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_2 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.
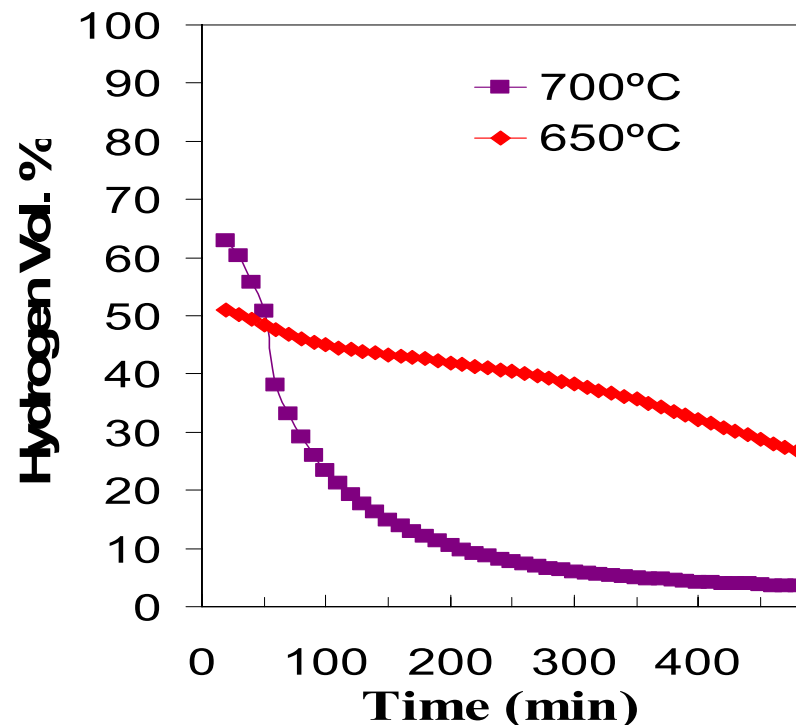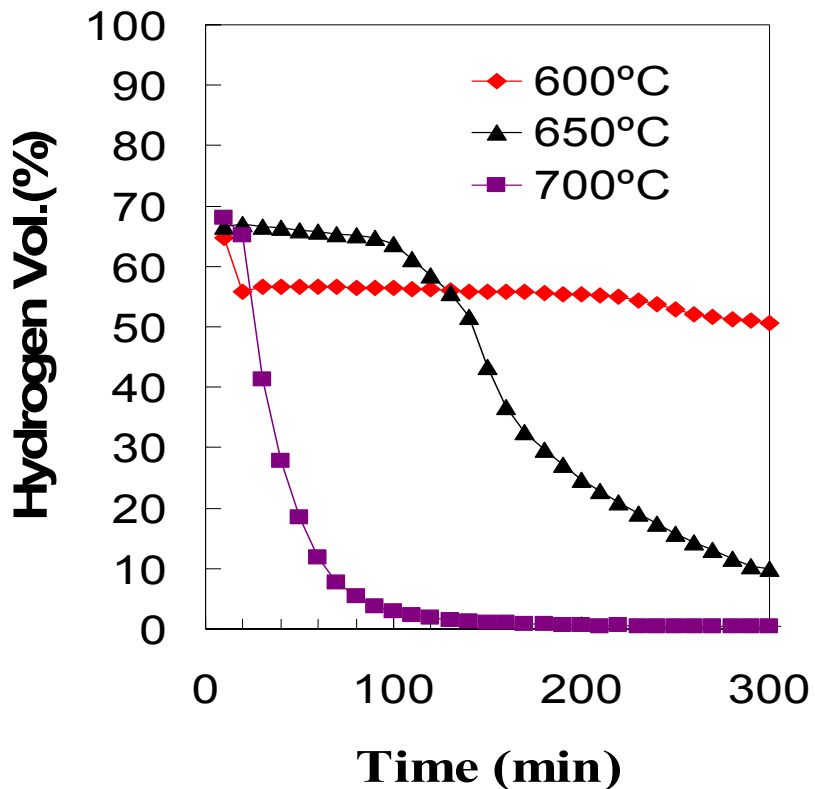
1. Catalytic dehydrogenation of alkanes – Gerald Huffman and Naresh Shah, CFFS and Dept. of Chem. & Materials Engr., University of Kentucky
2. Carbon-assisted electrolysis of water – Mohindar Seehra, Dept. of Physics, West Virginia University
3. Hydrogen by Supercritical Reforming of Water – Ram Gupta, 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
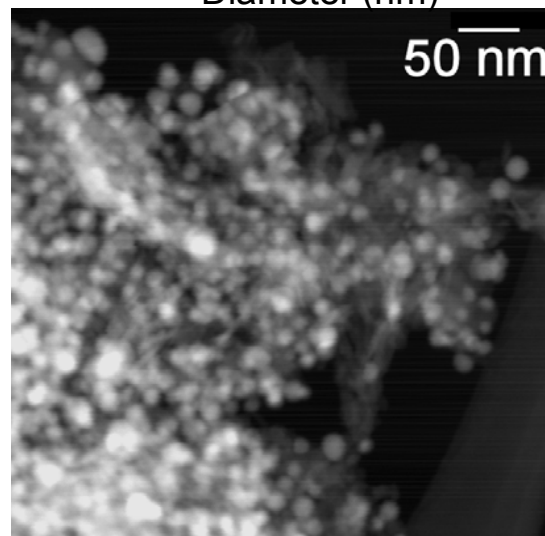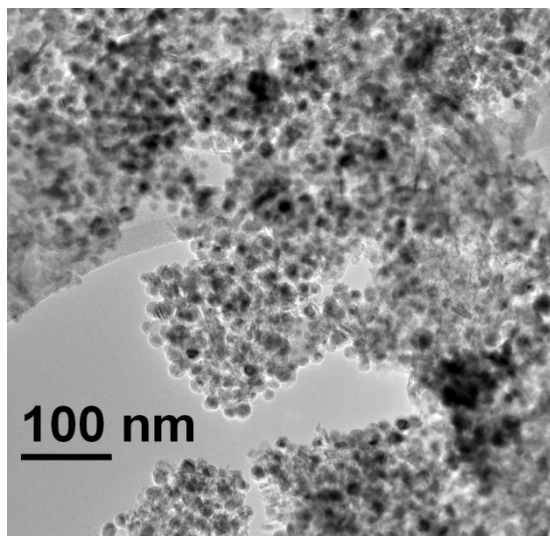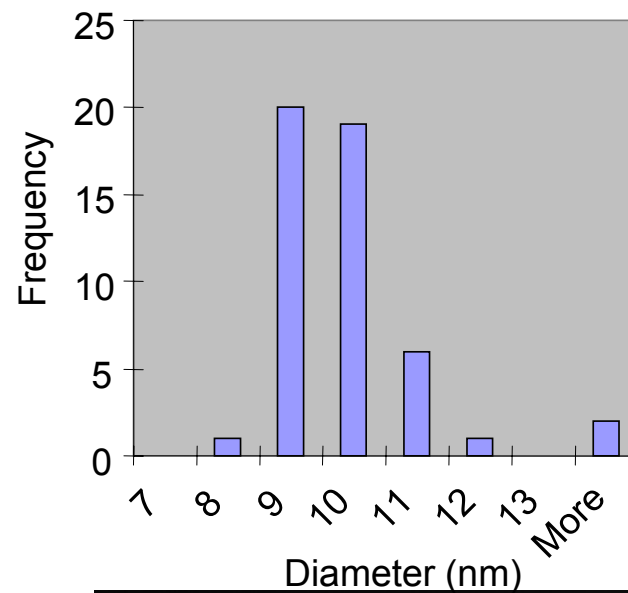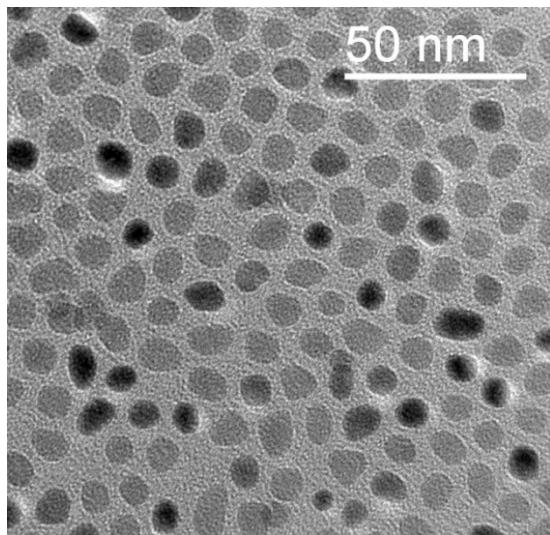

Top – TEM image and size distribution of as-synthesized 10 nm Fe-Ni nanoparticles.
Bottom – TEM and STEM images of the same nanoparticles on Mg(Al)O support.

