



Effect of Silica Nanoparticles on Syngas (H₂/CO/CO₂) Permeability in Polyetherimide Membrane

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Abstract

As an alternative fuel to fossil fuels, hydrogen has the highest energy density content of all current fuels. Membrane separation is known as one of the effective technologies in hydrogen separation and purification. PEI-silica nanocomposite membranes were synthesized and the permeation of H₂, CO and CO₂ as the gases produced by the synthesis gas were studied. By embedding a small percentage (5%) of hydrophobic silica in PEI membrane, the permeability of H₂, CO₂ and CO became 1.5, 1.6 and 1.9 times higher than the permeability of the pure membrane, respectively. Furthermore, at high loads of nanoparticles (20 wt%), H₂ permeability reached the level of pure membrane permeability, while CO permeability was significantly reduced. Thus, the selectivity of H₂/CO in this membrane reached 66, which is 3.4 times higher than the selectivity of the pure membrane.

Keywords: Hydrogen separation, PEI membrane, Hydrophobic Silica, Nanocomposite membrane

Introduction

The importance of hydrogen as a potential green fuel has increased dramatically over the last decades, owing to the growing universal acknowledgement of energy supplies and sustainable resources alongside notable advances in fuel cell technology. This fuel can be obtained from both renewable and non-renewable energy sources. Nowadays, industrially available hydrogen is mostly produced from Steam Methane Reforming (SMR) reaction which resulted in a mixture of gases including hydrogen, carbon monoxide, carbon dioxide, methane and water vapour [1].

During the last decades, Membrane separation technology has become one of the essential processes for gas separation. Membrane technology exhibits a high-yielding, easily handled and affordable process which is environmentally compatible. Between different membrane materials, polymeric membranes are one of the prominent materials for gas separation membranes, due to their superior processability and adjustability to be processed into various modules [2]. Polyetherimide (PEI) as an amorphous glassy polymer has some considerable advantages that make it a suitable membrane material in gas separation field [3]. However, the trade-off between selectivity and permeability is a major problem in polymeric membranes. Therefore polymer-inorganic nanocomposite membranes have emerged with rapid growth in the last decades, show the promising



potential for solving the trade-off problem of polymeric membranes. The combination of the high selectivity and thermal resistance of inorganic materials with adaptability and ductility of the polymeric membranes improves the implementation of gas separation through these membranes [4].

Among various inorganic filler, silica has attracted remarkable attention in the nanocomposite membranes fabrication. A non-porous filler as silica increases the tortures pattern of the membrane matrix and reduces the diffusion of the larger gas molecules.

Most of the studies on cooperating nanosilica and polymers have been used synthesized silica produced with the sol-gel method. Although good control could be achieved on the nano-silica properties, these types of silica are hardly reproducible. Therefore, the nanosilica used in this study is purchased from a reputable manufacturer and can be used without any further treatment. The utilized polymer is also an industrial grade that makes the membrane of this study easily duplicable.

The aim of our study is to broaden current knowledge of commercial nano-silica influence on the separation performance of the PEI membranes. Also, having a profound knowledge of gas permeability and selectivity can help the new polymer design which can lead to better performance of polymeric membrane for the desire application.

Experimental

Granular polyetherimide (Ultem® 1000) and NMP was purchased from SABIC Co. and Merck Co., respectively. Hydrophobic fumed silica (SiO₂) was obtained from Evonik Co. H₂ (99.95%), CO₂ (99.95%) and CO (99.9%) were supplied by Oxygen Yaran Co.

The pure membrane was prepared with the same procedure explained by Arabi et al [5]. The resulting film was immediately put in the oven at 80 °C. After 24 h, the membrane went out from the oven and peeled off from the glass plate.

The procedure of fabricating nanocomposite membranes by solution blending method was different than fabricating pure membrane. At first step, 5-20 wt% of SiO₂ based on the polymer weight was dispersed in the NMP (ex: M15 (20 wt% solution) contains 15g polymer and 5 g nanoparticles). For better dispersion of particles and broking up the crystal agglomeration, the solution was exposed to ultrasonic waves using an ultrasonic bath between every step for 15 minutes. The polymer was added in 3 parts to obtain a homogeneous particle distribution in polymeric solution and the final part of the polymer was kept stirring for one whole day to completely dissolve into nanocomposite solution for affording a uniform structure of nanoparticle distribution. Finally, the membranes were cast like as the pure membrane. As the final stage, the nanocomposite membrane with as detached from the glass sheet, and the thickness of was prepared membranes measured 18-24 μm by a digital calliper device.

