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Chromium oxide intermetallic diffusion barrier for palladium membrane supported on porous stainless steel

Sutheerawat Samingprai[a], Supawan Tantayanon[b,c,*], Yi Hua Ma[d]

[a] Graduate Program of Petrochemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[b] Green Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[c] National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand
[d] Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609, USA

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ABSTRACT

Dense palladium membrane on oxidized porous stainless steel (oxPSS) tube was prepared. Its hydrogen permeance was observed to decline at the temperature higher than 400 °C. SEM–EDX analysis of the cross-section of the annealed tube at 500 °C indicated the occurrence of the intermetallic diffusion. The heat treatment study of the palladium membrane on oxPSS disks in hydrogen atmosphere at various temperatures was essentially carried out. Their SEM–EDX analysis results confirmed that the *in situ* metal oxide barrier could not inhibit the intermetallic diffusion in hydrogen atmosphere. The chromium oxide layers at different thicknesses were then developed on oxPSS disks before palladium plating by controlled chromium elctrodeposition followed by oxidation in air at 700 °C. The similar heat treatment study and SEM–EDX analysis of these disks revealed that the presence of chromium oxide layer could suppress the intermetallic diffusion. Then, the dense palladium membrane tube with chromium oxide layer was prepared and its heat treatment in hydrogen atmosphere was studied. The result showed the steady increase in hydrogen permeance with increasing temperature.

1. Introduction

Hydrogen has long been used in several industrial applications including food, pharmaceuticals, chemical processing, electronics, metal production and fabrication, and petroleum recovery and refinery. Currently it has been of great interest as a clean alternative energy. Steam reforming of hydrocarbons is the major source of hydrogen production. Many reports on methane steam reforming using the catalytic palladium membrane reactor were published [1–6]. A few reports on methane dry reforming in the catalytic palladium membrane reactor were recently published as well [7–9]. Although the process was not optimized, the feasibility of achieving the enhancement of the CH_4 conversion and CO and H_2 selectivity beyond the limits stipulated by thermodynamic equilibrium during reforming of methane to synthesis gas was convincingly demonstrated by the use of a palladium membrane reactor comparing to a conventional reactor as reported by Galuszka et al. [7]. Among several types of membranes [10–14], the palladium and palladium alloy membranes were tested to have high selectivity [15–17]. Although palladium supported on porous stainless steel had several advantages comparing to other supported materials, its use at high temperature would cause the long-term stability problem due to the intermetallic diffusion of the metal elements from the support into palladium layer.

Accordingly, much attention had been paid on preventing the intermetallic diffusion by creating an additional layer between the stainless steel support and palladium layer. These include tungsten and a tantalum oxide layer [18], aluminium oxide [19], zirconia and titania [20], zeolite [21] and tungsten oxide [22]. Silica [23] was also used as a diffusion barrier between the palladium–copper active layer and nickel–porous stainless steel composite membranes.

In 1998, Ma and his co-workers had introduced an oxide-layer diffusion barrier by controlled *in situ* oxidation of the porous stainless steel supports prior to palladium and palladium/silver metal deposition [24–28]. They also reported that the oxidation had little effect on the mean pore size of the porous stainless steel indicating that oxidation did not constrict the internal pore system even at 800 °C [27]. They further explained that the oxide layers formed at temperatures equal or higher than 500 °C was effective in terms of preventing intermetallic diffusion on hydrogen permeance. They also showed that the structure of the oxide layer formed at 600 °C in air was similar to the one formed at 800 °C, which composed of an iron oxide rich layer on top of a chromium oxide layer [26]. However, the suitable material as the intermetallic diffu-

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[*] Corresponding author at: Green Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand. Tel.: +66 2 218 7641; fax: +66 2 218 7598.
E-mail address: supawan.t@chula.ac.th (S. Tantayanon).

