Project ID # PD002

Biomass-derived Liquids Distributed (Aqueous Phase) Reforming

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Pacific Northwest National Laboratory

DOE Merit Review
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Pacific Northwest NATIONAL LABORATORY

Institute for INTERFACIAL CATALYSIS

Overview

Timeline

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

Barriers

A: Reformer Capital Cost

C: Operation & Maintenance

D: Feedstock Issues

E. Greenhouse Gas Emissions

Budget

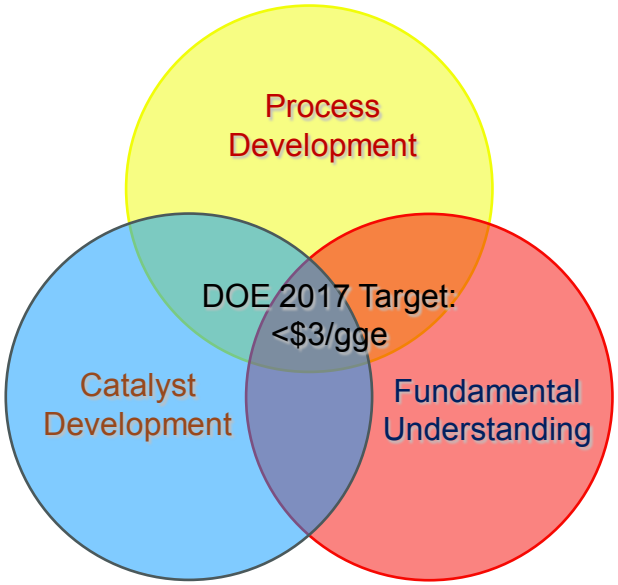
- Funding received in FY04: $100K
- Funding received in FY05: $500K
- Funding received in FY06: $0K
- Funding for FY07: $550K
- Funding for FY08: $600K
- Funding for FY09: $600K
- Funding for FY10: $450K

Collaborations

- ORNL—high resolution TEM studies

Project Objective

- Develop bio-derived liquids aqueous phase reforming technology for hydrogen production that can meet the DOE efficiency and cost targets
  - Enhance catalyst performance by increasing catalyst activity and hydrogen selectivity
  - Develop mechanistic understanding of reaction pathways and means to control product distributions consistent with application end-use



Project Milestones

Aqueous Phase Reforming	
Summarize effect of catalyst and support pretreatment and preparation methods on performance of Pt/C and Pt-Re/C catalysts	9/30/09 milestone met
Provide a report summarizing kinetic data, catalytic and non-catalytic reaction pathways, and pH effects with glycerol and sorbitol feedstock	9/30/09 milestone met (glycerol only)
Preliminary process economic analysis for CH_4 co-production for solid oxide fuel cell application	1/31/10 (complete)
Complete process and catalyst optimization to maximize H_2 and C_1 with glycerol feed	4/30/2010 milestone met
Demonstrate full conversion of glucose/sorbitol with <5% carbon retained as C_2^+ oxygenated product	9/30/2010 in progress

Technical Approach

- Detailed study of Pt-Re/C catalyst
  - Compare catalytic performance with Pt/C with glycerol
  - Quantify the effect of Re addition on Pt/C performance
    - Activity
    - Product selectivity--modification of reaction pathways
  - Develop advanced catalyst characterization methods to understand interactions between the components
    - XPS analysis of metal oxidation state changes (PNNL-EMSL)
    - XANES analysis of Pt-Re interaction (BNL)
    - In situ TEM for changes in metal dispersion (Ariz State, ORNL)
- Examine and quantify effect of base addition on catalyst performance
- Evaluate options for co-production of hydrogen with CH_4 for compatibility with SOFC for power generation
- Extend knowledge of glycerol APR to sorbitol APR

Recent Progress on APR

- Found evidence for dual-functionality of Pt-Re/C under hydrothermal APR environment:
  - Pt-Re alloy formation provides increased activity toward H_2 production
  - Acidic ReOx present facilitates alternate reaction pathways
- Advanced the understanding of glycerol APR over Pt-Re/C
  - Addition of Re increases conversion of glycerol, but also provides additional reaction pathways competing with H_2-generating C-C cleavage pathway
  - ReOx formed under APR conditions facilitates C-O scission, which consumes H_2 and leads to higher selectivity to alcohols and C_2^+ alkanes
  - H_2 productivity increases with addition of Re at expense of H_2 selectivity
  - Addition of KOH to glycerol feed over Pt-Re/C neutralizes acidity of ReOx and depresses C-O scission pathways, resulting in increased H_2 yield via C-C cleavage
- Preliminary results from APR of sorbitol have been obtained

Fuel Production From Reforming Of Bio-liquids

Agriculture

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

Forest residue

Hydrolysis: Acid or Enzymatic

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

Reforming → **Fuel**

Aqueous phase reforming

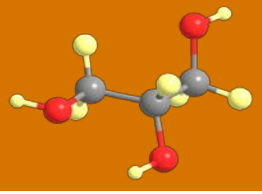
Cortright et al. *Nature* 418 (2002)

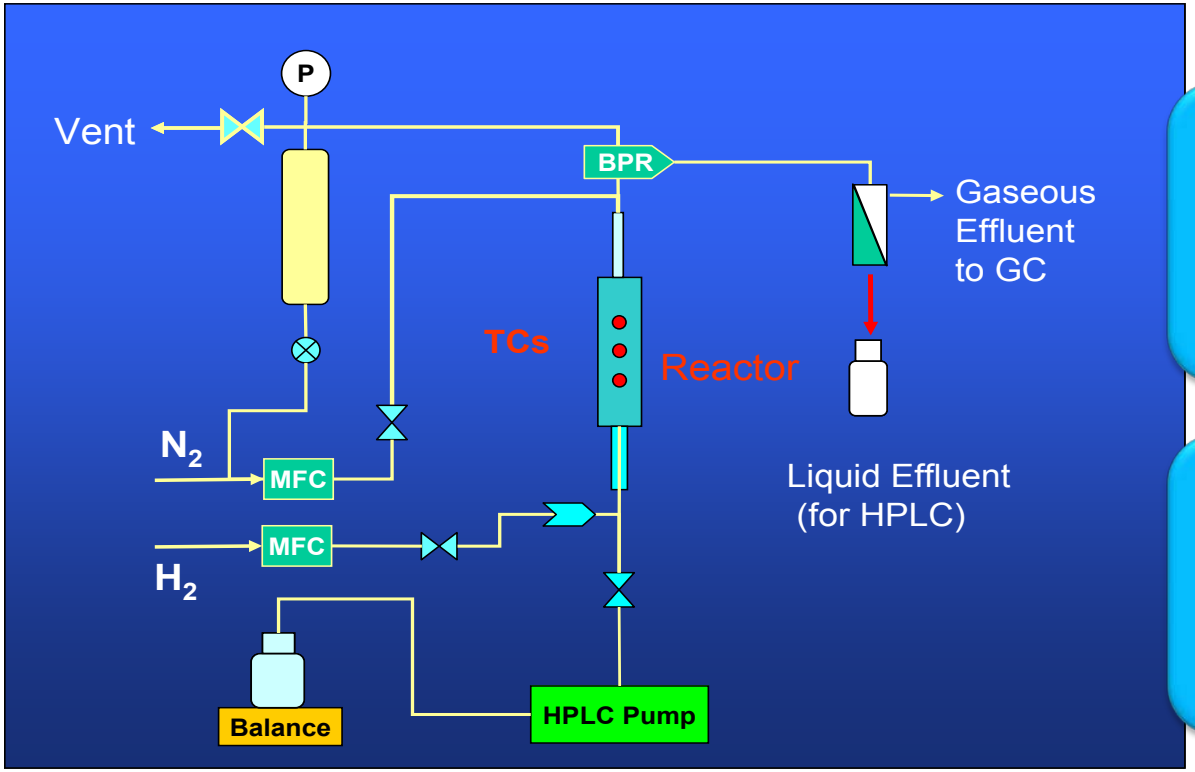
Operates at low temperatures compared with conventional reforming, reducing energy costs and favoring water gas shift reaction

Allows processing of biomass feedstock that are difficult to vaporize without decomposition

Compatible with wet feedstock utilization

Reaction Test on APR of Glycerol





Pt is chosen based on its good activity for C-C cleavage

Carbon is chosen as the support due to its higher hydrothermal stability than silica and alumina

- Isothermal microchannel reactor with oil heating jacket
- Aqueous feed is pumped into the reactor with pre-heating
- Catalyst is reduced in-situ at 280 °C before use.
- Reaction runs typically at 225 °C, 420 psig.

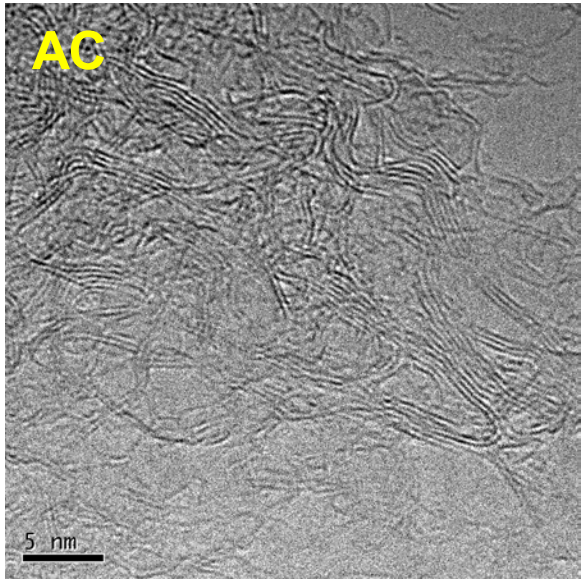
Catalyst Preparation: Incipient Wetness Impregnation

