

# Bio-derived Liquids Reforming

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## Timeline

- ▶ Project start date: Oct. 1, 2004
- ▶ Two projects consolidated in 2007
  - Aqueous phase reforming of sugar and sugar alcohols
  - Vapor phase reforming of ethanol
- ▶ Project end date: September 2009
- ▶ Percent complete: 80%

## Budget

- ▶ Funding received in FY04: \$100K
- ▶ Funding received in FY05: \$500K
- ▶ Funding received in FY06: \$0K
- ▶ Funding for FY07: \$550K
- ▶ Funding for FY08: \$600K
- ▶ Funding for FY09: \$600K

## Barriers

- A: Reformer Capital Cost
- C: Operation & Maintenance
- D: Feedstock Issues
- E. Greenhouse Gas Emissions

Target: Hydrogen Production Cost  
2012: \$3.80/gge  
2017: <\$3.00/gge

## Collaborations

- ▶ Virent Energy Systems –Exchange of technical information, collaboration on catalyst characterization

# Overall Approach Hydrogen Production From Reforming Of Bio-derived Liquids

## ► Agriculture

- Rotational crops
- Energy crops (switch grass, poplar, etc)
- Oil crops
- Rotational crop residue
- (stover, wheat & rice straws, etc)

## ► Forest residue

## ► Municipal solid waste

## ► Animal waste

Hemi-cellulose

Cellulose

Hydrolysis:  
Acid or  
Enzymatic

C5, C6 sugars:  
Xylose, Arabinose  
Glucose  
Or sugar alcohols

Gasification

Lignin

Syngas  
CO + H<sub>2</sub>

Fermentation

Ethanol

ESR

Aq. reforming

Hydrogen

WGS

Hydrogen

- Hemicellulose- and cellulose- derived sugars and ethanol are used as feedstocks, and they are different in thermal stability and bond structures.
- Both vapor phase reforming of ethanol (ESR) and aqueous-phase reforming of sugars are studied to maximize the hydrogen productivity and selectivity.

# Specific Approaches

## *Aqueous phase reforming (APR):*

- ▶ Use glycerol as a model compound
- ▶ Improve hydrogen selectivity and productivity by understanding role of:
  - key catalyst components and carbon support
  - based addition on reaction pathways (pH, identify of base)
- ▶ Collaborate with Virent Energy Systems to develop fundamental catalyst understanding and guide improved catalyst formulations

## *Ethanol steam reforming (ESR):*

- ▶ Compare performance of two distinct catalysts and gain fundamental understanding of metal-support interactions
  - Rh/CeO<sub>2</sub>-MO<sub>2</sub> (precious metal)
  - Co/ZnO (base metal)
    - Carry out information exchange with Ohio State University to better define the needs in further catalyst development
- ▶ Demonstrate viability of low-to-moderate temperature reforming ( $\leq 550^{\circ}\text{C}$ ) under realistic operating conditions (no feed dilution, ambient-to-elevated P, close to stoichiometric S/C, high SV)
- ▶ Use the H<sub>2</sub>A analysis to guide the R&D effort and down-select single catalyst composition; propose go/no decisions

# 2009 Project Objectives: Relevance to DOE Hydrogen Program

**Overall Objective:** Evaluate and develop bio-derived liquid reforming technologies for hydrogen production that can meet the DOE 2017 cost target of <\$3.00 /gge

*Relevance to DOE hydrogen program*

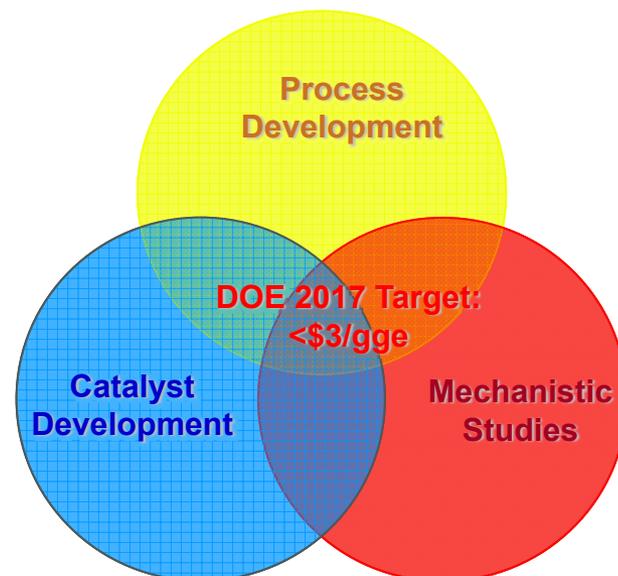
- ▶ *Domestic resource*
- ▶ *Distributed production*
- ▶ *Near-term introduction of H<sub>2</sub>*
- ▶ *Near-zero net GGE*

**Aqueous Phase Reforming (APR):** Improve overall catalyst activity, selectivity, and life

**Ethanol Steam Reforming (ESR):** Identify catalyst compositions for low-to-moderate temperature reforming with necessary activity, selectivity, life/regenerability under realistic operating conditions

*Relevance to DOE hydrogen program*

- ▶ *reduction in capital cost, operation & maintenance*



# Project Milestones

Aqueous Phase Reforming	
Summarize preliminary EXAFS and XANES studies of Pt-Re/C catalysts in quarterly report	3/31/09 (milestone met)
Summarize effect of catalyst and support pretreatment and preparation methods on performance in a written report	9/30/09 (on track)
Report summarizing kinetic data, catalytic and non-catalytic reaction pathways, and pH effects with glycerol and sorbitol feedstock	9/30/09 (on track)

Ethanol Steam Reforming	
Demonstrate 200 hour life at full ethanol conversion under continuous operation with Rh/CeO <sub>2</sub> -PrO <sub>2</sub> or best alternative Rh-based catalyst.	6/30/09 (milestone met)
Summarize the effect of elevated operating pressure and process conditions (space velocities) on the performance of the Rh/CeO <sub>2</sub> -PrO <sub>2</sub> and Co/ZnO catalysts in a quarterly report	9/30/09 (met for Co; in progress)
Provide comparative H <sub>2</sub> A analysis of Rh- based and Co-based catalysts under best achieved conditions for down-selection of the catalyst system and to demonstrate feasibility to meet 2017 DOE target for H <sub>2</sub> production cost	9/30/09 (on track)

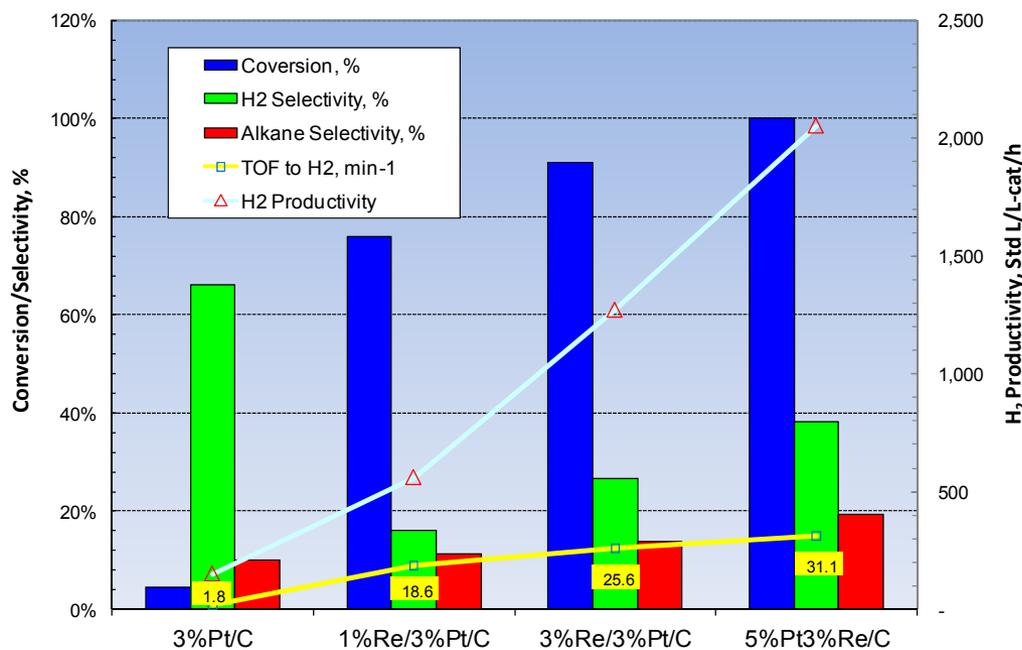
***Go/no go decisions have not been established for this project***

# Technical Accomplishments: Aqueous Phase Reforming (APR)

- ▶ Demonstrated that addition of Re to Pt/C catalyst significantly increases activity with modest decrease in H<sub>2</sub> selectivity
- ▶ Provided increased fundamental understanding of the interaction between Pt and Re on carbon-supported catalyst.
  - Re does not increase the dispersion of Pt.
  - Enhancement of Pt activity by Re is due to the charge transfer from Pt to Re, leading to weakened CO-Pt interaction.
- ▶ Demonstrated that metal dispersion and particle size stability (both catalyst activity and stability) are affected by the type of carbon support used.
- ▶ Identified role of base addition on catalyst performance.
  - Short term hydrogen selectivity increase
  - Rapid catalyst deactivation due to homogeneous chemistry in basic medium

