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SAPO-34 Zeolites/Polyamide (PA) Mixed-Matrix Membranes with Enhanced CO_2/CH_4 Separation Performance

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Abstract

A novel mixed-matrix membrane (MMM) comprising semi-fluorinated aromatic polyamide (PA) and Submicron SAPO-34 zeolites filler was synthesized and evaluated for gas separation capabilities targeting CH_4, N_2, O_2 and CO_2. Mixed-matrix formulations represent a promising strategy to mitigate the permeability-selectivity compromise inherent in polymer membranes by integrating fillers. The properties of the filler are pivotal in dictating the performance of MMMs. MMMs were synthesized with varying weight percentages (0%, 5%, and 10%) of Submicron SAPO-34 zeolites filler incorporated into the semi-fluorinated PA matrix. The MMM incorporating 10 wt% Submicron SAPO-34 displayed CO_2 permeability and a selectivity of 44.20 for CO_2/CH_4 gas pairs, showcasing enhanced CO_2/CH_4 separation performance credited to the existence of Submicron fillers. SEM imaging confirmed the uniform combination of Submicron SAPO-34 filler into the polyamide matrix. This investigation presents a promising pathway for developing efficient and high-performance separation membranes.

Keywords: *Gas Permeability; Mixed-matrix Membranes; Poly(amide); SAPO-34*

Introduction

Membrane technology has developed as a proficient process for gas separation, due to the advantageous combination of cost-effectiveness, straightforward processing, and the innovative nature inherent in polymer materials (Usman, 2022). Particularly within the realm of gas separation, the operation of polymeric membranes for CO_2 separation has garnered significant attention due to its diverse potential applications, including carbon capture and natural gas refinement. Membranes are commonly categorized into groups based on their material composition: inorganic, polymeric and mixed organic-inorganic materials. Polymer membranes are favoured in manufacturing applications due to their low production prices, decent mechanical strength, flexibility, informal processing, and toughness related to inorganic membranes (Cardoso *et al*., 2023). However, they face limitations in gas separation performance, often characterized by the Robeson upper bound limit, which represents a trade-off between permeability and selectivity. Mixed matrix membranes (MMMs) offer a possible solution by incorporating high-execution zeolites, inorganic molecular sieves, into polymer matrices to enhance

separation performance (Cardoso *et al*., 2024a). MMMs combine the rewards of polymeric membranes with greater separation performances, surpassing the upper bound limits by Robeson. The addition of inorganic fillers to the matrix is anticipated to improve membrane belongings beyond those of consistent polymer membranes. The creation of MMMs often encounters challenges in weak filler-polymer matrix contact and poor filler distribution within the polymer matrix phase (Cardoso *et al*., 2024a). Polyamides (PAs) have been extensively studied as matrices for gas separation membranes due to their excellent chemical and thermal stability, as well as the selectivity of glassy polyimides, making them suitable for various gas separation processes, especially CO_2 separation. MMMs, which combine with polymer membranes and filler particles, exhibit an inclusive variety of gas separation application prospects. Crystalline zeolites (Hassan *et al*., 2023) inorganic structures possess of molecular dimensions formed by TO_4 (T = Si, Al, or P) with uniform-sized pores and are widely employed in adsorption and separation processes (Usman, 2022). SAPO-34 zeolite, CHA structure as a silicoaluminophosphate is shaped by the neutral $AlPO_4$ framework of Si atoms. The chemical composition of SAPO-34 is represented as $(Si_xAl_yP_z)O_2$, where x = 0.01–0.98, y = 0.01–0.60, z = 0.01–0.52, and x + z = y. SAPO-34's structure comprises eight-membered rings with a diameter of 9.4 Å (3.8 × 3.8), exhibiting unique shape selectivity, molecular sieving properties with a pore diameter of 0.38 nm, close to the kinetic diameter of CH_4, and a strong CO_2 adsorption capacity (Cardoso *et al*., 2024b). Its microporous nature, with a zeolitic pore volume of 0.310 $cm^3\ g^{-1}$ and pore sizes of 3.8 Å, makes it suitable for the adsorption of gas molecules (Carter *et al*., 2017). SAPO-34 possesses an approximate BET surface area of 600 $m^2\ g^{-1}$. The impact of adding SAPO-34 as a filler on the gas permeation properties of other polymers such as polyetherimide (Mirfendereski & Mazaheri, 2024), PEBAX, polyethersulfone, and polysulfone has been investigated (Ignatusha *et al*., 2024).

