Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 36 (2010) 1193–1199

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of cellulose buffer layer on synthesis and gas permeation properties of NaA zeolite membrane

Nandini Das [*]

Ceramic Membrane Division, Central Glass and Ceramic Research Institute, CSIR, 196, Raja SC Mullick Road, Jadavpur, Kolkata 700032, India

Received 11 December 2008; received in revised form 22 September 2009; accepted 7 December 2009
Available online 28 January 2010

Abstract

NaA zeolite membrane coating was successfully synthesized on a porous alumina substrate by hydrothermal treatment. The effects of synthesis parameters like, seeding type (ex situ, in situ), time, temperature, sol concentration, coating stages, application of intermediate layer, etc. on membrane characteristics were investigated. A continuous membrane was formed on a seeded substrate. Surface seeding (ex situ crystallization) not only accelerates the zeolite crystallization process on the support surface, but can also enhance the formation of homogeneous NaA zeolite layer. The NaA zeolite membrane with a synthesis time of 4 h shows the best microstructure and the quality of membrane was improved by employing the multi-stage coating. But the main problem associated with membrane synthesis was crack formation, and it can be reduced by applying intermediate layer, between support surface and seed layer. A thin cellulose layer was applied to the support surface before applying seed crystals. The performance of the membranes was evaluated by gas permeation measurement. The permeance of O_2, N_2 decreased as kinetic diameter of gases increased. The permselectivity of O_2/N_2 was 1.9–2.34. This value showed the molecular sieving effect of NaA zeolite membrane.

Keywords: A. Films; A. Grain growth; B. Microstructure-final; E. Membrane

1. Introduction

In recent years, attempts to develop zeolite membranes for separation and catalytic application have been intensified. Considering their molecular sieving properties and uniform pore size, high thermal resistance, and high mechanical strength, zeolite membrane have attracted great interest for application in many important industrial processes [1,2].

Among the various types of zeolite species, especially NaA zeolite has the potential to sieve out molecules in a continuous process, by strong interaction, due to its hydrophilicity. As a result it has been commercially applied to alcohol dehydration and solvent dewatering [3,4].

There are many reports on the improvement of the formation stages of the membranes like microwave heating [5], addition of intermediate silane layer to increase the adhesion between gel layer and supporting substrate [6], vacuum seeding [7], etc.

The in situ hydrothermal synthesis appears to be the best studied method, in which the porous support is immersed into the synthesis solution, and then the membrane is formed by direct crystallization. However, it is difficult to prepare high quality membrane by this in situ crystallization method directly [8]. Coating the zeolite seed on the support surface before hydrothermal synthesis, which is also called as secondary growth method, is an effective approach to develop a high quality zeolite membrane. It is well known that the presence of seed on the support surface plays an important role in membrane formation. Synthesis with seeds gives a better controlled of the membrane formation process by separating the crystal nucleation and growth with a shortened crystallization time [9]. In addition, the secondary growth ensures the formation of the phase pure zeolite crystal on the support. The secondary growth method which was proposed by Lovello et al. [10] exhibit many advantages such as better control over membrane microstructure, and higher reproducibility [11].

In this work, zeolite membrane layer was synthesized on alumina substrate by secondary growth method. An intermediate layer made of cellulose, was applied between seeds and support substrate of the membrane which acts to increase the

---

[*] Tel.: +91 33 2483 8082; fax: +91 33 2473 0957.
E-mail address: dasnandini@cgcri.res.in.

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.01.014

mechanical strength and adherence of the seeds with supports. The synthesized membrane was characterized using SEM and XRD. The ultimate performance of the membrane was characterized by gas permeation measurement.

2. Experimental

A porous alumina disc of diameter 22 mm (cut from 5 kDa, 47 mm *diameter disc*) and thickness 3 mm collected from Sterlitech UK was used as substrate for the preparation of zeolite membrane. Before coating, the substrates were cleaned with acetone in a ultrasonic cleaner (vibracell, USA) for 5 min just to remove dust particles and oily matter. The cleaned substrates were coated with 3% alcoholic solution of cellulose, followed by attachment of zeolite seeds. The cellulose layer was applied by dip coating method. Initially porous alumina substrate was dipped into cellulosic solution. Dipping time was varied from 1 to 30 s and repeated for 5 times. Table 1 describes the details of application of cellulose layer. Then the substrate was dried at 100 °C for 2 h. A thin layer of cellulose was formed on support surface.

The modified support was coated with NaA zeolite crystals as nucleation seed. In order to get a uniform seed layer on the support surface, the seeds should be dispersed homogeneously on the support surface and amount of nucleation seeds should not be too large other wise the membrane layer will be too thick and uneven.

