

Producing Hydrogen from Ethanol in a Microfuel Processor: Recent Developments and Challenges

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Abstract: In the contemporary era of energy crunch, hydrogen fuel, obtained from ethanol, is a potentially strong contender as an energy carrier based on a renewable source. Moreover, acknowledging the critical importance of distributed power devices and systems on one hand and the importance of microscale engineering on the other, we envisage developing an ethanol-based distributed hydrogen production device of the order of one kW using Steam Reforming of Ethanol (SRE). In this paper, the key issues related to this microscale hydrogen production strategy are discussed in view of potential application for polymer electrolyte membrane (PEM) fuel cells. The design challenges and issues related various essential micro-devices, viz., the pre-heater, reformer, Water Gas Shift (WGS) reactor, Carbon Monoxide Preferential Oxidation (CO-PrOX), required for efficient production of H₂ with very low concentration of CO contamination, are discussed. Various production schemes are carefully evaluated for the purpose. Need for integration of micro-devices is emphasized to obtain a compact fuel processor system.

Keywords: Hydrogen energy, Decentralized production, Micro-reactor, Water-gas shift reaction, CO preferential oxidation.

1. Introduction

Unless definitive measures are not implemented soon enough, the world is heading towards a severe and prolonged energy crunch in the not-too-distant future. In the historical background of the decarbonization pattern of primary fuel usage, hydrogen is emerging as a natural choice for more secure and cleaner energy carrier (Barreto, Makihira, and Riahi 2003). Hydrogen can be produced from a variety of sources including fossil fuels (coal, natural gas, LPG, gasoline, diesel, methane, propane, wind, solar, methanol, ethanol, bio-diesel etc.) but to decrease the dependence on fossil fuels fully or partially, current situation strongly demands that hydrogen be produced from a renewable source. In this context, ethanol/bio-ethanol is a promising biomass derived liquid fuel for hydrogen production (Balat, Balat, and Öz 2008; Kim and Dale 2004). Hydrogen can be produced from a variety of feed stocks using a variety of methods; a brief review of these methods is presented below.

2. Hydrogen production methods

Methods of hydrogen production can be broadly classified as (a) thermo-chemical, (b) electrolysis of water, (c) photochemical, and (d) biological.

2.1 Thermo-chemical processes

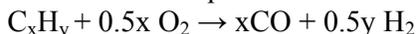
2.1.1 Steam reforming (SR)

Steam reforming refers to the reaction between steam and a hydrocarbon, typically producing hydrogen in the process. Use of natural gas or naphtha as a raw material is an industrial process. Typical reactions are highly endothermic in nature. Depending on the purity of hydrogen required, WGS and PrOX reactors are also appended to this process. The industrial catalyst used for this reaction is Ni/ α -Al₂O₃. While the steam/carbon ratio required for this reaction is 2, generally 2.5-3.0 molar ratios are used to avoid coke formation. Since this is an endothermic and kinetically controlled reaction, temperatures in the range of 1073-1173 K are used to obtain desirable reaction rates. Main disadvantages of this

process include the formation of CO₂, a global warming gas, as a byproduct, and the use of non-renewable natural gas feedstock.

2.1.2 Partial Oxidation

Partial oxidation (PO) is another industrially used process to produce H₂ or syngas from hydrocarbons, with following stoichiometric equation:



PO compares better than SR as it is not only non-catalytic but also does not require external thermal energy input. The process requires temperatures of 1400-1700 K and pressures ranging from 30-100 bar. Pure oxygen is used instead of air to avoid the N₂ separation step. Catalyst may be used to appreciably reduce the reaction temperature. The primary disadvantage of this process as compared to SR is low hydrogen yield.

2.1.3 Auto-Thermal Reforming (ATR)

Combining the features of SR and PO, ATR has been developed, utilizing both steam and oxygen along with the feedstock (Freni, Calogero, and Cavallaro 2000). The oxygen to fuel ratio is sub-stoichiometric and can be altered to adjust the process temperature. The hydrocarbon feed stock first reacts with oxygen and the released heat is used for steam reforming reaction. This takes place on reforming catalyst placed after the burner in the reactor. In this process the hydrogen yield is more than that in PO but less than that in SR. Moreover, this process does not require any external heat to be supplied.

