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ZIF-67 Nanosheet/Polyamide (PA) based Mixed-Matrix Membranes for efficient CO_2/CH_4 separation

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Abstract

Mixed matrix membranes (MMMs) were prepared from Semi fluorinated aromatic polyamide (PA) as matrix phase and filler ZIF-67 nanosheets (NS) as spread medium for separation of CO_2/CH_4. An ordered microporous framework of integral ZIF-67 nanosheets (NS) filler was used for membrane preparation. The morphology of ZIF-67 is flake like with incorporation 3%, 6%, 9% and 12% weight percent of loading in polymer. 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 filler to Mixed-matrix preparation which is a promising technique in current scenario. The ZIF-67 nanosheets MOF-808 play a crucial part in defining the performance of MMMs. Characterization technique like XRD, DSC and SEM were used to clarify properties and structure of MMMs. Single-gas permeation data showed that ZIF-67 filler of 12 wt% loading incorporated in the polymer matrix increased the selectivity and permeability. This study provides a feasibly rational design of MMMs in membrane separation scenarios.

IndexTerms - Poly(amide), ZIF-67 nanosheets (NS), Gas permeability and Mixed-matrix membranes.

1. Introduction:

Membrane separation technology is an attractive technique for CO_2 separation due low cost, and simple operation energy operative equipment investment.[1] For gas separation Polyamide (PA) membranes have been mainly explored as a matrix with excellent thermal stability and chemical. Membranes polymeric materials are suffering from a trade-off relationship between selectivity and gas permeability, i.e. 2008 Robeson upper bound. To discontinuity the Robeson upper bound strategies like hybrid polymer have been explored. The dual role properties of polymer membranes and filler particles in mixed matrix membranes (MMMs) affect gas separation.[2] Fillers like metal-organic frameworks (MOF) and zeolitic imidazolate frameworks (ZIFs) have been widely used. ZIFs a subclass of MOFs, composed of Zn and Co transitional metals connected via imidazole-based linkers which offer outstanding affinity with polymer matrix.[3] ZIF- 67 has a pore size of about 0.34 nm formed by bridging 2-methyl imidazolate anions and cobalt cations matches with kinetic diameters of CO_2 (0.33 nm). ZIF-67 has a perfect pore size of $CO_2$and selective adsorption abilities combine with the MMMs enhanced performance of CO_2 separation in polymers. The ZIF-67 NS has stable [211] crystal face with polyhedral morphology improves the oriented nanosheets (NS).[3] The ZIF-67 NS loading ratios in polymer matrix of MMMs are characterized via morphology MMMs and studied gas permeation. The membrane with MOF loading ratio of 12.0 wt% performs a highly improved gas separation performance owing to the nanosheets morphology. Single gas permeability tests of CH_4, N_2, O_2 and CO_2 through the MMMs have been tested.[4] Incorporating ZIF-67 NS in MMMs significantly enhances separation performance of CO_2/CH_4 gases.

