

# Investigation of Bio-ethanol Steam Reforming over Cobalt-based Catalysts

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**PDP-6**

# Overview

## Timeline

- ❖ Start Date - May 1, 2005
- ❖ End Date - April 31, 2009
- ❖ 40% Complete

## Budget

- ❖ Total project funding
  - \$1,145,625 (DOE)
  - \$299,715 (OSU cost share)
- ❖ Funding received in FY05
  - \$100,000 (DOE)
  - \$10,458 (OSU Cost share)
- ❖ Funding received in FY06
  - \$185,000 (DOE)
  - \$147,987 (OSU cost share)
- ❖ Funding received in FY07 (to date)
  - 290,473 (DOE)
  - \$25,037 (OSU)

## Barriers

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

## Partners

- ❖ NexTech Materials, Ltd. - Catalyst manufacturing scale-up
- ❖ PNNL - Economic analysis and feasibility considerations, deactivation studies



# Objectives and Prior Work Summary

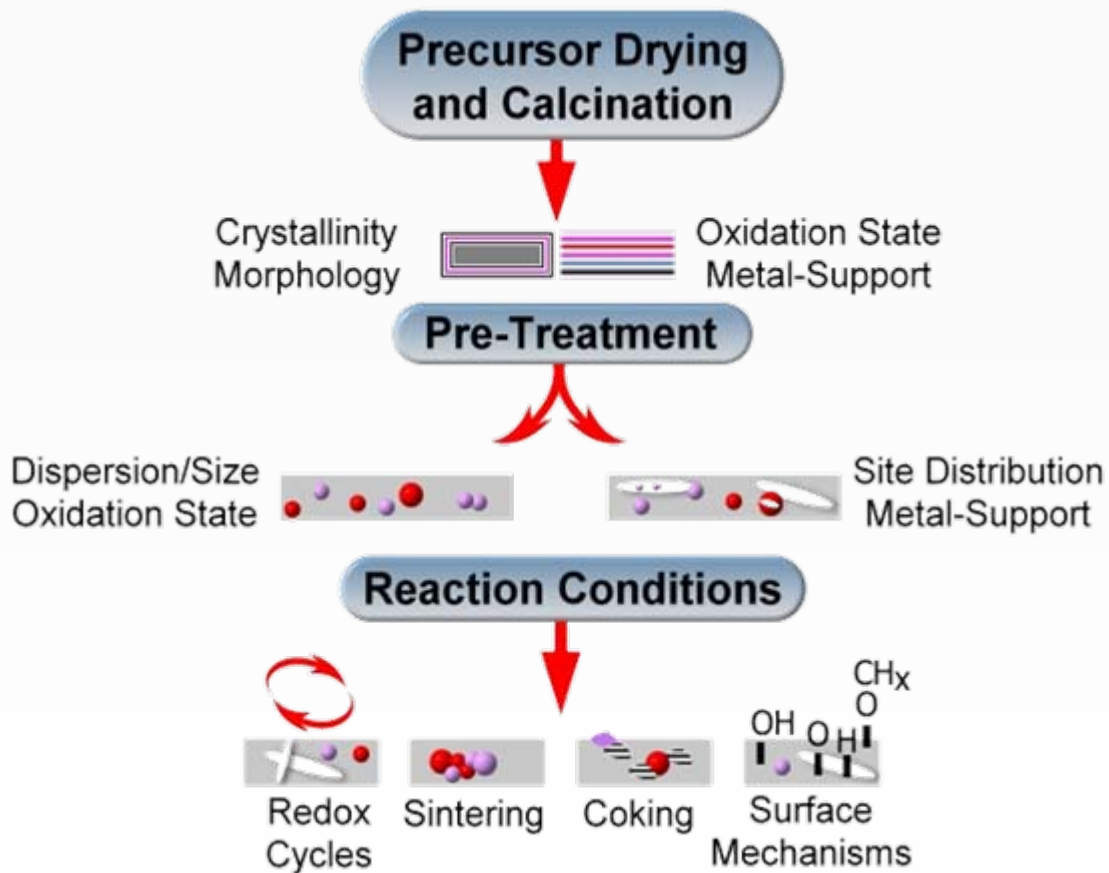


- ❖ **Overall:** To acquire a fundamental understanding of the reaction networks and active sites in bio-ethanol steam reforming over Co-based catalysts that would lead to
  - Development of a precious metal-free catalytic system which would enable
    - Low operation temperature (350-550°C)
    - High EtOH conversion
    - High selectivity and yield of hydrogen
    - Minimal byproducts such as acetaldehyde, methane, ethylene, and acetone
  - Understanding of the catalyst deactivation and regeneration mechanisms
  - Low cost for commercialization.
- ❖ **June 2005-Sep 2006**
  - Launching the project, setting up the experimental systems and establishing the experimental protocols
  - Investigating the effect of synthesis parameters on catalyst performance
  - Testing activity of the initial catalyst system.
- ❖ **FY06:**
  - Understanding the competing reaction networks
  - Identifying active sites during reaction
  - Optimizing catalyst pretreatment parameters



# Approach

## Supported Co-catalysts



### ❖ Preparation

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

### ❖ Calcination

- Temperature

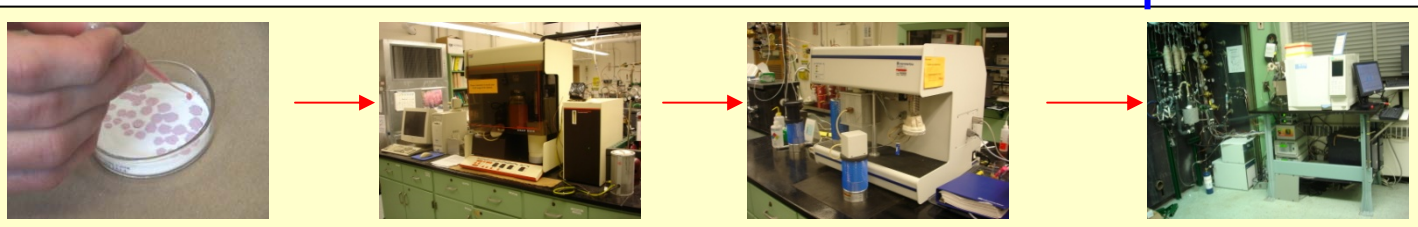
### ❖ Reduction

- Temperature
- Time

### ❖ Reaction

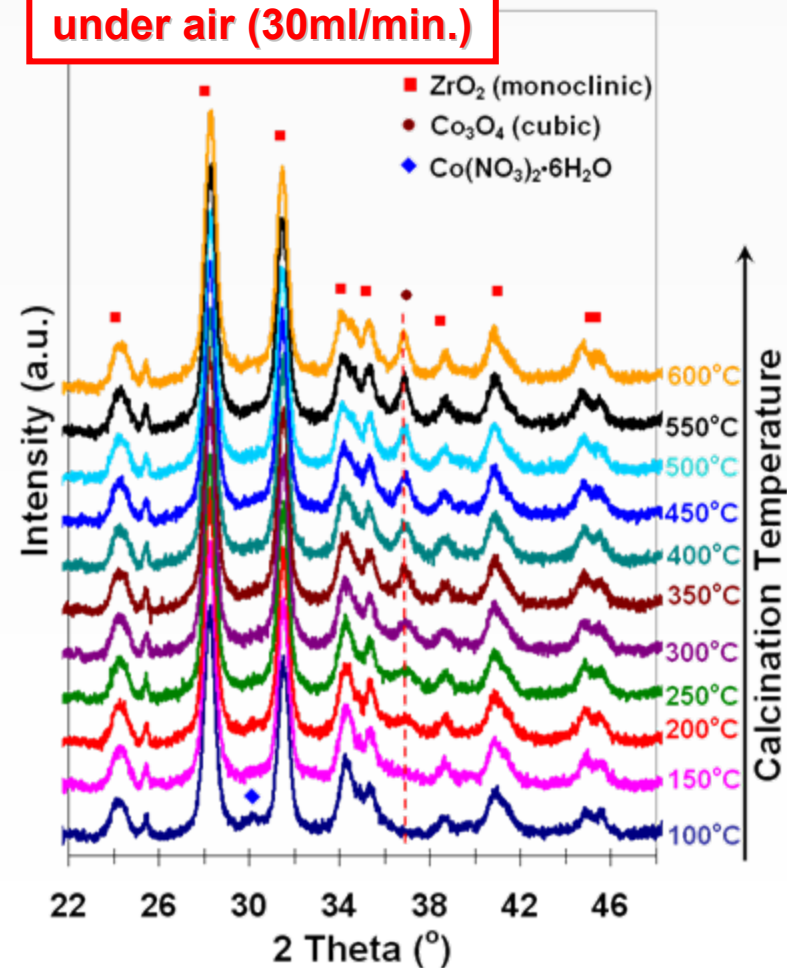
- GHSV
- EtOH:Water ratio
- Temperature
- Oxygen addition
- Deactivation

### ❖ Deactivation/Regeneration



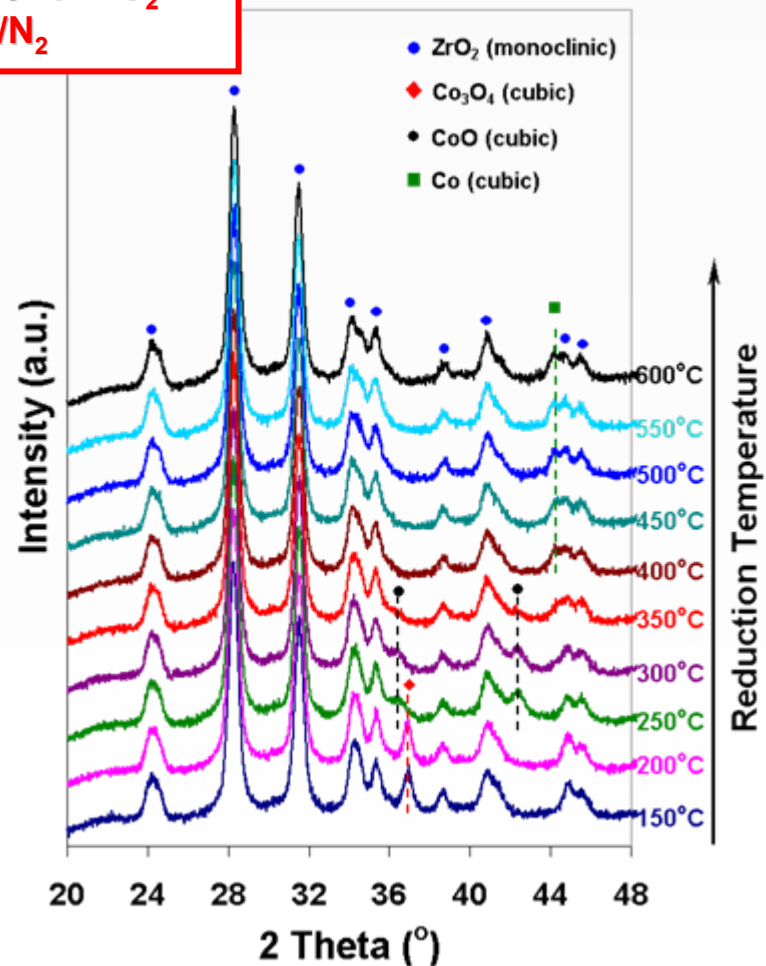
## Catalyst evolution: From precursor to active phase

10 wt% Co/ZrO<sub>2</sub> (IWI)  
under air (30ml/min.)



The decomposition of the crystalline cobalt precursor and formation of Co<sub>3</sub>O<sub>4</sub> during calcination process have been observed.

10 wt%Co/ZrO<sub>2</sub>  
5% H<sub>2</sub>/N<sub>2</sub>



Two step reduction, i.e., Co<sub>3</sub>O<sub>4</sub>→CoO, and CoO→Co, has been confirmed.

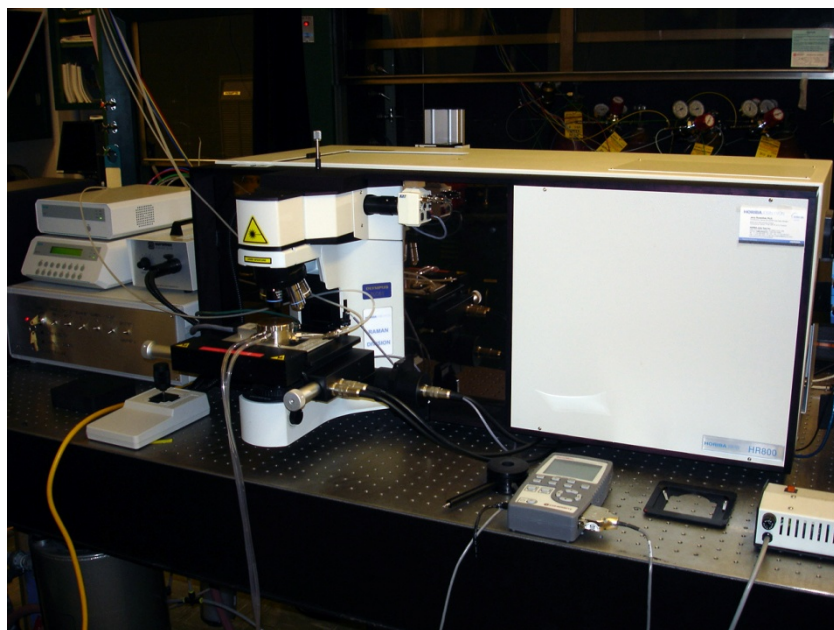
# Further Characterization of the Calcination step

## LABRAM HR-800 High Resolution Raman Microscope

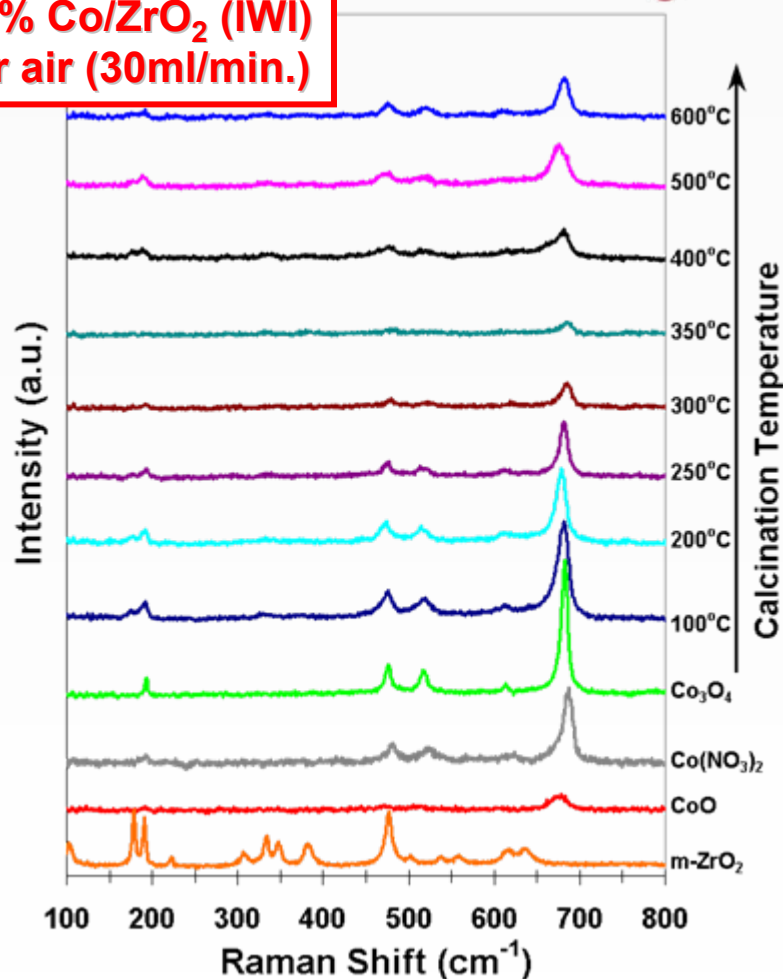
OLYMPUS BX41 microscope

In the current study:

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



10 wt% Co/ZrO<sub>2</sub> (IWI)  
under air (30ml/min.)



