Investigation of Bio-ethanol Steam Reforming over cobalt based catalysts

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The Ohio State University

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PDP-7

Overview

Timeline

- Start Date - May 1, 2005
- End Date - April 31,2009
- 20% Complete

Barriers

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

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)

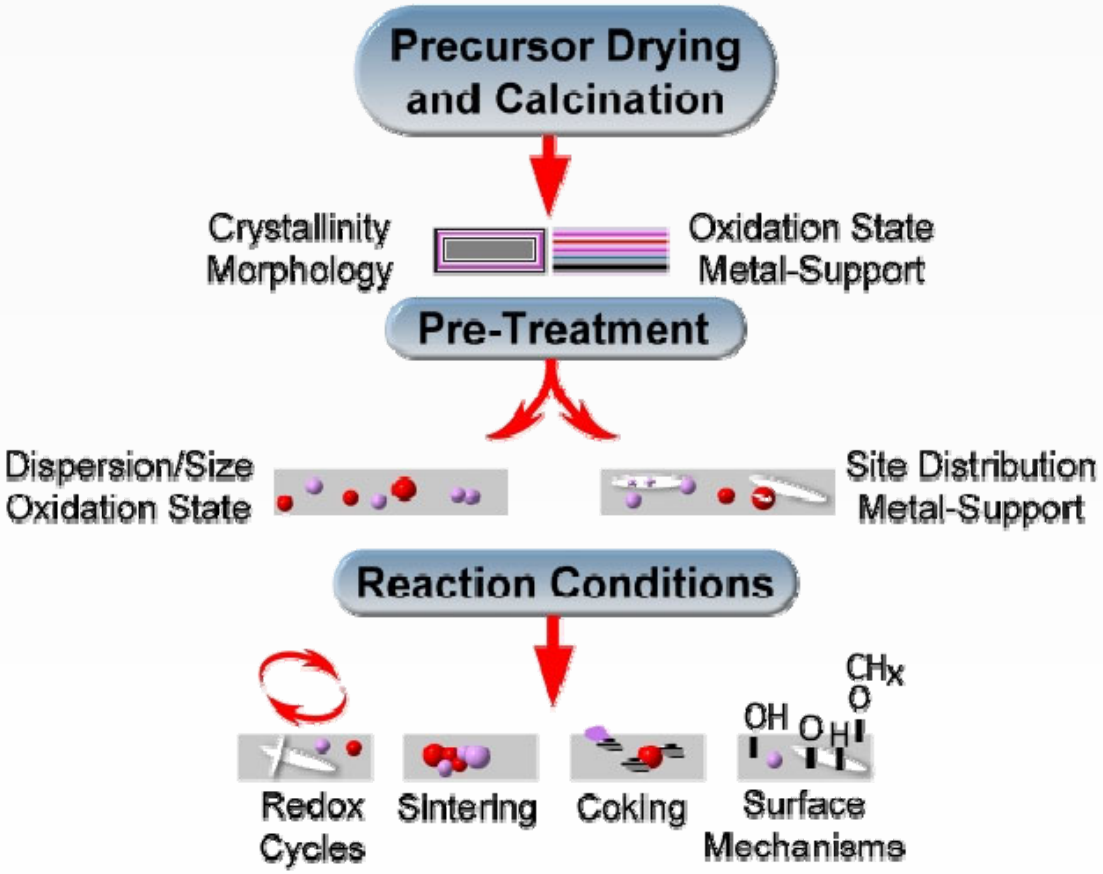
Partners

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

Objectives

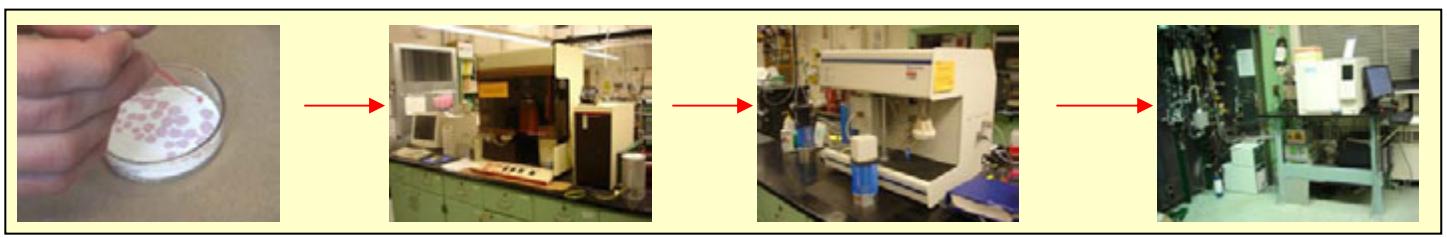
- To acquire a fundamental understanding of the reaction networks and active sites in bio-ethanol steam reforming over Co-based catalysts that would lead to
  - Development of a precious metal-free catalytic system which would enable
    - Low operation temperature (350-550 ° C)
    - High selectivity 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**



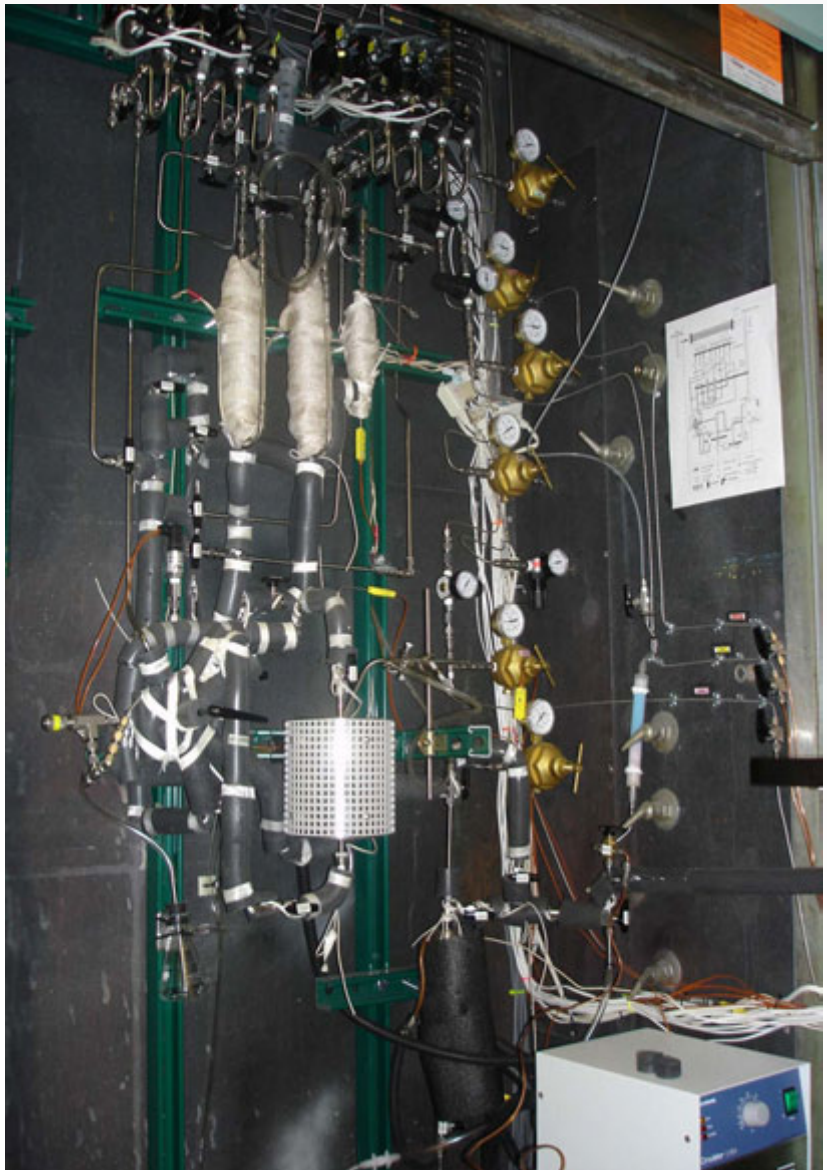
Technical Accomplishments/Progress/Results from Year 1

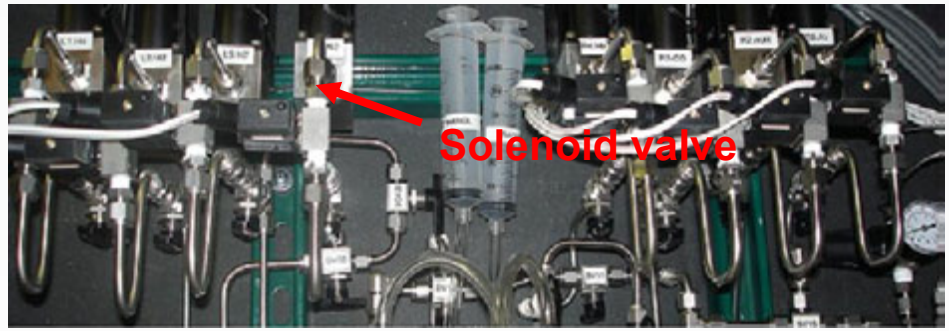
Catalysts Synthesis:
Role of the supports, precursors and synthesis techniques

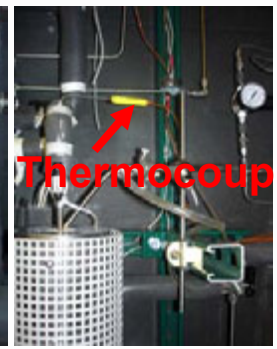
Catalyst	Precursor	Support/Preparation	
$10\%Co/ZrO_2$	**$Co(NO_3)_2 \bullet 6H_2O$**	**ZrO_2 (Commercial)**	IWI
$1\%Ru - 10\%Co/ZrO_2$	$Co(NO_3)_2 \bullet 6H_2O$ $RuCl_3$	ZrO_2 (Commercial)	
$1\%Re - 10\%Co/ZrO_2$	$Co(NO_3)_2 \bullet 6H_2O$ $ReCl_3$	ZrO_2 (Commercial)	
$1\%Rh - 10\%Co/ZrO_2$	$Co(NO_3)_2 \bullet 6H_2O$ $RhCl_3$	ZrO_2 (Commercial)	
$10\%Co/ZrO_2$	$CoCl_2$	ZrO_2 (Commercial)	
10% Co/ZnO(1)	$Co(NO_3)_2 \bullet 6H_2O$	Nano-powder ZnO	
10% Co/ZnO(2)	$Co(NO_3)_2 \bullet 6H_2O$	100+ Mesh ZnO	
10% Co/ZnO(3)	$Co(NO_3)_2 \bullet 6H_2O$	decomposition of $Zn(NO_3)_2 \bullet 6H_2O$ at 500^oC	
10% Co/ZnO(4)	$Co(NO_3)_2 \bullet 6H_2O$	decomposition of $3ZnO \bullet 2ZnCO_3 \bullet 3H_2O$ at 500^oC	
$10\% Co/SiO_2$	$Co(NO_3)_2 \bullet 6H_2O$	Fumed SiO_2	
10% Co/MgO	$Co(NO_3)_2 \bullet 6H_2O$	MgO (commercial)	
$10\% Co/V_2O_5$	$Co(NO_3)_2 \bullet 6H_2O$	V_2O_5 (commercial)	
$10\% Co/CeO_2$	$Co(NO_3)_2 \bullet 6H_2O$	CeO_2 (commercial)	
$10\% Co/Y_2O_3$	$Co(NO_3)_2 \bullet 6H_2O$	Y_2O_3 (commercial)	
$10\% Co/ Al_2O_3$	$Co(NO_3)_2 \bullet 6H_2O$	Al_2O_3 (commercial)	
$10\% Co/ TiO_2$	$Co(NO_3)_2 \bullet 6H_2O$	TiO_2 (commercial)	
$10\% Co/ La_2O_3$	$Co(NO_3)_2 \bullet 6H_2O$	La_2O_3 (commercial)	
$10\% Co/ Sm_2O_3$	$Co(NO_3)_2 \bullet 6H_2O$	Sm_2O_3 (commercial)	
$10\% Co/5ZrO_2 \bullet ZnO$	$Co(NO_3)_2 \bullet 6H_2O$	Co-Impregnating $Zn(NO_3)_2 \bullet 6H_2O$ into ZrO_2 along with $Co(NO_3)_2 \bullet 6H_2O$	
$10\% Co/10ZrO_2 \bullet ZnO$	$Co(NO_3)_2 \bullet 6H_2O$		
$10\% Co/15ZrO_2 \bullet ZnO$	$Co(NO_3)_2 \bullet 6H_2O$		
$10\%Co/ZrO_2$	$Co(NO_3)_2 \bullet 6H_2O$	Zr propoxide	Sol-Gel

