# Methane steam reforming operation and thermal stability of new porous metal supported tubular palladium composite membranes

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## ARTICLE INFO

## ABSTRACT

In 2009 cooperation between Plansee SE, Austria (PSE), Karlsruhe Institute of Technology, Germany (KIT) and the Engineering Division of Linde AG, Germany (LE) was set up with the aim to develop new tubular palladium composite membranes and a membrane reformer system for small scale on-site hydrogen production.

This paper presents for the first time in detail KIT and LE laboratory results of the new membranes. They are composed of a porous metal support, a porous ceramic diffusion barrier and a dense Pd layer which was produced by physical vapor deposition (PVD) as an activation step and two additional methods: electroless plating (ELP) and electro plating (EP).

Ideal $H_2/N_2$-permselectivities between 700 and almost 10,000 were measured at 600 °C and hydrogen transport kinetic parameters were determined for both membrane types. PVD/ELP-membranes reached a 15% higher $H_2$-permeability than PVD/EP-membranes. Moreover, stability tests were carried out indicating that the membranes are resistant to temperature and feed gas changes, to thermal cycling in $N_2$-atmosphere between room temperature and 650 °C, and to short-term high-temperature methane steam reforming (MSR) at 700 °C. Long-term operation for several hundred hours at realistic operating conditions proved that MSR can be performed without degradation of the membranes. Without optimizing membrane area versus feed load, a maximum methane conversion of 60% was achieved at a $H_2$-recovery of 70% at 650 °C, 16 bar(a) and a S/C of 3 without the use of sweep gas.
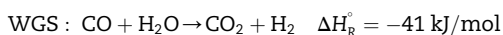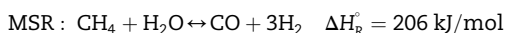
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## 1. Introduction

Natural gas steam reforming plays an important role in global hydrogen production [1]. The major chemical reactions are the steam reforming of methane as main component in natural gas (MSR reaction) followed by the water-gas shift reaction (WGS reaction).

$$MSR : CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_R^\circ = 206 \text{ kJ/mol}$$

$$WGS : CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_R^\circ = -41 \text{ kJ/mol}$$

The sum of both reactions gives the overall reaction (SUM).

$$SUM : CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad \Delta H_R^\circ = 165 \text{ kJ/mol}$$
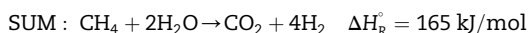
The standard industrial process uses large reformer units where the chemical reactions take place in long catalyst-filled reactor tubes at about 800–900 °C and up to 30 bar(a) [2]. On the one hand the applied conditions guarantee high methane conversion but also lead to a high CO content in the outlet stream due to the exothermic character of the WGS reaction. Therefore the outlet gas stream has to be conditioned in a second reactor in order to convert undesired CO into $CO_2$ and $H_2$. This so called shift converter is often operated as a high temperature shift unit (340–450 °C) and may be followed by a second low temperature shift unit (200–250 °C). Afterward the process stream is prepared for the hydrogen separation which is done by pressure swing adsorption (PSA) in a complex, pseudo-continuous purification process. Due to the high temperature level in the reformer, high pressure export steam is produced to increase the overall efficiency of the process.

For small-scale on-site production (<500 $m_N^3$/h $H_2$), however, the use of a PSA-unit does not seem economically attractive. Moreover, export steam, which is a very useful product in large chemical production facilities, is usually not gratified at small-scale production sites.

The idea of process intensification of natural gas steam reforming by using a membrane reformer dates back to the year 1987 when Oertel et al. [3] suggested this new process. In such an apparatus a $H_2$-selective membrane is integrated into the reaction zone for in-situ removal of the produced hydrogen. As a result, for small-scale applications the above mentioned disadvantages of the conventional process are overcome. First of all the produced hydrogen requires no further purification, and second, due to the shifted chemical equilibrium as a consequence of the hydrogen removal similar methane conversion levels can be achieved at lower temperature. This effect saves energy and increases the efficiency of the process without the need to export steam. Among different possible types of membranes, dense metal membranes made of palladium and other metals [4] combine best the most important features for this process: high hydrogen flux and high selectivity at high temperature (400–600 °C). In order to increase the hydrogen flux, free-standing, relatively thick Pd-membranes (50–100 μm) that have been developed in the 1960s have been replaced by composite membranes consisting of a thin selective Pd-layer (2–20 μm) and a porous support for the mechanical strength.

Pioneering work in preparing a composite membrane via electroless plating of the Pd-layer has been done by Uemiya et al. [5] on porous Vycor glass tubes (1988), by Way [6] on porous ceramic tubes (1993) and by Shu et al. [7] on stainless steel tubes (1994). They also investigated the performance of their membranes at different operating conditions in lab scale membrane reformers, indicating that significantly higher methane conversions than equilibrium conversion without $H_2$ removal can be achieved at moderate temperatures of 400–550 °C. Shu et al. [7] reported a methane conversion almost twice as high as the equilibrium conversion at 500 °C, atmospheric operating pressure, vacuum on the permeate side and a steam-to-carbon ratio (S/C ratio) of 2–4. After them many others have investigated experimentally the influence of temperature [8,9], reaction pressure [10,11], S/C ratio [9,12,13], feed flow rate [9,11,12], sweep gas flow rate [9,12] or permeate $H_2$-partial pressure [14], membrane area [11], membrane permeance [15] and catalyst activity [16] on methane conversion and hydrogen recovery in lab-scale membrane reformers. In order to further investigate and verify these lab results extensive simulation work of membrane reformers has been done for example by Barbieri and Di Maio [17], Gallucci et al. [18,19] and De Falco and co-workers [20,21]. Also, research papers have been published dealing with several observed side effects like competitive adsorption [22,23], concentration polarization [24,25] or coke formation [26] in membrane reformers.

Already in 1996 Japanese industrial driven developers engineered a 4 $m_N^3$/h pilot membrane reformer that was able to operate a 5 kW fuel cell [27]. The same party developed a 40 $m_N^3$/h unit equipped with planar Pd-based membranes that is to date the most advanced industrial scale version of a membrane reformer for natural gas steam reforming [28].

In 2009 cooperation between Plansee SE, Austria (PSE), Karlsruhe Institute of Technology, Germany (KIT) and the Engineering Division of Linde AG, Germany (LE) was set up with the aim to develop a membrane reformer for small scale on-site hydrogen production for applications with medium purity (∼99.95%) and low product pressure requirements (2–3 bars). The goal of the industrially driven project is the demonstration of this technology on a pilot scale based on new tubular palladium composite membranes.

This paper presents for the first time in detail KIT and LE laboratory results of the membranes which were developed and produced by PSE and KIT. At first, the $H_2$ transport properties and ideal $H_2/N_2$-permselectivities of the membranes are compared to literature values. Second, results of thermal cycling and repeated feed gas changes as well as results of long-term methane steam reforming (MSR) for several hundred hours are shown in order to demonstrate the stability of the new membranes. The membranes are composed of a porous metal support, a porous ceramic diffusion barrier and a dense Pd layer. The selective Pd layer was produced by physical vapor deposition (PVD) as an activation step and two additional methods: electroless plating (ELP) and electro plating (EP). The PVD/EP-membrane tubes made by PSE are unique in a way that they were produced with the well-known and industrially proven thin film production methods without using the laboratory ELP-technique applied by KIT.