In this study, the variable feed pressure/constant volume permeation method was used to measure the pure gas permeability. All permeability tests were performed at 6 bar and 25°C. The gas permeability was obtained from the steady-state growth rate of gas pressure (d_p/d_t) in the permeate chamber through the following expression [6]:

$$P = \frac{273.15 \times 10^{10} \times V l}{A \times T (p_0 \times 76)} \left(\frac{dp}{dt} \right) \quad (1)$$

Where P is the gas permeability (Barrer); V is the dead-end vessel volume in the downstream chamber (cm³); l and A are the effective thickness (cm) and area (cm²) of the membrane, respectively; T is the operating temperature (K); p₀ is the feed pressure (bar) and d_p/d_t is the slope of the plot obtained from the test.



Gas transport through a dense polymer has been explained by sorption-diffusion theory. In this model, the permeability as an indicator of membrane efficiency is a product of gas diffusion and solubility in the membrane. ($P_i = D_i \times S_i$ (2))

Furthermore, the ability of the gas molecules to diffuse through the membrane showed by selectivity term and the ideal selectivity of two pure components in the same test condition could be calculated through dividing their permeability. ($\alpha_{ij} = P_i/P_j$ (3))

Results and discussion

FTIR Characterization

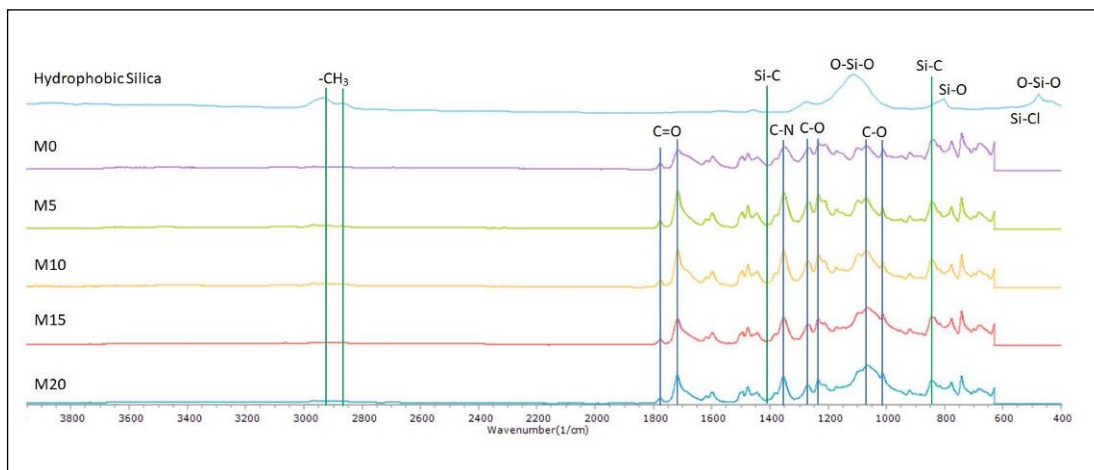


Figure 1 FTIR Spectrum of hydrophobic silica, Ultem membrane and nanocomposite

The structural characteristics of nanosilica, PEI and nanocomposites membranes containing 5-20 wt% of nanofiller are shown in Fig.2. PEI revealed bands on 1013, 1070 and 1270 cm^{-1} represent the vibration of the C-O bonds in the ether groups. The absorption at 1356 cm^{-1} is due to C-N stretch in the phthalimide rings. Also, the bands in 1776 and 1715 cm^{-1} are related to the asymmetric and symmetric stretch of imide carbonyl groups. The top spectrum in Fig.2 is related to the hydrophobic silica. The distinctive peaks of siloxane group at 477, 800 and 1114 cm^{-1} characterize the bending vibration, symmetric and asymmetric stretching vibration of Si-O-Si units, respectively. The Si-C bending and stretching bonds are represented at 845 and 1419 cm^{-1} wavelengths, respectively. The peaks between 2814 and 2938 cm^{-1} are referenced to symmetric and asymmetric stretching vibration of CH_3 of the alkyl groups. While the bonded carbonyl peaks became sharper in nanocomposite IR spectra, their place has not changed. It is clear that higher absorbance for bonded carbonyl in the nanocomposite membranes refers to a decrease in the polymeric phase and an increase in the inorganic phase. Besides, the fixed wavenumbers for bonded and free C=O in all the membranes confirm the weak physical interaction between polymer and filler. Since no new peaks and no substantial shift in the locations of the peaks have been observed, it can be concluded that no chemical reaction has been taken place between the polymer and the nanoparticle.

