Hydrogen Energy

CH3F7: Energy course contribution

Martin Wills

Why hydrogen?

1) Converting hydrogen to energy

2) Generation:.

3) Storage and transport:.

THE UNIVERSITY OF WARWICK

Hydrogen as a reagent and a carrier of energy: overview

Why consider using hydrogen? The 'trump card':

-releases a large amount of energy upon combustion and produces only water.

$$2\,H_2 \quad + \quad O_2 \longrightarrow 2\,H_2O \quad (+\text{ energy})$$

-**Uses:**
-Can be used directly in combustion or in a fuel cell to produce electricity.
- Hydrogen is produced primarily for use as a reagent, for example to produce ammonia for fertiliser and hydrocracking (making large hydrocarbons into smaller more useful ones).

Why not use hydrogen?
A carrier of chemical energy (not a primary source as it is not naturally available).
A highly explosive gas. Safe storage is a major challenge.

-At present, most is made by steam reforming of fossil fuels, which is unsustainable.

-Electrolysis of water using clean electricity is a sustainable alternative – but why not just use the electricity directly in the first place?

Bottom line –hydrogen is an energy *carrier*, like a battery (with the associated pros and cons).

Why hydrogen?

1) <u>Converting hydrogen to energy (the good and bad news)</u>

Potential energy content of hydrogen-

High per kg but low per litre:

Table: Comparison of energy density of various hydrogen sources with a hydrocarbon.

	Hydrogen gas, 200atm	Liquid hydrogen (0.07kg/L @ 20K)	Glucose $C_6H_{12}O_6$	Material containing 6% H by mass	Hexane C_6H_{14} (0.67 kg/L)
Moles H_2 per kg	-	500	33.3	25	-
Moles H_2 per litre	8.33	35	-	-	-
Energy/ kJ/mol	237.2	237.2	237.2 (1)	237.2 (1)	4,017 (2)
Energy/ kJ per kg	-	118,600 (14.2L)	7,898 (1)	7,116 (1)	46,711 (2)
Energy/ kJ per L	1,975	8,302	-	-	31,296 (2)

(1) by combustion of the hydrogen component only.
(2) by combustion of the full hydrocarbon.

Glucose has as much hydrogen energy per kg as a litre of liquid hydrogen and a storage material containing 6% H by mass.

At 700 Bar (70 megapascals) you could get about 7000 kJ / Litre – just about possible. But you need to use energy to compress it.

Potential energy content of hydrogen in organic molecules-

An aspect of hydrogen generation from organic molecules is that potentially up to half the hydrogen comes from water.

i.e. Organic molecules lever hydrogen out of water!

(nb a bit simplistic as I have ignored the energy cost/gain of the reaction shown)

$$C_6H_{12}O_6 + 6\ H_2O \longrightarrow 12\ H_2 + 6\ CO_2$$

Glucose; 6 out of 12 hydrogen molecules are from water.

Value of hydrogen produced:
15,813 kJ per Kg of glucose

$$C_3H_8O_3 + 3\ H_2O \longrightarrow 7\ H_2 + 3\ CO_2$$

Glycerol; 3 out of 7 hydrogen molecules are from water.

Value of hydrogen produced:
18,050 kJ per Kg of glycerol

But why not just burn the biomass in the first place – carbon capture and storate (CCS)?.

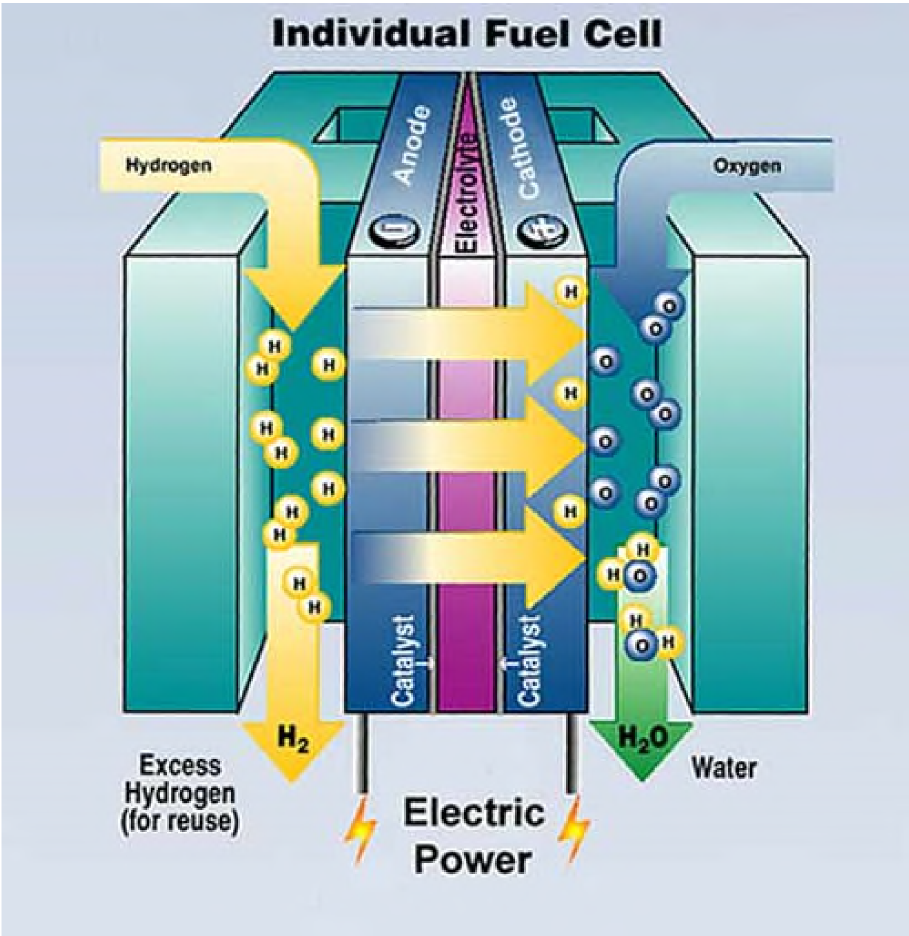
Using Hydrogen to Generate Power: Fuel Cells

Operation of Fuel Cells:

Protons and electrons are separated at the anode.

Electrons take a path which allows them to do work, then return to the cathode.

At the cathode, electrons 'rejoin' the protons with the electrons and oxygen to give water (hence a driving force).



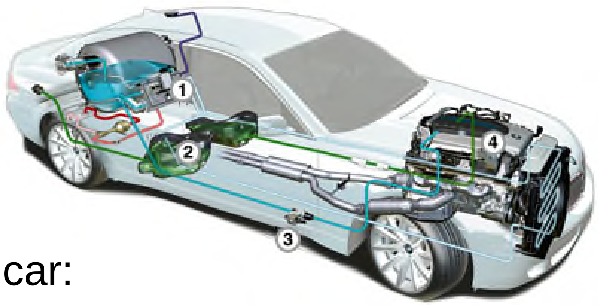
PEM (Proton Exchange Membrane*) fuel cell shown.

*** Sometimes called 'polymer electrolyte membrane' or some other variant.**

Alternatively, you can burn it, but this is usually less efficient.

