Hydrogen production via natural gas steam reforming in a Pd-Au membrane reactor. Comparison between methane and natural gas steam reforming reactions

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| ARTICLE INFO	ABSTRACT
	High-purity hydrogen to be fed directly to a PEMFC was produced by carrying out natural gas steam reforming under moderate operating conditions in a Pd-Au composite membrane reactor packed with a commercial Ni-based catalyst. The Pd-Au composite membrane with a thickness of approximately 12 μm was fabricated by using both electroless and electroplating techniques to deposit Pd and Au layers, respectively, over a porous stainless-steel support. After annealing, the membrane showed a hydrogen permeance of 1.30×10^{-3} mol/s-m²-Pa$^{0.5}$ at 450 °C, and near-infinite ideal selectivity of H2/Ar at pressures lower than 300 kPa and at temperatures lower than 400 °C. The natural gas reforming reaction was performed at 450 °C with a steam-to-methane ratio of 3.5 and gas hourly space velocity of 2600 h^{-1} at different operating pressures varying from 100 kPa to 300 kPa. As a comparison, the steam methane reforming reaction was also carried out at the same operating conditions. The natural gas reforming reaction showed better performance than the steam methane reforming reaction and reached > 80% conversion of the higher hydrocarbons and almost 65% of hydrogen recovery at 450 °C and 300 kPa. High-purity hydrogen was obtained in all the experimental tests. No coke formation was observed. Post-reaction analysis of the membrane is discussed via scanning electron microscope and energy-dispersive X-ray spectroscopy.

1. Introduction

Over the past decade, there has been an increase in the application of hydrogen as an energy vector due to its environmentally friendly quality and wide range of energy applications [1]. Currently, close to 50% of the hydrogen global demand is produced via steam reforming of natural gas [2], which is the most economic technology among all hydrogen production pathways [3]. Although natural gas (NG) consists mostly of methane, its composition can vary widely depending on the geologic reservoir from which it is recovered. Well location, geological conditions, and extraction method can dictate the level of impurities, e.g., water, nitrogen, hydrogen sulfide and higher-order hydrocarbons, contained within the natural gas. Once *raw* natural gas is processed (e.g., sulfur removal, etc.), it can enter the pipeline distribution system followed by consumption of the end-use product. The NG consumed in the U.S. has a standard heating value of approximately 1000 BTU/ft³ (1000 kJ/28 L) at STP [4]. Hence, given that the standardization is based on the heating value rather than the gas composition, a compositional range of gases, largely determined from a safety perspective by the Pipeline and Hazardous Materials Safety Administration sector of the U.S. Department of Transportation, can be found within NG [5]. The maximum compositional limit for various components of pipeline-quality NG [6–9] is shown in Table 1.

Currently, the conversion of NG to hydrogen takes place in a conventional reformer at harsh operating conditions. The general reaction describing NG steam reforming (SR) can be described as [10]:
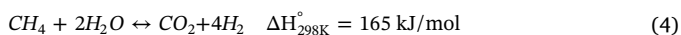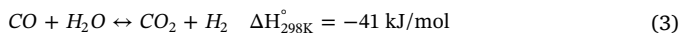
$$C_xH_y + xH_2O \leftrightarrow \left(x + \frac{y}{2}\right)H_2 + xCO \tag{1}$$
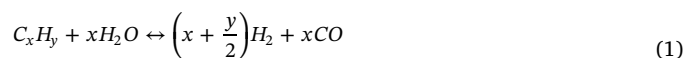
where x is the number of carbon atoms and y is the number of hydrogen atoms within the hydrocarbon feed. For example, if the feed is methane, as described previously, Eq. 1 reduces into Eq. (2). Furthermore, the three main reactions governing the steam methane reforming (SMR) process are [11]:
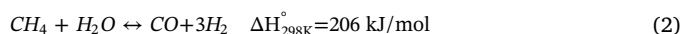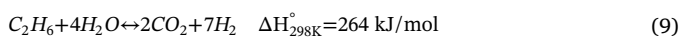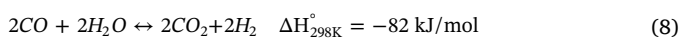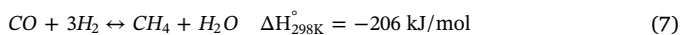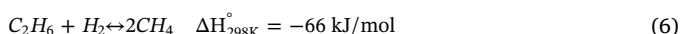
$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^{\circ}_{298K} = 206 \text{ kJ/mol} \tag{2}$$

Table 1
Maximum composition limits of various components for pipeline quality natural gas.