In this nucleation seeds coating process, the support substrate were dipped in a 1–3% NaA zeolite ($d_{50} \sim 100$ nm) suspension in deionized water, for different time span ranging from 5 to 10 times with a duration of 15 s. After the dipping procedure, the seeded supports were dried at 100 °C for 24 h.

The zeolite A (NaA) membranes were synthesized hydrothermally without applying seeds on porous support discs (in situ) before crystallization and also with dispersed seeds on modified substrate surface (ex situ). The materials used for the synthesis were sodium meta silicate nonahydrate (Qualigens fine chemicals, India) aluminium chloride (S.D. fine chemicals, India), sodium hydroxide (Merck India), and distilled water. Two reactant mixtures were prepared respectively dissolving sodium meta silicate and aluminium chloride in freshly made sodium hydroxide solution (molar ratio of NaOH/Si and NaOH/Al were 1:0.2317 and 1:0.072 respectively). The total amount of sodium hydroxide was distributed between the corresponding silicate and aluminate solutions, while the water was divided evenly. After aging the separate mixture for 1 h, they were mixed slowly under stirring at room temperature. The resulting mixture was stirred vigorously for 15–30 min to produce a homogeneous sol. The molar composition of the sol used for the synthesis was Al_2O_3:SiO_2:Na_2O:H_2O 1:1:50:500. The seeded/unseeded substrate was placed vertically in an autoclave. Crystallization was continued under autogenous pressure in a hot air oven at 65 °C for 2–6 h. Repeated crystallization for second stage and third stage was carried out to improve the quality of the membrane. After synthesis, the zeolite coated membrane was washed thoroughly with deionized water until the pH of the washing liquid became neutral. The crystalline structure of the as synthesized membrane was determined by XRD pattern. XRD was carried out on a Philips 1710 diffractometer using CuK_α radiation ($\alpha = 1.541$ Å).

Microstructure and morphology of growth layer was examined using scanning electron microscopy (SEM: model Leo, S430i, UK). Single gas permeation was measured by a specially designed permeation cell developed in our laboratory. The gas permeance of the membranes was measured by soap film flow meter under the feed pressure of 1–3.5 kg/cm^2 and at room temperature.

3. Results and discussion

In order to evaluate the membrane, the effect of different synthesis condition like synthesis temperature, time and initial gel composition on membrane formation was investigated and the as synthesized membranes were characterized by XRD and SEM. Fig. 1a–c shows the SEM micrographs of the zeolite membrane formed at 65 °C for 2–6 h from clear sol. It is clear, that at 65 °C, zeolite formation of zeolite crystal was positive after 2 h. SEM images indicate that NaA zeolite grains were scattered on the substrate surface. No continuous membrane was formed up to 6 h (Fig. 1c). As uniform, continuous coating through out the support was not formed, it was difficult to detect the zeolite phase on the support by XRD. Formation of zeolite phase was detected by the characterizing the powders formed in the reaction medium (not shown in figure). To increase the zeolite formation on membrane surface, synthesis temperature was increased up to 90 °C. Fig. 1d shows the SEM micrograph of the zeolite membrane prepared at 90 °C for 6 h. As shown in figure (Fig. 1d), the size and shape of those crystals were not uniform. Some cabbage like spherical crystals was formed, indicating the presence of some other phases. This was satisfied by XRD pattern of those zeolite powders (Fig. 2).

Table 1
Details of application of cellulose layer and seed layer on membrane substrate.

Sample ID	Cellulose concentration	Dipping time (30 s each)	Seed concentration	Dipping time	Remark on synthesized membrane
C1 1	1%	1 time	1%		Crack
C1 2	1%	5 time	2%	5 times	Crack
C3 1	3%	5 times	1%	5 times	Small cracks on the surface
C3 2	3%	5 times	2%	5 times	No cracks on the surface
C3 3	3%	5 times	3%	5 times	No cracks on the surface, uniform crystal size, good interlocking of the crystals.