Initial focus of the characterization and activity study

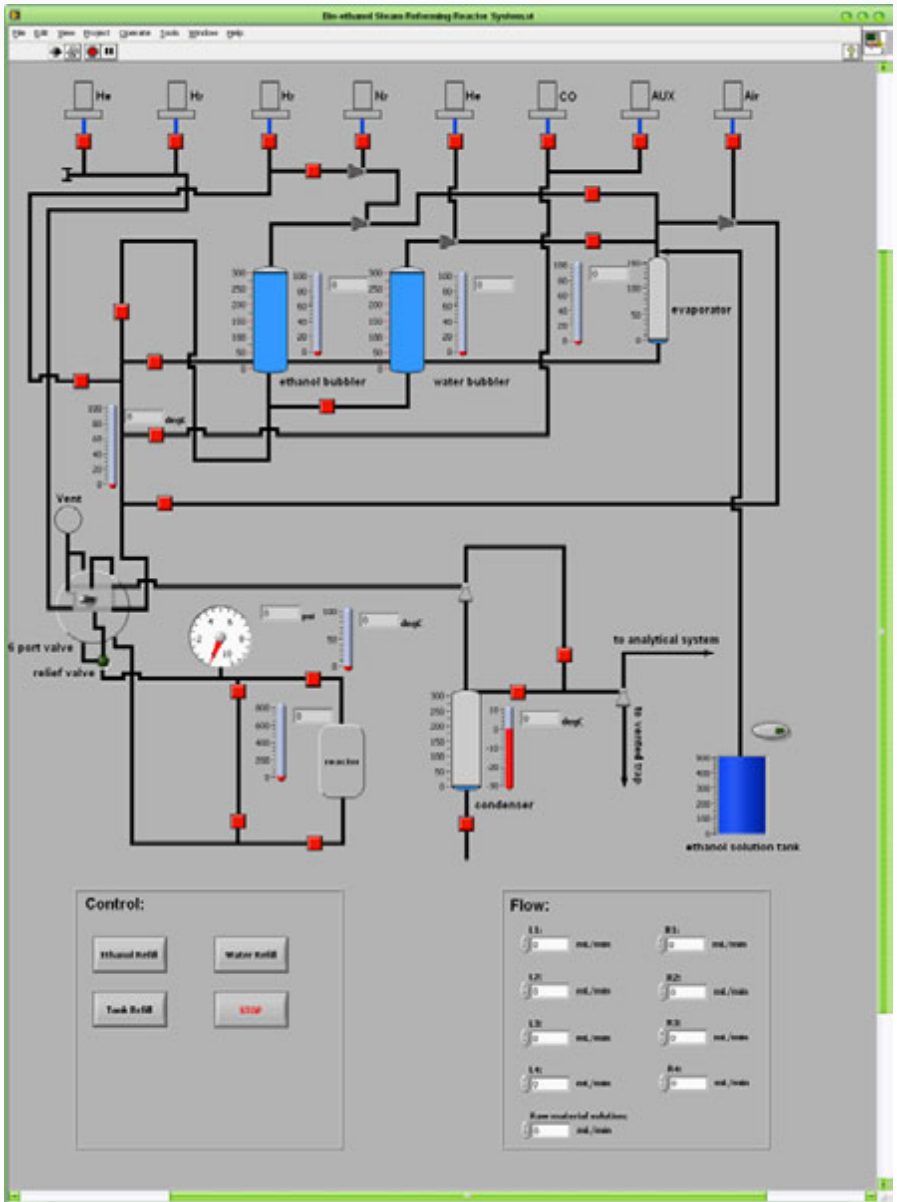
Reactor System: Designed and built

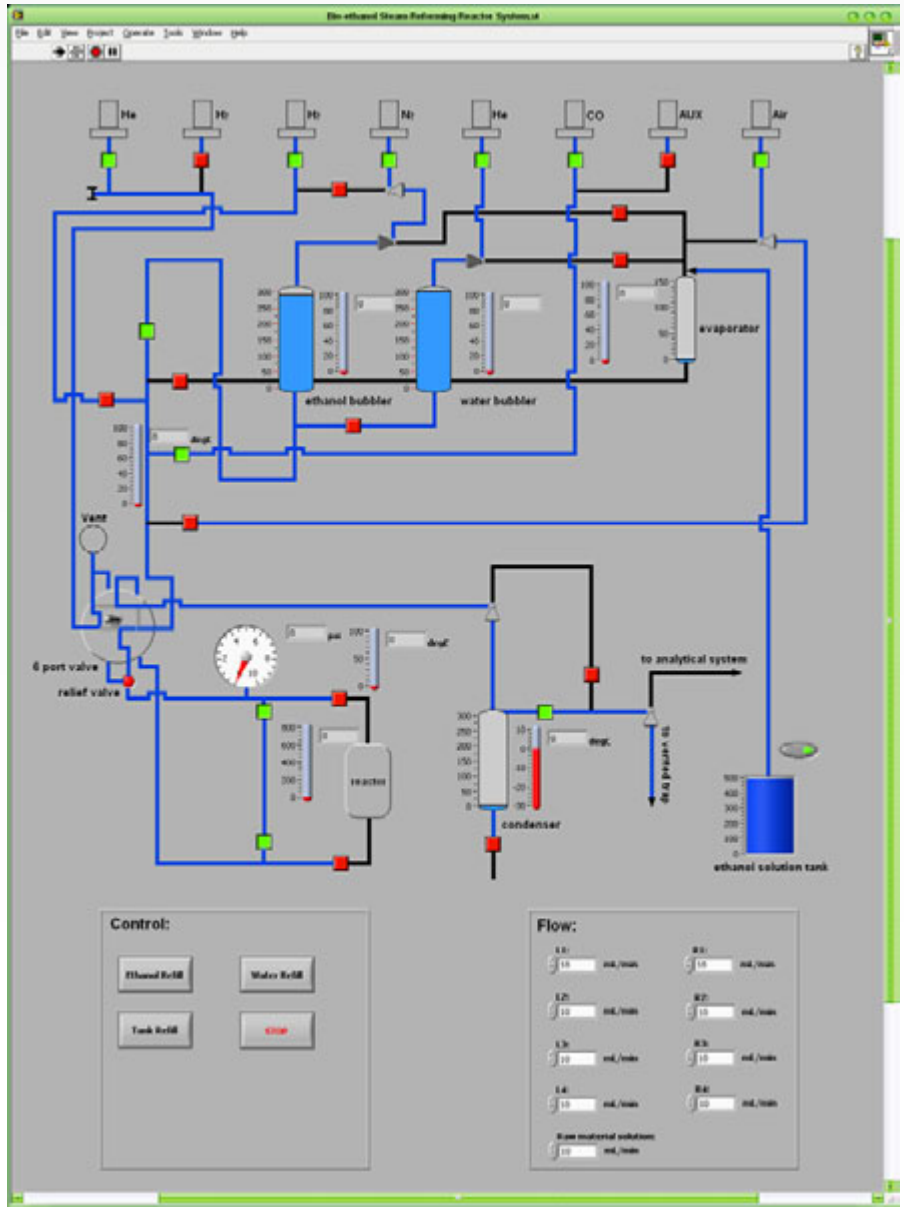




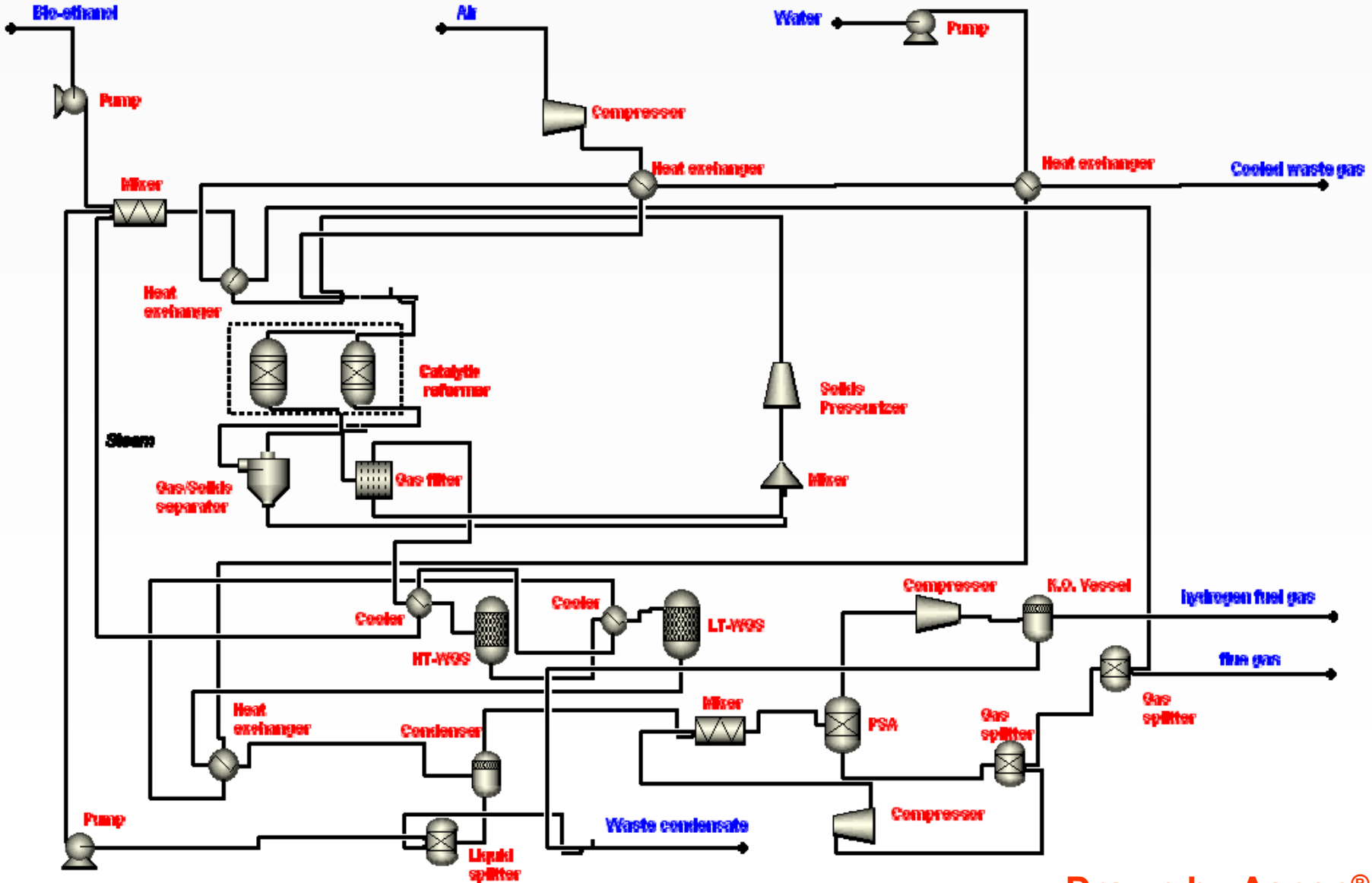


System automation and User Interface using labView





Preliminary Flow Chart for Economic Analysis



Drawn by Aspen®

Thermodynamic Analysis

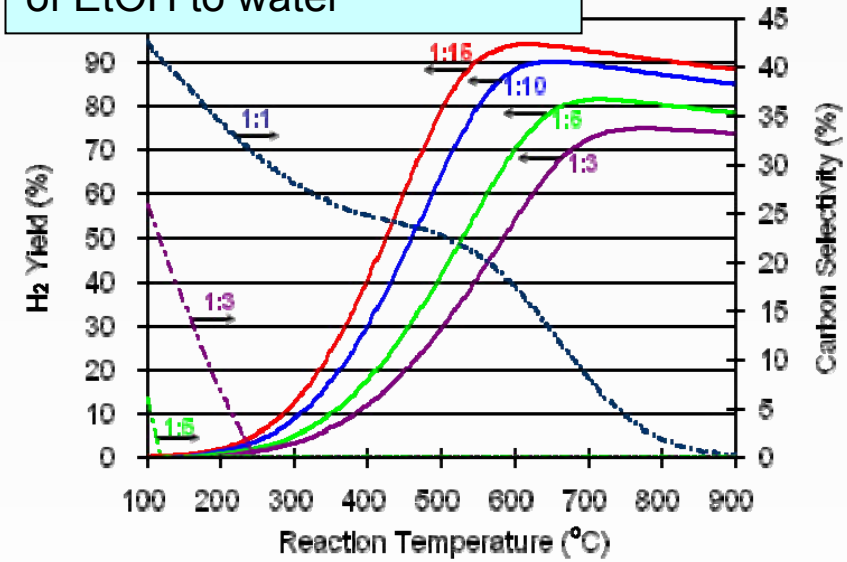
Definitions

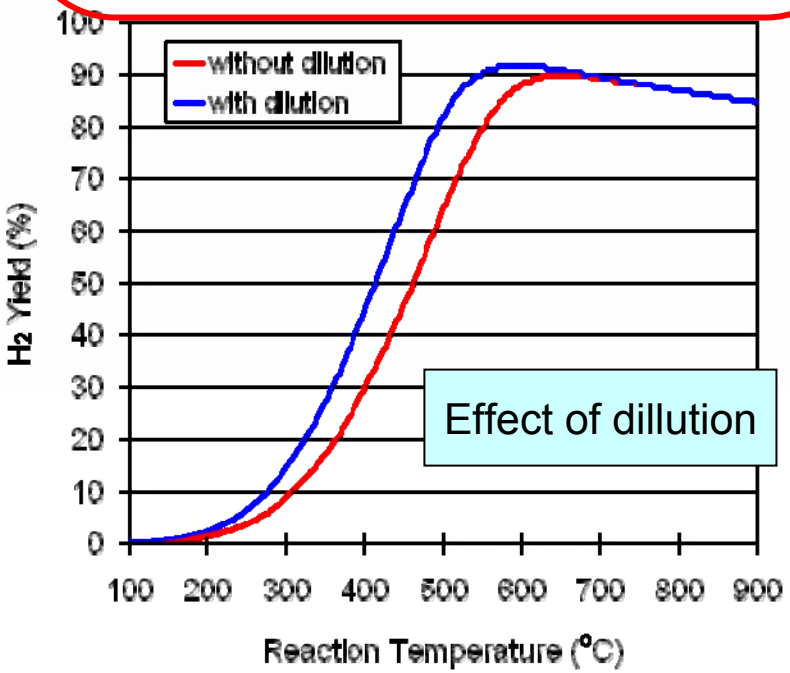
$$H_2 \text{ Yield } \% = \frac{\text{mol of } H_2 \text{ produced}}{\text{mol of EtOH fed} \times 6} \times 100$$

