

*2007 DOE Bio-Derived Liquids to Hydrogen Distributed
Reforming Working Group (BILIWG) Meeting*

Investigation of Bio-Ethanol Steam Reforming over Cobalt-based Catalysts

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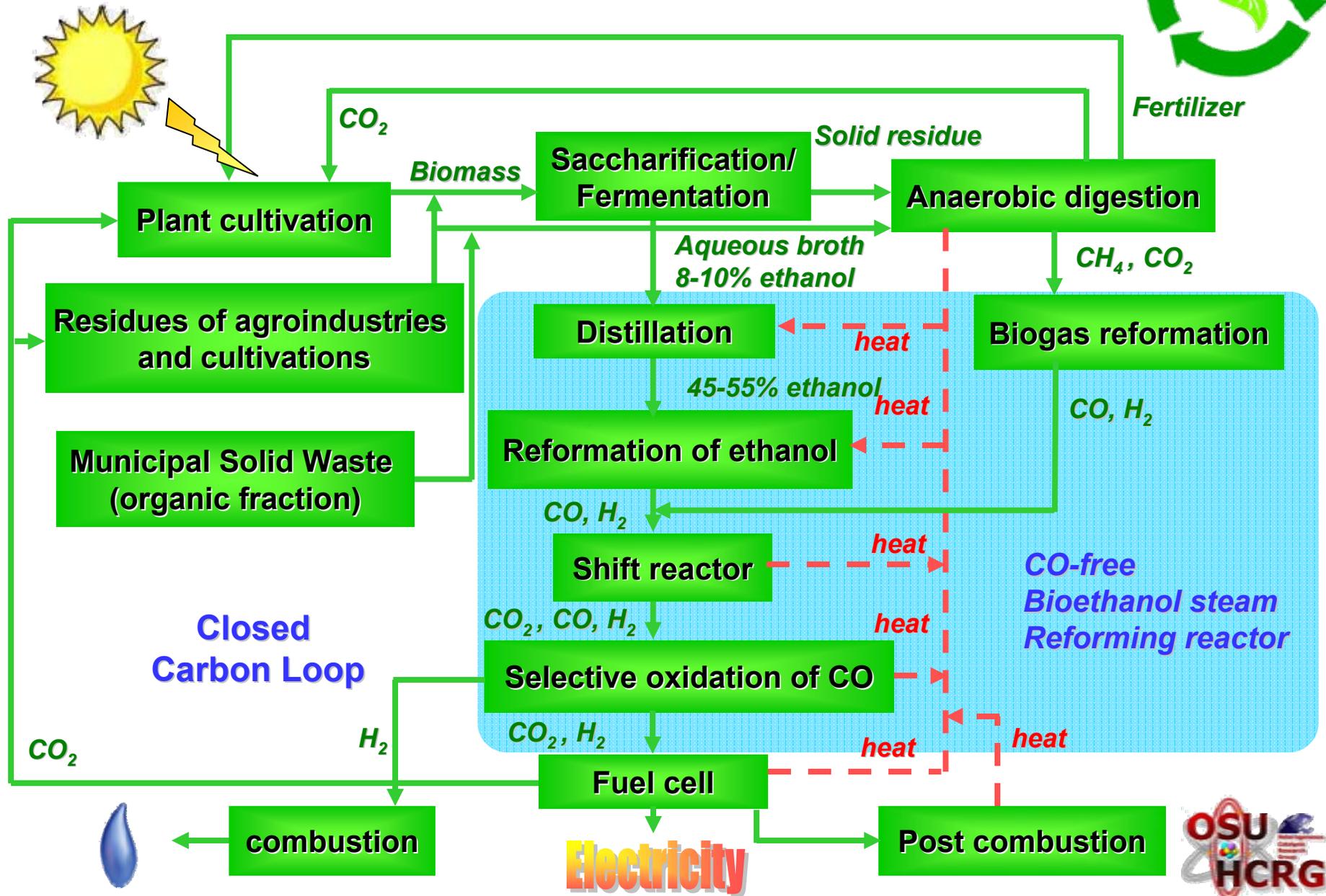
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Biomass to Hydrogen (Environmentally Friendly)



Technical Approach

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

Supported Co-catalysts

❖ Preparation

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

❖ Calcination

- Temperature

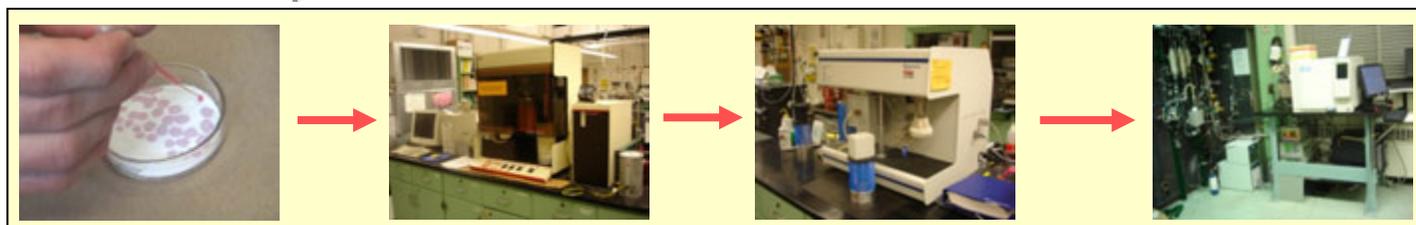
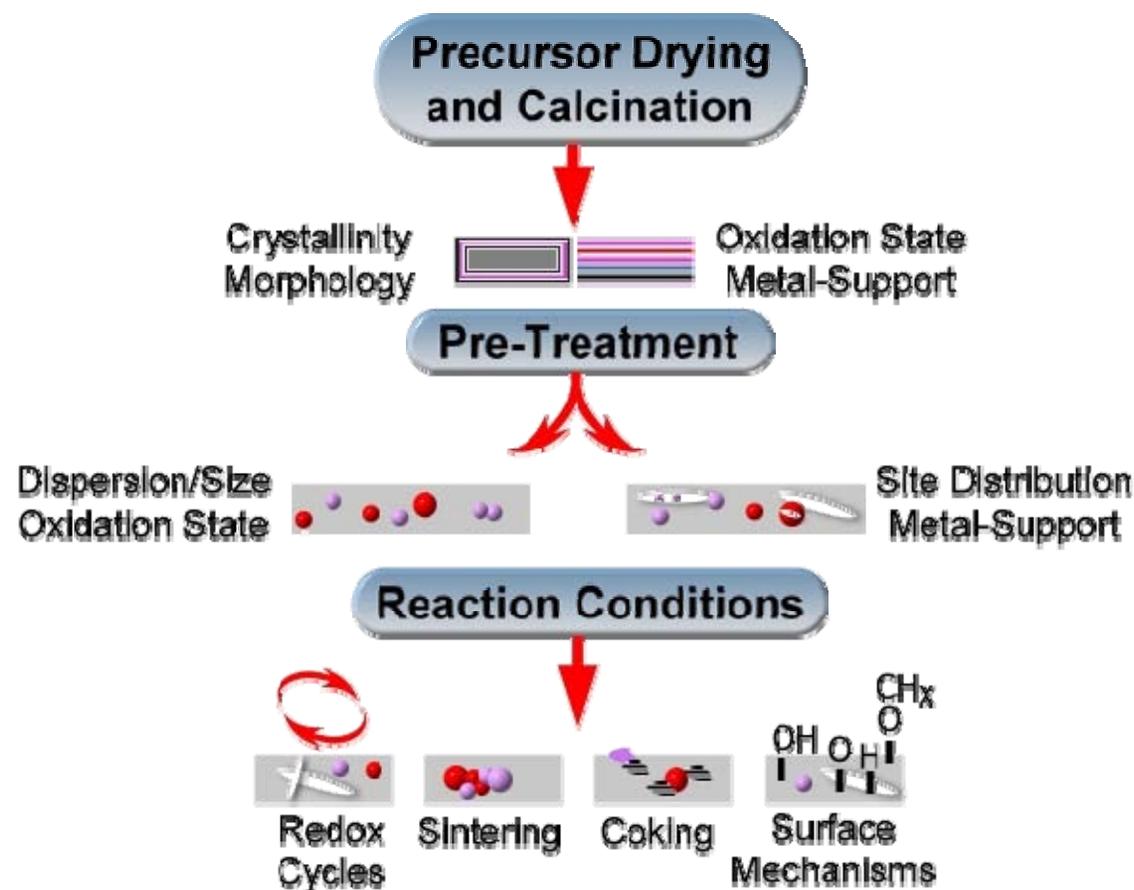
❖ Reduction

- Temperature
- Time

❖ Reaction

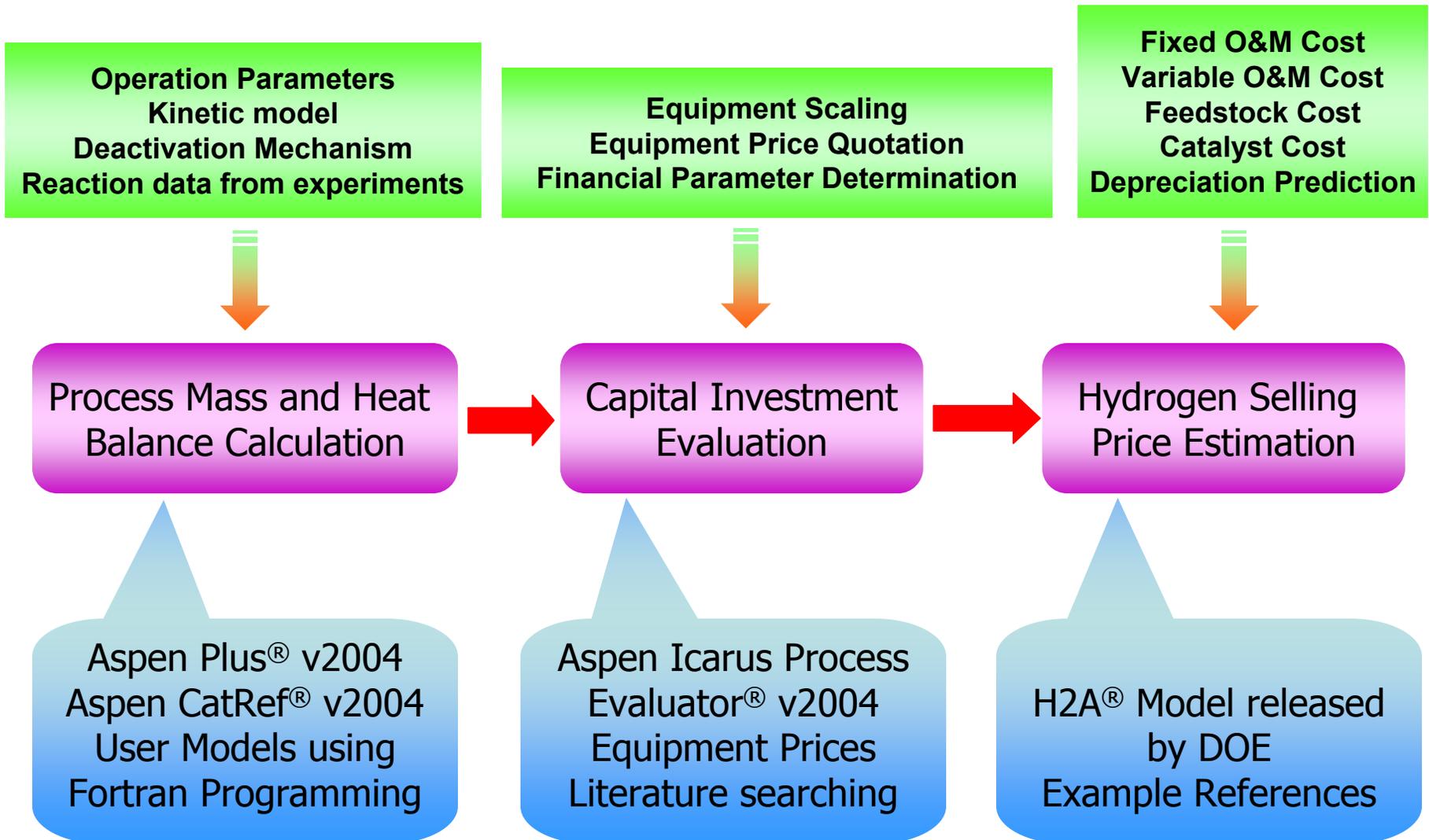
- GHSV
- EtOH:Water ratio
- Temperature
- Oxygen addition
- Deactivation

❖ Deactivation/Regeneration

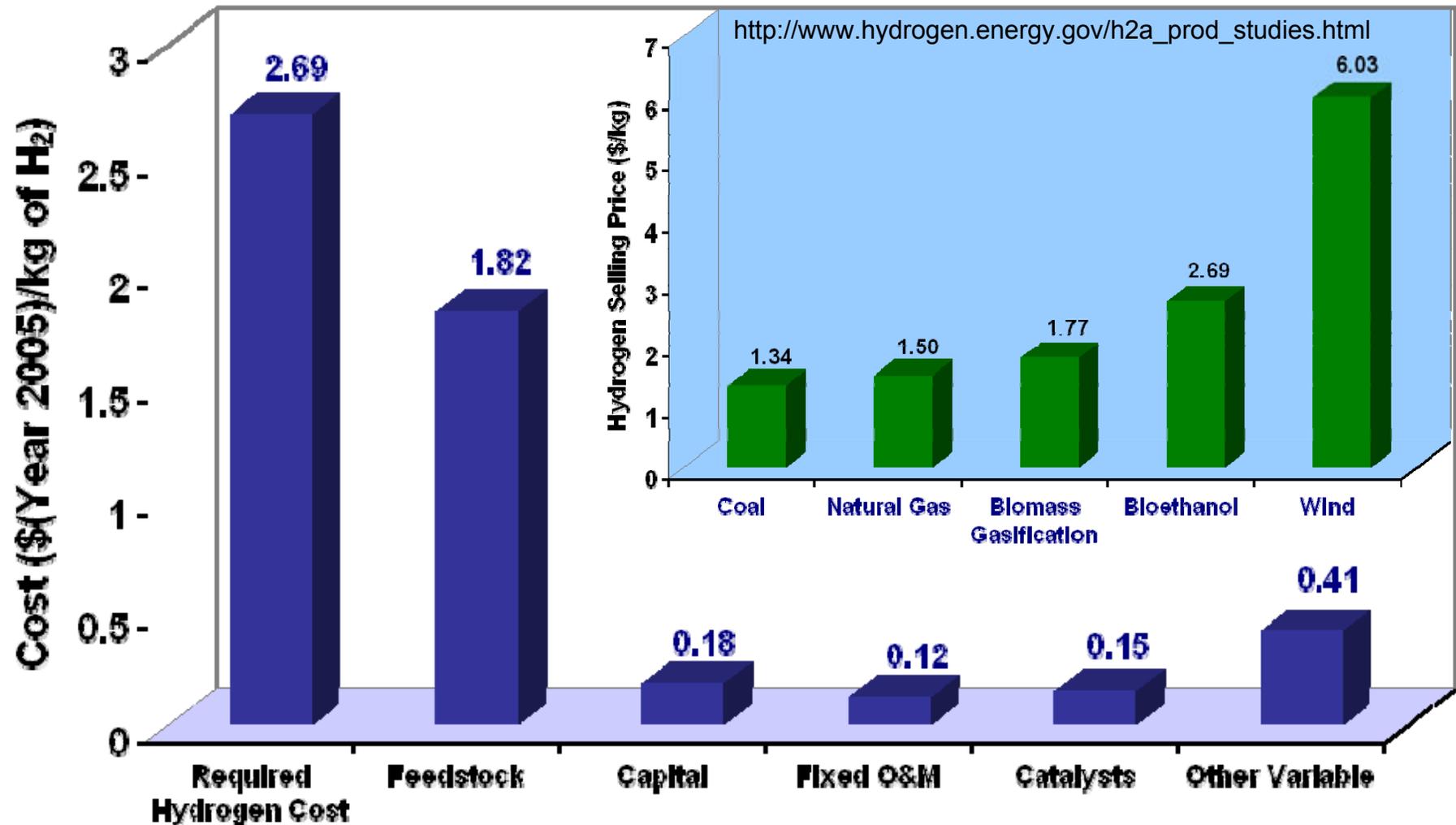




Overview of the Economic Analysis Strategies

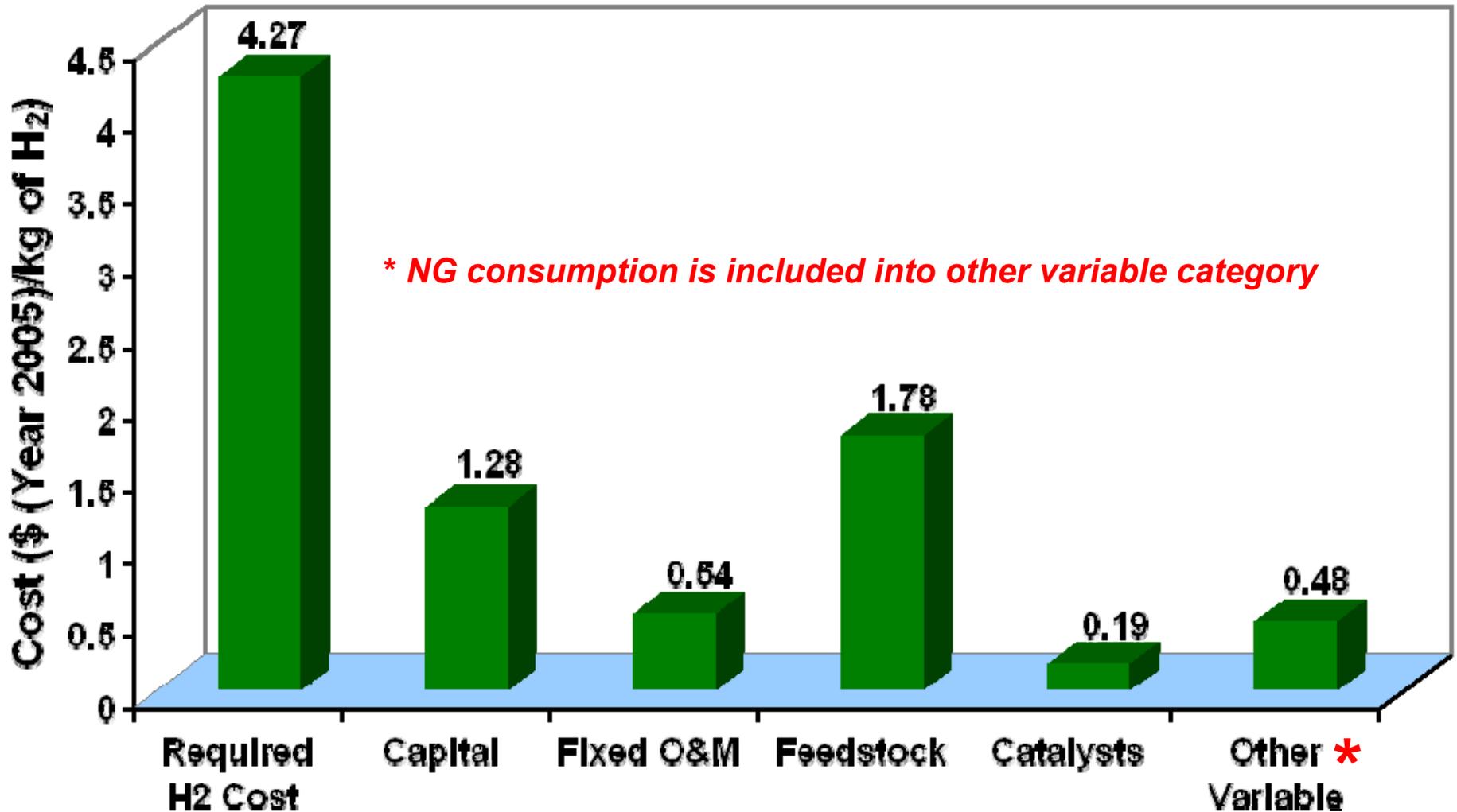


Economic Analysis – Central Production at 150,000kg H₂/day



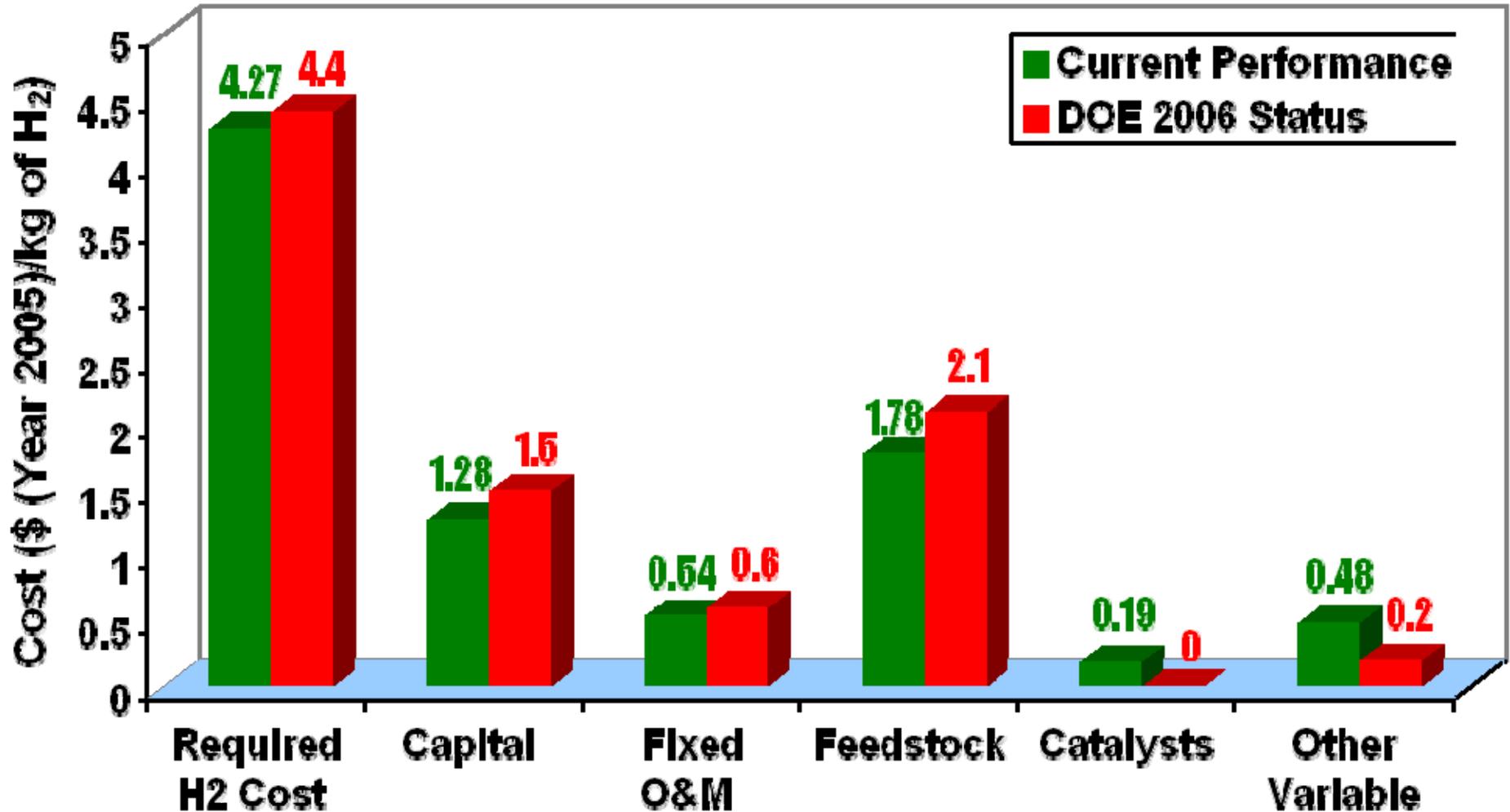
- ❖ 90% H₂ yield with ethanol to water of 1 to 10 and 70% capacity factor are assumed;
- ❖ The ethanol cost utilized is \$1.07/gal and electricity cost used is \$0.08/kWh;
- ❖ “OSU” catalyst is used for bioethanol steam reforming with 3,000h⁻¹ GHSV and 1,000h lifetime;
- ❖ Commercial catalyst is used for HTS reaction with 3000h⁻¹ GHSV and 5 years lifetime at \$4.67/lb.

Economic Analysis – Forecourt Production at 1,500kg H₂/day



- ❖ 90% H₂ yield with ethanol to water of 1 to 10 and 70% capacity factor are assumed;
- ❖ The ethanol cost utilized is \$1.07/gal and electricity cost used is \$0.08/kWh;
- ❖ “OSU” catalyst is used for bioethanol steam reforming with 3,000h⁻¹ GHSV and 1,000h lifetime;
- ❖ Commercial catalyst is used for HTS reaction with 3,000h⁻¹ GHSV and 5 years lifetime at \$4.67/lb.