CoO is an intermediate in calcination of the catalyst precursor before the Co<sub>3</sub>O<sub>4</sub> phase forms.

# Further Characterization of the Reduction step

## ❖ Sample:

➤ 10%Co/ZrO<sub>2</sub>

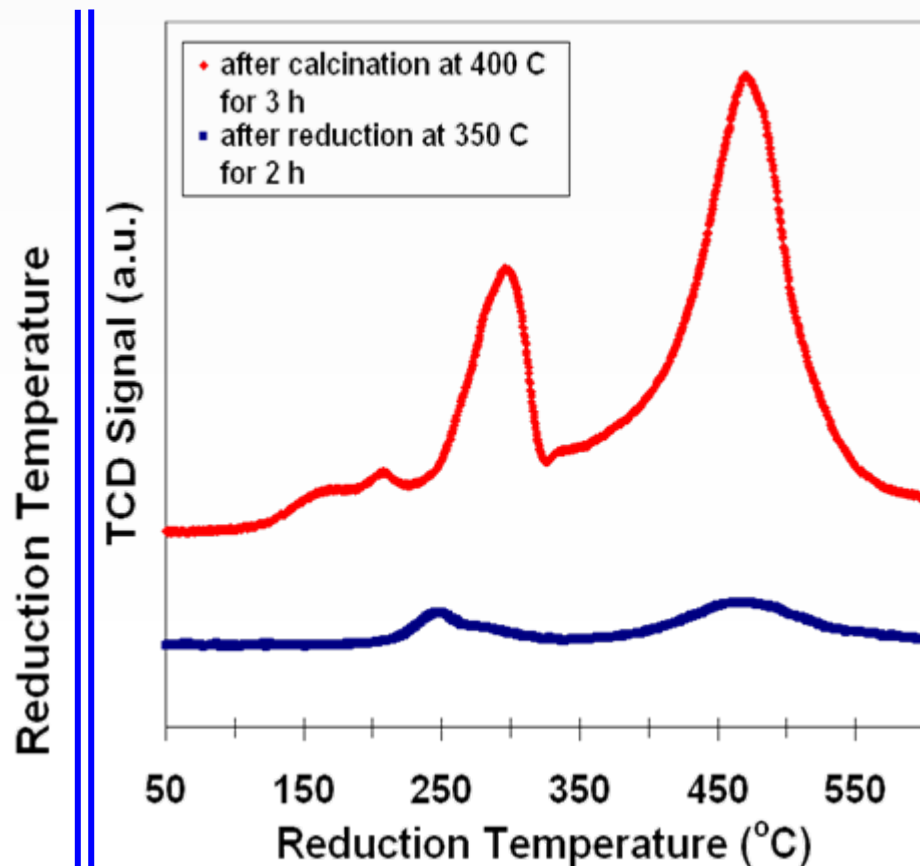
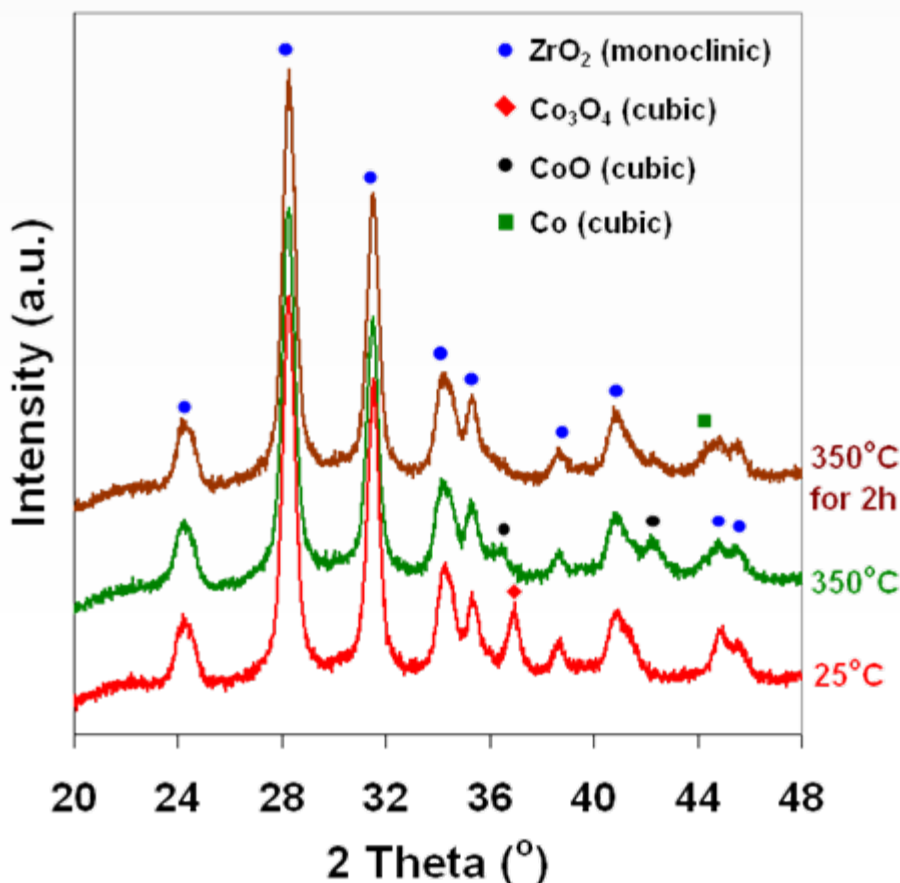
## ❖ Calcination:

➤ 400°C for 3h;

## ❖ Reduction:

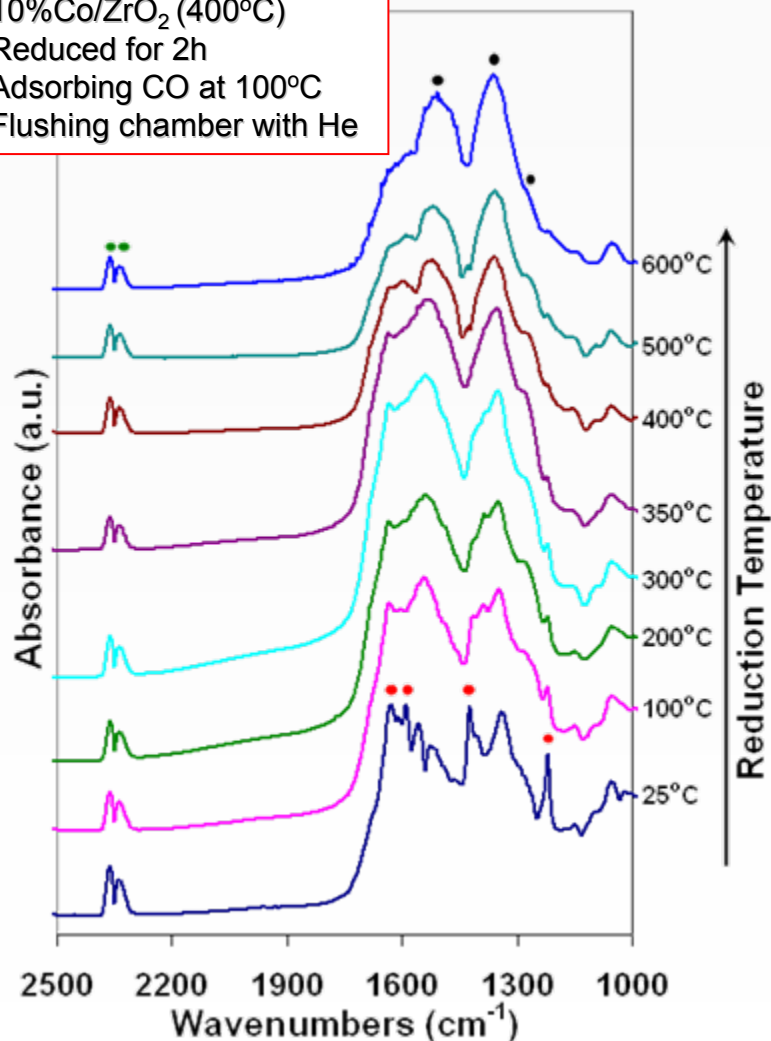
➤ 350°C for 2h under 5%H<sub>2</sub>/N<sub>2</sub>;

Most of the cobalt oxide has been reduced to metal Co after described activation treatment



# In-Situ DRIFTS - CO Chemisorption

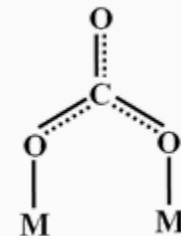
10%Co/ZrO<sub>2</sub> (400°C)  
 Reduced for 2h  
 Adsorbing CO at 100°C  
 Flushing chamber with He



Carbonate formation on the surface correlates well with the metallic surface area.

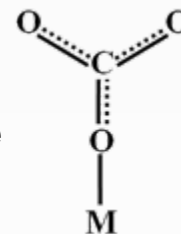
● **Bidentate carbonate** [1,2]

1631, 1591,  
 1425, 1220 cm<sup>-1</sup>



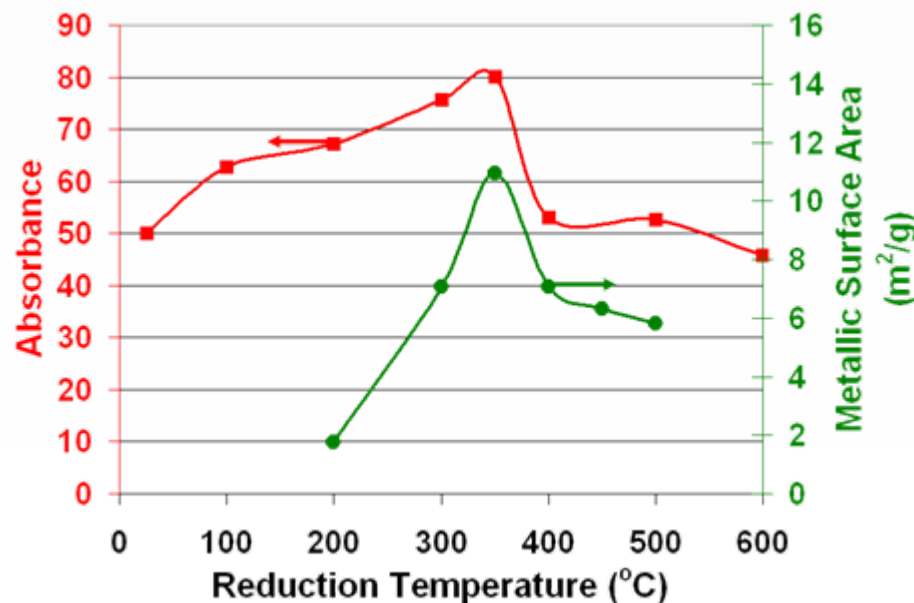
● **Adsorbed CO<sub>2</sub>**

2368, 2343cm<sup>-1</sup>  
 O=C=O stretching



● **Monodentate carbonate**

1530, 1373 cm<sup>-1</sup>

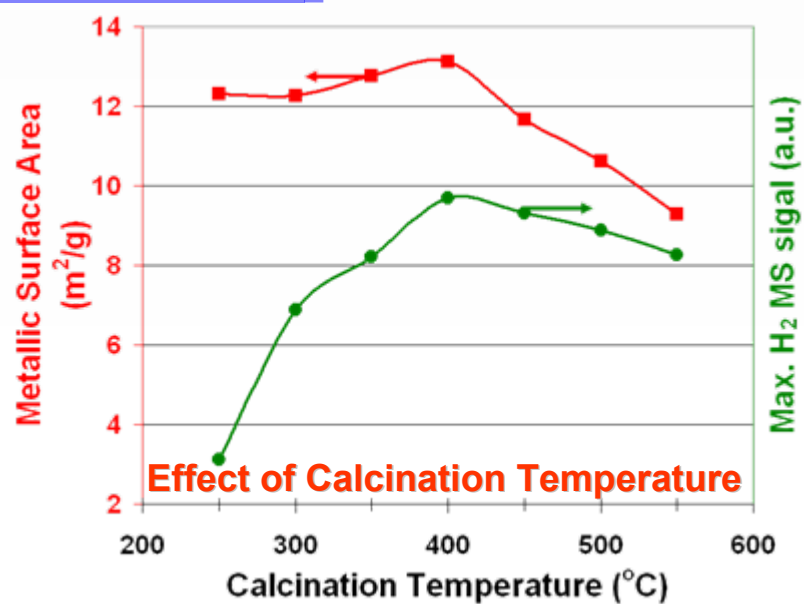
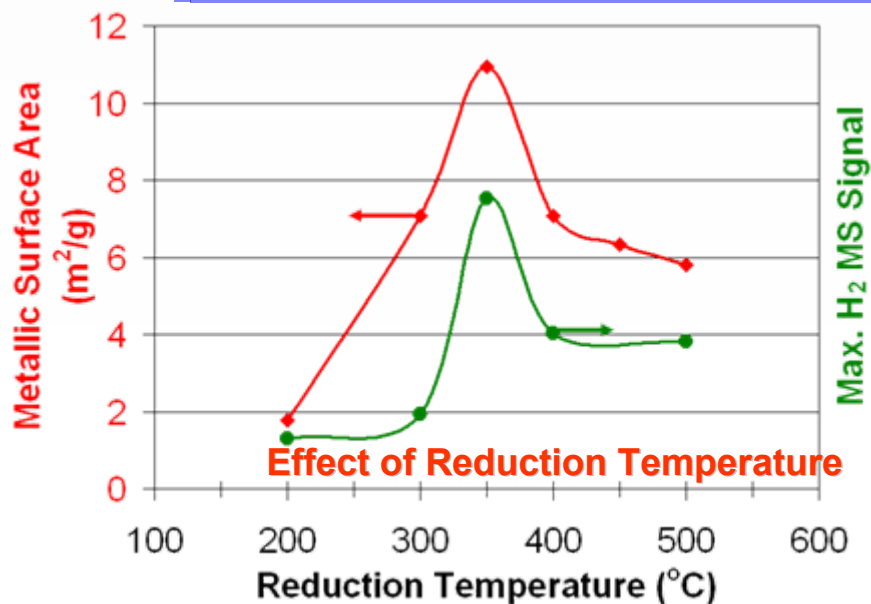
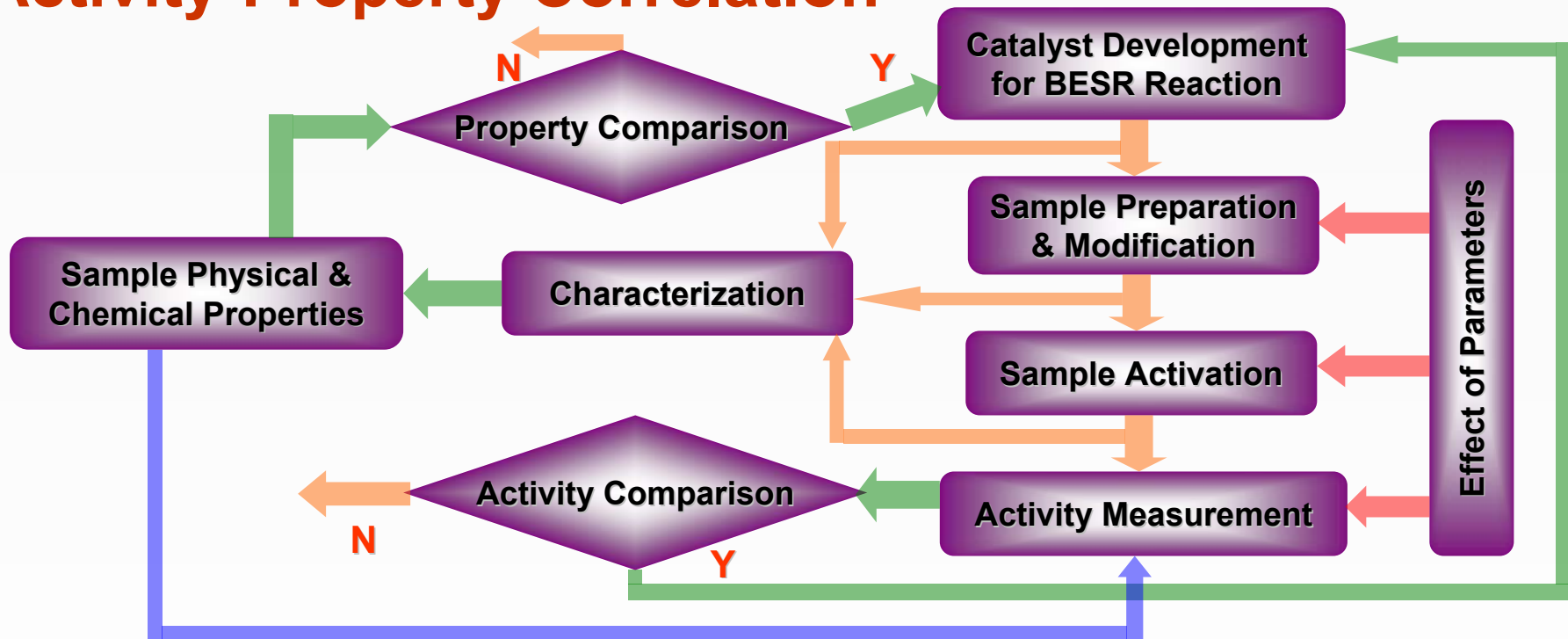