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

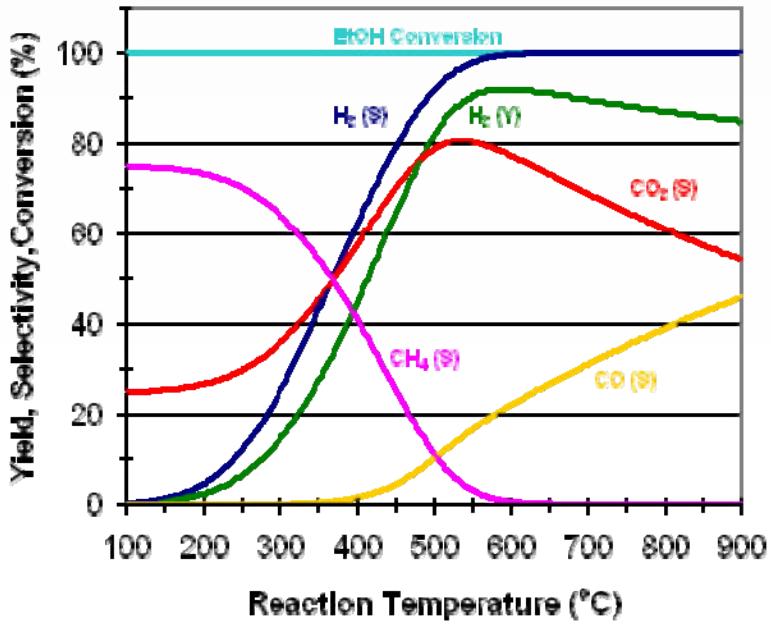
$$\text{Conversion } \% = \frac{\text{mol of EtOH converted}}{\text{mol of EtOH fed}} \times 100$$

Effect of different molar ratio of EtOH to water





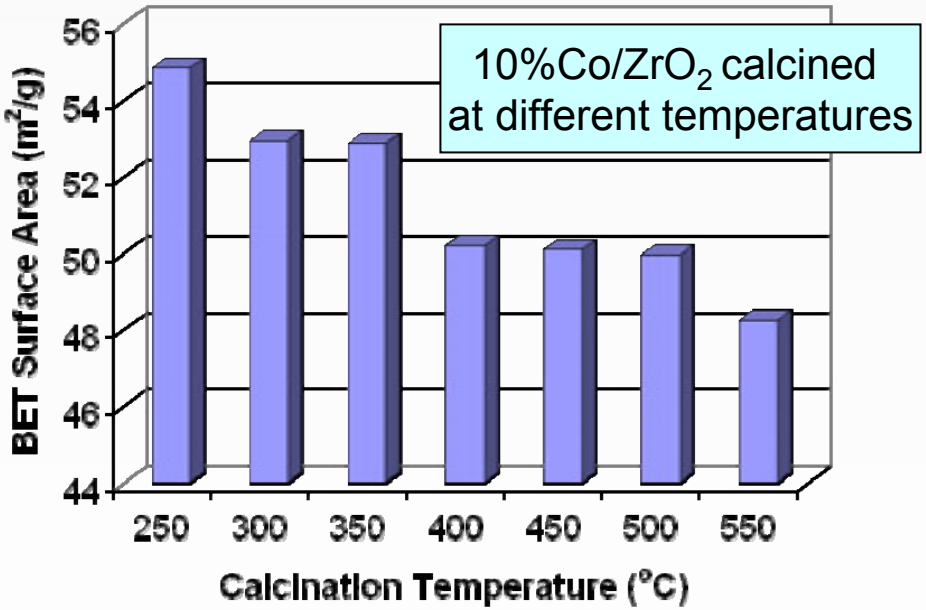
Effect of dillution

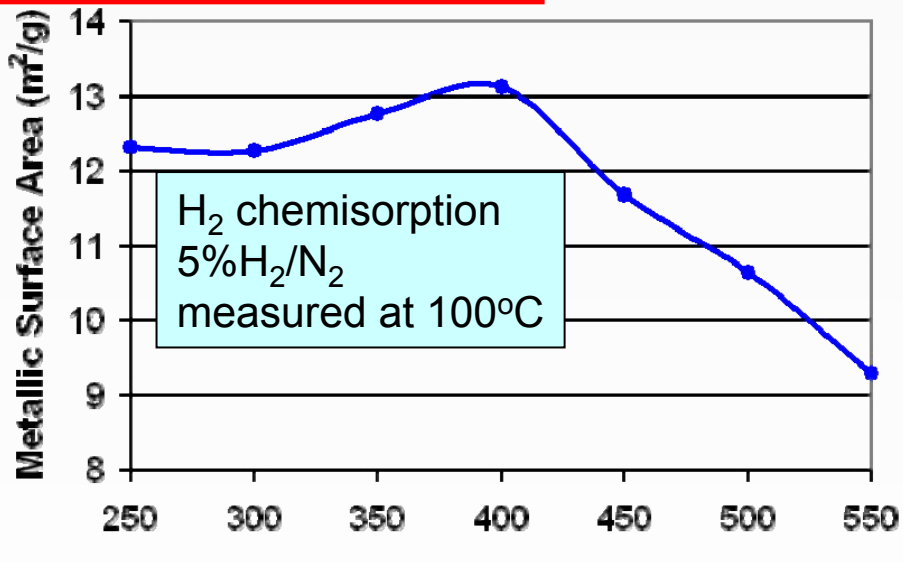


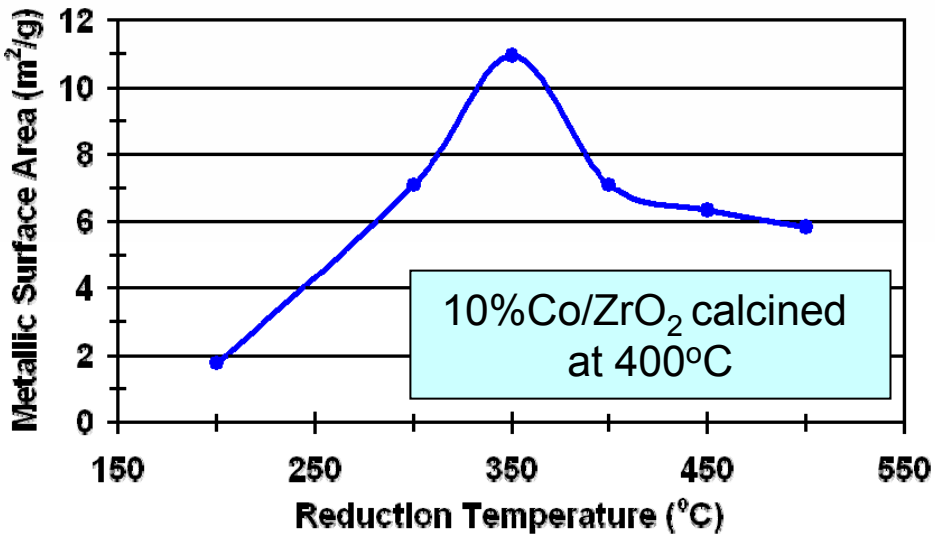
Technical Accomplishments/Progress/Results from Year 1

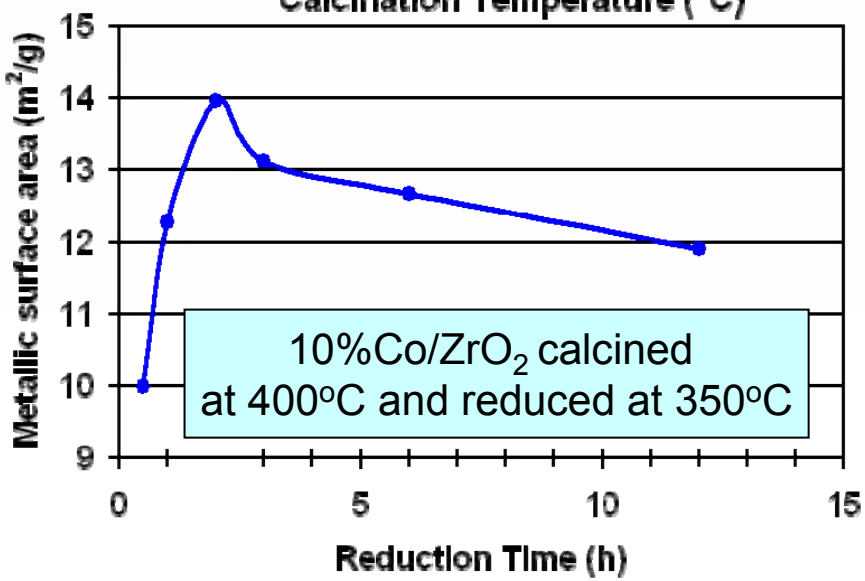
Effect of synthesis parameters

Optimum in Calcination T, Reduction T and Reduction time





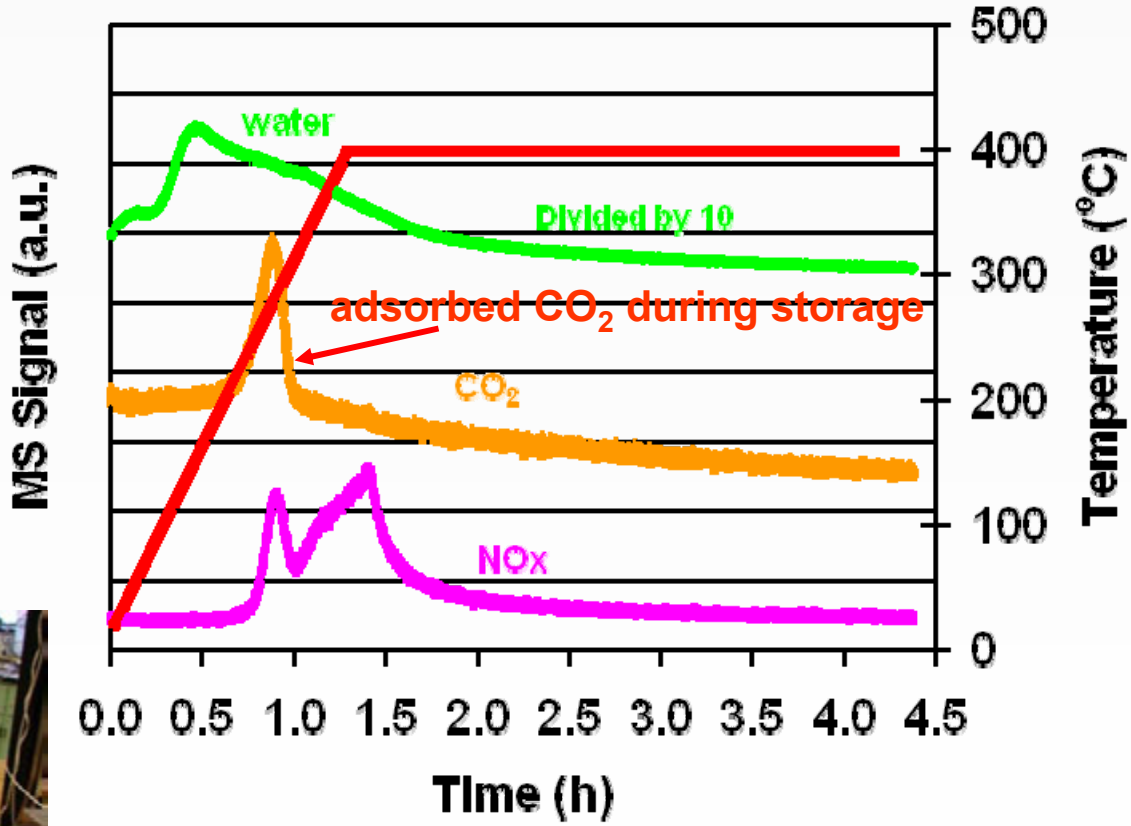




Mass spectrometry duringTemperature-programmed Calcination: Evolution of the catalyst precursor

In the current study:

- Ions followed:
  - 18 for water;
  - 44 for CO_2;
  - 30 for NOx;
  - 12 for verifying the assignment of 44 signal (not shown);



Cirrus MS

- **Sample:**
  - **10%Co/ZrO_2**
- **Calcination:**
  - **Temperature: 400°C;**
  - **Time: 3h;**
  - **Ramp rate: 5°C/min.**