Catalytic dehydrogenation of alkanes

Time-on-stream (TOS) H_2 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
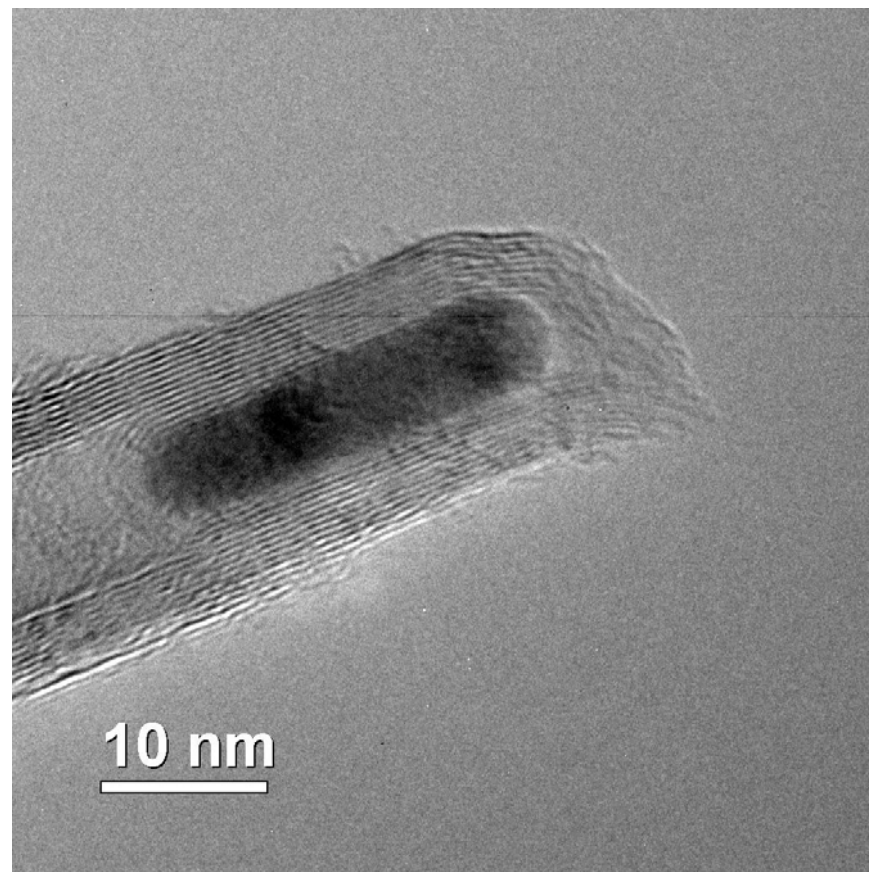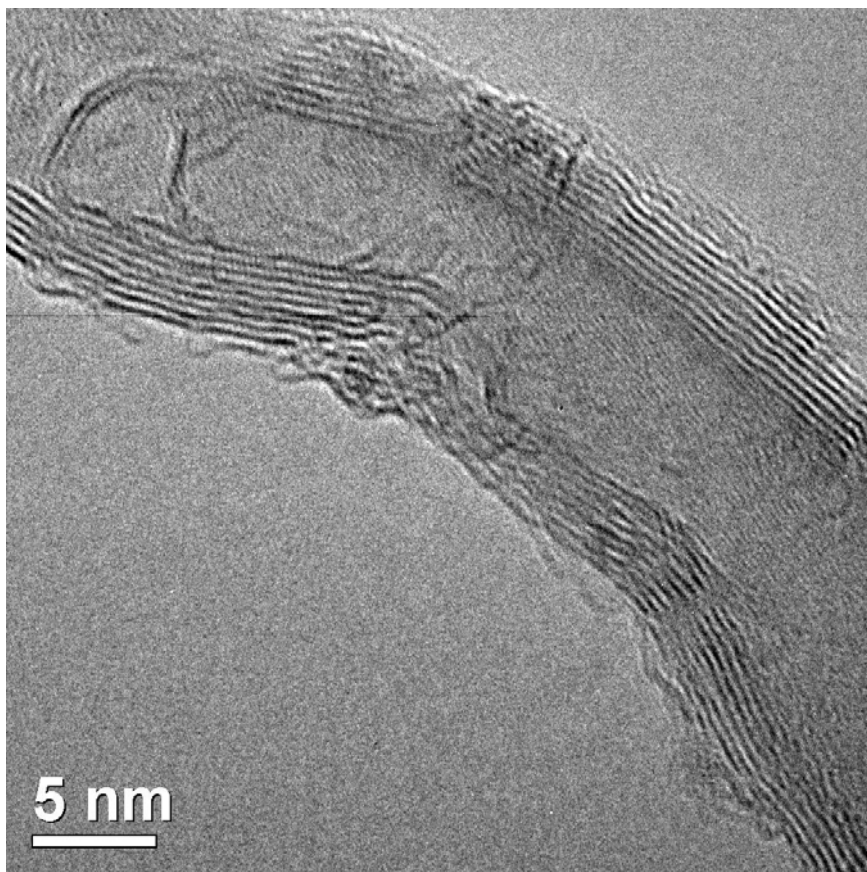
HRTEM images of carbon nanotubes (MWNT) produced during ethane dehydrogenation at 600ºC over Fe-Ni nanoparticles (10 nm, 0.2 wt%) supported on Mg(Al)O after removal of support in dilute nitric acid solution at room temperature. Some Fe-Ni nanoparticles remain within the MWNT tips.