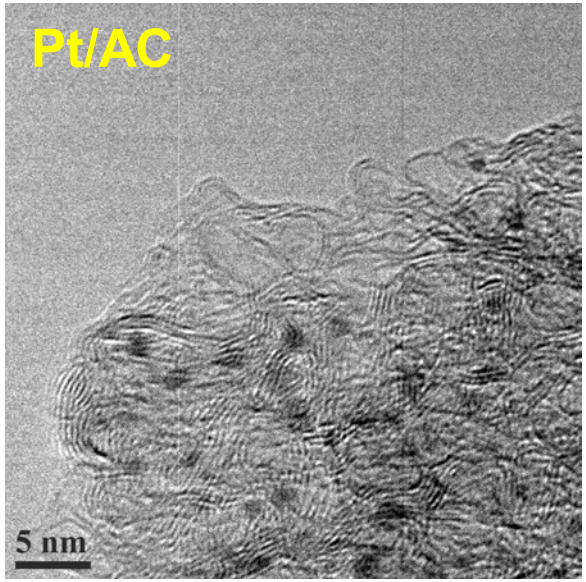
$Pt(NH_3)_4(NO_3)_2$

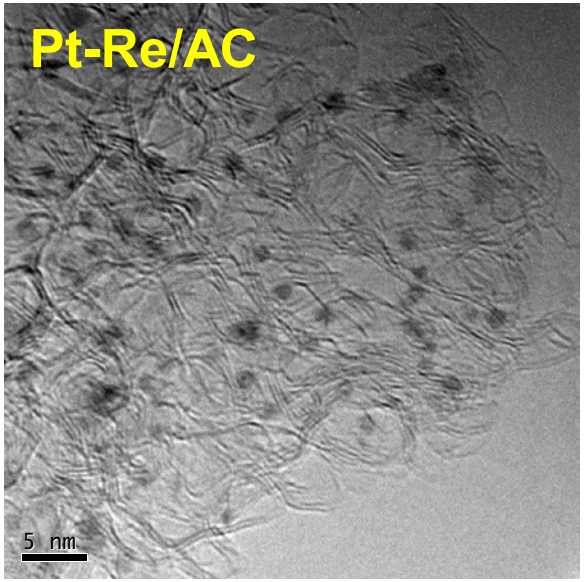
$HReO_4$

BET 570 m^2/g

P.V. 0.42 cc/g







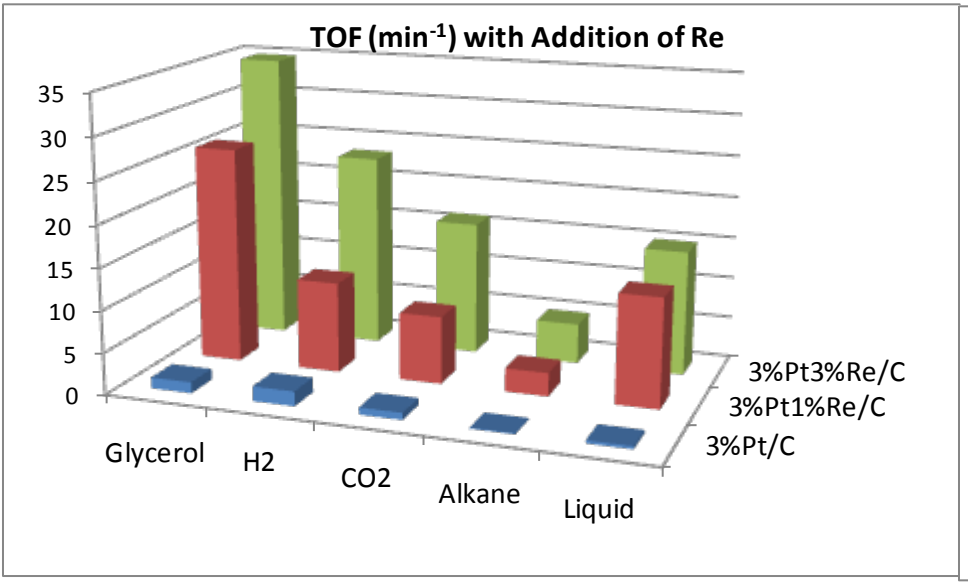
Prepared Catalysts—Metal Surface Areas and Dispersion

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

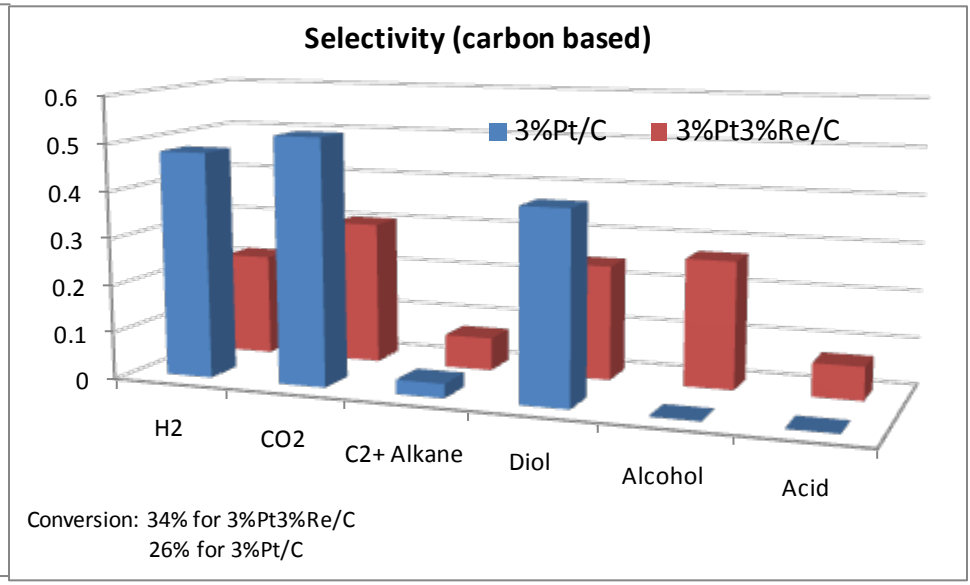
* wt.% -- g metal/100g carbon ** based on CO chemisorption

Addition of Re to Pt/C Results in …..

Higher Activity



Different Selectivity



T = 226 ºC, P = 420 psig, feed rate = 0.06 moles glycerol/gcat-h; TOF is calculated based on CO chemisorption

- Addition of Re results in significant enhancement in activity and different selectivity
- What is the role of Re?

Elucidating the Role of Re by Characterization and Testing

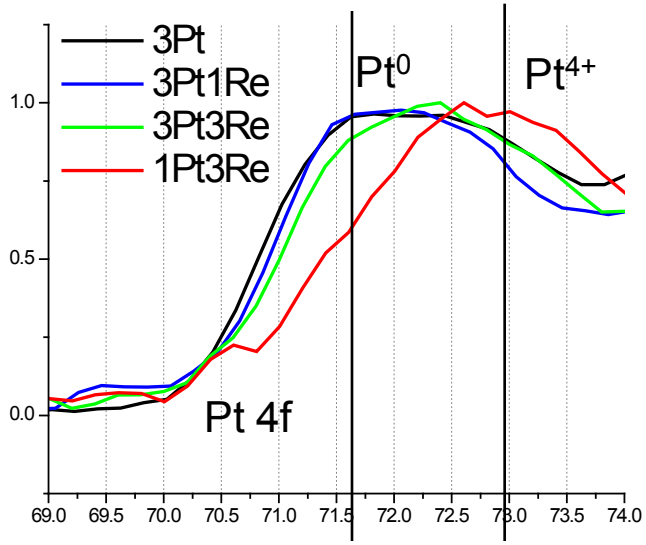
Electronic Structure of PtRe/C under H_2 pretreatment

Structure and composition of PtRe/C under hydrothermal conditions

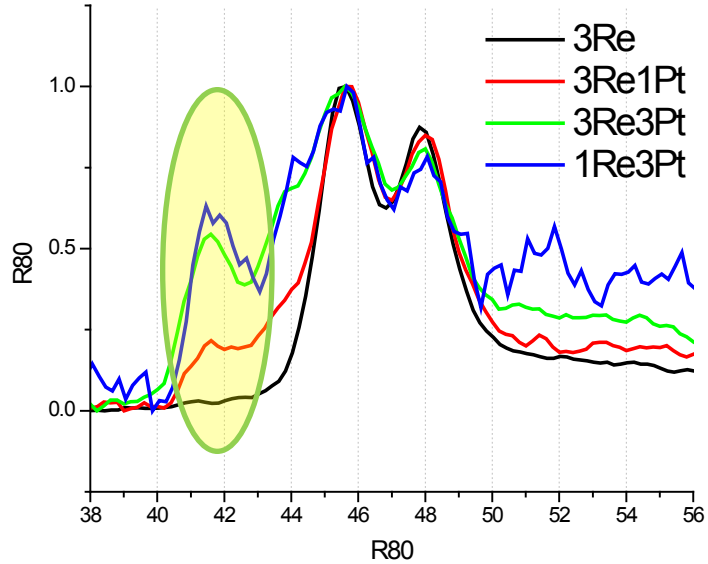
Correlation with activity and selectivity