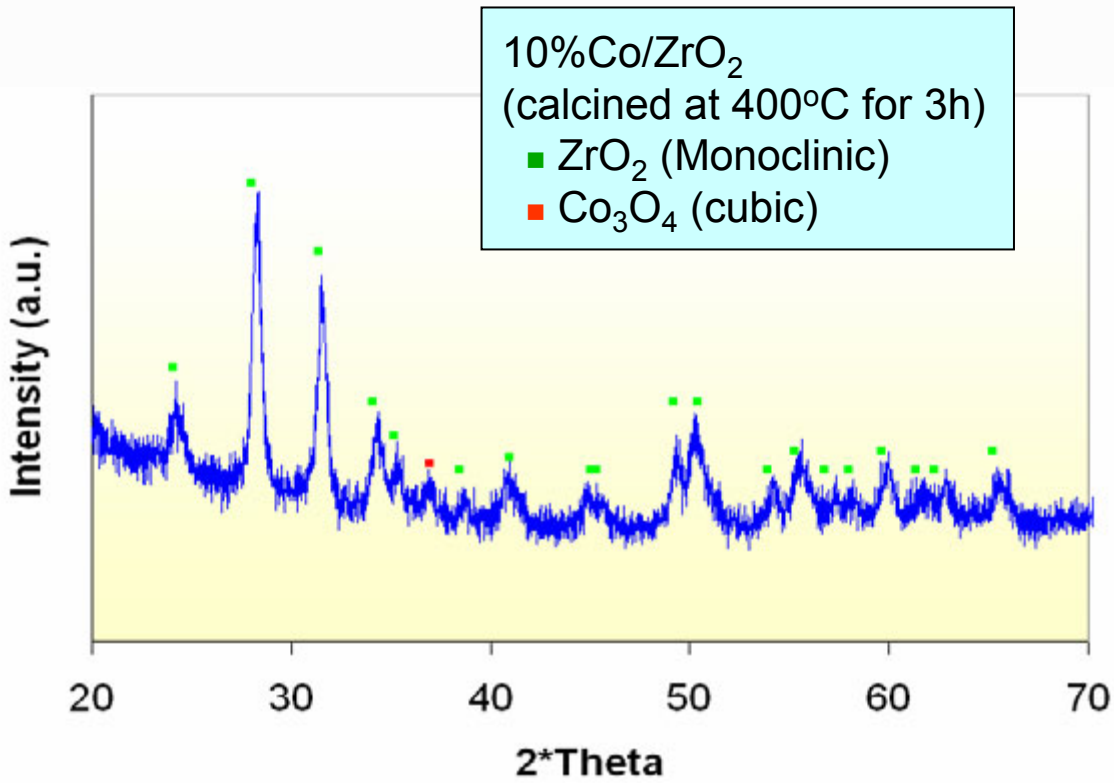
Technical Accomplishments/Progress/Results from Year 1

XRD Following Calcination

Crystalline phase of the support: Monoclinic
Catalyst phase: well-dispersed, not highly crystalline

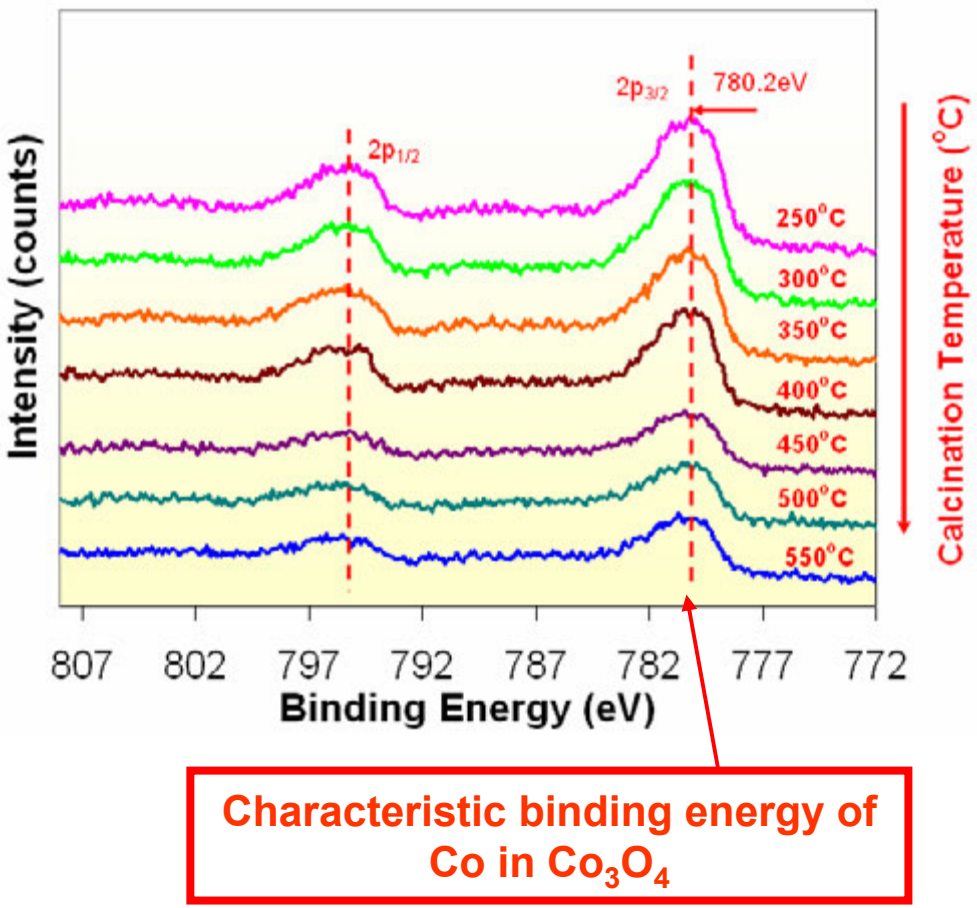
Bruker D8 Advance Diffractometer

Monochromatic Cu Ka1 X-ray source (1.5406 Å)



X-ray photoelectron spectroscopy following calcination

10%Co/ZrO_2
calcined at different temperatures for 3h



Characteristic binding energy of Co in Co_3O_4

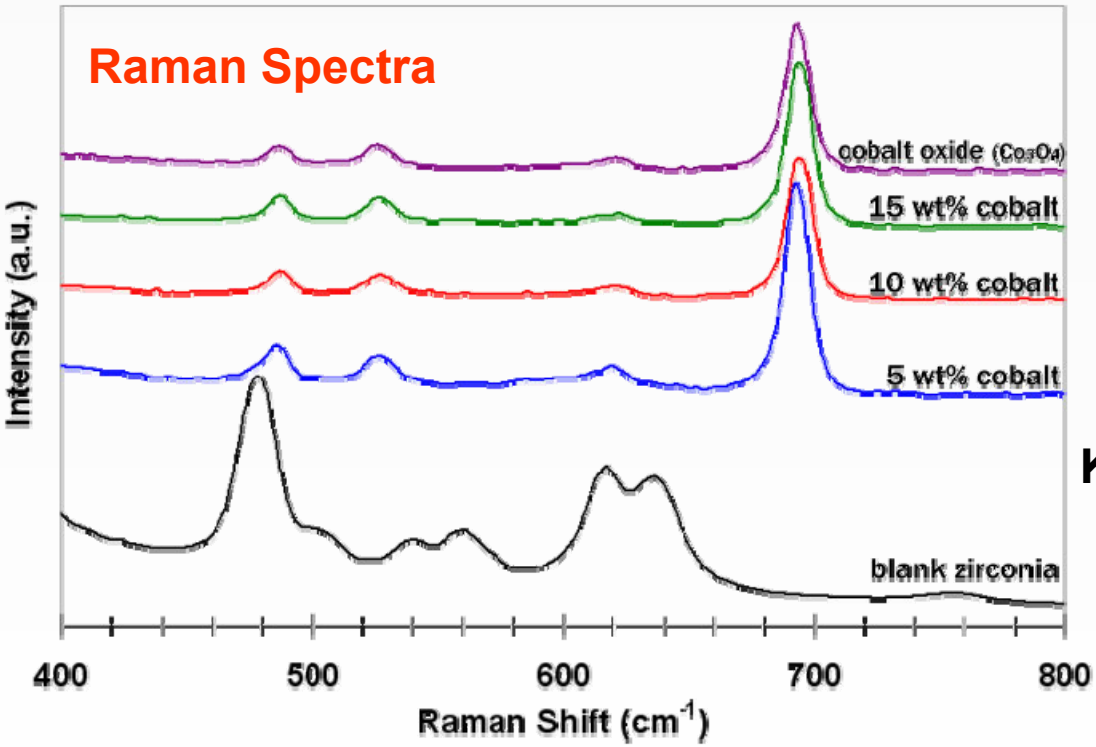
Kratos Axis Ultra XPS

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.

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

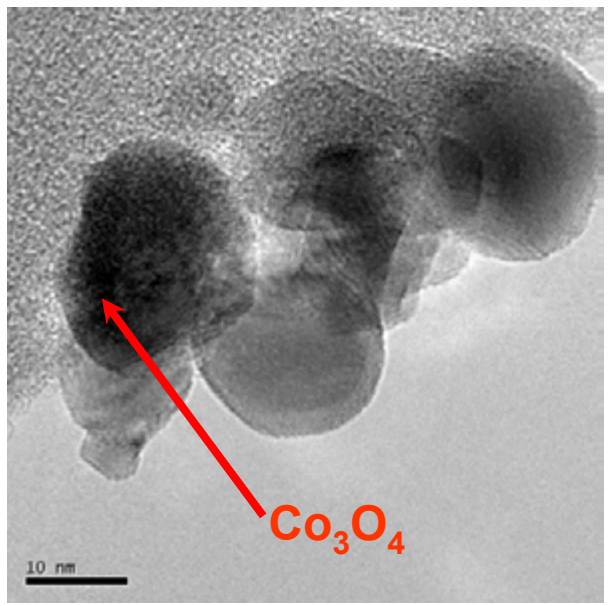
Tecnai TF-20 TEM

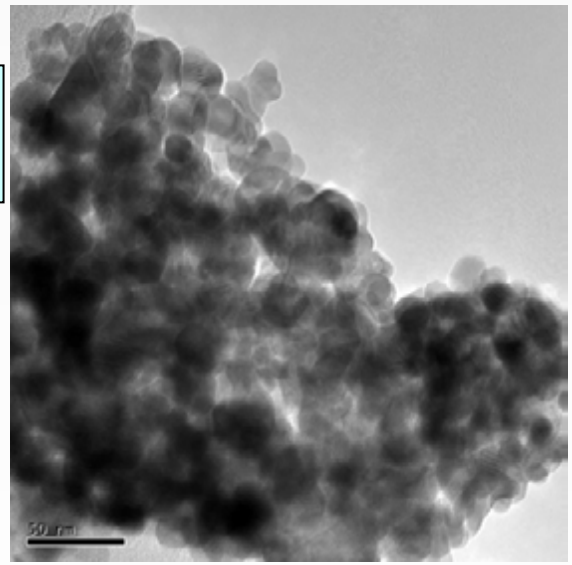
In the current study:

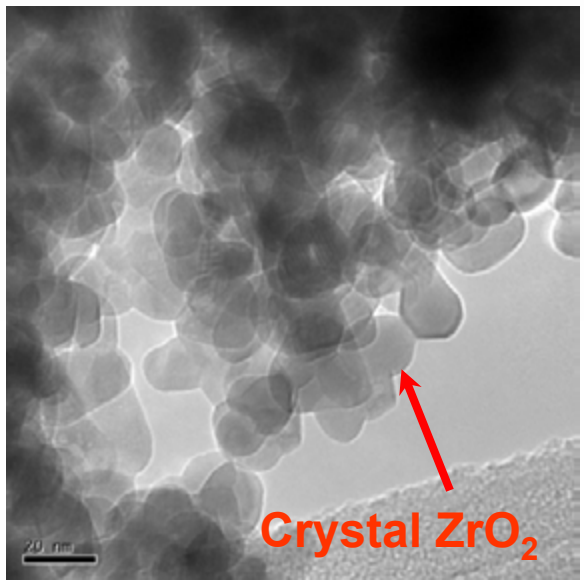
- Samples were dispersed in ethanol.
- Supported by lacey-formvar carbon on a 200 mesh Cu grid.