# APR Background: Rhenium Addition Increased the TOF of Pt by >10x

T = 226°C, P = 425psi, feed rate 0.06 moles glycerol/gcat-h



*TOF based on available metal sites by CO chemisorption*

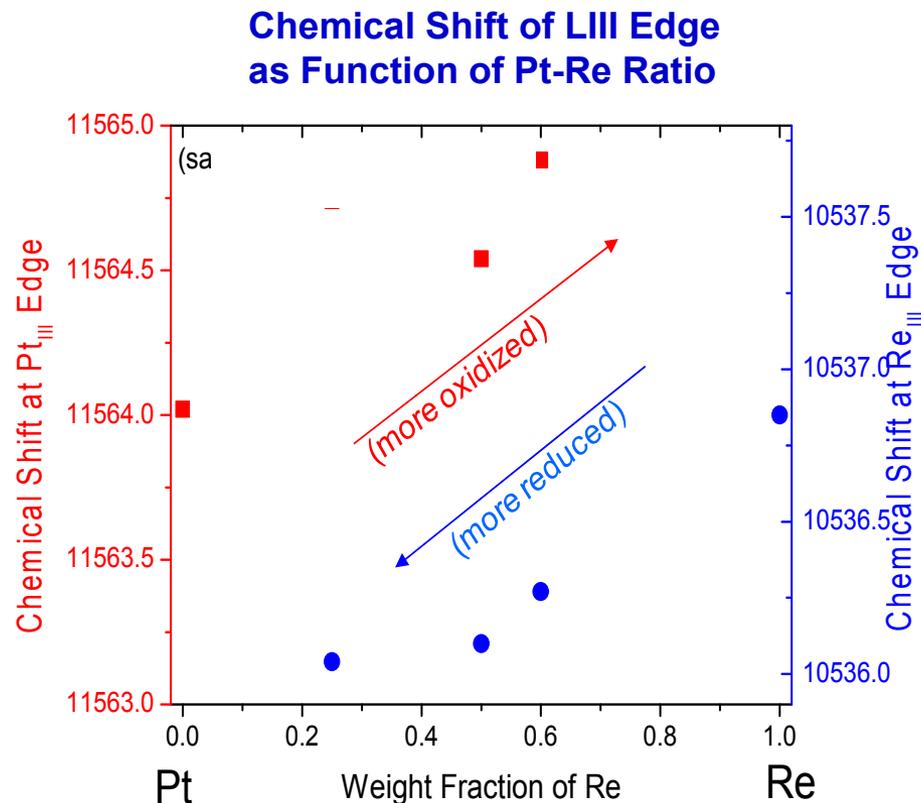
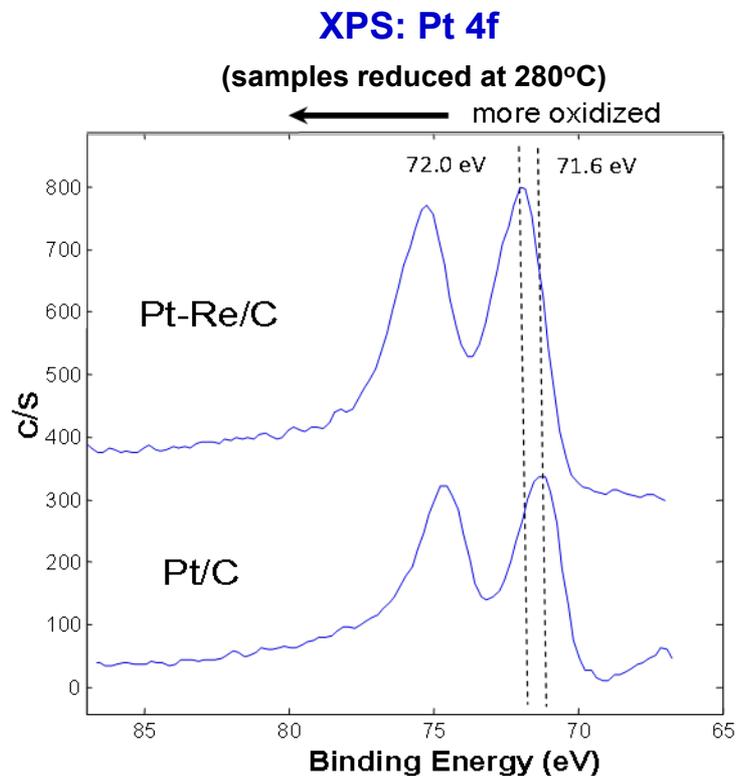
## Chemisorption by H<sub>2</sub> and CO

(samples reduced at 280°C)

	3Pt/C (calcined)	3Pt3Re/C (calcined)
CO uptake (μmol/g)	116.23	67.15
H uptake (μmol/g)	147.42	116.54
CO:H ratio	0.79	0.58

- ▶ Addition of Re increases catalyst activity and hydrogen productivity, with some decrease in H<sub>2</sub> selectivity (relative to alkanes) compared with Pt/C
- ▶ Chemisorption confirmed that Re addition led to weakened CO adsorption relative to H<sub>2</sub>

# APR Technical Accomplishments: *in situ* XPS and XANES Characterization of Pt-Re/C

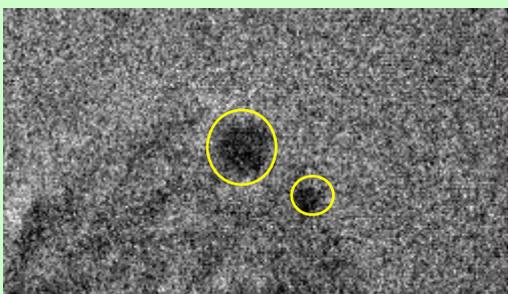
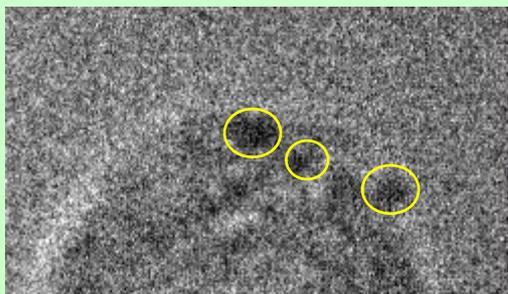
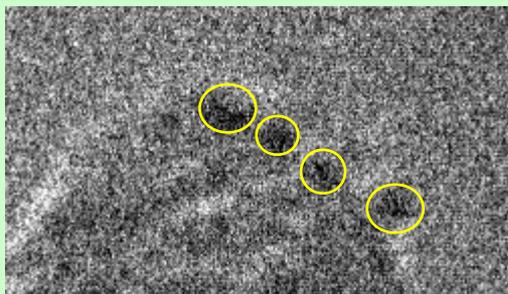


- ▶ The binding energy of Pt in reduced Pt-Re/C indicates that Pt is weakly oxidized
- ▶ Addition of Re results in opposing chemical shifts for Pt and Re LIII edges, consistent with charge transfer

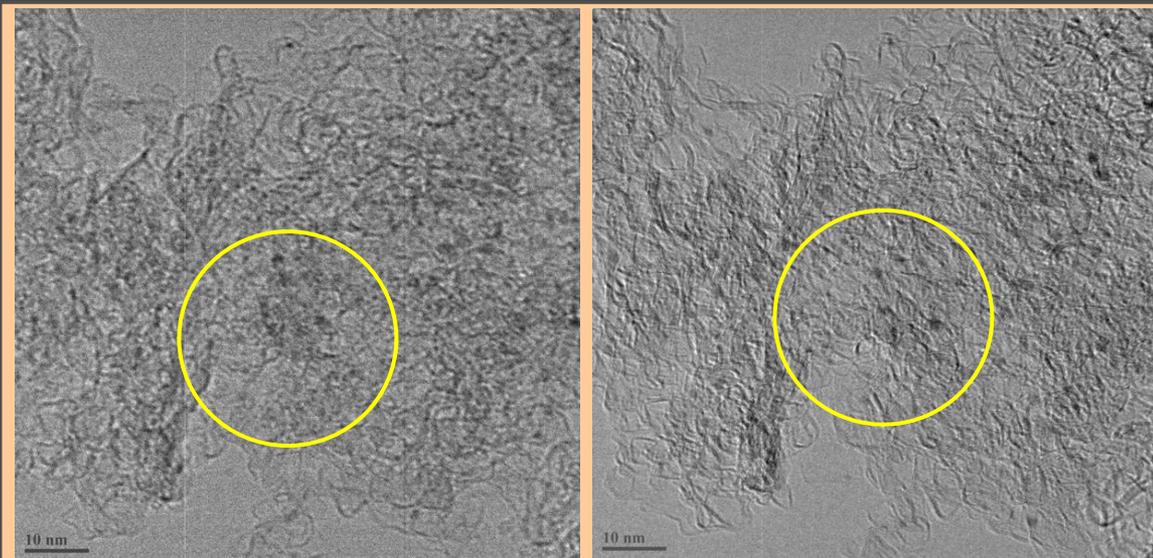
Work carried out in collaboration with Virent Energy Systems

