

Hydrogen Production via Reforming of Bio-derived Liquids

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U.S. Department of Energy
Bio-Derived Liquids to Hydrogen Distributed Reforming Working Group
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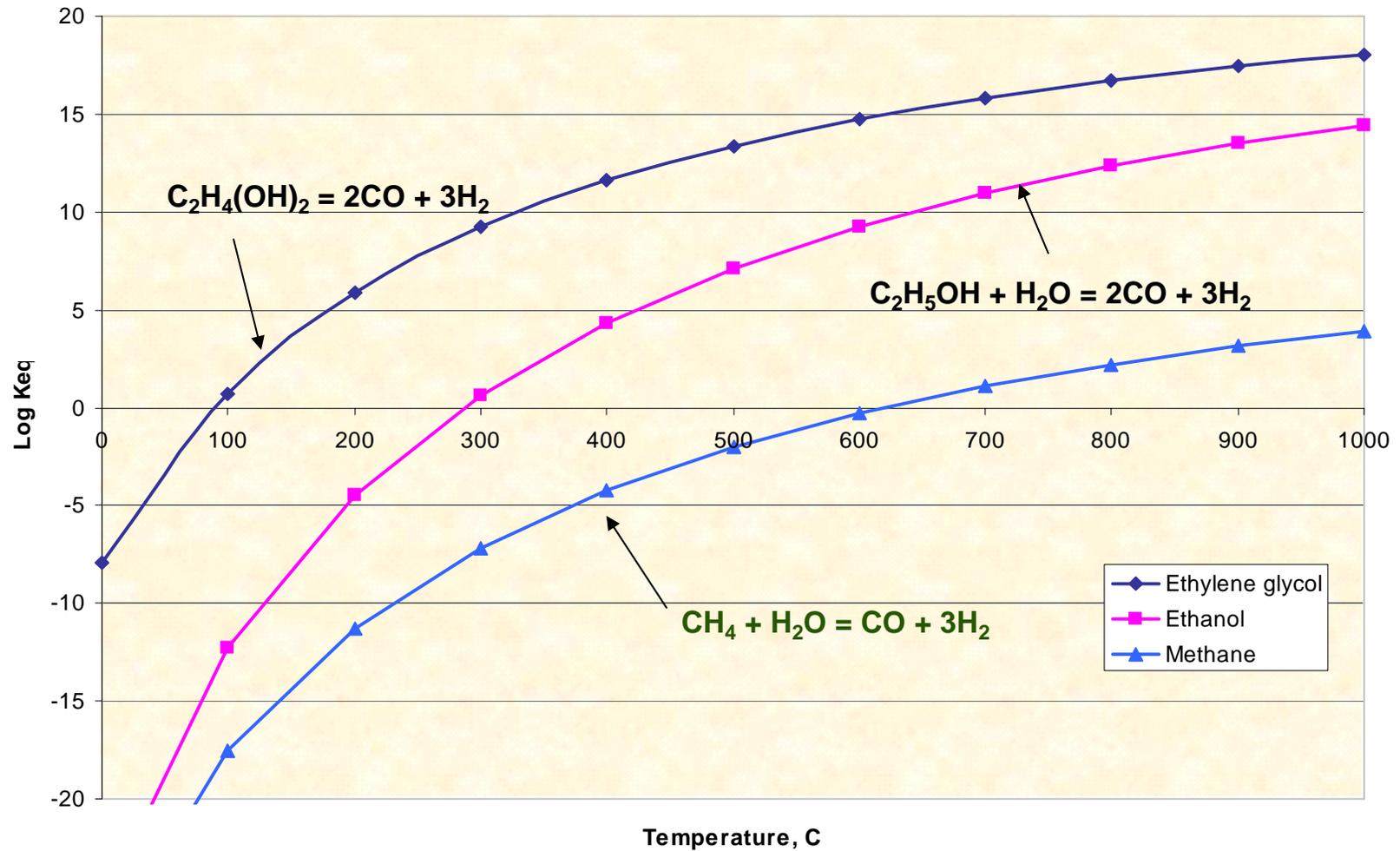
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Hydrogen Potential from Different Feedstocks

Feedstock	Formula	MW feedstock	moles/kg	moles H ₂ / mol feed	g H ₂ / kg feed	g H ₂ /kg feed w/wgs
Methanol	CH ₃ OH	32	31.3	2	125	188
Ethanol	C ₂ H ₅ OH	46	21.7	4	174	261
Ethylene glycol	C ₂ H ₆ O ₂	62	16.1	3	97	161
Glycerol	C ₃ H ₈ O ₃	104	9.6	4	77	135
Glucose	C ₆ H ₁₂ O ₆	180	5.6	6	67	133
Sorbitol	C ₆ H ₁₄ O ₆	182	5.5	7	77	143
Hexane	C ₆ H ₁₄	86	11.6	13	302	442
Methane	CH ₄	16	62.5	3	375	500

Thermodynamic Considerations



Aqueous Phase Reforming

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Advantages of Aqueous Phase Reforming

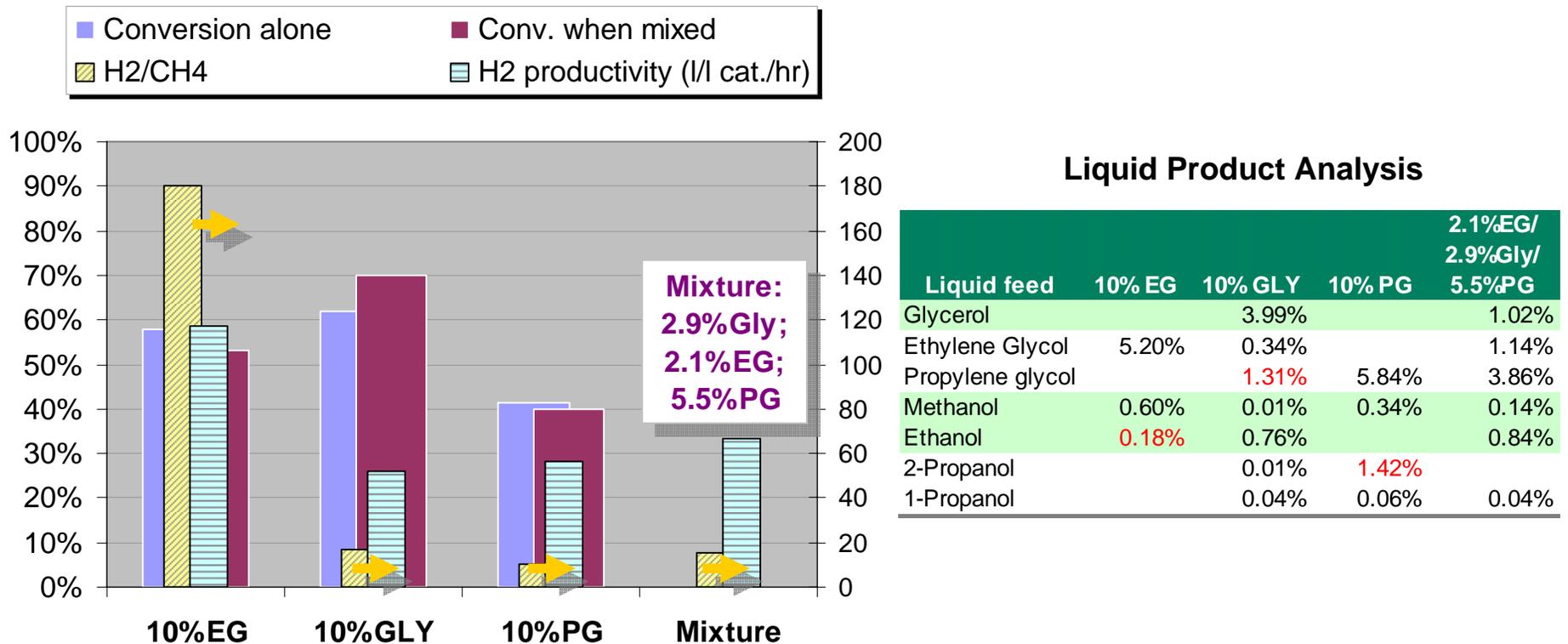
- **Eliminates energy required to vaporize water**
- **Allows processing of bioproducts that cannot be vaporized without decomposition**
- **Operates at low temperatures compared with conventional reforming, reducing energy costs**
- **Water gas shift reaction occurs simultaneously with reforming**
- **Pressurized product is compatible with membrane or pressure swing H₂ purification**

