

# Novel Methods of Hydrogen Production Using C1 Chemistry

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Project ID #  
**PDP22**

# Overview

## Timeline

- Start: Oct. 1, 2005
- End: Sept. 30, 2008
- 28 % complete

## Budget

- Total project funding
  - DOE - \$4,500,000
  - CFFS - \$1,125,000
- Funding received in FY06 - \$1,000,000

## Barriers

- Produce hydrogen from coal with minimum CO<sub>2</sub> production.
- Hydrogen storage/carrier media.

## Partners

**CFFS:** Univ. of Kentucky, West Virginia Univ., Univ. of Pittsburgh, Univ. of Utah, Auburn Univ.

**Advisory Board:** Eastman, ConocoPhillips, Chevron Texaco, US Air Force, US Army

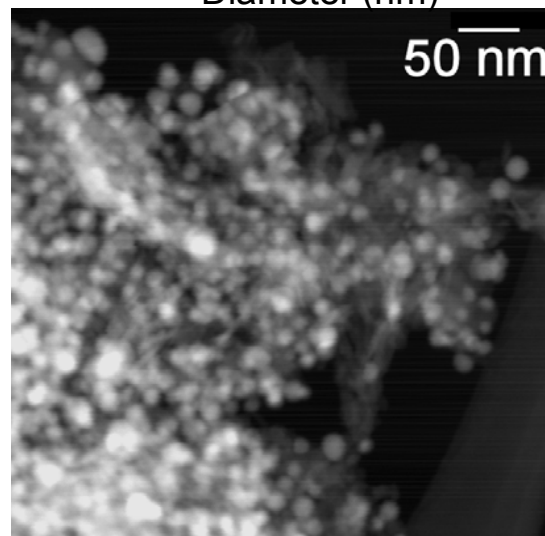
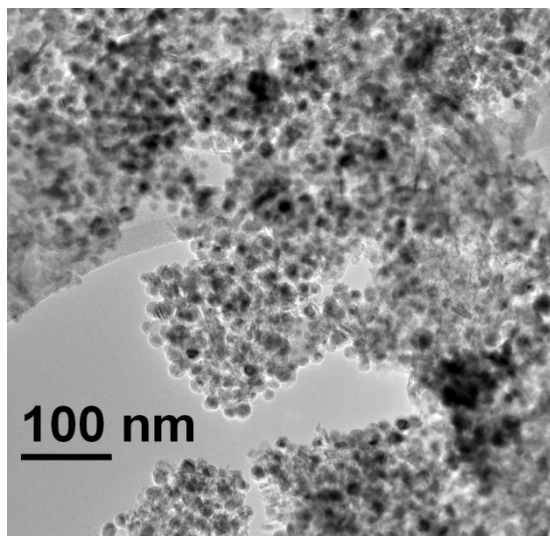
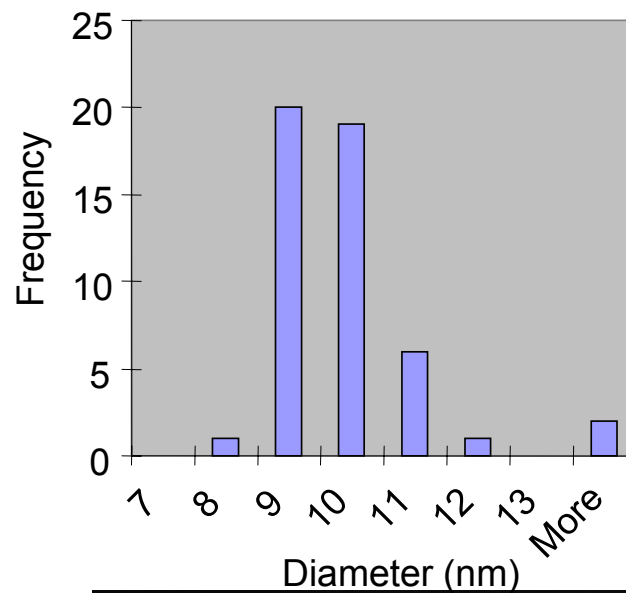
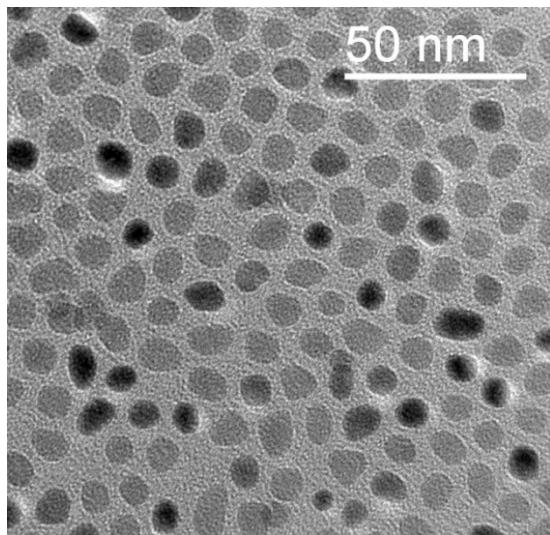
# Objectives and Approach

- Develop novel technology for producing hydrogen from coal, natural gas and biomass using C1 chemistry.
- Develop better methods of producing hydrogen-rich liquids and gases from coal, natural gas, and biomass using C1 chemistry.

The Consortium for Fossil Fuel Science (CFFS) is a research center with participants from five universities - Kentucky, West Virginia, Pittsburgh, Auburn, and Utah. This poster briefly describes the following novel methods of hydrogen production developed in this consortium.

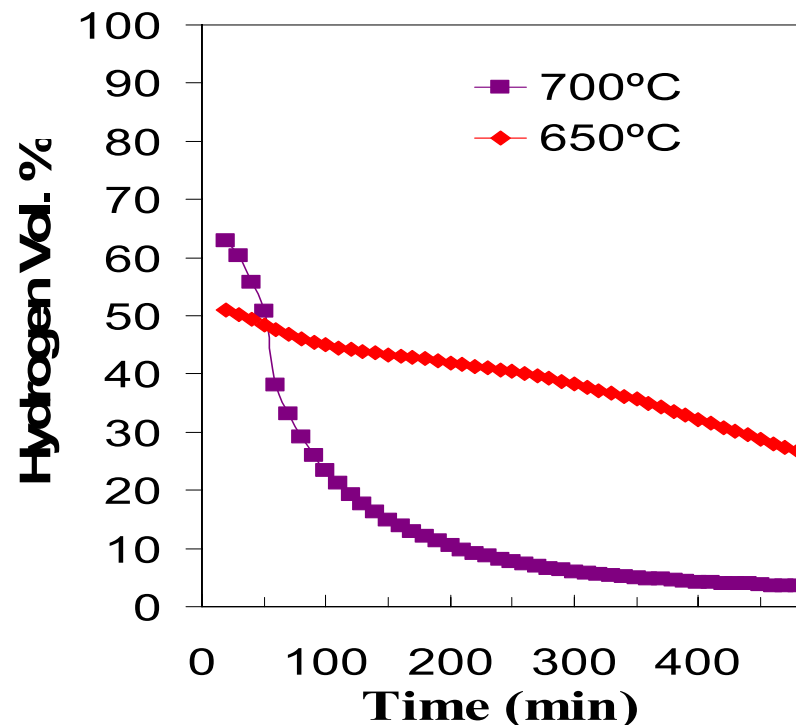
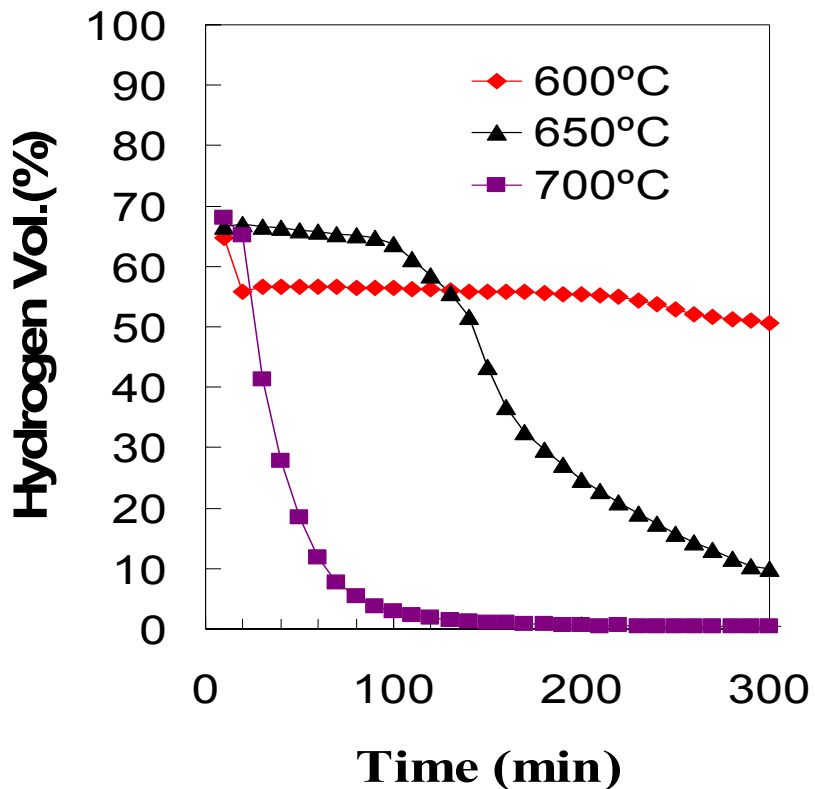
1. Catalytic dehydrogenation of alkanes – Gerald Huffman and Naresh Shah, CFFS and Dept. of Chem. & Materials Engr., University of Kentucky
2. Carbon-assisted electrolysis of water – Mohindar Seehra, Dept. of Physics, West Virginia University
3. Hydrogen by Supercritical Reforming of Water – Ram Gupta, Dept. of Chem. Engr., Auburn University
4. Hydrogen from Polyols – Irving Wender and Jack Tierney, Dept. of Chemical Engineering, University of Pittsburgh
5. High activity WGS catalysts produced by gas phase incorporation of Pd on very high surface area ceria – Edward Eyring and Richard Ernst, Dept. of Chemistry, University of Utah