10%Co/ZrO_2
calcined at 400°C for 3h

- **Average Particle size of Co_3O_4:**
  24nm;



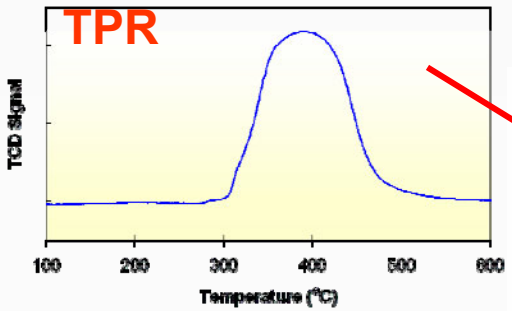




Technical Accomplishments/Progress/Results from Year 1

Reduction Characterization by Temperature - programmed Reduction

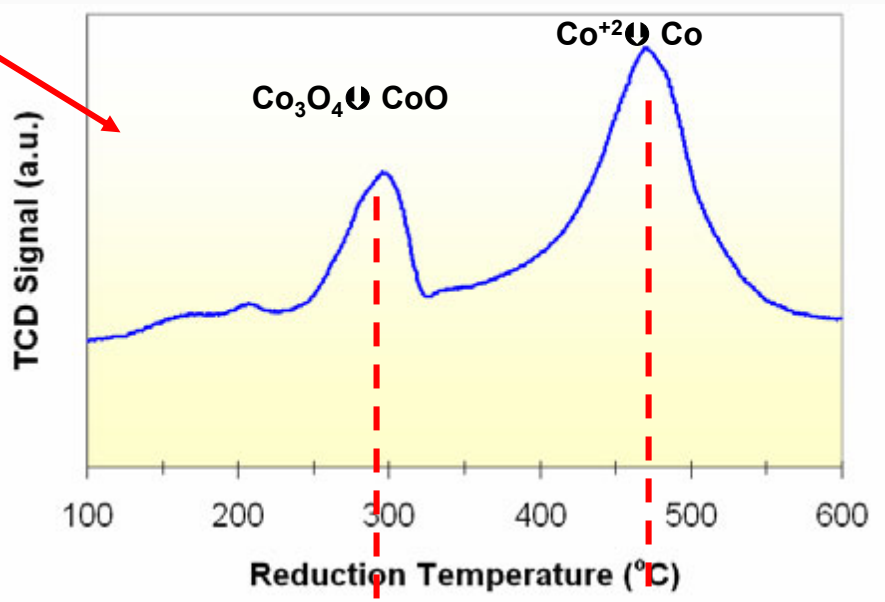
CuO as the Standard for Hydrogen Consumption



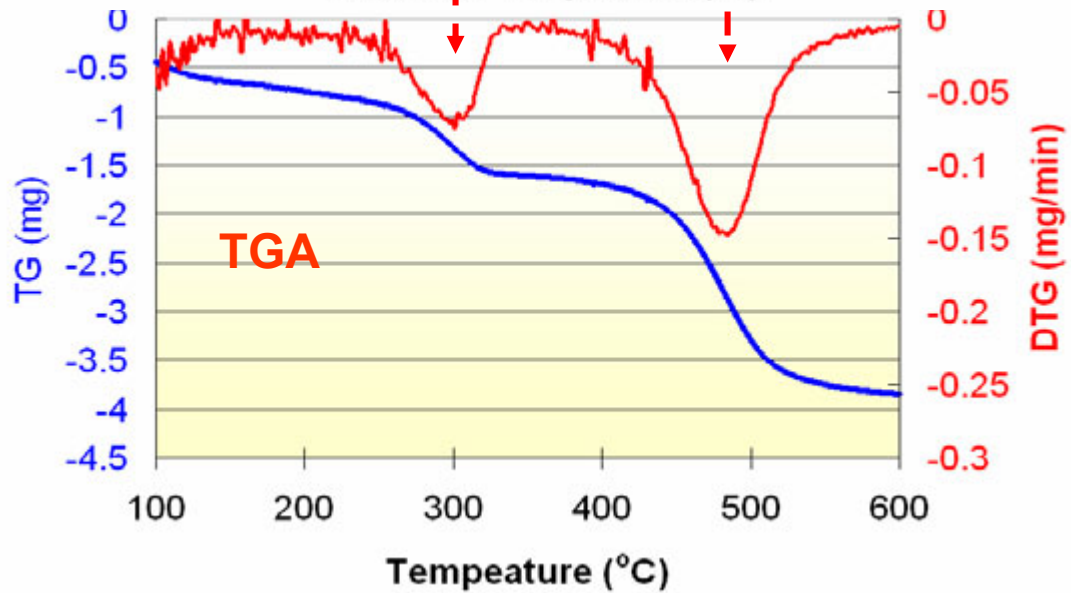
In the current study:

10%Co/ZrO_2
Calcined at 400°C for 3h;
Reduced under 5%H_2/N_2
at ramping rate of 5°C/min.;

Reduction proceeds in two discrete steps.

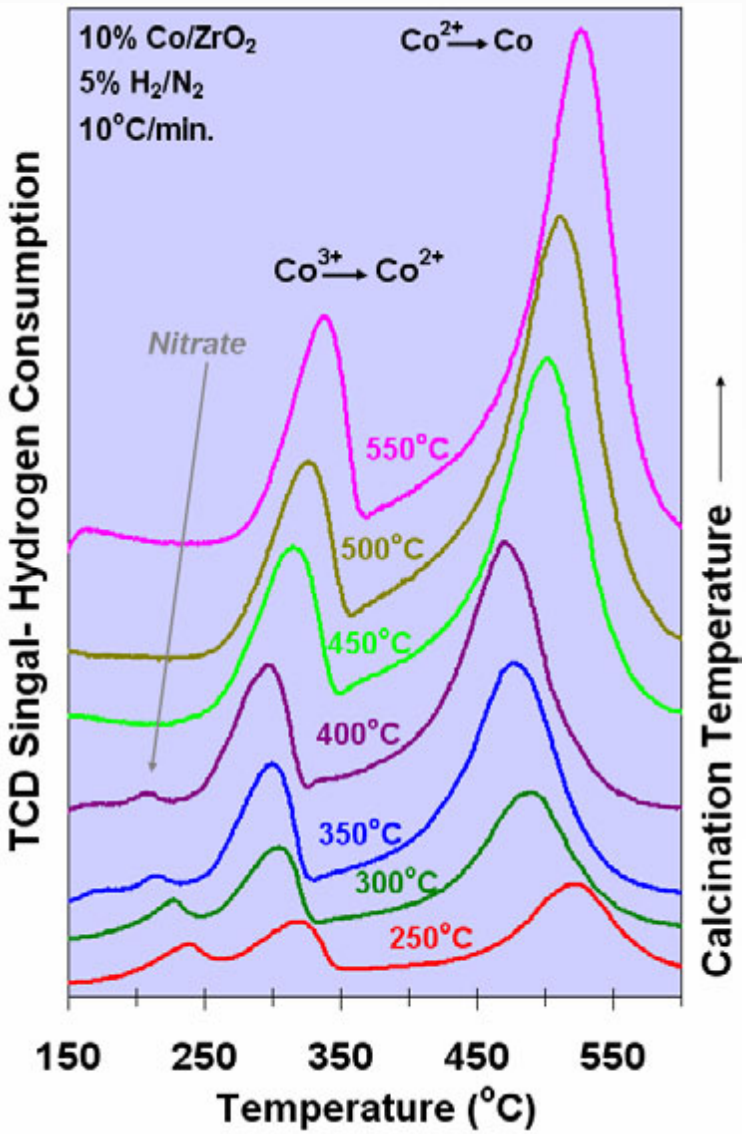


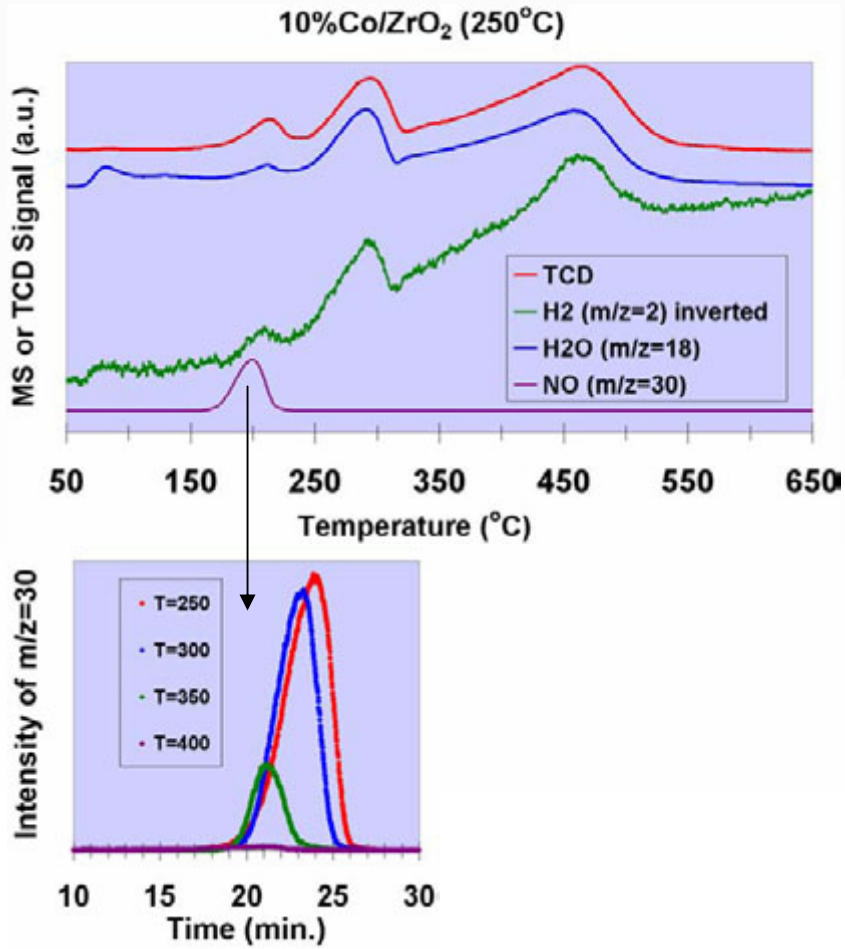
Setaram TGDSC-111



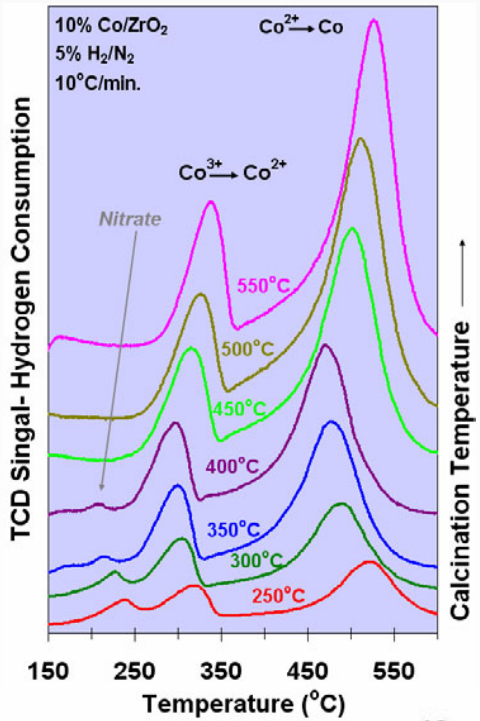
Reduction Behavior-TPR

Nitrate evolution observed during reduction using Mass Spectrometry experiments

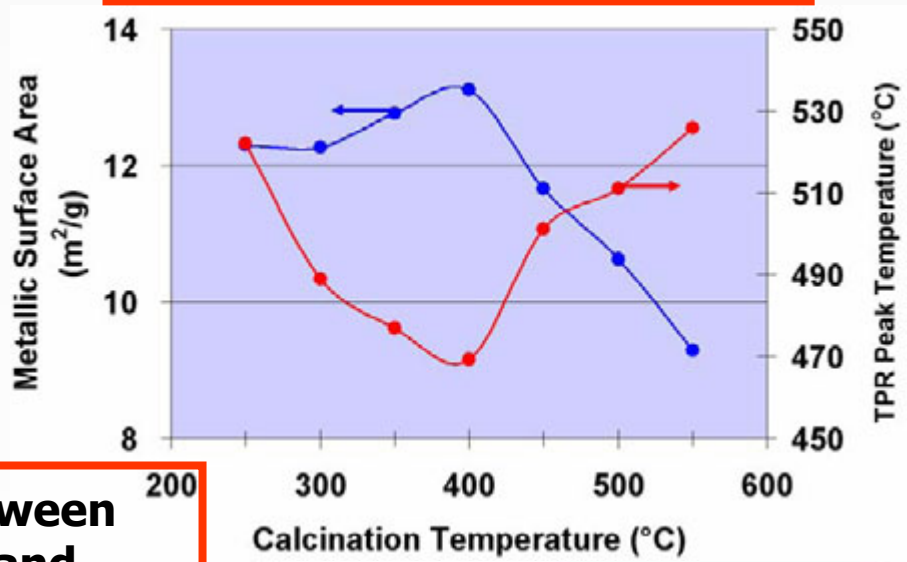




Effect of Reduction Process

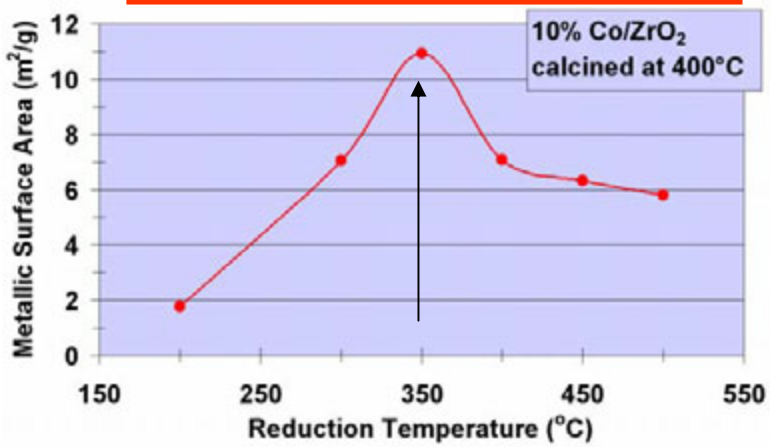


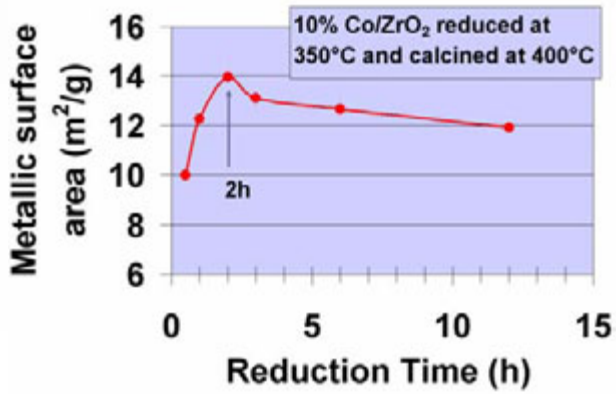
Correlation between dispersion and reducibility