Early Results With Plug Flow Reactor

	current	literature*	current	literature*
Catalyst	3%Pt/Al ₂ O ₃			
Feed	10% sorbitol/H ₂ O	1% sorbitol/H ₂ O	10% sorbitol/H ₂ O	1% sorbitol/H ₂ O
Temperature, °C	225	225	265	265
Feed rate (g sorbitol/g catalyst-h)	0.08	0.008	0.08	0.008
Sorbitol conversion, %	88.3		99.9	
Carbon % in gas phase product, %	58.3	61.0	95.7	90.0
H ₂ productivity (l H ₂ /l catalyst-h)	91.3		140.9	
Gas phase composition, mole%				
H ₂	58.9	61.0	57.0	54.0
CO ₂	35.5	35.0	33.8	36.0
CH ₄	4.7	2.5	7.2	6.0
C ₂	0.9	0.7	2.2	2.3
H ₂ /CH ₄	12.5	24.4	8.1	9.0
H ₂ /CO ₂	1.7	1.7	1.7	1.5

* R.D. Cortright, R.R. Davda & J.A. Dumesic, *Nature* 418 (2002) 964

Polyols Study With 3% Pt/Al₂O₃ Catalyst



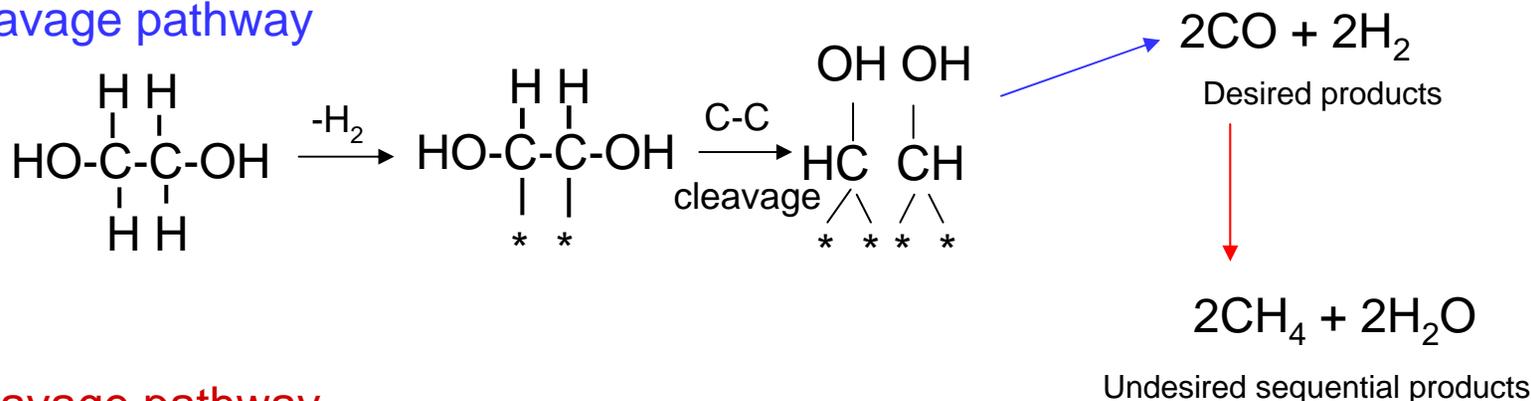
➤ **Feedstock dependence**

- Conversion: GLY>EG>PG, H₂/CH₄ ratio: EG>>GLY>PG, H₂ productivity: EG>GLY≈PG

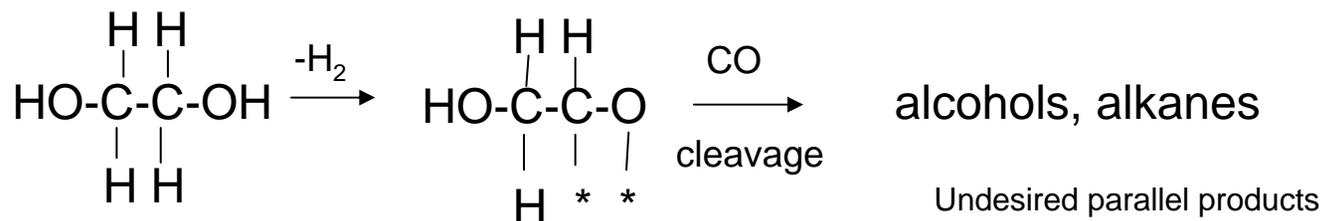
➤ **Mixed feed test showed enhanced glycerol conversion, suppressed ethylene glycol conversion, and lower than anticipated H₂/CH₄ ratio – indicates competitive adsorption occurs**

Kinetic Control of Reaction Pathways* is Essential For Good Hydrogen Production

C-C cleavage pathway



C-O cleavage pathway



Good catalyst should have good C-C cleavage and water gas shift activity, low C-O bond cleavage and methanation activity

* Adapted from Davda et. al., *Appl. Catal. B*, **56** (2005), 171-186

Effect of Feed Rate on Sorbitol Products (Microchannel Reactor, Virent Catalyst)

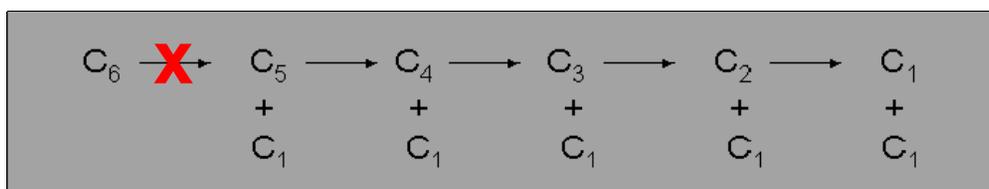
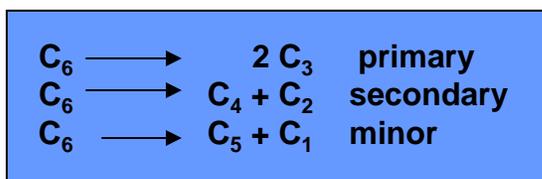
Run Temp. °C	225	225	225	225
BPR (psi)	420	420	420	420
Sorbitol Conc. (wt%)	10%	10%	10%	10%
WHSV (g sorbitol/g-cat/h)	1.0346	2.0692	3.1038	4.1384
Contact Time, min	7.68	3.84	2.56	1.92
Sorbitol Conversion	100.0%	96.8%	88.3%	78.7%
% Carbon in gas-phase effluent	71.55%	56.28%	36.30%	22.57%
Hydrogen	54.13%	52.22%	49.15%	47.23%
CO ₂	37.72%	41.44%	44.77%	46.64%
Ethane+ethylene	2.06%	1.70%	1.58%	1.48%
Methane	6.09%	4.49%	4.29%	4.43%
CO	0.00%	0.15%	0.21%	0.23%
H ₂ /CH ₄	8.90	11.63	11.46	10.67
H ₂ /C ₂	26.30	30.73	31.08	31.99

- Liquid products at incomplete conversion of sorbitol may provide information on reaction pathways and intermediates
- Higher space velocities result in greater production of liquid products with only modest changes in gas phase product composition

Effect of Feed Rate on Sorbitol Products (Microchannel Reactor, Virent Catalyst)

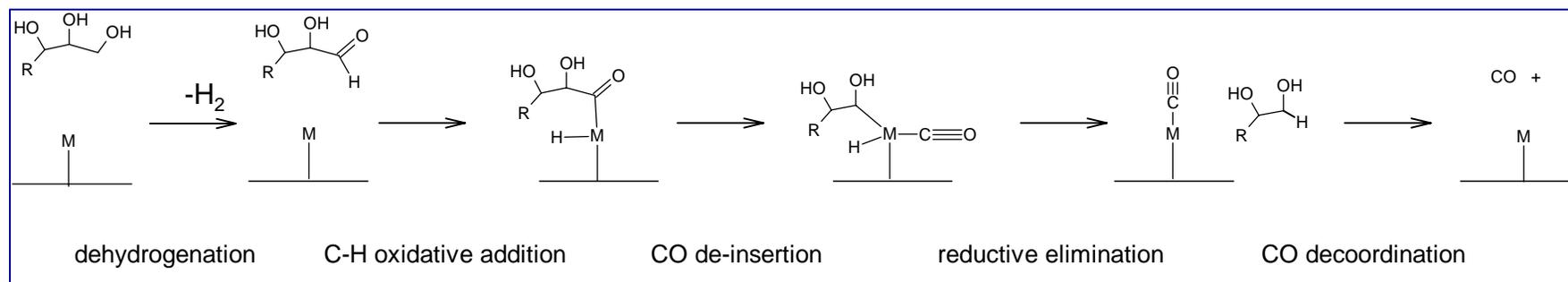
WHSV g sorbitol/g catalyst-h)	1.0	2.1	3.1	4.1
Liquid phase composition (wt%)				
Glucose (C ₆ H ₁₂ O ₆)	0.036	0.029	0.037	0.05
Sorbitol (C ₆ H ₁₄ O ₆)	0.002	0.33	1.23	2.172
Glycerate (C ₃ H ₅ O ₄)		0.153	0.307	0.347
Xylitol (C ₅ H ₁₂ O ₅)	0.004	0.107	0.236	0.29
Erythritol + threitol (C ₄ H ₁₀ O ₄)		0.191	0.316	0.342
Glycerol(C ₃ H ₈ O ₃)	0.004	0.504	0.822	1.018
1,2,4-Butanetriol (C ₄ H ₁₀ O ₃)		0.09	0.132	0.144
Acetic acid (C ₂ H ₄ O ₂)	0.075	0.1	0.098	0.085
Ethylene Glycol (C ₂ H ₆ O ₂)		0.275	0.39	0.428
Propylene glycol (C ₃ H ₈ O ₂)		0.796	0.897	0.941
1,3-Propanediol (C ₃ H ₈ O ₂)	0.001	0.168	0.161	0.219
Methanol (CH ₃ OH)		0.171	0.199	0.154
1,2-Butanediol(C ₄ H ₁₀ O ₂)		0.148	0.166	0.162
Ethanol(C ₂ H ₆ O)	0.036	0.261	0.235	0.216
2-Propanol(C ₃ H ₈ O)	0.223	0.182	0.128	0.088
1-Propanol(C ₃ H ₈ O)		0.147	0.167	0.12