Modification of Pt Electronic Structure by Addition of Re

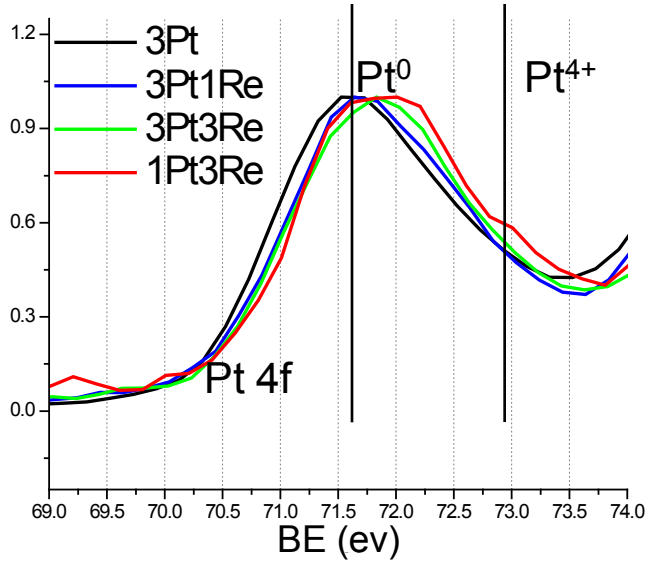
Pt-Re/C reduced at 80 °C



Re 4f Reduced @ 80°C

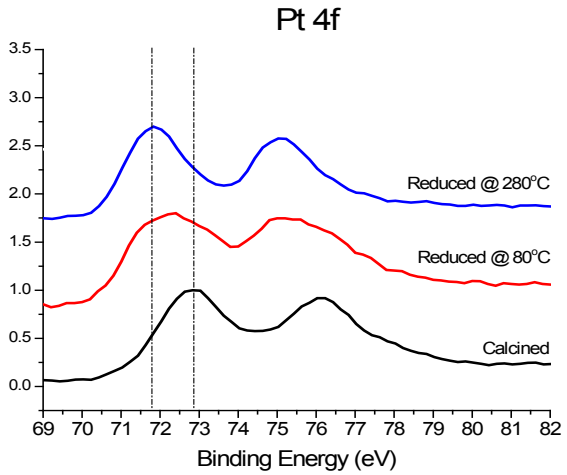


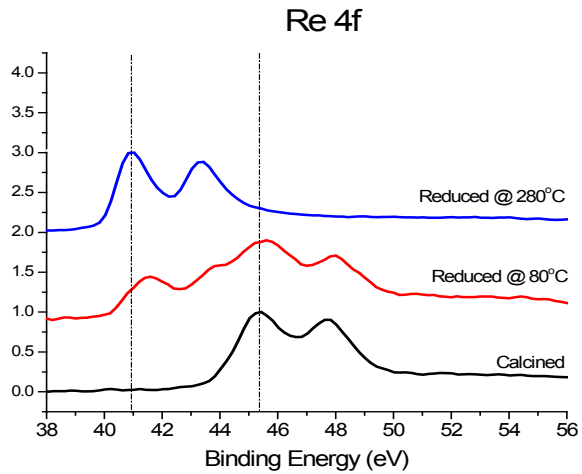
Pt-Re/C reduced at 280 °C



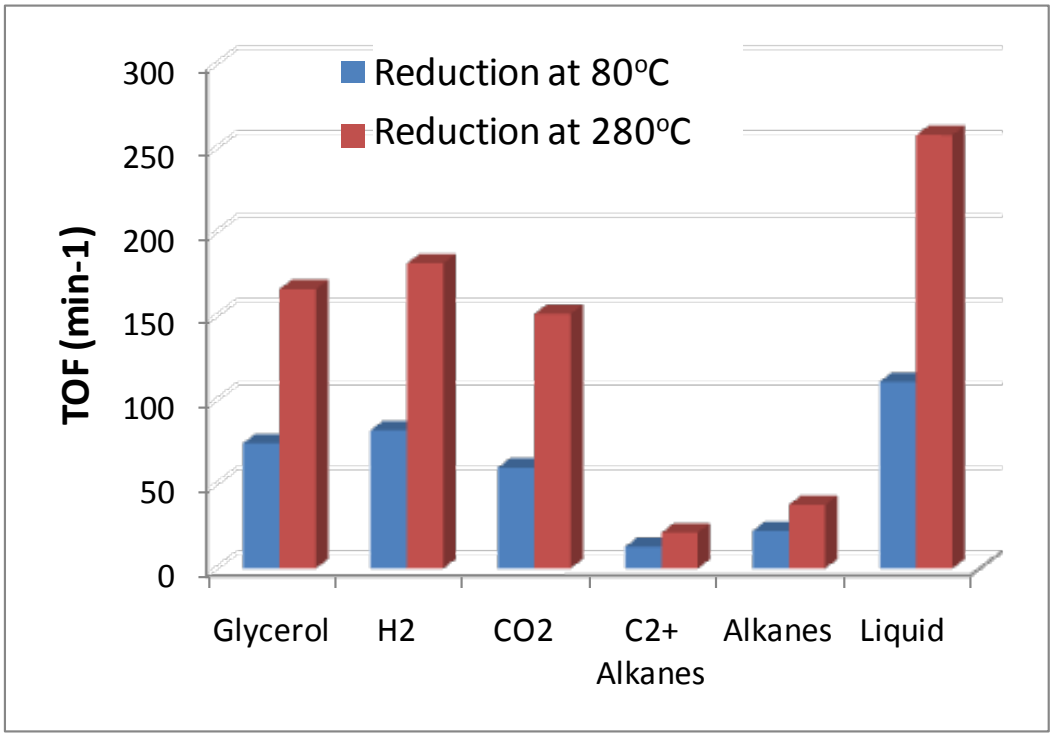
- Addition of Re retards reduction of Pt at lower temperature
- Pt appears to facilitate reduction of Re at 80°C
- Binding energies of Pt increase with addition of Re when reduced at 280°C, suggesting charge transfer from Pt to Re

Fully Reduced Pt and Re Results in Higher Activity





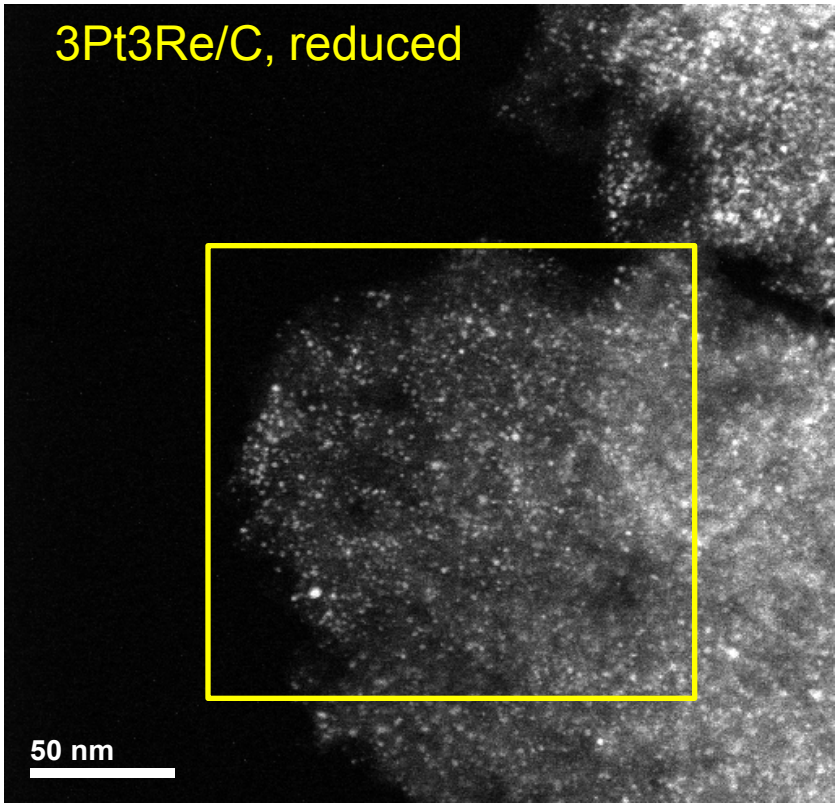
3%Pt-3%Re/C

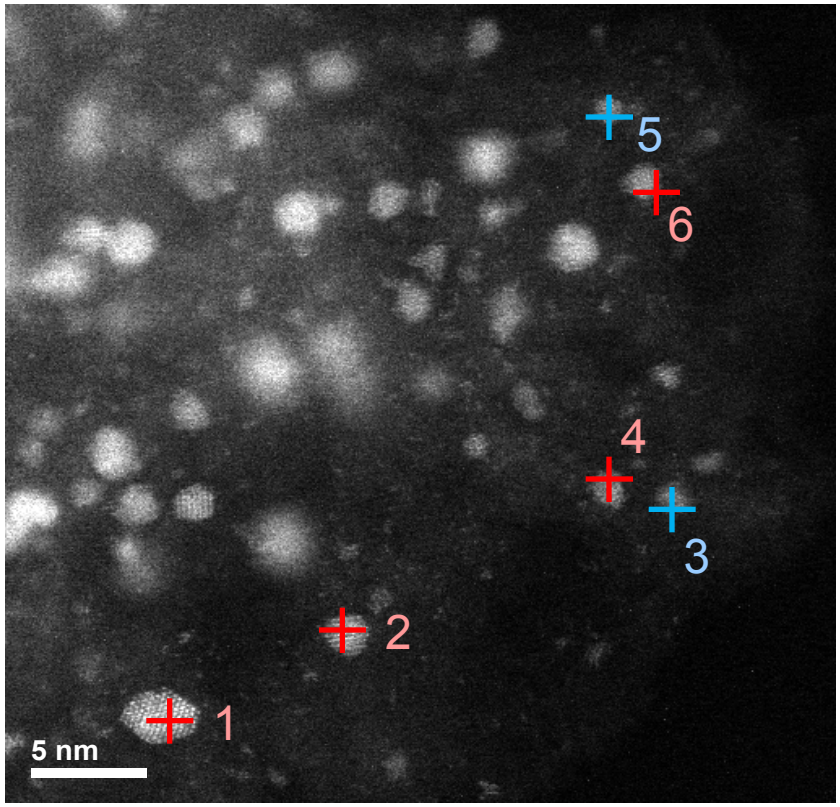


T = 226 °C, P = 420 psig, feed rate = 0.06 moles glycerol/gcat-h
TOF is calculated based on CO chemisorption

- Reduction at 280 °C fully reduces Pt and Re, which may forms Pt-Re alloy particles.
- Fully reduced Pt and Re results in higher activity

EDS Shows Pt Rich and Re Rich Particles

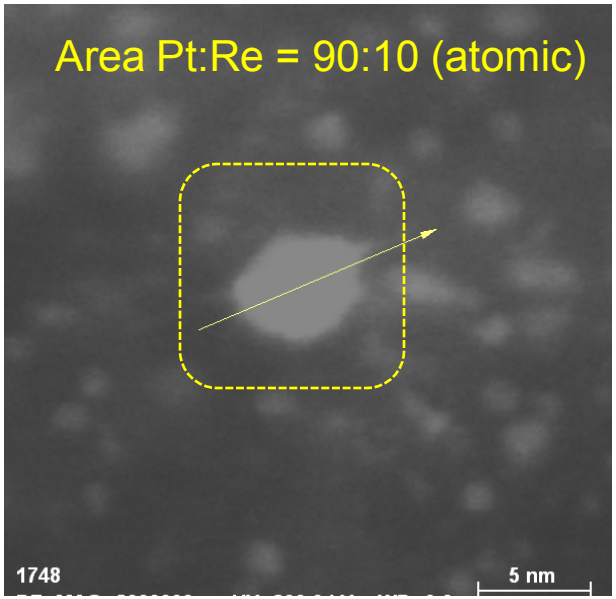


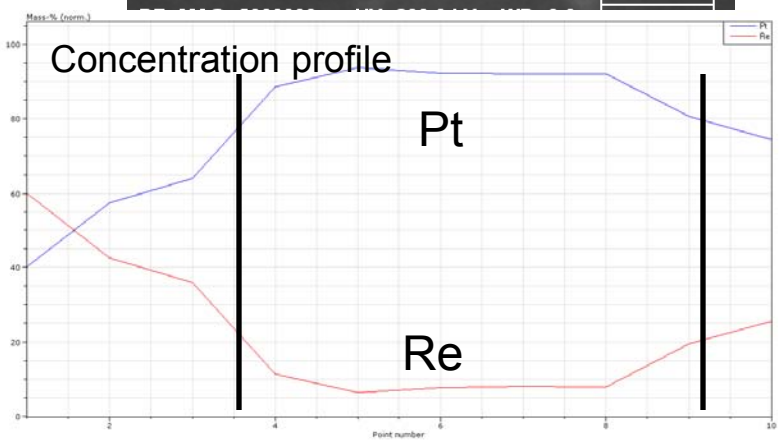


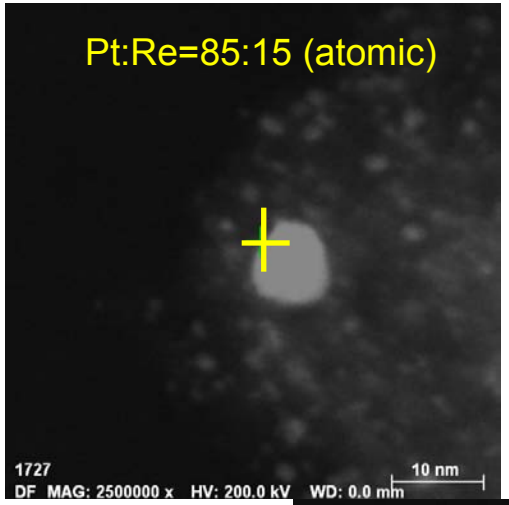
Atomic Ratio	Area	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6
Pt	54.5	88.4	76	15	74	13	84
Re	45.5	11.6	24	85	25	87	16

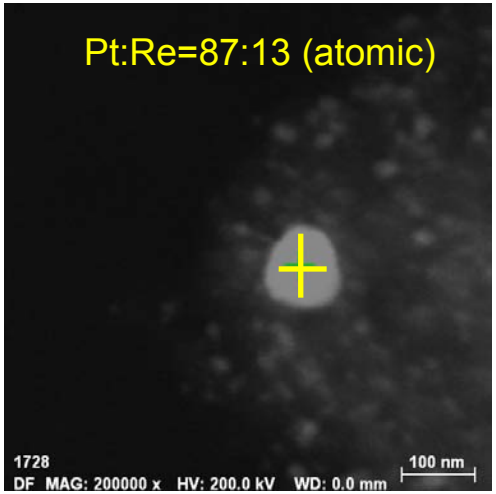
- Pt-Re phase diagram also predicts Pt-rich phase and Re-rich phase