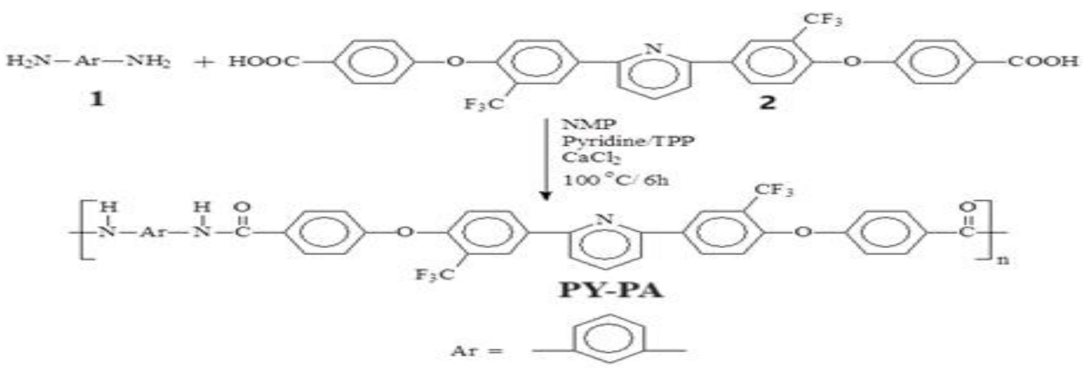
2. Experimental

2.1. Materials, Membrane Characterization & Gas Separation Measurements

2-Methylimidazole (MeIm), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and N, N-dimethylformamide (DMF) were purchased from SD Chemicals. 2,6-bis[3'-trifluoromethyl-4'(4" carboxyphenoxy)benzyl]pyridine (2) acid[4] has been prepared reported earlier. m-Phenyl diamine monomer was purchased from SD Chemicals, India. 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 (thickness around 60-80 µm) at 3.5 bar of applied gas pressure and at 35 °C. The permeability coefficient, ideal perm selectivity (α), were resolute as stated by earlier literature.[4]

2.2. Polymerization

The aromatic diamine, Triphenylamine (1) was reacted with dicarboxylic acid monomer (2) in equal molar ratio with NMP as solvent and $CaCl_2$, pyridine and TPP, as condensations agent (**Scheme 1).** For polymerization of PY PA a mixture of m- triphenylamine (6.87 g, 6.22 mmol) (1) and dicarboxylic acid, 2,6-bis[3'-trifluoromethyl-4'(4" carboxyphenoxy)benzyl]pyridine (2) (0.414 g, 6.87 mmol), 0.23 g calcium chloride, 6 mL NMP, 1.4 mL pyridine and 1.2 mL, 6.32 mmol of TPP were in a 50 mL R.B. flask associated with condenser. Nitrogen atmosphere was used through the process. The magnetic stirrer used for stirring in heating condition for 6 h at 110 °C. The highly viscous solution was poured in methanol (500 mL). Fibrous polymer was obtained with constant stirring.[4]



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

2.3. Preparation of ZIF-67 nanosheets

Deionized water 20 mL, Ethanol 20 mL, DMF 20 mL and $Co(NO_3)_2 \cdot 6H_2O$ (2.0 g) were mixed under stirring. After that MeIm (0.5 g) was added. After dissolution the MeIm and the solution mixture moved into a 100 mL stainless steel autoclave (Teflon-lined) at 160 °C temperature. Solution mixture was maintained 12 h. After completion of reaction, solution was cooled. The final product collected through centrifugation and washed. Under vacuum ZIF-67 NS were dried for 24 h at 120 °C.[5]

2.4. Polymeric Membrane Preparation

Polymer 10-15% (w/v) is dissolved by DMAc solvent and formed a homogeneous solution. Homogeneous solution cast onto clean glass Petri dishes and polymeric membrane was formed. The Petri dishes kept at 80 °C and put it in oven for overnight. Oven temperature heated to 150 °C and maintain temperature for 6h. The obtained polymer membranes were put in hot water. Flexible polymer membrane thickness varied from 60-80 µm. **Table 1** summarized physical properties of the polymeric membrane**.** Fractional free volume (FFV) determine from the density values (ρ) of the polymers by using the following Eq. $FFV = (V-1.3V_w)/V$ where V is the specific volume ($V = 1/\rho$), V_w = vander Waals volume.[6]

2.5. Preparation of ZIF-67 NS-PY-PA MMMs

0.4 g Polymer membrane (PY-PA) was dissolved in DMF of 3 mL solution. DMF solution was used for dispersion of ZIF-67 NS by ultrasonication and stirring for 30 min. Polymer solution was added to the ZIF-67 NS suspension with constant stirring for 2 h. MOF suspension was stirred overnight. The membranes casted in clean glass Petri dishes. The Petri dishes was placed in an oven heated at 80 °C overnight, followed by slow heating to 150 °C and then kept for 6h.[5] Membrane thickness obtained from 60-80 µm. The MMMs weight ratio kept constant by using this formula filler/(filler + polymer). Weight percent of loading of ZIF-67 NS fillers in MMMs were changed to 3%, 6%, 9% and 12%.