2.1.4 Pyrolysis

Hydrocarbons, when heated to ~1600°C, are converted to pure carbon and H₂, with no other significant side products. This, therefore, is quite a viable process for H₂ production; of course, till fossil fuel based feedstock is economically available.

2.2 Electrolysis

Electrolysis of water, i.e. applying electricity to split it, is the process by which almost 100% pure hydrogen can be obtained. This is the next commonly used industrial method, after steam reforming of methane. At present, conventional alkaline electrolyte based electrolysis is economical, only if cheap

electricity is available. Research is primarily focused on the feasibility of using solid oxide steam electrolyzer, PEM electrolyzer etc. (Barbir 2005; Grigoriev, Porembsky, and Fateev 2006; Ni, Leung, and Leung 2008a, b; Ouweltjes et al. 2007; Wang, Vohs, and Gorte 2007).

2.3 Photochemical decomposition

Photo-catalytic splitting of water, using nano-sized TiO₂ catalyst, is a potentially feasible process for production of hydrogen from water. Very low process efficiency is the main hurdle. This low efficiency is attributed to (i) rapid recombination of photo generated electron/hole pair and, (ii) backward reaction (Koca and Sahin 2002; Ni et al. 2007b). Some sacrificial reagents such as S²⁻/SO₃²⁻ (Koca and Sahin 2002), Ce⁴⁺/Ce³⁺ (Bamwenda and Arakawa 2001) and IO₃⁻/I⁻ (Abe et al. 2001) and electron donors such as methanol (Ashokkumar 1998) are under study for enhancing production. Catalyst modification techniques, such as noble metal loading (Anpo and Takeuchi 2003; Bamwenda et al. 1995), ion doping (Choi, Termin, and Hoffmann 1994), dye sensitization (Choi 2007) and metal ion implantation are also being studied (Li et al. 2008).

2.4 Bio-hydrogen

Biological hydrogen production is carried out by several methods including direct and indirect bio-photolysis, photo-fermentation and dark-fermentation, the latter being the most efficient (Levin, Pitt, and Love 2004). Dark-fermentation involves the use of anaerobic bacteria (*Clostridium pasteurianum*, *C. butyricum*, and *C. beijerinckii* e) grown in the dark on carbohydrate rich substrates to produce H₂ and CO₂ and traces of CH₄, CO, and H₂S. By using *Rhodospirillum rubrum*, H₂ can be produced from WGS reaction when only CO is available (Kerby, Ludden and Roberts 1995). The main disadvantage of this method is the very slow rate of production.

3. Why use ethanol?

All the methods mentioned above have some inherent limitations (such as dependence

on fossil fuel, low rates/process efficiency, etc.) which hinder their use for sustainable energy generation, at least at this point of time. In this context, ethanol steam reforming is a viable process for generating energy from biomass based fuel. Ethanol is a promising future bio-fuel because of its relatively high hydrogen content (on molar basis), non-toxicity, ease of storage and handling safety. Ethanol can be readily produced from renewable feed stocks such as sugar cane, municipal solid waste and agro-waste. Another advantage of using ethanol is that the CO_2 produced during steam reforming reaction is equal to the CO_2 required for biomass growth and thus provides a closed cycle for CO_2 consumption. Therefore, no net pollutants are released into the environment. Primary demerit includes high reforming temperatures ($\sim 600^\circ\text{C}$).

4. Why use micro-reactors?

During the last two decades, technological developments in micro-manufacturing systems have gained considerable momentum (Gad-el-Hak 2002). Recently, micro-devices and systems (popularly known as micro-reactors), having their characteristic dimensions typically of the order of few micrometers, have attracted the interest of chemical process industry because of certain inherent advantages (Kiw-Minsker and Renken 2005; Ehrfeld, Hessel, and Haverkamp (Ed.) 2007; Ehrfeld, Hessel, and Lowe 2000).