Hydrogen transport applications already exist:

Hydrogen as a fuel for transport applications**:**



Hyundai ix35 production hydrogen car:
Launched in 2013.
http://www.hyundai.co.uk/about-us/environment/hydrogen-fuel-cell

Lots of hydrogen-powered vehicles already exist:

Hydrogen in buses in cities = lower pollution, but can also ensure hydrogen supply is in place. More challenging situation for private vehicle owner:

Examples of Fuel Pumps-

Not many worldwide at present

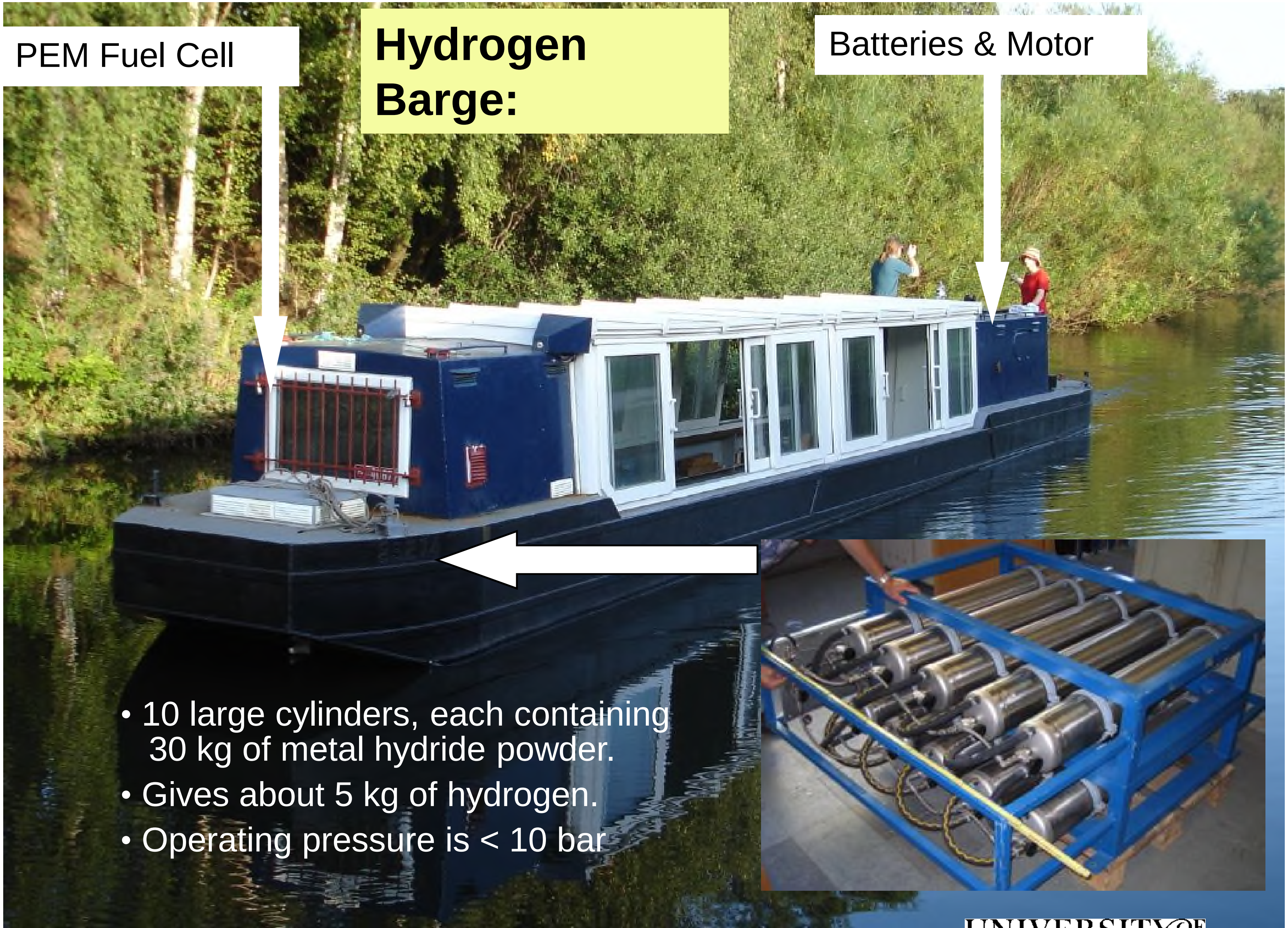
Hydrogen filling station in California

Eleven new hydrogen refuelling stations opened throughout the world in 2013, bringing the total number of hydrogen refuelling stations in operation to 186 as of March 2014.This is the result of the sixth annual assessment by H2stations.org, a website of Ludwig-Bölkow-Systemtechnik (LBST) and TÜV SÜD (http://www.tuev-sued.de/)

See also: http://www.netinform.net/h2/H2Stations/Default.aspx

No shortage of hydrogen through.

Hydrogen Barge:



- 10 large cylinders, each containing 30 kg of metal hydride powder.
- Gives about 5 kg of hydrogen.
- Operating pressure is < 10 bar

Hydrogen cars and filling station at Birmingham.

And a visit to Warwick

Hexis Solid Oxide Fuel Cell (SOFC) for home heating (also work with hydrocarbons but need high temperatures)

Research Test Stations - Birmingham

Recent article in Chemical and Engineering News (the Weekly Magazine of the American Chemical Society):
(November 17th 2014). Some quotes and some paraphrasing…

‘In 2007 GM’s test model used 80g of Pt in its fuel cells, today’s workhorse model is using below 30g’. A 10g stack of fuel cells is in development.

‘Since 2008 Toyota have reduced the cost of a car fuel cell system by 95%, and they now fit in a small car (not a massive SUV).’

‘Over the last decade, improvements in fuel cell technology have lapped battery technology three or four times’ (Batteries are heavy and slow to recharge, filling a hydrogen tank can take 3 minutes*).

‘Toyota is weaving its own carbon fiber tanks that compress the gas to 70 megapascals’ (nb this gives about 690 atmospheres and about 7000 kJ/litre, compared to 31,000 kJ/litre for a typical hydrocarbon, and a range of up to 400 miles).

‘Future hydrogen power drivers can thank innovations in chemistry and materials science for some of the most critical improvements.’

But there are still obstacles to overcome.
* MW comment – hybrid vehicles (petrol+ battery are exceptions as the battery charges during driving).

Why hydrogen?

2) Generation (the less good news):

Hydrogen is cheap and easy to make. Methods of hydrogen production include:

Steam reforming	CH_4	$\longrightarrow$	$H_2 + CO_2$ (via CO)
Electrolysis	H_2O	$\longrightarrow$	$H_2 + O_2$
Algae Bioreactors	Hydrocarbons	$\longrightarrow$	$H_2 + CO_2$
Fermentation (Dark or Light)	Fatty acids + bacteria	$\longrightarrow$	$H_2 + CO_2$
photoelectrochemical water splitting	H_2O	$\longrightarrow$	$H_2 + O_2$
Chemical catalysis	HCO_2H alcohols	$\longrightarrow$	$H_2 + CO_2$ H_2 + ketones or CO_2
	biomass		H_2 + high value products

The carbon in any hydrocarbon has to end up as something, usually it's CO or CO_2

Electrolysis or photoelectrochemical water splitting is a great method for making ‘green’ hydrogen – if the source of electricity is itself ‘green’ (i.e. solar, wind, wave, hydroelectric, tidal…):

Electrochemical or photoelectrochemical water splitting $\quad H_2O \longrightarrow H_2 + 0.5\ O_2$

Electrolysis relies on fairly obvious and simple technology, although this is always being improved and made more efficient.

But then again…why not just use the electricity directly, why have hydrogen at all…?

Steam reforming is a long established process:

(hydrogen generation for energy and synthesis)

From oil

C_nH_{2n+2} + n H_2O $\longrightarrow$ (2n+1) H_2 + n CO

requires high temperatures and catalyst

or

'syngas' or 'town gas'

If you have a lot of coal:

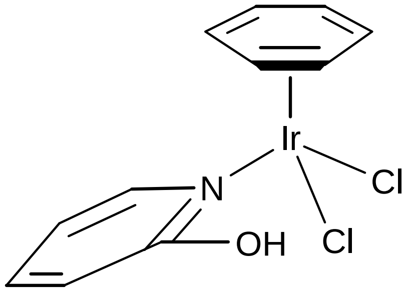
C + 2 H_2O $\longrightarrow$ 2 H_2 + CO $\longrightarrow$ C_nH_{2n+2} + n H_2O

Fischer–Tropsch Process (Co or Fe catalyst)

Cheap gas via fracking – a threat to sustainable energy generation?

Development of some chemical catalysts for hydrogen generation.