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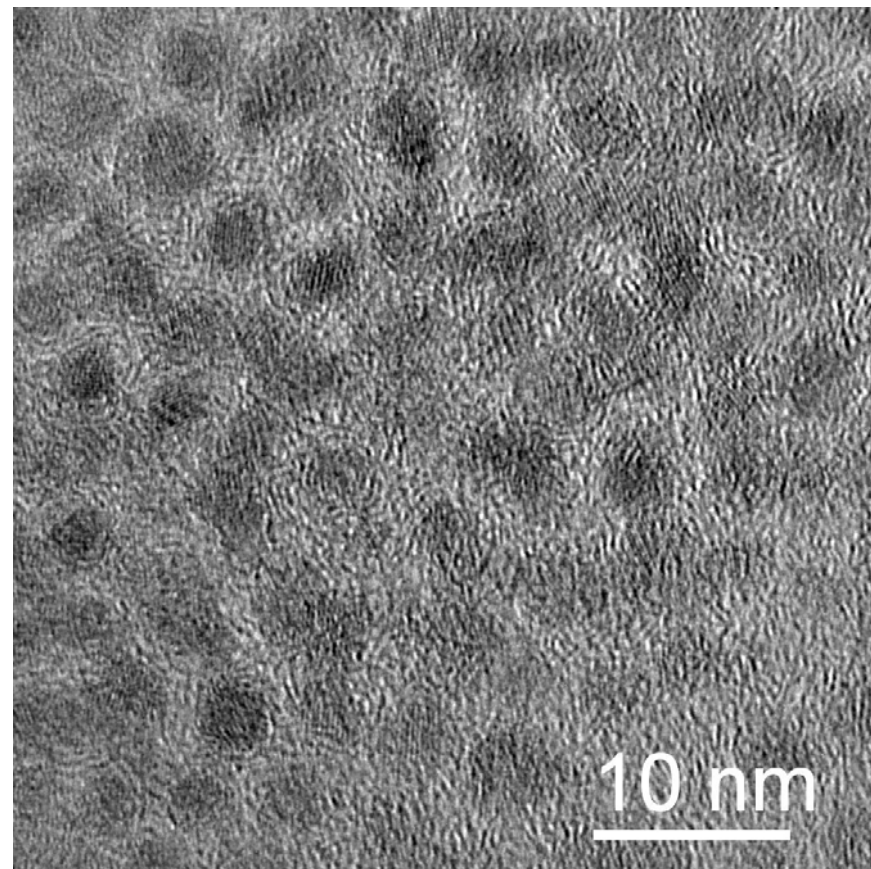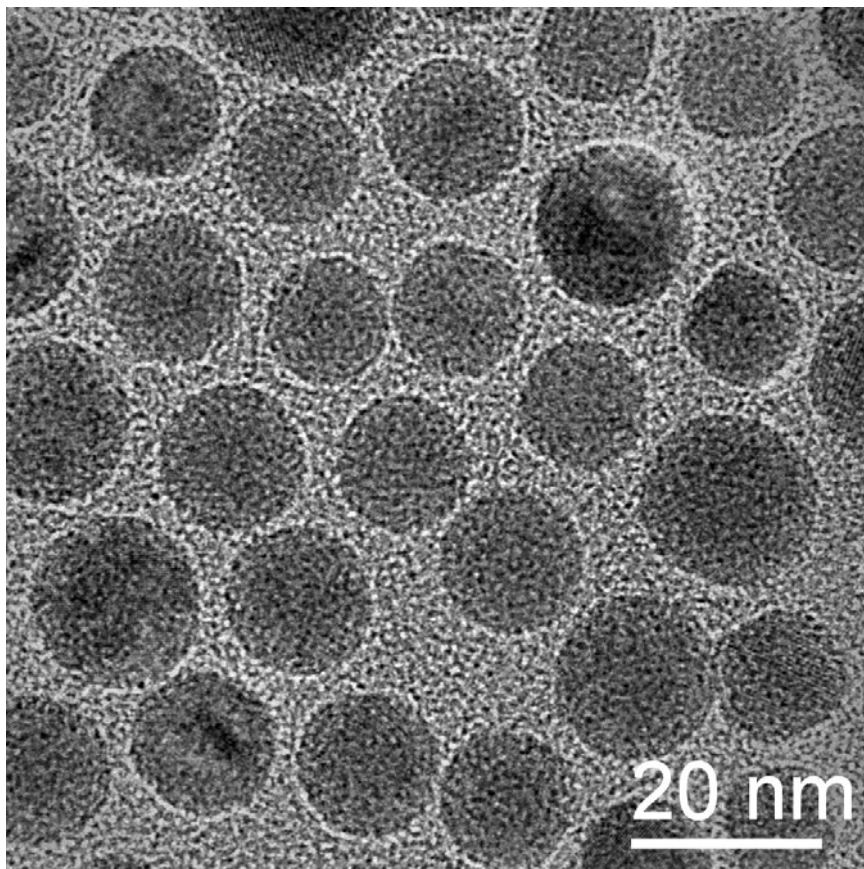
TEM images of 12 nm and 4 nm Fe oxide particles prepared for use in lower alkanes dehydrogenation experiments. (*Hyeon et al, Nature Materials, 3, 2004, 891; Sun et al, J. Am. Chem. Soc, 126, 2004, 273*).

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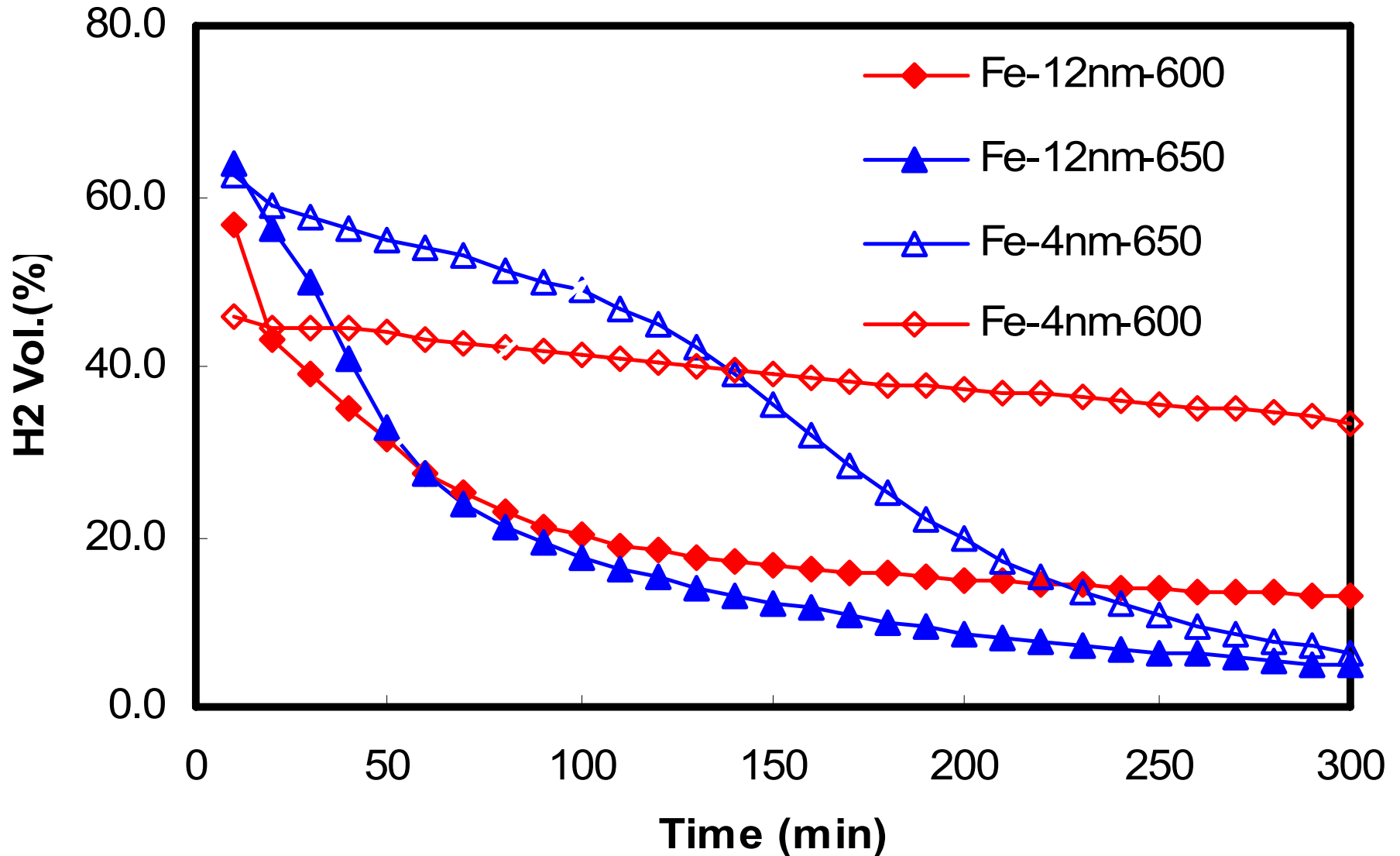
Hydrogen production by catalytic dehydrogenation