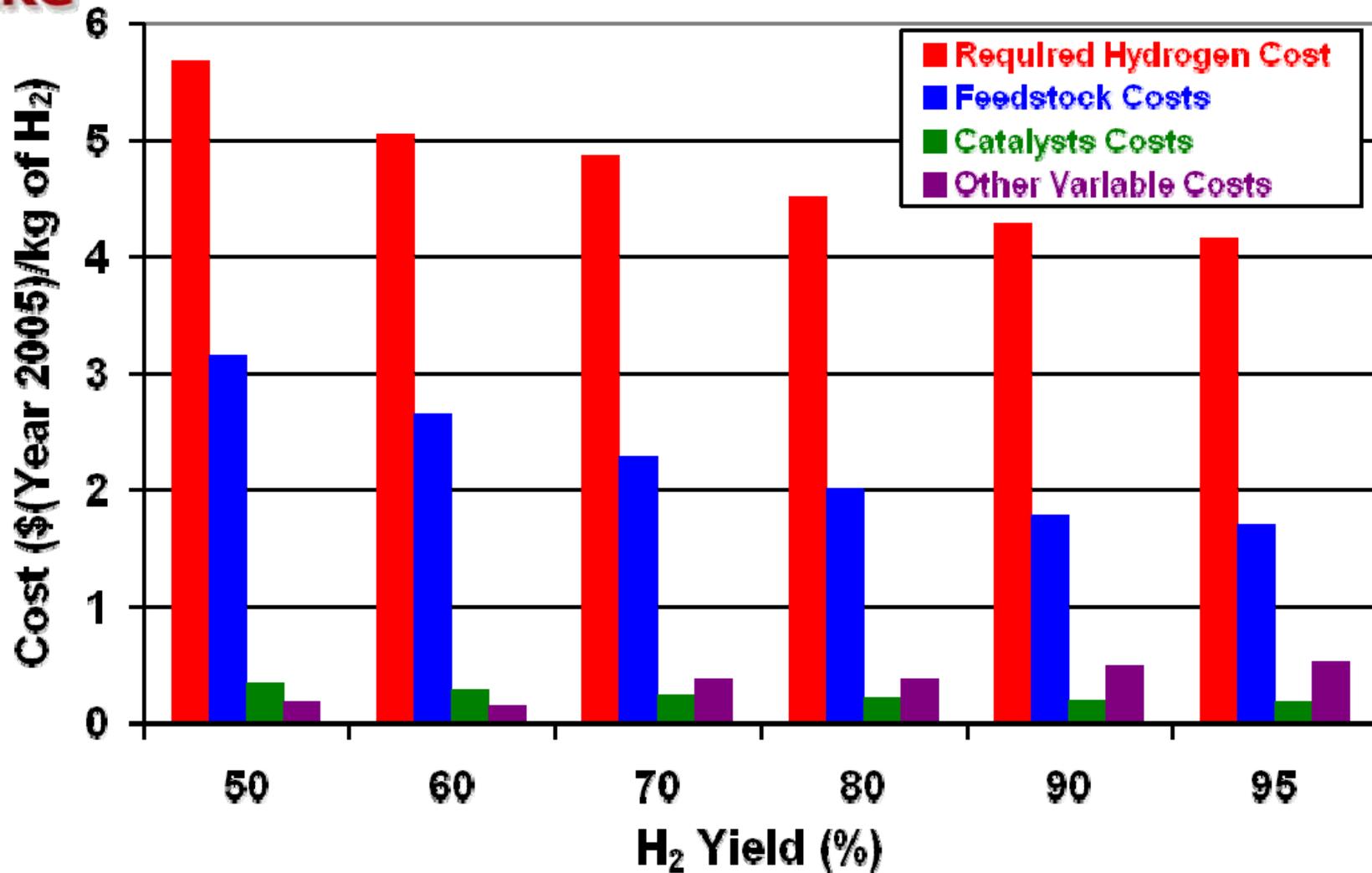
Economic Analysis – Forecourt Production at 1,500kg H₂/day



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

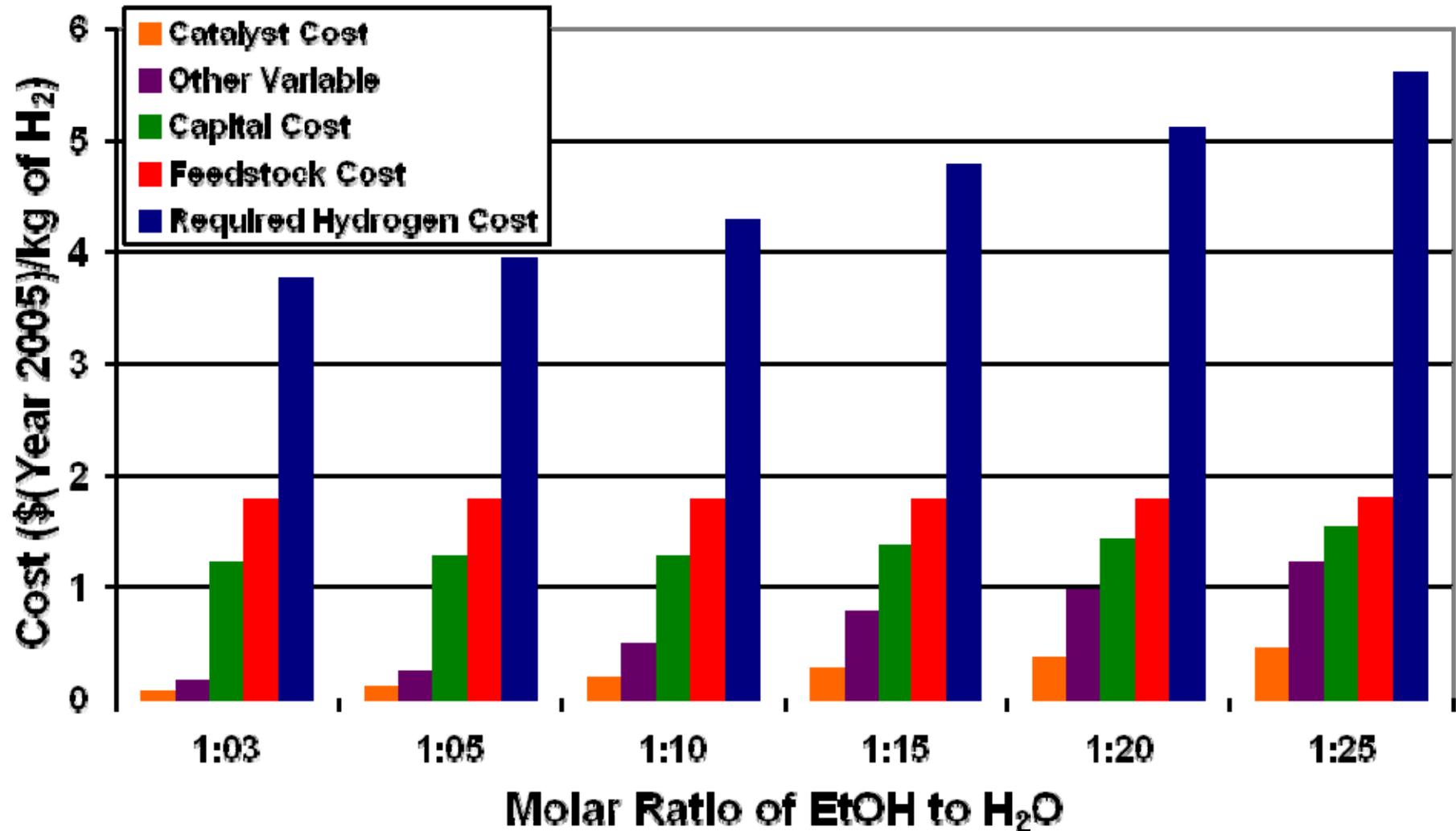


Sensitivity Analysis – Influence of Hydrogen Yield



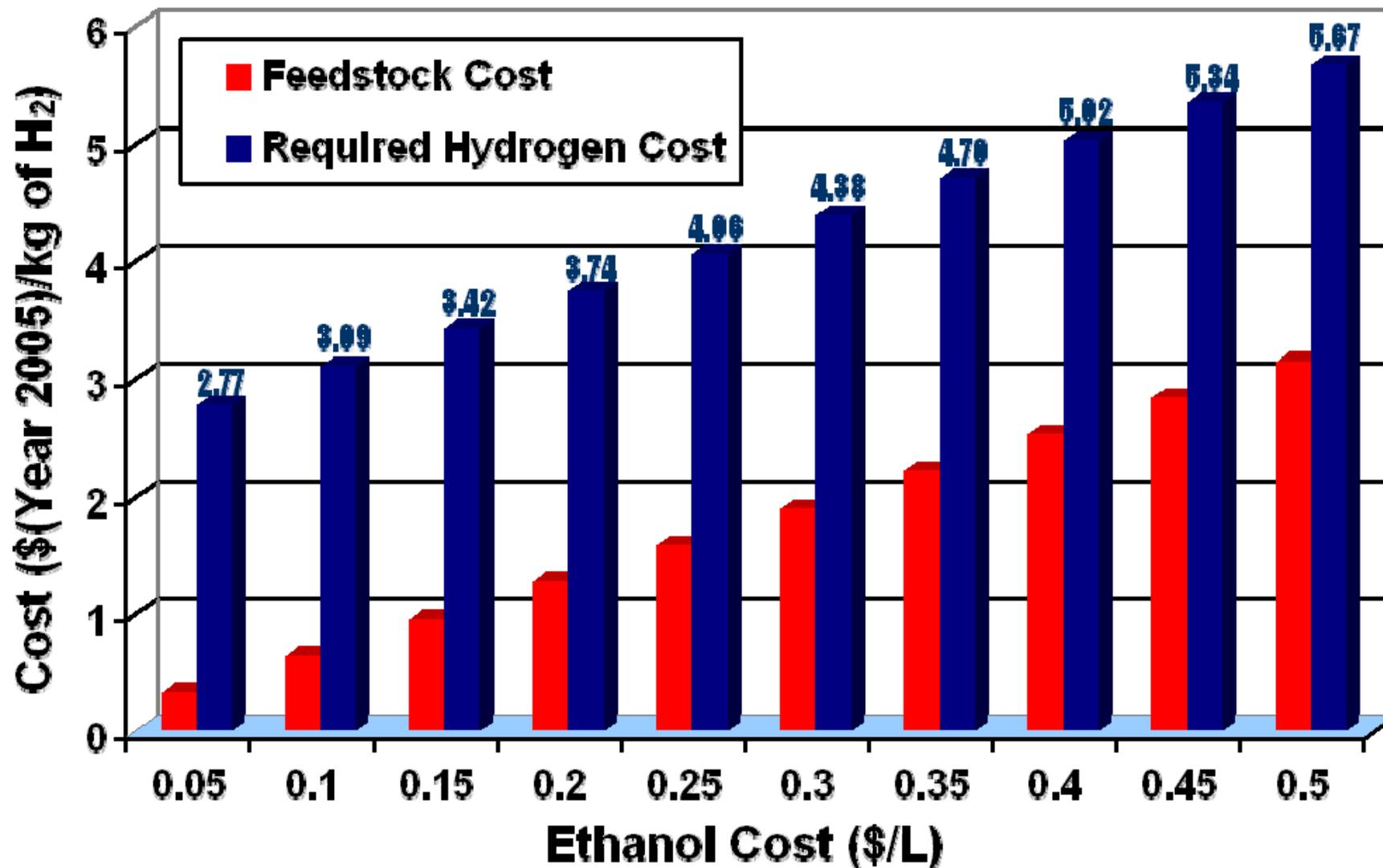
- ❖ Ethanol to water molar ratio of 1:10 is assumed;
- ❖ Various H₂ yields are based on the activity data over the catalysts developed in our lab.

Sensitivity Analysis – Influence of Molar Ratio of EtOH to H₂O



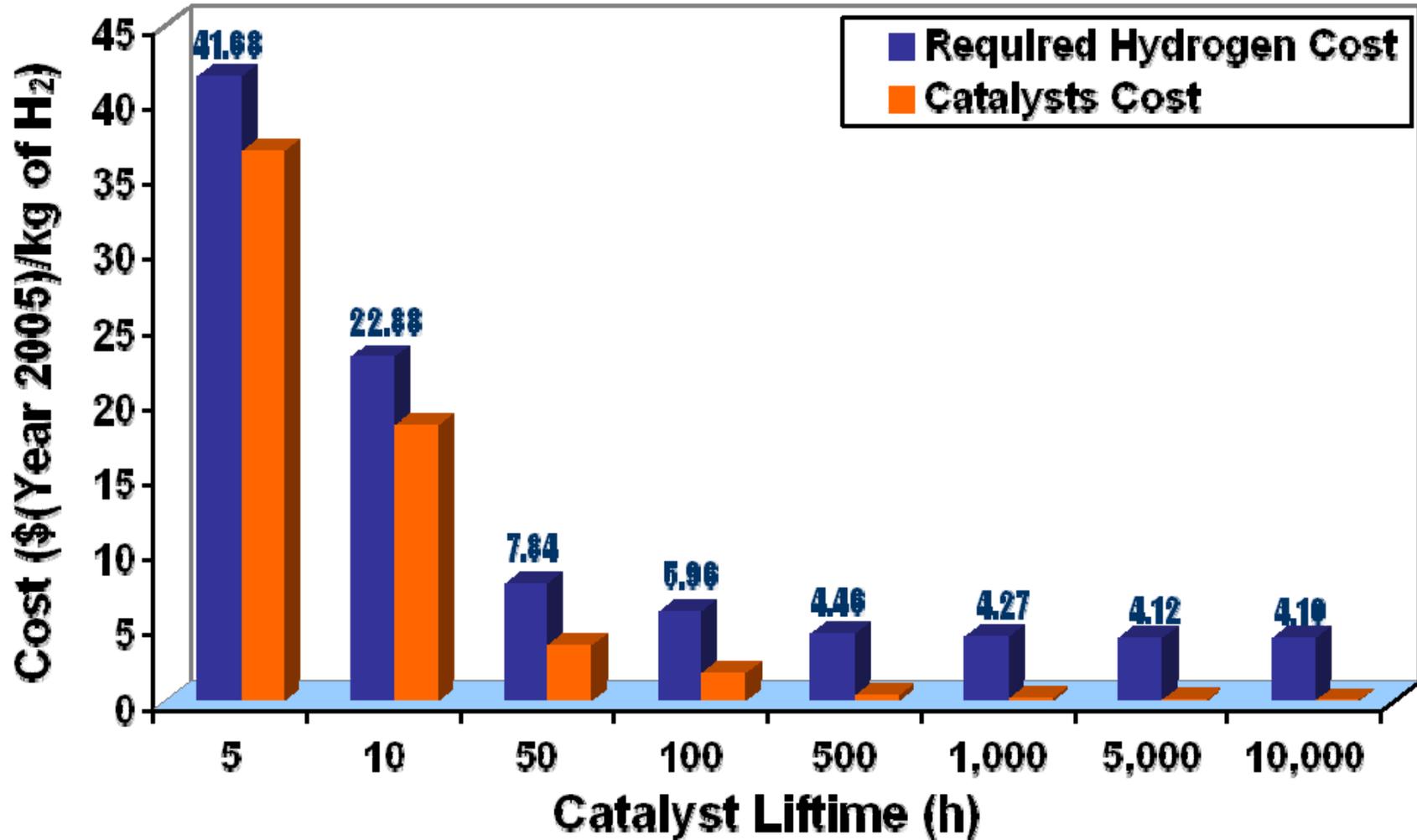
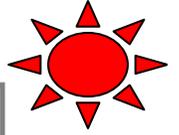
- ❖ 90% H₂ yield and 70% capacity factor are assumed;
- ❖ Catalysts loading is dependent on the total flowrate of reactants stream;
- ❖ Same catalysts system is used for bioethanol steam reforming and HTS reaction.

Sensitivity Analysis – Influence of Ethanol Cost Variation



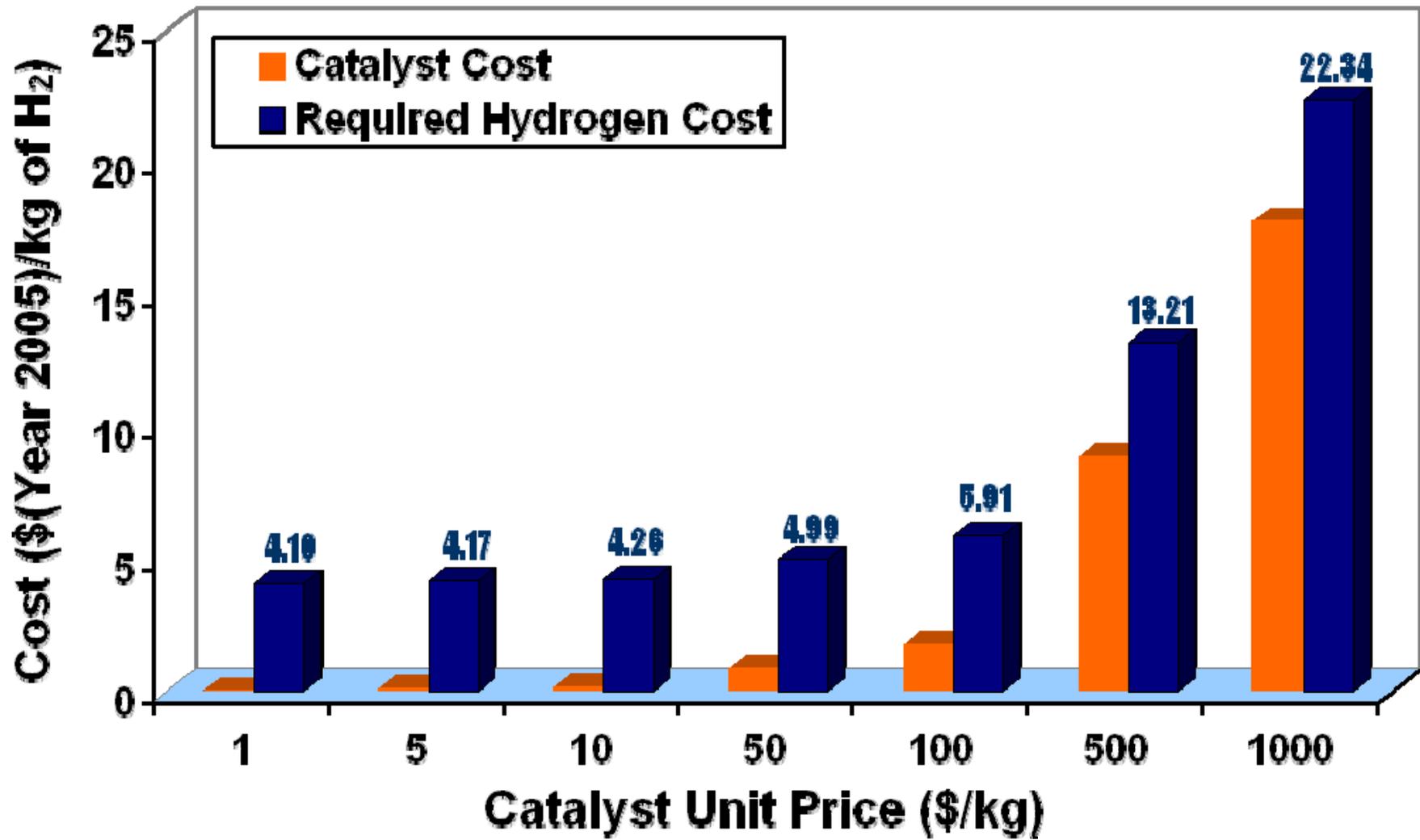
- ❖ 90% H₂ yield with ethanol to water molar ratio at 1:10 is assumed;
- ❖ Ethanol cost has a significant impact on the required hydrogen selling price.

Sensitivity Analysis – Influence of Catalyst Lifetime (stability)



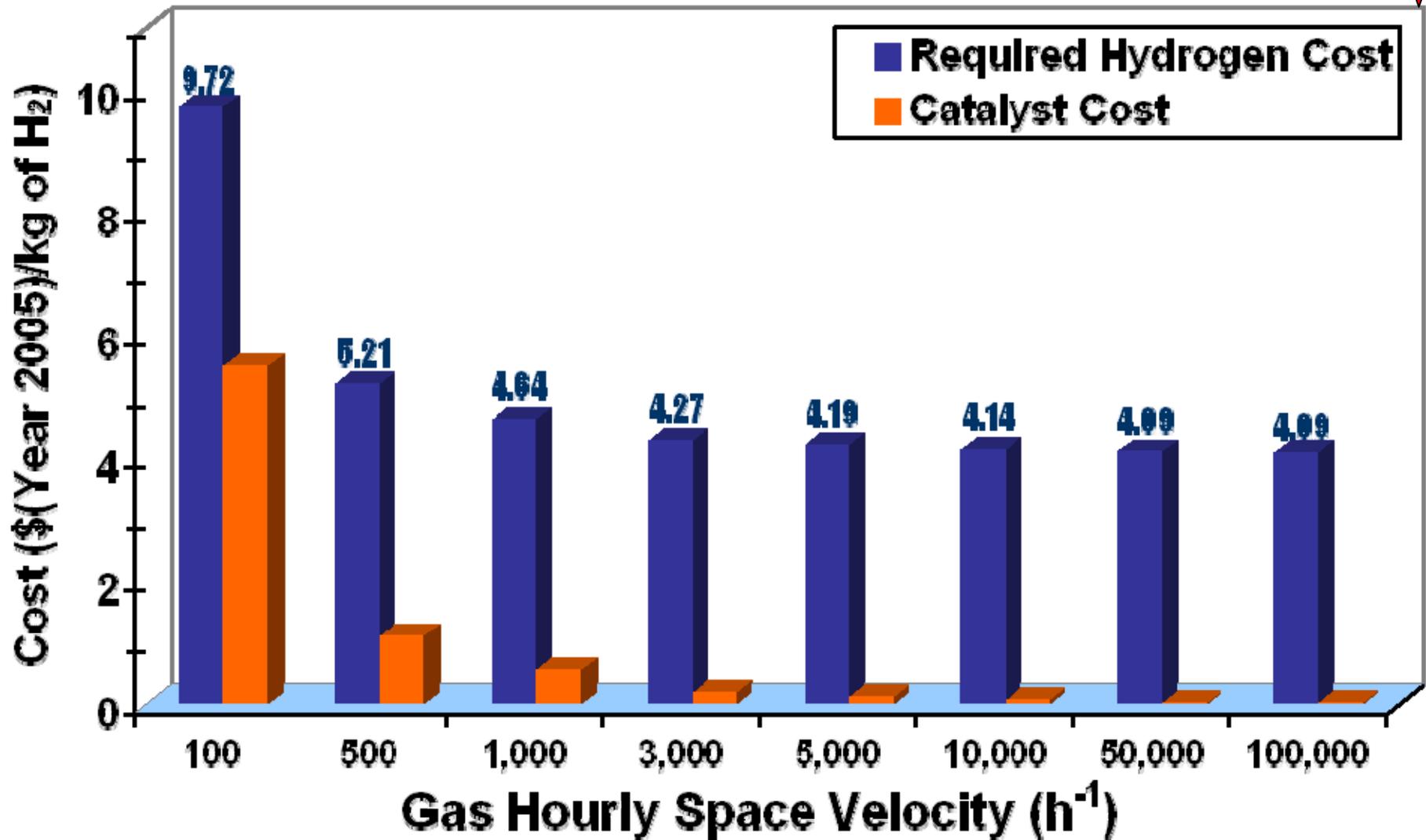
- ❖ 90% H₂ yield with ethanol to water molar ratio at 1:10 is assumed without dilution;
- ❖ The catalyst charged for BESR is assumed to have price of \$4.67/lb and 3,000h⁻¹ GHSV;
- ❖ Commercial catalyst is used for HTS reaction with 3,000h⁻¹ GHSV and 5 years lifetime at \$4.67/lb.

Sensitivity Analysis – Influence of Catalyst Unit Price



- ❖ 90% H₂ yield with ethanol to water molar ratio at 1:10 is assumed;
- ❖ The catalyst charged for BESR is assumed to have 3,000h⁻¹ GHSV and 1,000h lifetime;
- ❖ Commercial catalyst is used for HTS reaction with 3,000h⁻¹ GHSV and 5 years lifetime at \$4.67/lb.

