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Development of a Compact Steam Reformer Using a Palladium Membrane for the Production of Hydrogen

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1 Motivation

The Linde Group is a world leading gases and engineering company with almost 48,000 employees working in around 100 countries worldwide. Linde provides customers worldwide with all kinds of gases by cylinder, trailer, truck or even with dedicated production plants at the customers' site. The number of applications for hydrogen is rising mainly within users of small capacities (< 500 Nm^3/h H_2) compared to industrial consumption. Supply with hydrogen for this capacity involves delivery by truck. The shift of the supply to an onsite production is favoured for some cases due to economical, ecological and safety reasons. Scale-down of existing production technologies is economically not preferred. One reason is the high share of invest costs for the control and instrumentation of the pressure swing unit, which is costly even for smaller units.

Therefore a new development applying palladium membrane technology in a H_2 reformer unit (membrane reformer) was initiated for small scale applications, e.g. heat applications, glassware manufacture and hydrogen fuel stations for mobile applications. A compact design with fewer subunits compared to conventional reformers and improved economic characteristics can be achieved with the new technology. By applying a palladium membrane for the production of H_2, the equilibrium of the involved reactions can be shifted towards the product which will improve the efficiency of the process.

$$CH_4 + 3\,H_2O \leftrightarrow CO + 3\,H_2 \qquad \text{(Eq. 1)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{(Eq. 2)}$$

Membrane reformers have attracted a lot of interest over the last years, mostly in connection with fuel cell systems. But the concept of removing hydrogen from a reactor through an integrated membrane dates back to Gryaznov as early as 1969 [1]. Recently, research in the field of methane steam reformer including palladium (alloy) membranes was performed by several academic groups worldwide (reviews are given e.g. by Lukyanov et al. [2] or Dittmeyer and Caro [3]). The most advanced industrial application of a membrane reformer for natural gas steam reforming was published by Mitsubishi Heavy Industries together with Tokyo Gas [4]. Their work is based on studies of Kikuchi, Uemiya and co-workers, see e.g. [5, 6]. The membrane reforming system integrates flat rectangular membrane elements and has a hydrogen production capacity of $40m_N^3/h$, succeeded to produce 99.999% pure H_2 with an efficiency of 81.4% [7].

There are three options to apply the palladium membrane: thick self-supporting palladium or thin layers of palladium on a metal or a ceramic support. Preferred geometries for the membranes are tubular or plate shaped systems.

2 Project Scope & Partner

Following the demand for a small scale hydrogen production plant by the gas producing division Linde Gas, the R&D department of Linde Engineering division was commissioned to start an evaluation to identify existing technologies, their commercial and technical status as well as their availability. No technology was identified to match with Linde technologies.

A customized concept was developed to fit best with the Linde steam reformer technology. So the idea of combining a tubular membrane technology on a metal support with a conventional reformer from the Linde portfolio seemed promising.

The project has been set up and a cooperation team has been formed which covers industrial partners for the production and user side as well as an academic partner. In this joint development Linde, Plansee and KIT have set up an interdisciplinary team. Several work packages have been defined and assigned to the project partners (see Figure 1). Plansee as a world leading company in the fabrication of powder metallurgical components for high performance applications is responsible for the development and production of the membrane tubes, Linde as the producer of hydrogen and the group of Prof Dittmeyer at the Institute of Micro Process Engineering with long-time experience in heterogeneous gas-phase reactions in microstructured reactors as well as preparation and use of palladium composite membranes.

We are targeting an innovative small scale steam reformer for the production of hydrogen by using a palladium membrane for the separation of pure hydrogen.

The project aims at the demonstration of the new technology in a laboratory commercial scale pilot plant.