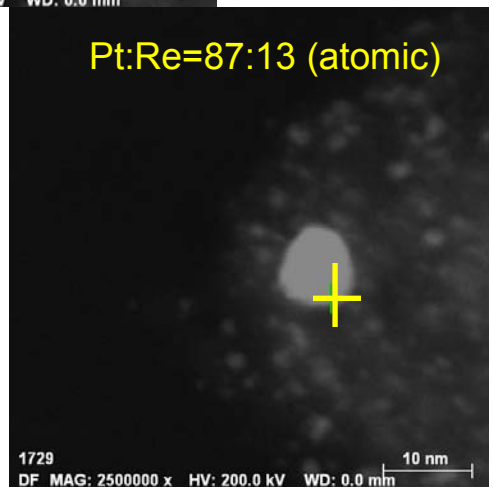
EDS Line Scan Shows Homogeneous Composition within the Individual Particles











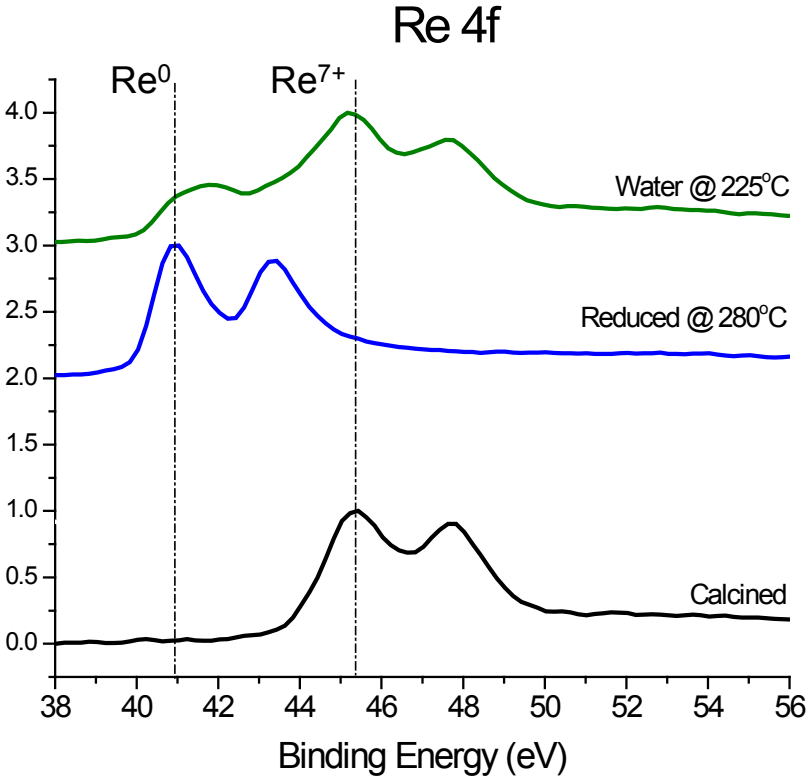
Line scan or spot scans on single particles shows uniform Pt and Re composition in the bulk part of particles, indicating formation of Pt-Re alloy

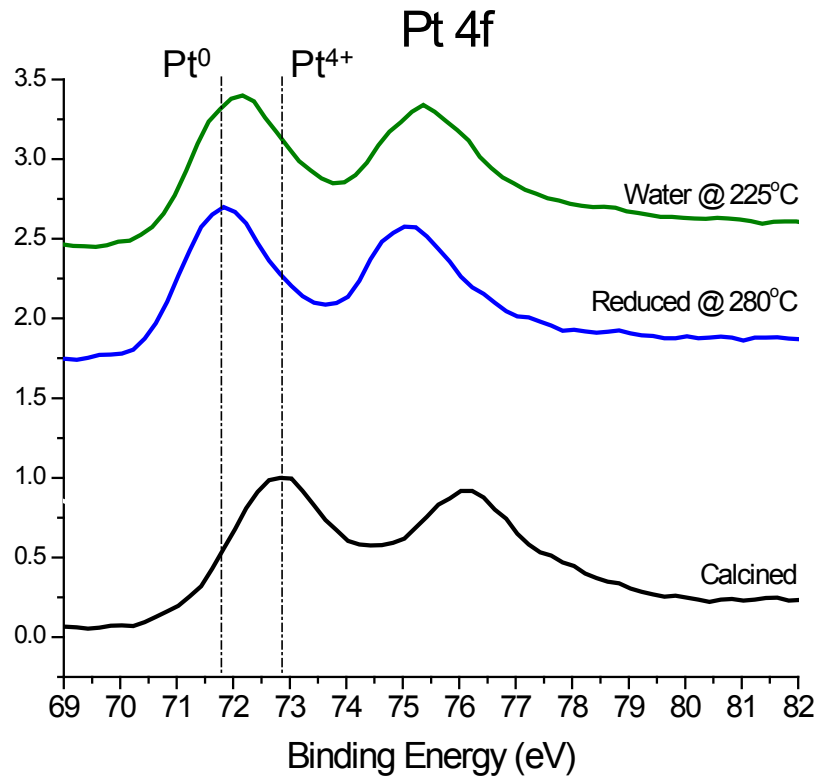
Summary on Pt-Re interaction after reduction

- Pt facilitates the reduction of Re
- Reduction at 280°C is required to fully reduce Pt and Re and maximize activity of glycerol APR
- Charge transfer (XPS) and uniform composition (TEM) suggests formation of Pt-Re bimetallic particles
- Modification of Pt electronic structure may account for enhancement of activity.

Pt-Re Interaction under Hydrothermal conditions

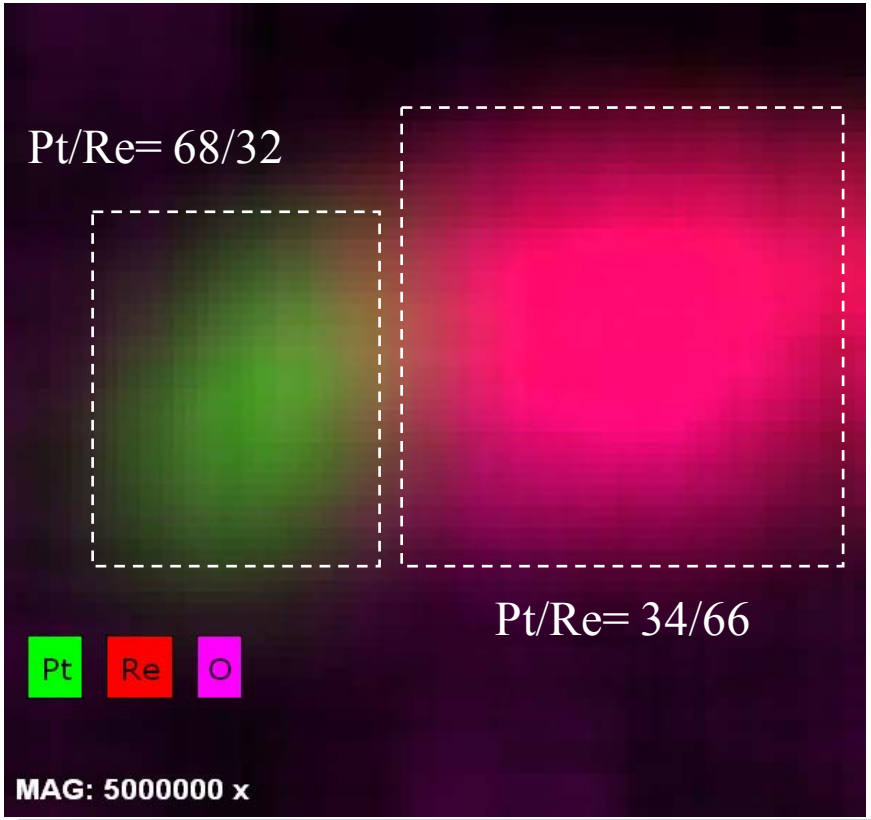
3%Pt-3%Re/C

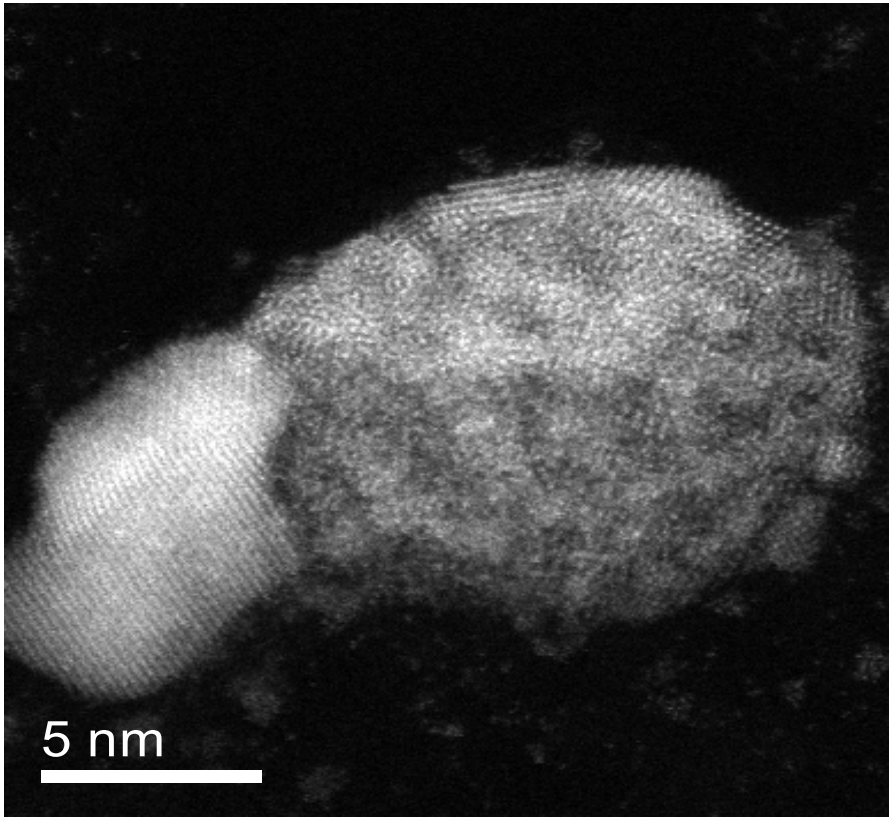




- Exposure to water results in oxidation of Re and Pt (Pt to a much smaller extent)
- Surface ReOx may form under hydrothermal conditions

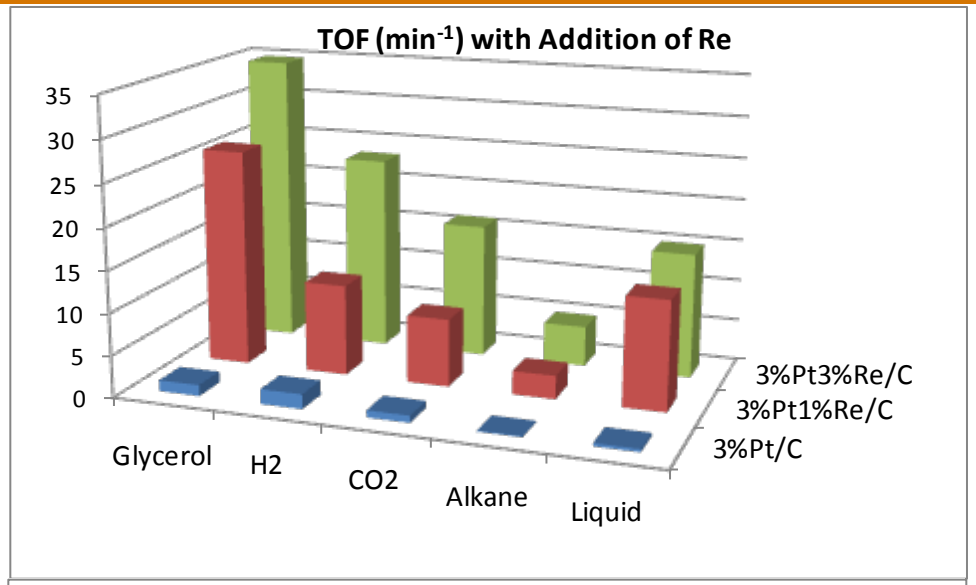
Model Catalyst (Pt:Re=1:1)

