Emulsion-based synthesis of NaA zeolite nanocrystals and its integration towards NaA membranes

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Abstract. NaA zeolite nanoparticles (seed crystals) of size 50–65 nm were synthesized using water-in-oil (w/o) type emulsions at a considerably low temperature of $65 \pm 1^\circ\text{C}$ in a short duration of 2 h. The emulsions were stabilized using non-ionic surfactants e.g. sorbitan monooleate (Span 80), sorbitan monolaurate (Span 20), polyoxyethylene(5)nonylphenylether with ethoxy numbers of 5 (Igepal CO-520) and polyoxyethylene sorbitan monooleate (Tween 80) of hydrophilic-lipophilic balance (HLB) values of 4.3, 8.6, 10 and 15 respectively. Among the surfactants, the intermediate HLB values of 8.6 (Span 20) and 10 (Igepal CO-520) were effective in synthesizing highly dispersible NaA nanoparticles of size 50–65 nm. The membrane prepared hydrothermally in multi-steps at $65 \pm 1^\circ\text{C}$, using the Span 20-derived seed crystals deposited on porous support, showed the formation of high quality interlocked NaA coating. Single gas nitrogen (N_2) permeation of the membrane exhibited a permeance value of $1.01 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at ambient temperature (30°C).

Keywords. Zeolite nanocrystals; emulsion synthesis; hydrothermal technique; NaA membrane; microstructure.

1. Introduction

Zeolites are three-dimensional silicate and aluminosilicate microporous crystalline solids with well-defined structures (Breck 1974; Barrer 1978). Depending on the Si/Al mole ratio, varieties of zeolites having pore sizes from 0.3 to 1 nm are obtained. Due to varying pore dimensions, zeolites can interact very selectively with molecules depending on their size, shape and chemical characteristics. Further, with increase in the Si/Al mole ratio, the hydrophilicity in the zeolite structure decreases, thus giving rise to varying applications, such as catalysis, adsorption, gas separation, ion exchange, etc (Breck 1974; Barrer 1978; Ramsay and Kallus 2000). The micrometer-sized zeolites e.g. NaA, NaX, NaY, Mordenite, etc. used for the above-mentioned applications have been reported to be synthesized mainly hydrothermally by several workers during 70s (Breck 1974; Chatterjee *et al* 1974; Chatterjee *et al* 1975; Barrer 1978). However, the reduction of particle size of the zeolites from micrometer to nanometer size range gives rise to dramatic changes in their properties, and subsequently the performance of the zeolites in traditional applications such as sorption and catalysis significantly increases (Ramsay and Kallus 2000; Mintova and Bein 2001; Yang *et al* 2007).

The increase in surface energy resulting from the increase in surface to volume ratio of the particles causes significant change in their properties. The main interest of the colloidal suspensions of nanozeolites (seed crystals) over the conventional micrometer-sized zeolites is in the preparation of thin films, membranes, composites and hierarchical structures with unique properties for their applications in medicine, optoelectronics, sensors, fuel cells, hydrogen production, etc. The nano-sized zeolites are effective in controlling the film thickness and membrane structure by *ex situ* process over *in situ* process (Ramsay and Kallus 2000; Mintova and Bein 2001; Yang *et al* 2007; Das *et al* 2009). It is obvious that the synthesis of nano-zeolites and its use as seed layer might play an important role for controlling the zeolite membrane structure.

Synthesis of nanoparticles with narrow size distribution is an essential requirement for practical purposes. In addition to the hydrothermal technique, the emulsion method is well accepted for the synthesis of nanoparticles due to its several advantages i.e. controlled growth, small size and narrow size distribution, better purity, etc. (Dutta *et al* 1995; Chatterjee *et al* 2000; Guo *et al* 2005; Lee and Shantz 2005; Naskar and Chatterjee 2005; Liu *et al* 2006; Naskar *et al* 2006; Das *et al* 2009). Both ionic and non-ionic surfactants are used for the synthesis of zeolite particles (Lee and Shantz 2005; Liu *et al* 2006; Das *et al* 2009). In our previous study, we have shown the effect of non-ionic surfactants in tailoring the size of the oxide and

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sulphide particles (Chatterjee *et al* 2000; Naskar *et al* 2006). The gradual increase in HLB value of the surfactants showed the formation of smaller particles (Chatterjee *et al* 2000; Naskar *et al* 2006). In the present study, we have examined the role of some non-ionic surfactants of varying HLB values in synthesizing NaA zeolite nanoparticles, which are not yet well studied. The main reason for considering the non-ionic surfactant is to reduce the electrostatic interaction between the surfactants and the aqueous ions present in the system. Such interactions are known to affect the nucleation and growth of the zeolites (Lee and Shantz 2005; Liu *et al* 2006; Das *et al* 2009). Keeping the above points in view, in the present investigation we report (i) an effective water-in-oil (w/o) type emulsion technique in presence of non-ionic surfactants of HLB values 4.3, 8.6, 10 and 15 for the synthesis of zeolite nanoparticles, (ii) role of surfactants on the formation of zeolite nanoparticles and (iii) characteristics of NaA membranes grown hydrothermally on the emulsion-derived NaA seed-coated support.