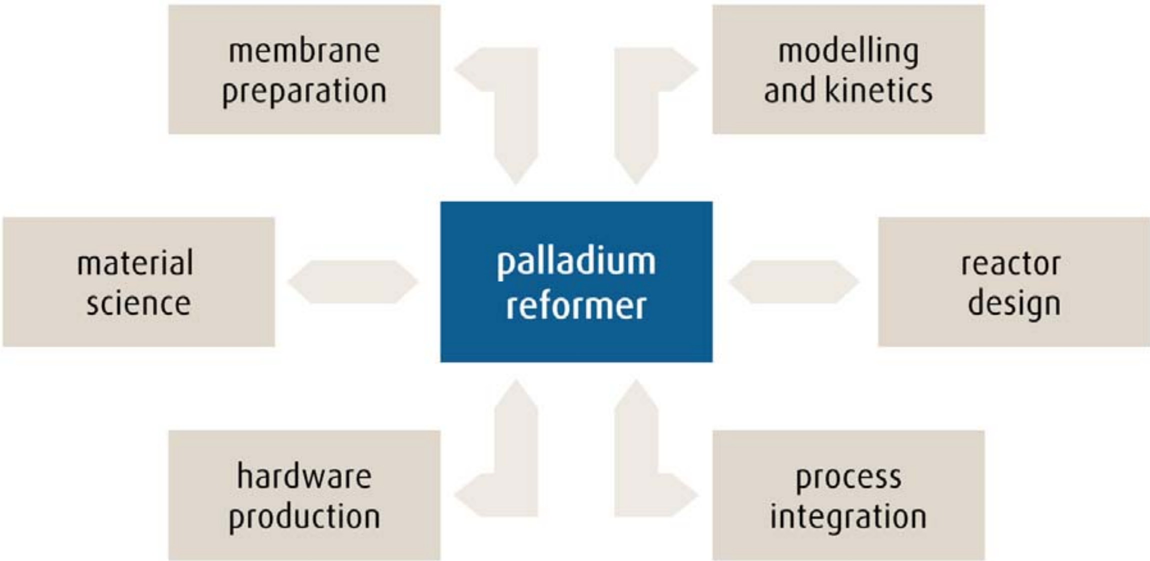

Figure 1: Interdisciplinary project cooperation.

Basis for the development of a membrane reformer is a stable and reliable membrane, so a metal supported membrane is the first choice. Therefore a diffusion barrier becomes necessary and helps to adjust the porosity of the layers. This diffusion barrier has to be adapted to the support and to the Pd membrane layer. A number of test samples are produced and these membranes are then evaluated in a new designed lab test rig, providing data about the performance of the membrane tubes, which can be used for the simulation. The next steps are the design and engineering of the reformer and adjustment of the additional units.

3 Development of Support Tubes and Diffusion Barrier

In order to maximize the hydrogen flux a thin-film composite membrane design is beneficial requiring a structural support. Metallic and ceramic substrates would be both applicable. However, metallic substrates offer a number of advantages, such as high strength, easy joining and similar thermal expansion coefficient to the selected Pd-membrane.

Plansee developed a ferritic alloy called ITM for new types of solid oxide fuel cells. As a result of fundamental development the oxide dispersion strengthened (ODS) alloy Fe26Cr (Mo, Ti, Y_2O_3) turned out to be most suitable for this application. New powder metallurgical (P/M) techniques for the fabrication of porous sheets and tubes of ITM were established. These substrates with high quality surfaces are used for fuel cells and high temperature membranes.

The metallic diffusion between the FeCr-matrix of the metallic substrate and the Pd-membrane must be prevented by a porous ceramic diffusion barrier layer (DBL), which is located directly at the substrate/membrane interface. Based on several years of experience in developing diffusion barrier layers for metal supported fuel cells Plansee adapted this technology and was able to demonstrate the functionality. It shows a high open porosity which improves the gas diffusion towards the separating membrane.