- 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 > 600ºC and stacked cone nanotubes at T ≤ approximately 500ºC

- 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 :

Anode : $C(s) + 2H_2O(l) \rightarrow CO_2(g) + 4H^+ + 4e^-$

Cathode : $4H^+ + 4e^- \rightarrow 2H_2(g)$

Net reaction : $C(s) + 2H_2O(l) \rightarrow CO_2(g) + 2H_2(g)$
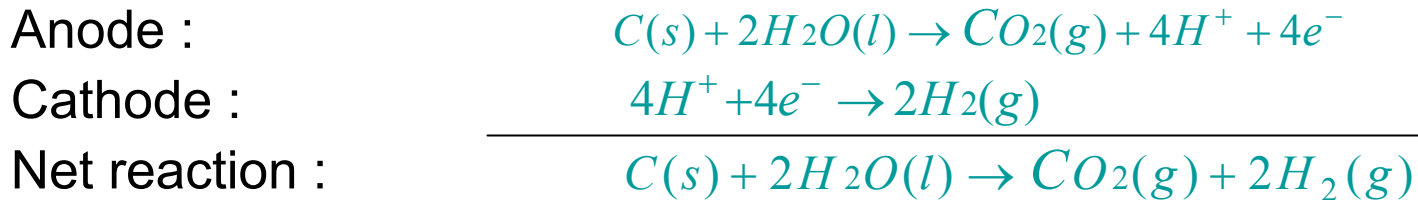
$\Delta G = \Delta G \ (product) - \Delta G \ (reactants)$

    $= -94.26 \ (CO_2) + 2(56.7) = 19.27$ kcal/ 2mol $H_2O = 9.6$ kcal/mol H_2O,

             compared to 56.7 kcal/mol H_2O without carbon

$$E^0 = -\frac{\Delta G}{nF} = -0.21V$$

compared to $E^0 = -1.23V$ for electrolysis of water without carbon.

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

Carbon-assisted electrochemical hydrogen production

Potentiostat

Cathode
Pt coil

Anode
Pt plate

Reference
electrode
Ag/AgCl

To
Gas Chromatograph

3.7 M H$_2$SO$_4$ +
carbon as
electrolyte at anode

3.7 M
H$_2$SO$_4$ as
electrolyte

3.7 M H$_2$SO$_4$
as electrolyte

Glass frits
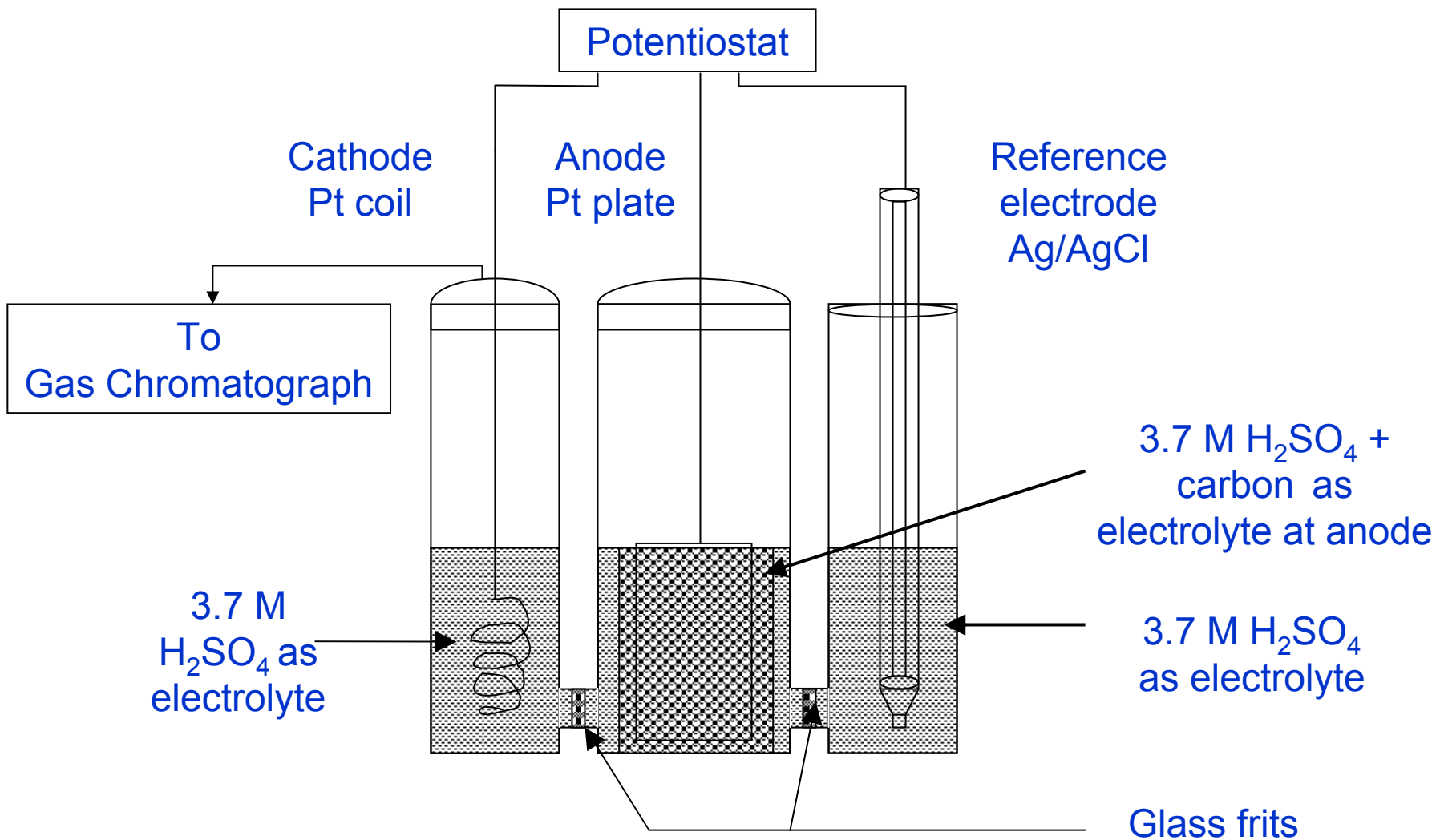
Working electrode area : 6.8 cm^2 ;Counter electrode area : 2.55 cm^2

Carbon-assisted electrochemical hydrogen production

t_H = time needed to produce the same amount of H_2

amount of carbon = 0.08 g/cm^3

t_H(min)/H$_2$

Current (mA)

