Synthesis and Characterization of ZIF-8 Filler for Preparation of Mixed Matrix Membrane

R.M. Abhang, K.S. Wani, V.S. Patil

Abstract— Development of mixed matrix gas separation membranes by utilizing nano sized inorganic particle with polymer matrix is new approach for improving the separation properties of polymeric membranes. To overcome the several challenges of mixed matrix membrane (MMM) like dispersion, contact of fillers with polymer, percentage of filler loading, size and shape of crystal, stability of membrane in harsh conditions, selective separation of gases needs to find material in such a way that the permeability of polymer should match with the permeability of inorganic fillers. Zeolitic imidazolate framework (ZIFs) a subclass of metal organic framework is an emerging class of porous solid nano sized crystals comprised of imidazolate linkers and metal ions with structure similar to zeolite. It exhibit permanent porosity and high hydrothermal and chemical stability. Due to their molecular sieving effect, facile syn sis and compatible with the polymers, it reveals its importance during preparation of mixed matrix membrane.

The main focus of this study was to synthesis ZIF-8 nano crystals in water and methanol at room temperature and characterization using x-ray diffraction (XRD) to ensure its size, surface area and crystalline porous nature. The review was taken on the methodology of preparation of mixed matrix membrane, its compatibility with polymer, significance and utilization for gas separation.

Index Terms — Filler, Mixed Matrix Membrane (MMM), Polymer, Synthesis, Significance, Zeolitic Imidazolate Framework (ZIF-8).

1 INTRODUCTION

A relatively new class of family of metal organic framework based on imidazolate linkers known as Zeolitic imidazolate frameworks (ZIFs) are promising crystalline porous materials [1],[2],[3] for many technological applications especially in gas storage, gas separation, and catalysis and chemical sensing, construction of advanced nanotechnology devices [1].

The ZIF-8 nanoparticles exhibit zeolite like structures [4] or tunable framework with ultrahigh porosity, chemical and thermal stability [2], [3], [5]. Generally, divalent metal cations such as Zn, Co and N atoms of bridging imidazolate anions are bonded for ZIF production and M-Im-M (M= Co and Zn) bridges are build with a bond angle of 145^0C [1], [3],[5]. These imidazolate linkers in ZIF framework increases the hydrophobicity [3] of the substance and provides a better interfacial property between the filler and polymer matrix than aluminosilicate zeolites. ZIF-8 has sodalite (SOD) topology with a pore size of 0.34 nm [1], [6], [3]. It has large pores of 11.6 A^0 which is two times larger than SOD zeolites. The pores are accessible through small channels (3.4 A^0). It exhibits thermal stability up 400^0C and it has a BET surface area around 1300 to 1600 m^2/g or even more [1], [6], [4], [3]. The important textural properties of the ZIF-8 found in the literature [4], [7],[3] are as shown in table 1.

Generally, the ZIF-8 crystals in the range of nanometers have been used in -thin films with dual micro- and mesoporosity for selective adsorption and sensing of vapors, supported membranes with random and preferred crystal orientation for gas separation, capillary coatings for the chromatographic separation of alkanes, fabricating porous composite nano fibers by electro spinning [8], [7].

The surface area of inorganic filler material in mixed matrix membranes is an important issue, because the higher the adsorption capacity of filler, the better the gas permeation performance of membranes [4], [9]. It was found that, ZIF-8 has high selective adsorption ability [5] to CO_2 which is attractive property for development of selective membrane materials. CO_2 has a smaller kinetic diameter 0.33 nm and much higher critical temperature compared to N_2 and CH_4 as shown in table 2. The smaller kinetic diameter and high critical temperature (higher condensability) of CO_2 support in higher diffusion and solubility coefficients and hence higher permeability compared to N_2 and CH_4.