Cardoso *et al*. (2024a) investigated the combination of SAPO-34 with polyethersulfone (PES), observing significant enhancements in CH_4, CO_2 and H_2 permeabilities, albeit at the expense of decreased CO_2/CH_4 ideal selectivities. (Peydayesh *et al*., 2013; Alibak *et al*., 2022) developed SAPO-34/Matrimid 5218 MMMs, demonstrating notable improvements of 97% and 55% in permeability of CO_2 and selectivity of CO_2/CH_4, respectively, highlighting effective filler-polymer medium adhesion. (Carter *et al*., 2017) fabricated MMMs utilizing silica, SAPO-34, and ZIF-8, attributing pore size as the primary factor influencing gas permeability, with increased permeability observed. (Messaoud *et al*., 2015) reported a technique of dip-coating for SAPO-34/polyetherimide MMMs, attaining optimal molecular filtering routine with 5 wt% SAPO-34 MMMs, exhibiting high CO_2 permeability and selectivity. Zhao *et al*. (2014) discussed SAPO-34/Pebax1657 MMMs fabricated via solvent evaporation, wherein SAPO inclusion notably enhanced CO_2 permeability while maintaining constant selectivity. Santaniello

et al., (2020) described the incorporation of 200 nm SAPO-34 in a polyhexafluoropropylene PHFP matrix, resulting in MMMs with improved selectivity and permeability.

Despite extensive research on MMMs utilizing SAPO-34 for CO_2/CH_4 separation, there is limited investigation into incorporating particles into the semifluorinated aromatic polyamide (PA) matrix and the influence of SAPO-34 on the performance of membrane gas separation. This study goals to explore the effects of PA, SAPO-34 on final separation properties, specifically focusing on PA/SAPO-34 influences for CO_2/CH_4 parting. Characterization of MMMs with varying SAPO-34 loading ratios includes assessing structure, morphology, and gas permeation properties. Notably, membranes with a lesser Zeolite cargo ratio of 10.0 wt% exhibit significantly improved performance compared to pristine polymer membranes. Permeation tests (CO_2, CH_4, N_2 and O_2) are conducted on prepared MMMs, demonstrating the significant promotion of CO_2/CH_4 gas separation performance by incorporating SAPO-34 into PA. Furthermore, the study investigates the effects of SAPO-34 cargo on MMM construction and permeation belongings using Differential Scanning Calorimetric (DSC) techniques and scanning electron microscopy (SEM).

Experimental

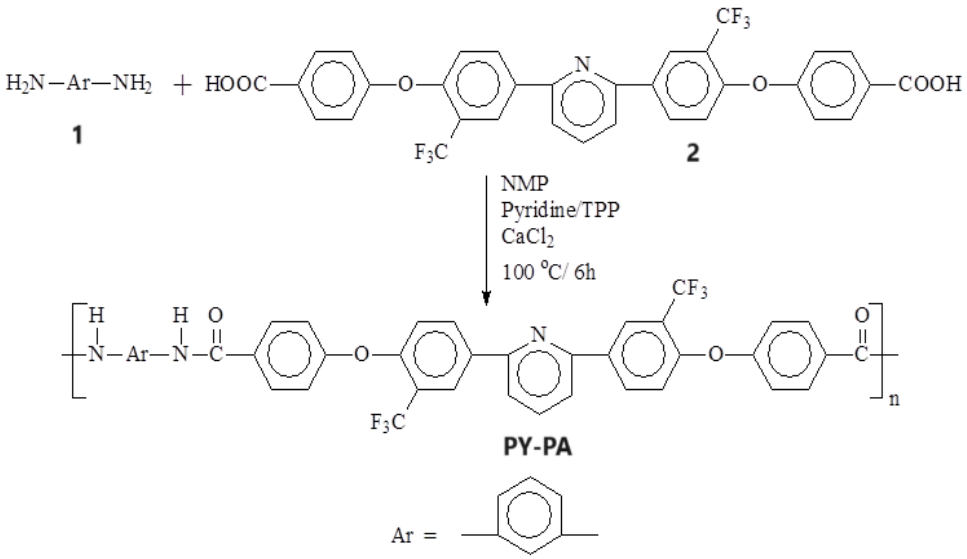
Materials, Membrane Characterization and Gas Separation Measurements