3. Results and discussion

3.1. Preparation polymer and their properties

Polyamide Prepared by the polycondensation reaction of the dicarboxylic acid monomer (2) with aromatic diamine monomer (1) shown in **Scheme 1**. Elemental analyses, FTIR-ATR and NMR spectroscopic confirmed Polymer structures. Amide group characteristic absorption bands of 3325-3276 cm^{-1} for N-H stretching and 1644-1671 cm^{-1} for carbonyl group stretching in the FTIR-ATR spectra confirmed the polymer structures. ^{1}H-NMR spectra also confirm polymer repeat unit structures. ^{1}H-NMR spectrum recorded in pyridine-d_5. The singlet proton at 11.39 ppm for amide proton obtained from ^{1}H-NMR spectra. Polymrs Physical properties are enlisted in Table 1. The data's are almost consistent with our previously reported results.[4]

Table 1. Properties of the polyamide

Polymer	η_{inh} (dL g^{-1})[a]	Density (g cm^{-3})[b]	V_w (cm^3 mol^{-1})[c]	T_{d10} (°C)[d]	T.S. (MPa)[e]	FFV
PY-PA	0.37	1.228	318.7	407	79.0	0.117

[a]η_{inh} = inherent viscosity. [b]Density (g cm^{-3}) at 30 °C. [c]V_w = Vander Waals volume, [d]10% degradation temperature measured by TGA. [e]Tensile strength. FFV = Fractional Free Volume.

3.2. Morphology: Synthesis of Nanoparticles of ZIF 67 NS

Synthesized ZIF-67 samples showed in the XRD spectra of **Fig. 1** the, indicates that the ZIF-67 structure was successful synthesis. The [211] and [422] crystal faces of ZIF-67 shows two main peaks at 13° and 26° observed in XRD spectra. Spectra validates that along [211] crystal face the ZIF-67 NS grows, steady with literature results.[5]

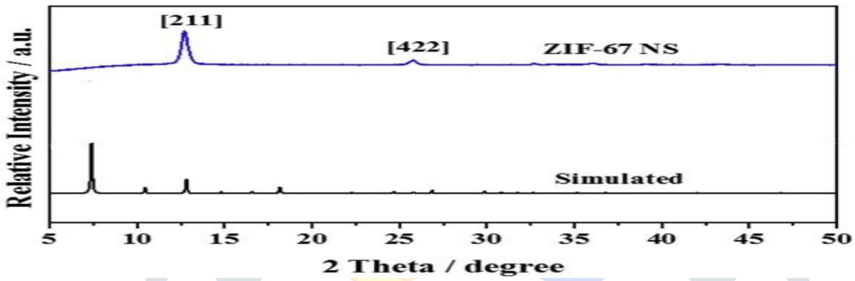


Fig. 1. XRD patterns of ZIF-67 NS.[5]

Fig. 2 shown in SEM image proves the morphology of stacked layer nanosheet. Solvent (DMF and ethanol) provides porous and rough surface structure because corrosion from the solvent and coordination recombination between cobalt ion and imidazole group. Nucleation and growth of ZIF-67 crystal occurs due to meetings of cobalt ions meets with MeIm at room temperature. Efficiency of molecular level of membrane contribute to insight and selectivity of membrane shows uniformity of previous reported results.[5]

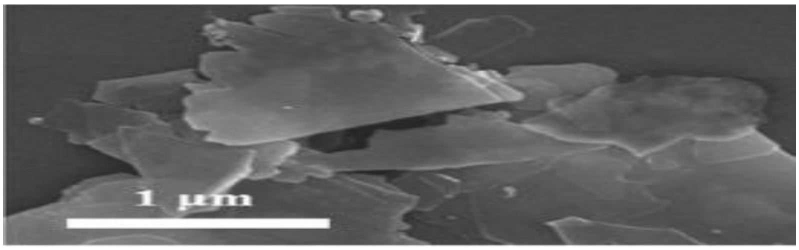


Fig. 2. SEM images of ZIF-67 NS.[5,7]

