

# Catalysis and the hydrogen economy

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Perspectives regarding the current and future production of hydrogen are offered. It is important to appreciate that most of the world's current production of H<sub>2</sub> is captively produced and not easily committed to a major new market need (such as H<sub>2</sub> for fuel cells). The size and capital investment, energy intensiveness, as well as delivery issues restrict the simple extension of existing SMR plants to fill the void needed in H<sub>2</sub> production for a H<sub>2</sub> economy. Forecasts suggest future H<sub>2</sub> needs exceed 14 times the world's current production of H<sub>2</sub>; this volume coupled by restrictions of CO<sub>2</sub> co-production would seem to limit the options for future H<sub>2</sub> production. Production of H<sub>2</sub> by new process technologies, including CH<sub>4</sub> decomposition, CO<sub>2</sub> reforming, biohydrogen, photodecomposition of water, etc. are discussed. Catalysis will play multiple roles in all aspects of H<sub>2</sub> production. Multiple needs exist for catalysts with respect to the photodecomposition of water, CPO based processes, highly active and low cost WGS catalysts, catalysts to assist in the capture and storage of CO<sub>2</sub>, improved hydrocarbon reforming, improved electrocatalysts and photocatalysts, improved hydrodesulfurization catalysts, and biophotolytic catalysts for decomposing water. Today, no single technology seems to offer a near term solution, although it appears that solar, photodecomposition of water offers a potential solution with respect to sustainability issues, the amount of H<sub>2</sub> needed, no CO<sub>2</sub> co-product, and energy needs; however the solar photodecomposition of water has many technical hurdles remaining which suggest it is decades away from large scale, cost effective implementation.

**KEY WORDS:** hydrogen production; hydrogen markets; H<sub>2</sub> economy; infrastructure; fuel cells; solar photodecomposition of water; biohydrogen.

There are lots of opportunities for catalysis to participate in and drive a potential H<sub>2</sub> economy. Major technical hurdles remain along the pathway to market acceptance of H<sub>2</sub> as a major energy source; in particular, the means to produce vast amounts of low pressure, high purity H<sub>2</sub> at low cost remains a serious challenge. Beyond the pressing need for alternative routes to producing H<sub>2</sub>, technical hurdles remain in H<sub>2</sub> purification, development of lower cost and long-lived fuel cells, H<sub>2</sub> delivery, and H<sub>2</sub> storage [1,2]. This manuscript will offer some perspectives regarding the production of hydrogen, briefly discuss opportunities for H<sub>2</sub> as a major energy source and describe potential routes to H<sub>2</sub> generation for a totally new business-supplying H<sub>2</sub> for fuel cells. The assumption will be made that ultimately the world's future energy needs will be met by H<sub>2</sub>, and this H<sub>2</sub> will be used to power fuel cells.

Today, hydrogen is largely produced by steam methane reforming (SMR – the multi-step, endothermic reaction of a hydrocarbon, usually methane, with excess steam to produce H<sub>2</sub> and CO [3]). In the United States, CH<sub>4</sub> accounts for 95% of the feedstock for H<sub>2</sub> [4]. Most of today's hydrogen is used in applications demanding huge volumes of H<sub>2</sub> (e.g., NH<sub>3</sub> synthesis, refineries and methanol synthesis), often with captive production of an

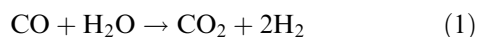
entire H<sub>2</sub> plant to a single customer. Refineries today, largely because of environmental controls on sulfur levels in fuels and/or on the slate of products made in the refinery, are net consumers of H<sub>2</sub>, which is often made up by a stand-alone H<sub>2</sub> plant at or adjacent to the refinery site. On the other hand, merchant H<sub>2</sub> is usually sold to smaller volume customers and is a small fraction (~3%) of the total H<sub>2</sub> produced today. Because of economies of scale, hydrogen plants are very large [often 70–100 MMscfd (millions of standard cubic feet per day) at ~\$70 million/plant [4]], and these plants are highly heat and energy integrated. Today, these plants sometime serve as distribution sites for compressed gas (cylinder or pipeline) or liquid H<sub>2</sub>. Building smaller (< 500,000 scfd) SMR H<sub>2</sub> plants is less cost effective [5] with much of the cost associated with the feedstock. Today, most customers need high pressure H<sub>2</sub> because the processes using that H<sub>2</sub> require high pressures (such as hydrodesulfurization, ammonia synthesis, methanol synthesis, GTL, hydrogenation of fats and oils, etc.), and the energy to compress low pressure H<sub>2</sub> at the customer's site becomes prohibitive. High pressure (~400 psig) needs for smaller customers (merchant H<sub>2</sub>) are met by shipping H<sub>2</sub> as a liquid, in cylinder tank trucks, or via pipeline, but at a much higher cost than the cost to very large customers. This higher cost H<sub>2</sub> would be much too expensive when added to the cost of producing fuel cells to provide a new energy resource. In addition, almost all of today's current merchant and

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captive production of H<sub>2</sub> is co-produced with large amounts of CO<sub>2</sub>.