Due to its wide range of potential applications, a few studies aimed for production of nanometer sized ZIF-8 crystals and various investigations tried to control the crystal size. Therefore, there are needs to synthysis ZIF-8 to assess nature, size and shape in accordance with the formation of MMM [13]. The main objective of this study was to synthesis the ZIF-8 nano crystals in water and methanol by a one hour stirring method at room temperature, its characterization using XRD and to ensure its compatibility with polymer to fabricate mixed matrix membrane. It is expected that ZIF-8 nanoparticles yield better contact with polymer matrix and reduction in interfacial voids due to their large surface area. Also evaluate the methodology of their significance in fabrication of MMM [7], [3].

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TABLE 1
TEXTURAL PROPERTIES OF THE ZIF-8

MOF Type	Pore topology	Pore diameter (nm)	Specific BET Surface area m^2/g	Approximate Particle size (nm)
ZIF-8	Cage/ Window	1.16 /0.34	1214	170

TABLE 2
GENERAL PROPERTIES OF GASES CO_2, N_2 AND CH_4

Gas	Molecular Mass (g/mol)	Critical Temperature (^{0}K)	Kinetic Diameter (nm)
CO_2	44	304	0.33
N_2	28	126	0.36
CH_4	16	190	0.38

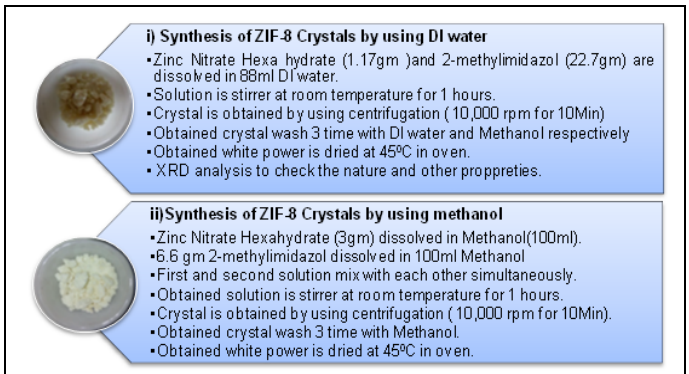

Fig.1. Synthesis methodology of ZIF-8 crystals- i) Using deionized (DI) water ii) Using Methanol.

2. EXPERIMENTAL METHODS

2.1 Materials

Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$], Methanol were obtained from Fisher Scientific and 2-methylimidazole [$C_4H_6N_2$] was obtained from Sigma-Aldrich (India). Deionized water was used as solvent for the synthesis of ZIF-8. All chemicals were used as received without any further purification.

2. 2 Synthesis of ZIF-8

The ZIF-8 crystals were synthesized [9] by the room temperature synthesis method [5] with some modifications by using methanol and deionized water. In this method a solution of 3 gm of [$Zn(NO_3)_2.6H_2O$] in 100 ml of methanol and another solution of 6.6 gm of 2-methylimidazole in 100 ml of methanol were prepared and then mixed with each other under vigorous stirring for one hour at room temperature. After stirring, the resulting ZIF-8 crystals were separated by centrifugation at approximately 10000 rpm for 10 minutes, followed by washing with methanol two to three times. ZIF-8 crystals were dried under vacuum at 45^{0}C for four to five hours and stored dry for further analysis and use. Similarly, ZIF-8 synthesized by using deionized water with proper proportion of Zinc Nitrate Hexahydrate (1.17gm) and 2-methylimidazol (22.7gm) are dissolved in 88ml deionized water. Synthesis methodology applied for ZIF-8 crystals is as shown in Fig 1.

3. SIGNIFICANCE OF ZIF-8 AS FILLER IN MMM

Developing defect-free mixed matrix membrane remains biggest challenges [8], [3], [11]. Membrane defected through particle agglomeration [13], unselective voids formation, and filler pore blockage and "sieve-in-cage" morphology leads to low separation properties. Utilizing nano-size filler like ZIF-8 into polymer matrix would overcome several challenges in developing MMM by providing good dispersion in polymer matrix, high contact of polymer-filler even at low filler loading by using separation properties of both polymer and filler [14], [8].