Reported organometallic catalysts for hydrogen generation from alcohols:



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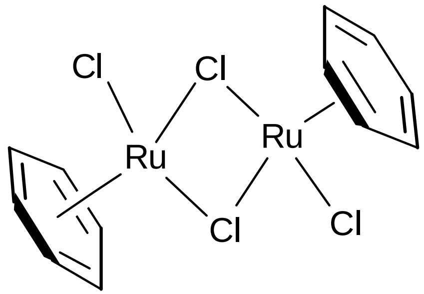

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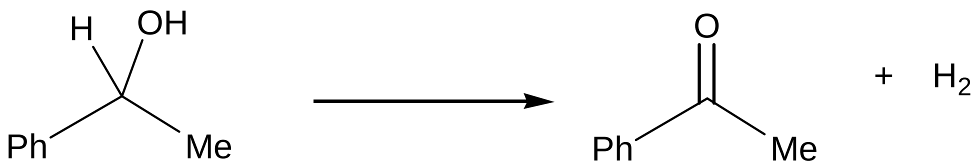
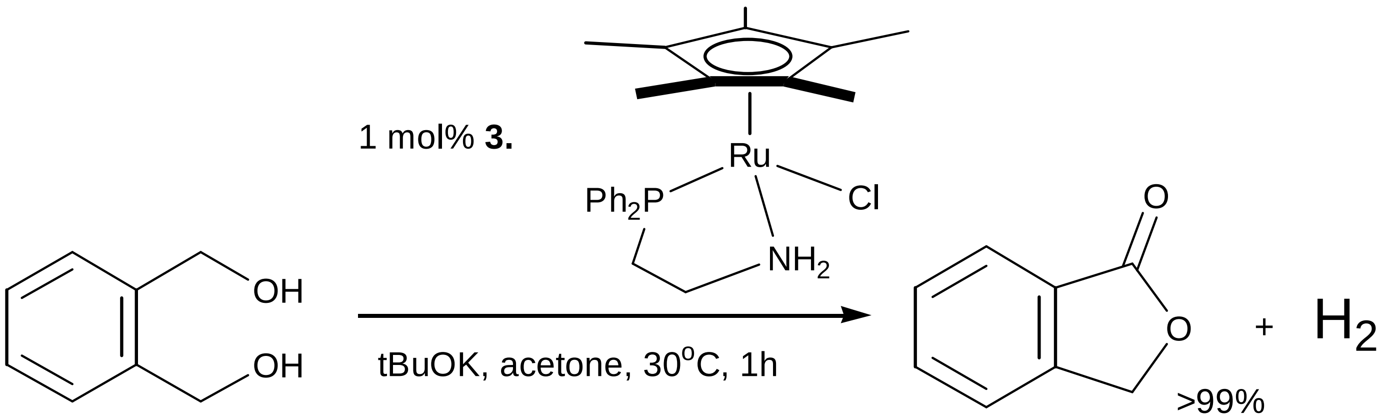
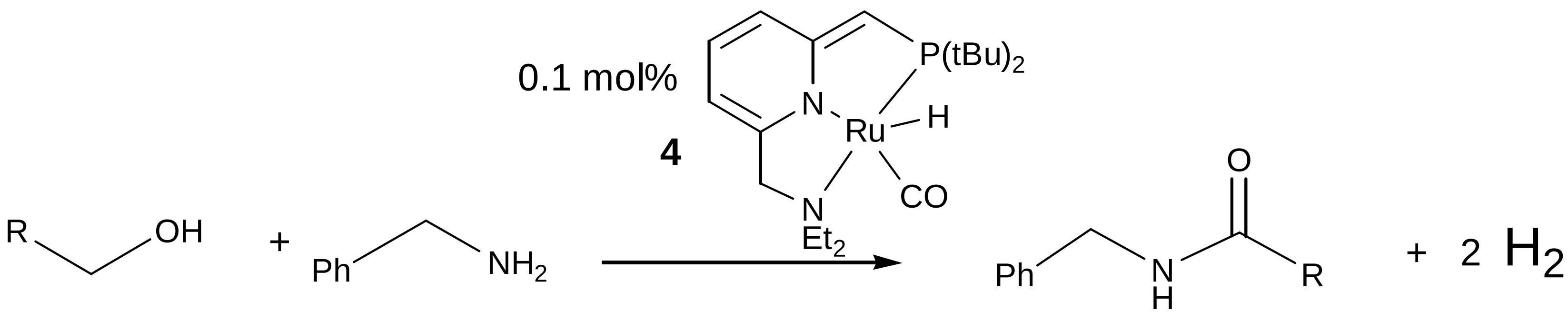


with **1**, 0.1 mol%, 20h reflux in toluene, 70% conversion.
with **2**, 5 mol%, 15 mol% LiOH, 48h in reflux in toluene, 100% conversion.

Catalyst **1**: K.-I. Fujita, N. Tanino and R. Yamaguchi, *Org. Lett.* **2007**, *9,* 109-111.
Catalyst **2**: G. R. A. Adair and J. M. J. Williams, *Tetrahedron Lett.* **2005**, *46*, 8233-8235.

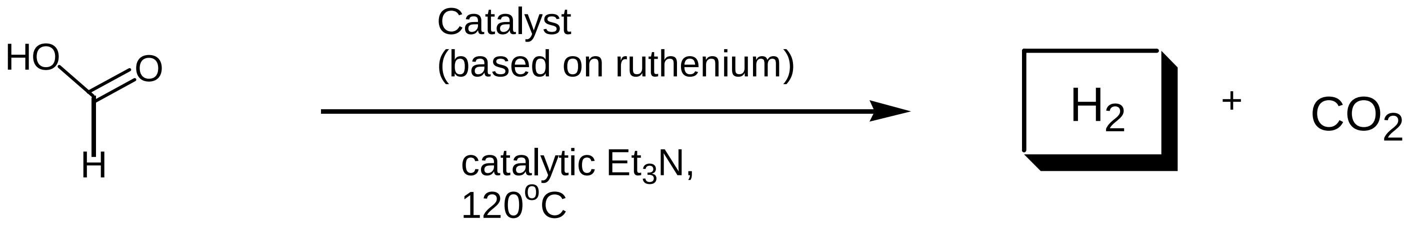
Reported organometallic catalysts for hydrogen generation from alcohols:





Catalyst **3**: M. Ito, A. Soaku, A. Shiibashi and T. Ikariya, *Org. Lett.* **2007**, *9*, 1821-1824.
Catalysts **4**: C. Gunanathan, Y. Ben-David and D. Milstein, *Science,* ***2007****, 317, 790-792.*

Wills group research – hydrogen generation from formic acid using ruthenium catalysts:



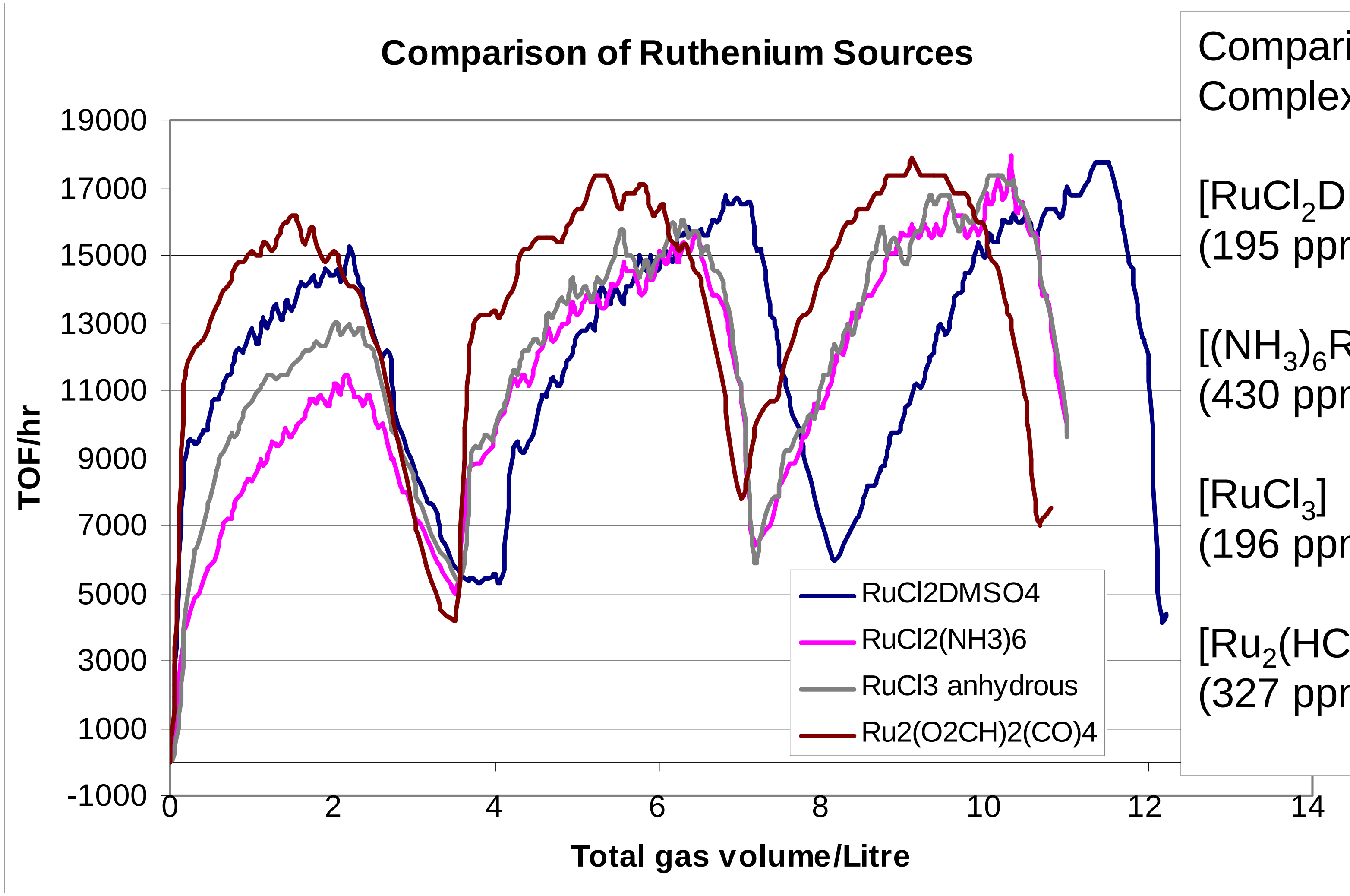
Can be run as a batch or continuous flow.

