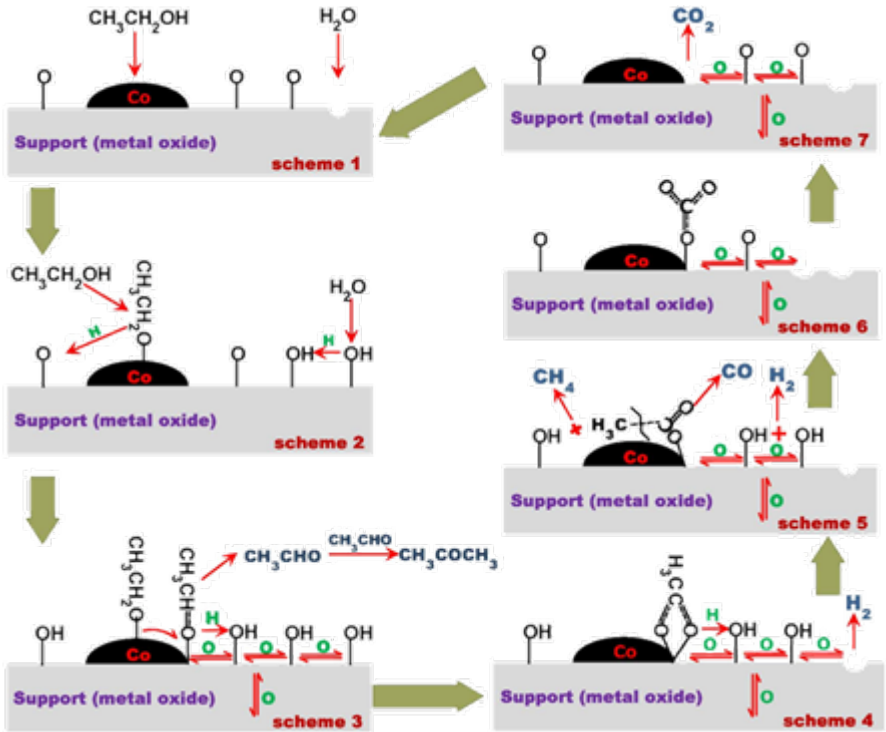


DOE Hydrogen Program

Our previous work on ethanol steam reforming over Co-based catalysts

- Novel catalyst synthesis and formulations
- Detailed catalyst characterization throughout its life history
- Detailed studies of the reaction network through TPReaction and TPD experiments
  - Acetaldehyde SR
  - Acetone SR
  - CH_4 SR
  - Reverse WGS
  - WGS
  - Methanation
- Detailed studies of the surface intermediates through *in-situ* DRIFTS during
  - Ethanol
  - Acetone
  - Acetaldehyde
  - Acetic acid
- Mechanistic investigations using isotopic labeling/DRIFTS





- ✓ **Established effect of synthesis parameters on the catalyst performance on supported Co catalysts**
- ✓ **Proposed a reaction network**
- ✓ **Proposed surface reaction steps and intermediates**
- ✓ **Achieved high H_2 yield over Co/ZrO_2 catalysts**

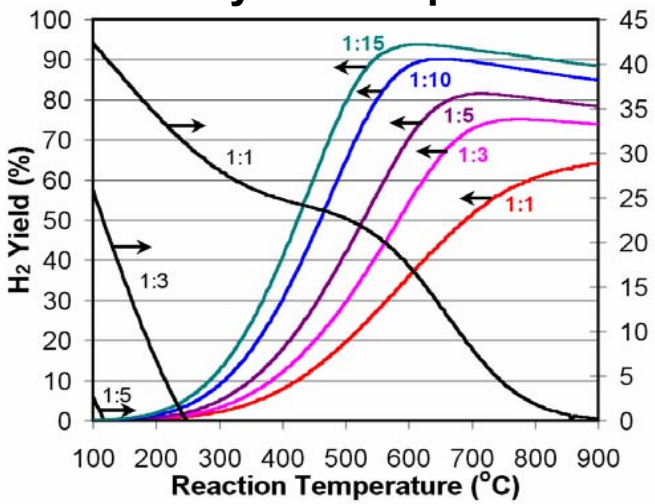
➢Song, H., Zhang, L., Watson, R.B., Braden, D., Ozkan, U.S., "Investigation of Bio-ethanol Steam Reforming over Cobalt-based Catalysts" ***Catalysis Today***, 129, 346-354 (2007).

➢Song, H., Zhang, L., Ozkan, U.S., "Effect of Synthesis Parameters on the Catalytic Activity of Co/ZrO_2 for Bio-ethanol Steam Reforming" ***Green Chemistry***, 9, 686-694 (2007).

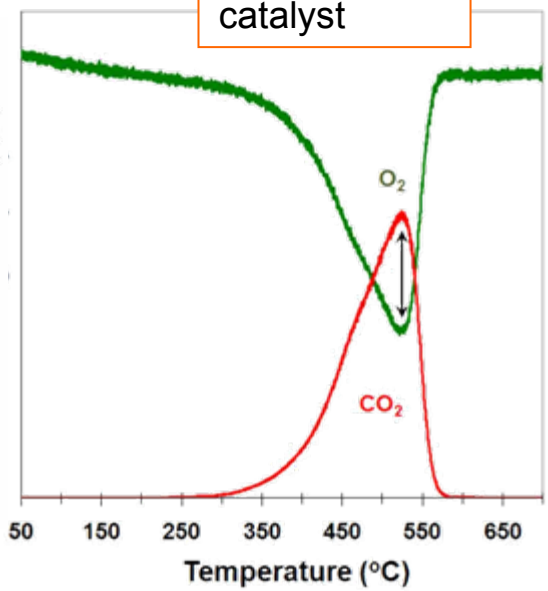
Stability issues

Stability of Co/ZrO_2 Catalysts

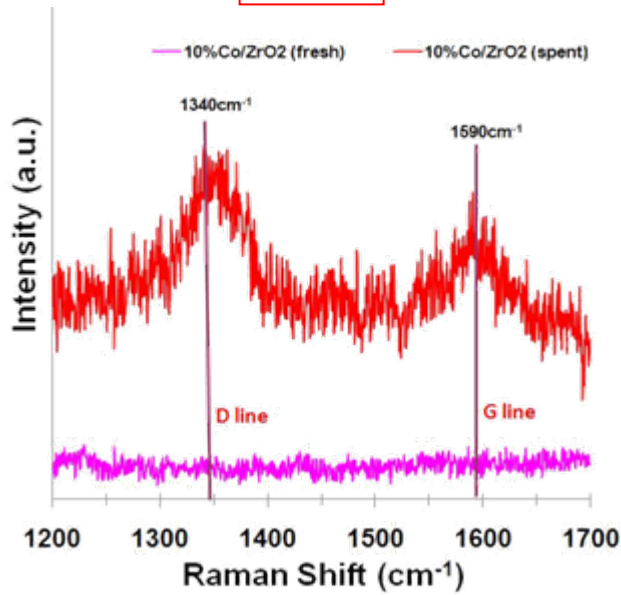
Thermodynamic equilibrium



TPO on spent catalyst

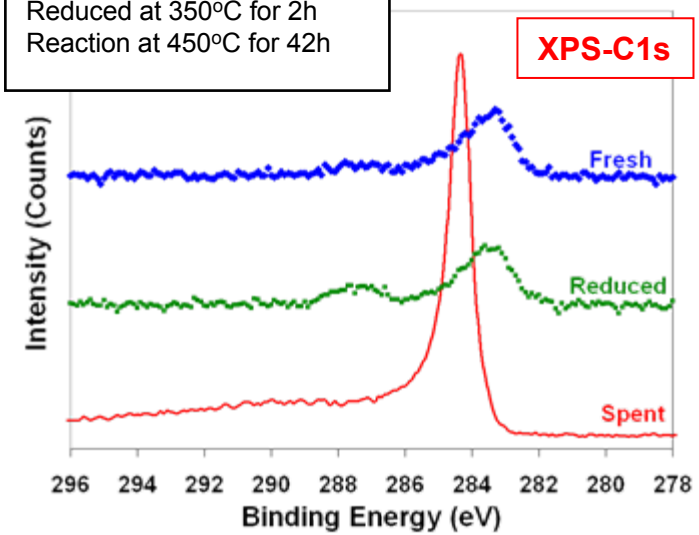


LRS



$10\%Co/ZrO_2$
Calcined at 400°C
Reduced at 350°C for 2h
Reaction at 450°C for 42h

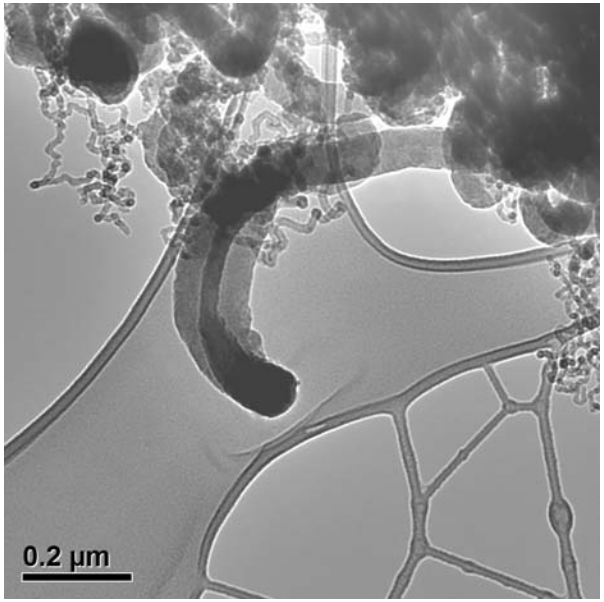
XPS-C1s

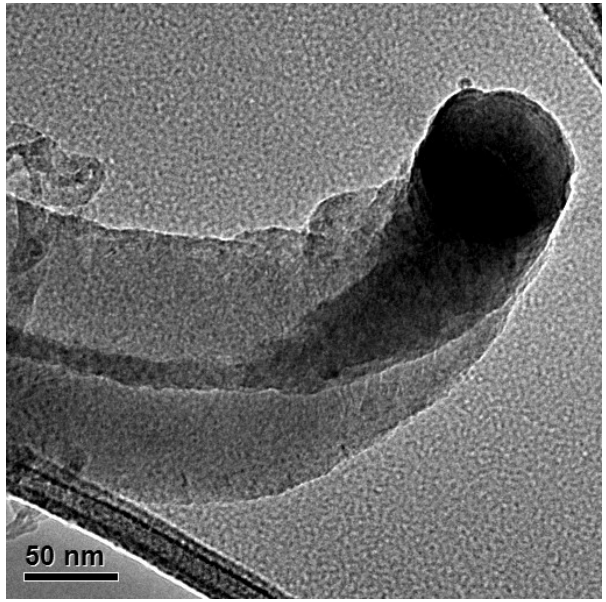


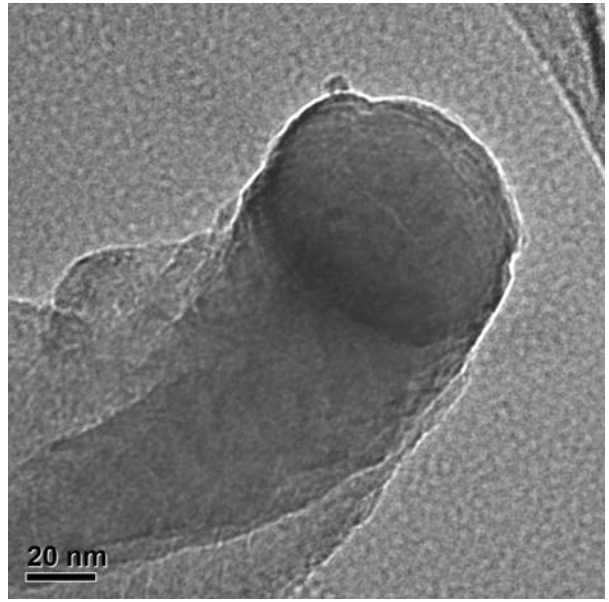
Although Co/ZrO_2 gave H_2 yields over 90%,at high temperatures (>450°C), deactivation of the catalyst was observed.

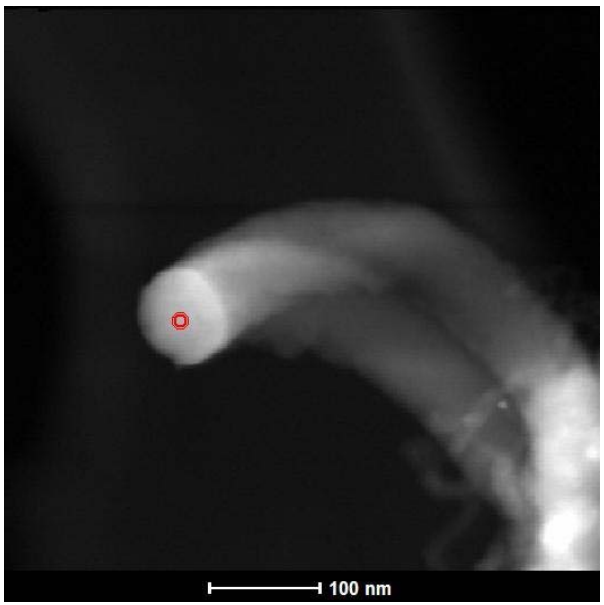
Post-reaction characterization through Temperature-Programmed Oxidation, LRS, and XPS showed coke formation on the surface.

