STUDY OF PERMEATION OF GASES THROUGH CERAMIC SUPPORTED POLYMERIC AND ZEOLITE MEMBRANES

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Abstract

Membrane separation process is one of the novel techniques for separation of CO_2 from various effluent gas mixtures. Membrane operations are recognized as feasible and economical operations over conventional technologies for gas separation due to a higher flexibility to tolerate fluctuations in feed composition and flow rate. In this present work Hydroxy Ethyl Cellulose (HEC) membrane prepared on Silicon carbide (SiC) tube and ZSM-5 membrane casted on α-Al_2O_3 tube support is used to study the permeation characteristics of various gases. Pour and decanting technique is used to coat HEC membrane on SiC tube whereas seed growth hydrothermal technique is used to prepare ZSM-5 zeolite membrane. Scanning electron microscope (SEM) and X-ray diffraction techniques (XRD) are used to characterize the membranes.

Single component permeation experiments are conducted for measurement of permeability coefficients which are essential for understanding and designing the membrane modules. Both the membranes have shown good permeation characteristics for all the gases. Ideal selectivity values are calculated from the pure component permeances.

***Keywords:** Gas separation, Polymeric membrane, Zeolite membrane, Permeability coefficient, Ideal selectivity*

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1. INTRODUCTION

Human activities, such as the burning of oil, coal and gases, and deforestation, have increased greenhouse gases (GHGs) like CO_2 concentrations in the atmosphere. Presently over 85% of world energy demand is supplied by fossil fuels [1] because of their low cost, availability, existing reliable technologies for energy production and energy density. These fossil-fueled power plants are responsible for approximately 40% of total CO_2 emissions, among which coal fired thermal power plants are the main contributors [2]. An average of 2.76, 2.28, or 1.62 t of CO_2 is released into the atmosphere, respectively, as a result of firing 1 t of solid, liquid, or gaseous fuel [3]. Among the GHGs (Carbon Dioxide, Methane, Nitrous Oxide and Fluorinated Gases) CO_2 is the largest contributor in regard of its present in the atmosphere contributing to 60% of global warming effects [4]. Thus the reduction of carbon dioxide emissions from the fossil fuel power plants is required to mitigate the adverse environmental impacts due to climate change. There are a variety of possibilities to reduce carbon emissions, ranging from the enhancement of energy efficiency to the replacement of fossil based energy production, and the use of efficient carbon capture techniques. One way to achieve a reduction is the use of gas separation through membranes, which is significantly efficient compared with conventional separation processes. Membranes are thin semi-permeable barriers that selectively separate some compounds from others. Membranes can be made of polymeric, liquid, hybrid, dense inorganic materials or microporous inorganic materials like zeolites.

Zeolites are polycrystalline aluminosilicates having a framework structure that has an uniform molecular-sized pores [5]. They have been used extensively as bulk catalysts, ion exchange material, molecular sieves, adsorbents and membranes. The zeolite membranes have chemical, mechanical, and thermal stability that has not observed in many types of membranes. Haiyang J et al., (2004) [6] given a review on synthesis methods for MFI-type zeolite membranes. Bonhomme F. et al., (2003) [7] prepared the high silica ZSM-5 membranes on porous α–alumina via hydrothermal synthesis and reported the permeation characteristics of membranes for gases such as H_2, CO_2, O_2, CH_4, N_2 CO, He and SF_6. Hasegawa Y et al., (2001) [8] synthesized NaY-type zeolite membranes ion-exchanged with alkali metal cations such as K, Rb, Cs on the outer surface of α-alumina tube by hydrothermal process. López A. B., et al. (2012) [9] analyzed the effect produced by the presence of ZSM-5 zeolite in an alumina tube upon the permeation rate of different gases.

The permeation through polymeric membranes are described by Paul and Yampolskii (1994) [10] using solution-diffusion mechanism. Solubility and diffusion of the specific gas through the polymeric membrane dictates the separation of the gaseous species. Stern S. A. (1994) [11] has studied the structure, permeability and selectivity relationships on selected rubbery polymers such as silicon polymers and glassy polymers such as polyacetylenes, polyimides, polycarbonates etc. Aitken C. L et al., (1992) [12] studied on gas transport properties through polysulfones for various gases. Xu Z.-K et al., (2002) [13] studied gas transport and separation properties of H_2, CO_2, O_2, N_2 and CH_4 on poly(arylene ether) membrane. Illing G. et al., (2001) [14] studied the permeability and ideal separation factors for various gas pairs such as H_2/CO_2, O_2/N_2, H_2/N_2 etc., through dense polyaniline membrane. Lin H. et al., (2004) [15] studied the effect of pressure on the solubility, diffusivity and permeability of various individual gases in poly ethylene oxide at 35°C. Taek-Joong Kim et al., (2013) [16] studied the effect of pH on CO_2 separation using polyvinylamine based composite membrane. These membranes are either having low permeability or low selectivity, however, commercialization of membrane gas separation requires the high permeability and high selectivity.

