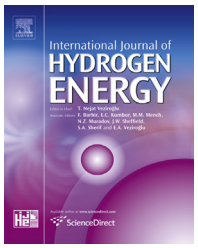
Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



# Ultra-compact microstructured methane steam reformer with integrated Palladium membrane for on-site production of pure hydrogen: Experimental demonstration

*T. Boeltken, A. Wunsch, T. Gietzelt, P. Pfeifer*, R. Dittmeyer*

*Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

ARTICLE INFO

*Article history:*
Available online 11 July 2014

*Keywords:*
Microstructured membrane reactor
Palladium membrane
Methane steam reforming
Rh-based catalyst
Compact system
Laser welding

ABSTRACT

A novel metal-based modular microstructured reactor with integrated Pd membrane for hydrogen production by methane steam reforming is presented. Thin Pd foils with a thickness of 12.5 μm were leak-tight integrated with laser welding between microstructured plates. The laser-welded membrane modules showed ideal $H_2/N_2$ permselectivities between 16,000 and 1000 at 773 K and 6 bar retentate pressure. An additional metal microsieve support coated with an YSZ diffusion barrier layer (DBL) facilitated the operation at temperatures up to 873 K and pressures up to 20 bar pressure difference. The membrane permeability in this configuration is expressed with Q = 1.58E-07*exp(−1460.2/T) mol/(msPa$^{0.5}$).

In the first proof-of-concept reaction experiments the influence of W/F ratio (0.33–1.32 $g_{Cat}h/mol_{CH_4}$), S/C ratio (3 and 4), temperature (773 and 823 K) and retentate/reformate pressure (6–12 bar) was studied. Methane conversion of 87% and a hydrogen recovery of 92% were obtained at a W/F ratio of 0.33 $g_{Cat}h/mol_{CH_4}$, corresponding to a GHSV of 29,000 $h^{-1}$, a temperature of 823 K and a feed pressure of 12 bar without the use of sweep gas.

The microstructured membrane reactor showed a promising performance for the production of pure hydrogen in a very compact and modular system.



## Introduction

The process intensification potential of compact reactors with integrated Pd-based membranes for distributed production of pure hydrogen by steam reforming of natural gas or methane (MSR) has been highlighted in recent publications [1,2]. The approaches to apply innovative reactor types refers to technical solutions, where on-site hydrogen production is favored instead of delivery of hydrogen in compressed or liquefied state via truck transportation.

The Pd-based membrane selectively separates the hydrogen from the reactor in high purity. In consequence, further complex purification steps, such as pressure swing

* *Corresponding author*. Tel.: +49 (0) 721 60824767.
E-mail address: peter.pfeifer@kit.edu (P. Pfeifer).
http://dx.doi.org/10.1016/j.ijhydene.2014.06.091

adsorption (PSA) are elided. Additionally, the membrane is improving reaction kinetics of the steam reforming (Eq. (1)), and the concurrent water gas shift (Eq. (2)) by shifting the thermodynamic equilibrium due to the extraction of hydrogen from the reaction zone. As a consequence, reaction temperatures can be decreased, while maintaining high conversion [3].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0_{298K} = 206\ kJ/mol \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298K} = -41\ kJ/mol \tag{2}$$

In literature, tubular membranes with diameters of around 2–10 mm with catalyst particles supplied as a packed bed around the membrane tube are frequently described [2–6].

However, for an optimized system efficiency, and high catalyst and membrane utilization several design parameters of a membrane reactor need to be considered:

- A sufficiently large membrane area per catalyst volume is required to achieve a good match of hydrogen production rate and hydrogen flux through the membrane [7], given the case that the activity of the catalyst is high enough to keep up with the shift of the thermodynamic equilibrium.
- The gas transport of generated hydrogen from and through the hydrogen producing catalyst bed may be significantly limited (concentration polarization) [8]. This results in a reduced driving force for hydrogen permeation, and a lower utilization of the Pd membrane when the hydrogen flux through the membrane is high. The application of thin membranes for reducing the system costs is consequently increasing the importance of this aspect.
- Good heat integration is crucial for the endothermic steam reforming reaction. Heat transfer limitation results in more fuel consumption for the burners and temperature gradients can have a remarkable effect on the overall system performance.

