

Celebration of Earth Day at the Institute for Catalan Studies, 2010

Energy from hydrogen. Hydrogen from renewable fuels for portable applications*

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Resum. L'hidrogen molecular és una font d'energia neta per al medi ambient, però no es troba disponible a la Terra. La reformació amb vapor de substàncies derivades de la biomassa constitueix una ruta valuosa per a la producció d'hidrogen molecular, i té l'avantatge que és neutre des del punt de vista del CO₂ i que no requereix grans infraestructures per a la seva implementació. En aquests moments s'estan desenvolupant catalitzadors per a la reformació selectiva, entre d'altres, de bioalcohols i dimetil èter a hidrogen i diòxid de carboni, tot i que el seu ús en reactors de parets catalítiques per a aplicacions reals encara no està del tot resolta. D'aquests, els reactors estructurats recoberts d'aerogels són molt prometedors perquè la transferència de massa és excel·lent i són capaços de dispersar nanopartícules de metalls actius per a la reacció. El comportament d'aquests sistemes millora considerablement quan s'empren en microreactors. Els microreactors basats en micromonòlits de silici en què s'integra la reacció de reformació i l'oxidació selectiva del monòxid de carboni generat són una opció prometedora per a la producció d'hidrogen *in situ* i sota demanda en les aplicacions portàtils de les piles de combustible.

Paraules clau: energia · hidrogen · catalitzador · microreactor

Summary. Molecular hydrogen is an environmentally clean source of energy, but it is not available on Earth. Steam reforming of bio-derived compounds represents a valuable route for the generation of molecular hydrogen and has the advantage that it is CO₂-neutral and it requires a limited amount of additional infrastructure for implementation. At present, suitable catalysts for selective bio-alcohol and dimethyl ether reforming into hydrogen and carbon dioxide are being developed, but their use on structured wall reactors for practical application is still under way. Among them, aerogel-based coated structures appear very promising due to their very high mass transfer rates and their ability to disperse highly active metal nanoparticles. The performance of these systems improves considerably by using microreaction technologies. Microreactors based on silicon micromonoliths together with integrated downstream carbon monoxide selective oxidation hold a promising future for the effective on-site and on-demand generation of hydrogen from renewable fuels in portable fuel cell applications.

Keywords: energy · hydrogen · catalyst · microreactor

Motivated by fossil fuel depletion, harmful gas emissions from combustion engines, increasing world energy demand and non-homogeneous distribution of energy resources, hydrogen and fuel cells are receiving increasing attention as new tools for the management of energy [19,37]. Excluding nuclear fuels, hydrogen is the most efficient energy source on a weight basis (Table 1).

In the same way that electrons serve today as an energy carrier in the form of electric power, hydrogen can also transport and store energy. A vital distinction, however, is that hydrogen is a chemical, so it is much easier to store than electric-

ity, allowing more flexibility and autonomy in the management of energy. The energy stored in hydrogen can be efficiently released in fuel cells, where hydrogen is oxidized electrochemically with oxygen (or air) to yield electricity, water and residual heat (eq. 1), thus offering an environmentally clean way to manage energy (the only byproduct is water!).



However, it should be kept in mind that the generation and transportation of hydrogen, as well as its conversion into electricity in fuel cells, require an input of energy that should be evaluated carefully from proper exergy, environmental and economical considerations [17]. That is, depending on the source and procedure employed in the generation of hydrogen and—if required—its storage and transportation, the use of hydrogen as an energy carrier may represent a solely academic exercise or a true technological breakthrough. This includes not only accurate energy balances, but also environmental

* Based on the lecture given by the author at the Institute for Catalan Studies, Barcelona, on 29 April 2010 for the celebration of Earth Day at the IEC (*2a Jornada de Sostenibilitat i Canvi Climàtic*).

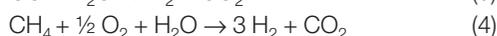
Table 1. Energy density of several processes

Process	MJ/kg
Hydrogen nuclear fussion	625,000,000
Uranium nuclear fission	88,000,000
Hydrogen combustion	142
Natural gas combustion	54
Gasoline combustion	47
Coal combustion	15–33
Wood combustion	6–17

concerns, safety and cycle life assessments. Recent research advances in nanoscience, catalysis, modeling, and bio-inspired approaches offer exciting new opportunities for addressing challenges for hydrogen and fuel cell technologies.

