



STUDIES ON DEVELOPMENT AND CHARACTERIZATION OF MFI TYPE ZEOLITE MEMBRANE ON CERAMIC SUPPORTS FOR CO₂ SEPARATION

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Abstract: In the present study, a thin layer of MFI-type silicalite zeolite membrane is synthesized on porous silicon carbide supports (discs and tubes) by direct in situ crystallization and secondary growth technique via hydrothermal treatment for CO₂/N₂ separation. The influences of synthesis conditions are studied. The membranes are characterized for the formation of zeolite by X-Ray Diffractometer (XRD) and crystal morphology by SEM. The permeation of single gases viz: H₂, N₂, CO₂, Ar, SF₆, and separation of mixed gases viz: H₂/N₂ and CO₂/N₂ are evaluated using gas chromatography. After optimizing conditions for disks samples, preparation of membrane on tubular silicon carbide supports will be taken up in an industrial reactor. The membrane module will be fabricated and tested for its performance. The secondary growth technique method resulted in uniform and thin layer of zeolite membrane on both disk and tubular supports. Single gas permeability results shows the permeability through the developed membrane is in the order of H₂>CO₂>N₂>Ar. The highest separation factor for CO₂/N₂ mixed gas is obtained for MFI membrane formed on disk sample by secondary growth method.

Keywords – MFI-type silicate zeolite, XRD, SEM, Gas separation

I. INTRODUCTION

The need to face the big issue of global warming, associated to the increment in energy demand (that is expected to grow to 30% by 2040 [1]) and the depletion of fossil fuels reserves, requires concrete actions of the international community in terms of reduction of CO₂ emissions and use of greener industrial technology, based on renewable sources and Process Intensification principles. Membrane technology moves in this direction, having the potentiality to achieve better performance, lower energy consumption and volume of equipment compared to the traditional processes [2]. In gas separation, membranes can be typically divided into polymeric, inorganic and mixed matrix [3], in which inorganic materials (e.g., zeolites) are used as fillers to be incorporated in a polymeric structure. Polymeric membranes are widely used, presenting a low fabrication cost, associated to ease processing, tuneability and scalability. Nevertheless, they do not assure high chemical and thermal stability and, moreover, have important limitations related to the permeability/selectivity trade-off, as shown by the Robeson's upper bound [4]. On the contrary, inorganic membranes, which are divided into dense (i.e., metallic and perovskite) and porous structures (e.g., carbon, amorphous silica and zeolite), show high chemical and thermal stability, even though have a lower packing density, and in some cases their scalability is more complex than for polymer membranes. Porous inorganic membranes, as the zeolite ones, assure higher flux and chemical stability than the dense structures [3]. The major drawbacks that limited their applications in the past were the high

fabrication costs and difficult in reproducibility. However, some efforts are made to reduce the fabrication costs of support, which may constitute the 70% of the total membrane cost [3]. The difficulty in scale-up of zeolite membranes for development of membrane modules, which was a big problem in the past [5], is now overcome in liquid separation as demonstrate several applications especially regarding water/alcohol pervaporation [6,7,8,9,10]. As discussed by Caro *et al.* [6] and, more recently, by Feng *et al.* [11], LTA membranes are applied for de-hydration of mixtures containing water and bioethanol. Also in gas separation, some attempts to scale up were carried out [12, 13]. In particular, Himeno *et al.* [12] set up a pilot plant for biogas produced in a sewage plant for CO₂:CH₄ separation using a DDR membrane. The authors obtained a CH₄ purity of 90% and 97% of CO₂, respectively, without loss of performance under operation up to 40 h. Li *et al.* [13] demonstrated the possibility to scaled-up a SAPO-34 membrane from 5 to 25 cm of length, maintaining the CO₂/CH₄ selectivity of the shorter membrane (about 250). However, further efforts will have to be made in reduction of fabrication cost and improvements in reproducibility to allow an ever-growing development of membranes for gas separation on industrial scale.

Zeolites represent an important class of the inorganic materials and consist of aluminosilicates with a microporous and crystalline structure. Their framework is characterized by tetrahedral building block TO₄, in which two T atoms (silicon or aluminum) are connected by oxygen in T-O-T bonds to form pores and channels [14,15]. In the zeolite structure, a SiO₄ group results neutral, whereas the AlO₄ group has a negative charge of -1. Thus, exchangeable cations (e.g., Na⁺, K⁺, etc.) can be located in the structure to compensate this charge. IZA, International Zeolite Association [16] classified zeolites with a three letters identification code. Based on the pore size, zeolites are distinguished into small, medium, large and ultra large structures. The Si/Al ratio, on which the adsorption capacity strongly depends, ranges from 1 (as in the case of zeolite X) to infinity (for ZSM-5 [17]). Zeolites improve their capacity to adsorb molecules when the aluminum content in its framework is higher (i.e., Si/Al is lower), since their structure become more polar [3]. Microporous character, uniform dimension of pore size, ability of ion-exchange, high thermal stability and surface area make zeolites suitable in several applications, such as adsorbent in pressure swing adsorption, catalysts for several chemical reactions, separation of liquid and gas mixtures [14]. In gas separation field, zeolites can be used in membrane shape for the separation of mixtures containing CO₂, exploiting their preferential adsorption of carbon dioxide compared to the other components that permits to achieve a high selectivity. Here, it is discussed the possibility to use zeolite membranes for separation of CO₂ from CH₄, H₂ and N₂. CO₂ and H₂ are the main products of syngas upgrading; their separation is needed in several processes, such as methanol and ammonia production. Finally, CO₂ and N₂ are the main components of the exhausted flue gas, whose release in the atmosphere without capturing CO₂ is the one of the main contributors to greenhouse gas emissions.

Objectives of this work are to develop the MFI-type silicalite zeolite membranes by secondary (seeded) growth technique on the micro porous Silicon Carbide supports. To separate Carbon dioxide from other calibration mixtures, which are exhaust from thermal power plants. Characterization of the membrane was performed by XRD and SEM analysis, also aimed at testing the membranes in a membrane test module. Important goal of this research to up scaling the preparation of silicalite zeolite membrane on Silicon Carbide tubular (200mm) supports to pilot plant basis.

Zeolite membranes consist of a thin zeolite layer, which is typically deposited on a porous support (as α -alumina) to obtain a membrane with high mechanical stability that can be used for separation of CO₂, light gases and hydrocarbons (Figure 1). Most of resistance to mass transport is given by the zeolite selective layer, even though porous support provides a further resistance, which depends on the pore size. This resistance may affect the separation performance of the membrane, especially when the ratio of the support permeance over the zeolite permeance is lower than 10 [3]).

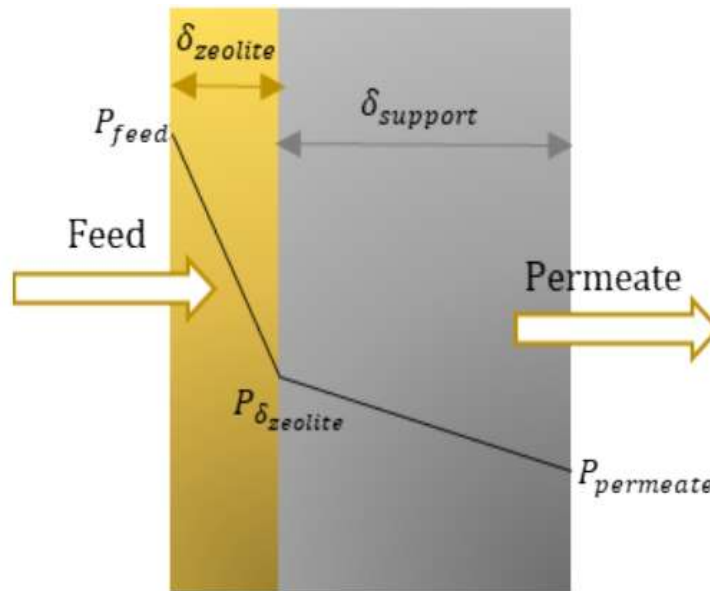


Fig. 1. Schematic view of a supported zeolite membrane.

$$\text{Permeance}_i = \frac{\text{Permeating Flux}_i}{\text{Driving force}_i} \quad (1)$$

$$\text{Selectivity}_{i,j} = \frac{\text{Permeance}_i}{\text{Permeance}_j} \quad (2)$$

$$\text{Permeability}_i = \text{Permeance}_i \cdot \text{Thickness} \quad (3)$$

The permeation properties of a zeolite membrane can be expressed in terms of permeance and selectivity of the components present in the feed mixture. Permeance is defined as the ratio of the permeating flux over the driving force of component i (Eq.1). Selectivity provides information regarding the ability of the membrane to separate one desired component from a mixture, being defined as the ratio between permeance of two components (Eq.2).

