Preparation and characterization of polysulfone mixed matrix membrane incorporated with palladium nanoparticles in the inversed microemulsion for hydrogen separation

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ABSTRACT

Polysulfone (PSf) membrane shows acceptable gas separation performance, but its application is limited by the "trade-off" between selectivity and permeability. In this study, PSf mixed matrix membranes (MMMs) incorporated with palladium (Pd) nanoparticles in the inversed microemulsion were proposed for hydrogen (H_2) separation. Pd nanoparticles can be kinetically stabilized and dispersed using electrostatic and/or steric forces of a stabilizer which is typically introduced during the formation of Pd nanoparticles in the inversed microemulsion. Pd nanoparticles were synthesized by loading ($PdCl_2$) into the polymeric matrix, polyethylene glycol (PEG) which acts as reducing agent and stabilizer. The dry–wet phase inversion method was applied for the preparation of asymmetric PSf MMMs. The effects of Pd (0–4 wt%) on the membrane characteristics and separation performance were studied. Experimental findings verified that the MMMs are able to achieved a high H_2/N_2 selectivity of 21.69 and a satisfactory H_2 permeance of 46.24 GPU due to the changes in membrane structure from fully developed finger-like structure to closed cell structure besides the growth of dense layer. However, the selectivity of H_2/CO_2 decreased due to the addition of PEG.

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1. Introduction

Hydrogen (H_2) is the utmost important gas product which is not only useful for chemical production such as hydrocracking, hydrodesulfurization, and Haber process, but also applicable in the energy industry as a clean fuel. H_2 can be directly produced from steam reforming of hydrocarbon, followed by gas purification. Besides pressure swing adsorption and cryogenic separation, membrane separation appears to be an attractive alternative in H_2 purification as it offers: (1) high energy efficiency, (2) cost effectiveness per foot print, (3) simplicity in operation, and (4) environmentally friendly.

Palladium (Pd) dense membranes supported on porous material are generally used for hydrogen separation at high temperature because of their excellent affinity towards hydrogen atoms [1]. The separation of H_2 via Pd membrane involves the reversible adsorption of H_2 molecules at the Pd surface, followed by rapid dissociation and diffusion of atomic H_2 into the metal lattice, where it occupies the octahedral interstitial sites with an increase in the lattice constant [2]. The diffusion of H_2 into the Pd lattice provides larger H_2 storage capacity, and the dissociation of H_2 into the active

atomic H_2 leads to its desirable separation properties [3]. Despite of high selectivity and permeance in H_2 separation, the reliability of Pd membrane remains one of the major problems in H_2 separation. Corrosion causing structural changes usually occur during the use of Pd membrane, causing reduction in its separation performance. For Pd alloy membranes, atomic inter-diffusion of metals between the Pd-based film and the substrate happens at high temperature, resulting performance deterioration. Pd and Pd based membranes also suffered from hydrogen-embrittlement cracking during thermal cycling and readily evidence surface contamination by sulphur-containing species [4]. The use of nano-sized Pd grains was reported as an alternative method to minimize the lattice distortion resulted from the α–β-phase transition. The improvement is due to the increment of the H_2 concentration on the grain surface and subsurface compared with the interior sites of the nano-Pd particles [5].

Besides inorganic membranes, polymeric membranes have also been commercialized as they are lower in cost. Polymeric membranes possessed good ability to cope with high pressure-drops and they can be easily scaled up. H_2 separation from highly supercritical gases such as methane, carbon monoxide and nitrogen can be easily achieved by polymeric membranes, because of the extremely high diffusion coefficient of H_2 relative to all other molecules except helium. Even though solubility factor is not favourable for H_2, the diffusion contribution dominates and gives overall high selectivity.

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Polymeric membranes for H_2 separation in gas producing plants have been commercialized under companies like Air Products, Linde, BOC and Air Liquide [6]. Polysulfone (PSf) has been used as the principal membrane material for Air Products since 1980. However, their application is limited by the "trade-off" between selectivity and permeability [7]. Hence, mixed-matrix membranes (MMMs) have been developed to couple the good processing flexibility of polymers and the outstanding gas-separation properties of inorganic materials. MMMs comprise of inorganic particles (e.g. zeolite, carbon, metal and metal oxides) as the dispersed phase and a polymer matrix as the continuous phase. Ahn et al. [8] have shown a remarkable enhancement in H_2 gas permeability from 11.8 to 22.7 barrer by introducing nonporous nanosized silica particles in the PSF membrane. Aside, Khan et al. [9] have prepared the polysulfone acrylate-zeolite MMMs and the results showed the increment of H_2 separation by 545.7% after incorporation of 25 wt% Zeolite 3A into PSf-acrylate. However, common obstacles of MMMs including poor interfacial adhesion and filler agglomeration have to be resolved before membrane formation. Nanoparticles are typically thermodynamically unstable and they tend to agglomerate. In the preparation of conventional MMMs, zeolite, silica, and other nanofillers are mechanically dispersed or chemically modified [10]. Mechanical dispersion is limited to low filler concentration while chemical modification may involve pore blockage.

