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ARTICLE

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CO_2/CH_4 SEPARATION PERFORMANCE OF MIXED-MATRIX MEMBRANES BASED ON MOF 808/POLYAMIDE

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Semi fluorinated aromatic polyamide (PY PA) based Mixed-Matrix Membranes (MMMs) using MOF-808 as filler were prepared.MOF-808 incorporated at 5%, 10%, and 15% weight percent of loading in polyamide matrix. MMMs were explored for single gas separation (CH_4, N_2, O_2 and CO_2) performances. Permeability-selectivity trade-off of polymer has been overcome with incorporation of MOF-808 filler. The MOF-808 is incorporated into the polyamide matrix membrane as a result membranes exhibits a significantly higher CO_2 permeability (91 bar) and CO_2/CH_4 selectivity (44).

Introduction

Mixed-matrix membranes (MMMs) consisting of hybrid membrane materials, as filler particles fixed in apolymeric matrix. Membrane-based separation technology is an interesting for CO_2 separation due to its simple operation and energy operative equipment asset[1]. Polyamides (PAs) have been mainly explored as a matrix for gas separation membranes with outstanding chemical and thermal stability. Polymeric membranes are suffering from a trade-off relationship between gas permeability and selectivity, i.e. 2008 Robeson upper bound. To break the Robeson upper bound strategies like MMMs have been explored. Metal-organic frameworks (MOFs), MOF-808 have been widely applied in gas separation and gas adsorption. MOF-808 has tetrahedral cages with an internal aperture of 4.8 Å. MOF-808 has a kind of porehas a size about 1.8 nm andit is unfavorable for CO_2capture. Kim et al.[2] prepared thin-film composite mixed-matrix membranescopolymer, where PBE/MOF-808 exhibits CO_2 permeance (1069 GPU) and CO_2/N_2 selectivity (52.7). Wang et al.[3] developed pore-optimized MOF-808 (MOF-808@PVAm) membrane at loading of 33.33 wt.% displayed CO_2 selectivity of 181 and permeance of 2753 GPU. Vankelecom et al.[4] correlate MOF-808/Matrimid 5218 MMMs for CO_2/N_2 separation performance. In this work, semi fluorinated aromatic polyamide (PY PA) with pyridine moiety in polymer backbone have been chosen as polymeric matrix. Filler material MOF-808 were chosen for functionalization in the MMM that provides a stage for presenting different filler loadings. The Gas permeation and morphology of the MMMs with different ratios MOF-808 loading are characterized. The prepared MMMs have been tested for single gas permeation tests separations. CO_2/CH_4 Separation performance of gas is also meaningfully helped by incorporating MOF-808 into PY PA.

Experimental

Materials, Membrane Characterization and Gas Separation Measurements: Acid, 2, 6-bis [3'-trifluoromethyl-4'(4''carboxyphenoxy)benzyl] pyridine (2) has been prepared reported procedure. An automated Diffusion Permeameter (DP-100-A) manufactured by Porous Materials, Inc., USA was used to measured the permeability of gases through the polymer membranes. The permeability coefficient (P) and ideal perm selectivity (α) were determined according to reported procedure[5].

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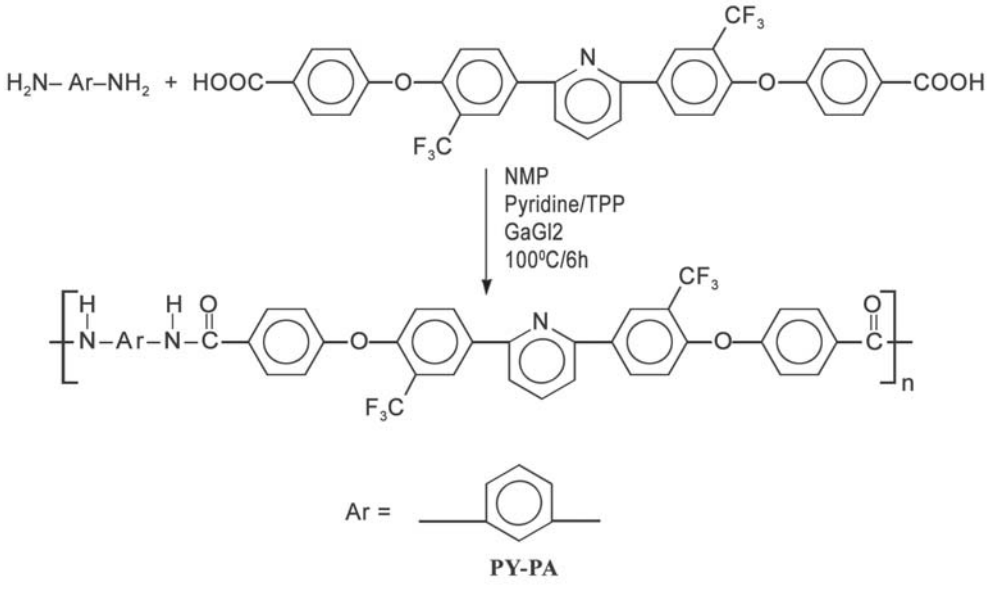

Scheme 1. Preparation of the polyamide (PY PA)[4].