2. Experimental

2.1 Synthesis of NaA zeolite nanoparticles

In the present investigation, water-in-oil (w/o) type emulsions were used for the synthesis of zeolite nanoparticles. For such synthesis, sodium hydroxide (G.R., Merck, Mumbai, India, purity > 98%), aluminium chloride hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (A.R., S.D. Fine Chemicals, Mumbai, India, purity > 99.5%) and sodium metasilicate nonahydrate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (G.R., Qualigens Fine Chemicals, Mumbai, India, purity > 99%) were used as the starting materials. Required quantities of NaOH and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in a fixed volume of deionised water under agitation in a tightly covered polypropylene container. Appropriate quantity of sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) was added to the above solution under vigorous stirring, leading to the formation of a clear solution. The molar ratio of the solution was maintained as $50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 1000\text{H}_2\text{O}$. This solution was used as the water phase (w) of w/o type emulsions. An organic solvent i.e. *n*-heptane (G.R., Merck, Mumbai, India, purity > 99%) acted as the oil phase (o). A support solvent was prepared by mixing 1 vol% of the non-ionic surfactant, e.g. Span 80 (Fluka Chemie AG, Neu-Ulm, Switzerland) in *n*-heptane. For the preparation of the w/o type emulsions, the water phase was dispersed as droplets in the support solvent under a constant mechanical agitation of 500 rpm and kept under such condition for 10 min for equilibration. The volume ratio of the water phase: support solvent was kept constant at 1:4 in all the experiments.

The stabilized emulsion was then placed in an oil bath at $65 \pm 1^\circ\text{C}$ for 2 h under stirring (500 rpm). The entire

emulsion was cooled down to the ambient temperature (30°C) followed by addition of a known volume of methanol (G.R., Merck, Mumbai, India, purity > 99%) (volume ratio of emulsion: methanol = 1:5). Immediate flocculation of particles occurred which were collected by centrifugation at 9000 rpm. The particles were washed thrice with methanol, each time collecting the particles centrifugally as described above followed by the dispersion in the washing solvents. The washed particles were dried at 80°C for 4 h. Following the same procedure separate experiments were performed using other surfactants, i.e. Span 20 (Fluka Chemie AG, Neu-Ulm, Switzerland), Igepal CO-520 (Sigma Aldrich, Teutonia Ave., Milwaukee, WI 53209, USA) and Tween 80 (Fluka Chemie AG, Neu-Ulm, Switzerland).

2.2 Preparation of NaA seed-coated supports

Porous alumina-based discs of diameter 47 mm and thickness 2.5 mm (Sterlitech Co. (Kent, WA 98032-1911, USA), were used as the support for the preparation of the LTA type (e.g. NaA) zeolite membrane. The support was cut into small pieces of discs of diameter about 20 mm. They were cleaned with acetone in a ultrasonic cleaner for 5 min to remove loose particles and greasy materials created during cutting into small pieces followed by drying in air at 100°C for 5 h for the removal of water and acetone from the support surface.

The NaA nanocrystals obtained from Span 20 and Tween 80 stabilized reverse emulsions, were used to prepare dispersion of NaA seeds. For the preparation of 4 wt% NaA dispersions, the required amount of the seed was dispersed in deionized water under sonication. The seed-coated support was prepared by using a dip coating machine (Dip Master; Model: 200, CHEMAT Technology Inc, North Ridge, California, USA). For this purpose, the blank porous support of 20 mm diameter was dipped into the NaA dispersion in a single step for 20 s and withdrawn with a speed of 10 cm/min. The seed-coated support was dried at room temperature for 4 h followed by drying in an air oven at 100°C for 2 h.

2.3 Preparation of NaA zeolite membrane

Figure 1 illustrates schematically the steps involved in the preparation of NaA zeolite membranes. Two clear zeolitic solutions, solution A and solution B were prepared at room temperature (30°C) under stirring. The molar composition of solution A was kept as $50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 1000\text{H}_2\text{O}$ and that of solution B was maintained as $50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 2300\text{H}_2\text{O}$. For the preparation of membranes, each zeolitic solution was kept in Teflon lined stainless steel autoclaves. The NaA seed-coated substrate was immersed into the above clear precursor solution by hanging through a Teflon thread

Figure 1. Schematic representation of the preparation of NaA zeolite membranes.

