

Investigation of Bio-ethanol Steam Reforming over cobalt based catalysts

Umit S. Ozkan (P.I.)
Hua Song, Lingzhi Zhang

Heterogeneous Catalysis Research Group

The Ohio State University

May 16, 2006



Project ID#: DE-FC36-05GO15033

PDP-7

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- ❖ Start Date - May 1, 2005
- ❖ End Date - April 31, 2009
- ❖ 20% 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 (to date)
 - \$120,000 (DOE)
 - \$149,314 (OSU cost share)
- Additional funding needed for FY06
 - \$194,619 (DOE)
 - \$58,909 (OSU)

Barriers

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

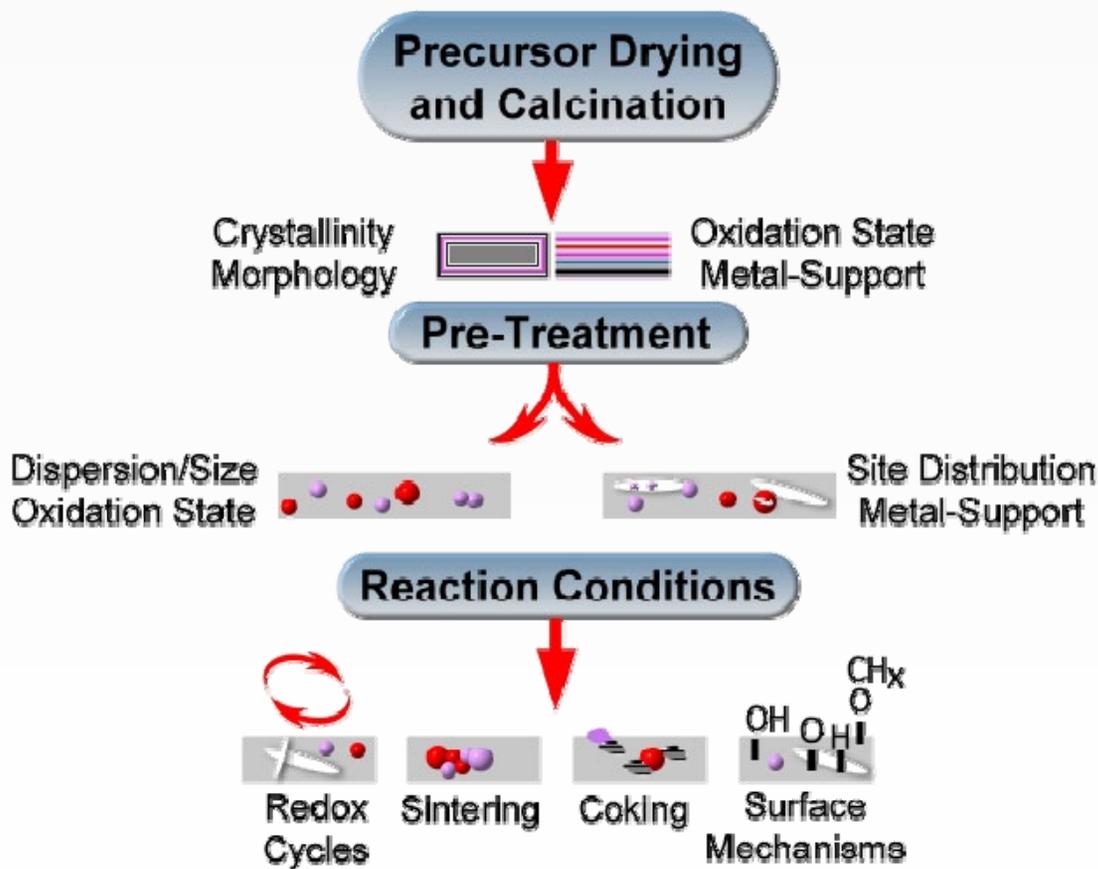
Partners

- ❖ NexTech Materials, Ltd. - Catalyst manufacturing scale-up
- ❖ RTI - economic analysis and feasibility considerations

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 ° C)**
 - ❖ **High selectivity and yield of hydrogen**
 - ❖ **High EtOH conversion**
 - ❖ **Minimal byproducts such as acetaldehyde, methane, ethylene, and acetone**
 - ❖ **Understanding of the catalyst deactivation and regeneration**
 - ❖ **Low cost for commercialization.**

Approach



Supported Co-catalysts

❖ Preparation

- IWI, SG
- Precursor
- Precursor solution
- Promoter
- Support
- Cobalt loading

❖ Calcination

- Temperature

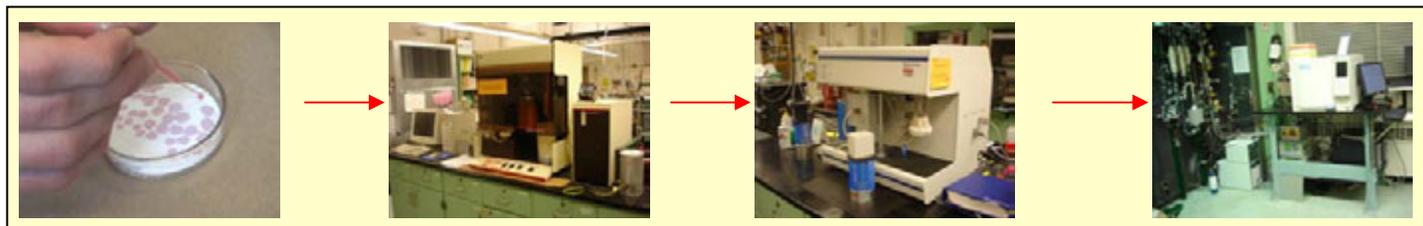
❖ Reduction

- Temperature
- Time

❖ Reaction

- GHSV
- EtOH:Water ratio
- Temperature
- Oxygen addition
- Deactivation

❖ Deactivation/Regeneration



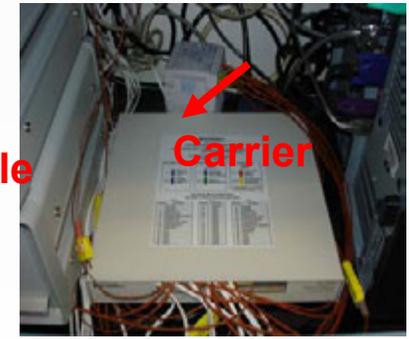
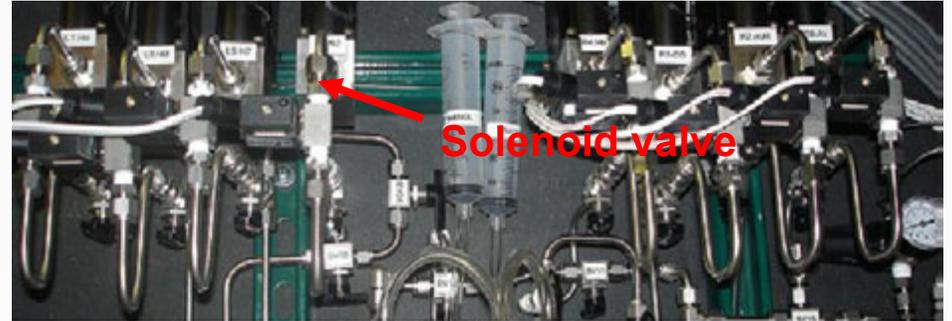
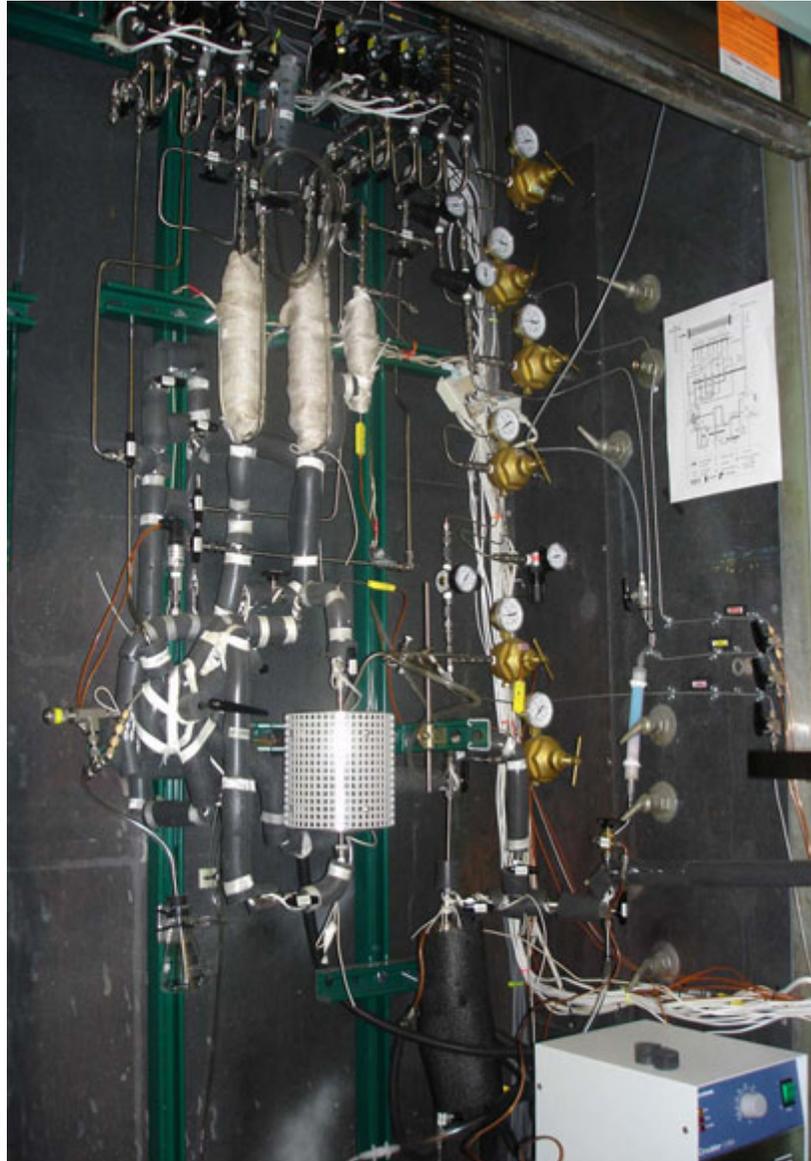
Technical Accomplishments/Progress/Results from Year 1

Catalysts Synthesis: Role of the supports, precursors and synthesis techniques

Catalyst	Precursor	Support/Preparation	
10%Co/ZrO₂	Co(NO₃)₂ • 6H₂O	ZrO₂ (Commercial)	IWI
1%Ru -10%Co/ZrO ₂	Co(NO ₃) ₂ • 6H ₂ O RuCl ₃	ZrO ₂ (Commercial)	
1%Re -10%Co/ZrO ₂	Co(NO ₃) ₂ • 6H ₂ O ReCl ₃	ZrO ₂ (Commercial)	
1%Rh -10%Co/ZrO ₂	Co(NO ₃) ₂ • 6H ₂ O RhCl ₃	ZrO ₂ (Commercial)	
10%Co/ZrO ₂	CoCl ₂	ZrO ₂ (Commercial)	
10% Co/ZnO(1)	Co(NO ₃) ₂ • 6H ₂ O	Nano-powder ZnO	
10% Co/ZnO(2)	Co(NO ₃) ₂ • 6H ₂ O	100+ Mesh ZnO	
10% Co/ZnO(3)	Co(NO ₃) ₂ • 6H ₂ O	decomposition of Zn(NO ₃) ₂ • 6H ₂ O at 500°C	
10% Co/ZnO(4)	Co(NO ₃) ₂ • 6H ₂ O	decomposition of 3ZnO • 2ZnCO ₃ • 3H ₂ O at 500°C	
10% Co/SiO ₂	Co(NO ₃) ₂ • 6H ₂ O	Fumed SiO ₂	
10% Co/MgO	Co(NO ₃) ₂ • 6H ₂ O	MgO (commercial)	
10% Co/V ₂ O ₅	Co(NO ₃) ₂ • 6H ₂ O	V ₂ O ₅ (commercial)	
10% Co/CeO ₂	Co(NO ₃) ₂ • 6H ₂ O	CeO ₂ (commercial)	
10% Co/Y ₂ O ₃	Co(NO ₃) ₂ • 6H ₂ O	Y ₂ O ₃ (commercial)	
10% Co/ Al ₂ O ₃	Co(NO ₃) ₂ • 6H ₂ O	Al ₂ O ₃ (commercial)	
10% Co/ TiO ₂	Co(NO ₃) ₂ • 6H ₂ O	TiO ₂ (commercial)	
10% Co/ La ₂ O ₃	Co(NO ₃) ₂ • 6H ₂ O	La ₂ O ₃ (commercial)	
10% Co/ Sm ₂ O ₃	Co(NO ₃) ₂ • 6H ₂ O	Sm ₂ O ₃ (commercial)	
10% Co/5ZrO ₂ • ZnO	Co(NO ₃) ₂ • 6H ₂ O	Co-Impregnating Zn(NO ₃) ₂ • 6H ₂ O into ZrO ₂ along with Co(NO ₃) ₂ • 6H ₂ O	
10% Co/10ZrO ₂ • ZnO	Co(NO ₃) ₂ • 6H ₂ O		
10% Co/15ZrO ₂ • ZnO	Co(NO ₃) ₂ • 6H ₂ O		
10%Co/ZrO ₂	Co(NO ₃) ₂ • 6H ₂ O	Zr propoxide	Sol-Gel

