

# Hydrogen Production Via Aqueous Phase Reforming

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# Outline

- ▶ Brief introduction to aqueous phase reforming (APR)
- ▶ Catalyst selection and preparation
- ▶ APR of glycerol using Pt/C and Pt-Re/C catalysts
- ▶ Observed reaction pathways: implications re catalyst surface properties
- ▶ Generation of surface acidity under APR conditions
- ▶ Challenges in extending APR to bio-oil conversion
- ▶ New analytical developments: in situ EXAFS/XANES for APR catalyst characterization



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# Motivation

- ▶ US DOE (Fuel Cell Office) has interest in the production of hydrogen from renewable sources (biomass)
- ▶ Aqueous phase reforming is a “low intensity” method to generate hydrogen, notably from polyols, sugars, and sugar alcohols derived from biomass
- ▶ Glycerol can serve as a “model compound” that has the desired functionality and can be considered a renewable resource
- ▶ The catalytic chemistry of aqueous phase reforming is not well understood, offering the opportunity for significant advances in understanding of catalysts and catalytic reactions in aqueous systems



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Overview of biomass conversion by aqueous phase reforming

Glycerol APR: characterization and testing of Pt/C and Pt-Re/C

Pt-Re interaction during APR : generation of acidity

APR of bio-oil

New analytical developments

Summary and conclusions

# Background

- ▶ Conversions of biomass compounds in aqueous phase, under sub-critical and super-critical conditions, have been studied for several years (catalytic and non-catalytic)
- ▶ Pioneering work in aqueous phase catalytic reforming with specific aim of hydrogen production was carried out by Dumesic and co-workers\*
- ▶ Virent Energy Systems developed the technology further to commercial unit production
- ▶ Although work continues in APR for hydrogen production, many groups have shifted focus to production of liquid fuels, which has a shorter term (more immediate and economic) horizon
- ▶ Understanding and improving performance of catalysts and conditions for APR remains a key focus for ongoing work in this area

\* Cortright, Davda, and Dumesic, Nature 418, 29 Aug 2002



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# Advantages and Limitations of APR

- ▶ Operation at low temperatures (225-275°C), compared with conventional reforming, reduces energy costs of water vaporization and favors the forward water gas shift reaction, facilitating hydrogen production in a single reactor
- ▶ Operation at elevated pressures (up to 30 atm) favors H<sub>2</sub> purification/separation by membrane or PSA
- ▶ Allows processing of biomass feedstocks that are difficult to vaporize without decomposition
- ▶ Compatible with wet feedstock utilization



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# Biomass Structures



## Agriculture

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



## Forest residue



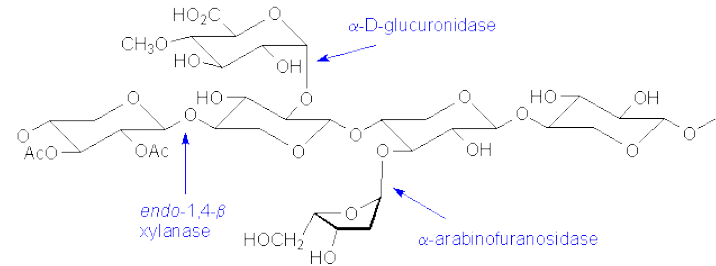
## MSW



## Animal waste

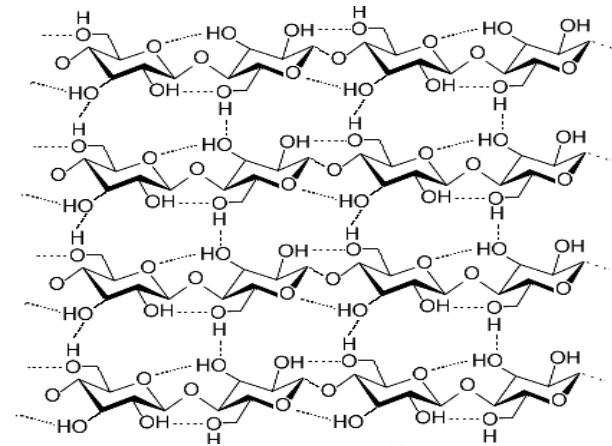
Hemi-cellulose

23-32%



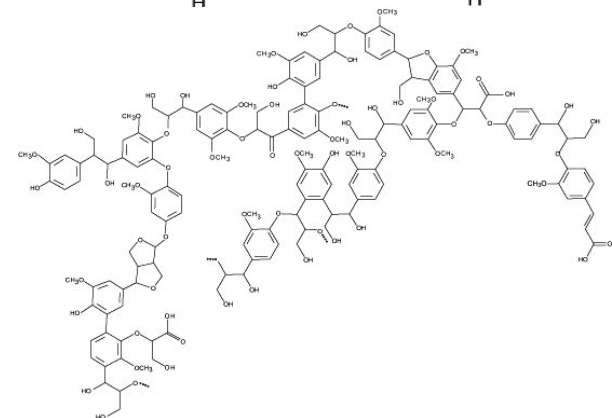
Cellulose

38-50%



Lignin

15-25%



# Biomass Conversion Routes to Hydrogen



## Agriculture

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



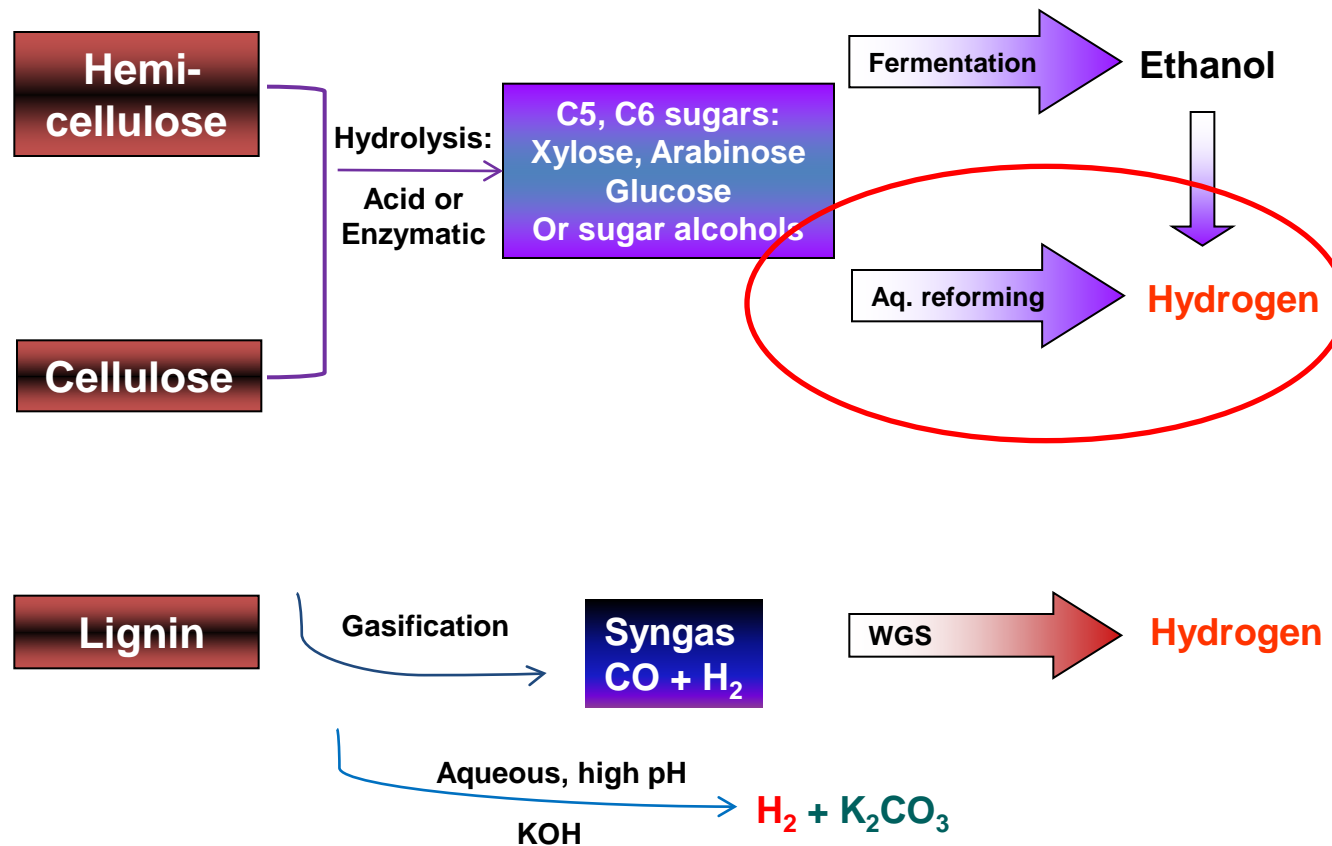
## Forest residue



## MSW



## Animal waste

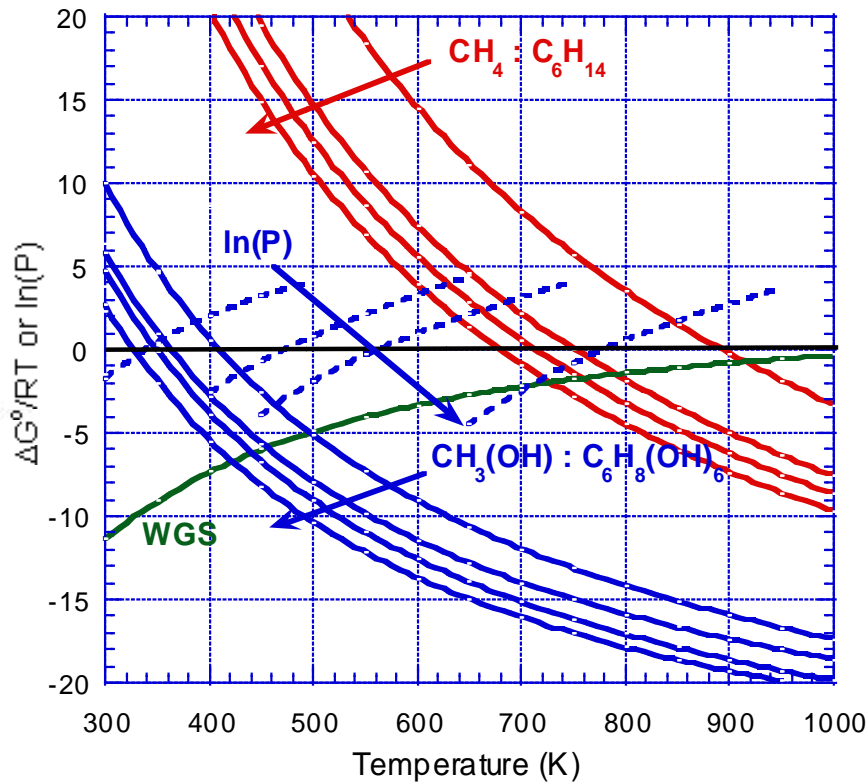


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# Reforming Thermodynamics



## Reforming of Hydrocarbons



## Reforming of Oxygenated Compounds



## Water-Gas Shift



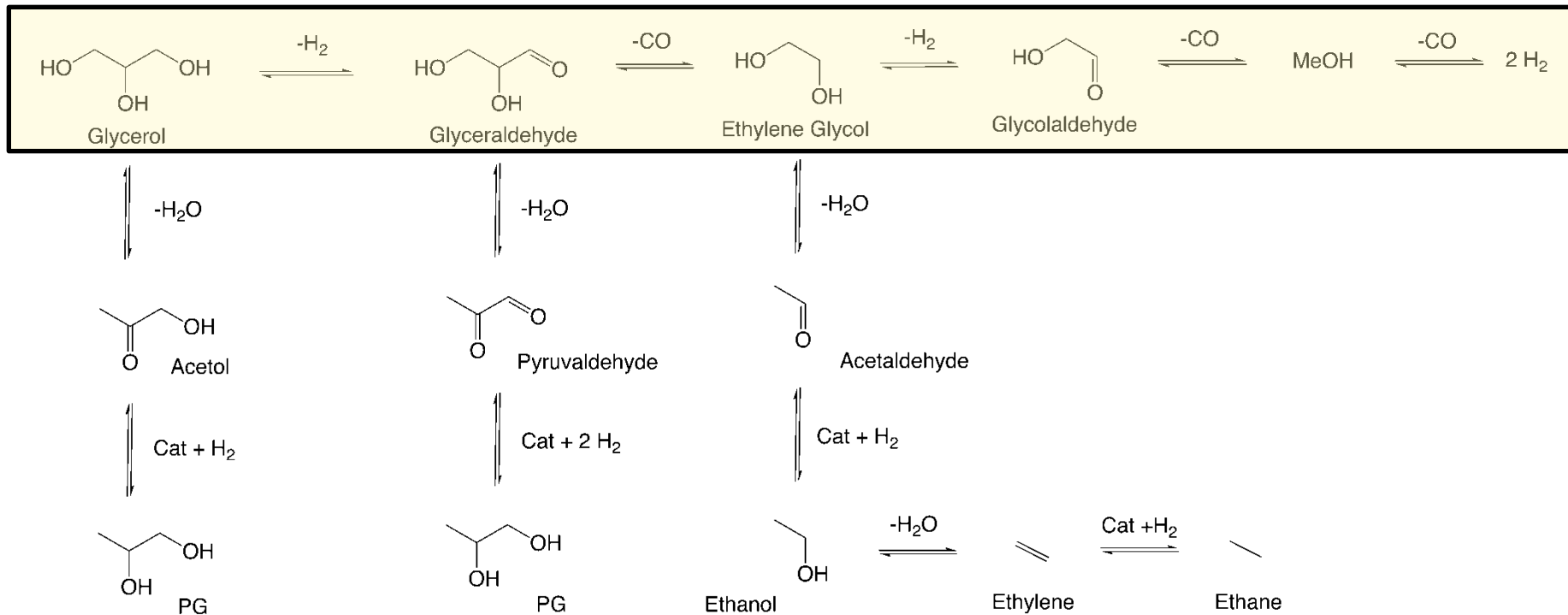
**Equilibrium is favorable for reforming of oxygenated compounds (especially polyols) and for WGS reaction at moderate temperatures**