[1] Mattos, L.V., Noronha, F.B. J. Catal. 233(2005) 453-463;

[2] Mattos, L.V., Noronha, F.B. J. Power Sources 152 (2005) 50-59; **8**

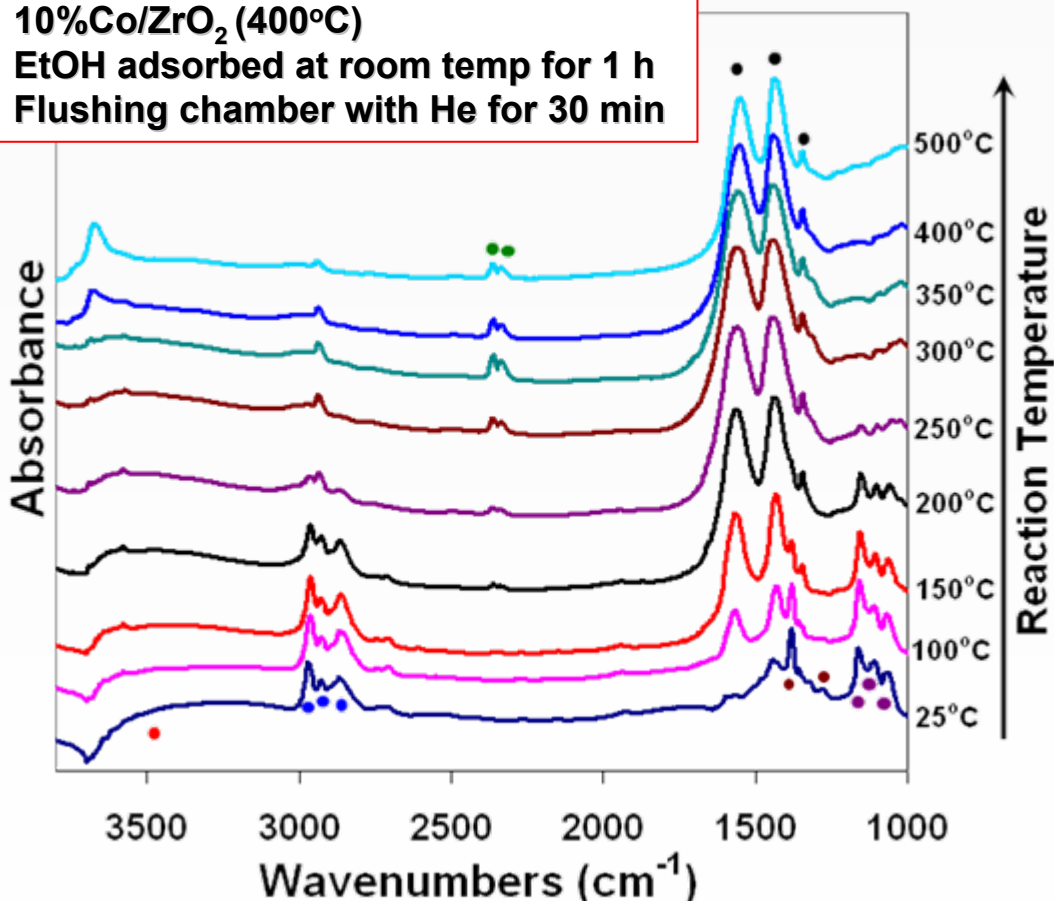


# Activity-Property Correlation



# Reaction Network and Intermediates: *In-Situ* DRIFTS-Ethanol TPD

10%Co/ZrO<sub>2</sub> (400°C)  
EtOH adsorbed at room temp for 1 h  
Flushing chamber with He for 30 min



- Ethanol molecules are adsorbed onto the surface at room temp
- Interaction with OH groups
- Ethoxy, acetate and carbonate intermediates
- CO (characteristic peaks: 2200~2000cm<sup>-1</sup>) is not observed

- **M-OH**  
3650~3150cm<sup>-1</sup>, O-H stretching
- **CH<sub>3</sub>- or CH<sub>3</sub>CH<sub>2</sub>-**  
2970, 2928, 2867cm<sup>-1</sup>:C-H stretching
- **Monodentate and bidentate ethoxy species** [1]  
1161, 1110, 1066cm<sup>-1</sup>  
CCO stretching
- **Acetates** [2]  
CH<sub>3</sub>COO  
1552, 1441, 1346cm<sup>-1</sup>
- **Adsorbed CO<sub>2</sub>**  
2361, 2338cm<sup>-1</sup>  
O=C=O stretching
- **Molecularly adsorbed ethanol** [3]  
1383cm<sup>-1</sup>: C-H bending  
1294cm<sup>-1</sup>: OH bending

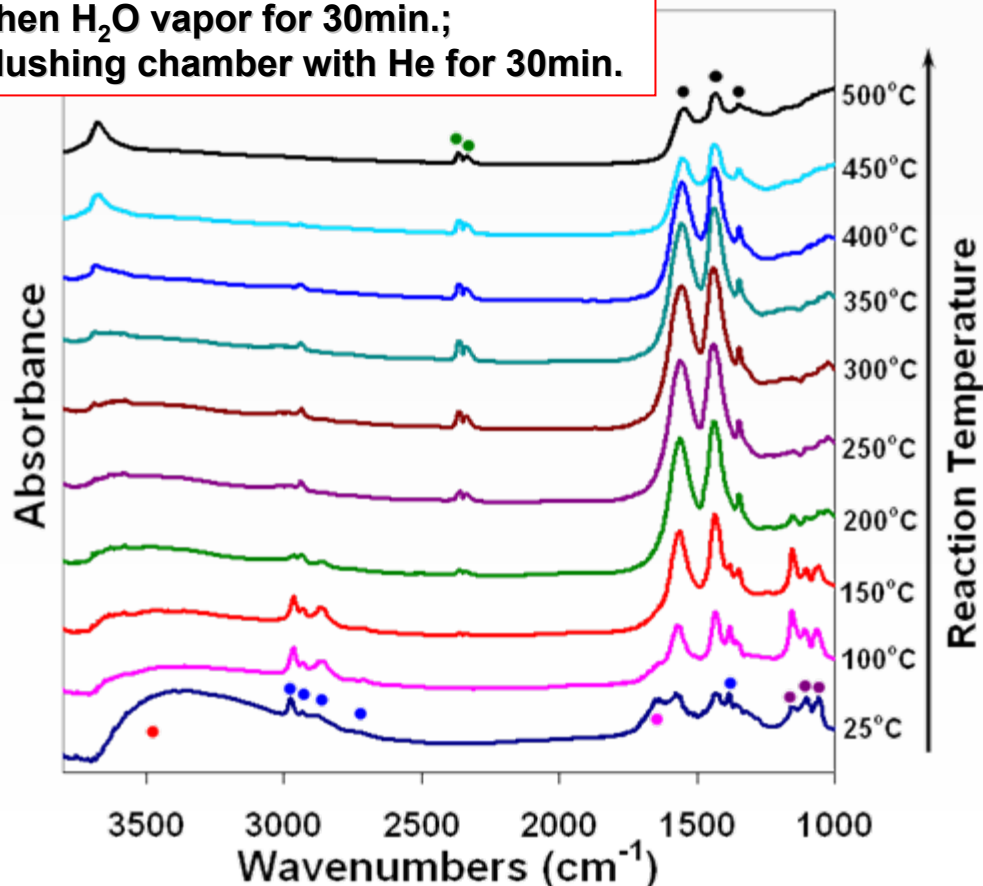
[1] Erdöhelyi, A., et al. Catal. Today, 116 (2006) 367.

[2] Guil, J.M., et al. J. Phys. Chem. B, 109 (2005) 10813

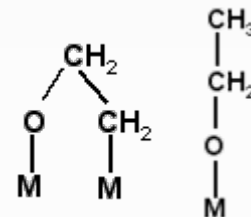
[3] Raskó, J., et al. Appl. Catal. A: Gen., 299 (2006) 202

# Reaction Network and Intermediates: *In-Situ* DRIFTS - EtOH+H<sub>2</sub>O Reaction

10%Co/ZrO<sub>2</sub> (400°C)  
Introducing EtOH vapor for 1h;  
Then H<sub>2</sub>O vapor for 30min.;  
Flushing chamber with He for 30min.



- **M-OH**  
3650~3150cm<sup>-1</sup>, O-H stretching
- **CH<sub>3</sub>- or CH<sub>3</sub>CH<sub>2</sub>-**  
2962, 2927, 2865 cm<sup>-1</sup>:C-H stretching  
1385cm<sup>-1</sup>: CH<sub>3</sub>- bending
- **Monodentate and bidentate ethoxide**  
1169, 1106, 1063cm<sup>-1</sup>  
CCO stretching
- **Acetates**  
CH<sub>3</sub>COO  
1569, 1429, 1348cm<sup>-1</sup>
- **Adsorbed CO<sub>2</sub>**  
2361, 2336cm<sup>-1</sup>: O=C=O stretching
- **Molecularly adsorbed H<sub>2</sub>O**  
1654cm<sup>-1</sup>

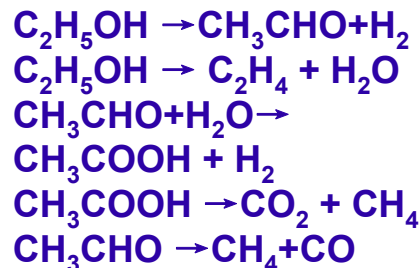


- Water and ethanol molecules are adsorbed onto the surface at room temp
- Interaction with OH groups
- Water facilitates formation of ethoxy and acetate surface intermediates at lower temp.,
- CO (characteristic peaks: 2200~2000cm<sup>-1</sup>) is not observed

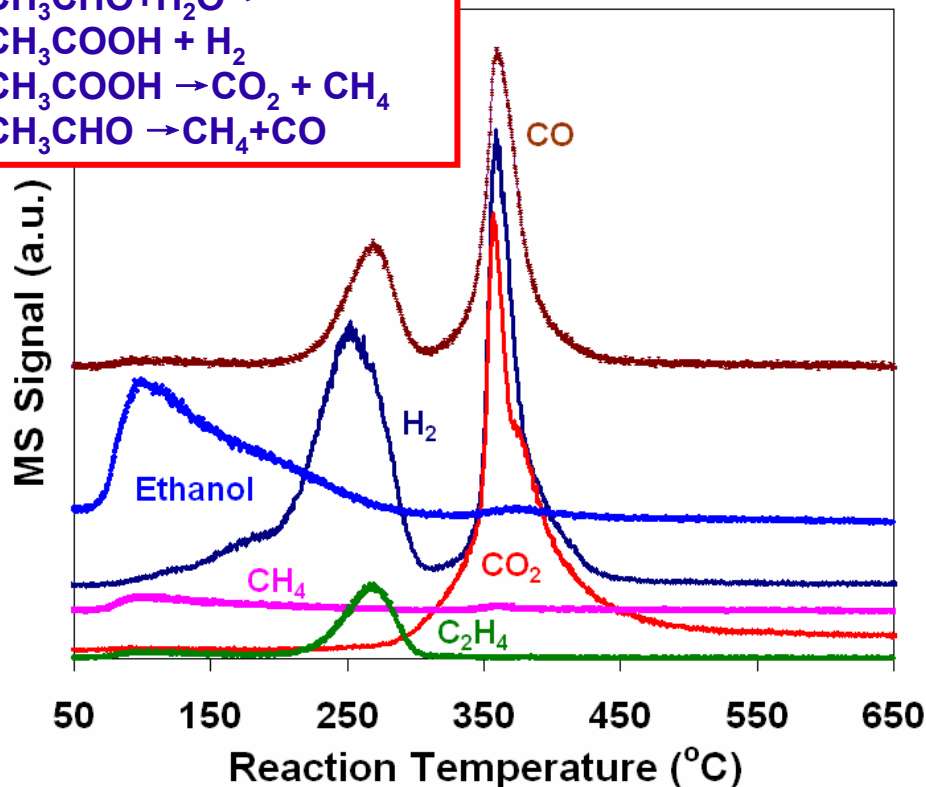
# Reaction Network and Intermediates:



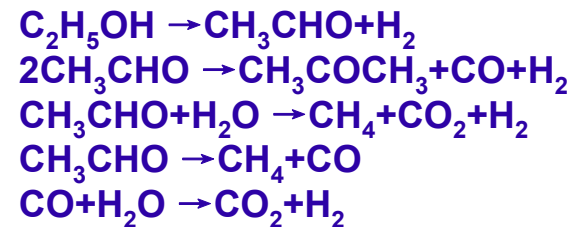
- ❖ Sample:
  - 10%Co/ZrO<sub>2</sub>;
- ❖ Calcination:
  - 400°C for 3h;
- ❖ Reduction:
  - 350°C for 2h;
- ❖ Before reaction:
  - Flowing EtOH for 1h;



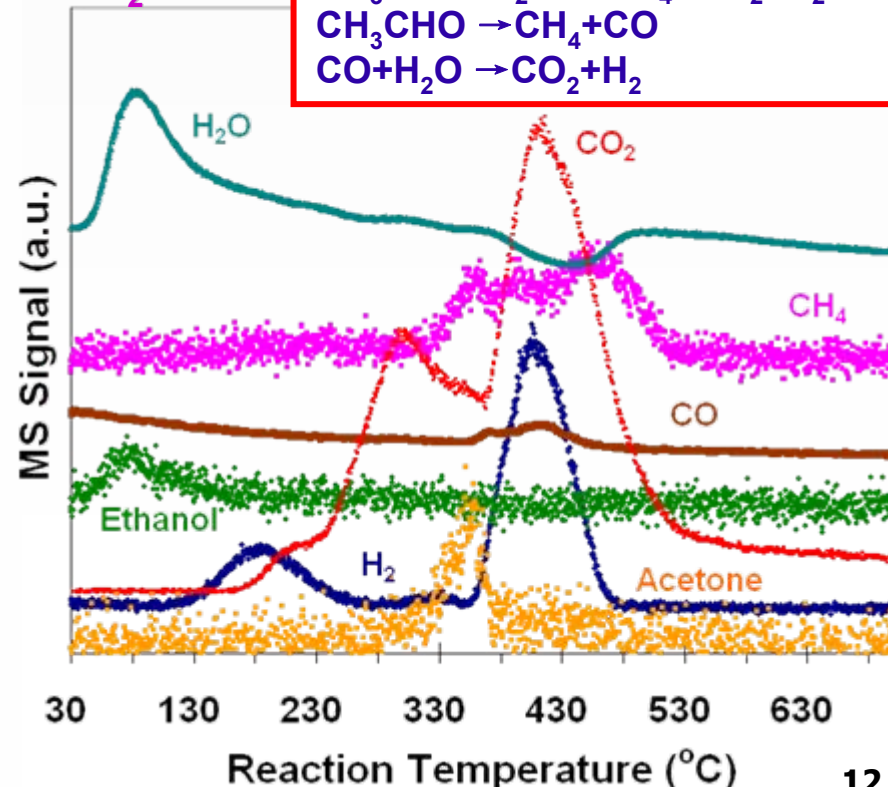
EtOH TPD



- ❖ Sample:
  - 10%Co/ZrO<sub>2</sub>;
- ❖ Calcination:
  - 400°C for 3h;
- ❖ Reduction:
  - 350°C for 2h;
- ❖ Before reaction:
  - Flowing mixture of EtOH:H<sub>2</sub>O(1:10) for 1h