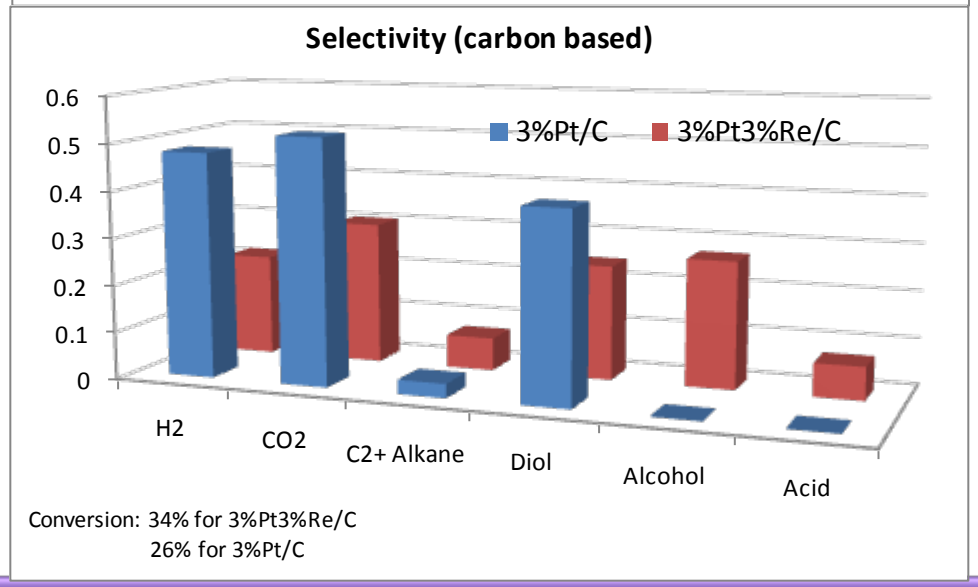




- Reduction was carried out in the airlock chamber of TEM. The non-flowing system allows small amount of residual water on the surface, similar to hydrothermal conditions in APR process.
- The Pt-Re/C consists of 2 phases
  - PtRe bimetallic phase rich in Pt
  - Pt embedded in a ReOx rich phase
- Oxygen is detected in Re rich phase.

Dual-Functionality of Pt-Re





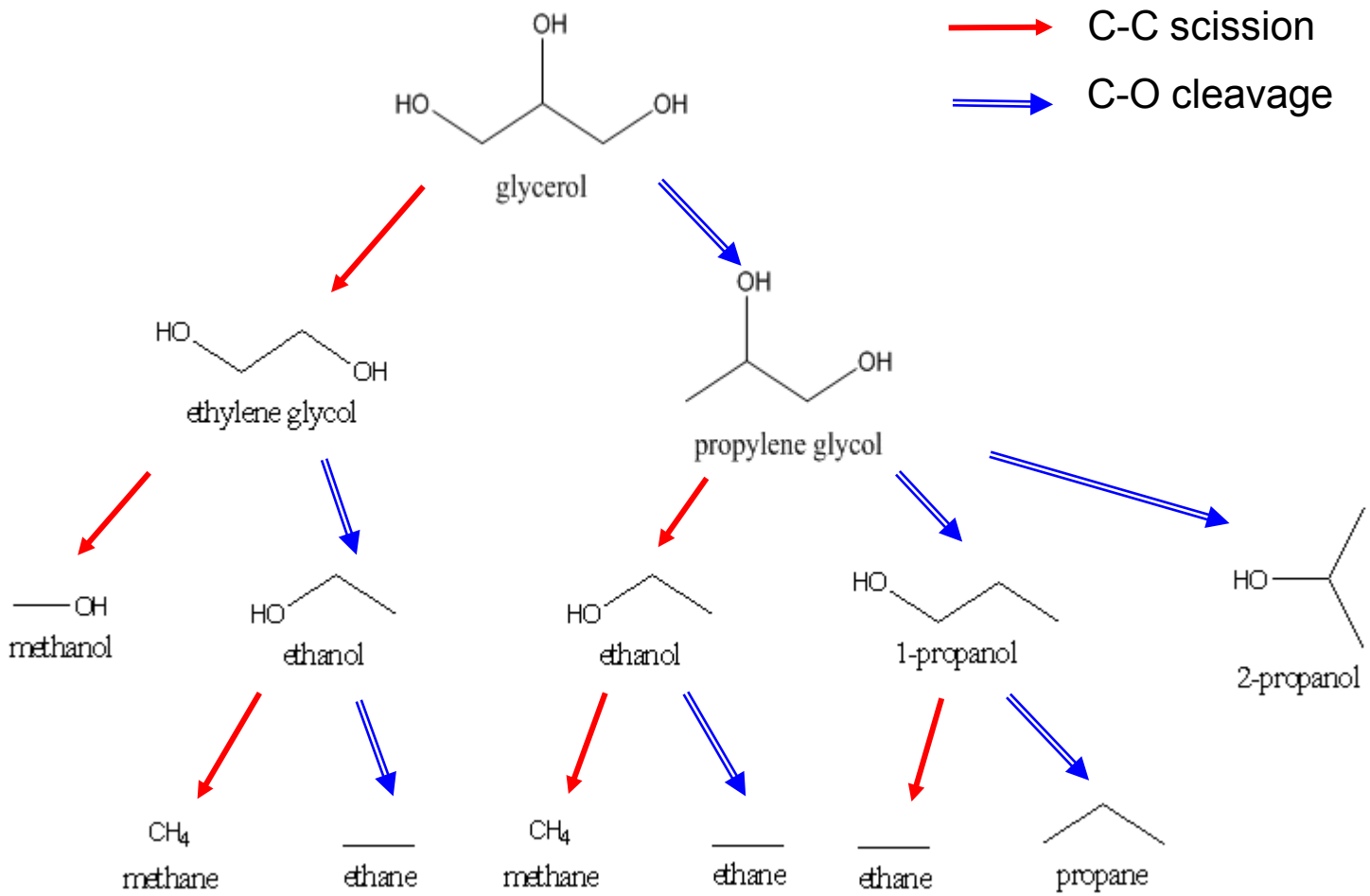
T = 226 ºC, P = 420 psig, feed rate = 0.06 moles glycerol/gcat-h
TOF is calculated based on CO chemisorption

What is the role of Re?

Electronic effects from alloying (PtRe)

Separate reaction pathways due to oxidized Re (ReOx)

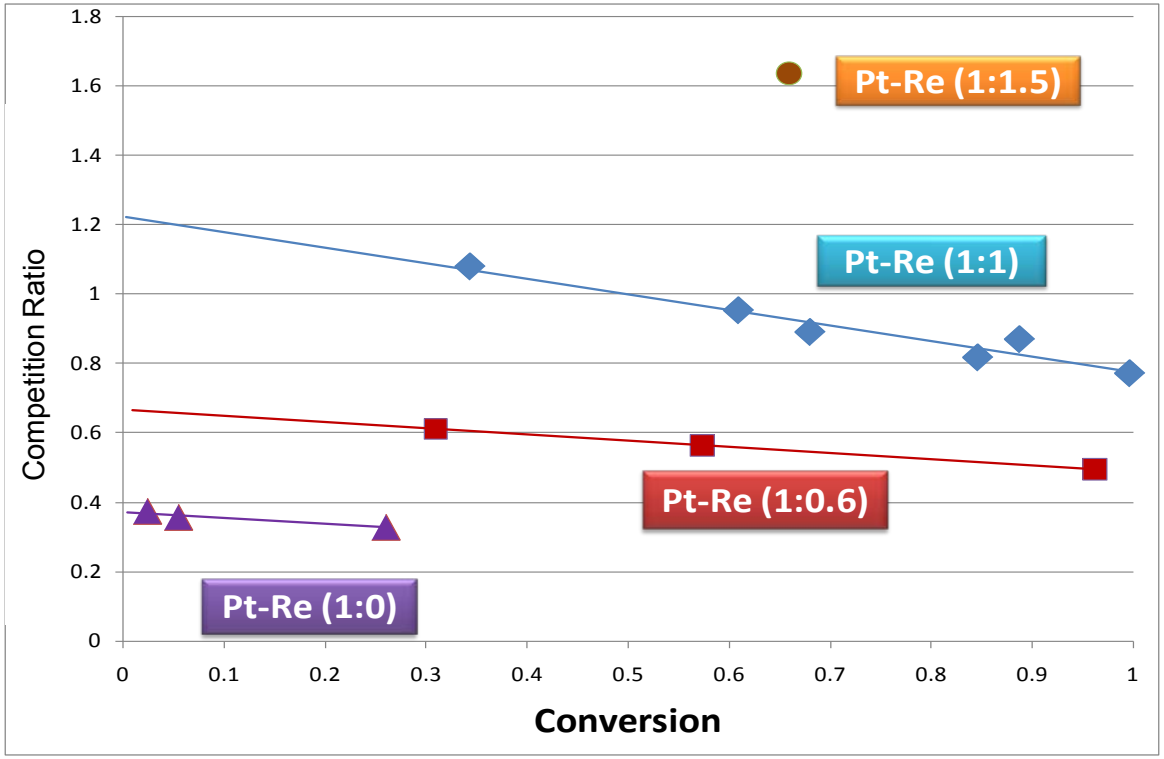
Definition of Competition Ratio: C-O vs. C-C Scission



$$\frac{\text{C-O Scission}}{\text{C-C Scission}} = \frac{\text{Sum of all dehydrated products for each dehydration step by mole}}{\text{Moles of } CO_2}$$