Correlation between reduction and cobalt dispersion

- **Reduction time (GHSV H_2) and temperature important also**

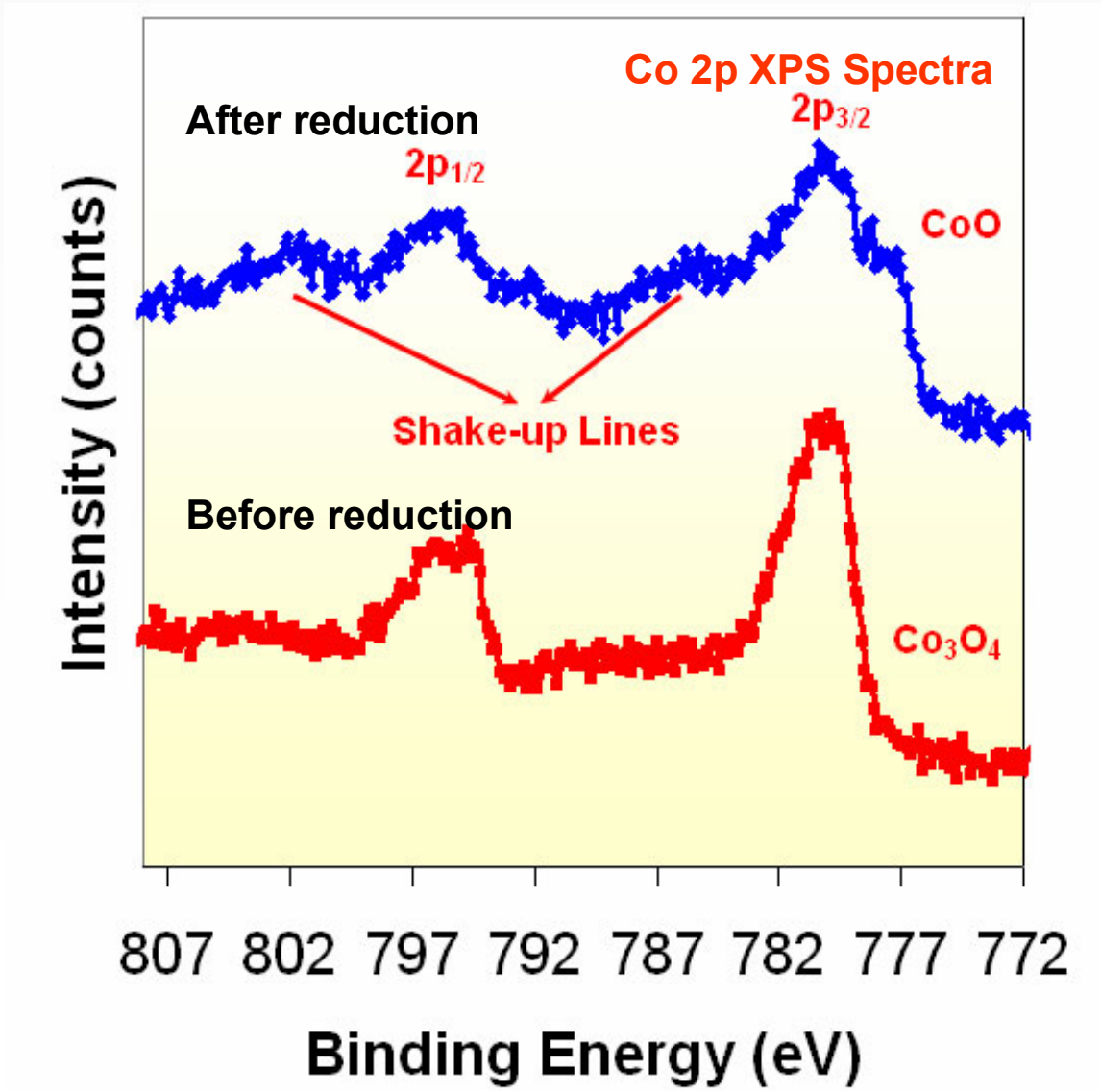




Reduction Characterization using X-ray photoelectron spectroscopy

Following reduction, Co is in +2 oxidation state.

- **Sample:**
  - **$10\%Co/ZrO_2$**
- **Calcination:**
  - **Temperature: 400°C;**
  - **Time: 3h;**
- **Reduction:**
  - **Temperature: 350°C;**
  - **Time: 2h;**
- **XPS:**
  - **X-Ray source: (Al $K_{\alpha 1}$);**

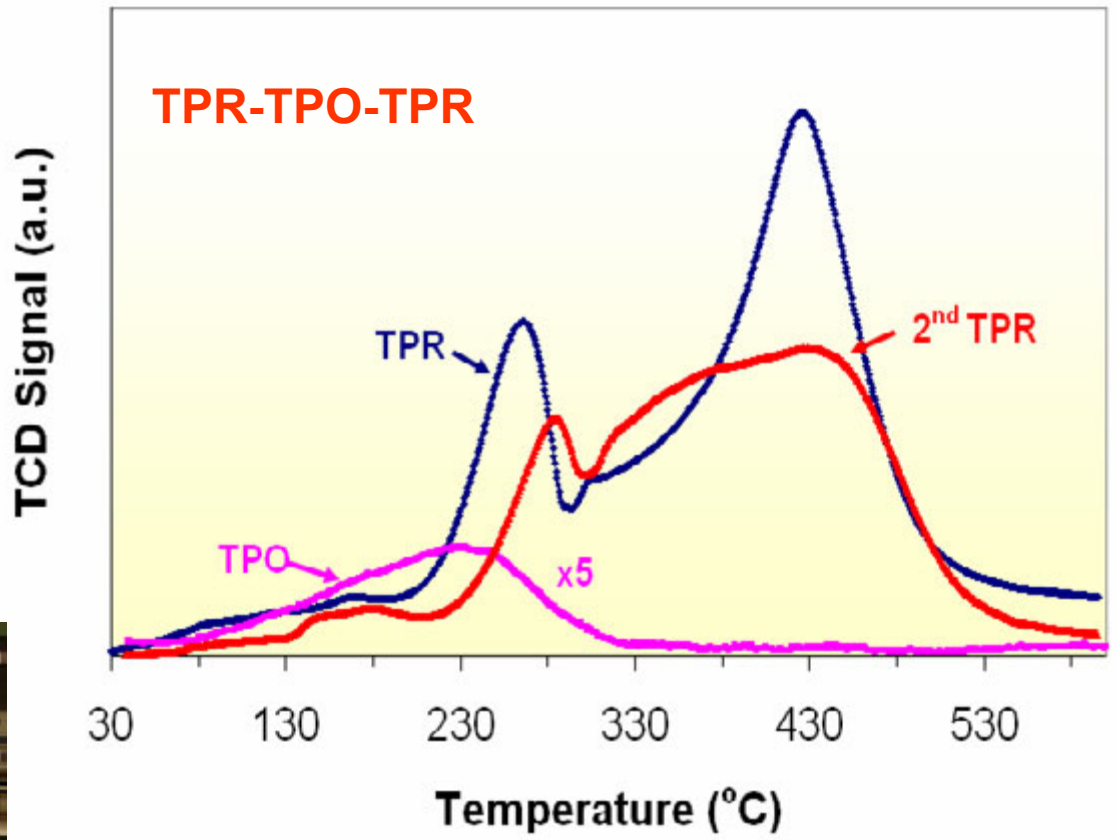


Technical Accomplishments/Progress/Results from Year 1

Reduction Characterization through consecutive TPR-TPO-TPR

Higher reduction temperatures could lead to sintering.

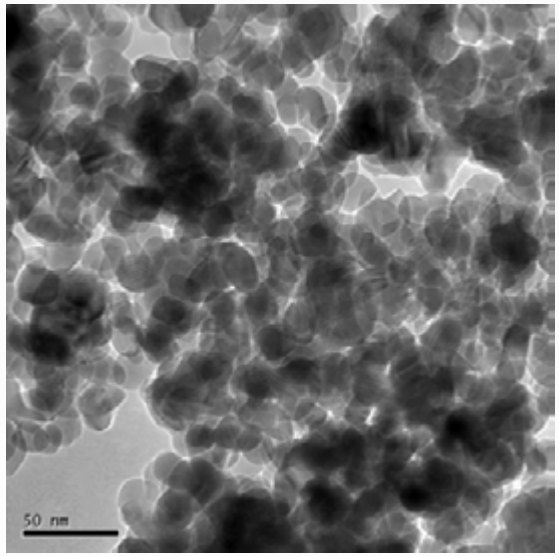
- **Sample:**
  - **10%Co/ZrO_2;**
- **Calcination:**
  - **Temperature:400°C;**
  - **Time: 3h;**
- **1st TPR**
  - **Reduction gas: 10%H_2/He;**
  - **Ramp rate:10°C/min.;**

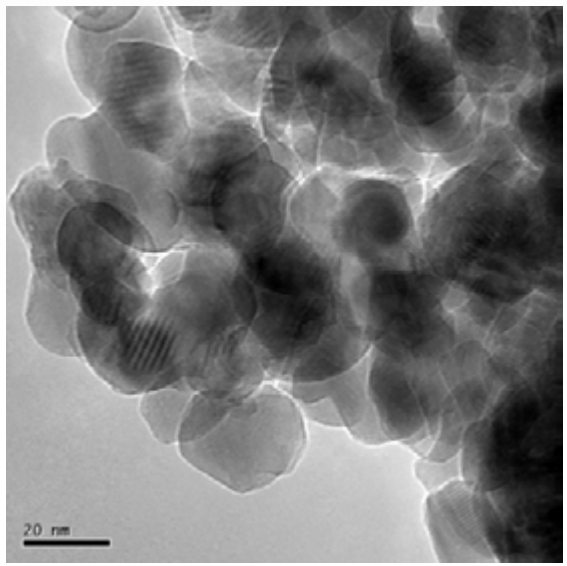


- **TPO**
  - **Temperature: up to 600°C;**
  - **Oxidization gas: 10%O_2/He;**
  - **Ramp rate: 5°C/min.;**
- **2nd TPR**
  - **Same as the 1st run;**

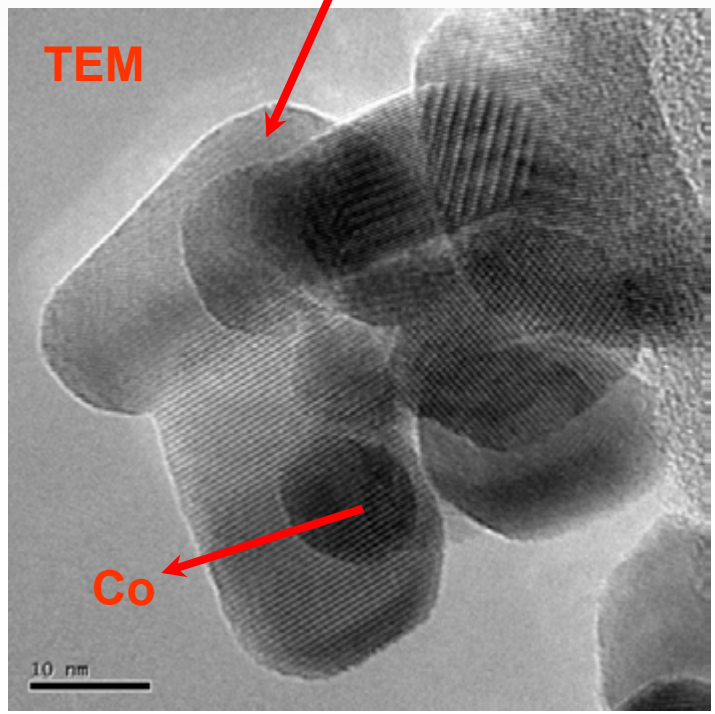
TEM Following Reduction

- **Sample:**
  - 10%Co/ZrO_2
- **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.