Component	Maximum [mol%]
Methane	> 96
Ethane	10
Propane	5
Butane	2
Nitrogen	4
Carbon Dioxide	4

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^{\circ}_{298K} = -41 \text{ kJ/mol} \tag{3}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H^{\circ}_{298K} = 165 \text{ kJ/mol} \tag{4}$$

However, NG contains several other hydrocarbons (HCs) as shown in Table 1, that react across the same catalytic bed, typically comprised of Ni, thereby leading to additional reactions [12]. Therefore, for SR of ethane, the following reactions are known to be prevalent [13]:
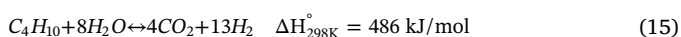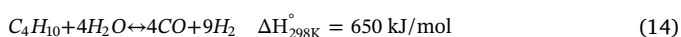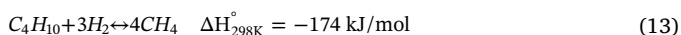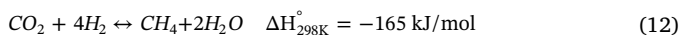
$$C_2H_6 + 2H_2O \leftrightarrow 2CO + 5H_2 \quad \Delta H^{\circ}_{298K} = 346 \text{ kJ/mol} \tag{5}$$

$$C_2H_6 + H_2 \leftrightarrow 2CH_4 \quad \Delta H^{\circ}_{298K} = -66 \text{ kJ/mol} \tag{6}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H^{\circ}_{298K} = -206 \text{ kJ/mol} \tag{7}$$

$$2CO + 2H_2O \leftrightarrow 2CO_2 + 2H_2 \quad \Delta H^{\circ}_{298K} = -82 \text{ kJ/mol} \tag{8}$$

$$C_2H_6 + 4H_2O \leftrightarrow 2CO_2 + 7H_2 \quad \Delta H^{\circ}_{298K} = 264 \text{ kJ/mol} \tag{9}$$
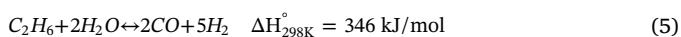
Similarly, the dominant pathways for SR of propane are [14]:

$$C_3H_8 + 3H_2O \leftrightarrow 3CO + 7H_2 \quad \Delta H^{\circ}_{298K} = 499 \text{ kJ/mol} \tag{10}$$

$$C_3H_8 + 6H_2O \leftrightarrow 3CO_2 + 10H_2 \quad \Delta H^{\circ}_{298K} = 375 \text{ kJ/mol} \tag{11}$$
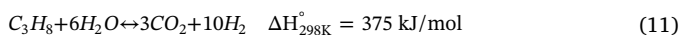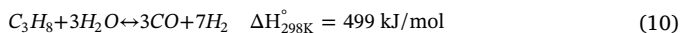
Also, the pathways for SR of butane [15] are:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H^{\circ}_{298K} = -165 \text{ kJ/mol} \tag{12}$$

$$C_4H_{10} + 3H_2 \leftrightarrow 4CH_4 \quad \Delta H^{\circ}_{298K} = -174 \text{ kJ/mol} \tag{13}$$

$$C_4H_{10} + 4H_2O \leftrightarrow 4CO + 9H_2 \quad \Delta H^{\circ}_{298K} = 650 \text{ kJ/mol} \tag{14}$$

$$C_4H_{10} + 8H_2O \leftrightarrow 4CO_2 + 13H_2 \quad \Delta H^{\circ}_{298K} = 486 \text{ kJ/mol} \tag{15}$$

Additionally, a complex network of side reactions can take place to form various HC species. Comprehensive literature studies relating to the industrial process of NG reforming are available in terms of catalyst deactivation, kinetics, energy evaluation, life cycle analysis, among other parameters [16–19].

The industrial reformed stream contains mainly H_2 and by-products such as CO_2 and CO. In order to obtain pure hydrogen, the industrial reformer is followed by water gas shift (WGS) reactors and equipment for hydrogen separation and purification. In the context of process intensification, the membrane reactor (MR) can be used to perform SR reactions and remove pure hydrogen within the same device. In particular, metallic MRs have been proven to efficiently produce hydrogen from SMR at lower temperatures and pressures than current industrial conditions [20–24].