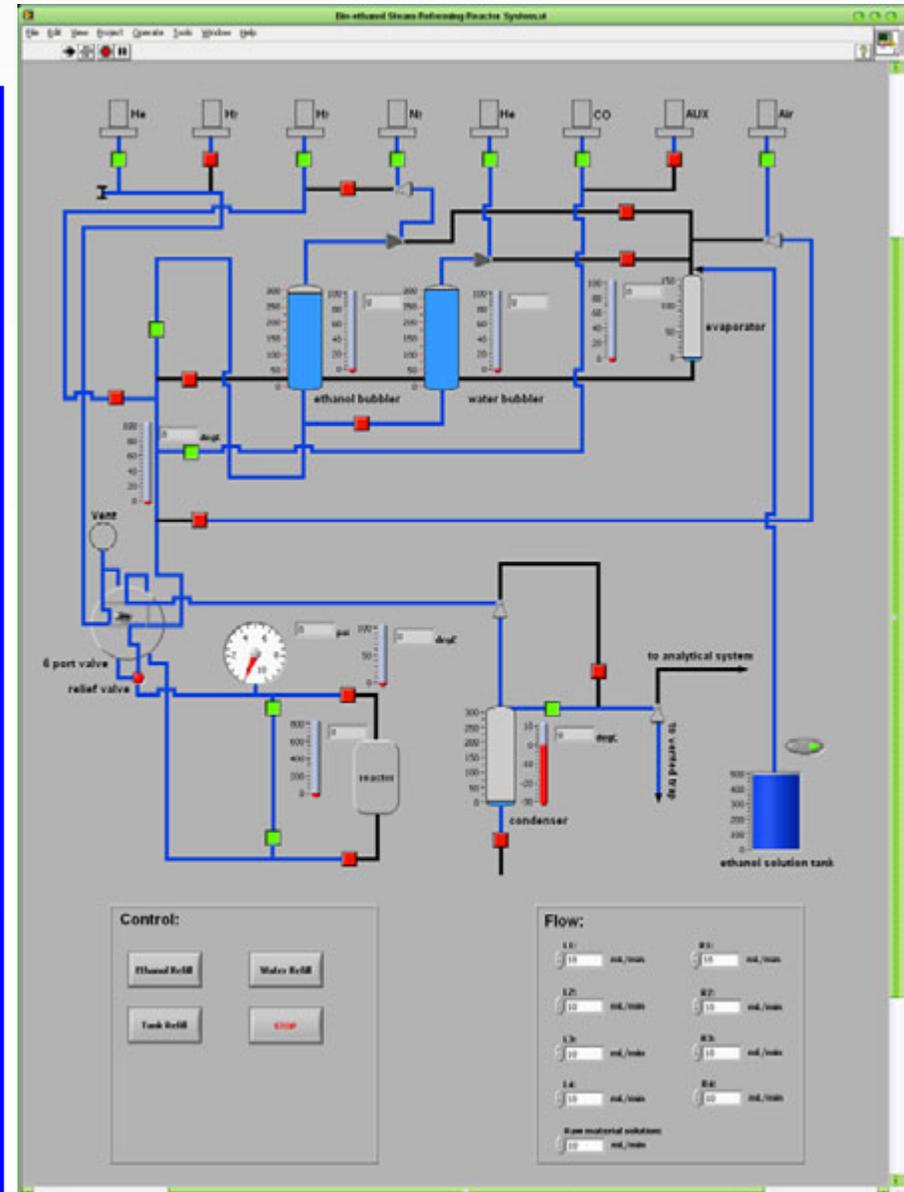
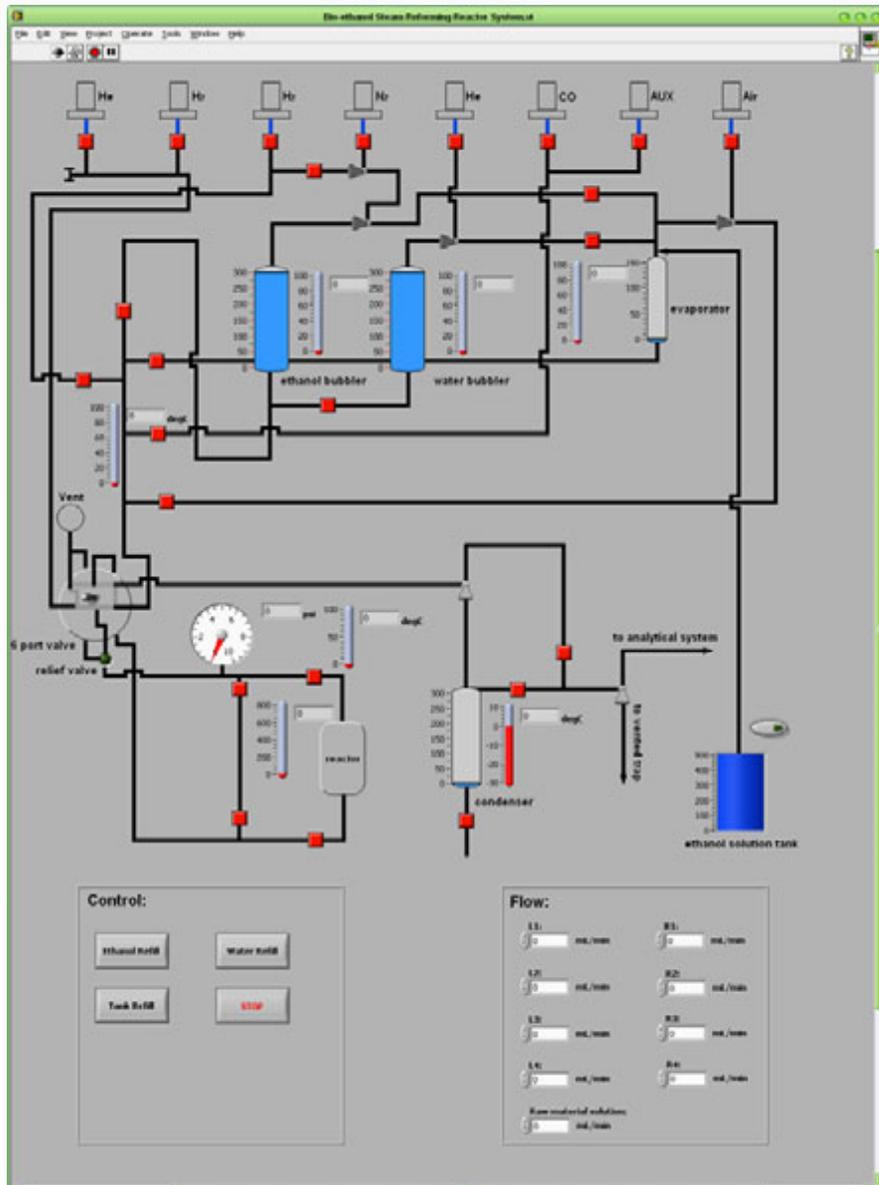
Initial focus of the characterization and activity study

Reactor System: Designed and built



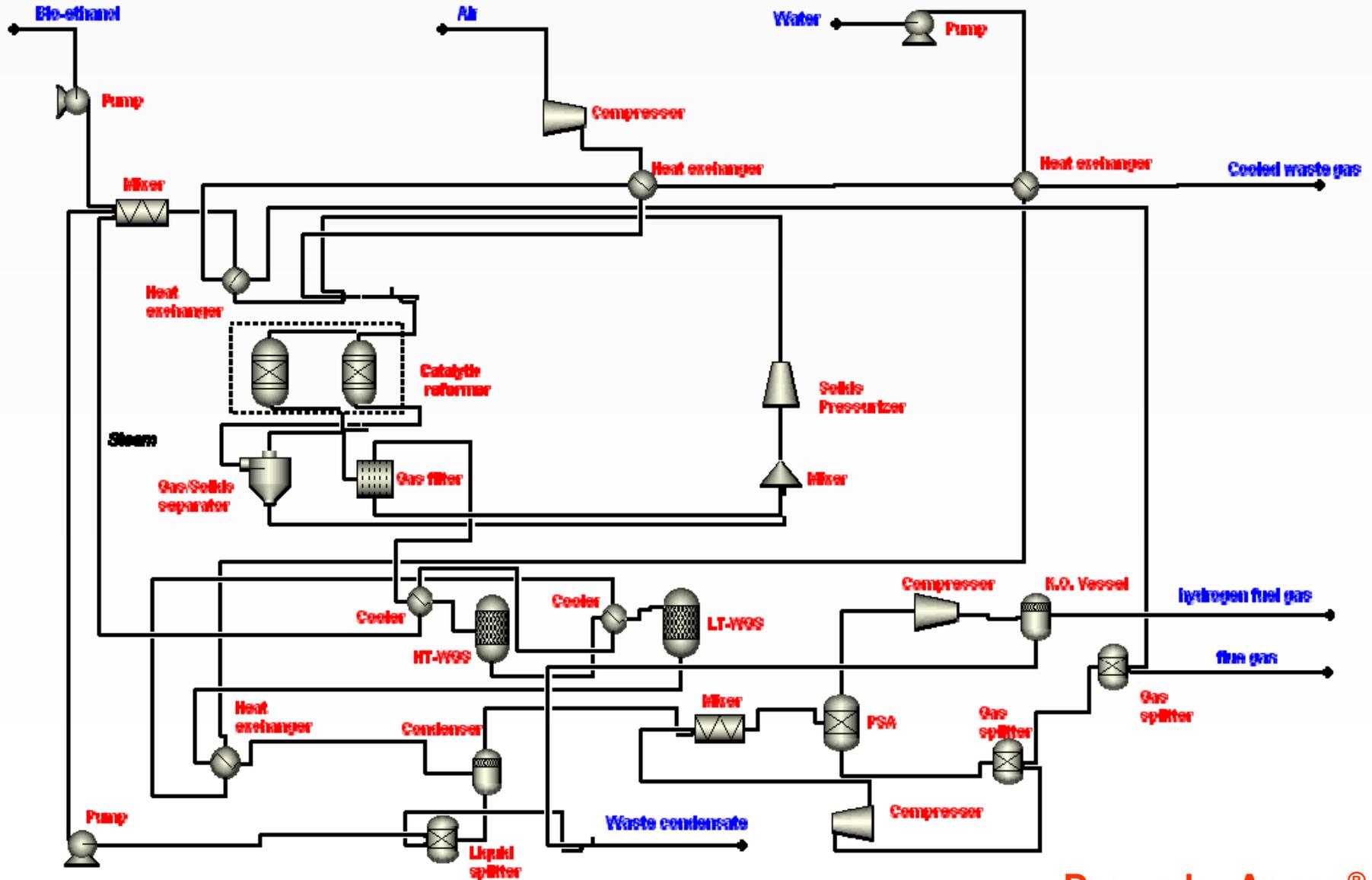
Technical Accomplishments/Progress/Results from Year 1

System automation and User Interface using labVIEW



Technical Accomplishments/Progress/Results from Year 1

Preliminary Flow Chart for Economic Analysis



Drawn by Aspen®

Technical Accomplishments/Progress/Results from Year 1

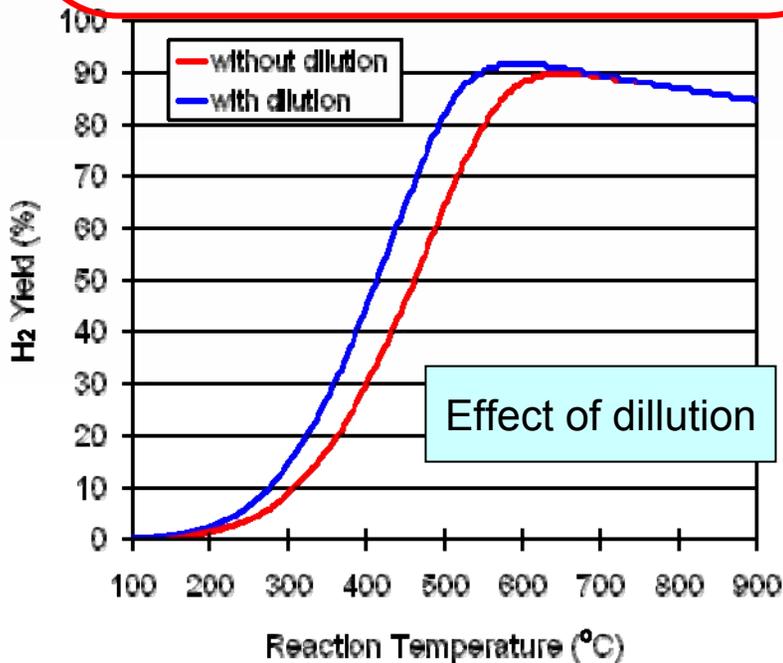
Thermodynamic Analysis

Definitions

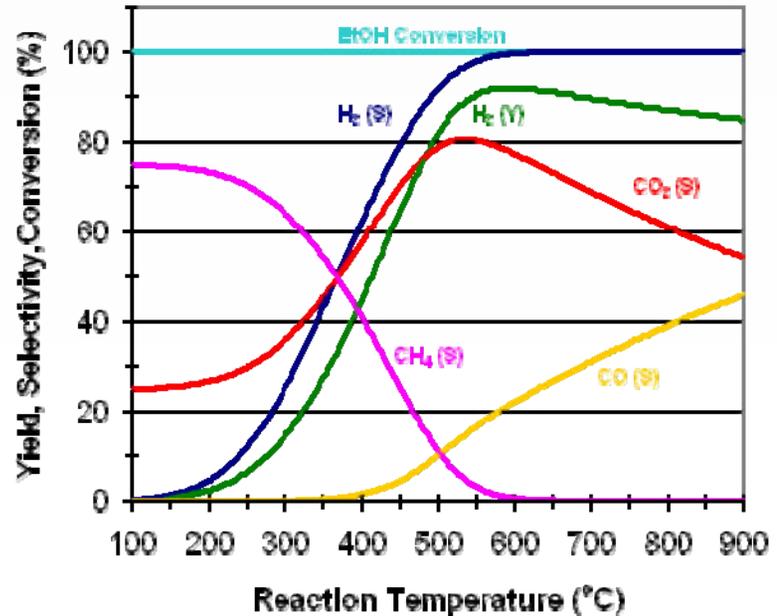
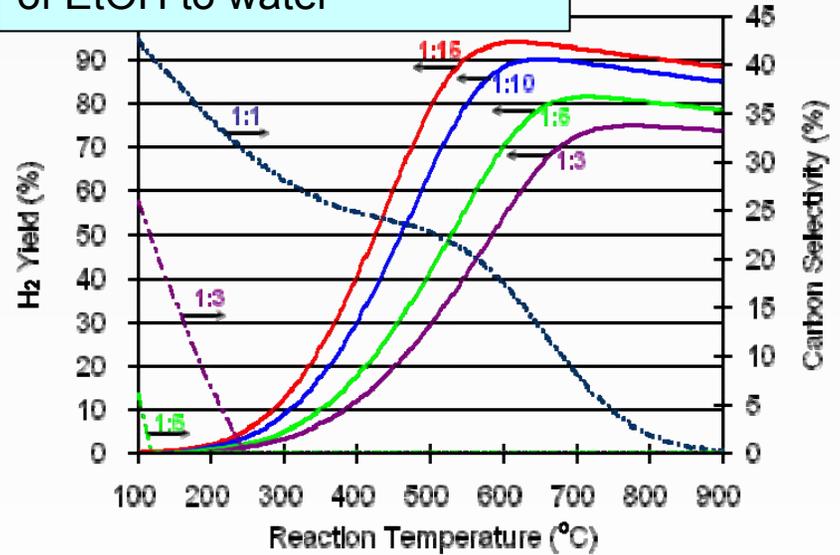
$$\text{H}_2 \text{ Yield \%} = \frac{\text{mol of H}_2 \text{ produced}}{\text{mol of EtOH fed} \times 6} \times 100$$

$$\text{Selectivity \%} = \frac{\text{mol of certain product}}{\text{mol of total products}} \times 100$$

$$\text{Conversion \%} = \frac{\text{mol of EtOH converted}}{\text{mol of EtOH fed}} \times 100$$