4 Optimisation of the Pd-coating and Characterisation

The support tube of sintered ITM with the ceramic diffusion barrier layer on top is coated with a palladium layer by Electroless Plating (ELP) (see Figure 2). The Electroless Plating procedure is based on the reduction of a meta-stable palladium salt complex on a substrate surface activated by palladium seeds. The growing Pd grains form a film and the microstructure of this film has an important effect on the permeation properties. The Pd grain growth is determined by the ELP conditions, including the rate, duration, temperature, and supply of reactants. The basic procedure has been described already by Shu et al. in 1991 [8]. However, many researchers worldwide are still working on improvements of this technology as witnessed by approximately 5 research papers per year in the last decade. The optimisation of Pd-coating aims for the minimization of the palladium thickness while maintaining dense pore-free membrane characteristics. The minimization of the Pd membrane thickness reduces the costs for the precious metal palladium and enhances the hydrogen flow through the Pd membrane. But very thin Pd layers show an enhanced tendency for defects through which all gases can diffuse and consequently lead to impurities in the produced hydrogen flow. Thus, the Pd membrane is characterized by its hydrogen permeability and its selectivity (to separate hydrogen from other gases) as well as its long term stability.

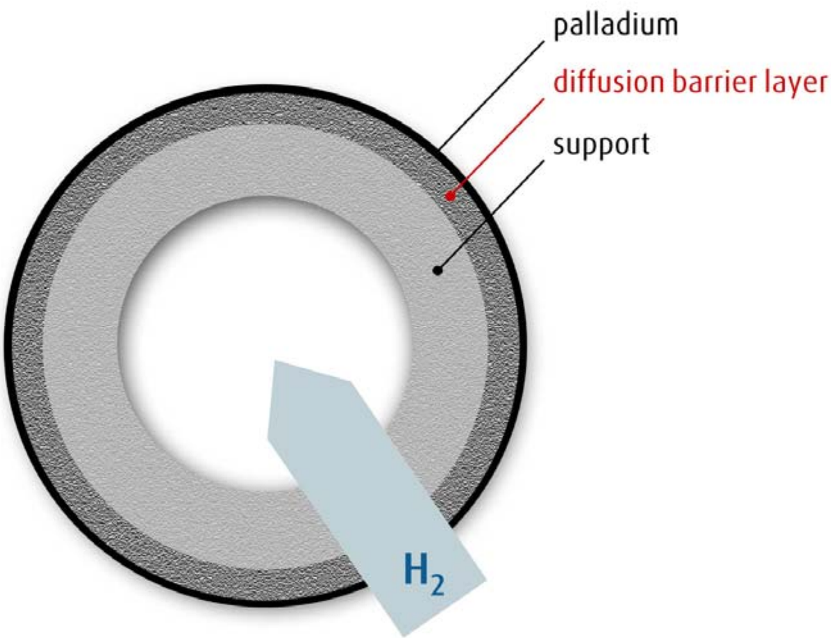

Figure 2: Cross-section of the membrane tube.

For achieving high hydrogen fluxes, high hydrogen selectivity and high long term stability the complete system of support material, diffusion layer and palladium membrane has to be optimized (see Figure 3). A large porosity of the metallic support and the ceramic diffusion layer is needed for high hydrogen flows. The ceramic layer should provide a multitude of small pores by avoiding large pores and obtain a smooth surface with modest roughness for enabling the growth of a thin and well adhering Pd layer. The palladium coating procedure is optimized by adapting the ELP conditions to enable homogeneous Pd coating of the total DBL surface without any defects or impurities.

