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Hydrogen generation from renewables
Steam reforming of ethanol and dimethyl ether over structured catalysts

ABSTRACT

Ethanol and dimethyl ether can be efficiently reformed with steam over appropriate catalysts for generating hydrogen. Both substrates provide a valuable example of the use of renewable chemicals for energy applications. At temperatures as low as 623 K, a mixture of ethanol and water at S/C=1.5 can yield as much as 92 percent H_2 over honeycomb structures coated with cobalt-based catalyst layers, with only 1 percent carbon monoxide. Dimethyl ether can be similarly reformed at 823 K. At S/C=1.5, hydrogen yields up to 80 percent are obtained over honeycombs coated with copper-zinc supported over ZrO_2. The performance of these systems improves considerably by using microreaction technologies, not only by increasing the surface-to-volume ratio, but also for allowing autothermal regimes.

KEYWORDS

Hydrogen, steam reforming, bio-fuel, ethanol, dimethyl ether, catalytic monolith, microreactor.

INTRODUCTION

Motivated by the possibility of using hydrogen as an energy carrier and the growing implementation of fuel cells, hydrogen production technologies are currently being investigated and developed thoroughly. Catalytic steam reforming of fuels has attracted much attention as an efficient technology for hydrogen production because it provides high hydrogen production yields at reasonable cost (1, 2). In addition, it can be used for supplying hydrogen to portable fuel cells while avoiding safety and storage issues related to gaseous or liquid hydrogen. Among several substrates, the use of alcohols for steam reforming is attractive due to their high volumetric energy density, low cost, safety, and easy transportation. In particular, methanol and ethanol are preferred since they are renewable fuels that can be readily produced from biomass (Figure 1). It merits to be highlighted that a bioalcohol-to-H_2 system is CO_2 neutral. Dimethyl ether (DME) is also considered a promising candidate for reforming technologies (3). 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 yields 6 mol H_2 per mol of substrate and half of H_2 originates from water:

$$C_2H_5OH + 3\,H_2O \;\rightarrow\; 6\,H_2 + 2\,CO_2 \qquad 1.$$
$$(CH_3)_2O + 3\,H_2O \;\rightarrow\; 6\,H_2 + 2\,CO_2 \qquad 2.$$
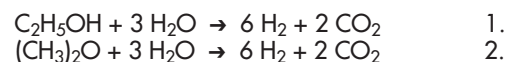
In practice, however, the reforming processes are never complete and usually compete with secondary, undesired reactions, such as decomposition to carbon monoxide and methane, reverse water gas shift, methanation, dehydration and polymerization into C_{2+} hydrocarbons, carbon deposition, etc. For that reason, the election of an appropriate catalyst is crucial for achieving large H_2 yields and long lifetime.
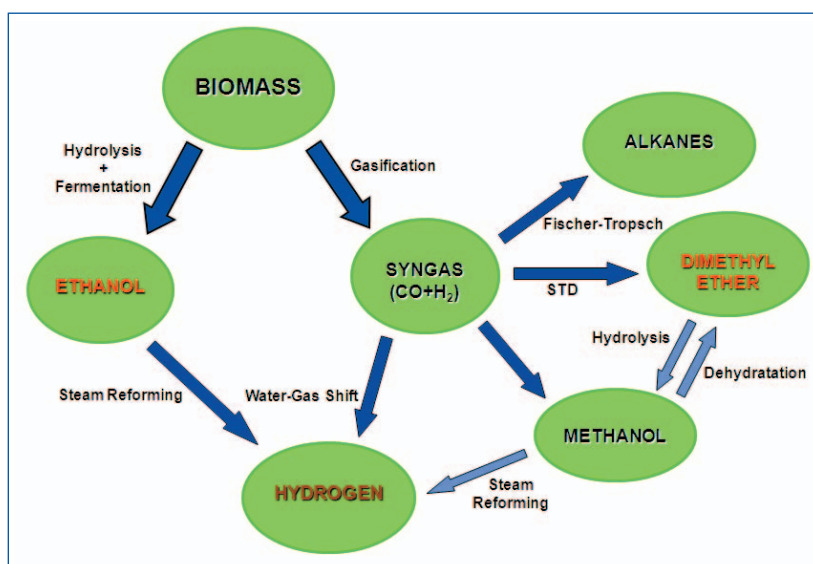