# Catalytic dehydrogenation of alkanes



Top – TEM image and size distribution of as-synthesized 10 nm Fe-Ni nanoparticles.  
Bottom – TEM and STEM images of the same nanoparticles on Mg(Al)O support.

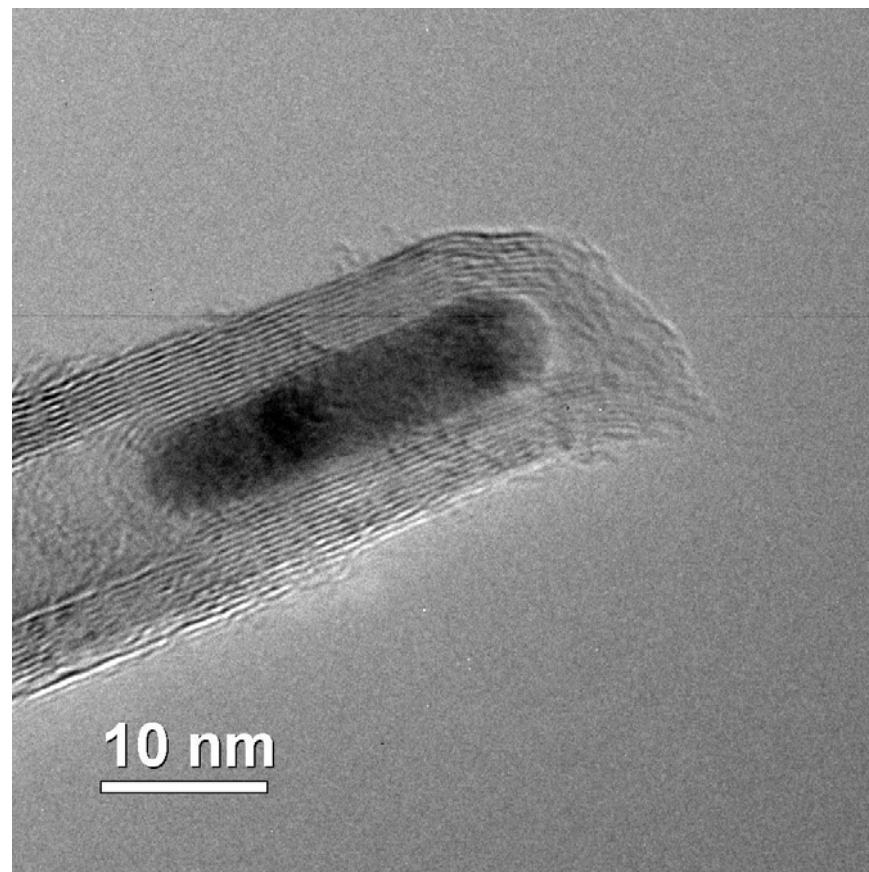
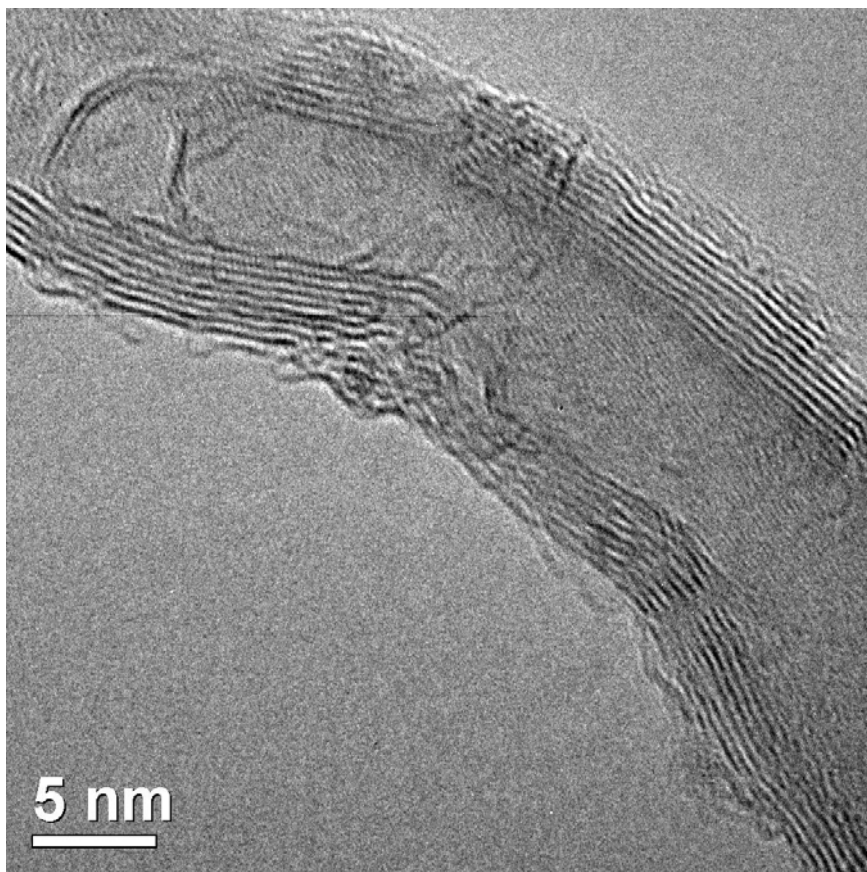
# Catalytic dehydrogenation of alkanes



Time-on-stream (TOS) H<sub>2</sub> production by methane dehydrogenation over Mg(Al)O supported: (Left) 0.2 wt% Fe-Ni (12 nm) nanoparticles; (Right) 5 wt% FeNi prepared by incipient wetness (IW) method.