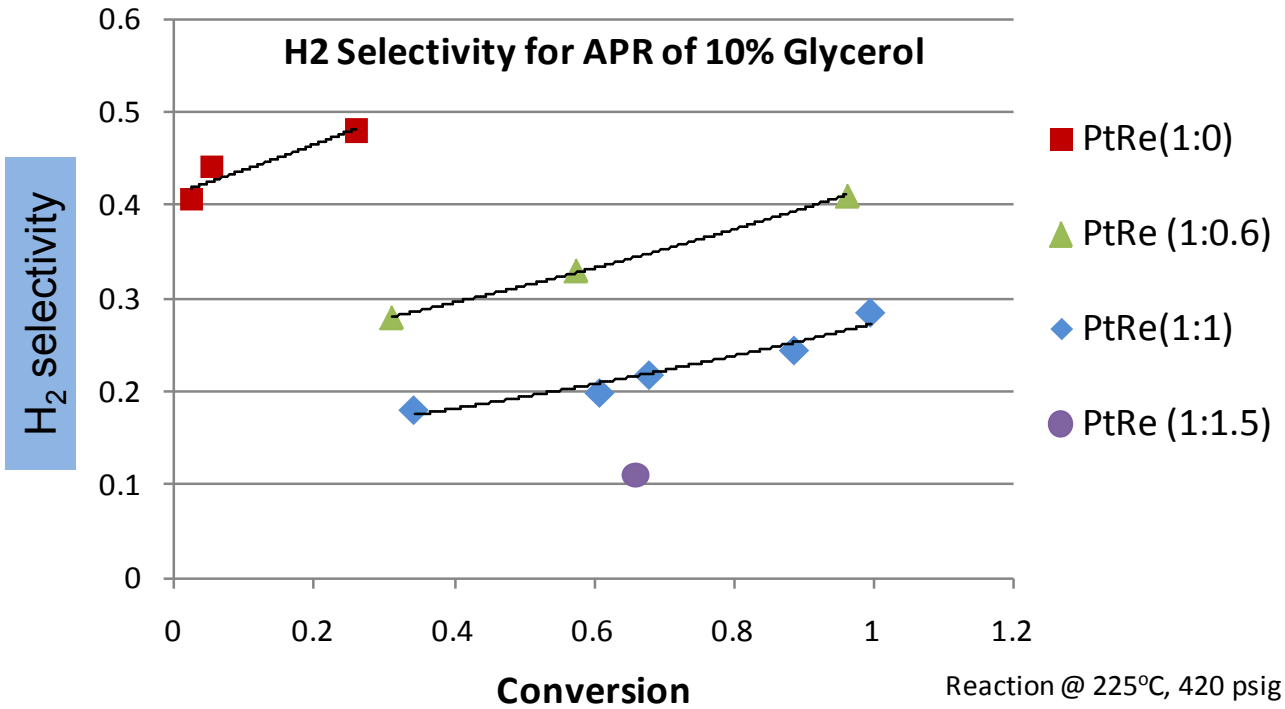
Addition of Re Facilitates the Dehydration Reaction (C-O Scission Pathway)

C-O scission/C-C scission (competition ratio) for different PtRe ratio



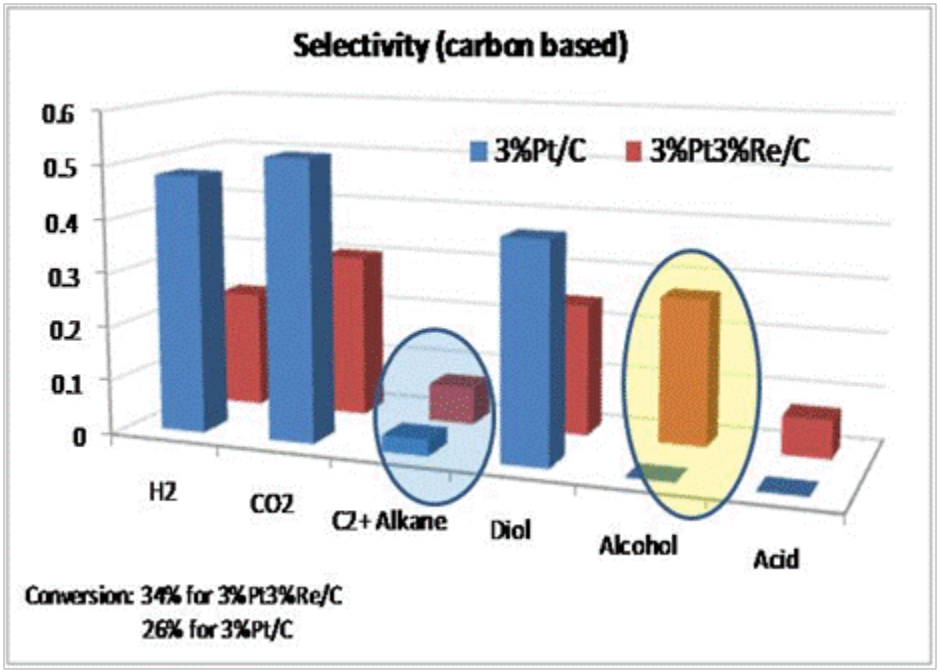
- Supported ReOx has been reported to be acidic. NH_3 TPD confirmed acidity of ReOx
- Larger amount of Re added to Pt results in higher dehydration selectivity (effect of ReOx)

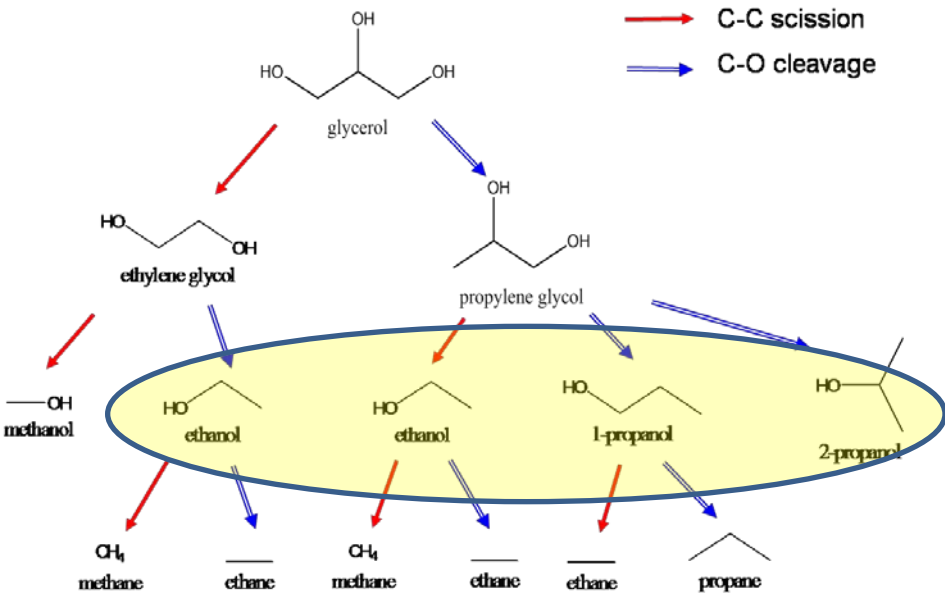
Addition of Re Affects Hydrogen Selectivity



- H_2 selectivity is defined as measured H_2 yield over theoretical H_2 yield from converted glycerol
- Higher Pt/Re ratio resulted in higher H_2 selectivity
- Lower hydrogen selectivity with addition of Re is due to more consumption of H_2 through C-O cleavage pathway (more ReOx)

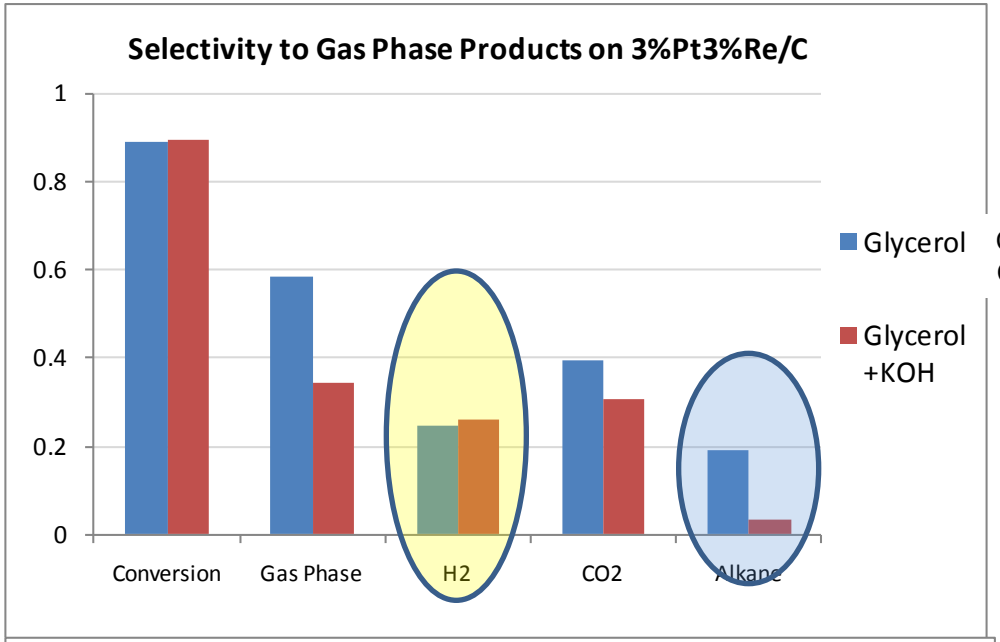
Addition of Re Affects Reaction Pathways

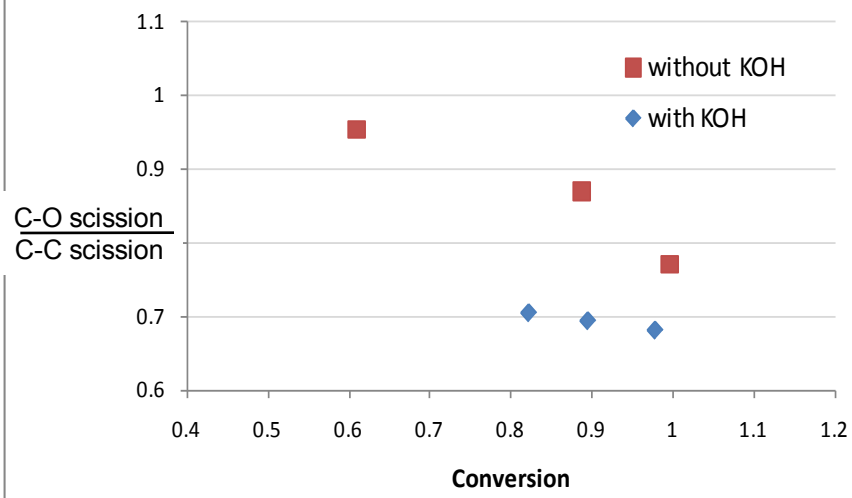


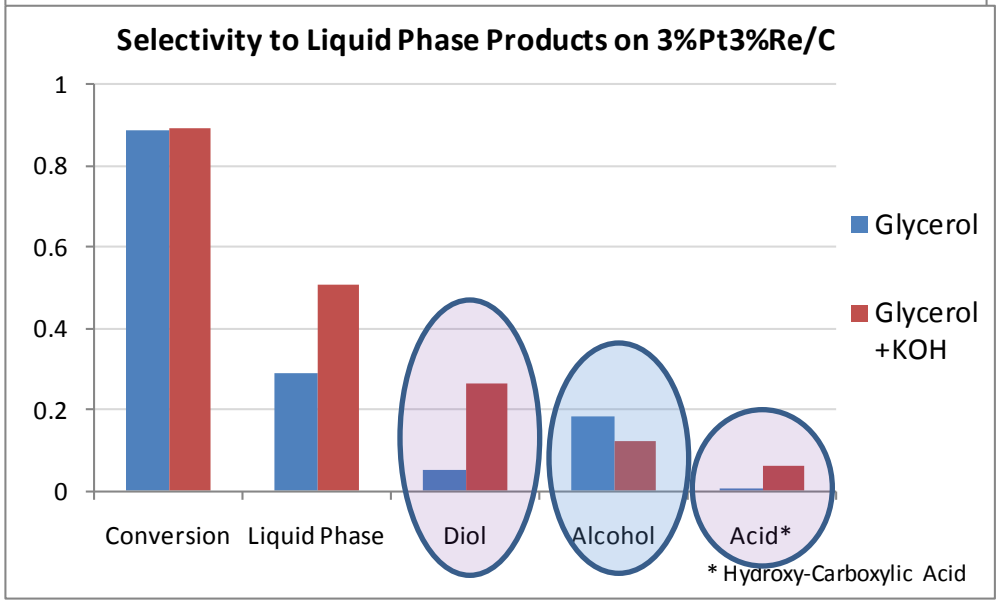


- Lower hydrogen selectivity with addition of Re indicates more hydrogen consumed by dehydration pathways
- Dehydration pathways result in less accumulation of diols and more formation of alcohols and C_2^+ alkanes