However, permeance provides a measure of the permeation of a component through a specific membrane layer and not allow a real comparison of the separation properties among different materials, since the membrane thickness can be different. On the contrary, this comparison can be done using the permeability (Eq.3)

II. LITERATURE REVIEW

Yutao Liu et al;(2021) In this study, we propose a multi-function integration strategy for the design of COF fillers considering entire morphological structure, aperture adjustment and channel decoration, as well as interface optimization. Eunhee Jang et al;(2017) In this study, we adopted an in-situ counter diffusion method to fabricate a ZIF-8 membrane; Zn sources, already placed inside a porous support, were allowed to diffuse out and react with the 2-methylimidazole (mim) molecules in the bulk phase. Because the reaction rates between the Zn source and the mim molecule were very high, their diffusion rates played a key role in determining the final properties of the membranes. The performance at 300 °C was completely degraded due to the eventual conversion of ZIF-8 into ZnO phases. Seyed Mohammad Reza Razavi et al; (2015) In this study, a mathematical model is proposed for prediction of CO₂ absorption from N₂/CO₂ mixture by potassium threonate in a hollow-fiber membrane contactor (HFMC). Salman Qadir et al;(2023) The two different mixtures, CO₂/CH₄ and N₂/O₂, were investigated to obtain concentration gradient and mass flux profiles of CO₂ and O₂ species in an axial direction. This study allows assessing the feed pressure's impact on the HFM system's overall performance. These results demonstrate that the increment in feed pressures decreased the membrane system's separation performance. The results show that increasing inlet pressure and a higher concentration gradient resulted in higher flux through the membrane. K. Fooet al;(2023) This paper reviews the computational parameters and boundary conditions involved in model simulations, including the general assumptions made for the gas separation process. This review also describes the effect

of obstacles (feed spacers) and various unsteady flow approaches for improving performance. Finally, challenges and future perspectives in CFD simulation involving membrane gas separation are provided.

III. MATERIALS AND METHODS

3.1 Materials: The solution was prepared using the following components: Colloidal silica, (with 40% water) tetrapropylammonium hydroxide, TPAOH (1M solution, MERCK) and distilled water. In the present study the samples of Silicon Carbide of discs with dimensions 30mm dia and 3mm thickness. Tubes of 200mm length with 13mm OD were used for zeolite coating.

3.2. Experimental procedure:

In this work the porous Silicon Carbide supports with 2 μ m average pore size and porosity of 35-40% were used as supports. As earlier discussed two types of supports i.e. discs and hollow tubes are used for coating. The supports were obtained from CTI pilot plant in the mode of axial pressing for the disc supports and extruding method for tubular supports. For preparing the silicalite zeolite membranes the discs having 30mm dia with 3mm thickness, whereas in the case of tubes 202 mm length with 7mm ID and 13mm OD. After firing the SiC supports were washed and cleaned with distilled water in ultrasonic cleaner, and then supports are dried in conventional oven.

3.2.1. Synthesis of silicalite zeolite membrane by in situ method:

A clear solution containing colloidal silica, TPAOH and distilled water was prepared as follows. The clear homogeneous solution with following molar ratio of 49.9SiO₂:12TPAOH:277H₂O was obtained by adding 25 ml of TPAOH and 50 ml distilled water to a measured amount of 25 ml of colloidal silica solution was stirred for 4 hr using magnetic stirrer, after continuously stirring, then the solution became homogeneous form and leave the solution up to 2 hrs for ageing.

The SiC porous support discs were placed vertically by a ceramic supports to prevent the sedimentation on top of the membrane with in the Teflon lined stainless steel autoclave of 100 ml volume, and synthesis solution was added to a level approximately 5mm above the discs. After placing the SiC disk and adding the solution, the autoclave was sealed and placed into a constant temperature oven preheated at the synthesis temperature at 150°C for 24 hr the, at autogenous pressure. Flow chart is shown in Fig 2. All syntheses were conducted without stirring. After the specified reaction time was completed, the autoclave was removed from the oven and quenched with tap water. After cooling, the disks were washed thoroughly with distilled water until the solution reaches 7 P^H and dried in air at ambient temperature for over night and then drying at slower rates at 40°C, 60°C, 80°C and 100°C respectively for certain time intervals. The SiC supports are covered by a thin layer of silicalite zeolite micron sized crystal were grown on the surface can visually under microscope.