SAPO-34 zeolite synthesis utilized phosphoric acid (H_3PO_4, 85 wt% aqueous solution, Merck), aluminum triisopropylate ($Al(i\text{-}C_3H_7O)_3$), tetra-ethyl ammonium hydroxide (TEAOH, Merck), and Ludox AS-40 colloidal silica sol (SiO_2, Aldrich). The synthesis of 2,6-bis[3'-trifluoromethyl-4'(4'' carboxyphenoxy)benzyl]pyridine (2) acid was earlier described (Bisoi *et al*., 2015). The m-phenyl diamine monomer was procured from SD Chemicals, India. The permeation of O_2, N_2, CO_2 and CH_4 gases was restrained over the polymer membranes utilizing an automated Diffusion Permeameter (DP-100-A) manufactured by Porous Materials, Inc., USA, at a temperature of 35°C and functional gas pressure of 3.5 bar.

Polymerization

Aromatic diamine, Triphenylamine (1), was reacted with a dicarboxylic acid monomer (2) in a 1:1 molar ratio with NMP as a solvent and triphenyl phosphite (TPP), $CaCl_2$, and pyridine, as illustrated in Scheme 1. The polymerization (PY PA) proceeded as follows: a mixture of the diamine, m-triphenylamine (0.686 g, 6.01 mmol) (1), and 2,6-bis[3'-trifluoromethyl-4'(4''-carboxyphenoxy)benzyl]pyridine (2) (0.494 g, 6.01 mmol), $CaCl_2$ (0.25 g), pyridine (1.2 mL), NMP (3 mL) and TPP (1.2 mL, 4.94 mmol), in a round-bottom flask and reflux condenser. The blend was intense at 110°C for 6 hours. Subsequently,

the mixture was transferred to methanol, resulting in the formation of a fibrous polymer. The fibrous polymer (PY-PA) was then dried in a vacuum (Bisoi *et al*., 2015).



Scheme 1: Preparation of the poly(amide)s (PY PA) (Bisoi *et al*., 2015)

SAPO-34 zeolite synthesis

The hydrothermal technique was used for SAPO-34 zeolite synthesis. Initially, silica and tetraethylammonium hydroxide (TEAOH) were allowed to hydrolyze for 16 hours at room temperature. Subsequently, aluminum triisopropylate $Al(OiPr)_3$ was stimulated for 15 minutes in water, and phosphoric acid (H_3PO_4) was supplementary dropwise to form an alumina gel. The 1.0 Al_2O_3:1.0 P_2O_5:0.3 SiO_2:1.2 TEAOH:60 H_2O molar composition was used. A teflon-lined, stainless steel autoclave is used for crystal formation and growth. The product was recovered by centrifugation at 2700 rpm for 10 hours. The precipitate was dried (Messaoud *et al*., 2015).

Polymeric Membrane Preparation

Polymeric membranes were cast in clean glass Petri dishes at 80°C and 150°C in an oven 6 hours. Membranes were extracted from Petri dishes in hot water. Membranes were dried under vacuum at 160°C for 4 hours. The flexible membranes were obtained.

Physical properties are summarized in Table 1 for membranes. The fractional free volume (FFV) is calculated using the equation $FFV = (V-1.3V_w)/ V_w$, where V represents the specific volume ($V = 1/\rho$), density values (ρ). The Hyperchem computer program was used for van der Waals volume (V_w) calculation (Hypercube, 2019).