Where are you, hydrogen?

Although hydrogen is the most abundant element in the universe [38], it does almost not exist naturally in its molecular form on Earth. Therefore, pure hydrogen must be produced from other hydrogen-containing compounds such as fossil fuels, biomass, or water. Each method for producing hydrogen requires a source of energy, namely, thermal (heat), electrolytic (electricity), or photolytic (light) energy. Today, most hydrogen is produced industrially from the steam reforming of fossil fuels such as natural gas and oil, and from coal through gasification processes [31]. The steam reforming of natural gas takes place in two steps. First, natural gas is cleaned and reacts with steam at high temperatures ($>800^{\circ}\text{C}$) over a nickel-based catalyst. From this, a mixture of mainly hydrogen and carbon monoxide is obtained (eq. 2). Then, carbon monoxide reacts in a second stage with more steam at a low temperature to produce a mixture of mainly hydrogen and carbon dioxide (the well known water gas shift reaction, eq. 3). The energy balance of the production of hydrogen by steam reforming can be improved by using a combination of steam and air at the reactor inlet (eq. 4), which may approach an autothermal regime ($\Delta H_{\text{reaction}} \sim 0$).



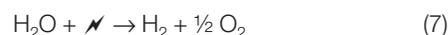
Steam reforming of fossil fuels, however, leads to carbon dioxide emissions that contribute negatively to the atmospheric CO_2 balance. One molecule of carbon dioxide is produced for each carbon atom participating in the above reactions. Therefore, the production of hydrogen from fossil carbon sources cannot be regarded as environmentally friendly, although it is certainly better than its combustion in combustion engines. For that reason, considerable efforts are directed towards the reforming of natural gas with CO_2 instead of steam [9]: the so-

called dry reforming of methane (eq. 5), or its direct decomposition into hydrogen and solid carbon over appropriate catalysts (eq. 6) [2].



Of course, the use of fossil sources, although technologically solved and well established, cannot be regarded as the best option for the production of hydrogen from a sustainability point of view, and other routes for producing hydrogen have been investigated thoroughly. In fact, one of the main advantages of using hydrogen as an energy carrier is that it can be produced by a great variety of processes that include almost all forms of energy (Fig. 1). In the long term, only water and biomass in all its forms can be considered as appropriate raw materials for hydrogen production.

Hydrogen can be obtained by decomposition of water into oxygen and hydrogen gas by means of an electric current being passed through it (eq. 7). In fact, electrolysis of water has been known since 1800, when William Nicholson (1753–1815) and Anthony Carlisle (1768–1840) first demonstrated it in England with the aid of a voltaic pile. Today hydrogen is generated most efficiently from energy usually supplied in the form of heat and electricity through high-temperature electrolysis. Also, wind power is widely used as a renewable power technology for generating electricity. Combining this electricity with water electrolysis, wind can provide hydrogen in an effective way [15]. Moreover, hydrogen can serve as an excellent buffer for excess energy produced in windmills.



While nuclear-generated electricity could be used for electrolysis, too, nuclear heat can be directly applied to split hydrogen from water through thermochemical cycles. Thermochem-

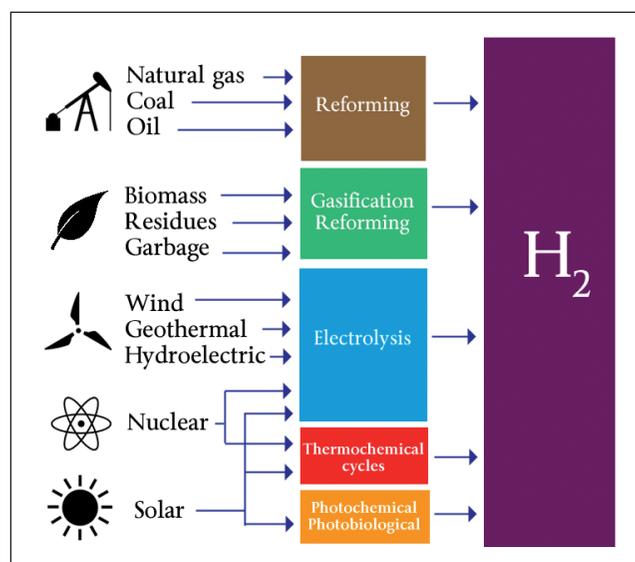
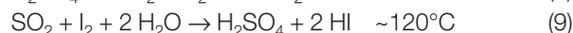