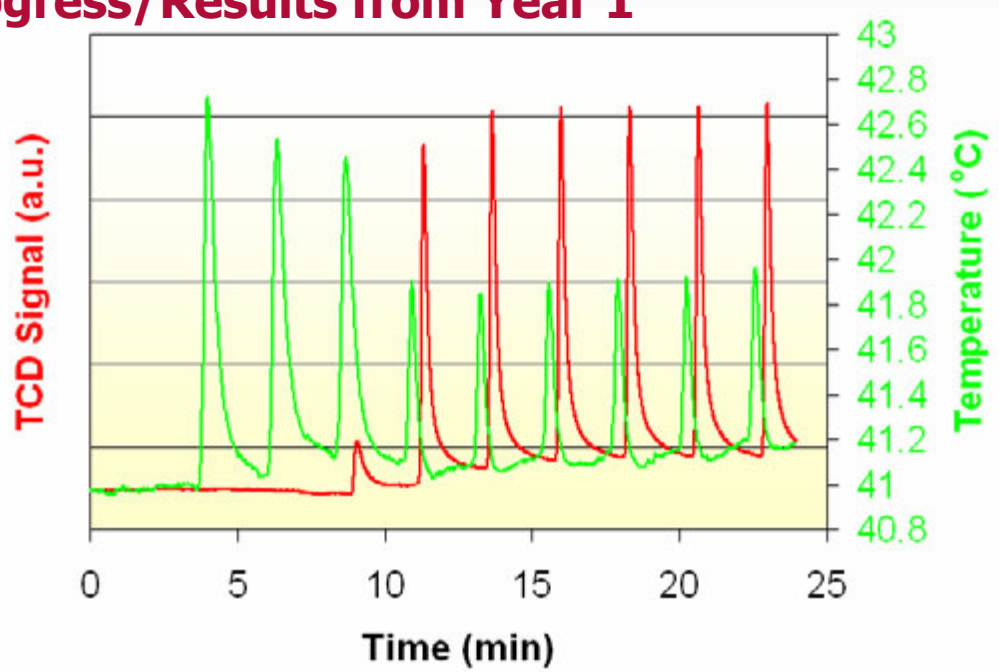


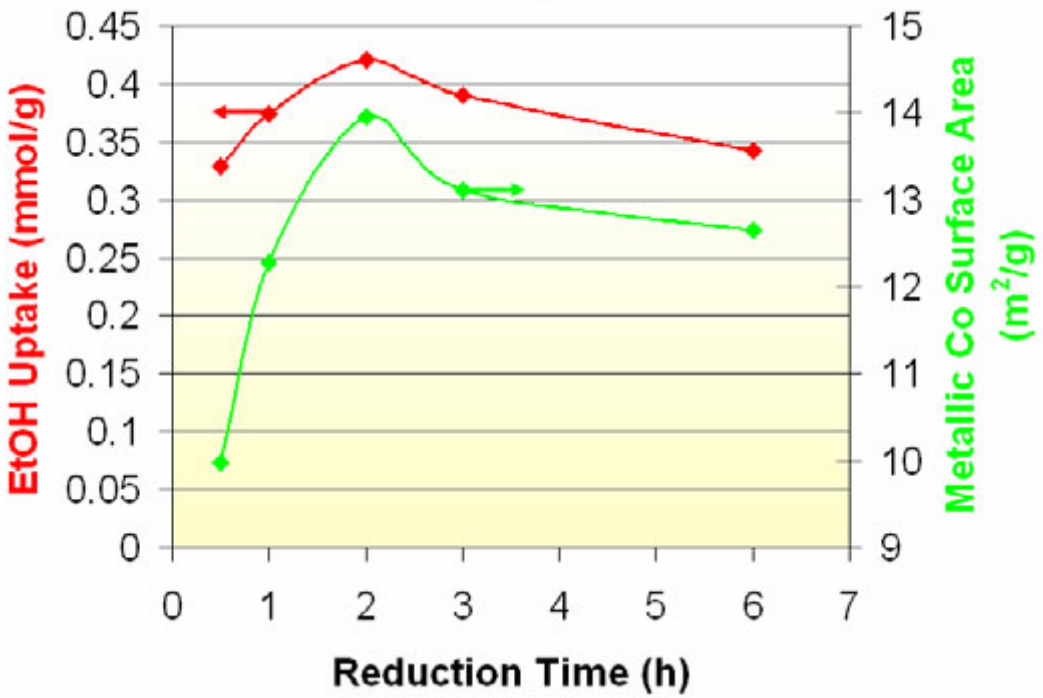
Technical Accomplishments/Progress/Results from Year 1

Characterization of Ethanol Adsorption Behavior by Pulsed Chemisorption

Strong correlation exists between ethanol uptake and metallic surface area.

- **EtOH Pulse Chemisorption:**
  - 10%Co/ZrO_2(calcined at 400°C);
  - Reduced at 350°C for different time;
  - Pulsed ethanol vapor injection at room temperature;



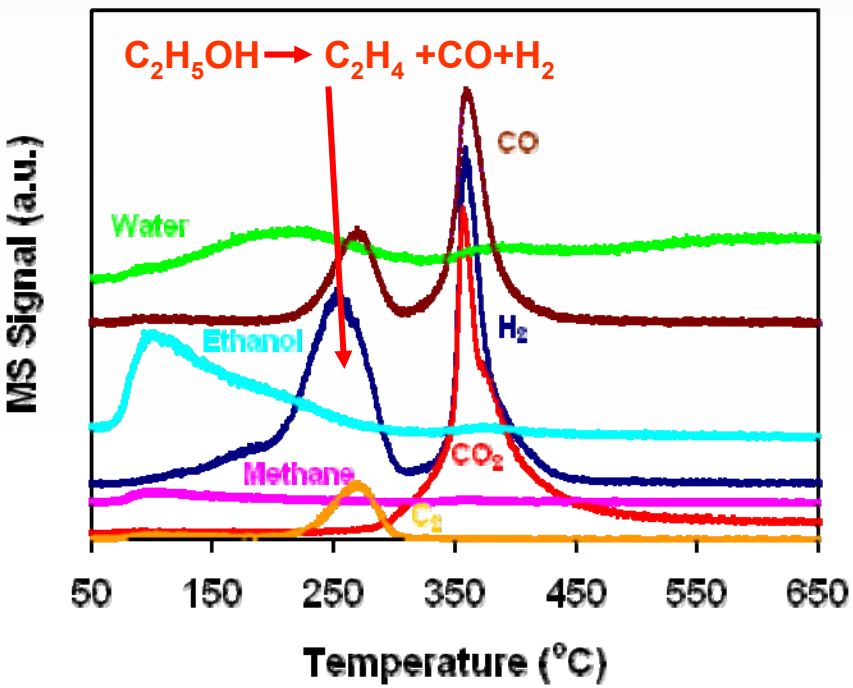


Technical Accomplishments/Progress/Results from Year 1

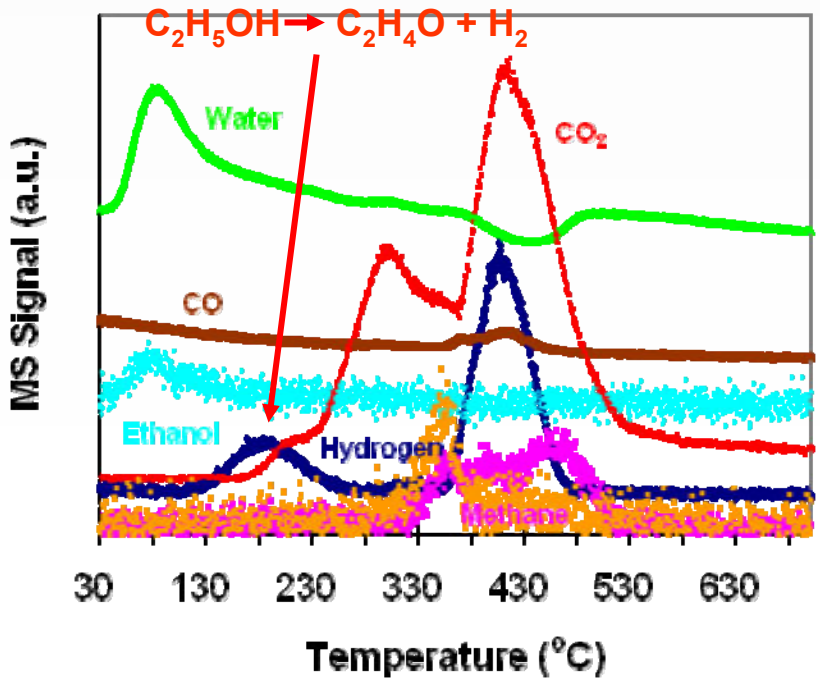
Characterization of competing reactions: Temperature-programmed Desorption

Different reactions dominate at different temperature regions.

- **Sample:**
  - 10%Co/ZrO_2;
- **Calcination:**
  - 400°C for 3h;
- **Reduction:**
  - 350°C for 2h;
- **Before reaction:**
  - Flowing EtOH for 1h;



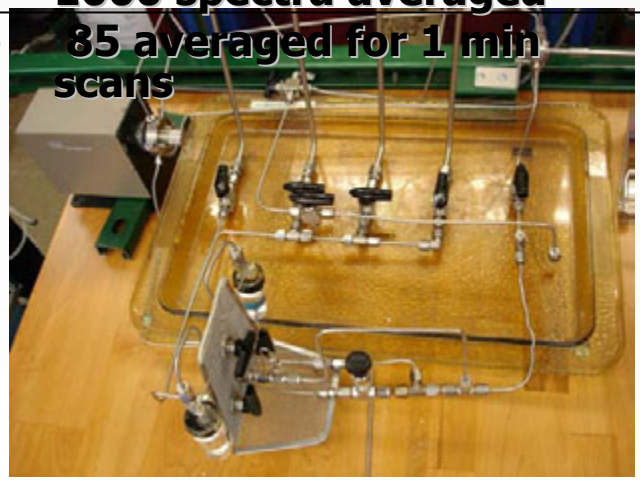
- **Sample:**
  - 10%Co/ZrO_2;
- **Calcination:**
  - 400°C for 3h;
- **Reduction:**
  - 350°C for 2h;
- **Before reaction:**
  - Flowing mixture of EtOH:H_2O(1:10) for 1h



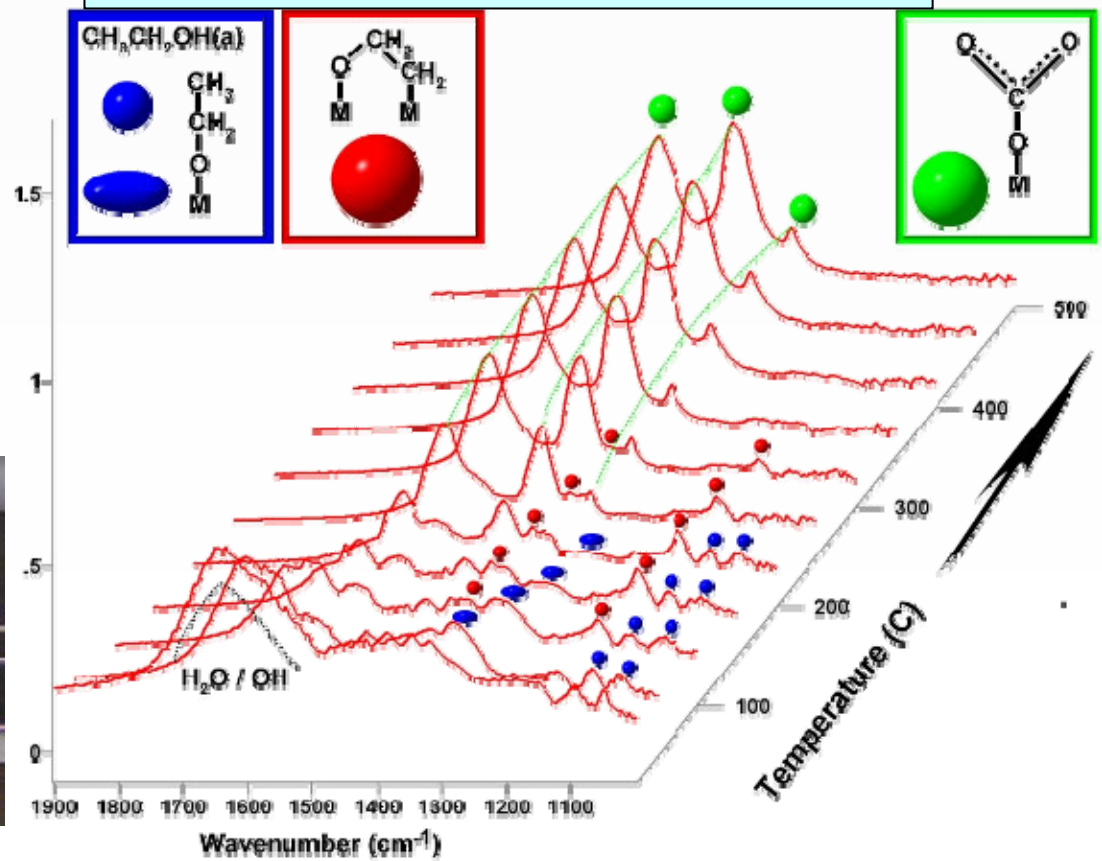
In-situ DRIFTS-TPRxn

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**

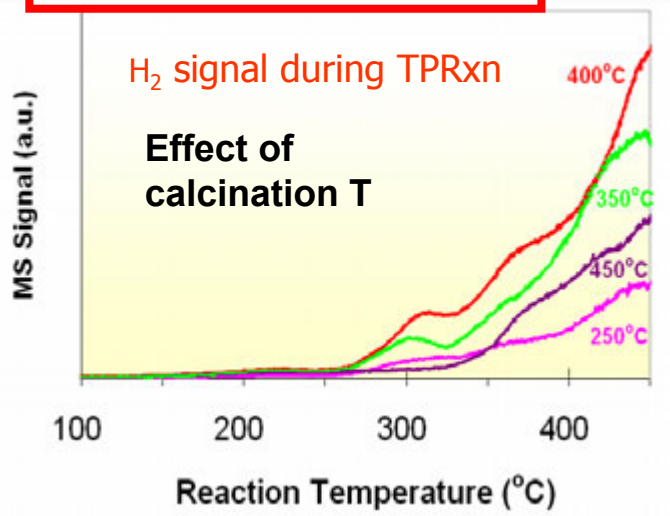


10%Co/ZrO_2 ; Calcined at 400°C/12h;
Reduced at 350°C under 5%H_2/He for 1h;
Ethanol +water adsorption at room T for 1h;
Spectra taken during TPRxn at 10°C/min under He flowing at 30ml/min.