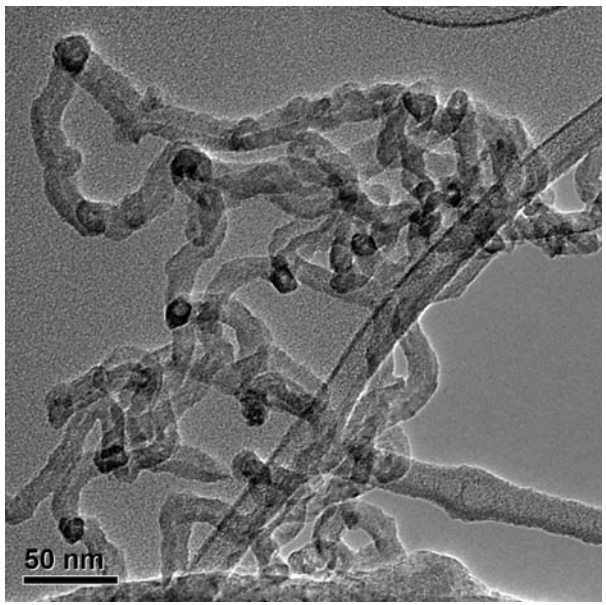
Carbon Deposition on Co/ZrO_2 was Verified by TEM











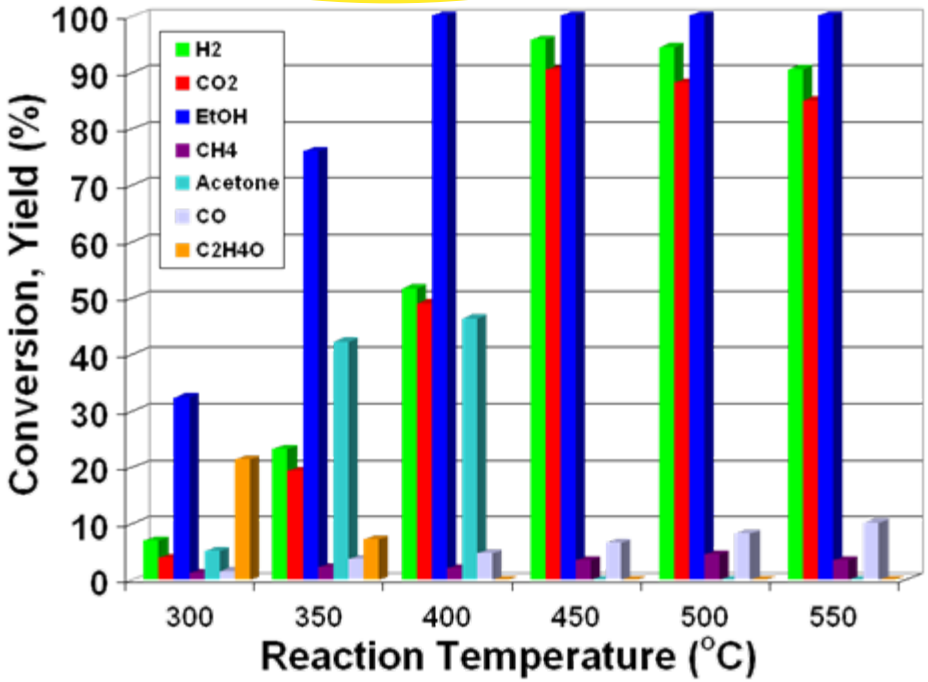
Tecnai TF-20 TEM

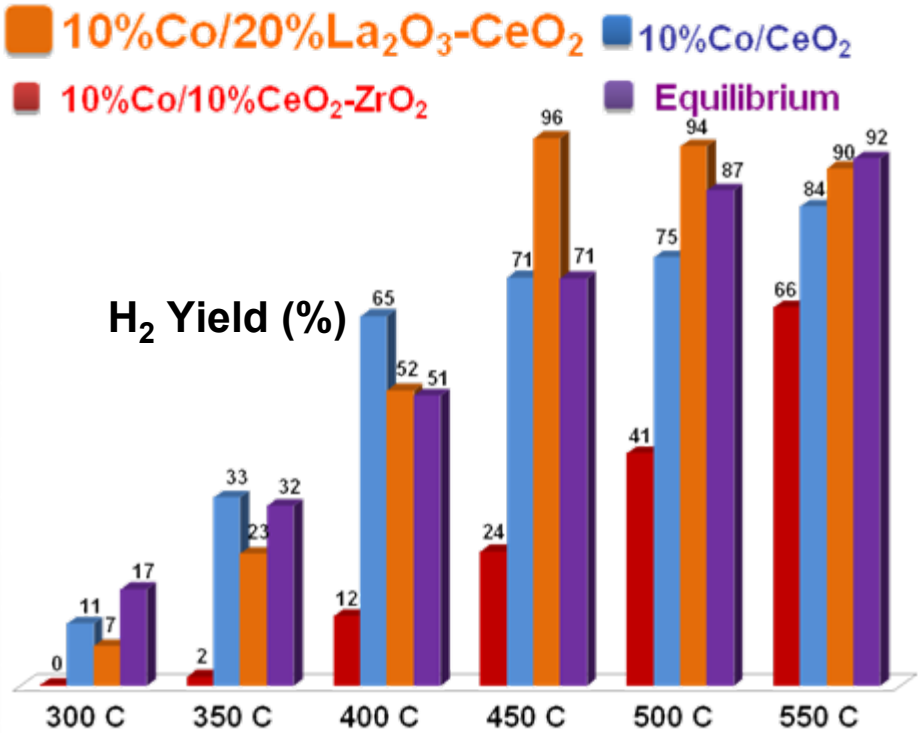
In the current study:

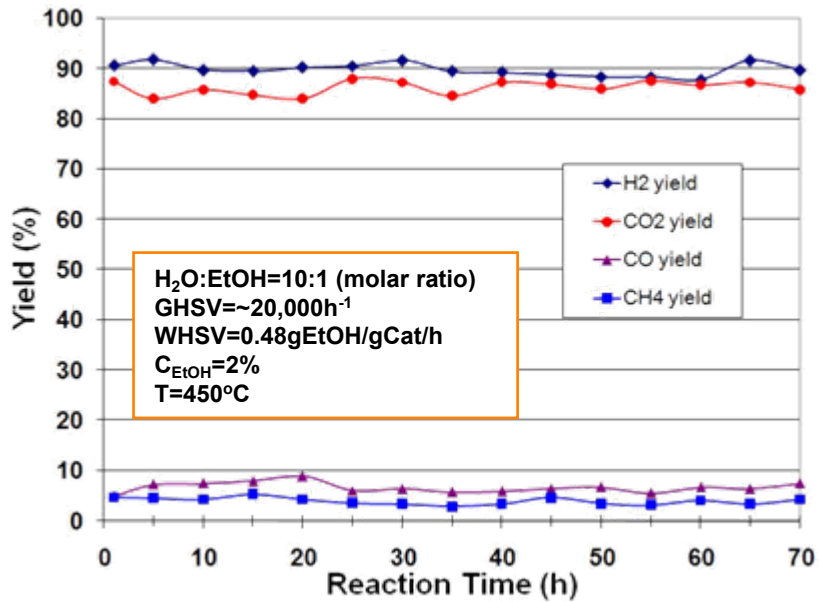
- Samples were dispersed in ethanol.
- Supported by lacey formvar carbon on a 200 mesh Cu grid.

Next generation of catalysts

Efforts to improve stability by lanthanide incorporation

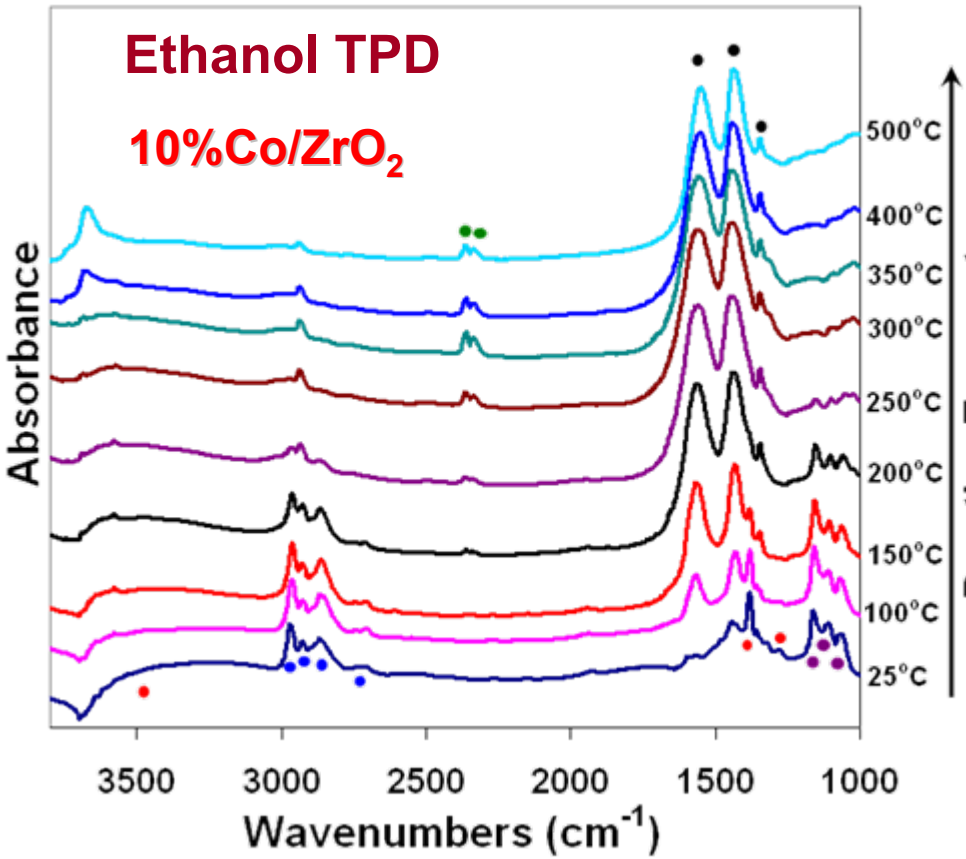




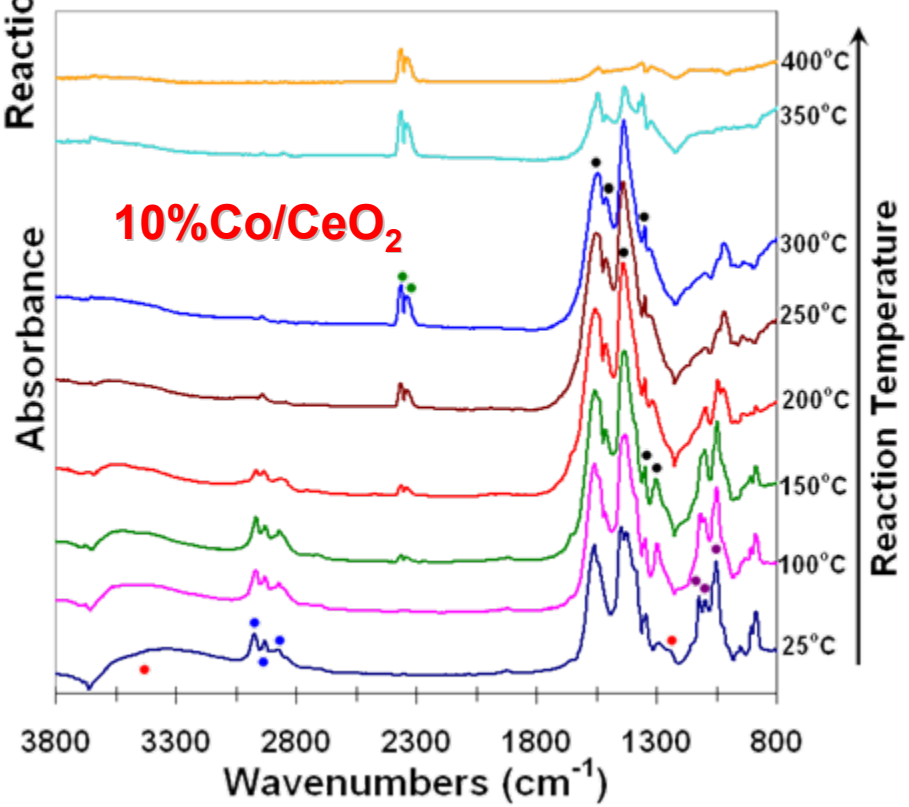


- With modified formulations, high hydrogen yields can be achieved at lower temperatures and catalyst stability is improved
- Activity is stable during TOS (over 70 hrs)
- Hydrogen yield is ~90% during TOS

Evidence of Activity and Stability Improvement through In-Situ DRIFTS during EtOH TPD



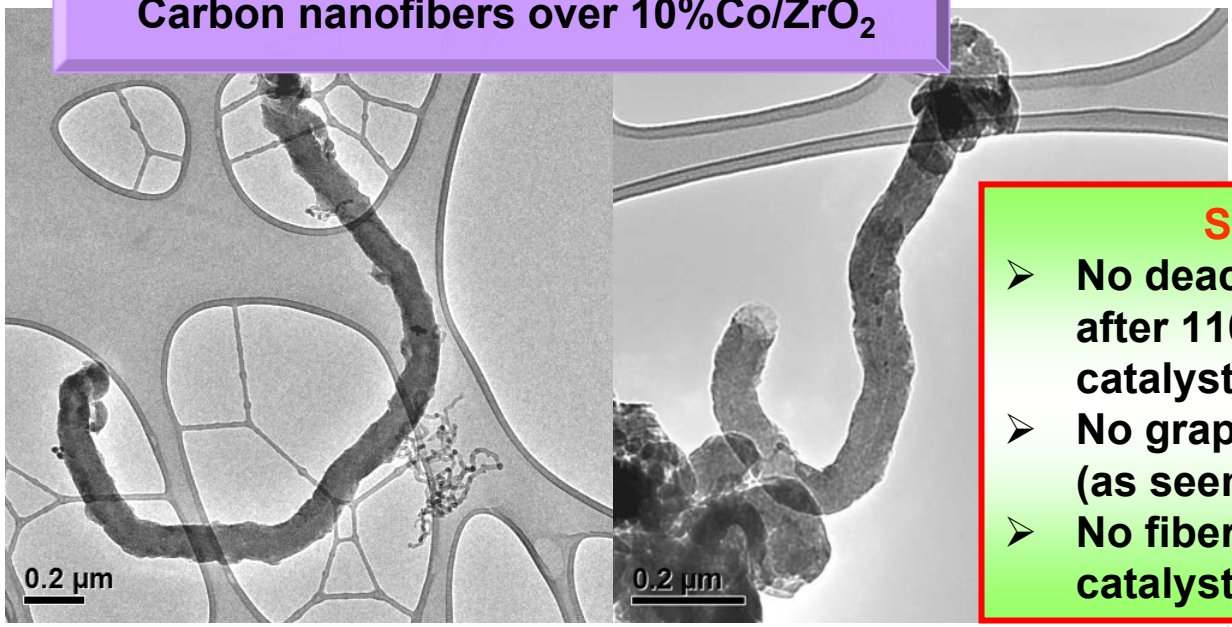
- CH_3- , -CH_2-
- Adsorbed CO_2
- Acetates or carbonates at various adsorbed forms
- Ethoxide species
- Molecularly adsorbed ethanol



High oxygen storage capability of ceria facilitates the appearance and disappearance of the reaction intermediates at much lower temperatures.