Figure 1. Common routes for hydrogen production from biomass-derived renewables

Considerable work has been carried out on catalytic steam reforming of methanol and ethanol for hydrogen production using conventional packed bed reactors (4-6), but the use of structured and micro-structured catalytic wall reactors is relatively new. In addition to compactness and light weight, the advantages of catalytic walls and microreactors include rapid mass and heat transport due to large surface area to volume ratios, low pressure drop and no reactor blocking, good structural and thermal stability, and precise control of process conditions with higher product yields. Micro-structured reactors also provide built-in safety because large volumes are avoided. Numerous micro-devices for on-site production of hydrogen from methanol steam reforming at 533-723 K have been reported (4), but although catalytic ethanol steam reforming is gaining interest rapidly, the higher temperatures required for C-C bond breaking has prevented extensive work in this field (7, 8). The use of structured catalytic wall reactors for the steam reforming of DME has been reported very recently over Pd-Pt-Zn/Al_2O_3 (9) and Cu-Zn/CeO_2-ZrO_2 (10) catalytic honeycombs. Monolithic supports can be an attractive replacement for conventional catalytic pellets because they offer many advantages in terms of efficiency, cost and operation conditions (11).

Ethanol and dimethyl ether can be efficiently reformed with steam over appropriate catalysts for generating hydrogen.

STEAM REFORMING OVER HONEYCOMBS

Low-temperature ethanol steam reforming
Currently, the generation of hydrogen through bioethanol steam reforming at low temperature is being widely investigated (5, 6). The reaction (equation 1) has been extensively studied over catalysts based on Ni, Ni/Cu, Co, and noble metals (Pd, Pt, Rh and Ru) (12, 13).

The reaction is reversible and highly endothermic, which accounts for the requirement of reforming temperatures usually above 873 K.

At such high temperatures ethanol is mainly reformed into a mixture of H_2 and CO, and it is necessary to pass the reformate through a water gas shift reactor in order to generate further hydrogen and eliminate CO. However, cobalt-based catalysts are particularly effective for ethanol steam reforming (ESR) at lower temperatures, 623–673K, where the water gas shift reaction is also operative. We have developed several preparation procedures for developing cobalt-based catalytic honeycombs and tested them in ESR.

Outstanding results in terms of stability, fast activation, and fast response in oscillating environments for hydrogen supply were obtained over honeycombs coated with cobalt nanoparticles dispersed in aerogels (14). 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 and excellent mass transfer properties that favour the accessibility to the catalytically active centres (15).

A typical preparation procedure involved immersion of monoliths into a sol of silica precursor tetraethoxyorthosilicate (TEOS), incomplete gelation using water-ethanol as solvent and HNO_3-HF as catalysts, complete gelation under continuous rotation in liquid ethanol, and subsequent impregnation of the cobalt precursor (16). Finally, monoliths were dried under supercritical conditions of ethanol (6.28 MPa, 516 K). A BET surface area of 645 m^2 g^{-1} and an average BHJ pore size of 19 nm were estimated. Catalytic honeycombs activated at very low temperature (580-590K), were resistant to oxidation (563-613K), exhibited good selectivity towards the reforming products, H_2 and CO_2, and did not deactivate after 100 h of continuous operation under ESR conditions. On-board reformers may benefit from these honeycombs coated with catalytic aerogels 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.

Dimethyl ether steam reforming
Traditionally, DME is obtained industrially from syngas through a two-step process using copper-based and zeolite catalysts, although a one-step method called STD process (synthesis gas-to-dimethyl ether) has been recently developed for the synthesis of DME in a single reactor with hybrid catalysts (17). DME can be produced from renewable sources as well, such as biomass-derived syngas and methanol. A bifunctional catalyst is needed to carry out the steam reforming of DME (equation 2). To our best knowledge, there was only one work with catalytic monoliths with Pd-Pt-Zn systems supported on alumina or zeolites and they were used for autothermal reforming of DME (9). This encouraged us to undertake a survey of new honeycomb catalysts for DME steam reforming.

We have prepared a wide range of new catalytic formulations using ionic oxides with acidic and redox properties as supports and Pd, Cu, and/or Zn as active phases. The honeycomb structures were first washcoated with the support particles (CeO_2, ZrO_2, CeO_2-ZrO_2, MnO_2, SnO_2, Al_2O_3, WO_3 and WO_3-ZrO_2), and then the active phases were incorporated to the support using various impregnation methods and characterized by electron microscopy and X-ray diffraction techniques as well as by NH3-TPD analysis.

Among catalytic honeycombs loaded with Cu and/or Zn, the best performance in terms of activity, stability and selectivity was obtained over monoliths containing a mixture of copper and zinc as active phase and ZrO_2 as support.