Therefore, the present work is aimed to prepare Hydroxy Ethyl Cellulose (HEC) polymeric membrane on Silicon carbide (SiC) tube supports and ZSM-5 zeolite membrane on α-Al_2O_3 tube supports. These membranes are used to study the permeation characteristics of various gases like CO_2, N_2, H_2, O_2, etc. Ideal selectivity values are calculated from the obtained permeability values.

2. MATERIALS AND EXPERIMENTAL METHODS:

2.1 HEC Polymeric Membrane Preparation:

The clear 3.7 wt% of HEC (LOBO Chemicals, Mumbai) solution is prepared by mixing HEC in distilled water for 4-24 hourrs. The solution is left for an hour to remove the entrapped air bubbles. This bubble free solution is used for preparing HEC dense film or direct coating on ceramic support.

2.1.1 Preparation of HEC Dense Film:

The homogeneous bubble free solution is used for casting the dense HEC membrane by pouring the solution on clean polythene film and spreading the solution of desired thickness. Then the solvent is evaporated at the ambient temperature to get dry membrane over the polythene. The membrane is peeled off from the polythene.

2.1.2 Preparation of HEC Film on Ceramic Tube:

The ceramic support tubes (Tube Length: 200mm, ID: 7.25mm, OD: 13.25mm, effective membrane surface area, 4.553E-03m^2) are first boiled in water for 2-3 hours so that the pores of the ceramic support are cleaned and occupied with water. Then the bubble free HEC solution is poured inside the tube and left for 5-10 min. The excess polymeric solution is drained off to get uniform membrane over the inside surface of the tube.

2.2 ZSM-5 Membrane Preparation on α-Al_2O_3 Tube:

The hydrothermal synthesis method is used to prepare the ZSM-5 membranes on α-Al_2O_3 support tubes. In this regard, a synthetic (precursor) solution consisting of SiO_2: TPAOH: H_2O is prepared by mixing the components in 100: 10: 1800 molar ratio. This solution is stirred for 3 hours at room temperature. The α-Al_2O_3support tubes (Tube Length: 126 mm, I Diameter: 6 mm, thickness: 1.5 mm) is dipped into the precursor solution for 3-4 hour at room temperature. Then saturated supports are removed from the solution and kept in the Teflon autoclave which is maintained at 100°C. It is left for 12 hours to grow initial seeds on the supports. Actual hydrothermal synthesis is carried out for 24 hours at 150°C to grow ZSM-5 membrane on seeded supports. After these the tubes are dried by keeping in hot air oven for 24 hours at 100°C. Then the supported membrane is calcinated by keeping in furnace at 550°C at a rate 0.4°C and left for 5 hours. The membranes are cooled to room temperature at a cooling rate of 0.4°C.

2.3 Membrane Characterization:

2.3.1 Scanning Electron Microscope

The surface and the cross section of the membranes are studied using Scanning Electron Microscope (Leica make model number s440) with EDAX attachment. Before taking SEM picture the membranes are coated with gold using sputter coater. The polymeric membranes are positioned vertically and horizontally, whereas zeolite membrane and dense polymer films are taken horizontally.

2.3.2 X Ray Diffraction

X-ray diffraction technique is used to find the nature of the surface of the polymeric membrane and ZSM-5 membrane. XRD curves of the membranes are obtained using Panalytical make - model Xpert pro, with inbuilt ICDD data and expert high score soft ware.

2.4 Permeation Experiments:

Pure gas permeation experiments were conducted in order to find the permeability of the gases through the membranes. Freshly prepared membrane is placed in the stainless steel test fixture (Permeation cell) and tightened by placing proper gaskets so that no leakage takes place. Figure-1 shows a view of a permeation cell used for dense film and Figure-2 shows the schematic experimental diagram used to conduct the permeation experiments. Pure gases (Carbon Dioxide, Oxygen, Hydrogen and Nitrogen) are passed through the membrane from the gas cylinder and upstream pressure is regulated using pressure regulator. The permeate flow rate of the gas is measured at atmospheric pressure with the help of Standard Rotometer/soap bubble meter at the atmospheric conditions. The same experimental setup with different permeation cell is used to study the permeation characteristics through tube membranes.