- Glycerol and propylene glycol are most predominant products
- C₄ and C₂ polyols are in approximate balance
- Oxygenated products are more consistent with random C-C cleavage than sequential C₁ cleavage



Reaction Pathways

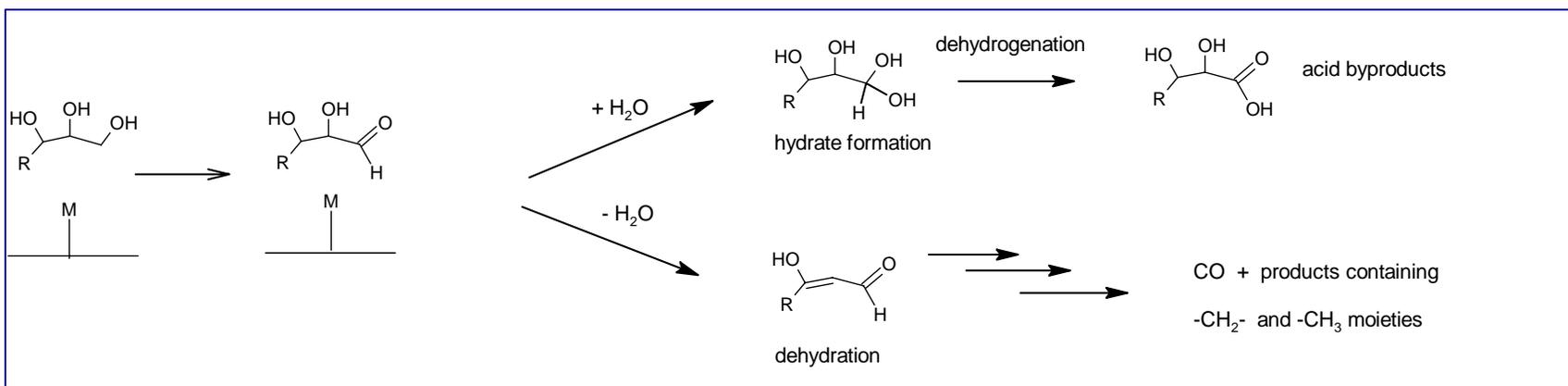
- **Random C-C cleavage reduces hydrogen selectivity**
 - Production of glycerol from sorbitol requires hydrogenation
$$\text{C}_6(\text{OH})_6\text{H}_8 + \text{H}_2 \rightarrow 2 \text{C}_3(\text{OH})_3\text{H}_5$$
 - Production of propylene glycol from glycerol requires combination of hydrogenation plus dehydration
$$\text{C}_6(\text{OH})_6\text{H}_8 + 3\text{H}_2 \rightarrow 2 \text{C}_3(\text{OH})_2\text{H}_6 + 2\text{H}_2\text{O}$$
- **Catalyzed terminal cleavage, if possible, could lead to improved hydrogen selectivity**



First step is dehydrogenation to form the corresponding aldehyde;
Wilkinson's catalyst (organometallic); heterogeneous examples?

Origins of Reaction By-products

- Hydration followed by dehydrogenation of aldehyde hydrate leads to acid formation.
- Dehydration (to α, β -unsaturated carbonyls) generates methane and products containing $-\text{CH}_2-$ and $-\text{CH}_3$ moieties
 - Maximizing hydrogen production requires avoiding dehydration of reaction intermediates that subsequently hydrogenate to final alkane products



Hydrate formation and dehydration are usually acid- or base-catalyzed reactions and might be promoted by the catalyst support (Al_2O_3). Understanding support effects could be critical to improving selectivity.

Conclusions and Path Forward

– Aqueous Phase Reforming

Conclusions

- Identifying reaction intermediates can be important for catalyst design to increase hydrogen selectivity and productivity
- Catalyst modification may help hydrogen selectivity through controlling certain classes of reactions

Path Forward

- Focus on the sorbitol and xylitol feedstocks and improve hydrogen productivity by better understanding and controlling
 - Formation of intermediates
 - Reaction pathways of these intermediates
- Innovate the reaction engineering to improve the space time yield of hydrogen.

Hydrogen Production from Steam-reforming of Ethanol

➤ “Bioethanol”

- Higher energy density than lithium ion batteries
- Clean and renewable - potentially CO₂ neutral
- Cost competitive
 - selling price decreased from \$5.66/gge in 2001 to \$2.26/gge in 2005
- Low temperature activation possible

➤ Steam reforming of ethanol

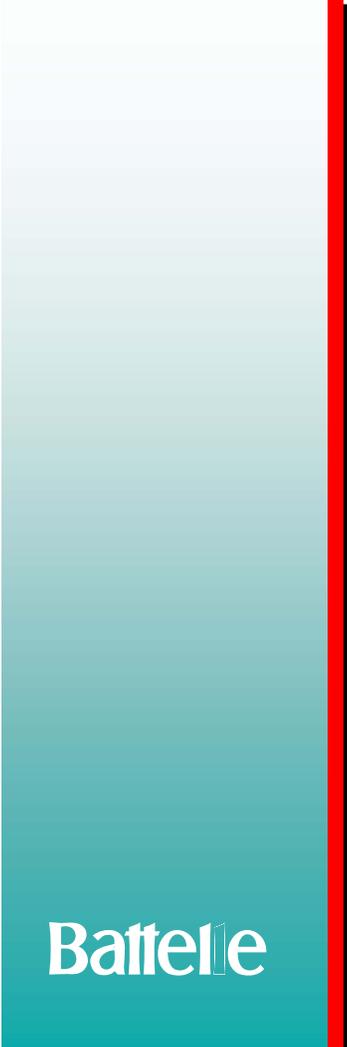
- As-fermented aqueous solution has a water/alcohol ratio: ~6:1 to 9:1+
- Reforming fermentation-derived feedstocks reduces the cost associated with the purification

Ethanol Aqueous Phase Reforming

T, WHSV, Concentration Effects (MC Reactor, Virent Catalyst)

Run Temp. °C	225	225	225	230	235	225
Pressure, psi	441	440	442	482	520	463
EtOH Conc. (wt%)	10%	10%	10%	10%	10%	20%
WHSV (g substrate/g-cat/h)	1.03	3.08	5.14	5.14	5.14	2.04
EtOH Conversion, %	99.6%	82.3%	66.9%	78.0%	85.2%	92.9%
% Carbon in gas-phase effluent	89.6%	74.1%	55.3%	70.9%	81.8%	81.8%
% Carbon in liquid-phase effluent	1.3%	21.8%	37.4%	26.6%	18.9%	8.8%
Carbon Balance	90.9%	95.9%	92.7%	97.6%	100.8%	90.6%
Hydrogen Productivity (STD L/L-cat/h)	626.2	1687.2	2188.3	2682.9	3062.2	1175.4
Product Composition, %						
Hydrogen	48.57%	50.69%	51.87%	50.63%	50.32%	49.48%
CO ₂	24.21%	23.54%	22.11%	23.75%	24.05%	24.37%
Ethane	0.99%	1.02%	1.29%	1.10%	1.02%	0.88%
Methane	26.23%	24.67%	24.58%	24.39%	24.49%	25.26%
CO	0.00%	0.09%	0.16%	0.12%	0.11%	0.00%
H ₂ /CH ₄	1.85	2.06	2.11	2.08	2.05	1.96
H ₂ /C ₂	49.13	49.89	40.21	45.90	49.11	56.26
H ₂ /CO ₂	2.01	2.15	2.35	2.13	2.09	2.03
Liquid Analysis						
Acetic acid (C ₂ H ₄ O ₂)	0.186	0.904	0.941	0.964	0.895	0.902
1,3-Propanediol (C ₃ H ₈ O ₂)		0.004	0.003	0.0104	0.00583	
Ethanol(C ₂ H ₆ O)	0.044	2.042	3.656	2.462	1.686	2.022
2-Propanol(C ₃ H ₈ O)	0.014	0.006	0.004	0.004	0.004	0.006
Unkown		0.012		0.0154	0.0135	0.0258