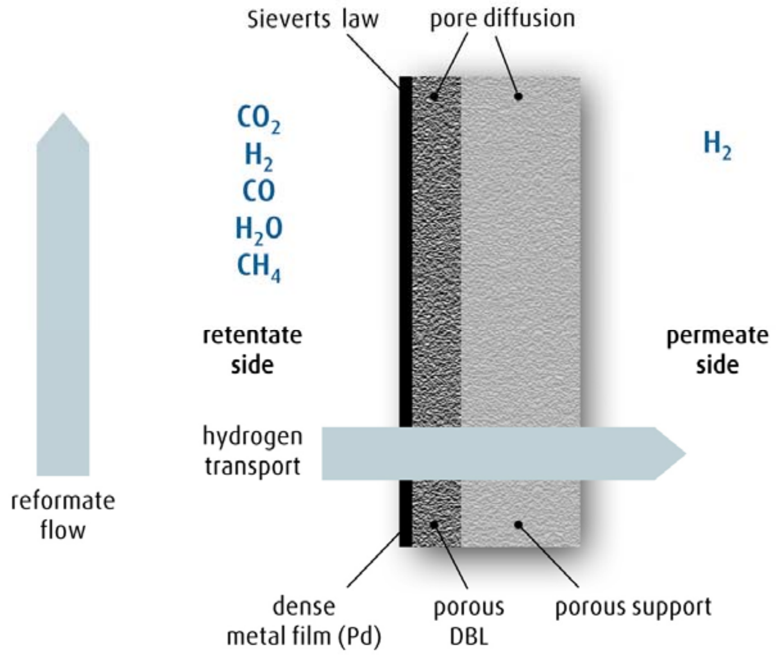

Figure 3: Membrane system consisting of metal support tube, ceramic diffusion barrier layer and dense palladium coating.

Palladium membranes show the feature of selective hydrogen transport. By placing the membrane directly into the steam reformer reactor, it is possible to withdraw pure hydrogen where it is generated. By doing so, shifting of the equilibrium of reforming and shift reactions towards the products is achieved, which improves the overall efficiency. By removing hydrogen through the membrane, the pure hydrogen product is obtained directly from the reformer tubes without further purification steps, e.g. pressure swing adsorption and CO-shift-converter which are necessary in the conventional reformer design (see Figure 4).

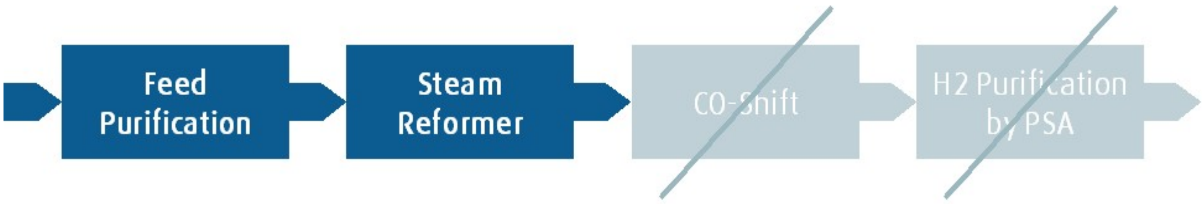

Figure 4: Units necessary for membrane reformer technology.

References

[1] Gryaznov, V.M.: Dokl. Akad. Nauk SSSR., 189, No. 4, (1969),pp 794-796

[2] Lukyanov, B.N.; Andreev, D.V.; Parmon, V.N.: Catalytic reactors with hydrogen membrane separation; Chem. Eng. J., 154 (2009), pp 258-266

[3] Dittmeyer, R.; Caro, J.: Catalytic Membrane Reactors in Handbook of Heterogeneous Catalysis, Edts. Ertl, G.; Knözinger, H.; Schüth, F.; Weitkamp, J.; , 2nd edition, 2008, Wiley-VCH Verlag, Weinheim, pp 2198-2248

[4] Yasuda, I.; Shirasaki, Y.: Development and Demonstration of Membrane Reformer System for Highly-efficient Hydrogen Production from Natural Gas; Materials Science Forum, Vols. 539-543 (2007,) pp 1403-1408

[5] Uemiya, S.; Sato, N.; Ando, T.; Matsuda, T.; Kikuchi, E.; Steam reforming of methane in a hydrogen-permeable membrane reactor , Journal of Applied Catalysis 67 (1990), pp 223-230

[6] Kikuchi, E.; Nemoto, Y.; Kajiwara, M. Uemiya, S.; Kojima, T.; Steam reforming of methane in membrane reactors: comparison of electroless-plating and CVD membranes and catalyst packing modes; Catalysis Today, 56 (2000), pp 75-81

[7] Green Car Congress: Tokyo Gas, Mitsubishi Heavy Improve Hydrogen Separation Membrane Reformer, 4 May 2008, http://www.greencarcongress.com/2008/05/tokyo-gas-mitsu.html

[8] Shu, J.; Greandjean, B.P.A.; Van Neste, A.; Kaliaguine S.: Catalytic palladium-based membrane reactors: A review Canadian Journal of Chemical Engineering, 69 (1991), pp 1036-1060