Potential E^0(volts)
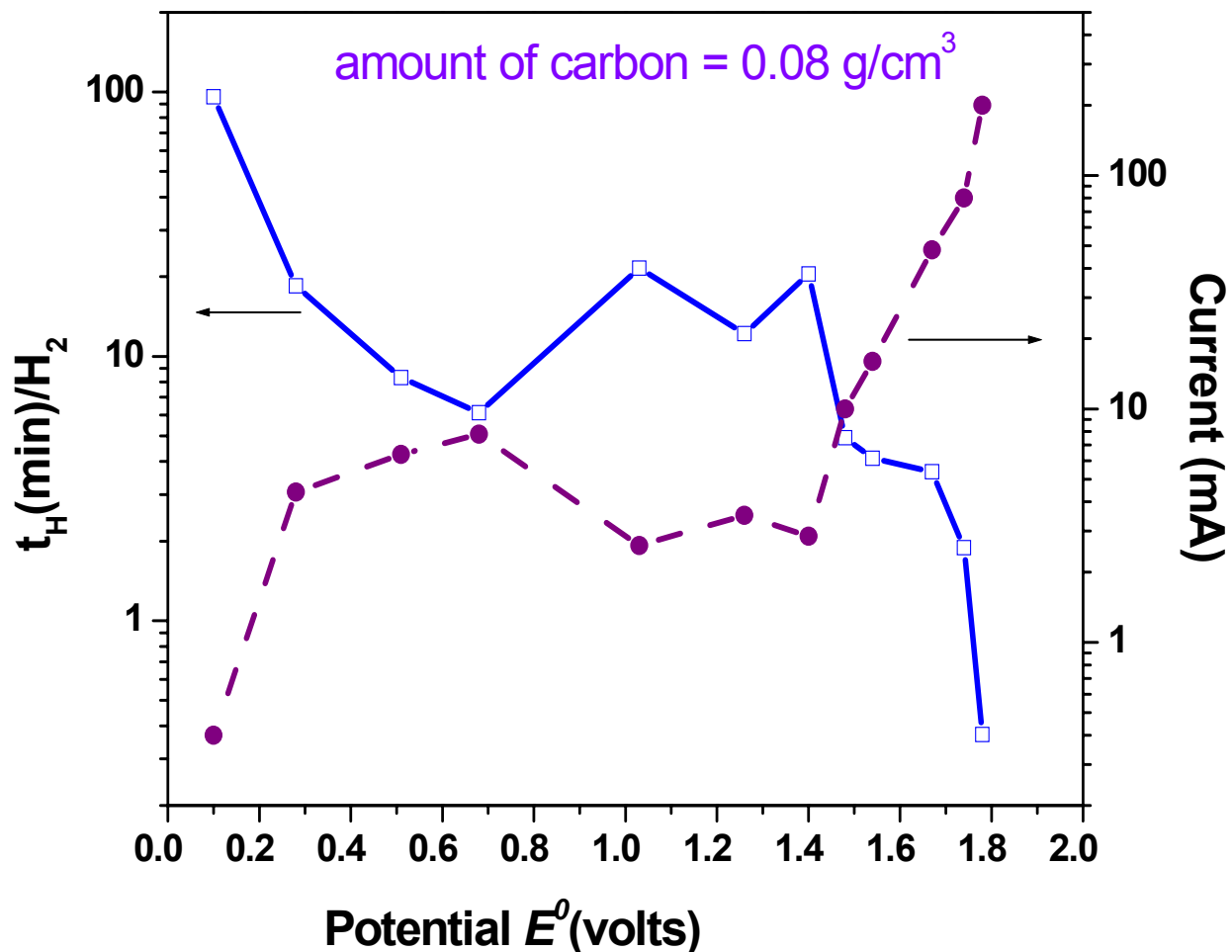
H_2 is produced at voltages as low as 0.1V, but time required to produce the same amount of H_2 is higher and the corresponding current is lower.

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 = 3.6×10^6 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
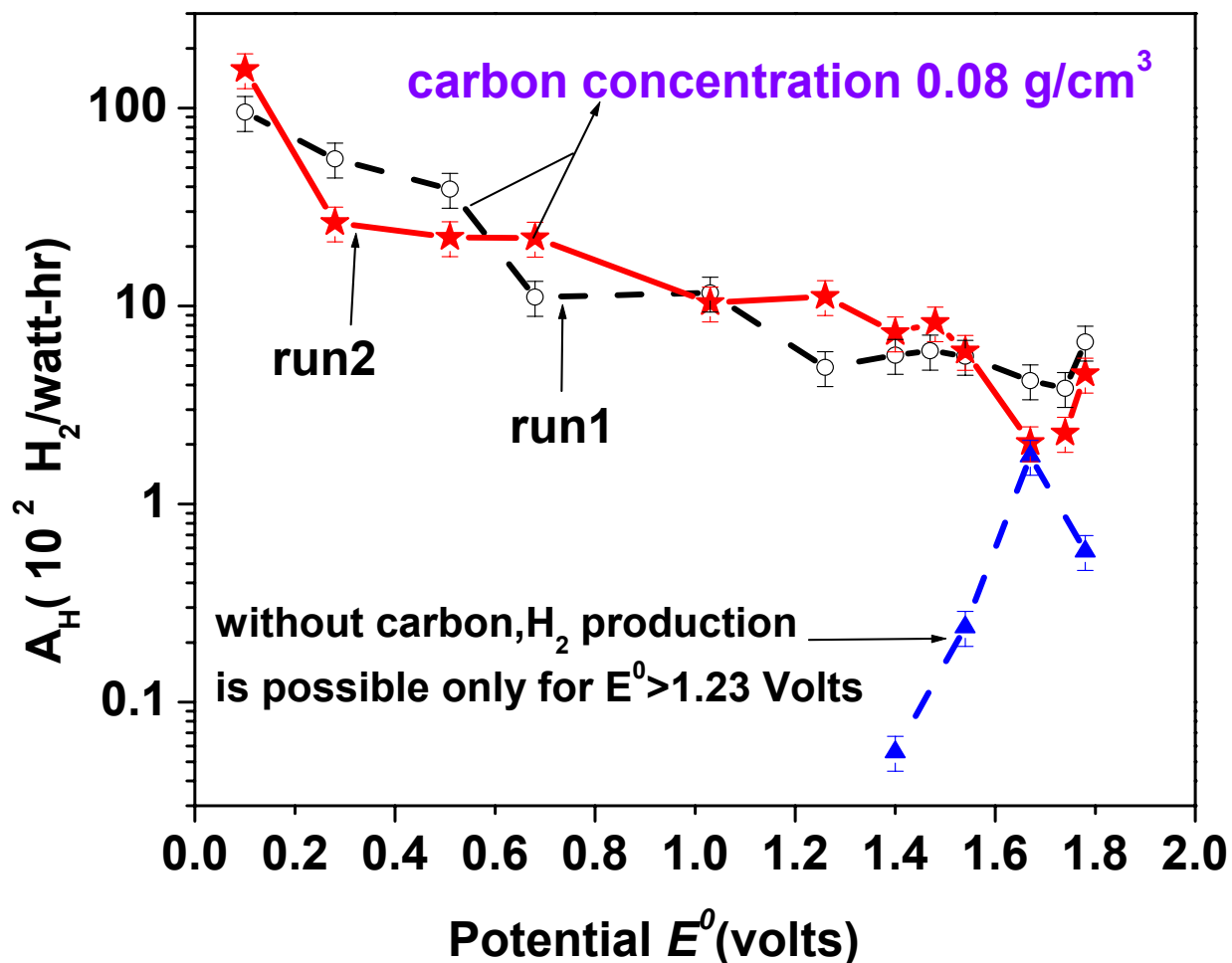
Carbon-assisted H_2 production at lower voltages is considerably more energy efficient, although it takes somewhat longer to produce the same amount of H_2. Use of catalysts to reduce this time is being investigated.