- No need to vaporize the excess water in bio-ethanol (8-12wt% ethanol), pressurized reformat readily for membrane separation
- Stable catalyst life (>300 hrs)
- Excellent CO₂ selectivity (nearly 100% efficiency in WGS)
- H₂ productivity approximately doubled when ethanol feed concentration increases from 10 to 20%
- Relatively low productivity 3000 l/l/hr at 235°C vs 48,000 l/l/hr at 350°C (vapor phase reforming)
- Equal molar of CH₄ and CO₂ formation
- Acetic acid is primary product observed in liquid phase effluent



Vapor Phase Reforming of Ethanol

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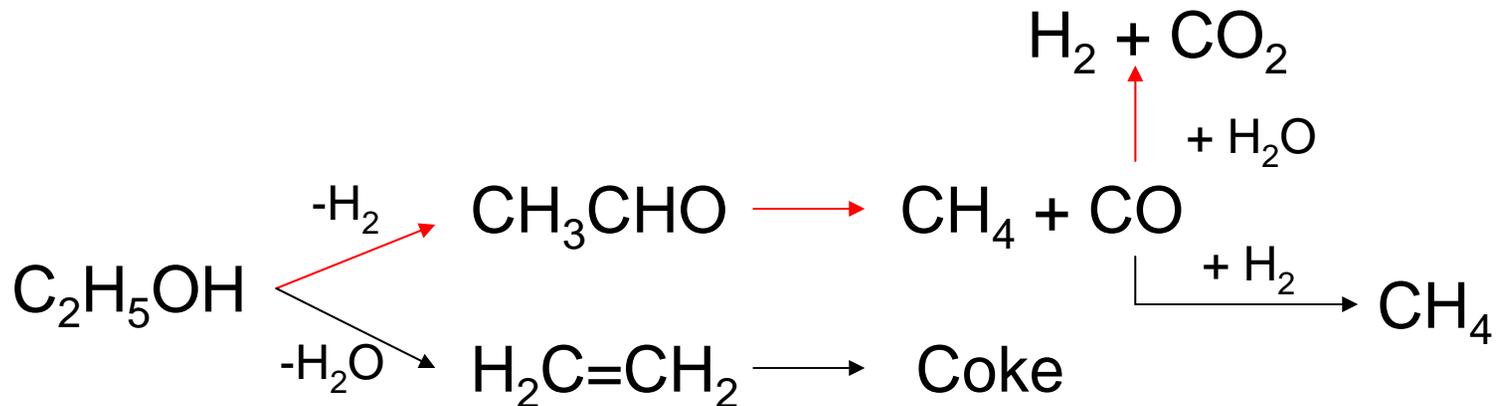
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Ethanol Vapor Phase Reforming

- **Low temperature SR (<500°C)**
 - Potentially less energy intensive
 - More directly matches with H₂ membrane separation
 - Catalyst deactivation poses challenges
- **High temperature SR (>500°C)**
 - High temperatures facilitates subsequent conversion of parallel product methane
 - Need CO clean up unless for SOFC
 - Catalyst deactivation could be masked by excess activity
- **Oxidative SR (e.g., work at U of Minnesota and Penn State)**
 - Stable catalyst life
 - Dilution of N₂ in reformat
 - Not amenable to membrane separations

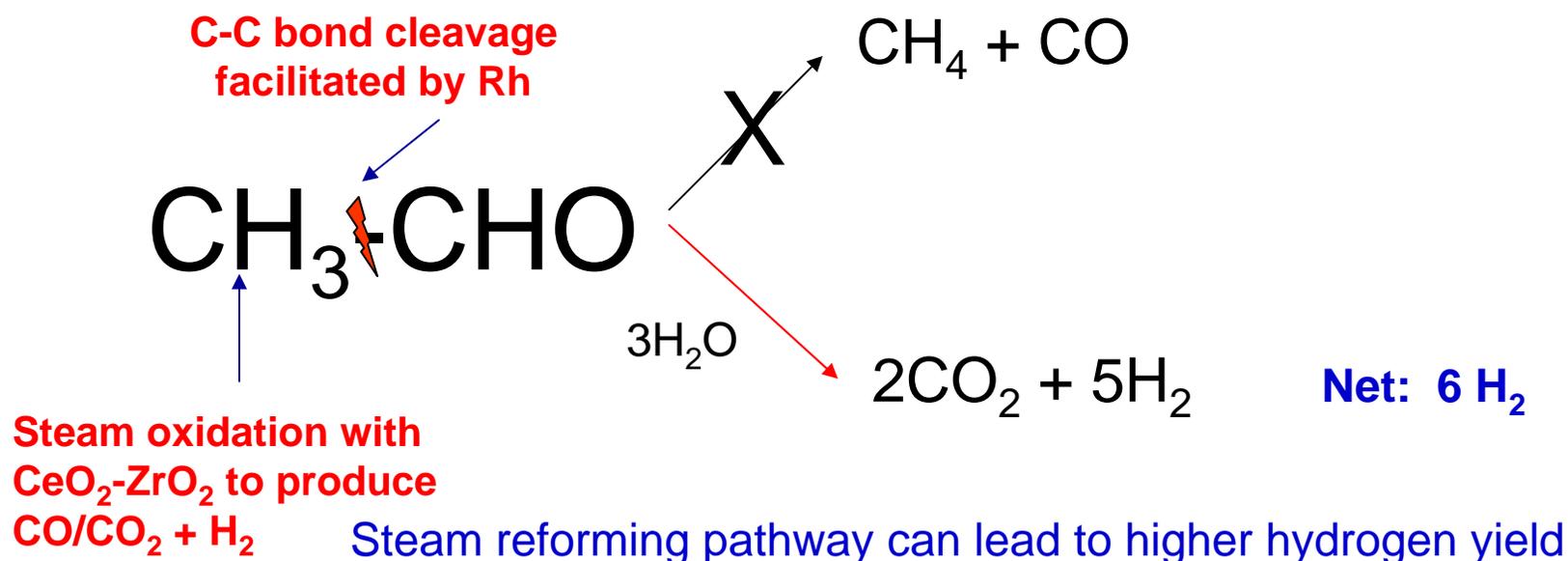
Possible Pathways for SR of Ethanol

Theoretical yield: 6 mol H₂ / mol EtOH



- Dehydrogenation is a preferred pathway to minimize coke formation
- Low methanation activity is desired
- At low temperatures, methane is more difficult to activate – likely forming a 50% CO+CO₂ and 50% CH₄ product mixture via acetaldehyde decomposition

Concept: Increase Hydrogen Selectivity Through CH_3CHO Intermediate

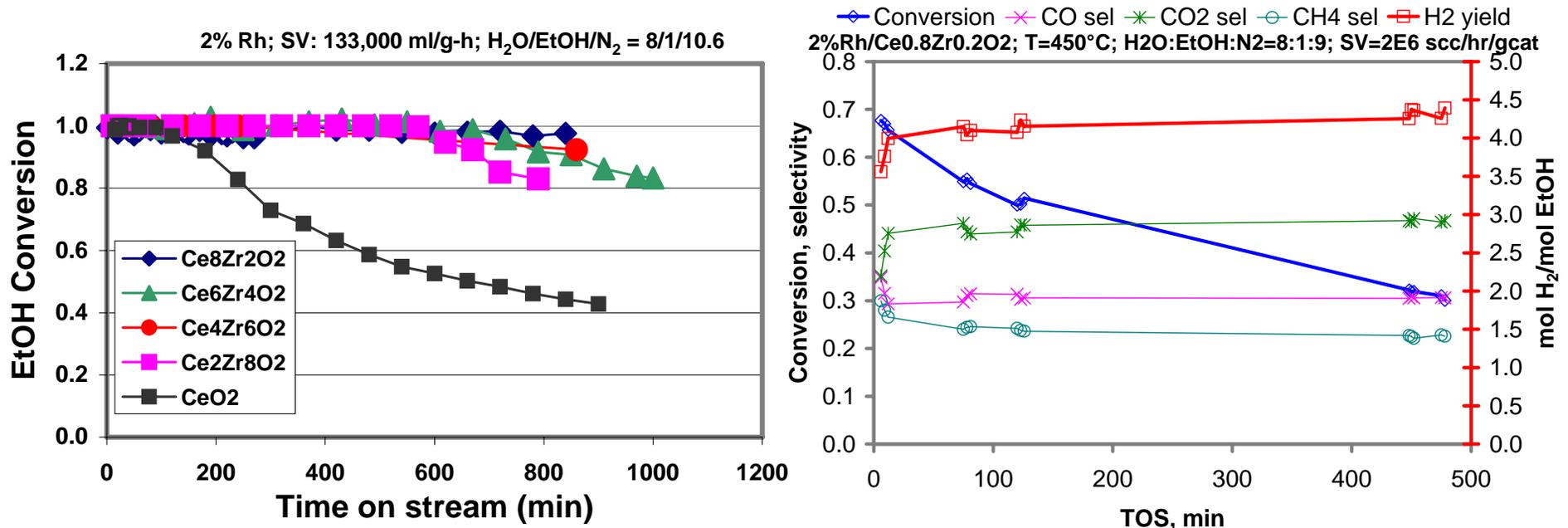


Previous work with 2wt%Rh on CeO₂-ZrO₂

Catalyst	X _{EtOH} (%)	H ₂ /EtOH (m/m)	S _{CH4} (%)	S _{CO} (%)	S _{CO2} (%)
2%Rh/Ce _{0.8} Zr _{0.2} O ₂	100	4.3	25	11	64
2%Rh/Ce _{0.6} Zr _{0.4} O ₂	100	4.0	26	18	56
2%Rh/Ce _{0.4} Zr _{0.6} O ₂	100	4.0	27	20	53
2%Rh/Ce _{0.2} Zr _{0.8} O ₂	95	3.6	28	21	50
2%Rh/CeO ₂	53	1.9	22	32	39