Ref: R.R. Davda, J.W. Shabaker, G.W. Huber, R.D. Cortright, J.A. Dumesic; Applied Catalysis B: Environmental 56 (2005) 171–186



# Plausible Reaction Pathways for APR of Glycerol and Other Polyols

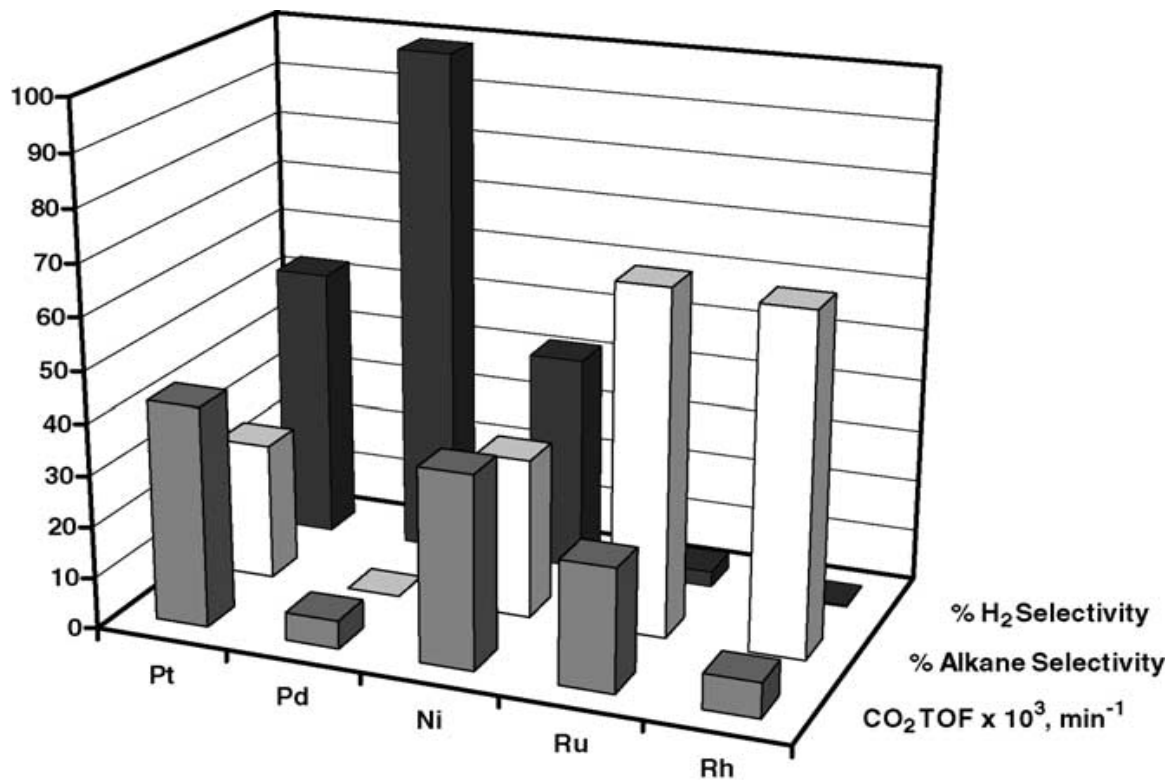
Desired pathway for hydrogen production →



APR chemistry is best realized with poly-hydroxy species such as sugars, sugar alcohols, polyols

# Catalyst Metal Selection: Pt is the Preferred Metal

aqueous phase reforming of ethylene glycol

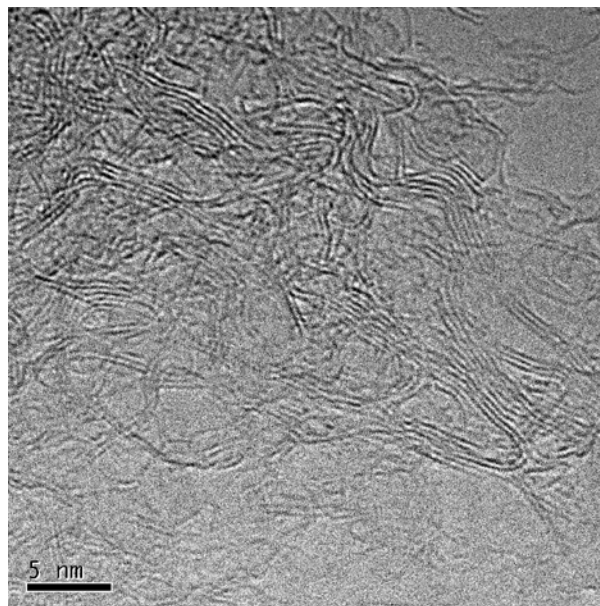


R. R. Davda, et al., Appl. Catal. B., 56 (2005), 171-186

Pt has good C-C cleavage capability, Ni makes too much methane

# Catalyst Support Selection

- ▶ APR reaction occurs in liquid water/steam environment
- ▶ Conventional metal oxide supports such as silica and alumina have low hydrothermal stability
- ▶ Hydrothermally stable supports include  $\text{ZrO}_2$ , carbon
- ▶ Carbon was selected due to its ability to facilitate high metal dispersion



TEM of activated carbon

Overview of biomass conversion by aqueous phase reforming

Glycerol APR: characterization and testing of Pt/C and Pt-Re/C

Pt-Re interaction during APR : generation of acidity

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Summary and conclusions

# Objectives

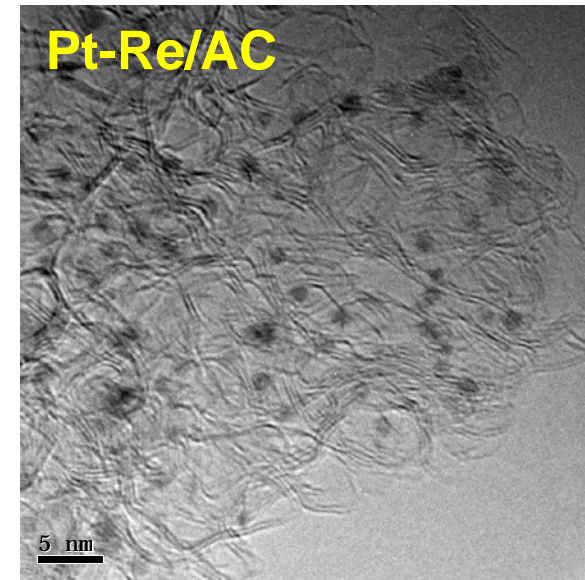
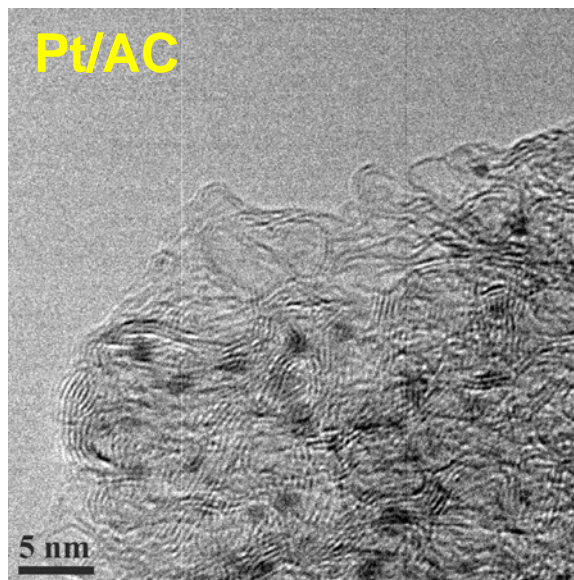
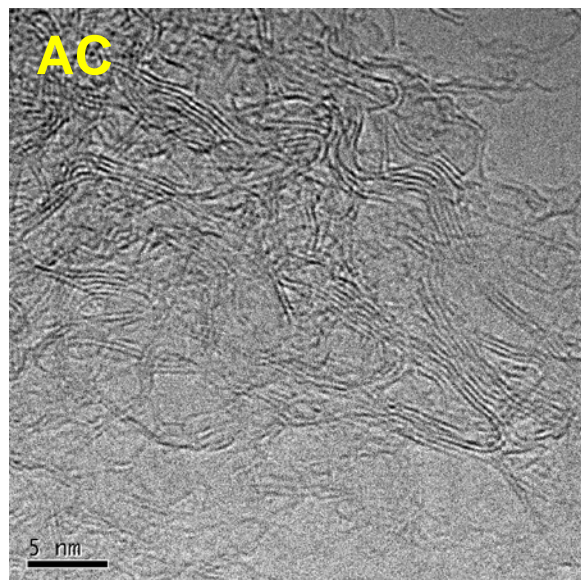
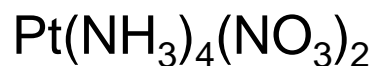
- ▶ Early work in aqueous phase reforming pointed to Pt/C as the best catalyst for hydrogen production from polyols, but overall productivity is low
- ▶ A number of promoters and bimetallics have been examined to increase the activity of Pt for APR
- ▶ Re has been found to be an effective activity promoter for Pt/C
  - Pt-Re forms an alloy over a broad range of compositions
  - The selectivity of Pt-Re/C was found to be different from Pt/C
  - Hydrogen selectivity was lower although hydrogen productivity was higher
- ▶ A broad range of oxygenated products are observed with Pt-Re/C that are not observed with Pt/C
  - Performance is consistent with generation of acid-catalyzed reaction pathways
- ▶ We present some comparative studies of Pt/C and Pt-Re/C, including an examination of the nature of the acidity generated by the addition of Re and its effect on catalyst performance



# Catalyst Preparation: Sequential Incipient Wetness Impregnation

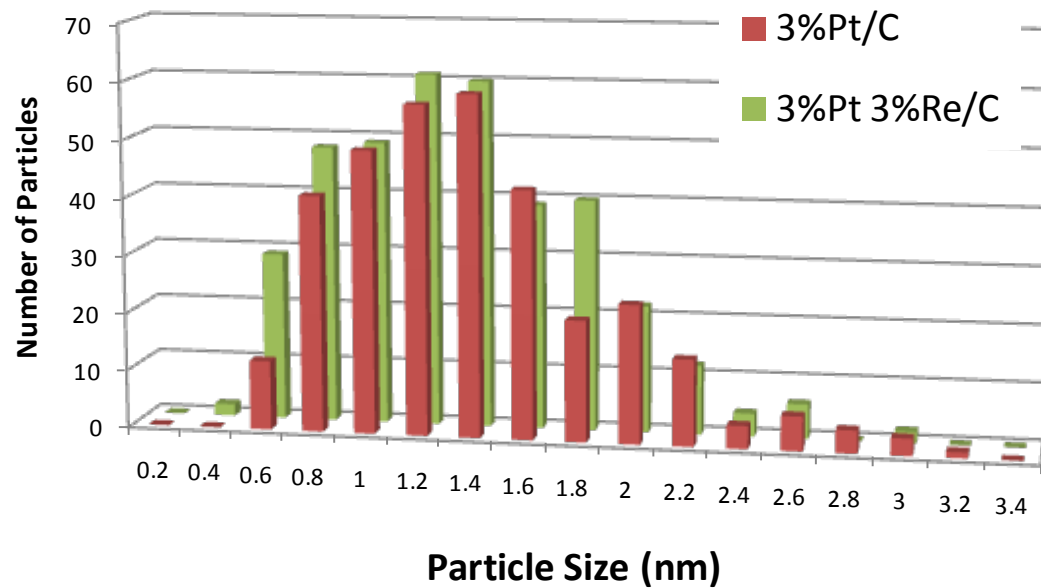
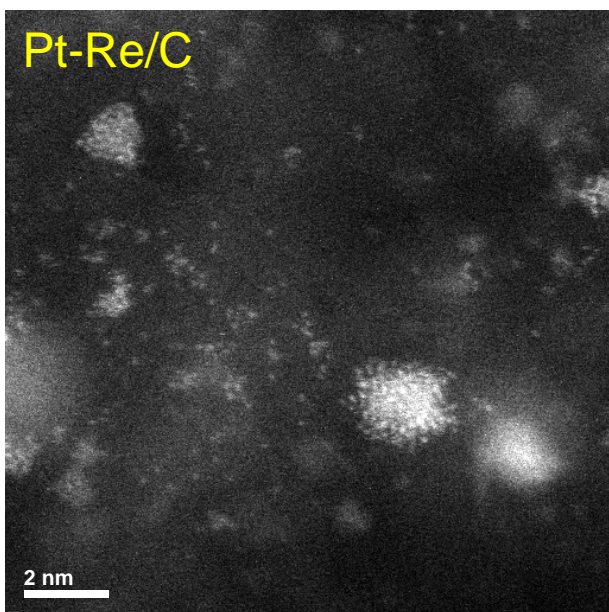
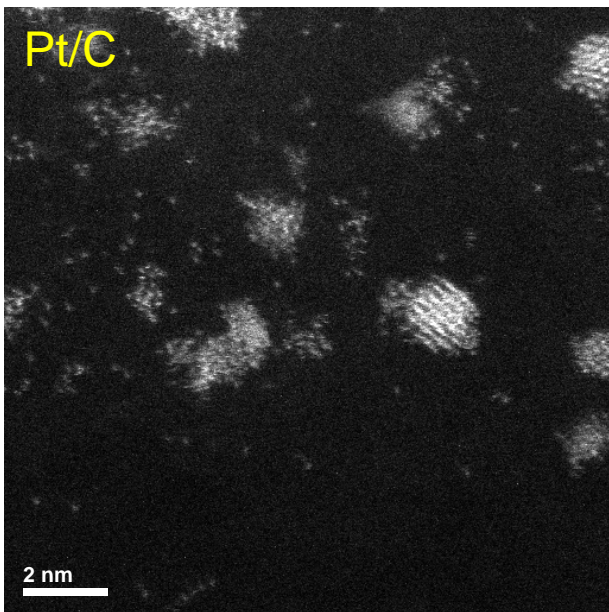
BET 570 m<sup>2</sup>/g

P.V. 0.42 cc/g



Co-impregnation not feasible with these metal precursors  
Recent work with co-impregnation ( $\text{H}_2\text{PtCl}_6$ ) shows poorer dispersion

# Morphology of Pt-Re Nanoparticles on Carbon Following Calcination and Reduction



- Pt and Pt-Re are highly dispersed on carbon
- The size distributions of Pt and Pt-Re are similar