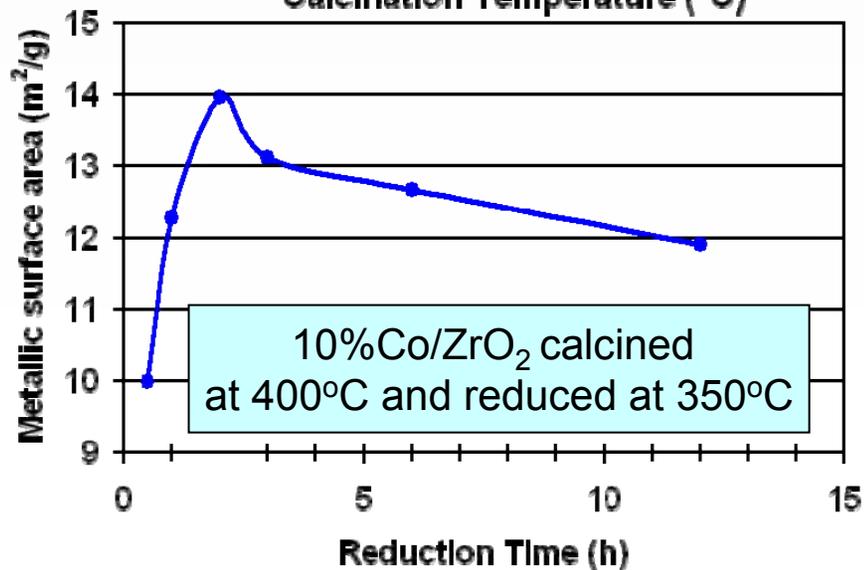
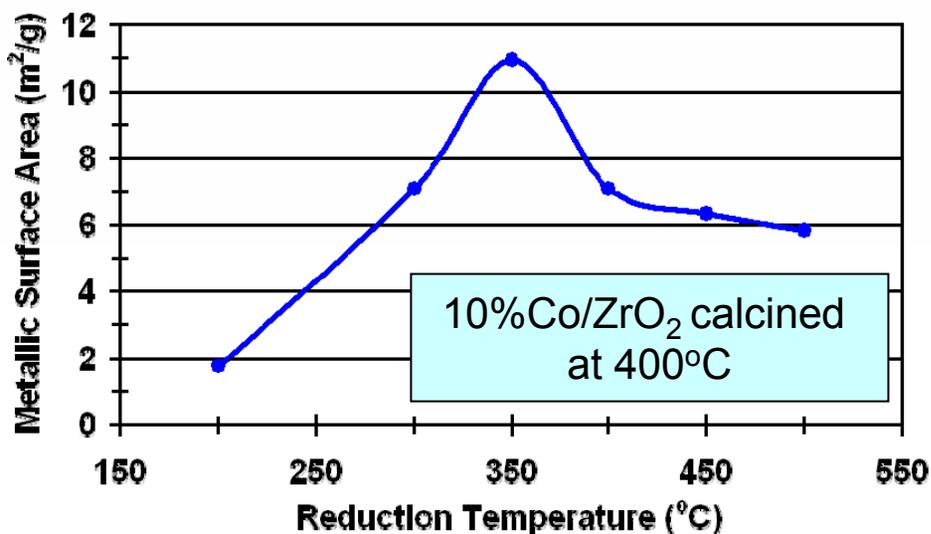
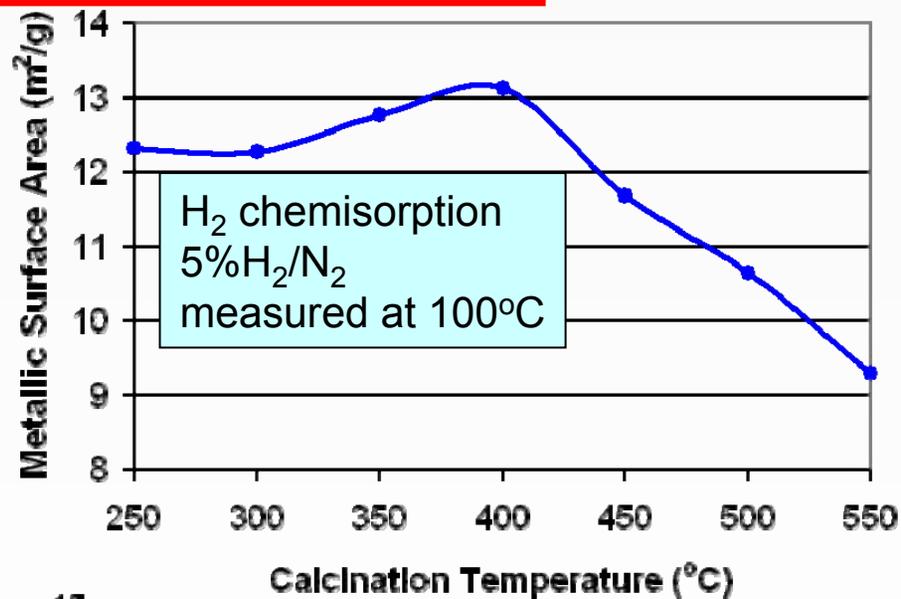
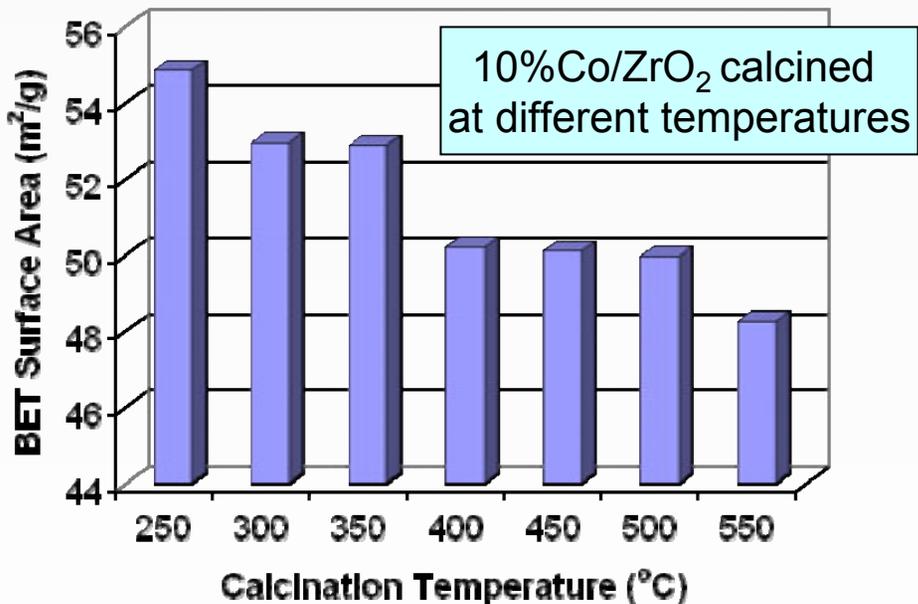
Effect of different molar ratio of EtOH to water



Technical Accomplishments/Progress/Results from Year 1

Effect of synthesis parameters

Optimum in Calcination T, Reduction T and Reduction time



Technical Accomplishments/Progress/Results from Year 1

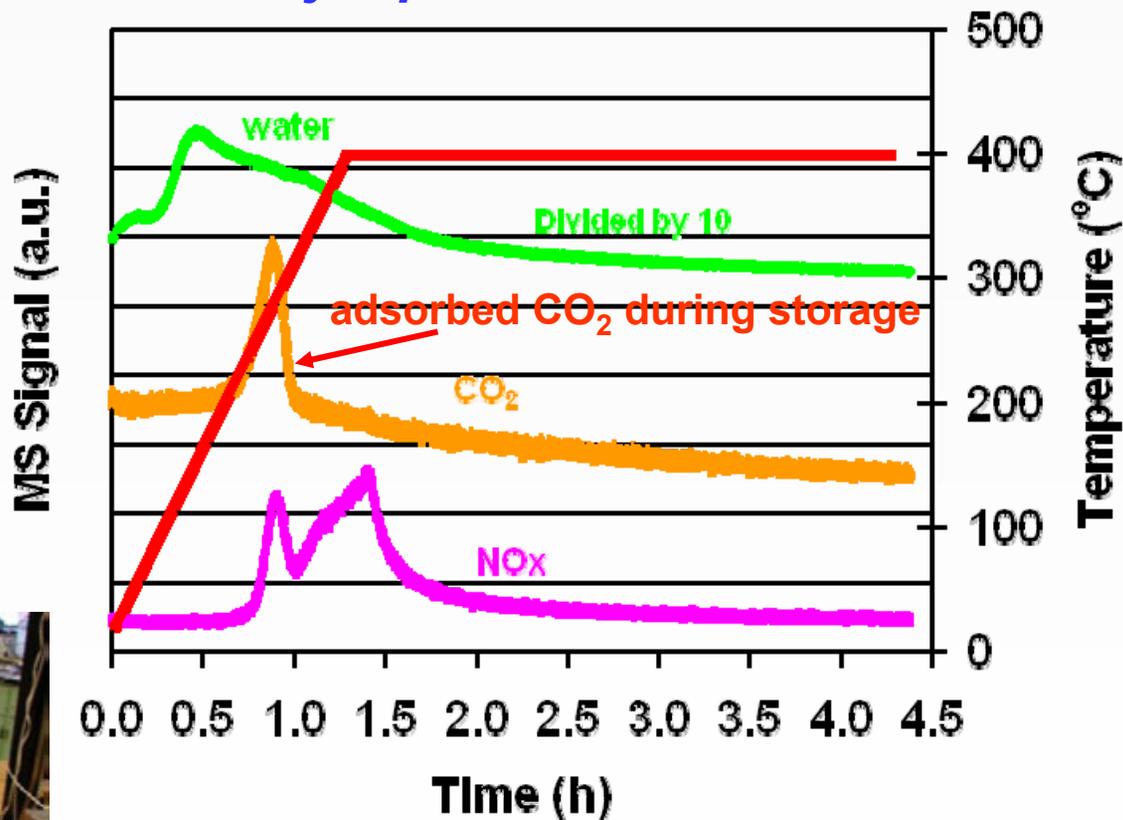
Mass spectrometry during Temperature-programmed Calcination: Evolution of the catalyst precursor

In the current study:

❖ Ions followed:

- 18 for water;
- 44 for CO₂;
- 30 for NO_x;
- 12 for verifying the assignment of 44 signal (not shown);

Cirrus MS



❖ Sample:

- 10%Co/ZrO₂

❖ Calcination:

- Temperature: 400°C;
- Time: 3h;
- Ramp rate: 5°C/min.