Fig-1: Permeation cell used for Flat membranes

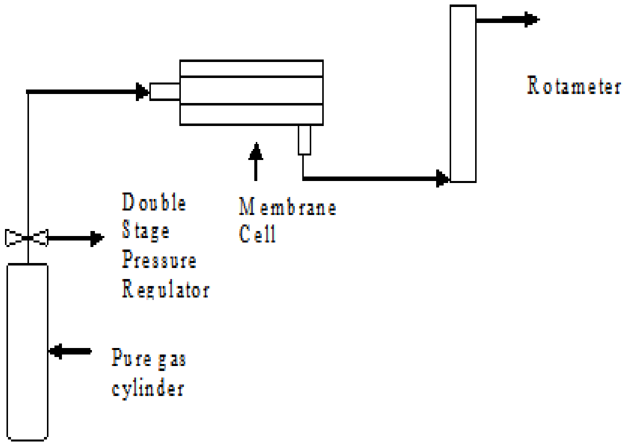
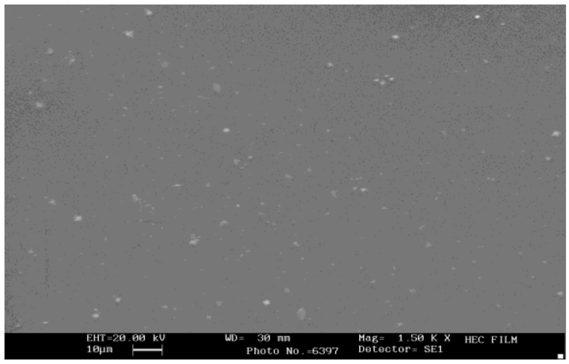


Fig-2: Schematic experimental setup to conduct permeation experiments

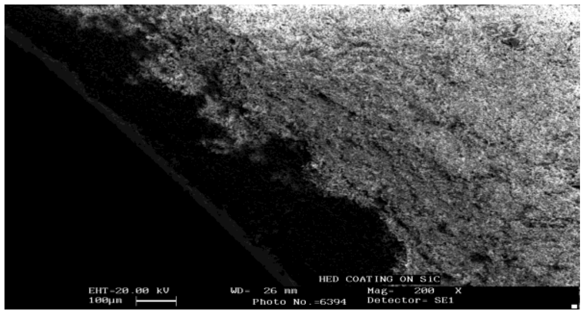
3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscope

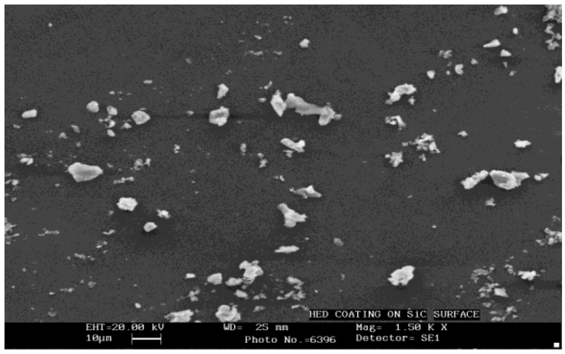
The Figure- 3 a – d shows the SEM images that are taken for the different membranes of dense HEC film and membranes on ceramic supports. Figure -3 a shows the surface of the plain HEC dense film and figure clearly shows that the membrane is highly dense. Figure -3 b gives the cross section of the HEC membrane on the SiC support and thickness of the top layer is estimated to be 50 µm. Figure-3 c is the SEM picture of HEC membrane surface on the SiC support. The presence of white regions may be due to the improper coating of HEC on SiC. Figure-3 d is the SEM image of zeolite membrane coated on α-Al_2O_3.The figure clearly indicates the formation of zeolite crystals.