EtOH+H<sub>2</sub>O TPD

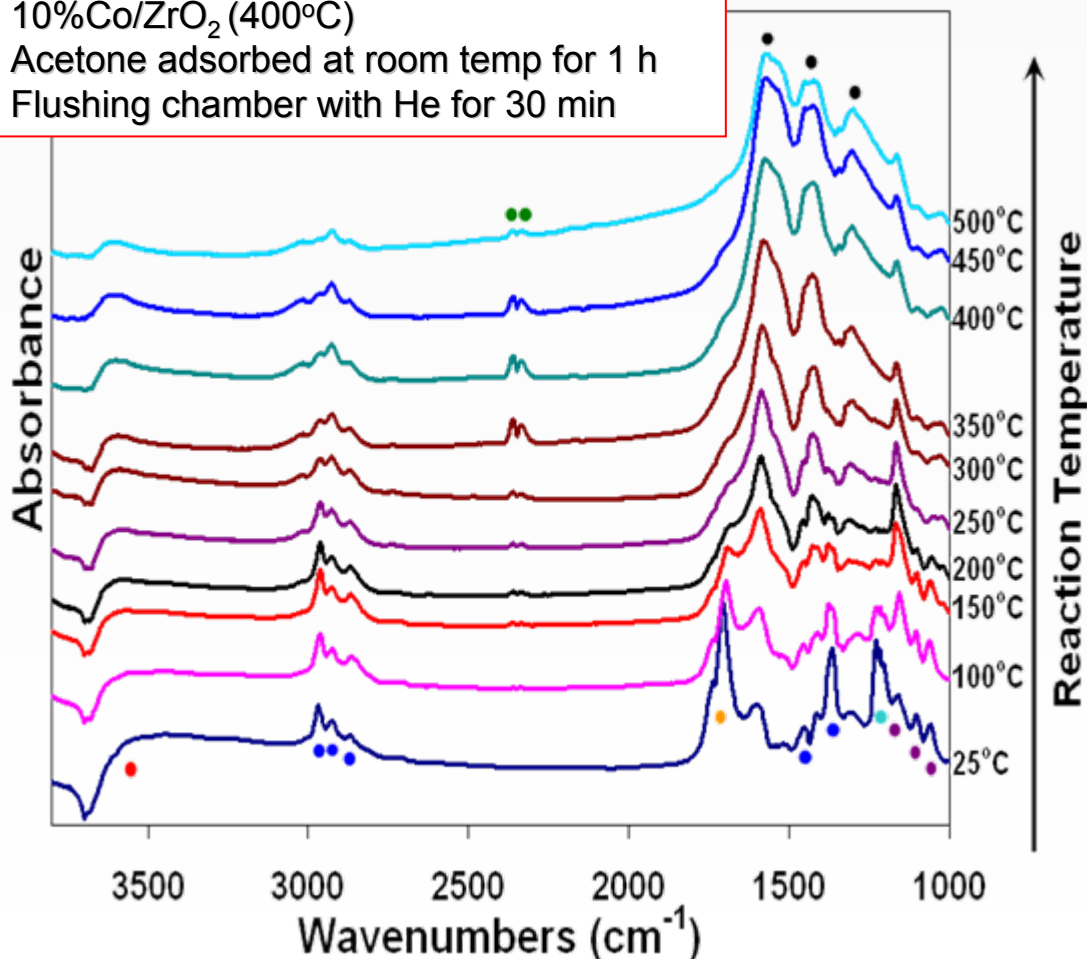


# Reaction Network and Intermediates: *In-Situ* DRIFTS-Acetone TPD

10%Co/ZrO<sub>2</sub> (400°C)

Acetone adsorbed at room temp for 1 h

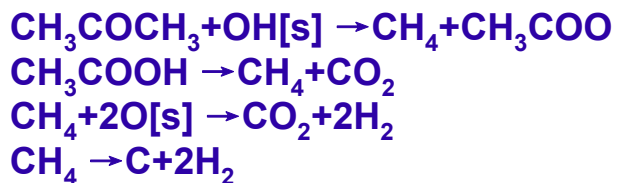
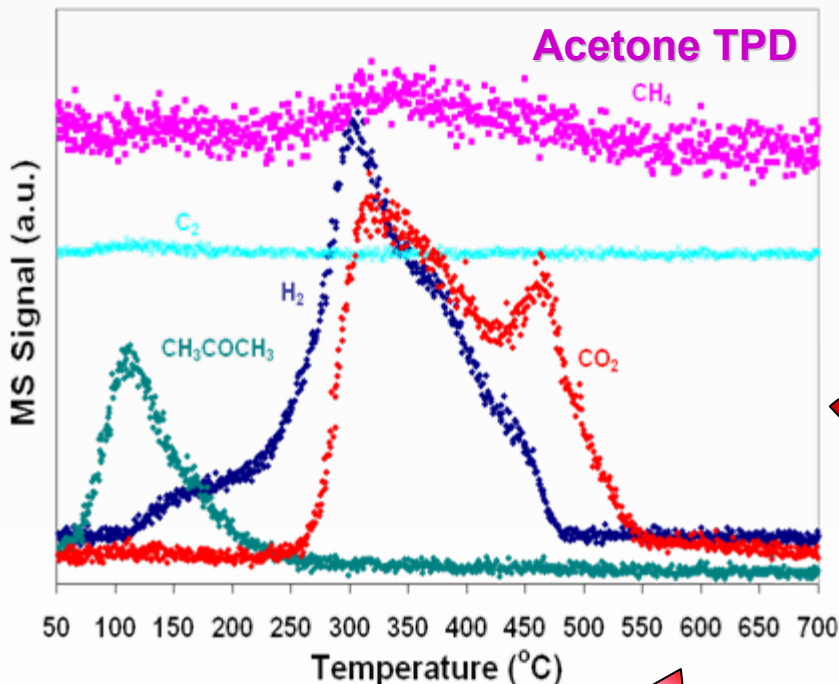
Flushing chamber with He for 30 min



- **M-OH**  
3650~3150cm<sup>-1</sup>, O-H stretching
- **CH<sub>3</sub>-**  
2963, 2927, 2865cm<sup>-1</sup>:C-H stretching  
1456, 1371cm<sup>-1</sup>: CH<sub>3</sub>- bending
- **Adsorbed CO<sub>2</sub>**  
2361, 2336cm<sup>-1</sup>  
O=C=O stretching
- **Acetates**  
1580, 1440, 1310cm<sup>-1</sup>
- **Monodentate and bidentate acetoxide**  
1170cm<sup>-1</sup>: C-C stretching  
1107, 1066cm<sup>-1</sup>: C-O stretching
- **O=C- carbonyl group:**  
1745cm<sup>-1</sup>
- **C-C-C group stretching:**  
1232cm<sup>-1</sup>

- Acetone molecules are adsorbed onto the surface at room temp.
- Evidence of C-C-C and C=O
- The cracking of acetone at lower temperatures
- Acetate species form at higher temperatures compared to ethanol TPD

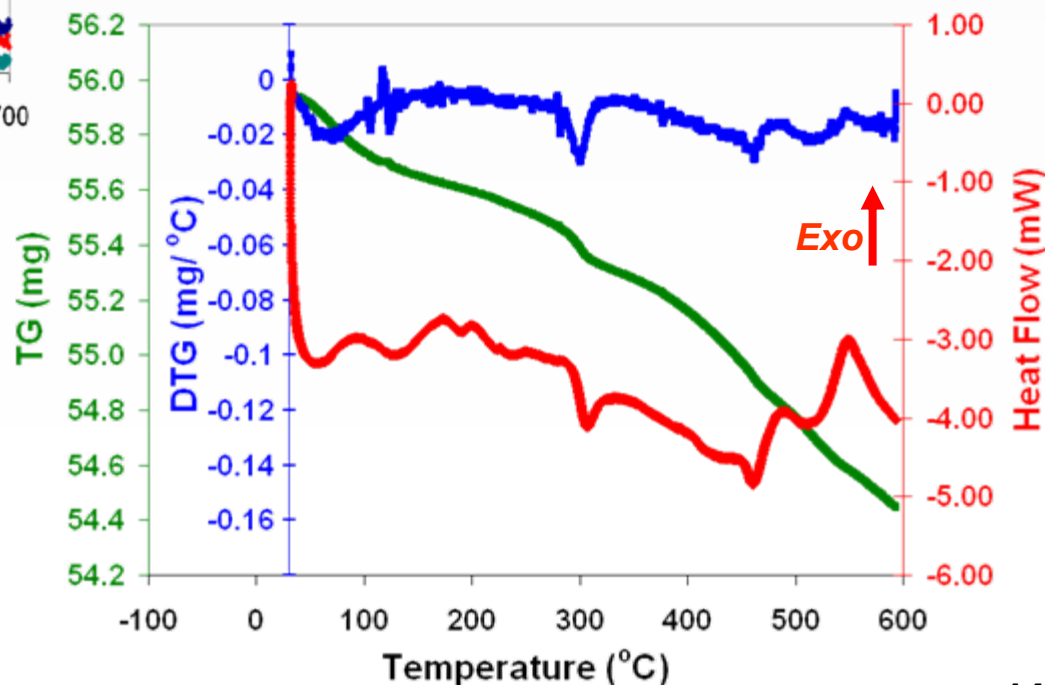
# Reaction Network and Intermediates: Acetone TPD (MS-TGA-DSC)



10 wt% Co/ZrO<sub>2</sub>

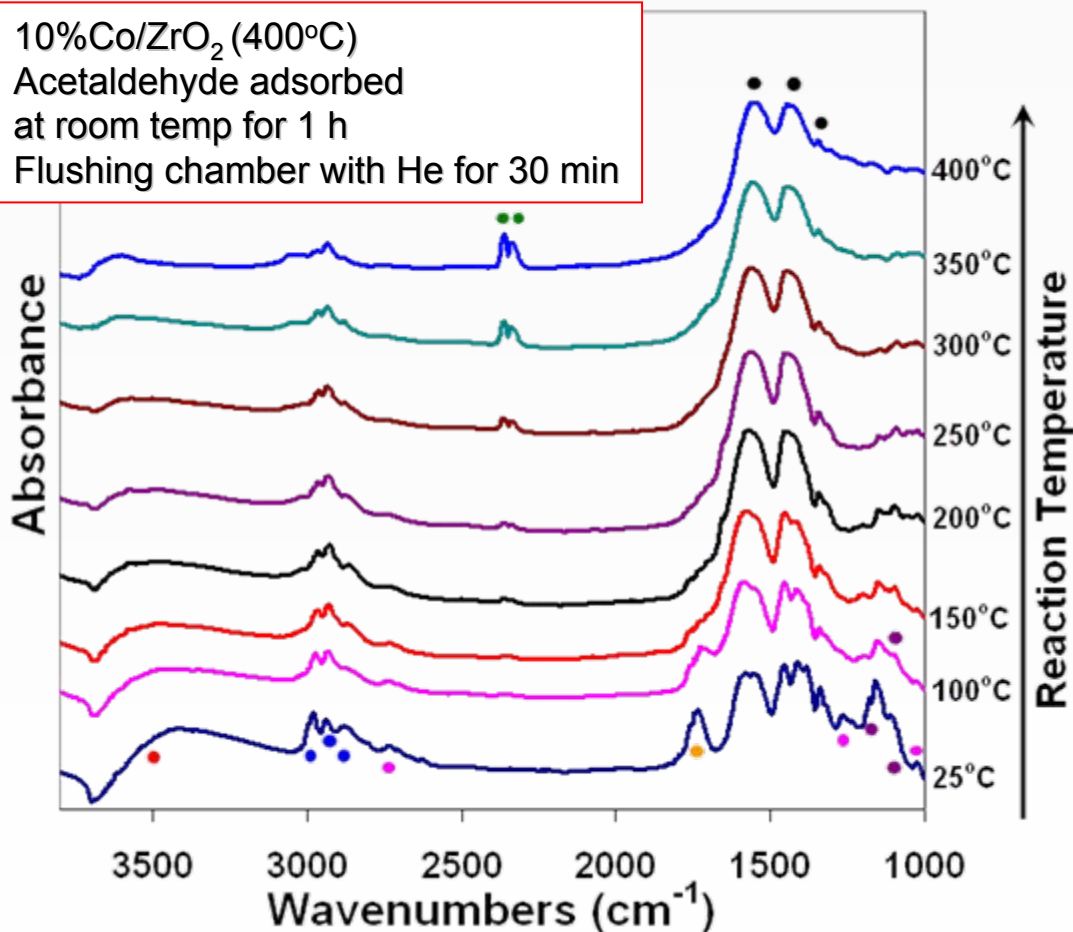


- ❖ **Sample:**  
10%Co/ZrO<sub>2</sub>
- ❖ **Pretreatment:**  
400°C for 30min.;  
Reduced at 350°C for 2h under 5%H<sub>2</sub>/He;  
400°C for 1h under He to remove moisture
- ❖ **Adsorption:**  
Acetone vapor was generated by flowing He at room temperature;
- ❖ **Desorption:**  
Under He at ramping rate of 5°C/min



# Reaction Network and Intermediates: In-Situ DRIFTS-Acetaldehyde TPD

10%Co/ZrO<sub>2</sub> (400°C)  
Acetaldehyde adsorbed  
at room temp for 1 h  
Flushing chamber with He for 30 min



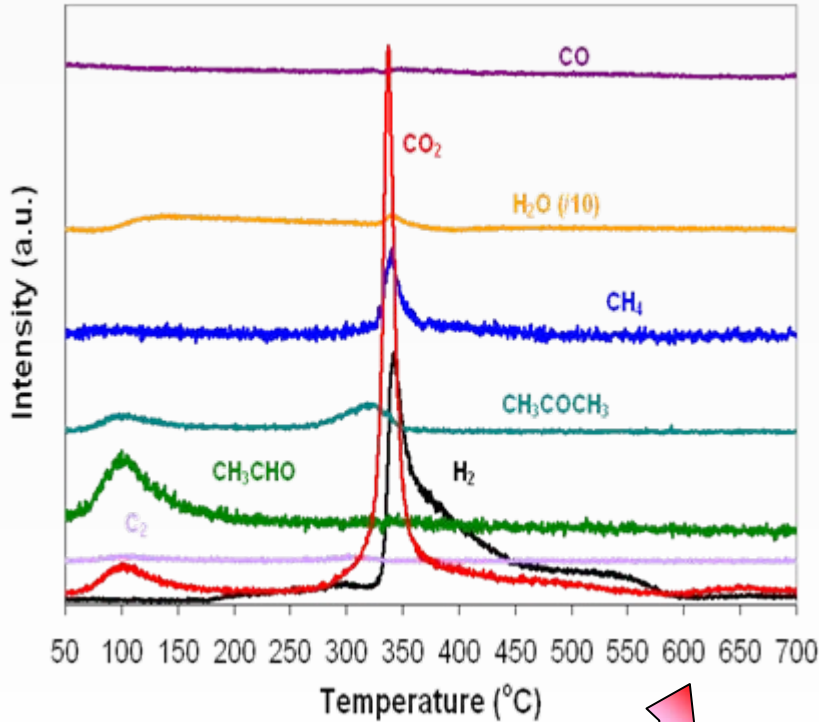
- **M-OH**  
3650~3150cm<sup>-1</sup>: O-H stretching
- **CH<sub>3</sub>- or CH<sub>3</sub>CH<sub>2</sub>-**  
2980, 2940, 2889cm<sup>-1</sup>:  
C-H stretching
- **Adsorbed CO<sub>2</sub>**  
2366, 2355cm<sup>-1</sup>:  
O=C=O stretching
- **Acetates**  
1556, 1442, 1360cm<sup>-1</sup>
- **Adsorbed acetaldehyde** [1,2]  
2736, 1267, 1025cm<sup>-1</sup>
- **Monodentate acetoxides**  
1180, 1161, 1100cm<sup>-1</sup>  
CCO stretching
- **Molecularly adsorbed acetaldehyde**  
1745cm<sup>-1</sup>: O=C- stretching