The obvious discerning characteristics of micro-reactors are compact size, light weight, and lower material and energy consumption. Secondly, smaller linear dimensions lead to increased specie gradients (momentum flux, concentration, temperature) which are particularly important for chemical reactor processing. This results in rapid heat and mass transport, and short diffusion lengths. Faster system response gives better process control and high product yields. Besides these, the attractive feature of micro-reactors is their high surface to volume ratio compared to conventional chemical reactors. Because of smaller passage size, flow through micro-reactors usually remains laminar. Thus, the heat/mass transfer coefficients become

inversely proportional to the channel hydraulic diameter; of course there is increase in corresponding momentum flux transfer i.e. pressure drop. Nevertheless overall heat/mass transfer to pressure drop ratio is increased.

The higher heat and mass transfer characteristics of micro heat exchangers are an added advantage for utilizing the full potential of catalysts used, especially during endothermic/exothermic reactions. Thus, local hot-spot formations are avoided because of high heat removal capacity. Secondly, because of higher reaction temperature, catalysis can be utilized effectively requiring a smaller volume. This leads to low operating cost and higher system efficiency. Finally, because of smaller reactants and products inventories, high level of safety is achieved.

5. Integrated reactor system for steam reforming of ethanol and CO clean-up

The production of H_2 from ethanol includes the reaction of ethanol with steam, followed by steps to reduce the CO content of the product stream. As shown in Figure 1, water and ethanol are mixed together and then fed to a pre-heater where flow boiling of the mixture takes place by application of external heat input. The gas phase mixture is further superheated to the desired reaction temperature. The pre-heated vapor is fed to the reformer, where the mixture reacts to form hydrogen as well as other compounds, such as CO_2 , CO and CH_4 . As the produced hydrogen is rich in CO ($\sim 10 \text{ mol}\%$), a cleanup unit needs to be attached after the reformer. As shown in the figure, three possible routes are being investigated for reducing the CO content in the product stream: (a) membrane separation; where the effluent is passed through a membrane after reforming, which allows only H_2 molecules to pass through it. In this way 99.99% pure hydrogen can be produced (Ockwig and Nenoff 2007). (b) & (c) are chemical routes in which CO is reduced to ppm levels by WGS followed by either PrOX or selective methanation of CO.

The routes described above involve several thermal and chemical transport processes i.e. endothermic/exothermic catalytic reactions, flow boiling of liquid mixtures, single phase

and two-phase heat exchange, etc. In contrast to conventional reactor and heat exchanger systems, microreactors provide unique features not only in the integration of various thermochemical processes described above, but also by meeting the demands of space optimization in distributed systems. Heat resistant materials like Klingsil® can be used to avoid unwanted heat exchange between the devices while making the overall system compact. In recent times, the relative merit of microreactors has been studied by many groups (Holladay, Wang, and Jones 2004; Kolb et al. 2006; Kolb et al. 2007).

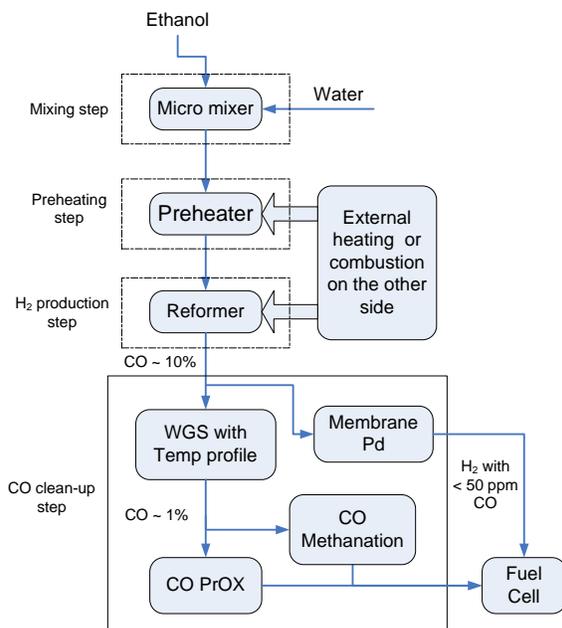
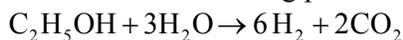


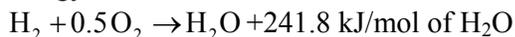
Figure 1: Schematic of an integrated reactor system for distributed generation of hydrogen from ethanol and water.

