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Laser synthesis of palladium–alumina composite membranes for production of high purity hydrogen from gasification

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Abstract

This paper describes a special method of laser-based deposition to synthesize palladium–ceramic composite membranes. Thin film Pd was deposited on a ceramic substrate by Nd-YAG laser irradiation of coating precursor $PdCl_2$ on γ-alumina substrate. The parameters of the laser processing technique were optimized to synthesize metal–ceramic composite membranes. The physical and chemical characteristics of Pd coated γ-alumina membranes were studied and compared with various other alumina membranes referenced in the literature. Hydrogen permeation experiments were performed in a $CO + CO_2 + CH_4 + H_2$ environment under typical catalytic steam gasifier exit conditions. The Pd–ceramic composite showed good mechanical and thermal stability and resulted in a hydrogen permeability flux of about 0.061 mol/m^2 s. The activation energy of the Pd membrane was found to be 5.39 kJ/mol in a temperature range of 900–1300 °F.

Keywords: Palladium membranes; Hydrogen permeation; Ceramic membranes; Laser deposition; Inorganic membranes; Catalytic steam gasification

1. Introduction

The demand for hydrogen has increased rapidly in recent years because of steady depletion of fossil fuel reserves and greenhouse effects caused by the combustion of these fuels. Hydrogen is important raw material for chemical industries and it is an alternative clean energy source to replace fossil fuels. Production of hydrogen from gasification has achieved increasing importance in recent years. However, the production of hydrogen and the other desirable gases from separate steps of gasification and gas separation are limited by the inherent thermodynamic equilibrium established at the given conditions. For several reversible reactions in gasification, preferential removal of one or more of the products during reaction will cause a shift in equilibrium, thereby overcoming possible thermodynamic limitation and pushing the reaction in the desired direction. High temperature membrane can bring about such selective removal of species during reaction, and therefore, reactor incorporating such membrane can be used to increase the reaction yields of desirable products. It is claimed that reactors incorporating such membranes to perform in situ separation would offer several advantages over conventional fixed bed reactors without built-in membranes in the areas of higher energy efficiency, lower capital and operating costs, compact modular construction, low maintenance cost and ease of scale up.

2. Literature review

Combining the chemical reaction and separation steps in a single processing vessel has been investigated in several studies. Examples include the dehydrogenation of ethane [1], cyclohexane [2] and ethylbenzene [3]; the hydrogenation of acetylene [4]. Uemiya et al. [5] studied the water-gas shift reaction using a palladium membrane reactor in which the product hydrogen permeated the membrane to provide CO conversions in excess of those associated with the ‘‘normal’’ equilibrium conversion. H_2S decomposition studies were conducted in a porous-glass membrane reactor by Kamayema et al. [6,7] who succeeded in selective separation of H_2 from the reacting mixture and reported conversions twice as high as

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possible from thermodynamic equilibrium. The dehydrogenation of cyclohexane in reactors using platinum impregnated vycor [8], palladium (tube) [9] and porous glass [10] membranes resulted in conversions 2.5–5 times higher than equilibrium conversion. The dehydrogenation of methanol and *n*-butane was studied by Zaspalis et al. [11] in alumina membrane reactors and about 50% increase in conversions were obtained in the membrane mode of operation as compared to the fixed-bed mode of operation without the membrane.

Membrane-based separation processes are today finding widespread and ever increasing use in the petrochemical, food and pharmaceutical industries, in biotechnology, and in a variety of environmental applications, including the treatment of contaminated air and water streams [12]. The most direct advantage of a membrane separation process, over more conventional separation counterparts such as adsorption, absorption, distillation, etc., results in energy saving, and in the reduction of the required initial capital investment.