Hydrogen Production by Reforming in Supercritical Water

- H$_2$O is both a reactant and the solvent
- Direct high-pressure H$_2$ 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]
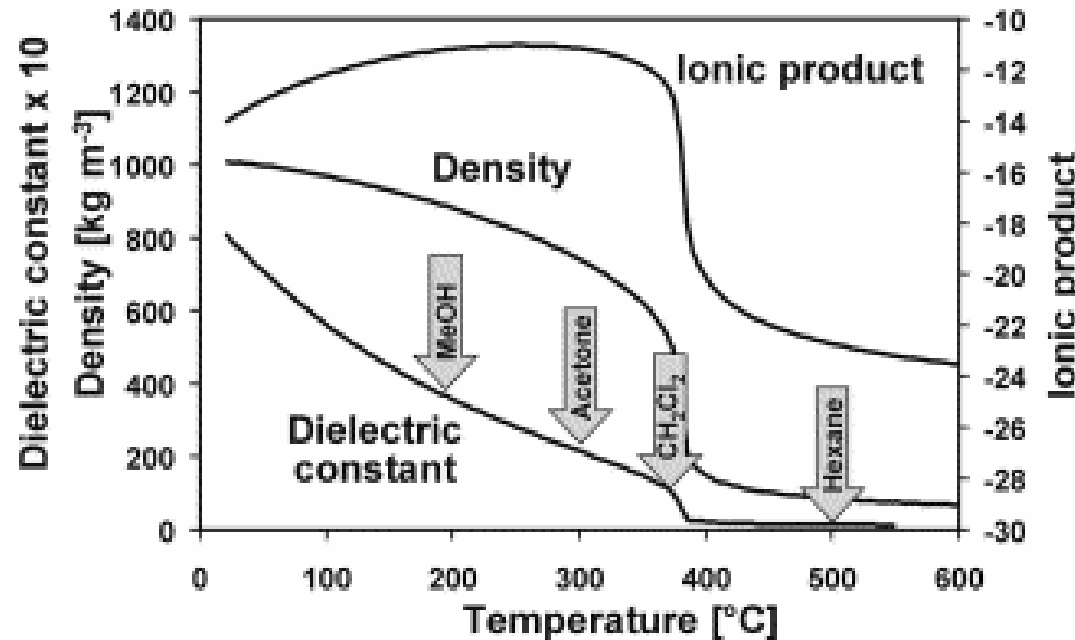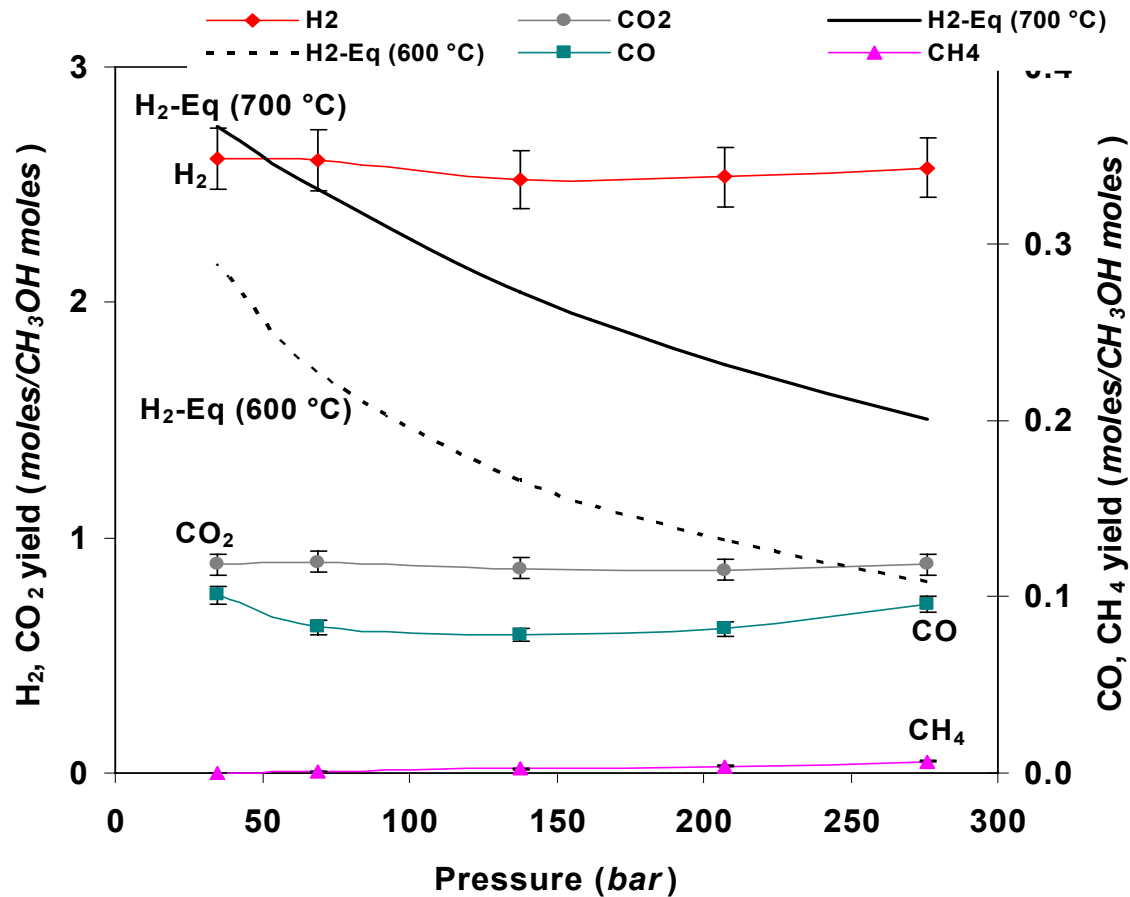
Experimental Setup - H$_2$ Production by Reforming in Supercritical Water
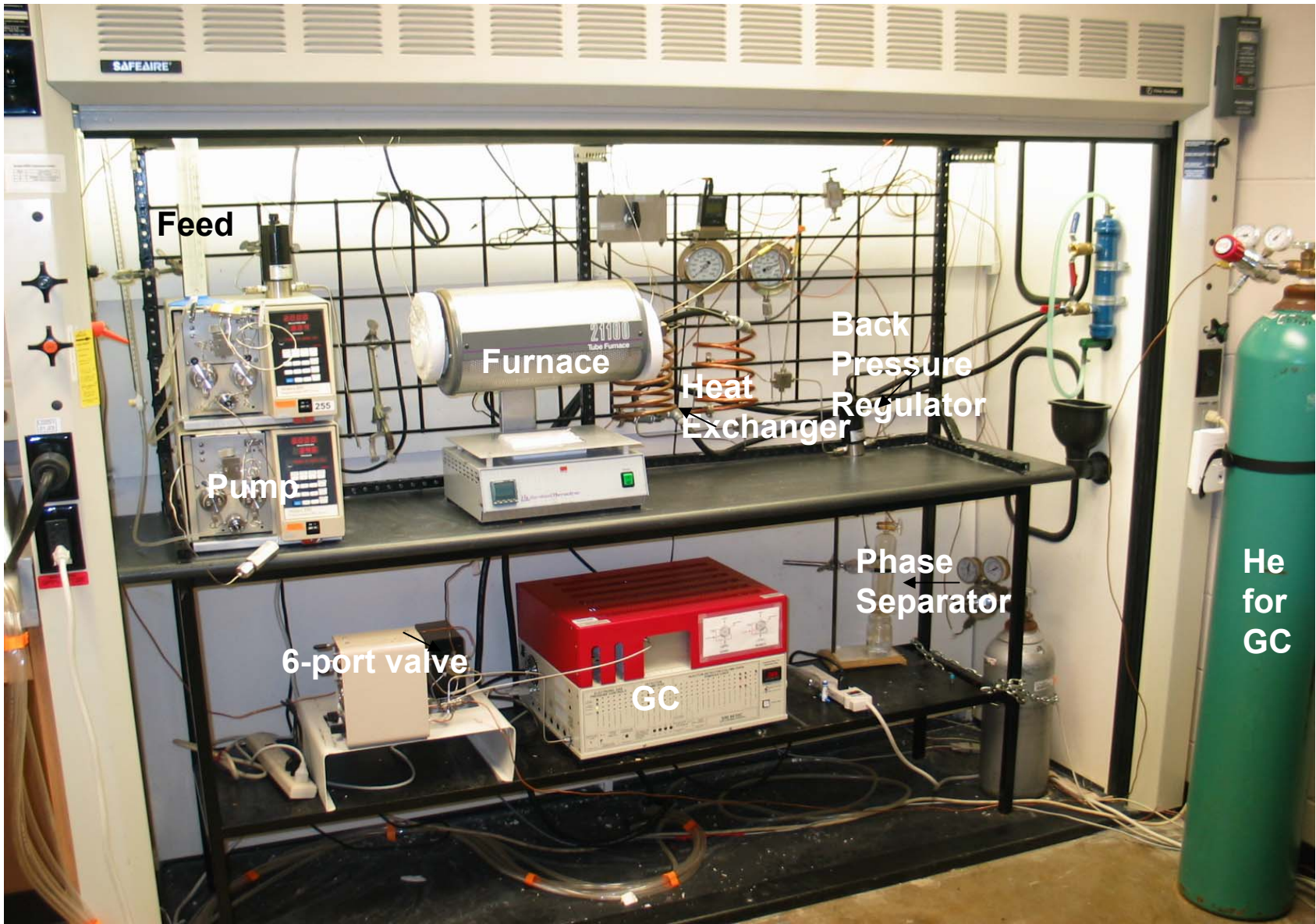
Hydrogen Production by Reforming in Supercritical Water