A comparison of selectivity values obtained over honeycombs coated with ZrO_2 and Cu-Zn/ZrO_2 is shown in Figure 2.
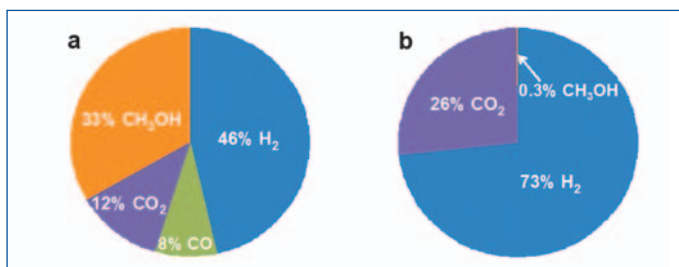

Figure 2. Product distribution obtained under dimethyl ether steam reforming conditions over ZrO_2 (a) and Cu-Zn/ZrO_2 (b) catalytic honeycombs at 693 K and S/C=1.5

Over ZrO_2, the simultaneous occurrence of methanol and reforming products at the reactor outlet evidences that the support is not only adequate for the hydration of DME into methanol (first step of the reforming process), but also to initiate the second step of the reforming process, which is the steam reforming of methanol. The addition of Cu and Zn to ZrO_2 honeycombs results in the main transformation of DME into the reforming products, H_2 and CO_2, providing a new and cheap material for the production of hydrogen from a renewable source.

AUTOTHERMAL REFORMING OVER MICROCHANNEL REACTORS

Reforming reactions show strong thermal effects and conventional fixed-bed reactors exhibit poor heat transfer characteristics. Microchannel metal reactors with cross sections of the channels below 0.5 mm^2 have been therefore introduced in recent years to achieve better heat transfer rates in hydrogen production technologies. In addition to miniaturization and the achievement of remarkable increases on the specific contact area, the small dimensions of microchannels allow better reaction control by achieving previously inaccessible residence times and flow pattern homogeneity. Also, microreactors appear as a novel technology for boosting the implementation of on-board generation of hydrogen for mobile applications, thus avoiding limitations imposed by hydrogen storage. However, the deposition of thin catalysts layers and their adherence onto the metallic substrates is challenging and novel methods are currently being developed (18).

We have recently reported a microreactor for the generation of hydrogen from ethanol under autothermal regime (8).

A two-side platelet microreactor with hemicylindrical microchannels was designed and manufactured (see Figure 3) for transferring the heat released during ethanol total catalytic oxidation over a $CuMnO_x$ catalyst ($\Delta H°_{673}$=-1262.3 kJ mol^{-1}) in one side of the platelet to its reverse side, where ethanol steam reforming occurred at low temperature over a CoO_x-ZnO catalyst ($\Delta H°_{673}$=+208.4 kJ mol^{-1}). The overall efficiency of the microreactor, determined by comparing the amount of ethanol required in the combustion side for autothermal operation with respect to the amount dictated by thermodynamics and by considering the amount of hydrogen generated with respect to stoichiometric values, was about 70 percent.

ESR OVER Si MICROMONOLITHIS. A NEW *TURN ON THE SCREW*

The rapidly growing market for power sources for new portable electronic devices has moved researchers to investigate in the development of miniaturized fuel cell systems, including hydrogen production and purification stages (19). However, conventional microreactor technologies can hardly reach channels dimensions under 0.1 mm. In recent pioneering work, we have reported the breakthrough application of micromonolithic silicon layers for hydrogen production by ethanol steam reforming (20, 21). Channel diameters ~3-4 μm with a density of channels of ca. $4x10^4$

Outstanding stability, fast activation, and fast response in oscillating environments for hydrogen supply are obtained over honeycombs coated with metal nanoparticles dispersed in aerogels

channels mm^{-2} are achieved through photo-assisted electrochemical etching in ca. 200 μm-height silicon wafers. A perfectly parallel array of channels are obtained with a depth/diameter ratio >65. By means of a novel deposition method, the walls of the channels can be successfully coated with homogeneous thin layers of cobalt catalysts.

With the resultant geometry, the specific contact area increases up to fabulous values of $3x10^5$ m^2 m^{-3}.

We have implemented *in-series* several functionalized silicon wafers of 16 mm diameter, with ca. $8x10^6$ channels each, inside a stainless steel casing. In addition to inlet/outlet conduits and flow direction facilities, the casing includes a preheating/evaporation section and place to house electrical microcartridges to provide the heat of reaction and evaporation and to fix the operation temperature of the system. A snapshot of the manufactured microreformer is shown in Figure 4. The unit was tested successfully for ESR under practical operating conditions. Non-diluted ethanol/water liquid mixtures were fed directly using a pump. A parametric sensitivity study regarding operation

$$C_2H_5OH + 3 H_2O \rightarrow 6 H_2 + 2 CO_2$$

heat   microchannel

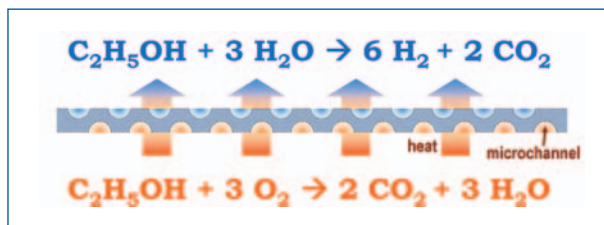$$C_2H_5OH + 3 O_2 \rightarrow 2 CO_2 + 3 H_2O$$

