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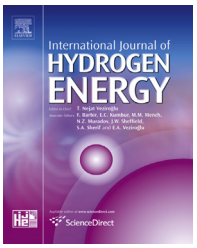

Syngas upgrading in a membrane reactor with thin Pd-alloy supported membrane

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ABSTRACT

In hydrogen production, the syngas streams produced by reformers and/or coal gasification plants contain a large amount of H_2 and CO in need of upgrading. To this purpose, reactors using Pd-based membranes have been widely studied as they allow separation and recovery of a pure hydrogen stream. However, the high cost of Pd-membranes is one of the main limitations for scaling up technology. Therefore, many researchers are now pursuing the possibility of using supported membranes with as thin as possible Pd-alloy layers.

In this work, the upgrading of a syngas stream is experimentally investigated in a water gas shift membrane reactor operated in a high temperature range with an ultra-thin supported membrane (3.6 micron-thick). The membrane permeance was measured before and after catalyst packing and also after reaction for 2100 h of operation in total.

Membrane reactor performance was evaluated as a function of operating conditions such as temperature, pressure, gas hourly space velocity, feed molar ratio, and sweep gas. A CO conversion significantly higher than the thermodynamics upper limit of a traditional reactor was achieved, even at high gas hourly space velocities and a 25% less reaction volume than that of a traditional reactor was enough to achieve a 90% equilibrium conversion.

Introduction

As indicated in the EU-White Paper [1] on renewable and alternative energy, and according to leading energy scenarios, the use of hydrogen as an energetic vector is expected to become more and more important. In July 2014, BP and GE announced plans to develop jointly up to 15 new hydrogen power plants to generate electricity over the coming decade [2]. The hydrogen required is planned to be derived from fossil

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fuels, including coal and natural gas and the plants will include carbon capture technologies reducing the CO_2 emissions by 90% [3]. If one considers that, at present, 96% of hydrogen is directly produced from fossil fuels and that 4% ca. is produced indirectly by using electricity generated through them [4], the need to find new efficient and competitive technologies able to maximize hydrogen production from fossil fuels while lowering emissions of CO_2 and other pollutants appears evident. Up to now, most H_2 is obtained industrially from natural gas via steam reforming, although other alternative sources (i.e., bio-alcohols steam reforming) have been attracting great attention owing to the use of biomass as a renewable source [5–8].

The stream produced by reformers and/or coal gasification plants contains around 50% molar of hydrogen (on a dry basis) and between 40 and 45% molar of CO, which is usually reduced in an upgrading stage producing more hydrogen at the same time, by water gas shift (WGS) reaction. The upgrading stage of traditional processes consists of a multi-stage CO-shift process based on two catalytic reactors: the first operates at high temperatures (about 350–400 °C) to take advantage of the faster reaction rates, whereas the other operates at low temperatures (around 220–300 °C) to refine the carbon monoxide conversion, thus allowing a lower final CO concentration (less than 1% molar) [9].

$$CO + H_2O = CO_2 + H_2 \quad \Delta H^0_{298} = 41 \text{ KJ mol}^{-1}$$

The H_2 rich stream coming out from the last reactor is fed to a pressure swing adsorption (PSA) unit for H_2 separation from other gases. Most often another reaction unit is added for oxidizing CO to CO_2, to meet the purity targets for fuel cells uses (CO concentration lower than 10–20 ppm).

Among the technologies for hydrogen production/purification, membrane reactors (MRs) have received increased interest, particularly in the case of Pd-based membranes owing to their infinite selectivity to hydrogen, which offers the possibility of recovering a pure hydrogen stream during the reaction, circumventing the need for any downstream separation step. The MR, in fact, combining the reaction and separation in the same unit, involves various synergistic benefits. As an example, for equilibrium-limited reactions (as for WGS), the continuous removal of a reactant from the reaction environment shifts the reaction towards the formation of products, making it possible to reach a higher conversion than that of more traditional reactors (the so-called "shift effect"). In addition, combining the reaction and the separation allows the elimination of various operation units, including not only the number of reactors and separators, but also pressure vessels, heat exchangers etc. Additionally, the reduction of the percentage of CO in the system reduces coking of metal catalysts surfaces, implying longer lifetime. This means an intensified process with a reduced plant size and a higher yield. In some cases, the interesting results achieved at laboratory level thanks to this effect have even led to several patents [10–15].

However, most the studies on WGS in MRs were carried out in low and medium temperature range (180–250 and 250–320 °C, respectively) by using CuO-based catalysts, owing to the thermodynamics constraints on the reaction [16–21]. Only few works in the literature explored the combination of a high temperature WGS catalyst with Pd-based membranes [19,22–28]. An interesting review on the recent advances of this technology for high temperature applications is proposed by Cornaglia et al. [29].

Rather than the thermodynamics limitations, fast kinetics and promoted permeation are the main advantages offered by the high temperature. However, a fundamental role is played by the characteristics of the membrane used in the reactor. In fact, until now one of the main hurdles limiting the large-scale development of these MRs is the high cost of Pd-based membranes, partly owing to the cost of palladium that could further increase if Pd membranes are exploited on a large industrial scale [30]. For this reason, great efforts were made to obtain thin Pd-layers on appropriate supports in order to maximize the permeate flux, minimize the support influence and reduce the cost related to Pd [31,32].

A recent review [33] reported how thin and stable membranes are nowadays produced with selectivities higher than 10,000 (the accepted target to produce ultra-pure hydrogen for fuel cell applications) and high fluxes. In comparison to pure Pd, it is well known that Pd–Ag alloy membranes have up to 70% higher H_2 permeability (Pd77Ag23) and are more resistant to hydrogen embrittlement (PdH α-β transition at low temperature) [34]. Electroless plating is a most commonly reported method on the preparation of thin Pd-based membranes particularly with respect to operational flexibility, simple equipment, cost performance and applicability to non-conductive materials of any shape [33].

Various papers in the open literature refer to thin Pd-alloy membranes used for hydrogen separation [35–45], whereas only few were used for reaction [23,46]. In this context, this work presents an analysis of the performance of an MR using an ultra-thin Pd-based membrane prepared by electroless plating along with an Fe–Cr-based commercial catalyst for the WGS reaction carried out at high temperature range (360–400 °C). CO conversion and hydrogen production, as well as reaction volume are analysed as functions of feed pressure, temperature, sweep factor, H_2O/CO feed molar ratio and GHSV for various configurations. In addition, the influence of catalyst presence and thermal cycles on membrane permeation properties are evaluated for the whole experimental campaign to estimate the membrane stability.

Materials and methods

Membrane preparation

An alumina tube 10/7 mm o.d./i.d. with pore size of 100 nm (provided by Rauschert Kloster Veilsdorf) was used as membrane support. As is known, porous support improves the mechanical strength of the membranes but it may impose resistance to hydrogen permeation; therefore, asymmetric supports with gradual decrease of pore size are usually used. For the preparation of thin Pd membranes (less than 5 μm) smooth and uniform pore size distribution is required; permeation through pores with less than 50 nm diameter follows the Knudsen mechanism; therefore, the permeation will increase with pressure but decrease with temperature.

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