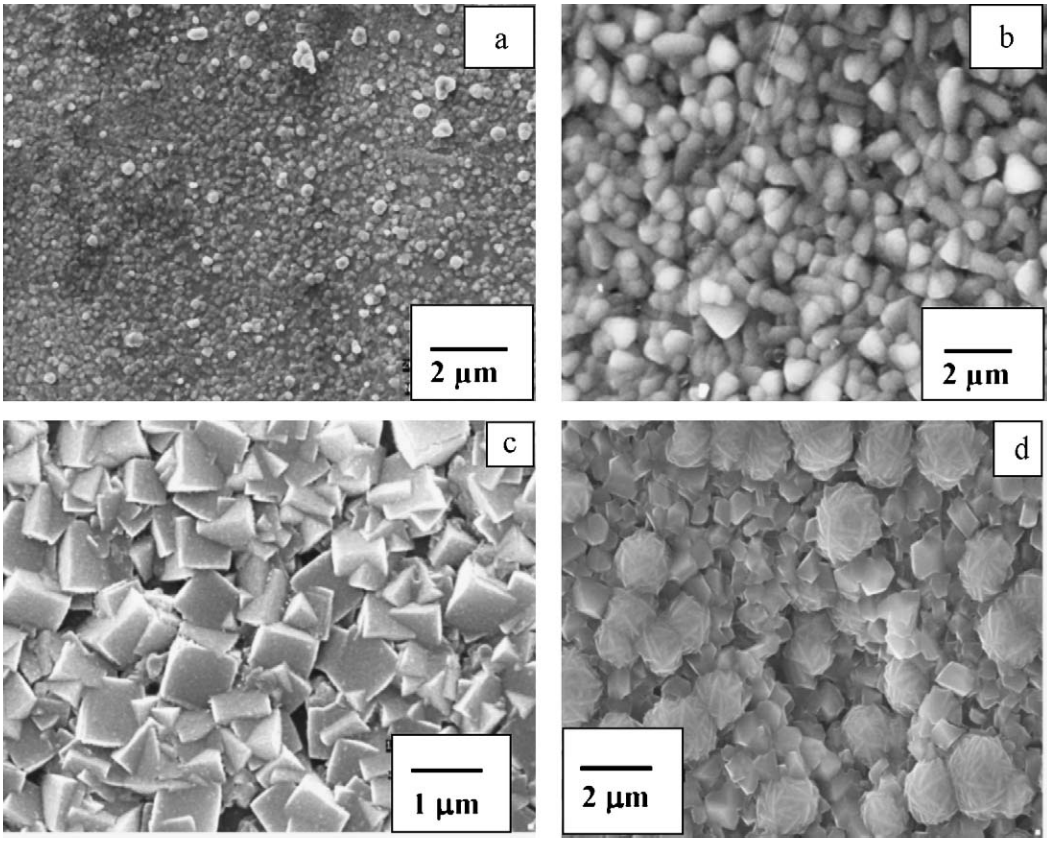

Fig. 1. SEM micrographs of NaA zeolite membrane on unseeded substrate synthesized for (a) 65 °C, 2 h; (b) 65 °C, 4 h; (c) 65 °C,6 h; (d) 90 °C, 4 h

In order to increase the zeolite formation on support surface, initial sol concentration was changed from half concentration to double concentration of total oxide content. No formation of zeolite phase in case of half oxide content, as shown in Fig. 3a. At this lower concentration, the nucleation and crystal growth does not occur in the reaction medium but the gel was formed and the covered the substrate. The SEM image of synthesized zeolite membranes with double sol concentration was shown in Fig. 3c. Some different type zeolite crystals along with NaA crystals were formed. This result suggests that higher reagent concentration forced to form large number of nuclei in the reaction medium. Those nuclei form agglomerates, which after crystal growth form irregular shaped particles and interlocked dense structure did not formed with those type of particles. But in case of optimum concentration of the sol, at 65 °C for 6 h only NaA crystals were formed.

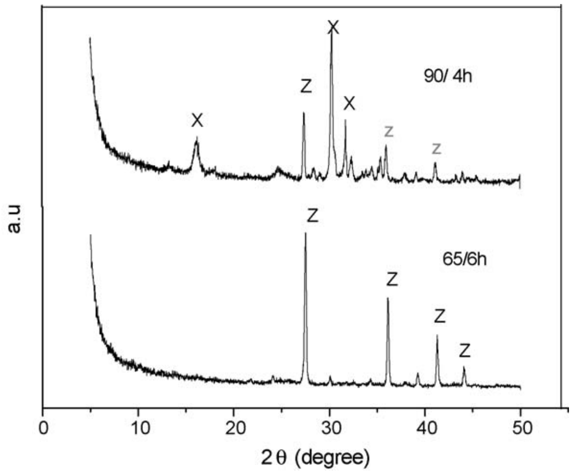

Fig. 2. XRD pattern of NaA zeolite synthesized at different time and temperature.

Thus it was clear from above observations, that to get a uniform coating of zeolite membrane layer on substrate, a seed layer of same type of zeolite must be distributed on substrate surface. Each seed on the surface acts as nucleation point for formation of zeolite from sol.