Technical Accomplishments/Progress/Results from Year 1

XRD Following Calcination

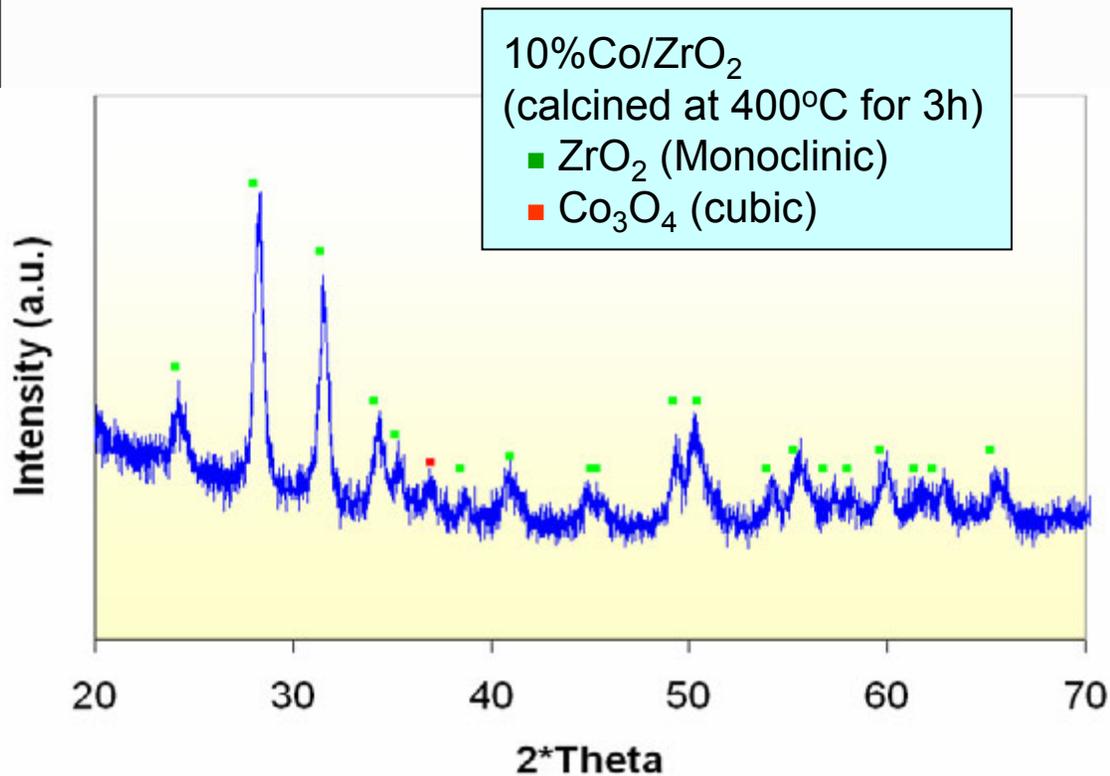
Crystalline phase of the support: Monoclinic

Catalyst phase: well-dispersed, not highly crystalline

Bruker D8 Advance Diffractometer



Monochromatic Cu Ka1 X-ray source
(1.5406 Å)



Technical Accomplishments/Progress/Results from Year 1

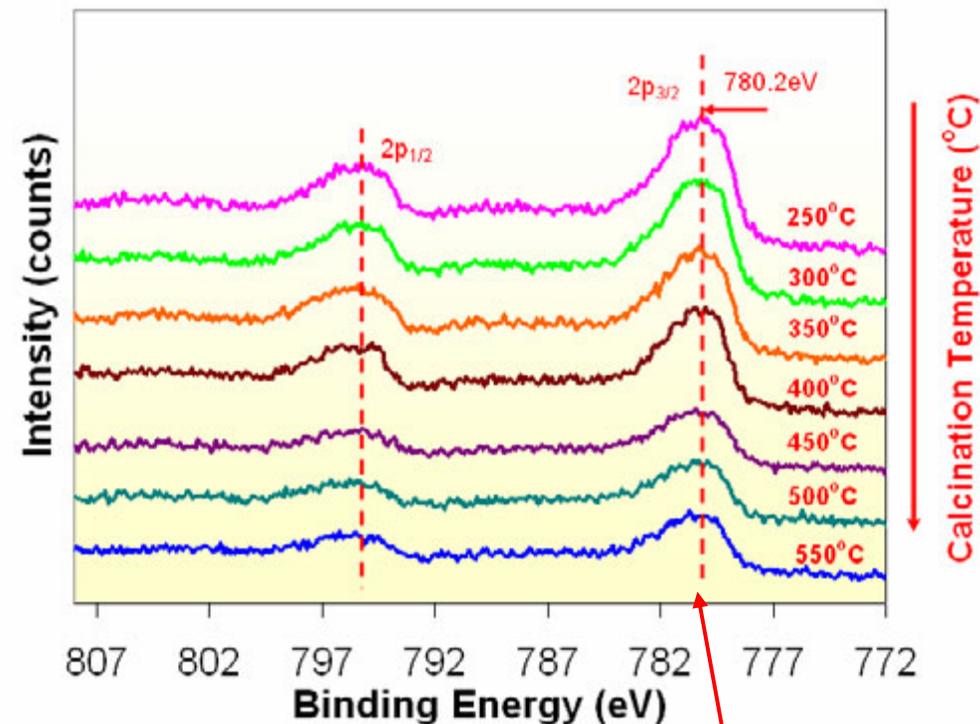
X-ray photoelectron spectroscopy following calcination

10%Co/ZrO₂
calcined at different temperatures for 3h

Kratos Axis Ultra XPS

In the current study:

- ❖ Supported on carbon tape
- ❖ Survey from 1200 eV to 0 eV and scans of Co 2p, O 1s, Zr 3d, and C 1s regions.
- ❖ Used to determine surface content and oxidation state of surface species.

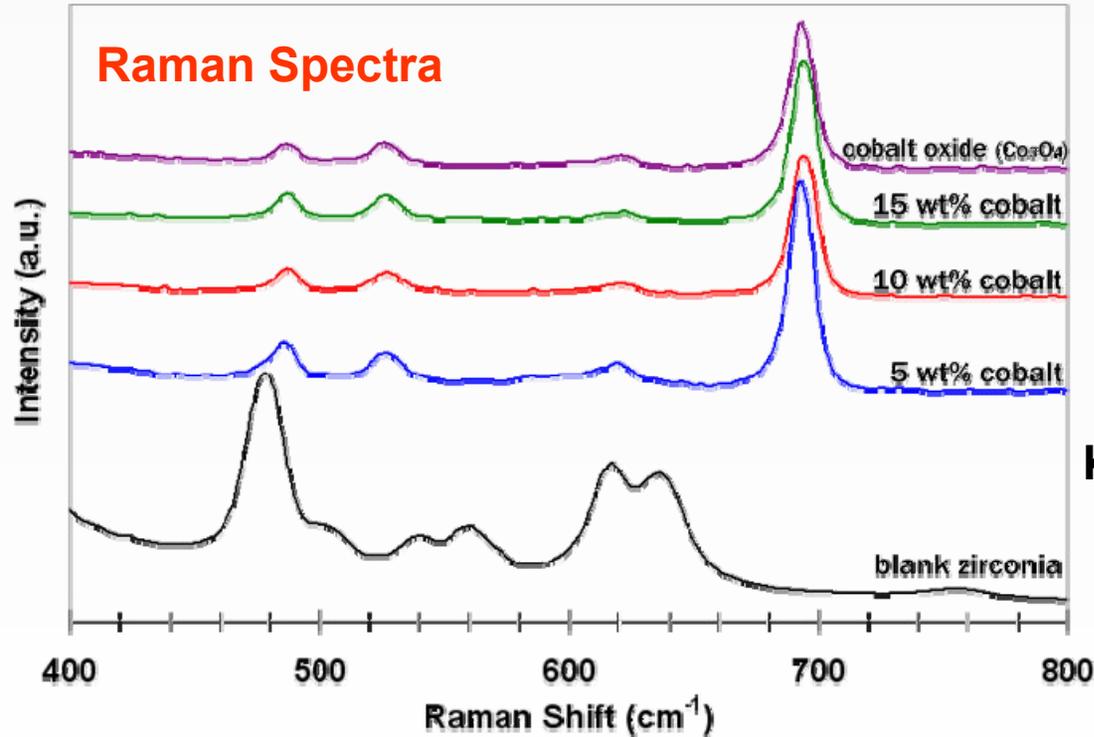


Characteristic binding energy of
Co in Co₃O₄



Technical Accomplishments/Progress/Results from Year 1

Laser Raman Spectroscopy Following Calcination



Well-dispersed samples;
complete surface coverage

Kaiser Laser Raman Spectrometer

❖ Sample:

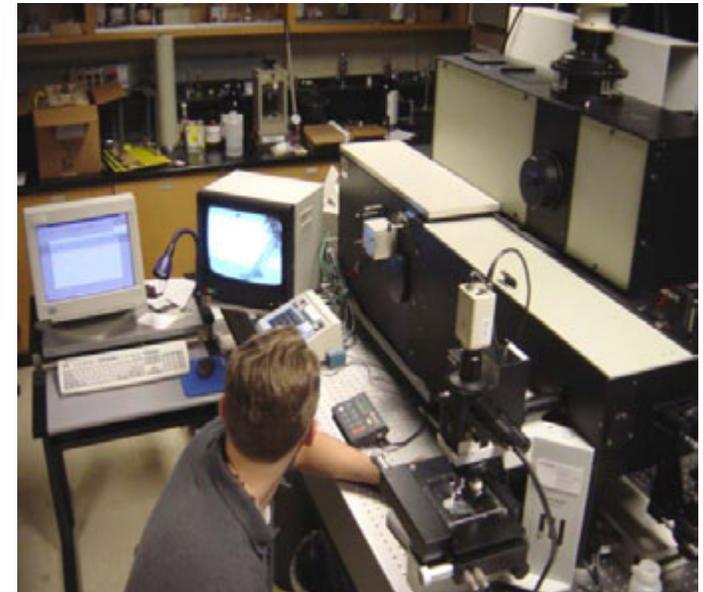
➤ ZrO_2 , Co/ZrO_2 , Co_3O_4

❖ Calcination:

➤ Temperature: **400°C**

➤ Time: **3h**

➤ Loading: **5%, 10%, 15%**;



Technical Accomplishments/Progress/Results from Year 1

Transmission Electron Microscopy (TEM) Following Calcination

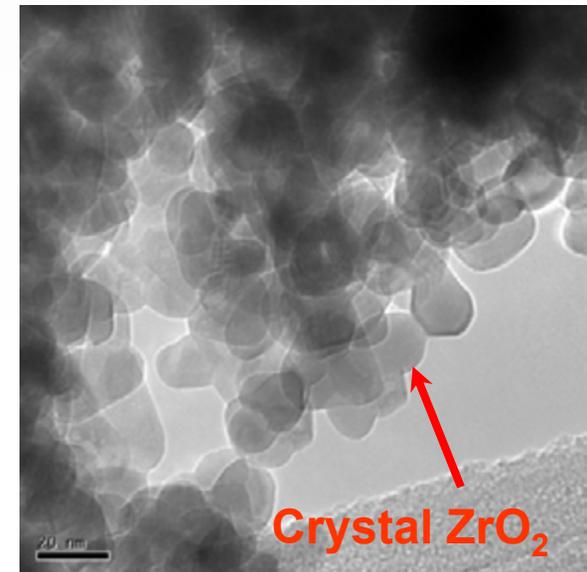
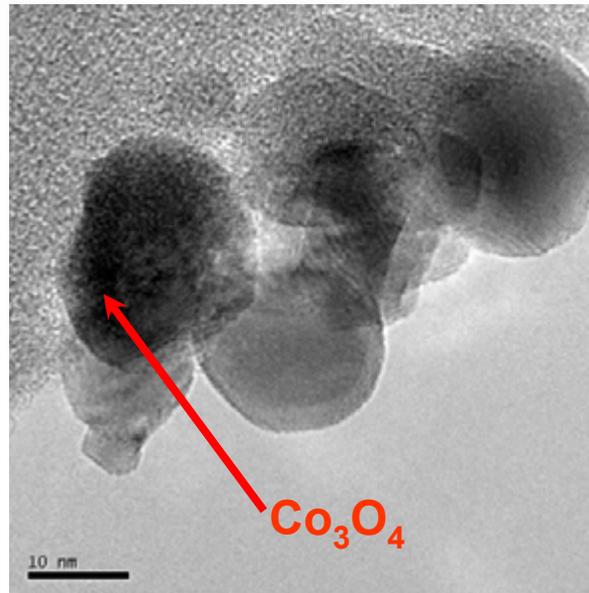
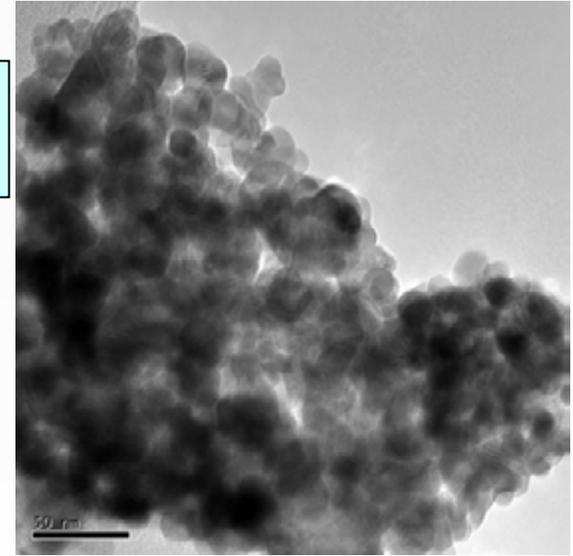
Tecnai TF-20 TEM

In the current study:

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

10%Co/ZrO₂
calcined at 400°C for 3h

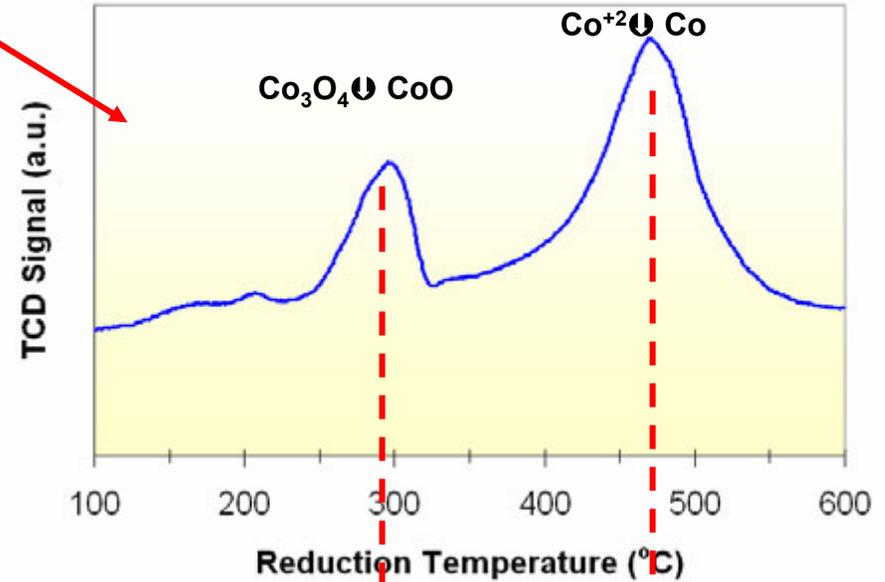
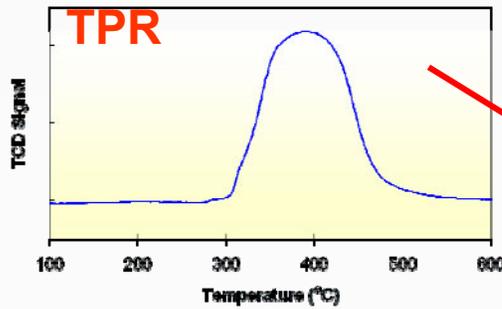
- ❖ Average Particle size of Co₃O₄:
24nm;