Sensitivity Analysis – Influence of Gas Space Velocity

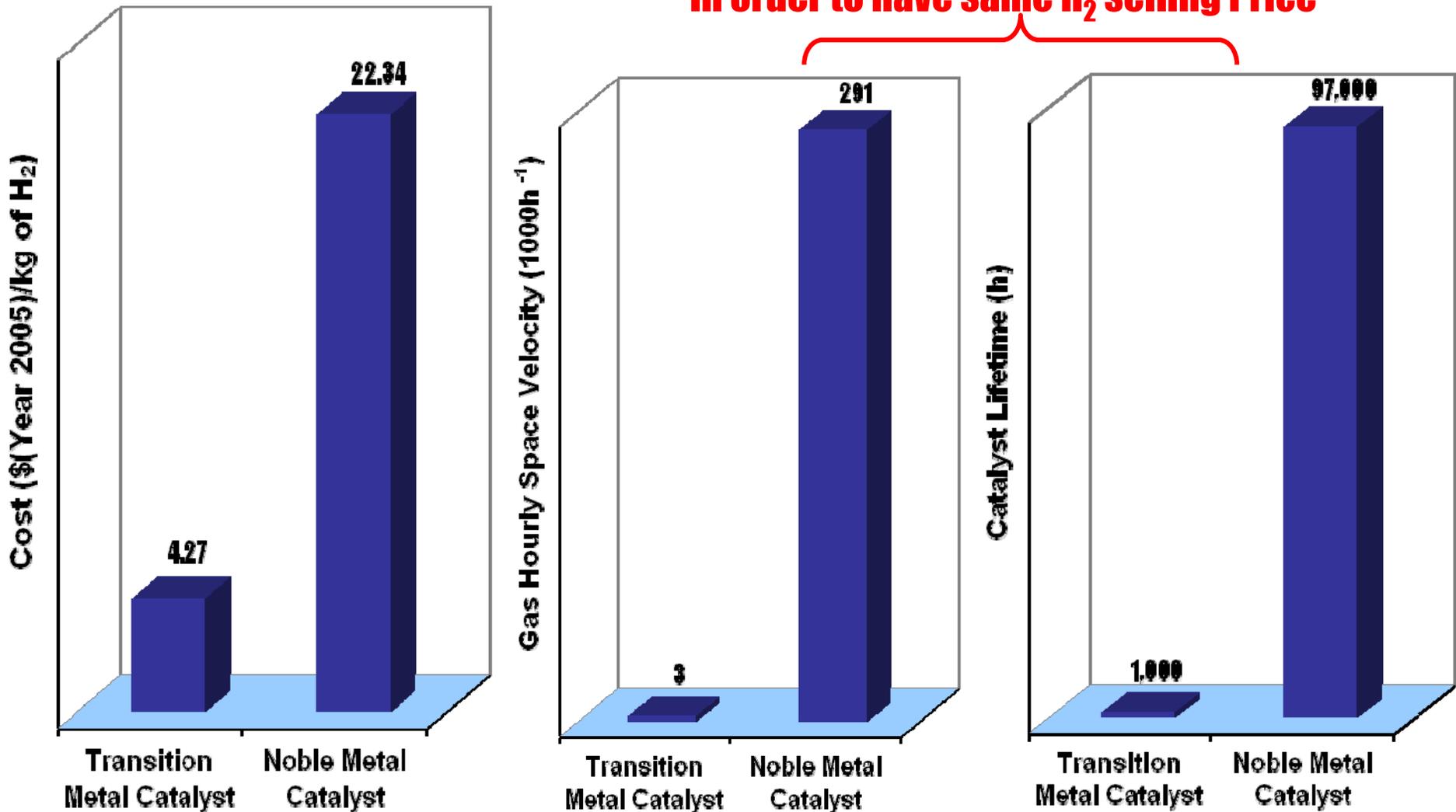


- ❖ 90% H_2 yield with ethanol to water molar ratio at 1:10 is assumed without dilution;
- ❖ The catalyst charged for BESR is assumed to have price of \$4.67/lb and 1,000h lifetime;
- ❖ Commercial catalyst is used for HTS reaction with $3,000\text{h}^{-1}$ GHSV and 5 years lifetime at \$4.67/lb.



Sensitivity Analysis – Noble vs. Non-noble Catalysts

In order to have same H₂ selling Price



- ❖ 90% H₂ yield with ethanol to water molar ratio at 1:10 is assumed without dilution;
- ❖ The noble catalyst charged for BESR is assumed to have price of \$1,000/kg;
- ❖ Commercial catalyst is used for HTS reaction with 3,000h⁻¹ GHSV and 5 years lifetime at \$4.67/lb.

Economic Analysis – Assessment of Status



❖ **Uncertainty areas during economic analysis:**

- Bioethanol reformer cost information;
- Water-gas shift reactor cost information;
- PSA equipment and corresponding operation cost information;
- Process optimization to improve energy efficiency for cost reduction;

❖ **Strategies to reduce the uncertainties:**

- Manufacturer consultations;
- Literature searching;
- Collaboration efforts with partners;

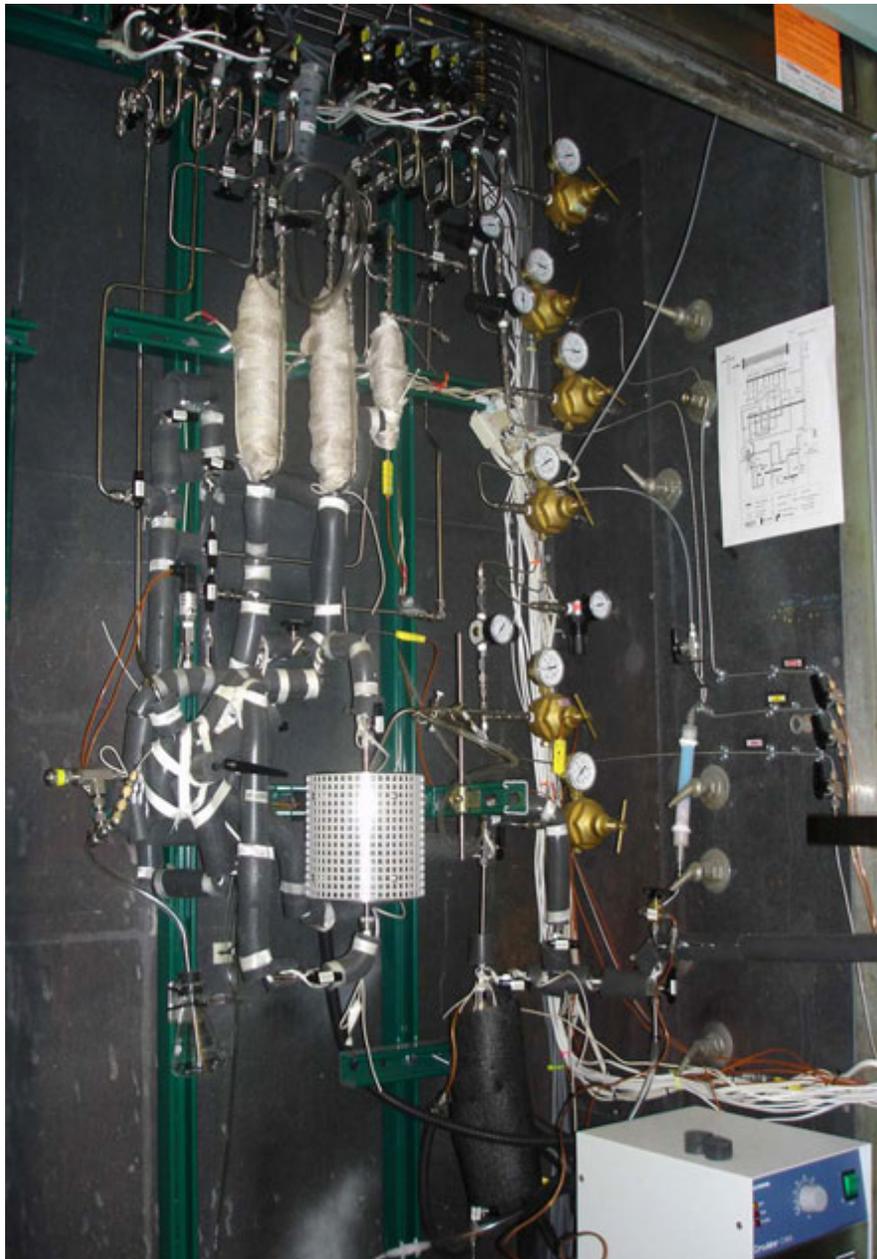
❖ **Timeline for addressing these uncertainties:**

- 2 quarters.

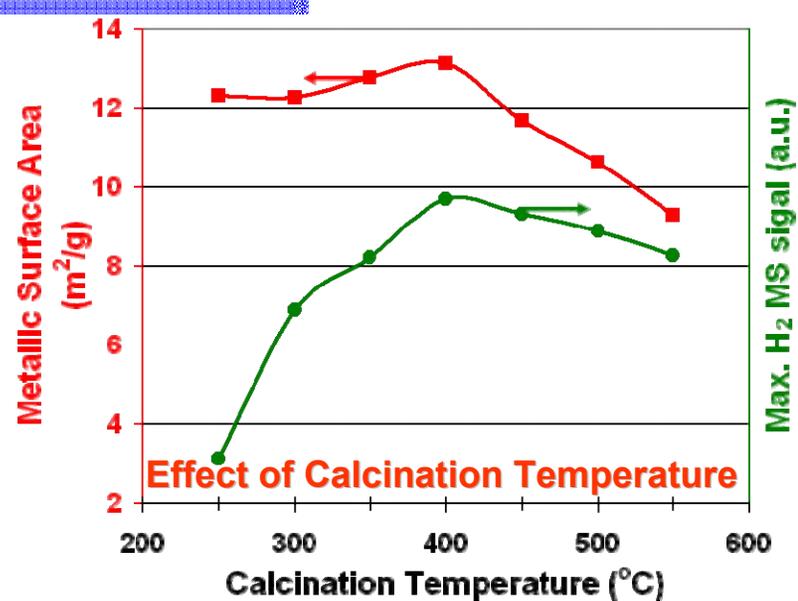
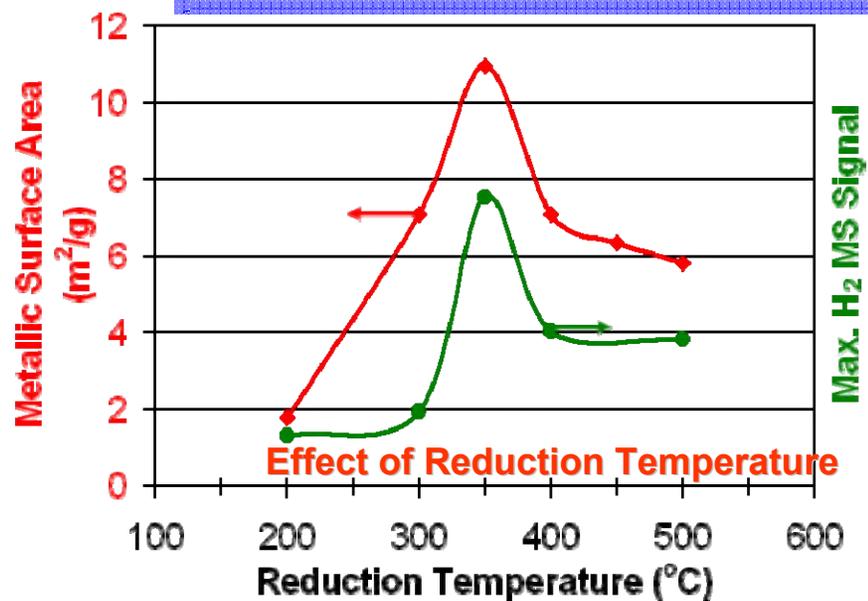
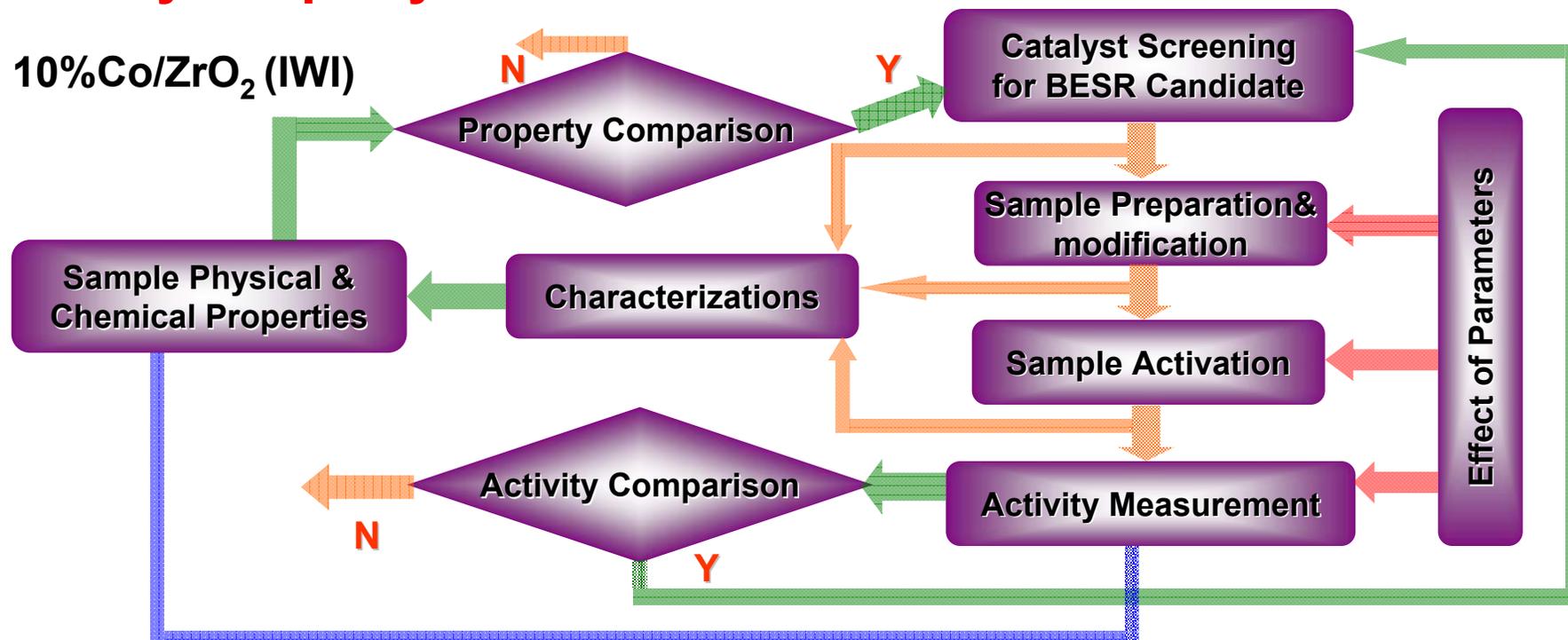


Highlights of Accomplishments

Design, Installation and Shake-up of a Reactor System



Activity-Property Correlation



Stability of Co/ZrO₂ Catalysts



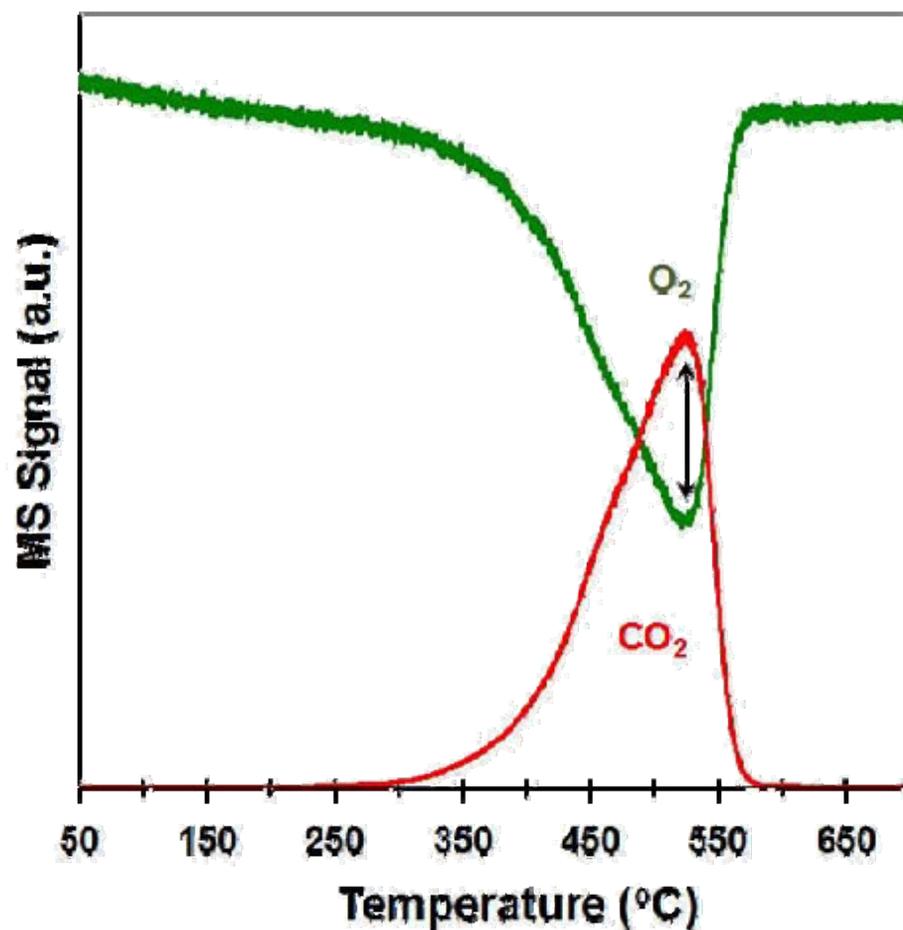
Time on Stream experiment:

EtOH: H₂O: dilution=1:10:75

GHSV=5,000h⁻¹

C_{EtOH}=1.2%

TPO on spent catalyst

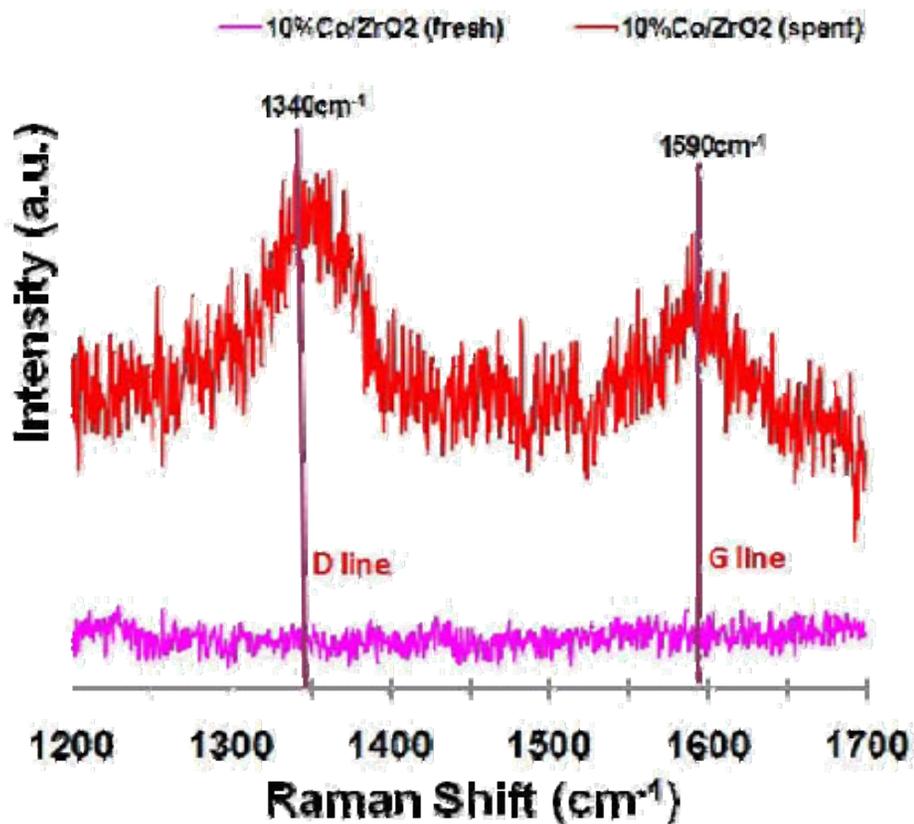


At high temperatures (>450°C), deactivation of the catalyst was observed.

Post-reaction characterization showed coke formation on the surface.



Coke Formation on the Surface of Co/ZrO₂ Catalysts was Verified by Raman Spectroscopy and XPS

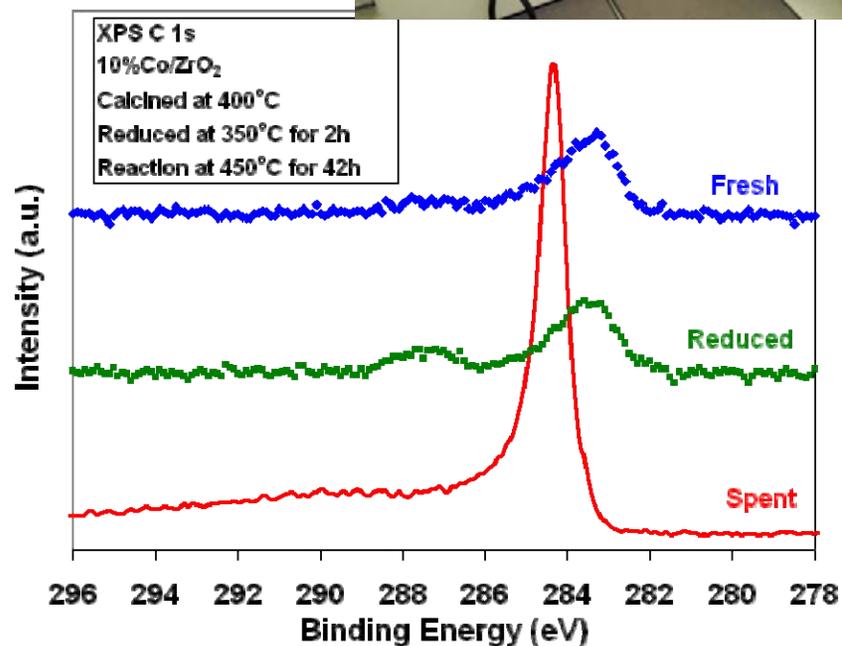
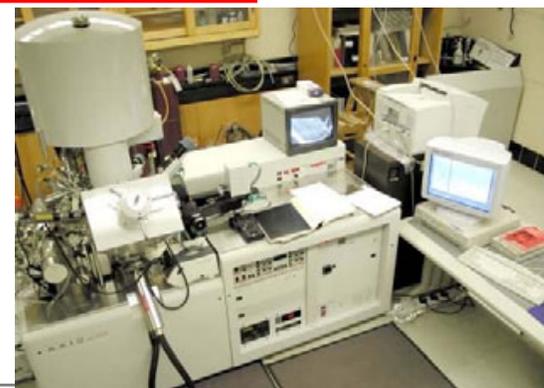


Time on Stream experiment:

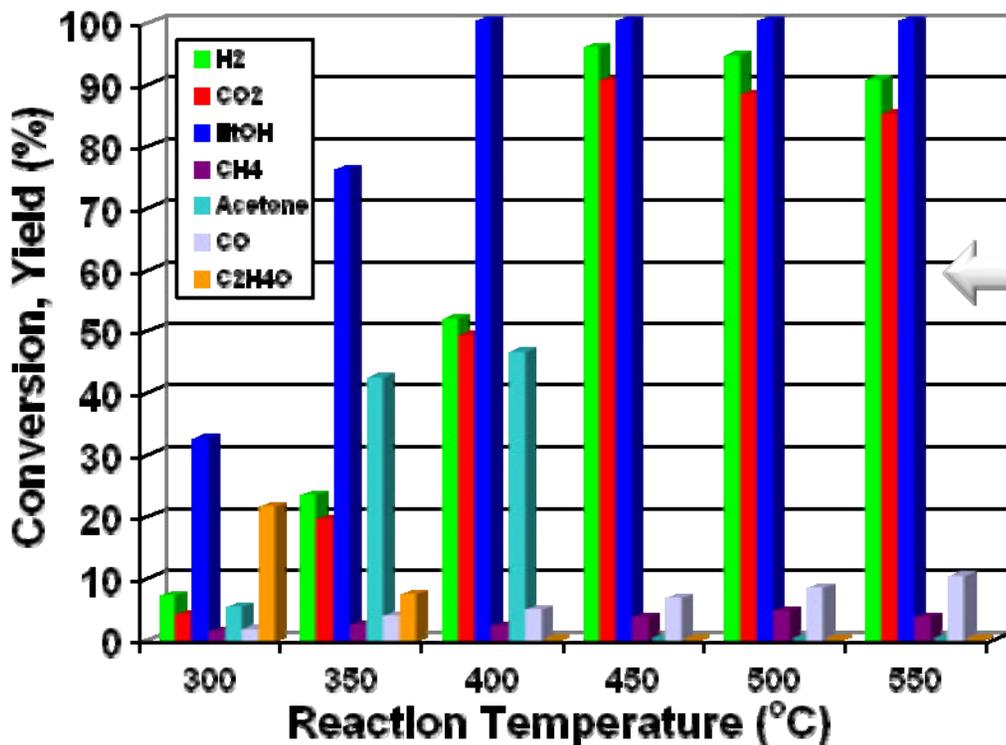
EtOH: H₂O=1:10

GHSV=5,000h⁻¹

C_{EtOH}=1.2%



Modified Formulations: Activity and Stability Improvement

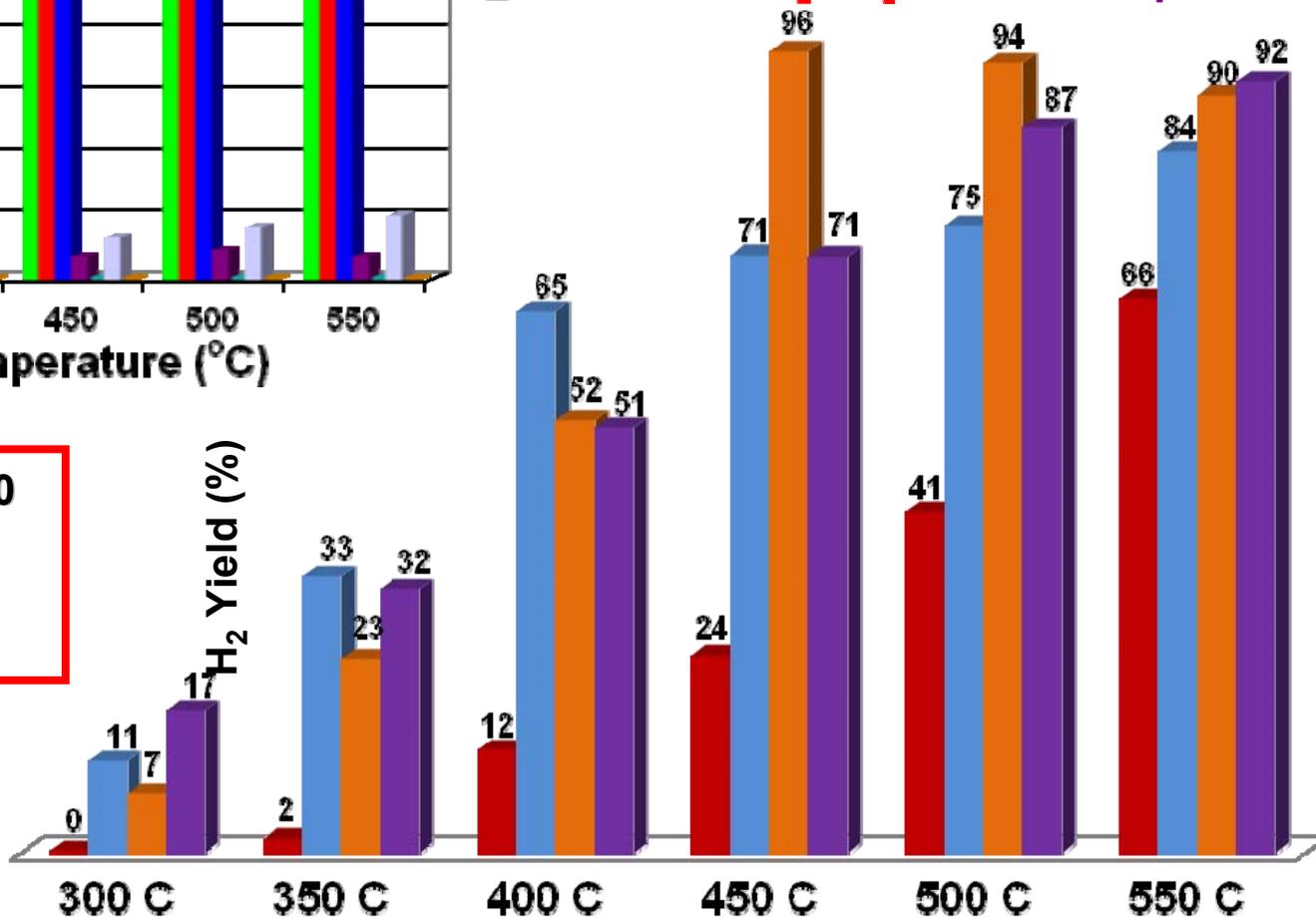


With modified formulations, high hydrogen yield can be achieved at lower temperature and catalyst stability is improved

