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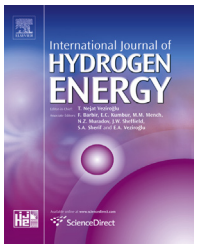

Development of thin Pd–Ag supported membranes for fluidized bed membrane reactors including WGS related gases

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ABSTRACT

This paper reports the preparation, characterization and stability tests of Pd-based thin membranes for fluidized bed membrane reactor applications. Various thin membranes have been prepared by simultaneous Pd–Ag electroless plating. A simple technique for sealing of the produced membranes is reported and discussed. The membranes have been characterized for single gas permeation, and afterwards used for permeation of mixtures of gases and under fluidization conditions. The membranes have shown very high permeation rates and perm-selectivity when used as permeators. When applied in fluidized bed reactors it has been found that the membranes are stable as long as no interaction between the fluidization catalyst and the membrane surface occurs. For some catalysts a strong chemical interaction between the catalyst and the membrane surface has been observed which caused a drastic decrease in the membrane flux.

Introduction

High purity hydrogen is required in many processes, such as semiconductor manufacturing, fuel cells applications, chemical industry, analytical instruments, computer and aerospace industries, recovery of radioisotopes of hydrogen in nuclear reactors [1]. On the other hand, hydrogen production and separation can be also exploited for pre-combustion (decarbonization) route for carbon capture and sequestration (CCS) from fossil-fuel fired power stations [2]. Most of the hydrogen (>80%) is currently produced by steam reforming of natural gas in large multi-tubular fixed-bed reactors. In small-scale applications, partial oxidation reactions and auto-thermal reforming (combination of partial oxidation (exothermic) and steam reforming (endothermic))

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are also considered. These reactions are (generally) equilibrium limited and produce a hydrogen-rich gas mixture containing carbon oxides and other by-products. The carbon monoxide can be converted to carbon dioxide producing more hydrogen via the Water Gas Shift (WGS) reaction where steam is introduced as reactant (Equation (1)). WGS is thermodynamically favored at low temperatures and kinetically favored at high temperatures. The traditional two-stage WGS process consists of a first reactor operated at 300–450 °C (to efficiently convert the biggest part of CO) and a second reactor that works at lower temperatures at 200–300 °C to convert the last part of CO.

$$CO + H_2O \leftrightarrow H_2 + CO \quad \Delta H = -41.1\ kJ/mol \tag{1}$$

During the last few years more attention has being paid on hydrogen perm-selective membrane reactors operated with commercial ferrochrome based catalysts which can integrate the WGS reaction and in-situ extraction of ultra-pure H_2 in one-stage and accordingly shift the equilibrium and thus intensify the process (improving yields and selectivities and reducing downstream separation costs, while also reducing the required reactor volume) [3]. New noble metal catalysts have been developed and have been tested in packed-bed membrane reactors. Results have shown that improving membrane characteristics enhances the reactor performance, but it would be more beneficial to develop a more active catalyst with higher activity to facilitate the use of thinner catalyst beds with a higher specific membrane area and lower concentration polarization across the catalyst bed. Most recently, fluidized bed membrane reactors have been introduced to overcome the mass transfer limitations prevailing in packed bed reactors because of their excellent gas–solid contact and heat and mass transfer characteristics [4,5]. However, these reactors have not been exploited yet for the WGS reaction.

Among the membranes for H_2 separation, the Pd-based membrane shows the highest permeability and exclusive selectivity for H_2 due to the unique permeation mechanism.

In order to achieve the hydrogen separation targets defined by the Department of Energy of the United States (DOE) [6], very thin Pd membranes (less that 5 μm) are required. In comparison to Pd, it is well known that Pd–Ag alloy membranes have higher H_2 permeability up to 70% ($Pd_{77}Ag_{23}$) and are stronger against hydrogen embrittlement (PdH α–β transition at low temperature) [1]. Common dense metal layer deposition technologies include physical vapor deposition (PVD, including magnetron sputtering, thermal evaporation or pulsed laser evaporation), chemical vapor deposition (CVD or MOCVD) and electroless plating (ELP) [7]. The electroless plating (ELP) method is the most used method for 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. Pacheco Tanaka et al. developed a method for the simultaneous plating of Pd–Ag with the desired composition of metals [8]. This was achieved by uniform deposition of nanoparticles of Pd nuclei on the surface of the substrate and careful control of the composition of the plating solution; various Pd–Ag ratios were prepared by this method and the H_2 permeation properties observed were studied and related to the embrittlement phenomenon [9]; recently, the method was improved and a synchronized deposition of Pd/Ag was obtained [10].

Thin Pd-based membranes are generally supported on porous substrates including stainless steel and ceramic materials of planar or tubular configuration [2]. Porous ceramics are the most common substrate material, owing to their excellent chemical stability. However, Pd-based membranes deposited on a ceramic support showed gas leak problems after some thermal cycles, due to the detachment of the Pd membrane layer that is deposited on the glass used to join ceramic dense and porous parts. The presence of leaks causes a decline in the hydrogen selectivity. The most promising sealing approach is based on using graphite. In some works, graphite gaskets were applied onto the faces of the two ends of the membrane tube [11,12], but the sealing is poorly gas-tight and the membrane can be easily broken by mechanical stress induced by the sealing compression. The membrane tube can be also sealed to a metal tube with connectors. The design of the connector is critical, because it should limit the pressing force and avoid damage to the thin membrane layer during operation [13,14].

In this paper we will present results on Pd–Ag alloy supported on alumina tubes. The Pd–Ag membranes were prepared by simultaneous electroless plating. A membrane sealing procedure based on graphite ferrules and stainless steel connector was optimized to be able to connect the ceramic supported Pd-based membrane to dense metal tubes. These sealed membranes showed high hydrogen permeance and selectivity, in the order of the targets for DOE 2015. In addition, the resistance of the membranes to catalyst fluidization in novel fluidized bed WGS membrane reactors is investigated and discussed.

Experimental

Membrane preparation

Tubular alumina supports with an outside pore size of 100 nm were provided by Rauschert Kloster Veilsdorf. The supports have an external diameter of 10.0–10.5 mm and an internal diameter of 7 mm. For proper handling during membrane preparation, the alumina porous tubes were cut and connected to dense alumina tubes (provided by OMEGA with 6 mm OD and 4 mm I.D.), one end was closed, using an enameled glass (ASF1761, Asahi Glass Co., Ltd.) as shown in Fig. 1. The glass was applied in the junction point between the porous and dense support and cures at 1000 °C in air for 30 min (heating rates of 4 °C/min from room temperature to 200 °C and then of 12 °C/min to 1000 °C).

Pd–Ag thin layers were deposited on the alumina tubes by using a simultaneous (Pd and Ag) electroless plating technique. Firstly, the surface of the alumina tube was activated by seeding it with Pd nuclei prior to electroless plating following the procedure reported by Pacheco et al. [8]. The surface completely turned black due to uniform covering of palladium nuclei. By this procedure, a large number of fine palladium particles were deposited on the surface.