H_2 from 10 wt.% methanol using Monel-400 ($Ni_{0.67}$ $Cu_{0.33}$) 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

$$C_6H_5CH_3 + 14H_2O \Leftrightarrow 7CO_2 + 18H_2$$
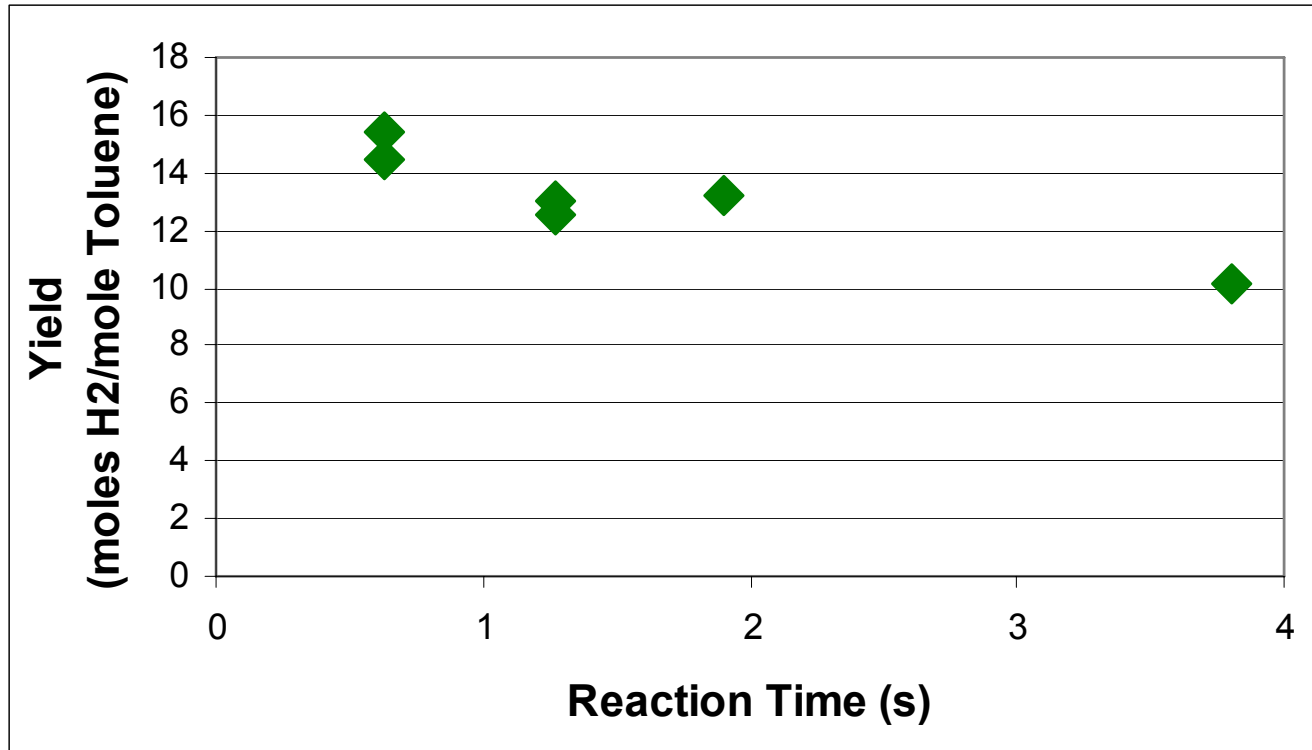
Inconel reactor, Ru/Al_2O_3 catalyst, 800°C, 3500 psi, 2.1 wt% toluene in water feed

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.
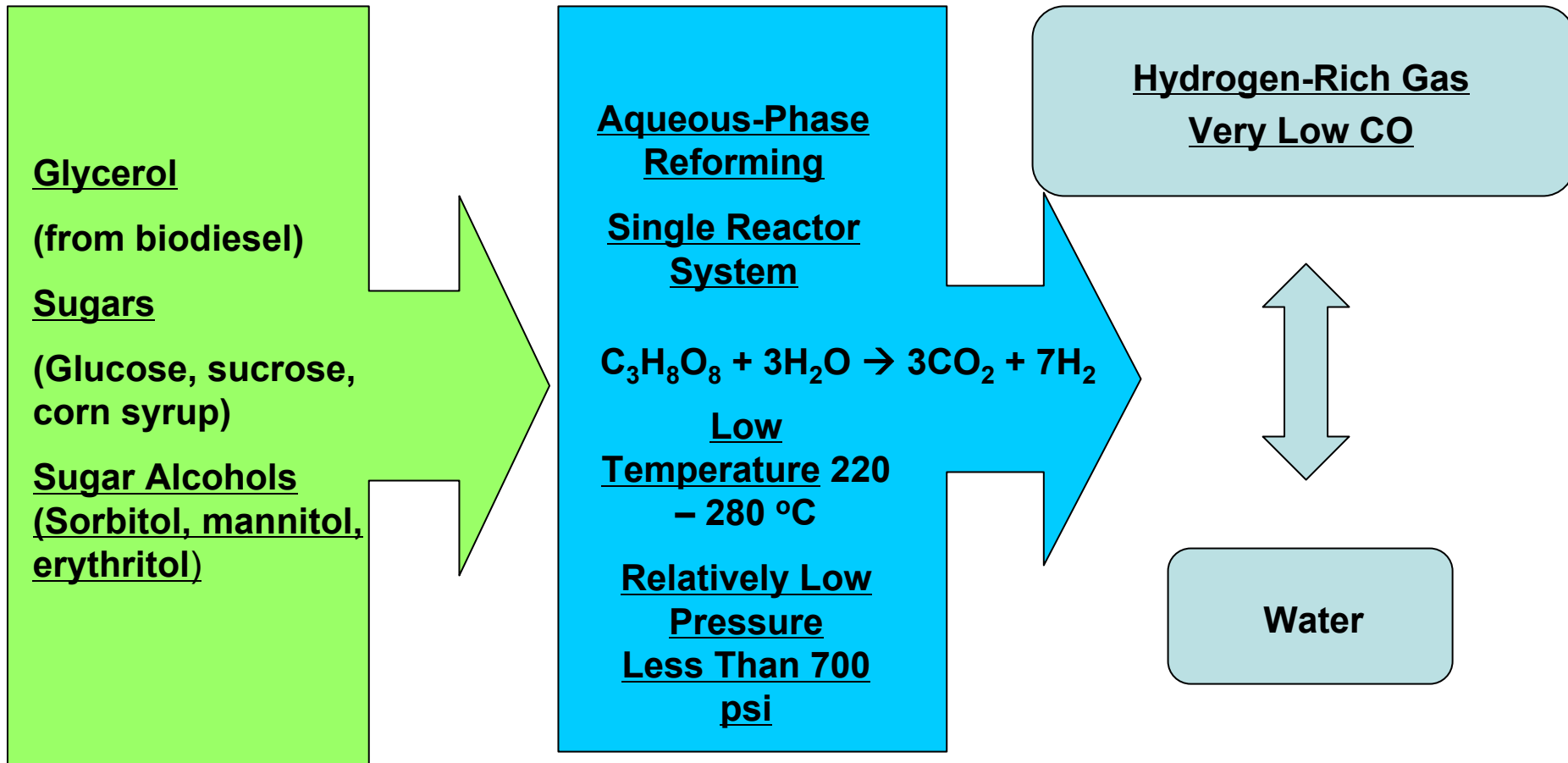
- They can be reacted with water in a single step reactor at 200-250°C and sufficient pressure to prevent vaporization of the water to produce a high yield of hydrogen and low CO.