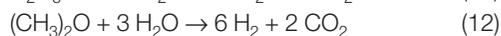
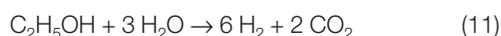
Fig. 1. Routes and sources for producing hydrogen. Given the variety of processes for its production, hydrogen is considered an excellent energy carrier for many applications.

ical cycles are processes where water is decomposed into hydrogen and oxygen via chemical reactions using intermediate compounds that are recycled. There are several hundreds of different thermochemical cycles which have been considered for hydrogen generation [1]. Among them, the sulfur-iodine cycle is one of the most widely studied (eqs. 8–10). These processes can be even more efficient than high-temperature electrolysis. Similarly, thermochemical cycles can also be achieved by concentrating solar thermal power.



Photobiological water splitting is another method for producing hydrogen. In this process, hydrogen is produced from water using sunlight and specialized microorganisms, such as several green algae and cyanobacteria. Just as plants produce oxygen during photosynthesis, these microorganisms consume water and produce hydrogen as a byproduct of their natural metabolic processes. Photocatalytic and photobiological water splitting is in the very early stages of research but offers long term potential for sustainable hydrogen production with low environmental impact [14]. Biological hydrogen can also be produced in bio-reactors that use waste streams as a feedstock. To sum up, hydrogen can be obtained from water by a variety of processes in a great variety of locations. This means autonomy and adaptability, two key parameters when considering future energy scenarios.

Another appealing and sustainable source of hydrogen is biomass in the form of wood residues, non-edible parts of food crops, garbage, etc. Since biomass is renewable and consumes atmospheric CO_2 during growth, it can have a smaller net CO_2 impact compared to fossil fuels (Fig. 2). In that context, the catalytic steam reforming of renewable fuels derived from biomass has attracted much attention as an efficient technology for hydrogen production because it provides high hydrogen production yields at reasonable cost [20]. Among several renewable fuels, the use of alcohols (methanol and ethanol) for steam reforming is attractive due to their high volumetric energy density, low cost, and easy transportation [22]. Dimethyl ether (DME) is also another promising candidate for reforming technologies [23]. The steam reforming of DME is performed in two consecutive steps; namely the hydrolysis of DME to form methanol over a solid acid catalyst, followed by the steam reforming of methanol. The relatively inert, non-corrosive and non-carcinogenic character of DME may help to promote its practical usage with respect to harmful methanol. The overall reactions for both ethanol and DME steam reforming yield 6 mol H_2 per mol of substrate and, more important, half of H_2 originates from water (eqs. 11 and 12, respectively).



In practice, however, the reforming processes are never complete and usually compete with secondary, undesired re-

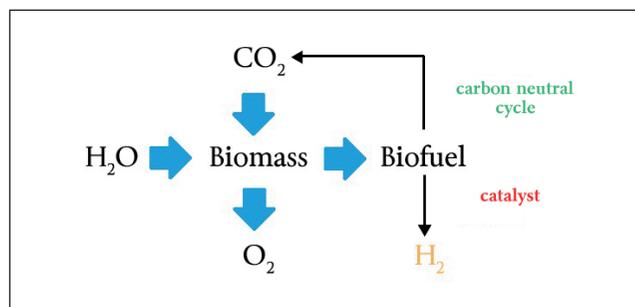


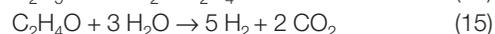
Fig. 2. The steam reforming of renewable bio-derived substrates is ideally CO_2 neutral.

actions, such as decomposition to carbon monoxide and methane, reverse water gas shift, methanation, dehydration and polymerization, carbon deposition, etc. For that reason, the election of an appropriate catalyst is crucial for achieving large H_2 yields and long lifetime [39].

Ethanol as a source of hydrogen

Bio-ethanol is the most widespread renewable alcohol and, for that reason, the generation of hydrogen through ethanol steam reforming at low temperature is currently being thoroughly investigated. Ethanol can be reformed with steam to a hydrogen-rich mixture over selected catalysts (eq. 11). Although thermodynamics predicts that it is possible to obtain complete ethanol conversion at 573 K and 68% H_2 on a dry basis, the C-C bond scission involved in the reforming mechanism often requires higher operating temperatures (the reaction is highly endothermic, $\Delta H_{673}^\circ = +208.4 \text{ kJ/mol}$), thus favoring side reactions which result in considerably lower hydrogen yield.

