2010 DOE Annual Hydrogen Program 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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PD001

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This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start Date - May 1, 2005
- End Date - April 31, 2010
  (no-cost extension requested)
- 90% 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)
- Funding received in FY10
  - No funding

Barriers

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

Partners

- Argonne National Laboratory
  - Advanced Photon Source Synchrotron techniques
- Chemistry Dept. at OSU (Prof. Hadad)
  - Molecular simulation
- NexTech Materials, Ltd.
  - Catalyst manufacturing scale-up
- Directed Technologies Inc.
  - Economic analysis and feasibility considerations
- PNNL
  - Sharing findings

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°C)
    - High EtOH conversion
    - High selectivity and yield of hydrogen
    - High catalyst stability
    - Minimal byproducts such as acetaldehyde, methane, ethylene, and acetone
    - Ease of operation
  - Addressing the barriers
    - Fuel Processor Capital Costs
    - Operation and Maintenance
    - Feedstock Issues

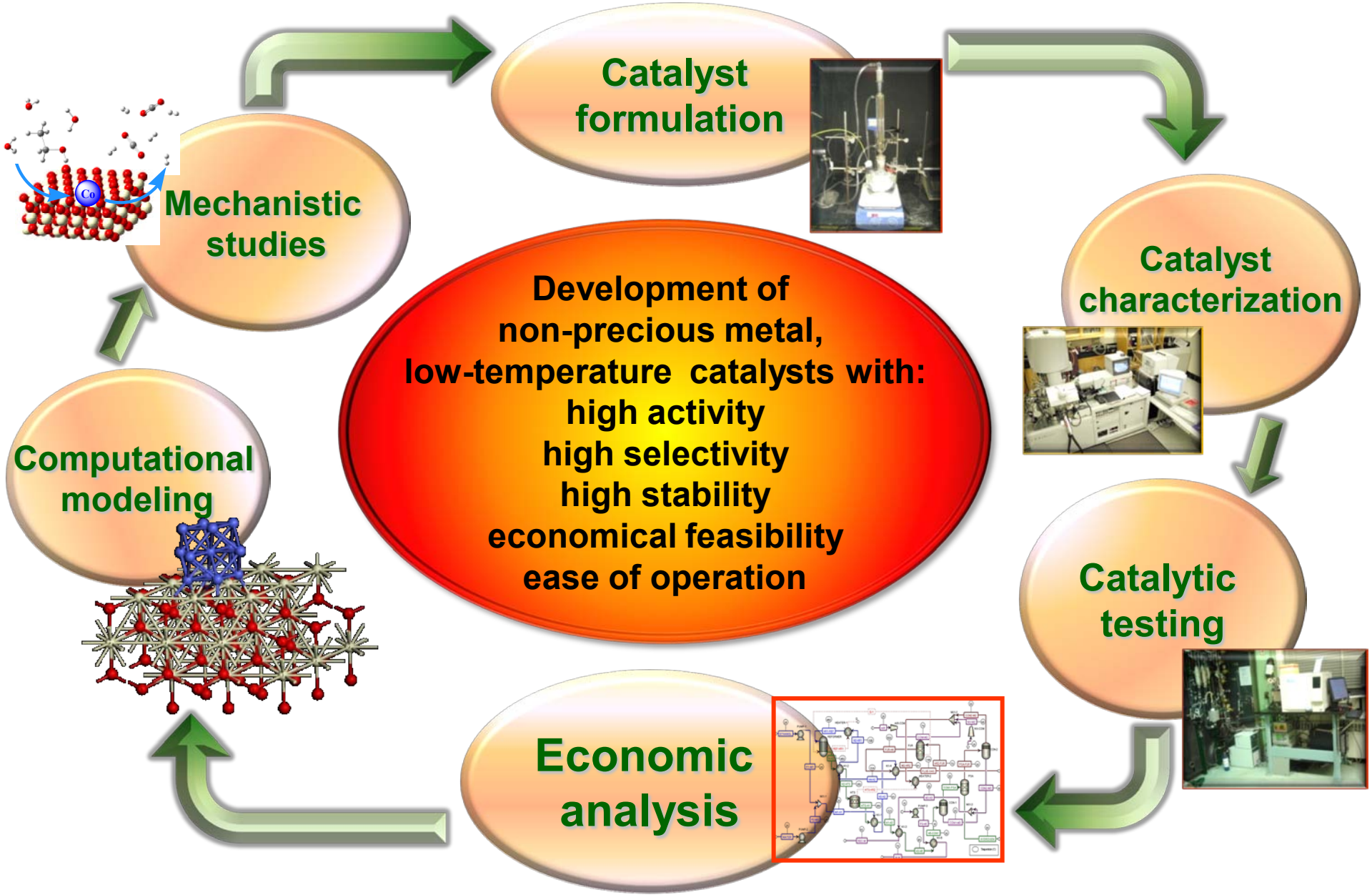
Approach

Milestones and Progress

	Tasks	Progress	% comp
1	Setting up the experimental systems, establishing protocols, training	Built, installed a reactor system and established experimental protocols; Completed a HAZOP review for the ethanol reforming reactor system; Went through a safety inspection conducted by a DOE Safety Panel.	100%
2	Economic analysis	Completed an initial economic analysis based upon a 1,500 kg/day of hydrogen process using H2A model.	95%
3	Catalyst synthesis and optimization	Prepared over 100 batches of catalysts; Investigated the effect of support, promoters, precursors, active metal loading, synthesis techniques and parameters on catalytic performance.	95%
4	In-situ, pre- and post-reaction characterization	Completed characterization studies using CO, N_2O and H_2 chemisorption, X-ray diffraction, temperature programmed reduction, oxidation, desorption, and thermogravimetric analysis, differential scanning calorimetry. 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; XANES and EXAFS studies using the Synchrotron Facilities at Argonne National Laboratories Advanced Photon Source.	90%
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; Examined the role of pre-treatment procedures. Initiated studies with dimethyl ether (DME) steam reforming.	90%
6	Information dissemination	Published 12 articles in refereed journals, five articles in conference proceedings, and gave 27 presentations, one key-note lecture and several invited lectures.	90%
7	Data analysis, reproducibility tests, literature awareness	Built a literature data base; Data analysis and reproducibility tests are performed in conjunction with the experiments.	90%

Technical Approach

An integrative approach - Iterative with feed-back



Technical Accomplishments and Progress

Understanding how to control the most important catalytic properties

Synthesis method
IWI, SG, CCT
solvothermal, hydrothermal

Support effect
ZrO_2, SiO_2, Al_2O_3
CeO_2

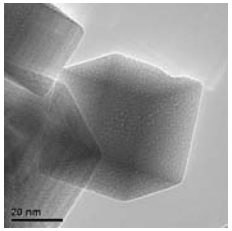
Formulation
Loading, dopants
promoters

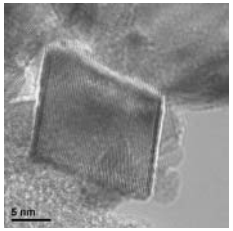
Precursor effect
$Co(NO_3)_2$, $CoCl_2$, $CoSO_4$, $CoCO_3$
$Co(AcAc)_2$, CoAc, $Co_2(CO)_8$ CoC_2O_4