Zeolitic Imidazolate frameworks (ZIFs) come out as potential filler due to organic linkers exist in its structure [3] have good interaction with polymer. Besides, ZIFs consist of enormous surface area, high adsorption capacity; ease to modifications and high affinity towards certain gas gives the edge for ZIFs to be implemented as filler. ZIF-8 show good chemical stability against polar and non polar solvents, reorientation of its structure at high pressure and high mechanical strength [8], [3], [15].

Another concern regarding MMM is the amount of filler loading. High filler loading would provide higher penetrant-filler interaction and increase MMM separation properties [13]. However, it also likely leads to particles agglomeration. Increased filler loading increase its separation performance, but eventually leads to particle agglomeration and deteriorating its performance. It should be noted that high filler loading would directly reflect on membrane production cost. In contrast, incorporating small amount of filler given significant improvement on membrane separation properties, but highly unlikely for particles to agglomerate [13], [11]. Minimum filler loading with significant improvement of membrane performance would be the ideal MMM. The details investigation of percentage loading of ZIF-8 nano filler in various polymers for separation of single and binary gases with its important significance on performance [6],[9],[14],[16],[2],12] of MMM studied in table 3.

4. PREPARATION METHODOLOGY OF ZIF-8 BASED MMM

Mixed matrix membrane consists of an inorganic or inorganic-organic hybrid material in the form of micro or nano particles or fillers [13], [11] incorporated into a polymeric matrix as shown in Fig. 2.

TABLE 3
SIGNIFICANCE OF ZIF- 8 NANO FILLER IN MIXED MATRIX MEMBRANE

Polymer	Loading of ZIF-8 nano filler (Wt. %)	Separation of single gases	Separation of binary gases	Significance
Matrimid-5218	15- 80	H_2,O_2,N_2, CO_2,CH_4, C_3H_8	H_2/CO_2 CO_2/CH_4	i) At this loading, loss of mechanical strength, leading decrease in flexibility. ii) Permeability increases up to 40% loading due the presence of more polymer free volume. iii) Most of the gas pairs O_2/N_2, CH_4/N_2, H_2/O_2, H_2/CO_2, H_2/N_2 no significant change in the ideal selectivity up to 40 % loading. i) However, higher loading of 50 & 60 % of ZIF-8 decreases the permeability for all gases & increases selectivity consistent with the influence of ZIF-8. ii) In case of gas pairs of small gases, such as H_2/O_2, H_2/CO_2, H_2/CH_4, CO_2/CH_4 etc. 50 wt% of ZIF% improved ideal selectivity.
PI – Matrimid-9725	10, 20, 30	H_2,N_2, O_2, CH_4, CO_2,	CO_2/CH_4, CO_2/N_2	i) CO_2 concentration 10 to 75 (Vol. %) of ZIF-8 compared with MIL- 53 (Al) and $Cu_3(BTC)_2$, Permabilities increases for all three, but selectivity slightly increases with MIL and $Cu_3(BTC)_2$ and constant for ZIF-8. ii) At 35^0C and 10 bar pressure for a 35/65 (Vol %) CO_2/CH_4, slight improvement in CO_2 permeance of ZIF-8 with other two. At Same conditions CO_2/N_2, CO_2 permeance constant for all three.
Ultem	13	CO_2, N_2	CO_2/N_2	i) Hollow fiber asymmetric composite membrane prepared by dry -jet wet method. ii) Good adhesion and permeability increases, 20% perm selectivity enhancement over pure polymer. iii) Mixed gas transport measurement promising perm selectivity as high as 32% in the hybrid membrane. iv) It may be used for large scale gas separation such as CO_2 capture from flue gas, but limitation of low permeability of Ultem.
6FDA-DAM	---	C_3H6, C_3H_8	C_3H_6/C_3H_8	i) Good adhesion, well dispersed, clusters of ZIF-8 with sizes larger than single ZIF-8 crystals were found in the film at higher loading 48%. Still enhancement of C_3H_6 permeability and C_3H_6/C_3H_8 selectivity . ii) C_3H_6 and ideal selectivity C_3H_6/C_3H_8 with 48% loading were found to 258% and 150% higher than pure 6FDA-DAM. Using Maxwell model, C_3H_8 permeability of 277 barrer, selectivity C_3H_6/C_3H_8 ideal selectivity of 122.
PPEES	10, 20, 30	CO_2	---	i) ZIF 8 particle size reduced after sonication, but crystal structure remains unchanged.
PEEBAX-2533	35	CO_2, CH_4, N_2, O_2	CO_2/N_2	i) Permeability increases with increasing filler content. CO_2/N_2 selectivity slightly decreases from 33.8 to 32.3 at dry and humidified conditions.