3.3. Processing of Mixed Matrix Membranes

TGA (Fig. 3) curve shows the thermal stabilities of PY-PA and PY-PA/ZIF-67 NS MMMs. Weight loss of all membranes fall in range of 305 °C and 435 °C because of decomposition of main chain of polyamide. Membranes are stable up to 300 °C, representing good latent capacity as a result it can be used in industrial claims.

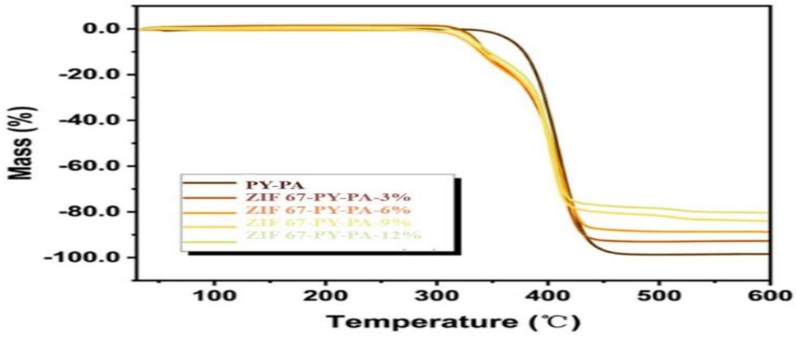


Fig. 3. TGA curves of ZIF 67-PY-PA-12% MMMs.[5,7]

SEM images in **Fig. 4a-c** shows the morphology of top-view of the pure polymer and the ZIF-67-NS/PY-PA membranes. Fig. 4a shows that pure membrane (PY-PA) has a smooth surface and rougher surfaces for ZIF-67-NS/PY-PA membranes. Main reason for this observation is minimization of intermolecular hydrogen bonds as loading of ZIF-67 in polymer matrix. Fig. 4b–c, shows that at low loadings of ZIF-67 NS distributed well in the polymer matrix.[7] At 12.0 wt % loading on the membrane agglomeration of ZIF-67 occurs.[8] SEM image revels that ZIF-67 is well-matched in polymer, due to ZIF-67 has electron-rich properties for strong electrostatic interactions with polymer.

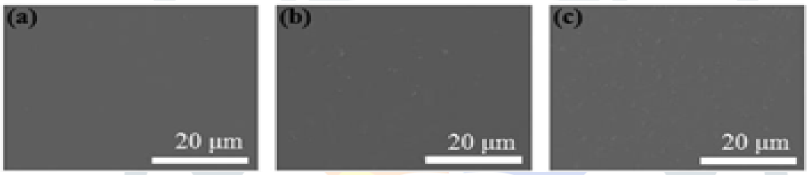


Fig. 4. SEM images of (a) pure PY-PA membrane and MMMs with different ZIF-67 loading (b & c) 3 and 9 wt %.[5,7,8]

3.2. Transport properties

3.2.1. Effect of ZIF 67 in gas transport properties

The pure gas permeation measurements of all MMMs were made at 3.5 bar and 293 K. Permeability and ideal selectivity values were measured using the constant-volume method, and for four CO_2, O_2, N_2 and CH_4 gases through MMMs and tabulated in the **Table 2.** Gas permeability follow the order of P (CO_2) > P (O_2) > P (N_2) > P (CH_4); which follow their kinetic diameter, CO_2 (3.3 Å) < O_2 (3.46 Å) < N_2 (3.64 Å) < CH_4 (3.8 Å).[7] Solution-diffusion model follow transport mechanism. Permeability of the MMMs membrane knowingly enhances by incorporation of ZIF-67 NS. ZIF-67 NS particle dispersed properly in MMMs which in turn increases CO_2/CH_4 selectivity at loading (0 wt % to 12.0 wt %). At 10 wt% loading shows highest selectivity because of decent interactions between the filler and the polymer matrix.[9] CO_2 molecules interact nitrogen atoms on the imidazole ligands in ZIF-67 as a result CO_2 solubility increases which increases selectivity increased interactions, hence sorption, in a polar environment like the ZIF-67 NS framework.