Effect of Addition of KOH on Glycerol APR over Pt-Re/C







- Addition of KOH neutralizes acidity of ReOx and depresses dehydration pathways over Pt-Re/C, resulting in less alkanes and alcohols
- Lower selectivity to dehydration results in higher RHY
- KOH also facilitates the Canizzaro reaction, resulting in more acids and diols in the liquid products

Conclusions on Pt-Re and the Role of Re

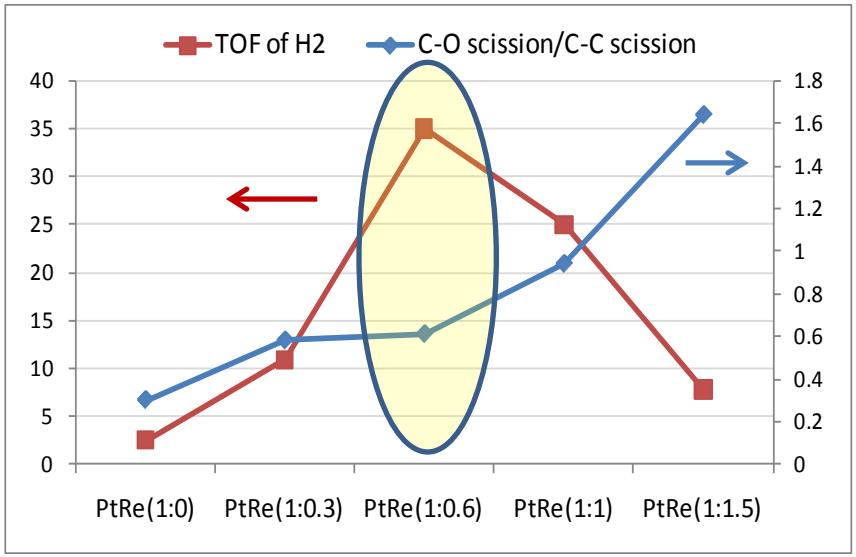
- Pt facilitates the reduction of Re
- Reduction at 280°C is required to fully reduce Re and maximize the catalyst activity.
- Under reaction conditions, the surface of Pt-Re/C appears to consist of
  - A PtRe bimetallic phase
  - A ReOx-rich phase
- Re increases the activity of the Pt/C catalyst by:
  - Electronic effect – charge migration in PtRe bimetallic particles
  - Facilitating dehydration pathways → ReOx rich phase (acid sites)
- Addition of base neutralizes the acidity of ReOx and results in lower alkane selectivity and higher H_2/CO_2

Potential Linkage of APR with Solid Oxide Fuel Cell (SOFC) Operation

- SOFC is more tolerant of impurities and flexible in feedstock than PEMFC, for example CH_4 byproduct has feedstock value with SOFC
- Orienting the APR product distribution toward a SOFC-compatible feed might provide benefits in catalyst operation and/or process efficiency
- Our results have shown that high H_2 selectivity and methane/alkane selectivity can be achieved by adjusting reaction conditions such as flow rate and adding base

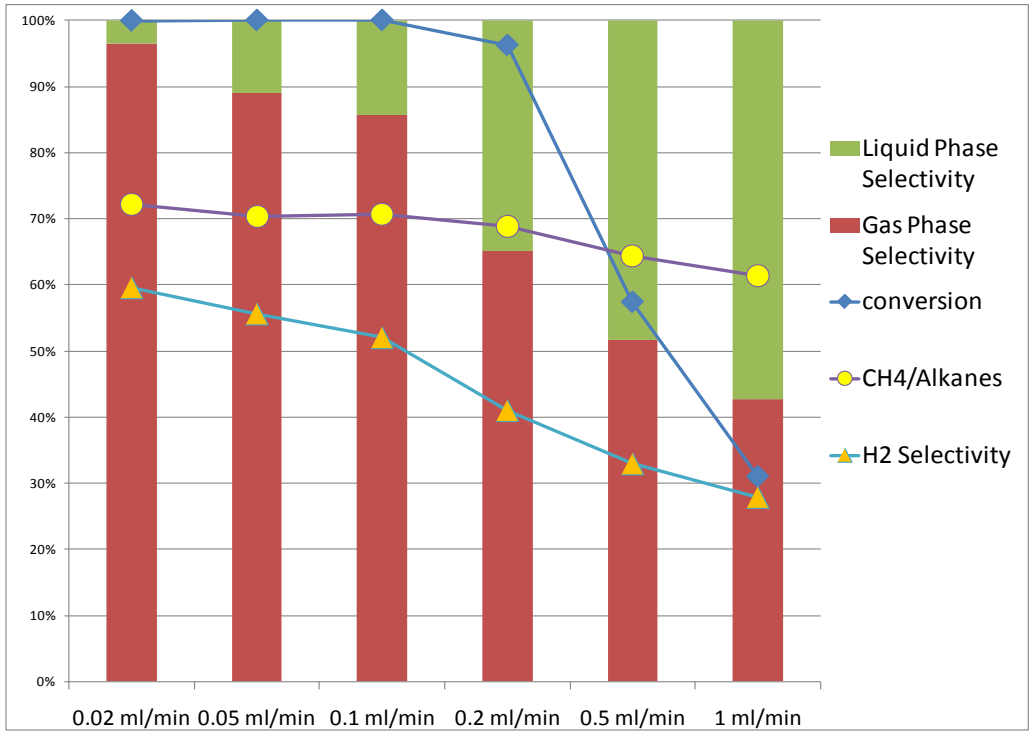
Study of Glycerol APR for SOFC Application

Catalyst Composition Study



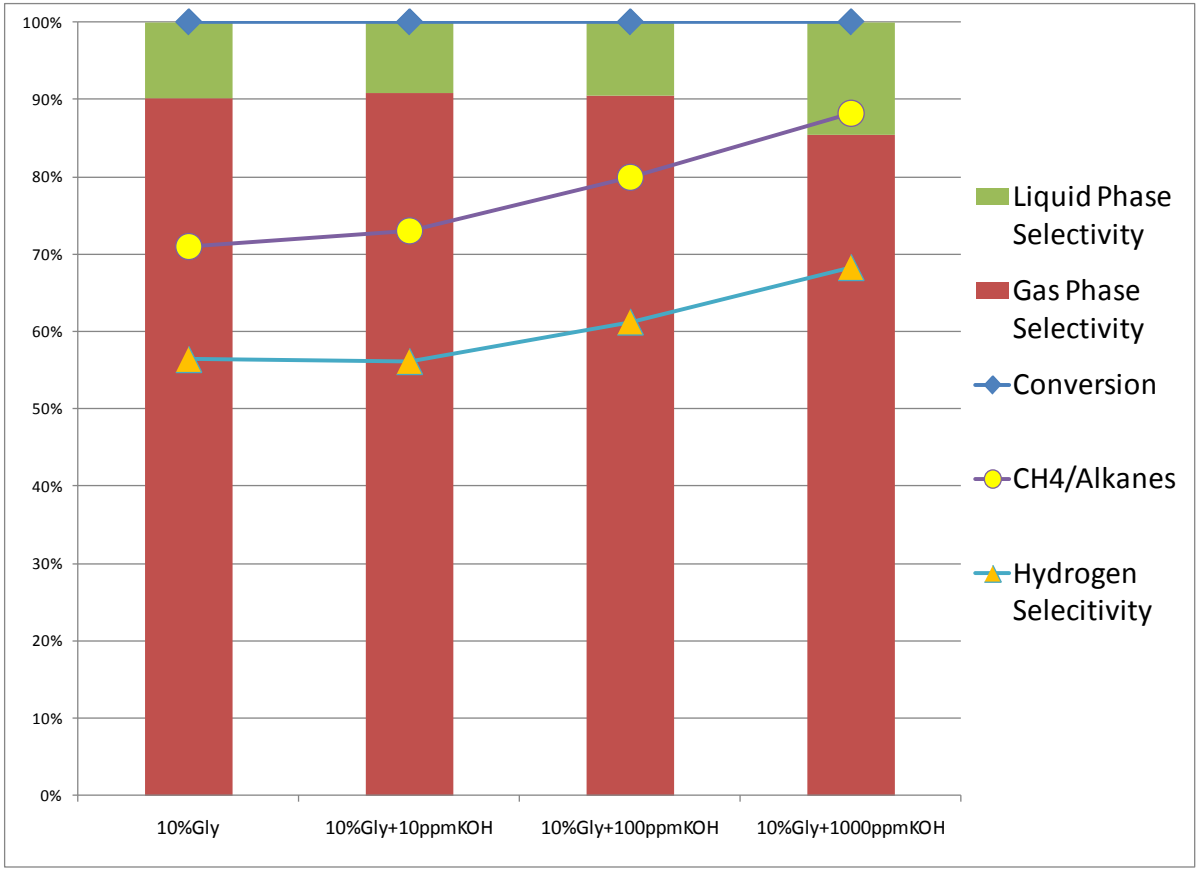
200 mg of catalyst, 225 ºC, 420 psig, 0.2ml/min

Effect of Residence Time over 5%Pt-3%Re/C



- By lowering flow rate and increasing residence time, high H_2 and CH_4 selectivity can be achieved with minimal liquid phase byproduct.