# APR Technical Accomplishments: *In situ* TEM Characterization of Pt-Re on Two Different Carbon Supports During Reduction at 280°C

evolve with time



Carbon Black



Start of Reduction

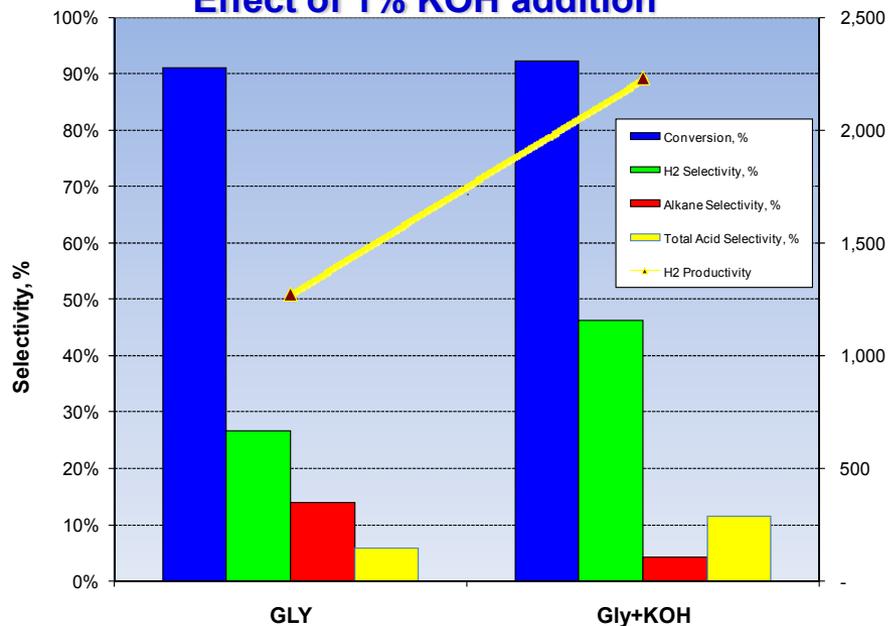
End of Reduction

Activated Carbon

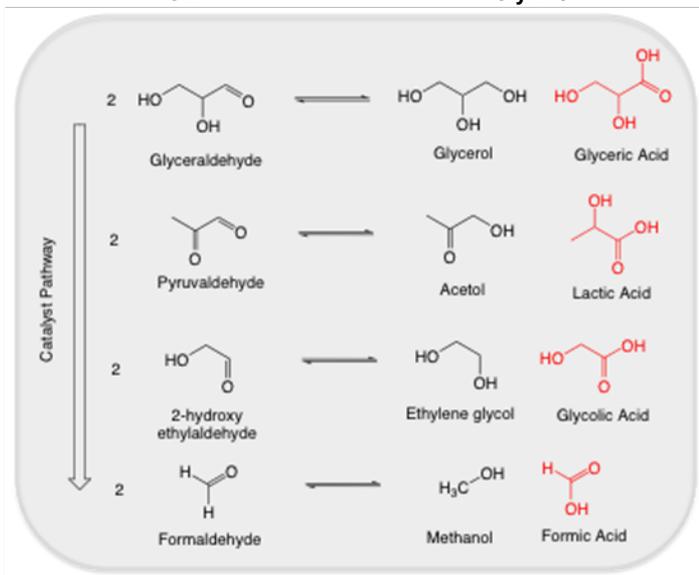
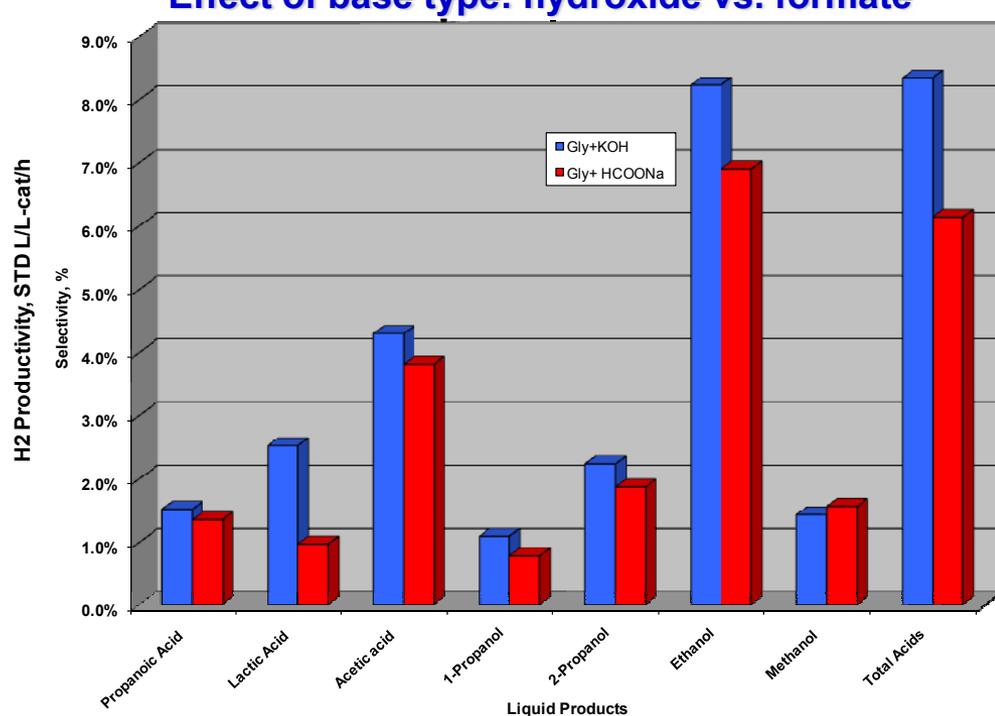
- ▶ Pt-Re coalesces on carbon black while Pt-Re is stable on activated carbon under reduction and E-beam exposure
- ▶ Surface functional groups affect the dispersion and stability of Pt-Re particles
- ▶ No apparent influence of Re on metal particle size

# APR Technical Accomplishments: Addition of Base Affects Product Selectivity

## Effect of 1% KOH addition



## Effect of base type: hydroxide vs. formate



	KOH	CHOONa
Conversion, %	100	99.9
Conversion to Gas Products (C based), %	70.6	81.2
Hydrogen Productivity, STD L/L-cat/h	3459	4070
Hydrogen Selectivity, %	55.2	66.8

- ▶ 1% KOH addition increased hydrogen productivity and selectivity, reduced alkane selectivity, but increased acid formation.
- ▶ Acid formation by cannizzaro disproportionation was reduced using formate, leading to increased hydrogen productivity and selectivity.

# APR: Future Work

- ▶ Determine role of Re under representative APR-type reaction conditions using *in situ* XANES and XPS, including structure characterization of Pt-Re using EXAFS.
- ▶ Complete study of sample preparation effects on activity and selectivity.
  - Pt and Re precursors, deposition sequence
  - Carbon pretreatment or pre-oxidation
- ▶ Suggest alternative base metals of similar properties to Pt-Re to lower the catalyst cost.
- ▶ Improve hydrogen productivity and selectivity by exploring additives that may retard dehydration pathway to acids on Pt-Re/C

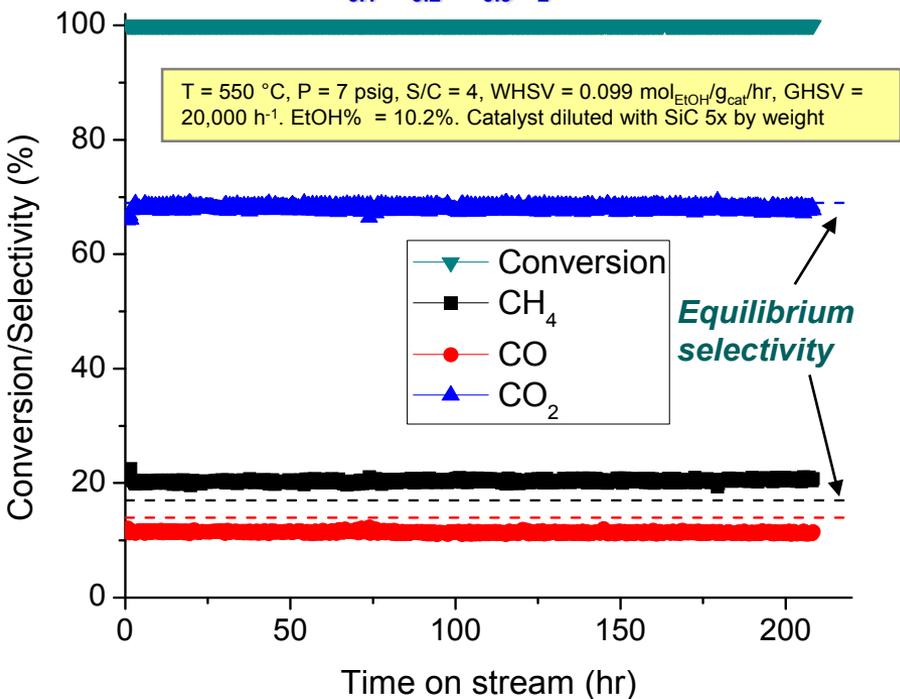
# Technical Accomplishments: Ethanol Steam Reforming (ESR)