Different Carbon Deposition Mechanisms

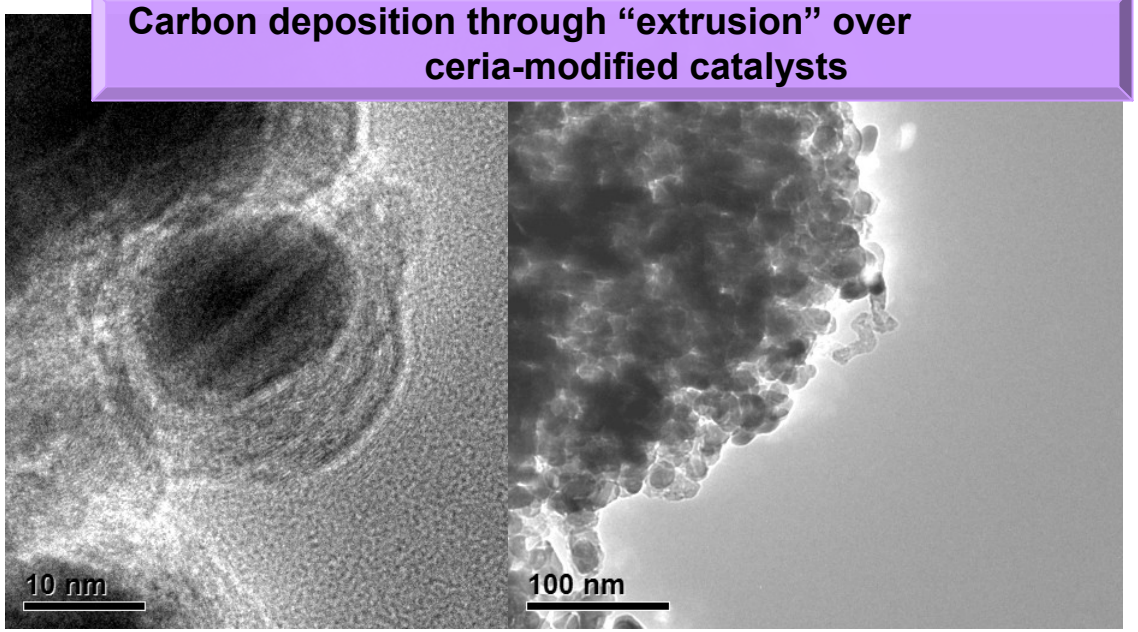
Carbon nanofibers over 10%Co/ZrO_2

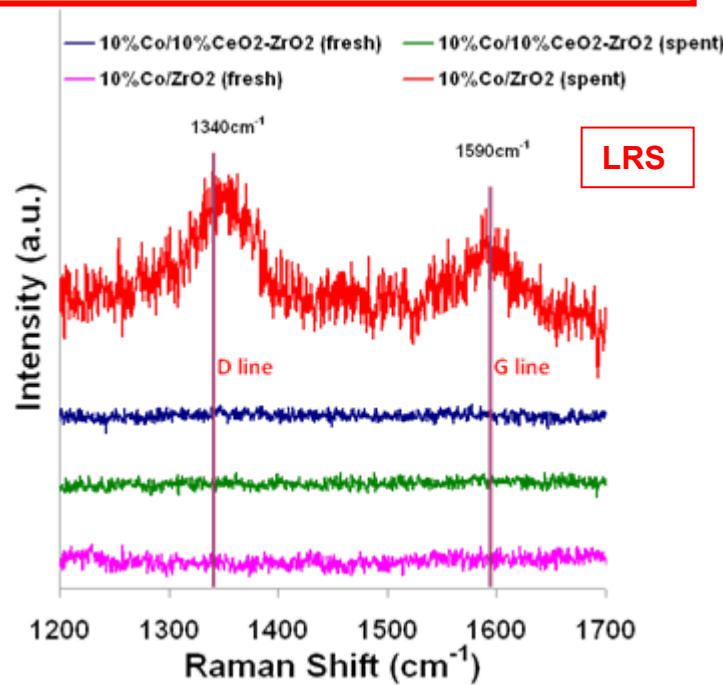


Stability test at 450°C

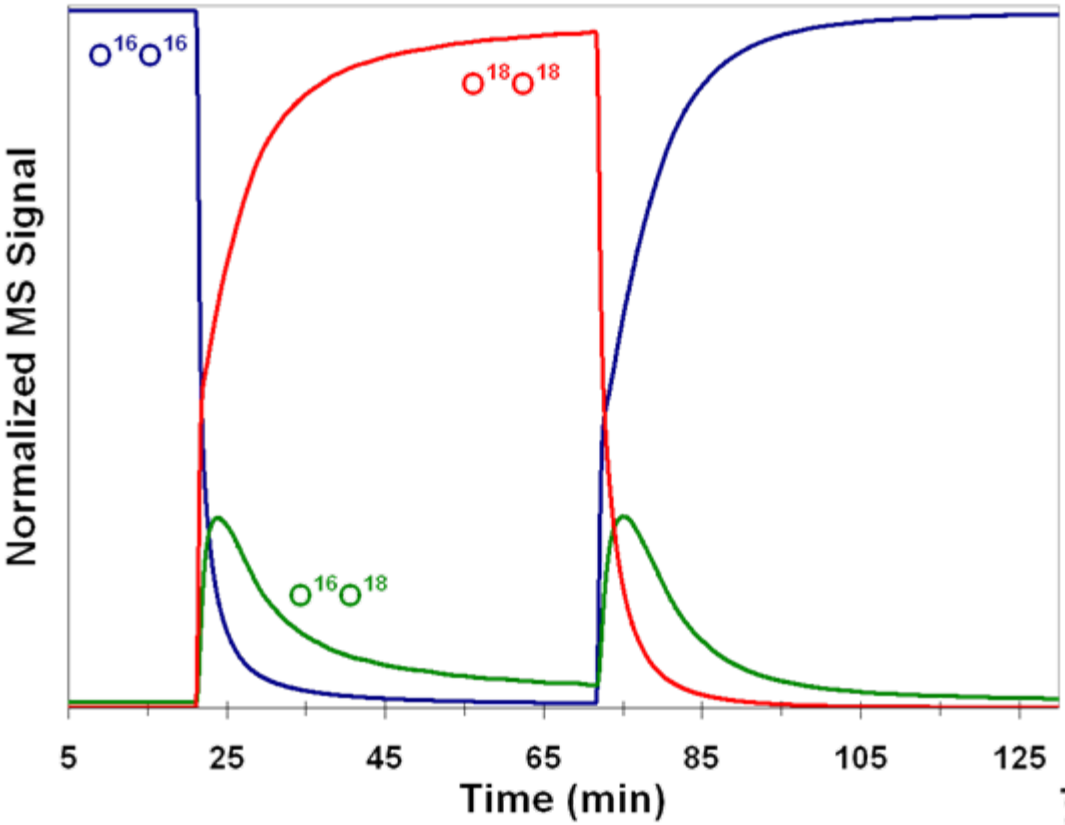
- No deactivation was observed even after 110h run over ceria-modified catalysts.
- No graphite formation on the surface (as seen through LRS).
- No fiber growth on ceria-modified catalyst (as seen through TEM).

Carbon deposition through "extrusion" over ceria-modified catalysts





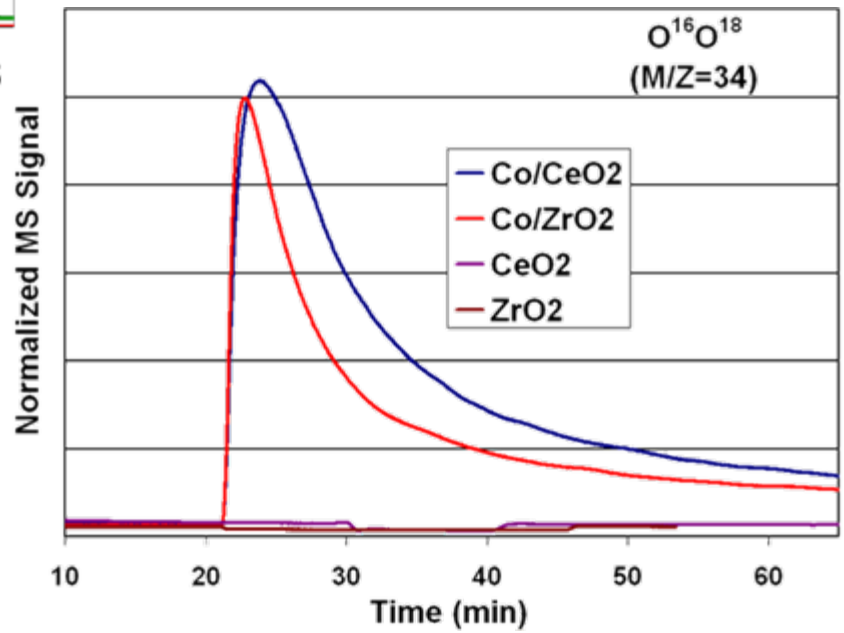
$^{16}O_2/^{18}O_2$ Exchange Experiment over Co/CeO_2



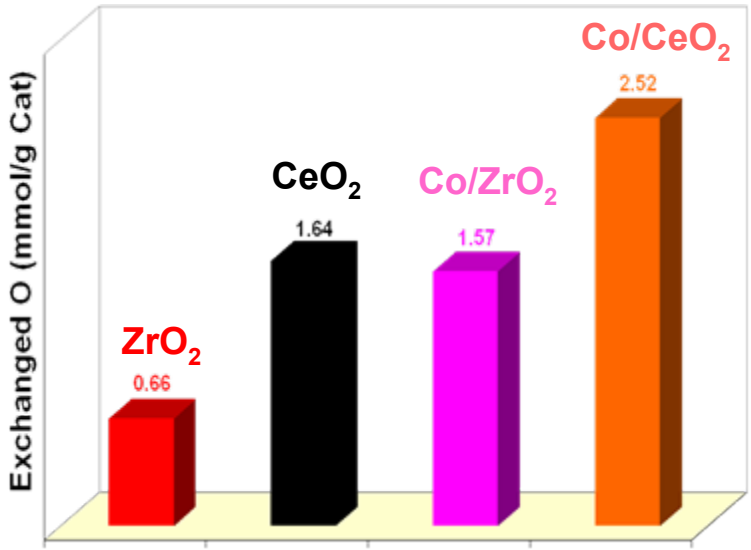
Experimental Parameters

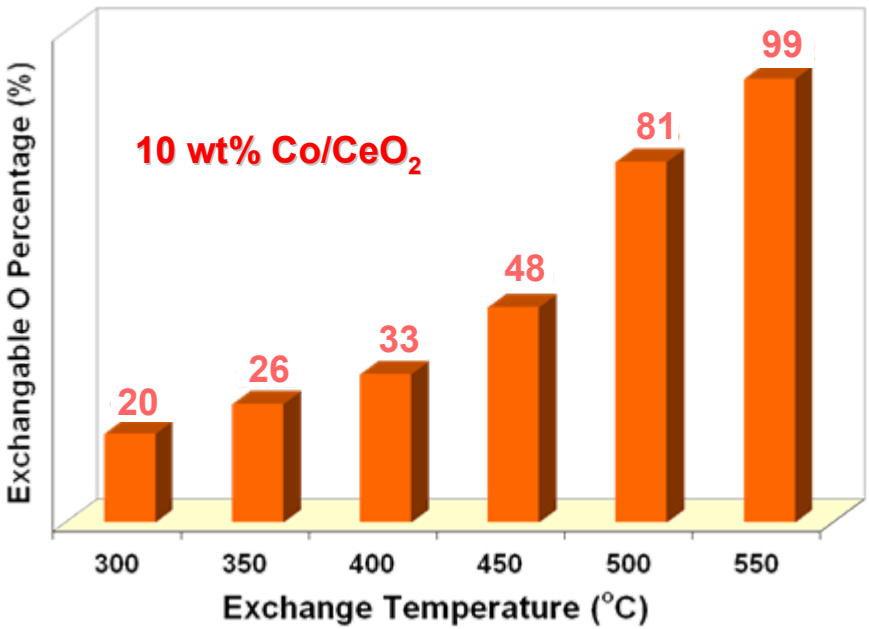
- $2\%^{16}O_2$/He-Ar flows through sample;
- The isotopic switch experiment is performed at 300°C;
- Flow is switched to $2\%^{18}O_2$/He without perturbing the system;
- $2\%^{16}O_2$/He flow is switched back when the signals (m/z=32, 34, 36) are stable.