It is envisaged to develop an ethanol-based hydrogen production device of the order of one kW using steam reforming of ethanol (SRE) coupled with fundamentals of microscale engineering. The stoichiometry of the reaction for maximum hydrogen production by catalytic ethanol steam reforming process is:



$$\Delta H_{298}^\circ = 174 \text{ kJ/mol}$$

The produced hydrogen is made to react with oxygen (or air) to form water and thermal energy:



Thus, stoichiometry requires a mixture of 2.4 ml/min of $\text{C}_2\text{H}_5\text{OH}$ and 2.23 ml/min of H_2O for producing 1 kW of thermal energy equivalent. In real-time practice, to avoid coke formation and to enhance the selectivity towards reforming reaction, a steam-rich mixture is desired (Ni, Leung, and Leung 2007a). Thus, assuming water to ethanol molar ratio of 1:6 (Stoichiometry = 1:3), the amount of water required would be 4.5 ml/min. By assuming a W/F_{A0} of 1.00, (W = weight of the catalyst and F_{A0} = molar flow rate of the reactant A (i.e. ethanol), the amount of catalyst required would be 2.5 g. With this data, if the cross section area of the microchannel is of the order of $\sim 500 \mu\text{m}^2$, the length of reactor is of the order of $\sim 50 \text{ mm}$, catalyst layer thickness of $\sim 30 \mu\text{m}$, number of microchannels per reactor plate ~ 25 , the number of reactor plates required works out to be about 30.

5.1 Preheater design issues

The catalytic steam reforming of ethanol for hydrogen production is highly endothermic ($\Delta H_{673}^\circ = 208.4 \text{ kJ/mol}$), which accounts for the requirement of high reforming temperatures usually around $\sim 873 \text{ K}$ (Casanovas et al. 2008c). A preheater, consisting of a phase-change heat exchanger and a superheater, are therefore needed to convert the liquid phase reactants (water and ethanol) to superheated gas phase, before entering the micro-reactor. In this background, the fundamental understanding of thermo-hydrodynamics of flow boiling of pure fluids and binary mixtures is a precursor to design the catalytic reformer.

5.1.1 Flow boiling of pure and binary liquids in mini/microchannels

While flow boiling studies in conventional sized channels dates back to the development of steam boilers and nuclear power reactors, the advent of miniaturization in many engineering systems, for example, emergence of small tonnage unit refrigeration industry, provided the impetus to similar studies in mini/micro geometries (Kandlikar 2002).

In recent times, the focus is on experiment, computations, as well as theoretical research on

sub-millimeter/ micron sized geometries. In early 1980s, Tuckerman and Pease (1981) first demonstrated experimentally that flow boiling of water through microchannels is capable of removing high heat flux. Shortly after the initial work of Tuckerman and Pease (1981), Wu and Little (1984) also conducted experiments on flow friction and heat transfer characteristics in microchannels. Since then there has been an unprecedented upsurge of on flow boiling through mini/microchannels using a variety of fluids and passage dimensions. The primary issues in flow boiling of liquids in micro channel geometries which are being addressed, include, amongst others, (a) fundamental physics of nucleation and bubble growth in confined geometries, (b) effect of surface roughness on transport mechanisms, (c) effect of aspect ratio of the flow channels on transport behavior (d) correct handling of the boundary conditions (e) additional effects due to surface energy of the tube material, electrokinetic forces, wettability, etc., (f) flow instability in single channel and parallel channel arrays (g) relative importance of nucleate and convective boiling, etc. The current status of the understanding of flow boiling in mini/microchannels has been reviewed from time to time by several authors (Bertsch, Groll, and Garimella 2008; Cheng and Mewes 2006; Garimella and Sobhan 2003; Kandlikar 2002; Kakac et al. (Eds.) 2005; Thome 2004; 2006).