- ▶ Demonstrated that Rh based catalyst life can be significantly increased by operating at a significantly reduced weight hourly space velocity (WHSV) and balancing metal and support functions.
- ▶ Showed that Co/ZnO exhibits excellent hydrogen (and CO<sub>2</sub>) selectivity at low space velocities and low EtOH feed concentration and partial pressure
  - Increasing EtOH partial pressure, decreasing S/C results in lower H<sub>2</sub> (and CO<sub>2</sub>) selectivity
- ▶ Preliminary H<sub>2</sub>A analysis indicates that Co/ZnO is superior to Rh/Y-Pr-CeO<sub>x</sub> catalyst based on results to date
  - Better selectivity toward H<sub>2</sub>, lower toward CH<sub>4</sub> with Co/ZnO
  - Lower catalyst cost, eliminate water gas shift

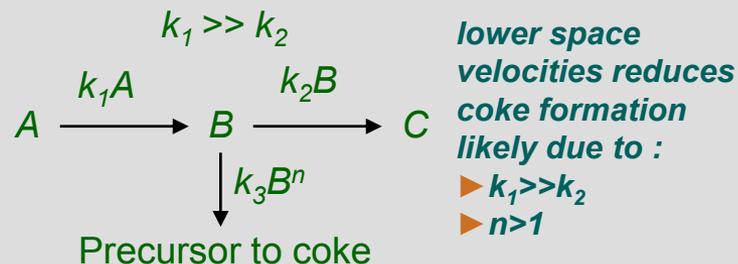
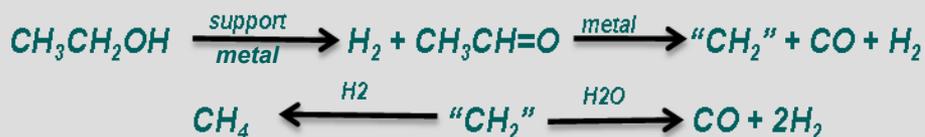
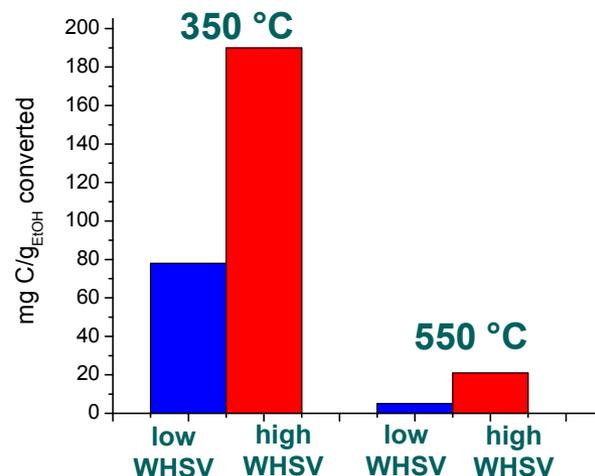
Caveat: data on elevated pressure operation, catalyst lifetime and regeneration effectiveness and protocols still need to be incorporated

# ESR Technical Accomplishments: Rhodium Based Catalyst

2.3% Rh/Y<sub>0.1</sub>Pr<sub>0.2</sub>Ce<sub>0.9</sub>O<sub>2</sub> WHSV 23x lower



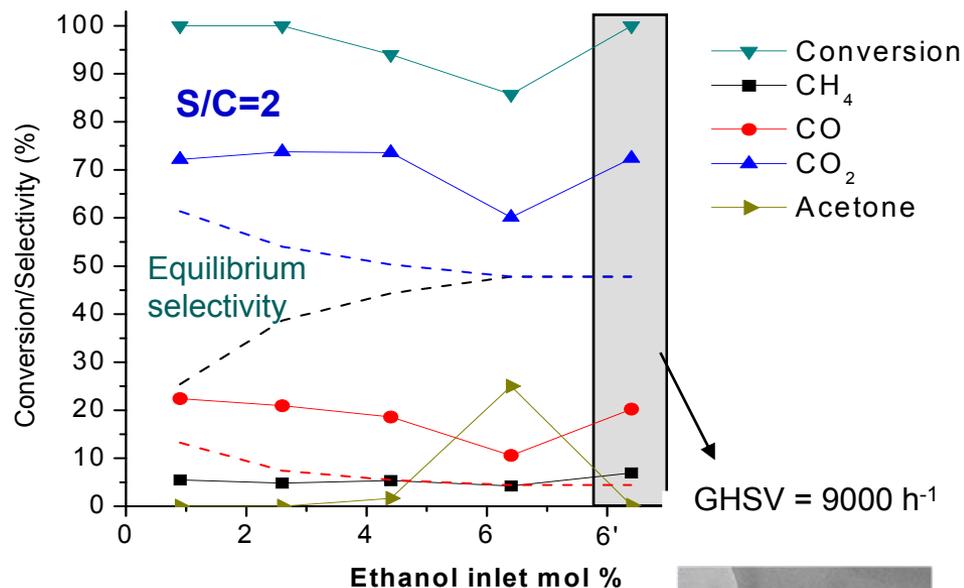
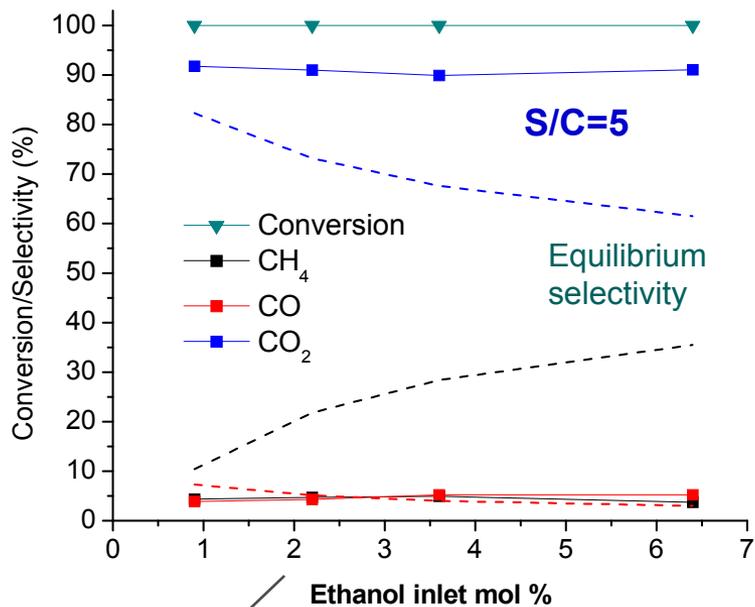
Amount of Carbon Deposited (per gram ethanol converted) as a Function of Temperature and WHSV



- ▶ Demonstrated 200hr time-on-stream stable performance
- ▶ Catalyst deactivation rate is slower at 550°C and a lower WHSV as evidenced by less carbon deposited after same amount of ethanol was fed into reactor
- ▶ Balance of metal and support activities led to extended catalyst life (temperature and space velocity dependent)

# ESR Technical Accomplishments: Cobalt Based Catalyst

Conversion/Selectivity as a Function of Ethanol Partial Pressure on Co/Zn at 450°C



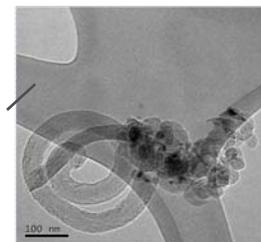
Typical literature conditions

- ▶ Co performs well under literature conditions
- ▶ Good performance can also be achieved at a lower S/C and higher ethanol partial pressure if operated at a lower SV
- ▶ Amount and type of coke formation is a concern

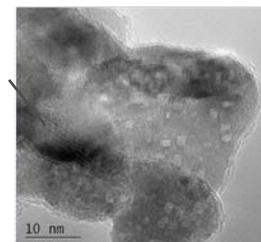
Carbon Deposited after Same Amount of Ethanol Fed

Catalyst	mg C/g <sub>EtOH</sub> converted (x 10 <sup>-3</sup> )
Rh/YPrCe, S/C = 4	7
Co/ZnO, S/C = 5	900
Co/ZnO, S/C = 2	810
Co/ZrO <sub>2</sub> , S/C = 5	2000
CoZn/ZrO <sub>2</sub> S/C = 5	1600

