Temperature Dependence Study of Gas Permeability in Metal Doped Composite Polymeric Membrane

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Abstract: Polycarbonate (PC) membrane and PC base hydrogen active intermetallic compound $Fe_{0.5}Ti_{0.5}$ particles doped composite membrane have been prepared by solution cast method. The membranes have been characterized by H_2 and CO_2 permeability and selectivity measurements with increasing temperature. Higher gas permeation has been observed with increasing temperature. In case of doped composite membrane H_2/CO_2 gas pair selectivity first increases then decreases with temperature whereas in case of pure PC it decreases with temperature.

The effect of doping increases the activation energies for permeation of H_2 and CO_2 in the doped membrane in comparison to pure PC. Doping was found to suppress plasticization effect in polycarbonate. The doped membrane was analyzed by optical micrograph.

INTRODUCTION

Hydrogen separation from various gases in important in both refinery and chemical processing. There is an increase demand for hydrogen in renewable energy related applications such as clean fuel for vehicles and fuel cells [1]. Glassy polymers are widely used as gas barrier or as gas separation membranes because of their low cost, energy efficiency and easiness to mold in a desired shape. There widespread use in gas separation has however been limited by the difficulty of preparing membrane with the desired combination of high selectivity and permeability. It is unfortunate that as the selectivity of a polymer membrane increases, permeability invariably decreases and vice versa [2]. Many attempts have been made to overcome this fundamental limitation. The addition of micron-sized zeolite porous particles to organic polymers in the hope of combining the mechanical elasticity and process ability of polymers with strong size selectivity characteristics of spatially well defined zeolite pores has been investigated. Commercialization of this approach has been hampered by poor polymer / zeolite adhesion and inadequate zeolite particle dispersion in a polymer [3]. Addition of fumed silica particles in glassy amorphous poly (4-methyl-2 pentyne) enhances both membrane permeability and selectivity for large organic molecules over small permanent gases. An unexpected increase in permeability for small penetrant molecules (methane) for poly (4-methyl-2-pentyne) based nano composite membrane with an unusual permselectivity for large organic molecules over small permanent gases have been reported by Merkel *et al*. [4].

The porous polymer beads of the chelate-resin-Fe (II) complex are quite useful as an adsorbent for nitrogen monoxide [5]. Thus the concentrated recovery or the removal of a trace amount of gas is successfully achieved when the appropriate chemical adsorbent is chosen. By forming polymer-metal complex, the active metals can be easily handled and attain the advantages of polymeric materials. Since the coordination of gaseous molecules to the metal complex is stronger than the physical adsorption or solubilization into polymers, the polymer metal complex provide higher selectivity for gas separation. Thus a chemical adsorbent can be prepared by immobilization of proper metal ions by ligands, which can be fixed on the polymer chain by covalent bonding [6].

In the present work doped composite membrane was prepared by adding sub micron sized $Fe_{0.5}Ti_{0.5}$ particles in polycarbonate. $Fe_{0.5}Ti_{0.5}$ has high affinity for hydrogen, it can absorb large amount of hydrogen [7] and desorb it at increased temperature or decreasing pressure. The permeability of the composite membrane for H_2 and CO_2 along with H_2/CO_2 selectivity has been studied at different temperatures. Activation energies for permeation for H_2 and CO_2 have been calculated from Arrhenius plots.

EXPERIMETAL

PC and doped membrane of thickness 50-55um were prepared by solution cast method [8]. The doped composite membrane was prepared by physically

adding sub micron sized $Fe_{0.5} Ti_{0.5}$ particles in concentration of 2wt% in PC during solvent preparation. Before adding into PC solution, $Fe_{0.5} Ti_{0.5}$ was treated with acetic acid in the hope of immobilizing it by legend and fixing it on to the PC chain. The details of the permeability cell and the process involved have been given elsewhere [8]. Permeability was calculated by using the formula

$$P = \frac{Gas\ flux \times membrane\ thickness}{Pressure\ difference} \qquad (1)$$

Permeability is defined as the product of diffusion coefficient and solubility coefficient. Selectivity of the membrane for gas A relative to gas B is given by the equation.

$$\alpha = {PA}/{PB} \qquad (2)$$

Effect of temperature on permeability is expressed by an Arrhenius-type relationship

$$P = Po\ exp{Ep}/{RT} \qquad (3)$$

Where Ep is activation energy for gas permeation. The temperature has been varied from 302K to 358K, well below the glass transition temperature (423K) of PC with upstream gas pressure fixed at 30 psi for the composite membrane and 20 psi for pure PC.