Flow boiling of binary mixtures is inherently more complicated than the pure fluid counterpart due to the fact that (a) there is no unique boiling point temperature for a given operating pressure (b) the overall transport mechanism may be limited by the preferential mass transfer process of the less volatile component during phase change, (c) the composite thermo-physical properties of the mixture may substantially vary from those determined from linear mixing laws, and, (d) the bulk liquid contact angle, an important quantity required for understanding boiling mechanism, usually shows highly non-linear behavior with concentration. There are, comparatively, not only few studies available on this topic, most of them are confined to flow

boiling studies of binary mixtures of refrigerants (Celata, Cumo, and Setaro 1994; Kandlikar 1998; Cheng and Mewes 2006; Stephan 1995; Thome 1996; Levy, Koyfman, and Jelinek 2006; Hewitt 2002).

There are very few studies reported in the literature on flow boiling of binary mixtures in mini/microchannels; prior to 1994, almost no publications exist in open literature (Cheng and Mewes 2006; Peng, Peterson, and Wang 1996). Peng and co-workers (Peng and Wang 1994; Peng et al. 1996) first conducted a sequence of experiments to investigate the flow boiling of subcooled binary mixtures (methanol and water) flowing through a variety of microchannels. They investigated the impact of microchannel scale, geometric configuration, liquid velocity, liquid subcooling, and liquid concentration on the flow boiling.

Peng and Peterson (1996) also conducted experiments on flow boiling of subcooled binary mixtures of methanol and water. For smaller mole fractions of the more volatile component (methanol), heat transfer was augmented, and then reached the maximum value at a characteristic mole fraction. The effect of the aspect ratio on the convection heat transfer also varied as a function of the mole fraction of the mixture.

Recently, Cheng and Mewes (2006) have extensively reviewed flow boiling of mixtures in small and mini channels. They have included the investigations during 1996-2005, a majority of which focus on refrigerant mixtures. They proposed the basic equation for binary mixture to determine the heat transfer coefficient as:

$$h_{mix} = \frac{q''}{T_w - T_b} \quad (1)$$

where, T_b is the bubble point temperature of the binary mixture and T_w is the wall temperature. For pure fluids, the bubble point temperature equals the saturation temperature.

Peng and Wang (2000) reviewed experimental and theoretical advances in boiling phase-change and transport phenomena in microchannels and microstructures, including bubble formation, phase transition and the fluid flow and heat transfer characteristics. Their investigations showed that flow boiling heat transfer of pure water,

pure methanol, and water-methanol binary mixtures through rectangular and triangular microchannels display some unusual phenomena and characteristics. The experimental results showed that microchannel size, geometric configuration, and mole fraction of water-methanol binary mixtures have a significant impact on the flow boiling, especially for nucleate boiling, and on bubble formation and growth in microchannels. They proposed two new concepts, 'evaporating/boiling space' and 'fictitious boiling', to explain the unusual phase-change transport phenomena, although these concepts were not substantiated with enough evidence.

Though ethanol is being used industrially for a long time, its use for the study of flow boiling in mini/microchannels hardly exists in literature. Suzuki, Kawamura, and Ueno (2003) investigated subcooled flow boiling of ethanol-water mixtures in a horizontal rectangular channel. They observed that micro-bubble emission boiling occurs in transition boiling and the heat fluxes are about 50 percent higher than water at the same superheat of heating surface. The maximum heat fluxes of the mixtures reached 8.0 MW/m^2 at 40K of liquid subcooling and 0.5 m/s of liquid velocity. Xie, Yu, and Zhao (2005) experimentally investigated flow and heat transfer characteristics by taking 30% of ethanol-water solution in microchannels. This solution is the most commonly used coolant in the aviation sector. They found that wall temperature has maximum influence on convection heat transfer. No investigation has presented the explicit effect of liquid concentration on the flow boiling heat transfer.

The state-of-the-art on flow boiling of binary mixtures in microchannels suggests that the following issues need immediate research:

- (i) Many more systematic experiments in this area are indeed needed. The effect of component composition on transport behavior is not very clear.
- (ii) The interplay between heat transfer and flow patterns is still unclear. Robust visualization of two-phase flow in microchannels continues to pose a challenge.
- (iii) A generalized and robust heat transfer

model is still not available which takes into account the complex interplay between channel shapes/sizes, component compositions, mass diffusion, flow pattern etc.

(iv) For practical applications, empirical/ semi-empirical correlations for pressure drop and heat transfer are also not available.