The steam reforming of ethanol has been extensively studied over catalysts based on Ni, Ni/Cu, Co, and noble metals (mostly Pd, Pt, Rh, and Ru) and has been widely reviewed [18,33,40]. Over noble metals, the reaction proceeds through three steps [20]. First, ethanol decomposes into a mixture of methane, carbon monoxide and hydrogen at a moderate temperature (eq. 13), then CO reacts with steam and transforms into CO_2 (eq. 3) and, finally, methane is reformed at high temperature (eqs. 2 and 3). The reaction scheme is totally different over cobalt-based catalysts [24], where ethanol first dehydrogenates into acetaldehyde at low temperature (eq. 14), and then acetaldehyde reacts with steam to yield more hydrogen (eq. 15). The generation of hydrogen from the steam reforming of ethanol over cobalt systems has been attained at temperatures as low as 340°C , but the drawback is carbon deposition, which poisons the surface of the catalyst. The addition of alkaline promoters results in a better resistance towards poisoning by carbon deposition [25].



Usually, these fundamental studies have been performed over powdered catalyst samples and catalytic pellets, but they

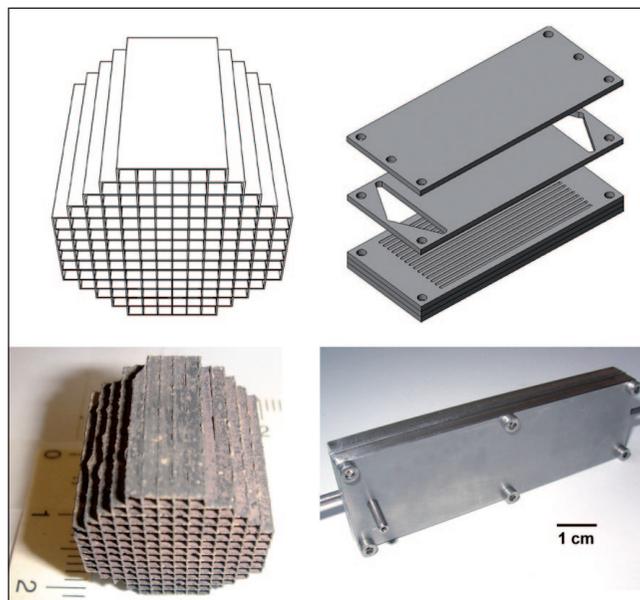


Fig. 3. Catalytic walls in monolithic (left) and microchannel (right) structures.

are definitely not adequate for practical use due to attrition and pressure drop, which may eventually result in dangerous operation regimes and low performance. For that reason, catalytic walls are preferred. Among different possible catalytic wall geometries, catalytic plates [32] and honeycomb structures [6] are preferred (Fig. 3). These supports are attractive for real application because they offer many advantages in terms of scalability, efficiency, stability, cost and operation conditions. However, the deposition of a catalyst layer over these structures may be difficult and several approaches have been adopted, including direct washcoating, chemical vapor deposition, electrophoretic techniques, in situ routes, etc. [6,32,34]. Recently, we have reported outstanding results in the steam reforming of ethanol in terms of hydrogen yield, fast activation and fast response in oscillating environments over honeycombs coated with catalytic cobalt-talc nanolayers dispersed in aerogels [11,12,28].

Aerogels are extremely light materials obtained by removing the solvent from gels under supercritical conditions. The result is an open porous material with very high surface area (>600 m²/g) and excellent mass transfer properties that favor the accessibility to the catalytically active centers. In addition, talc layers delaminate under steam and their structure partially breaks

