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Preparation, characterization and gas permeation properties of PDMS/PEI composite asymmetric membrane for effective separation of hydrogen from H_2/CH_4 mixed gas

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ABSTRACT

In this work, PDMS/PEI membranes were synthesized and sorption and permeation of H_2/CH_4 mixture were studied. The influence of pressure, temperature and feed composition were investigated. It was shown that permeances increased and selectivity decreased with an increment in the feed temperature. Increasing feed pressure caused a decline in gas permeance and increased selectivity. Higher concentrations of hydrogen in the feed declined the selectivity. The effect of different non-solvents was explained by their effect on precipitation time and it was concluded that water made the membrane denser while isopropanol forms a sponge-like structure. Coagulation bath temperature made the membrane denser. Film casting and dip-coating techniques were used to prepare selective membranes. Obtained selectivity results introduced dip-coating as a better method than film casting. Sequential coating improved selectivity of the prepared membrane. Finally, sequential coating with different concentrations was applied and enhanced selectivity significantly from about 22 to more than 70.

1. Introduction

Hydrogen energy technologies can play a vital role in solving problems related to the environment sectors [1–5]. The constant increasing demand for purified hydrogen has resulted in a greater focus towards extensive research studies on the advancement of the technologies for generation and purification of hydrogen with higher efficiency and lower production cost [6].

Abbreviations: GC, gas chromatograph; GPU, 10^{-6} cm^3 (STP). cm/(cm^2. s. cmHg); NMP, N-methyl-2-pyrrolidinone; PDMS, polydimethylsiloxane; PTMSP, (Poly [1-(trimethylsilyl)-1-propyne]); PEI, polyetherimide; SEM, scanning electron microscopy; TCD, thermal conductivity detector.

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There are primarily four convectional techniques for gas separation including absorption, adsorption, cryogenic distillation and membrane processes. The membrane separation process offers a number of advantages in terms of no phase change, no usage of sorbent materials, small footprint, low maintenance requirements, high process flexibility and high energy efficiency [7–11]. Membranes offer an attractive potential technology to offset traditional bulky and often less environmentally friendly means of separation [12,13]. Gas separation by polymer membranes is a proven technology that has found a wide range of industrial applications [14]. Polymer membranes are widely used in separation processes as they have acceptable film forming capability, toughness and flexibility [15]. They have gained important places in chemical technology and have been applicable to various separation processes of many chemicals and gases [16].

With a growing awareness of the importance of conserving natural resources and environmental aspects, companies are enthusiastic about finding ways to reduce flare gases and to recycle them [17]. Hydrogen containing a methane gas mixture is found to a great extent in the tail gases of petroleum refineries, ammonia and olefin plants [3,18]. Therefore, hydrogen recovery is of interest for the reduction of waste and decreasing environmental disadvantages.

In the olefin plant of Marun Petrochemical Company, hydrogen is used as fuel for cracking furnaces and the hydrogenation process and in poly-olefin plants; it is used to terminate polymer reaction. Because of the inadequate purity of methane for use as balance gas in the ethylene oxide plant of the Marun Petrochemical Co., the stream after turbo-expanders, containing hydrogen and methane, is sent to flare. Hydrogen recovery from this tail gas is an economical and environmental policy of this company. It can help to recycle hydrogen as a valuable resource and to purify methane for use instead of nitrogen to increase loading of the ethylene oxide plant by reducing the recycled gas compressor duty [5].

The majority of industrial membrane processes for gas separations utilize glassy polymeric membranes because of their high gas selectivity and good mechanical properties [17]. Commercially available polyetherimide (PEI) has several important advantages as a membrane material. This polymer has good chemical and thermal stability. The studies on gas permeation in the PEI dense film reveal that PEI exhibits impressively high selectivity for many important gas pairs [19,20]. The selectivity of about 30–40 was reported by Peinemann in 1987 for CO_2/CH_4 separation with PEI flat-sheet asymmetric membranes [21]. The results for porous and dense PEI hollow fiber membranes were obtained by Kneifel and Peinemann for He/N_2 separation and the selectivity of about 170 was achieved [22]. PEI hollow fiber membranes were synthesized by Wang and Teo for the separation of N_2 from He, H_2, CO_2, CH_4 and Argon [19]. PEI/metal complex asymmetric hollow fiber membranes were used by Kurdi and Tremblay for O_2/N_2 separation [23]. The influence of various non-solvents on the morphology of PEI membrane was investigated by Ren et al. [24]. The hollow fiber PEI membrane with an ultra-thin dense-selective layer for O_2/N_2 separation was fabricated by Peng et al. and the selectivity of about 2–7.5 was reported [25]. The CO_2 sorption and transport behavior of PEI membrane was studied by Simons et al. and the selectivity was reported of about 40–60 for CO_2/CH_4 separation [26]. PEI membrane with formamide as an additive was prepared by Zhang et al. and separation factors of 7 and 153 for O_2/N_2 and H_2/N_2 were achieved. Also, separation factors of 6.9 and 107 for O_2/N_2 and H_2/N_2, was reported by them for PEI membrane coated with Poly [1-(trimethylsilyl)-1-propyne] (PTMSP) [27,28].

Polydimethylsiloxane (PDMS) is the most commonly used elastomeric membrane material for the heavy hydrocarbons separation processes [29,30]. Due to structural properties such as unique flexibility of the siloxane backbone, low intermolecular forces between the methyl groups and high bonding energy of the siloxane bond, it can be used as a coating layer for preparation of a defect free membrane by the phase inversion method [27,31,32]. Several studies have investigated the effects of coating conditions such as concentration of coating solution, solvent type, coating temperature and number of coating layers on membrane performance [33–35].

In this research, asymmetric PEI membranes coated by PDMS were synthesized and optimum conditions for membrane preparation such as suitable non-solvent, coagulant bath temperature, coating method, and coating parameters were determined and the prepared membranes were characterized and evaluated for H_2/CH_4 separation. Effects of pressure, temperature and feed composition as operating mixed gas permeance and selectivity were investigated. Operating parameters were selected similar to real tail gas streams in the Marun Petrochemical Company and refineries of Iran. The influence of different non-solvents on the membrane structure and behavior were demonstrated by precipitation time and the difference of solubility parameters between solvent and non-solvents was confirmed by membrane morphology and gas permeation experiments. For the first time, sequential coating with different concentrations of PDMS solutions was introduced as an effective technique to remarkably increase selectivity. Experimental results confirmed the ability of prepared membranes for H_2/CH_4 separation.

2. Experimental

2.1. Materials

Polyetherimide (PEI) was obtained from Sigma–Aldrich (USA) in pellet form. Ethanol, methanol isopropanol, n-Hexane and anhydrous 1-methyl-2-pyrrolidinone (EMPLURA®, 99.5%, water<0.1%) were supplied from Merck (Germany).

Demineralized water used in the experiments had maximum conductivity of 0.2 μS/cm. Polydimethylsiloxane (PDMS and curing catalyst) was bought from Z-mark Co. (Italy). The pure gases including CH_4 (99.9%) and H_2 (99.9%) were supplied from Technical Gas Services. These gases were used in permeation measurement experiments.

2.2. Membrane preparation

The detailed description for preparation of asymmetric PEI membranes were explained in our previous study [36]. Before