■ 10%Co/20%La₂O₃-CeO₂
■ 10%Co/CeO₂
■ 10%Co/10%CeO₂-ZrO₂
■ Equilibrium

EtOH: H₂O: dilution=1:10:40
 GHSV= \sim 20,000h⁻¹
 WHSV=0.48gEtOH/gCat/h
 C_{EtOH}=2%

Sample activation is observed after activity test



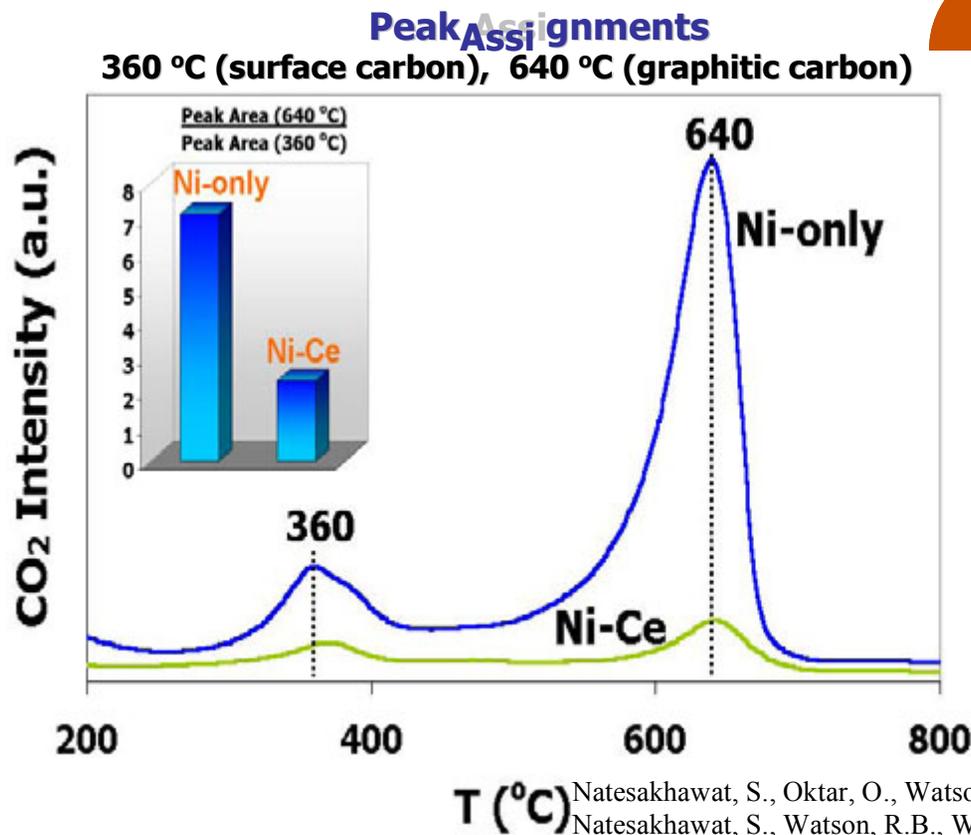
**Catalyst modification for improved
resistance to coking:**

**Doping of the active metal with a
lanthanide element.**

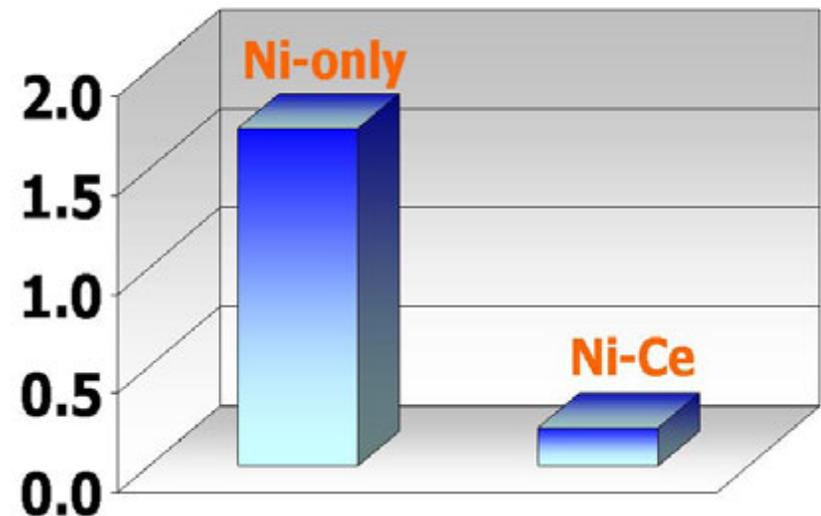
**Similar phenomena observed in
propane steam reforming
over Ni/Al₂O₃ and Ce-doped Ni/Al₂O₃**

Temperature-programmed Oxidation (TPO)

- Post-reaction samples after 20 hr of propane steam reforming at 500 °C and $H_2O/C_3H_8 = 4$.
- Oxidizing agent: 1% O_2/He



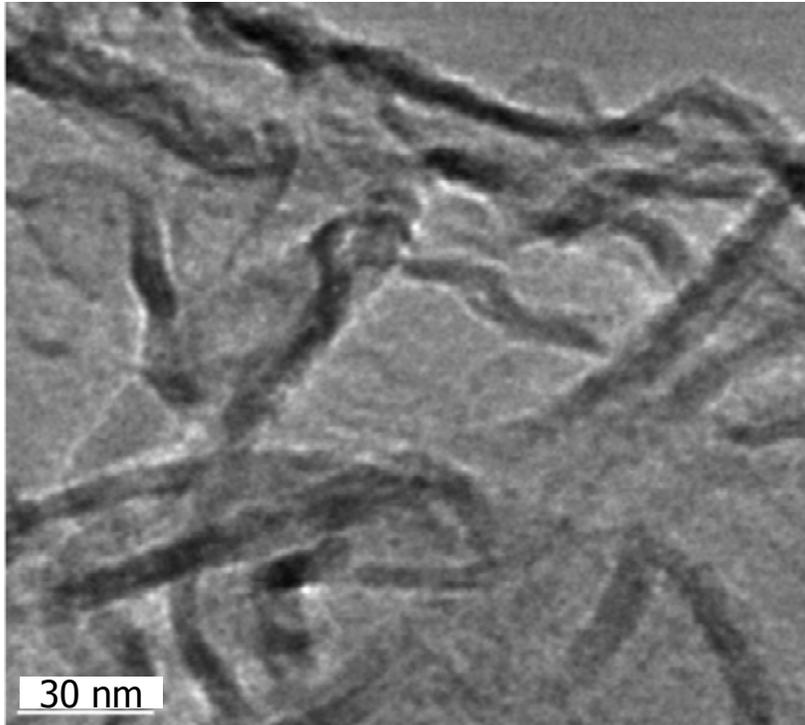
Carbon Formation (g C/m²x10⁻³)



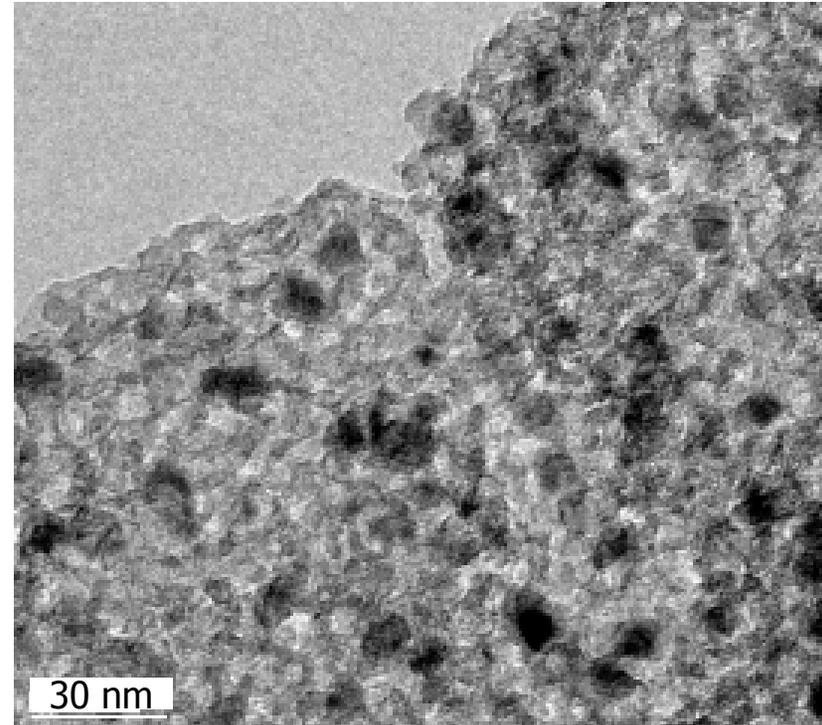
Ce Promotion Inhibits Coke Formation

Transmission Electron Microscopy (TEM)

Ni-only



Ni-Ce



*TEM images were taken from samples after 20 hr of propane steam reforming (500 °C, H₂O/C₃H₈ = 4)

- Clear evidence of significant amounts of carbon filaments over Ni-only catalyst after SR of propane.

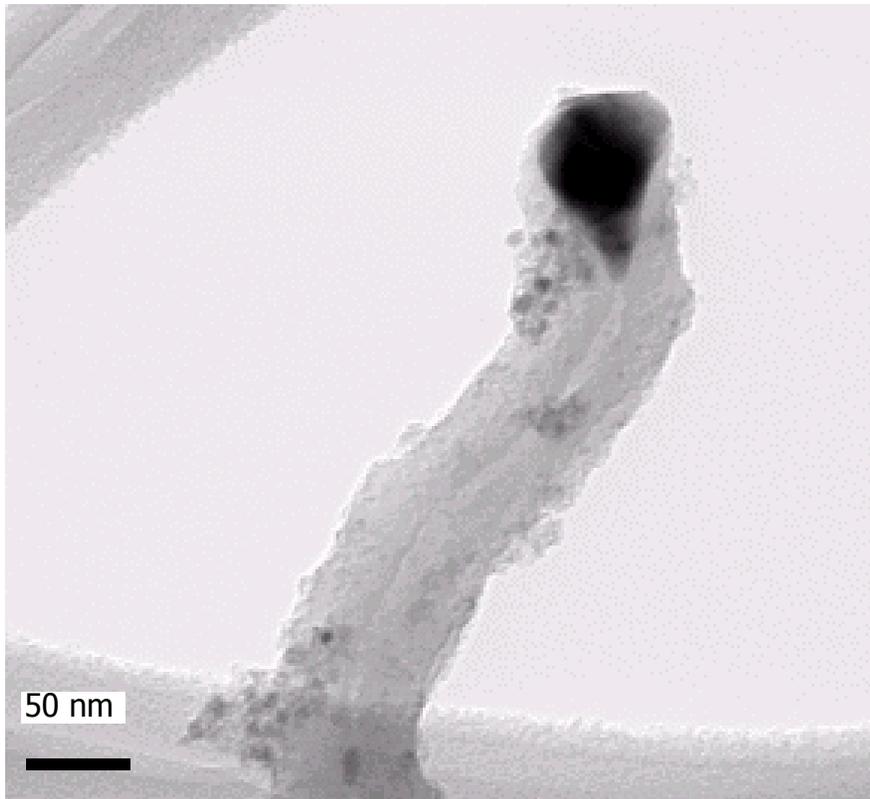
- No carbon filaments observed on post-rxn Ni-Ce catalyst due to improvement in coking resistance.

Natesakhawat, S., Oktar, O., Watson, R.B., Ozkan, U. S., *Journal of Molecular Catalysis A*, **241**, 133-146 (2005)

Natesakhawat, S., Watson, R.B., Wang, X., Ozkan, U. S. , *Journal of Catalysis*, **234**, 496-508 (2005).

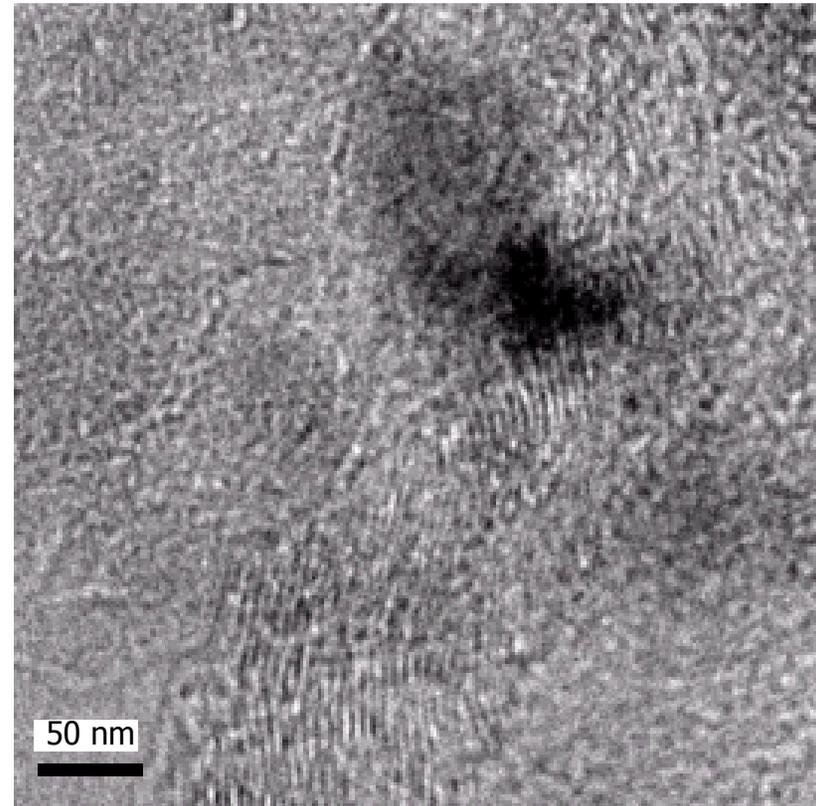
Morphology of Carbon Deposits

Ni-only



- A filament-like structure of carbon species on post-rxn Ni-only catalyst is clearly observed [A nickel particle is seen at the tip of carbon filament].

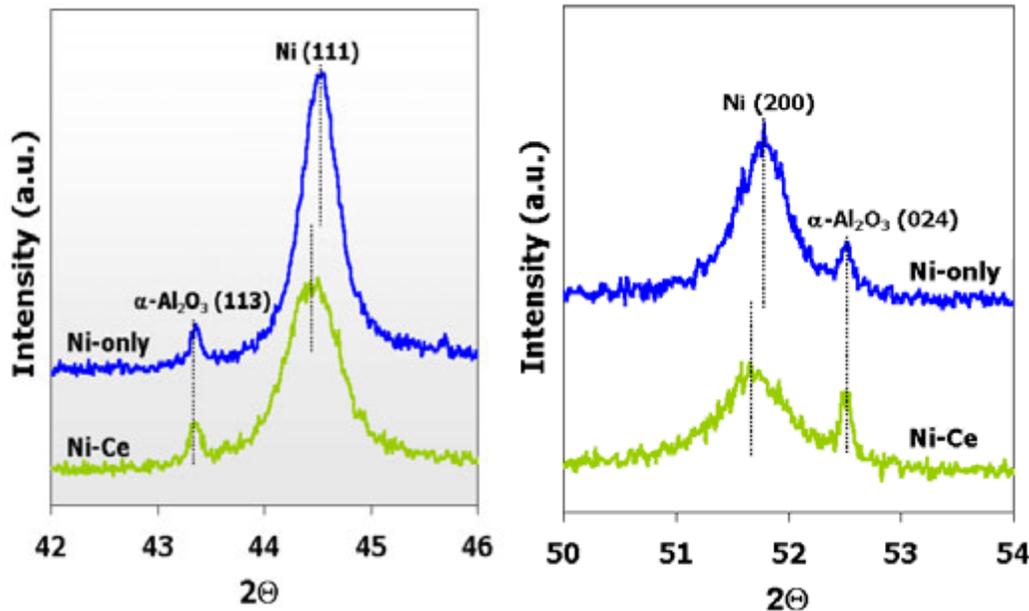
Ni-Ce



- "Extruded" carbon on post-rxn Ni-Ce catalyst is observed [Nickel particle remains on the alumina support surface].

In situ XRD

[$\alpha\text{-Al}_2\text{O}_3$ was used as an internal standard]



Lattice parameter

	a (nm)	
Pure Ni (JCPDF 4 850)	Ni-only	Ni-Ce
0.5238	0.5239	0.5278

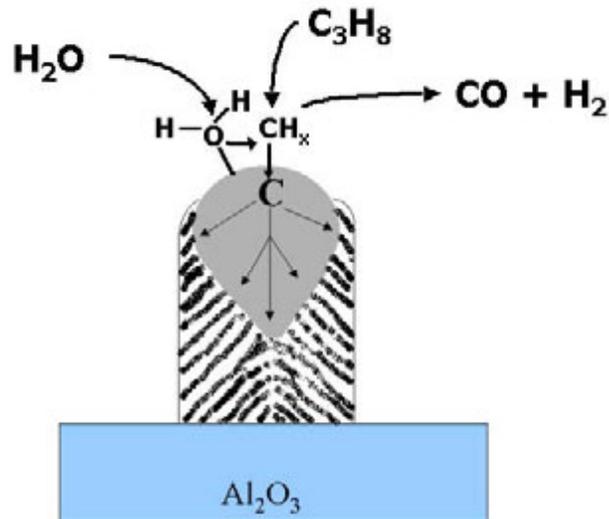
* Catalysts were reduced *in situ* under 5% H_2/N_2 at 700 °C.

- *In situ* XRD result suggests that Ce is incorporated into Ni catalysts, leading to a change in lattice parameter of Ni crystallite.
- Incorporation of ceria in nickel results in reduction of carbon dissolution/diffusion through Ni crystallites.

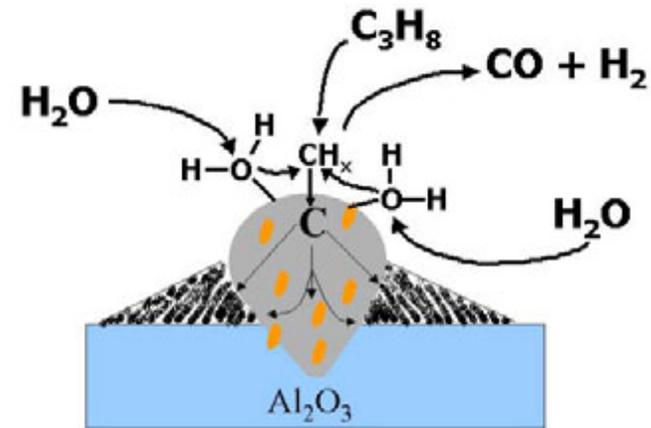
Natesakhawat, S., Oktar, O., Watson, R.B., Ozkan, U. S., *Journal of Molecular Catalysis A*, **241**, 133-146 (2005)

Natesakhawat, S., Watson, R.B., Wang, X., Ozkan, U. S. , *Journal of Catalysis*, **234**, 496-508 (2005).