450°C, SV: 133,000 ml/g-h; H₂O/EtOH/N₂ = 8/1/10.6, Data obtained at 10 h TOS

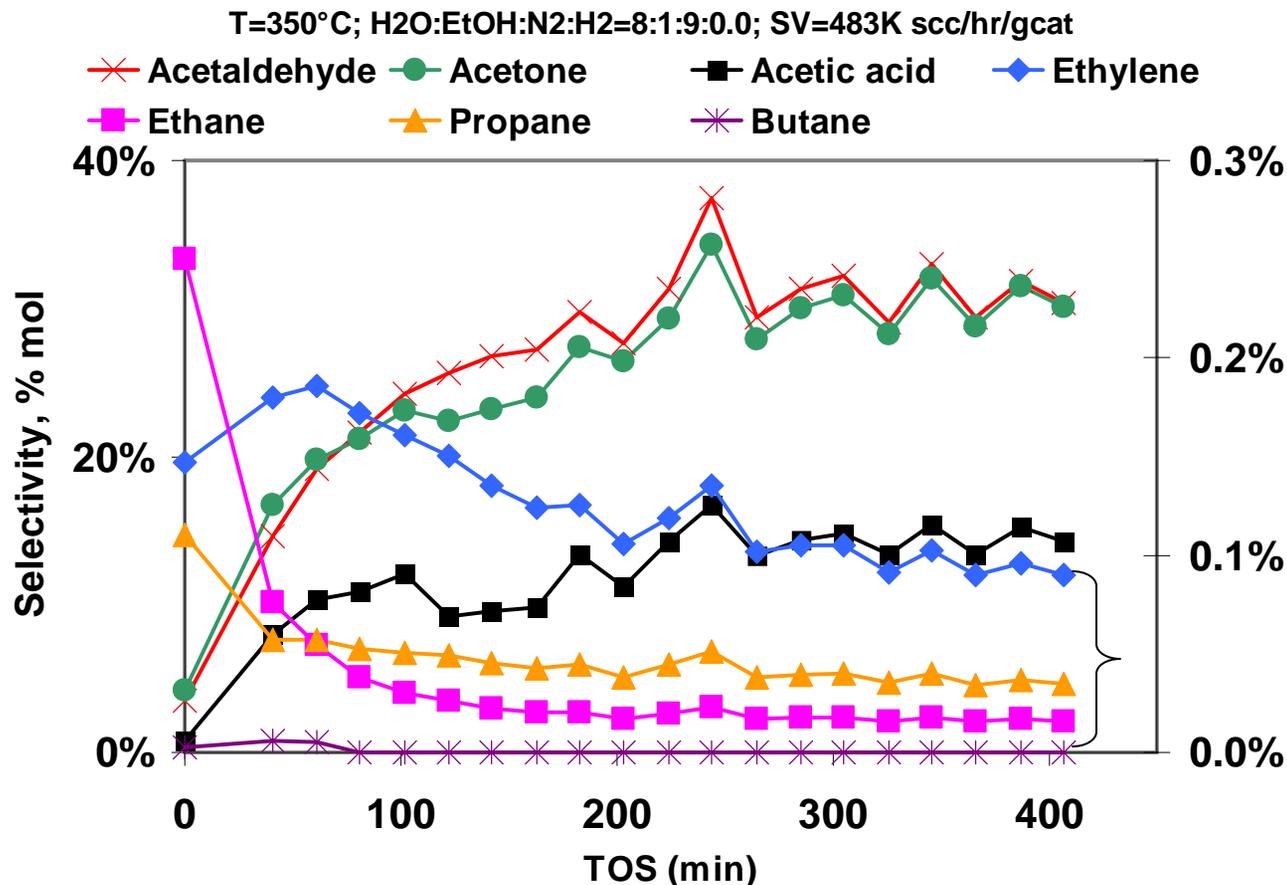
Catalyst Deactivation Issues



- At lower SV (133,000 cc/g/hr), deactivation was observed at TOS > 600 min
- At higher SV (2,000,000 cc/g/hr), a continuous deactivation was observed although selectivities to CO, CO₂, CH₄ were unchanged

Causes of deactivation?

Other Products Can Be Monitored During Reaction and Deactivation



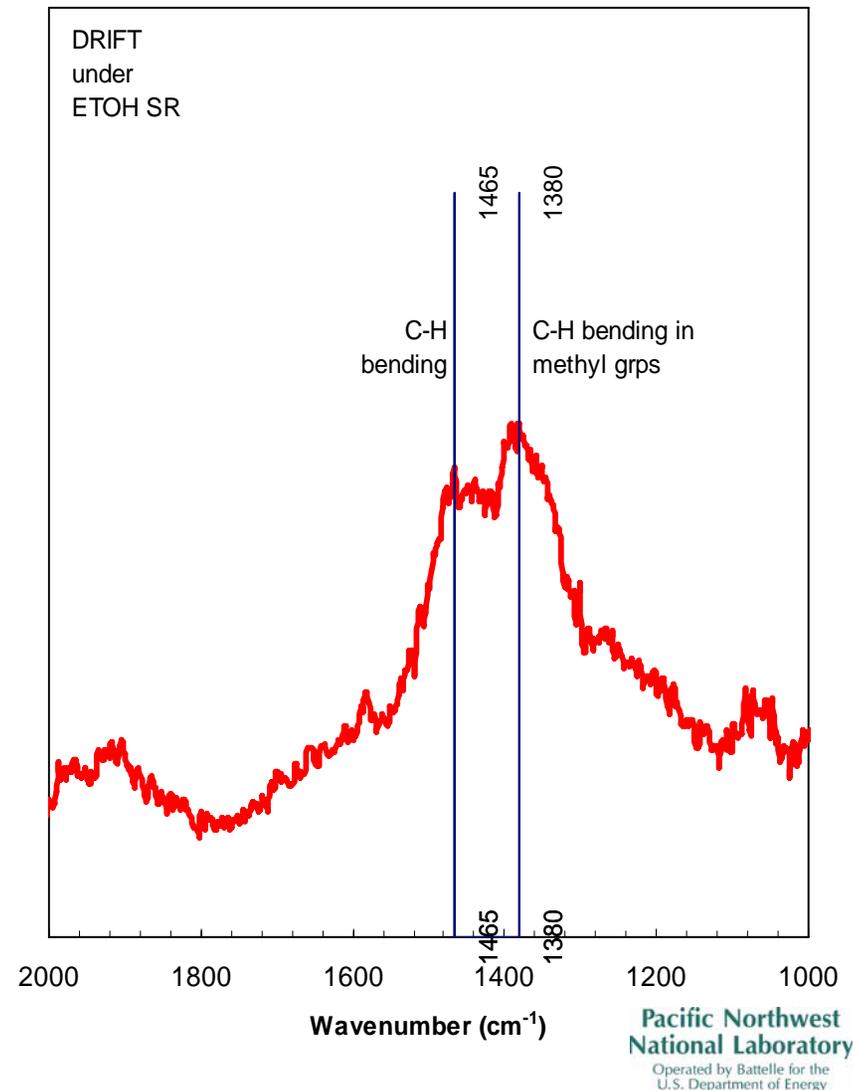
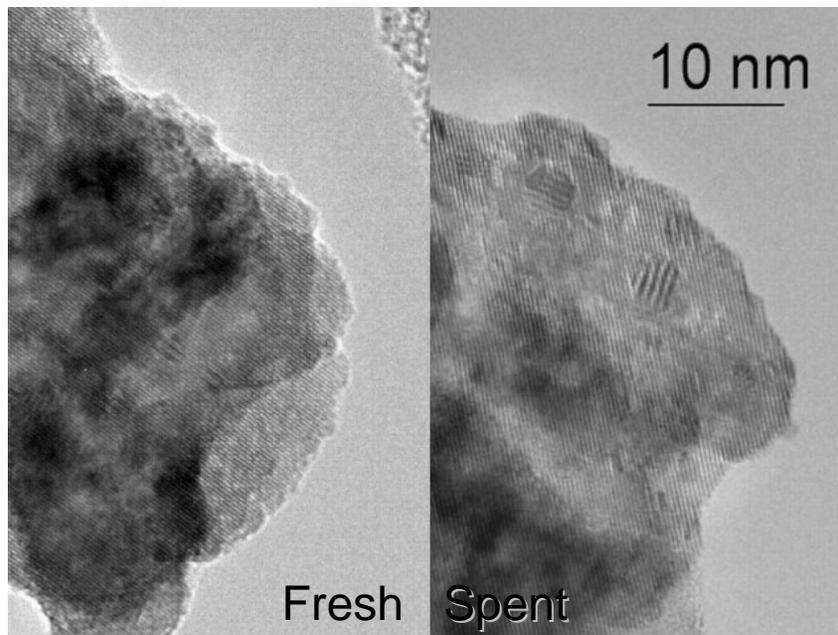
- Major byproducts/intermediates are the oxygenates acetaldehyde, acetone, and acetic acid, and they increase as catalyst deactivates
- Hydrocarbon byproducts decrease as catalyst deactivates