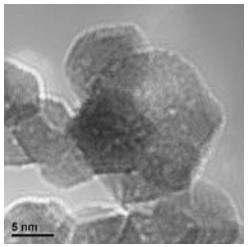
Impregnation medium
water, ethanol
ethylene glycol

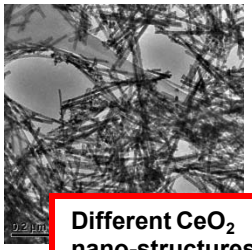
Support Morphology
3-D ordered macroporous
cubic, cuboid, belt
rod, plate, polyhedron

Pre-treatment/ activation parameters
calcination temp., calcination time
reduction temp., reduction time



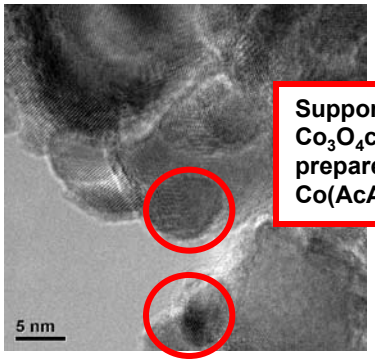






Different CeO_2 nano-structures

Metal Dispersion
Reducibility
Oxygen mobility
Surface acidity
Metal-Support Interaction
Support nano-structure



Supported Co_3O_4 crystalline size prepared by $Co(AcAc)_2$: 3-6 nm

Activity, Selectivity, Stability

Catalytic performance

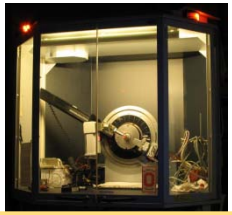
Results published in

- *Catalysis Letters*, **132**, 422-429 (2009).
- *J. Molecular Catalysis*, **318**, 21-29 (2010).
- *Applied Catalysis A* doi:10.1016/j.apcata.2010.04.01
- *Green Chemistry*, **9**, 686-694 (2007).
- *Journal of Physical Chemistry A*. **114**, 3796-3801 (2010).

Technical Accomplishments and Progress

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

N_2 Physisorption



X-Ray Diffraction

Laser Raman Spectroscopy

DRIFTS

Mass Spectrometry

Surface area
Pore volume
Pore size
Pore size distribution
Crystalline phase
Particle size
Molecular structure
Oxidation state
Coordination environment
Weight variation
Surface energetics
Adsorption/desorption
Reduction/oxidation characteristics
Morphology
Particle size
Elemental analysis
Surface intermediates

X-ray photoelectron Spectroscopy

Thermogravimetry Scanning calorimetry

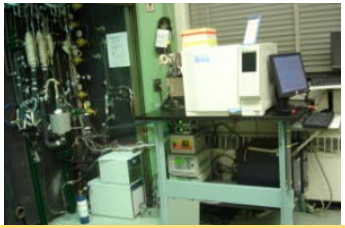
Adsorption desorption

Electron microscopy EDX

X-ray Absorption Spectroscopy

Technical Accomplishments and Progress

Understanding the Reaction Network



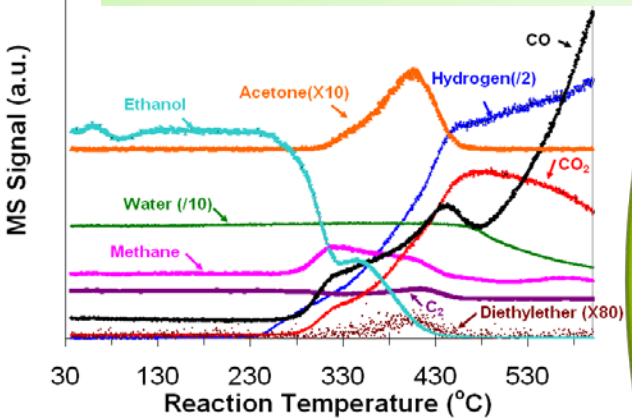
Steady-state reaction experiments

Transient response experiments

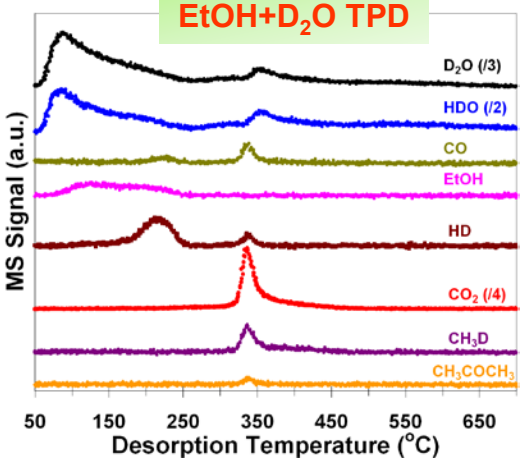
Isotopic labeling experiments

A complex network of reactions catalyzed by different sites

Ethanol steam reforming
Temperature programmed reaction



EtOH+D_2O TPD



$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$
$$CH_3CH_2OH \rightarrow CH_4 + CO + H_2$$
$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O$$
$$CH_3CHO \rightarrow CH_4 + CO$$
$$2CH_3CHO \rightarrow CH_3COCH_3 + CO + H_2$$
$$CH_3CHO + 3H_2O \rightarrow 2CO_2 + 5H_2$$
$$CH_3CH_2OH + H_2O \rightarrow 2CO + 4H_2$$
$$CH_3CH_2OH + 2H_2O \rightarrow 2CO_2 + 6H_2$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$CO_2 + H_2 \rightarrow CO + H_2O$$
$$C_2H_4 \rightarrow coke$$
$$CH_4 \rightarrow C + 2H_2$$
$$2CO \rightarrow CO_2 + C$$

Results published in
Song, H., Zhang, L., Ozkan, U.S., "Reaction Networks in Ethanol Steam Reforming over Supported Co Catalysts," *Industrial and Engineering Chemistry Research*, accepted