The use of these two materials with different flux and selectivity provides the possibility to better design of gas separation membrane with easy processability and performance [12], [11]. If porous inorganic additive ZIF-8 added to the organic poly mer could be applied with a pore diameter larger than the kinetic diameter (Table 2) of one gas component but smaller than the other one a strong improvement of permeability would be expected [14],[7].

The major technical barrier for mixed matrix membranes is the preparation of well dispersed and wetted additives at high

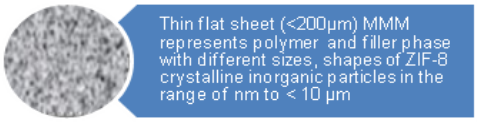

Fig.2. Schematic representation of a mixed matrix membrane with different size and shape of ZIF-8

loading. Superior MMM permeability and performance selectivity can be achieved by matching the properties of the polymer and ZIF. Generally, several main issues, such as the tunable synthesis of the sub-micrometer ZIF nanoparticles, defect-free interface [11] between the polymers and ZIFs and the controllable dispersion of ZIFs within the polymer. Particle size and shape affect dispersion and wetting, behavior of polymer and particle interactions, its functionality are the important parameters must be considered during fabrication of membrane [16], [2], [8].

Traditionally, the substrate supported MMMs are prepared through several steps including solution-blending, dip-coating and solution-casting. These membranes can be formed by selecting polymer and ZIF with specific permeability and performance selectivity and the amount of ZIF with a desired concentration which is necessary for the preparation of MMMs is added to an organic polymer solution of known composition under stirring [11]. The resulting mixture is sonicated [16] or stirred for some time until an apparently homogeneous suspension is obtained [11]. The suspension is cast or coated onto a substrate to form membranes, followed by heating and drying under vacuum. Finally, the membrane is cooled down to room temperature under vacuum.
Similarly thin flat thin film mixed matrix membrane prepared from homogeneous suspension [11] of polymer and ZIF-8 can be cast on the glass plate. The detail stepwise procedure is shown in Fig-3.

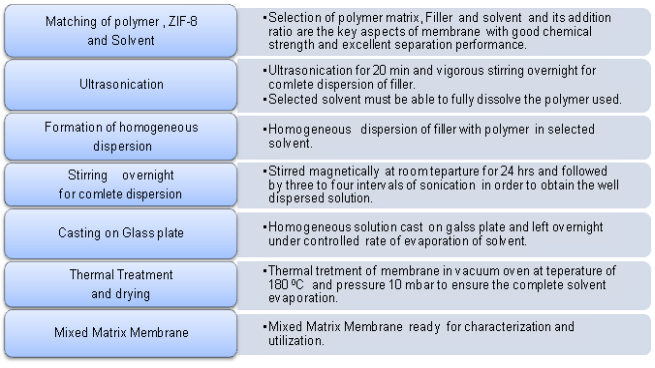

Fig.3. Detail procedures for the preparation of flat thin film mixed matrix membranes.

5. Results and Discussion

The schematic graphical representation of synthesized ZIF-8 crystalline powder by room temperature synthesis method and synthesis procedure of ZIF-8 crystals by using deionized water and by using methanol as shown in Fig. 4 [a] and [b].

The X Ray Deffractometer (XRD) analysis [16], [5] were used to confirm the phase purity of ZIF-8 and found to be similar to the earlier literature. It is a nondestructive analysis to measure wavelength of sample and to identify structure. The XRD will emit X-rays to the sample and the X-rays diffracted at different angles and intensity by CuKa irradiation with a wavelength (λ) 1.54A^0 at room temperature.