Preparation of SAPO-34 MMMs

For mixed matrix membranes (MMMs) preparation, PY-PA solution was dissolved in DMF of 0.6 g of polymer. Ultrasonication is used for the dispersion of SAPO-34 in DMF. A polymer solution was added to the SAPO-34 suspension and stirred overnight. Membranes were fabricated by casting the homogeneous polymer solution in DMF onto clean glass Petri dishes. And heating to 80°C to 150°C continued for 6 hours. This process yielded free-standing, stretchy membranes. To maintain consistency, the weight ratio of filler to total filler and polymer was kept constant for MMMs. MMMs were arranged with SAPO-34 loadings of 0%, 5%, and 10% by weight of the fillers. This approach ensured the systematic investigation of the belongings of varying SAPO-34 loading (Nawaz *et al*., 2024).

Results and Discussion

Polymer Synthesis and Their Properties

Polyamide was produced via the typical polycondensation-based phosphorylation with dicarboxylic acid (2) and diamine (1) (Scheme 1). Repeat unit structures of polymers confirmed NMR. The polymer repeat unit structures were consistent with ^{1}H-NMR spectra. The ^{1}H-NMR spectrum in pyridine-d_5 of PY-PA displayed a singlet above 11.39 ppm (amide proton). Physical properties were found to be consistent with the previously reported results (Bisoi *et al*., 2015).

***Table 1**: Physical properties of the polyamide*

Polymer	η_{inh} (dL g^{-1})[a]	Density (g cm^{-3})[b]	V_w (cm^3 mol^{-1})[c]	FFV
PY-PA	0.37	1.228	318.7	0.117

[a]η_{inh} = inherent viscosity at 30 °C. [b]Density measured at 30 °C. [c]V_w = Vander Waals volume, FFV = Fractional Free Volume (Bisoi et al., 2015).

Morphology: Synthesis of Nanoparticles of SAPO-34

Figure 1 illustrates the XRD spectra, showcasing the distinctive peaks of pure SAPO-34. High crystallinity specifies the synthesis of zeolite. Clearly visible in the picture are the cubic crystals of SAPO-34, aligning with previously reported findings (Wang *et al*., 2024). The sheet-like morphology in the SEM image depicted in Figure 2 confirms SAPO-34 crystals. Crystals exhibit an average length of 750 nm and a thickness of 75 nm. These observed particles display flat outer tops with a cubic morphology, distinguishing the crystals of SAPO 34. This observation aligns with the conclusions stated by Wang *et al*. (2024). Additionally, Messaoud *et al*. (2015) demonstrated the fabrication of both plate-like and cubic SAPO-34 morphologies. Initially, plate-like SAPO-34 is produced for use as seeds, followed by the formation of cubic SAPO-34.

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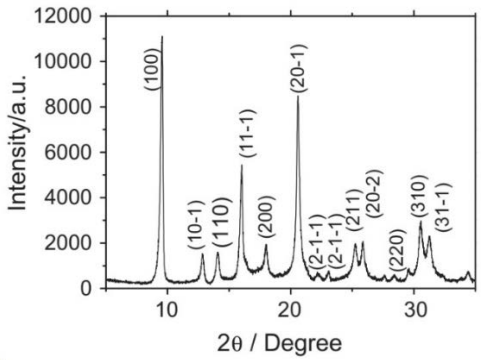

Figure 1: XRD patterns of SAPO-34 *(Messaoud et al., 2015)*

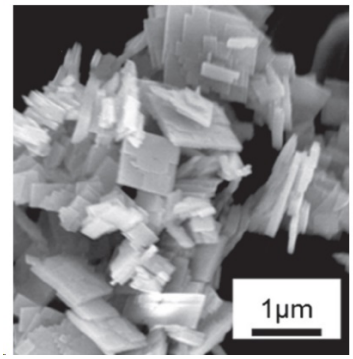

Figure 2: SEM images of SAPO-34 *(Messaoud et al., 2015)*

Processing of Mixed Matrix Membranes

Notably, the glass transition temperature (T_g) values ranged from 274 to 278ºC in DSC subversions (Figure 3), with no idea of crystallization temperatures. The T_g of pristine PY-PA was determined to be 274°C, consistent with previously reported findings. Disturbance in the stacking of polymer matrix is the reason for increased T_g values, which suggest the incorporation of SAPO-34 (Peydayesh *et al*., 2013).