- Hydrogen yield and selectivity for a series of polyols ranging from C_2 to C_6 have been measured using a flow reactor and a variety of experimental conditions.

Hydrogen Production from Biosustainable Polyols

Glycerol

(from biodiesel)

Sugars

(Glucose, sucrose, corn syrup)

Sugar Alcohols (Sorbitol, mannitol, erythritol)

Aqueous-Phase Reforming

Single Reactor System

$C_3H_8O_8 + 3H_2O \rightarrow 3CO_2 + 7H_2$

Low Temperature 220 – 280 °C

Relatively Low Pressure Less Than 700 psi

Hydrogen-Rich Gas Very Low CO

Water

Hydrogen Production from Selected Polyols

Reactant	Feed Conc. (wt%)	H$_2$ Yield (mole %)	H$_2$ 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$_2$O$_3$; CO < 400 ppm

Hydrogen yield based on total hydrogen in polyol

Hydrogen from Polyols - Catalyst Specificity

GLYCEROL

$$H_2-C-C-C-H_2$$

Pt   Cu

H_2 $CH_3CHOHCH_2OH$

HYDROGEN   1,2-PROPANEDIOL
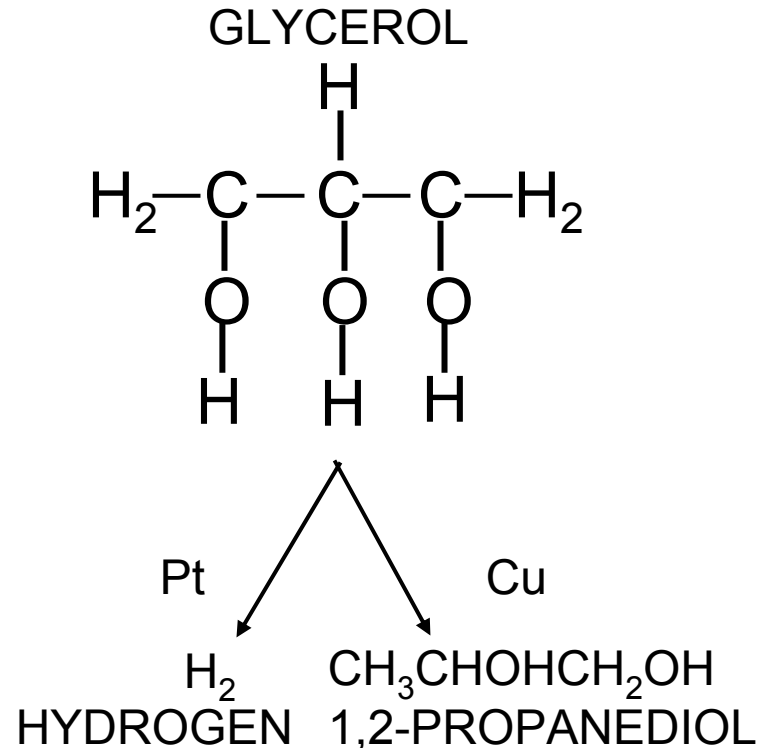
Experiments with glycerol, a by-product of biodiesel manufacture, have shown that it can be converted to hydrogen by splitting the O-H bond using a Pt catalyst or to chemicals by splitting the C-C bond using a Cu catalyst.

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

$Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$
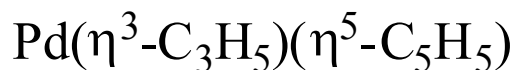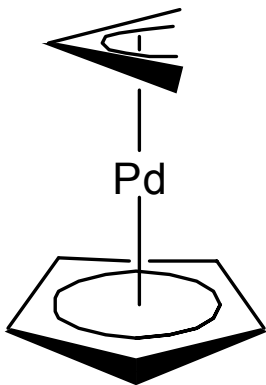
Pd (%)	Incorporation Method	Activity @ 200 ºC (mmol-H_2/g-cat h)	Improvement @ 200 ºC w/ GPI
1	solution	4.2	
1	gas-phase	7.2	71%
2	solution	4.3	
2	gas-phase	11.0	155%
5	solution	11.6	
5	gas-phase	18.7	61%

Production of very high surface area (S_A) Ceria aerogel

- Very high surface ceria
  - Maximum BET S_A = 375 m^2/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
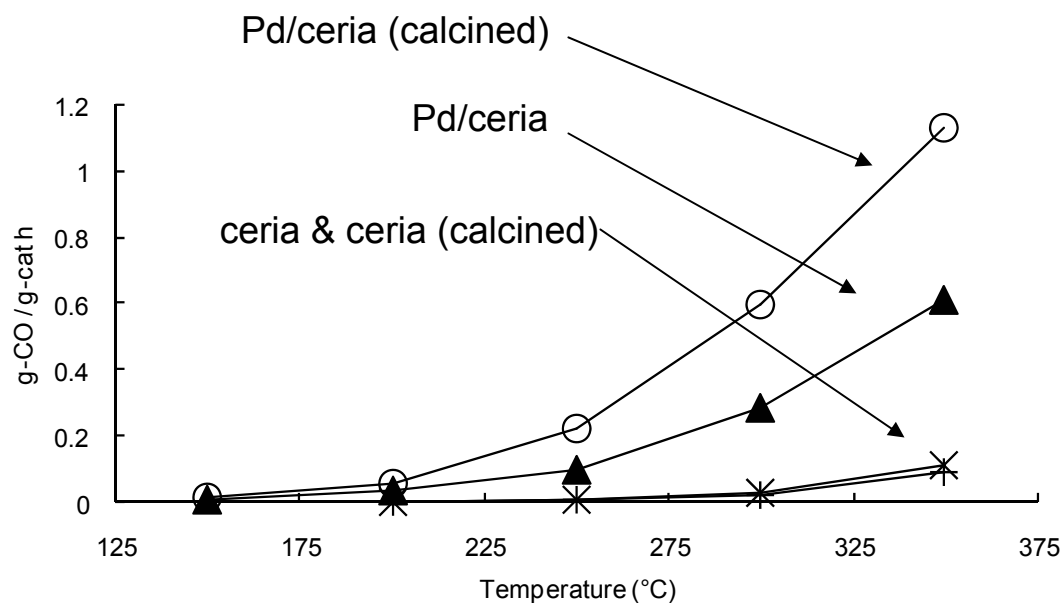
Catalyst type	Arrhenius Activation Energy
Pd/ceria (calcined)	(53.7 ± 0.8) kJ/mol
Pd/ceria	(52.7 ± 0.8) kJ/mol
ceria	(77.2 ± 1.5) kJ/mol
ceria (calcined)	(74.3 ± 2.0) kJ/mol

- Pd/ceria BET S_A = 283 m^2/g
- Pd/ceria (calcined) BET S_A = 137 m^2/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)