Technical Accomplishments and Progress

Identifying the surface species and elucidating the surface mechanisms

Molecular modeling

Isotopic labeling
Mass spectrometry

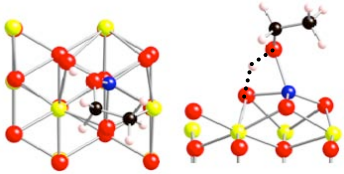
Temperature-programmed desorption

Calorimetry

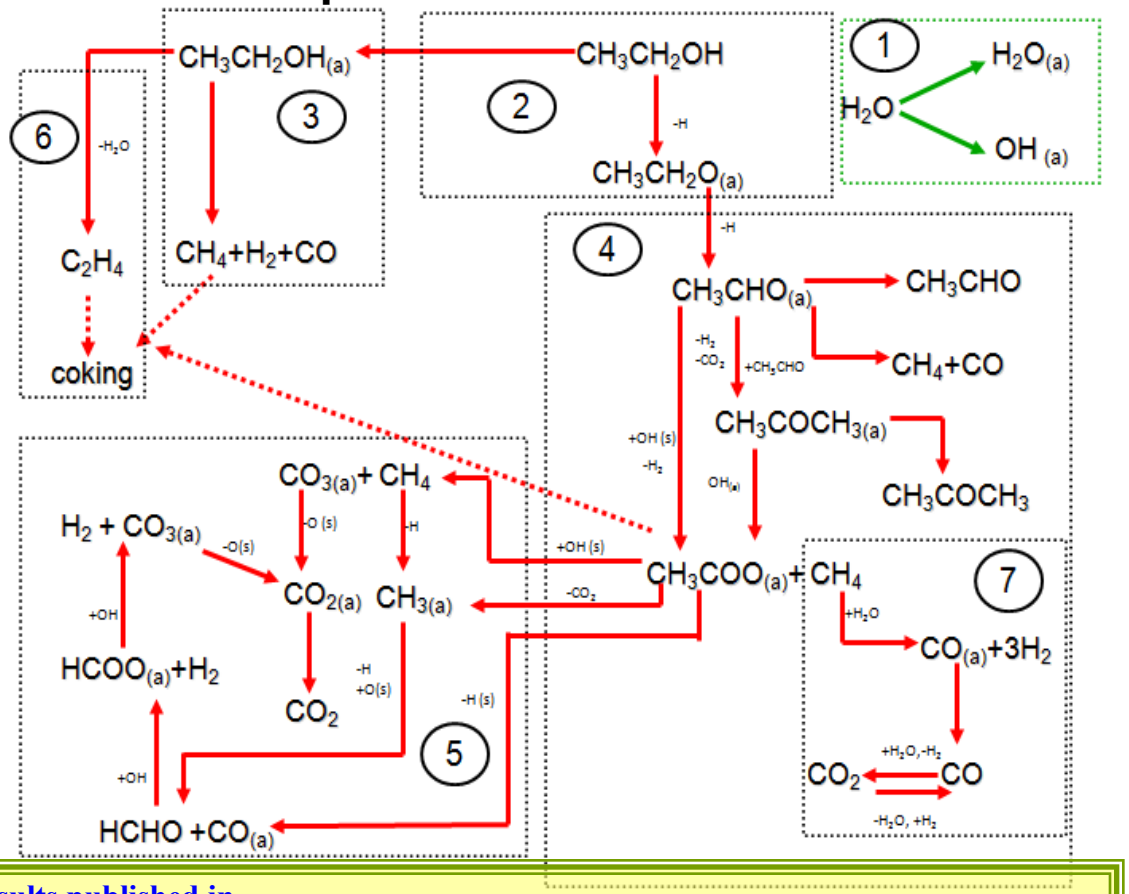
Thermogravimetry

In-situ vibrational spectroscopy

Multiple pathways that directly impact the yield, selectivity and stability



Proposed mechanism



Results published in

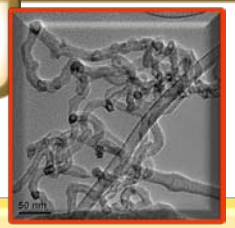
- Song, H. Zhang, L. Watson, R.B., Braden, D., Ozkan, U.S., "Investigation of Bio-ethanol Steam Reforming over Cobalt-based Catalysts," *Catalysis Today*, **129**, 346-354 (2007).
- Song, H. and Ozkan, U.S., "Adsorption/desorption Behavior Ethanol Steam Reforming Reactants and Intermediates over Supported Cobalt Catalysts," *J Phys. Chem*. Accepted

Technical Accomplishments and Progress

Understanding the major deactivation mechanisms

Primary modes of deactivation

Coking



Sintering

Factors that lead to coking

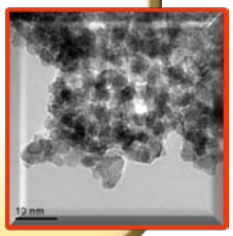
- High surface acidity
- Low oxygen mobility
- Low metal-support interface

Factors that lead to sintering

- Low dispersion
- Low oxygen mobility
- High operating temperatures
- Need for pre-reduction with H_2

Findings from this project that allow us to prevent deactivation

- Increasing oxygen mobility by creating anion vacancies in the support
- Neutralizing acidic sites
- Improving dispersion by using organic ligands in the synthesis
- Improving activity to reduce the operating temperature
- Eliminating the need for pre-reduction with H_2



Results published in

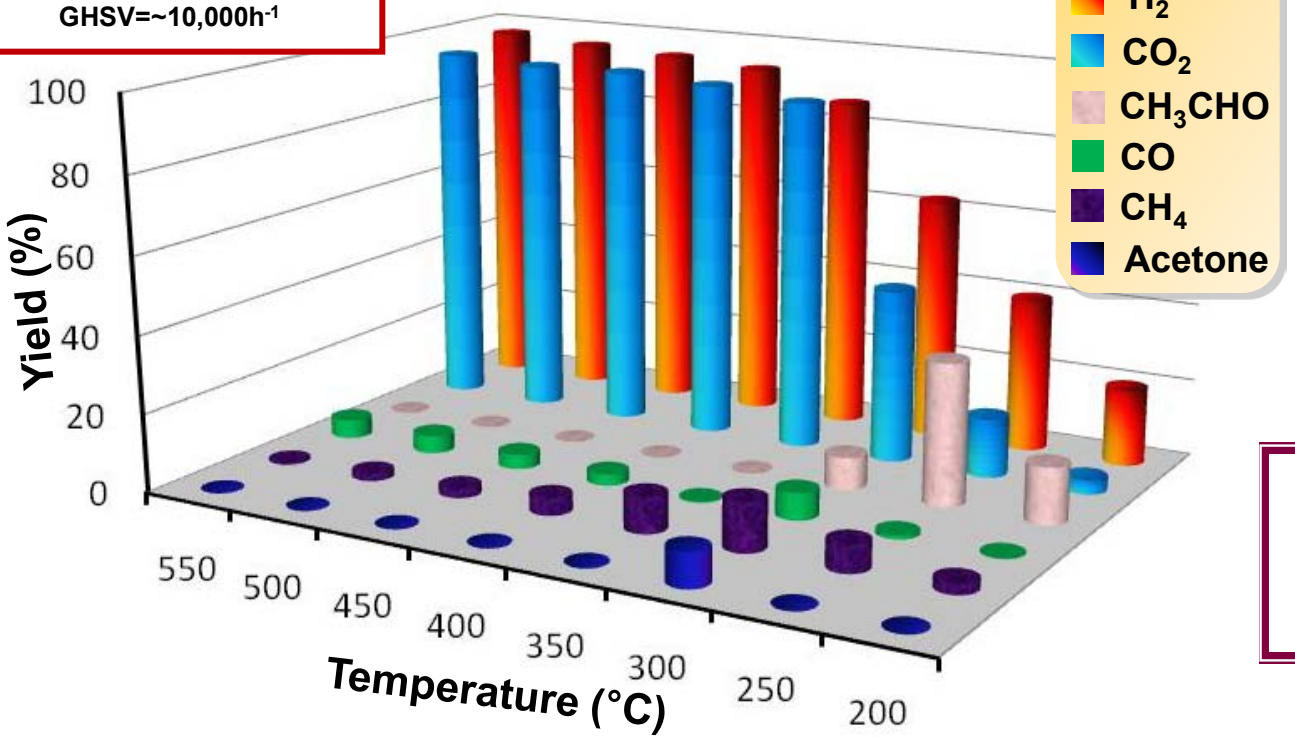
Song, H., Ozkan, U.S., "Ethanol Steam Reforming over Co-based Catalysts: Role of Oxygen Mobility ," *J. Catalysis*, **261** 66-74 (2009).