apart by the hydrogen generated during the reaction, resulting in a strong enhancement of exposed catalytic centres (Fig. 4). The aerogel host immobilizes the resulting nanolayers, which typically measure ca. 10×10×2 nm [12] but, at the same time, assures excellent mass transfer and diffusion regimes. This allows fast response to varying loading environments, such as those encountered in real fuel cell applications. On-board reformers for the generation of hydrogen in mobile applications may benefit from this technology since they can be heated to the reaction temperature in air (i.e. they do not require long activation treatments prior to use) and they are stable under start-up/shut-down cycles. However, at the reactor outlet, in addition to the hydrogen that is needed to run a mobile fuel cell (i.e. low temperature proton exchange membrane fuel cells, PEMFC), there is also CO₂ coming from the reforming process (eq. 11) and minor amounts of other byproducts such as carbon monoxide and methane. It is well known that the electrocatalysts of PEMFC become poisoned by carbon monoxide molecules because they bind strongly over the Pt particles of the electrocatalysts. Therefore, the removal of CO from the hydrogen stream down to a few parts per million (ppm) is mandatory. Hydrogen can be easily separated from the rest of molecules at the reactor outlet by palladium-based membranes (Fig. 5) which, in addition to hydrogen separation, increase the yield of the reaction by the constant removal of H₂ from the reaction mixture [35]. Alternatively, CO can be abated by catalytic preferential oxidation (eq. 16), whereas a selective catalyst must be used in order to oxidize CO and avoid hydrogen losses.



Towards miniaturization: microreaction technology

The range of applications of fuel cells spans from commercially stationary large power plants to automotive and other mobile devices as well as portable electronic gadgets requiring less than 1 Watt electrical output [4]. Market analyses expect portable applications to enjoy widespread market success sooner than automotive or stationary fuel cells. This has moved researchers to investigate in the development of miniaturized fuel cell systems, including reformers for the on-site generation of hydrogen [21]. At present, portable electronic devices show remarkably improved performances, which lead to greater con-

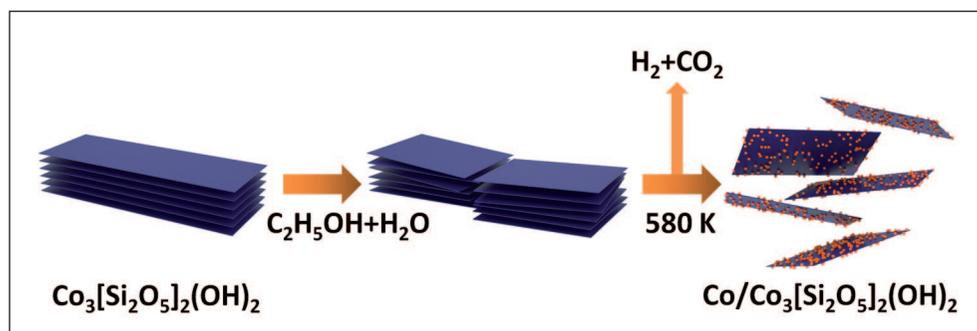


Fig. 4. Cobalt talc nanolayers embedded in an aerogel host act as excellent composite materials for the steam reforming of bio-alcohol. Under reaction, cobalt talc delaminates and metallic nanoparticles develop on the surface.



Fig. 5. Bio-ethanol reformer equipped with catalytic monoliths and a separation membrane selective to hydrogen. The permeate is hydrogen of high purity that can be feed directly into a low-temperature fuel cell for mobile applications.

sumptions of electrical power. Moreover, the tendency towards miniaturization and the wireless revolution is being restrained by battery life. Fuel cells last much longer than batteries and do not need to be replaced. Already existing prototypes demonstrate that fuel cells about the same size as lithium-ion batteries pack almost four times as much power [3]. However, fuel cell implementation in handheld electronics could be restrained if hydrogen feeding and/or refueling is not properly solved. Although considerable work has been performed on hydrogen production via reforming reactions using conventional reactors, the scale reduction required for this market renders their utilization impractical. Furthermore, reforming reactions show strong thermal effects and conventional fixed-bed reactors exhibit poor heat transfer characteristics. Microreactors assess both the problems of moving down the scale and increasing the heat transfer rate by the deposition of the catalyst directly on the reactor walls and the introduction of new manufacture techniques which permit, along with the miniaturization involved, the achievement of remarkable increases in the specific contact area [13]. The small dimensions attained for microchannels and their high reproducibility (Fig. 3) allow for better reaction control by achieving previously inaccessible residence times and flow pattern homogeneity.

