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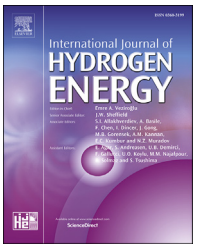

Deposition of TS-1 zeolite film on palladium membrane for enhancement of membrane stability

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ABSTRACT

A thin TS-1 zeolite film was successfully fabricated on palladium membrane using an assembly method combined with secondary growth technique. The preparation of TS-1-Pd composite membrane involved three stages: (1) deposition of palladium layer on porous alumina support through electroless plating; (2) assembly of silicalite-1 zeolite seeds on the palladium layer; (3) growth of TS-1 layer from the zeolite seeds over the top surface of the palladium layer using hydrothermal synthesis method. The detailed microstructure of the TS-1-Pd composite membrane was examined by SEM, EDX, XRD, FT-IR and UV–vis. This architecture allows the composite membrane to remain stable for 10 days of hydrogen permeation tests at 773 K and tolerate 30 cycles in gas exchanging tests, even for 5 days of hydrogen permeation tests at 423 K. Furthermore, the presence of a TS-1 zeolite film on palladium membrane effectively protected the palladium membrane from the contamination from the hydrocarbon, therefore greatly enhanced its operation stability.

Introduction

Hydrogen as a clean energy carrier has drawn much attention in the last decades [1–6]. For production of hydrogen, a variety of techniques have been developed, such as steam reforming of hydrocarbons, partial oxidation of fossil fuels, electrolysis of water, etc. However, hydrogen is not the only product from above mentioned methods. Therefore, obtaining highly pure hydrogen from the gas mixtures is the key point. Membrane technologies are expected to play a key role in separation and purification of hydrogen. Among various H_2-permeable membranes [7], palladium and palladium alloy membranes seems to be excellent candidates for applications in hydrogen separation and purification [8–14], fuel cells [15,16], steam reforming [17–19] and H_2-related reactions [20–22] due to their excellent hydrogen permselectivity.

Based on the configuration, palladium-based membranes can be classified as two main types, palladium foil [23] and supported palladium membrane [24–31]. Compared to palladium foil, the supported palladium membrane has attracted intense interest owing to its low cost, excellent H_2 permeability and high physical strength. Despite extensive contributions which have been made on the preparation of supported palladium membranes, the membrane stability is

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still an obstacle for their applications in industries [32–35]. For instance, most studies focused on the preparation of palladium-based membrane on the outer surface of porous support [36–40]. Under such way, the palladium membranes can be easily polluted and scratched during the operation, resulting in a decrease of their H_2 permeation performance and stability, even failure.

On the other hand, palladium membranes are often exploited for dehydrogenation process of hydrocarbons, such as dehydrogenation of propane to propylene [41] and dehydrogenation of ethylbenzene to styrene [42,43]. By combining separation and catalytic functionalities in a single membrane reactor, instantaneous removal of hydrogen in the reaction zone by permeation through a membrane can increase the conversion. However, degradation of palladium membrane is often observed when they were applied to separate hydrogen from those carbon-containing gas mixtures. During the separation process of hydrogen, the palladium layer directly exposed to the feeding gas was prone to be contaminated and poisoned by carbon, resulting in a loss of hydrogen permeability [44,45].

Recently, a novel strategy to enhance the stability of palladium membrane has been reported, in which a zeolite film as a protective layer was deposited on the surface of palladium membrane. This sandwich-like structure significantly improved the membrane stability. Abate et al. [46] reported that a TS-1 zeolite film was fabricated on the palladium membrane by secondary growth technique, including seeding of palladium membrane with TS-1 nanocrystals followed by hydrothermal synthesis. During the seeding process, polymers have to be used to increase the adhesion between TS-1 particles and the palladium membrane. Yu et al. [47] used the dilute acid to pre-treat palladium membrane to form the imperfections of palladium membrane. This morphology will improve the adhesion of zeolite film on the palladium membrane. Evidently, fabricating a continuous and compact zeolite film on a palladium membrane is quite challenging, owing to their different chemical characteristics.