SEM Characterization

The structural morphology of neat PEI and MMMs is presented in Fig.3. The cross-section image of the pure membrane in Fig.3 (a) confirms the entirely dense structure of the prepared membrane. The homogeneous distribution of the nanoparticles into the polymer matrix can be witnessed in Fig.3 (b-d)), confirming the thoroughly mixing as well as the good compatibility



of silica particles in the polymer phase. The validity of this matter can also be demonstrated by cross-sectional EDAX and mapping of 20% silica membranes in Fig.4.

However, as the load of nanoparticles rises up, particles adhesion occurs and cause some aggregates in the matrix. The size of these clumped-up particles was ≤ 60 nm approximately as shown in Fig.4(a); therefore a new hybrid construction with silica interior the polymeric network is formed. Also, when the detachment of silica and polymer chains occurs as a result of weak bonding, a different population of nanovoids is constituted between the accumulated nanoparticles and silica-polymer interface as identified in the 5%-silica nanocomposite image in Fig.3 (b-d).

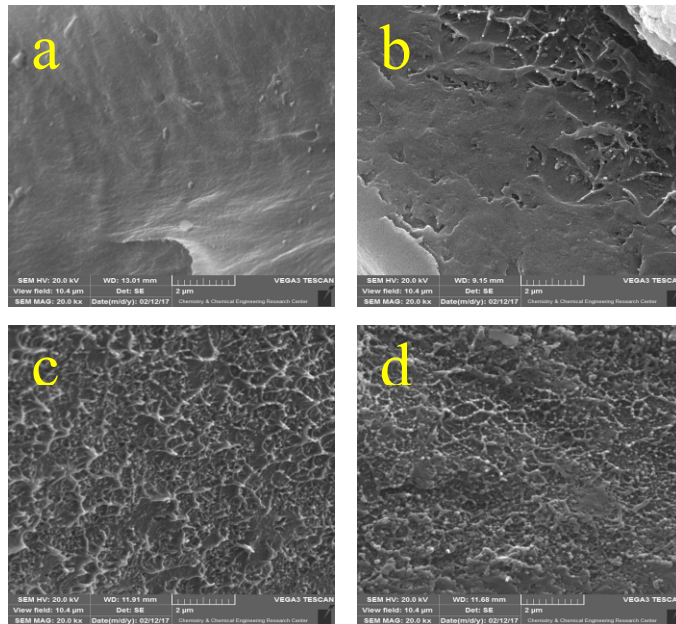


Figure 2 Cross sectional SEM images of pure and nanocomposite membranes (a) M0 (b) M5, (c) M10, (d) M20

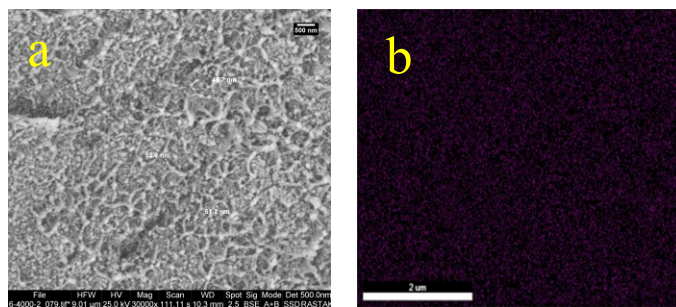


Figure 3 (a) EDAX Image, (b) EDAX map of M20 nanocomposite membrane

Gas permeation

Single gas permeation analysis was carried out to investigate the potential of pure and nanocomposite membranes in separation H₂, CO and CO₂. Fig.5 presents the permeability of neat PEI and 5-20% silica nanocomposite membranes. The permeability of gases in pure and hybrid membranes decreases with increasing the penetrate molecules size, H₂>CO₂>CO, which is in agreement with the results observed for glassy polymers in previous studies [7]. Generally, the gas permeability through M5 has increased compared to the pure membrane for all of the analyzed gases. This behaviour can be explained by the cross-section image of this membrane in Fig.3 (b). Since the detachments occur between polymer matrix and nanoparticles, some voids created around the nanoparticles and certainly affect the gas



behaviour in the nanocomposite membrane. Also, the impermeable phase was not large enough to reduce the membrane permeable phase. These created free volumes had shortened the penetrating path and increase the solubility and thus permeability [8]. Based on laboratory density measurements and FFV calculations, it was determined that the free volume of the polymer phase has increased in the membrane containing 5% nano-silica. This phenomenon can be explained by the laws of fluid mechanics of the low viscosity solution, the distribution of silica was not as uniform as that of a higher viscosity solution, and the formation of a surface vacuum at the filler-polymer interface in the M5 membrane was higher than in other membranes [9]. Consequently, the permeability of three gases is increased in the membranes with lower loaded of inorganic filler (Fig.5)