The optical micrographs of the samples were taken using LABOMED (10 X) microscope. The measuring scale is attached with the eyepiece having an accuracy of 0.1 micron.

RESULTS AND DISCUSSION

Temperature dependence of H_2 and CO_2 permeability coefficients for pure PC and for doped membranes, with concentration of dopant 2wt% in the temperature range 302 K to 358 K are shown in figure 1 and 2 respectively. Temperature dependence of H_2/CO_2 selectivity for pure PC and doped composite membranes are shown in fig. 3.
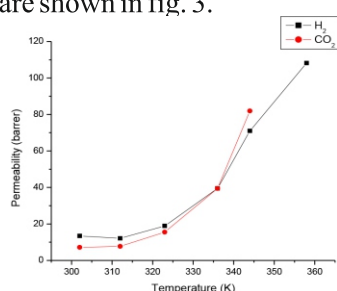

Fig. 1. *Temperature dependence of permeability of H_2 and CO_2 in pure PC.*
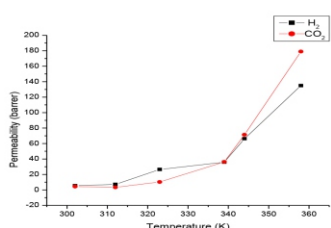

Fig. 2. *Temperature dependence of permeability of H_2 and CO_2 in 2wt. % doped composite membrane.*

Since size of H_2 molecule 2.89A° is smaller than CO_2 molecule 3.3A°, therefore, it diffuses through the polymer matrix faster and consequently, has larger permeability. It is observed that for pure PC, permeability increases with increasing temperature for both the gases, whereas selectivity of pure PC for H_2/CO_2 pair decreases with temperature. The permeation process is explained on the basis of free volume molecular theory. The free volume in the polymer is created by inefficient chain packing and transport of the penetrant depends on the available free volume as well as energy of the penetrant molecule to overcome attractive forces of polymer chains. Any change in the temperature produces thermally induced chain segments rearrangements leading to less resistive passage to the opening of transient gaps for penetrants jumps based on difference in their sizes and thus leading to decrease in mobility selectivity but with increased permeability [4,9]. At the same temperature lower gas permeability in the doped membrane is due to the fact that filler particles obstruct penetrant mobility through the polymer. The reduced permeability in filled polymer is attributed to the increase in diffusion path length and decrease in available free volume for penetrant transport through polymer matrix.
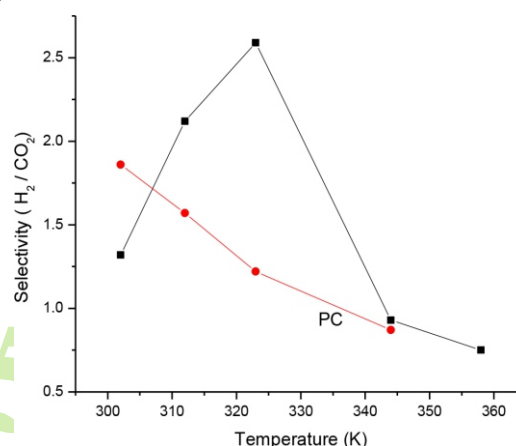

Fig.3. *Temperature dependence of H_2/CO_2 selectivity for pure PC and 2 wt. % doped composite membrane.*

In case of doped membrane the highest selectivity of 2.6 is obtained at 323K, higher than that of pure PC at this temperature. This is due to the initial adsorption of

H_2 by $Fe_{0.5}Ti_{0.5}$ to a greater extend than CO_2 and desorbing it at higher temperature leading to higher H_2 permeability and hene H_2/CO_2 selectivity. A comparative statement of the selectivity verses temperature is shown in figure3.