5.2 Steam reforming of ethanol (SRE)

The reactions involved in catalytic steam reforming of ethanol for hydrogen production have been studied extensively over catalysts based on Co, Ni, Ni/Cu as well as noble metals such as Ru, Rh, Pt, and Pd. Cobalt and copper based catalysts are more efficient at low temperatures. Rh based catalysts are more efficient in breaking the C-C bond but are relatively less active for the WGS reaction. Some bimetallic catalysts (Rh-Ni) have been tried to enhance the WGS reaction (Sheng et al. 2002). Research efforts on development of active, selective and stable catalysts for SRE have increased significantly in the last decade and several reviews have been recently published (Cheekatamarla and Finnerty 2006; Haryanto et al. 2005; Ni et al. 2007a; Vaidya and Rodrigues 2006; Xuan et al.). The high temperatures required to obtain reasonable reaction rates increase the coke formation, catalyst sintering and eventual catalyst deactivation. To alleviate this problem, a double layer catalyst system has been proposed. The first layer contains Cu based catalysts to facilitate dehydrogenation reaction and the second layer contains Ni or Rh based catalysts to facilitate C-C bond rupture and to steam reform the acetaldehyde formed on the first catalyst layer (Vaidya and Rodrigues 2006). However, at these conditions the chances for side reactions to form methane and carbon monoxide are very high, and thus, the selection of catalyst is critical in this type of configuration.

The heat required for the endothermic reforming reaction can be supplied in several ways: (a) external heat input (by electrical heating), (b) auto-thermal reforming, (c) combination of combustion/steam reforming reactors with heat exchange between the two, so that heat generated in combustion reaction

can be utilized in the steam reforming reaction. For any of the heat supply system mentioned above, micro-devices can be used for efficient heat integration.

Men et al. (2007) studied SRE in a microchannel reactor at atmospheric pressure in the temperature range of 400-600°C, over various noble and non-noble metal catalysts. Washcoating method was used to coat the catalyst support and metals were impregnated onto the washcoated supports. The activity of doped Rh catalysts was very high at low temperatures as compared to that of monometallic Rh catalysts. The catalyst doped with Ni and Ce was tested for stability for 50 hrs and no deactivation was found for this catalyst during this period.

Casanovas et al. (2008c) used a two sided microchannel plate, one side with reforming catalyst and the other side with combustion catalyst, to produce hydrogen from ethanol in auto-thermal mode. In this study four different methods were used for preparing coated plates, such as washcoating, in-situ co-precipitation, in-situ urea-assisted precipitation and sol-gel. In-situ urea-assisted precipitation was found to be better among the four methods used, in terms of adherence and final catalyst loading. Efficiency of the microreactor was calculated to be 71% by using the formula

$$\eta = 100 \times \text{mol of H}_2 / (\text{mol. of ethanol} \times 6 \times 0.858)$$
where, the factor 0.858 arises due to the fact that 14.2% of total ethanol will be consumed in combustion reaction. Differences in both micro structure of catalyst coatings and catalytic behavior were not observed even after exposure to thermal cycling for 24h between 298-773 K.

Casanovas et al. (2008b) used 3 different types of catalytic wall reactors, viz. conventional monoliths (Casanovas et al. 2008a), microchannels (Casanovas et al. 2008c) and micromonoliths (Llorca et al. 2008) for SRE at low temperature. CoO₃ catalyst coated reactors were prepared by in-situ thermal decomposition of cobalt hydroxide salts. Significant difference in activity was observed among the three reactors studied. Micromonoliths performed better than the other two reactors. The performance decreased as size of the channel increased.

Wang et al. (2008) fabricated ceramic micro-components by “deep X-ray lithography and lost-mold” technology with dimensions 300 μm width, 400 μm height and 20 mm length. The components so fabricated were tested for SRE with 300 nm Ni film-catalysts, coated through sputtering process. The results from this study revealed that, the sputtered catalyst show better performance even at lower temperatures.

5.3 CO clean up step

Effluent from ethanol reformer typically contains more than 10% CO. In many applications it is desirable to reduce the CO content to ppm levels, for example, in PEM fuel cell applications. Two routes have been suggested in the literature: (i) membrane separation and (ii) WGS followed by selective methanation of CO or PrOX.