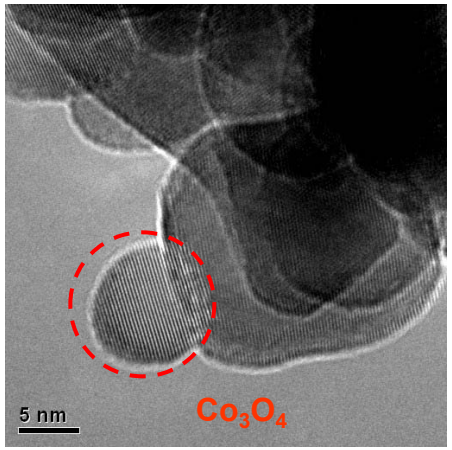
Song, H. Ozkan, U.S., :Changing the Oxygen Mobility in Co/Ceria Catalysts by Ca Incorporation: Implications for Ethanol Steam Reforming," Invited paper. *Journal of Physical Chemistry A*. **114**, 3796-3801 (2010).

Technical Accomplishments and Progress

A catalyst formulation with high activity, selectivity and stability

EtOH:H_2O=1:10 (molar ratio);
C_{EtOH}=7.5vol.%;
WHSV=~1.08gEtOH/gCat/h;
GHSV=~10,000h^{-1}





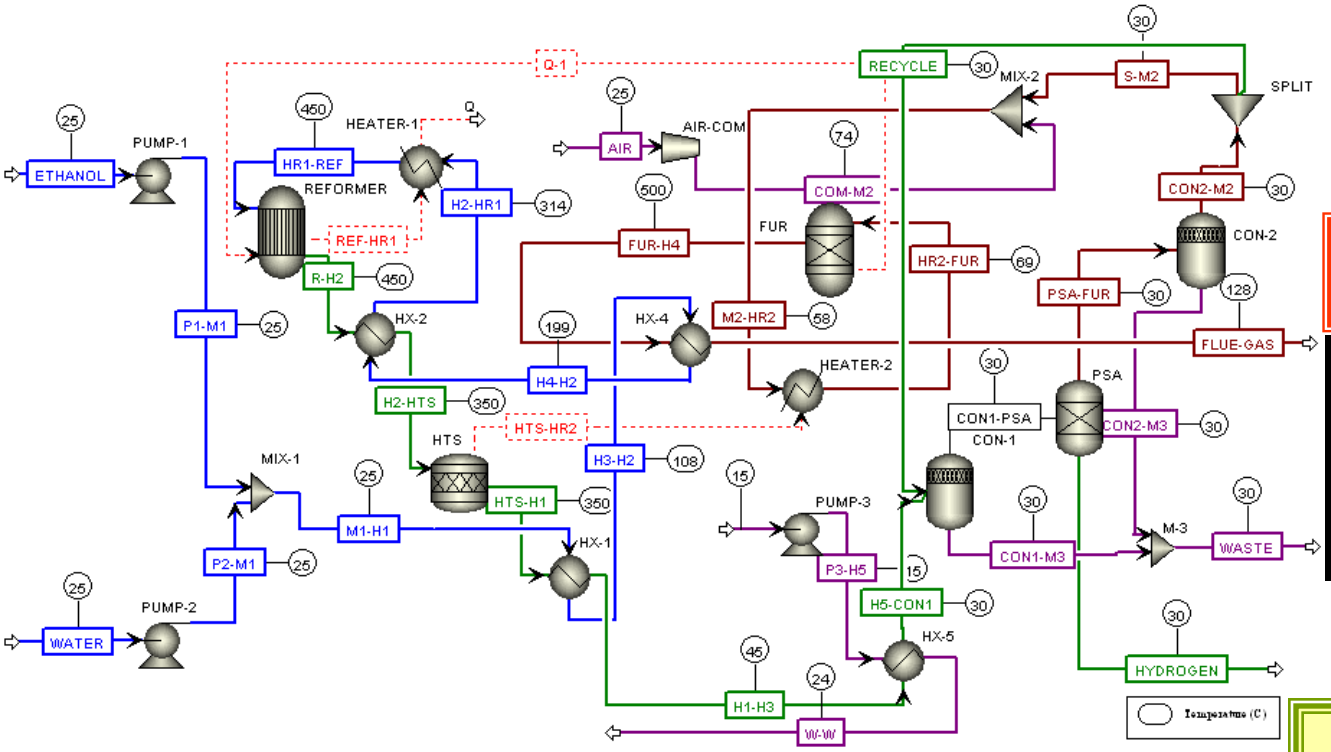
Co/CeO_2 catalyst prepared by a reverse microemulsion technique

- Over 95% H_2 yield
- No liquid by-products above 300°C
- Stable activity in accelerated aging study

Results published in
Song, H., Tan, B. and Ozkan, U.S., "Novel Synthesis Techniques for Preparation of Co/CeO2 as Ethanol Steam Reforming Catalyts," *Catalysis Letters*, **132**, 422-429 (2009)

Technical Accomplishments and Progress

Economic analysis



Forecourt Production Scale - (1,500 kg H_2/day)