The success of microreaction technology is well established today since it has proven to provide excellent mass and heat

transfer properties, as well as uniform flow patterns and residence time distributions in many applications [13]. In addition to rapid mass and heat transport, due to large surface area to volume ratios, the advantages of microreactors include compactness and light weight, good structural and thermal stability, and precise control of process conditions with higher product yields. Microreaction technologies enable process intensification because conversion rates are significantly enhanced due to short diffusional distances, resulting in a considerable decrease in the amount of catalyst required with respect to conventional reactors. Also, microreaction technology provides enhanced safe operation in the management of hydrogen-producing reactions because large volumes are avoided, permitting the use of process parameters of otherwise explosive regimes. Therefore, microreactors appear as an invaluable technology for boosting the implementation of on-board, on-demand generation of hydrogen for portable applications, thus avoiding limitations imposed by hydrogen storage. Numerous micro-devices for on-site production of hydrogen from methanol steam reforming at 260–450°C have been reported [36], but the high temperatures required for the steam reforming of renewable ethanol has prevented extensive work in this field [26].

Men et al. from the Mainz Institute of Microtechnology (IMM) tested several catalyst formulations based on Ni, Rh, Co, and Ni-Rh for the steam reforming of ethanol in a microchannel reactor (channels 500 μm width and 250 μm depth) [30]. The best results were obtained over Ni-Rh/CeO₂, which showed no deactivation during a 100 h catalytic test at 923 K. Casanovas et al. from the Technical University of Catalonia (UPC) developed a microreactor for the generation of hydrogen from ethanol under an autothermal regime [7]. A two-sided platelet microreactor was designed for transferring the heat released during ethanol total catalytic oxidation over a CuMnO_x catalyst ($\Delta H_{673}^{\circ} = -1262.3$ kJ/mol) in one side of the microreactor to the other side, where ethanol steam reforming occurred at low temperature over a CoO_x/ZnO catalyst (Fig. 6). The overall efficiency of the microreactor, determined by comparing the amount of ethanol required in the combustion side for autothermal operation with the amount dictated by thermodynamics, and by considering the amount of hydrogen generated with respect to stoichiometry, was about 70%. Görke et al. from the Institute for Micro Process Engineering (Karlsruhe) used a microchannel reactor (channels 200 μm width and depth) to produce hydrogen by ethanol steam reforming over a Rh/CeO₂ catalyst [16]. For temperatures above 898 K, a space time yield

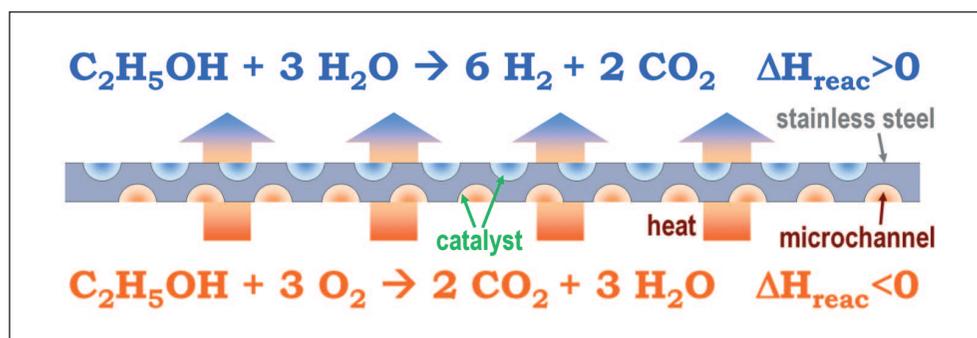


Fig. 6. Heat can be transferred efficiently in microreactors for autothermal operations. For example, ethanol can be catalytically reformed in the microchannels of one side of the microreactor (endothermic process) and combusted (exothermic process) in the other side.

four times higher than that obtained in conventional reactors was reached. Cai et al. from CNRS and the University of Lyon used a microreactor with channels 500 μm wide and deep, loaded with an Ir/CeO₂ catalyst, and hydrogen productivity was found significantly higher than in conventional fixed-bed reactors, essentially due to better heat and mass transfers [5].

These are pioneering examples reported in the open literature concerning the generation of hydrogen from ethanol using microreactor technologies. However, the natural trend in miniaturization of fuel cell systems is being carried out with increasing difficulty by actual micro-reforming units. To further reduce the hydrogen generation scale while maintaining system efficiency can hardly be attained by using conventional geometries and/or manufacture techniques of present-day microreactors. Therefore, the development of breakthrough technologies capable to provide higher hydrogen generation rates per unit volume and, at the same time, enable downscaling is required.