Generally to get a good seeding layer, the seeds must have suitable size so that the size of the seeds should be small but should not penetrate into the support pores [12]. The formation of NaA zeolite membrane on the seeded alumina support with different synthesis time was investigated and the as synthesized membranes were characterized by XRD and SEM. According to the formation mechanism of zeolite membrane on the porous support, the nucleation of zeolite on the support/gel interface and in the bulk synthesis mixture are competitive processes [13]. In order to form a continuous zeolite membrane on the support surface, the nucleation of zeolite in the bulk synthesis mixture must be inhibited, while the nucleation of zeolite at the support gel interface should be promoted. By increasing the nucleation point on the support surface, a continuous NaA zeolite membrane layer, can be obtained. In the synthesis of continuous membrane layer seed crystals must be added before synthesis.

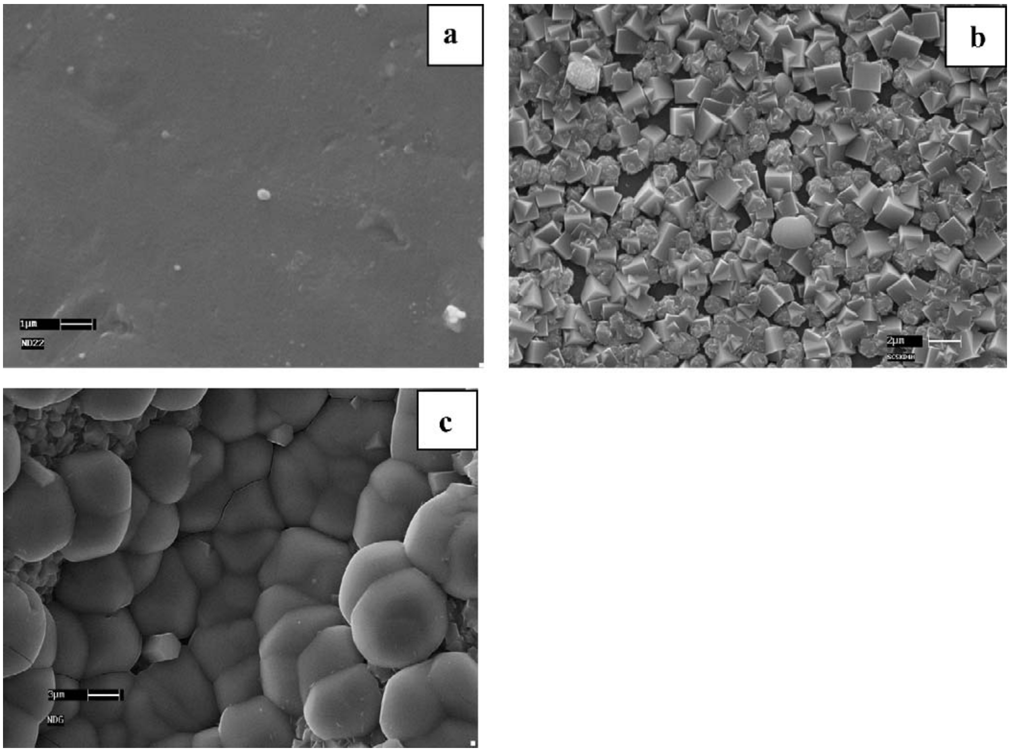

Fig. 3. SEM micrographs of NaA zeolite membrane on unseeded substrate synthesize sol with (a) half oxide concentration, (b) standard concentration and (c) double concentration.

Fig. 4 shows the XRD pattern of as synthesized membrane on the seeded alumina support, synthesized for 2–6 h along with support surface.

The membrane formed after 2 h showed very weak peaks of zeolite NaA besides strong peaks of alumina substrate. The membranes after 4 and 6 h clearly showed every peak for zeolite A. The morphology of these membranes was observed with scanning electron microscope. Fig. 2 shows the SEM photograph of the gradual change of seeded surface (Fig. 5a) from 2 h (Fig. 5b) to 4 h (Fig. 5c and d) of synthesis. The seed crystals which have size less than 2 μm were distributed homogenously on the support surface. After 2 h of synthesis, the support surface started to cover with NaA zeolite layer. The packing of the layer was not dense. Some pores were still present on the membrane layer and the grains were not interlocked. After 4 h, the surface was completely covered with NaA zeolite crystal. An interlocked packed zeolite layer was formed. No space between the particles was found by SEM.