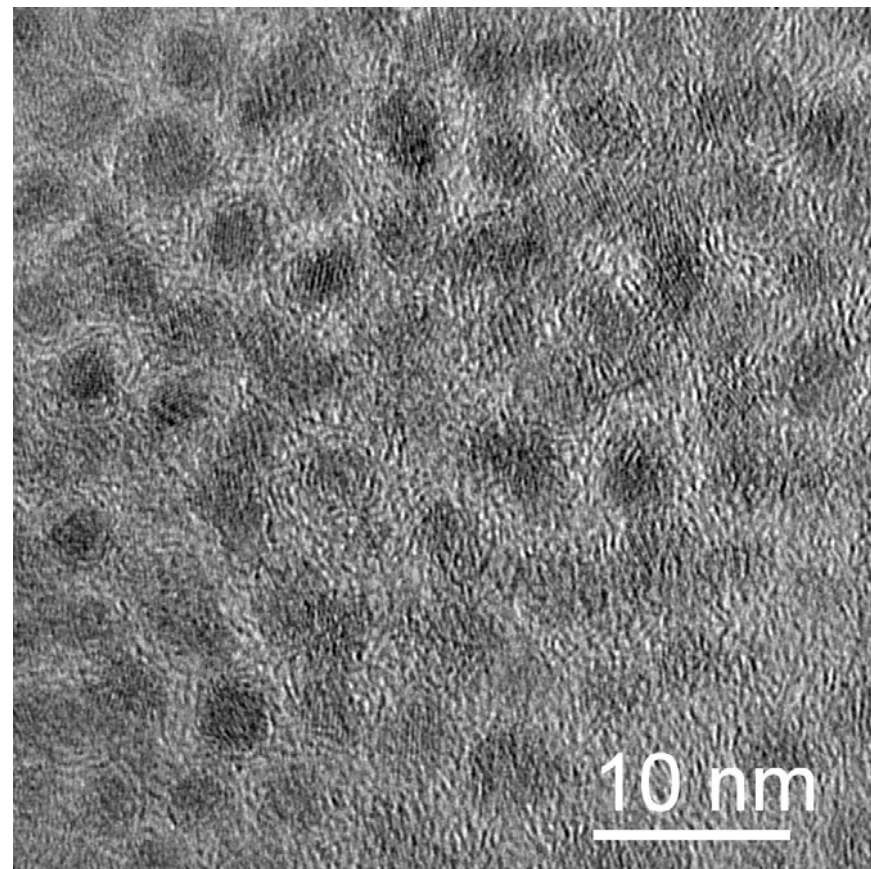
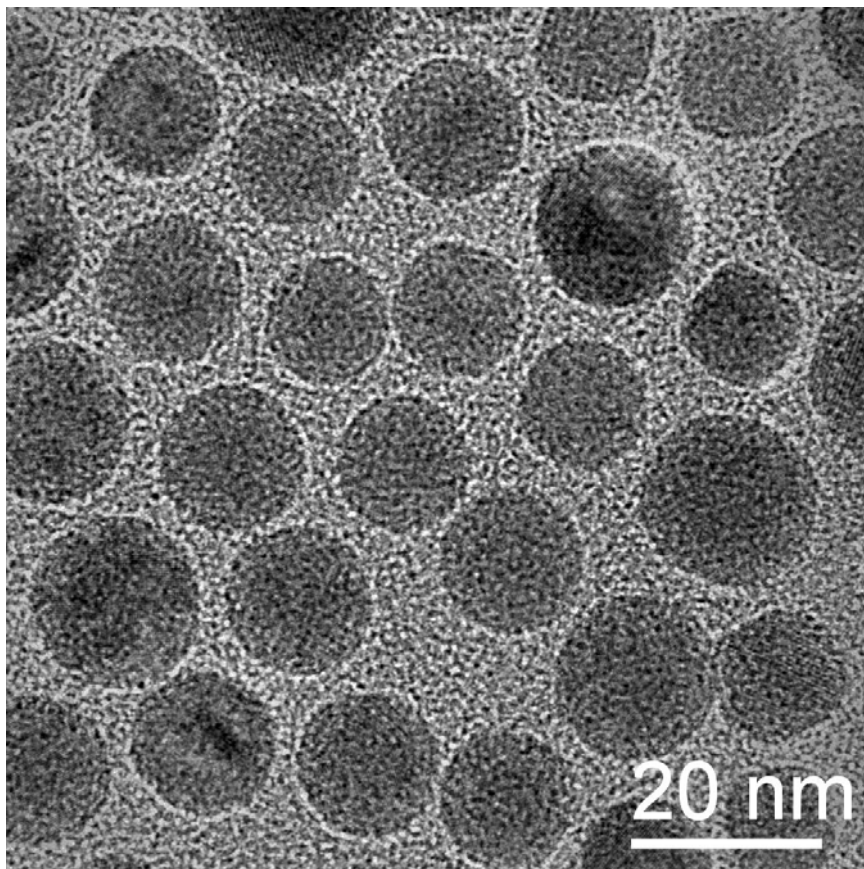
# Catalytic dehydrogenation of alkanes



HRTEM images of carbon nanotubes (MWNT) produced during ethane dehydrogenation at 600°C over Fe-Ni nanoparticles (10 nm, 0.2 wt%) supported on Mg(Al)O after removal of support in dilute nitric acid solution at room temperature. Some Fe-Ni nanoparticles remain within the MWNT tips.



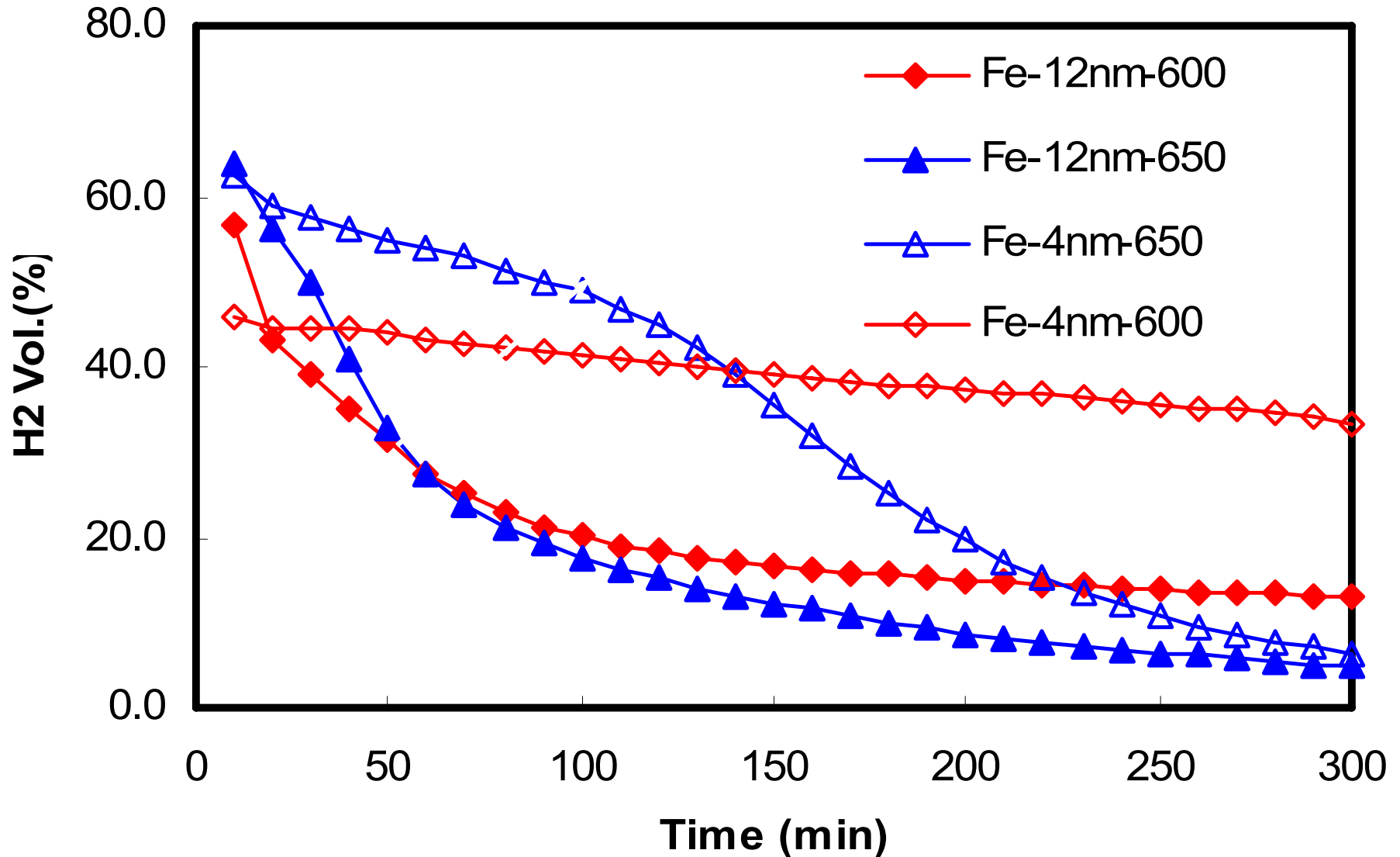
# Catalytic dehydrogenation of alkanes



TEM images of 12 nm and 4 nm Fe oxide particles prepared for use in lower alkanes dehydrogenation experiments. (*Hyeon et al, Nature Materials, 3, 2004, 891; Sun et al, J. Am. Chem. Soc, 126, 2004, 273*).