Production Cost $/kg	Total Cost (Production/ Storage/Disp.) $/kg
2.75	4.63

- **Economic analysis based on Aspen Plus and DOE-H2A model.**
- **Agreement with Directed Technologies independent analysis.**
- **Based on conservative estimates for catalyst life-time and GHSV.**

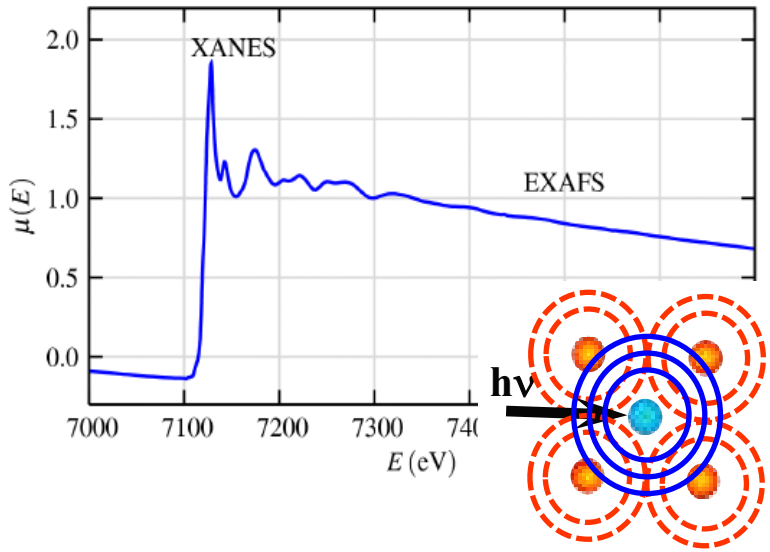
Results published in

Song, H. and Ozkan, U.S., "Economic Analysis of Hydrogen Production through a Bio-ethanol Steam Reforming Process: Sensitivity Analyses and Cost Estimations," *International Journal of Hydrogen Energy*, ***35***, 127-134 (2010).

Technical Accomplishments and Progress

Understanding the effect of catalyst pre-treatment

Recent Progress



New capability

New collaboration

New insight

XAFS spectroscopy was utilized to provide insight on the oxidation state and the local coordination environment of Co during ethanol steam reforming with Co/CeO_2

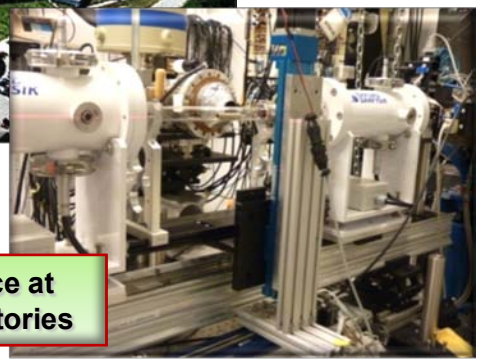
X-ray absorption spectroscopy capability was recently added

XAFS (X-ray Absorption Fine Structure) spectroscopy provides information on the local atomic structure of a selected element, including:

- formal oxidation state
- coordination
- bond distances
- nature of immediate neighbors

Advanced Photon Source (APS) at the Argonne National Laboratories was utilized

The APS is a third generation synchrotron facility with the nation's most brilliant X-ray beams



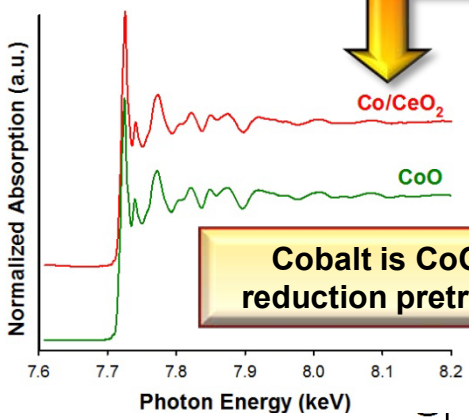
Advanced Photon Source at Argonne National Laboratories

Technical Accomplishments and Progress

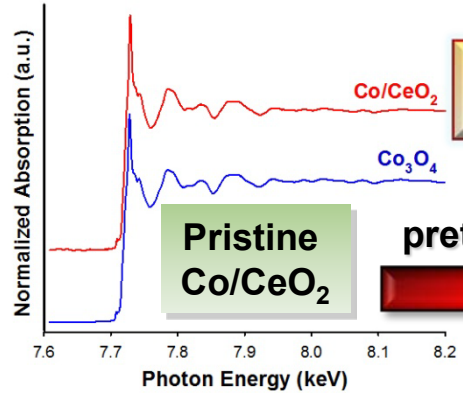
Understanding the effect of catalyst pre-treatment