'A Continuous-Flow Method for the Generation of Hydrogen from Formic Acid', Artur Majewski, David J. Morris, Kevin Kendall and Martin Wills, *ChemSusChem,* 2010, **3**, 431-434.

'Insights into hydrogen generation from formic acid using Ru complexes', David J. Morris, Guy J. Clarkson and Martin Wills, *Organometallics*, 2009, **28**, 4133-4140. (om900099u).

A review:
Hydrogen generation from formic acid and alcohols using homogeneous catalysts
Johnson, Tarn C.; Morris, David J.; Wills, Martin, *Chem. Soc. Rev.* 2010, **39**, 81-88.
(160 citations).

Comparison of activity of four Ru catalysts.



Comparison of Ru Complexes:

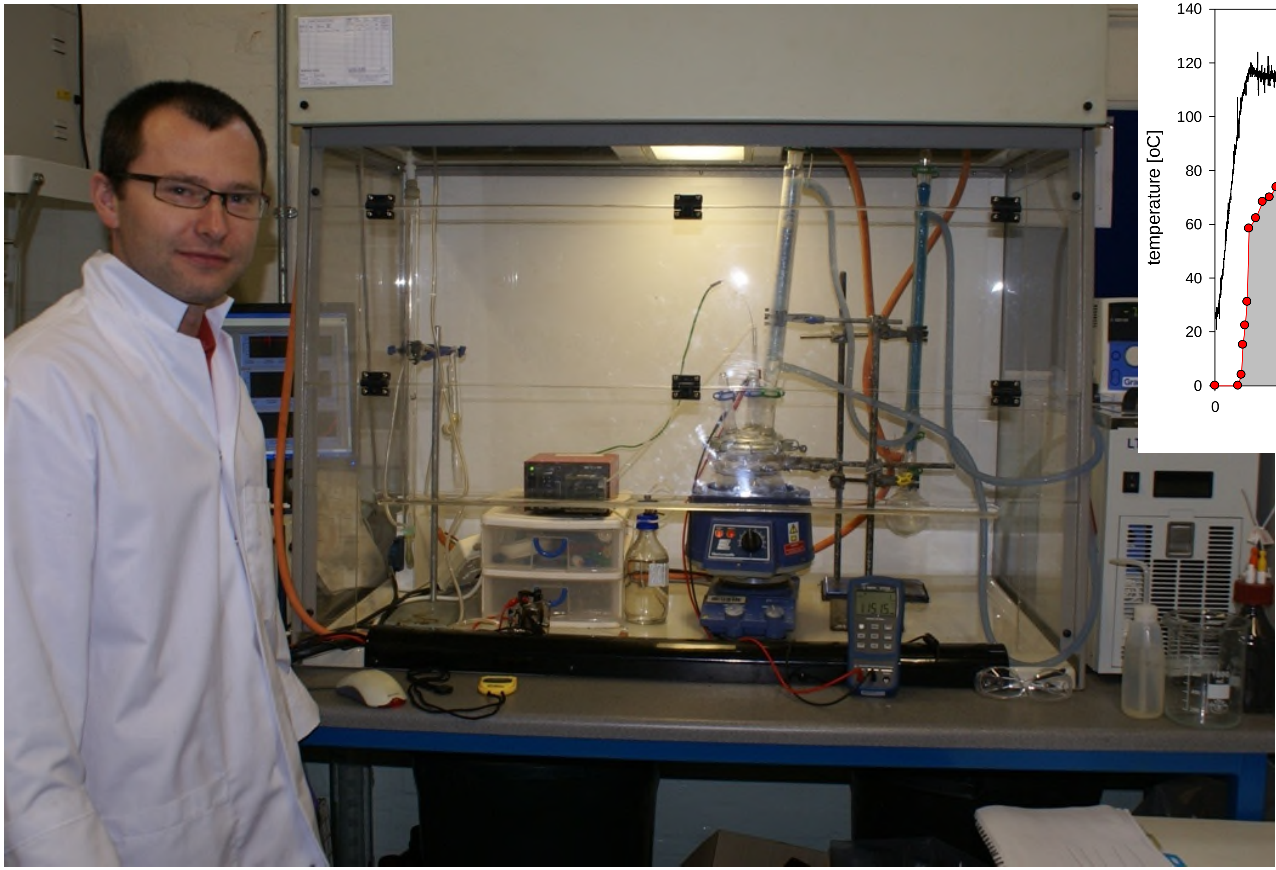
$[RuCl_2DMSO_4]$
(195 ppm CO)

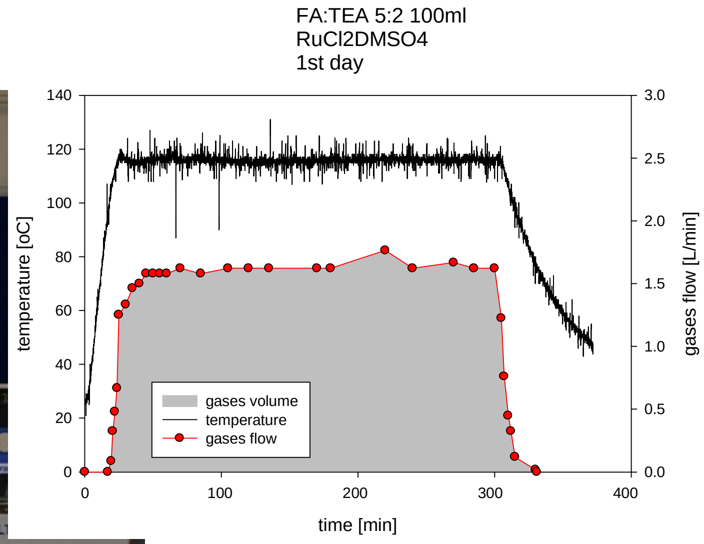
$[(NH_3)_6RuCl_2]$
(430 ppm CO)

$[RuCl_3]$
(196 ppm CO)

$[Ru_2(HCO_2)_2(CO)_4)]$
(327 ppm CO)

Medium scale hydrogen generation from formic acid:

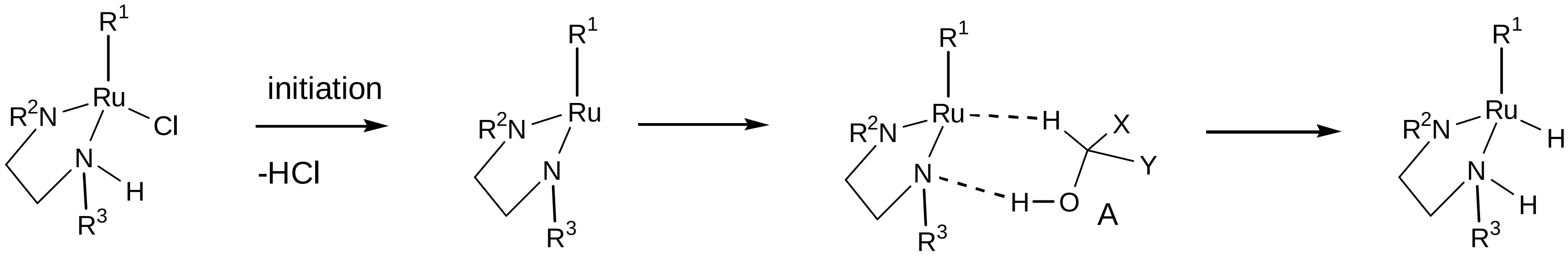




Larger scale set up which allows continuous formation of hydrogen from formic acid, with Artur Majewski.