# Effect of nanoparticles size on time-on stream (TOS) hydrogen production by catalytic dehydrogenation of methane over Fe/Mg(Al)O.

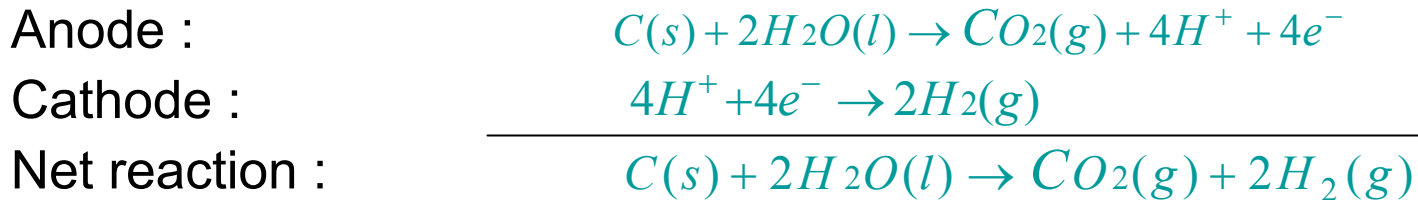


# Hydrogen production by catalytic dehydrogenation

- Catalytic dehydrogenation of alkanes produces pure hydrogen and carbon nanotubes in one step. No carbon oxides are produced. Binary Fe-M on various supports exhibit excellent activity and productivity.
- Multiwalled nanotubes are produced at  $T > 600^{\circ}\text{C}$  and stacked cone nanotubes at  $T \leq$  approximately  $500^{\circ}\text{C}$
- A new Mg(Al)O support has been produced from Mg-Al hydrotalcite precursor. It has high surface area and is easily dissolved in nitric acid, which greatly simplifies nanotube cleaning.
- Fe-Ni nanoparticles of uniform size (10 nm) have been synthesized and dispersed on Mg(Al)O. These catalysts exhibit better activity for hydrogen production than Fe-Ni/Mg(Al)O prepared by incipient wetness technique.
- 4 nm and 12 nm Fe nanoparticles on Mg(Al)O exhibit reasonably good activity for dehydrogenation but not as good as Fe-Ni nanoparticles.

# Carbon-assisted electrochemical production of hydrogen at room temperature

Coughlin et al (J.Appl.Electrochem.10,729,1980) proposed the electrochemical gasification of carbons :

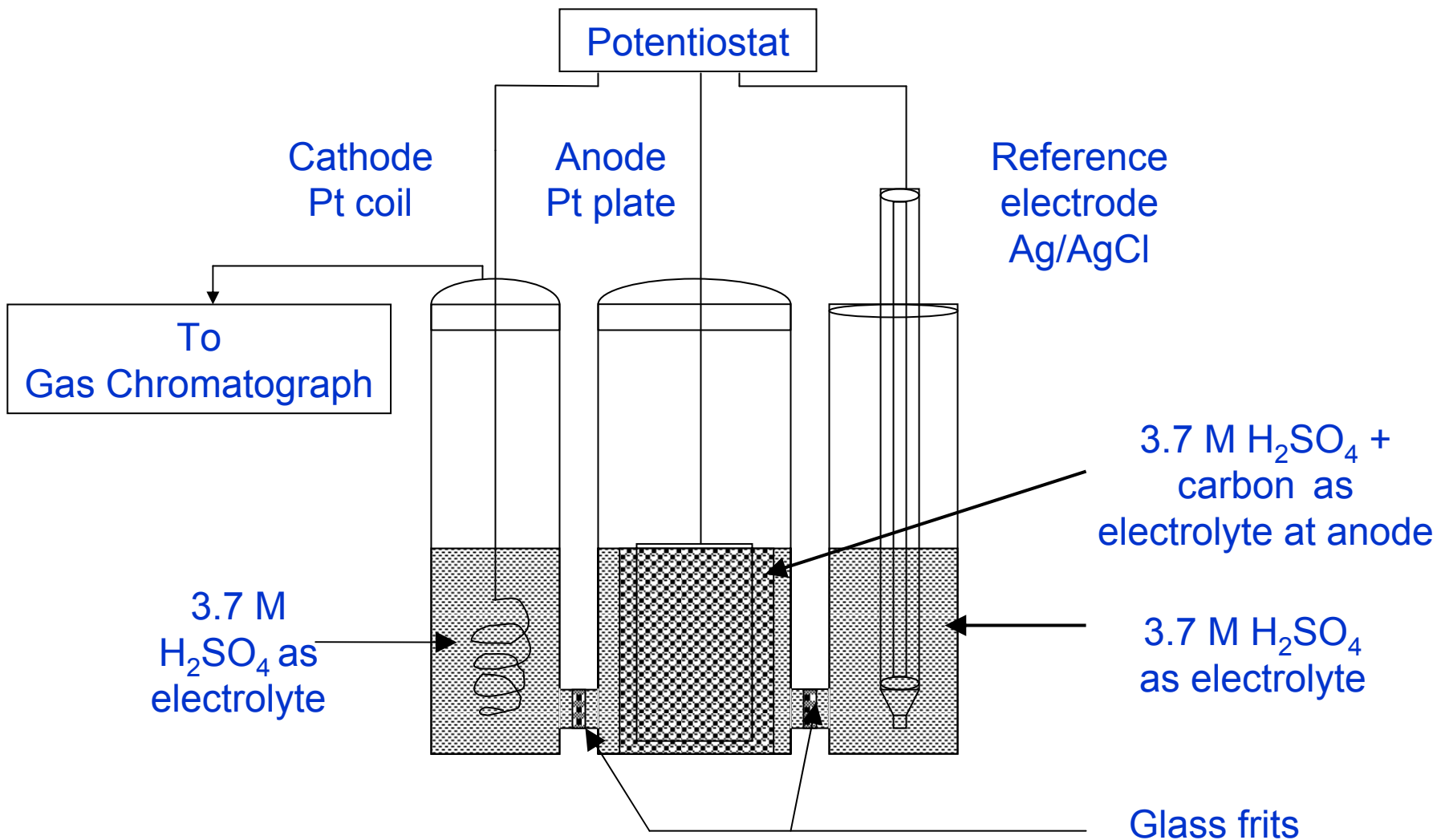


$$\begin{aligned} \Delta G &= \Delta G (\text{product}) - \Delta G (\text{reactants}) \\ &= -94.26 (\text{CO}_2) + 2(56.7) = 19.27 \text{ kcal/ } 2\text{mol H}_2\text{O} = 9.6 \text{ kcal/mol H}_2\text{O}, \\ &\quad \text{compared to } 56.7 \text{ kcal/mol H}_2\text{O without carbon} \end{aligned}$$

$$E^0 = -\frac{\Delta G}{nF} = -0.21V \quad \text{compared to } E^0 = -1.23V \text{ for electrolysis of water without carbon.}$$

\* For details, see Seehra et al, Appl. Phys. Lett. 90, 044104 (2007).