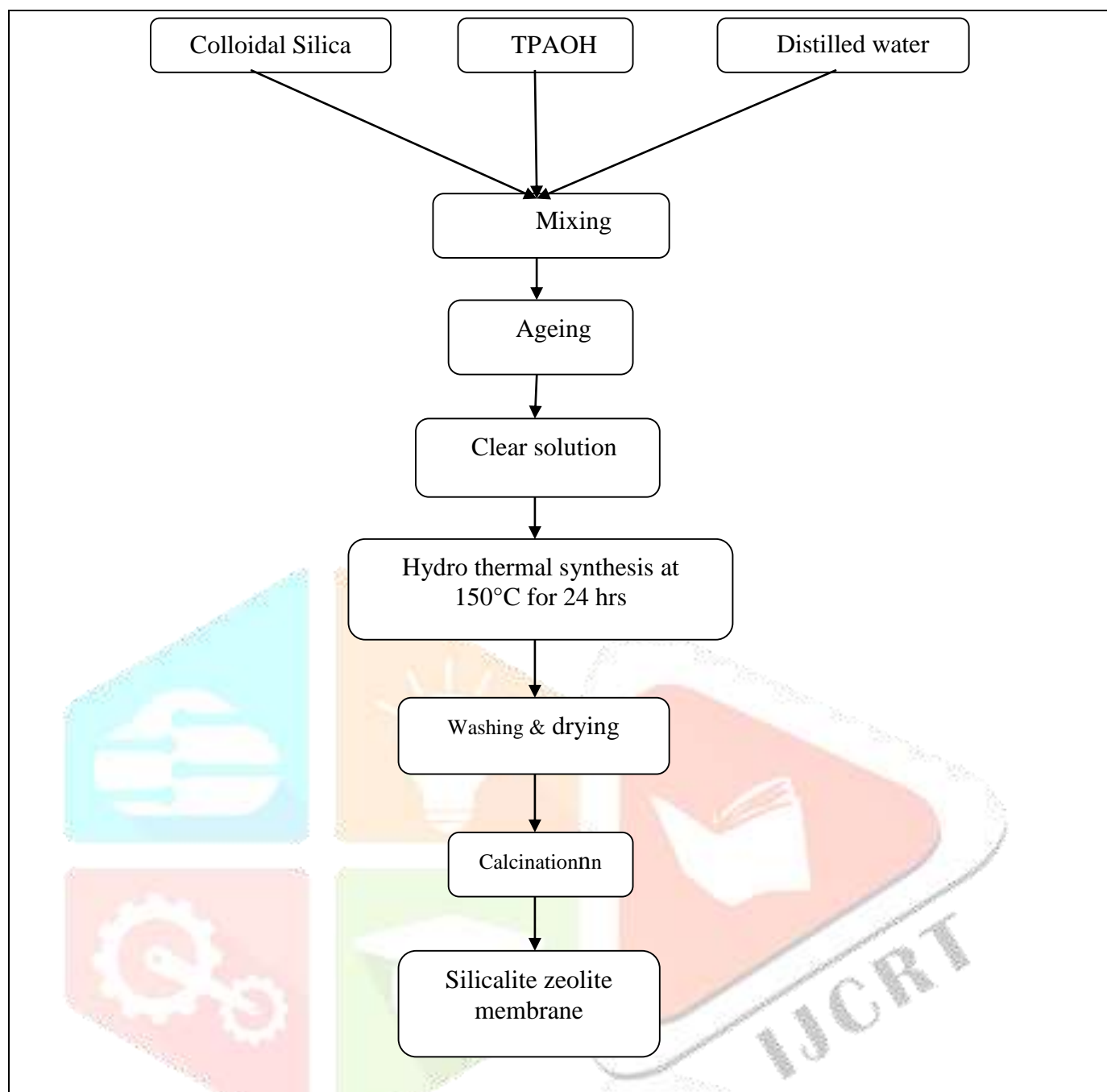


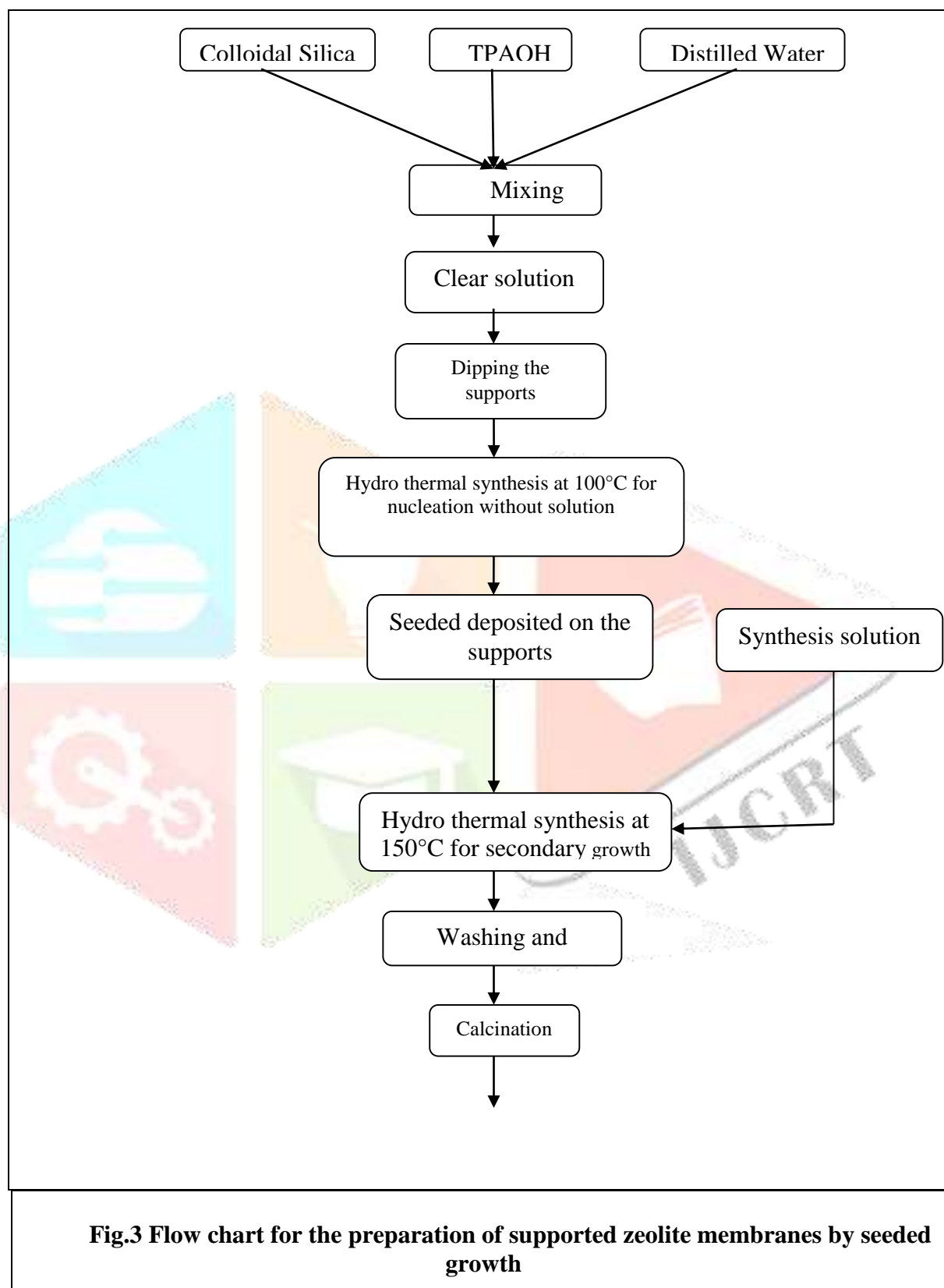
Fig 2. scheme of procedure for the preparation of supported zeolite membranes by in situ crystallization

3.2.2. Synthesis of silicalite zeolite membrane by seeded growth technique:

Seeded method is an alternative method for preparing the silicalite zeolite membranes. The basic aim of the present study is that the preparation of high silica zeolite membrane in the absence of alumina source with very thin membrane layer on the SiC supports for high temperature stability. Seeded method or secondary growth technique involves two steps: 1. nucleation of seeds, 2. membrane growth. In this technique two types of supports were used for coating i.e., discs and tubes. Materials used and zeolite synthesis solution was prepared by the same procedure used in the direct in situ crystallization

Before conducting the hydrothermal process nucleation of the seeds were developed, nucleation is a process, in which micron sized seeds are pre deposited on the SiC supports for better controlling the membrane layer in post hydrothermal process. In this present study we followed some new technique to seed deposition. To grow the seeds, the SiC disc supports were dipped in synthesis solution for 1 min after dipping the samples taken out from solution and kept for natural drying to precipitate the solution on the surface. Schematic flow chart shown in Fig.3 these dipped samples were placed in autoclave for pre-hydrothermal treatment at 100°C for 12 hr without the synthesis solution; after completing the specified

reaction time, the autoclave was opened and the zeolite synthesis solution was added. The autoclave is heated for hydrothermal treatment at 150°C for 24 hr and 36 hr. The autoclave was taken out from oven and quenched for cooling. The resulting silicalite membranes were washed with distilled water and dried in over night by natural drying.



Calcination is carried out in programmable high temperature furnace for removing the template or structure directing agent. As the template molecule is inside the pores of the zeolite after synthesis, a continuous zeolite film with essentially non zeolitic pores should be impermeable to gases. In this work tetrapropylammonium hydroxide (TPAOH) act as a template which block the membrane pores in hydrothermal treatment until. In calcination process (OKAY high temperature furnace) the program set as

heating up to 600°C at the rate 0.5°C/min; soaking for 4hrs.and cooling to room temperature at the rate of 2°C/min. After calcination of the zeolite membranes are ready for gas permeability testing.

3.3 Experimental setup

3.4. Gas permeation measurements:

Membrane performances were evaluated by measuring single gas and binary gas permeation. In both, the membrane was held inside a stainless steel module, fitted with O-rings to prevent leakage from the retentate side to the permeate side.