Ni-only



Ni-Ce

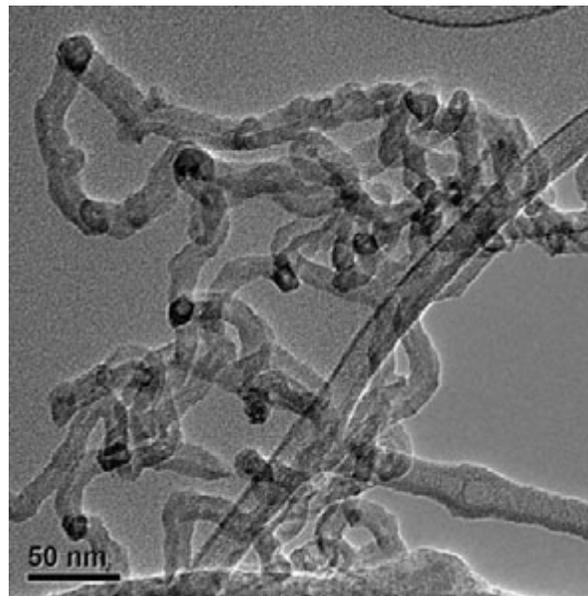
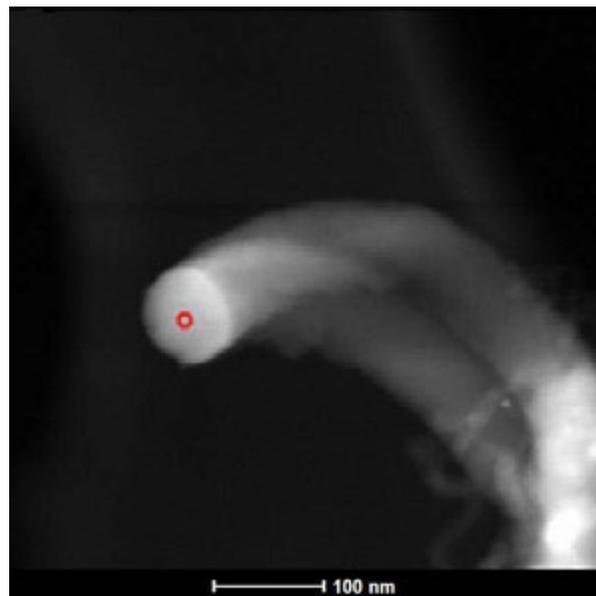
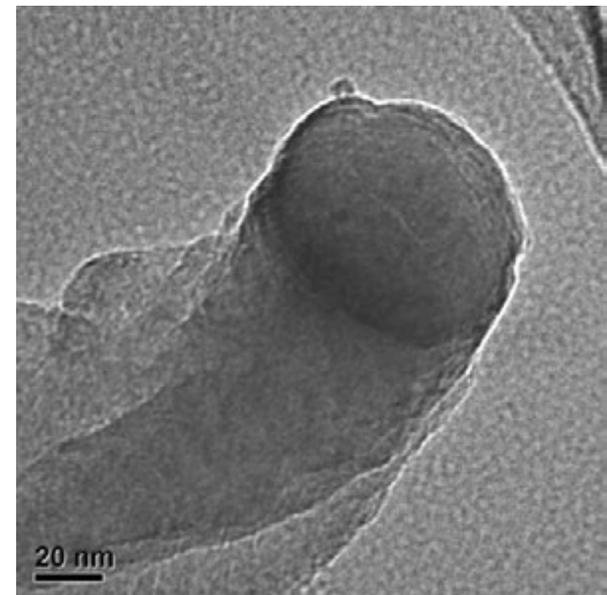
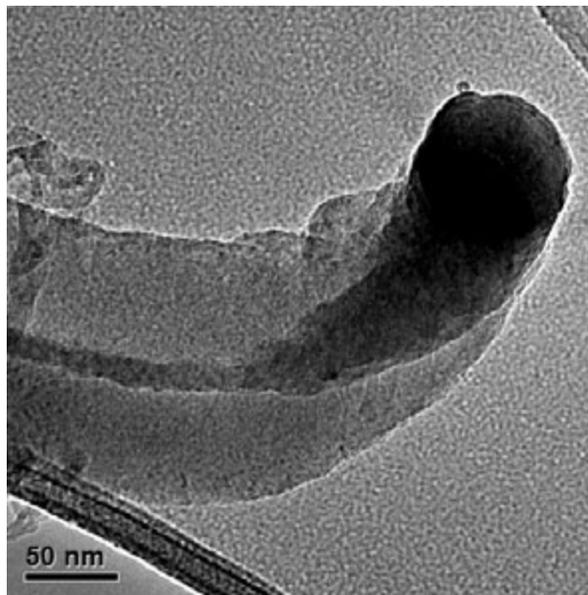
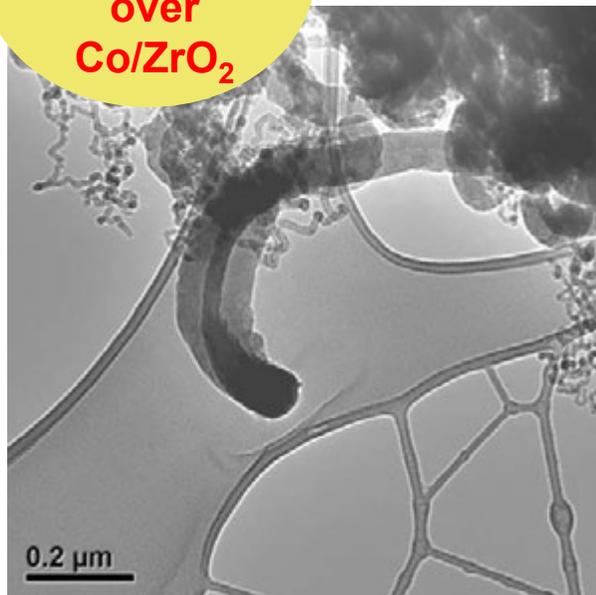


Cerium promotion not only increases SR activity but also inhibits coke formation possibly due to

- Higher concentration of active surface oxygen due to increased water adsorption
- Minimization of dehydrogenation of dissociated hydrocarbon fragments
- Enhancement in carbon gasification through oxygen mobility
- Inhibition of carbon dissolution through nickel due to incorporation of Ce
- Inhibition of carbon diffusion through nickel particles

Carbon Deposition on Co/ZrO₂

Similar phenomena over Co/ZrO₂



Tecnai TF-20 TEM

In the current study:

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

Carbon Nanofibers Growth over Deactivated Catalysts



10%Co/ZrO₂ (IWI)

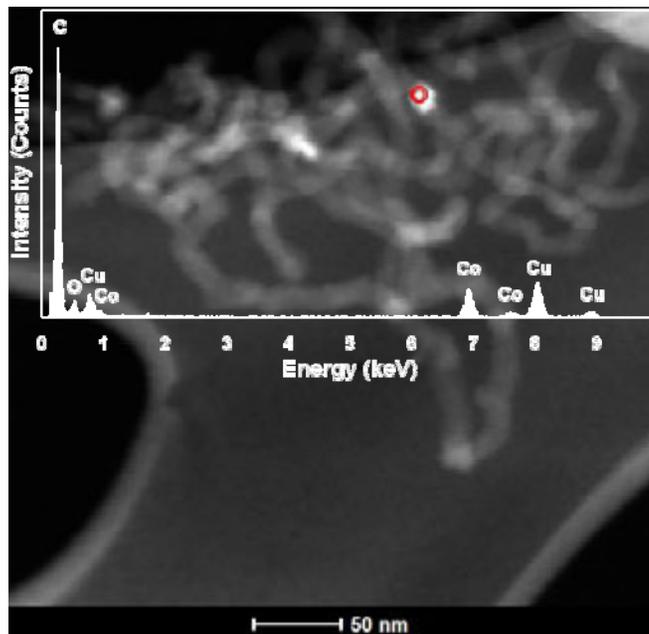
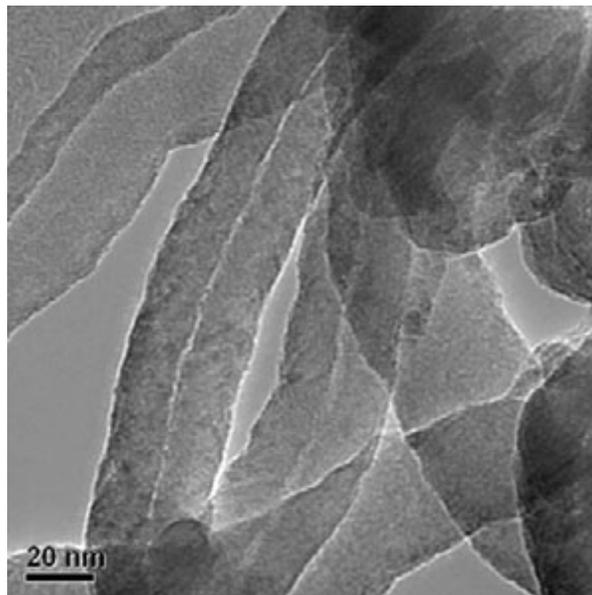
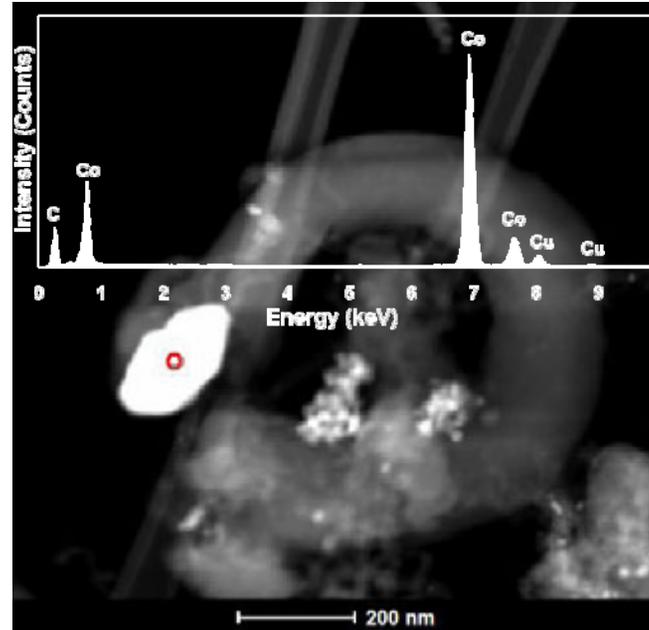
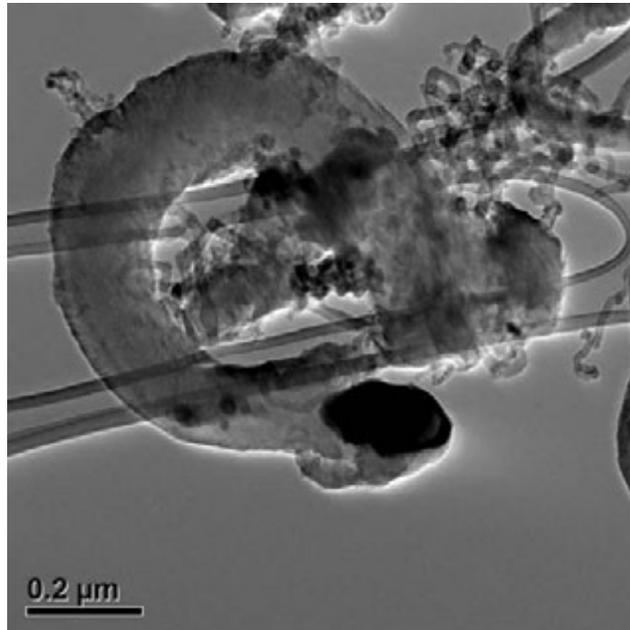
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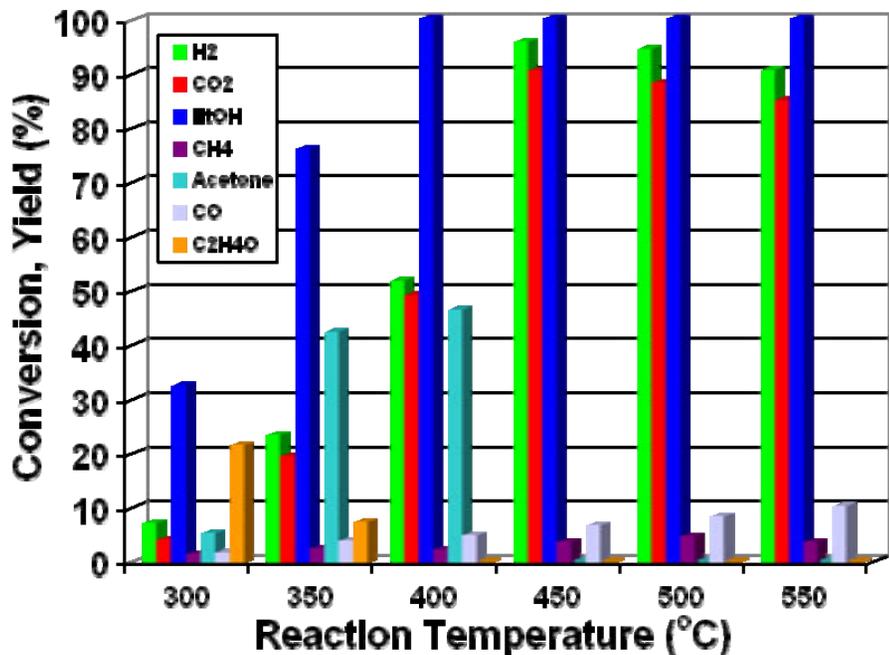
- ❖ Samples were dispersed in ethanol.
- ❖ Supported by lacey formvar carbon on a 200 mesh Cu grid.

The diameter of the carbon nanofiber is dependent on cobalt particle size;

Co particles identified through EDXA analysis.



Much Higher Stability-coking is suppressed



10%Co/20%La₂O₃-CeO₂ (CP)

metal precursor: Co(NO₃)₂, Ce(NO₃)₃, La(NO₃)₃

pH value: 7.5 ~ 8.5;

Precipitant: Na₂CO₃.

EtOH: H₂O: dilution=1:10:40

GHSV=~20,000h⁻¹

WHSV=0.48gEtOH/gCat/h

C_{EtOH}=2%

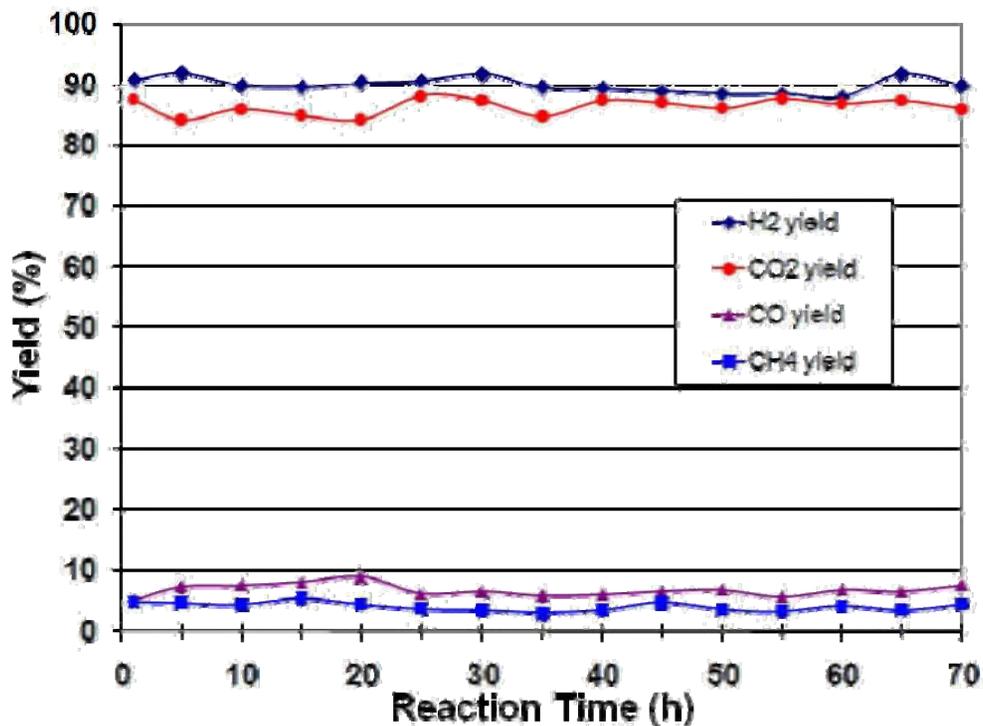
H₂O:EtOH=10:1 (molar ratio)

GHSV=~20,000h⁻¹

WHSV=0.48gEtOH/gCat/h

C_{EtOH}=2%

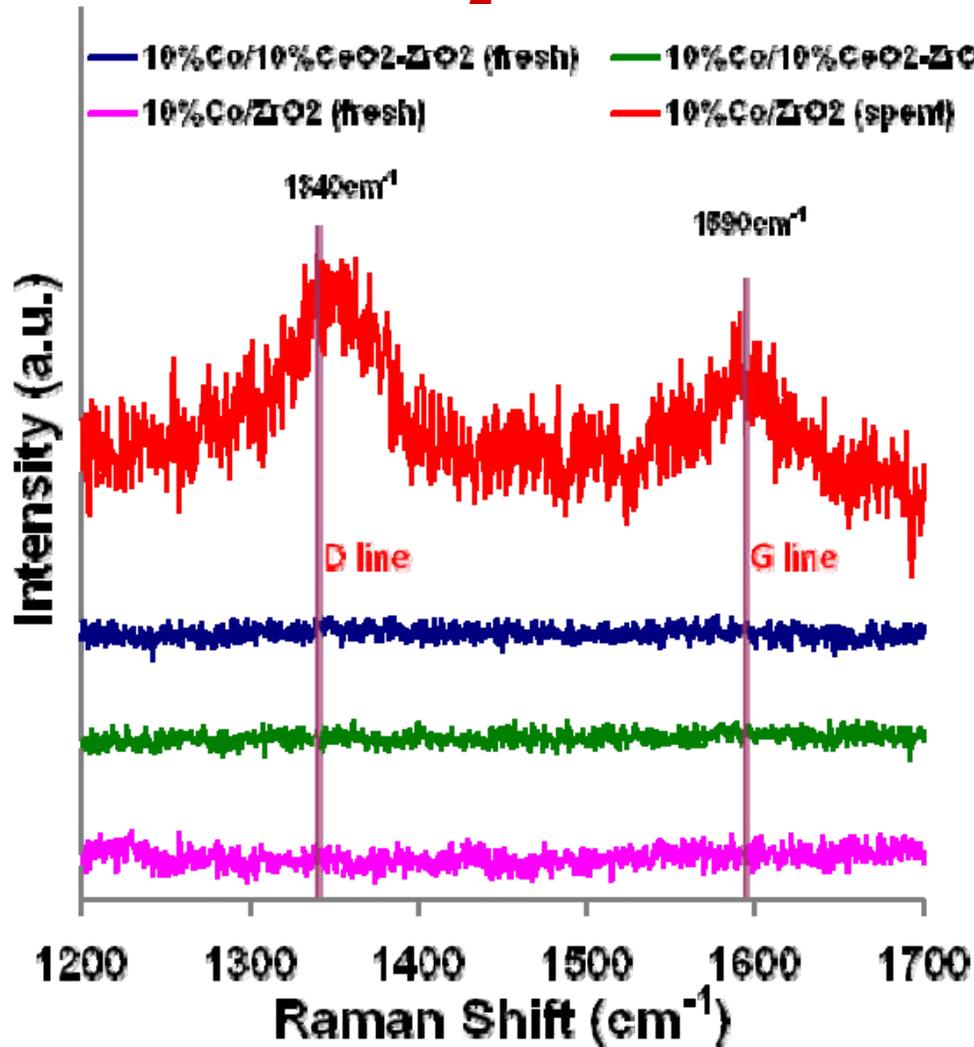
T=450°C



❖ Activity is stable over 70 hrs

❖ Hydrogen yield is ~90% during the test time period

Effect of CeO₂ Addition on Sample Stability



Time on Stream experiment:

EtOH: H₂O: dilution=1:10:75

GHSV=5,000h⁻¹

C_{EtOH}=1.2%

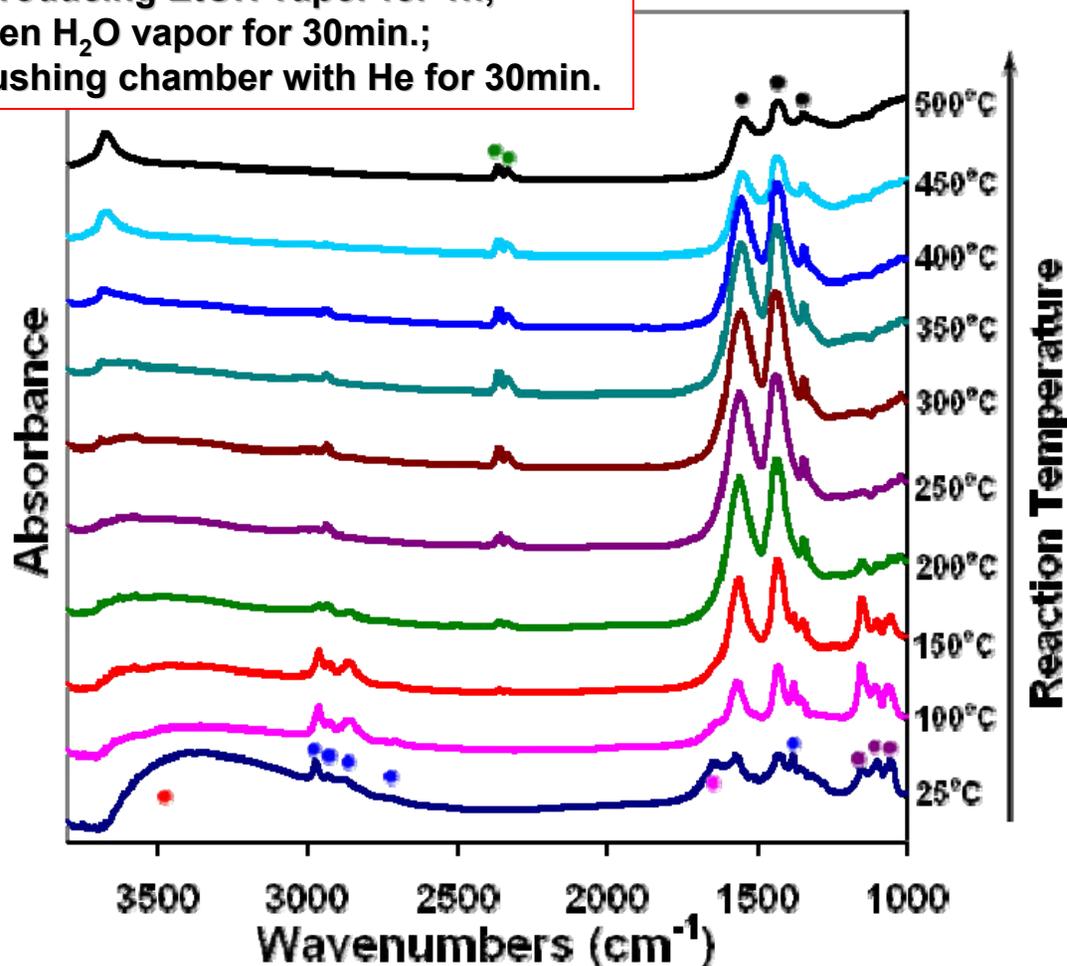
Stability test at 450°C

No deactivation was observed even after 110h run over ceria-modified samples. No coke formation on the surface.

Proof of Activity Improvement through In-Situ DRIFTS EtOH+H₂O Reaction

10%Co/ZrO₂ (400°C)

Introducing EtOH vapor for 1h;
Then H₂O vapor for 30min.;
Flushing chamber with He for 30min.



● **M-OH**

3650~3150cm⁻¹, O-H stretching

● **CH₃- or CH₃CH₂-**

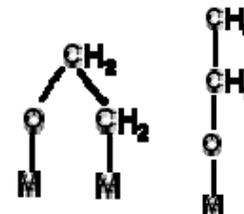
2962, 2927, 2865 cm⁻¹:C-H stretching

1385cm⁻¹: CH₃- bending

● **Monodentate and bidentate ethoxide**

1169, 1106, 1063cm⁻¹

CCO stretching



● **Acetates**

CH₃COO

1569, 1429, 1348cm⁻¹

● **Adsorbed CO₂**

2361, 2336cm⁻¹: O=C=O stretching

● **Molecularly adsorbed H₂O**

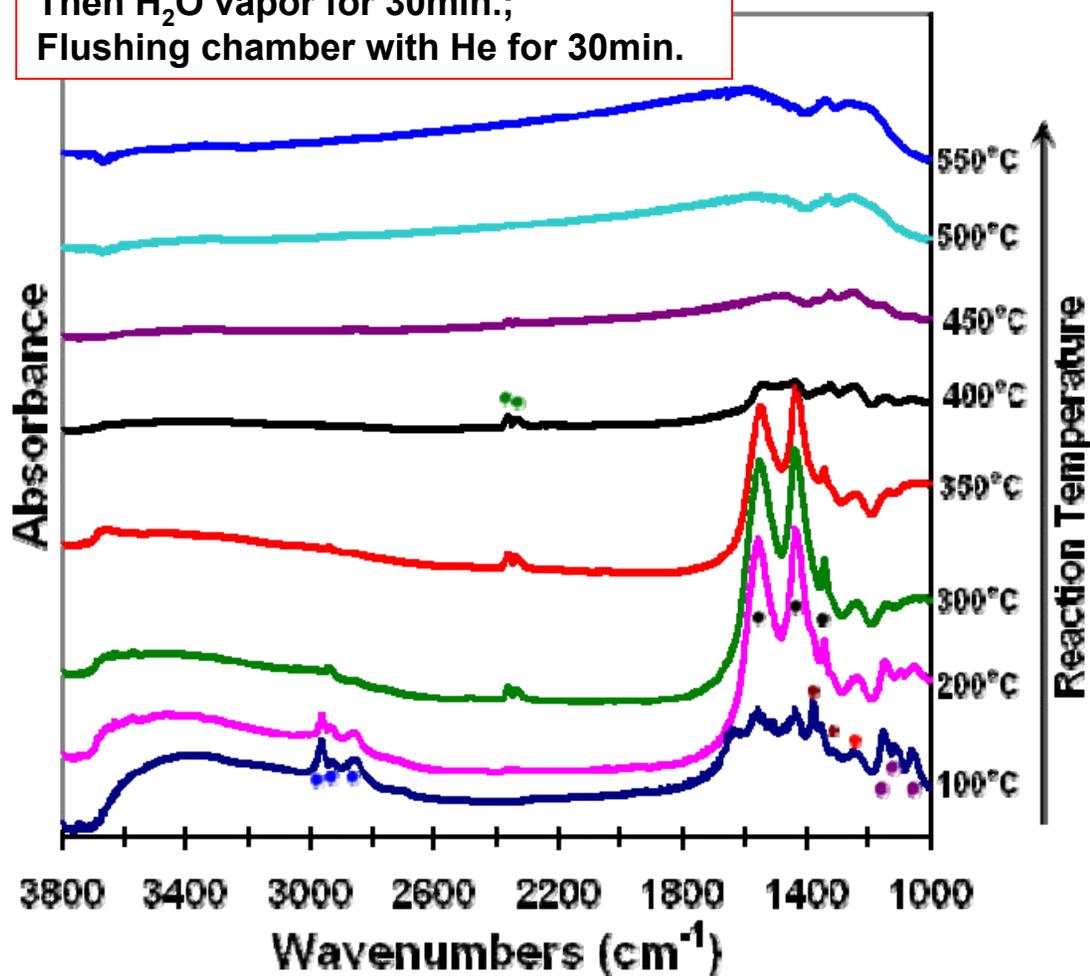
1654cm⁻¹

- Water and ethanol molecules are adsorbed onto the surface at room temp
- Interaction with OH groups
- Water facilitates formation of ethoxy and acetate surface intermediates at lower temp.,
- CO (characteristic peaks: 2200~2000cm⁻¹) is not observed

Proof of Activity Improvement through In-Situ DRIFTS

EtOH+H₂O Reaction

10%Co/10%CeO₂-ZrO₂ (400°C)
 Introducing EtOH vapor for 1h;
 Then H₂O vapor for 30min.;
 Flushing chamber with He for 30min.