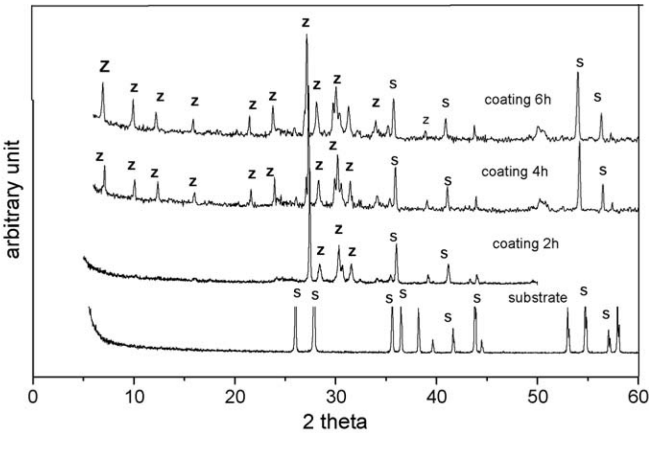

Fig. 4. XRD spectra of synthesized zeolite coating on seeded support where '*z*' denotes NaA peak and '*s*' denotes substrate peak.

From these figures it is clear that after 4 h of synthesis, the zeolite crystals grew and interlocked to from dense membrane structure. Surface seeding cannot only accelerate the formation of the NaA zeolite on the support, but also inhibit the transformation of the NaA zeolite into other types of zeolites. A continuous NaA zeolite membrane can be formed on the seeded support. The main advantage with seed crystals is that they are easily inter-grown. In seed film method, the final film thickness can be controlled by varying crystallization time and size of the seed crystals [12–14]. The SEM images showed that although a continuous NaA zeolite membrane was obtained after coating the seeds, a crack of width 2–3 μm still existed in the obtained membrane after interlocking of zeolite crystals properly. The films are fragile since zeolite grains were not strongly bonded to the support surface.

The main cause of cracking of zeolite layer is lack of good adherence between zeolite layer and substrate layer. To obtain a crack free membrane layer on the substrate, an intermediate layer (buffer layer) was applied. The intermediate layer was made of cellulose solution and seed sol. It increased the anchoring property of the seed layer and support layer. As the zeolite crystals were grown from seed surface, the bonding between support layer and grown membrane layer became strong. Addition of a buffer layer can also enhance the mechanical strength and integrity of the film. Fig. 6 shows the

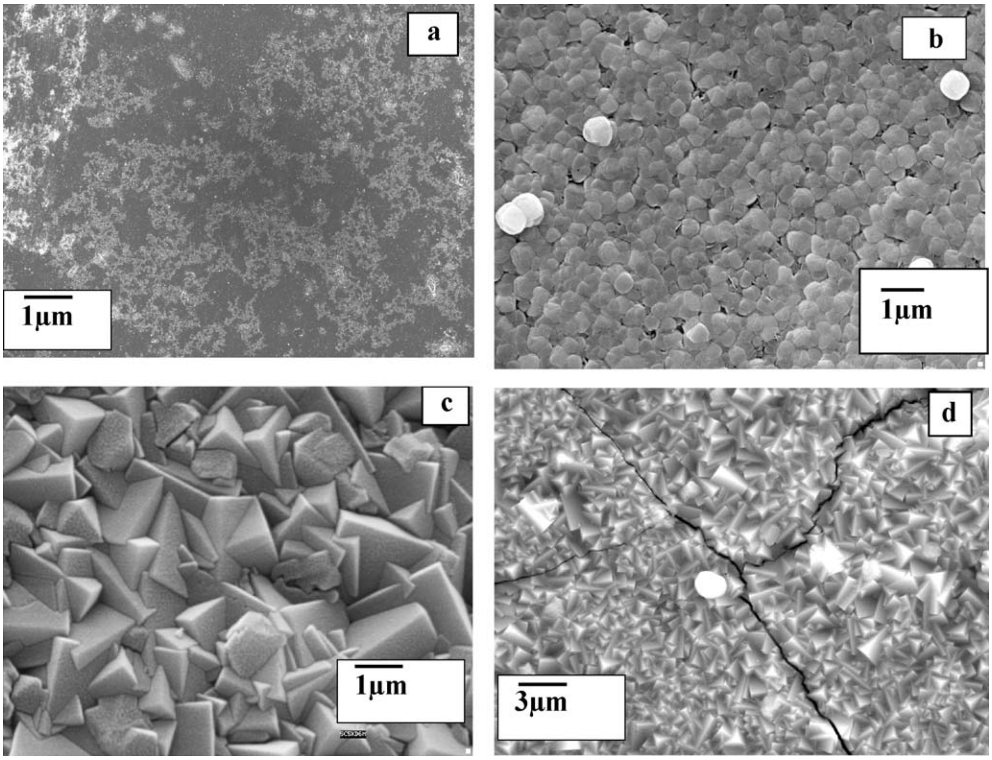

Fig. 5. SEM micrograph of (a) seeded support, (b) coating formation after 2 h of synthesis, (c) interlocked coating formed after 4 h and (d) severe cracks on coating surface