Examination of Catalyst Deactivation

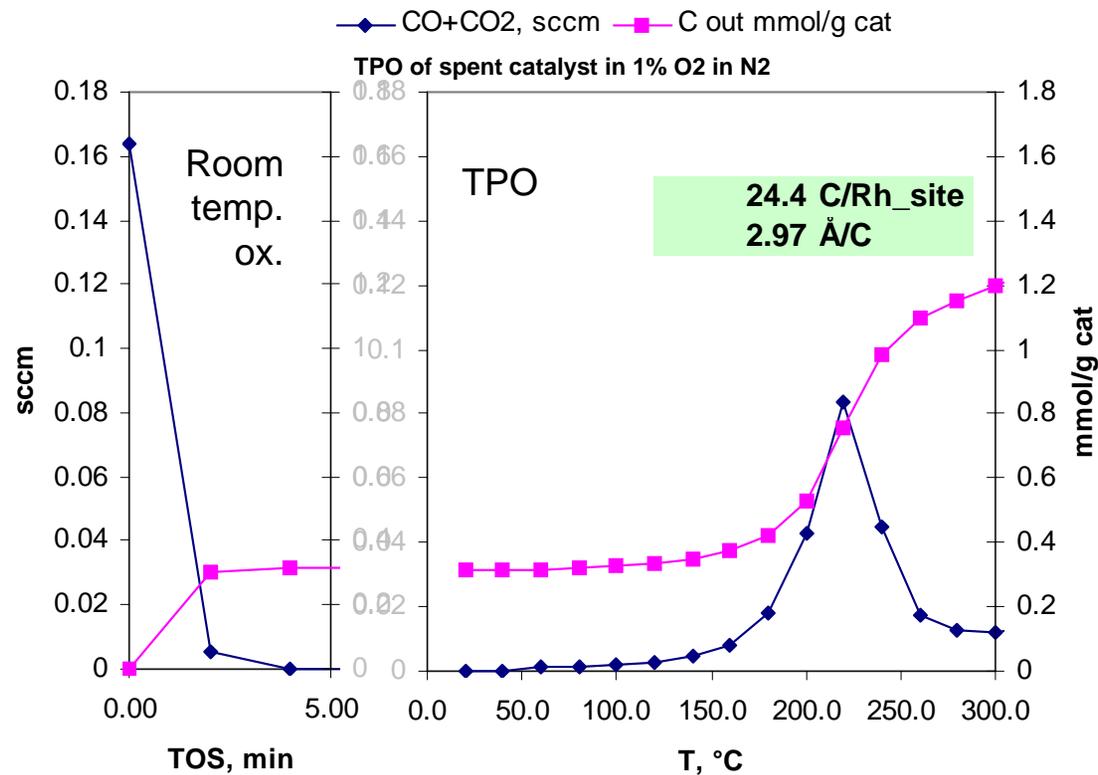
- **Two major causes considered**
 - Metal sintering or loss of surface area
 - Fouling by carbonaceous residues
- **Investigation methods included**
 - HRTEM – look for carbonaceous material, textural damage
 - FTIR – examine surface species
 - Dispersion and surface area – count available Rh sites
 - TPO and *in-situ* regeneration of spent catalyst – evidence for, and amount of, carbonaceous deposits

Catalyst Surface Changes

- TEM indicates no major cluster of carbon; no major textural change
- *In situ* FTIR indicates some carbonaceous deposit present
 - Need to quantify amount



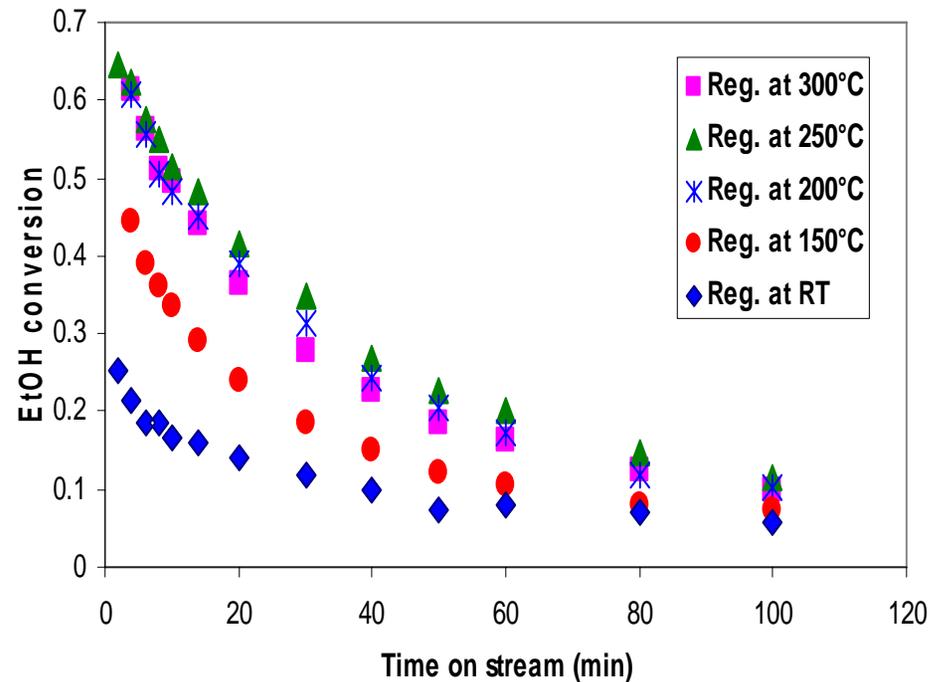
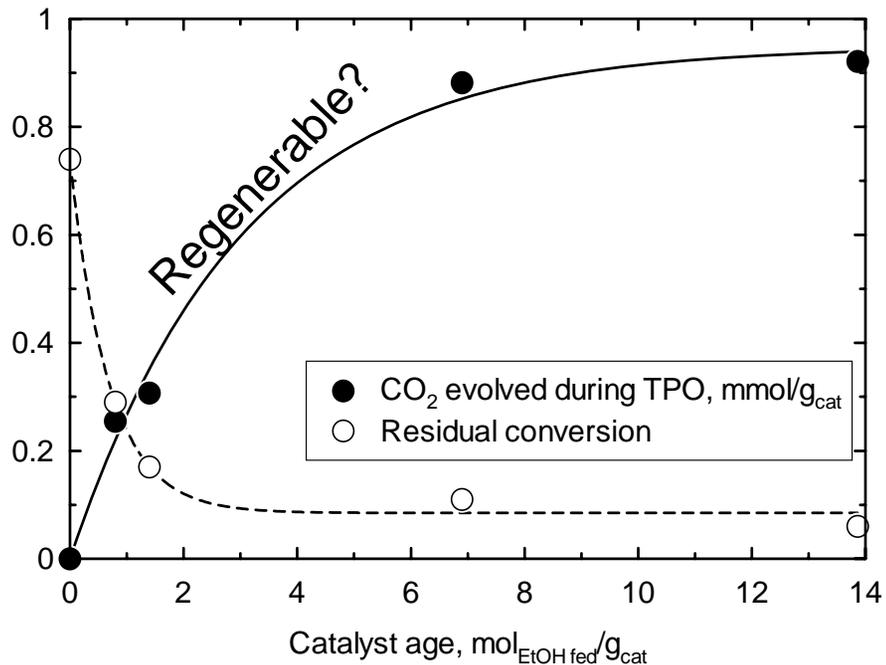
Amount of Surface Carbonaceous Deposition