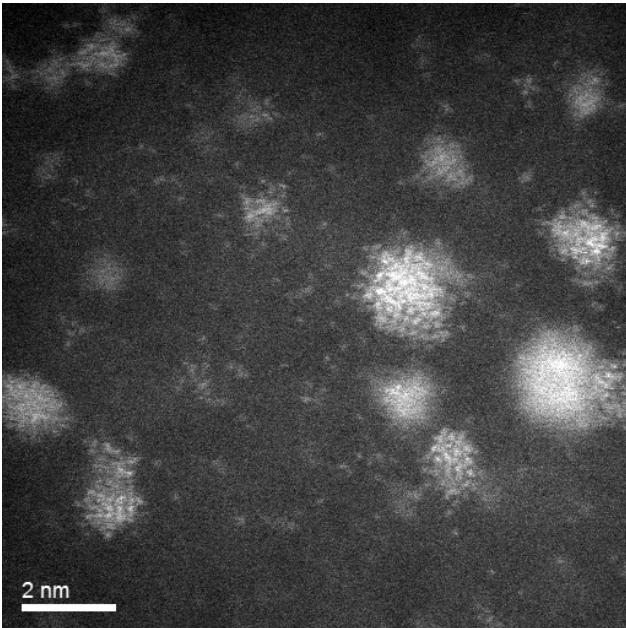
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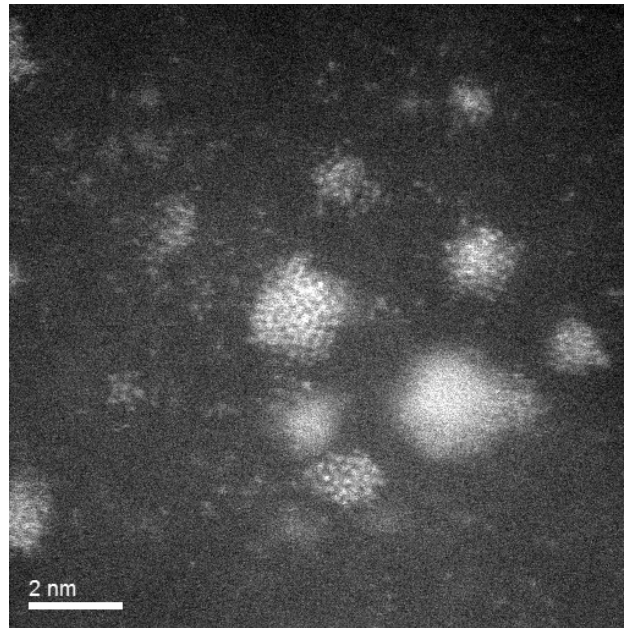


# Morphological Change of Pt-Re on Carbon

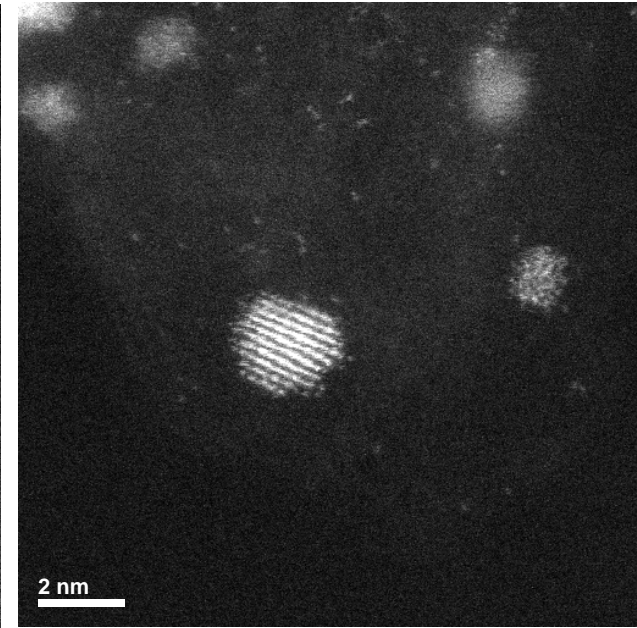
Calcined Pt-Re



Reduced Pt-Re

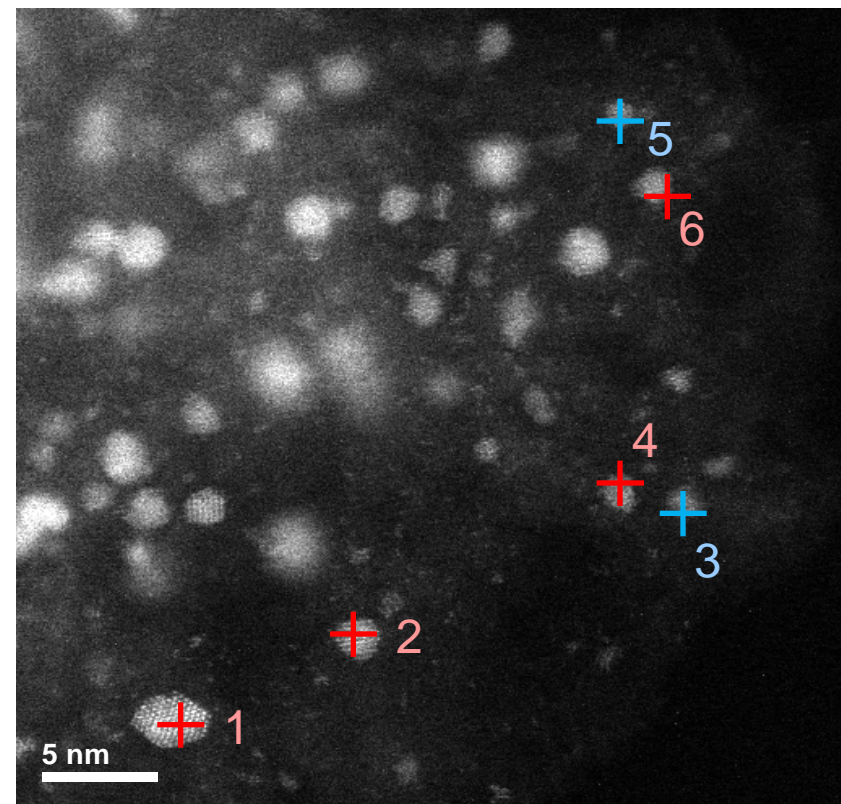
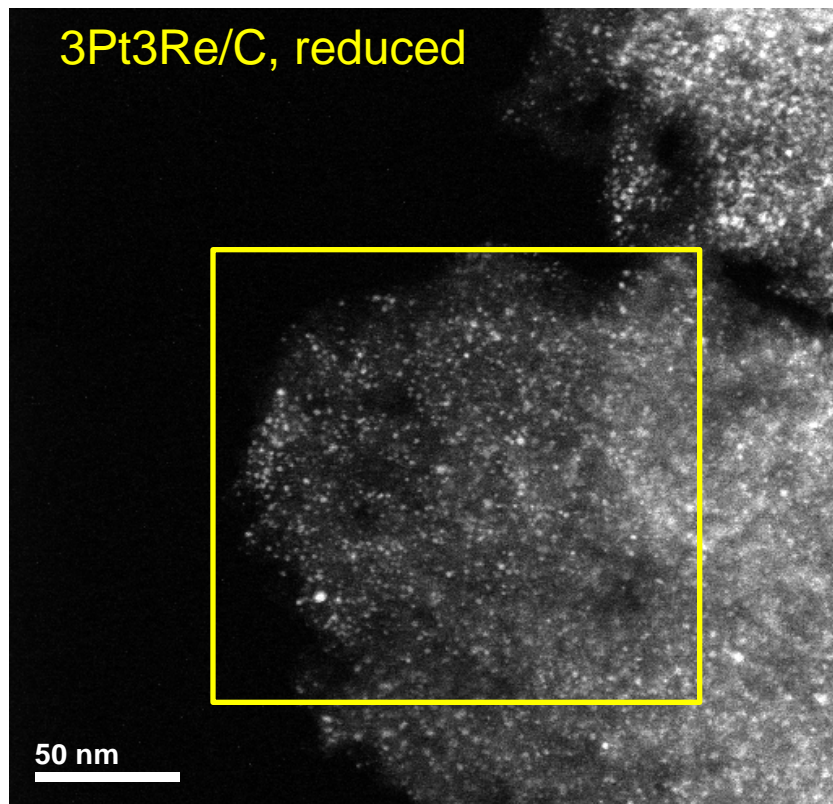


Spent Pt-Re



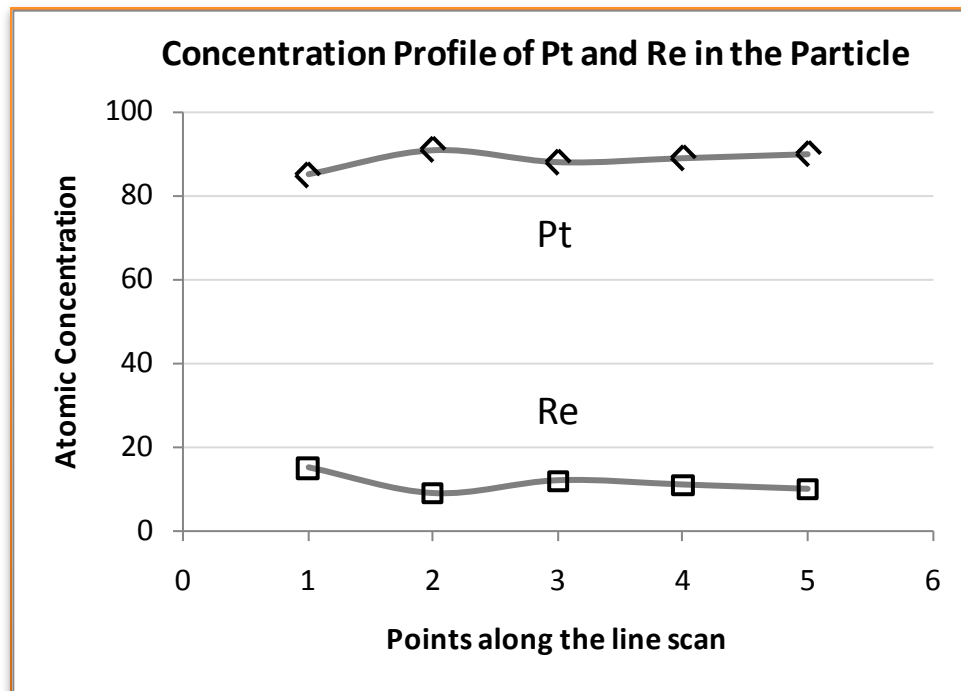
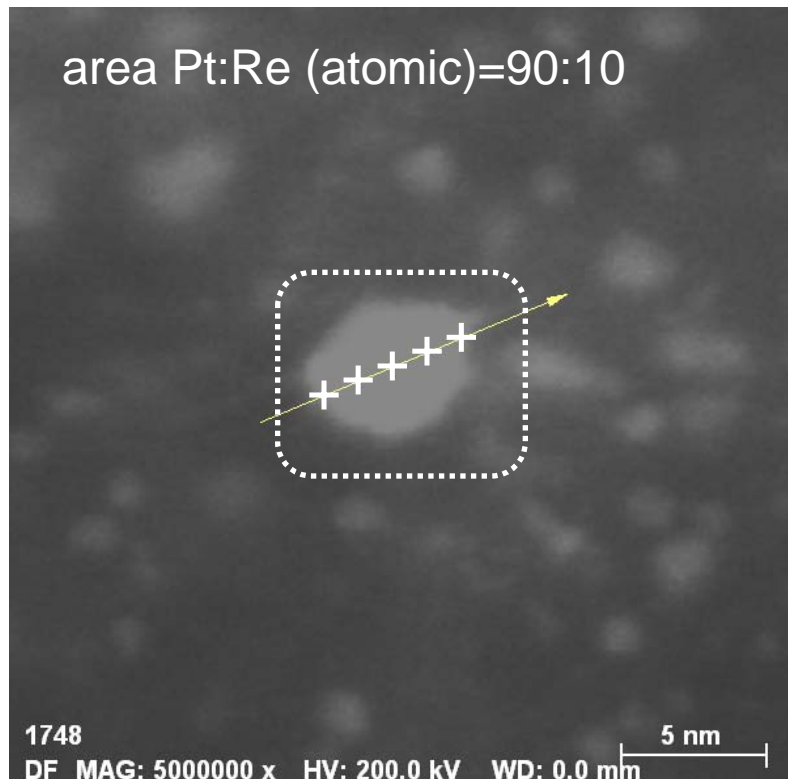
- ▶ *In-situ* TEM shows reduction does not change the size distribution of Pt-Re
- ▶ Processing under the APR eliminates single atoms or small clusters

# EDS Shows Pt-Rich and Re-Rich Particles



Atomic Ratio	Area	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
Pt	54.5	88.4	76	15	74	13	84
Re	45.5	11.6	24	85	25	87	16

# Line Scan on a Large Catalyst Particle



- ▶ Pt and Re concentration profile in the particle is almost constant
- ▶ Compositional uniformity suggests formation of Pt-Re alloy