Temperature Programmed Reaction

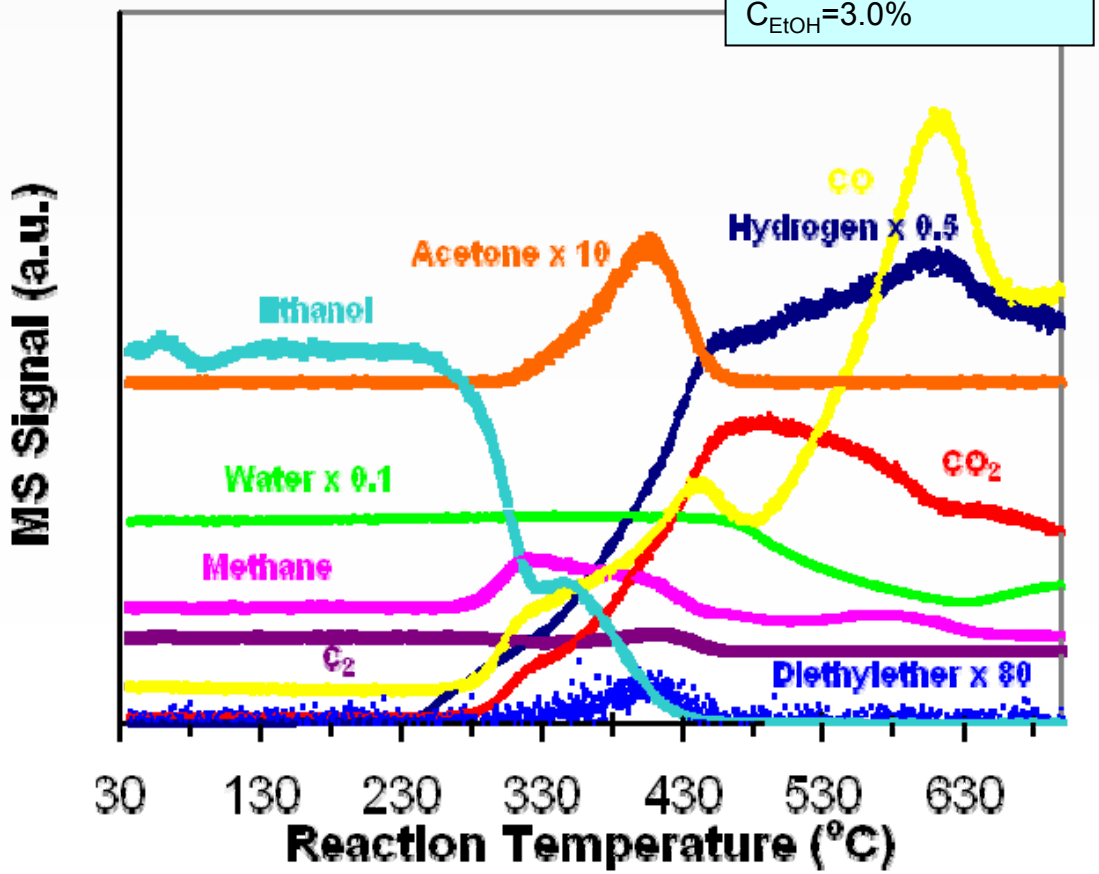
Calcination temperature has a strong effect on the H_2 yield.



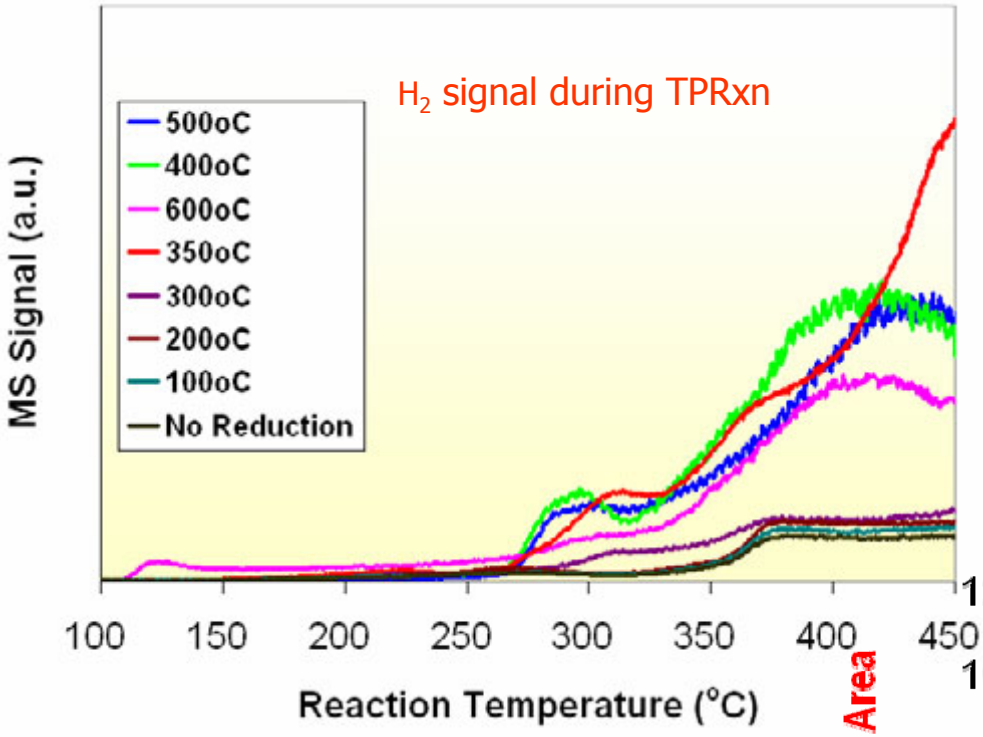
MKS Cirrus Mass Spectrometer

Different reactions dominate at different temperature regions.

10%Co/ZrO_2; Reaction mixture of EtOH and water (1:10 molar) in He GHSV=15065h^{-1}; C_{EtOH}=3.0%

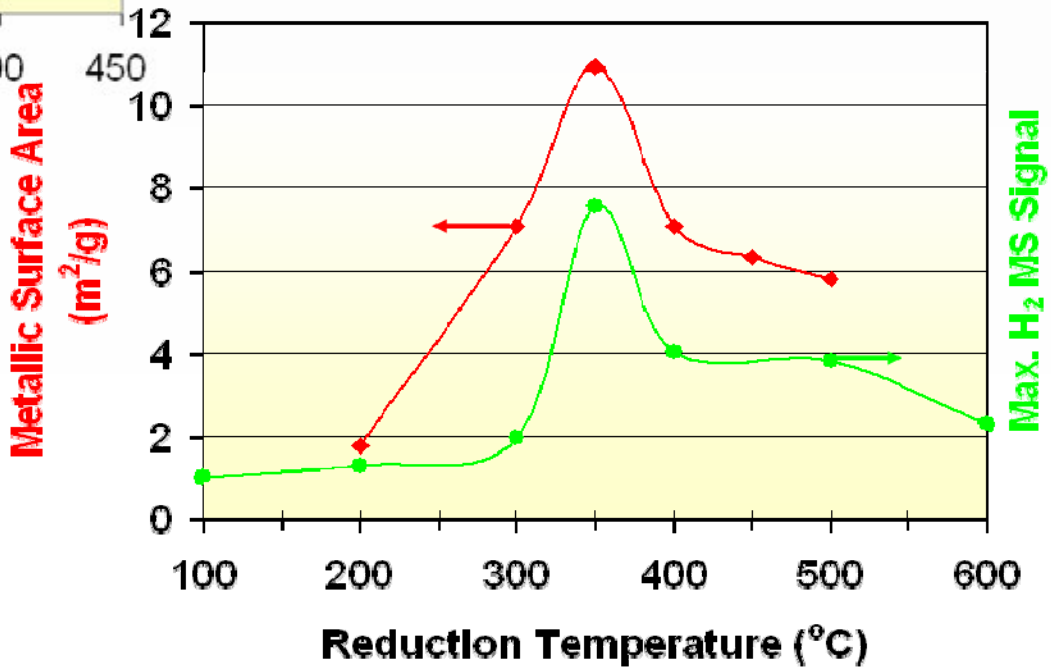


Temperature Programmed Reaction



H_2 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

$$H_2\ \text{Yield}\ \% = \frac{\text{moles of } H_2 \text{ produced}}{6 \times (\text{moles of ethanol fed})} \times 100$$

Carbon containing product A Yield %:

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

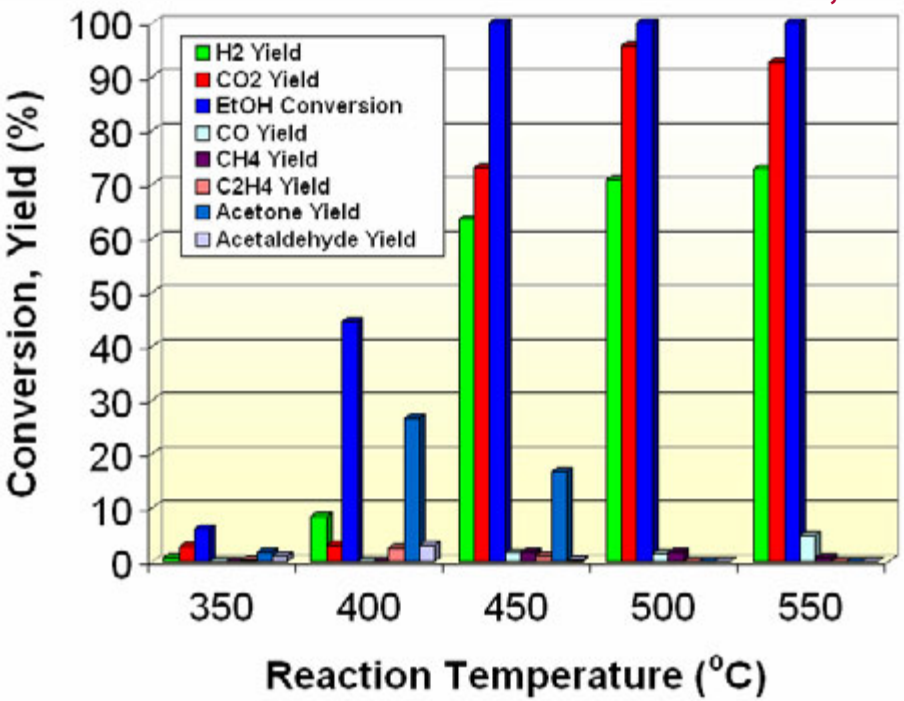
$$\text{EtOH Conversion}\ \% = \frac{\text{moles of ethanol converted}}{\text{moles of ethanol fed}} \times 100$$

Demonstrated high H_2 yields (over 70%) at GHSVs approaching 100,000 hr^{-1} (significantly higher than those reported earlier).

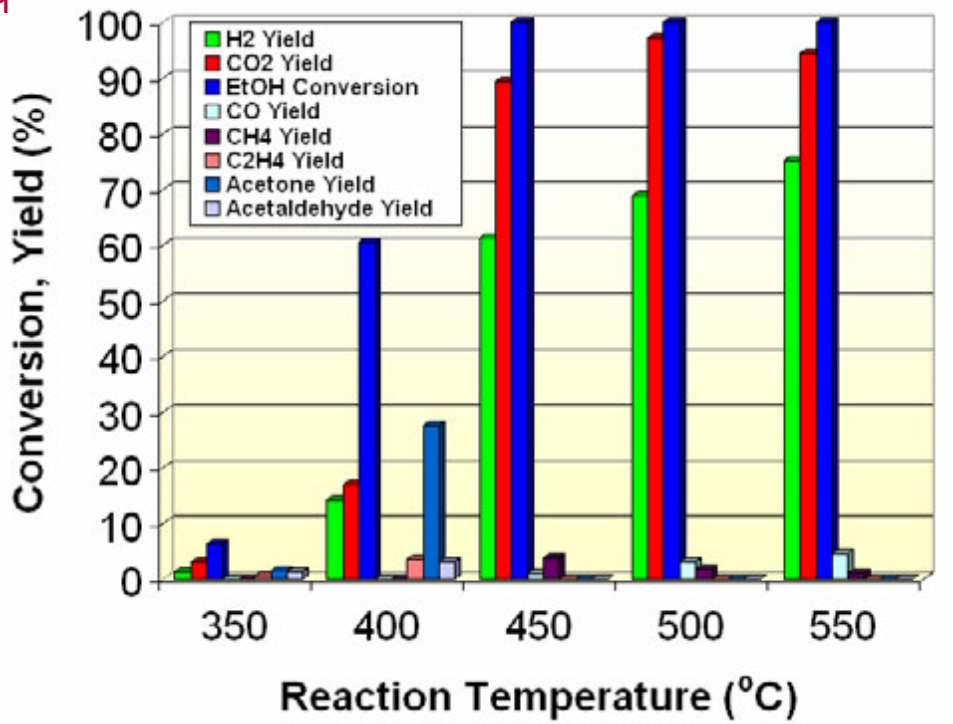
Reaction Conditions:

10%Co/ZrO_2(400°C);
Reduced under 5%H_2/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 H_2 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.

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