- Acetaldehyde molecules are adsorbed onto the surface room temp.;
- Part of the adsorbed acetaldehyde is reduced to ethoxide
- Part of the acetaldehyde is oxidized to acetate at room temperature;
- Acetaldehyde is the surface intermediate during ethanol TPD

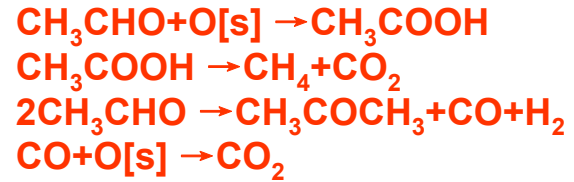
[1] Carlo Resini, et al. React. Kinet. Catal. Lett., 90 (2007) 117-126

[2] J. Llorca, et al. J. Catal., 227(2004) 556-560

# Reaction Network and Intermediates: Acetaldehyde TPD (MS-TGA-DSC)



10 wt% Co/ZrO<sub>2</sub>



## ❖ Pretreatment:

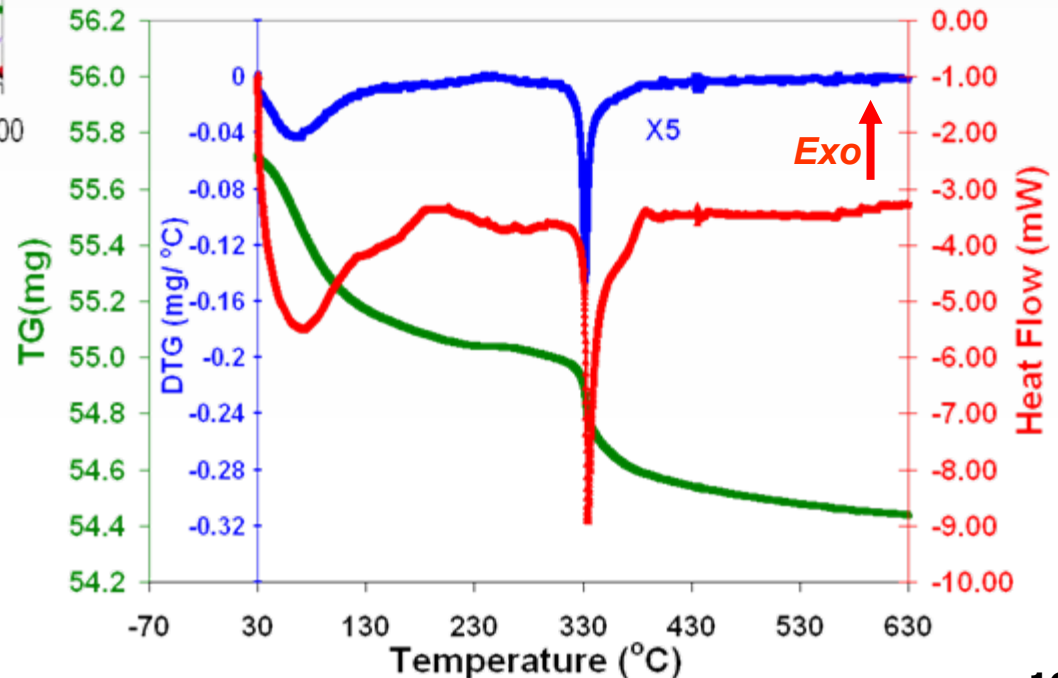
400°C for 3h;  
Reduced at 350°C for 2h  
Under 5% H<sub>2</sub>/He;

## ❖ Adsorption:

Use He as the carrier gas to generate  
CH<sub>3</sub>CHO vapor at room temperature for 1h;  
Flow He to purge the line;

## ❖ Desorption:

Under He (10°C/min.)



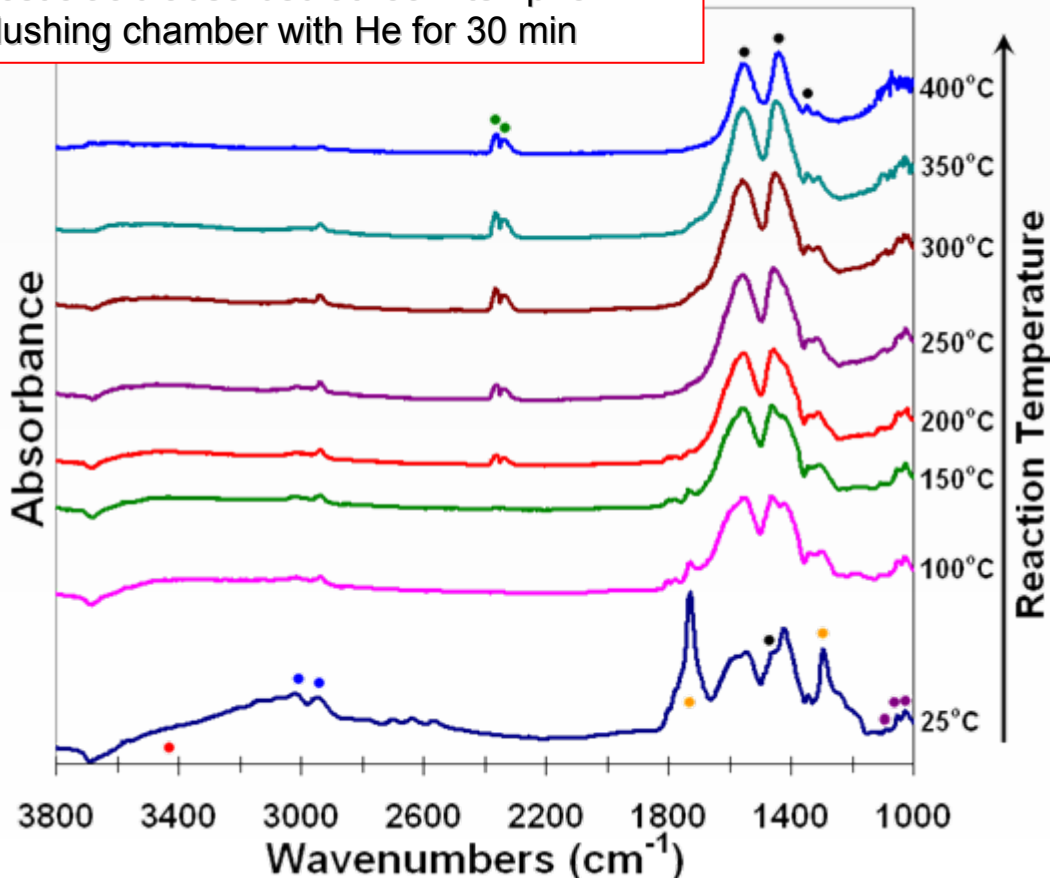


# Reaction Network and Intermediates: In-Situ DRIFTS-Acetic Acid TPD

10%Co/ZrO<sub>2</sub> (400°C)

Acetic acid adsorbed at room temp for 1 h

Flushing chamber with He for 30 min



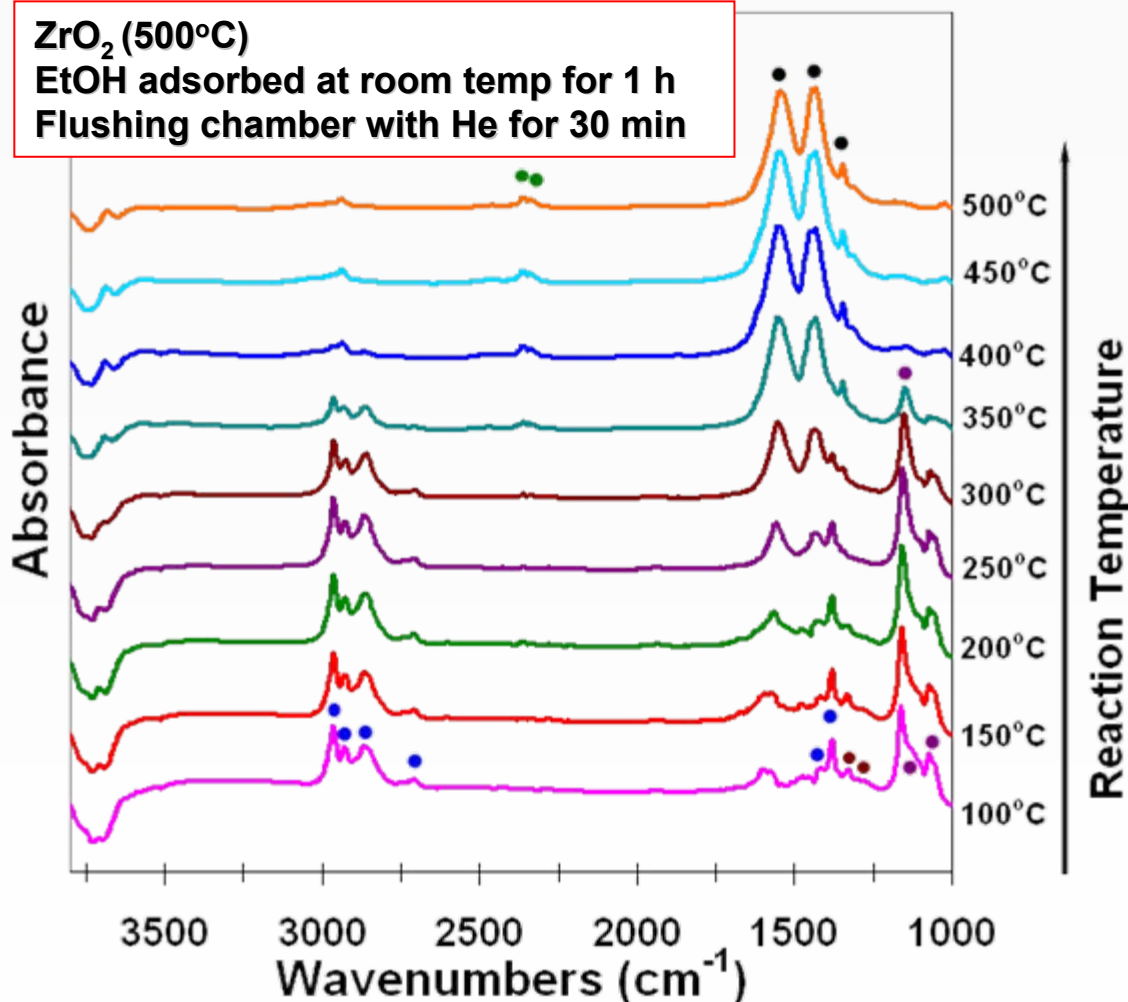
The assignment of surface acetate species is confirmed

- **M-OH**  
3650~3150cm<sup>-1</sup>, O-H stretching
- **CH<sub>3</sub>- , -CH<sub>2</sub>-**  
3050~2800cm<sup>-1</sup>:C-H stretching
- **Adsorbed CO<sub>2</sub>**  
2366, 2345cm<sup>-1</sup>  
O=C=O stretching
- **Surface Acetates**  
1558, 1465, 1446, 1350cm<sup>-1</sup>
- **Monodentate and bidentate ethoxide**  
1091, 1053, 1026cm<sup>-1</sup>  
CCO stretching
- **Molecularly adsorbed acetic acid**  
1728cm<sup>-1</sup>: O=C- stretching  
1297cm<sup>-1</sup>: OH bending

- Acetic acid molecules are adsorbed onto the surface at room temp.
- Surface acetates are observed even at room temp.
- Molecularly adsorbed acetic acid disappears along with increase of temp.
- Linearly adsorbed CO<sub>2</sub> present without experiencing carbonate intermediate.

# In-Situ DRIFTS-Ethanol TPD on Bare Support

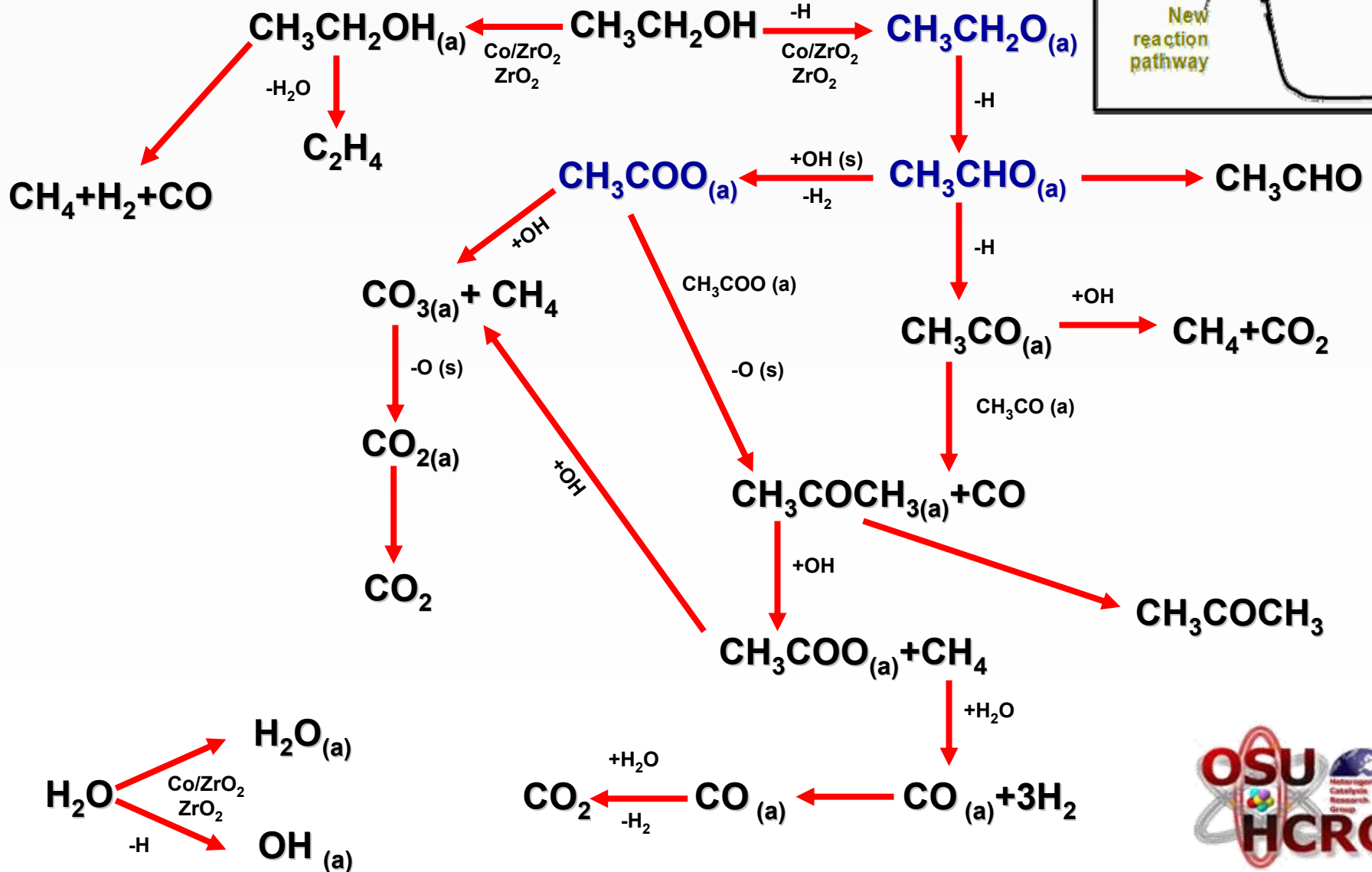
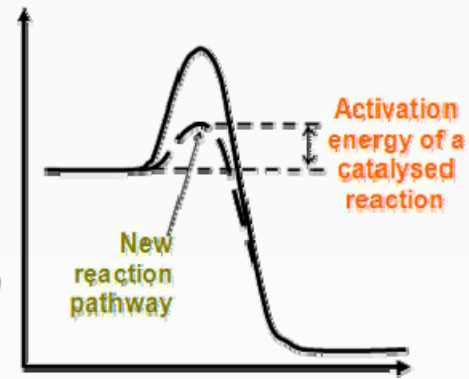
ZrO<sub>2</sub> (500°C)  
EtOH adsorbed at room temp for 1 h  
Flushing chamber with He for 30 min