● Monodentate and bidentate ethoxide

2968, 2935, 2871cm⁻¹: C-H stretching

1155cm⁻¹: C-C stretching;

1139cm⁻¹: C-O stretching (mono)

1061cm⁻¹: C-O stretching (bi)

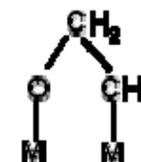


● Acetates

CH₃COO

1562, 1440cm⁻¹: COO stretching

1348cm⁻¹: CH₃ bending



● Molecularly adsorbed ethanol

1380, 1340cm⁻¹

● Adsorbed CO₂

2370, 2347cm⁻¹

● -OH group: 1267cm⁻¹ bending

➤ The presence of CeO₂ facilitates the conversion of ethanol, leading to the appearance and disappearance of surface reaction intermediates at much lower reaction temperature

Highlights of Accomplishments (cont'd)

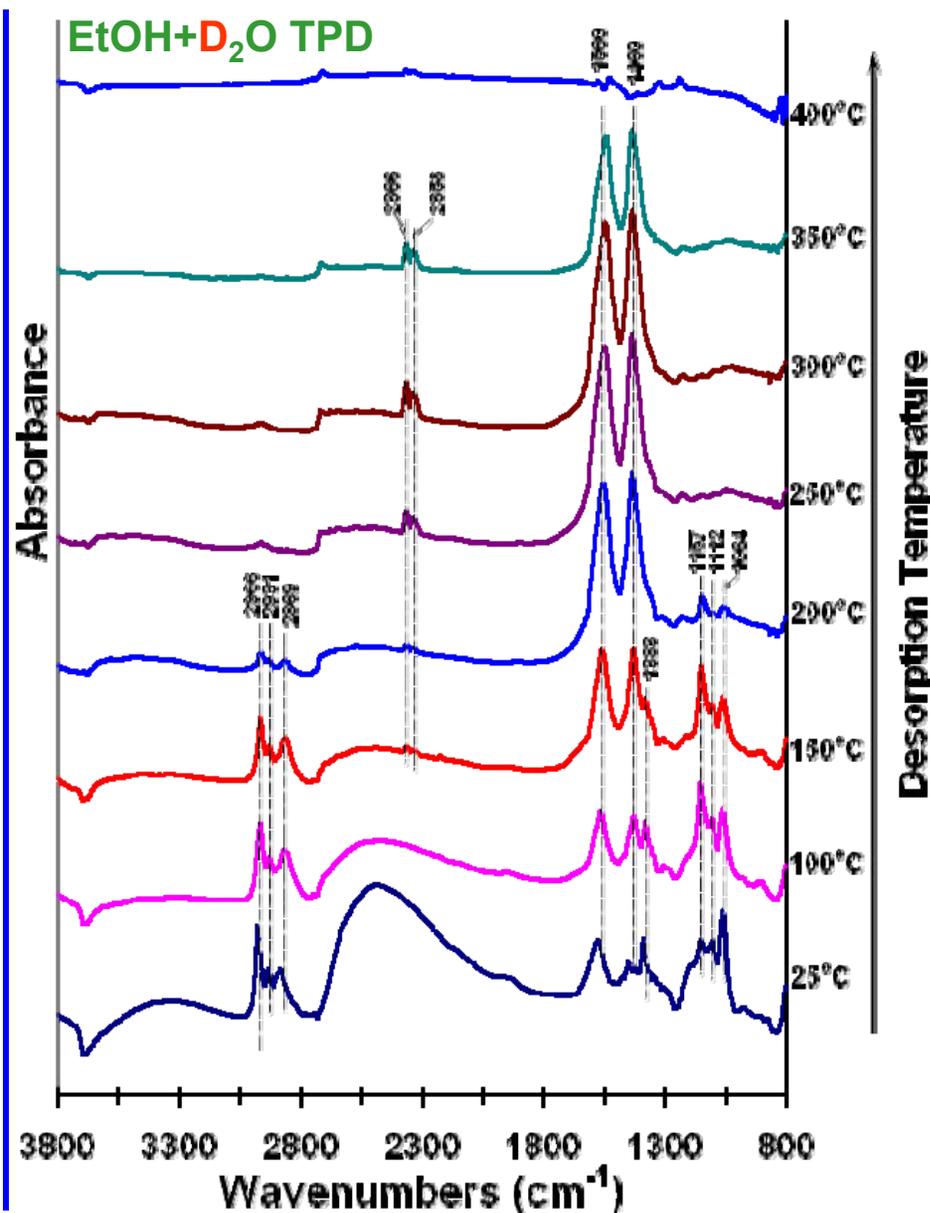
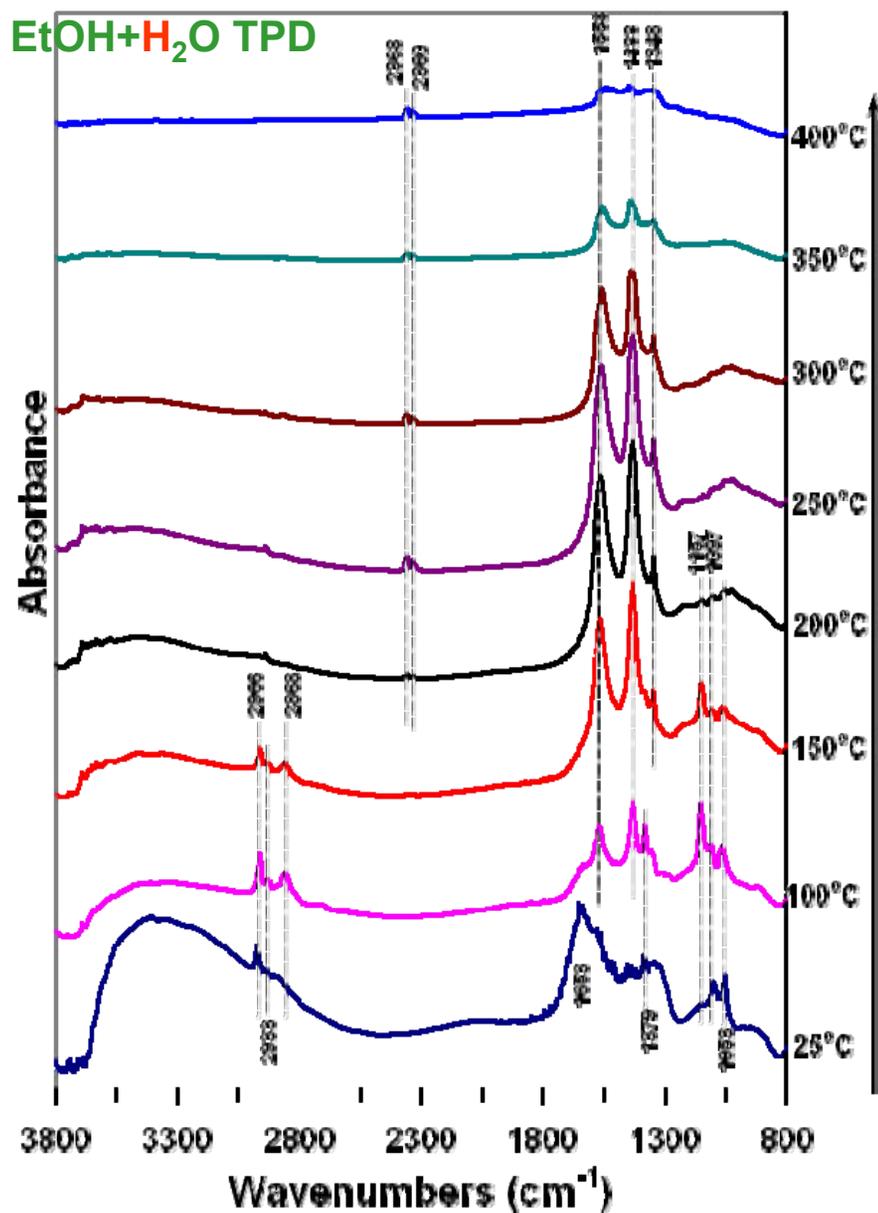


- Detailed studies of the reaction network through TPReaction and TPD experiments
 - Acetaldehyde SR
 - Acetone SR
 - WGS
 - Reverse WGS
 - CH₄ SR
 - Methanation
- Detailed studies of the surface intermediates through in-situ DRIFTS during
 - Ethanol SR
 - Acetone
 - Acetaldehyde
 - Acetic acid

In-Situ DRIFTS – Isotopic Effect over 10%Co/ZrO₂

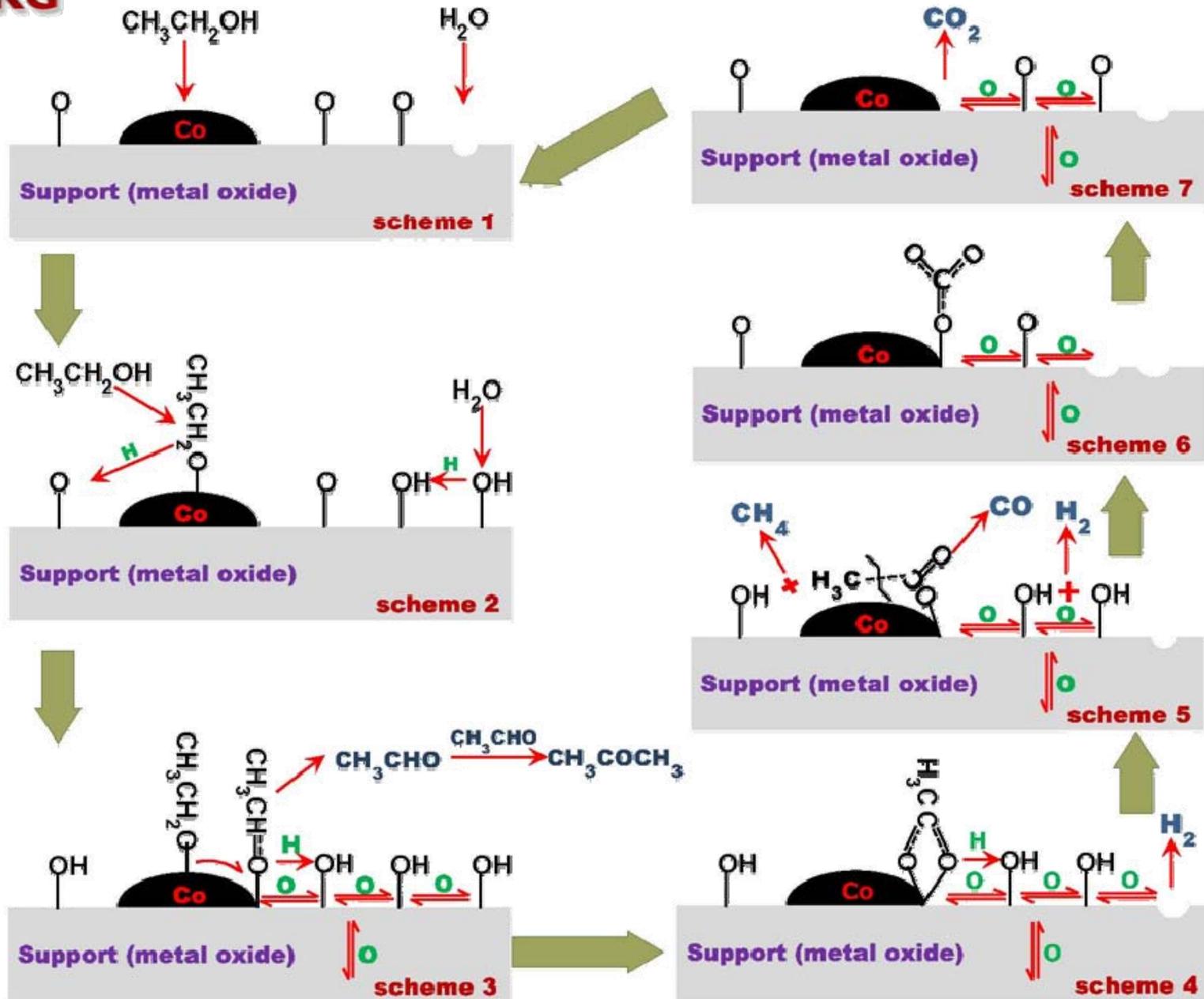


Water participates in ESR by providing the surface OH groups

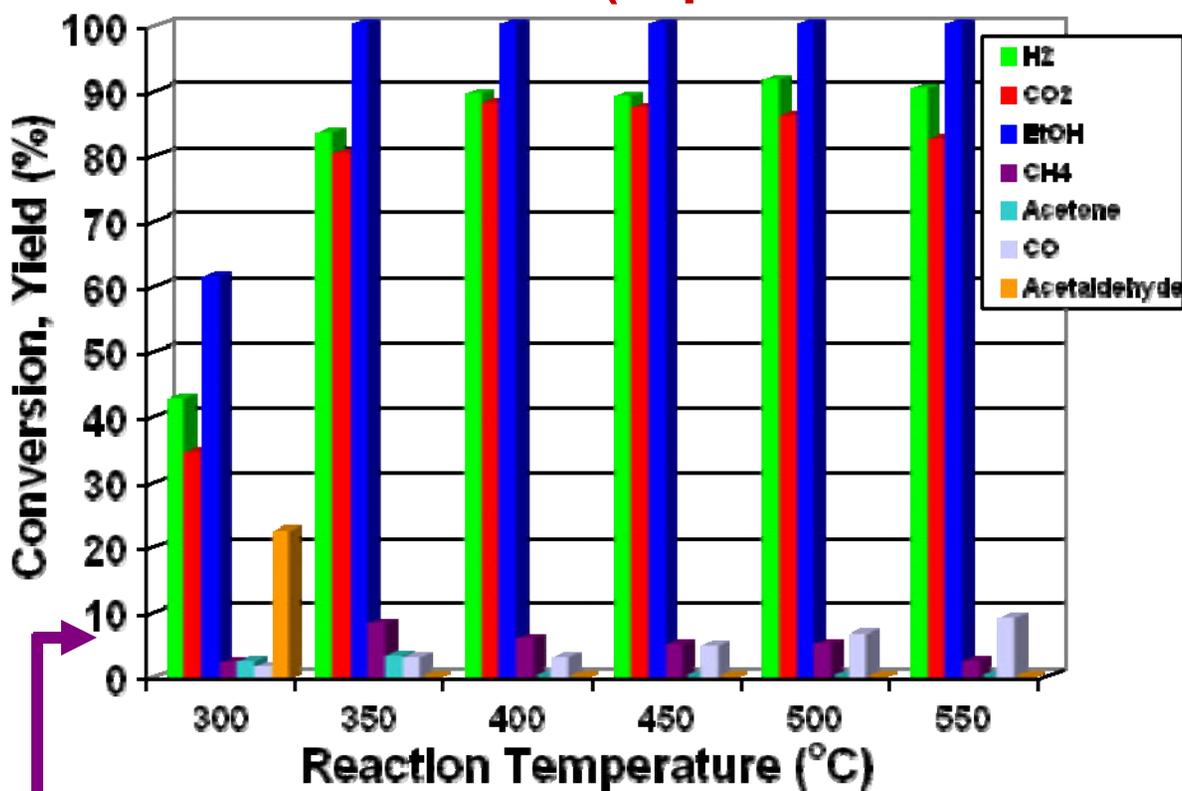




Reaction Mechanism Identification – Schematic Pathway



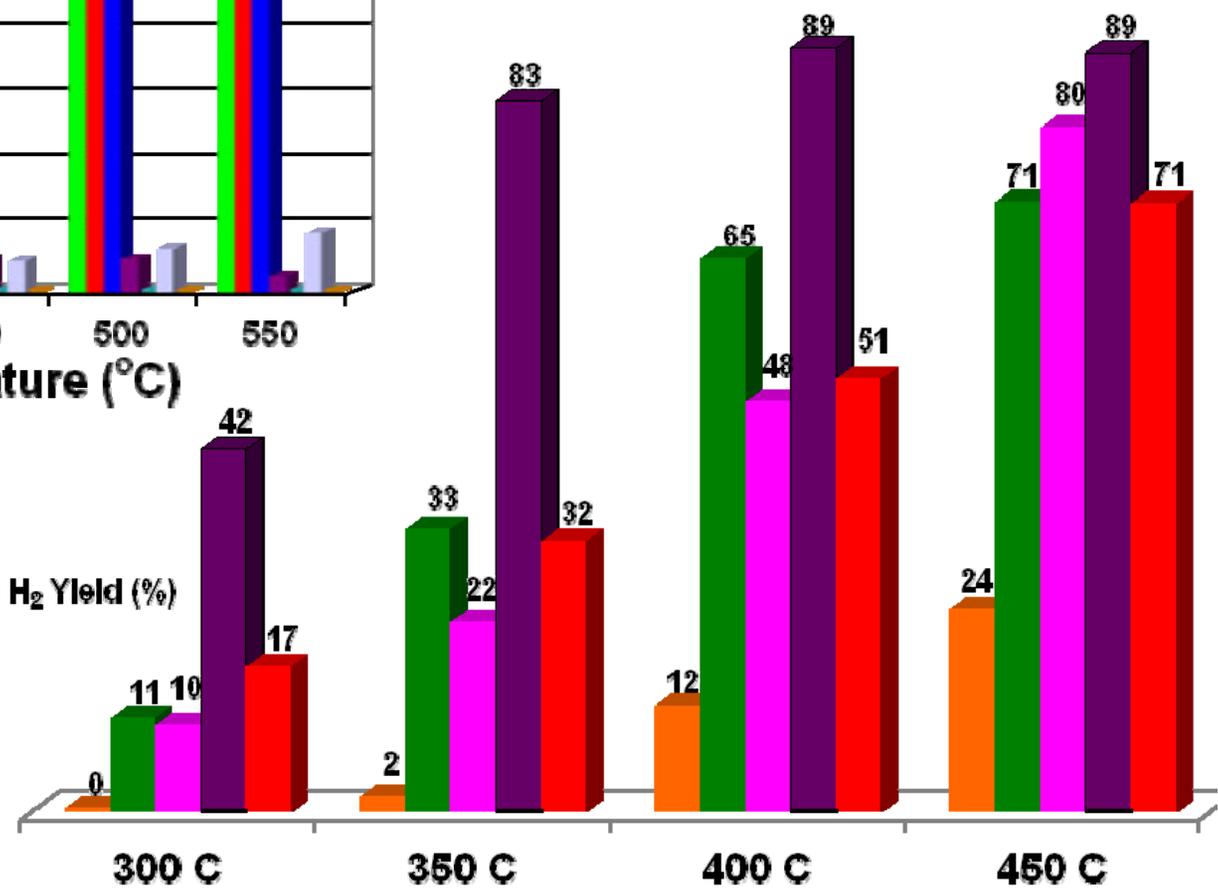
Effect of the Impregnation Medium on Activity (Aqueous vs Ethanol)



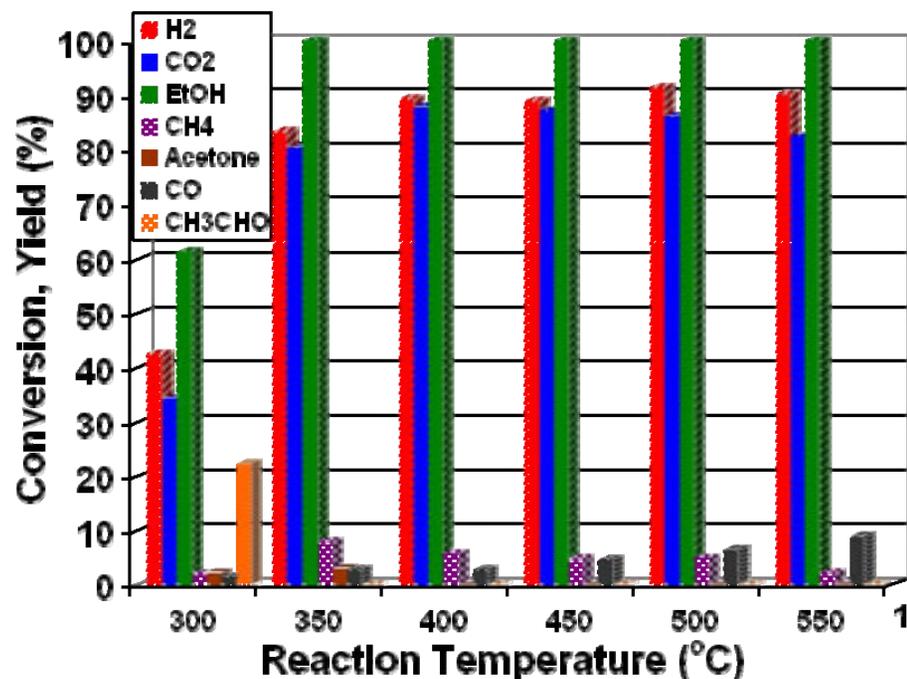
With EtOH impregnation, higher hydrogen yields can be achieved at lower temperatures.

- 10%Co/10%CeO₂-ZrO₂ (Orange)
- 10%Co/CeO₂ (A) (Green)
- 1%Re-10%Co/CeO₂ (Magenta)
- 10%Co/CeO₂ (E) (Purple)
- Equilibrium Calculation (Red)

H₂O:EtOH=10:1(molar ratio)
 WHSV=0.48gEtOH/gCat/h
 GHSV=~20,000h⁻¹
 C_{EtOH}=2%



Superior Performance of Catalyst Impregnated in Ethanol



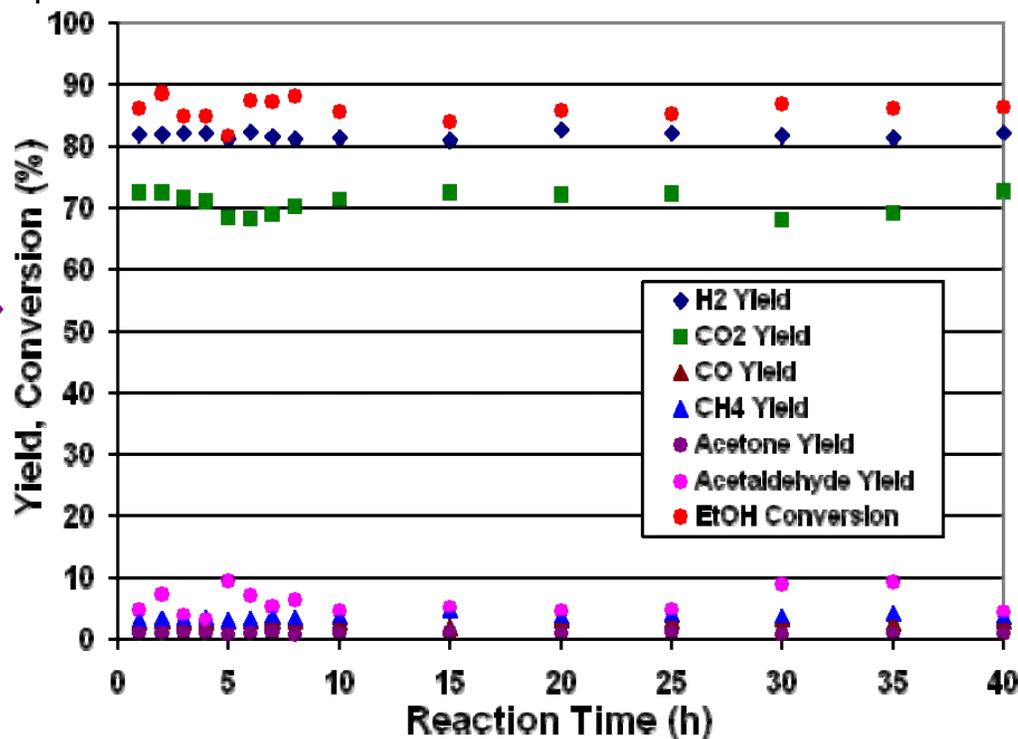
10%Co/CeO₂ (EtOH IWI)

EtOH: H₂O: dilution=1:10:40
 GHSV~20,000h⁻¹
 WHSV=0.48gEtOH/gCat/h
 C_{EtOH}=2%

H₂O:EtOH=10:1 (molar ratio)
 GHSV~20,000h⁻¹
 WHSV=0.48gEtOH/gCat/h
 C_{EtOH}=2%

T=350°C

- ❖ Activity is stable over 40 hrs
- ❖ Hydrogen yield is over 80% during the test time period



Evolution during Temperature-Programmed Calcination



Cirrus MKS Mass Spectrometer

In the current study:

❖ Ions followed:

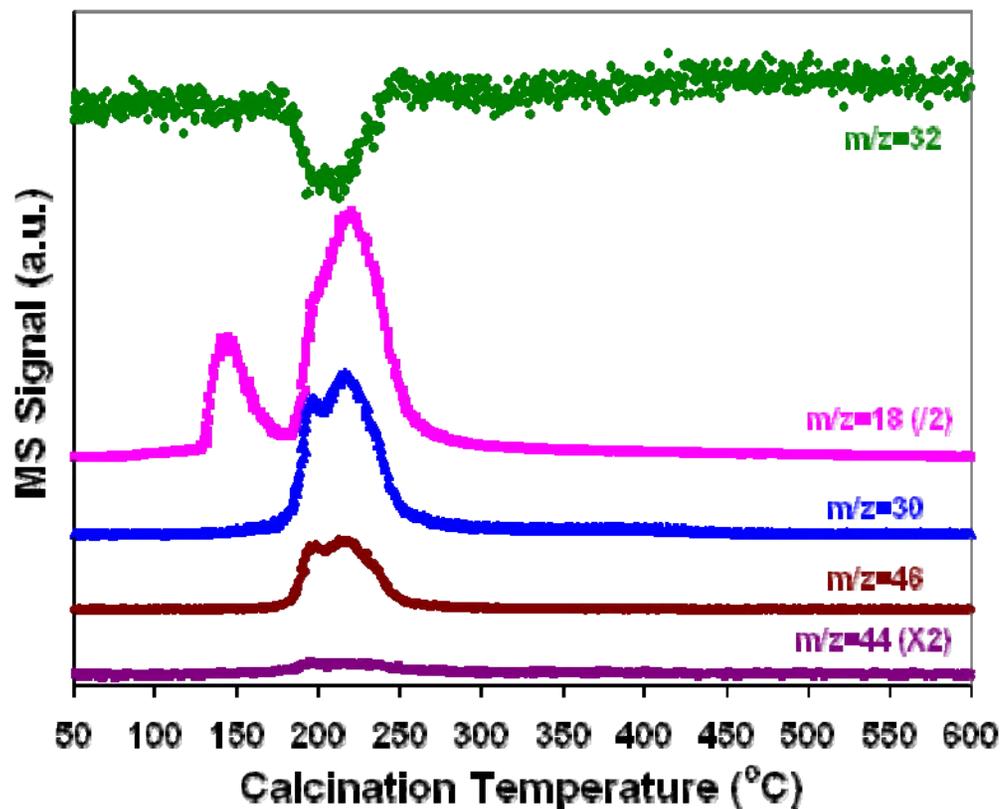
- 18 for water;
- 32 for O₂;
- 44 for CO₂;
- 30 for NO_x;
- 46 for NO₂;