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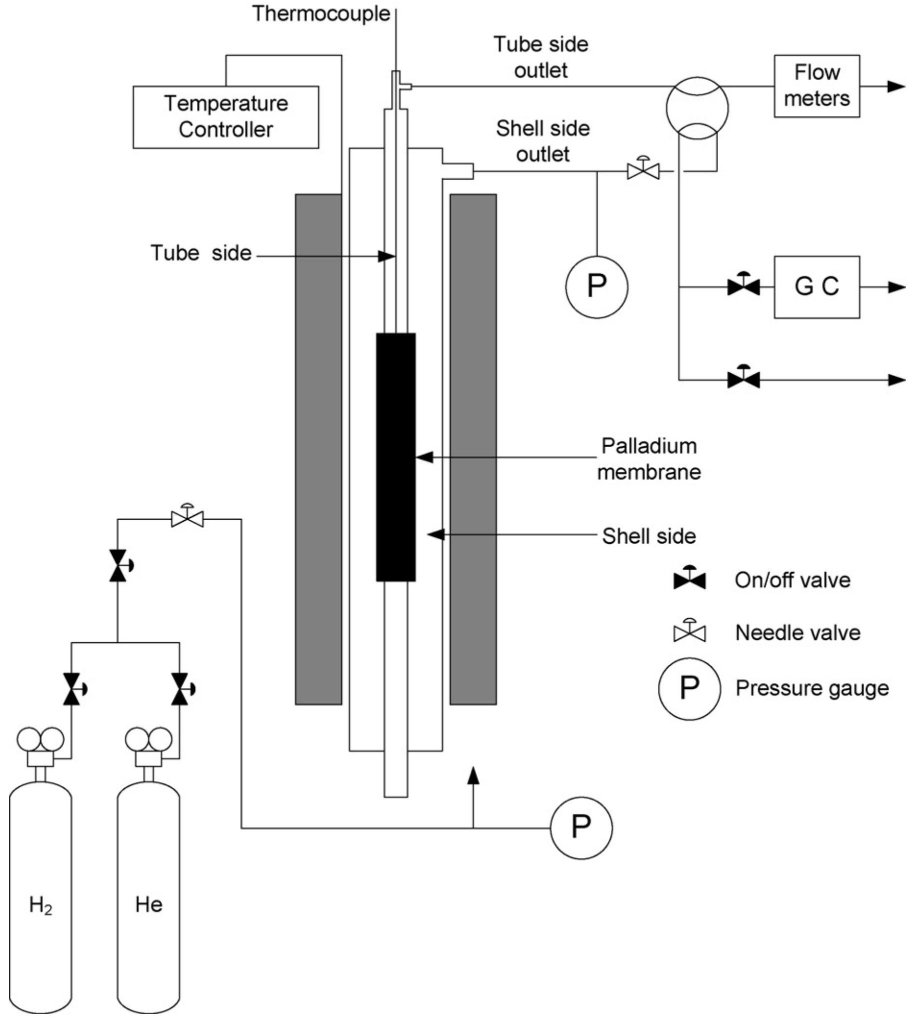

Fig. 1. Experimental setup for permeation measurement.

sion barrier should at least have the Tamman temperature higher than palladium (640 °C or 913 K) and stainless steel (550–560 °C or 823–833 K), as the rate of diffusion of metal elements at the interface between two metallic layers would become greatest when they were at or above their Tamman temperature [24]. Therefore, chromium oxide, with Tamman temperature of 1081 °C (1354 K), can be one of the potential candidates. As no literature reports on using chromium oxide as the intermetallic diffusion barrier, it is interesting to investigate its performance.

In this study, the incremental formation of chromium oxide layer on top of the *in situ* mixed oxides on porous stainless steel was described and its performance as an intermetallic diffusion barrier between palladium membrane and porous stainless steel was discussed.

2. Experimental

2.1. Palladium membrane preparation

A porous 316L stainless steel (PSS) tube, welded to non-porous stainless steel tube at both ends, was purchased from Mott Metallurgical Corporation (Farmington, CT). It had 9 mm in outer diameter, 70 mm long, 1 mm wall thickness, 0.1 μm average pore size and 17% porosity. The PSS disks were prepared by cutting a 1 mm thick media-grade 0.1 μm 316L PSS sheet into 1 cm^2 pieces and then a small hole with 1 mm diameter was drilled at one corner of the disk for hanging during metal deposition. All PSS supports were cleaned before activation and metal deposition, with the alkaline solution containing 5 ml/l of a household detergent. PSS supports were then thoroughly washed with deionized water (DI water) until the rinsing water had pH 7 and finally immersed in iso-propanol. All cleaning steps were carried out in ultrasonic bath at 60 °C. The supports were dried at 120 °C for 4 h. The cleaned PSS tubes and disks were oxidized at 450 °C with heating rate 4 °C/min in air in the muffle furnace. The weight of each oxidized PSS (oxPSS) support was recorded. Prior to palladium plating, the surface of oxPSS supports was activated by the consecutive immersion in $SnCl_2$ (0.1 g/l in 0.01 M HCl), $PdCl_2$ (0.1 g/l in 0.01 M HCl) with intermediate rinsing in DI water between both solutions. Then the activated PSS supports were rinsed with 0.01 M HCl. A two-step immersion sequence in $SnCl_2$ and $PdCl_2$ solution was generally repeated 3 times. A perfectly activated layer had a dark-brown color and smooth surface. Then the activated supports were deposited with palladium using the typical palladium plating solution composed of 4.0 g/l of $Pd(NH_3)_4Cl_2{\cdot}H_2O$, 198 ml/l of 28% NH_4OH, 40.1 g/l of Na_2EDTA, and 5.6–7.6 ml/l of 1 M N_2H_4 at 60 °C for 90 min. It was then cleaned with the warm DI water and let it at room temperature. Plating and cleaning were repeated for 3 times more. Finally, they were dried at 120 °C for 4 h. In case of the plated tube, it was subjected to the helium permeation flux measurement. If it was not dense, it would be submitted to another plating cycle. The palladium layer thickness