Recent Progress

Reduction pretreatment with H_2



Cobalt is CoO after reduction pretreatment



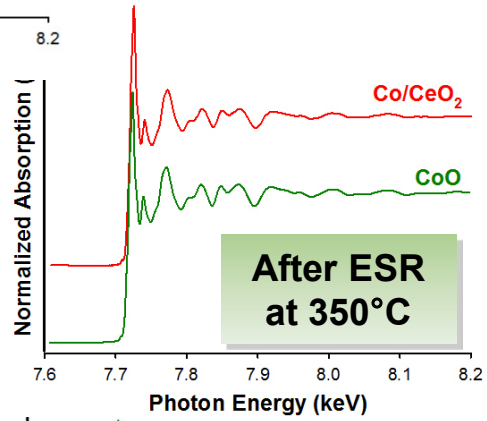
Co_3O_4 over pristine catalyst

Pristine Co/CeO_2

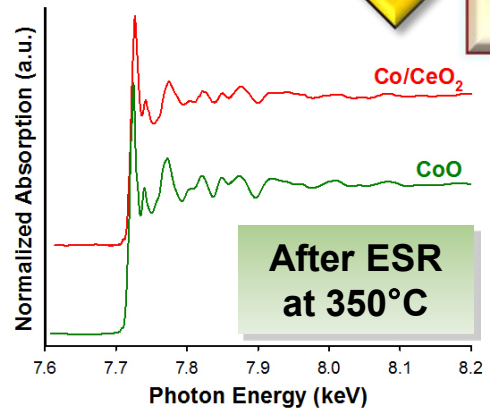
No pretreatment

Co_3O_4 is reduced to CoO during reaction at 350°C

Reaction after reduction pretreatment

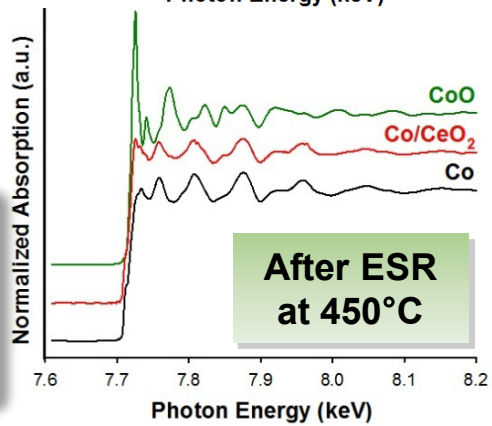


After ESR at 350°C

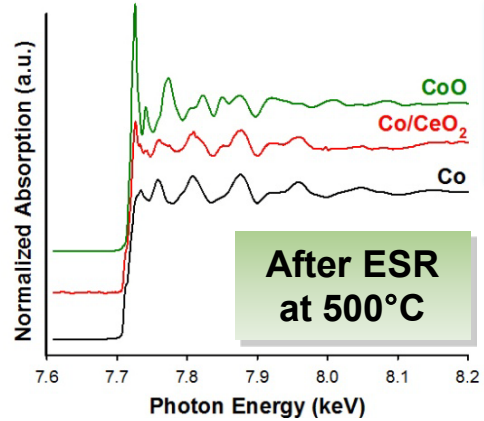


After ESR at 350°C

CoO is further reduced to metallic Co during reaction



After ESR at 450°C



After ESR at 500°C

CoO is further reduced to metallic Co during reaction

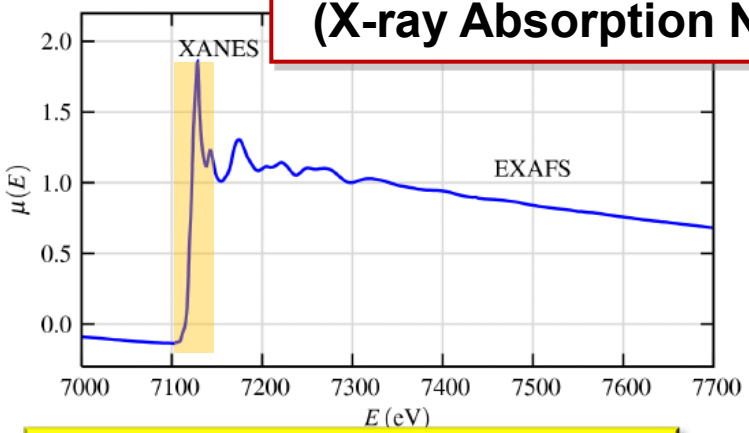
Co reduction takes place under reaction conditions

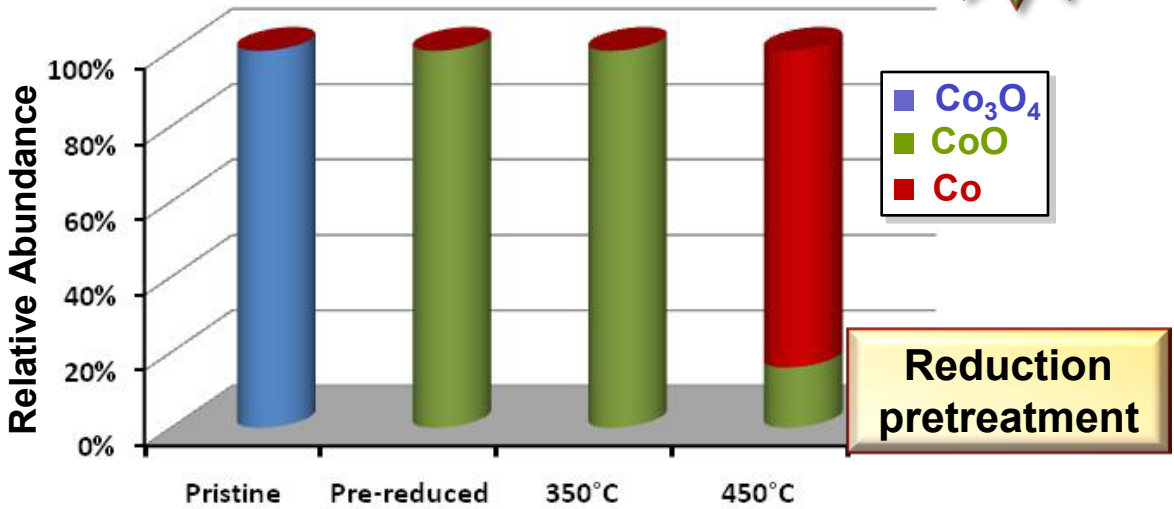
Technical Accomplishments and Progress

Understanding the effect of catalyst pre-treatment

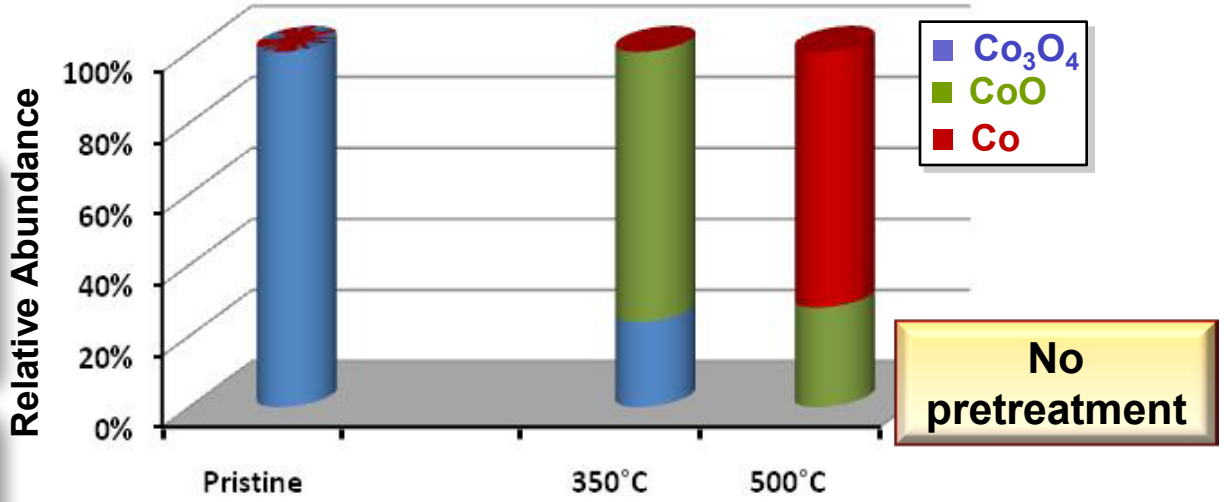
Recent Progress

XANES Spectroscopy (X-ray Absorption Near Edge)





- Catalyst reduction takes place under reaction conditions
- Both samples converged to the same oxidation state for cobalt regardless of pretreatment
- XPS over post ESR samples further supported the conclusion