Fig. 4(a) The membrane module used in gas permeation experiments

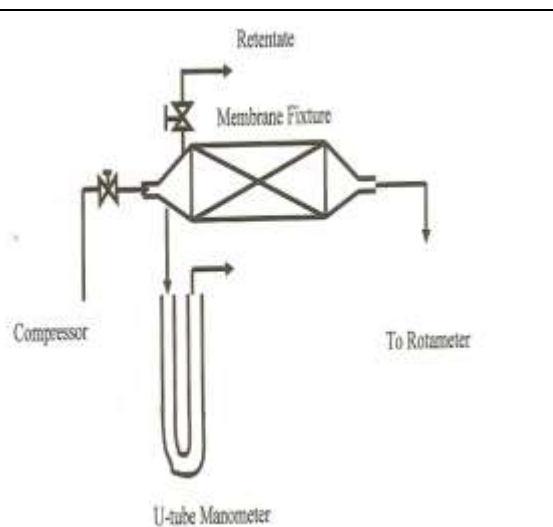


Fig. 4(b) Membrane setup used for gas separation

After synthesis and calcination of the membrane, the all single gas permeances of CO₂, N₂, O₂, H₂ Argon and SF₆ through the membranes were measured. Ideal selectivity of CO₂/N₂ and N₂/H₂ are calculated by taking the ratios of single gas permeances. All flux and permeability were measured at room temperature. Single gas permeation measurements were carried out by the constant pressure-variable volume method. The schematic drawing of the permeation setup is shown in Fig 4(b). The permeate side was connected to the flow meter to measures the floe rate for flux calculations then open to atmosphere and the feed side was kept at a gauge pressure of 4 bar.

The exit streams from both retentate and permeate sides were analyzed by injecting the sample at fixed volume in gas chromatography (GC-2014 model). The Helium is used as a carrier gases to analysis the calibration mixtures at rate 25 LPM. The GC can be analyzed by standard peaks by area percentage which is analyzed by manual integration to know the actual composition of the sample. For the gas separation in this work the CO₂/N₂ separation factor (α_{CO_2/N_2}) was calculated as follows:

$$\alpha_{CO_2/N_2} = \frac{Y_{CO_2}/Y_{N_2}}{X_{CO_2}/X_{N_2}}$$

Where X and Y are, respectively, the molar fractions at the feed streams and the permeate

3.5 CO₂/N₂ Gas separation:

The basic aim of this work is to separate CO₂ from N₂ as these from the major constituents of the thermal power plant flue gases. Calibrated Mixed gases of similar compositions (CO₂:15% and N₂:85% by volume) and N₂/H₂ and pure (99.99%) of all single gases like CO₂, N₂, H₂, O₂, Argon, SF₆ were procured from Bhorukha Gases Limited, Bangalore.

The carrier gas and CO₂/N₂ mixture gas cylinders were connected to the membrane holder through flow control mechanisms. The carrier gas was used to direct the flow of the permeate. The feed side and the retentate side both were connected to pressure gauges. The permeate was connected to a sample collector or bladder in which the permeate gas was collected. The cylinder was opened carefully to maintain a constant pressure desired and permeate collected was for gas chromatograph analysis.

In the experiments, first standard CO₂/N₂ mixture was injected for conditioning the system, after giving the standard peaks of N₂ and CO₂ the gas mixture was passes through the zeolite coated membrane at different feed pressures which is passing through the membrane collected in sample collector as permeate and inject with the help of needle some required amount through the injector. In the analysis note down the retention time at what time peaks are obtained. Using the manual integration the separation factors were calculated. Repeat the process for different samples at different pressures. Testing conditions of GC as follows:

Testing conditions for gas chromatography (GC 2014 SIMHADZU)

- Column (left) : CARBOSPHERE (new column)
- Length of carbosphere column : 6m
- Column (right) : Molecular sieve
- Length of molecular sieves : 2m
- Oven temperature : 40°C
- Injector temperature : 200°C
- Detector temperature : 250°C
- Pre-heater temperature : 150°C
- Sample injection : 0.5 ml
- Carrier gas : Helium
- Carrier gas flow rate (left) : 25 ml
- Carrier gas flow rate (right) : 25 ml
- Detector : TCD (Thermal Conductivity Detector)
- Current : 80 mA
- Cylinder gas pressure : 6 bar
- Gas purifier pressure : 6 bar
- Calibration graph : CO₂/N₂ Peak analysis

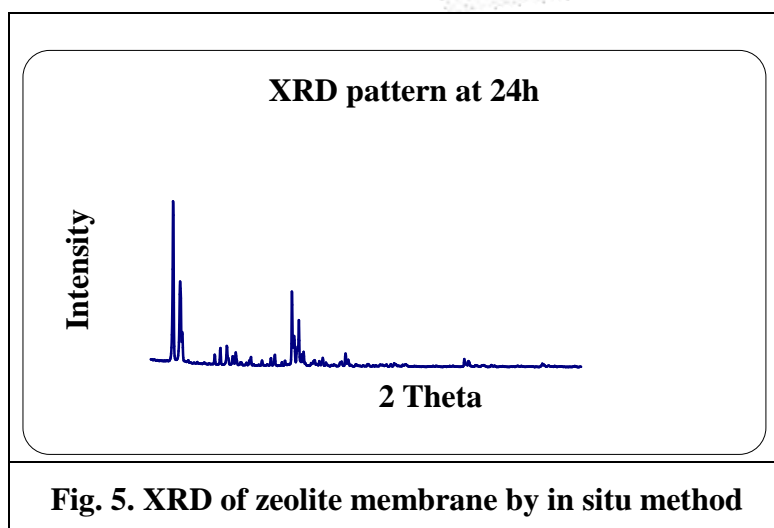
IV. RESULTS AND DISCUSSIONS

In this present work the characterization of the zeolite membranes carried out as follows.

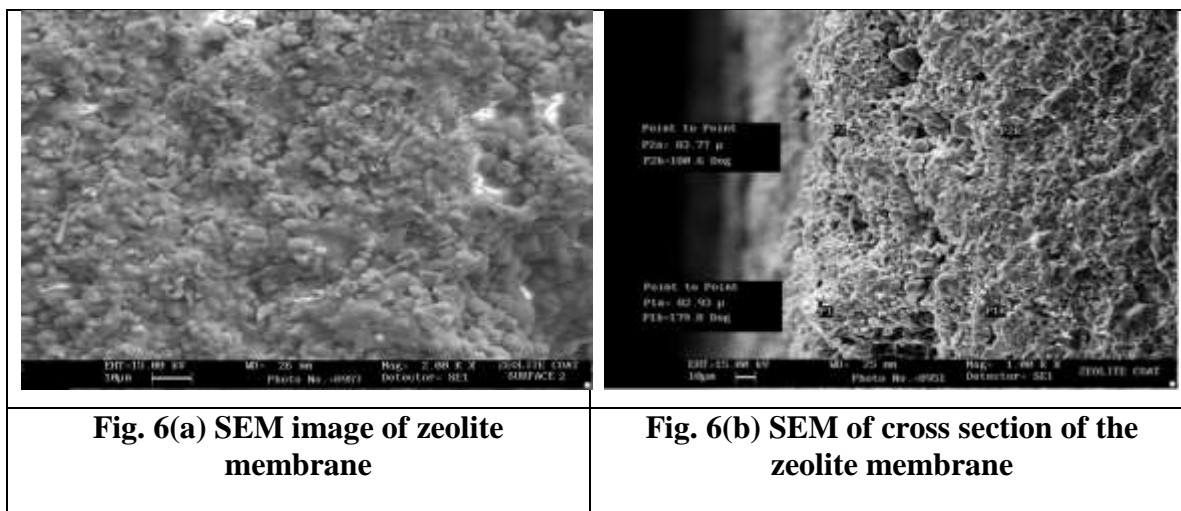
- a. X-Ray diffraction (XRD)
- b. Scanning Electron M microscopy