# Carbon-assisted electrochemical hydrogen production

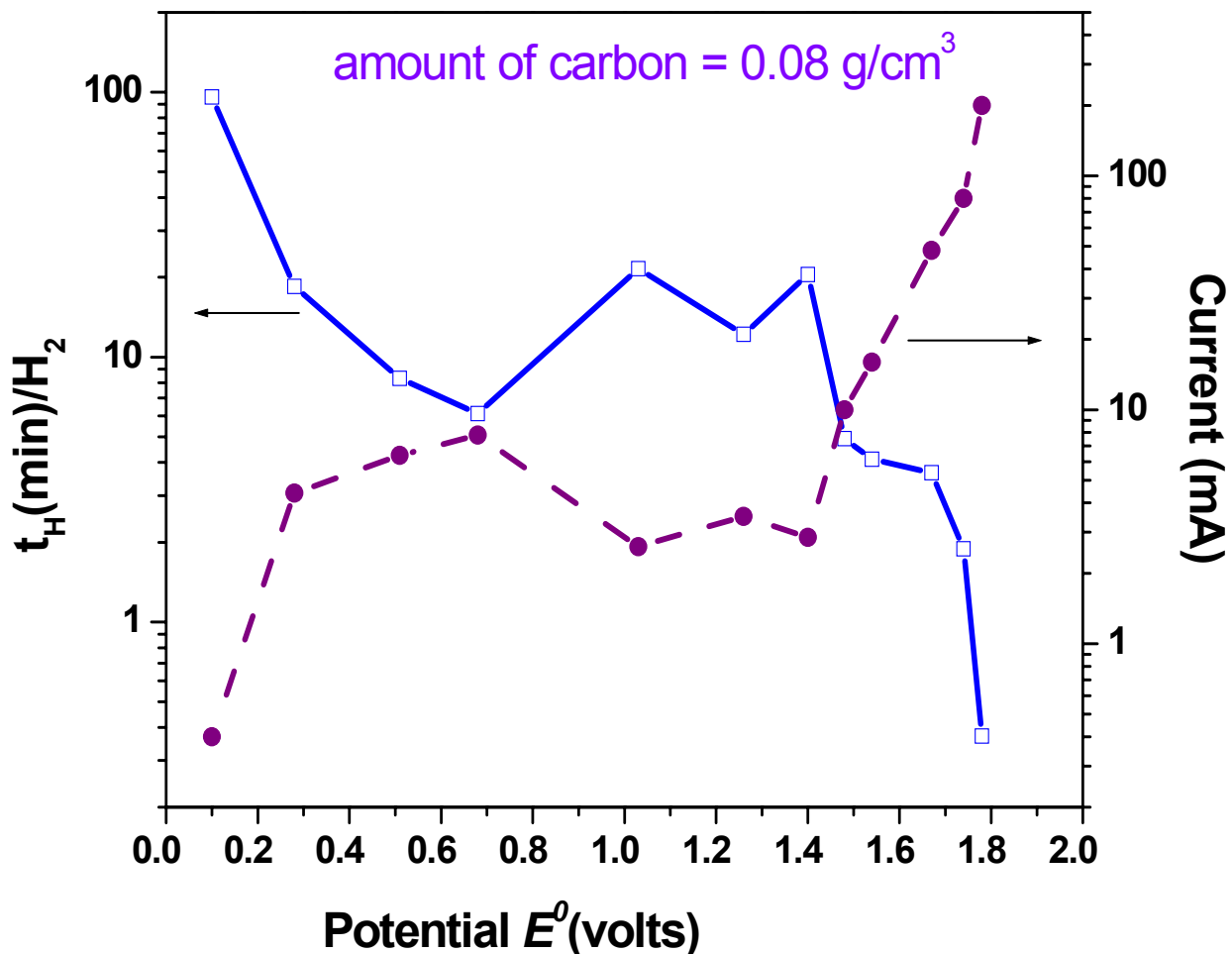


Working electrode area : 6.8 cm<sup>2</sup> ; Counter electrode area : 2.55 cm<sup>2</sup>



# Carbon-assisted electrochemical hydrogen production

$t_H$  = time needed to produce the same amount of  $H_2$



$H_2$  is produced at voltages as low as 0.1V, but time required to produce the same amount of  $H_2$  is higher and the corresponding current is lower.

# Energy requirements for carbon-assisted electrochemical hydrogen production

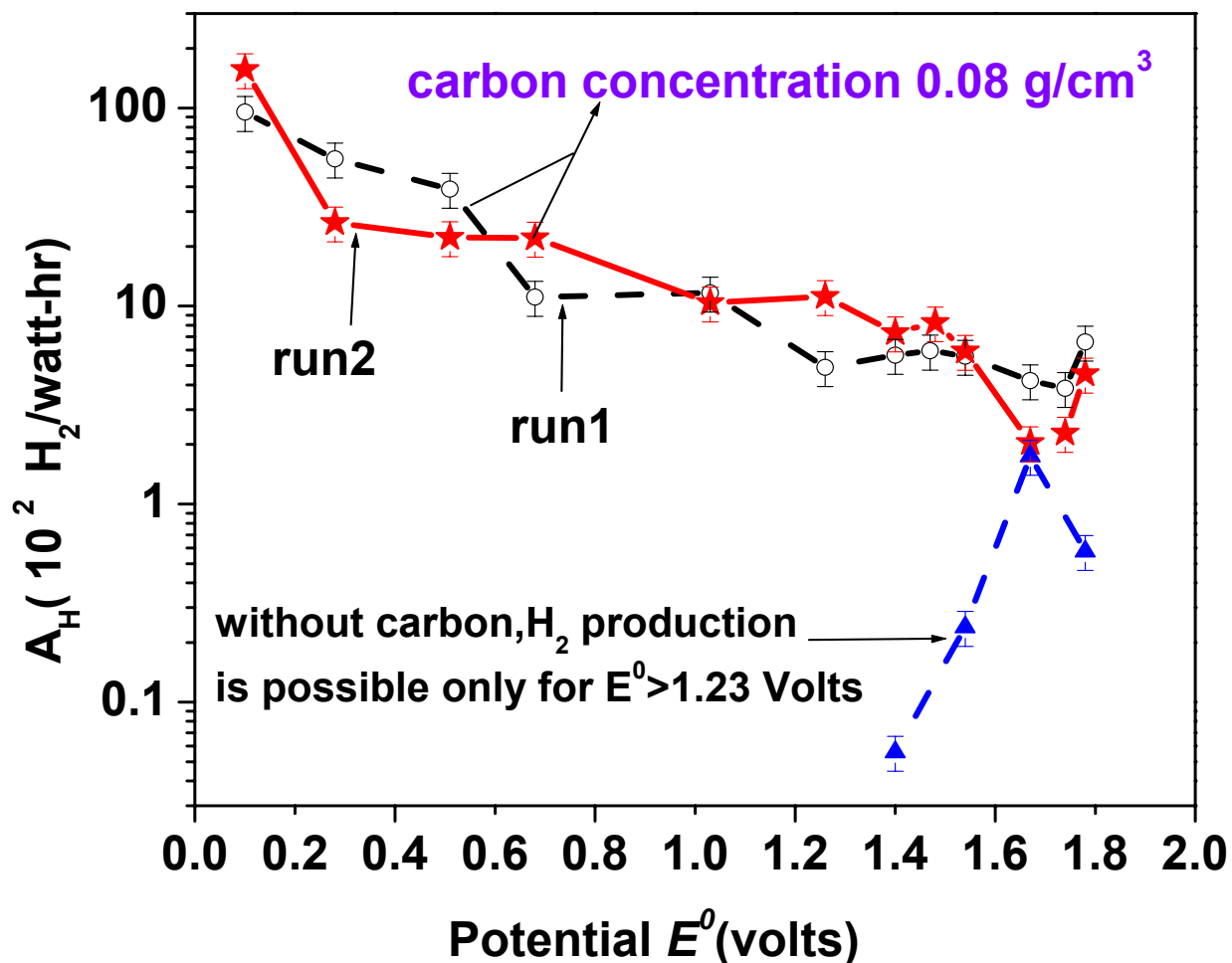
- Power =  $I E_0$  (Joules /sec or watt)
- Energy needed =  $\int P dt = I E_0 t$
- 1 kiloWatt-hour =  $10^3$  Joules/sec x 3600 sec =  $3.6 \times 10^6$  Joules

$E_0$ (volts)	$I_0$ (mA)	Power= $E_0 I_0$ ( $10^{-4}$ watts)	$t_H$ (min/ $H_2$ )	$E_0 \cdot I_0 \cdot t_H$ ( $10^{-4}$ watt-hr/ $H_2$ )	$A_H$ ( $10^2$ $H_2$ /watt-hr)
0.1 (Carbon)	0.4	0.4	95.9	0.64	156.3
0.28(Carbon)	4.4	12.32	18.5	3.8	26.3
0.51(Carbon)	6.38	32.54	8.3	4.5	22.2
1.78(Carbon)	200	3560	0.37	22.0	4.54
1.67 (No Carbon)	65	1085.5	3.16	57.2	1.75

Energy consumption to produce same amount of  $H_2$  goes up sharply as  $V$  increases. But the time requirements go down with increasing  $V$ .