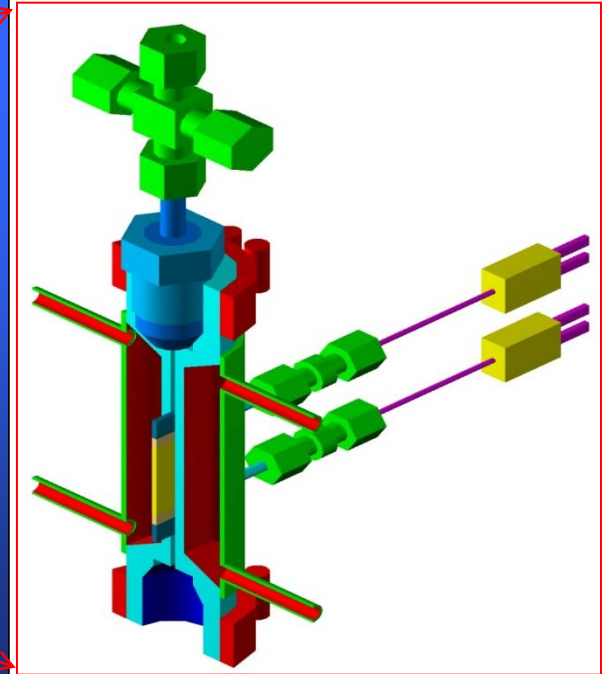
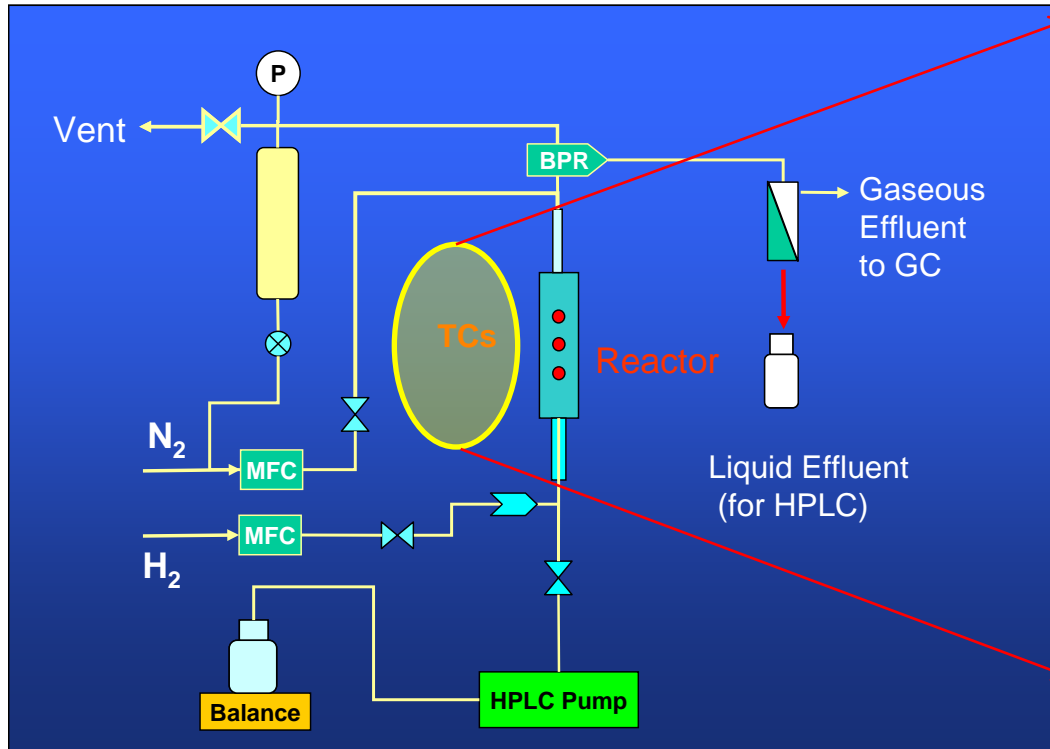
# Addition of Re to Pt/C Decreases the Number of Available Sites as Determined by CO or H<sub>2</sub> Adsorption

Catalyst	Pt (wt.%)*	Re (wt.%)*	CO uptake (μmol/g)	H uptake (μmol/g)	H/CO	Metal Dispersion (%)**
3%Pt/C	3	0	116.2	147.4	1.27	75.6
3%Pt1%Re/C	3	1	69.5			45.2
3%Pt3%Re/C	3	3	67.1	116.5	1.74	43.6
3%Re/C	0	3	0.9	0.8		N/A

\* wt.% -- g metal/100g carbon    \*\* based on CO chemisorption

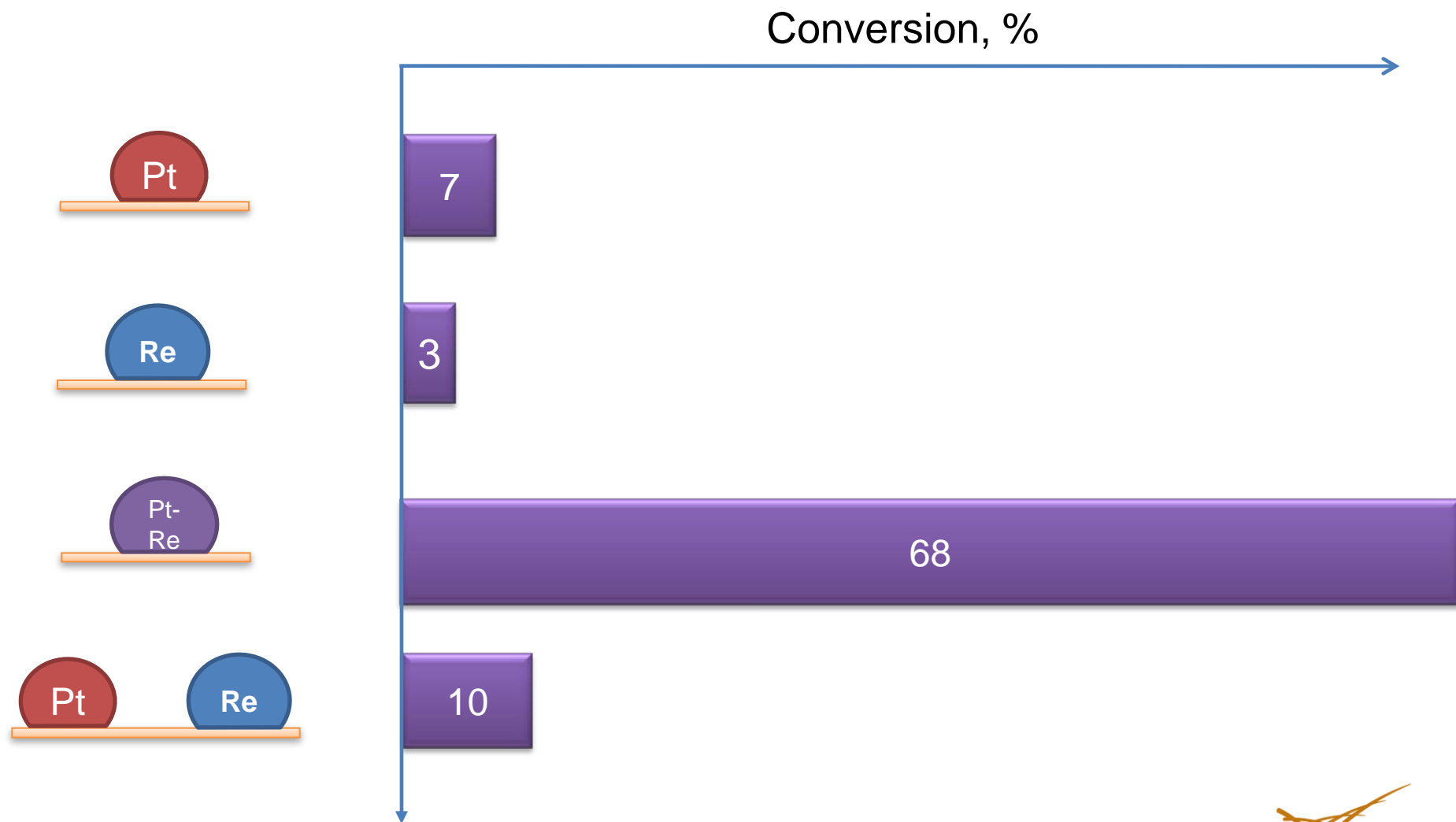
Perhaps we are not measuring all the active sites by this method

# APR Reaction Test System



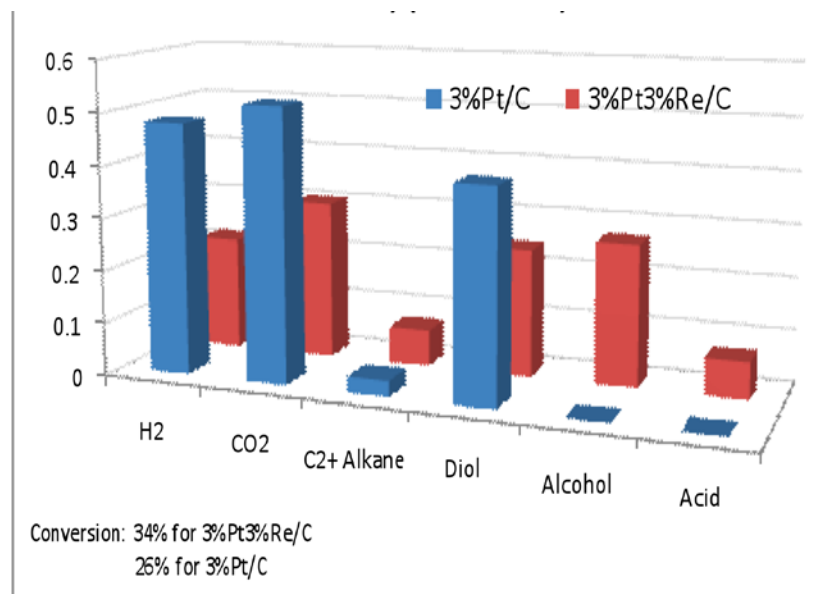
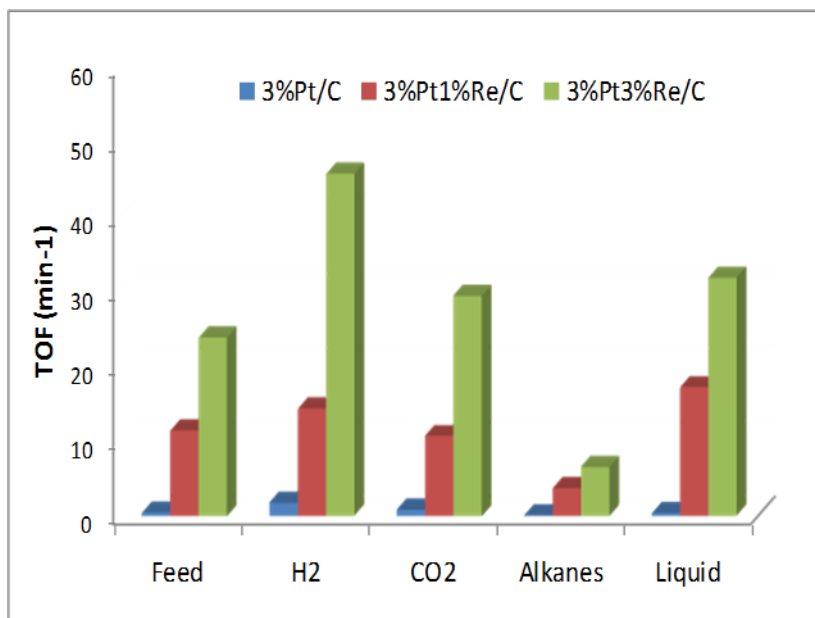
- ▶ Isothermal microchannel reactor with oil heating jacket
- ▶ Aqueous bio-liquid is fed into system by HPLC pump
- ▶ Catalyst is reduced in-situ at 280°C before use.
- ▶ Typical operation: 225°C, 420 psig, 200 mg catalyst

# Comparative Catalyst Activity Test With Glycerol



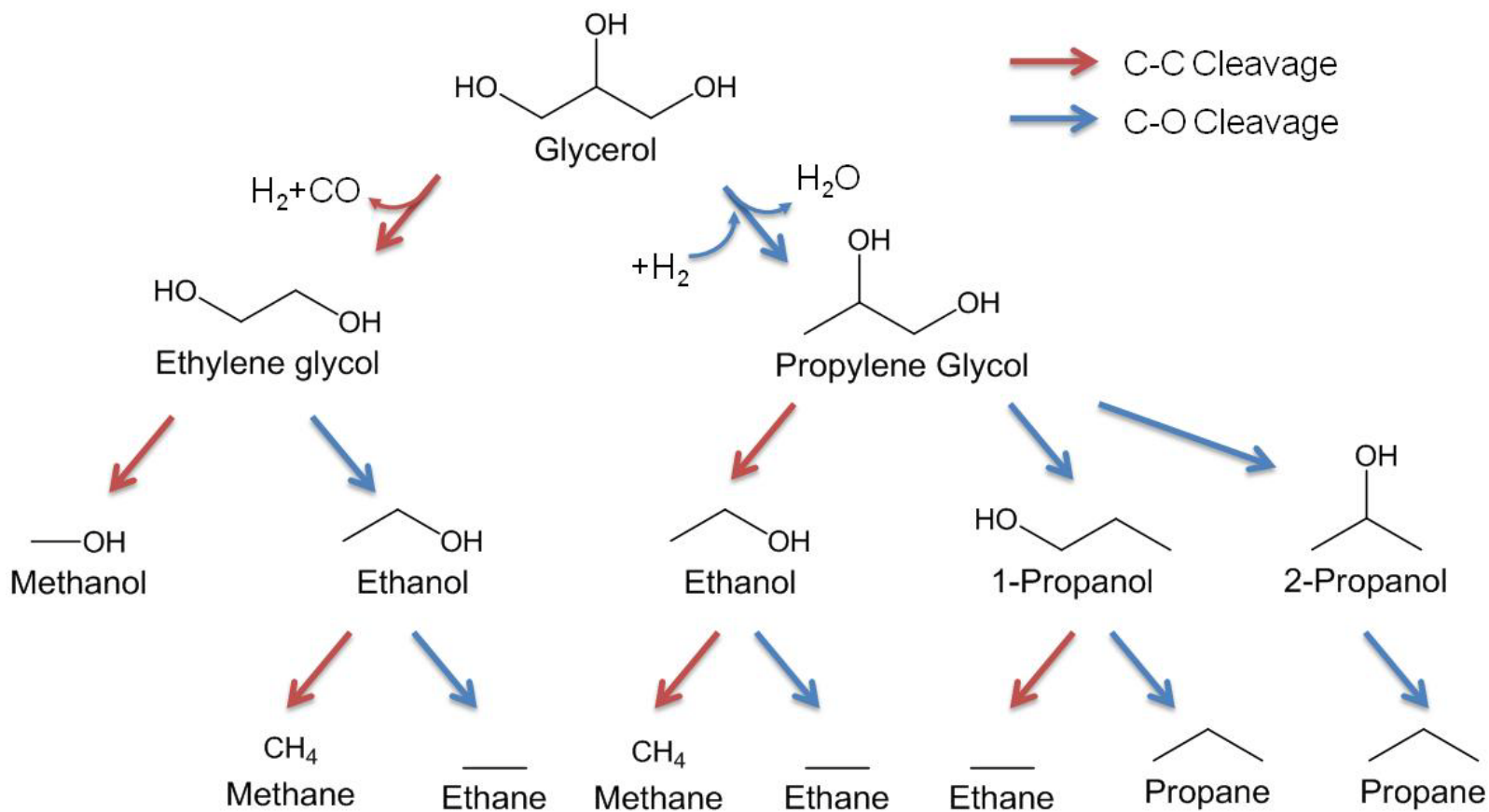
- T = 225 °C, P = 420 psig, feed rate = 0.06 moles glycerol/gcat-h