This paper presents a novel method to fabricate a TS-1 zeolite film on the palladium membrane using an assembly method combined with secondary growth technique to enhance the membrane stability. The microstructure and morphology of the TS-1-Pd composite membrane were characterized by SEM, EDX, XRD, FT-IR and UV–vis. The membrane stability was evaluated by long-term operation test, gas exchange cycling test. Moreover, the effect of propylene on hydrogen permeation properties of the TS-1-Pd composite membrane was also investigated.

Experimental

Materials

N_2H_4, Na_2EDTA, $SnCl_2$, HCl, NH_4OH, and TEOS, which were used for synthesis of palladium membrane and TS-1 zeolite film, were purchased from Tianjin Kermel Chemical Reagent Co. Ltd. The tetrapropyl ammonium hydroxide (TPAOH, 20 wt%) was prepared in the laboratory. The $PdCl_2$ was provided by Shanghai Jiuling Chemical Co. Ltd. A porous alumina tube (O.D. 13 mm, I.D. 9 mm, length 75 mm, nominal pore diameter 200 nm) was provided by Foshan Ceramics Research Institute of China.

Fabrication of TS-1-Pd composite membrane

Fabrication of palladium membrane

The palladium membrane was fabricated on the porous alumina support by electroless plating. Prior to plating, the substrate was activated by a $SnCl_2/PdCl_2$ method at room temperature. The activation process was composed of a two-step immersion sequence in an acidic $SnCl_2$ solution (2 g/L), followed by an acidic $PdCl_2$ solution (0.2 g/L). Then the palladium membrane was prepared by electroless plating at 318 K using the plating solution [48] containing $PdCl_2$ (3.5 g L^{-1}), Na_2EDTA(30 g L^{-1}), NH_4OH (15 M, 101 ml L^{-1}) and N_2H_4 (1 M, 16 ml L^{-1}).

Assembly of silicalite-1 (Sil-1) zeolite seeds on palladium membrane

The resulted palladium membrane was functionalized with 3-aminopropyltrimethoxysilane (APTMS). During this process, the palladium membrane was placed in APTMS solution of ethyl alcohol (1:40 v/v) in a sealed autoclave and was heated at 373 K for 4 h. The unreacted organic linkers were washed away from the surface palladium membrane with ethanol. Subsequently, the APTMS-treated palladium membrane was immersed in an autoclave containing 0.08 wt% silicalite-1(Sil-1) zeolite suspension of ethanol for 4 h at 373 K to assemble the zeolite seeds on the membrane surface. The Sil-1 zeolite seeds were synthesized from a solution with molar composition of 25 TPAOH:100 TEOS:2700 H_2O at 368 K for 24 h as described by Zhang et al. [49].

Growth of TS-1 zeolite

After seeding palladium membrane, the TS-1 zeolite layer was grown on the top surface of the palladium membrane using hydrothermal synthesis from a synthesis solution with a molar composition of 1 TEOS: 0.01 TBOT:0.18 TPAOH: 250 H_2O [50,51]. A seeded palladium membrane was immersed in the synthesis solution in a Teflon vessel, which was sealed in a stainless steel autoclave at 448 K for 72 h. Thereafter, the resulted TS-1-Pd composite membrane was rinsed with deionized water, dried overnight at 373 K and calcined for 6 h at 823 K in nitrogen atmosphere to remove the organic template.

Characterization

The morphologies of silicalite-1(Sil-1) zeoite seeds, palladium membrane, the seeded palladium membrane with Sil-1 zeolites and the TS-1-Pd composite membrane were examined by field emission scanning electron microscopy (FESEM, Hitachi S-4800). The X-ray diffraction (XRD) analysis was carried out with a D/Max2400 Rigaku X-ray diffractometer using Cu Kα radiation at 40 kV and 50 mA. Elemental composition of the samples was measured by Energy dispersive X-ray spectroscopy (EDXS, Bruker-quantax). Fourier transform infrared spectra (FT-IR) was recorded on an EQUINOX55 spectrometer (Bruker) using the KBr disk technique. The resulted samples

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