# Carbon-assisted electrochemical hydrogen production

$A_H = H_2$  produced  
per watt-hr



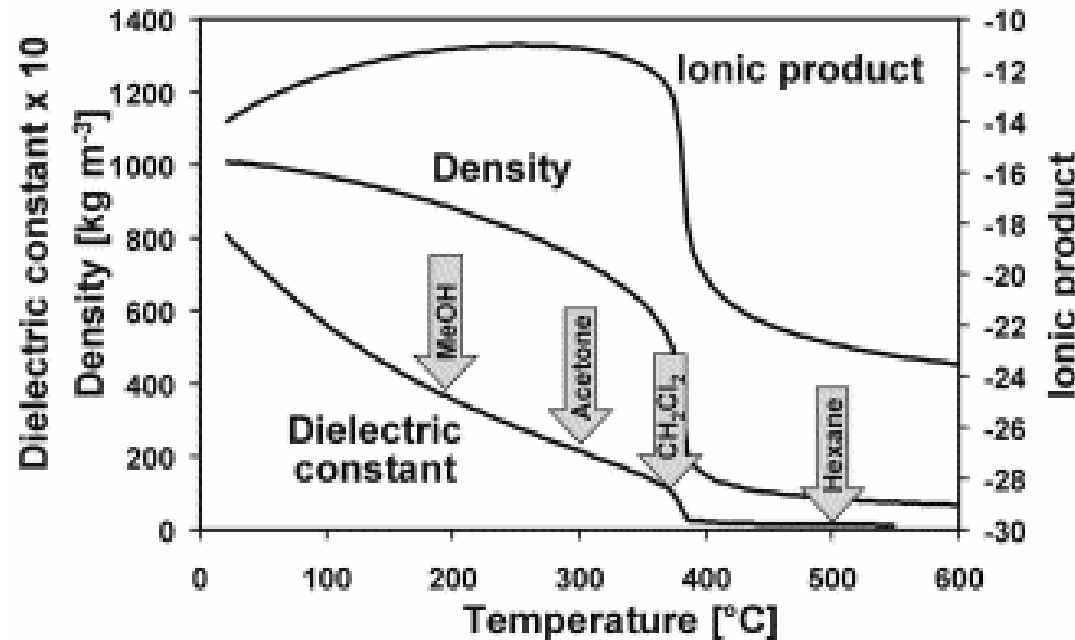
Carbon-assisted  $H_2$  production at lower voltages is considerably more energy efficient, although it takes somewhat longer to produce the same amount of  $H_2$ . Use of catalysts to reduce this time is being investigated.

# Hydrogen Production by Reforming in Supercritical Water

- H<sub>2</sub>O is both a reactant and the solvent
- Direct high-pressure H<sub>2</sub> is obtained
- Compact reactors: reactions time in seconds
- In-situ separation
- Energy integration
- Carbon dioxide can be easily sequestered
- Avoids char formation

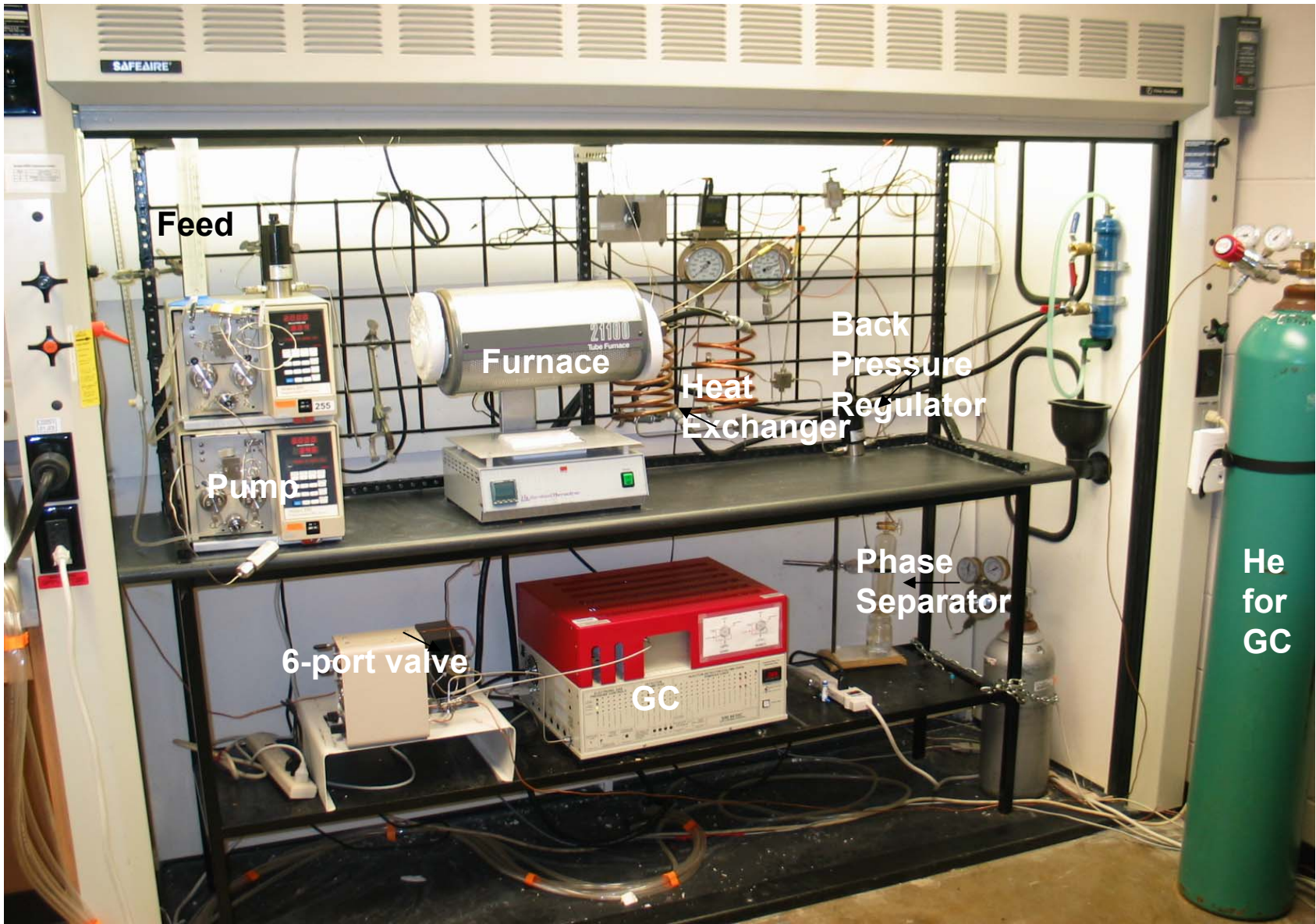
Supercritical water is like an organic solvent!

[Kritzer and Dinjus, Chemical Engineering Journal (2001), 83(3), 207-214]