➤ *In situ* TPO of carbonaceous deposit

- 1/3 of deposit removed at room temperature
- Rest of deposit peaks at ~210°C

Catalyst Regeneration

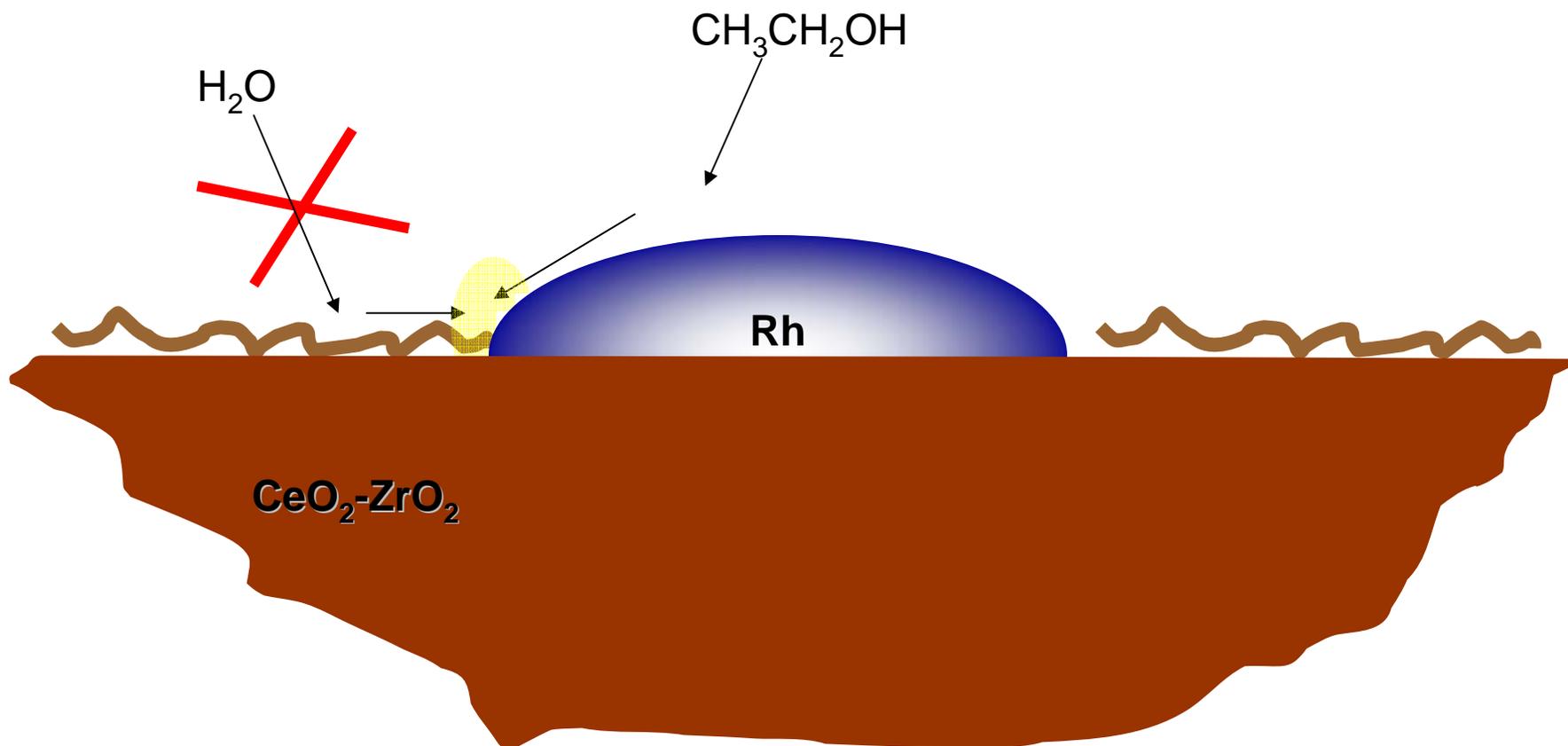


➤ Amount of carbonaceous deposit correlates with residual activity

➤ Activity is restored after regeneration at ~200 °C

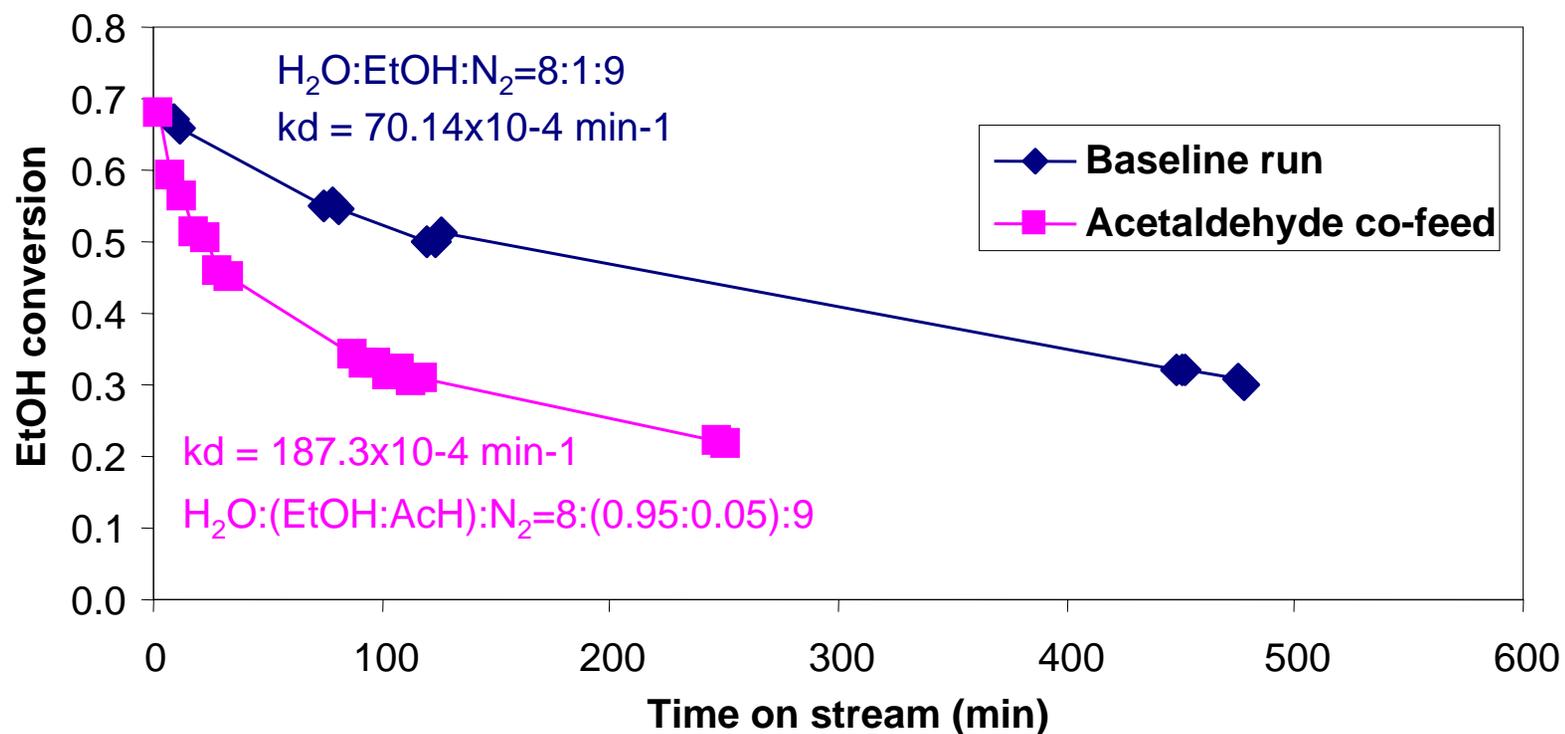
Roh *et al*, *Catal.Lett.*, 110 (1&2) (2006) 1-6