❖ Sample:

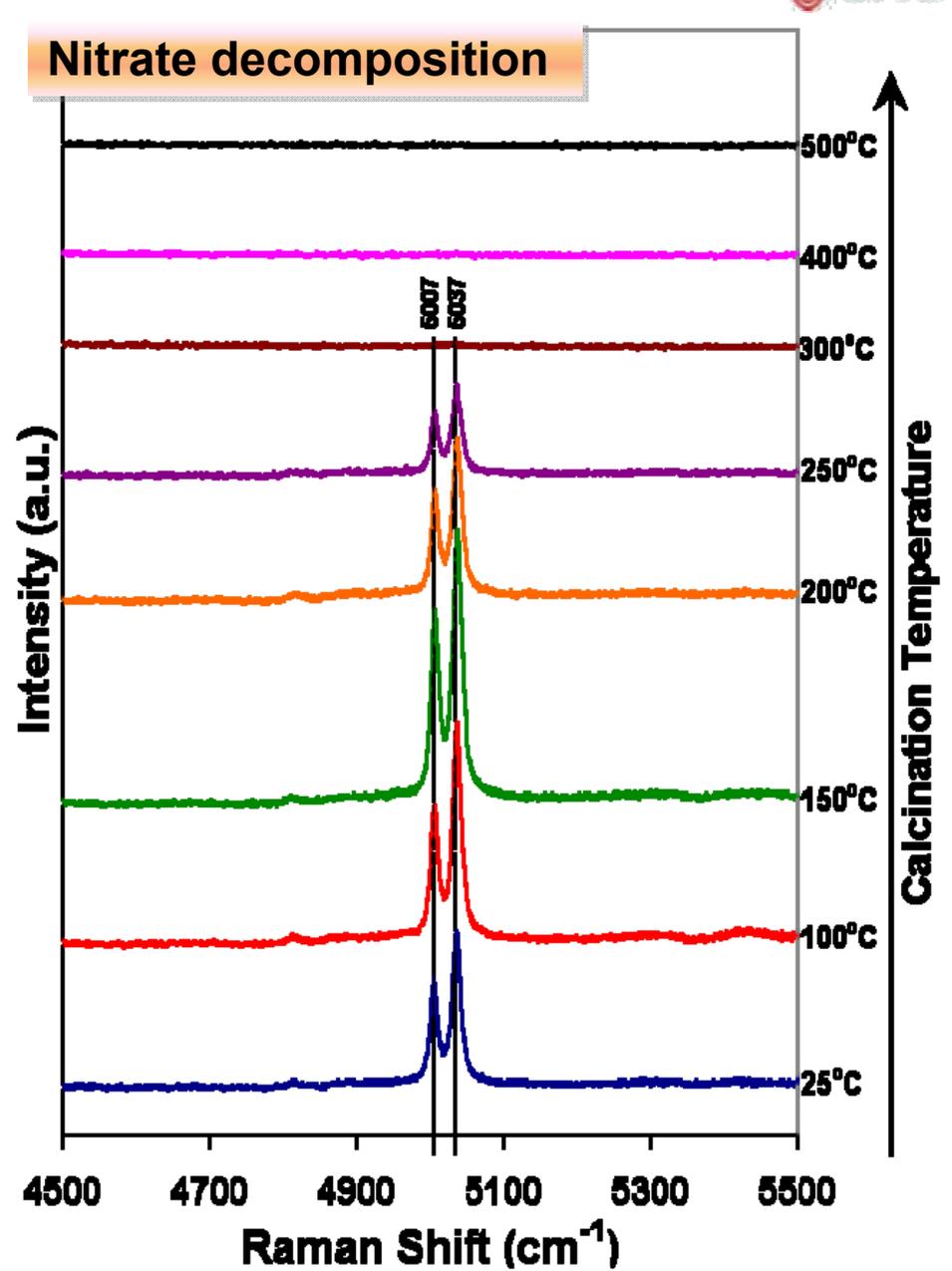
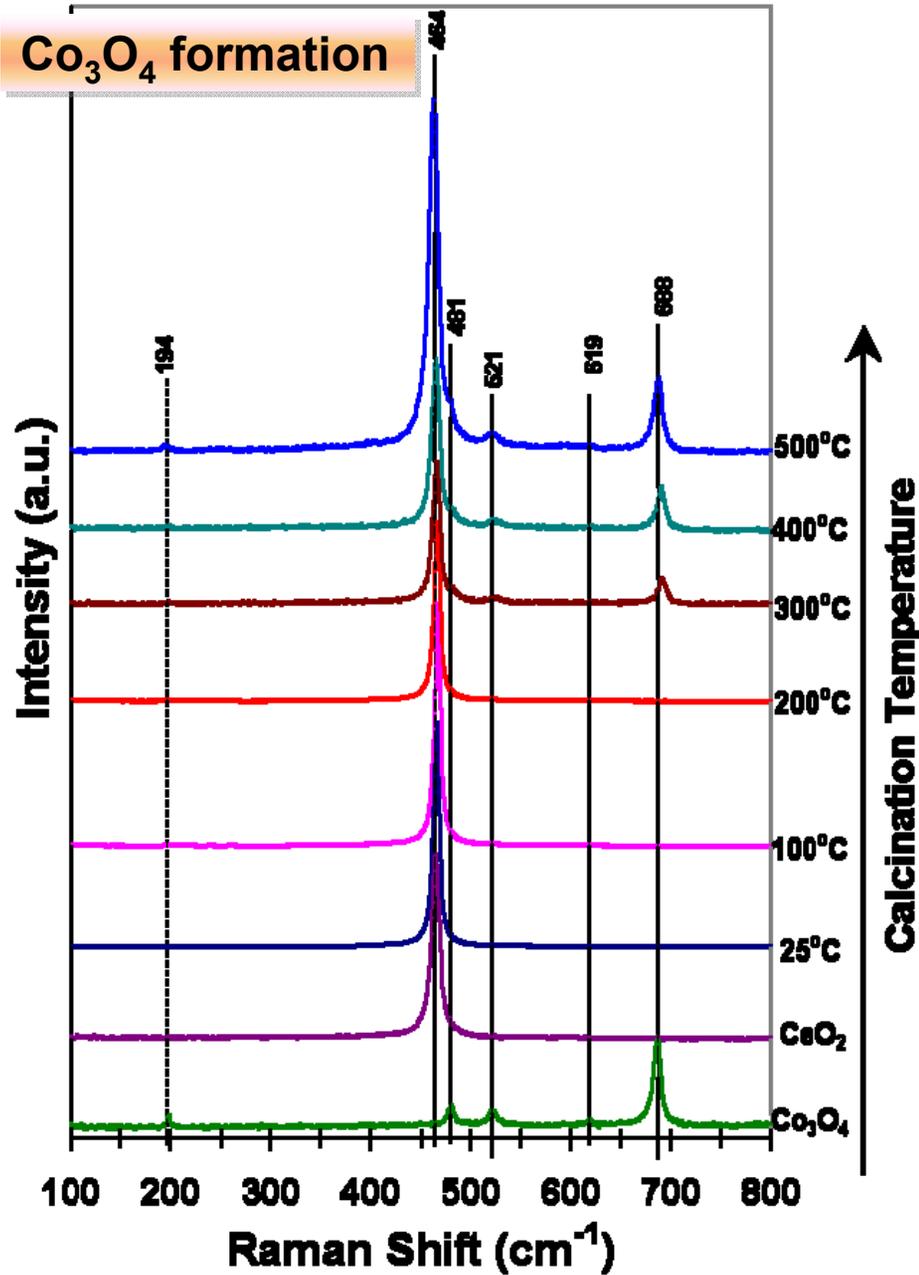
- 10 wt%Co/CeO₂ (EtOH IWI)
(Co(NO₃)₂ • 6H₂O as Co precursor)

❖ Calcination:

- Condition: **air**;
- Flow rate: **30ml/min.**;
- Ramp rate: **10°C/min.**



Evolution during Calcination – Raman Characterization



Evolution during Reduction

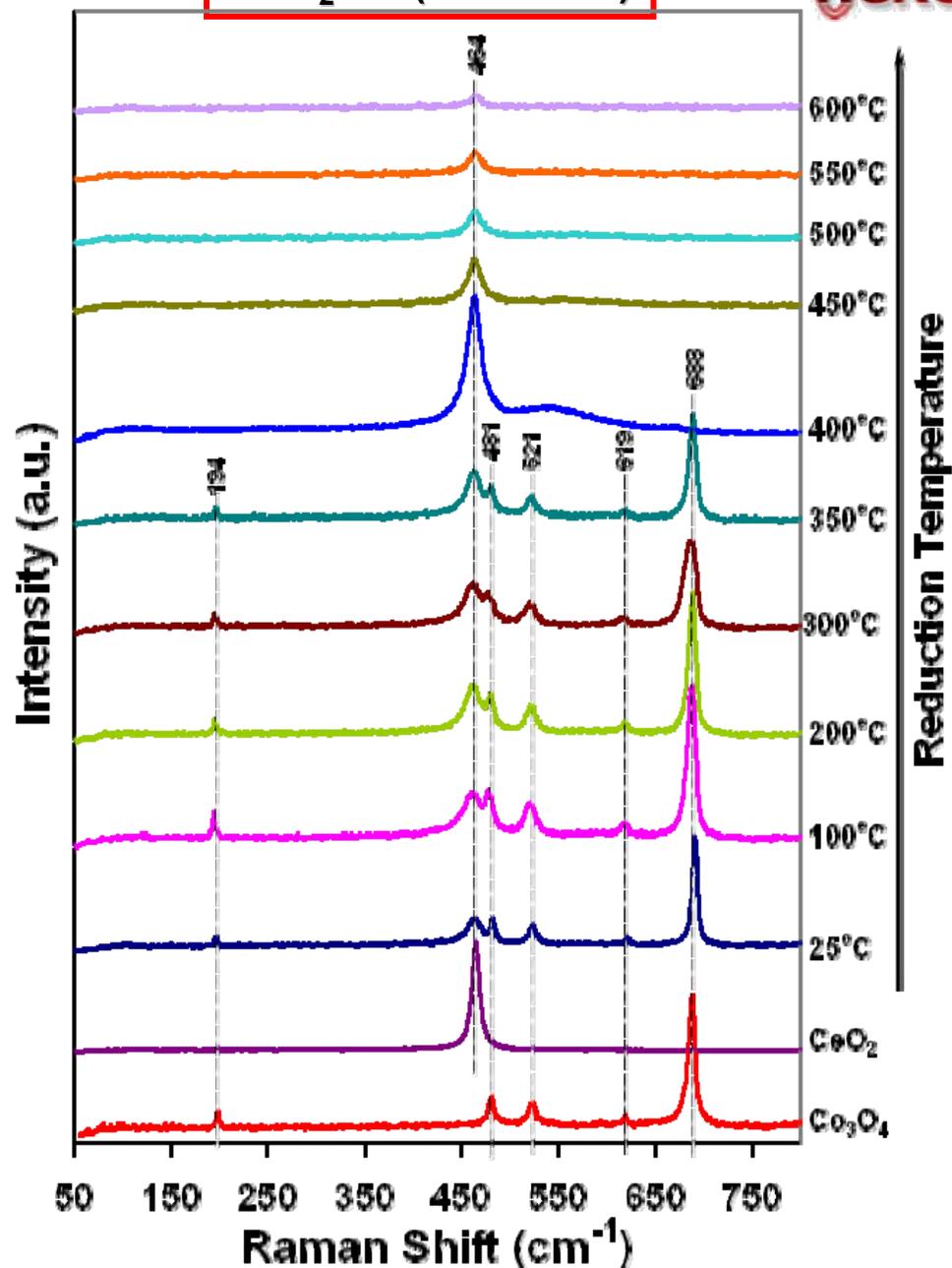
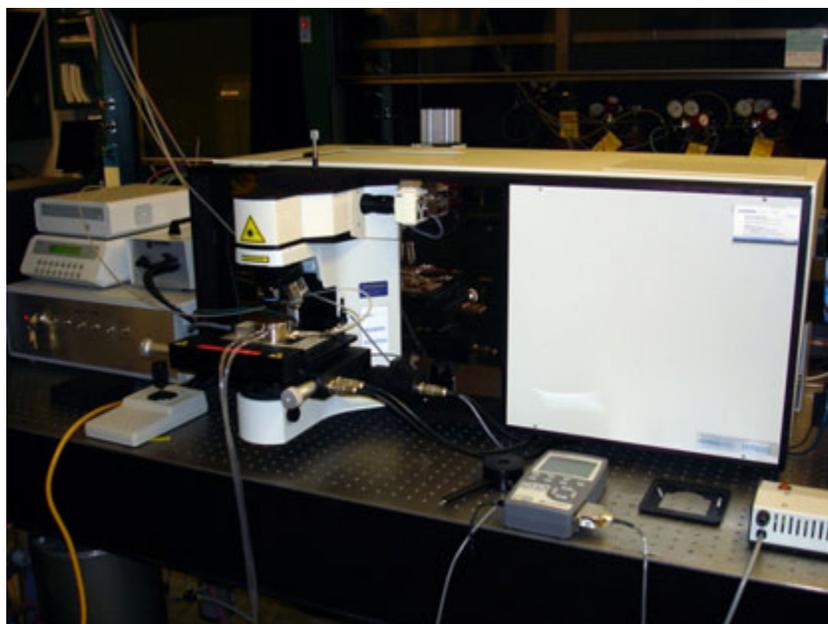
LABRAM HR-800 High Resolution Raman Microscope

OLYMPUS BX41 microscope

In the current study:

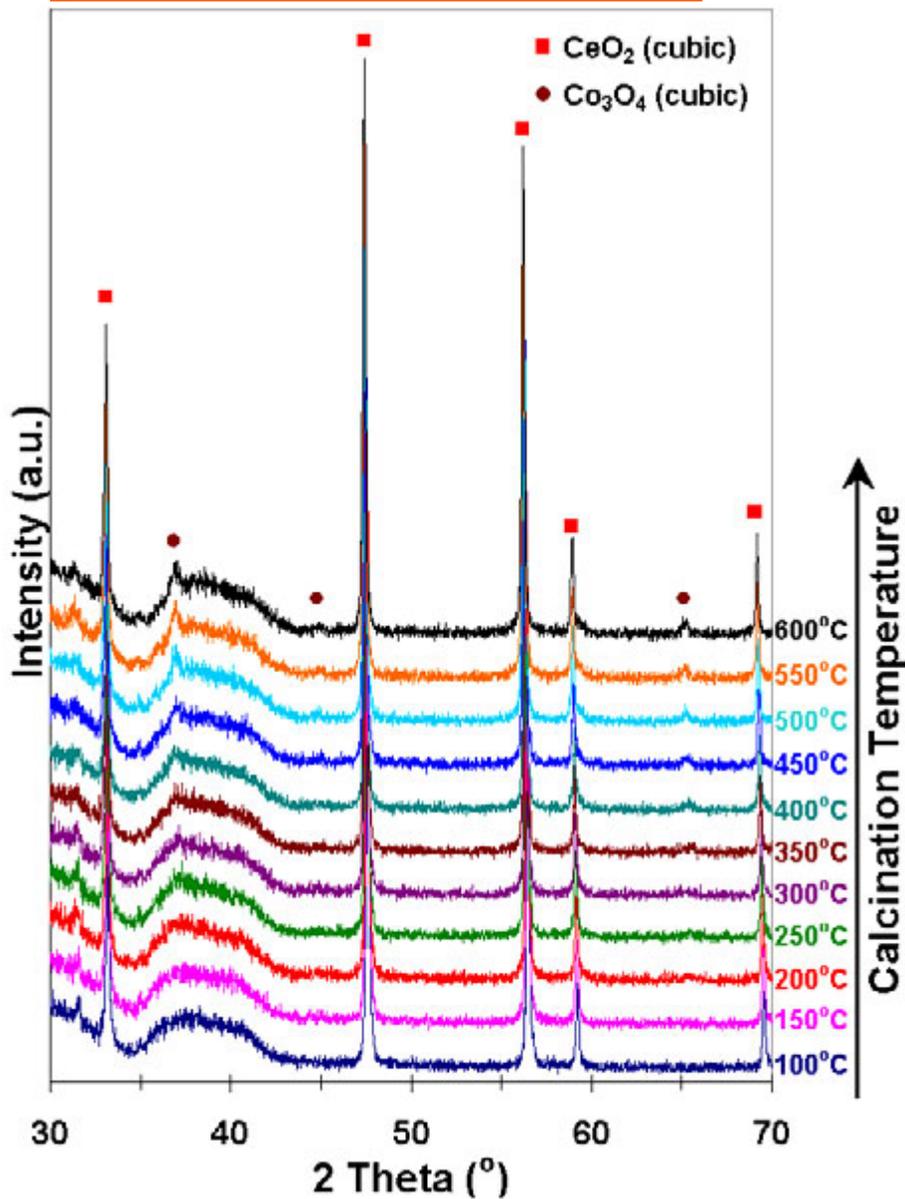
- ❖ Sample is placed in Operando Cell;
- ❖ 50X magnification;
- ❖ Argon ion green laser (514.5nm);
- ❖ 3mW.

10 wt% Co/CeO₂ (E)
5% H₂/He (30ml/min.)

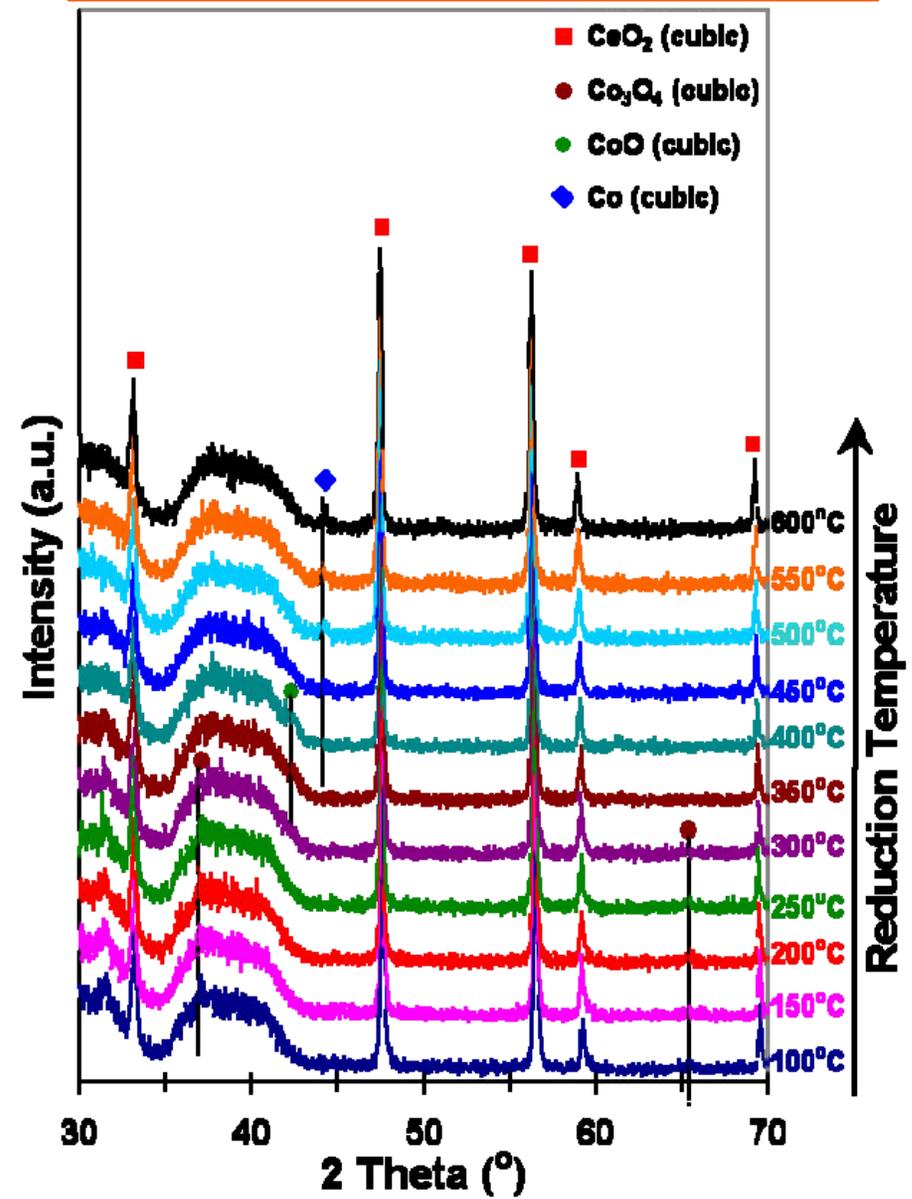


Characterization of Calcination and Reduction Steps through In-Situ XRD

Calcination - Co_3O_4 formation



Reduction – two Stage of reduction



Effect of Impregnation Medium

Kratos Axis Ultra XPS



10%Co/CeO₂ :

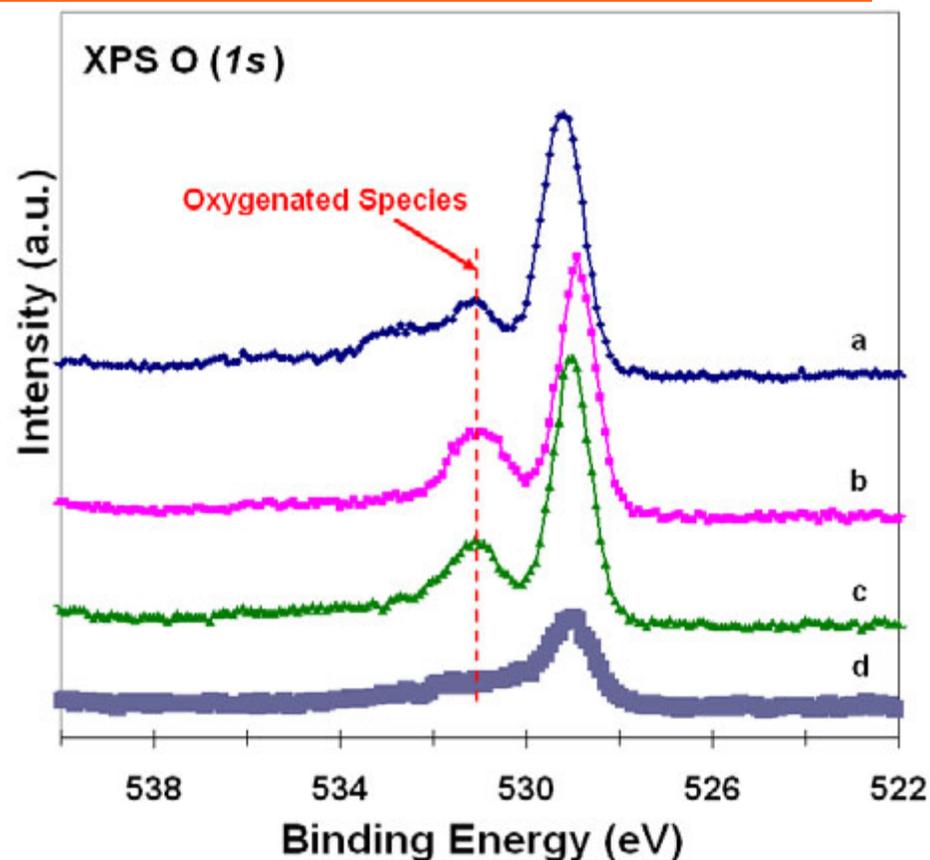
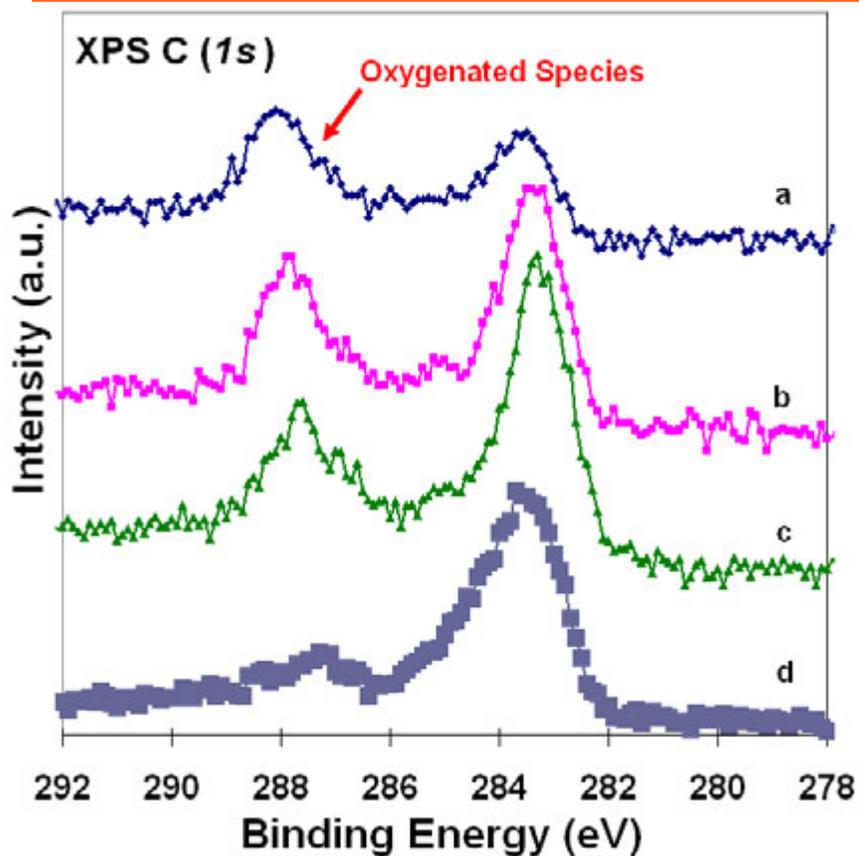
a: After calcination at 450°C for 3h (EtOH IWI);

b: After reduction at 400°C for 2h (EtOH IWI);

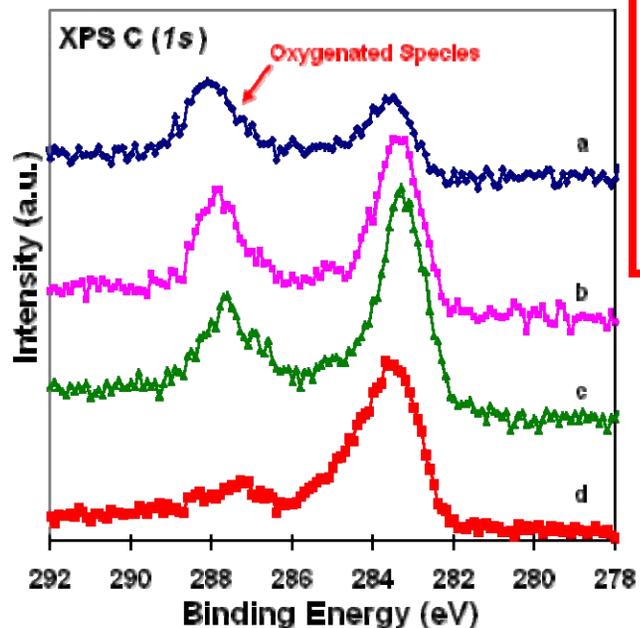
c: After reduction at 600°C for 2h (EtOH IWI);

d: After calcination at 450°C for 2h (H₂O IWI).