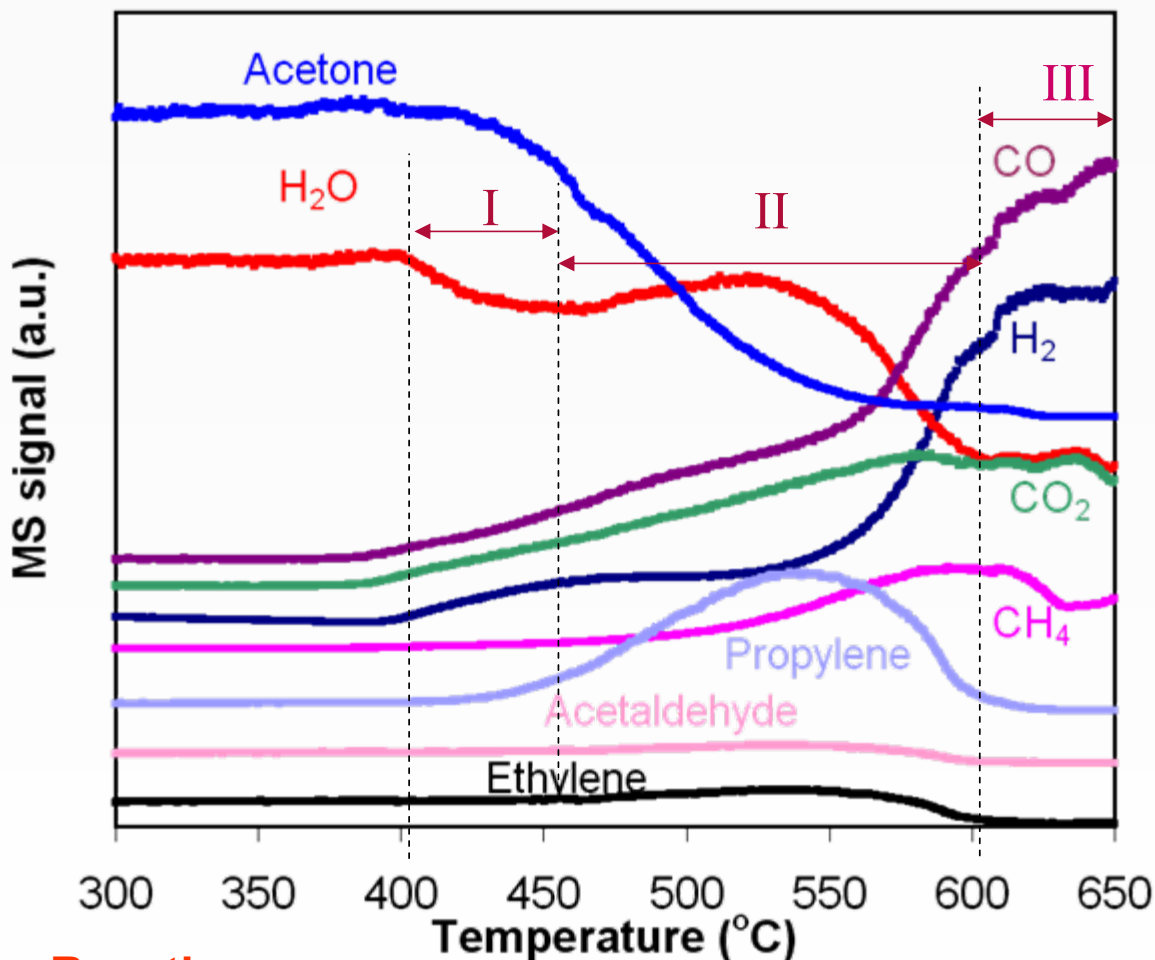
- **CH<sub>3</sub>- , -CH<sub>2</sub>-**  
3050~2800cm<sup>-1</sup>: C-H stretching  
1429, 1383cm<sup>-1</sup>: C-H bending
- **Adsorbed CO<sub>2</sub>**  
2368, 2352cm<sup>-1</sup>  
O=C=O stretching
- **Surface Acetates**  
1552, 1446, 1348cm<sup>-1</sup>
- **Ethoxide**  
1126, 1074cm<sup>-1</sup>: C-O stretching  
1182cm<sup>-1</sup>: C-C stretching
- **Molecularly adsorbed ethanol**  
1330cm<sup>-1</sup>: C-H bending  
1292cm<sup>-1</sup>: OH bending

- C-H bonding is observed at higher temp., compared with Co impregnated sample.
- C-C bonding is seen at higher temp., compared with Co impregnated sample.
- Ethoxide species disappear at higher temp., compared with Co impregnated sample.

# Possible Pathways of BESR over Co/ZrO<sub>2</sub>



# Effect of T on Reaction Network: TPRxn - Acetone +H<sub>2</sub>O



## Reactions:

- I.  $\text{CH}_3\text{COCH}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{CO} + \text{CO}_2 + 6\text{H}_2$
- II.  $\text{CH}_3\text{COCH}_3 + \text{H}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$ ;  $\text{CH}_3\text{COCH}_3 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{CH}_4$   
 $\text{CH}_3\text{COCH}_3 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{C}_2\text{H}_4 + 2\text{H}_2$
- III.  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ ;  $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$

## ❖ Sample:

10%Co/ZrO<sub>2</sub>

## ❖ Pretreatment:

400°C for 30 min;

Reduced at 350°C for 2h

under 5%H<sub>2</sub>/He;

Degassing at 400°C for 1h

under He

## ❖ Reaction:

CH<sub>3</sub>COCH<sub>3</sub>:H<sub>2</sub>O=1:10  
(molar ratio)

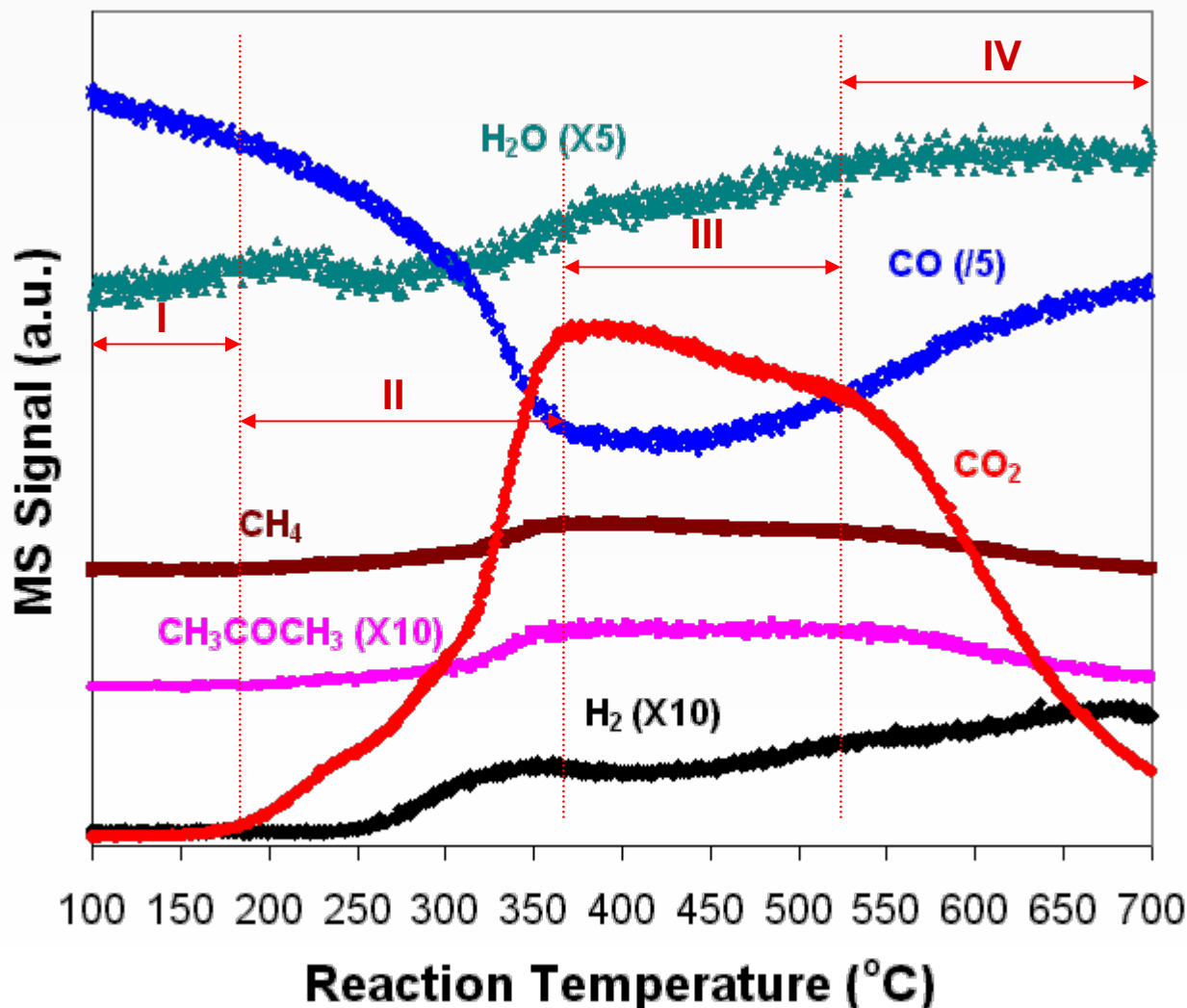
Total flow=55ml/min.

Ramp rate:10°C/min.

## ❖ Experiment:

Monitoring product stream  
with MS

# Effect of T on Reaction Network: TPRxn - Water Gas Shift



❖ **Sample:**  
10%Co/ZrO<sub>2</sub>

❖ **Pretreatment:**  
400°C for 3h;  
Reduced at 350°C for 2h  
under 5%H<sub>2</sub>/He;  
400°C for 1h under He to  
remove moisture

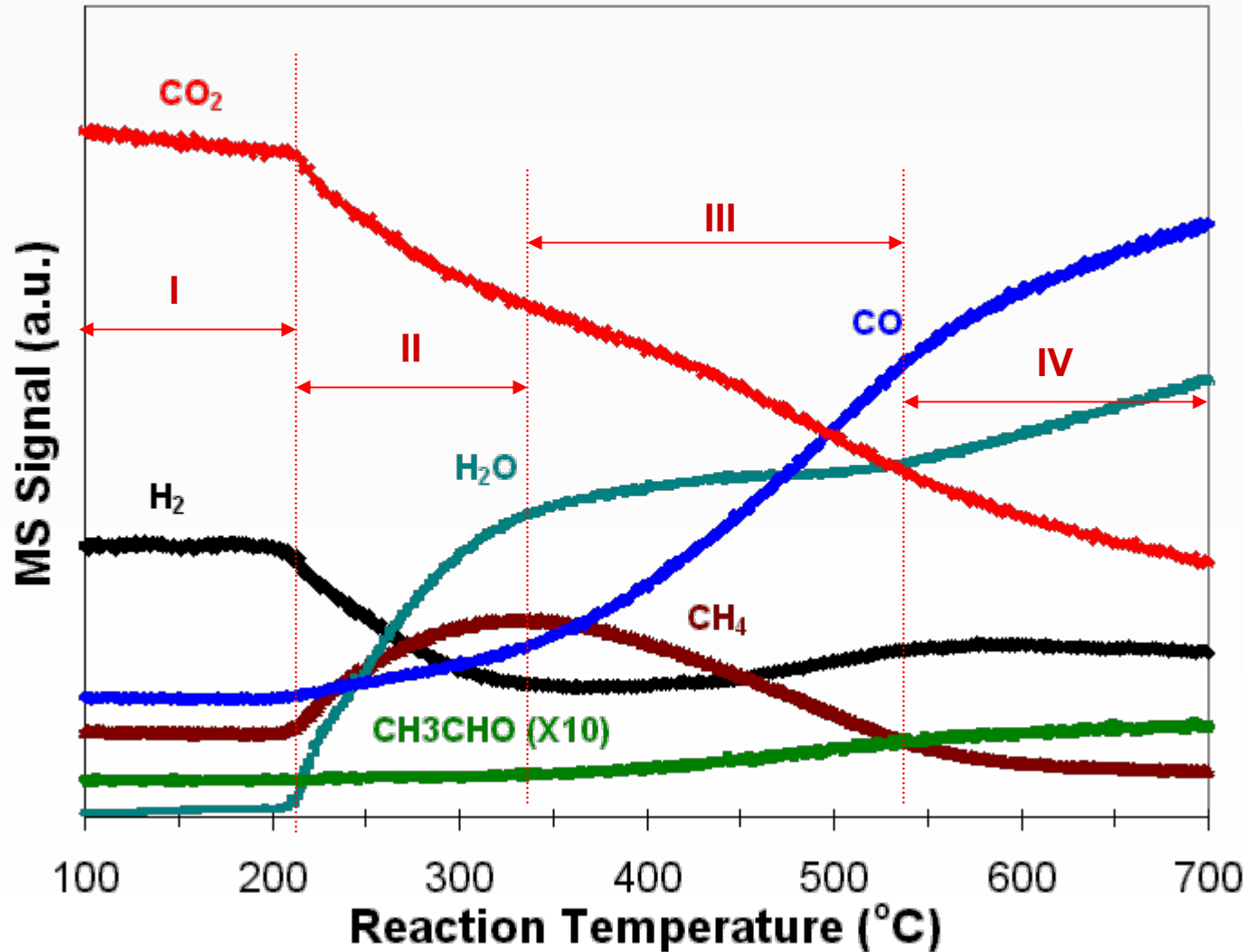
❖ **Reaction:**  
CO:H<sub>2</sub>O=1:8 (molar ratio)  
Total flow=51ml/min.  
Ramp rate:10°C/min.