Polymeric Membrane Preparation: Homogeneous polymer 10-15% (w/v) solutions put in DMAc solvent to casting onto glass Petri dishes. At 80 °C in an oven, Petri dishes were positioned for overnight. Membranes were slowly heating to 150 °C. The membranes were kept for 4h at 160 °C under vacuum forremoval of solvent and moisture[1]. Obtained membranes were flexible free standing in nature.

Polymerization: A polymerization reaction Scheme 1. (PY PA) is as follows: in a round bottom flask (50 mL) equipped with reflux condenser, a mixture of m-triphenylamine (0.880 g, 6.90 mmol), di amine (1) and 2,6-bis [3'-trifluoromethyl-4'(4''-carboxyphenoxy)benzyl]pyridine (2), dicarboxylic acid (0.510 g, 6.90 mmol), NMP (5 mL), pyridine (1.4 mL), calcium chloride (0.3 g) and triphenyl phosphite (TPP) (1.2 mL, 5.09 mmol) were added. The mixture was under nitrogen atmosphere heated for 6h at 110 °C using magnetic stirrer on continuous stirring. Fibrous polymer was obtained when the mixture was poured in methanol (500 mL) with constant stirring[5].

Preparation of MOF-808: MOF-808 was synthesized as follows: first, 5.08 g (24.2 mmol) 1,3,5-benzenetricarboxylate and 23.4 g (72.8 mmol) $ZrOCl_2 \cdot 8H_2O$ was used to taken in 500 mL round-bottom flask and dissolve in 182 mL H_2O and then 26.8 mL (712 mmol) formic acid was added. The mixture was stirred for 15 min with heated to 100 ºC under reflux for 5 h. The resulting MOF sludge was washed four times with water and ethanol[6].

Preparation of MOF-808/PY-PA MMMs: A PY-PA polymer solution was prepared by dissolving polymer of 0.5 g in 5 mL DMF.MOF-808 was dispersed for 30 min by ultrasonication in DMF and stirring. Then, polymer solution by 2 h further stirring of 10% of the volume was added to the MOF-808 suspension. The MOF suspension was stirred for overnight after added to the remaining volume of polymer solution. The membranes were prepared in DMF by casting polymer (homogeneous) solution solvent onto clean glass Petri dishes. The Petri dishes was placed at 80 °C overnight in an oven heated, followed by slow heating for 6h to 150 °C. The weight ratio of filler/(filler + polymer) was kept constant for all MMMs[6]. MOF-808 loading of 5%, 10% and 15% weight percent of fillers were used for preparation of MMMs.

Results and Discussion

Polymer Synthesis and their Properties: Phosphorylation polycondensation was used for Polyamide (PY-PA) preparationusing the dicarboxylic acid monomer (2) with aromatic diamine monomer (1) (Scheme 1). FTIR-

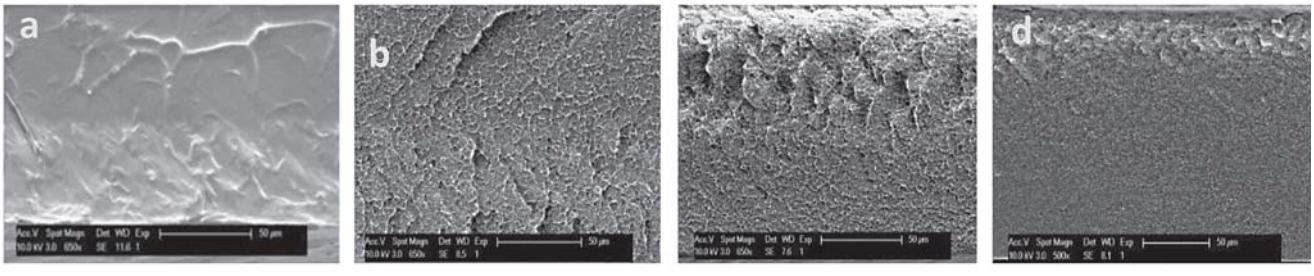

Fig. 1. SEMcross-section of (a) PY-PA membrane & MOF-808 loading (b, c & d) 5, 10 and 15wt %.

Table 1. Gas permeability coefficients (P) and permselectivities (α) values of the MMMs at 35 °C (3.5 bar).

MMMs	$P(CO_2)$	$P(O_2)$	$P(N_2)$	$P(CH_4)$	$\alpha(CO_2/CH_4)$	$\alpha(O_2/N_2)$
PY-PA	42.0	3.20	0.65	1.68	26.00	6.21
MOF-808-PY-PA-5%	55.0	5.28	0.91	1.21	33.50	6.62
MOF-808-PY-PA-10%	65.0	12.2	1.82	1.79	36.20	7.15
MOF-808-PY-PA-15%	91.0	14.1	1.74	2.52	44.30	9.65

P = gas permeability coefficient in barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cm^{-1} Hg^{-1}.