# Addition of Re Results in Higher TOFs For All Product Categories, With Significant Changes in Selectivity



- T = 226 °C, P = 420 psig, feed rate = 0.06 moles glycerol/gcat-h
- TOF is calculated based on CO chemisorption
- Carbon-based selectivity defined as total moles C in product relative to total moles C available from converted glycerol

# Following the Preferred Reaction Pathways is Key to Hydrogen Production



- ▶ C-C scission leads to production of  $\text{H}_2$  and  $\text{CO}_2$  (preferred)
- ▶ C-O cleavage leads to production of diols, alcohols, and alkanes and consumes  $\text{H}_2$
- ▶ A competition ratio can be defined as  $[\text{sum (C-O events)}/\text{sum (C-C events)}]$

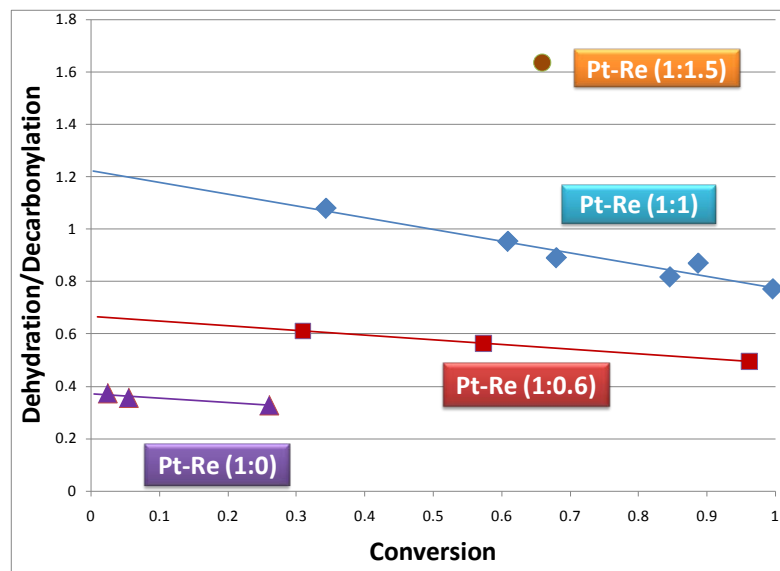
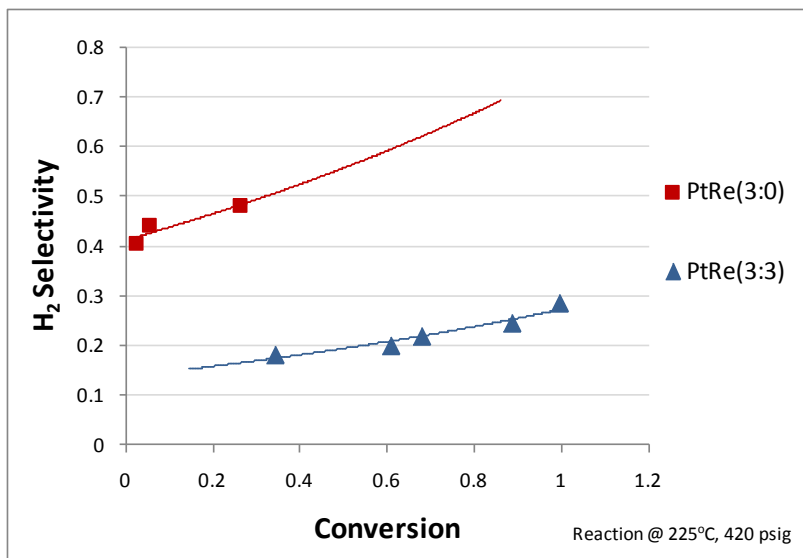


# Interaction Between Pt and Re: Reduction Produces a Strong Interaction

	3%Pt/C Unreduced	3%Pt/C Reduced	3%Pt3%Re/C Unreduced	3%Pt3%Re/C Reduced	Physical Mix Reduced	3%Re/C Reduced
Conversion	8.2%	7.4%	6.7%	68.2%	10.1%	2.6%
C-O/C-C	0.6	0.6	0.5	1.1	1.0	33.8
H <sub>2</sub> /CO <sub>2</sub>	2.3	2.3	2.3	2.0	1.8	
Glycerol APR @ 225 °C, 420 psig, WHSV = 6 hr <sup>-1</sup>						

- Low activity for both monometallic Pt/C and Re/C
- Both C-O and C-C breaking with Pt/C, mainly C-O breaking (dehydration) with Re/C
- Strong interaction between Pt and Re following reduction of the metal oxides results in dramatic change in activity and selectivity

# H<sub>2</sub> and Decarbonylation (C-C Cleavage) Selectivity Decrease With Increasing Re Content



- ▶ H<sub>2</sub> selectivity is defined as measured H<sub>2</sub> yield divided by theoretical H<sub>2</sub> yield from converted glycerol
- ▶ H<sub>2</sub> and decarbonylation selectivity increase with increasing conversion (decreasing space velocity)

Overview of biomass conversion by aqueous phase reforming

Glycerol APR: characterization and testing of Pt/C and Pt-Re/C

Pt-Re interaction during APR : generation of acidity

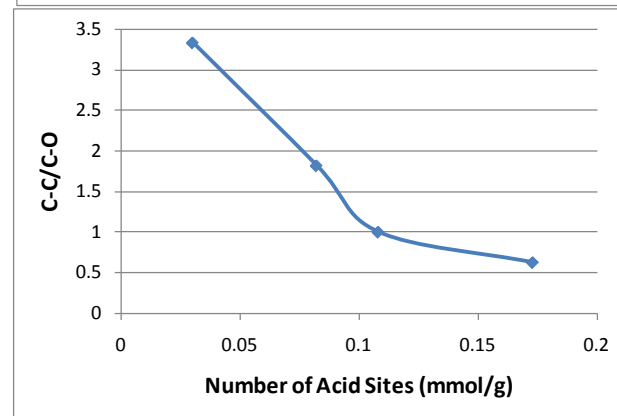
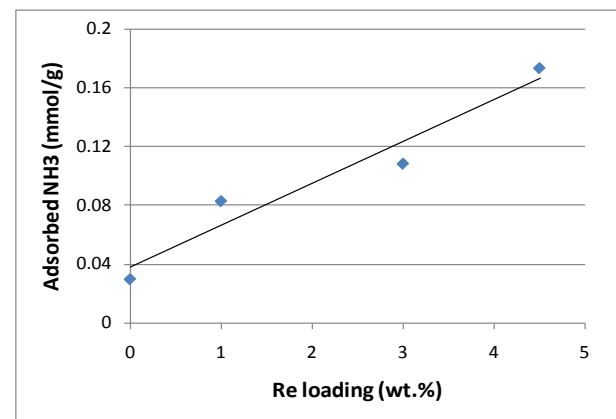
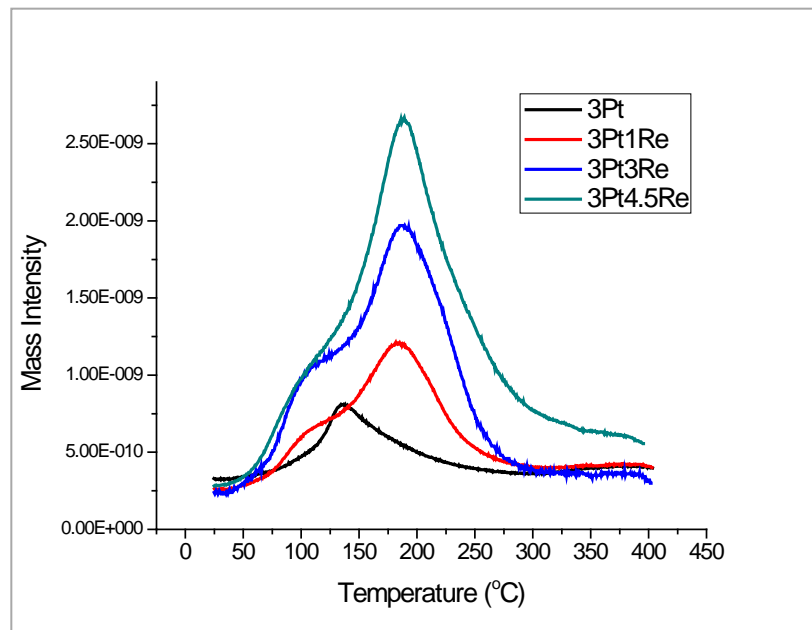
APR of bio-oil

New analytical developments

Summary and conclusions

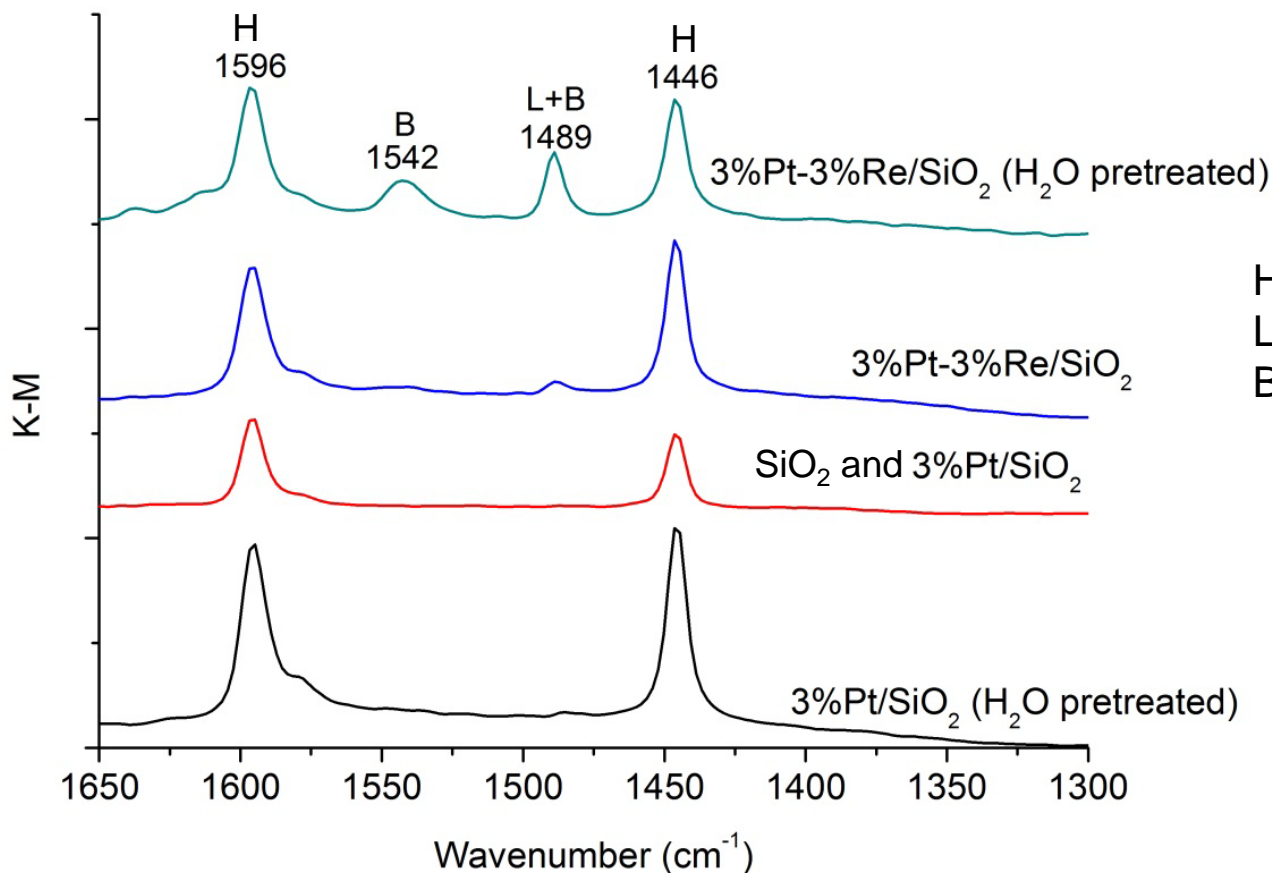
# Acidity of Pt-Re Following Steam Treatment

## Surface Chemistry Probed by NH<sub>3</sub> TPD



- Titration with base shows steam-treated Pt-Re is acidic
- Acidity increases with amount of Re in Pt-Re/C
- The acid strength is similar for different Pt/Re ratios
- Pt/C also displays some acidity, lower in strength than Pt-Re/C