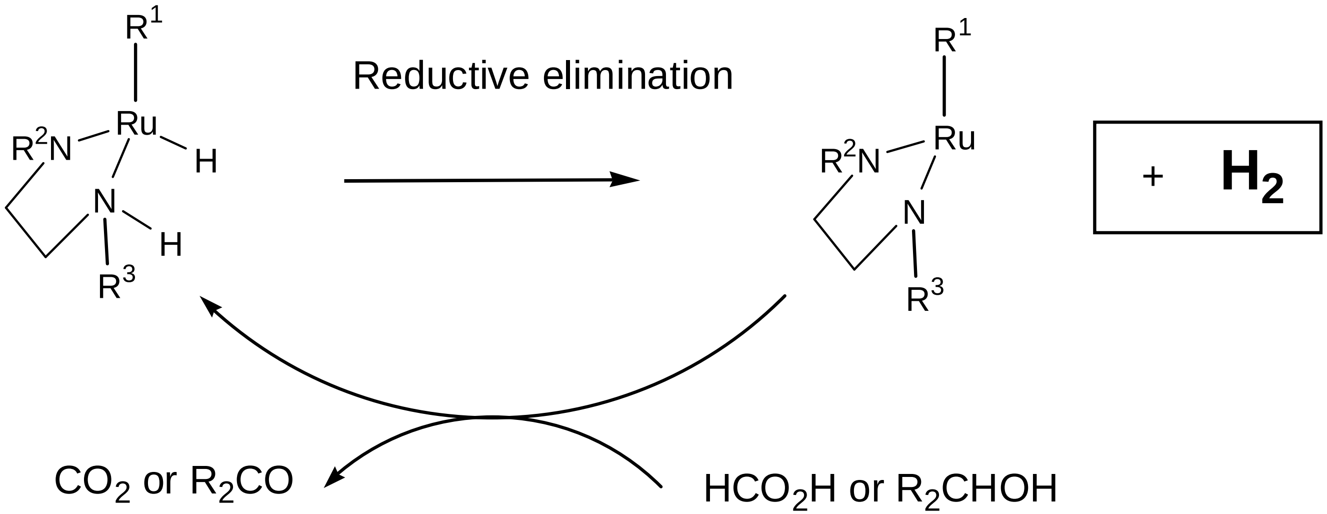
Hydrogen generation from organic molecules (Chemistry):

Hydrogen generation using organometallic catalysts: Initiation



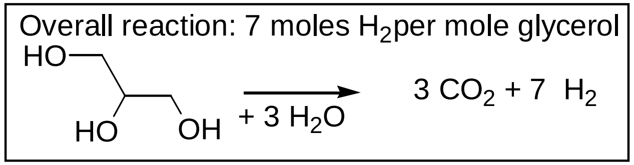
X,Y=O (formic acid)
X,Y=Me (isopropanol)

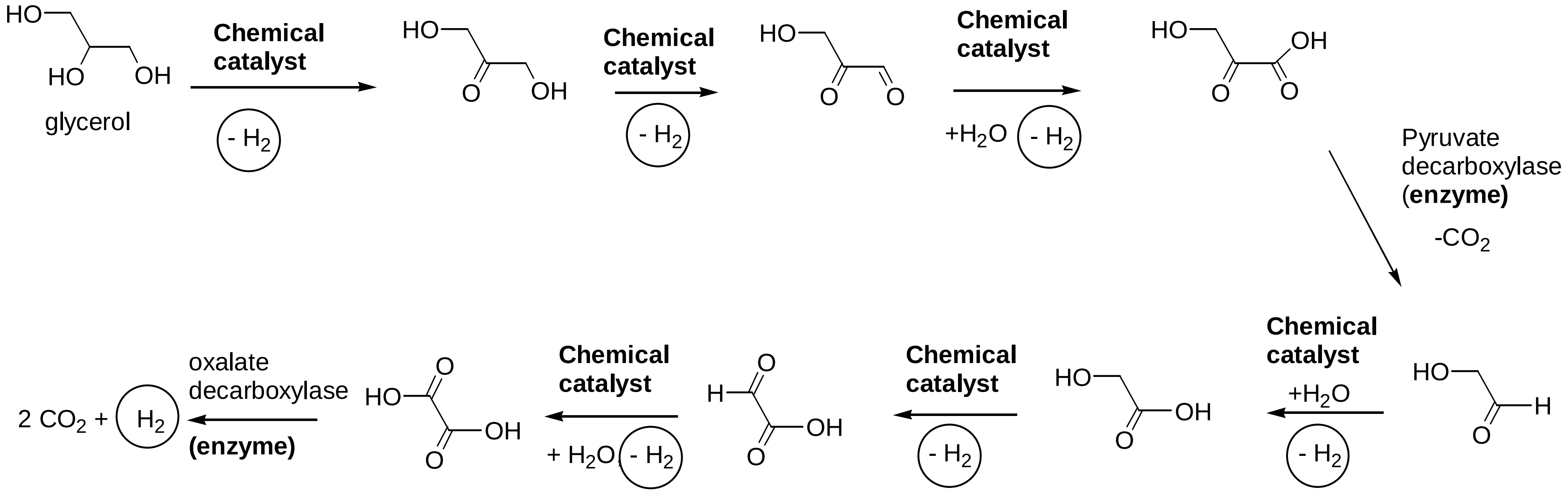
Catalytic cycle:



You can work out routes from complex molecules to hydrogen:

Glycerol to hydrogen with combined catalyst system:



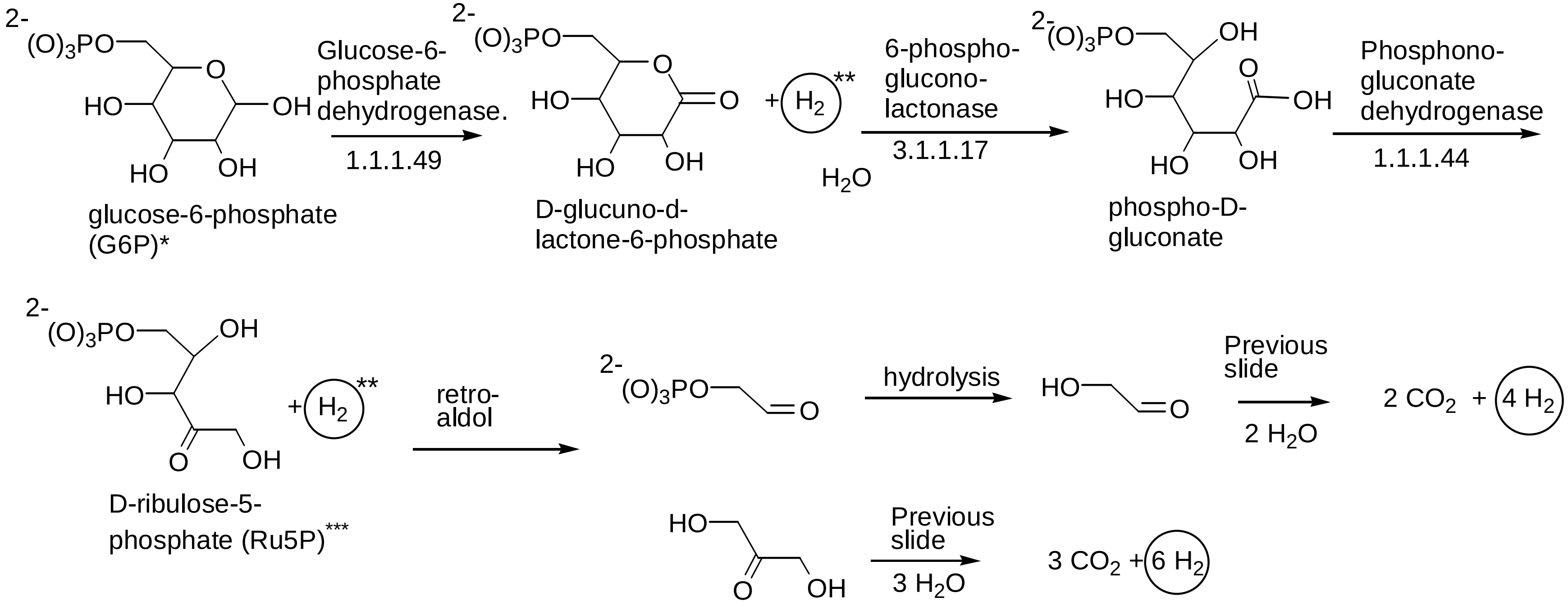


Hydrogen from glucose – with help from enzymes:

The pentose phosphate cycle (up to Ru5P)and its interception in this project at the 5C sugar stage to give hydrogen from glucose:

Overall reaction: 7 moles H_2per mole glycerol

$$\underset{C_6H_{12}O_6}{\text{Glucose}} \xrightarrow[+\ 6\ H_2O]{} 6\ CO_2 + 12\ H_2$$



* From glucose or from starch with glycogen phosphorylase then phosphoglucomutase.

** Hydrogen not formed directly: hydrogenase will be added to release H_2 from the formed NADH,which is the initial enzyme product.

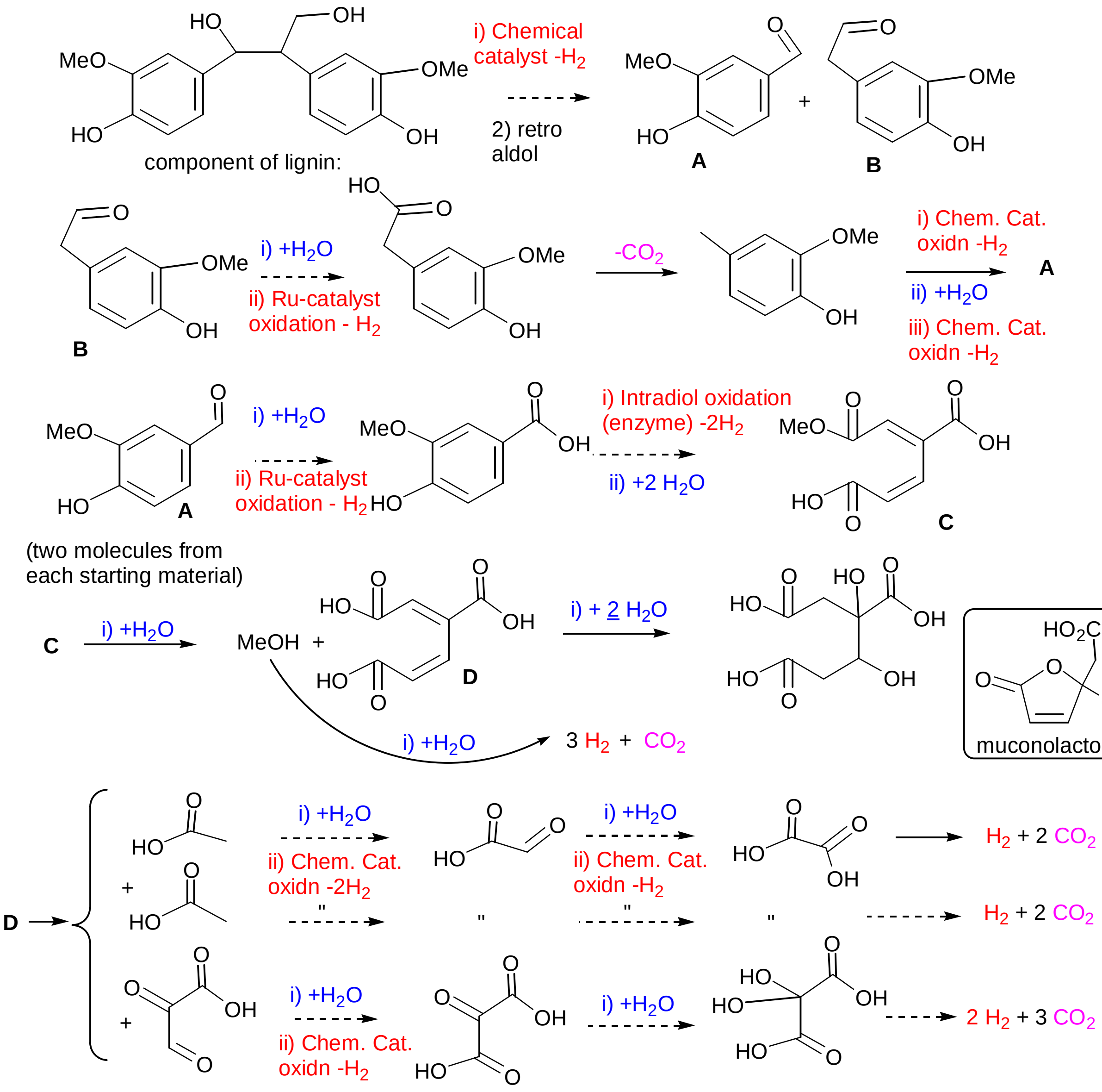
*** In the pentose phosphonate cycle, a series of 8 enzymes converts 6 molecules of Ru5P to five molecules of G6P and the cycle repeats

But is this ‘Green’ or not? You still end up with CO_2, and what about the other uses that glucose can be put to? Can this really supply the energy we need?

Hydrogen from lignin components (which would otherwise be waste)?:

overall : $C_{17}H_{20}O_6 + 28\ H_2O \dashrightarrow 38\ H_2 + 17\ CO_2$

Red = Hydrogen generation step.
Blue = water addition step.
Purple = carbon dioxide loss step.



Running total (from starting material):

Moles H_2 formed	Moles H_2O used	Moles CO_2 formed
1	0	0
4	2	1
10	8	1
16	16	3
24	20	7
32	24	11
$\boxed{38}$	$\boxed{28}$	$\boxed{17}$

Generating Hydrogen from Biomass:
(Biological Sciences, Warwick HRI)

Formation of hydrogen gas from Biomass in a Biomass reactor:

Biomass at Warwick HRI is used as fuel for enzymatic decomposition in the biomass reactor

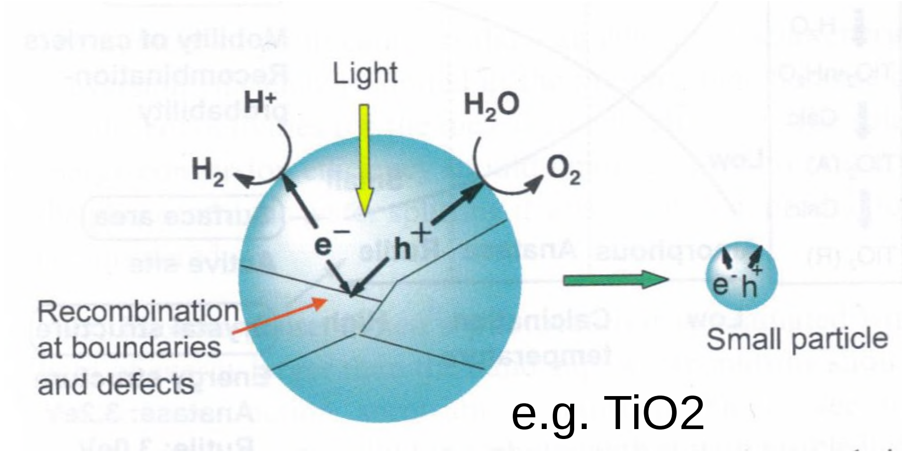
→

→ H_2

Contemporary efforts: '<u>Solar Fuels</u>'-– hydrogen can be made directly from (sun)light using semiconductors.