5.3.1 Membrane route

In the case of membrane reactor, the process is very simple and Pd membranes are highly selective for H₂ permeation and possess excellent mechanical characteristics. A low hydrogen recovery (~70% gas processed), requirement of high pressures on the reformer side and low pressure on the other side, failure at high temperatures, prohibitively high cost, are the limitations of this process (Ockwig and Nenoff 2007). To increase the overall productivity for H₂ using membranes, Karnik, Hatalis, and Kothare (2003) integrated WGS with a H₂ gas separator by preparing a composite membrane with four layers viz. Cu, aluminum, Spin on glass (SOG), and palladium. Out of these layers, Cu acted as a WGS catalyst and Pd separated the H₂ from the other gases. Also aluminum and palladium served to increase the mechanical strength.

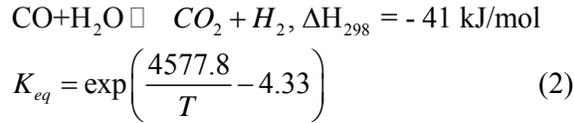
A micro-membrane with 66 nm Cu, 200 nm Al, 500 nm SOG, and 200 nm Pd withstood a maximum ΔP of 1 atm before failure. It was claimed that due to the nano-thin layer of Pd, the activation energy for hydrogen flux was decreased.

5.3.2 Chemical route

Water gas shift followed by preferential methanation or oxidation is widely studied for CO clean up.

i) Water-gas shift reaction

In WGS, the steam reacts with water to give CO₂ and H₂ as follows:



By this reaction, the CO content can be reduced from 10% to about 1%. WGS is mildly exothermic so the conversion of CO is thermodynamically controlled at high temperature; moreover the rates are very low at low temperature. Therefore, for every composition there will be an optimum temperature at which space-time yield is the highest. Two reactors are used to maximize the conversion: one at high temperature (HT-WGS) for achieving high rates and the other at low temperature (LT-WGS) to achieve high equilibrium conversion. Noble metal catalysts have reasonable activity even at low temperature and, with such catalysts; one can achieve high conversions in a single reactor, by maintaining a decreasing temperature profile along the reactor length.

Tonkovich et al. (1999) have applied microreactor technology to exploit fast intrinsic kinetics on 5%Ru/ZrO₂ catalyst and found that, with this technology, the fuel processor size can be 1 or 2 orders less than that of conventional processes. (Kolb, Pennemann, and Zapf 2005) employed microchannel reactors to screen and optimize the catalysts for WGS reaction. They tested a range of bimetallic catalysts (Pt/CeO₂/Al₂O₃, Pt/Rh/CeO₂/Al₂O₃) and Pt/CeO₂/Al₂O₃ was identified as the best candidate concerning selectivity and activity. The optimum platinum content was found to range between 3 and 5 wt.%, whereas the optimum ceria content ranged between 12 and 24 wt.%.

In a later work, the same group (Kolb et al. 2008), integrated WGS with PrOX, using the same catalyst as developed for WGS. With this integrated reactor and with steam/carbon ratio of 3.3 and O₂/carbon ratio of 0.67, the iso-

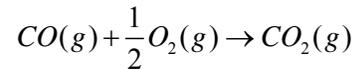
octane fuel was auto-thermally reformed completely, with CO content less than 50 ppm.

TeGrotenhuis et al. (2002) developed a model for calculate the optimum temperature profile to maximize the conversion in WGS, and compared this with an optimized two reactor system with inter-stage heat removal. The catalyst required for the latter system was 2.5 times more than that for the former system to achieve a conversion level of 93%.

