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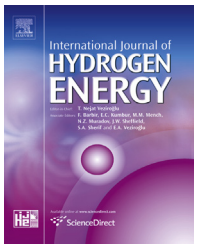

Preparation of palladium membrane on Pd/silicalite-1 zeolite particles modified macroporous alumina substrate for hydrogen separation

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ABSTRACT

A palladium composite membrane was successfully fabricated by electroless plating on a macroporous alumina tube. Pd/silicalite-1 zeolite particles were employed to reduce the pore size of the alumina support and improve its surface roughness. Moreover, the Pd^0 existed in the Sil-1 particle can avoid the time consuming sensitization and activation steps for palladium seeding. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS) and X-ray diffraction (XRD) analysis were conducted for analyzing the detailed microstructure of the palladium composite membrane. The hydrogen permeation performance of the resulting palladium membrane was investigated at temperatures of 623 K, 673 K, 723 K and 773 K. The hydrogen permeance of 1.95×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with an H_2/N_2 ideal selectivity of 1165 for the palladium membrane was obtained at 773 K. Furthermore, the resulting palladium membrane was stable for a long-term operation of 15 days at 673 K.

Introduction

Hydrogen has recently received much attention as a clean energy carrier. It is widely applied in various process sectors such as fuel cell and petroleum refining. The demand for the highly pure hydrogen has been increasing significantly. Therefore, the technology of hydrogen separation and purification is the key issue and many attempts have been made to produce pure hydrogen. Intense research efforts have been performed on the development of membranes for the production of hydrogen. Palladium-based membranes are very good candidates because of their good thermal stability, high permeation performance and unique selectivity for hydrogen [1–7]. The membrane cost, hydrogen permeation flux and permselectivity are considered as

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important factors for preparation of a palladium-based membrane. Numerous works have been devoted to the deposition of thin palladium films on various porous supports, such as porous glass [8,9], porous stainless steel [10,11] and porous ceramic [12–14], in order to make the palladium membrane more economically feasible for the separation and purification of hydrogen.

Surface topology of support is a key factor for preparing thin and dense palladium membrane [15,16]. Mardilovich and co-workers confirmed that the larger pore size of the support, the thicker of the palladium film is required to obtain dense membrane [17]. A proper solution is to modify the coarse surface of the porous substrates by some intermediate materials, including WO_3 [18], Al_2O_3 [19,20], ZrO_2 [21], CeO_2 [22], NaA zeolite [23] and pencil power [13]. The intermediate layer not only improved the pore size of the substrate and its surface roughness, but also behaved as a diffusion barrier to protect the membrane from the support contaminants. However, most of these intermediate materials are non-conductive. Therefore, electroless plating technique is a preferred technique for depositing palladium membranes on the surface of the non-conductive materials. During the process of electroless plating, the pre-seeding of the palladium nuclei as catalyst has to be carried out to make the palladium deposited. The conventional pre-seeding method used to activate the substrate is time-consuming, such as $SnCl_2/PdCl_2$ process. Although this activation is effective to deposit the palladium nuclei on the substrate, the tin contamination for the palladium membrane [24] and the generated waste liquid would be problematic. To investigate the significance of modifying the coarse surface of the porous substrate and seeding the Pd^0 nuclei on the support simultaneously, several works have been made. The studies carried out by Zhao et al. [25], Pan et al. [26] and Zhang et al. [27] claimed that thin palladium membranes were successfully deposited on porous alumina supports by a modified electroless plating procedure, which included seeding Pd^0 nuclei on the substrate by a sol–gel process of a Pd(II)-modified boehmite sol. Tong et al. [28] modified a macroporous stainless steel tube with Pd/aluminum hydroxide gel before deposition of the palladium membrane.

In this work, we propose a modification procedure for macroporous alumina substrates by Pd/silicalite-1 (Pd/Sil-1) zeolite particles and the subsequent eletroless plating of a palladium membrane. The microstructure of the resulting palladium membrane was characterized comprehensively by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). The permeation performance of the membrane at temperature range of 623 K~773 K was also investigated.

Experimental

Materials

The palladium membrane was deposited on a porous alumina tube supported by Foshan Ceramics Research Institute of China. The α-Al_2O_3 tube has a 75 mm length with nominal pore diameter of 3 μm and a porosity of about 40%. The inner and outer diameters of the tube substrate are 9 and 13 mm, respectively. The chemical used for synthesis of silicalite-1 zeolite particles included tetraethyl orthosilicate (TEOS) from Tianjin Kermel Chemical Reagent Co. Ltd. The tetrapropyl ammonium hydroxide (TPAOH, 20 wt.%) was prepared in the laboratory. The reagents for preparation palladium membrane including hydrazine (N_2H_4), Na_2EDTA and NH_4OH were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. The palladium chloride ($PdCl_2$) was supported by Shanghai Jiuling Chemical Co. Ltd.

Fabrication of palladium membrane

The preparation procedure of the palladium membrane is illustrated in Fig. 1 and involves: (1) coating of Sil-1 zeolite particles containing Pd (II) on the support surface; (2) reduction of Pd(II) to Pd^0 in Sil-1 zeolite particles by H_2 treatment; (3) formation of palladium film on the Pd/Sil-1 zeolite modified layer by electroless plating.

The Sil-1 zeolite particles were synthesized from a clear synthesis solution of 40 SiO_2: 5 $TPAO_2$: 2700H_2O at 373 K for 16 h according to the synthesis procedure proposed by Wong et al. [29] and Zhang et al. [30]. Thereafter, the fresh alumina tube was dip-coated for 10 s in a water Sil-1 solution which was composed of 2 wt. % Sil-1 zeolite particles (150 nm diameter), 0.8 wt.% $PdCl_2$ and 20 wt.% poly(vinyl) alcohol (PVA, MW = 1750 g mol^{-1}). The dip-coated tube was dried overnight in humid air (100% R.H.) to prevent crack-formation and delamination of the seed layer. The tube was calcined in air at 823 K for 6 h to remove the organic template and PVA binders.

The modified tube was activated in flowing H_2 at 623 K for 3 h to convert Pd(II) to Pd^0 nuclei. Followed the surface activation step, a dense palladium layer would be deposited on the outside surface of the seeded substrate by electroless plating. The plating solution [31] containing 3.5 g L^{-1} $PdCl_2$, 30 g L^{-1} Na_2EDTA, 101 ml L^{-1} NH_4OH (15 M) and 16 ml L^{-1} N_2H_4 (1 M) was kept at 318 K with a water jacket.

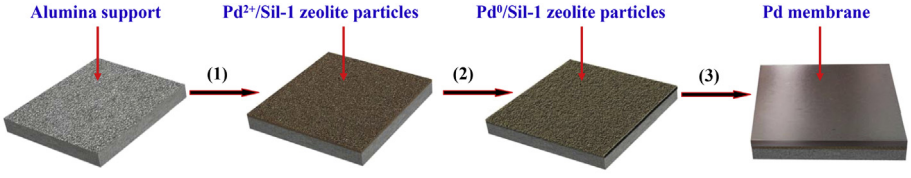

Fig. 1 – Fabrication scheme for palladium membranes:(1) coating of Pd^{2+}/Sil-1 zeolite particles on support; (2) conversion of Pd^{2+}/Sil-1 to Pd^0/Sil-1 by H_2 treatment; (3) deposition of palladium membrane by electroless plating.