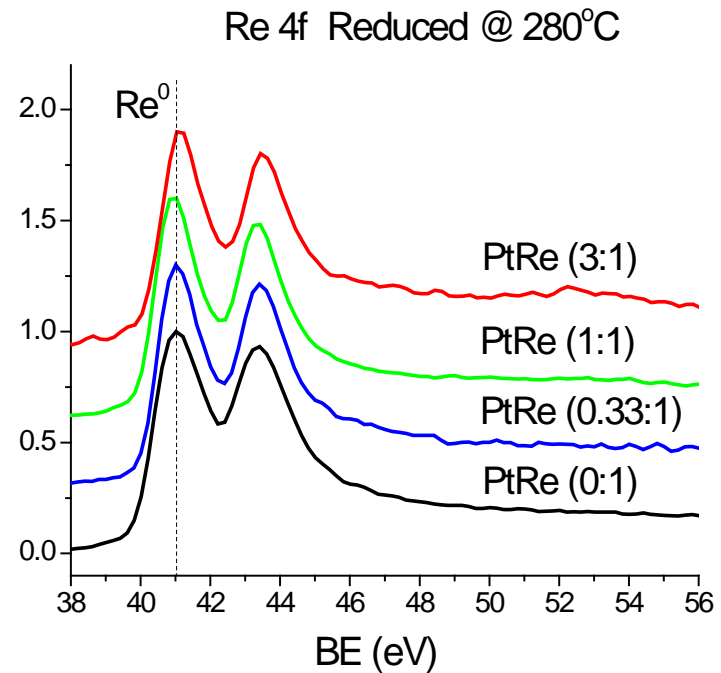
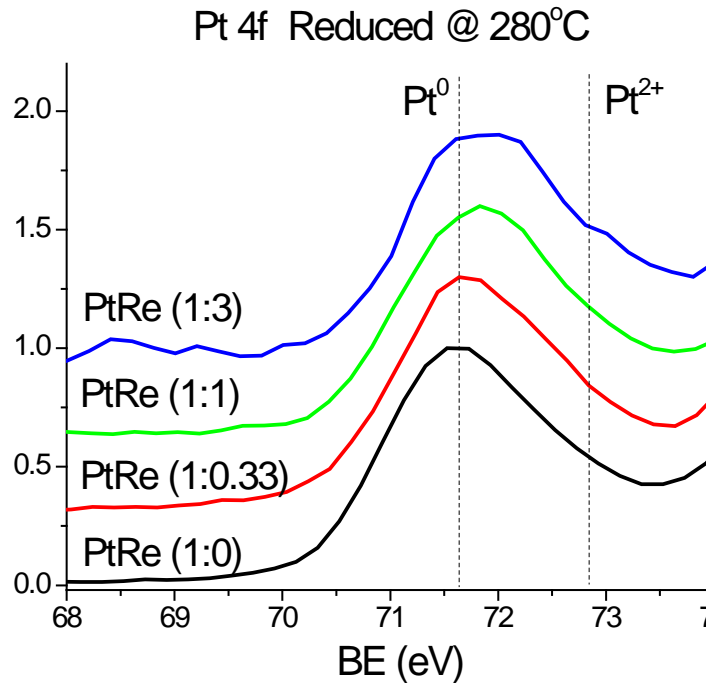
# Pyridine Adsorption on Pt-Re/C Confirms Presence of Brönsted Sites Following Steam Treatment



H = hydrogen bonded  
L = Lewis acid site  
B = Brönsted acid site

- Brönsted acidic sites appear only on the 3%Pt-3%Re/SiO<sub>2</sub> catalyst

# Pt-Re Interaction during Reduction – XPS Results



Pt and Re are fully reduced at 280°C

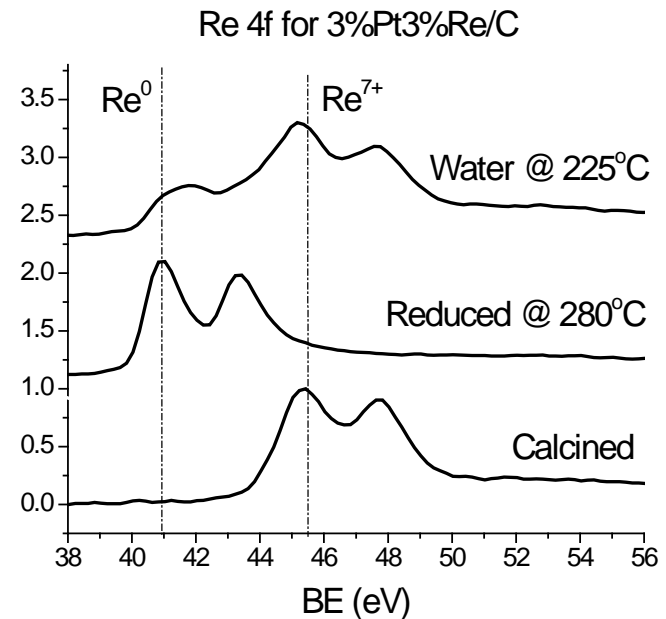
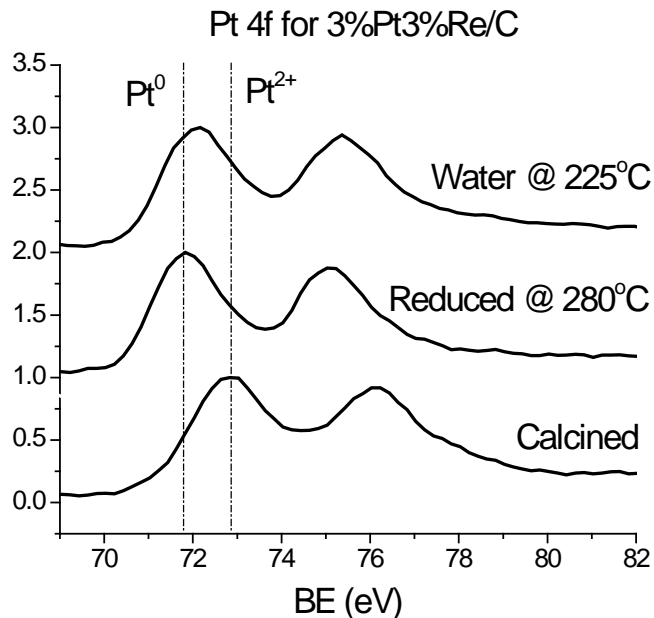


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# Pt-Re Interaction under Hydrothermal Conditions: Re Does Not Remain Reduced

Pt-Re exposed to water vapor at 225°C



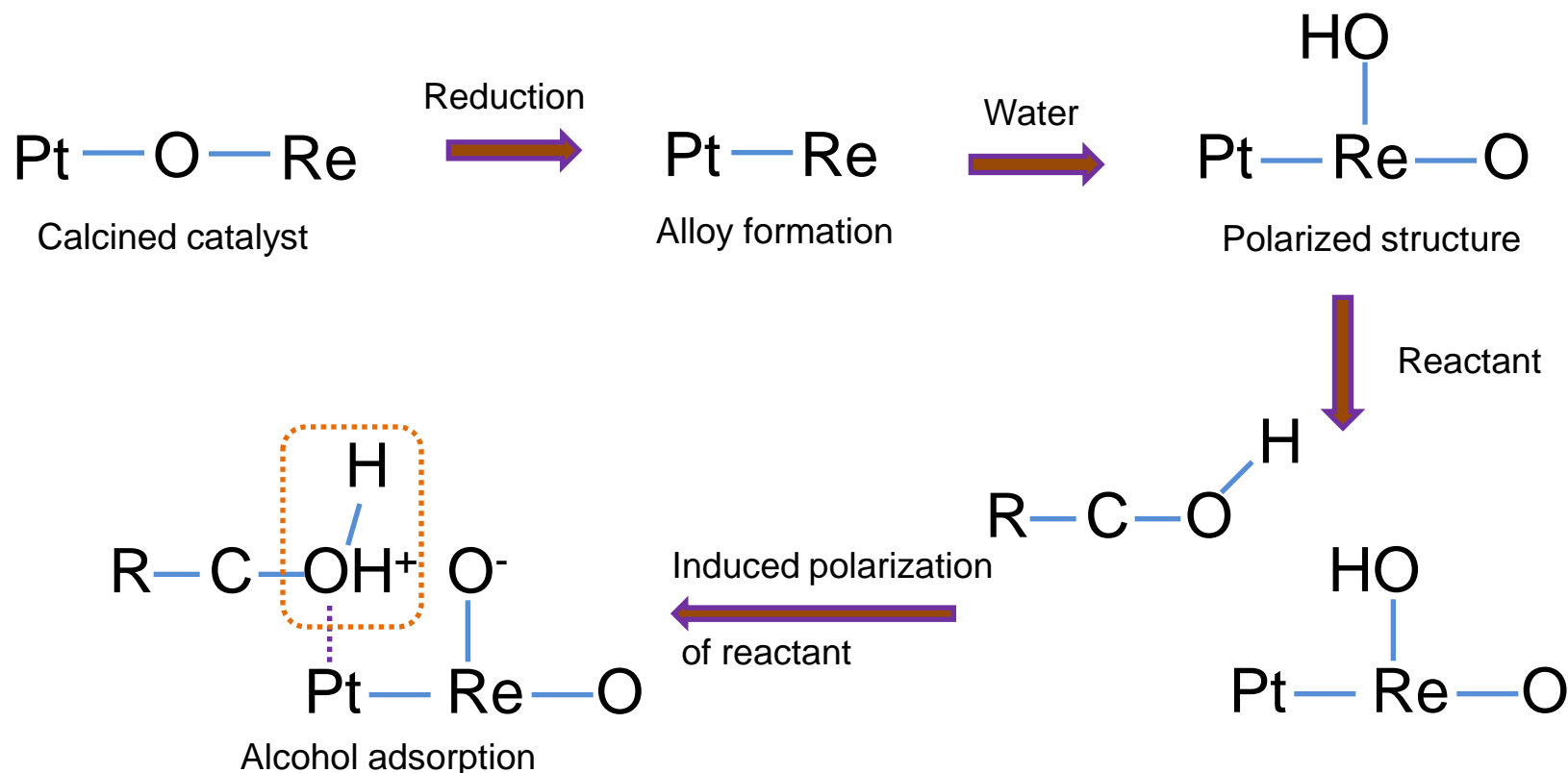
- ▶ Re is oxidized to higher oxidation states upon exposure to water
- ▶ Suggests loss of alloy structure under hydrothermal conditions



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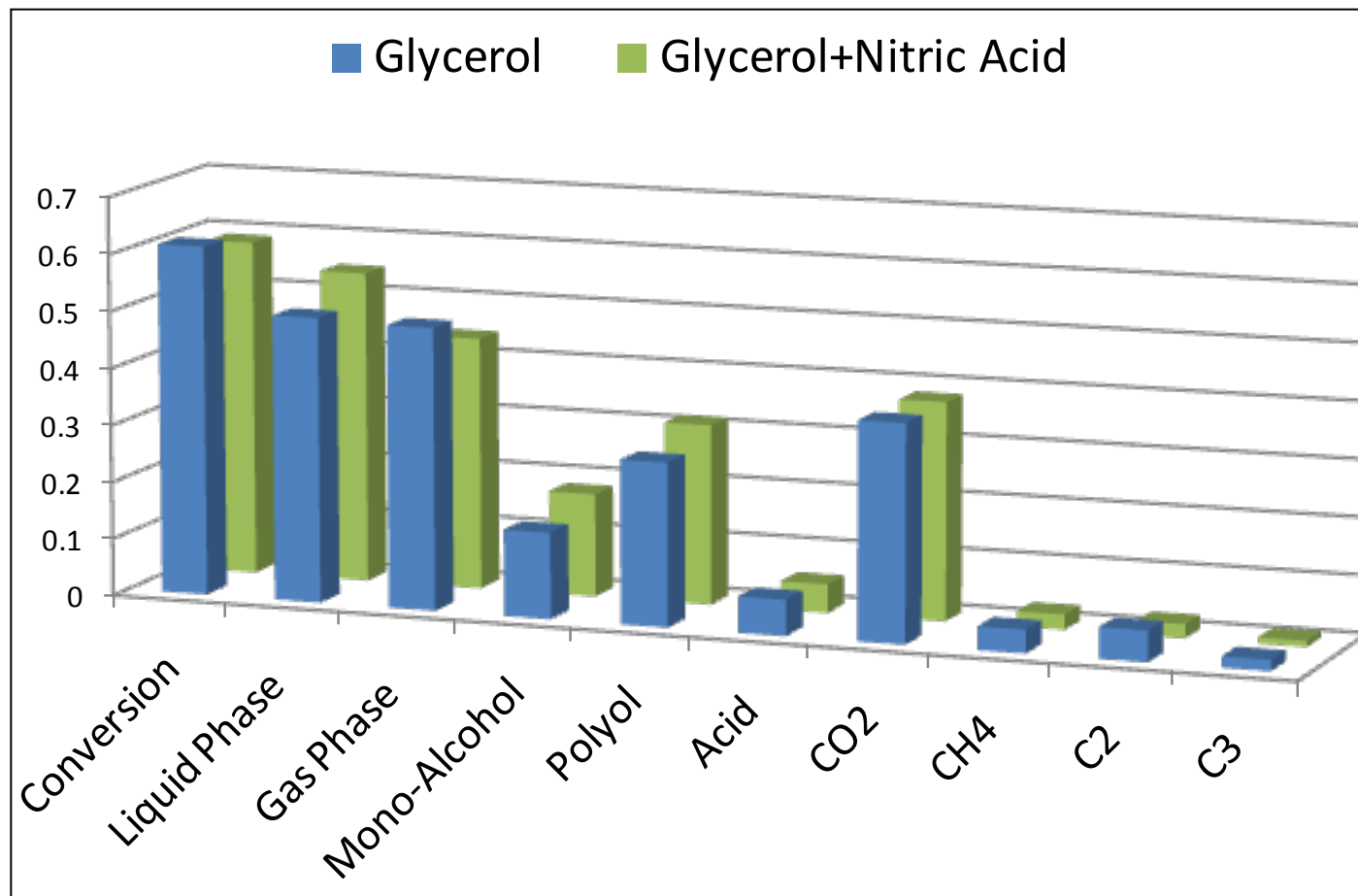
# Acidity of Pt-ReO<sub>x</sub>/C Will Affect Adsorption and Reaction Pathways at Pt-Re Interface



- ▶ Bonding to surface through reactant oxygen function could facilitate dehydration pathways
- ▶ This model does not explain simultaneous increase in C-C bond cleavage (at Pt-Pt sites?)
- ▶ Computational work needed for better understanding surface interactions