Producing hydrogen in silicon micromonoliths

A new turn of the screw in miniaturization of systems for hydrogen production has been accomplished by using silicon micromonoliths with millions of parallel microchannels per square centimeter with a diameter of only $\sim 3\text{--}4\ \mu\text{m}$ [8,27]. Such geometry is achieved through photo-assisted electrochemical etching in silicon wafers. The parallel channels, with depth/diameter ratios greater than 65, show spectacular reproducibility and a perfectly cylindrical shape, assuring excellent flow distribution (Fig. 7). By means of precisely designed methods, the channels walls can be successfully coated with homogeneous thin layers of appropriate catalysts. With the resultant geometry, the specific contact area increases ca. 100 times with respect to conventional microreactors reaching fabulous values of $10^6\ \text{m}^2/\text{m}^3$.

In-series units of functionalized silicon micromonoliths of 16 mm diameter, with ca. 8×10^6 channels each, have been tested successfully for ethanol steam reforming under practical operating conditions [29]. A parametric sensitivity study regarding operation temperature (400–500°C), feed concentration (liquid, steam-to-carbon = 1.5–6.5) and residence time (3–90 ms) has been performed to find optimal operation windows. Fuel con-

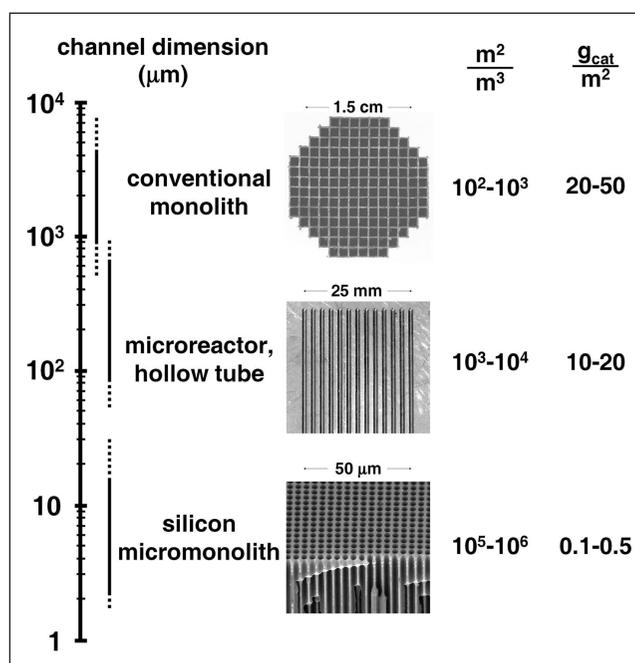


Fig. 7. Channel dimensions, specific contact area and catalyst loading of conventional monolithic structures, microreactors, hollow tubes, and silicon micromonoliths. For the generation of hydrogen in portable applications, silicon micromonoliths yield the best performance; they exhibit the highest contact area and lowest catalyst loading.

version, product selectivity, H₂ specific production rate and catalyst long-term stability have been evaluated at atmospheric pressure in a specifically conceived microreactor to quantify the reaction performance (Fig. 8). Nearly complete ethanol conversions are achieved for residence times of 70–80 ms. A typical selectivity distribution accounts for 64% H₂, 25% CO₂, 3% CO, and 7% CH₄ with negligible quantities (<1%) of other by-products or intermediates (e.g., acetone, acetaldehyde, ethylene). Specific production rates exceeding 3.2 L_N of H₂ per ml of liquid fed and cm³ of micromonolith are possible due to the great geometric area of the micromonoliths, which are much higher than those reported for classical microreactors (Fig. 7). Long term tests (24-h non-stop operation) have shown remarkable constancy in selectivity profiles and hydrogen productivity. After more than 250 h operation at realistic conditions no signs of catalyst deactivation have been observed [29].