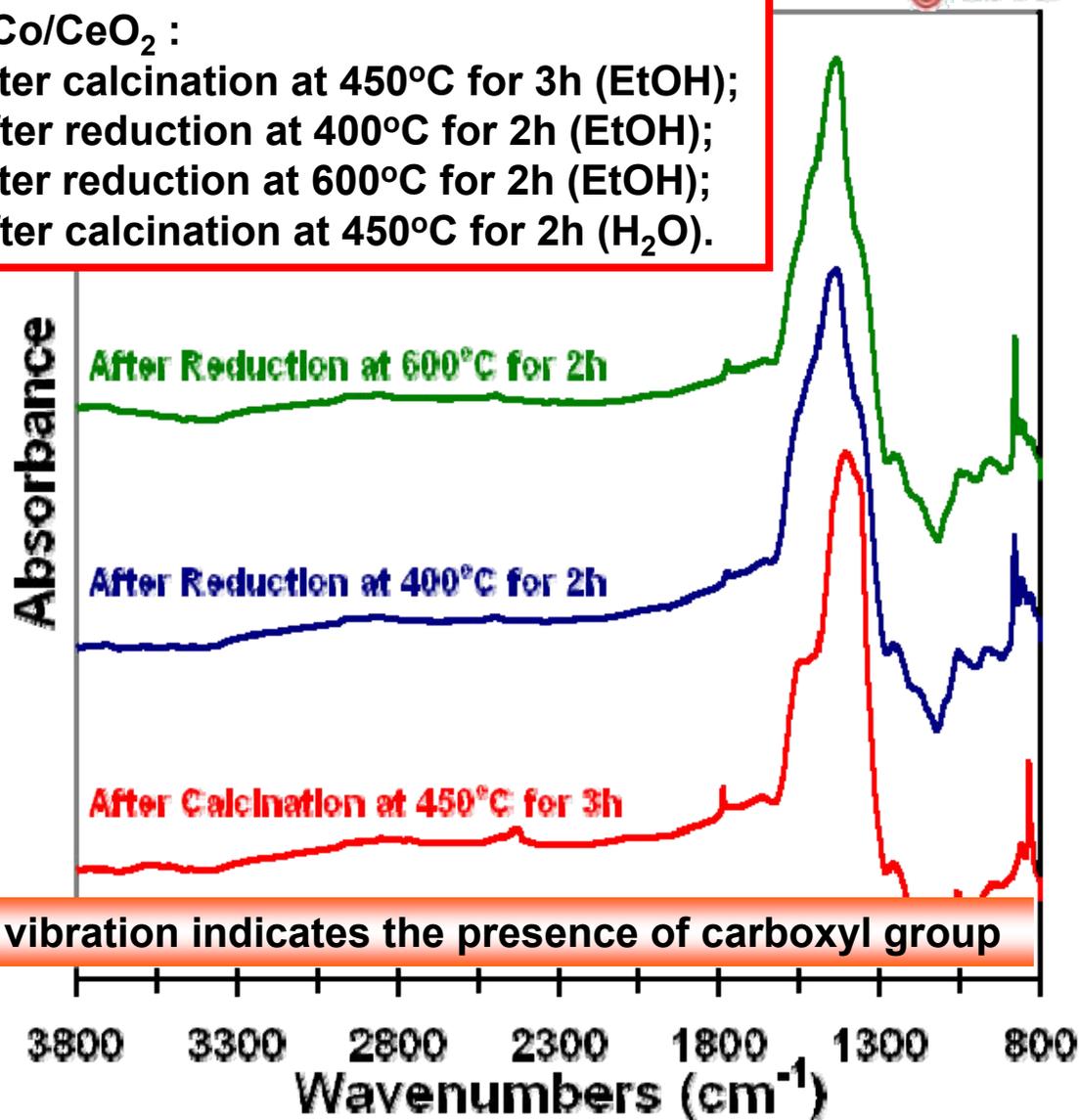
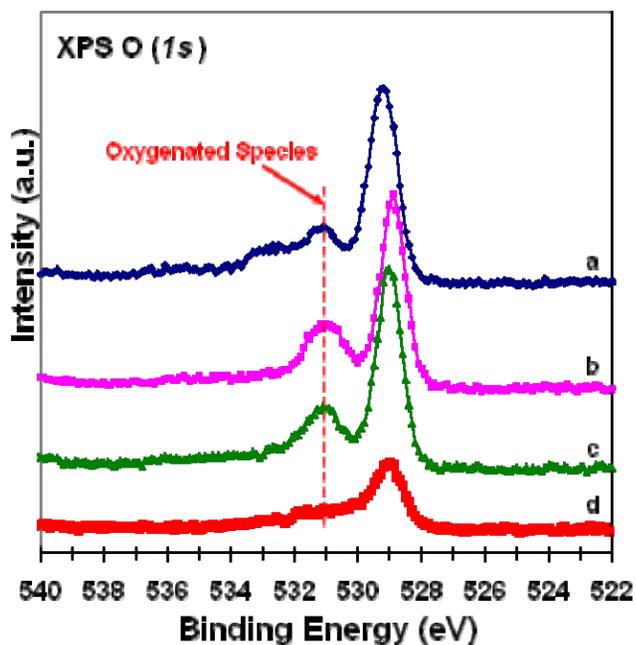
Oxygenated species remained on the surface even after reduction treatment



Effect of the Impregnation medium: Validation with FTIR Results



10%Co/CeO₂ :
a: After calcination at 450°C for 3h (EtOH);
b: After reduction at 400°C for 2h (EtOH);
c: After reduction at 600°C for 2h (EtOH);
d: After calcination at 450°C for 2h (H₂O).



C-O vibration indicates the presence of carboxyl group

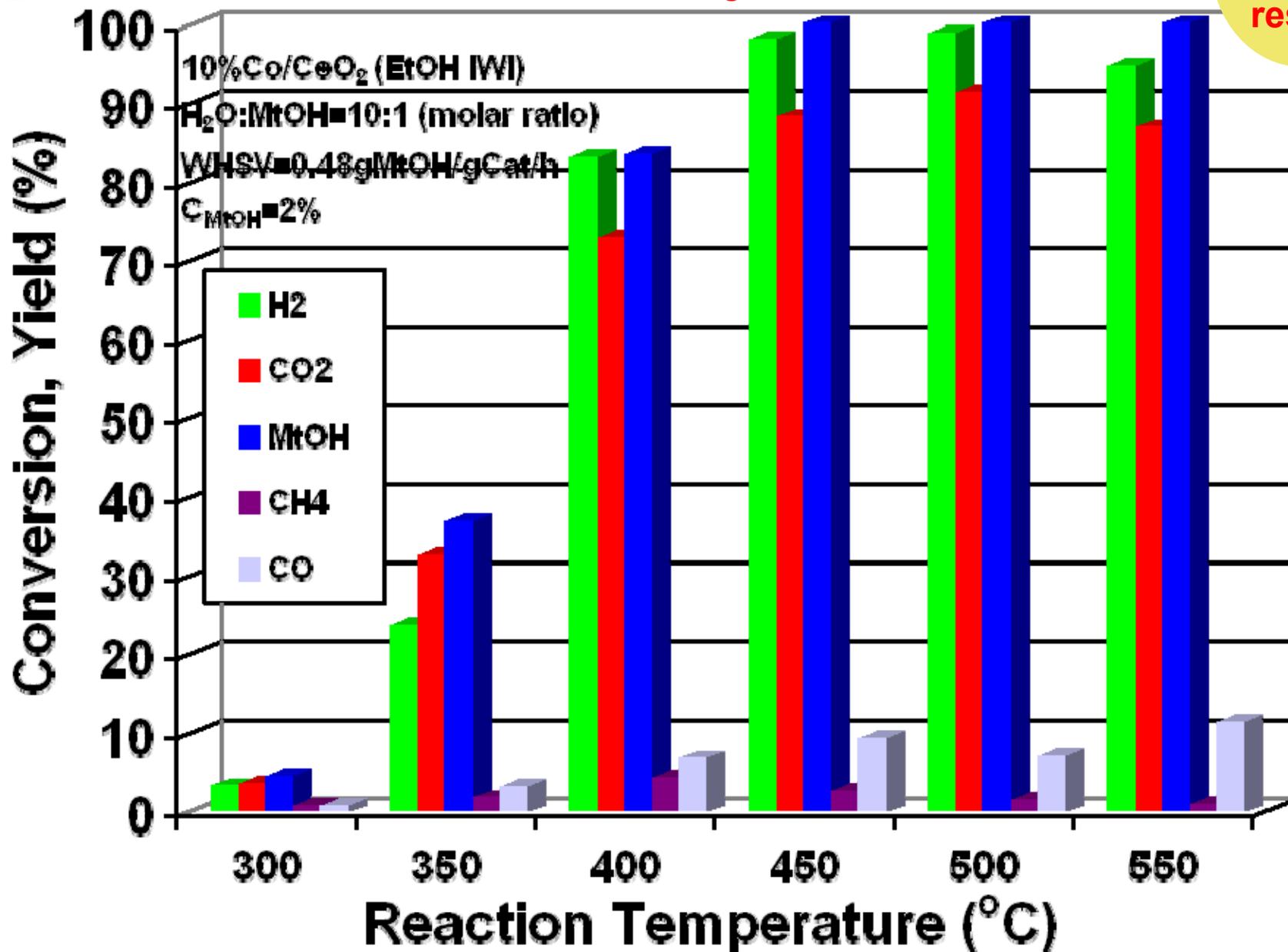
DI water impregnated sample is used for background



Steam Reforming of Bio-derived Liquids

Most recent results

Methanol Steam Reforming



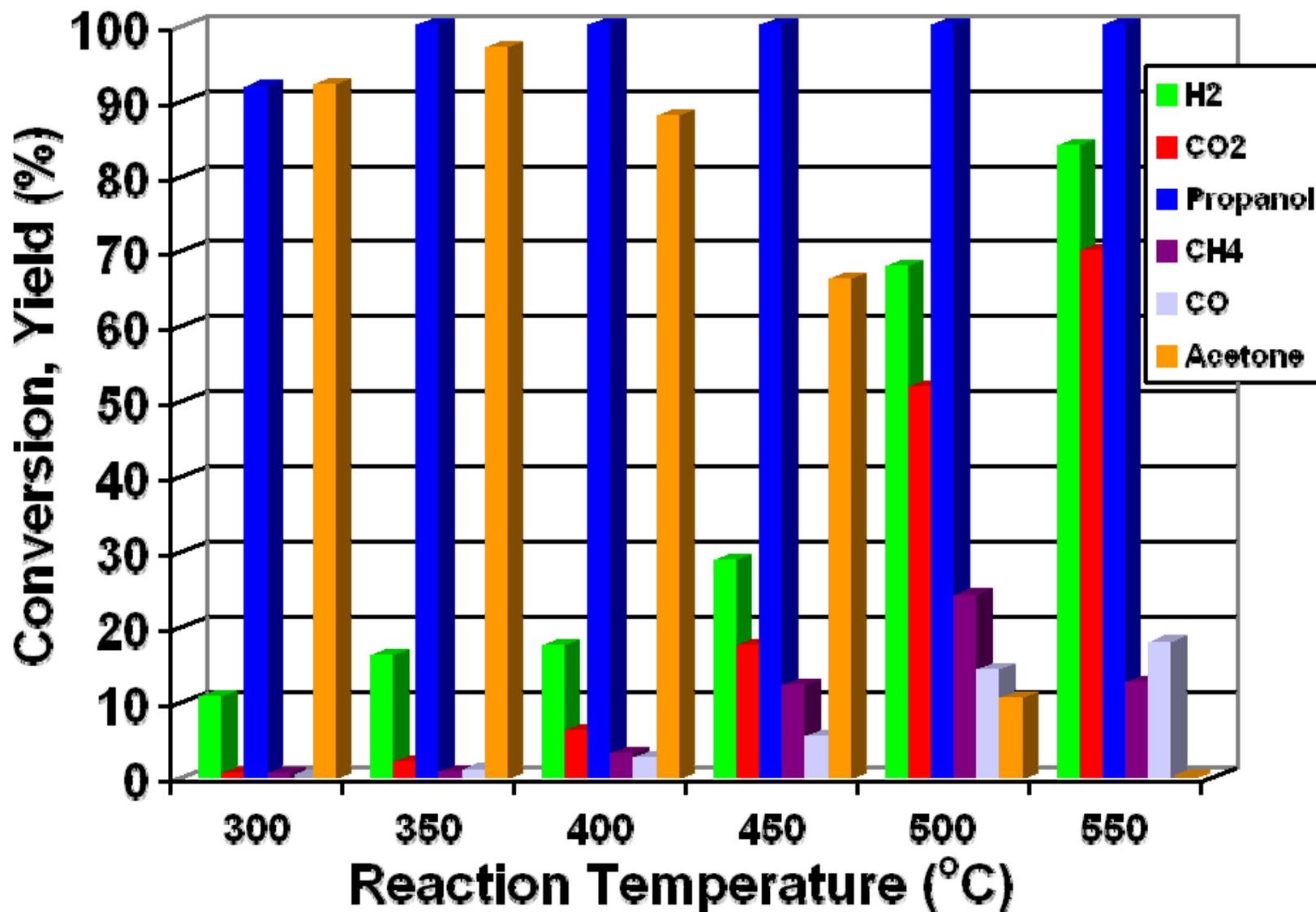
Steam Reforming of Bio-derived Liquids

2-Propanol

10%Co/CeO₂ (EtOH IWI), H₂O:PtOH=10:1 (molar ratio)

WHSV=0.48gPtOH/gCat/h, C_{PtOH}=2%

Most
recent
results

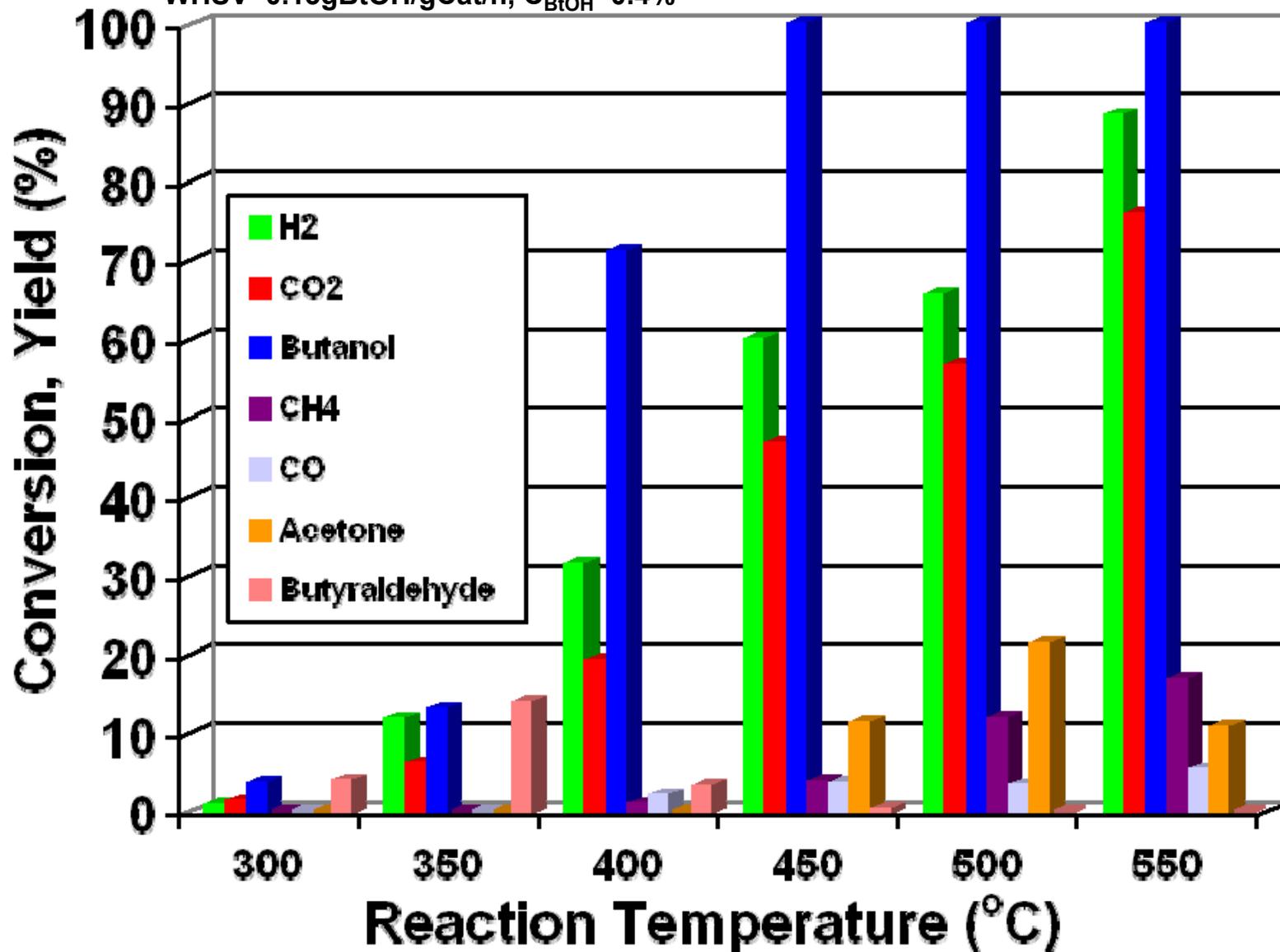


Steam Reforming of Bio-derived Liquids

Butanol

Most recent results

10%Co/CeO₂ (EtOH IWI), H₂O:BtOH=60:1 (molar ratio)
WHSV=0.13gBtOH/gCat/h, C_{BtOH}=0.4%





Summary



- Successful design, installation, shake-up of reactor system;
- Initial catalyst system development with excellent activity;
- Investigation of the reaction network;
- Identification of the active sites and reaction mechanism;
- Characterization of the deactivation mechanism;
- Modified catalyst system development with high stability while maintaining good activity;
- Further activity improvement, especially at lower reaction temperatures through modification of the catalyst synthesis technique
- Activity for steam reforming of various bio-derived liquids;
- Successful utilization of H2A model to perform economic analysis.



Future Work



- ✓ Longer time-on-stream stability studies;
- ✓ Catalyst system optimization to improve stability while maintaining high activity;
- ✓ Flexibility test of the catalyst system for reforming **other bio-derived liquids** (e.g., DME);
- ✓ Further investigation of the proposed reaction pathways;
- ✓ Further improvement of catalytic activity especially at lower temperatures
- ✓ Catalytic activity measurement when **impurities** are present in the reactants;
- ✓ Fine tuning of the economic analysis depending on availability of the reaction data;
- ✓ Catalytic activity measurements by varying the reaction parameters
- ✓ Further exploration of the relationship between catalyst properties and activity;
- ✓ Development of catalyst regeneration strategies over deactivated samples.
- ✓ Investigation of the catalyst scale-up through NexTech partnership

Main Points to Address from the Annual Review

- ✓ **Development of a system understanding**
- ✓ **Integration of an economic analysis**
- ✓ **Long term testing of the catalysts**
- ✓ **Effect of contaminants**
- ✓ **Coordination with industrial partner(s)**





Publications



- Song, H., Zhang, L., Ozkan, U.S., "Catalytic Hydrogen Production from Renewable Sources" Prepr. Am. Chem. Soc. Div. Fuel Chem., 51(2) (2006).
- Song, H., Zhang, L., Ozkan, U.S., "Effect of Synthesis Parameters on the Catalytic Activity of Co/ZrO₂ for Bio-ethanol Steam Reforming" *Journal of Green Chemistry*, 9, 686-694 (2007).
- Song, H., Zhang, L., Ozkan, U.S., "Promotional Effects on Co-Based Catalysts in Bio-ethanol Steam Reforming", Proceedings of the 2nd International Hydrogen Energy Congress, July 2007.
- Song, H., Zhang, L., Watson, R.B., Braden, D., Ozkan, U.S., "Investigation of Bio-ethanol Steam Reforming over Cobalt-based Catalysts" *Catalysis Today*, DOI: 10.1016/j.cattod.2006.11.028

Conference Presentations and Invited Lectures



1. Song, H. and Ozkan, U.S., "Fuel Cell Grade Hydrogen Production from the Bio-Ethanol Steam Reforming over Co-based Catalysts: An Investigation of Reaction Networks and Active Sites" *Ohio Fuel Cell Symposium*, May 2006, Canton, Ohio;
2. Song H., Zhang, L., Ozkan, U.S., "Investigation of bio-ethanol system reforming over cobalt-based catalysts", *232nd ACS National meeting & exposition*, San Francisco, CA, September 2006;
3. Song H., Zhang, L., Ozkan, U.S., " Investigation of bio-ethanol steam reforming over cobalt-based catalysts", *U.S. Department of Energy Bio-derived Liquids to Hydrogen Distributed Reforming Working Group Kick-Off Meeting*, Baltimore, MD, October 2006;
4. Song, H. Zhang, L., and Ozkan, U.S., "Catalytic Hydrogen Production from Renewable Sources" *OSU-Honda Research Forum*, Columbus, Ohio, February 2007.
5. Song, H., Zhang, L., Ozkan, U.S., "Investigation of Reaction Networks and Active Sites in Steam Reforming of Bio-ethanol over Cobalt based Catalysts" *233rd ACS National Meeting*, Chicago, IL, March 2007;
6. Song, H., Zhang, L., Ozkan, U.S., "Hydrogen Production from Bio-ethanol Steam Reforming over Cobalt-based Catalysts" *20th North American Meeting of North American Catalysis Society*, Houston, TX., June 2007;
7. Song, H., Zhang, L. and Ozkan, U.S., "Catalytic Hydrogen Production from Bio-ethanol on Co-based Catalysts," *2nd International Hydrogen Energy Congress*, Istanbul, Turkey, July 2007;
8. "Catalytic Hydrogen Production," *Universite Claude Bernard*, Lyon , France, October 2007;
9. "Catalytic Hydrogen Production through Steam Reforming, Water Gas Shift, and PROX Reactions", *Technical University of Eindhoven*, Eindhoven, The Netherlands, October 2007.

Acknowledgement



Department of Energy

*Ohio Wright Center of Innovation
for Fuel Cells*