Few studies exist in the literature dealing with hydrogen production in Pd and Pd-Ag MRs using *real* NG mixtures. For example, Shirasaki et al. produced pure hydrogen at a rate of 3.6 kg/h (40 m³/h) by using planar Pd-Ag membranes with a thickness of ∼ 20 μm and a NG mixture composed by 88.5% methane, 4.6% ethane, 5.4% propane, and 1.5% butane [25]. This study mainly focused on the overall principle of large-scale hydrogen production from reforming of NG via Pd-based MRs. The authors obtained an overall average energy efficiency of > 70% and a best value of 76.2% based on the HHV of pure hydrogen produced divided by the HHV of NG along with auxiliaries (i.e., air handling

equipment, heat needed for the reaction, cooling loads, NG compressor, etc.). Although the MR was operated for 3310 h and was subjected to 61 thermal cycles (from start up to shut down), it provided a hydrogen purity greater than 99.99% throughout the testing. In addition, the reformer system was optimized to realize a NG conversion of 83%, with the possibility of reaching 90% [26]. In another study [27], a mixture of CH_4 at > 90 mol.% and other HCs (C2-C4) were fed into a fluidized-bed membrane reformer (FBMR) obtaining a conversion of 58.6% based on the average CH_4 equivalent of all HC species at T = 600 °C and $p_{reaction}$ = 400 kPa. The 25-μm Pd-Ag$_{25}$ flat composite membrane deposited on porous stainless steel (PSS) used in the work produced a H_2 purity greater than 99.99% over a 395-h period. The same authors in another study illustrated a NG conversion of 81%, with a decreased of H_2 purity of 99.988% [28].

Although higher hydrocarbons are more reactive and enhance the overall H_2 production, they also increase the coke formation, which can rapidly deactivate the nickel catalyst, and decrease the membrane performance. Usually, an additional step called pre-reforming is added to the overall SMR process, which converts all the heavier hydrocarbons in CH_4, carbon oxides, H_2 and steam and it serves to avoid catalyst deactivation and to enhance heat recovery.

Therefore, the aim of this work is to use a thin Pd-Au membrane supported on PSS to perform the NG SR reaction and to evaluate how the heavier HCs and impurities, such as CO_2, present in NG may impact the Pd-Au MR performance in terms of conversion and hydrogen production. A comparison between SMR and NG SR reactions is also performed and evaluated. This paper will lay the foundation for a direct performance evaluation between different reactants, a first of its kind comparative analysis using MR technology.

2. Experimental details

2.1. Membrane fabrication and membrane reactor details

The composite Pd-Au/PSS membrane used in this work was fabricated at Worcester Polytechnic Institute's Center for Inorganic Membrane Studies. The commercial PSS support was purchased from Pall AccuSep, and it was already characterized by a deposited layer of zirconia on the outer surface. The outer diameter of the support was 1 cm and its total active length was 3.6 cm. The electroless plating was used to deposit a dense Pd layer by using a similar procedure to Ma et al. [29–31]. A thin gold layer was deposited on top of the palladium surface via conventional electroplating, which allows for obtaining films of desired thickness [32]. Notice that gold has been shown to enhance the properties of Pd-based membranes, such as permeance, stability and contaminant-recoverability [33], and therefore, it was used in this work. In addition, the optimum amount of gold is 5%, which has a negligible effect on the total cost of the membrane. Finally, to provide active sites on the asymmetric membrane, and to enhance the initial H_2 flux and decrease the overall time of annealing as shown within the literature [33], a pure Pd topmost layer was deposited.

The thickness of the membrane was estimated by gravimetric methods. Specifically, the final membrane was characterized by a Pd layer of approximately 12-μm thickness and a thin layer of 4.4 wt% Au, with a total active area of 11.3 cm². A photo showing the final membrane along with a schematic of the metallic layers on the PSS support is shown in Fig. 1.

One end of the membrane was welded to a 316-L nonporous-capped tube while the other end was welded to a nonporous tube. A commercial Ni-based catalyst supplied by Johnson Matthey Inc. was used. Before packing 3 g of catalyst in the annular region of the MR, it was crushed and sieved to an approximate particle size of 200–400 μm, in order to increase the available surface area for the reaction and to avoid pressure drop in the catalytic bed.

A cross-section of the MR system is shown in Fig. 2.