❖ **Experiment:** Monitoring  
product stream with MS

**I:** no reaction;    **II:**  $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$  ;  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$

**III:** same reactions as step II;    **IV:**  $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$  ;  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$

# Effect of T on Reaction Network: TPRxn - Reverse Water Gas Shift



❖ **Sample:**  
10%Co/ZrO<sub>2</sub>

❖ **Pretreatment:**  
400°C for 3h;  
Reduced at 350°C for 2h  
under 5%H<sub>2</sub>/He;  
400°C for 1h under He to  
remove moisture

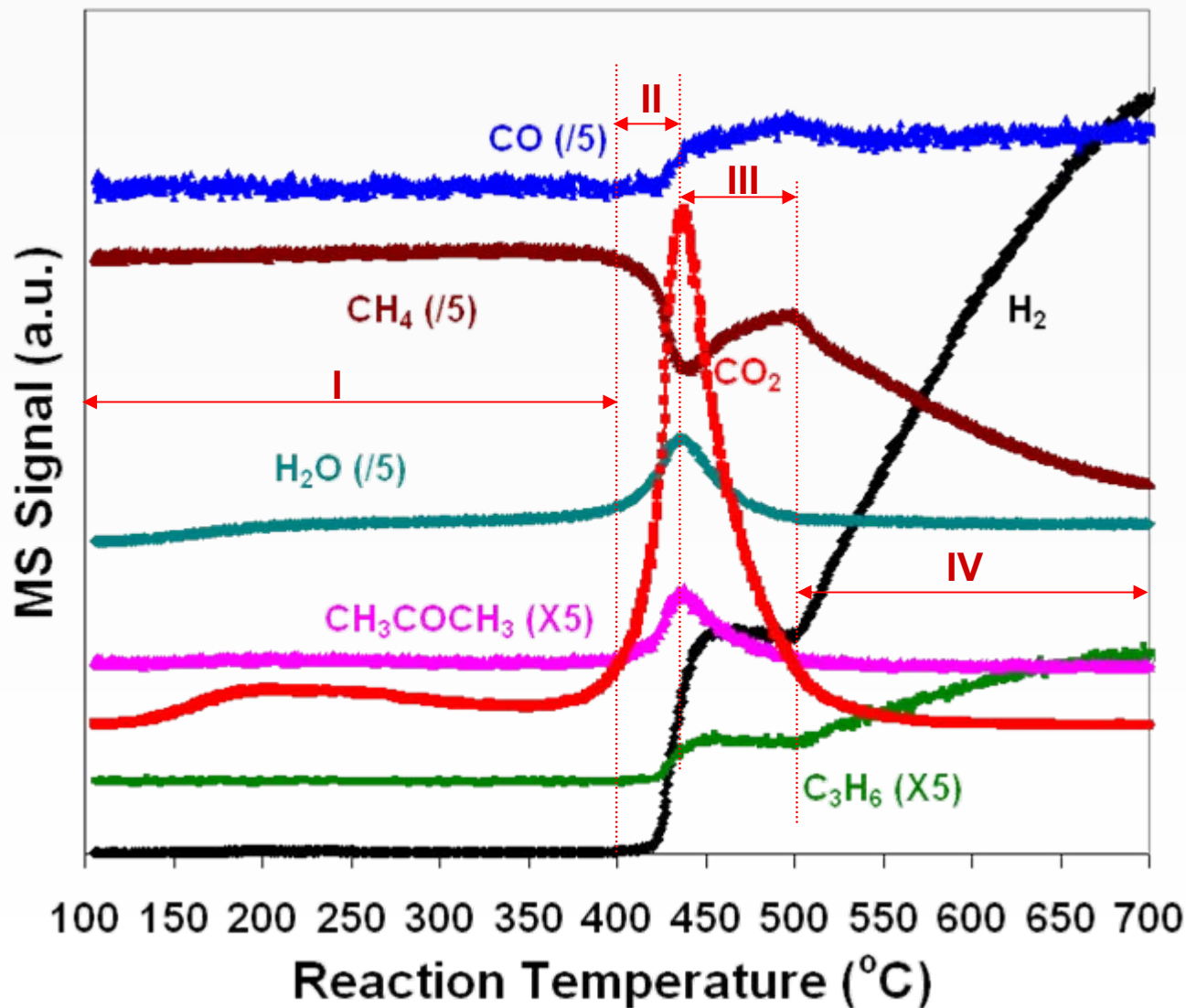
❖ **Reaction:**  
CO<sub>2</sub>:H<sub>2</sub>=1:1 (molar ratio)  
Total flow=60ml/min.  
Ramp rate:  
10°C/min.

❖ **Experiment:**  
Monitoring product  
stream with MS

**I:** no reaction;    **II:** CO<sub>2</sub> + 4H<sub>2</sub> ⇌ CH<sub>4</sub> + 2H<sub>2</sub>O;    CO<sub>2</sub> + H<sub>2</sub> ⇌ CO + H<sub>2</sub>O

**III:** CH<sub>4</sub> + 2H<sub>2</sub>O ⇌ CO<sub>2</sub> + 4H<sub>2</sub>    **IV:** CH<sub>4</sub> + H<sub>2</sub>O ⇌ CO + 3H<sub>2</sub>;    CO<sub>2</sub> + H<sub>2</sub> ⇌ CO + H<sub>2</sub>O

# Effect of T on Reaction Network: TPRxn-Methane Steam Reforming



❖ **Sample:**  
10%Co/ZrO<sub>2</sub>

❖ **Pretreatment:**  
400°C for 3h;  
Reduced at 350°C for 2h  
under 5%H<sub>2</sub>/He;  
400°C for 1h under He to  
remove moisture

❖ **Reaction:**  
CH<sub>4</sub>:H<sub>2</sub>O=1:8 (molar  
ratio)  
Total flow=51ml/min.  
Ramping rate:10°C/min.

❖ **Experiment:**  
Monitoring product  
stream with MS

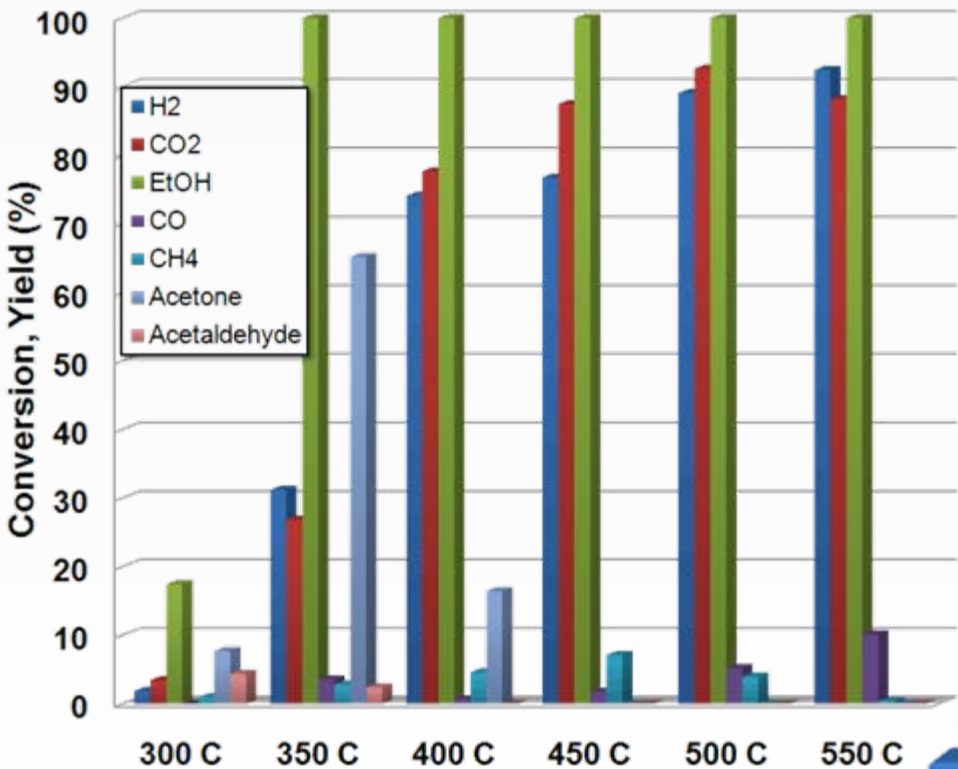
I: No Reaction    II: CH<sub>4</sub>+2H<sub>2</sub>O    III: CO<sub>2</sub>+2H<sub>2</sub>    IV: CH<sub>4</sub>

IV: CH<sub>4</sub>    I: CO<sub>2</sub>+4H<sub>2</sub> ; CH<sub>4</sub>+H<sub>2</sub>O    I: 3H<sub>2</sub>+CO; 2CH<sub>4</sub>+CO<sub>2</sub>    I: CH<sub>3</sub>COCH<sub>3</sub>+H<sub>2</sub>O

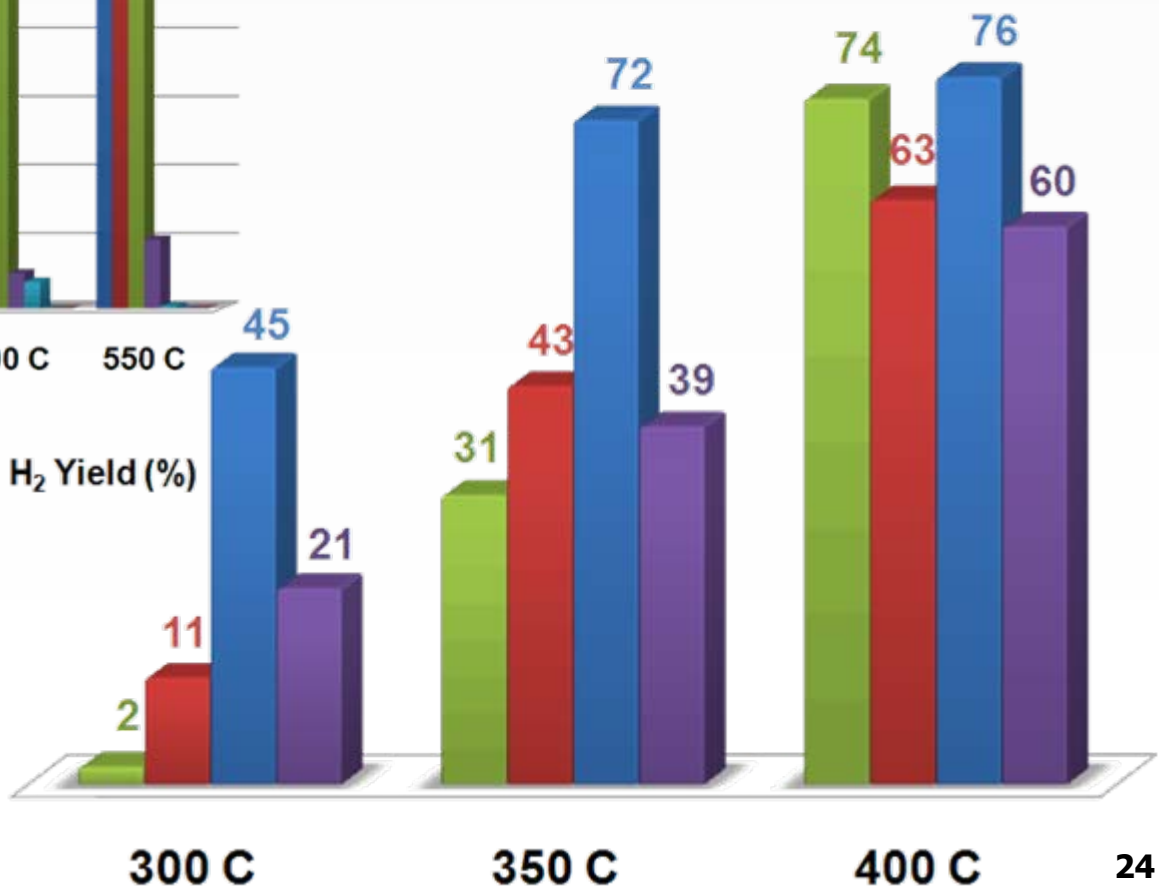
III: CO<sub>2</sub>+2H<sub>2</sub>    I: CH<sub>4</sub>+2H<sub>2</sub>O    IV: CH<sub>4</sub>    I: C+2H<sub>2</sub>; CH<sub>3</sub>COCH<sub>3</sub>+H<sub>2</sub>    I: C<sub>3</sub>H<sub>6</sub>+H<sub>2</sub>O

# Modification of the Initial Catalyst Formulation

With modified formulations, higher hydrogen yield can be achieved at lower temperatures



■ 10%Co/ZrO<sub>2</sub>     ■ 10%Co/10CeO<sub>2</sub>-ZrO<sub>2</sub>  
■ 1%Re-10%Co/10%CeO<sub>2</sub>-ZrO<sub>2</sub>     ■ Equilibrium Calculation



EtOH: H<sub>2</sub>O: dilution=1:10:75  
 GHSV=5,000h<sup>-1</sup>  
 C<sub>EtOH</sub>=1.2%



# Modification of the Initial Catalyst Formulation:

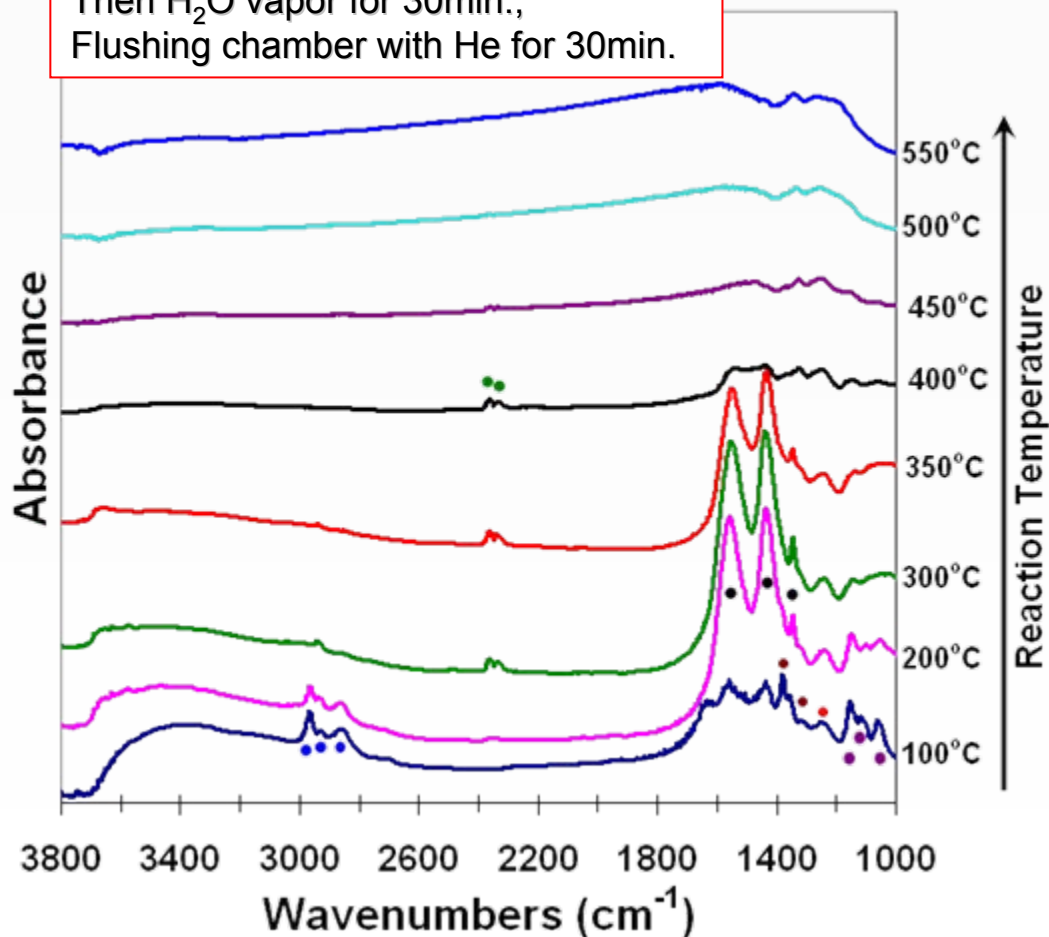
## In-Situ DRIFTS - EtOH+H<sub>2</sub>O Reaction

10%Co/10%CeO<sub>2</sub>-ZrO<sub>2</sub> (400°C)

Introducing EtOH vapor for 1h;

Then H<sub>2</sub>O vapor for 30min.;

Flushing chamber with He for 30min.