In view of the high selectivity and durability of Pd nanoparticles, Pd nanoparticles should be dispersed in the polymeric matrix. Unlike other inorganic filler, Pd nanoparticles can be kinetically stabilized using electrostatic and/or steric forces of a stabilizer without affecting the functionality and surface area of Pd nanoparticles. The stabilizer is typically introduced during the formation of Pd nanoparticles, and this is achieved via the chemical or electrochemical reduction or thermal decomposition of metallic precursors [11]. The subsequent interaction between the stabilizer and the surface of the nanoparticle is a highly dynamic one, with its strength and nature often controlling the long-term stability of a dispersion of the nanoparticles. Thermodynamically stable Pd nanoparticles can be synthesized within the polar droplets of inverse microemulsions. Within the droplets (hydrophilic pool) of inverse microemulsions or the so-called nanophase reactor, nanoparticles with controlled particle size can be prepared. The inner radius of the droplet is determined by the composition and structure of the microemulsions. Thus, inverse microemulsions with the desired micelle size must be prepared using the appropriate molar ratio of polar phase and surfactant. Some of these stabilizers such as polyethylene glycol (PEG) are actually additives used in the preparation of polymeric membranes [12]. Hence, it is proposed to utilize the thermodynamically stable Pd nanoparticles in appropriate stabilizers for the preparation of Pd/polymeric membrane. The effects of stabilizer on membrane morphology, as well as the permeability performance in MMMs were studied in this work.

2. Experimental

2.1. Material

In the synthesis of Pd nanoparticles, palladium chloride ($PdCl_2$, 59%, anhydrous, Merck) was used as Pd precursor while PEG ($HO(C_2H_4O)_nH$, M_w: 10,000, Aldrich) was utilized as both reducing agent and stabilizer. The methane dichloride (MdCl, CH_2Cl_2, Merck) was used as solvent.

Polymer solution used in this study consisted of PSf (C_6H_4-4-$C(CH_3)_2C_6H_4$-4-OC_6H_4-4-$SO_2C_6H_4$-4-$O)_n$, M_w: ~35,000, Aldrich), and tetrahydrofuran (THF, C_4H_8O, 99.8%, Aldrich), ethanol (EtOH, C_2H_6O, 99.8%, Merck) and N,N-dimethylacetamide (DMAc,

Table 1
The weight percentage of polymer, stabilizers and Pd nanoparticles in PSf/Pd MMMs.

Sample	Percentage (%)			
	PSf	PEG	MdCl	Pd
PSf	23	0	0	0
PSf(PEG)_3	23	3	0	0
PSf(PEG/MdCl)_3	23	3	3	0
Pd_1	23	1	1	1
Pd_3	23	3	3	3
Pd_4	23	4	4	4

$CH_3CON(CH_3)_2$, 99.8%, anhydrous, Merck), whereas distilled water was used as a coagulating medium. PSf was dried in an oven at 60 °C overnight before being used, while other organic chemicals were obtained in reagent grade purities and used as received.

2.2. Synthesis and characterization of Pd nanoparticles synthesis

During the preparation of Pd nanoparticles, $PdCl_2$ was added into the polymeric matrix at a temperature above the melting point of PEG (43 °C) with magnetic stirring. The resulting light yellow homogenous solution was further stirred for 2 h at the same temperature. During this process, the colour of the solution changed from light yellow to brown and finally turned black, indicating the formation of Pd metal. The process was then followed by ultrasonic irradiation of the solution using Elmasonic S Ultrasonic at 37 kHz for 1 h at the same temperature. Then the mixture of PEG and Pd nanoparticles was cooled immediately to ambient temperature to form a solidified mixture [13].

The particle size of the Pd nanoparticles was determined using Zeta Sizer (Nano Sizer Malvern, United Kingdom). The transmission electron micrographs (TEM) were obtained by employing CM200 FEG Philips microscope. A droplet of Pd/PEG in MdCl was placed onto a carbon-coated copper grid for TEM scanning after the evaporation of MdCl. The crystalline properties of the prepared samples were investigated by X-ray diffraction (XRD).

2.3. Synthesis and characterization of membrane

Asymmetric PSf flat sheet membranes were prepared by polymer solution consisted of 23 wt% of PSf (polymer), 33.4 wt% DMAc (less volatile solvent), 33.4 wt% THF (more volatile solvent) and 10 wt% EtOH (nonsolvent) were mixed by mechanical stirring for 24 h around 25 °C [7]. The MMMs solutions were prepared by adding the required amount of Pd nanoparticles (1, 3 or 4 wt%) into the polymer solution. The mixture was vigorously stirred for 2 h. Prior to casting, the solution was degassed for 30 min to eliminate micro-bubbles trapped in the solution. Casting process was performed by using a pneumatically controlled casting machine. The solution will be spread on a clean flat glass plate with a casting knife at a gap of 150 μm. This film was left for evaporation to form dense layer. Casting was carried out at ambient atmosphere. The prepared film will be rapidly immersed in a coagulation non-solvent bath (distilled water). After primary phase separation, the membranes were stored in fresh distilled water for 24 h to guarantee the complete phase separation and complete removal of the residual solvents. Then, the membrane will be immersed in methanol to reduce pore enlargement. At the final stage, the membrane will be dried for 24 h at room temperature [7]. The weight percentage of polymer, stabilizers and Pd nanoparticles in PSf/Pd MMMs were varied as stipulated in Table 1.

The dried membrane samples were characterized using a Fourier Transform Infrared spectrometer (FTIR) (Nicolet iS10, Thermo Scientific, USA). All spectra were obtained from 32 scans at 4.00 cm^{-1} resolution with wave numbers ranging from 400 to