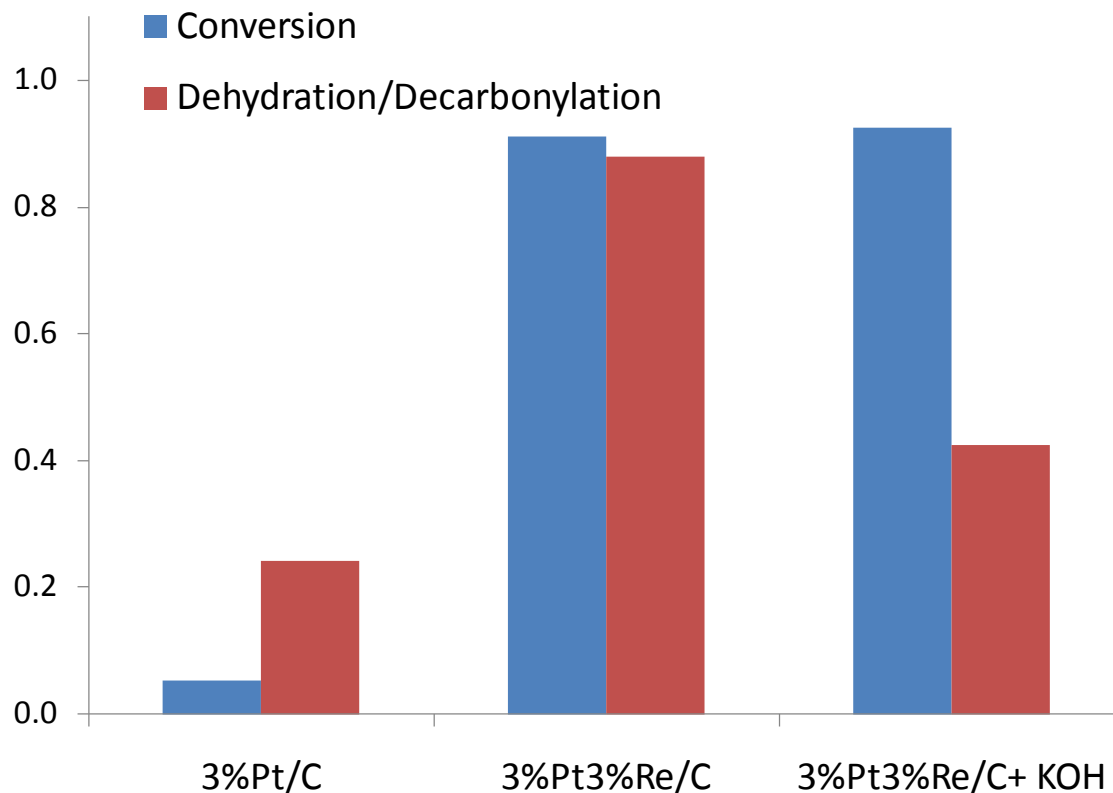


# Addition Of Soluble Liquid Acid to APR Medium Shows Little Effect on Selectivity From Pt-Re/C



- Nitric acid added to achieve a pH of 2
- Surface acidity appears to account for selectivity differences

# Addition of Base Affects Glycerol APR Selectivity

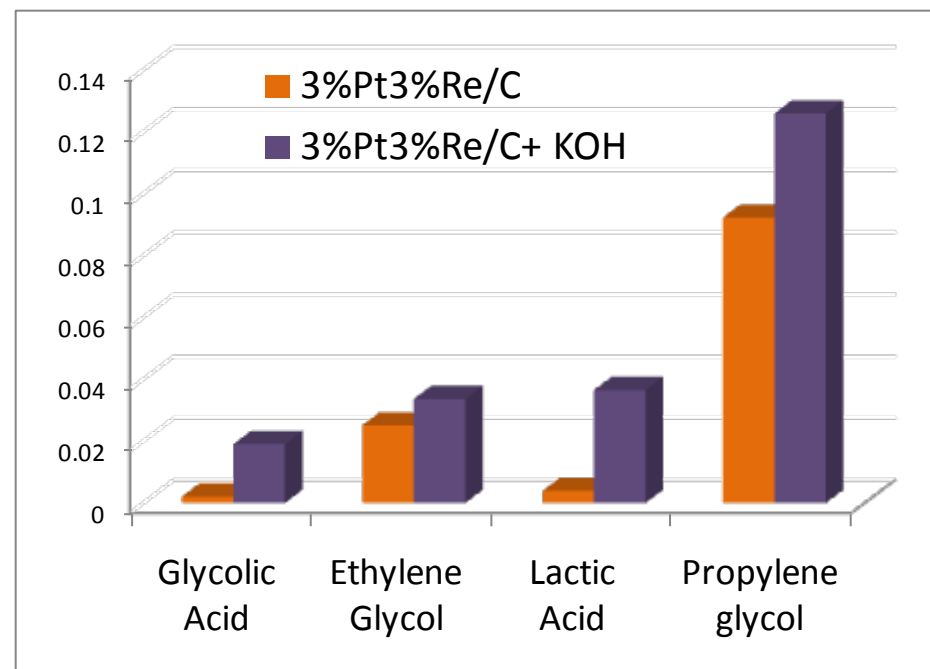
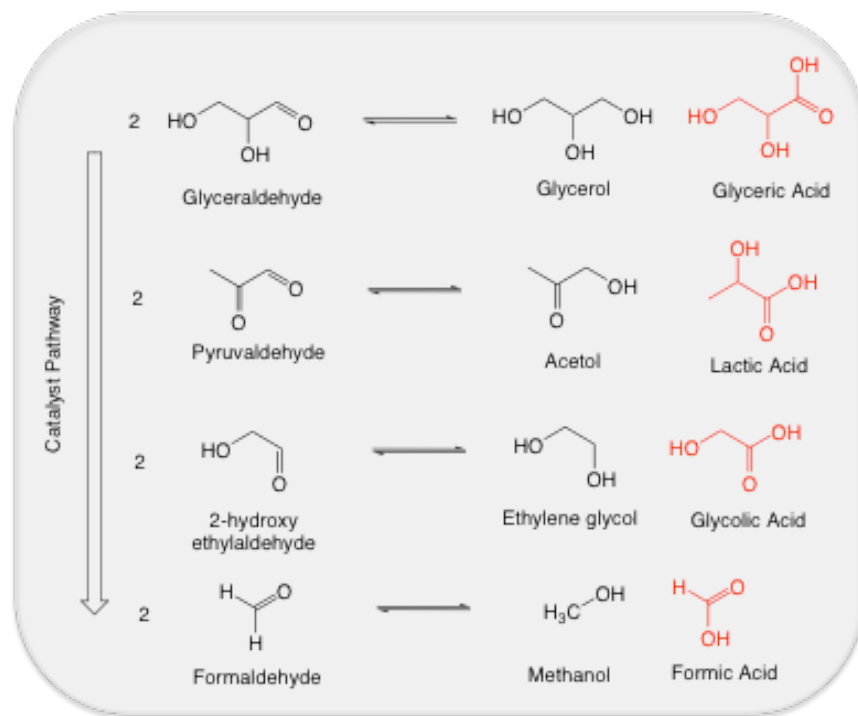


KOH neutralizes acid sites in Pt-Re/C and therefore depresses the dehydration pathway and makes decarbonylation more favorable



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# Addition of Base Alters Selectivity of Glycerol APR Through Undesirable Solution Phase Chemistry



Base also facilitates Cannizzaro reactions, leading to increased amount of acids and corresponding alcohols, e.g. lactic acid and propylene glycol

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APR of bio-oil

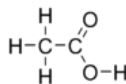
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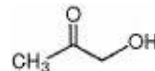
# Initial APR Tests Focus on Selected Representative Compounds

Representative Compounds

Acetic acid

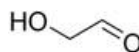


Hydroxyacetone



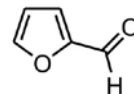
“acetol”

Hydroxyacetaldehyde



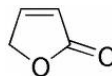
“glycolaldehyde”

Furfural

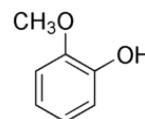


(insoluble ambient H<sub>2</sub>O)

2-furanone

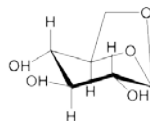


Guaiacol

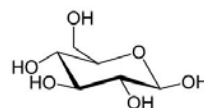


(insoluble ambient H<sub>2</sub>O)

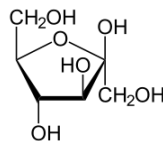
Levoglucosan



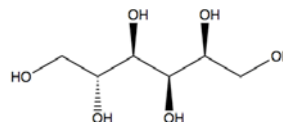
Glucose



Fructose



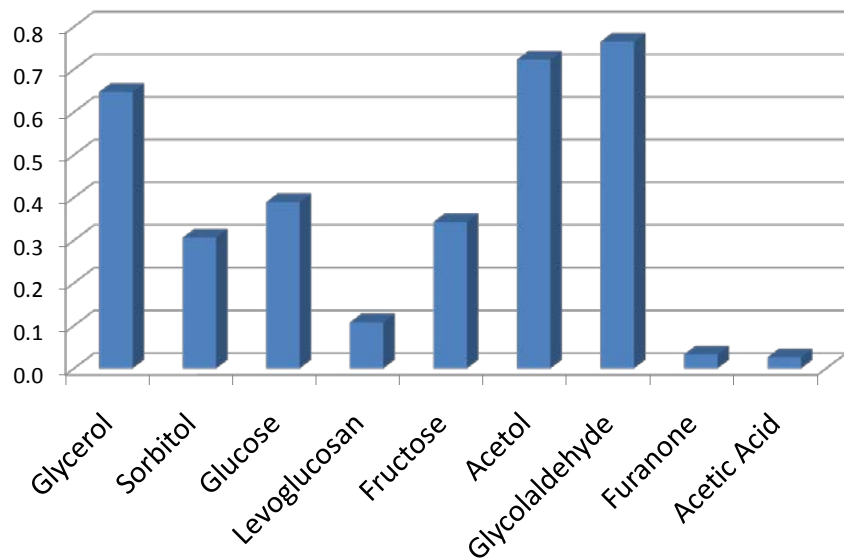
Sorbitol



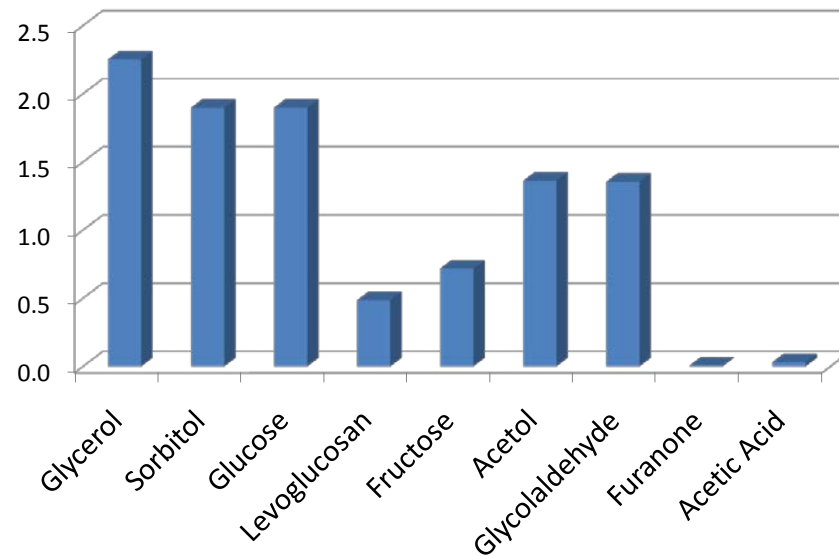
Each molecule poses special reforming requirements  
Acetic acid is especially prevalent in aqueous bio-oil and must be reformed

# APR of Bio-oil Components Under Standard Reaction Conditions

Conversion to CO<sub>2</sub> (carbon based)

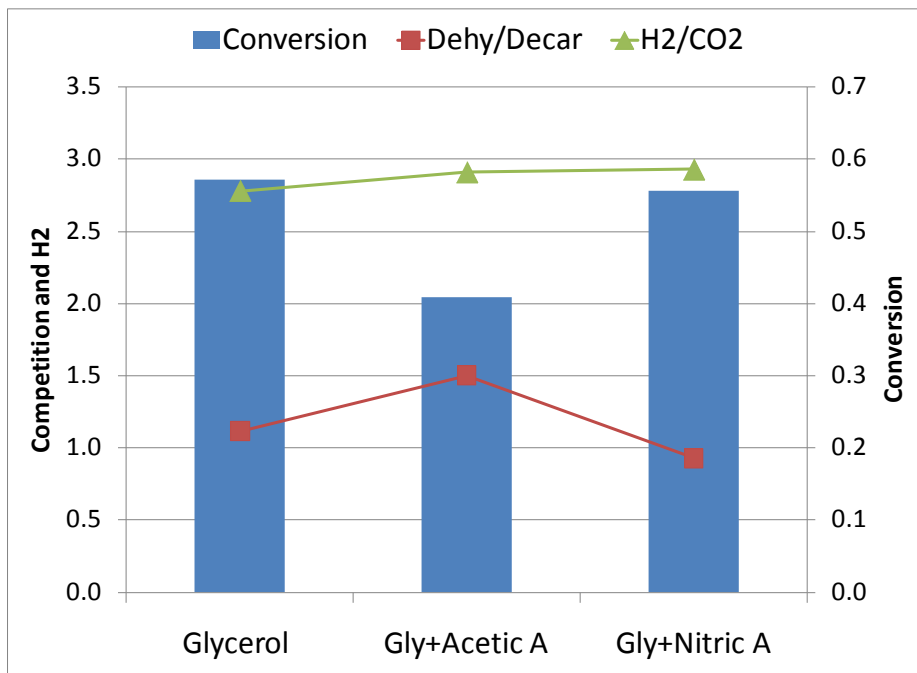


H<sub>2</sub> Yield (mol. H<sub>2</sub>/mol. Feed)