Using **inorganic semiconductor materials** to split water – has been known since 1972:

(using uv light)
Fujishima A, Honda K: Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38.



Hydrogen photogeneration catalysts and cells currently major area of worldwide research. Lots of work on different materials and modifications with additives.

At the moment they are not efficient, but this will inevitably improve with development.

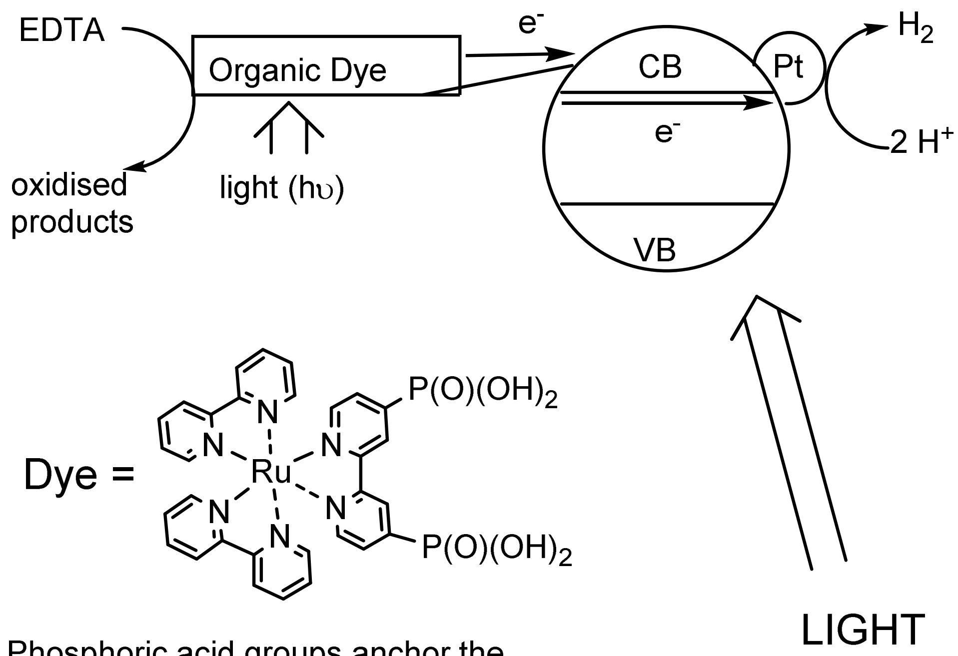
Catalysts/materials also eventually degrade so stability is also a major challenge!

How stable is chlorophyll? How is it regenerated?

A. Kudo and Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253-278.

‘Solar Fuels’-– hydrogen can be made (sun)light using catalysts on the semiconductor surface.

TiO_2 based system for hydrogen generation using a sacrificial reagent.



Ru(bipy)$_3$ complex widely used to trap photochemical energy by excitation of electrons in the complex.[8]

Phosphoric acid groups anchor the complex to the inorganic support.

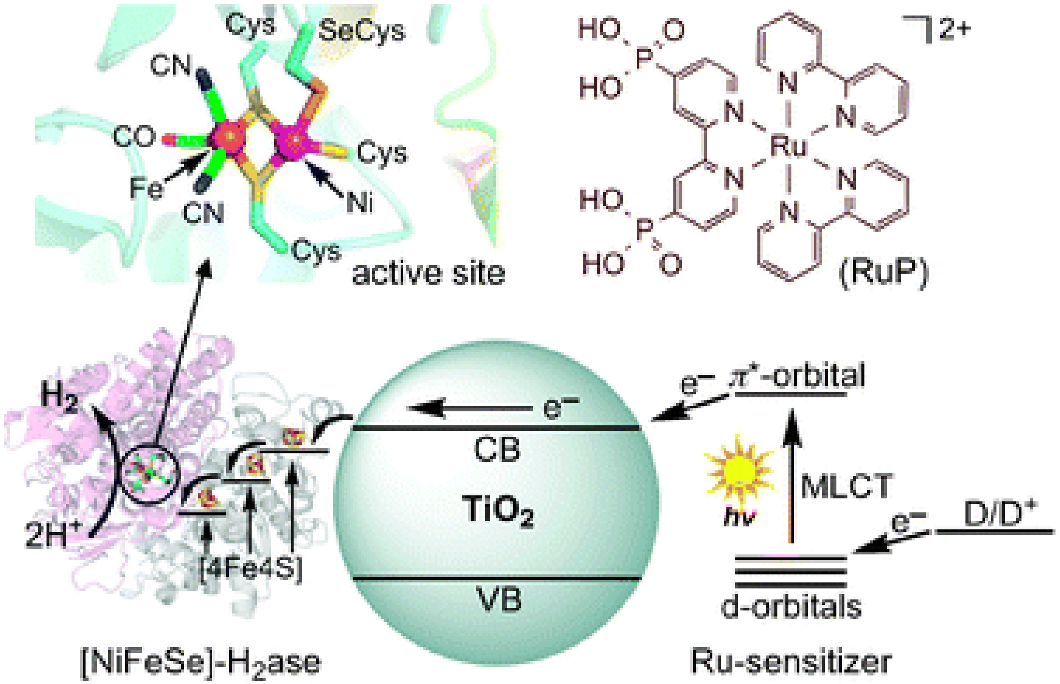
Inorganic photogeneration cells currently major area of research:

http://solarfuelshub.org/research/

‘Solar Fuels’-– hydrogen can be made (sun)light using a biological catalyst on the semiconductor surface.

Using supported enzymes and photosensitisers, with electrons from an organic donor:

Pd particles also achieve the proton reduction step.



Catalytic electrochemistry of a [NiFeSe]-hydrogenase on TiO2 and demonstration of its suitability for visible-light driven H2 production

Erwin Reisner, Juan C. Fontecilla-Camps and Fraser A. Armstrong, *Chemical Communications*, **2008**, 550-552.

Inorganic photogeneration cells currently major area of research:

http://solarfuelshub.org/research/

The ‘artificial leaf’ is already here:

Why is water splitting ‘equivalent’ to photosynthesis in energy terms?

Look at the energies:

$$CO_2 + H_2O \rightarrow 1/6\ C_6H_{12}O_6 + O_2 \quad E^o = 1.24\ V$$

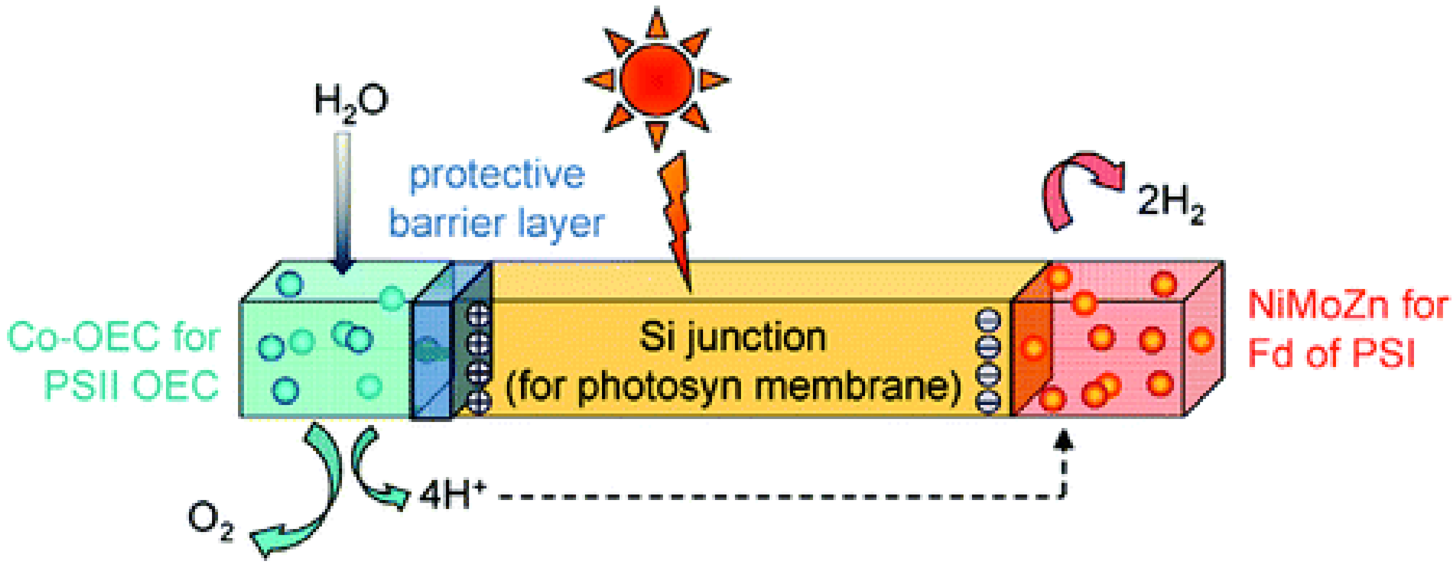
But: $$H_2O \rightarrow H_2 + 0.5\ O_2 \quad E^o = 1.23\ V$$!!!