- **m/z=34 signal is the result of a three-atom complex on the surface, suggesting dissociative adsorption of O_2;**
- **No cross-labeled O_2 on Co-free support;**
- **Showing that Co is effective in O-O bond breakage, more O-exchange over Ce-supported catalyst.**



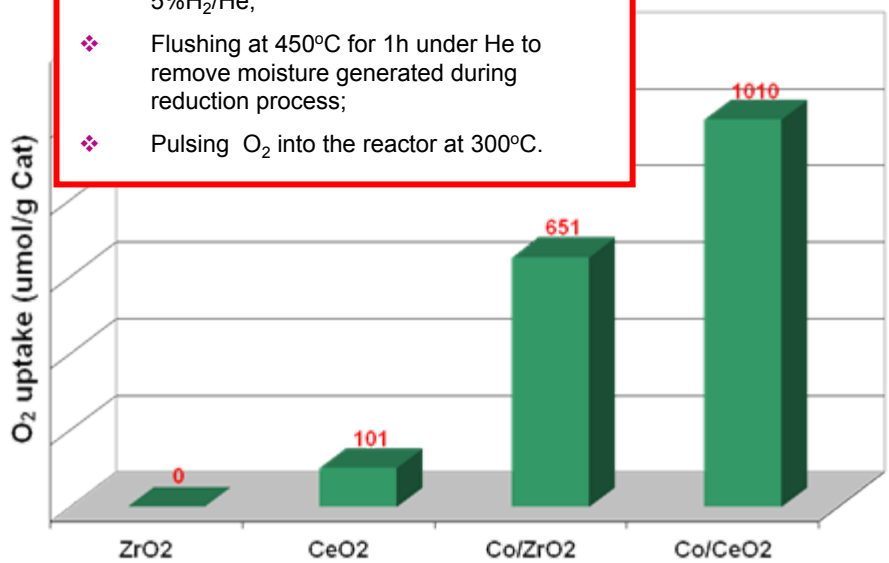
Oxygen Mobility Measurement Using $^{16}O_2/^{18}O_2$ Exchange





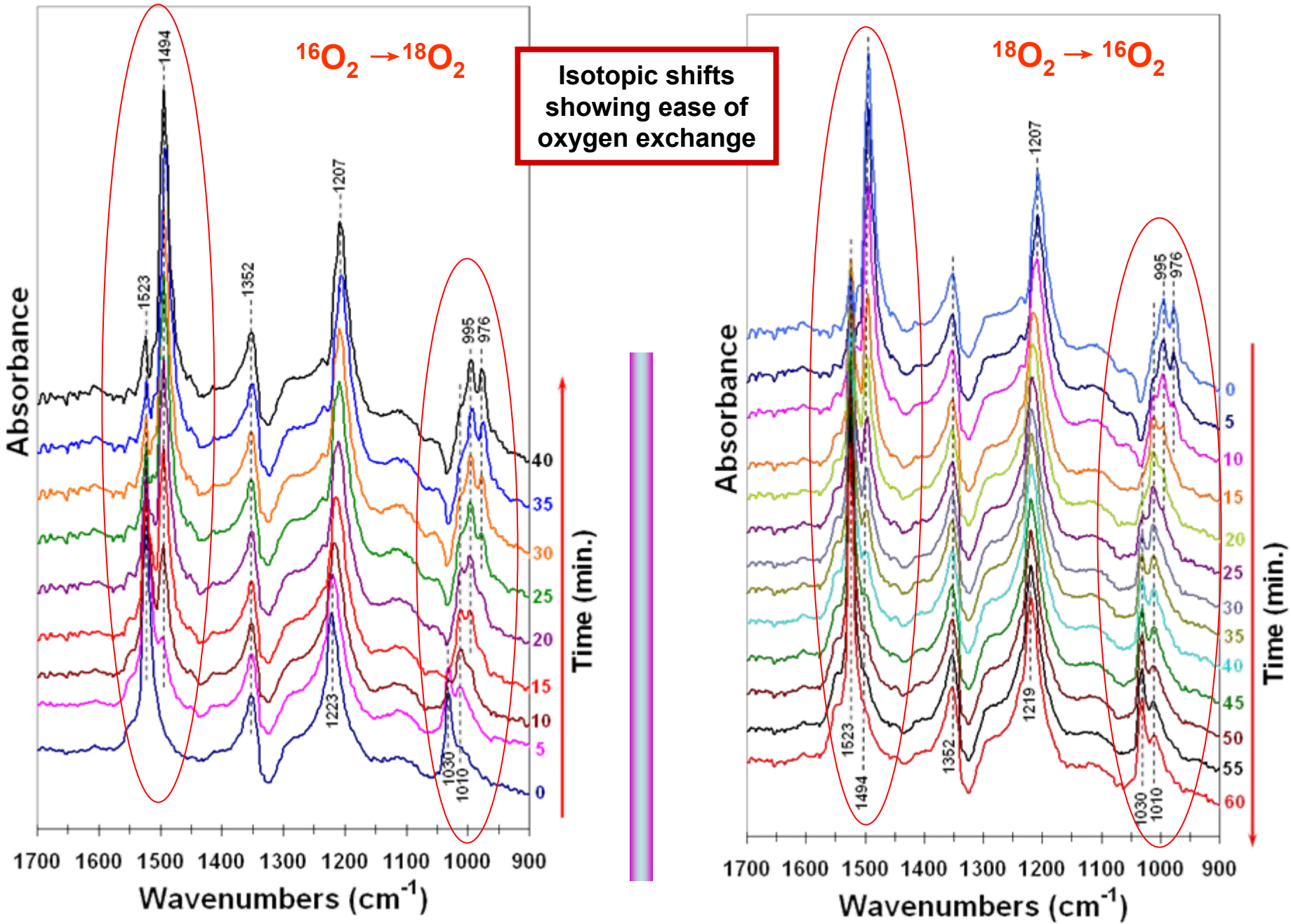
Reducibility Comparisons

- Pre-reduction at 400°C for 2h under 5%H_2/He;
- Flushing at 450°C for 1h under He to remove moisture generated during reduction process;
- Pulsing O_2 into the reactor at 300°C.

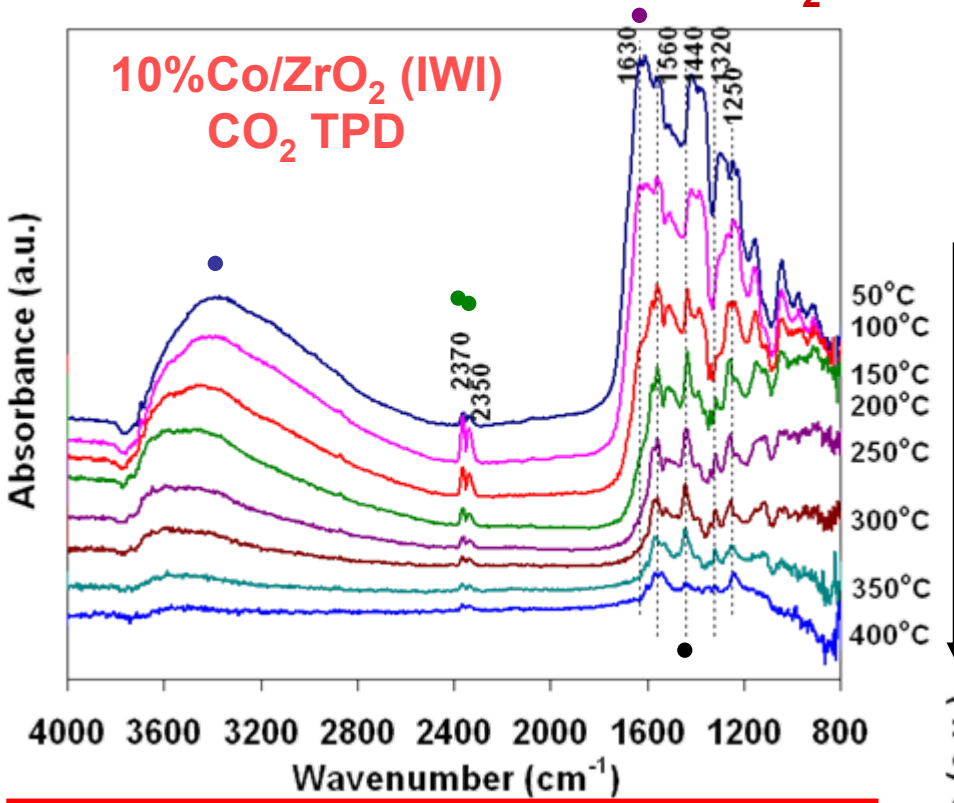


- Oxygen in CeO_2 is much more accessible (as seen through $^{16}O_2/^{18}O_2$ Exchange and reducibility tests;
- Co can facilitate oxygen adsorption dissociatively;
- At temperatures relevant for the reaction, significant % of oxygen from the bulk is accessible.

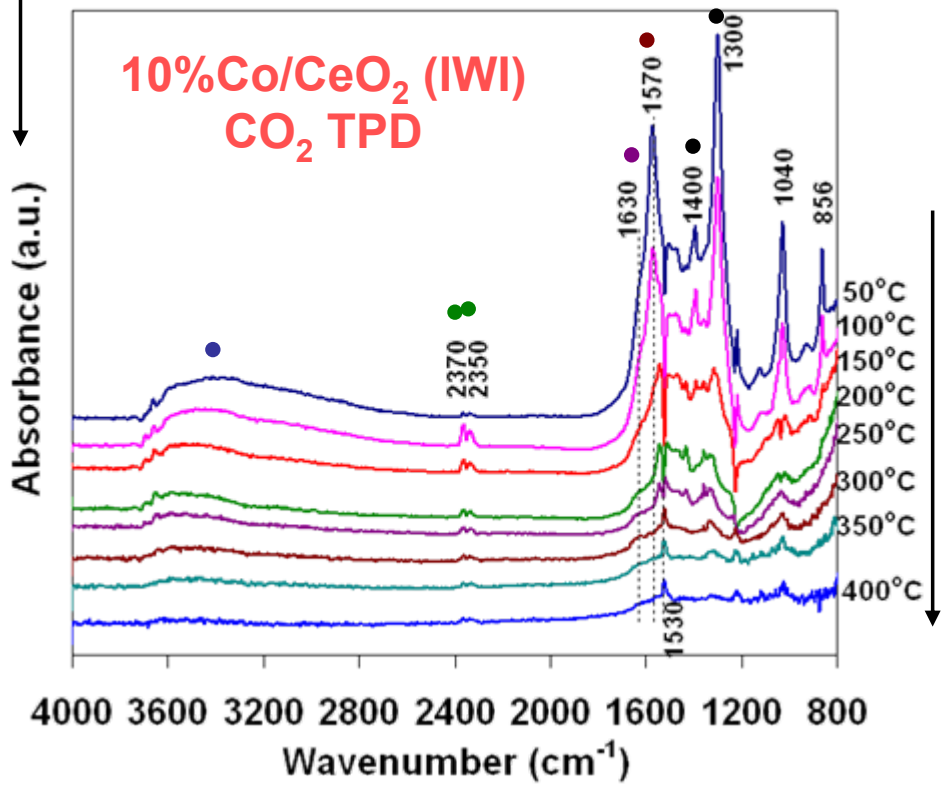
Time Resolved DRIFTS over 10%Co/CeO_2 Using $^{16}O_2$ / $^{18}O_2$



Surface Basic Sites Characterization: Use of CO_2 as a Probe Molecule



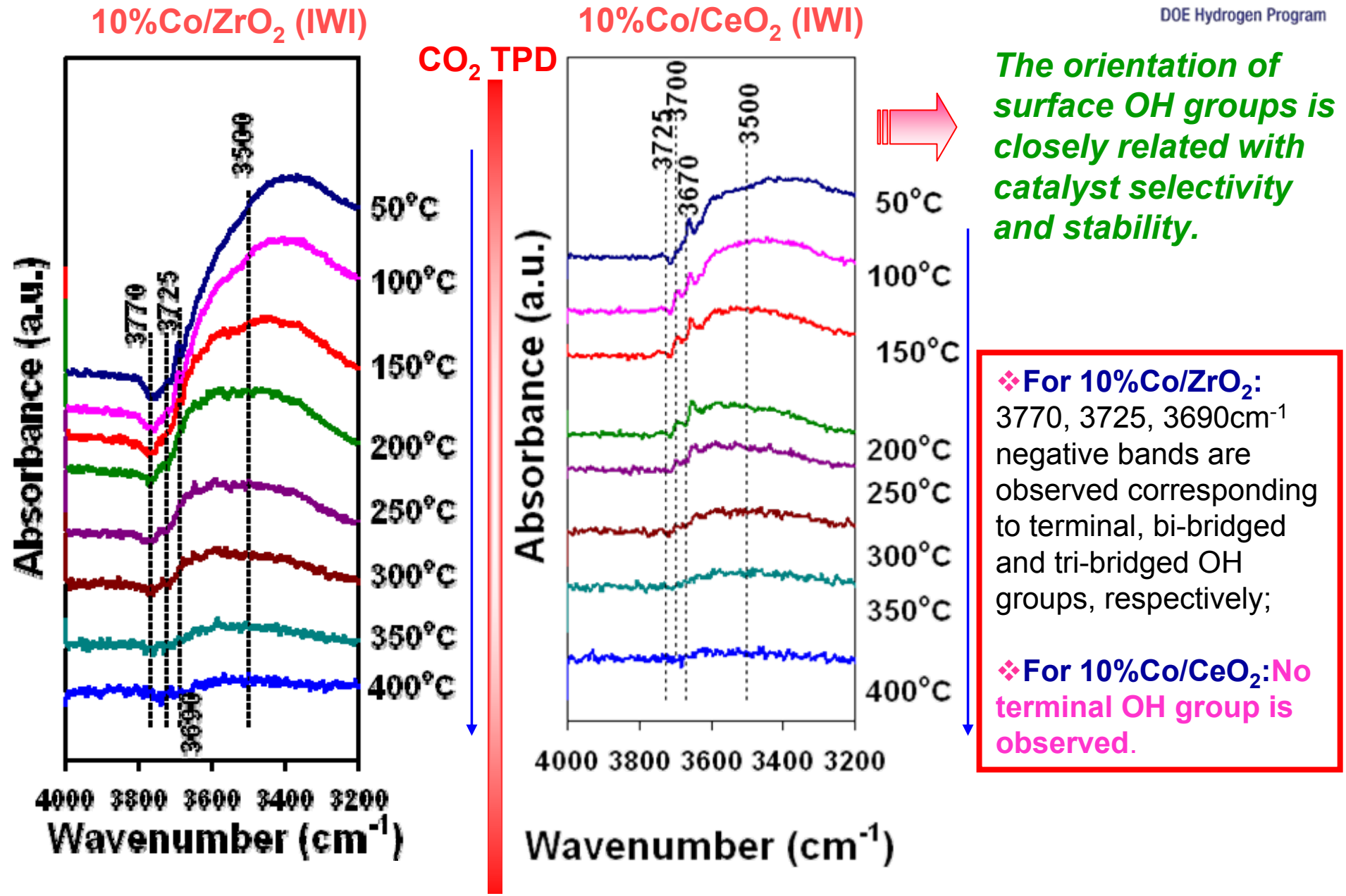
- OH: 3600-3000cm^{-1};
- Adsorbed CO_2: 2370, 2350cm^{-1};
- Molecularly adsorbed H_2O: 1630cm^{-1};
- Bidentate formate: 1570cm^{-1};
- Carbonate: 1440, 1400, 1300cm^{-1}.



- More O atoms are accessible on the surface of CeO_2 supported sample, leading to easier formation of formate and carbonate species;
- Stronger water band (both 3600-3000 cm^{-1} and 1630 cm^{-1} signals) are present on the surface of ZrO_2 supported sample, resulting from interaction between CO_2 and catalyst surface.