# Experimental Setup - H<sub>2</sub> Production by Reforming in Supercritical Water



Feed

Pump

6-port valve

Furnace

Heat Exchanger

GC

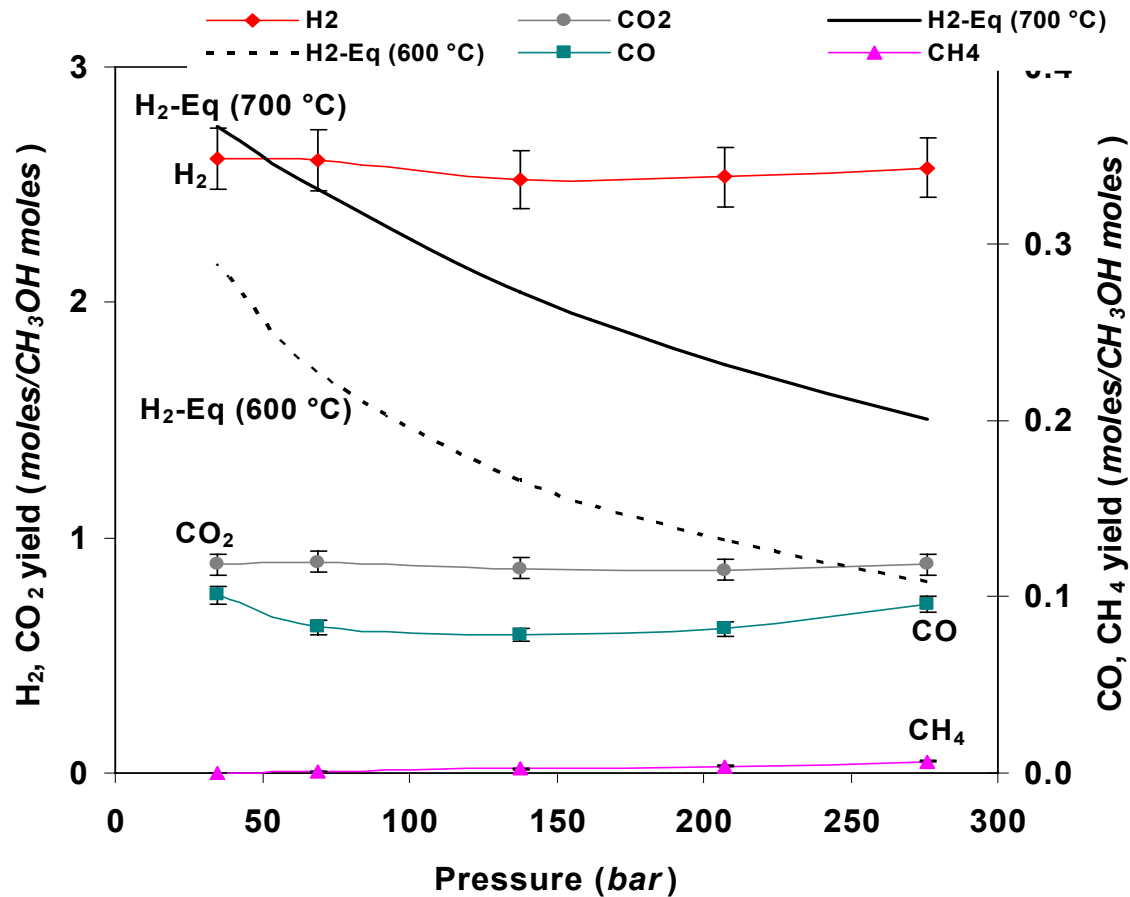
Phase Separator

Back Pressure Regulator

He for GC

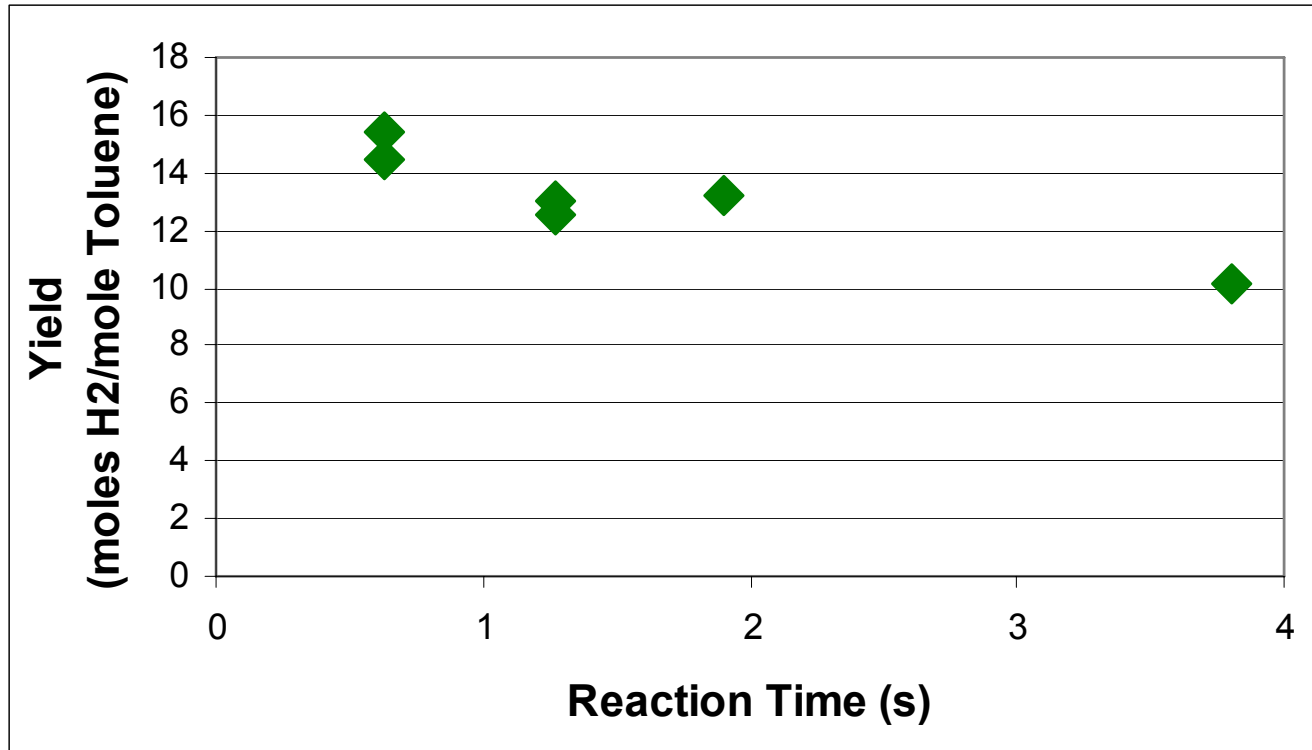
# Hydrogen Production by Reforming in Supercritical Water

H<sub>2</sub> from 10 wt.% methanol using Monel-400 (Ni<sub>0.67</sub> Cu<sub>0.33</sub>) Reactor - 600 °C, feed rate = 1 ml/min, reactor length = 1 m



[Gadhe, Jayant B.; Gupta, Ram B., Industrial & Engineering Chemistry Research (2005) 44, 4577-4585]

# Hydrogen Production by Reforming in Supercritical Water



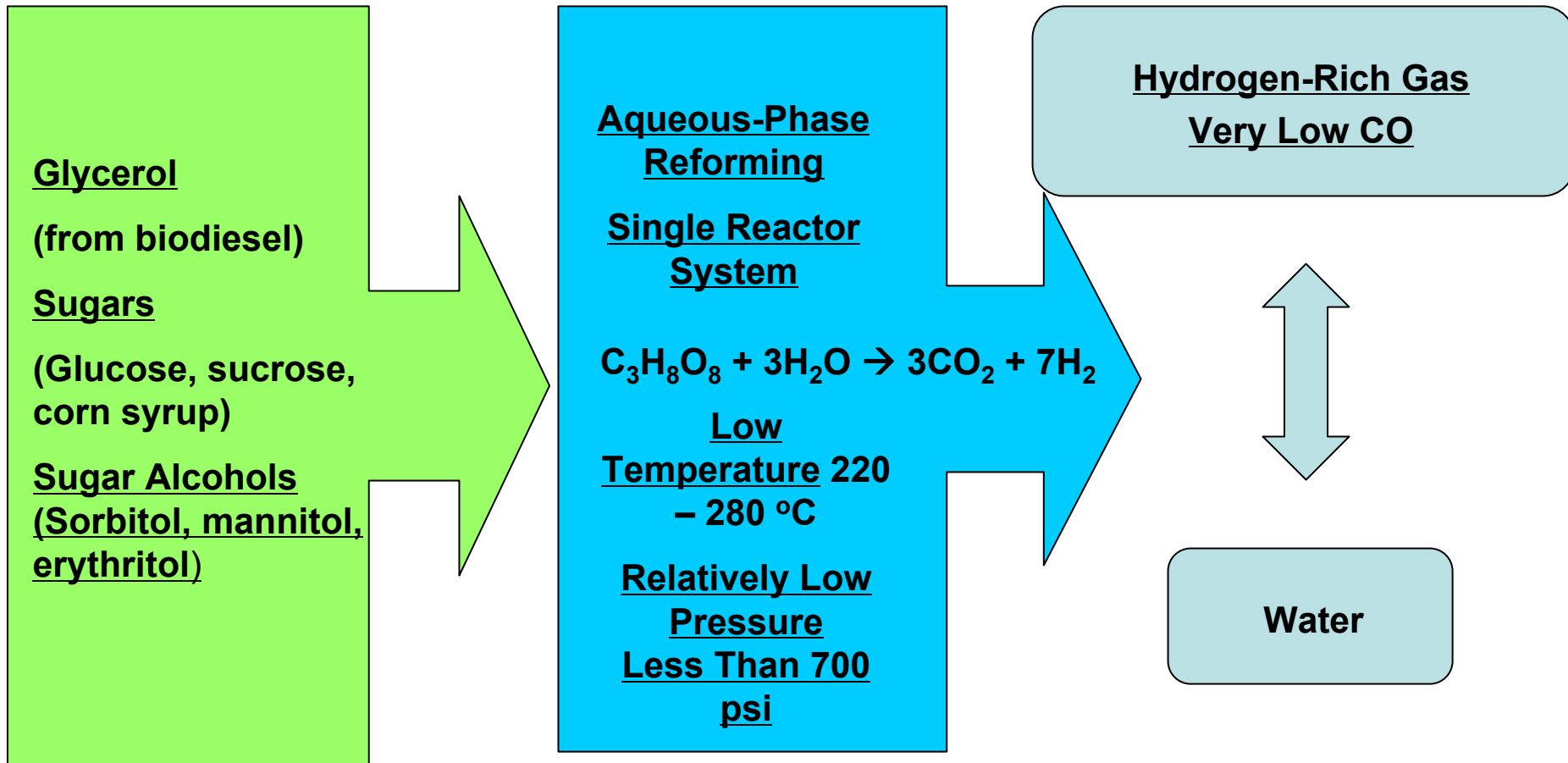
Inconel reactor, Ru/Al<sub>2</sub>O<sub>3</sub> catalyst, 800°C, 3500 psi, 2.1 wt% toluene in water feed

# Hydrogen from Polyols

- Polyols are alcohols which contain two or more adjacent hydroxyl groups connected to carbons. They can be obtained from natural materials such as sugars, fats or cellulose.
- They can be reacted with water in a single step reactor at 200-250°C and sufficient pressure to prevent vaporization of the water to produce a high yield of hydrogen and low CO.
- Hydrogen yield and selectivity for a series of polyols ranging from C<sub>2</sub> to C<sub>6</sub> have been measured using a flow reactor and a variety of experimental conditions.