Proposed Deactivation Mechanism



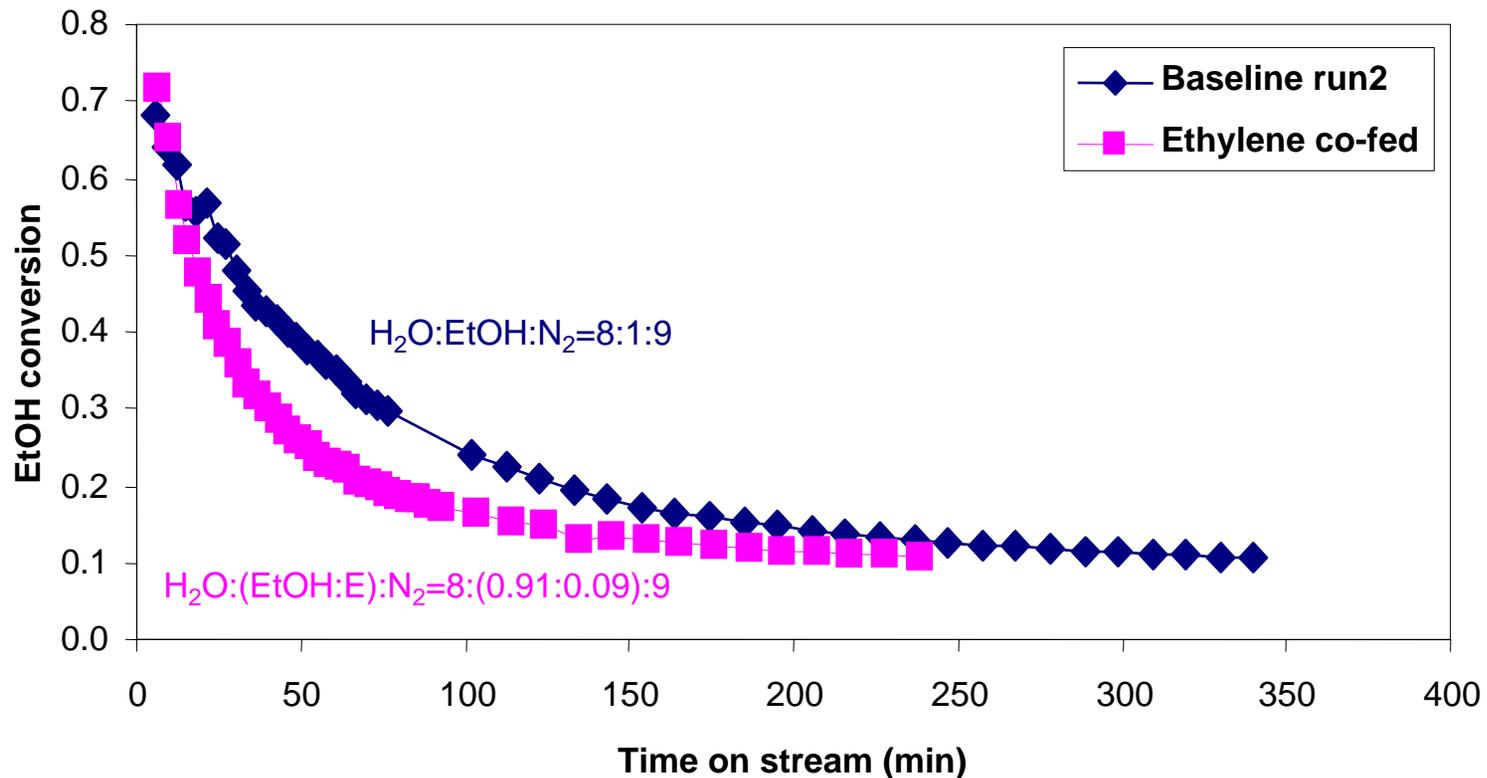
Effect of Co-Feeding Acetaldehyde on Catalyst Stability

2%Rh/Ce_{0.8}Zr_{0.2}O₂; T=450°C; SV=2,000,000cc/gcat/hr

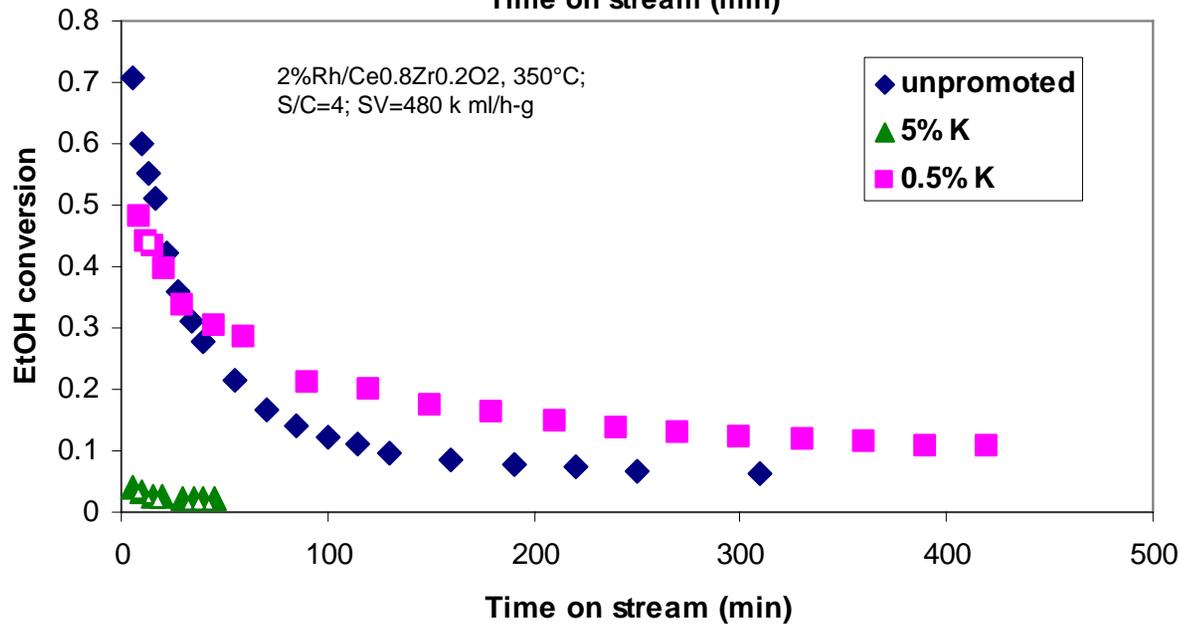
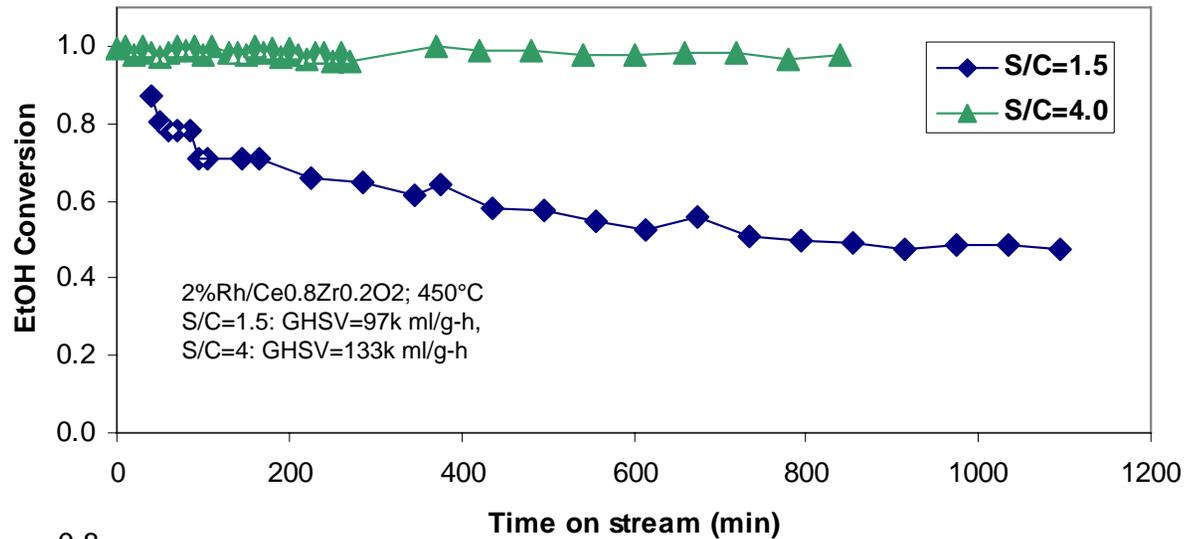


Effect of Co-Feeding Ethylene on Catalyst Stability

2%Rh/Ce_{0.8}Zr_{0.2}O₂; T=350°C; SV=487,000 scc/hr/gcat



Increasing S/C Ratio or Adding K Enhances Catalyst Stability



Conclusions – Vapor Phase Ethanol Reforming

- **Rh/Ce_{0.8}Zr_{0.2}O₂ is active for ethanol SR at T<450°C**
- **Rapid catalyst deactivation is observed**
 - “soft” carbonaceous deposits
 - Activity can be readily recovered by treatment with O₂ at 200°C
- **Ethylene and acetaldehyde both accelerate deactivation**
 - Acetaldehyde may be greater problem at low reforming temperatures
- **Excess steam reduces deactivation**
 - May displace intermediates on surface and facilitate reforming
- **K-doping improves steady state activity**
 - Likely due to facilitating H₂O adsorption on surface
- **Challenge: how to avoid deactivation when both postulated intermediates accelerate deactivation?**

Path Forward

- **Identify compositions and reaction conditions for stable vapor phase reforming**
 - Increase reaction temperature to minimize deposition of “soft carbonaceous deposits”
 - Identify the potential deactivation issue in the preheating zone
- **Innovate reaction engineering, e.g., integrate with membrane separation**
- **Obtain guidance from process economics**
 - e.g., trade off between low temperature and high temperature reforming