ATR spectroscopic methods were confirmed polymer repeat unit structures for amide group (N-H stretching) in the range of 3325-3276 cm^{-1} and carbonyl group stretching of 1644-1671 cm^{-1} established poly(amide) PY-PA structure.SEM morphology of the prepared MOF-808 showed that octahedral and crystalline MOF particles of an average size 350 nm with which is respectable agreement with the reported literature[6].

The SEM cross sections morphology of the pure polymer and the MOF-808/PY-PA membranes were showed by the SEM images in Fig. 1a-d. Fig.1 suggest a good incorporation of the particles in polymer matrix. Fig. 1b–d, showed that the MOF-808 are well dispersed in the MMMs at different loadings[7].

Gas Transport Properties: **Effect of Chemical Structures on Gas Transport Properties:** The pure gas permeation measurements of all MMMs were made at 3.5 bar and 293 K. Constant-volume and variable pressure method was used to study the single gas permeability of all the membranes, and the permeability and ideal selectivity values are tabulated in the Table 1 for four different gases (CO_2, O_2, N_2 and CH_4) of the MMMs. The gas permeability of four different gases follow the order of P (CO_2) > P (O_2) > P (N_2) > P (CH_4)[1]. Single gas permeation properties of MMMs was also investigated by changing filler loading (5, 10 and 15 wt%). A growth in the filler loading from 10 wt% to 15 wt% significantly improved the CO_2 permeability from 65 Barrer to 91 Barrer, while the also ideal selectivity from 34 to 44 due to the particle dispersion in the MMMs. The free volume of the membrane enhanced by introduction of MOF-808, thereby enhancing the diffusion capability of CO_2 within the membrane results selectivity increases.

Comparison of Gas Permeabilities of MMMs with Structurally Related Polymer Membranes: The gas permeability and perm selectivity values of these MMMs PAs (MOF-808/PY-PA-5-15%) was compared with different commercially available polymers (e.g., Matrimid®, Extem® and Ultem®)[5]. CO_2/CH_4 permselectivity vs. CO_2 gas permeability (Fig. 2) have been obtained in terms of the Robeson plots for better comparison. The addition of the filler pointedly improved the overall performance of the membranes MOF-808-PY-PA-15% shows permeability of CO_2 gases with an improvement in perm selectivity than other structurally analogous PAs, although the Robeson upper bound is not exceeded[8].

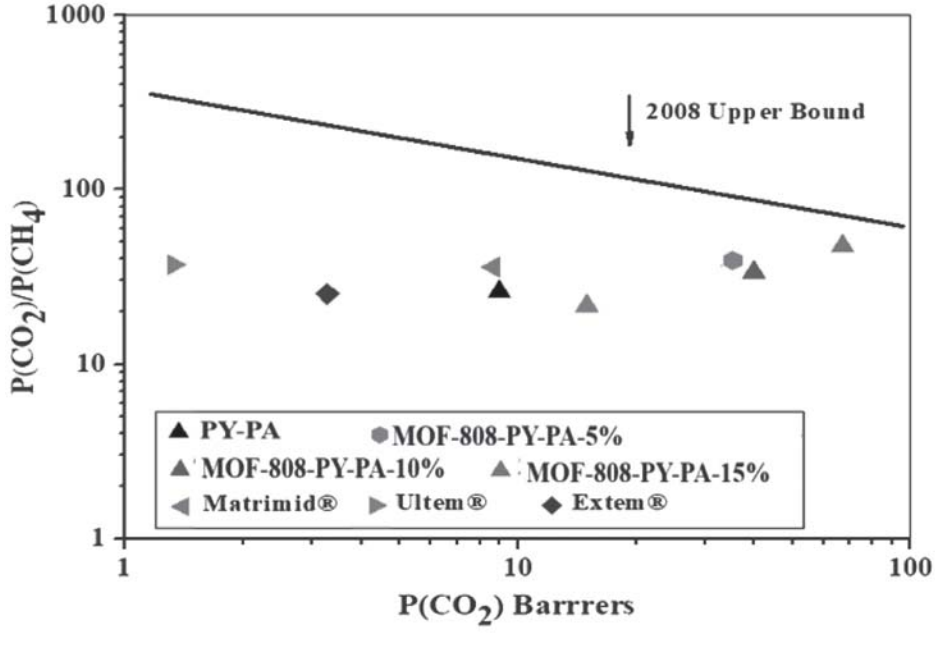

Fig. 2. Robeson plot of selectivity CO_2/CH_4 vs. permeability coefficients CO_2.

Conclusions

In summary, MMMs construction of MOF-808 as filler materials added into polymer matrix for effective separation of CO_2/CH_4. MOF-808 show a vital role in the performance of the MMMs. A fluorinated PY-PA membranes containing pyridine moiety was shared in polymer backbone to studied their properties. The obtained MOF-808/PY-PA MMMs exhibit improved gas

permeation performance related with the pure PY-PA membrane. The optimum CO_2 permeability (91barrer) and ideal selectivity (44.3) are realized by the MMM loaded with only 15.0% MOF-808 compared to those of the PY-PA membrane.

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