The 2003 global H<sub>2</sub> production was 17.0 trillion SCF with a growth of ~10%/year [5,6]. US demand for merchant H<sub>2</sub> in 2003 was 502 billion SCF [6], which was 67% of the global merchant H<sub>2</sub> sales or ~16% of total US H<sub>2</sub> production. Thus, the merchant (~3% of global) H<sub>2</sub> market in the US is small versus the captive (97% of global) H<sub>2</sub> market. The merchant H<sub>2</sub> market does not include the H<sub>2</sub> produced by a number of captive production operations (such as within methanol plants (9% of global H<sub>2</sub> consumption), for the production of NH<sub>3</sub> (57% of global H<sub>2</sub> consumption) or used internally (such as for hydrodesulfurization in the refinery)). It is estimated that it would take 600 million tons (or 233 trillion SCF of H<sub>2</sub>/year to satisfy a global energy market based only on H<sub>2</sub> [7]). "This is about fourteen times more than the total amount of H<sub>2</sub> now produced, globally!" Such a large gap in H<sub>2</sub> production capacity can only be filled by uncommitted H<sub>2</sub> (the merchant sales), new plants, and/or a totally new production process.

Today, H<sub>2</sub> is usually made from syngas, a mixture of CO and H<sub>2</sub>; H<sub>2</sub> producers are always trying to find ways to get more H<sub>2</sub> product from the CO in the syngas, usually by water gas shift reaction (WGS) (reaction 1). The present Fe–Cr and Cu–Zn water gas shift catalysts are efficient



when used in a commercial syngas generation facility, but they are not readily adaptable for use in stationary fuel cell power units or mobile fuel cells. Catalysts used in the fuel cell reformer must have a high level of activity at high space velocities. A typical syngas generation facility uses reformer catalyst beds having average volumes between 2 m<sup>3</sup> to about 240 m<sup>3</sup>, whereas today's stationary fuel cell reformer catalyst bed volumes are around 0.1 m<sup>3</sup>, and mobile fuel cell catalyst beds have volumes of about 0.01 m<sup>3</sup>. In addition, WGS catalysts must be able to withstand numerous shutdown and startup cycles, undergo special activation procedures, tolerate oxygen rich conditions, and show high tolerance to sulfur compounds [8]. New and much more active WGS catalysts need to be developed where syngas is part of the process stream for a fuel cell.

Fuel cells are seen as a potentially huge market for H<sub>2</sub>, with the attraction for H<sub>2</sub> being driven by a H<sub>2</sub> fuel cell's operation producing only water and no CO<sub>2</sub>. Thus, as long as the H<sub>2</sub> is derived from non-fossil fuel feedstock it is a truly green fuel. Forbes Magazine reports what many others have been saying, "It will be at least 2015, and more likely decades later, before fuel-cell-powered electric motors become a plausible competitor to gasoline engines. At the moment a fuel cell and set of motors cost 10 times as much as an internal combustion engine." [9]. Fuel cells will find smaller volume markets such as stationary power supply, convenience devices