In case of pure PC, permeability of CO_2 is found to rise very sharply to the value of 916.9 barrer at 358 K. If the permeability of H_2 is measured again at this temperature, it comes out to be 1298 barrer instead of the previous value of 108.2 barrer. The reason is that exposure of polymer to highly sorbing penetrant such CO_2 leads to a swelling of the polymer matrix and an increase in segmental mobility. This phenomenon of plasticization leads to an increase in the permeability of all penetrants but unfortunately with decrease in selectivity [9]. In case of composite membranes we do not observe very sharp rise in permeability as was observed for pure PC at 358 K temperature. This shows inhibition to chain mobility due to filler particles that leads to decrease in available free volume.

Temperature has large effect on gas permeation through dense polymer membrane as expressed by equation (3). Arrhinius plots of H_2 and CO_2 for pure PC is shown in fig4 and for doped composite membrane is shown in figure 5 respectively.
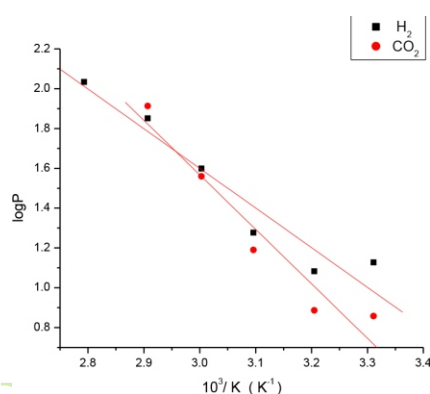

Fig.4. *Arrhinius plots of H_2 and CO_2 for pure PC*

The straight-line plots show that the temperature dependence of permeability follows Arrhenius type equation. The activation energies of H_2 and CO_2 for pure PC are found to be 16.5 KJ/mole and 22.7 KJ/mole respectively. As expected, activation energy for permeation of H_2 is less than that of CO_2. For the doped composite membrane these values are 22.6 KJ/mole and 28.4 KJ/mole respectively.
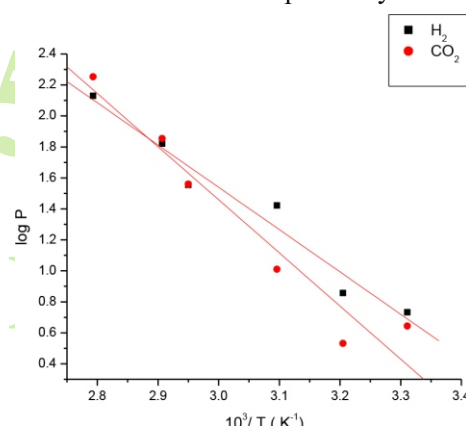

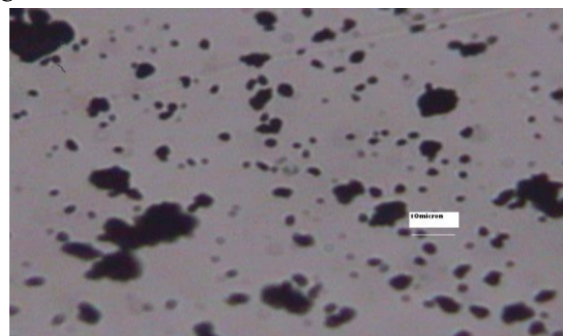**Fig. 5.** *Arrhinius plots of H_2 and CO_2 for 2 wt. % doped PC*

Fig.6. *Optical micrograph of the doped composite membrane*

The distribution $Fe_{0.5}Ti_{0.5}$ particles in PC is shown in the optical micrograph. The metal particles are well embedded and well dispersed in the polymer matrix. Some $Fe_{0.5}Ti_{0.5}$ particles aggregate into clusters ranging up to a hundred micron order. These clusters processes a highly fractal surface, which together with discrete primary particles yield a large polymer/filler interface, leading to increase in gas permeation.

CONCLUSIONS

Doping of fine particles of $Fe_{0.5}Ti_{0.5}$ in PC leads to changes in its permeability and selectivity properties. The doped composite membrane shows good H_2/CO_2 selectivity at higher temperature making it working at as hydrogen filter at high temperature. Dependence of permeability follows Arrhenius type equation. Doping suppress the phenomenon of plasticisation.

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