Technical Accomplishments/Progress/Results from Year 1

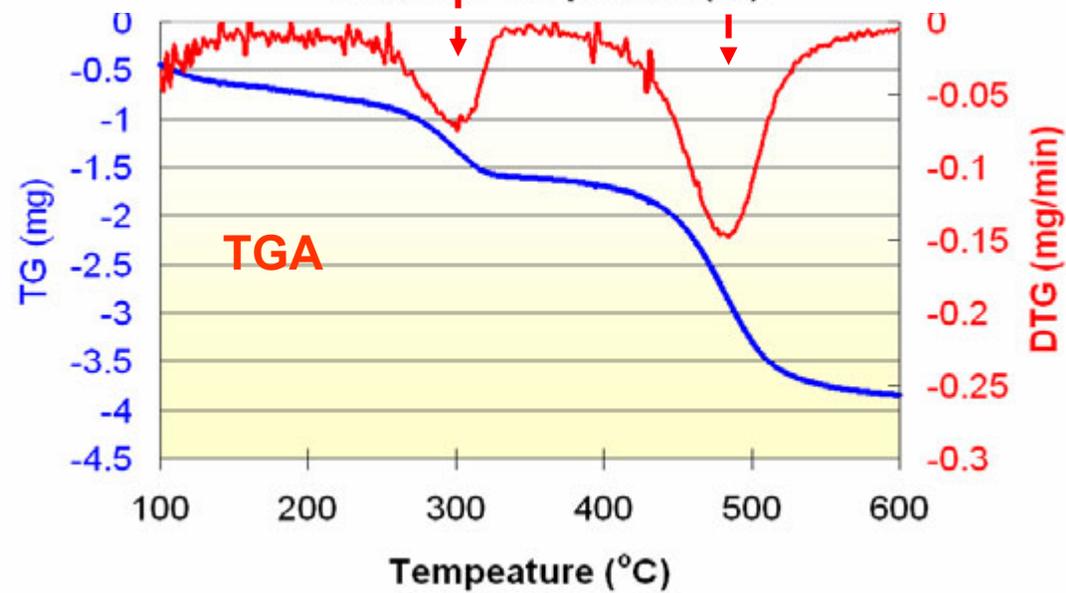
Reduction Characterization by Temperature - programmed Reduction

CuO as the Standard for Hydrogen Consumption



Reduction proceeds in two discrete steps.

In the current study:
10%Co/ZrO₂
Calcined at 400°C for 3h;
Reduced under 5%H₂/N₂
at ramping rate of 5°C/min.;

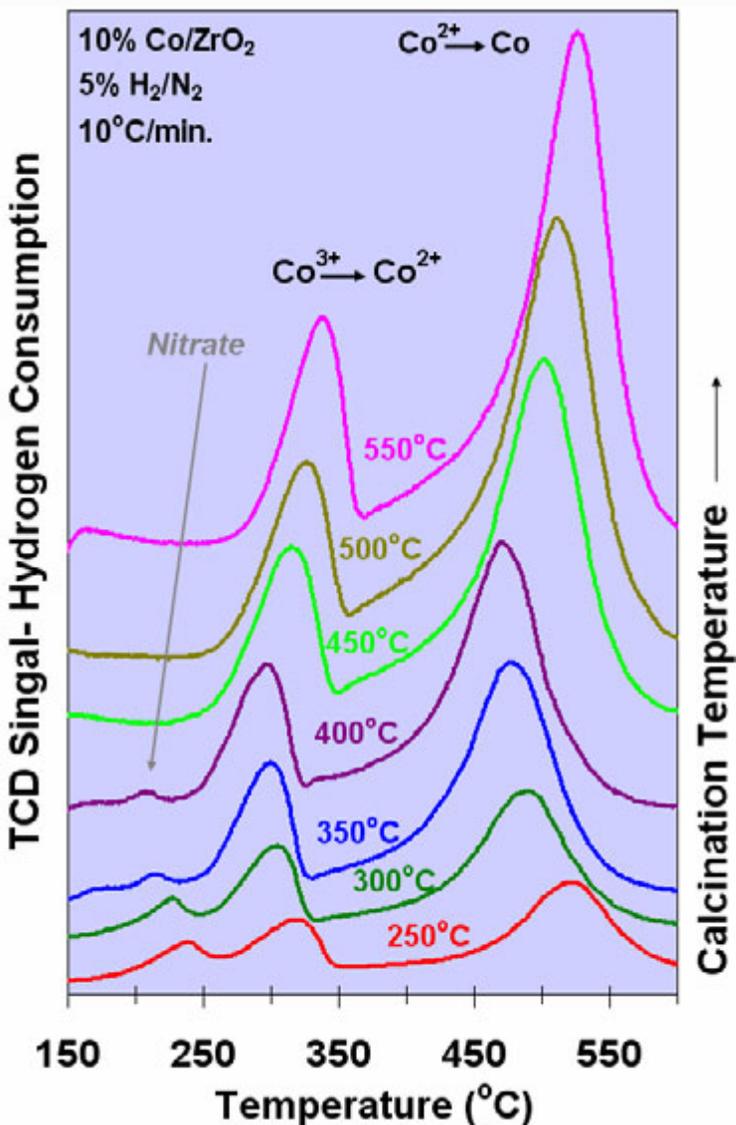


Setaram TGDSC-111

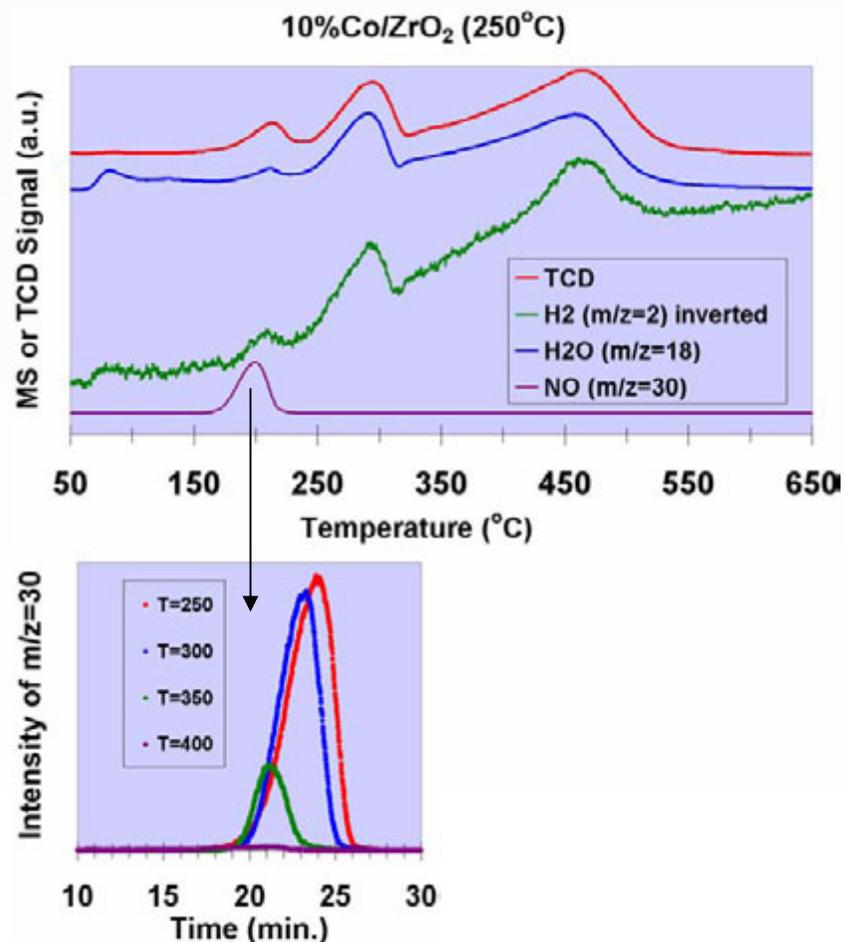


Technical Accomplishments/Progress/Results from Year 1

Reduction Behavior-TPR

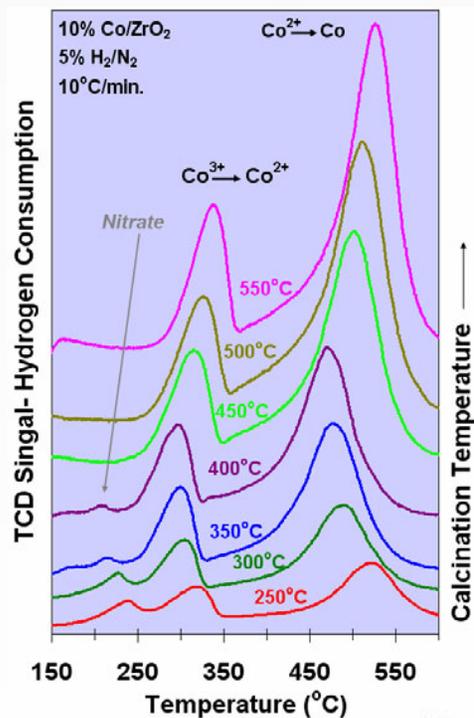


Nitrate evolution observed during reduction using Mass Spectrometry experiments

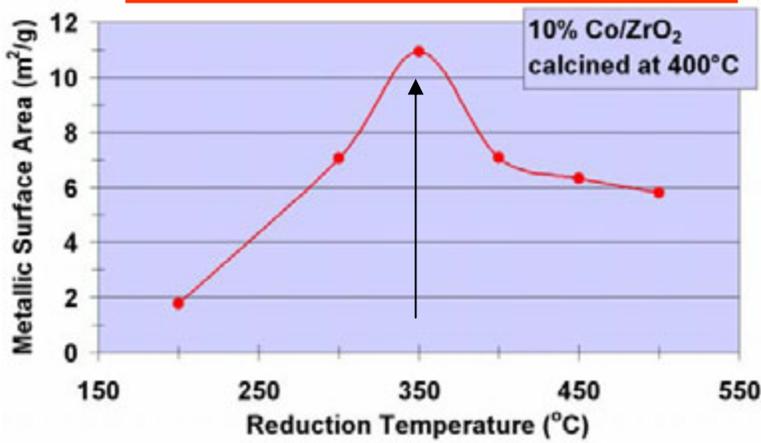


Technical Accomplishments/Progress/Results from Year 1

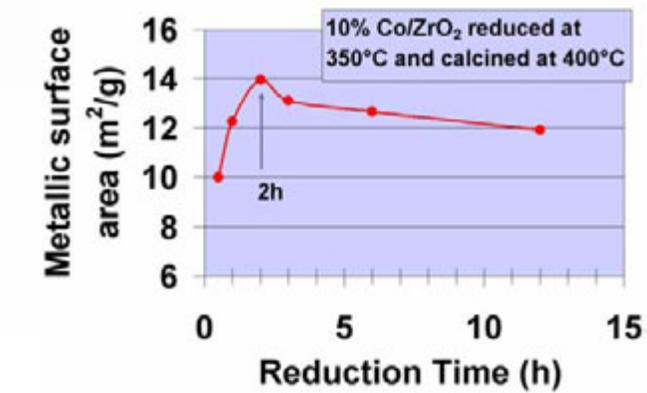
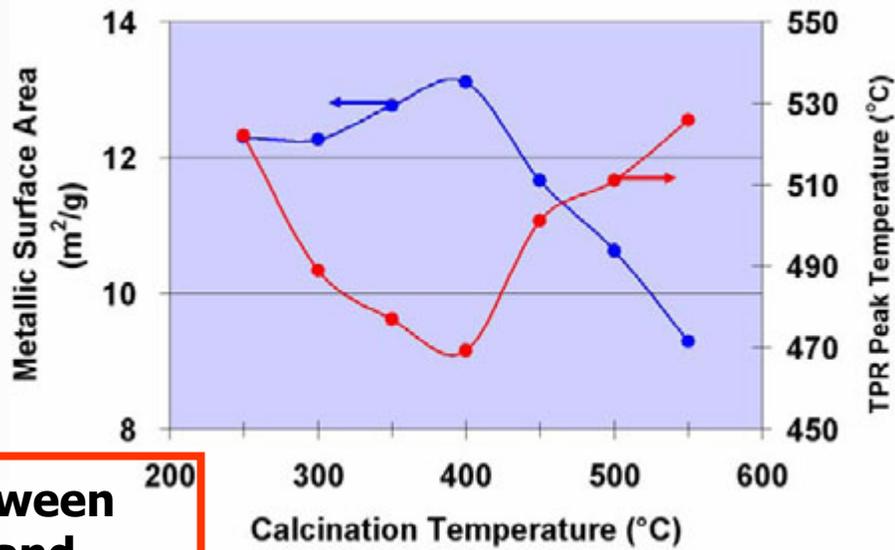
Effect of Reduction Process



Correlation between reduction and cobalt dispersion



Correlation between dispersion and reducibility



- Reduction time (GHSV H₂) and temperature important also

Technical Accomplishments/Progress/Results from Year 1

Reduction Characterization using X-ray photoelectron spectroscopy

Following reduction, Co is in +2 oxidation state.