Coke on Co catalyst

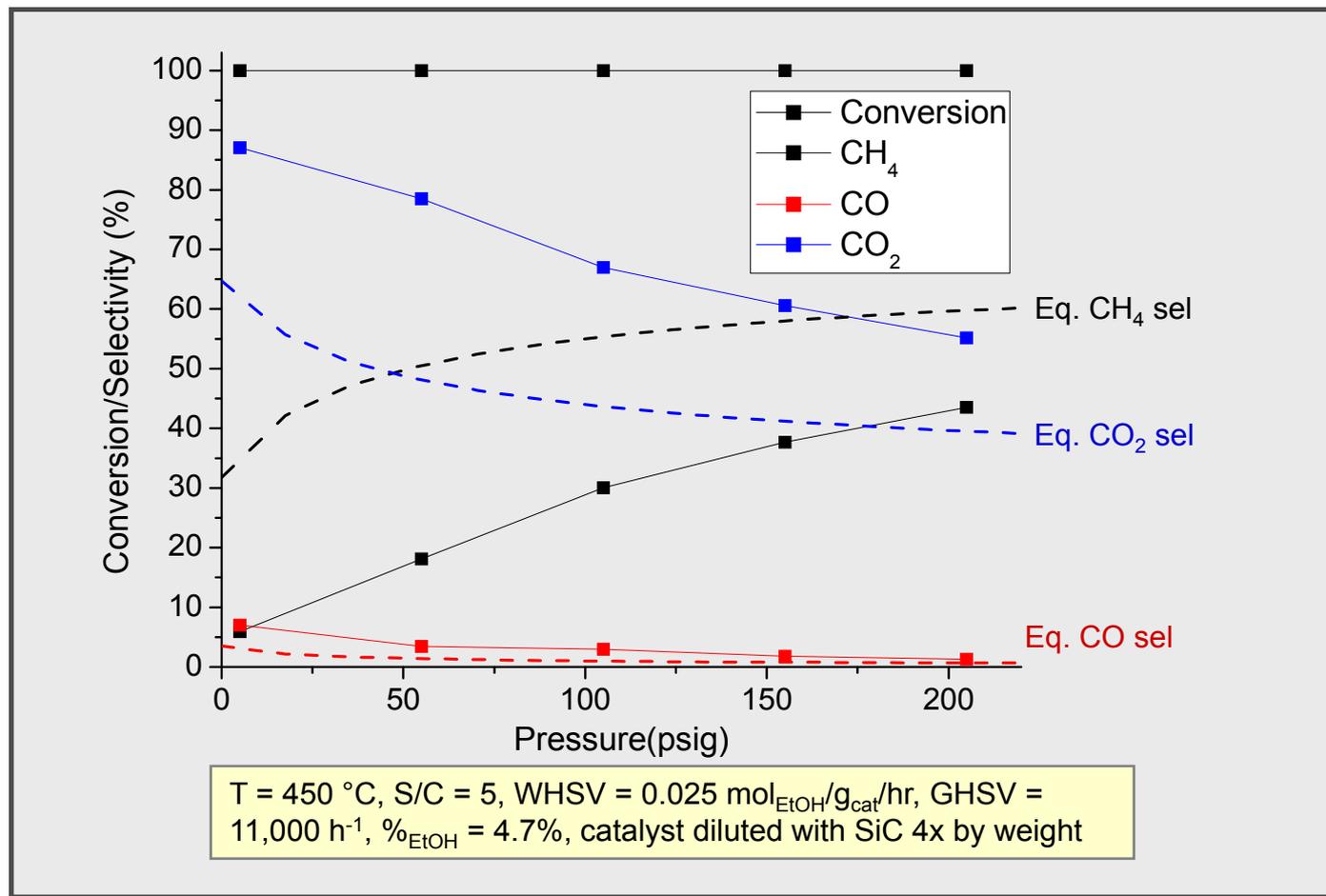


Coke on Rh catalyst



# ESR Technical Accomplishments: Cobalt Based Catalyst

## Effect of Total Reaction Pressure on Co/ZnO Selectivity



Higher reaction pressure results in increasing  
CH<sub>4</sub> selectivity toward equilibrium value

# Preliminary H2A Analysis: Ethanol Reforming Uninstalled System Cost Estimate

	<b>Rh catalyst</b>	<b>Co catalyst</b>
Feed Pumps	\$7,405	\$7,405
Feed Heating	\$51,433	\$51,433
Reformer and Catalyst	\$408,864	\$370,847
WGS and Catalyst	\$82,056	\$0
Raw Product Cooling	\$105,853	\$105,853
PSA	\$59,918	\$59,918
Fixed Cost Components	\$268,638	\$268,638
Storage Tank	\$138,934	\$138,934
Miscellaneous	\$98,417	\$86,409
<b>Total</b>	<b>\$1,221,519</b>	<b>\$1,089,439</b>

## Assumptions:

- ▶ Based on 2009 H2A EtOH Reforming Model
- ▶ Reference EtOH Capital = \$1,109,617
- ▶ Reformer feed rate:
  - 0.099 moles EtOH/g cat-h for Rh
  - 0.026 moles EtOH/g cat-h for Co
- ▶ Single pass 100% EtOH conversion
- ▶ H<sub>2</sub> yield:
  - 4.80 mol/mol EtOH for Rh
  - 5.04 mol/mol EtOH for Co
- ▶ WGS required for Rh, not for Co
- ▶ EtOH cost \$1.07/gallon (H2A assumption)
- ▶ 1500 kg H<sub>2</sub>/day
- ▶ 85% annual capacity factor
- ▶ Assumes no operating labor required
- ▶ Maintenance and repair: 5% of capital
- ▶ PSA H<sub>2</sub> recovery: 75%
- ▶ Selectivity unaffected by operating pressure

# Preliminary H2A Analysis EtOH Reforming Comparative Production Costs

**H2A Reference EtOH Reforming H2 cost = \$3.18/kg**

## Hydrogen Production Cost Contribution (\$/kg)

<b>Cost Component</b>	<b>Rh-based catalyst</b>	<b>Co-based catalyst</b>
Capital costs	0.63	0.57
Decommissioning costs	0.00	0.00
Fixed O&M	0.22	0.20
Feedstock costs	2.28	2.17
Other raw material costs	0.00	0.00
Byproduct credits	0.00	0.00
Other variable costs	0.05	0.05
<b>Total</b>	<b>3.19</b>	<b>2.99</b>

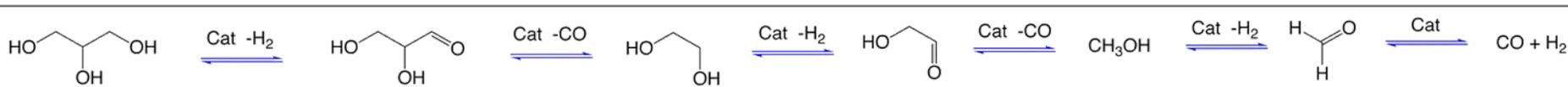
# Ethanol Steam Reforming: Future Work

- ▶ Complete elevated pressure studies for Rh and Co
  - Explore catalyst modifications (as needed) to reduce  $\text{CH}_4$  yield from elevated pressure operation
- ▶ Mitigate carbon formation on catalysts
  - Characterize type(s) of carbon deposited
  - Correlate carbon with time-on-stream and process conditions (S/C, P, SV, T)
  - Study the coke formation mechanisms to guide catalyst modification
- ▶ Investigate catalyst regeneration
  - Develop protocols
  - Quantify catalyst activity recovery through several cycles
- ▶ Complete H<sub>2</sub>A analysis of Rh and Co catalyzed processes
  - Down-select preferred catalyst system
  - Investigate more efficient, but more costly PSA designs
  - Estimate H<sub>2</sub> production cost to compare against 2017 target
  - Provide recommendations on go/no for technology approach

# Additional Slides

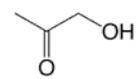
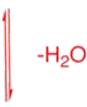
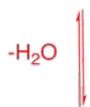
# Primary Reaction Pathways in APR of Glycerol Leading to Hydrogen (Desired) and Propylene Glycol (Not Desired)

*Desired reaction pathway*  $\longrightarrow$

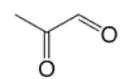


Glycerol

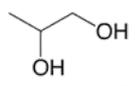
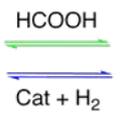
Glyceraldehyde



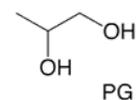
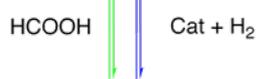
Acetol



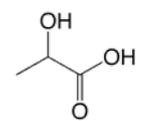
Pyruvaldehyde



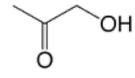
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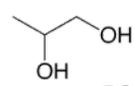
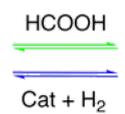
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Lactic Acid