Surface Basic Sites Characterization: Use of CO_2 as a Probe Molecule

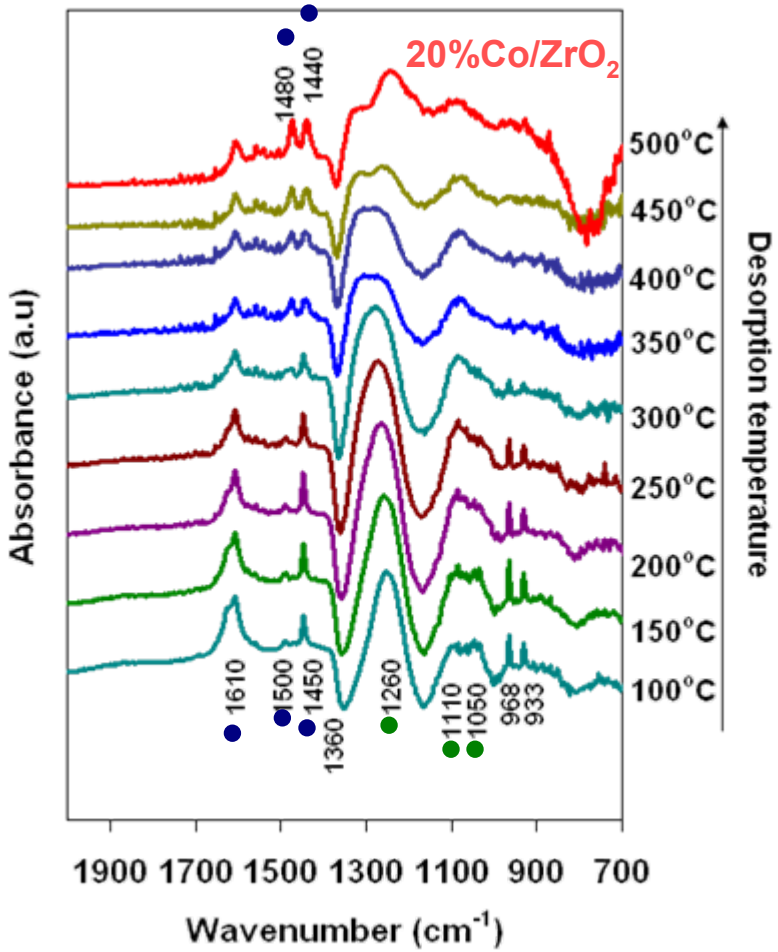
DOE Hydrogen Program



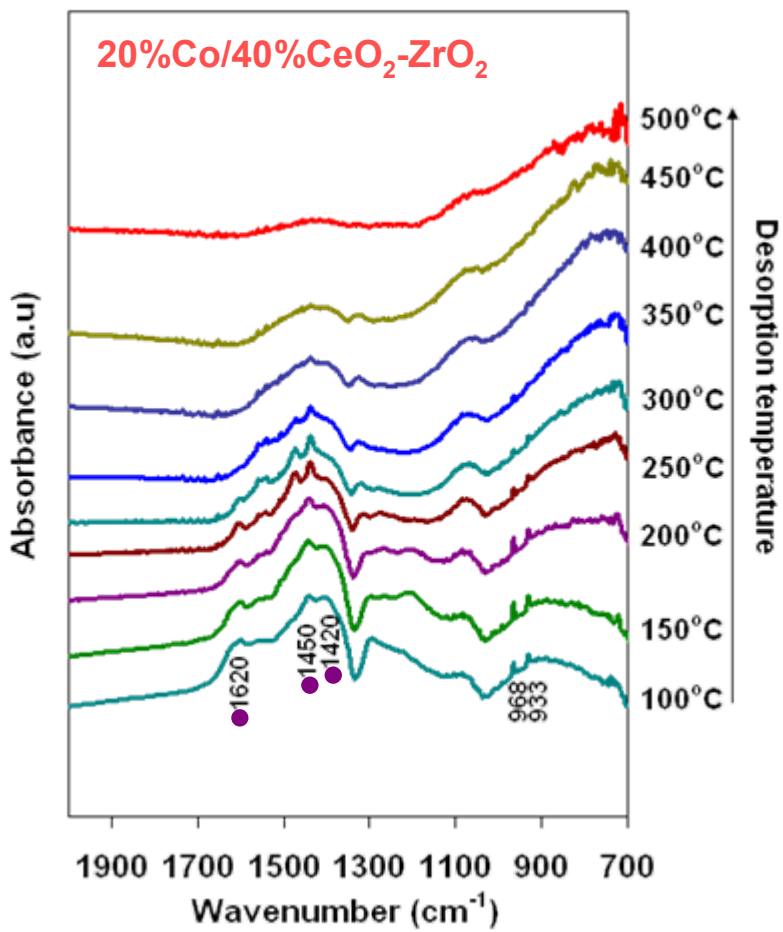
The orientation of surface OH groups is closely related with catalyst selectivity and stability.

- **For 10%Co/ZrO_2:** 3770, 3725, 3690cm^{-1} negative bands are observed corresponding to terminal, bi-bridged and tri-bridged OH groups, respectively;
- **For 10%Co/CeO_2:** No terminal OH group is observed.

Surface Acidic Sites Characterization
Use of NH_3 as a Probe Molecule



NH_3 TPD



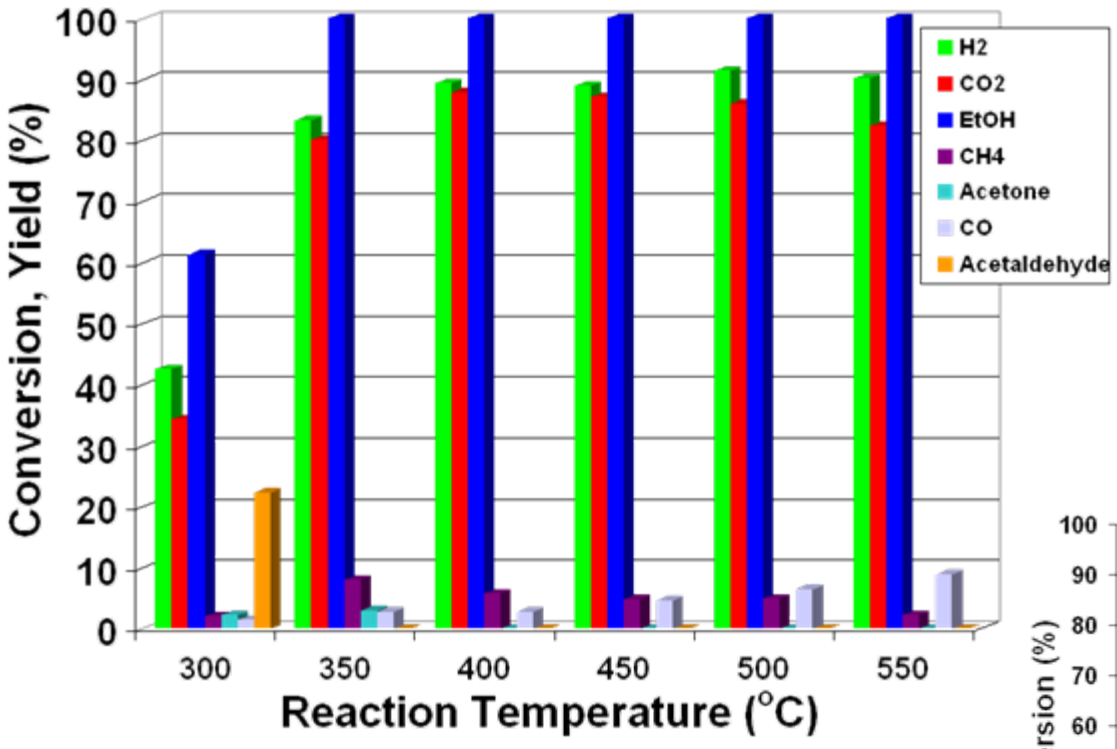
- NH_4^+: 1450, 1500cm^{-1} (asymmetric)
  1610cm^{-1} (symmetric)
- NH_3: 1260cm^{-1} (co-ordinatively bonded)
  1110, 1050cm^{-1} (molecularly)
- Brønsted acid sites: 1620, 1450, 1420cm^{-1}

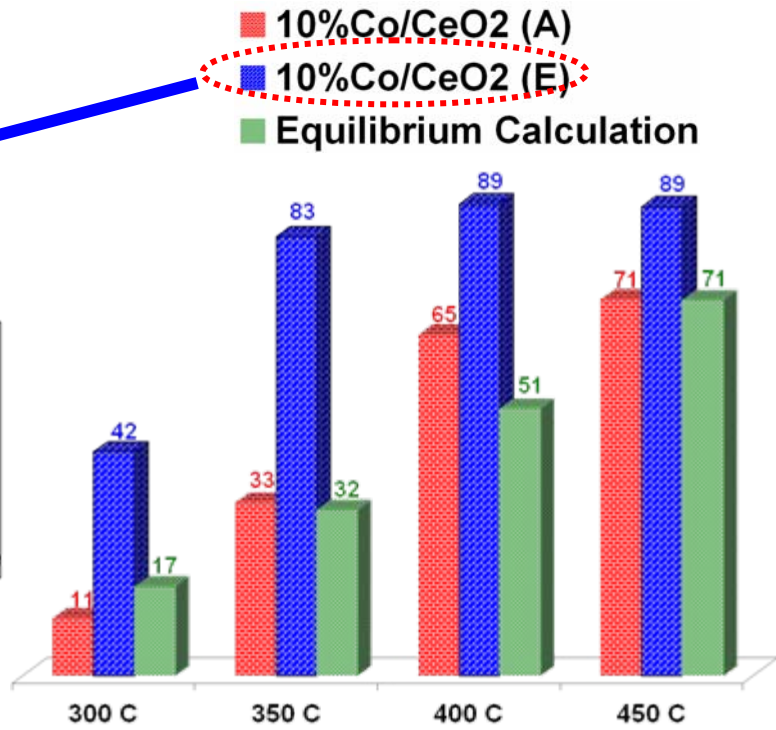
- More acidic sites are present over the surface of 20%Co/ZrO_2, resulting in stronger interaction with NH_3 probe;
- Surface acidity correlates well with coke formation.

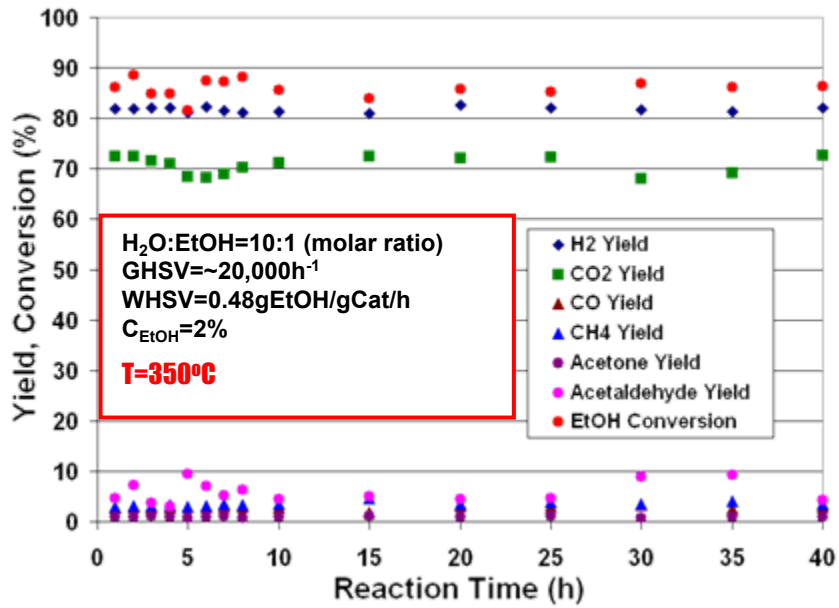
Effect of synthesis technique:

Impregnation medium

Aqueous vs Ethanol

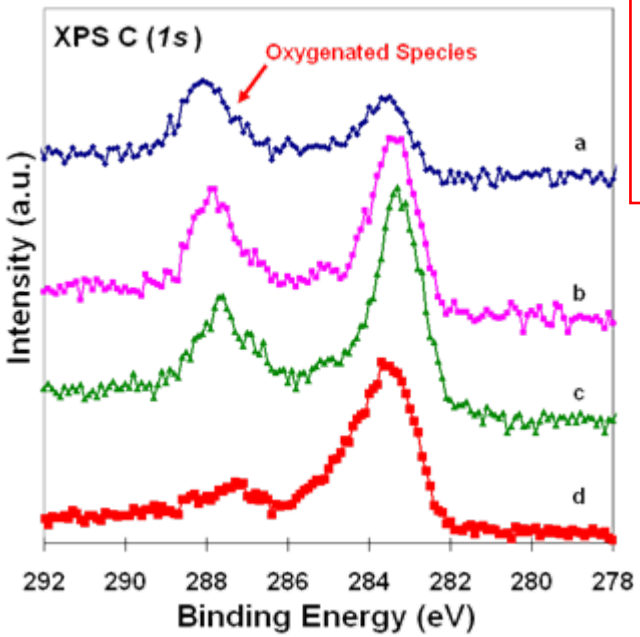


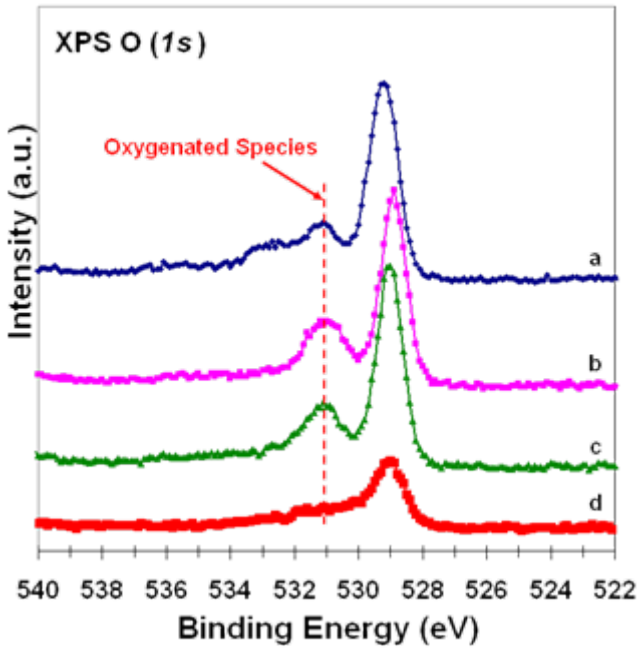




- With EtOH impregnation, higher hydrogen yields can be achieved at lower temperatures;
- Activity is stable during TOS experiment.