Tubular membrane reactors with large diameters offer a relatively small membrane area to catalyst volume ratio. Even when a membrane tube of only 1 cm in diameter is considered with an internal catalyst bed, only 400 $m^2/m^3$ of membrane surface area can be supplied. For high reaction rates and/or high permeance, this might not be sufficient.

In general, the mass transfer resistance in the gas phase is significantly reduced the closer membrane surface and catalyst are brought in contact [9]. However, direct contact between catalyst and membrane surface has to be avoided to prevent mechanical damage of the membrane or undesired reactions by active site-membrane contact.

More elaborate designs are described in literature to counteract the effect of concentration polarization. Van Sint Annaland and co-workers presented a (micro) fluidized-bed membrane reformer for the autothermal reforming of methane with reduced mass transfer resistance between catalyst and membrane, and potential hot spots are avoided as well [10,11].

A research group of KIERS in Korea reported a planar circular membrane module integrated in a housing and $H_2$ recovery could be increased by decreasing the distance between module wall and membrane surface from 2.5 mm to 0.4 mm [12,13]. Based on this design, a modular disk-type multi-membrane reformer for hydrogen production from methane steam reforming was presented that operates at pressures up to 21 bar [14].

Tokyo Gas has developed the world's largest membrane reformer so far for the production of 40 $Nm^3H_2/h$ from natural gas, and an efficiency of 81.4% was reported [15]. In this system, structured catalyst modules are used that are attached close to the membrane surface [16].

Microstructured reactors are characterized by high indirect heat exchange and high mass transfer rates, and are well documented in the literature [17,18]. The small lateral dimensions of the microchannels result in a large surface area to volume ratio, a feature that makes the incorporation of thin membranes attractive [19]. For example, microchannels with a channel depths of 200 μm coated with a catalyst layer of 10 μm inside the channel would result in a membrane surface area to catalyst volume ratio of 100,000 $m^2/m^3$, provided that every microstructured catalyst foil is in contact with the membrane. Due to this very high ratio, extremely active catalysts can be used to produce hydrogen at a rate comparable to the hydrogen removal rate through the membrane [20]. A membrane surface area to catalyst volume ratio of 100,000 $m^2/m^3$, however, may be too high for practical applications, and therefore the design of a microstructured membrane reactor should be adapted to the process needs in order to neither oversupply Pd membrane area nor expensive catalytic material. The small dimensions of the microchannels will minimize mass transfer effects towards the membrane [9]. Furthermore, up-scaling of this reactor type is possible by stacking multiple microstructured elements to a modular reactor. Hence, very compact systems are anticipated.

MEMS type membrane-integrated microreactors based on silicon and glass have been proven to produce hydrogen from steam reforming and partial oxidation of methanol [21,22]. For example, methanol conversion of up to 63% was obtained at 475 °C and atmospheric pressure, and hydrogen permeation through a 200 nm thin Pd–Ag alloy film resulted in a hydrogen recovery of 47% [22]. The pressure difference for these ultra-thin membranes was limited to 70 kPa and challenges, such as sealing of the metal membrane with the silicon based device and membrane stability at elevated pressures and temperatures remain. However, this chip-like membrane reactor type is interesting for fueling fuel cells in the Watt and sub-Watt range for portable applications [21,23].

A further step towards a technical system is an approach that originates from thin metallic plate-type heat exchangers that carry microchannels in the micrometer range and are coated with a catalyst layer or filled with a micro-packed bed. The advantage of metallic microreactors is that there is a variety of techniques available for bonding of metals [24]. Each bonding technique has to be well matched with the process parameters of the application of the device. Full-faced connections between the thin metallic foils can be achieved with diffusion bonding in vacuum at elevated temperatures close to the Tammann temperature, where self-diffusion processes of the crystals bond the metal parts. Pressing load and time influence the bonding result as well.