Additionally, the FFV calculation showed that the free volume of the polymer phase decreases with increasing nanoparticle load to 10,15 and 20 wt%. It is concluded that the available free volume in the polymer matrix is declined due to the presence of the nanosilica between polymer chains. As the amount of FFV in the polymer phase decreases, the gas molecules with larger size are more restricted than smaller gas molecules [10]. As can be seen from the permeability diagram in Fig.5, the decrease in permeability for CO was greater than that of CO₂ and H₂ by embedding more silica in the membranes.

Moreover, in the MMM, other two populations of voids were formed as a result of the bonding of nanoparticles to each other as well as their detachment from the polymer phase which are totally different with the polymer free volume [11]. The difference between the theoretical and experimental densities of the membranes shows that the largest amount of voids are in the M5 membrane and then decreases with increasing silica load percentage.

On the other hand, the tortuosity of the membrane was calculated using the volume fraction of the nanoparticles in the membrane, and it shows that the tortuosity of the membrane is slightly increased with increasing silica load. Therefore, it assumed that the voids create because of clumping up of the particles are somehow semi-selective voids, which accelerate the transmission of smaller gases and restrict the passing of large molecules like CO. This also reconfirms the trend of permeability of larger gases.

The selectivity of H₂/CO and H₂/CO₂ is shown in the Fig.6. As can be seen, the H₂/CO selectivity for the M5 membrane decreased slightly and then increases significantly, with the highest M20 membrane selectivity for these two gases. While, the selectivity of H₂/CO₂ has not changed significantly, which is a result of the CO₂ condensability as well as the increase in its permeability with the same rate as H₂. Nevertheless, the M20 membrane also reveals the highest selectivity for H₂/CO₂.

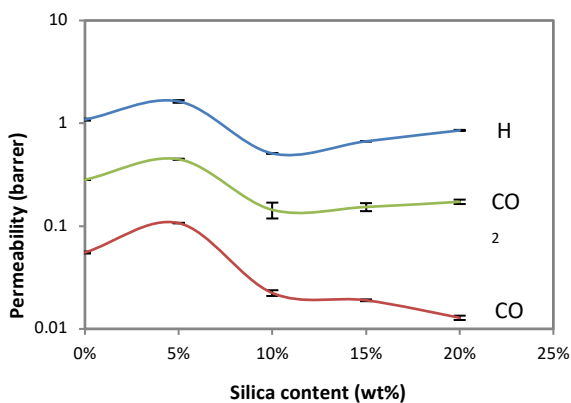


Figure 4 Permeability of analyzed gases at 6 bar,25 °C

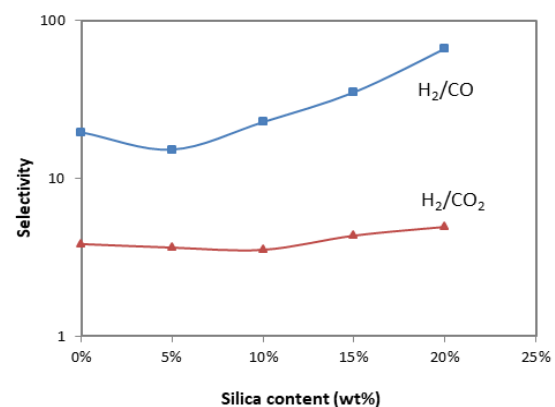


Figure 5 Selectivity of analyzed gases at 6 bar,25 °C



Conclusions

In this study, the effect of silica nanoparticles on the gas permeation properties of PEI was investigated. The gas permeation of prepared membranes increased with embedding 5% wt% of nanosilica into the membrane and decreased with adding more proportion of filler. With adding more silica different behaviours for analysed gases are witnessed, resulting of uniform distribution of nanoparticles and forming selective voids in the clumped up nanoparticles. The highest selectivity for H₂/CO and H₂/CO₂ is obtained in M20 membrane, and the permeability of all gases in this membrane is almost reached permeability in the pure membrane.

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