❖ Sample:

➤ 10%Co/ZrO₂

❖ Calcination:

➤ Temperature: 400°C;

➤ Time: 3h;

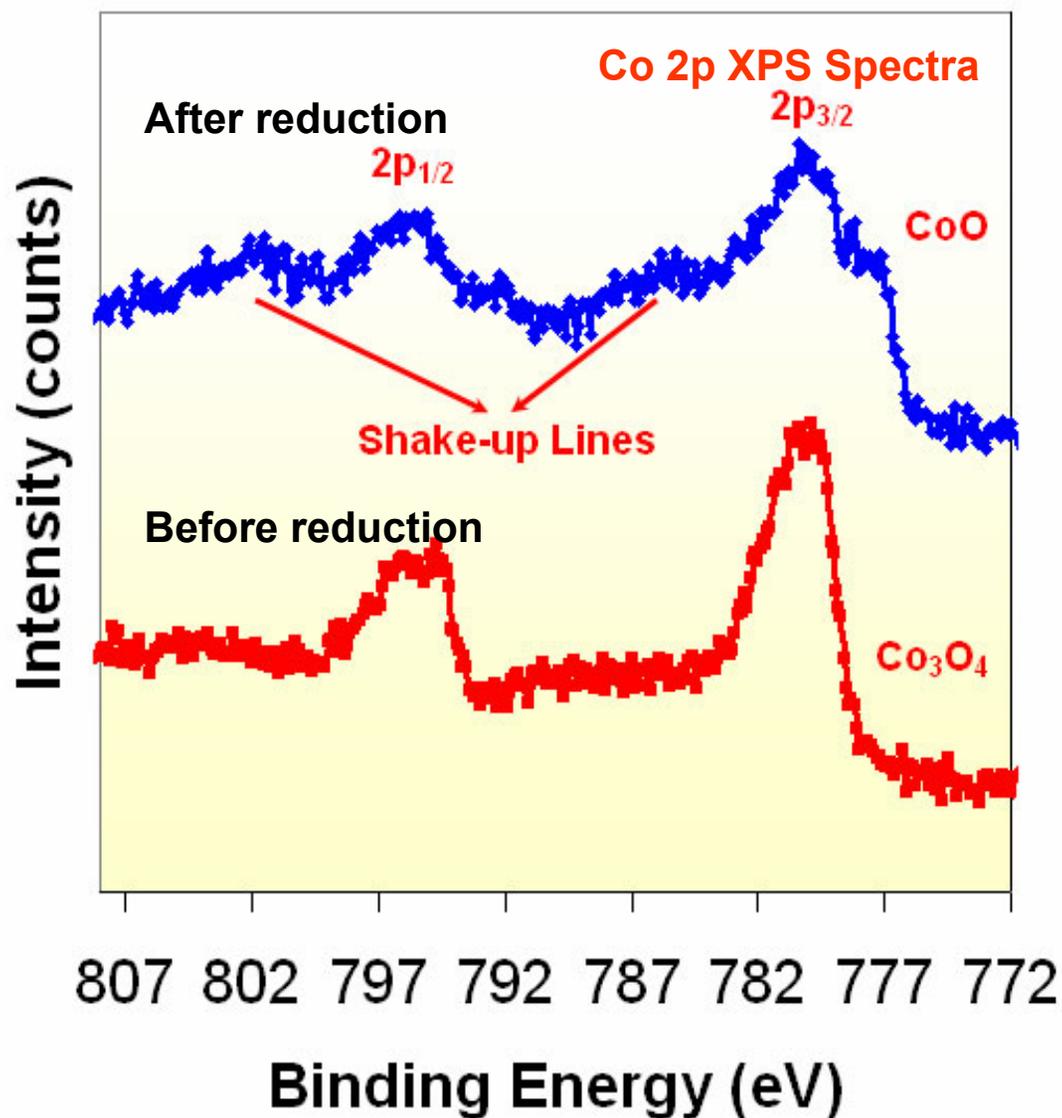
❖ Reduction:

➤ Temperature: 350°C;

➤ Time: 2h;

❖ XPS:

X-Ray source: (Al K_{α1});



Technical Accomplishments/Progress/Results from Year 1

Reduction Characterization through consecutive TPR-TPO-TPR

Higher reduction temperatures could lead to sintering.

❖ Sample:

➤ 10%Co/ZrO₂;

❖ Calcination:

➤ Temperature: 400°C;

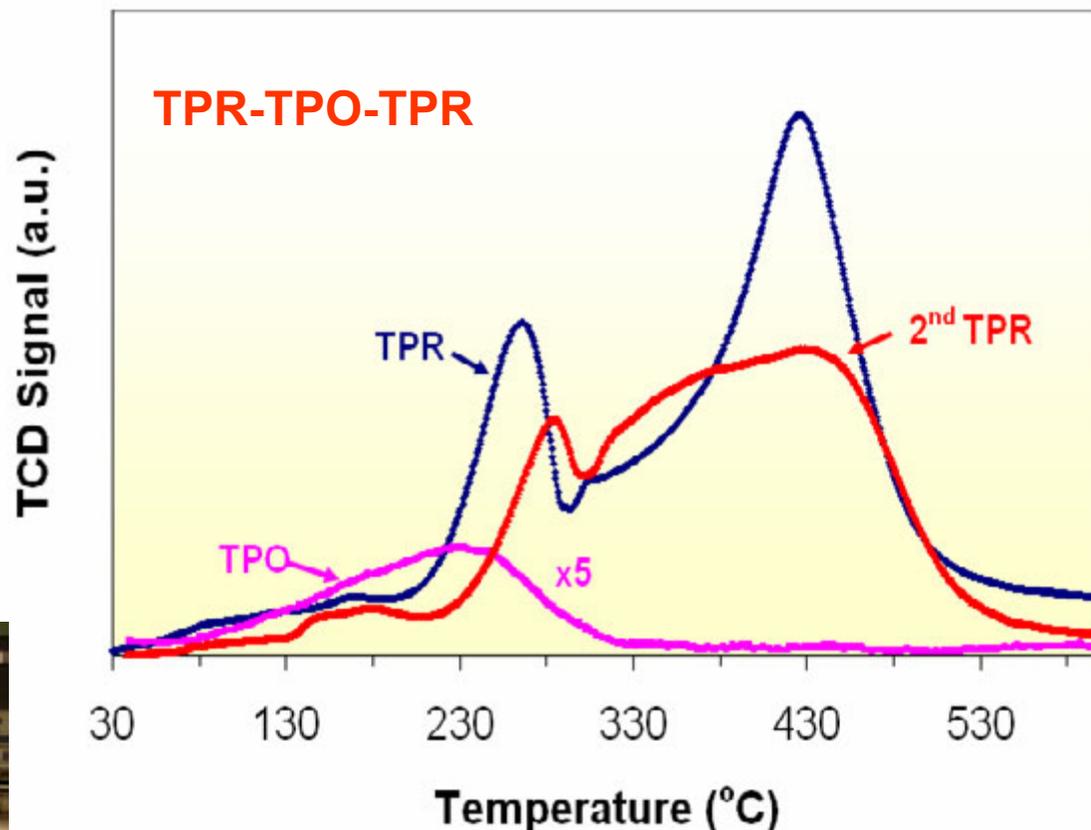
➤ Time: 3h;

❖ 1st TPR

➤ Reduction gas:

10%H₂/He;

➤ Ramp rate: 10°C/min.;



❖ TPO

➤ Temperature: up to 600°C;

➤ Oxidation gas: 10%O₂/He;

➤ Ramp rate: 5°C/min.;

❖ 2nd TPR

Same as the 1st run;

AutoChemII 2920



TEM Following Reduction

❖ Sample:

➤ 10%Co/ZrO₂

❖ Calcination:

➤ Temperature:

400°C

➤ Time:

3h

❖ Reduction:

➤ Temperature:

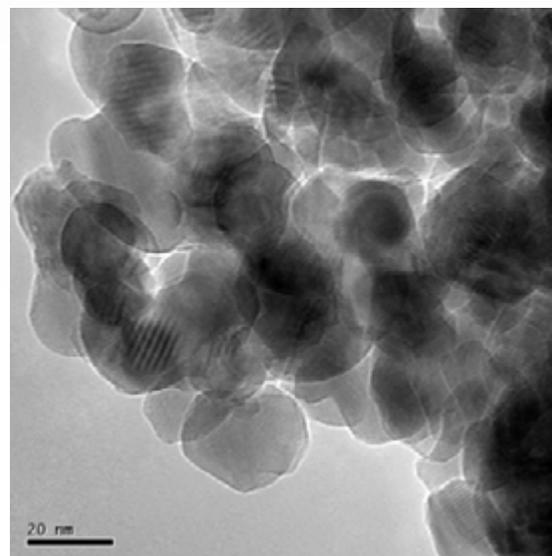
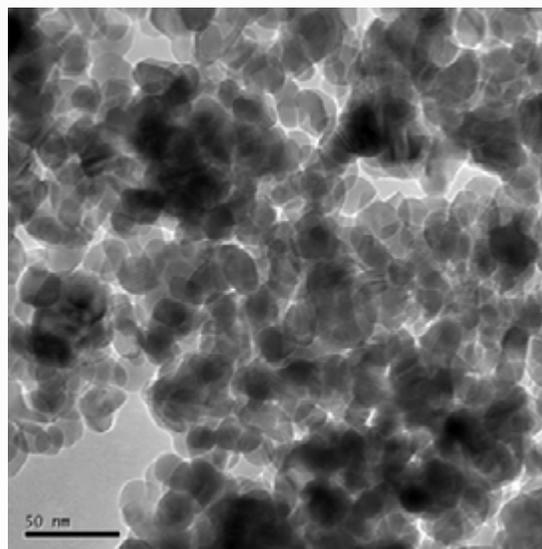
600°C

➤ Time:

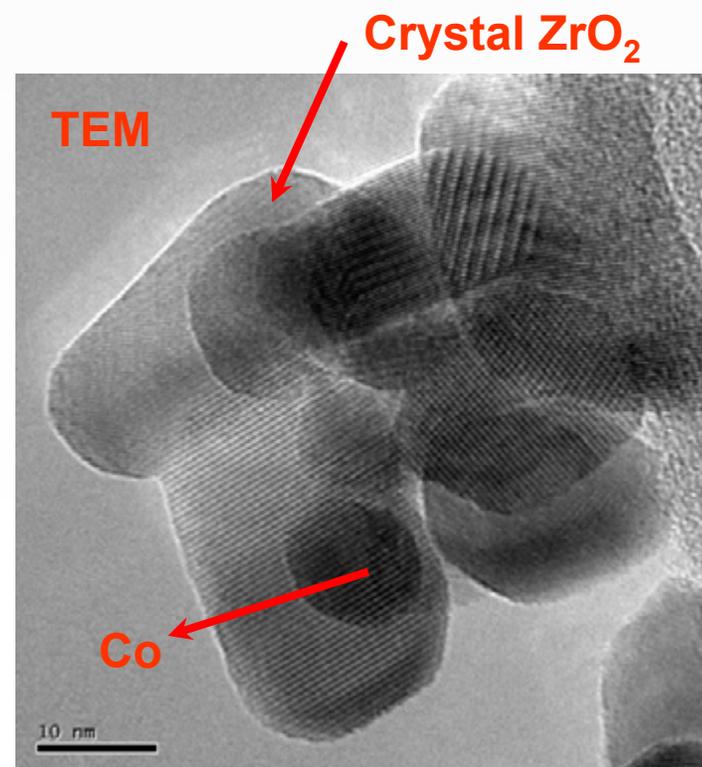
4h

➤ Ramp rate:

2°C/min.



Average Particle size
of Co following reduction:
12nm.



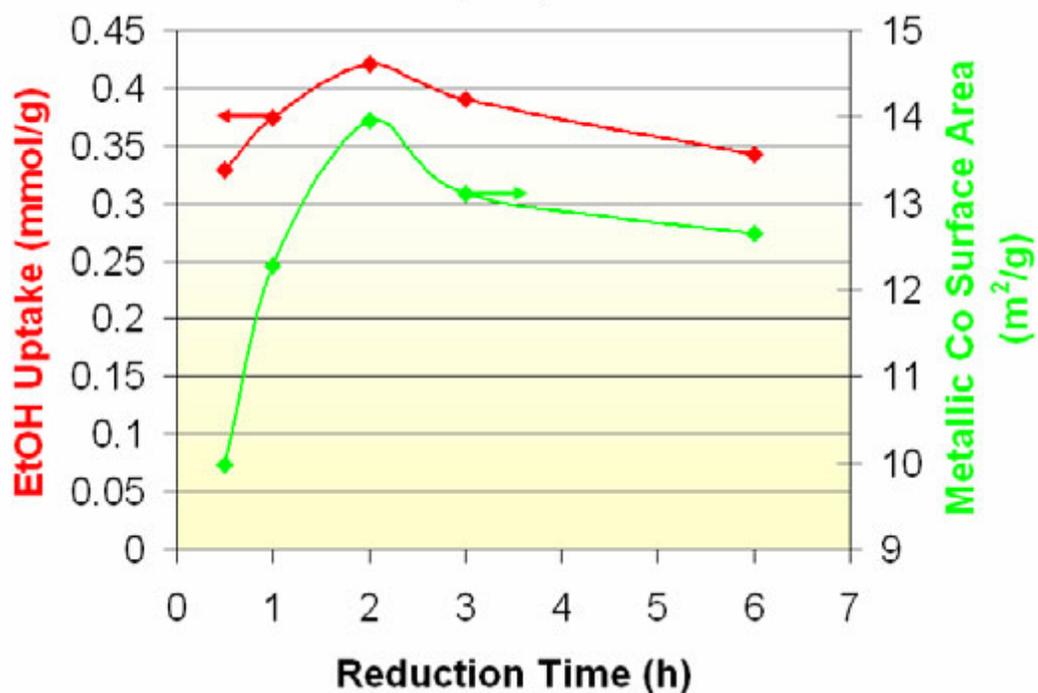
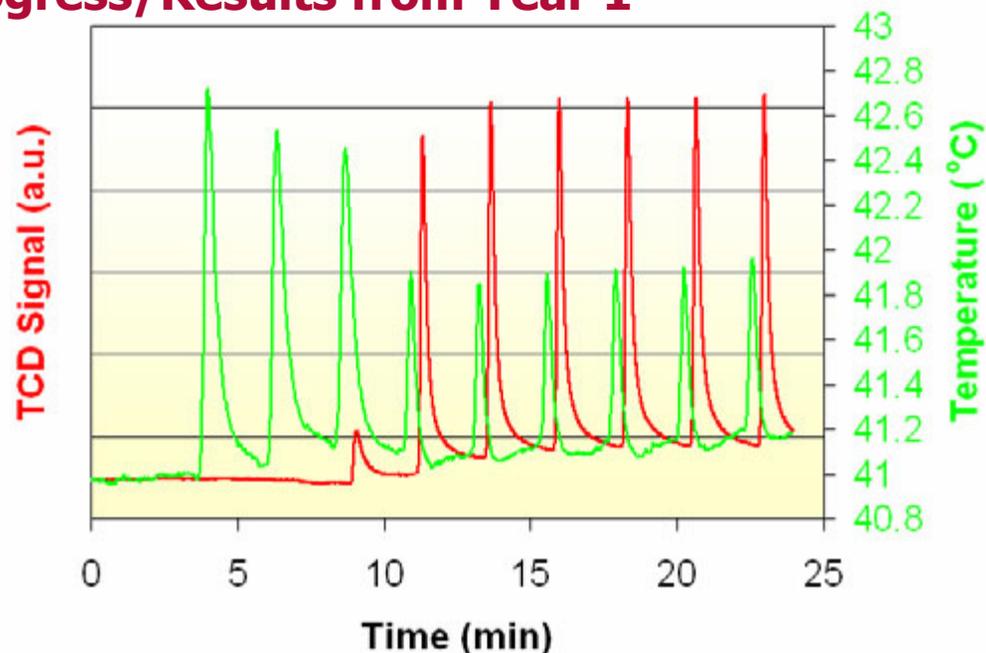
Technical Accomplishments/Progress/Results from Year 1

Characterization of Ethanol Adsorption Behavior by Pulsed Chemisorption

Strong correlation exists between ethanol uptake and metallic surface area.