4.1. Characterization of the zeolite membrane by in situ method:

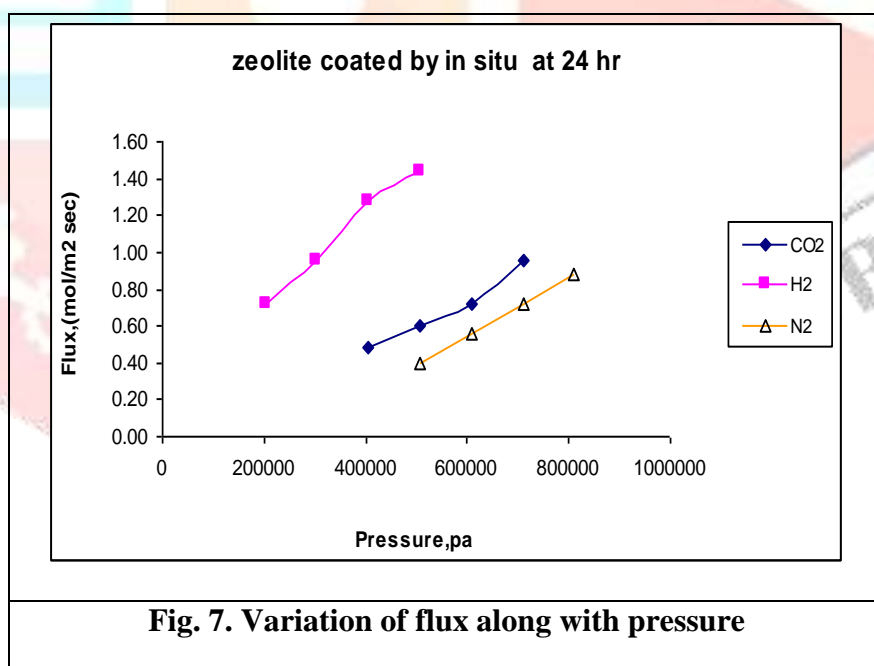
4.1.1. Characterization of the zeolite membrane by in situ method at 24hr:



XRD pattern in Fig.5. shows the zeolite membrane coated by in situ crystallization at 24hr. Zeolite coated at these conditions showing clearly high silica zeolite peaks on the SiC supports. SiC peaks are not found indicating complete coverage of zeolite crystals on SiC support.

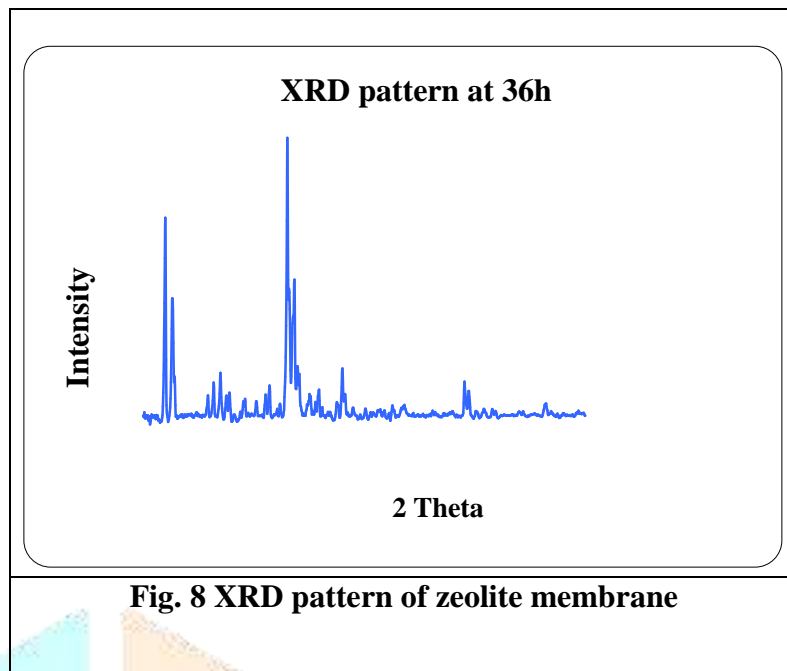


SEM image in Fig.6(a).shows the microstructure of the zeolite coated membrane on silicon carbide disc support at 24h. The picture showed the uniform porosity and crystal growth on the surface, the average size of the crystals is about $2\mu\text{m}$. By observing the SEM image, the zeolite layer was covered whole surface of the support which is also confirmed by XRD. The Fig. 6(b) shows the uniform coating and thickness of the zeolite membrane on the support is about $80\mu\text{m}$

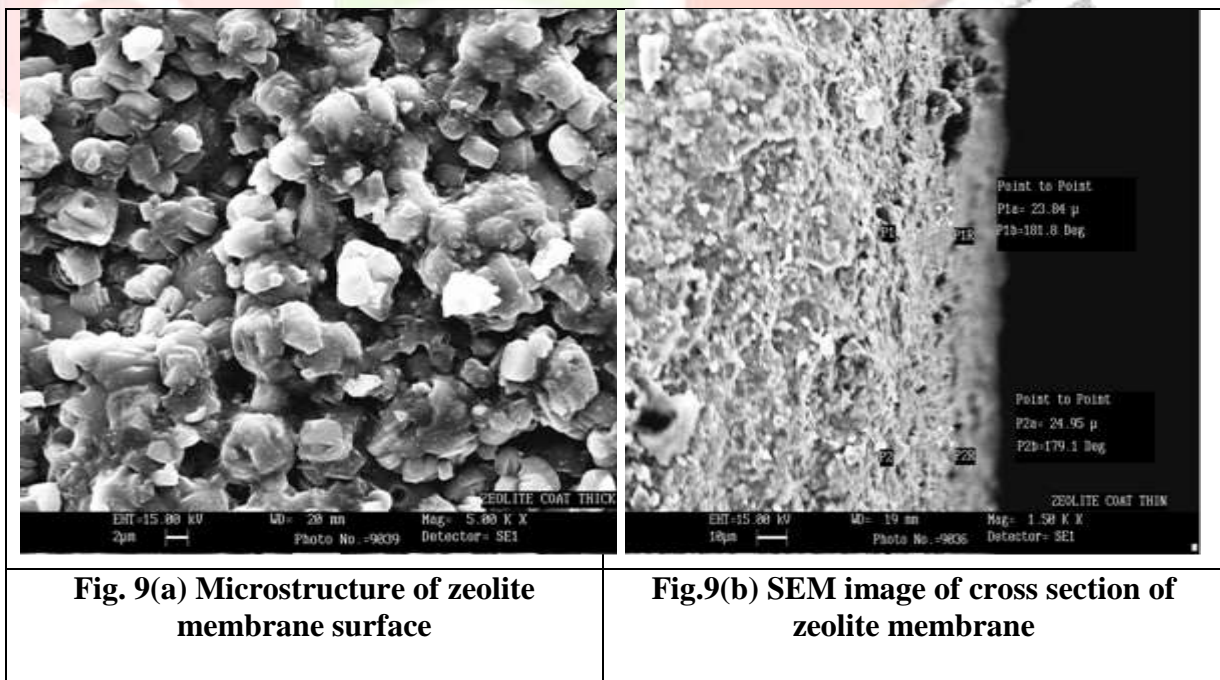


Permeability of the various gases through the zeolite membrane prepared by in situ crystallization for 24 hr. The flux v/s pressure is plotted in Fig.7. Permeability of H₂ is highest and N₂ is lowest. Permeability of CO₂ is much lower than H₂ but slightly more than N₂. The increasing of permeability with decreases in kinematic diameter of gases indicates that primary mechanism of transport is molecular sieving.