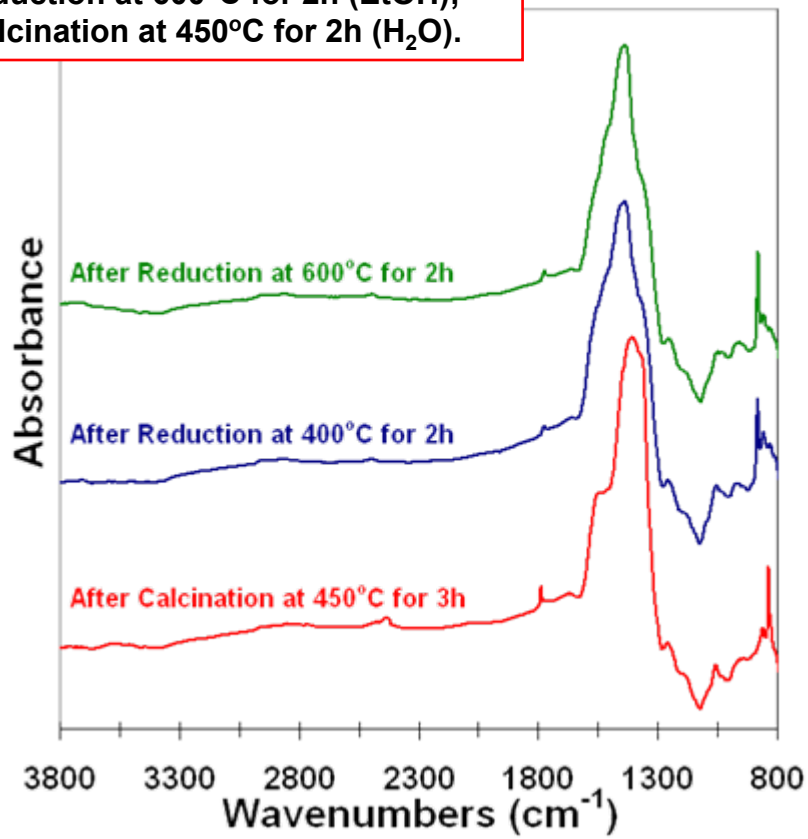
Effect of the Impregnation Medium: XPS and DRIFTS





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).

Spectrum of the sample impregnated in DI water is used for background



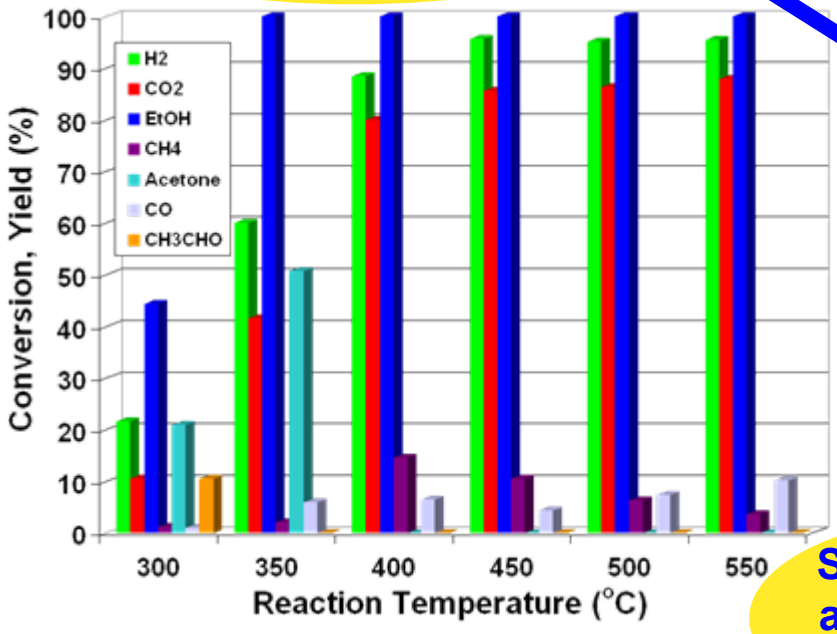
- **Presence of oxygenated species shown by XPS (C1s and O1s) and DRIFTS;**
- **C-O vibration indicates the presence of carboxyl group;**
- **Oxygenated species remained on the surface even after reduction treatment.**

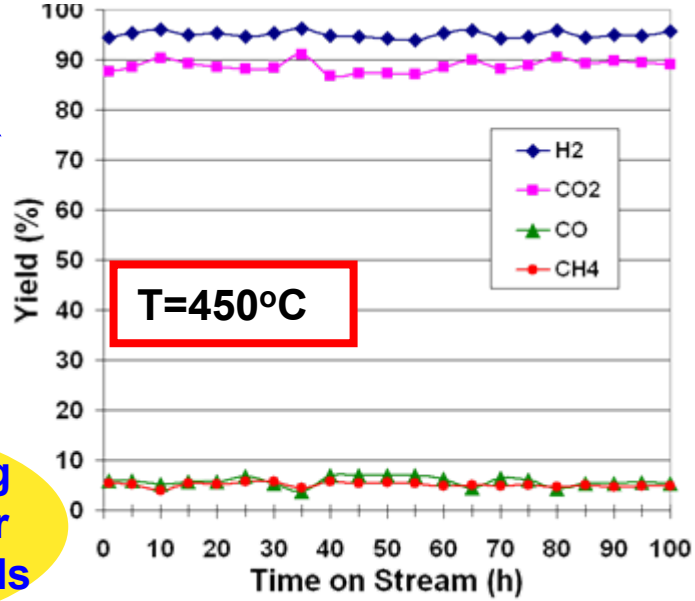
Effect of Bioethanol Impurities on Performance

H_2O:EtOH=23.5:1 (molar ratio)
GHSV=~15,000h^{-1}
WHSV=0.2gEtOH/gCat/h
C_{EtOH}=~1%
Co/CeO_2- E

Crude ethanol composition*	Vol. (%)
Ethanol	12
Water	86
Glycerol	1
Lactic acid	1

** Akande, A.J., et. al., Appl. Catal. A: Gen. 287 (2005) 159*





Steam reforming activity for other bio-derived liquids

- No performance loss due to crude EtOH impurities;
- Activity is stable over 100 hrs;
- Hydrogen yield is ~95% during the test time period;
- Significant Steam Reforming Activity for other Bio-derived Liquids.

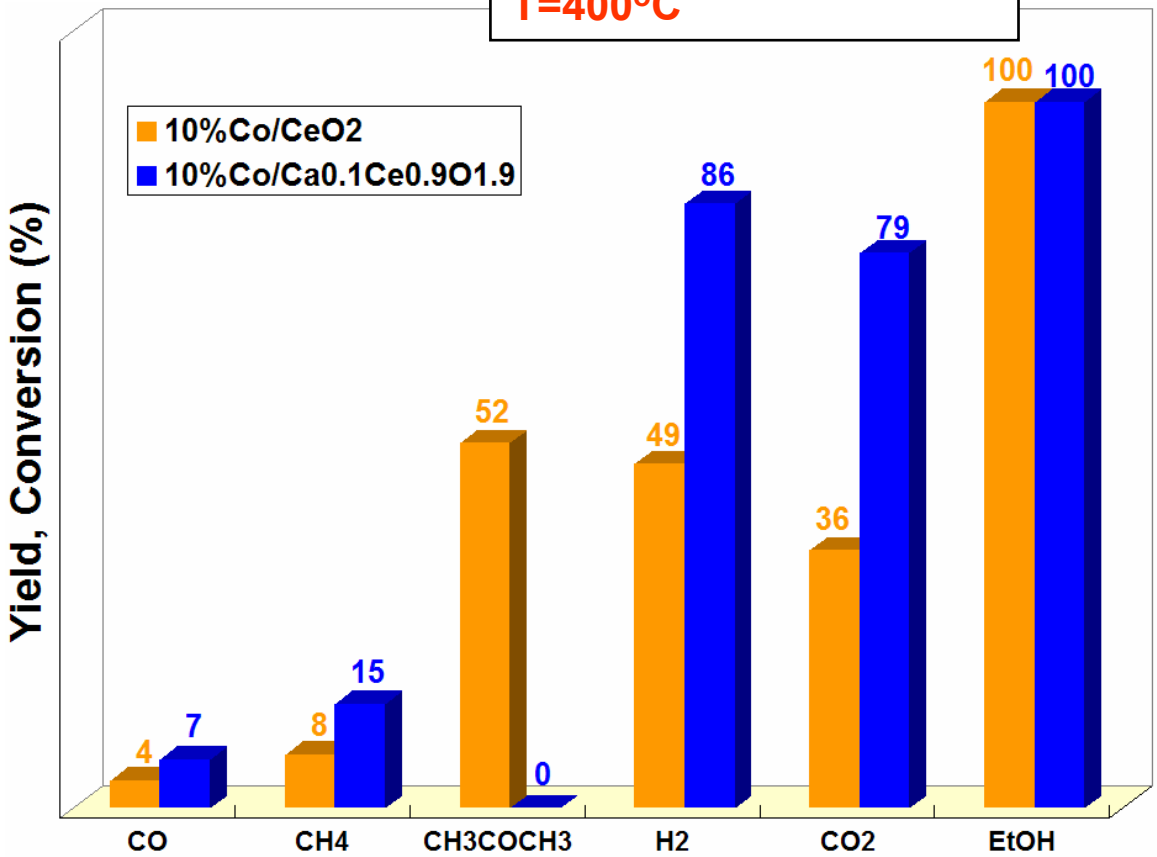
Bio-derived liquids	% H_2 Yield
Methanol	>95% at 450°C
1-propanol	>90% at 500°C
2-propanol	>80% at 550°C
Butanol	>85% at 550°C
Dimethyl ether	>80% at 550°C

Reaction tests under neat conditions

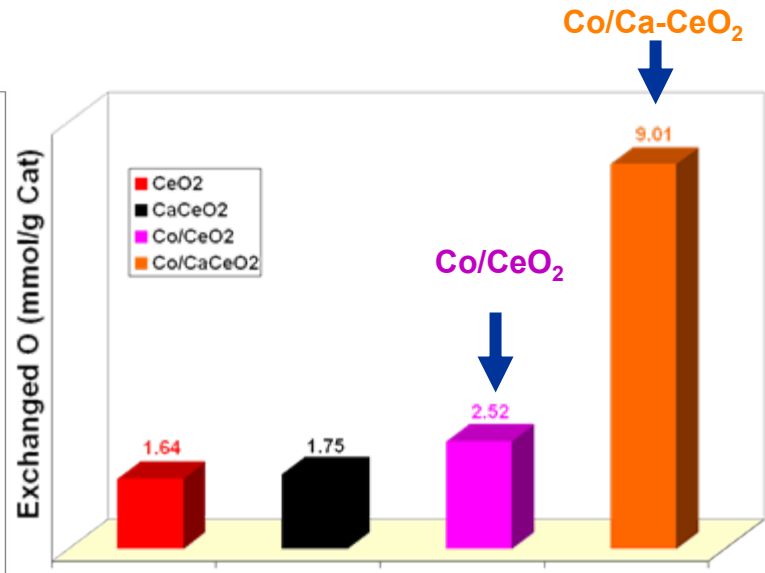
Further modifications to support

Vacancy creation through substitution by lower valence metals

EtOH:H_2O=1:10 (molar ratio);
C_{EtOH}=7.5vol.%;
WHSV=~0.54gEtOH/gCat/h;
GHSV=~5,000h^{-1}
T=400°C