Phase identification of the solid crystalline powder was by X-ray diffractometer using Ni filtered Cu-Kα radiation at a scan speed 3 deg. /min with continuous mode and sampling width 0.020 deg. The voltage and current were 30 kV and 15 mA. The sharp peak of below 20^0 (with 2θ of 18.04)

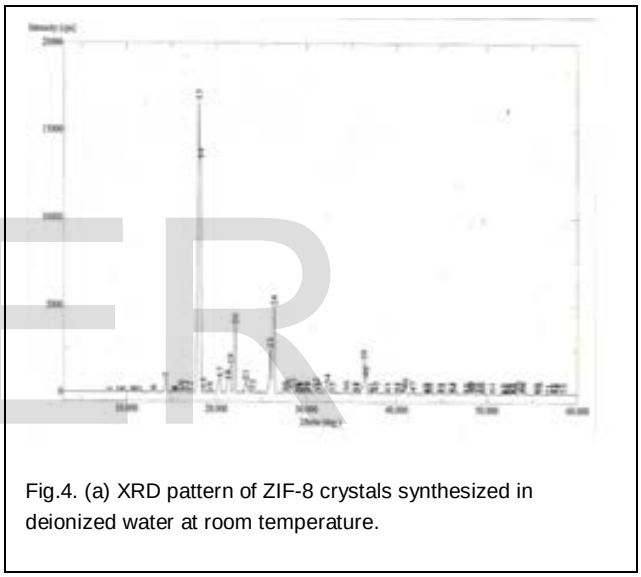

Fig.4. (a) XRD pattern of ZIF-8 crystals synthesized in deionized water at room temperature.

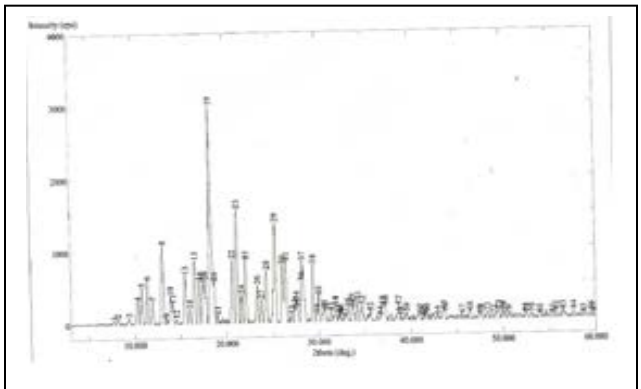

Fig.4. (a) XRD pattern of ZIF-8 crystals synthesized in deionized water at room temperature.

was observed on XRD diffractogram of the ZIF-8, indicating that a highly crystalline material was achieved (Fig. 4-a). Compared to the standard Basolite (Z-1200) of Sigma Adlrich (BET surface area 1223.19 m2/gm), the intensity of the synthesized ZIF-8 by both deionized water and methanol peaks, are specifically lower. The differences can be related to the guest molecule occupying by the ZIF-8 pores that causes pattern destructive and retarded gas uptake capacity.

6. Conclusion

The synthesized ZIF-8 can be added to the polymer matrix as a filler which altered the matrix properties and enhanced performance [11] i.e. selectivity and permeability's of mixed matrix membrane for gas separation because of superior interaction of the filler with matrix, due molecular sieving effects at good thermal stability of the membrane.

Synthesis and characterization of the ZIF-8 crystals in deionized water and methanol at room temperature characterized using X-ray diffraction (XRD) was carried out to ensure its crystalline nature and phase purity to check compatibility with polymer to fabricate mixed matrix membrane. The synthesized ZIF-8 XRD pattern compared with the well known Basolite (Z-1200) to validate the crystalline structure and found good agreement. Review propose that development of the methodology of preparation of ZIF-8 based mixed matrix membrane, its compatibility with polymer, significance and explore the potential applications for the gas separation.

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