(hence $CO_2 + H_2 \rightarrow 1/6\ C_6H_{12}O_6 + 0.5\ O_2 \quad E^o = 0.01\ V$)

‘…the production of the carbohydrate stores only 0.01 eV more energy than water splitting. Thus, solar energy storage in photosynthesis is achieved by water splitting; carbohydrate production is nature’s method of storing the hydrogen that is released from the water splitting reaction. Consequently, the key to duplicating photosynthesis lies squarely in the ability to achieve solar-driven water splitting by a direct method.’

Taken from: Daniel Nocera, *Acc. Chem. Res.*, 2012, 45 (5), pp 767–776.

The ‘artificial leaf’ is already here:



Need to use a ‘stack’ of these to achieve the required voltage for reduction.

Taken from: Daniel Nocera, *Acc. Chem. Res.*, 2012, 45 (5), pp 767–776.
Hydrogen photogeneration cells are currently a major area of worldwide research

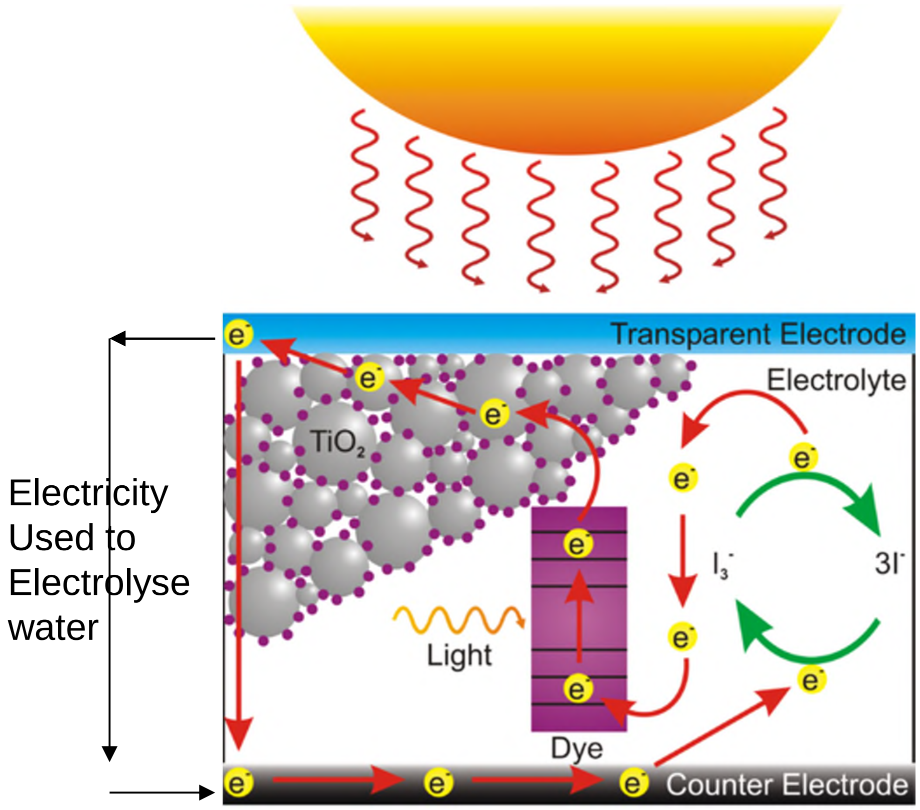
Hydrogen from sunlight using a photochemical cell.
(Graetzel cell)

Sunlight enters the cell through the transparent top, striking the dye on the surface of the TiO_2. Photons are absorbed and create an excited state of the dye, from which an electron can be "injected" directly into the conduction band of the TiO_2, and from there it to the clear anode on top.

Meanwhile, the dye molecule has lost an electron and this is provided by the iodide the in electrolyte below the TiO_2, oxidizing it into triiodide.

The triiodide then recovers its missing electron by diffusing to the bottom of the cell, to the counter electrode.

This completes the electrical circuit.



Why hydrogen?

3) Storage and transport (still a big challenge).

Hydrogen storage options:

Liquid hydrogen: Most compact and high-energy version but a lot of energy (about 30-40% of the energy value of the hydrogen) is required to compress it. Needs to be cooled and kept under very high pressure.

Compressed hydrogen: Up to 700 bar is a possibility – about 80% of the density of liquid hydrogen, but 200-250 bar is more readily achieved (this is the pressure of a cylinder we would use in a lab).

Hydrogen complexes of metals: Probably the safest way to store hydrogen but there is a limit to how much you can store. But Dr Hatton discussed this in good detail in his lecture 9.

Look at: http://energy.gov/eere/fuelcells/hydrogen-storage

See p31 of http://www.hi-energy.org.uk/Downloads/Hydrogen%20Fuel%20Cell%20Resource/3b-Hydrogen%20refuelling%20and%20storage%20infrastructure.pdf
For a table
Other options…on-site generation?

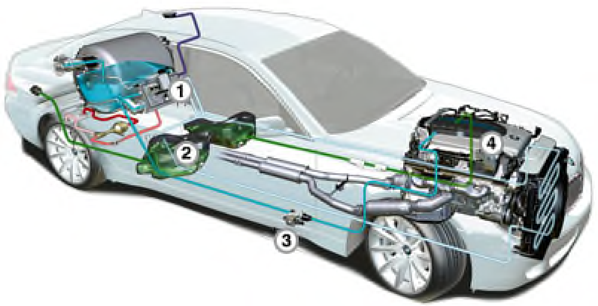
Hydrogen generation/storage schemes linked to solar and wind energy and transport applications:

Hydrogen is generated and stored at times of excess wind and solar energy, then used when required.

Hydrogen generation/storage schemes linked and transport applications:

Hydrogen as a fuel for
transport applications:

Which is the best for each transport method?



Why hydrogen?

Some issue to reflect on:

What is the best use of hydrogen energy – local generation, energy storage, transport…

What is the best way to generate hydrogen, and is this the best use of solar power (nb is solar power really ‘green’ when you have to pave over fields)?

What are the risks with hydrogen energy? Are they any worse than the risks with other energy sources (petrol also burns, nuclear!)?

Would you buy a hydrogen vehicle?

Will cheap renewable energy really solve the ‘energy crisis’?

Why hydrogen?

This is what I think:

What is the best use of hydrogen energy? Right now, petrol cars are quite efficient although hybrids are better. In urban areas, hydrogen can reduce local pollution levels so that's good. An ideal use would be local energy storage – generate and store hydrogen locally when there is an excess of 'green' power then consume it via a fuel cell when there is a deficit of other power sources available.

The best way to generate hydrogen is probably through the use of solar, wind, hydroelectric, tidal etc power sources. Solar fuel technology is probably a good bet. Steam reforming does not really provide any advantages – but is cheap.

Hydrogen is not really any more dangerous than other energy sources, but being a gas makes it appear to be more dangerous than it really is

Right now I would not buy a hydrogen vehicle because I couldn't afford one and it would be hard to fill it up. But in the future I might.

Solving the 'energy crisis'.