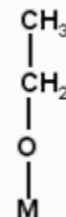
### ● Monodentate and bidentate ethoxide

2968, 2935, 2871cm<sup>-1</sup>: C-H stretching

1155cm<sup>-1</sup>: C-C stretching;

1139cm<sup>-1</sup>: C-O stretching (mono)

1061cm<sup>-1</sup>: C-O stretching (bi)

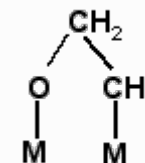


### ● Acetates

CH<sub>3</sub>COO

1562, 1440cm<sup>-1</sup>: COO stretching

1348cm<sup>-1</sup>: CH<sub>3</sub> bending



### ● Molecularly adsorbed ethanol

1380, 1340cm<sup>-1</sup>

### ● Adsorbed CO<sub>2</sub>

2370, 2347cm<sup>-1</sup>

### ● -OH group: 1267cm<sup>-1</sup> bending

➤ The addition of CeO<sub>2</sub> facilitates the conversion of ethanol, leading to the appearance and disappearance of surface reaction intermediate at much lower reaction temperature

# Investigation on alternative methods for Co-based catalyst synthesis

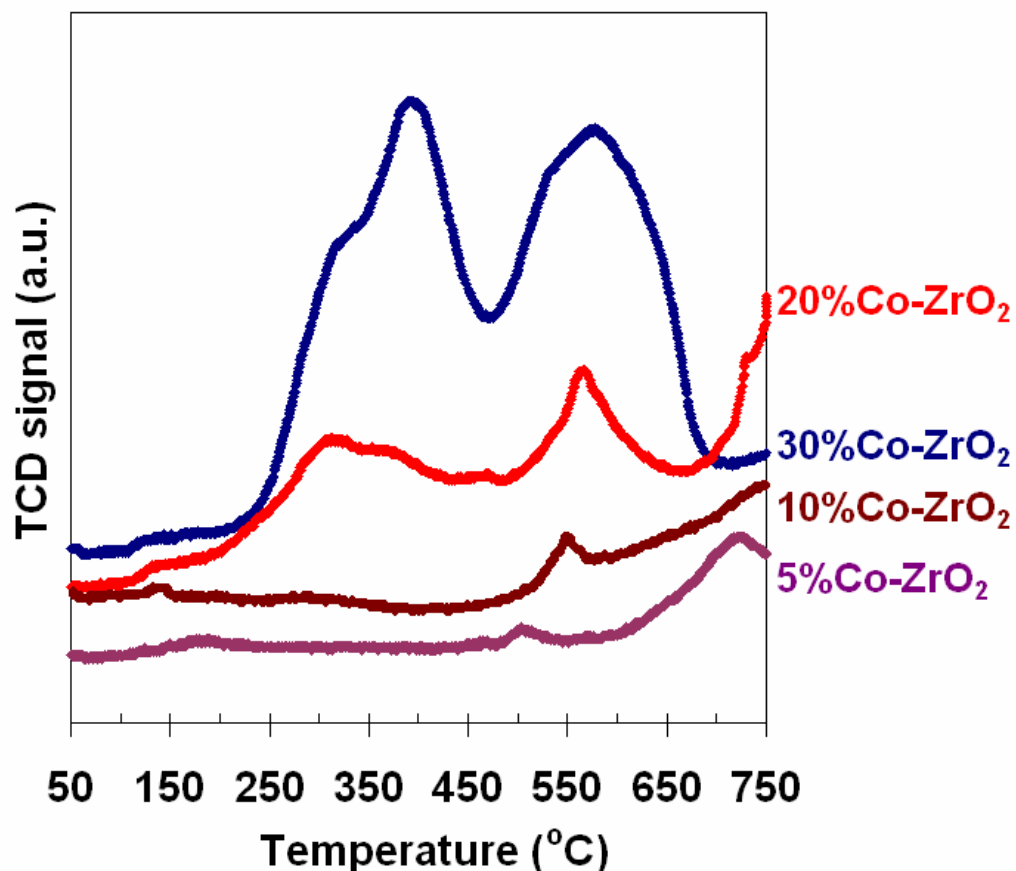
## Motivation of research on sol-gel synthesis of Co-ZrO<sub>2</sub> catalysts

- ❖ For IWI preparation, all active metals are dispersed on the surface, which may cause aggregation of metal particles or sintering at high temperatures--phenomena closely related to catalyst stability and selectivity,
- ❖ Sol-gel technique provides a way to uniformly distribute active metal particles in the sample. Particle size is easy to control by varying synthesis parameters

## So-gel CoZrO<sub>2</sub> catalyst preparation

- ❖ Zirconium propoxide and cobalt nitrate as precursor
- ❖ Mixing of zirconium propoxide and cobalt nitrate aqueous solution at 65°C and stirring for 1hr
- ❖ Oven dry at 110°C overnight
- ❖ Calcination in air before use

# Temperature programmed reduction for Co-ZrO<sub>2</sub> sol-gel catalysts with different Co loadings

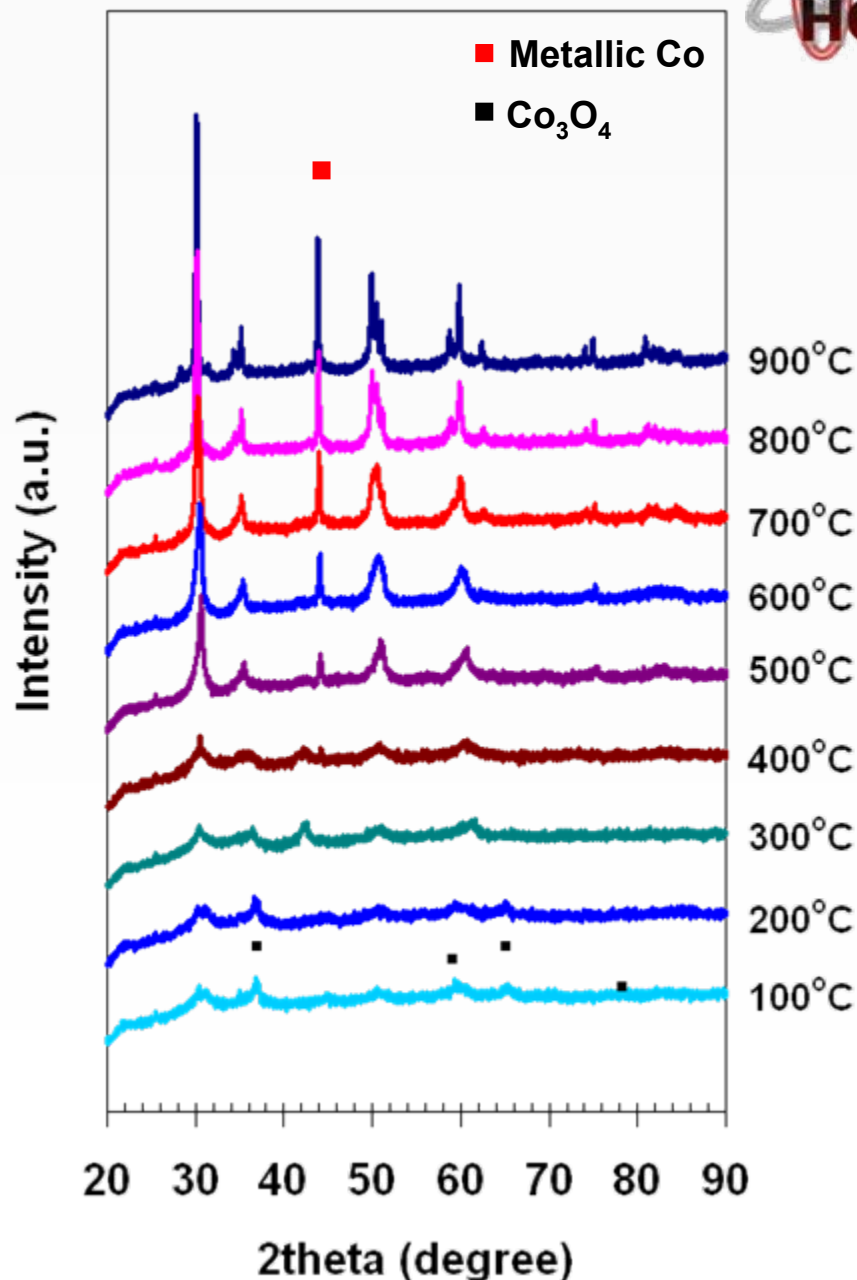


- ❖ With sol-gel preparation, there is better interaction between cobalt and the zirconia support. When Co wt% is less than 10%, there is hardly any reduction features till 500°C.
- ❖ With increasing Co loadings, there is more cobalt on the surface and is easier to reduce

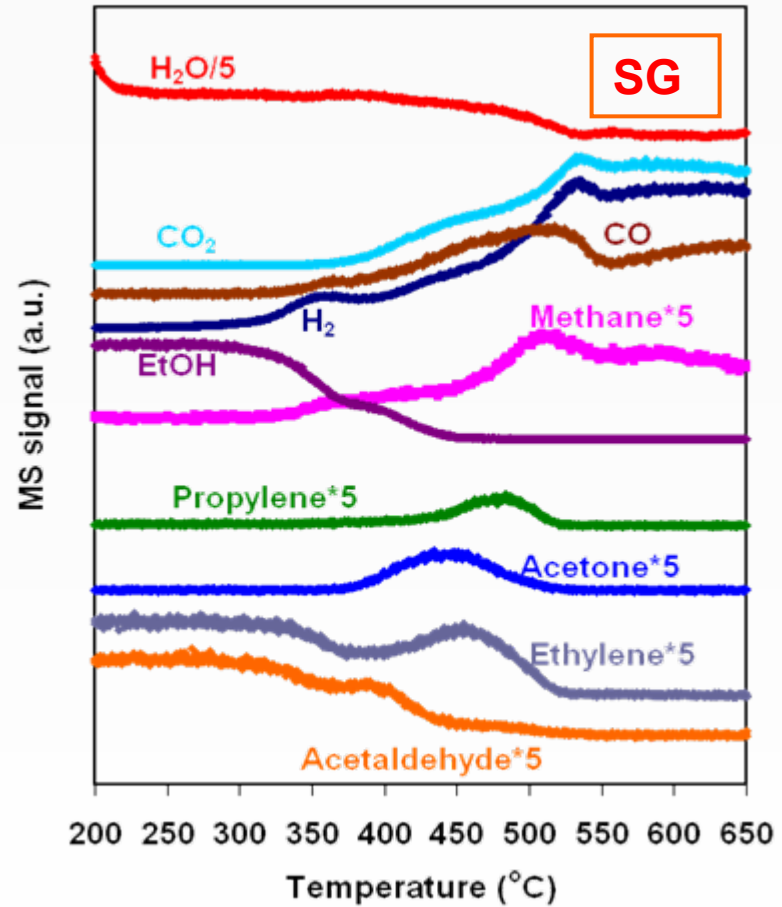
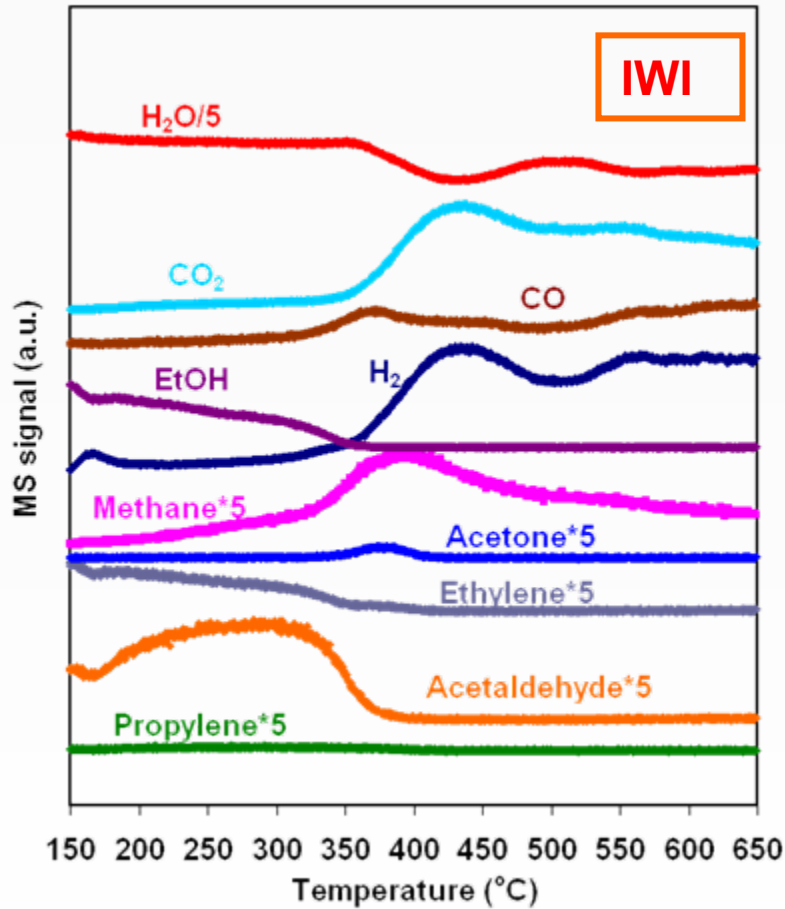
# In-situ XRD during Reduction

Reduction: 5%H<sub>2</sub>/N<sub>2</sub>  
SG-30%CoZrO<sub>2</sub>  
From 100°C to 900°C with 100°C/step

- ❖ Cool to 100C Monoclinic ZrO<sub>2</sub> with Co
- ❖ 900C Tetragonal ZrO<sub>2</sub> with a small amount of Monoclinic ZrO<sub>2</sub> and Metallic Co
- ❖ 800C Tetragonal ZrO<sub>2</sub> with a small amount of Monoclinic ZrO<sub>2</sub> and Metallic Co
- ❖ 700C Tetragonal ZrO<sub>2</sub> with a small amount of Monoclinic ZrO<sub>2</sub> and Metallic Co
- ❖ 600C Cubic ZrO<sub>2</sub> with Co phase
- ❖ 500C Cubic ZrO<sub>2</sub>, CoO and Co coexist
- ❖ 400C CoO and Co coexists together with Cubic ZrO<sub>2</sub>
- ❖ 300C Cubic ZrO<sub>2</sub> with CoO
- ❖ 200 C Co<sub>3</sub>O<sub>4</sub> phase with cubic ZrO<sub>2</sub>
- ❖ 100C Co<sub>3</sub>O<sub>4</sub> phase with cubic ZrO<sub>2</sub>



# 10%CoZrO<sub>2</sub> catalysts prepared by two different methods result in different product distributions



- (1) Pretreat: 400°C He for 30 min
- (2) Reduction: 600°C (350°C for IWI) 5% H<sub>2</sub>/He 2 hrs
- (3) Purge 400°C He for 1 hr
- (4) TPRxn with EtOH:H<sub>2</sub>O=1:10 using Cirrus MS

**It may be possible to affect the product distribution and stability by using new synthesis techniques based on organometallic chemistry.**

# Publications and Presentations

- ❖ Song, H. Zhang, L. Watson, R.B., Braden, D., Ozkan, U.S., “Investigation of Bio-ethanol Steam Reforming over Cobalt-based Catalysts” *Catalysis Today (in press)*;
- ❖ Song, H., Zhang, L., Ozkan, U.S., “Effect of Synthesis Parameters on the Catalytic Activity of Co/ZrO<sub>2</sub> for Bio-ethanol Steam Reforming” *Journal of Green Chemistry (in press)*;
- ❖ 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, Canton, Ohio, May 2006*;
- ❖ Song H., Zhang, L., Ozkan, U.S., “Investigation of bio-ethanol system reforming over cobalt-based catalysts”, *232<sup>nd</sup> ACS National meeting & exposition, San Francisco, CA, September 2006*;
- ❖ 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*;
- ❖ Song, H. Zhang, L., and Ozkan, U.S., “Catalytic Hydrogen Production from Renewable Sources” *OSU-Honda Research Forum, Columbus, Ohio, February 2007*;
- ❖ Song, H., Zhang, L., Ozkan, U.S., “Investigation of Reaction Networks and Active Sites in Steam Reforming of Bio-ethanol over Cobalt based Catalysts” *233<sup>rd</sup> ACS National Meeting, Chicago, IL, March 2007*.

# *Future Work*



- ❖ **Kinetic and mechanistic investigations coupled with *in-situ* characterization**
- ❖ **Performing economic analysis based on updated catalyst system knowledge database**
- ❖ **Performance optimization**
- ❖ **Investigation of catalyst deactivation and regeneration characteristics**
- ❖ **Catalyst scale-up through industrial partnerships**

# Project Summary

- ❖ **Target:** development of a catalytic system that does not rely on precious metals and that can be active and selective in the 350°C-550°C temperature range.
- ❖ **Relevance:** help to develop small-scale distributed hydrogen production technologies from renewable liquid energy sources.
- ❖ **Approach:** develop a systematic optimization strategy for evaluating the catalytic performance of different catalyst systems.
- ❖ **Accomplishments:**
  - Understanding the competing reaction networks
  - Identifying active sites during reaction
  - Optimizing catalyst system based on modification to the IWI sample and SG prepared catalyst
- ❖ **Future Work:** Mechanistic investigations coupled with in-situ characterization; economic analysis; deactivation/regeneration studies.



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