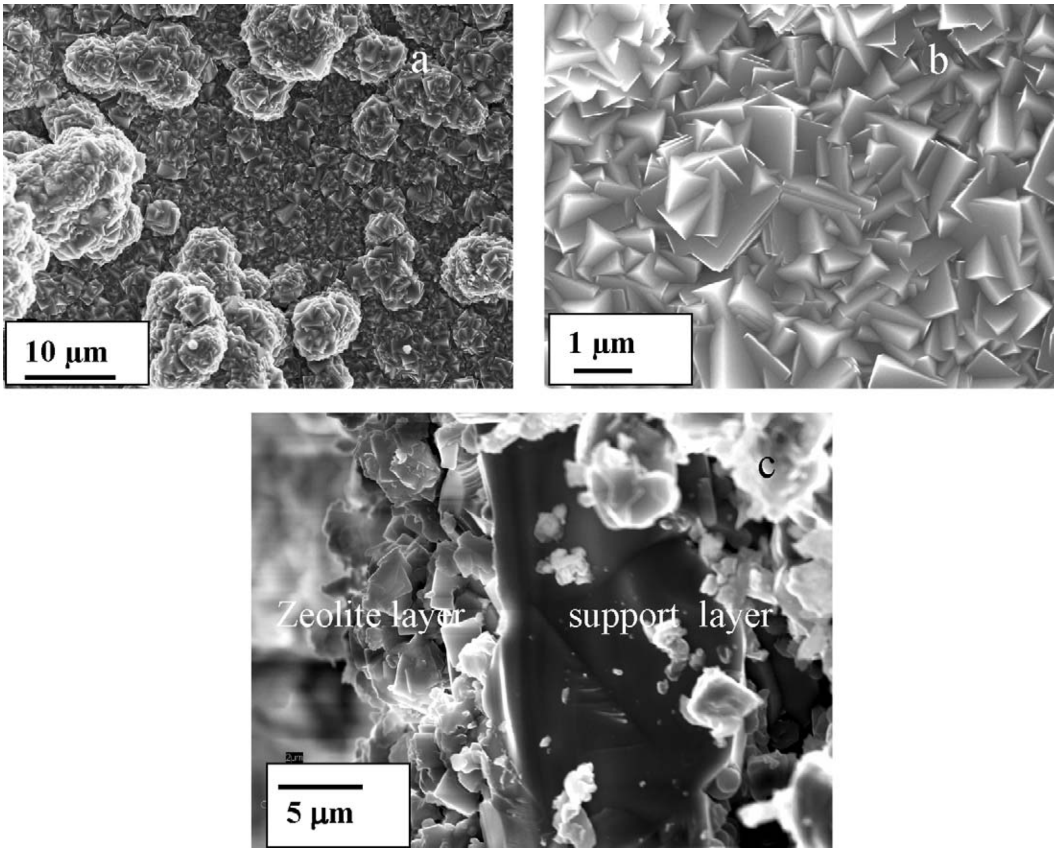

Fig. 6. SEM micrograph of seeded support with cellulose layer: (a) lower magnification, (b) higher magnification and (c) cross-sectional view

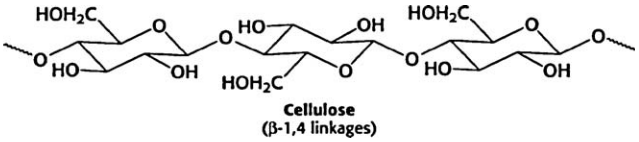

Fig. 7. Structure of cellulose.

Table 2
Gas permeance of seeded membrane (without buffer layer).

Time	Permeance (mol s^{-1} m^{-2} Pa^{-1})		Ratio O_2/N_2
	N_2	O_2	
Uncoated	17.82 × 10^{-6}	17.67 × 10^{-6}	0.991
Single stage	12.46 × 10^{-6}	15.78 × 10^{-6}	1.266
Two stage	6.41 × 10^{-6}	6.48 × 10^{-6}	1.010
Three stage	6.016 × 10^{-6}	6.23 × 10^{-6}	1.036

SEM micrograph of seeded support with buffer layer. Fig. 6a and b depicted the growth of membrane layer on that seeded support with different magnification and Fig. 6c showed the cross-section view of the membrane layer. The SEM image indicates the formation of compact layer of about 15–20 μm thickness. Some zeolite crystals were also grown in support pore surface.

Hydroxyl group of cellulose layer acts as binder between zeolite and support layer (Fig. 7). These chains are parallel, forming layers with OH group outside. These hydroxyl groups will form hydrogen bonds between hydroxyl ion and neighboring group. There fore an increase in hydroxyl group density causes a better attachment between the zeolite and the support, Fig. 8 shows the elemental analysis of zeolite layer. Layer I (alumina substrate) is rich in 'Al' and layer II, a nanoporous layer is made up of Ti (nanofiltration or uppermost surface layer of 'Sterlitech' membrane substrate contains TiO_2) and layer III, the zeolite layer, started to form at 32 μm and end at 48 μm (taking the distance form support surface layer which is rich in Ti (layer II)). The peak intensity of Si, Al, Na is high in these range.