Table 2. Gas permeability and permselectivities values of the MMMs.

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	44.0	3.20	0.65	1.68	26.00	6.21
ZIF 67-PY-PA-3%	62.0	5.18	0.95	1.31	36.50	6.62
ZIF 67-PY-PA-6%	68.0	13.1	1.55	1.56	37.50	7.03
ZIF 67-PY-PA-9%	76.0	14.2	1.72	1.72	38.20	7.65
ZIF 67-PY-PA-12%	82.0	16.1	1.82	2.22	41.30	9.05
Matrimid	8.70	1.90	0.27	0.24	36.00	7 .00
Ultem	1.33	0.41	0.05	0.03	36.90	8.00
Extem	3.28	0.81	0.13	0.13	25.20	6.20

[a]Gas permeability coefficient measured in barrer.

3.2.2. Corelation of gas permeabilities of MMMs with membranes

Fig. 5 is Robeson plots indicates CO_2/CH_4 permselectivity vs. CO_2 gas permeability. In Robeson plots our prepared membranes were compared with other reported membranes. All prepared membranes showed comparable or higher gas permeability and permselectivity and the values touches upper bound. The permselectivity data's of ZIF-67-PY-PA-12% for CO_2/CH_4 pairs were attributed to diffusivity selectivity values. The prepared MMMs showed gas-separation performance in terms Robeson's upper bound.[4]

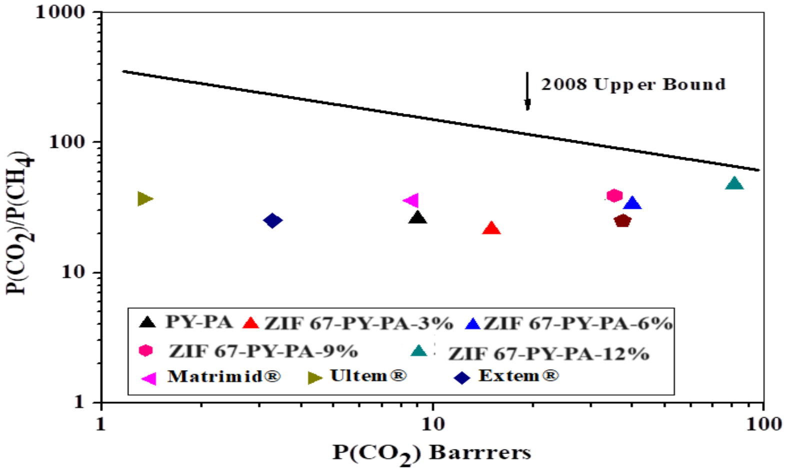


Fig. 5. Robeson plot of CO_2/CH_4 selectivity vs. CO_2 permeability.

4. Conclusions

Filler ZIF-67 Nanosheet used into the building of MMMs for effective CO_2/CH_4 separation. ZIF-67 Nanosheet play a vital part in the presentation of the MMMs. A fluorinated PA membranes comprising pyridine moiety moiety was combined in polymer spine to studied their properties. Mixed-Matrix Membranes (MMMs) were prepared by solvent evaporation with Semi fluorinated Polyamide (PY-PA) as base polymer and ZIF-67 as filler. The CO_2 permeability of 82 barrer and ideal selectivity of 41.3 are appreciated due to MMM loading of 12% ZIF-67 NS related pure membrane. Structural belongings of the ZIF-67 NS were attributed to increase selectivity and permeability. Approach of construction current membranes in gas separation ZIF-67 as filler might suggest a new direction.

5. Acknowledgment

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