(laptop computers, cell phones, etc.), and remote energy supply (where costs for alternative energy sources are very high). In the transition period (5–40 years) towards a truly green H<sub>2</sub> fuel source, fossil fuel feedstocks are viewed as a temporary solution. H<sub>2</sub> fuel cells do not need high pressure H<sub>2</sub>, nor are huge quantities of H<sub>2</sub> needed for each fuel cell; however, compressing the H<sub>2</sub> provides a way to transport more moles of H<sub>2</sub> to the customer. Today's costs for delivery of H<sub>2</sub> add a lot to the cost of H<sub>2</sub>, and the cost of delivering the H<sub>2</sub> is a function of production volume [10]. As mentioned above it has been estimated that 600 million tons of hydrogen yearly [7] would be needed to generate the energy that natural gas and oil now provide the world, which is much greater than the total amount of non-captive H<sub>2</sub> produced today via merchant hydrogen plants (9 million tons/year in US) [11]. Thus, the H<sub>2</sub> plants of any future H<sub>2</sub> economy are not likely to be met by the merchant H<sub>2</sub> plants of today; rather, they will need a new process for producing (with the ability to deliver) low pressure (~1 atm) H<sub>2</sub> at thousands of point source sites to supply thousands, if not many millions of fuel cells for transportation and stationary power at a competitive cost. If we had a way to supply H<sub>2</sub> at or near the location of the fuel cells, this would reduce the cost of H<sub>2</sub>. Just to produce 40 million tons of H<sub>2</sub>/year to fuel 100 million vehicles [12] (75% of the light duty vehicles in the US) or 25 million homes [13]), it would take 400 dedicated natural gas to H<sub>2</sub> plants [14]. Thus, the world will probably need an entirely new process for this new industry: H<sub>2</sub> for fuel cells. Without a clear source of these huge, new volumes of hydrogen required, the H<sub>2</sub> economy will stall. Even if we resolved how we are going to produce all this new H<sub>2</sub>, we must still get it to the thousands, if not millions of customers, needing it for energy [15] generation. Figure 1 shows the interaction of all these steps in generating, storing, transporting, recovering, producing and ultimately using this H<sub>2</sub> as a fuel. There are going to be purification needs for this fuel cell hydrogen, as well as distribution issues for transporting H<sub>2</sub> from the production areas to the thousands of customers, but none of this will happen without a means of producing the H<sub>2</sub> economically. Catalysis figures prominently in these alternative process approaches to producing fuel cell hydrogen, and now I would like to focus the balance of this article on how we might make this hydrogen for this new and emerging market.

In the future, the use of coal, which is available in huge quantities in the USA, Russia and China, might be an attractive source of H<sub>2</sub> coupled with CO<sub>2</sub> recovery and strict emissions controls, but such environmentally attractive plants do not exist today. Today, natural gas is a preferred source of H<sub>2</sub> and syngas. There are several methods of producing syngas from natural gas including [16–18]: (a) Steam-methane reforming ("SMR") which uses an endothermic, catalyzed reaction between natural

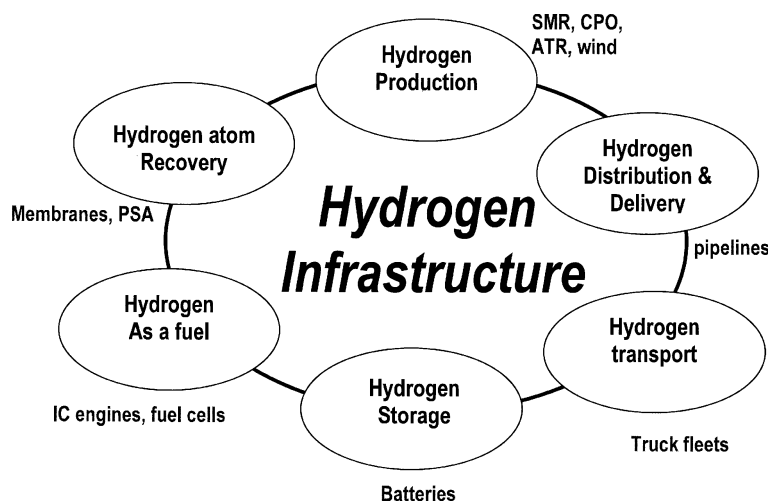


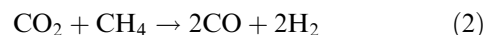
Figure 1.

gas and steam (accounts for more than 50% of merchant H<sub>2</sub> production today); (b) Partial oxidation (“POX”) of natural gas thermally with pure oxygen, which achieves a H<sub>2</sub> to carbon monoxide ratio in the resultant syngas in the range from 1.6–1.8 to 1; (c) Autothermal reforming (ATR) which uses a partial oxidation burner followed by a catalyst bed with a feed of natural gas, steam and oxygen to produce the a 2 to 1 H<sub>2</sub>/CO ratio in the resultant syngas (often preferred for large volume applications, such as GTL); and (d) Catalytic partial oxidation (CPO or CPOx) which is the reaction of natural gas with oxygen over a catalyst that permits flameless partial combustion to hydrogen and carbon monoxide. All these processes first produce syngas. Also, these plants co-produce CO<sub>2</sub> from the water gas shift process and hydrocarbon combustion [19]. For POX, ATR and CPO, the oxidation reaction in the primary heat-generating unit is exothermic and, thus, the syngas is produced at elevated temperature (generally >900 °C). If one uses WGS after these units (to covert CO value into H<sub>2</sub>), then heat must first be recovered since high temperature shift catalysts can not operate above 450 °C [16]. Further purification (by pressure-swing absorption) of the process stream to remove CO, CO<sub>2</sub>, and CH<sub>4</sub> requires removing more heat. Thus, H<sub>2</sub> plants are very carefully balanced for both energy and process steam generation and recovery. Because of the energy intensive operations and by product steam production, SMR is not attractive for low volumes of low pressure H<sub>2</sub>. Currently, CPO and ATR operations require added O<sub>2</sub>, which adds cost, especially for low volume H<sub>2</sub> production. If CPO could be adapted to safely handle air as a feed, it becomes an attractive route to H<sub>2</sub>. Both Shell [20] and ConocoPhillips [21] have been investigating scale up of O<sub>2</sub> based CPO approaches to syngas and H<sub>2</sub> production.