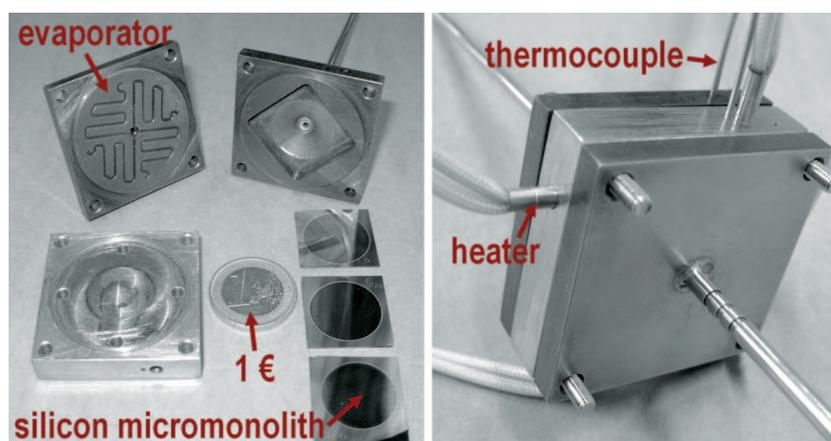


Fig. 8. Proof of concept of a microreactor containing silicon micromonoliths in-series for the generation of hydrogen from the reforming of bioethanol in small fuel cell application.

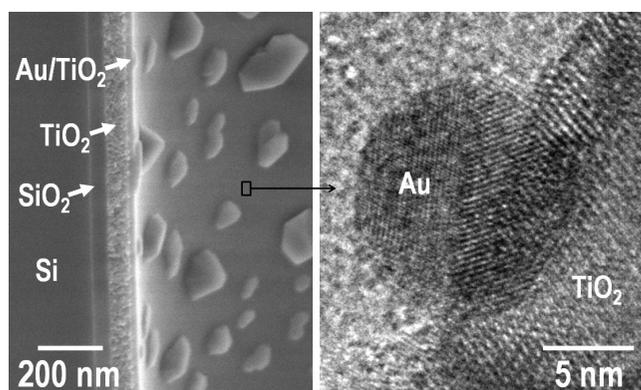


Fig. 9. Scanning electron microscopy image (left) of a transversal section of a SiO_2 -coated microchannel in a silicon micromonolith covered with a TiO_2 layer and gold nanoparticles, visible by transmission electron microscopy (right).

In addition to ethanol steam reforming, silicon micromonoliths are also very valuable for the purification of hydrogen-rich streams obtained in micro-devices, in particular for CO preferential oxidation (eq. 16) which, as discussed above, is mandatory in proton exchange membrane fuel cells. CO oxidation is a strongly exothermic reaction, therefore the ability of a reactor designed to eliminate the heat of reaction from the reaction medium to maintain adequate selectivity levels (i.e. avoid H_2 losses) is of crucial importance. The reproducibility achieved on the support geometry and the good thermal conductivity of the silicon matrix itself strongly prevents the formation of local hot spots during CO oxidation and, in addition, nearly isothermal conditions are feasible along with appropriate reaction rates. We have successfully coated silicon micromonoliths with a TiO_2 layer via an organometallic route and subsequently anchored gold nanoparticles over the TiO_2 support (Fig. 9). The resulting catalytic micromonolith has been tested for the preferential oxidation of CO in the presence of excess hydrogen in order to simulate reformer outlet streams and excellent performances have been encountered at the temperature of fuel cell operation [10]. The outstanding efficiency of silicon micromonoliths for the generation of hydrogen from renewable ethanol and its further purification under residence times of the order of milliseconds is remarkable. Summing up, micromonolithic silicon substrates have been successfully implemented for hydrogen production via ethanol steam reforming towards portable fuel cell feeding. This novel concept represents a landmark in miniaturization technology in general and in micro-scale energy production in particular.

Conclusions

Hydrogen is deemed to be a useful energy carrier in the foreseeable future. It can be produced by using a variety of energy sources and it can be efficiently converted into useful energy forms without detrimental environmental effects. Hydrogen can be used as a fuel in internal combustion engines, turbines and jet engines, even more efficiently than fossil fuels. Hydrogen can also be converted directly to electricity in fuel cells, with a

variety of applications in transportation, portable, and stationary power generation.

When renewable biomass is used to produce hydrogen, both the primary and secondary forms of energy become renewable and environmentally compatible, resulting in an ideal, clean and permanent energy system. Renewable fuels derived from biomass constitute a potential source of hydrogen. Furthermore, bio-derived compounds are available everywhere and can be conditioned for catalytic steam reforming processes and are particularly suitable for fuel cell feeding in portable applications through microreaction technology.

Acknowledgements

Funding from MICINN grant CTQ2009-12520 and from ICREA Academia Program (Autonomous Government of Catalonia) is acknowledged.

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