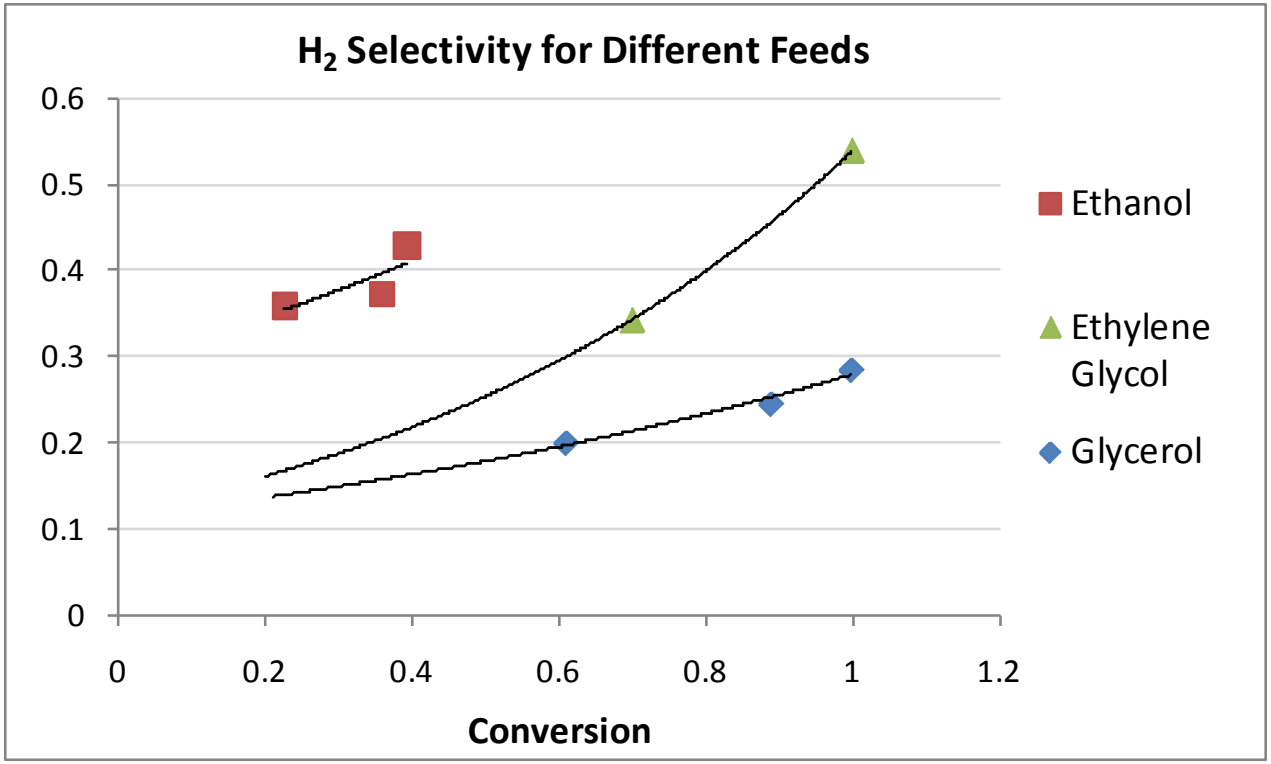
Study of Glycerol APR for SOFC Application with Base Addition



- At 100% conversion, addition of base increases hydrogen selectivity and depresses production of C_2^+ alkanes, favoring CH_4

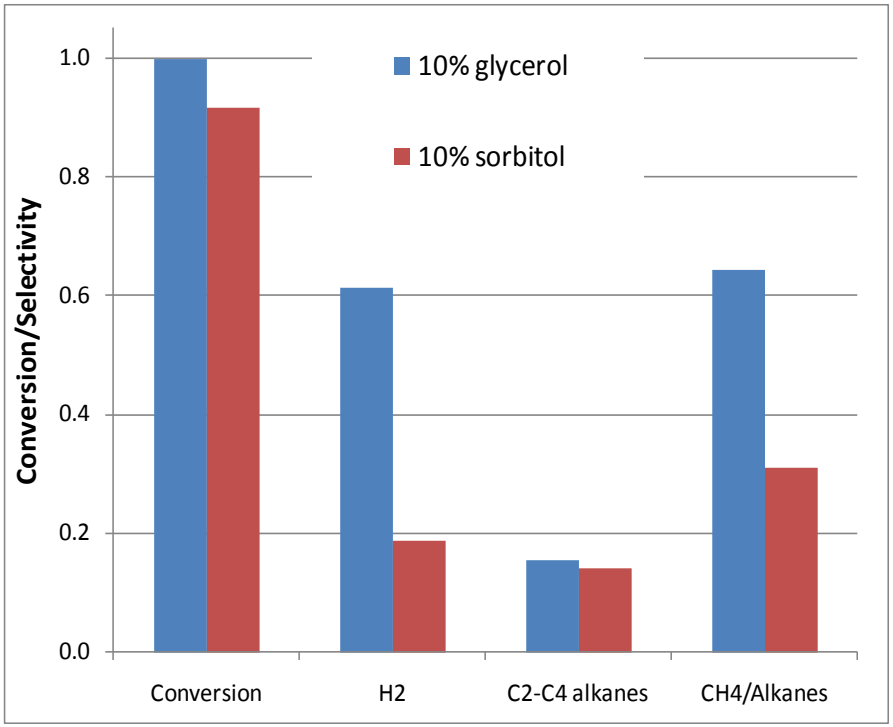
Extend the Lesson Learned to APR of Sorbitol

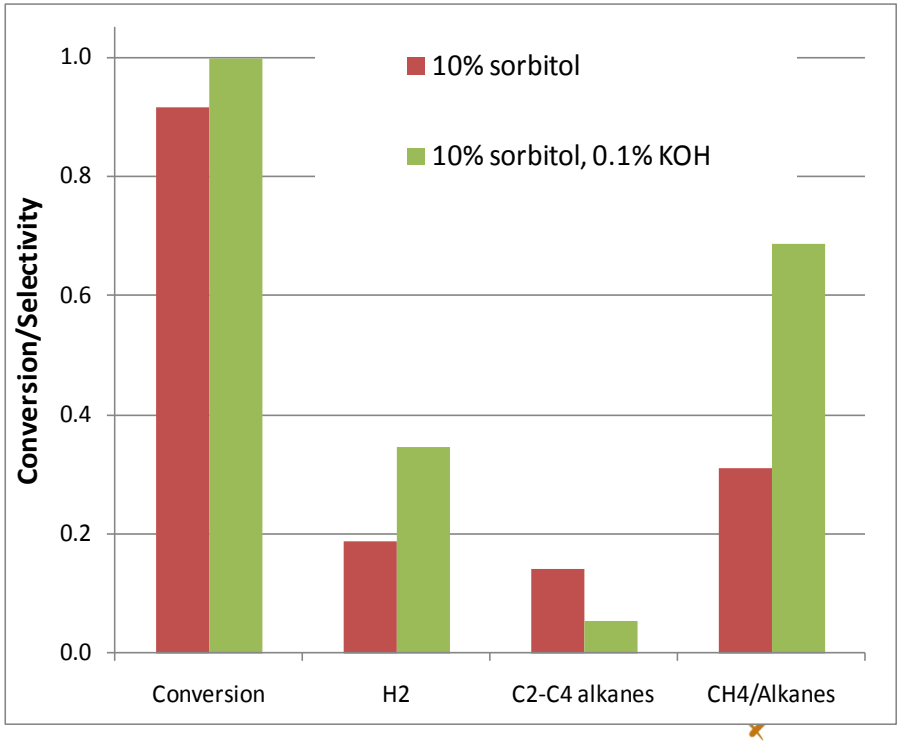
- Dehydration is more favored on polyols and longer chain polyols which results in lower H_2 selectivity.



APR of Sorbitol

- 5%Pt-3%Re/C showed the highest activity and selectivity
- Conditions favoring high H_2 selectivity:
  - 225-230°C and 370-415 psig
  - Longer contact time
  - Addition of base
- Hydrogen selectivity is lower with sorbitol than with glycerol under otherwise similar conditions





Preliminary Economic Analysis on Bio-Liquid Aqueous Phase Reforming for SOFC Feed

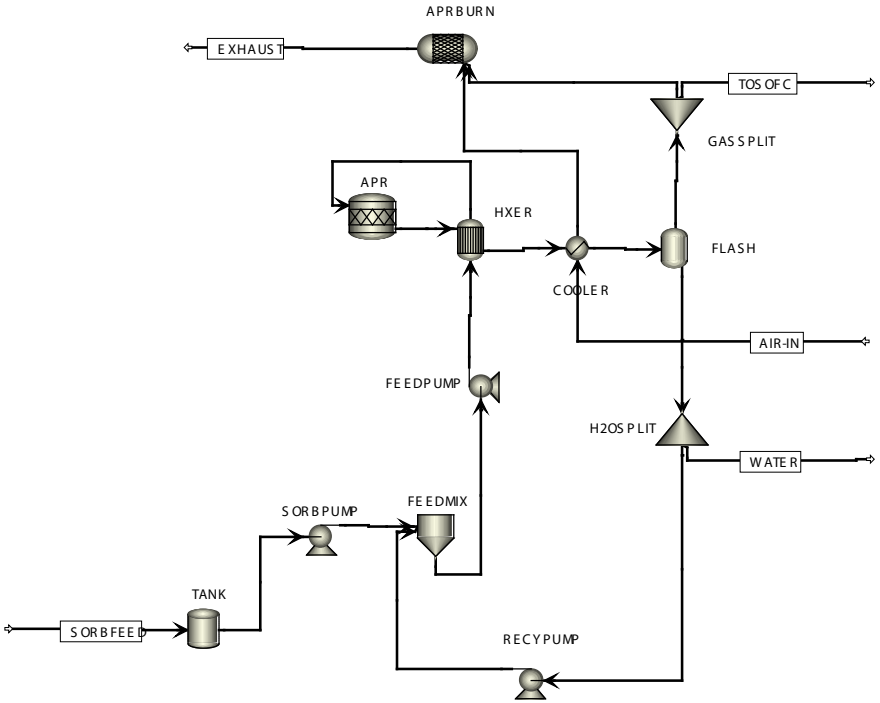
Bio-Alcohol Fuel Options

- Ethanol, Glycerol (refined), and Sorbitol (70 wt%) are all currently priced at about $0.30/lb.
- Energy content per gallon much higher for ethanol.
- Current $/MMBtu (based on HHV of fuel)
  - Ethanol - $21/MMBtu
  - Glycerol - $39/MMBtu
  - Sorbitol - $60/MMBtu

Bio-Alcohol Markets

- Ethanol already established as significant liquid fuel.
- Byproduct production of glycerol from biodiesel production is driving glycerol price down. European requirements for increased biodiesel use is expected to drive glycerol price down further.
- Sorbitol price primarily driven by market for high-fructose corn syrup, but can be produced from any source of glucose.

Aqueous Phase Reforming of Sorbitol



Pacific Northwest
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Performance

- Reformate Fuel Per Mole Sorbitol
  - Hydrogen – 6.6 mole
  - Methane – 1.0 mole
  - Ethane – 0.2 mole
  - Propane – 0.1 mole
- Conversion Efficiency = 79% if reformate provides reformation energy
- Conversion Efficiency = 109% if SOFC provides reformation energy

APR Direct Capital Costs
(ASPEN Process Economic Evaluator; March 31 2008 dollars)

Process Sized for 1 MW SOFC
First-Cut Design

Component	Direct Equipment, Material & Labor
Aqueous Phase Reformer	294,200
Reformate Cooler	236,700
APR Feed Mixing Tank	163,100
Reformate Flash Tank	123,600
APR Feed Preheater	140,700
Sorbitol Feed Pump	31,400
High Pressure Pump	74,300
Recycle Pump	31,300
Sorbitol Storage Tank	250,600
Total	**1,345,900**

Levelized Cost of Reformate $/kg H_2-equivalent

- Energy content of reformate constituents combined into equivalent quantity of hydrogen
- Cost includes feedstock, capital, and annual O&M costs
- Uses standard H2A assumptions for indirect construction costs, and annual O&M for distributed H_2 production.
- Levelized cost calculated for four scenarios.
  - $0.30/lb and $0.12/lb 70% sorbitol feedstock costs
  - Use of reformate or SOFC waste heat for reforming energy

Levelized Cost Results, $/kg H_2-equivalent

Sorbitol feedstock represents 95+% of hydrogen cost

Reforming Energy Source	70% Sorbitol @ $0.12/lb	70% Sorbitol @ $0.30/lb
Fuel Cell Waste Heat	3.06	7.61
Reformate	4.29	10.65