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Fabrication & performance study of a palladium on alumina supported membrane reactor: Natural gas steam reforming, a case study

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ABSTRACT

In this work, a synthetic mixture of natural gas is considered in a steam reforming process for generating hydrogen by using a membrane reactor housing a composite membrane constituted of a Pd-layer (13 μm) supported on alumina. The Pd/Al₂O₃ membrane separates part of the produced hydrogen through its selective permeation, although it shows a relatively low H₂/N₂ ideal selectivity (>200 at 0.5 bar of trans-membrane pressure and T = 425 °C).

The steam reforming reaction is performed at 420 °C, by varying the gas hourly space velocity between 4400 h⁻¹ and 6900 h⁻¹ and by using two different mixtures containing some common impurities found within natural gas pipeline. Specifically, the effect of N₂ and CO₂ as impurities in the feed line is analyzed. The reaction pressure and steam-to-carbon ratio (S/C) are kept constant at 3.0 bar (abs.) and 3.5/1, respectively.

The best performance of the Pd-based membrane reactor is obtained at 420 °C, 3.0 bar and 100 mL/min of sweep-gas, yielding a methane conversion of 55% and hydrogen recovery >90%.

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Introduction

A possible use of hydrogen, without direct greenhouse gas (GHG) emissions, is as a feed for the readily available technology of proton exchange membrane fuel cell. Natural gas (NG) steam reforming represents the primary industrial process for generating hydrogen, which is largely carried out in

conventional fixed bed reactors (FBRs) and is responsible of a massive emission of GHGs [1]. Nevertheless, the high purity requirements for the produced hydrogen are achieved in successive stages, represented by water-gas shift (WGS) reactors (high temperature and low temperature WGS reactors) and further H₂ separation/purification equipments (pressure swing adsorption (PSA), preferential oxidation reactors (PrOx), etc.), Fig. 1.

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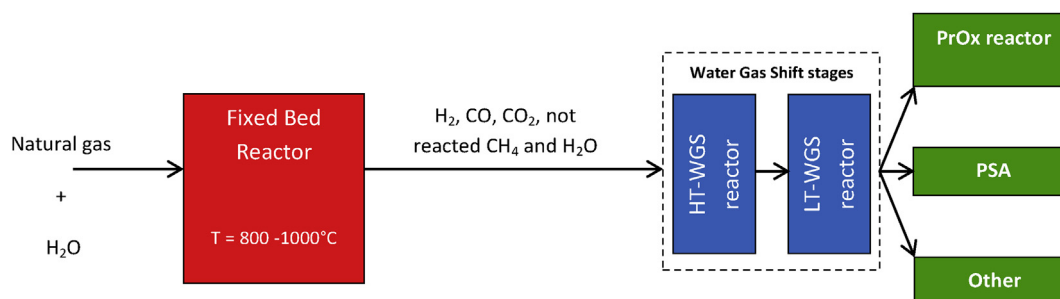


Fig. 1 – Scheme of the industrial hydrogen production process from natural gas steam reforming reaction.

In the last decade, a number of studies relating to steam reforming of NG and/or methane, being the main compound of the feed, analyzed the benefits of alternative solutions to the FBRs and, among them, the adoption of the membrane reactors (MRs) technology gained considerable attention [2–16]. In particular, Pd-based MRs can be useful for the simultaneous production and purification of high-grade hydrogen, without needing further separation/purification stages. Additionally, the Pd-based MRs work at milder operating conditions, both pressure and temperature, when compared to the FBRs. In recent years, Pd-based composite membranes, i.e. thin Pd or Pd/alloy layer supported on porous materials such as ceramics, stainless steel, or vycor glass have been considered due to their lower cost (thinner Pd-layers) and higher mechanical strength (porous support) compared to dense unsupported Pd-based membranes [10,17–20]. Among the different porous support, the ceramic ones show such benefits as high mechanical, chemical and thermal stability. Furthermore, compared to porous stainless steel, the ceramic supports make possible better performance in terms of H_2/N_2 ideal selectivity when used as a substrate for Pd-based composite membranes [21].

Several studies relating to the use of supported Pd-based membranes within steam methane reforming (SMR) reaction tests have been carried out at various temperatures, with most of them above 450 °C [2,3,5,9,22,23]. To our knowledge, only a few studies have dealt with experimental tests on SMR reaction at $T \leq 450$ °C. Kyriakides et al. performed SMR at 450 °C in a MR housing a Pd–Ru/alumina composite membrane with a deposited layer of ~ 5 μm and a Ni–Pt/CeZnLa based catalyst, reaching a methane conversion of around 40% at a reaction pressure of 10.0 bar [24]. Recently, Iulianelli et al. [18] studied SMR reaction in a MR allocating a porous stainless steel supported Pd–Au membrane (~ 7 μm of dense metallic layer) showing, at steady state condition, a H_2/N_2 ideal selectivity of around 500 at 420 °C and 0.5 bar of trans-membrane pressure. At this temperature, gas hourly space velocity (GHSV) = 4100 h^{-1} and 3.0 bar, the MR reached 40% methane conversion and 35% hydrogen recovery using a commercial Ni/Al₂O₃ catalyst, observing a severe coke formation due to the low temperature conditions. Finally, Anzelmo et al. [10] performed NG steam reforming at 400 °C in a MR allocating a highly H_2 perm-selective porous stainless steel supported Pd-based membrane (13 μm of Pd-layer). More than 80% of methane conversion was reached at 3.0 bar with a correspondent hydrogen recovery of 82%.

Therefore, the novelty of this work is to fabricate a composite membrane constituted of a dense Pd-layer supported on alumina and evaluate its performance within a MR for producing as much as pure hydrogen via steam reforming reaction of a synthetic mixture of NG at 420 °C. Moreover, two different mixtures are used for simulating a NG mixture; Mix 1 containing N₂ as impurity and Mix 2 containing both N₂ and CO₂. In particular, the addition of CO₂ was 3% of the total feed mixture, which is based on the natural gas pipeline standards within the USA [25].

Experimental details

Membrane preparation and membrane reactor module

Commonly, the deposition of a Pd and/or Pd-alloy layer onto porous substrates takes place via magnetron sputtering [26], spray pyrolysis [27], chemical vapor deposition [28,29], physical vapor deposition [30] and electroless plating (ELP) [31–33]. In this work, ELP technique has been used for preparing the composite membrane due to its important benefits in terms of uniformity of the thin palladium layer, simplicity of the required equipment and low cost.

The composite Pd-based membrane consists of ~ 13 μm Pd-layer deposited on a ceramic support, with a mean pore size of about 5 nm. The ceramic support was provided by Fraunhofer IKTS (Germany) and has a total length of 7.6 cm (active length of 6 cm) and an outer diameter of 1 cm.

This membrane was manufactured at Worcester Polytechnic Institute (USA) and its preparation was carried out by following these main steps: 1) support cleaning with distillate water, 2) support activation and 3) successive deposition of the Pd-layer by ELP. After each activation and deposition cycle, the membrane was placed in the oven at 140 °C to dry overnight. In total, the membrane was subjected to three cycles of activation and deposition and it showed a total active surface area of ~ 19 cm^2 . Fig. 2 shows the several steps of the fabrication process.

The membrane module used for housing the Pd/Al₂O₃ membrane was provided by CNR-ITM (Fig. 3a) consisting of a tubular stainless steel module having total length of 120 mm and an inner diameter of 15 mm. Graphite O-rings (99.5% C and 0.5% S), supplied by Gee Graphite Ltd., were placed at both membrane ends to prevent the permeate and retentate streams mixing with each other.

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