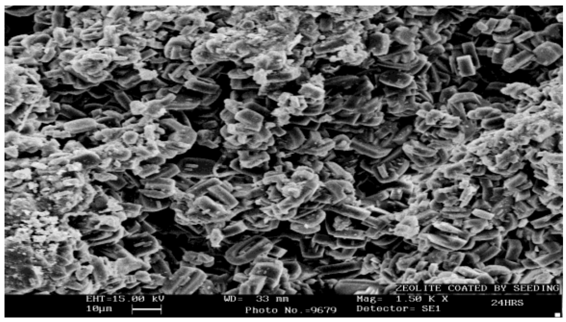
(a)



(b)



(c)



(d)

Fig-3: SEM images (a). Surface of Dense HEC film (b). Cross section of HEC Coating on SiC Support (c). Surface of HEC Coating on SiC Support (d). Formation of ZSM-5 Crystals on α-Al_2O_3 Support

3.2 XRD

XRD spectrums are also taken for the membranes for confirmation of membrane materials. Figure-4 shows the XRD spectrum of HEC film and HEC coated on SiC support. The peak position at 2θ of 21° for both the spectrums confirms the presence of HEC on SiC. The extra peaks at 2θ of 34, 35, 38, 60 and 72° may be due to the SiC. Figure 5 shows the XRD spectrum of zeolite on α-Al_2O_3 and the figure clearly shows the formation of ZSM-5.

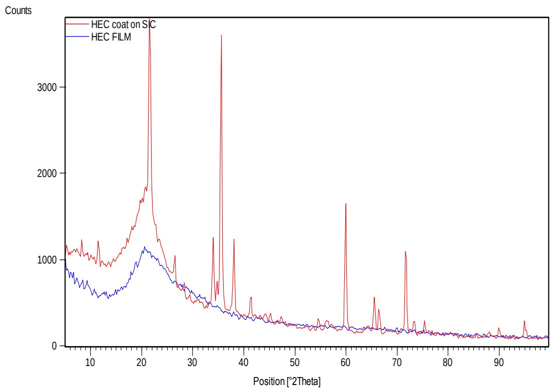


Fig-4: XRD spectrum of dense HEC film and HEC coated on SiC support

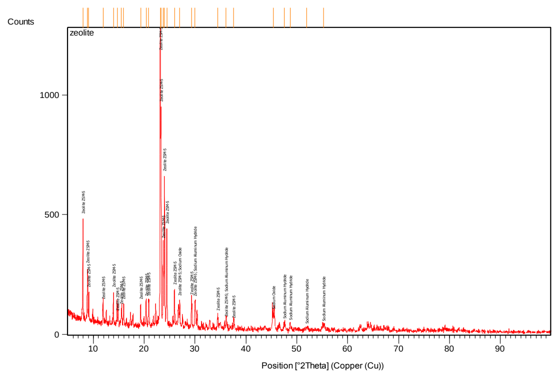


Fig- 5: XRD spectrum of ZSM-5 membrane

3.3 Permeation Results

Pure component permeation experiments of various gases (CO_2, O_2, N_2 and H_2) at various pressure drops are conducted for all the membranes. Figure–6, 7 and 8 gives the variation of the permeation flux with pressure drops for HEC film, HEC coated on SiC tube and ZSM-5 on α-Al_2O_3, respectively. As expected the flux through these membranes are increasing with increase in pressure. The Figure - 6 infers that the permeation flux of all the gases through dense HEC film is same at low pressures, however, at high pressures the CO_2 flux is high compared to other gases. A similar trend is also observed for HEC on SiC tube (Figure - 7). Further comparison of Figure- 6 & 7 shows that fluxes are little higher for HEC coated on inner surface of SiC tube. This may be due to improper coating of HEC on SiC and confirms SEM image (Fig- 3 c). The CO_2 flux at all pressures is high compared to Nitrogen flux for ZSM-5 coated on α-Al_2O_3 and the difference in the flux is high at high pressures. In addition to this the fluxes through ZSM-5 membrane is higher compared to HEC membranes. The study clearly shows that HEC and ZSM-5 are good candidates for CO_2 separation from the other gases.