Reduction pretreatment is not necessary for catalytic activity

Ease of Operation

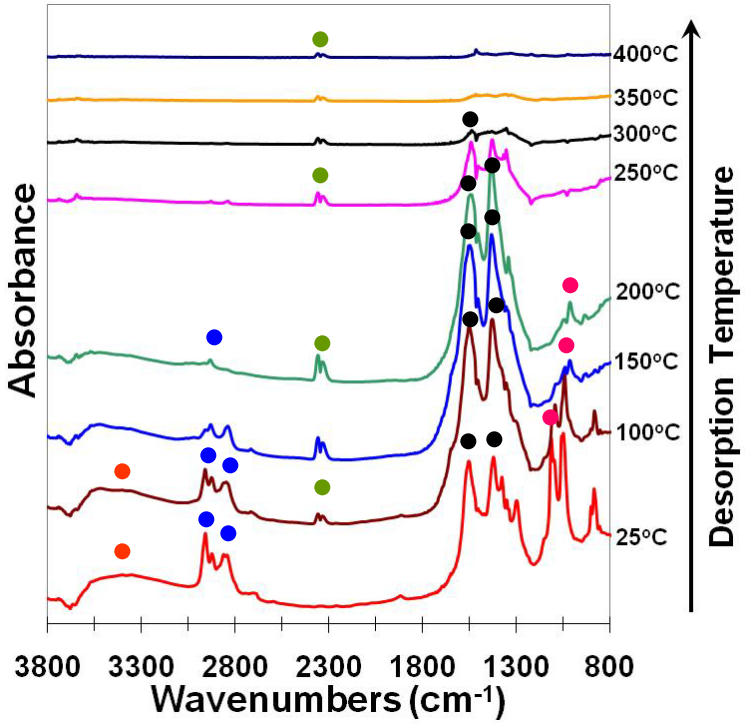
Technical Accomplishments and Progress

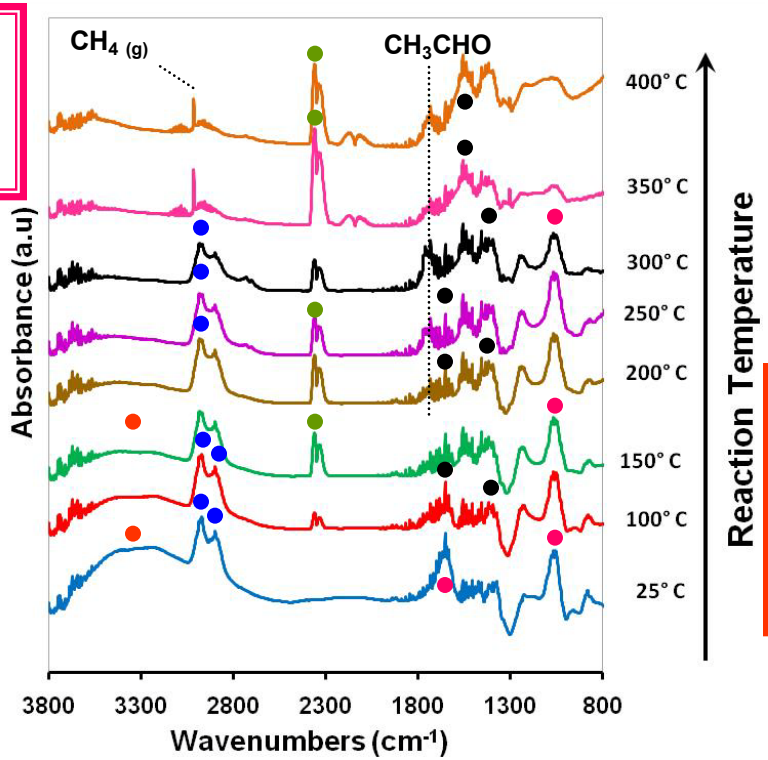
Vibrational spectroscopy under actual reaction conditions (operando)

Recent Progress

DRIFTS during Temperature-programmed desorption

- Thermal transformation of adsorbed species
- Provides limited information on the surface species during ethanol steam reforming



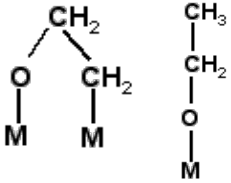


Acetaldehyde formation and decomposition to CH_4 and CO_2 can be directly observed.

DRIFTS during ESR Reaction

- Spectra collected while reaction is progressing
- Provides information on the surface species and mechanistic steps under true reaction conditions

- **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

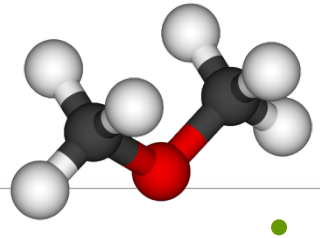


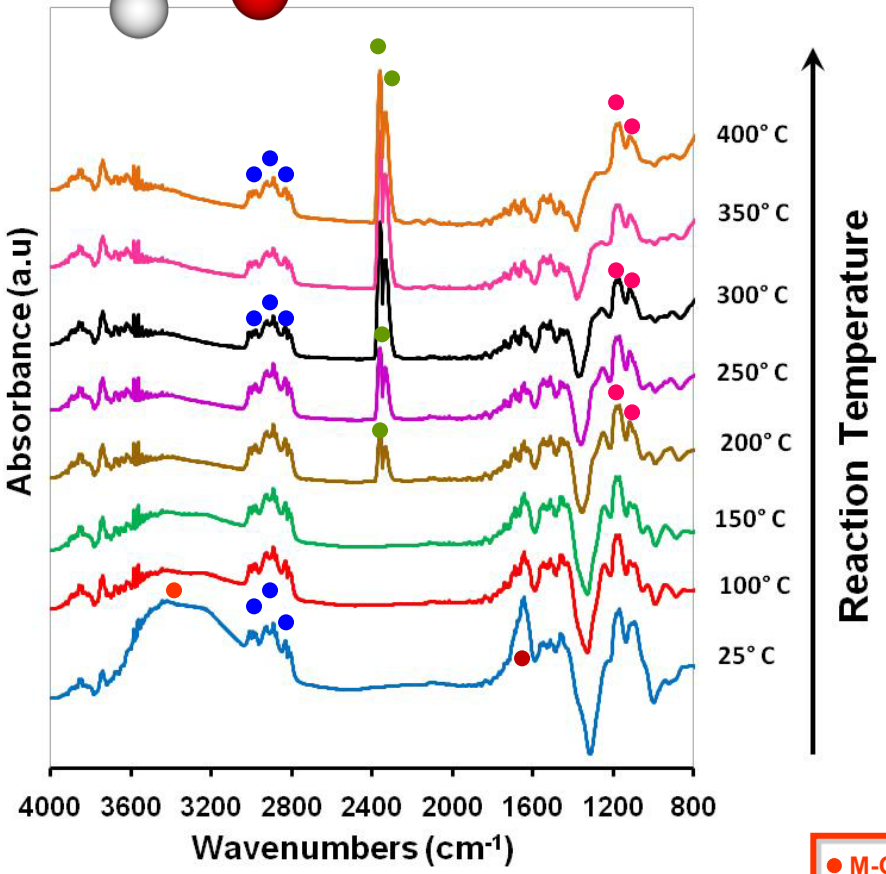
- **Acetates**
  CH_3COO
  1569, 1429, 1348cm^{-1}
- **CO_2**
  2361, 2336cm^{-1}: O=C=O stretching
- **Molecularly adsorbed H_2O**
  1654cm^{-1}