Figure 3. Two-side microchannel reactor for autothermal reforming of ethanol. Each side is coated with appropriate catalyst. The heat released in the ethanol oxidation side is transferred to the reforming side where hydrogen is selectively produced

temperature (673-773 K), feed concentration (S/C=1.5-6.5) and residence time (3-90 ms) was also performed to find optimal operation windows. Results were analyzed by means of a μ-GC. The fuel conversion, products selectivity, H_2 specific production rate and catalyst long-term stability were evaluated at atmospheric pressure to quantify the reaction performance. Almost complete ethanol conversions were achieved for residence times of 70-80 ms. As reported in Figure 4, a typical selectivity distribution accounts for 64 percent H_2, 25 percent CO_2, 3 percent CO and 7 percent CH_4, with negligible quantities (<1 percent) of other by-products or intermediates (e.g., acetone, acetaldehyde, ethylene). Specific production rates exceeding 3.2 L_N of H_2 per mL of liquid fed and cm^3 of micromonolith are possible due to the great geometric area of the micromonolith. Long term tests (24 h non-stop operation) show remarkable constancy in selectivity profiles and hydrogen productivity. After more than 250 h operation at realistic conditions not signs of catalyst deactivation are observed. Summing up, micromonolithic silicon substrates have been successfully functionalized and implemented for hydrogen production via ethanol steam reforming towards portable-fuel-cell feeding. This novel

Microreactors appear as a novel technology for boosting the implementation of on-board generation of hydrogen for mobile applications, thus avoiding limitations imposed by hydrogen storage

concept represents a landmark on miniaturization technologies in general and on micro-scale energy production in particular.

CONCLUSION

Steam reforming of renewable ethanol and dimethyl ether represents a valuable route for the generation of hydrogen and has the advantage that it requires a limited amount of additional infrastructure for implementation. At present, suitable catalysts for selective ethanol and dimethyl ether steam reforming are being developed, but their use on structured wall reactors for industrial application is still under way. Among them, aerogel-based coated structures appear very promising due to very high mass transfer rates and ability to disperse highly active metal nanoparticles. We have shown an excellent catalytic performance of Co-SiO$_2$ aerogels deposited onto commercial honeycombs for ethanol steam reforming at low temperature. In addition, the catalytic device is activated rapidly under reaction conditions and no conditioning of the catalyst is required prior to use. Microreactors based on silicon micromonoliths together with integrated downstream hydrogen separation by means of dense metal membranes or carbon monoxide selective oxidation/methanation hold a promising future for the effective on-site/on-demand generation of hydrogen from renewables in portable fuel cell applications. Due to their extremely high specific surface area, silicon micromonoliths show remarkable reaction rates per unit volume, even operating with residence times in the order of milliseconds. The reproducibility achieved on the support geometry and the good thermal conductivity of the silicon matrix itself strongly prevents from formation of local hot spots in autothermal processes and nearly isothermal conditions are feasible along with appropriate reaction rates.

Micromonolithic silicon substrates have been successfully functionalized and implemented for hydrogen production towards portable-fuel-cell feeding
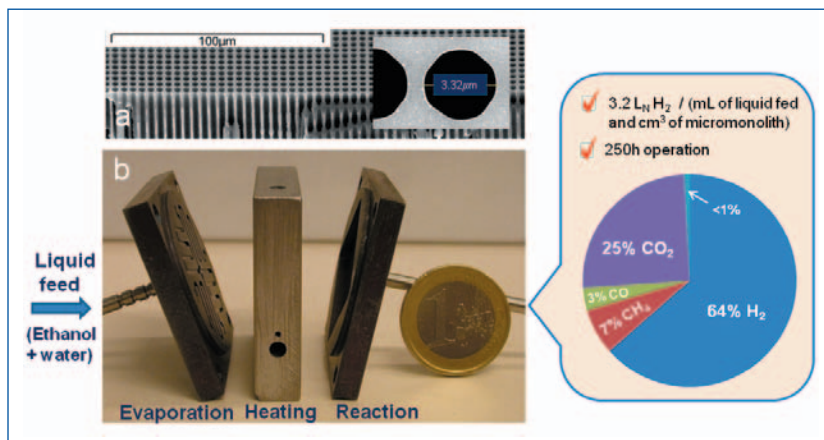

Figure 4. a) SEM image of a silicon micromonolith with detail of a single channel. b) Photograph of the dismantled microreactor for hydrogen production, with its three main sections and inlet/outlet pipes. The silicon micromonoliths are implemented in the "reaction" section. A typical performance is also presented

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