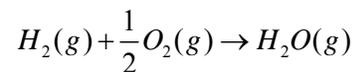
Baier and Kolb (2007) applied a simple one dimensional model to compare two configurations for WGS (a) combination of reactor/heat exchanger and (b) two stage reactor with intermediate water injection. The length required for configuration (a) was found to be 30% less than that required for configuration (b).

ii) CO preferential oxidation (PrOX)

In WGS reaction, it is difficult to achieve a CO concentration below 1%, because of thermodynamic constraint on equilibrium conversion. So generally PrOX is used to reduce the CO concentration below 50 ppm, which is the tolerance level of PEMFC. For PrOX reaction, the exit gases from the WGS reactor are mixed with the required amount of O₂ and passed over the PrOX catalyst. The main reactions that may take place are



$$\Delta H_{298}^0 = -283 \text{ kJ/mol}$$



$$\Delta H_{298}^0 = -241.8 \text{ kJ/mol}$$

If the oxygen content is not sufficiently high then there may be chances of reverse WGS



In a PrOX reactor, CO has to be oxidized preferentially in the presence of high concentration of H₂ and other hydrocarbon products. Hence, highly selective catalysts are required to maximize the CO conversion and minimize the conversion of H₂. Moreover, at PrOX conditions methanation of CO and CO₂ is also promoted by some catalysts and by that H₂ productivity will be reduced. Therefore, for PrOX reaction, catalyst selection is very important. The catalyst development for CO

PrOX in packed bed reactors has been reviewed recently by (Park, Lee, and Lee 2009). Whatever may be the catalyst, because of the lower rates at low temperature and lower selectivity towards CO PrOX at high temperature (Snytnikov et al., 2008), the temperature window for highest CO PrOX is limited and is less than 50°C. Moreover, the reaction is highly exothermic, so it is very difficult to maintain a constant temperature, which is essential for high activity of PrOX catalyst. In this context microreactors perform well. Several studies have been done to test the feasibility of using microreactors for PrOX. (Galletti et al., 2008; Guan et al., 2008; Kim and Dale, 2004; Snytnikov et al., 2008).

Gracia, Li, and Wolf (2003) selected catalysts for ProX with the hypothesis that a catalyst which promotes CO adsorption and reaction at low temperature would be a good catalyst. Accordingly, two families of catalysts were developed, and Pt/Al₂O₃ doped with CeO₂ was found to be best catalyst for PrOX at temperatures below 90°C.

Delsman et al. (2004) designed an integrated heat exchanger/reactor for PrOX by using a 3-D model CFD simulation for flow patterns, 2-D heat transfer model and finally 1-D model was used to simulate the integrated device. In their integrated device, one high temperature heat exchanger, one low temperature heat exchanger and PrOX reactor were integrated. With such a device, CO concentration can be reduced to 10 ppm while recovering heat with 90% efficiency.

Chen et al. (2004) conducted PrOX reaction in a microchannel reactor and compared the reactor performance with that of a monolithic reactor (MR). The smaller dimensions of MR resulted in high heat mass transport which in turn resulted in higher reaction rates even at low contact times of 4-6 ms. Srinivas et al. (2004) compared the performance of a Si microreactor with a packed bed microreactor by taking PrOX as a model reaction. They claimed that, wall coated microreactors do not suffer from any external mass transfer resistance.

Cominos et al. (2005) screened several noble metal based catalysts and their bimetallic

combinations for PrOX, and found Pt-Ru/ γ -Al₂O₃, Rh/Al₂O₃, Pt-Rh/ γ -Al₂O₃ to be the most active and Pt-Rh/ γ -Al₂O₃ to be the most stable catalyst.

6. Conclusions

As regards the fuel reformer, even though a large number of catalysts have been developed, the commercialization of this process requires more favorable catalysts, which can reduce the required reaction temperature and there by, the catalyst deactivation. Double layer catalyst system, with a careful selection of catalyst, may be a solution for this problem. Microreactor configuration is quite favourable for the implementation of double layer catalyst deposition scheme. Moreover, Micro-devices can also be effectively used for heat integration.

For WGS reaction, the required temperature profile can be maintained in microreactor systems. Even though the PrOX reactions are highly exothermic, the small temperature window (~50°C), required for high activity of PrOX catalyst, can be maintained in microreactors, through efficient heat exchange. Various micro-devices required for efficient generation of H₂ from ethanol, with very low concentration of CO, can be integrated with efficient heat recovery within the system, by using micro-reactor technology. In this paper we have tried to highlight the salient requirements and state of the art for the development of distributed hydrogen production system from bio-ethanol steam reforming.

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