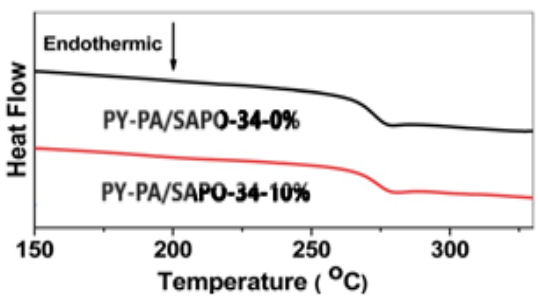

Figure 3: DSC curves of the MMMs *(Bisoi et al., 2015)*

The surfaces of the obtained MMMs are depicted in Figure 4. Both the PY-PA/SAPO-34-0% and PY-PA/SAPO-34-5% membranes exhibit no inadequacies and display similarity throughout the membrane. MMMs with distributed SAPO-34 crystals in the medium boost the performance of the membrane. However, the PY-PA/SAPO-34-10% membrane exhibited particle agglomeration. In Fig 4c, agglomeration ascends due to incompatibility between the SAPO-34 and matrix.

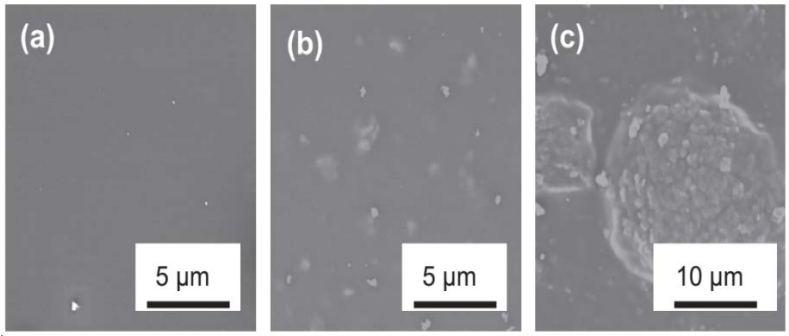

Figure 4: SEM images of PY-PA/SAPO-34 membranes with SAPO-34 loading of (a, b & c) 0 wt %, 5 wt % and 10 wt % (Usman, 2022)

Gas permeation

Effect of SAPO 34 on gas permeation properties

The gas permeation measurements of all MMMs were conducted at 3.5 bar and 293 K. The constant-volume method used for checking permeability of all the membranes of different gases (O_2, N_2, CO_2 and CH_4) in the MMMs is presented in Table 2. Gas permeability of the four different gases through these MMMs membranes follows the order of P (CO_2) > P (O_2) > P (N_2) > P (CH_4) (Bisoi *et al*., 2015). The solution-diffusion model used for transport mechanisms is broadly reported in the literature. Assimilation of SAPO-34 significantly enhances the permeability of the PA membrane, with an observed increase in gas permeabilities as the SAPO-34 concentration increases. This enhancement is attributed to SAPO-34's sieve effect on the gas molecule. The increased selectivity of CO_2/CH_4 with growing SAPO-34 loading (0 wt % to 10.0 wt %) is attributed to the decent dispersion of particles in MMMs. Mesopores in matrix pass gas molecules enhanced ideal CO_2/CH_4 selectivity.