However XRD and SEM can only indicate whether a continuous membrane formed on the support, they cannot confirm whether a high quality zeolite membrane formed. The quality of zeolite membrane can only be evaluated by gas permeation properties of the zeolite coated membrane.

The molecular kinetic diameter of O_2 and N_2 are 0.346 and 0. 364 nm. These are close to pore size of NaA zeolite. Table 2 shows the gas permeance properties of membrane prepared without intermediate layer. The permeance of N_2 and O_2 and, permselectivity of O_2/N_2 of NaA zeolite membranes with different synthesis stages was measured. After one stage synthesis, the SEM and XRD results were consistent with the results of gas permeation measurements. The N_2 and O_2 permeances of the substrates were 17.82×10^{-6} and 17.67×10^{-6} mol s^{-1} m^{-2} Pa^{-1}. As the reaction progressed for first stage, second stage and third stage coating, the permeance of N_2 changed to 12.46×10^{-6}, 6.41×10^{-6}, and 6.01×10^{-6} mol s^{-1} m^{-2} Pa^{-1}. The O_2 permenace through the membranes changed to 15.78×10^{-6}, 6.48×10^{-6} and 6.23×10^{-6} mol s^{-1} m^{-2} Pa^{-1} with coating stages. The permeability ratio changes from 0.99 to 1.036. These small changes of permeation values indicate the presence of large pores or cracks and voids.

In case of cellulose containing membrane layer, the gas permeances of O_2, N_2 decreased as the molecular kinetic diameter increased, which indicates that permeance was controlled by molecular sieving effect. Table 3 shows the permeation results of N_2 and O_2 for cellulose coated NaA zeolite membranes.

For NaA zeolite (applying intermediate layer) membrane with a single stage synthesis, perm selectivity of was increased

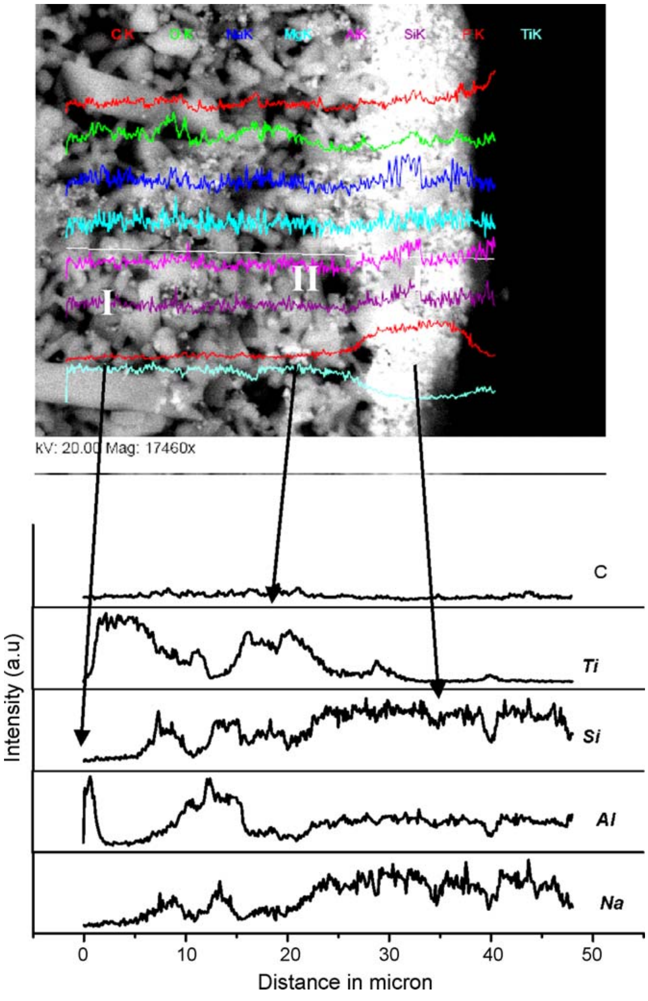

Fig. 8. Compositional elemental scan of NaA zeolite layer.

Table 3
Gas permeance results of as synthesized membrane with cellulose buffer layer.