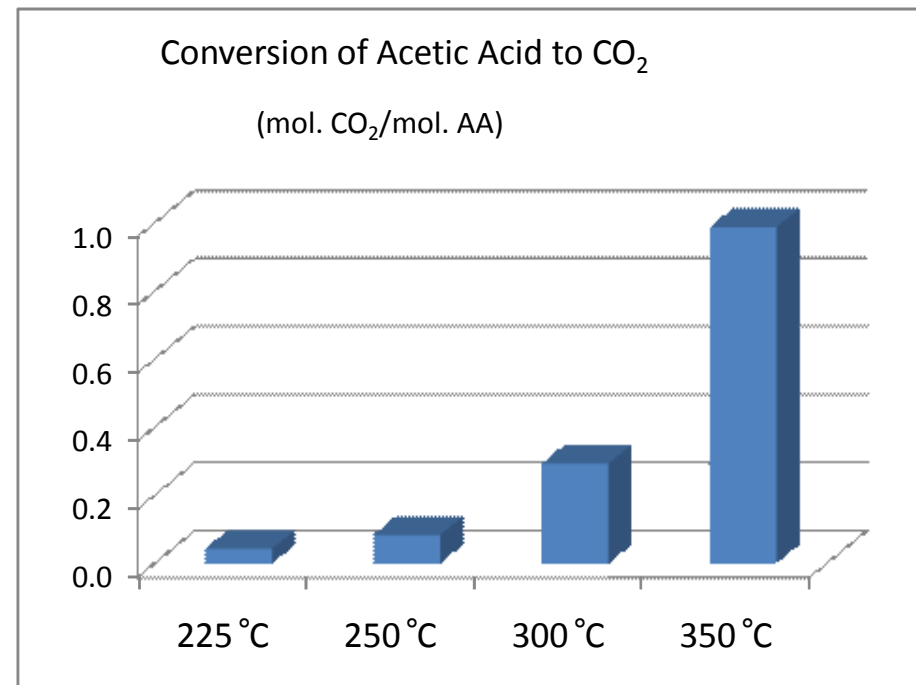


- Conditions: 225°C, 420psig, 0.1mL/min, all feeds with the same molar concentration
- Variability in reactivity is clearly demonstrated
- Furanone and acetic acid are especially unreactive at 225°C and have low available H<sub>2</sub> content

# Further Studies of Acetic Acid Reforming

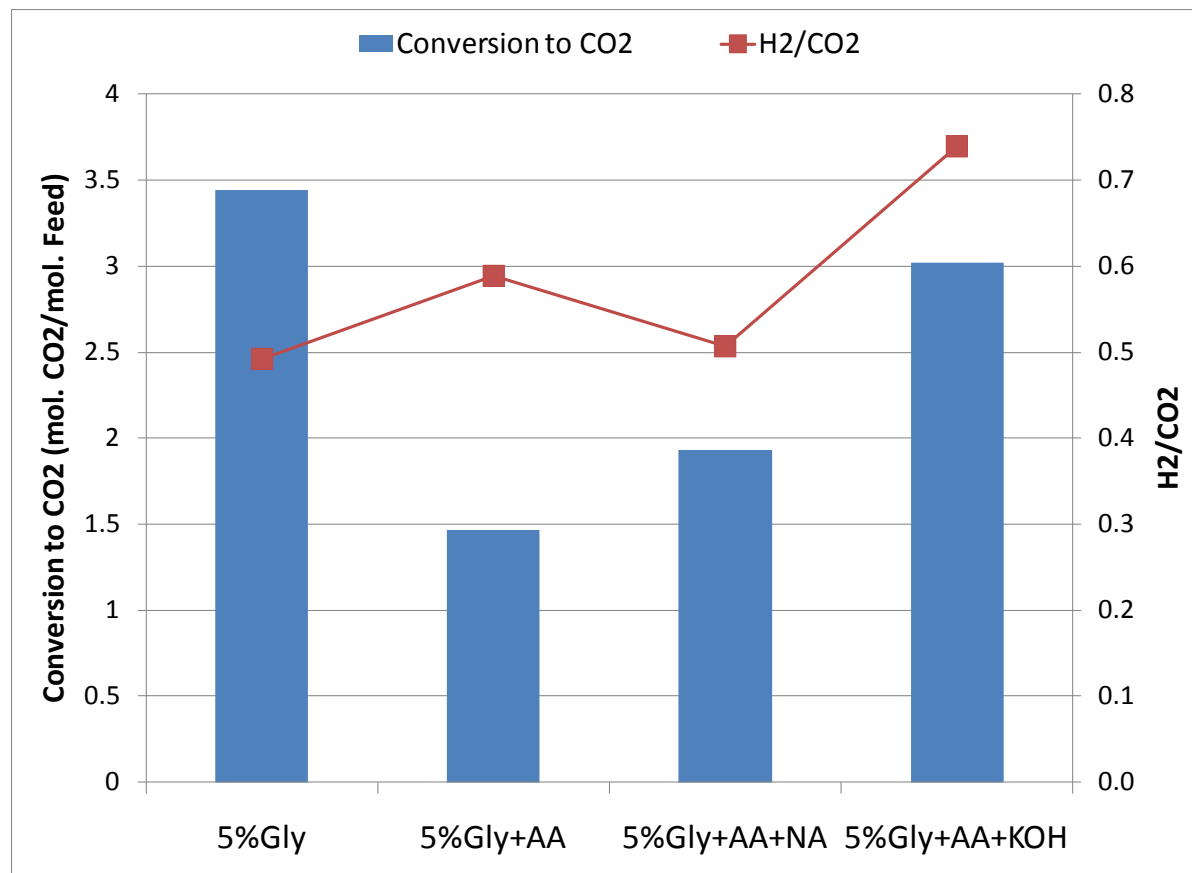


225°C, 420 psig



- ▶ Low conversion activity of acetic acid is not a result of an acidic medium affecting the catalyst
- ▶ Reduced activity may be due to carboxylic acid moiety bonding strongly to surface
- ▶ Acetic acid conversion can be significantly increased with increasing temperature, but best performance is at temperatures exceeding those possible with APR (gas phase reforming)

# Acid-Base Effects In Glycerol Conversion



- T = 225°C, 420 psig
- Acetic acid (AA): 3.26 wt.%; nitric acid (NA): 0.062 wt.%; KOH: 3 wt.%
- Addition of KOH neutralizes acidity of acetic acid, recovers activity of catalyst, and increases H<sub>2</sub> selectivity



Overview of biomass conversion by aqueous phase reforming

Glycerol APR: characterization and testing of Pt/C and Pt-Re/C

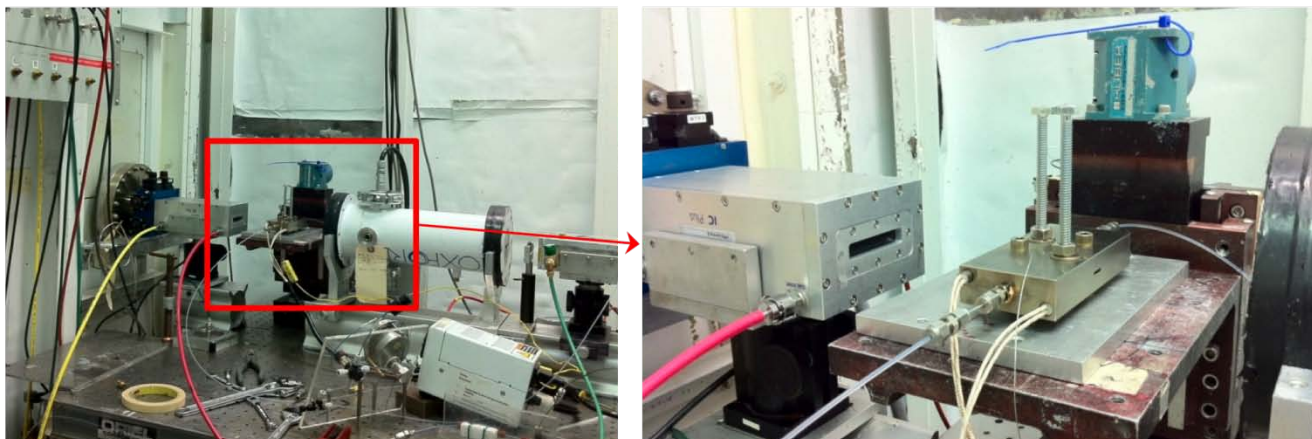
Pt-Re interaction during APR : generation of acidity

APR of bio-oil

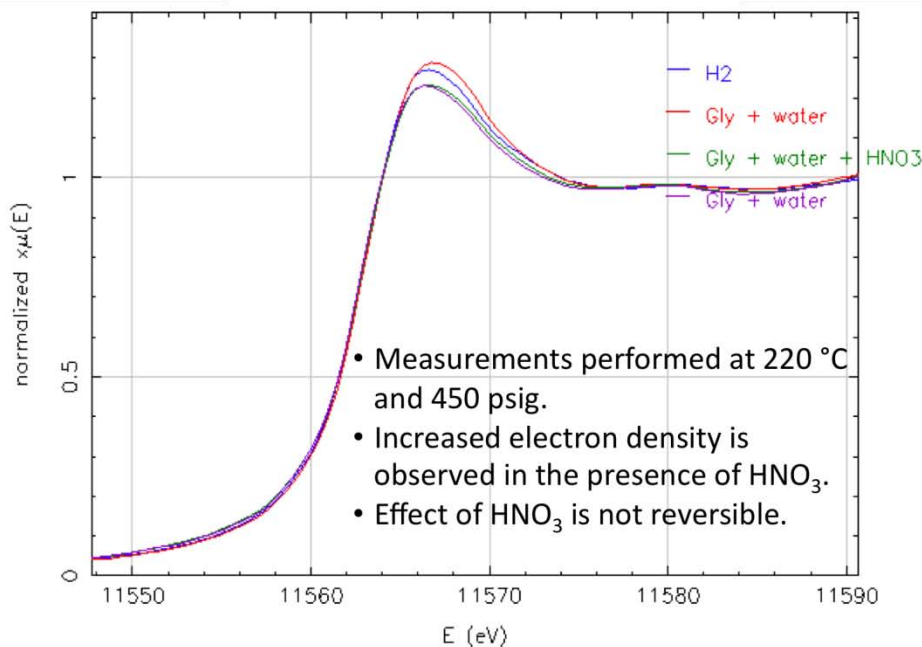
New analytical developments

Summary and conclusions

# X-ray Absorption Spectroscopy *in-situ* Cell

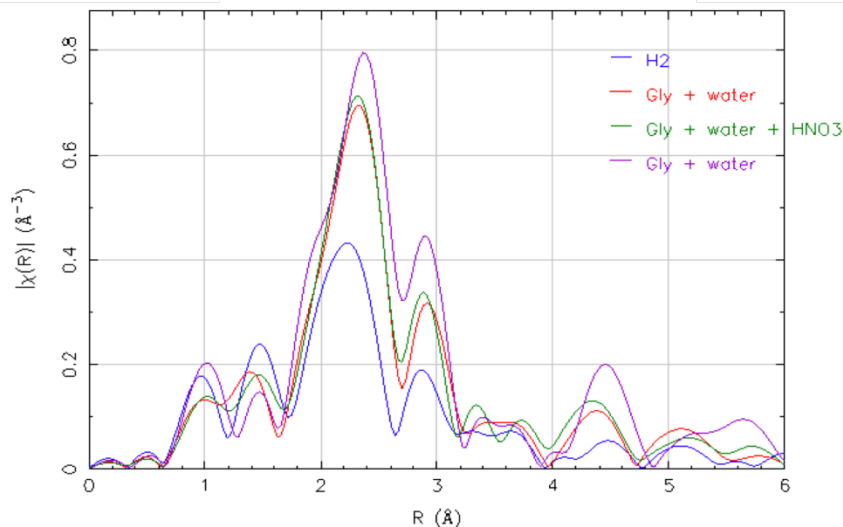


National Synchrotron Light Source (NSLS) beamline X18B at Brookhaven National Laboratory



- High P *in-situ* cell developed by PNNL staff in collaboration with BNL.
- Cell is used for collaborative work with UD.
  - The state of the catalyst (oxidation state and adsorbates) can be very different under gas phase vs. aqueous phase reaction conditions.
- Identification of adsorbates and their effect on the electron density can be studied under reaction conditions.

# X-ray Absorption Spectroscopy of Pt/C



Addition of HNO<sub>3</sub> results in:

- Increased electron density.
  - Increase in dehydrogenation activity.
  - Decrease in C-C cleavage activity.
- Effect is not reversible (both in XANES and catalytic).

		$N_{\text{Pt-Pt}}$	$\sigma^2$ (Å <sup>2</sup> )	$R_{\text{Pt-Pt}}$ (Å)	$E_0$ shift (eV, XANES)
3%H <sub>2</sub>	at 220 °C	7.2(5)	0.013(3)	2.73(2)	0.14
Glycerol + water	at 220 °C and 450 psig	10.5(1.4)	0.013(1)	2.76(1)	0.24
Glycerol + water + HNO <sub>3</sub>	at 220 °C and 450 psig	10.1(2.0)	0.009(1)	2.758(9)	0.07
Glycerol + water	at 220 °C and 450 psig	10.1(1.5)	0.010(1)	2.756(8)	0.12

- Sintering occurs under reaction conditions (in agreement with TEM).
- The changes in XANES are due to bonding with adsorbates.
- HNO<sub>3</sub> causes irreversible change in the catalyst (both XANES and catalytic).



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# Summary and Conclusions

- ▶ Pt and Pt-Re are highly dispersed on activated carbon
- ▶ Interaction between Pt and Re develops during reduction, and bimetallic or alloy nano particles form
- ▶ Pt-Re/C following reduction is significantly more active for APR of glycerol than is Pt/C
  - Yet, H<sub>2</sub> and CO chemisorption decrease with Pt-Re
  - Overall activity and hydrogen productivity increase is accompanied by greater selectivity to liquid alcohol products and alkanes
- ▶ APR reaction conditions lead to oxidation of the Re to form ReO<sub>x</sub> by steam, and possibly de-alloying the bimetallic
- ▶ Resulting catalyst shows evidence of surface acidity
  - NH<sub>3</sub> TPD results confirm increasing acidity with increasing Re loading
  - Bronsted acidity is verified by IR measurements
- ▶ Surface acidity favors a pathway of C-O bond breaking (dehydration), resulting in lower H<sub>2</sub> and CO (CO<sub>2</sub>) selectivity



# Summary and Conclusions

- ▶ Catalyst surface acidity, generated from oxidized Re, affects reaction pathways differently from effect of liquid (nitric) acid intentionally added to the feed
- ▶ Addition of base inhibits the dehydration pathways and results in greater hydrogen (and methane) production, along with homogeneous base-catalyzed products
- ▶ Both acid sites and metal sites have important roles in determining overall activity and conversion of substrate
- ▶ Role of Re in simultaneously increasing H<sub>2</sub> productivity is still not understood
- ▶ Hydrogen production by APR with bio-oil feedstock is significantly more challenging than with sugars or sugar alcohols
- ▶ Catalyst performance and understanding remains at the heart of an improved APR process

# Acknowledgement



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DOE Hydrogen Program

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# Thank you !



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