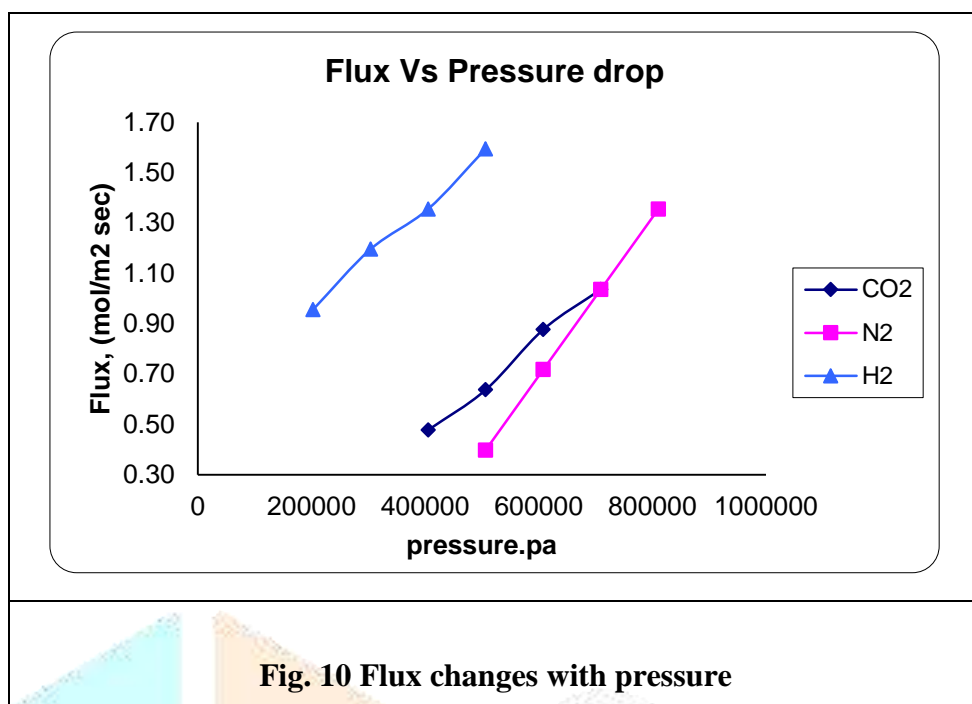
4.1.2. Characterization of the zeolite membrane by in situ method at 36hr:



XRD pattern in Fig.8 shows the zeolite membrane coated by in situ crystallization at 36hr. Zeolite coated at these conditions showing clearly high silica zeolite peaks on the SiC supports. SiC peaks are not found indicating complete coverage of zeolite crystals on SiC support.



SEM image in Fig.9(a).shows the microstructure of the zeolite coated membrane on silicon carbide disc support at 36h. The picture showed the uniform porosity and crystal growth on the surface, the average size of the crystals is about $5\mu\text{m}$. By observing the SEM image, the zeolite layer was covered whole surface of the support which is also confirmed by XRD. The Fig.9(b) shows the uniform coating and thickness of the zeolite membrane on the support is about $24\mu\text{m}$. This method given very less membrane thickness than the zeolite membrane given in direct crystallization



Permeability of the various gases through the zeolite membrane prepared by in situ crystallization for 36 hr. The flux v/s pressure is plotted in Fig.10. Permeability of H₂ is highest and N₂ is lowest. Permeability of CO₂ is much lower than H₂ but slightly more than N₂. The increasing of permeability with decreases in kinematic diameter of gases indicates that primary mechanism of transport is molecular sieving.

4.1.3 Mixed gas separation:

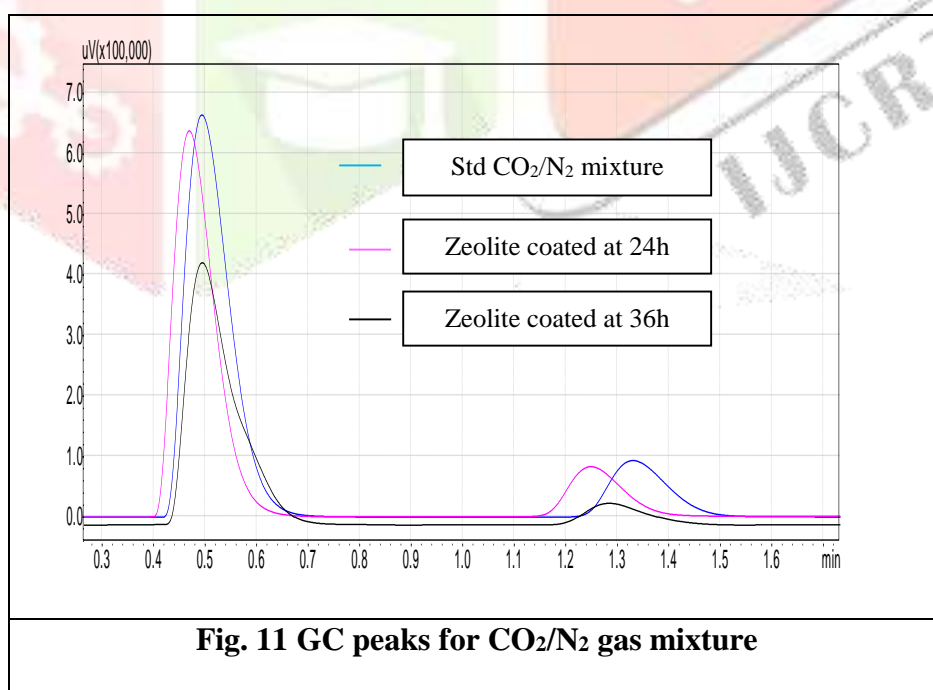


Fig.11 shows the CO₂ and N₂ peaks observed in GC for permeate gas through the zeolite membrane prepared by direct crystallization method at 24 and 36hr. Here feed gas was calibration gas mixture of CO₂ & N₂ with ratios of 15:85 (by volume %). From the gas chromatograph peaks and the area of the peaks the % of gases in permeate is calculated as follows

Feed gas: $\text{CO}_2:\text{N}_2 = 15:85$

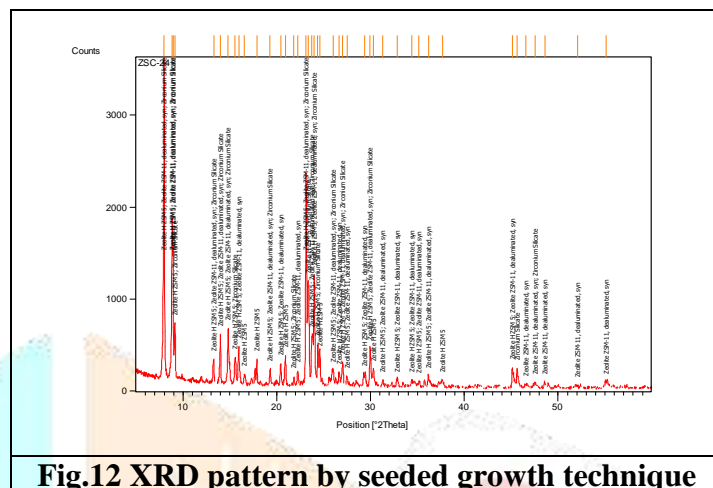
Permeate for 24 hr sample: $\text{CO}_2:\text{N}_2 = 15:85$ $\alpha_{\text{CO}_2/\text{N}_2} = 0$

Permeate for 36 h sample: $\text{CO}_2:\text{N}_2 = 2.5:96.5$ $\alpha_{\text{CO}_2/\text{N}_2} = 0.15$

The separation was not achieved at 24h hydrothermal synthesis time, whereas in the case of 36h synthesis time, the CO_2 was reduced to 2.5 from 15 % indicating good separation through the developed membrane; though separation factor is only 0.15.