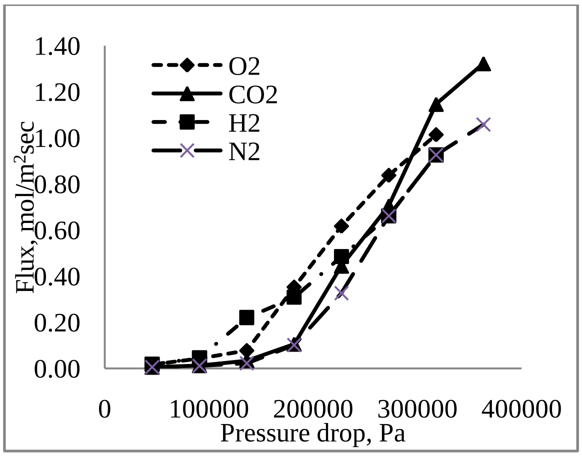


Fig-6: The Variation of the Flux with Pressure for Dense HEC Film

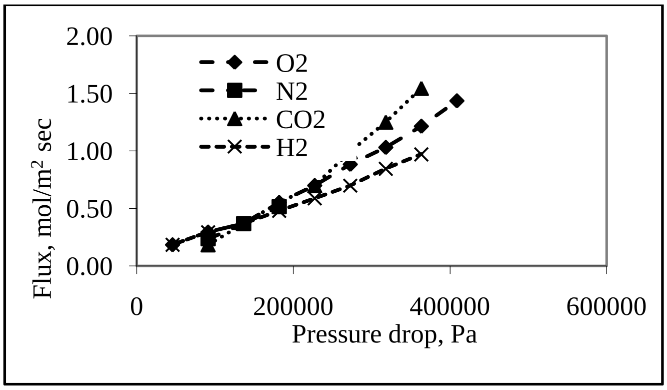


Fig-7: The Variation of the Flux with Pressure for HEC coated on SiC

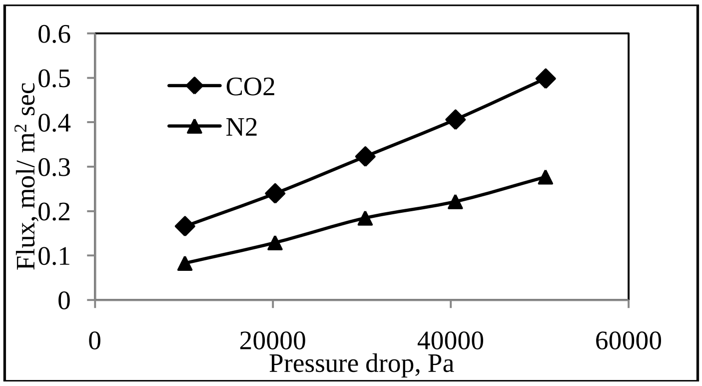


Fig-8: The Variation of the Flux with Pressure for ZSM-5 membrane

Permeance values are calculated from the ratio of flux to pressure drop across the membrane. The calculated average permeance values are given in Table-1. Even though the permeation flux of CO_2 is high at higher pressures for HEC membranes, the average permeance of O_2 is almost same that of CO_2, however these values are high compared to the N_2 and H_2.A permeance value of 0.161×10^{-5} mol/m^2 sec Pa for HEC film and 0.324×10^{-5} mol/m^2 sec Pa for HEC coated tube are obtained for CO_2.The permeance values for HEC coated tube is little higher than HEC film and this may be an uneven coating of the polymeric film on the surface and again confirms SEM image (Fig- 3 c). An average permeability value of $1.175x10^{-5}mol/m^2$ sec Pa is obtained for CO_2 for ZSM-5 membranes, this is 10 times higher compared to the dense HEC film membrane. Therefore ZSM-5 is having better permeation characteristics for CO_2 as compared to HEC film.

The ideal selectivity values for these membranes are calculated by taking the ratios of permeance and the obtained values are reported in Table-2. The ideal selectivity value for CO_2/N_2 is approximately 1.2 for HEC membrane and its value for ZSM-5 membrane is 1.86. So once again it may conclude that ZSM-5 membrane is better for CO_2-N_2.

Table-1: The Permeability Values of Gases for Different Membranes

Component Gas	Permeance ($mol/m^2 sec Pa$) * 10^5		
	HEC film placed on SiC disc	HEC coated on SiC tubes	ZSM-5 membrane on α-Al_2O_3 tubes
O_2	0.176	0.327	--
CO_2	0.161	0.324	1.175
N_2	0.133	0.271	0.632
H_2	0.160	0.289	--

Table-2: The Ideal Selectivity Values for Different Membranes

Gases	Ideal Selectivity		
	HEC film placed on SiC disc	HEC coated on SiC tubes	ZSM-5 membrane on α-Al_2O_3 tubes
CO_2/ O_2	0.9	0.99	--
CO_2/ N_2	1.21	1.19	1.86
CO_2/H_2	1.01	1.12	--

4. CONCLUSIONS

Membrane gas separation is one of the separation processes for separation of CO_2 from various effluent gases. So in the present work various membranes like HEC and ZSM-5 are prepared to study the single component permeation characteristics of various gases. The seed growth hydrothermal technique is used to prepare ZSM-5 zeolite membrane. SEM image and XRD spectra shows the formation of ZSM-5 zeolite on α-Al_2O_3. All the membranes have shown good permeation for all the gases and ZSM-5 have better separation characteristics compared to HEC.

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