Acetol



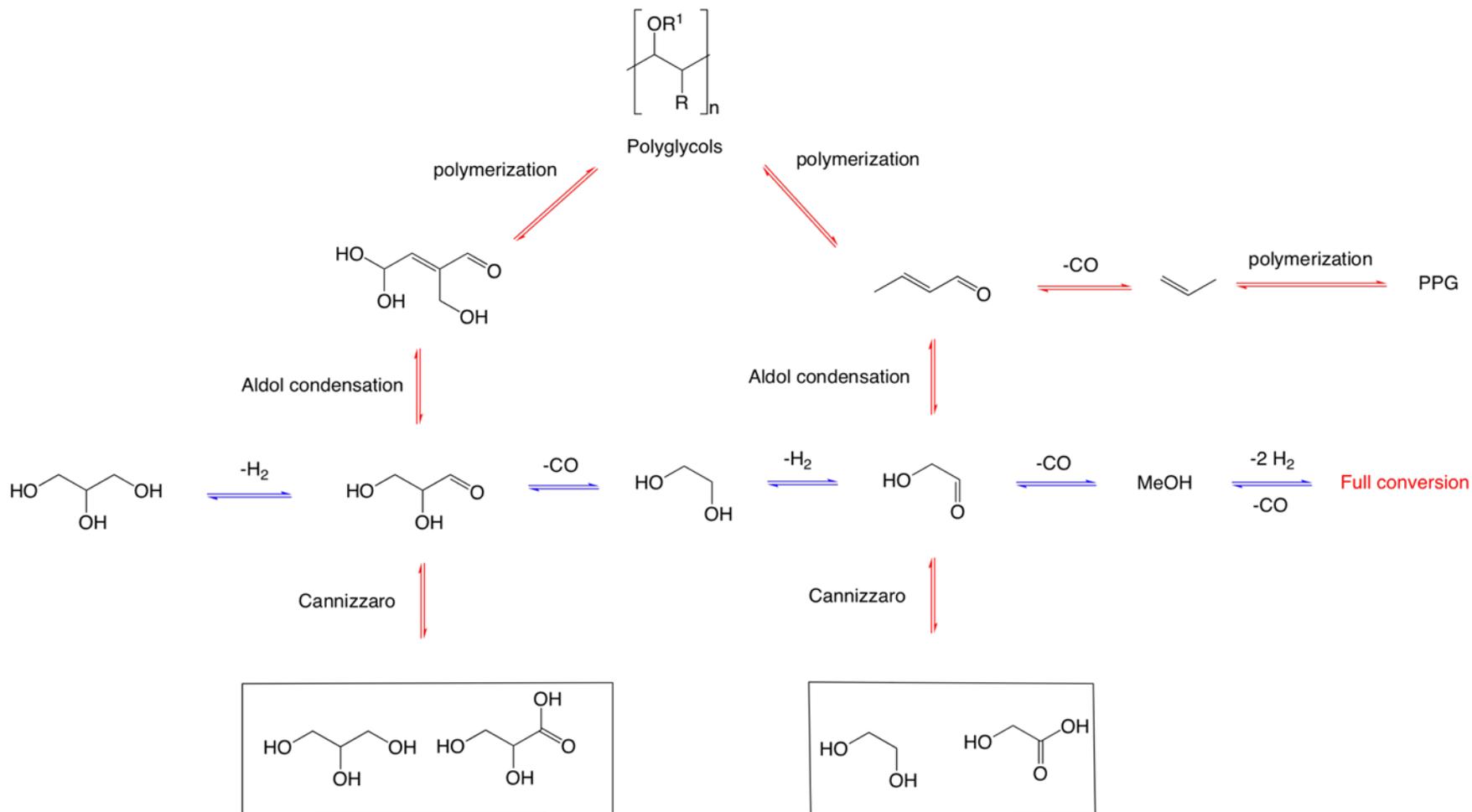
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*Possible undesired pathways to propylene glycol*

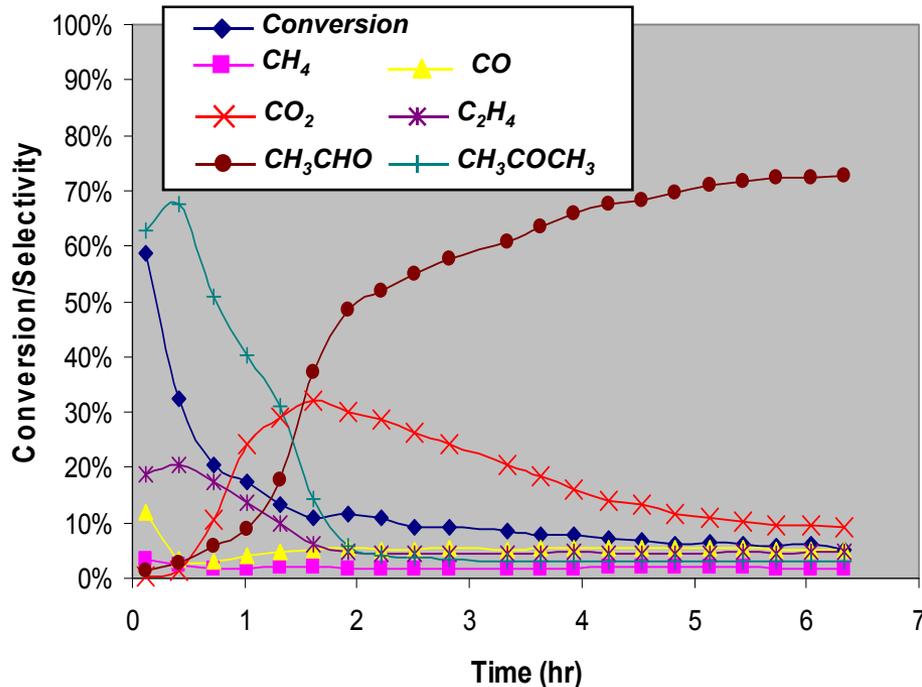


# Many Possible Pathways Compete With Hydrogen Production

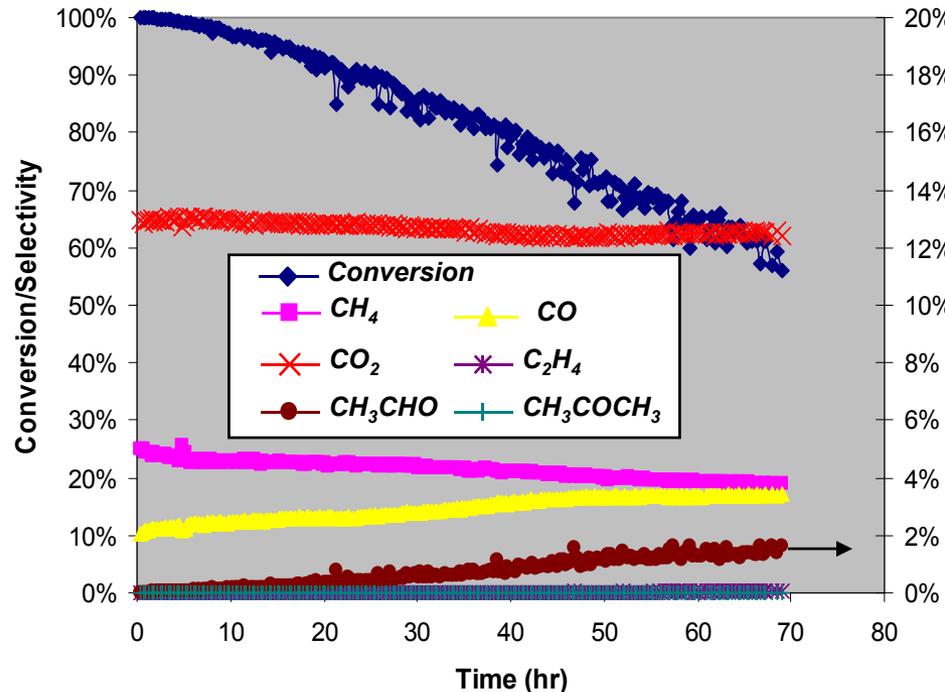


# ESR Technical Accomplishments: Rhodium Catalyst Role of Metal and Support Functions

$Pr_{0.1}Ce_{0.9}O_2$

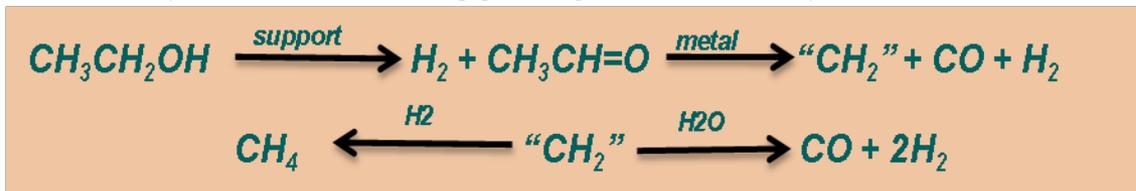


2.3% Rh/ $Y_{0.1}Pr_{0.2}Ce_{0.9}O_2$



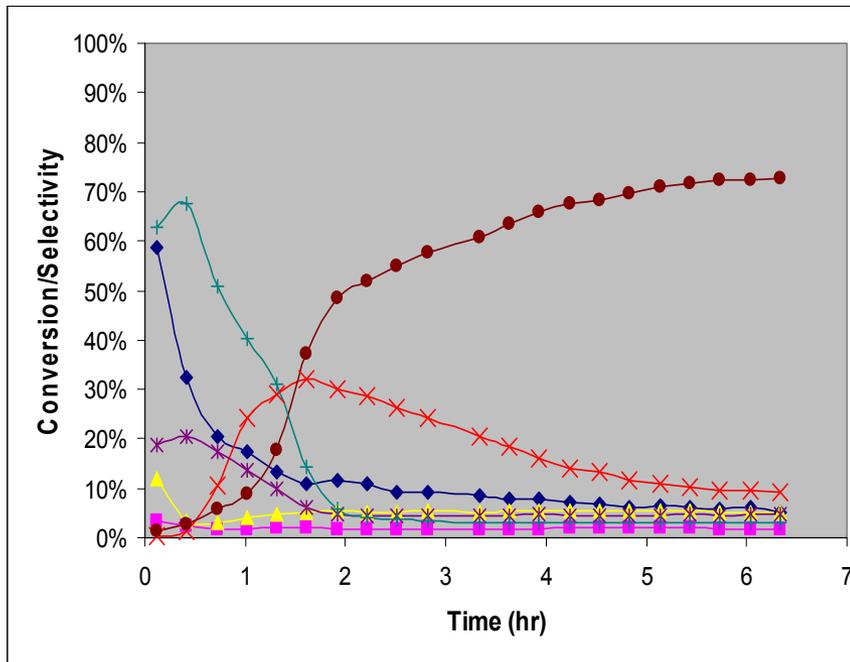
$T = 550\text{ }^\circ\text{C}$ ,  $P = 7\text{ psig}$ ,  $S/C = 4$ ,  $WHSV = 2.25\text{ mol}_{EtOH}/g_{cat}/hr$ ,  $GHSV = 436,000\text{ h}^{-1}\text{ \%}_{EtOH} = 10.6\%$ . Catalyst diluted with SiC 5x by weight