# Hydrogen Production from Biosustainable Polyols



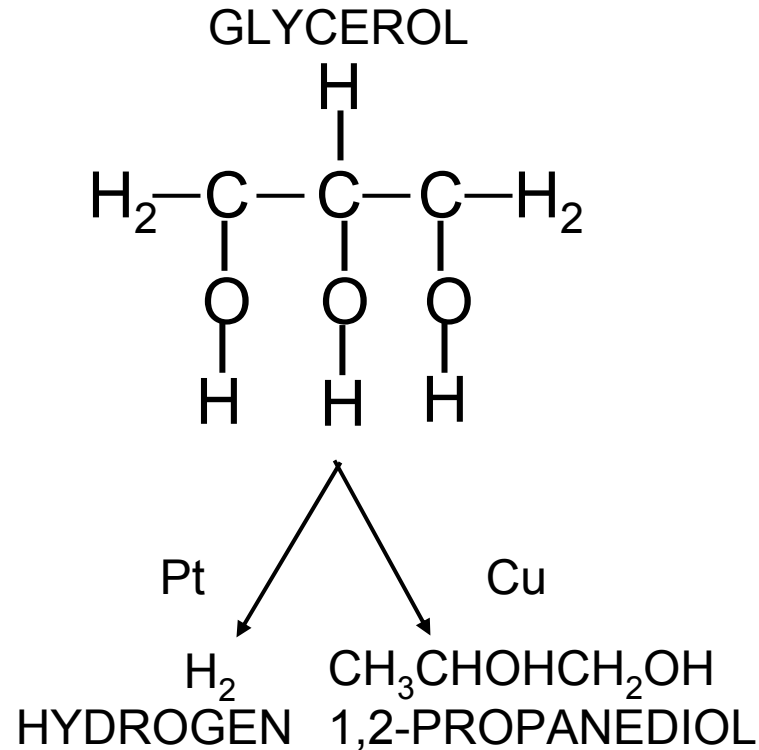
# Hydrogen Production from Selected Polyols

Reactant	Feed Conc. (wt%)	H <sub>2</sub> Yield (mole %)	H <sub>2</sub> Selectivity %
Ethylene glycol	1	67.7	82
	10	62.1	80
Glycerol	1	63.8	70
	10	61.7	68
Sorbitol	1	59.8	58
Sucrose	1	52.0	50
Glucose	1	47.2	33
Corn syrup (97% D-glucose)	1	46.8	31

Reaction Conditions: 220°C, 350 psi, 1 % PtAl<sub>2</sub>O<sub>3</sub>; CO < 400 ppm

Hydrogen yield based on total hydrogen in polyol

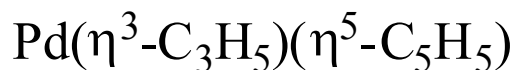
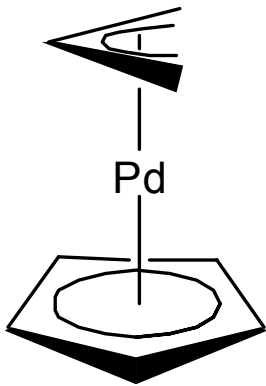
# Hydrogen from Polyols - Catalyst Specificity



Experiments with glycerol, a by-product of biodiesel manufacture, have shown that it can be converted to hydrogen by splitting the O-H bond using a Pt catalyst or to chemicals by splitting the C-C bond using a Cu catalyst.

# High activity WGS catalysts produced by gas phase incorporation (GPI) of Pd on very high surface area ceria

- Use of volatile, organometallic Pd source yields very small and well-dispersed Pd particles
- Comparison of GPI Pd with conventionally (solution based) applied Pd exemplifies significant advantages of GPI for Water-Gas Shift (WGS) reaction

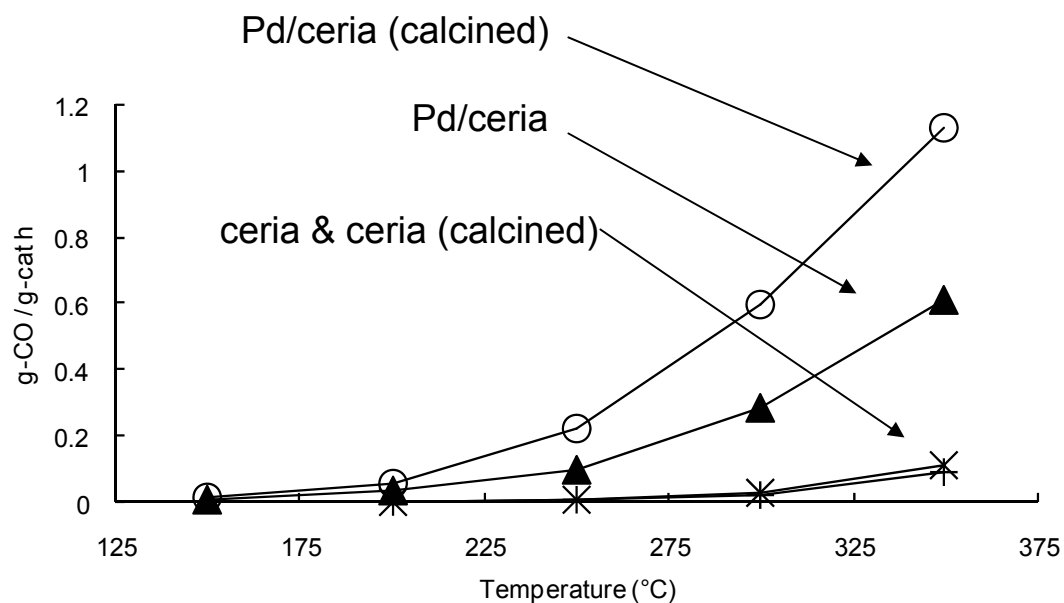


Pd (%)	Incorporation Method	Activity @ 200 °C (mmol-H <sub>2</sub> /g-cat h)	Improvement @ 200 °C w/ GPI
1	solution	4.2	
1	gas-phase	7.2	71%
2	solution	4.3	
2	gas-phase	11.0	155%
5	solution	11.6	
5	gas-phase	18.7	61%

# Production of very high surface area ( $S_A$ ) Ceia aerogel

- Very high surface ceria
  - Maximum BET  $S_A = 375 \text{ m}^2/\text{g}$
  - Synthesized by sol-gel chemistry
- Can be readily doped with precious metals for active WGS catalysts by multiple methods
  - GPI of volatile organometallic
  - Solvent incorporation with suspended, preformed nanoparticles

# WGS activity of high $S_A$ ceria aerogel



Catalyst type	Arrhenius Activation Energy
Pd/ceria (calcined)	$(53.7 \pm 0.8)$ kJ/mol
Pd/ceria	$(52.7 \pm 0.8)$ kJ/mol
ceria	$(77.2 \pm 1.5)$ kJ/mol
ceria (calcined)	$(74.3 \pm 2.0)$ kJ/mol

- Pd/ceria BET  $S_A = 283 \text{ m}^2/\text{g}$
- Pd/ceria (calcined) BET  $S_A = 137 \text{ m}^2/\text{g}$
- Pd incorporated via *GPI*



# Silica aerogel-supported ceria

- XRD data indicates relatively constant ceria crystallite size of 7 nm – with no observed sintering or agglomeration under practical conditions:
  - Independent of ceria loadings
  - Independent of calcination temperatures, up to at least 650 °C
  - After extreme reaction conditions, more harsh than intended application, (WGS at 350 °C)
- U.S. Patent Application (in progress)