Other approaches to H<sub>2</sub> include: CO<sub>2</sub> reforming, methanol reforming, CH<sub>4</sub> decomposition, oxidative dehydrogenation of hydrocarbons, electrolysis (with fuel

cells), renewable sources, photocatalysis of water, biomass conversion, biological H<sub>2</sub> production, and the use of nuclear energy for the thermal decomposition of water.

With so much co-product CO<sub>2</sub> available, it might seem that reacting CO<sub>2</sub> with CH<sub>4</sub> to produce CO and H<sub>2</sub> would be attractive (reaction 2). However, the problems here are substantial [22] including the need to purify, often impure, CO<sub>2</sub>. The reaction of CO<sub>2</sub> with CH<sub>4</sub> also produces low



levels of carbon by-product; as a by-product, there is a strong possibility that this carbon would eventually foul the surface of the catalyst. If one could overcome these substantial technical hurdles, one would still need to deal with the huge amounts of CO co-product from this reaction.

CH<sub>4</sub> decomposition into C and H<sub>2</sub> might also seem like an attractive option, but now huge amounts of co-product (3 tons of carbon for every ton of H<sub>2</sub> from reaction 3) would be produced,



given the large volumes of H<sub>2</sub> required for the H<sub>2</sub> economy. This added carbon could not be allowed to foul the catalyst [23] (a real challenge for a process demanding years of operation), and one would have to find an application for (or dispose of) large amounts of elemental carbon. If one were to assume using reaction 3 to produce even 50% global H<sub>2</sub> needs for fuel cells, reaction 2 would co-produce almost 1 billion tons of carbon/year, which is hundreds of times more than the global volumes than any single, major organic chemical and comparable to all the coal mined in the US and Europe in 2 years. [Even 40 million tons of H<sub>2</sub> would produce 120 million tons of carbon.] Oxidative dehydrogenation will also require producing a large amount co-product. In addition, oxidative addition often co-produces small amounts of carbon, which might foul any catalyst operating over long periods of time.

Electricity, when it is cheap, is a good way of producing  $H_2$  (by electrolysis), but it is expected that the costs of electricity [24] will continue to climb and the price of electricity will make this an unattractive approach as a means to produce the huge volumes of  $H_2$  needed to supply the emerging  $H_2$  economy.

The US DOE has evaluated many of these alternative approaches to producing  $H_2$ . In particular the use of nuclear energy [25] to supply all the future US needs for  $H_2$  energy would require the construction of more than 3000 new nuclear plants (versus the 103 now operating) [26]; the cooling water requirements for nuclear power would require vast amounts of water which demands location of most of these plants along the US coastline (about one every 10 miles) – an unlikely occurrence in addition to unresolved issues about spent nuclear fuel storage and safe management of the waste fuel for so many new plants. These issues suggest that nuclear energy will not be the dominant source of future energy needs for the USA, although it may become part of a long term solution.

The use of biological processes to produce  $H_2$  sounds attractive if one could really demonstrate such an approach for large volumes of  $H_2$  (versus the micromoles of product now generated in the lab) and the potentially  $CO_2$  free nature of this approach if water is the feedstock [27]. Small units show promise in laboratory scale testing of the concept, but big hurdles [28] remain for R&D to increase the rates and yields of  $H_2$  production by this approach (whether it be for biophotolysis (algae using solar energy to photodecompose water [29]), biological  $H_2$  conversion [30,31], biological catalyst for light energy conversion, hydrogen from living organisms, etc.).