Synthesis time	Permeance (mol s^{-1} m^{-2} Pa^{-1})		Ratio O_2/N_2
	N_2	O_2	
Substrate	18.32 × 10^{-6}	20.67 × 10^{-6}	1.12
One stage	5.82 × 10^{-7}	7.04 × 10^{-7}	1.20
Two stage	3.67 × 10^{-7}	7.12 × 10^{-7}	1.94
Three stage	2.11 × 10^{-7}	4.94 × 10^{-7}	2.34

to 1.20 comparing to that of only seeded membrane (Table 2). The permselectivity of N_2/O_2 was increased up to 2.34 for third stage synthesis which is much higher than Knudsen diffusion ratio, which indicates that the quality of the membrane was improved by applying third stage coating.

4. Conclusion

A high quality NaA zeolite membrane was successfully synthesized on a porous alumina substrate. Application of cellulose layer on support surface improves the quality of the membrane. When support was unseeded, the formation of coating layer was inhomogeneous. When the support was seeded, the formation of zeolite layer on the support was accelerated. A homogenous, continuous zeolite layer was formed on the seeded support. Cracking of the zeolite layer was the main problem for the synthesis of zeolite layer. To reduce the cracking, cellulose layer was applied on the support layer before zeolite layer synthesis. Gas permeation results indicated that non-zeolitic pores were present after single stage synthesis. After third stage synthesis the quality of the membrane was improved. The permeances of N_2 and O_2 increased as the molecular kinetic diameter of the gases decreased, which showed the molecular sieving effect of the NaA zeolite membrane. The permselectivity of O_2/N_2 was 2. 34. The quality of the as synthesized membrane with three stage synthesis gave the best results.

Acknowledgements

The author would like to thank CSIR, India for financial support in the project No. SIP 0023 and also thankful to Dr. H.S. Maiti, Director, CGCRI for his kind permission to publish the research work.

References

[1] J.C. Jansen, J.H. Koegler, H. van Bekkum, H.P.A. Calis, C.M. Van de Bleek, F.K. Kapteijin, J.A. Moulijin, E.R. Geus, N. van der Puil, Zeolitic coatings and their potential use in catalysis, Micropor. Mesopor. Mater. 21 (1998) 213–226.

[2] T. Bein, Synthesis and application of molecular sieve layer and membranes, Chem. Mater. 8 (1996) 1636–1653.

[3] K. Okamoto, H. Kita, K. Horii, K. Tanaka, M. Kondo, Zeolite NaA membrane: preparation, single gas permeation and pervaporation and vapor permeation of water/organic liquid mixtures, Ind. Eng. Chem. Res. 40 (2001) 163–175.

[4] J. Zaha, H.M. Krieg, J.C. Breytenbach, Pervaporation and related properties of time-dependent growth layers of zeolite NaA on structured ceramic supports, J. Membr. Sci. 284 (2006) 276–290.

[5] X. Xu, W. Yang, J. Liu, L. Lin, Synthesis of a high performance NaA zeolite membrane by microwave heating, Adv. Mater. 12 (3) (2000) 195–198.

[6] G. Yang, X. Zhang, S. Liu, K.L. Yeung, J. Wang, A novel method for the assembly of nano-zeolite crystals on porous stainless steel microchannel and then zeolite film growth, J. Phys. Chem. Solids 68 (2007) 26–31.

[7] A. Huang, Y.S. Lin, W. Yang, Synthesis and properties of A-type zeolite membranes by secondary growth method with vacuum seeding, J. Membr. Sci. 245 (2004) 41–51.

[8] L.C. Boudreau, T. Tsapatsis, A highly oriented thin film zeolite A, Chem. Mater. 9 (1997) 1705–1707.

[9] M. Tsapatsis, M.C. Lovallo, T.O. Kubo, M.E. Davis, M. Sadakata, Characterization of zeolite L, nanoclusters, Chem. Mater. 7 (1995) 1734–1736.

[10] M.C. Lovallo, M. Tsapatsis, Preferentially oriented submicron silicalite membranes, AIChE J. 42 (1996) 3020–3031.

[11] X.C. Xu, W.S. Yang, J. Liu, L.W. Lin, Synthesis and perfection evaluation of NaA zeolite membrane, Sep. Purif. Technol. 25 (2001) 475–486.

[12] N. Kuanchertchoo, S. Kulprathipanja, P. Aungkavattana, D. Atong, K. Hemra, T. Kirksomboon, S. Wongkaseujit, Preparation of uniform and nanosized NaA zeolite using silatrane and alumatrane precursor, Appl. Organomet. Chem. 20 (2006) 775–783.

[13] K. Aoki, K. Kusakabe, S. Morooka, Preparation of oriented A type zeolite membranes, AIChE J. 46 (1) (2000) 221–224.

[14] M. Kondo, M. Komori, H. Kita, Tubular-type pervaporation module with zeolite NaA membrane, J. Membr. Sci. 133 (1997) 133–141.