❖ EtOH Pulse Chemisorption:

- 10%Co/ZrO₂(calcined at 400°C);
- Reduced at 350°C for different time;
- Pulsed ethanol vapor injection at room temperature;



Technical Accomplishments/Progress/Results from Year 1

Characterization of competing reactions: Temperature-programmed Desorption

Different reactions dominate at different temperature regions.

❖ Sample:

➤ 10%Co/ZrO₂;

❖ Calcination:

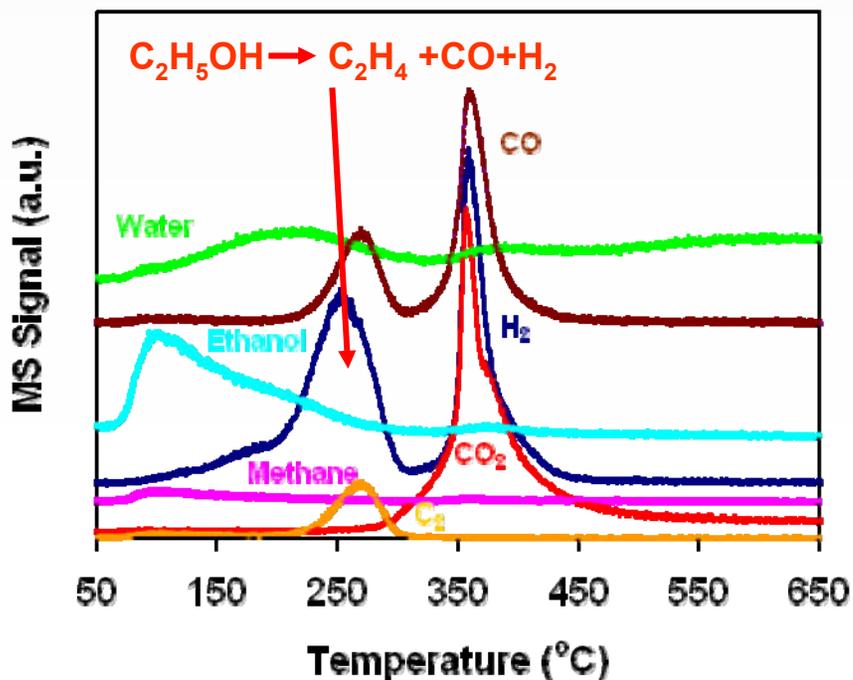
➤ 400°C for 3h;

❖ Reduction:

➤ 350°C for 2h;

❖ Before reaction:

➤ Flowing EtOH for 1h;



❖ Sample:

➤ 10%Co/ZrO₂;

❖ Calcination:

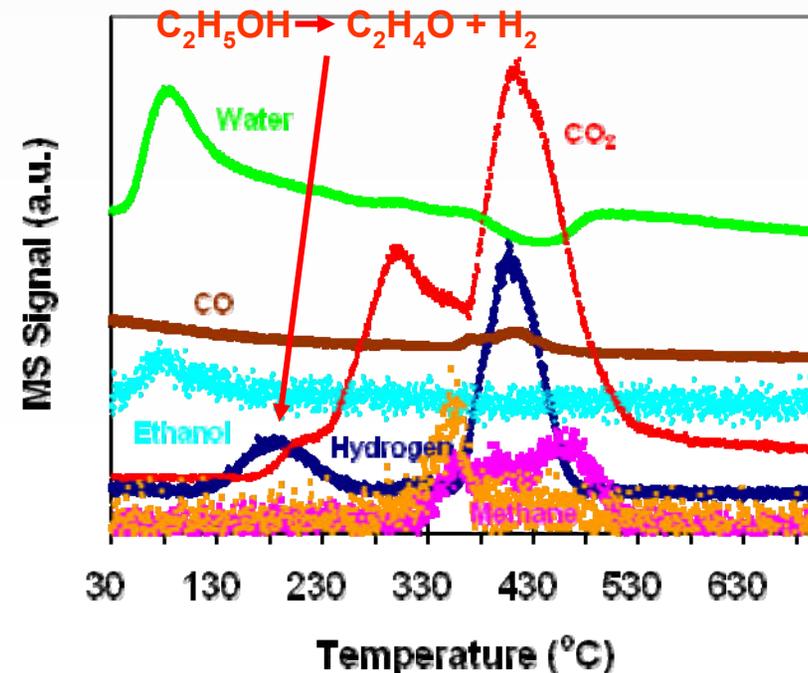
➤ 400°C for 3h;

❖ Reduction:

➤ 350°C for 2h;

❖ Before reaction:

➤ Flowing mixture of EtOH:H₂O(1:10) for 1h

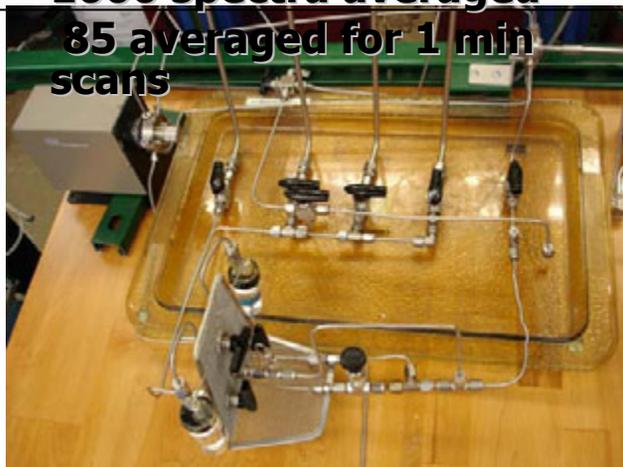


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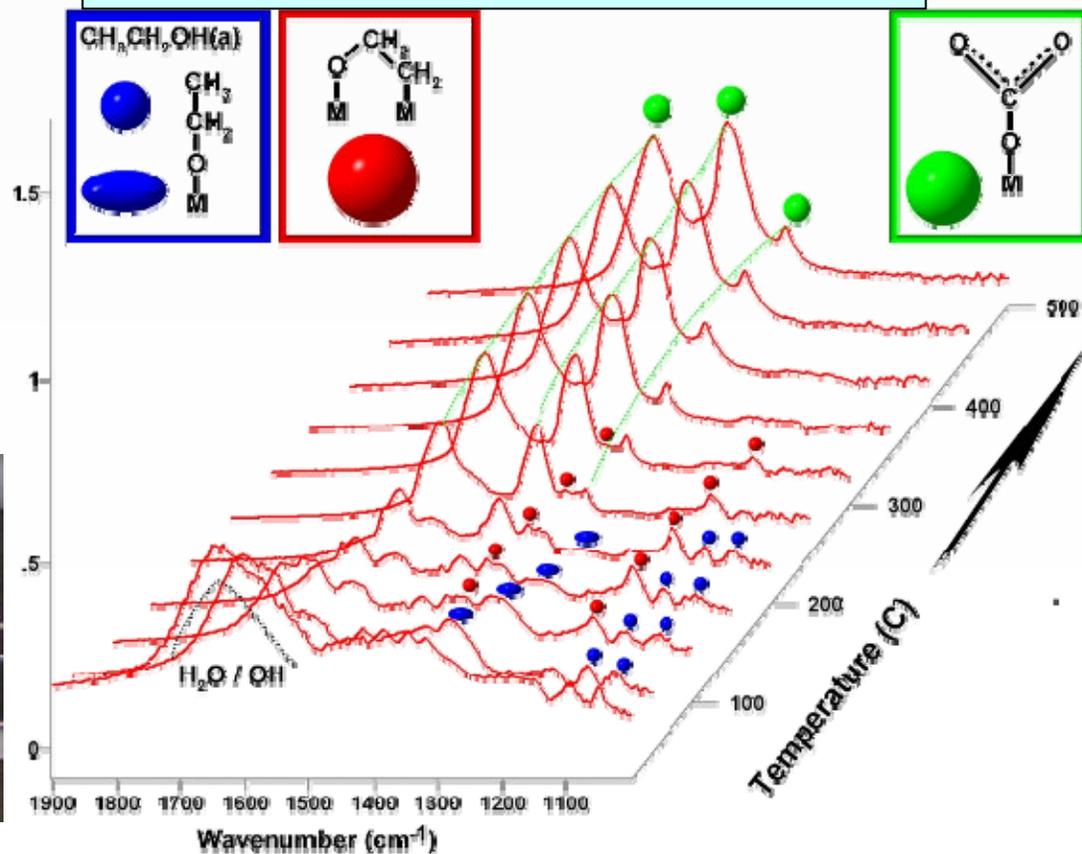
In-situ DRIFTS-TPRxn

Identification of surface species

- **Bruker IFS66 spectrometer**
- **Mid-IR range (400-4000 cm^{-1})**
- **MCT detector; KBr beamsplitter**
- **1000 spectra averaged**
- **85 averaged for 1 min scans**



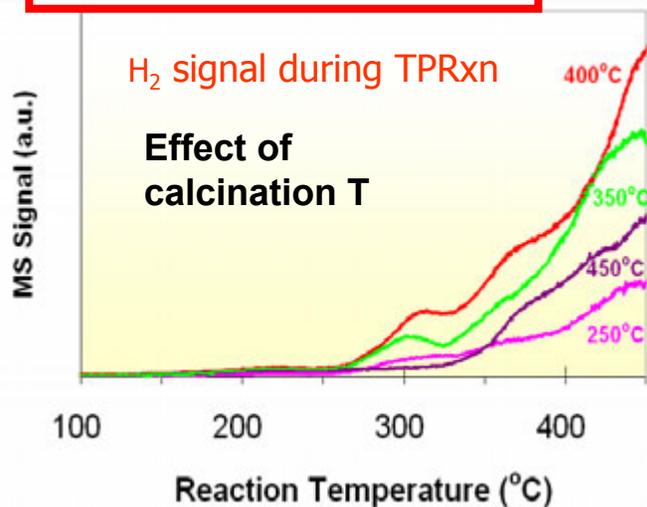
10%Co/ZrO₂; Calcined at 400°C/12h;
Reduced at 350°C under 5%H₂/He for 1h;
Ethanol +water adsorption at room T for 1h;
Spectra taken during TPRxn at 10°C/min under
He flowing at 30ml/min.



Technical Accomplishments/Progress/Results from Year 1

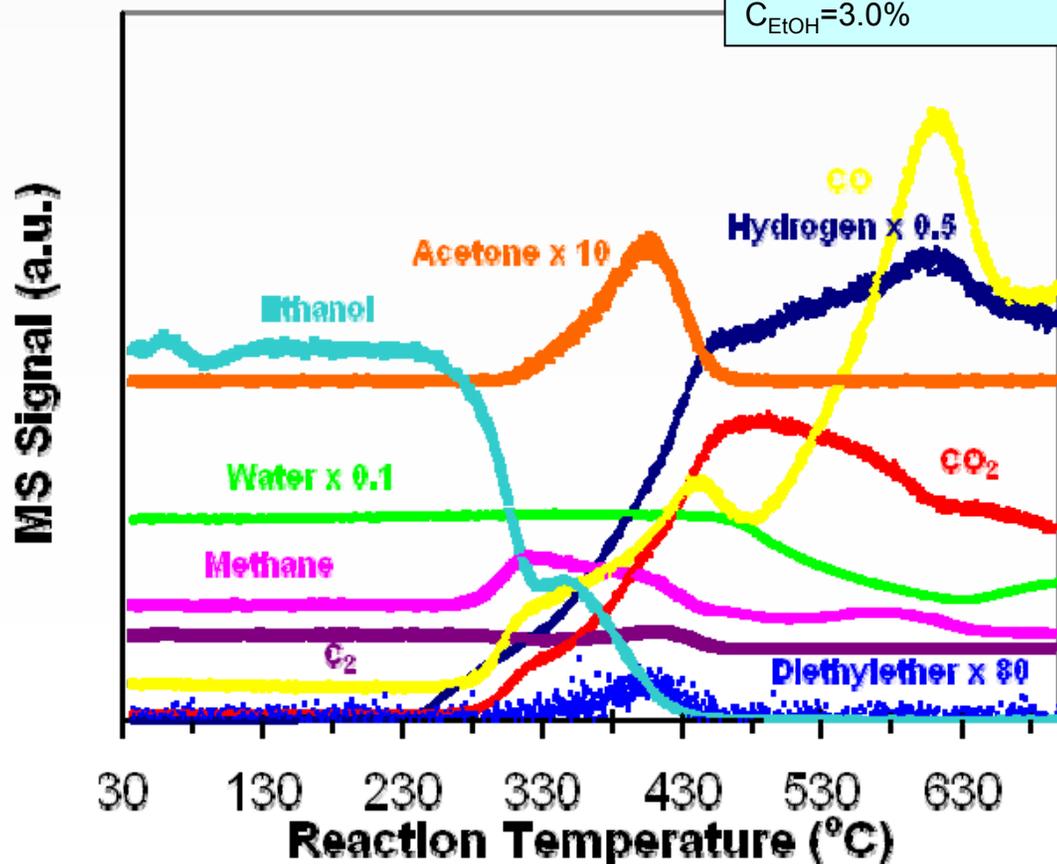
Temperature Programmed Reaction

Calcination temperature has a strong effect on the H₂ yield.