Membrane technology plays a very important role in hydrogen separation. Since the introduction of polysulfone fiber membranes, used in applications like the recovery of H_2 from ammonia purge gas and extraction of H_2 from petroleum cracking streams [13], there exists a considerable interest in the development of high-performance membranes for hydrogen-separation. Such membranes have the potential for profound improvements in efficiency for separation and purification of hydrogen in applications ranging from gasification to fuels refining. For example, substantial advantages can be gained in operating the water-gas shift reaction at very high temperatures provided that the low equilibrium conversion of carbon monoxide can be enhanced by removing a hydrogen permeate stream through use of a membrane reactor [9,14,15]. However, one particularly significant technical challenge is the development of hydrogen-separation membranes that can withstand severe operating conditions of temperatures up to 1300 °F, and hydrogen containing gas pressures up to 300 psi. These conditions are typical of catalytic steam gasification process.

For economic production of high purity hydrogen from gasification, an appropriate inorganic membrane should be capable for in situ use in separation of hydrogen at elevated temperature without reducing the feed stream temperature. The key factor is the availability of a membrane with adequate hydrogen selectivity and good thermal and mechanical stability. Pd-based composite membranes are expected to possess high thermal and mechanical stability and have sufficient hydrogen permeability and 100% hydrogen selectivity due to the unique property of hydrogen solubility in palladium and the solution–diffusion mechanism for hydrogen permeation through palladium [16]. Consequently, palladium-based membranes have received considerable attention for high temperature reaction and separation applications. The hydrogen permeability of palladium membranes is inversely proportional to the membrane thickness while the hydrogen selectivity is highly dependent on obtaining a dense structure in a thin palladium film. Therefore, a viable palladium membrane for high temperature reaction and separation should be a thin, defect-free, composite membrane.

Palladium is an attractive membrane material due to its ability to readily dissociate molecular hydrogen at its surface. Although some other metals, such as zirconium, niobium, tantalum and vanadium, exhibit significantly higher bulk hydrogen permeability, these metals form oxide layers by surface reaction limiting the hydrogen flux. Hydrogen embrittlement of these metals is also a reason for their less use for hydrogen separation. As a result, the direct replacement of palladium by cheaper refractory metals is sought for [17]. Since palladium is a precious metal, its efficient economic use for industrial applications makes it necessary to reduce the material costs by decreasing the thickness of palladium films. Meanwhile, the reduced thickness would result in higher hydrogen flux without compromising selectivity for hydrogen over other gases. The most significant improvement would be the development of new multilayer membranes consisting of at least two layers. An ultra thin palladium layer combined with a porous ceramic, where the microporous base provides the necessary mechanical support to the thin metallic layer.

Dense inorganic membranes consist of solid layers of metals, such as Pd, Pt, Pd/Ag alloys or solid oxides (such as ionic conductors). In order to increase the permeability by reducing the critical membrane thickness, the membranes are applied in the form of multi-layers. The thin dense inorganic membranes usually consist of dense top layers supported on porous ceramic base material. The multi-layer membranes generally have different morphologies with a gradual variation in the pore size of each layer so that good continuity and adhesion between layered can be achieved. The pore size of these membranes depends on the particle size and the methods by which they are prepared. Ceramic membranes are asymmetric layers structures composed of a separation layer, which fulfills the actual membrane function, and a ceramic support structure comprising of one to five layers [1,18]. The support structure which serves as a substrate is needed for general mechanical stability and must have larger pores than the separation layer to reduce the resistance to the desired species flux.

3. Preparation of palladium-based membranes

Membranes or metallic thin films may be prepared by a variety of methods, the choice of which depends on such factors as the nature of metal itself, the manufacturing facilities available on site, required thickness, surface area, geometrical form, purity, cleanliness, etc. Shu et al. [19] have provided a good review of the candidate methods such as alloy casting and rolling, physical vapor deposition (PVD), chemical vapor deposition (CVD), electroplating and electro less plating. From their review, they concluded that the preparation of the membrane to be applied in a particular application must be considered as an original problem of material design, and may therefore benefit from the wealth of original ideas and techniques developed currently in this field.

Laser induced surface improvement (LISI) is a process where a thin layer at the surface and/or subsurface region of a metal is melted by a laser beam with the simultaneous addition of precursor consisting of water soluble binder/vehicle and