4.2. Characterization of the zeolite membrane Secondary growth technique:

4.2.1 Characterization of the zeolite membrane Secondary growth technique at 24hr:



XRD pattern in Fig.12 shows the zeolite membrane coated by seeded growth technique at 24hr. Zeolite coated at these conditions showing clearly high silica zeolite peaks on the SiC supports. SiC peaks are not found indicating complete coverage of zeolite crystals on SiC support.

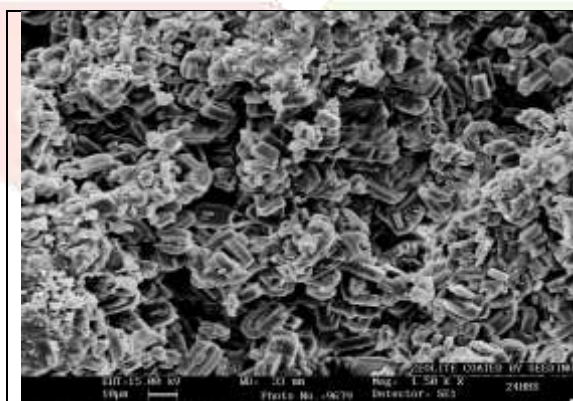


Fig.13(a) SEM surface image in secondary growth

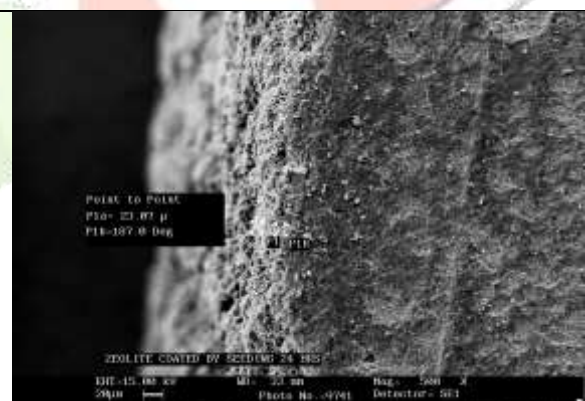
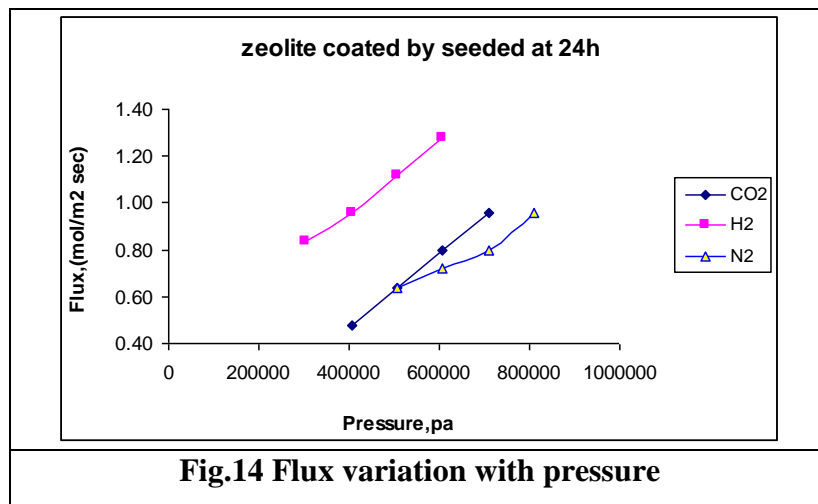


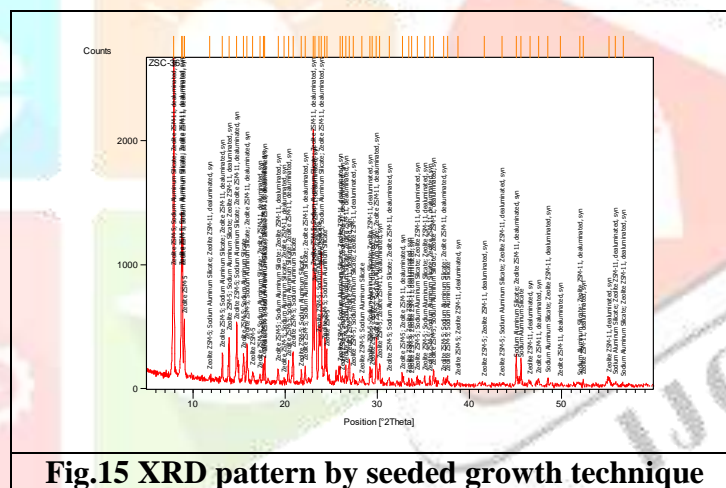
Fig.13(b) Cross section of zeolite membrane

SEM image in Fig.13(a).shows the microstructure of the zeolite coated membrane on silicon carbide disc support at 24h. The picture showed the uniform porosity and crystal growth on the surface, the average size of the crystals is about $4\mu\text{m}$. By observing the SEM image, the zeolite layer was covered whole surface of the support which is also confirmed by XRD. The Fig.13(b) shows the uniform coating and thickness of the zeolite membrane on the support is about $23\mu\text{m}$



Permeability of the various gases through the zeolite membrane prepared by seeded growth technique for 24 hr. The flux v/s pressure is plotted in Fig.14. Permeability of H₂ is highest and N₂ is lowest. Permeability of CO₂ is much lower than H₂ but slightly more than N₂. The increasing of permeability with decreases in kinematic diameter of gases indicates that primary mechanism of transport is molecular sieving.

5.3.2 Characterization of the zeolite membrane Secondary growth technique at 36hr:



XRD pattern in Fig.15 shows the zeolite membrane coated by seeded growth technique at 36hr. Zeolite coated at these conditions showing clearly high silica zeolite peaks on the SiC supports. SiC peaks are not found indicating complete coverage of zeolite crystals on SiC support.

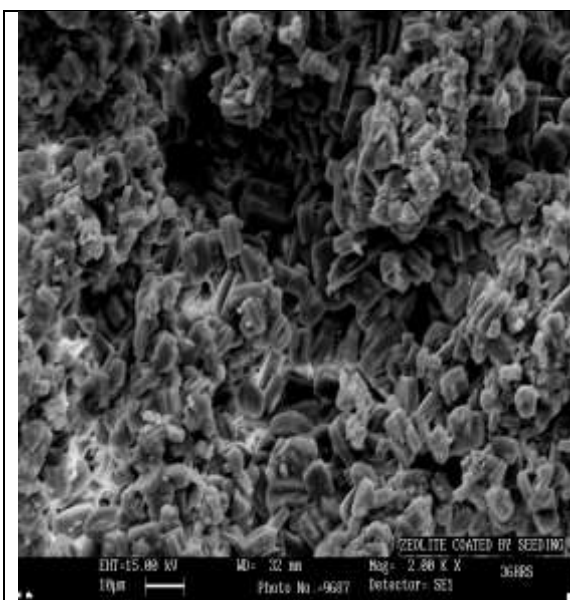


Fig.16(a) SEM image of zeolite surface by seeded growth

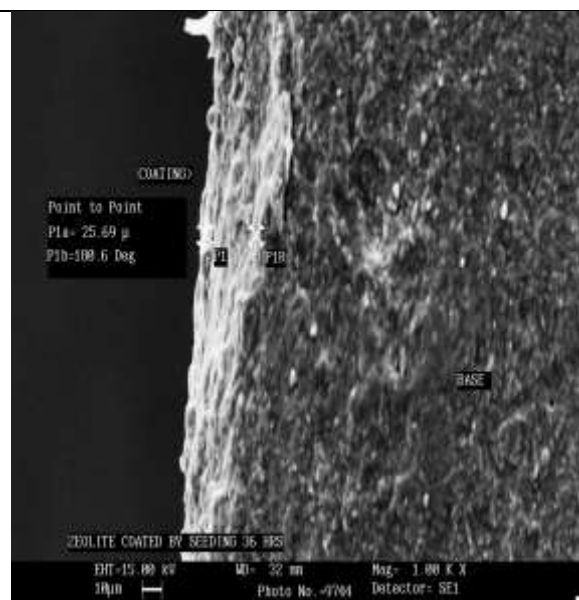


Fig.16(b) SEM for cross section of zeolite membrane

SEM image in Fig.16(a).shows the microstructure of the zeolite coated membrane on silicon carbide disc support at 36h. The picture showed the uniform porosity and crystal growth on the surface, the average size of the crystals is about $5\mu\text{m}$. By observing the SEM image, the zeolite layer was covered whole surface of the support which is also confirmed by XRD. The Fig.16(b) shows the uniform coating and thickness of the zeolite membrane on the support is about $23\mu\text{m}$