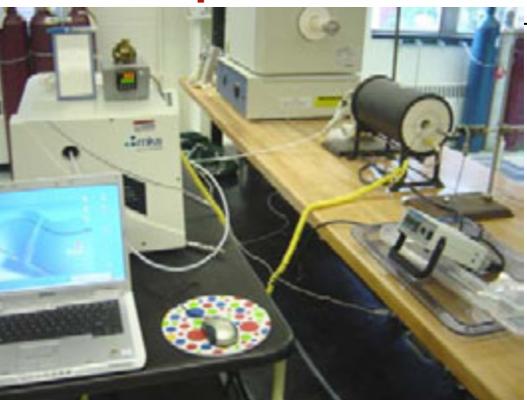


Different reactions dominate at different temperature regions.

10%Co/ZrO₂;
Reaction mixture of EtOH and water (1:10 molar) in He
GHSV=15065h⁻¹;
C_{EtOH}=3.0%

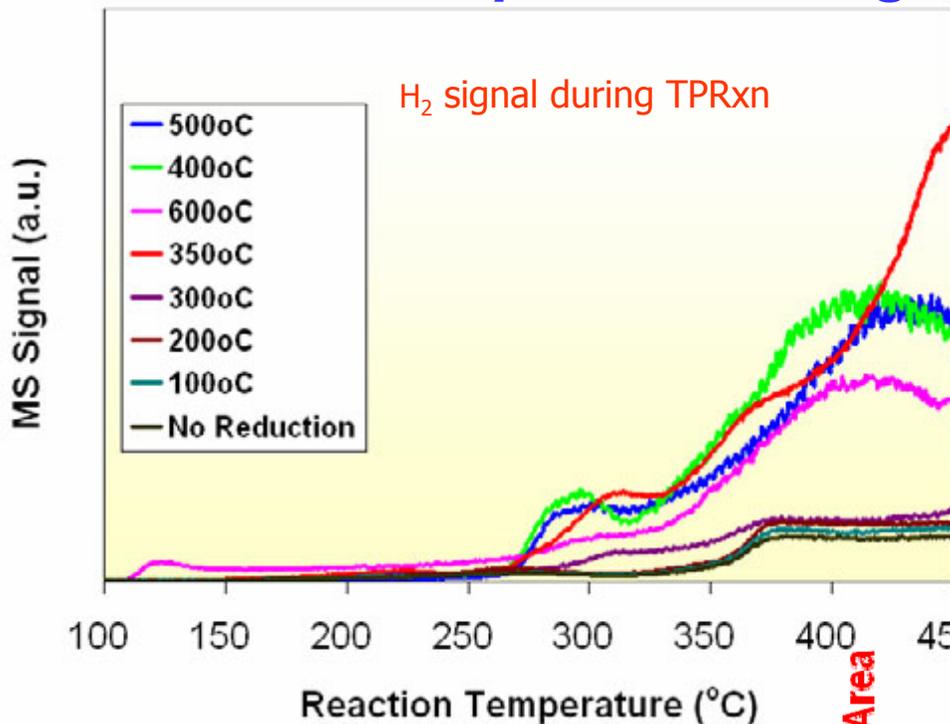


MKS Cirrus Mass Spectrometer



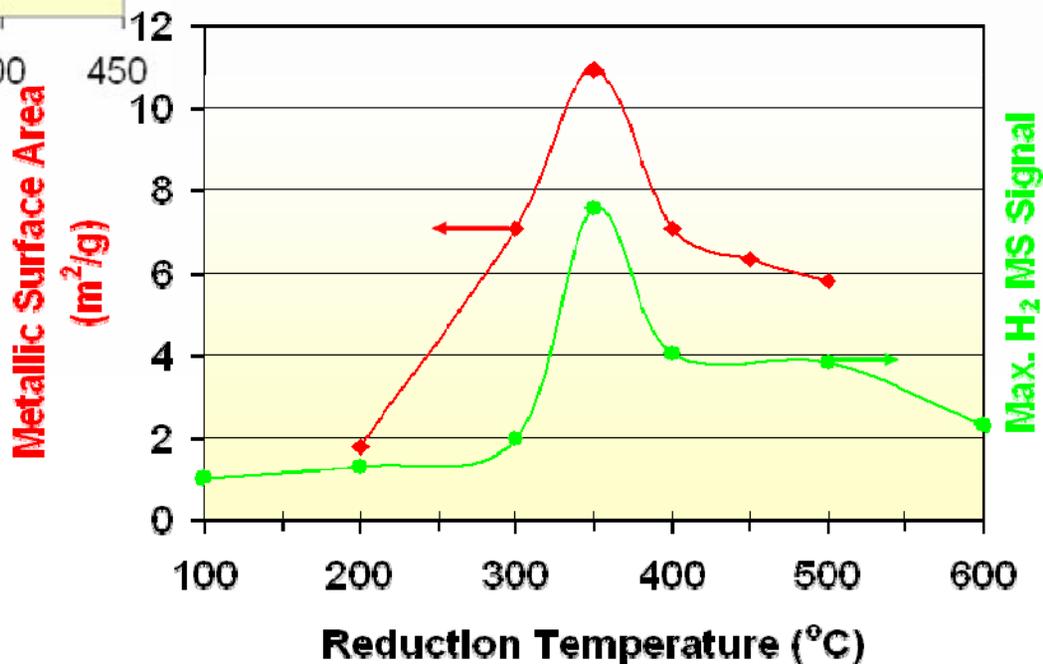
Technical Accomplishments/Progress/Results from Year 1

Temperature Programmed Reaction



H₂ yield correlates strongly with reduction temperature and, in turn, with metallic surface area.

Effect of reduction temperature



Technical Accomplishments/Progress/Results from Year 1

Steady-State Reaction Experiments: Initial data

$$\text{H}_2 \text{ Yield \%} = \frac{\text{moles of H}_2 \text{ produced}}{6 \times (\text{moles of ethanol fed})} \times 100$$

Carbon containing product A Yield %:

$$= \frac{(\text{moles of A produced}) \times (\# \text{ of carbon in A})}{2 \times (\text{moles of ethanol fed})} \times 100$$

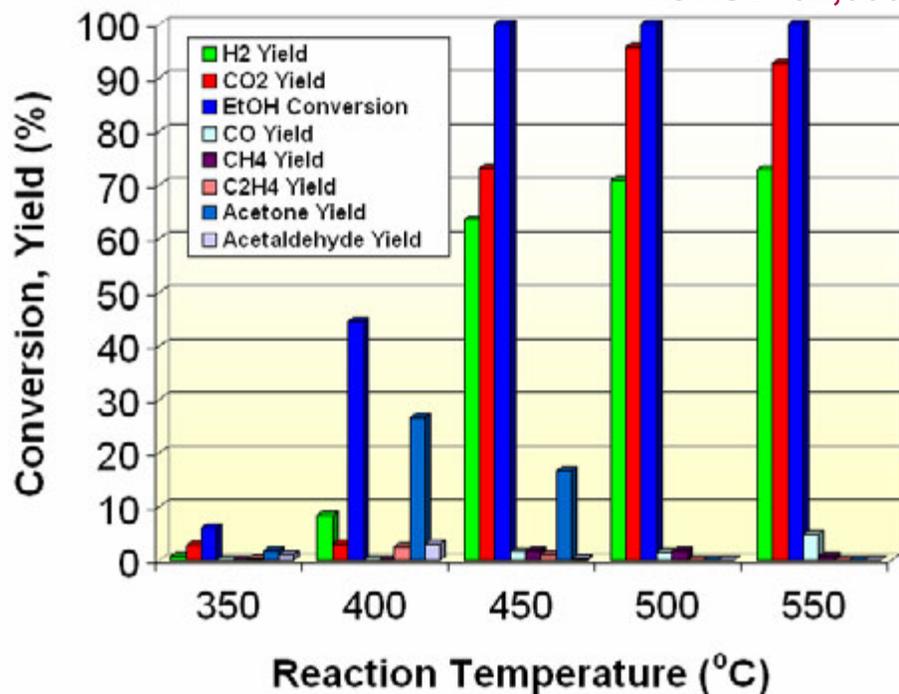
$$\text{EtOH Conversion \%} = \frac{\text{moles of ethanol converted}}{\text{moles of ethanol fed}} \times 100$$

Demonstrated high H₂ yields (over 70%)
at GHSVs approaching 100,000 hr⁻¹
(significantly higher than those reported earlier).

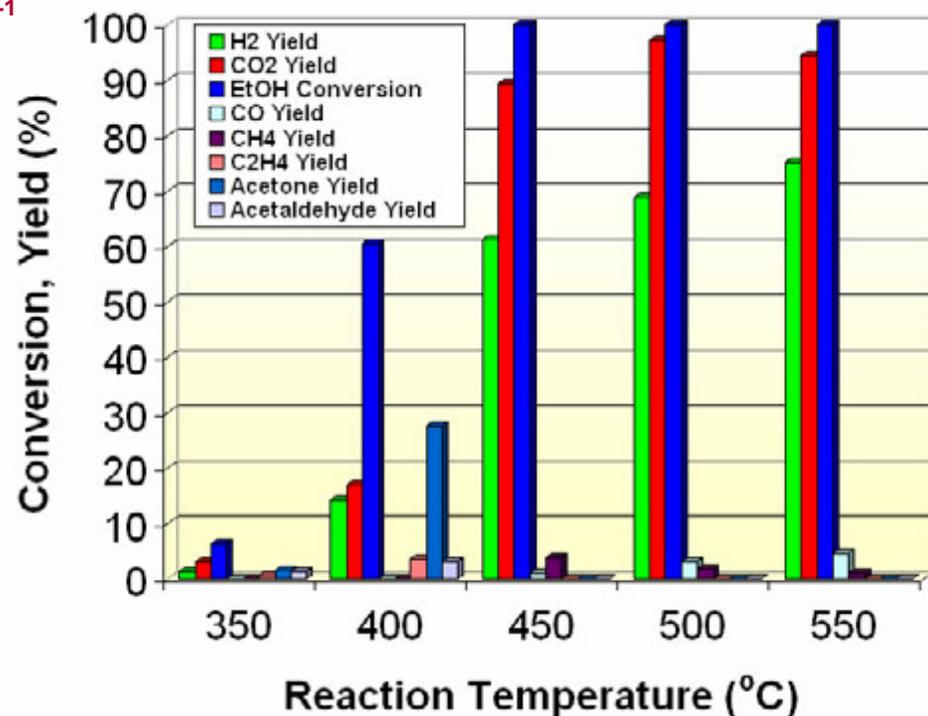
Reaction Conditions:

10%Co/ZrO₂(400°C);
Reduced under 5%H₂/He at 350°C for 2h;
EtOH:Water=1:10 (molar);
C_{EtOH}=1.1%;

GHSV=94,000h⁻¹



GHSV=47,000h⁻¹



Publications and presentations

- Watson, R.B., Ozkan, U.S., Matter, P.H., Braden, D., Song, H., "Alcohol Steam Reforming for Hydrogen Production" presented at the Annual Meeting of the American Institute of Chemical Engineers, Cincinnati, OH, November 2005.
- Ozkan, U.S., Song, H., Watson, R.B., Zhang, L., "Investigation of Bio-ethanol Steam Reforming over Co-based Catalysts" presented at the ACS National Meeting, Atlanta, GA, March 2006.
- Ozkan, U.S., Song, H., Watson, R.B., Zhang, L., "Investigation of Bio-ethanol Steam Reforming over Co-based Catalysts" *Prepr. Am.Chem.Soc. Div.Petr.Chem.*, 2006, 51(1)24).

Future Work

- ❖ **Kinetic and mechanistic investigations coupled with in-situ characterization**
- ❖ **Performing energy and mass balances and economic analysis using Aspen[®]**
- ❖ **Performance optimization**
- ❖ **Investigation of catalyst deactivation and regeneration characteristics**
- ❖ **Catalyst scale-up through industrial partnership**

Project Summary

- ❖ **Target:** development of a catalytic system that does not rely on precious metals and that can be active in the 350°C-550°C temperature range.
- ❖ **Relevance:** help to develop small-scale distributed hydrogen production technologies from renewable liquid sources.
- ❖ **Approach:** develop a systematic optimization strategy for evaluating the catalytic performance of different catalyst systems.
- ❖ **Accomplishments:**
 - Successful launching of the project and establishment of the experimental protocols
 - Understanding the effect of synthesis parameters on the catalyst performance and establishing correlations
 - Understanding the competing reaction networks
 - Significant H₂ yields at high GHSV and low temperatures in initial steady-state runs
- ❖ **Future Work:** Mechanistic investigations coupled with in-situ characterization; economic analysis; deactivation/regeneration studies.

Umit S. Ozkan

614-292-6623

Ozkan.1@osu.edu