**Both catalyst metal and support provide catalytic contributions**

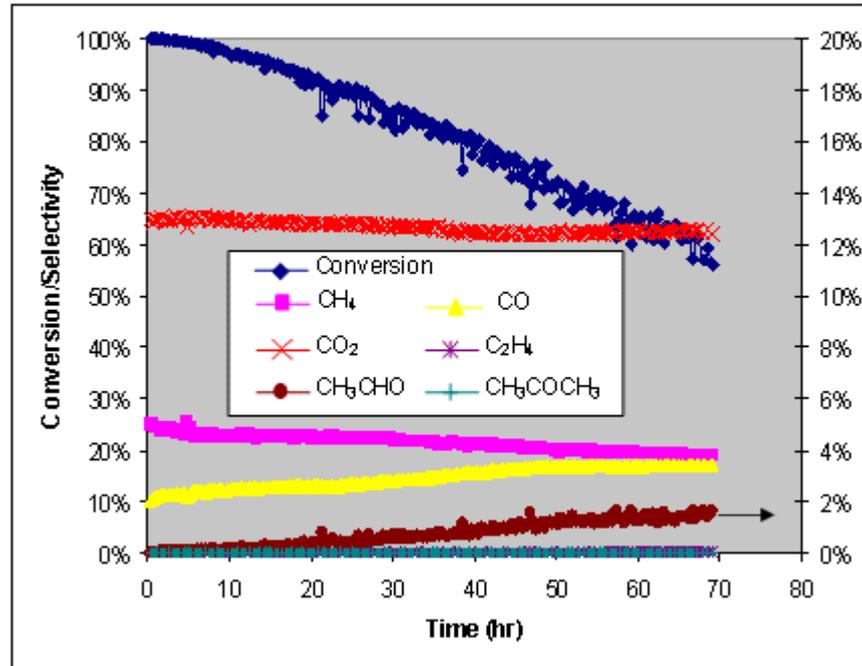


# ESR Technical Accomplishments: Rhodium Catalyst Role of Metal and Support Functions

$\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_2$

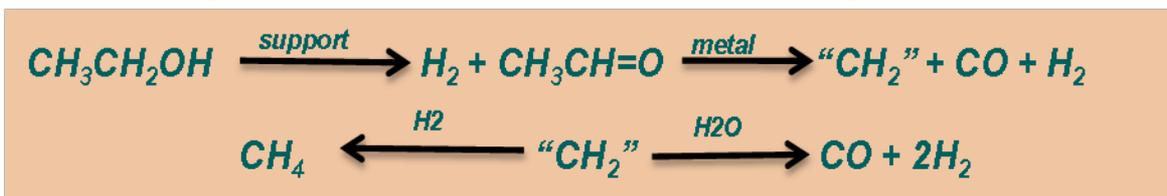


2.3% Rh/ $\text{Y}_{0.1}\text{Pr}_{0.2}\text{Ce}_{0.9}\text{O}_2$



$T = 550\text{ }^\circ\text{C}$ ,  $P = 7\text{ psig}$ ,  $S/C = 4$ ,  $\text{WHSV} = 2.25\text{ mol}_{\text{EtOH}}/\text{g}_{\text{cat}}/\text{hr}$ ,  $\text{GHSV} = 436,000\text{ h}^{-1}$ .  $\text{EtOH}\% = 10.6\%$ . Catalyst diluted with SiC 5x by weight.

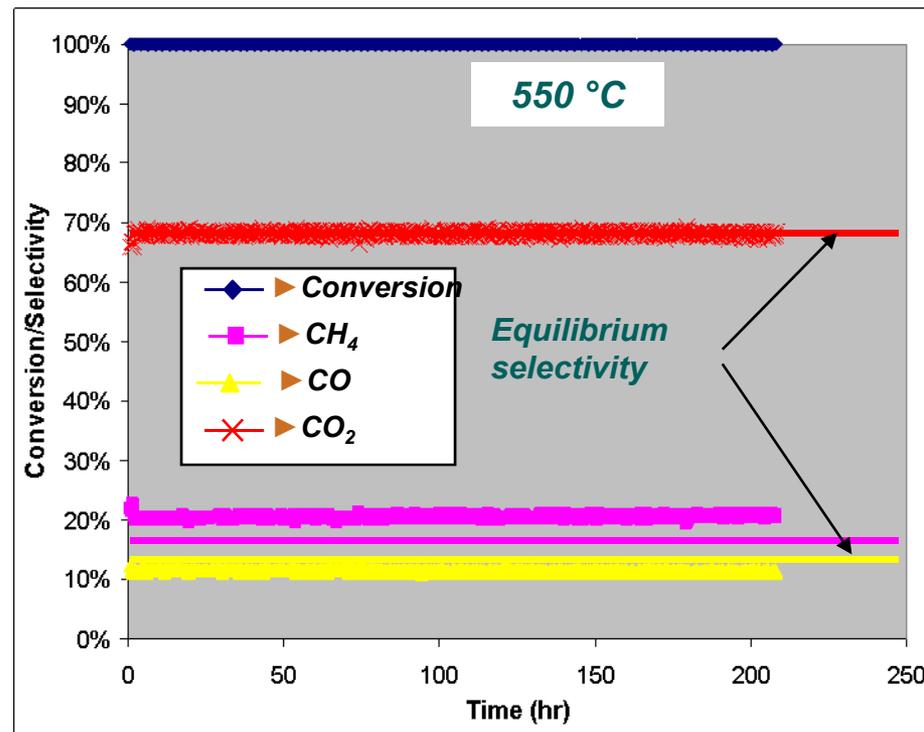
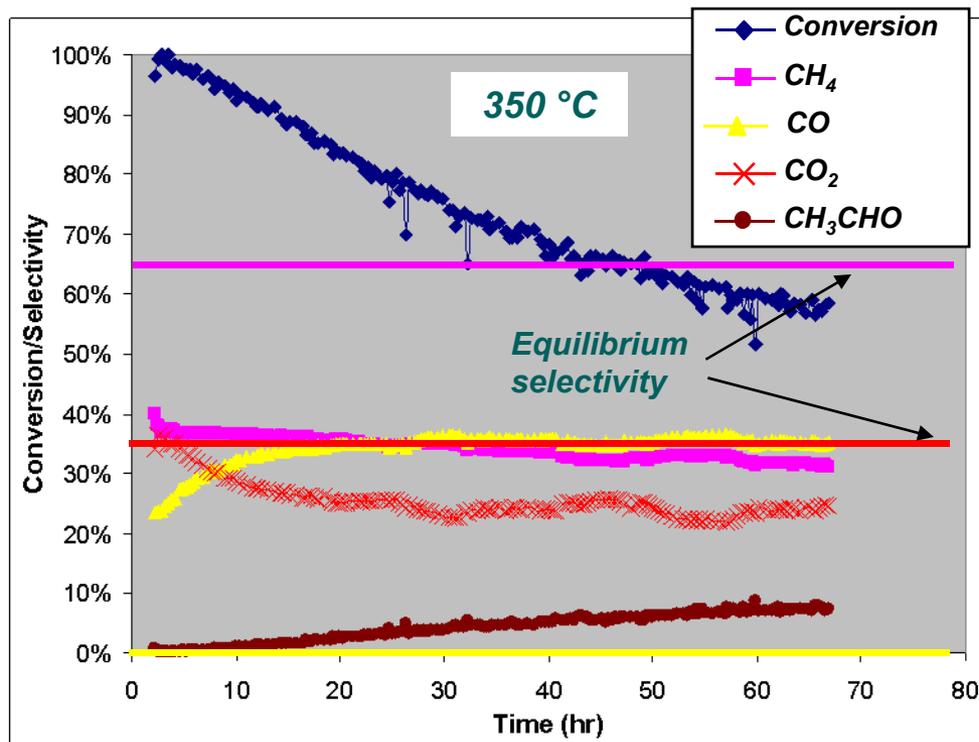
**Both catalyst metal and support provide catalytic contributions**



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INTERFACIAL  
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# ESR Technical Accomplishments: Rhodium Catalyst Effect of Reaction Temperature on Performance