Technical Accomplishments and Progress

Dimethyl ether steam reforming over Co-based catalysts

Recent Progress



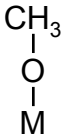


- Multi-source clean fuel which can be produced from a wide spectrum of feeds including lignocellulosic biomass
- Inert, non-carcinogenic, nonmutagenic, non-corrosive, and virtually non-toxic
- Hydrogen content is equal to that of ethanol

In-situ DRIFTS data show that Co/CeO_2 catalysts can be used in steam reforming of DME

Formation of various adsorption and oxidation products observed on the surface

- **M-OH**
  3650~3150cm^{-1}, O-H stretching
- **CH_3-**
  2962, 2927, 2865 cm^{-1}:C-H stretching
  1385cm^{-1}: CH_3- bending
- Surface Carbonates and methoxy region
  1176, 1166, 1101, 1079cm^{-1} v(OC)



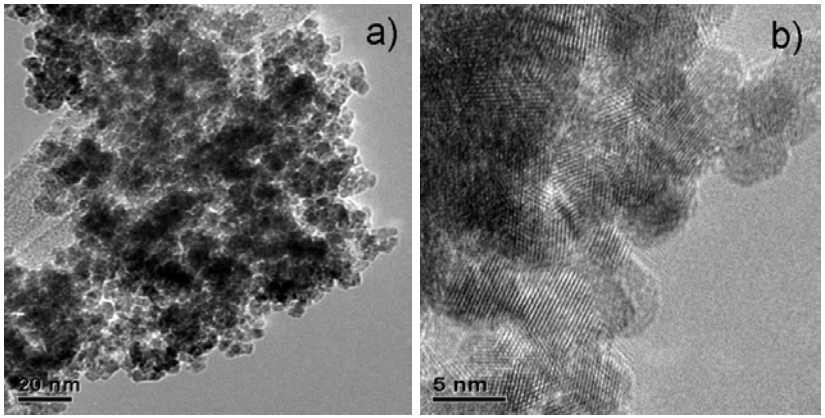
- **CO_2**
  2361, 2336cm^{-1}: O=C=O stretching
- **Molecularly adsorbed H_2O**
  1654cm^{-1}

Technical Accomplishments and Progress

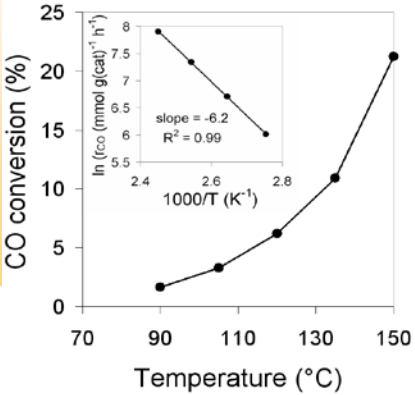
Active and selective catalysts for PROX

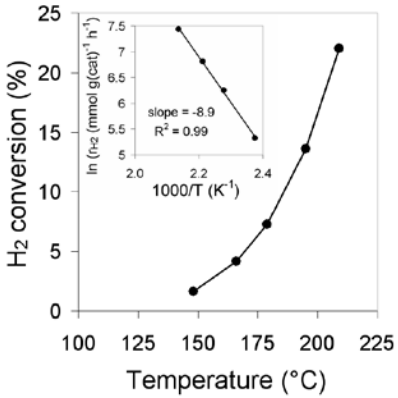
Recent Progress

- Co/CeO_2 nanoparticles were found to have high activity as Preferential Oxidation (PROX) catalysts for removing CO from H_2 streams.
- In the 150-180°C, high CO conversion (~100%) and high O_2 selectivity to CO_2 (>90%).
- Examined the effect of O_2 concentration, H_2 concentration, space velocity, temperature on conversion and selectivity
- Examined possible side reactions (WGS, r-WGS, methanation)
- Examined time-on-stream activity
- Measured activation energies for CO oxidation and H_2 oxidation



Nano-particles of CeO_2





Results published in

Woods, M. P. Gawade, P., Tan, B. Ozkan, U.S., "Preferential Oxidation of Carbon Monoxide on Co/CeO_2 Nano-particles," *Applied Catalysis B*: in press. doi:10.1016/j.apcatb.2010.03.015

Collaborations

- A new collaboration with Argonne National Lab (Dr. Jeffrey Miller and Dr. Christopher Marshall) has been initiated to incorporate XAFS studies in the project. Three consecutive proposals for "In-situ XAFS Characterization of cobalt-based catalysts for steam reforming of bio-derived liquids" have been submitted to Argonne National Laboratory to request beam time at the synchrotron facilities and they all have been accepted. Seven members of the P.I.'s team have registered as facility users at Advanced Photon Source of Argonne National Laboratory. Dr. Miller has been working closely with the team members in in-situ experimentation and data analysis.

- 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 presented at the ACS National Meeting in August 2009. A refereed journal article written jointly has been accepted for publication in *Journal of Physical Chemistry*. A second collaborative article is in preparation. A post-doctoral researcher and a graduate student are being jointly advised by the P.I. and Dr. Hadad.

- Collaboration with Nextech Materials, Inc. for scale-up of the catalyst manufacturing process is in place. A joint proposal (OSU and NexTech) to NSF has been accepted.

- Collaboration with PNNL. Sharing findings

- Directed Technologies, Inc. Economic analysis and feasibility considerations

Summary

Relevance:

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

Approach:

An integrative approach that combines catalyst synthesis, characterization, kinetic studies and molecular simulation 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, high selectivities and high stability at low temperatures

Collaborations:

New partnership with Argonne National Lab for XAFS studies

Active partnership with Chemistry Department on molecular simulation

Partnership with NexTech for catalyst manufacturing

Partnership with PNNL and Directed Technologies, Inc. for sharing findings

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 continued in conjunction 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 continued.
- Accelerated deactivation and regeneration studies (e.g., higher C/S ratio and GHSV) will be continued.
- Economic analysis will be fine-tuned based on process modification with no pre-reduction.
- 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. Accelerated deactivation studies will be coupled with in-situ XAFS studies. This will be a collaborative activity.
- Catalyst synthesis for best performing catalysts will be scaled-up through industrial partnership. This is a collaborative activity.
- Several more publications are in preparation and will be submitted within the next 6 months.