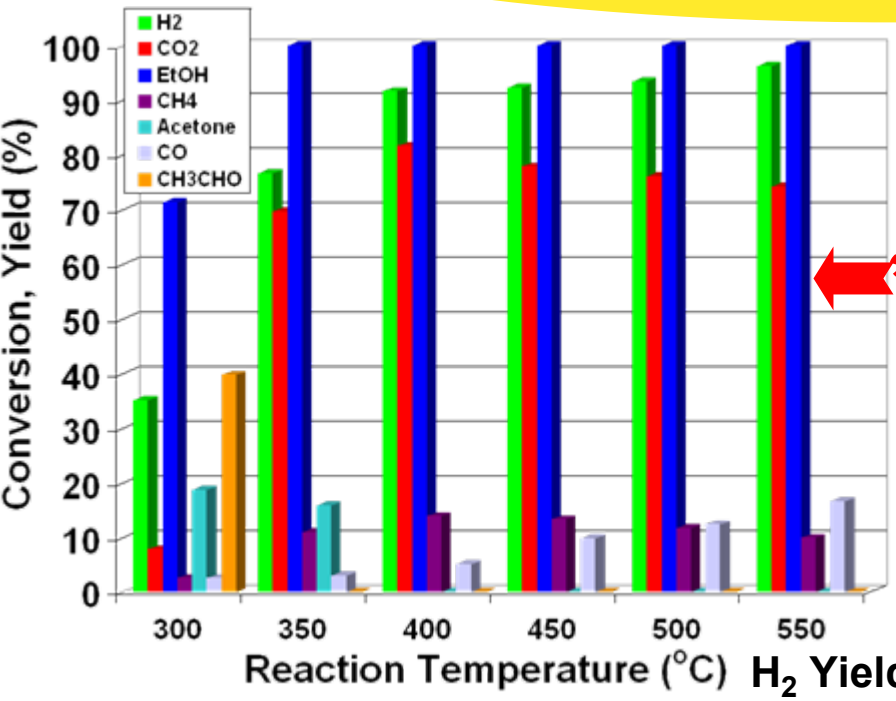


Oxygen Mobility Measurement Using $^{16}O_2/^{18}O_2$ Exchange



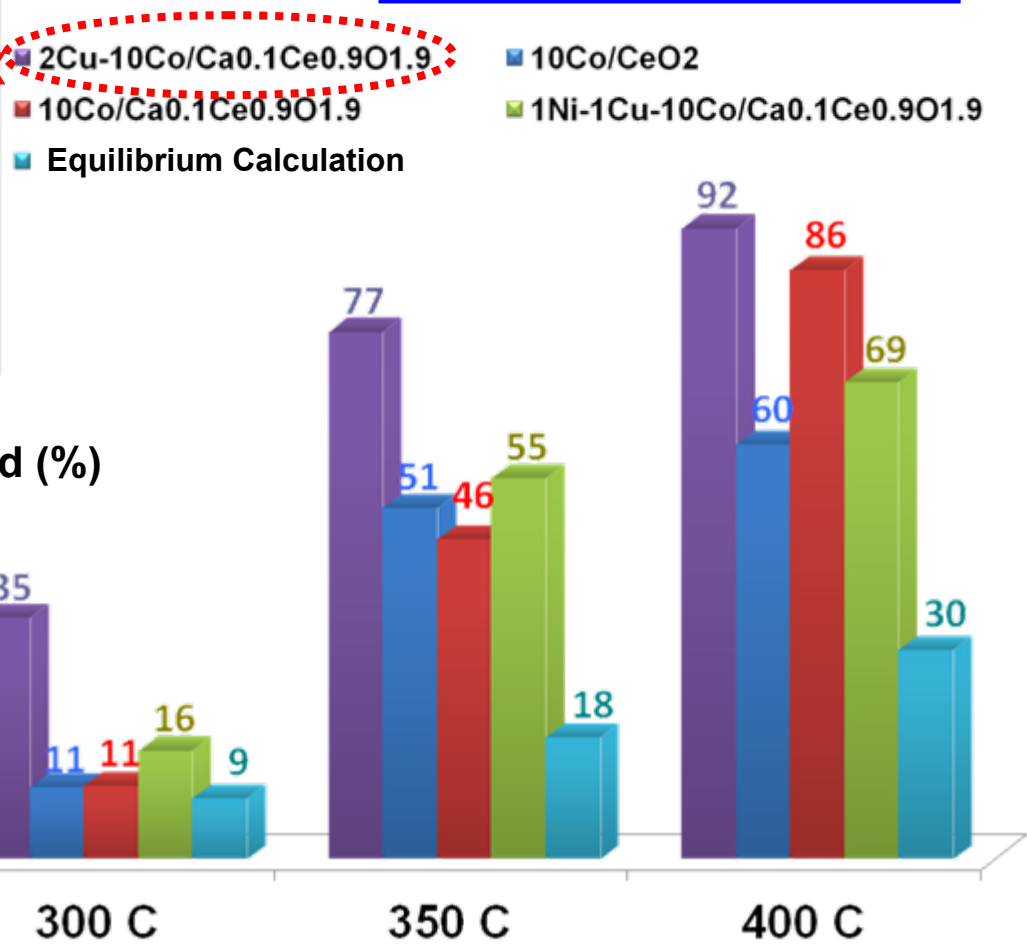
Ca doping can create oxygen vacancies, resulting in increased oxygen mobility, and much higher H_2 yield under neat conditions

Reaction tests under neat conditions
Further modifications to catalyst
Active metal promotion



H_2 Yield (%)

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



- Modified formulations lead to improved catalyst performance;
- Higher than 90% H_2 yield is obtained at T=400°C.

Collaborative effort

Combining experimental work with molecular simulation

Dr. Christopher M. Hadad
Professor of Chemistry
The Ohio State University
http://www.chemistry.ohio-state.edu/~hadad

- **Motivation for Molecular Simulation**
- Gaining theoretical insight into active sites, reaction intermediates, and reaction mechanisms;
- Experimental results interpretation grounded in theory;
- Testing the reliability of some experimental results;
- Investigating certain catalyst properties which are not directly observable experimentally;
- Reducing the time-consuming and cost-intensive catalyst screening process;
- Acquiring guidelines for catalyst formulation modifications to improve catalytic performance;
- Facilitating rational design of catalyst system.

Simulation approaches

- **Support surface representation**
- **Crystal plane selection**
- **Oxygen vacancy coordination**
- **Active metal anchoring**
- **Metal loading**
- **Metal particle size**
- **Doping/promoter effect**
- **Reactant adsorption**
- **Surface intermediates**
- **Reaction network**

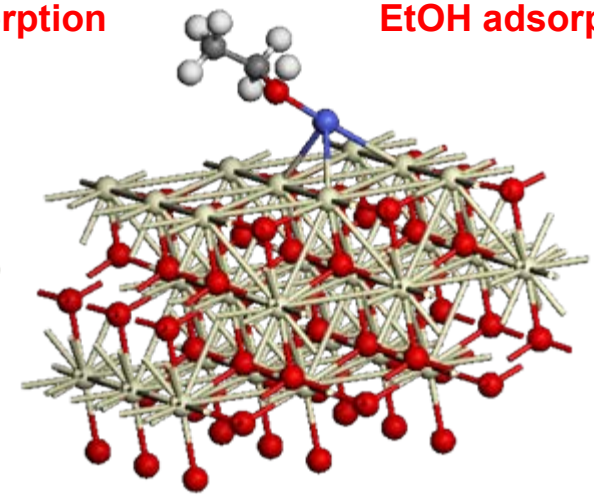
Simulation Approaches

- **Reactant adsorption:**

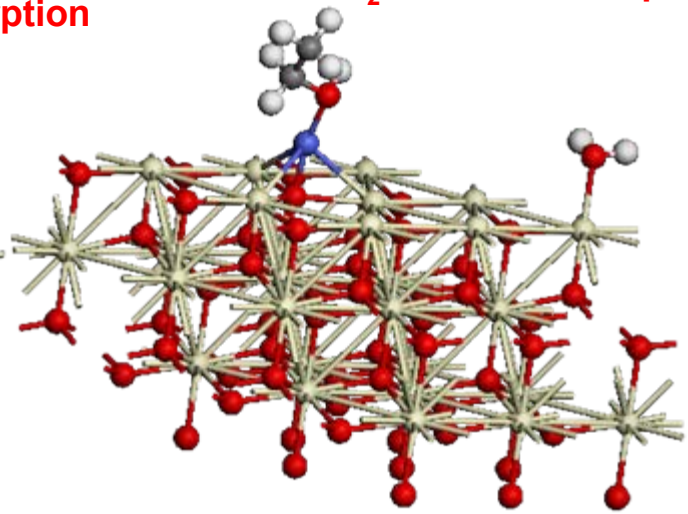
Co/CeO_2

H_2O adsorption

EtOH adsorption

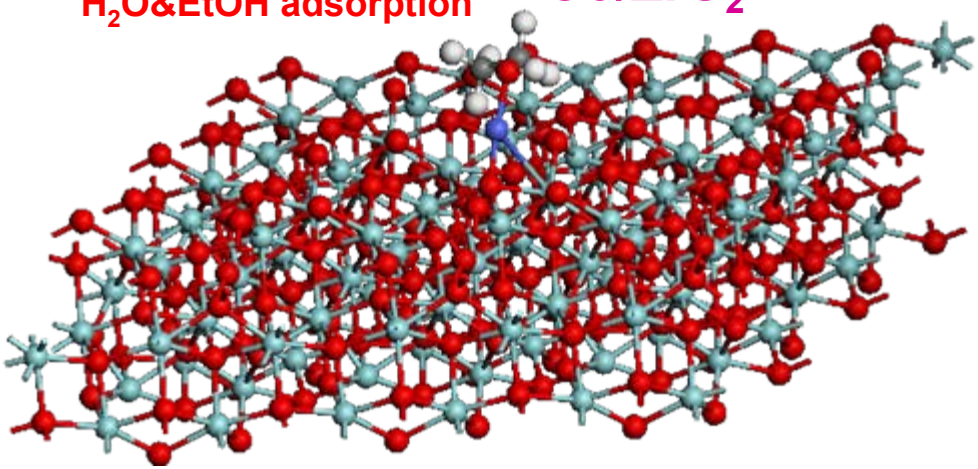


H_2O&EtOH adsorption



H_2O&EtOH adsorption

Co/ZrO_2

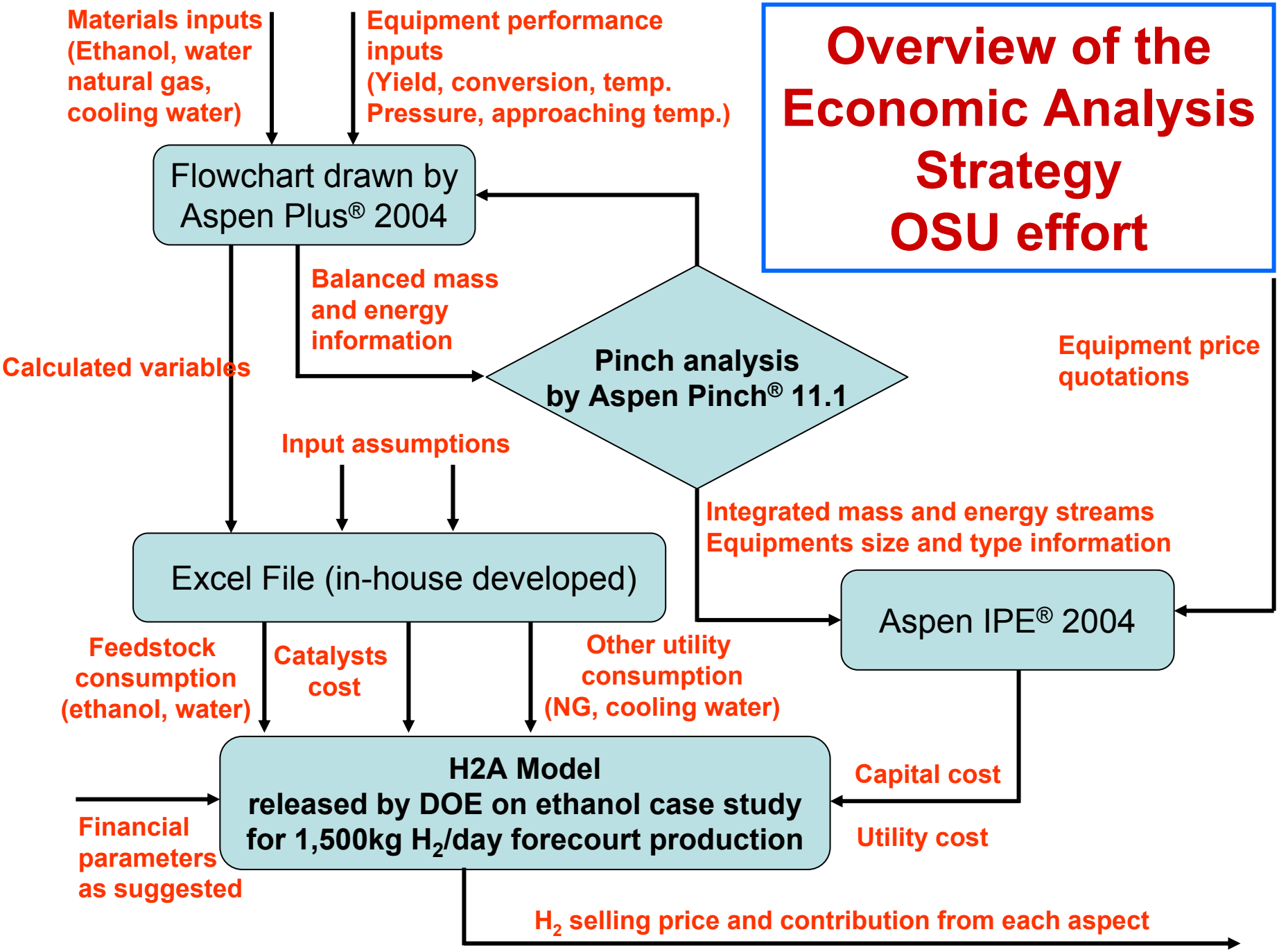


Ce O Co C H

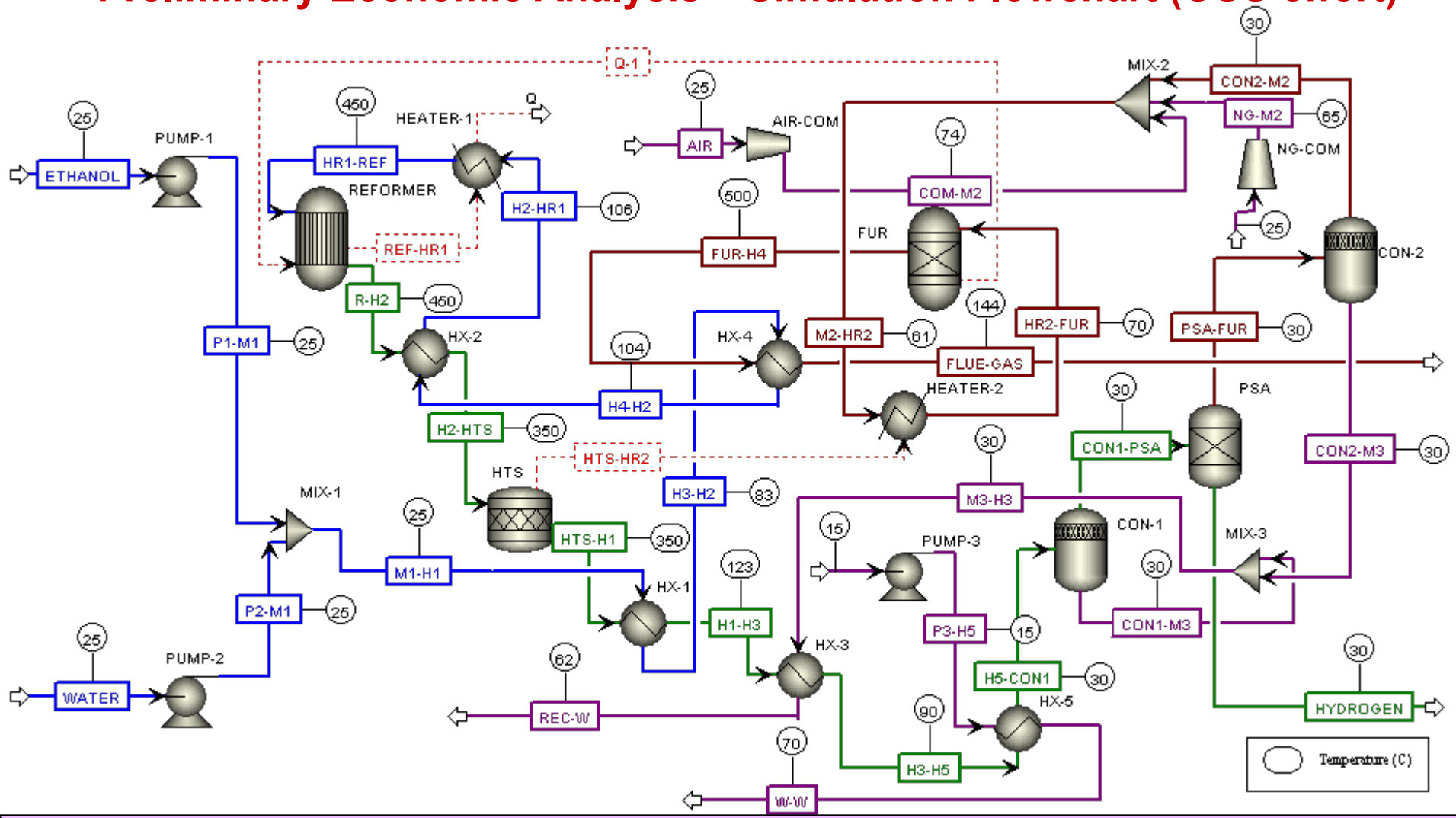
Ethanol Adsorption using TGA-DSC

Sample	Adsorption Energy (kcal/mol)
ZrO_2	-14.95
CeO_2	-16.14
$10\%Co/ZrO_2$	-15.33
$10\%Co/CeO_2$	-16.63