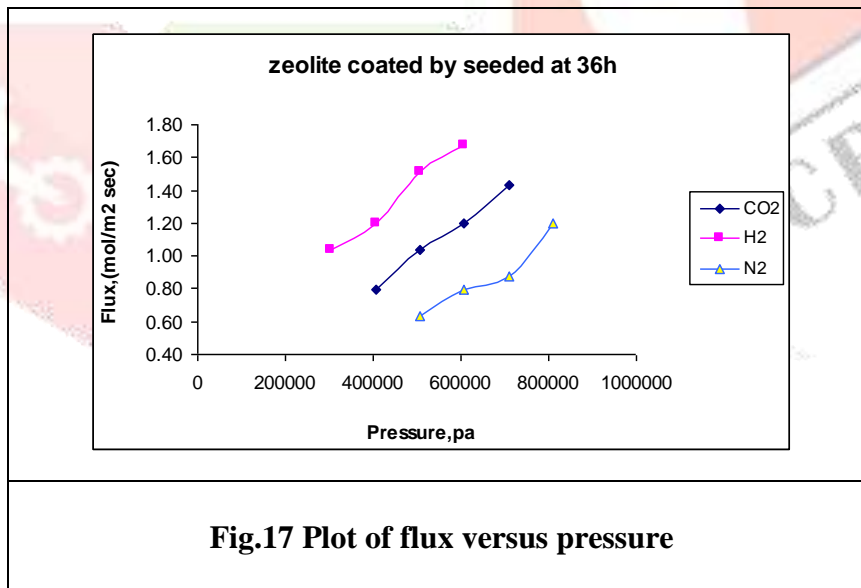


Fig.17 Plot of flux versus pressure

Permeability of the various gases through the zeolite membrane prepared by seeded growth technique for 36 hr. The flux v/s pressure is plotted in Fig.17. Permeability of H₂ is highest and N₂ is lowest. Permeability of CO₂ is much lower than H₂ but slightly more than N₂. The increasing of permeability with decreases in kinematic diameter of gases indicates that primary mechanism of transport is molecular sieving.

4.2.3 Mixed gas separation:

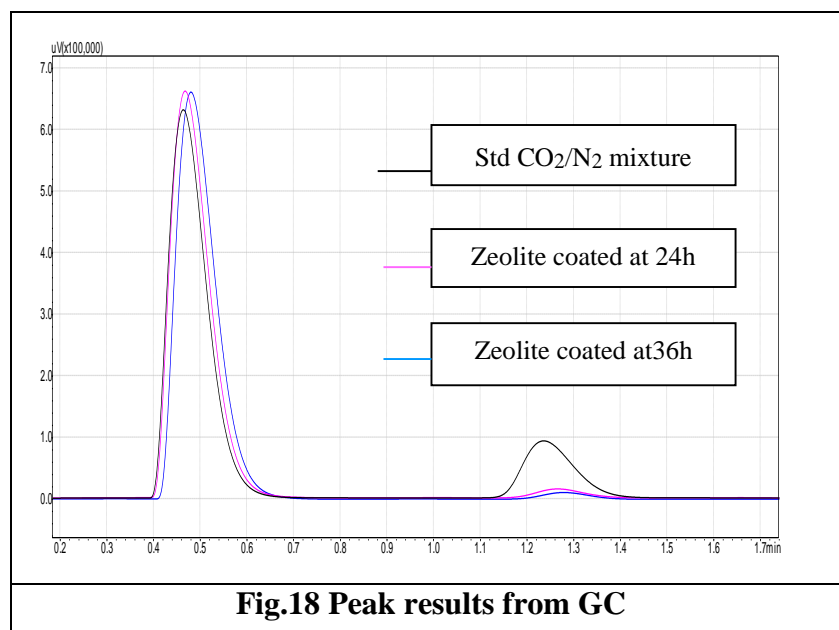


Fig.18 shows the separation between the CO₂ and N₂ by the zeolite coated membrane in secondary growth technique. The separation peaks of CO₂ and N₂ were analyzed by the gas chromatograph (GC). The highest separation achieved by this method at 36h hydrothermal synthesis time. The separation peaks are differs from the standard CO₂/N₂ mixture, the separation factor and ideal selectivities in different methods at different time parameters with area percentage of CO₂/N₂ mixture was tabulated in Table.1. The separation factor was calculated from their mole fractions of CO₂ and N₂ those are present in permeate and feed. The ideal selectivity of CO₂ to N₂ is the ratio of the individual permeability values. The ideal selectivity is slightly more than Knudsen factor. Indicating the pore sizes are higher than limits for molecular sieving. This is the fact that MFI zeolites have pores of .54 to.56 nm size where the gases used for permeation are of .33-.37nm. Hence surface diffusion mechanism is predominating than molecular sieving. Hence if the surface diffusion is increased by some modification or substitution in zeolite, much higher separation could be obtained.

Feed gas: CO₂: N₂ = 15:85 (by volume)

Permeate the 24 hr sample: CO₂: N₂= 3:96.5

Permeate the 36 h sample: CO₂:N₂= 4: 95

α_{CO_2/N_2} = separation factor is **0.18**

α_{CO_2/N_2} = separation factor is **0.24**

Table 1. Tabulation for separation factor results from various zeolite membranes
(Knudsen diffusion for CO₂/N₂ is **0.8**)

Method	Time in hr	% Area (CO ₂ /N ₂)	Separation factor	Ideal Selectivity (CO ₂ /N ₂)
In Situ	24	15:85	---	1.5
In Situ	36	2.5:96.5	0.15	1.6
Seeded Growth	24	3:96.5	0.18	1.2
Seeded Growth	36	4:95	0.24	1.6

6. CONCLUSIONS

Secondary growth technique method is a suitable method for preparation of zeolite membrane for separation of the very closer molecular diameter like, CO₂/N₂ gas mixtures. Direct in situ crystallization method has given less separation factor than the seeded method. For CO₂/N₂ gas separation the direct crystallization method is not preferable, due to high thickness of the membrane layer by the random growth of crystals on the support surface, this leads lower fluxes. Whereas, in the case of seeded growth technique, the membrane layer can be controlled by the pre-deposition of seeds on the support surface. The membrane thickness obtained in the direct method was larger than the secondary growth method. Experiments carried out without filtered colloidal silica leads the high thickness membrane hence the deposition of the particles on the support surface due to gravity settling. Four hour ageing time of the hydrothermal synthesis solution has given good coating rather than without ageing. From the permeability results, the flux values in both the methods are very low. It can be avoided by taking precaution for one side smooth coating. Low separation was observed by the tubular zeolite membrane compared to disc membranes. To enhance the separation results, the coating techniques have to be improved and also require a suitable autoclave.

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