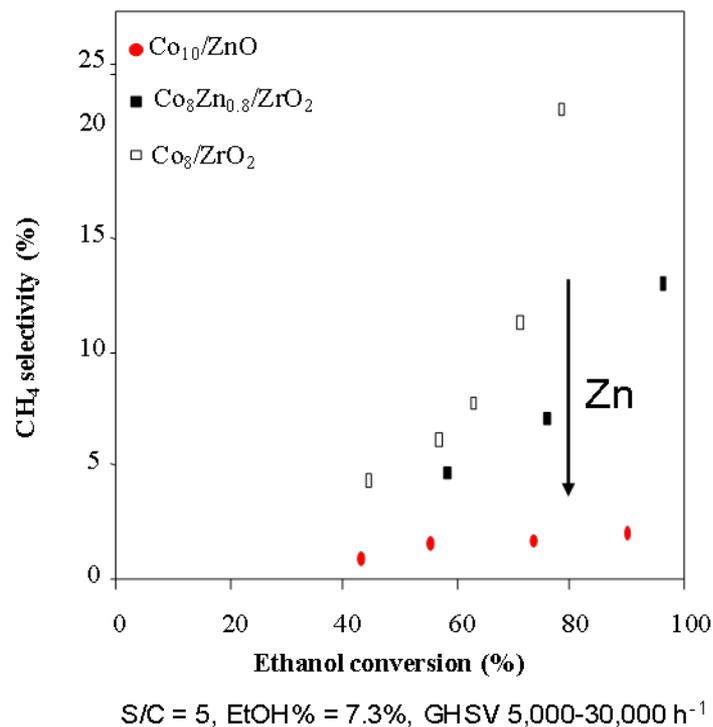
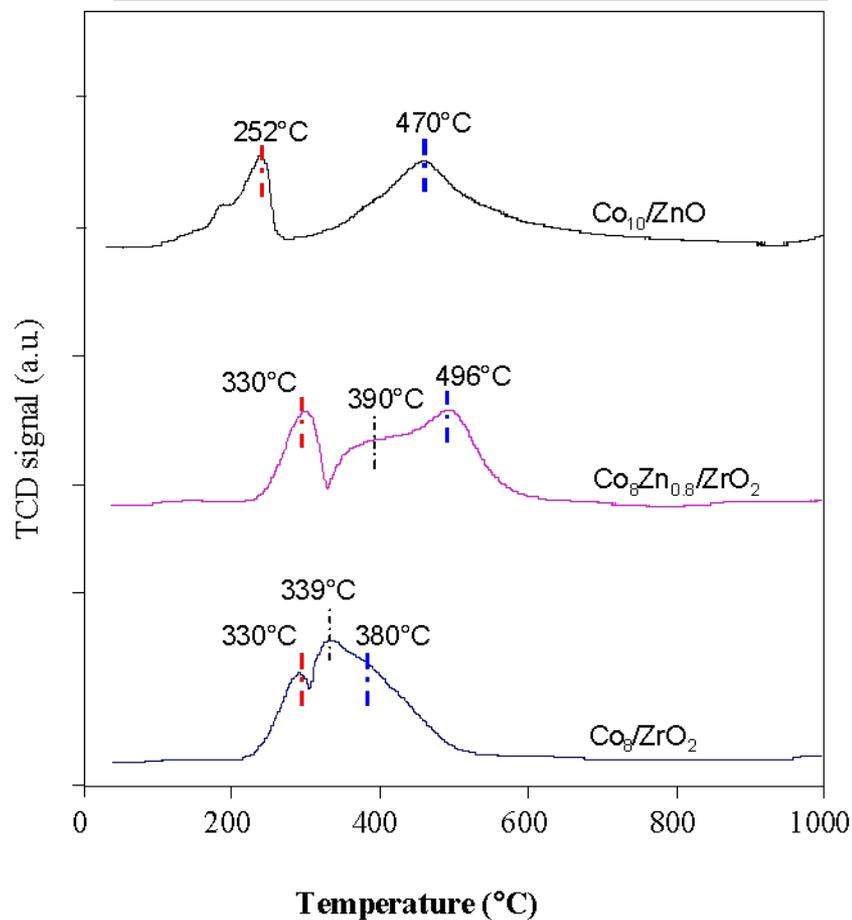
$P = 7$  psig,  $S/C = 4$ ,  $WHSV = 0.099 \text{ mol}_{\text{EtOH}}/\text{g}_{\text{cat}}/\text{hr}$ ,  $GHSV = 20,000 \text{ h}^{-1}$   
 $\text{EtOH} \% = 10.2\%$ . Catalyst diluted with SiC 5x by weight

At lower temperature, both catalyst support and metal are insufficiently active  
Catalyst: 2.3% Rh/Y<sub>0.1</sub>Pr<sub>0.2</sub>Ce<sub>0.9</sub>O<sub>2</sub>

# ESR Technical Accomplishments: Co Catalyst

## Effect of ZnO on Co Selectivity to CH<sub>4</sub>

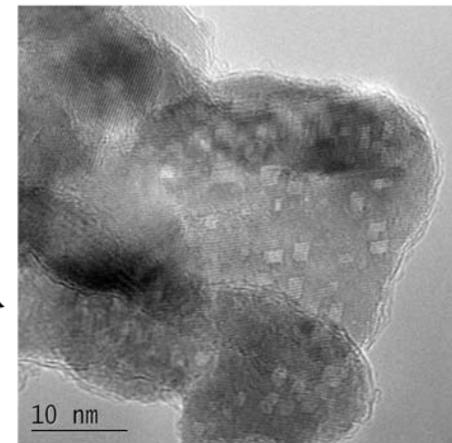
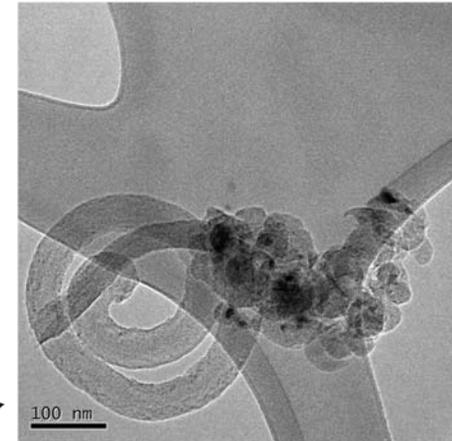
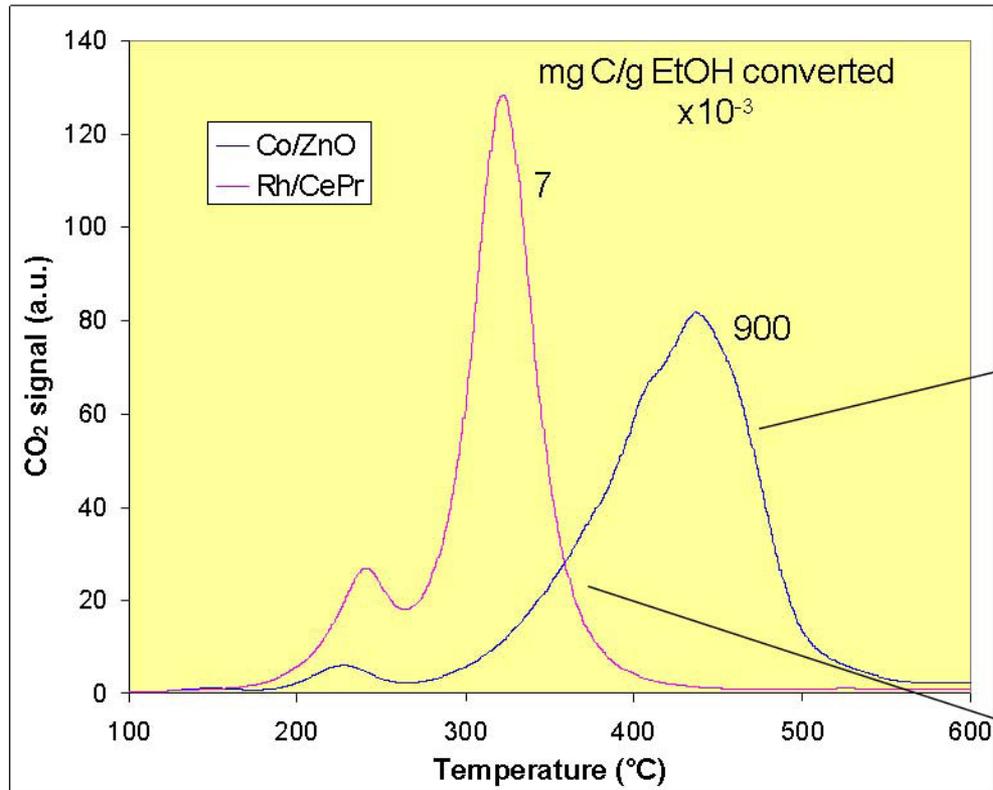
*Temperature programmed reduction (TPR) profiles of supported Co catalysts*



**Higher Co reduction temperature with ZnO support favors some unreduced Co (Co<sup>2+</sup>) and less methane formation**

# ESR Technical Accomplishments

## Different Type of Carbon is Deposited by Rh and Co Metals



- ▶ Carbon deposition is greater on Co than Rh catalyst
- ▶ Carbon type is different as is its effect on deactivation