Overview of the Economic Analysis Strategy OSU effort

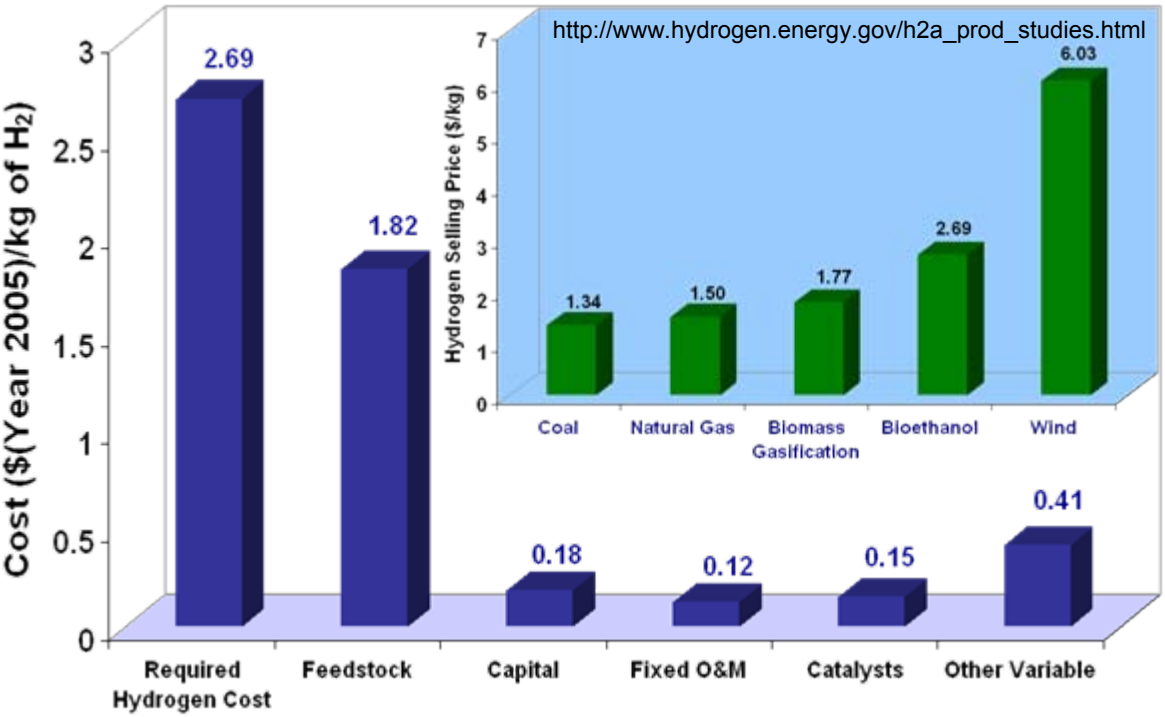


Preliminary Economic Analysis – Simulation Flowchart (OSU effort)



- 85% hydrogen recovery on PSA. NG used to supply energy required for reaction and heating;
- 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).

Central Production at 150,000kg H_2/day

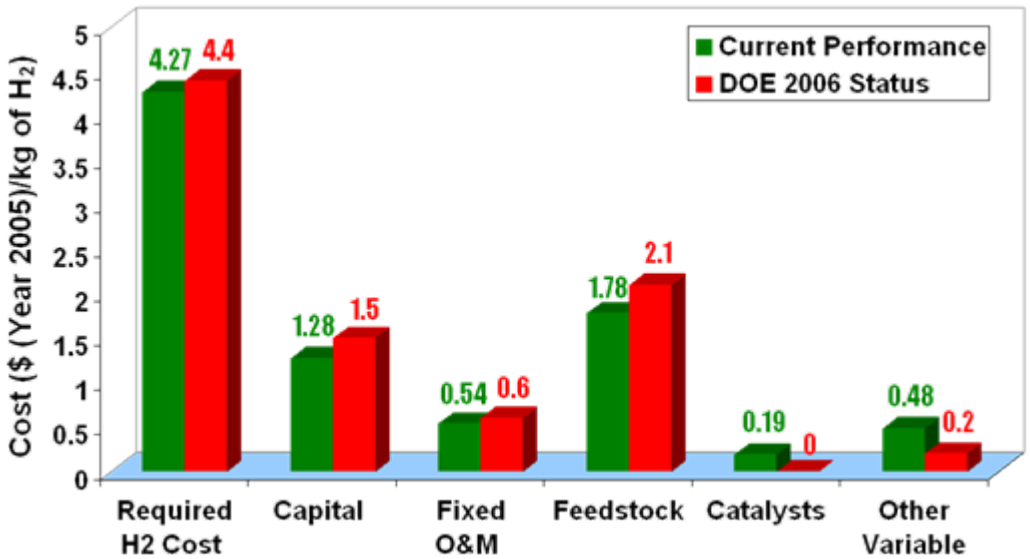


Preliminary Economic Analysis (OSU effort)

- 90% H_2 yield with ethanol to water of 1 to 10 and 70% capacity factor are assumed;
- The ethanol cost utilized is $1.07/gal and electricity cost used is $0.08/kWh;
- "OSU" catalyst is used for bioethanol steam reforming with 3,000h^{-1} GHSV and 1,000h lifetime;
- Commercial catalyst is used for HTS reaction with 3000h^{-1} GHSV and 5 years lifetime at $4.67/lb.

- Ethanol case study recently released by DOE is referenced;
- Same financial parameters and capital cost for forecourt station compression and storage are used;
- Catalysts contribution is not considered separately in the DOE technical plan;
- NG consumption is classified into other variable contribution instead of feedstock category.

Forecourt Production at 1,500kg H_2/day

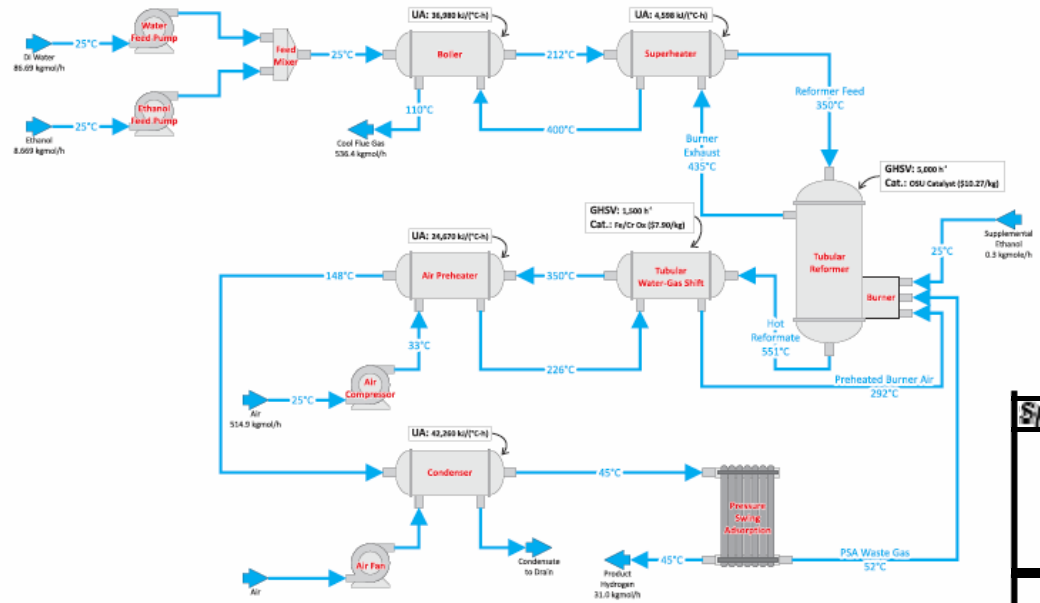


Capacity: 1500 kg/day
Ethanol Efficiency: 67.7%
Overall Efficiency: 66.9%
Elec. Load: 0.592 $kW_e/kg\ H_2$
Pressure: ~22 bar
H_2 Recovery: 31.0 kgmol/h
Capital Cost: $947,809

System 09: Tubular Medium-Temperature Ethanol System (OSU)

Economic Analysis provided by

Directed Technologies, Inc.



H2A Model H2 Production Cost Projections

(Production Only, Does Not Include Compression/Storage/Dispensing)

Specific Item Cost Calculation	
	OSU Catalyst System (Med. Temp. EtOH Reforming) (System #9) (Tubular Reformer)
Cost Component	Hydrogen Production Cost Contribution ($/kg)
Capital Costs	$0.576
Decommissioning Costs	$0.000
Fixed O&M	$0.176
Feedstock Costs	$2.355
Other Raw Material Costs	$0.000
Byproduct Credits	$0.000
Other Variable Costs (including utilities)	$0.063
Total	$3.170
Key Assumptions:	$1.07/gal EtOH 67.7% EtOH Efficiency 10:1 Steam/C Ratio 1 year catalyst lifetime $1,039k uninstalled production system capital cost

March 21, 2008

Brian James, Jeff Kalinoski
Directed Technologies, Inc.

Progress Summary

- Successful utilization of H2A model to perform economic analysis;
- Investigation of the reaction network;
- Identification of the active sites and reaction mechanism;
- Characterization of the deactivation mechanism;
- Modified catalyst system development with high stability while maintaining good activity;
- Further activity improvement, especially at lower reaction temperatures through modification of the catalyst synthesis technique;
- Activity for steam reforming of various bio-derived liquids;
- Activity in the presence of impurities;
- Excellent catalytic performance under neat reaction conditions;
- Initial work on molecular simulation for rational design of the catalyst system (collaborative effort);
- Economic analysis (OSU effort and collaborative effort);
- Up-to-date literature awareness and information dissemination activities.

Future Work

DOE Hydrogen Program

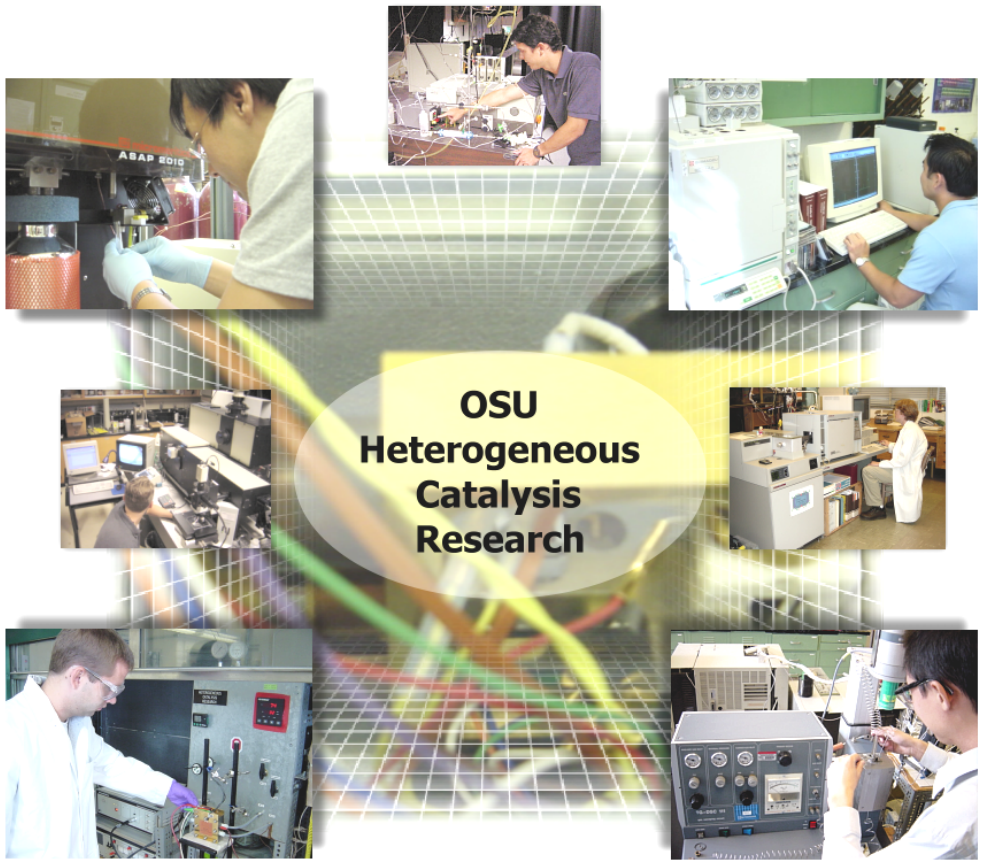
- Kinetic and mechanistic investigations coupled with *in-situ* characterization;
- Catalyst testing under more realistic conditions.
- Tuning economic analysis based on updated catalyst system knowledge database and the new H2A model; continued collaboration with Directed Technologies, Inc.
- Performance optimization;
- Long term time-on-stream experiments;
- Accelerated deactivation and regeneration studies;
- Performing molecular simulation for rational design of catalysts
- Catalyst scale-up through industrial partnership.

DOE Hydrogen Program

Acknowledgement

OSU HCRG

Department of Energy



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