***Table 2**: Gas permselectivities and permeability of the MMMs*

MMMs	P(CO_2)	P(O_2)	P(N_2)	P(CH_4)	α(CO_2/CH_4)	α(O_2/N_2)
PY-PA/SAPO-34-0%	65.0	12.2	1.59	1.54	36.50	7.86
PY-PA/SAPO-34-5%	78.0	13.9	1.77	1.65	37.30	7.79
PY-PA/SAPO-34-10%	80.0	14.1	1.91	2.33	44.20	9.13

P = gas permeability coefficient in barrer

Corelation of gas permeabilities of MMMs with membranes

The gas permselectivity, permeability and values of these MMMs (PY-PA/SAPO-34-0-10%) were related to the other polymers Matrimid, Extem, and Ultem (Bisoi *et al*., 2015). A thorough comparison of CO_2/CH_4 permselectivity vs. CO_2 gas permeability (Figure 5) and O_2/N_2 permselectivity vs. O_2 gas permeability (Figure 6) was conducted to obtain a better understanding through Robeson plots (Robeson, 2008). The data in Robson's line

touches indicate the separation capability of the membrane. In general, combination permeability and higher selectivity were observed for MMMs. The prepared membrane revealed better permeability than previously reported polymers. Here, the data's of MMMs in Robeson's upper bound was not surpassed, though the overall performance of the MMMs significantly improved. PY-PA/SAPO-34-10% displayed improved CO_2 gas permeability along with an enhancement in permselectivity compared to PAs. The optimal performance of MMMs was achieved with the highest SAPO-34 zeolite loading of 10wt%. These PAs demonstrated notable enhancements in gas-separation performance, as evidenced by their Robeson's trade-off points in the upper bound.

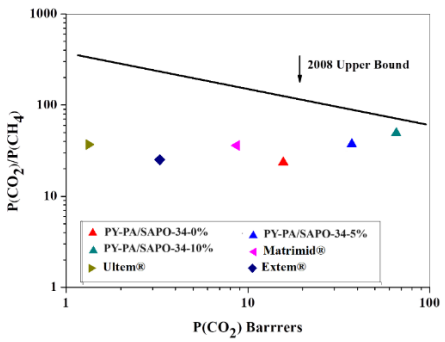

Figure 5: Robeson plot of CO_2/CH_4 selectivity vs. CO_2 permeability *(Bisoi et al., 2015)*

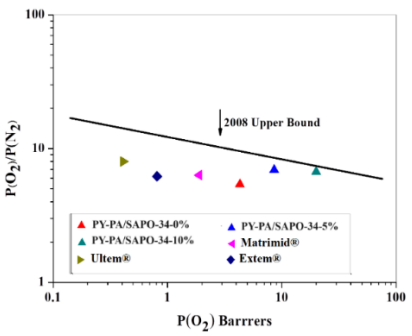

***Figure 6**: Robeson plot of O_2/N_2 selectivity vs. O_2 permeability* (Bisoi et al., 2015)

Conclusion

In summary, mixed-matrix membranes (MMMs) comprising semi-fluorinated polyamide (PY-PA) as the base polymer, along with incorporated SAPO-34, were prepared via a solvent-evaporation method. SAPO-34 filler materials were introduced to boost the proficiency of CO_2/CH_4 separation in the MMMs. SAPO-34 played a pivotal role in determining the performance of the MMMs. A fluorinated PA membrane containing a pyridine part in the polymer spine was hired to study its properties in combination with SAPO-34. Among the membranes tested, the one with 5 wt% SAPO-34 demonstrated a clear molecular sieving effect and exhibited the highest performance, with a permeability of CO_2 of 80 Barrer and a selectivity of CO_2/CH_4 of 44.2. The above findings suggest that PY-PA/SAPO-34 MMMs hold promise for gas separation applications. The preparation protocol employed for the MMMs occasioned in a uniform dispersal of SAPO 34 within the PY-PA. The experimental increase in permeability with growing SAPO-34 cargoes was attributed to the operational properties of SAPO-34, which exhibited excellent chemical compatibility with PY-PA. This innovative approach of incorporating SAPO-34 as filler materials into PY-PA-based MMMs presents a promising pathway for the enterprise of advanced membranes tailored for sustainable applications in gas transportation.

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