Renewable sources of energy (such as wind, tidal, dams, biomass) might provide local sources of  $H_2$ , but probably cannot meet the huge volumes of  $H_2$  required on a global scale as a major source of energy. This renewables shortfall has been discussed in a recent and excellent DOE report [26]. In this report they point out that solar is most likely the only source of energy capable of producing the huge volumes of  $H_2$  required to satisfy a  $H_2$  economy. While the land mass is expected to be great [32] (about the size of land for the State of Utah), this land requirement could be spread over vast areas of desert, un-used land, and even off shore. Step-out concepts would still be needed to grow and develop this approach while continuing to reduce the costs of solar cells, increase their energy efficiency [15] and to reduce the energy intensiveness of photovoltaic production processes. Delivery of this  $H_2$  to sun-starved industrial/residential regions still needs to be resolved. Solar, photocatalytic production of  $H_2$  (via photoelectrolysis or direct photodecomposition of water) is also drawing a lot of attention because it too, using water as a source of  $H_2$ , has the potential to provide  $H_2$  without  $CO_2$  co-production [33]. The direct photodecomposition

of water [34,35], while exciting, has many demanding, technical hurdles ahead (higher quantum yields, greater solar efficiency, long-lived catalysts, co-product free, etc.) and is forecast to be perhaps 40 years away (if certain technical hurdles can be met) from any widespread application.

In developing any new process there are always both technical and other, what I term, external challenges. For a  $H_2$  based energy source, there will be issues of feedstock. In the near term, while we struggle to find  $CO_2$  free approaches, we will have to rely on sustainable approaches or very efficient and environmentally acceptable uses of cheap feedstocks (such as coal or natural gas). Use of a fossil fuel may require  $CO_2$  sequestration as well. The type of feedstock one selects has a great deal of impact on the process route [8]. Partial oxidation (POX or CPO) processes prefer high purity oxygen as the oxidant, and one has to accept the cost and capital investment to produce large quantities of  $O_2$ . Purity (and separation) is another issue for  $H_2$ , which will depend on the source of the  $H_2$  and the cost of purification. If there is a co-product such as  $CO_2$  or steam, then a customer needs to be found for this co-product. The cost of capital can be a serious and confining limitation to the development of new technology. Environmental regulations will have to be considered, modified or addressed if the generation of this new source of  $H_2$  develops. Support by government and politicians [36] will be necessary for laws and subsidies to encourage the development of a major, new energy source.

In summary, there is no single, clear route for near term (3–10 years) production of the huge volumes of  $CO_2$  free (byproduct)  $H_2$  needed if a  $H_2$  economy is to emerge to serve the world's energy needs. Long term sources of energy should be sustainable, environmentally sound, and based on very efficient processes. Solar photocatalysis (perhaps 40 years away from any widespread application) probably has the greatest potential of meeting the volumes of  $H_2$  needed without  $CO_2$  co-product [37], as long as the significant technical and cost issues can be surmounted. If this did happen, it would create a huge, new market for  $H_2$ , which would be much bigger than today's  $H_2$  business. In the interim, I [38] suspect, low pressure, small volume sources of  $H_2$  for the thousands of  $H_2$  energy consumption devices will come from many different process approaches. Since most of today's  $H_2$  is captive and already committed, new  $H_2$  plants will need to be built to service this new and larger volume customer. Where sensible, merchant hydrogen plants might be scaled down (but there is a cost effective, lower limit), and where transportation of such high pressure  $H_2$  will not create a great deal of added cost, existing or new SMR, ATR, or CPO merchant  $H_2$  plants might be an interim source. Affordable  $CO_2$  sequestration needs to be applied as long as fossil fuels are the feedstock for the massive amounts of new

H<sub>2</sub> production for a H<sub>2</sub> based energy supply. In other regions of the world, because of different feedstock costs and availability, new process approaches may emerge or be more cost effective than elsewhere. Catalysis will play multiple roles in all aspects of H<sub>2</sub> production. Multiple needs exist for catalysts with respect to the photodecomposition of water, CPO based processes, highly active and low cost WGS catalysts, catalysts to assist in the capture and storage of CO<sub>2</sub>, improved hydrocarbon reforming, improved electrocatalysts and photocatalysts, improved hydrodesulfurization catalysts, and biophotolytic catalysts for decomposing water. Wind, hydrothermal, biomass, and wave/tidal energy recovery approaches may supply niche opportunities for H<sub>2</sub> energy. Nuclear too will probably play a small role. However, solar, photodecomposition of water appears the only major, but long term, solution to a CO<sub>2</sub> free means for the mass production of the huge volumes of H<sub>2</sub> needed if a H<sub>2</sub> economy is to emerge.

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