Table 1. Experimental conditions for the preparation of NaA zeolite membrane at $65 \pm 1^\circ\text{C}$.

Sample no.	Solution composition (mol)	Seed-coated support	Synthesis step	Time (h)
A-4	$50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 1000\text{H}_2\text{O}$	Span 20-derived	Single	4
A-4*	$50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 1000\text{H}_2\text{O}$	Tween 80-derived	Single	4
A-6	$50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 1000\text{H}_2\text{O}$	Span 20-derived	Single	6
A-6*	$50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 1000\text{H}_2\text{O}$	Tween 80-derived	Single	6
B-4-2	$50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 2300\text{H}_2\text{O}$	Span 20-derived	Second	4 + 2
B-4-2-2	$50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 2300\text{H}_2\text{O}$	Span 20-derived	Third	4 + 2 + 2
B-4-2-2-2	$50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 2300\text{H}_2\text{O}$	Span 20-derived	Fourth	4 + 2 + 2 + 2

attached to a Teflon rod fitted at the top of the each autoclave bomb. The sealed autoclaves were then placed in an oven preheated at $65 \pm 1^\circ\text{C}$. With the solution A, single step *ex situ* crystallizations on the seed-coated supports (prepared from Span 20 and Tween 80 derived seeds) were performed at $65 \pm 1^\circ\text{C}$ for 4 and 6 h to obtain the NaA membranes (A-4, A-4* from Span 20 and Tween 80 derived seeds respectively with 4 h reaction time each and A-6, A-6* from Span 20 and Tween 80 derived seeds respectively with 6 h reaction time each). However, with the solution B, multi-step *ex situ* crystallizations on the seed-coated supports (prepared from Span 20 derived seeds) were carried out at the same temperature. Table 1 shows the experimental conditions for the preparation of NaA membranes with solutions A and B. For multi-step *ex situ* crystallization with solution B, in the first step the seed-coated supports (prepared from Span 20 derived seeds) were immersed into the solution A and kept at $65 \pm 1^\circ\text{C}$ for 4 h to obtain the membrane A-4 as above. Membrane A-4 was treated with solution B at $65 \pm 1^\circ\text{C}$ for 2 h in the second step for the formation of membrane B-4-2. Further, in the third step, B-4-2 was treated under the same experimental conditions as in the second step to

obtain the membrane B-4-2-2 while in the fourth step, the B-4-2-2 was used for the formation of membrane B-4-2-2-2 under the above conditions. It is to be mentioned that in each step freshly prepared zeolitic solution B was used. The prepared membranes from solution A (single step for 4 and 6 h each) and from solution B (multi-steps, in each step) were thoroughly washed with deionized water until the pH of washing liquid became neutral followed by drying at 100°C for 4 h in an air oven.

2.4 Characterization of the zeolite particles and membranes

The zeolite particles were characterized by X-ray diffraction (XRD; Model: Philips, 1730, Philips, Almedo, The Netherlands) with Ni-filtered CuK_α radiation and transmission electron microscopy (TEM; Model: Tecnai G² 30ST (FEI Company, Eindhoven, The Netherlands). The microstructural feature of the membrane was examined by scanning electron microscopy (SEM; Model: S430i, LEO Electronic Microscopy Ltd, Cambridge, UK) and field emission scanning electron microscopy (FESEM,

Table 2. Single gas N₂ permeance of NaA zeolite membrane prepared under different experimental conditions

Sample no.	Synthesis step	Time (h)	Permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)
Support			19.32 × 10 ⁻⁶
A-4	Single	4	6.57 × 10 ⁻⁷
B-4-2	Second	4 + 2	2.14 × 10 ⁻⁷
B-4-2-2	Third	4 + 2 + 2	1.01 × 10 ⁻⁸
B-4-2-2-2	Fourth	4 + 2 + 2 + 2	1.06 × 10 ⁻⁷

Model: Zeiss, Supra^{TM} 35VP, Oberkochen, Germany). Formation of NaA zeolite in the membrane was confirmed by XRD.

The specific surface area of the particles, calcined at 500°C with a dwell time of 1h, was measured using the BET surface area analyzer (Model: Autosorb 1, Quantachrome Corporation, USA). Ignition loss due to removal of adsorbed organics and other volatiles was determined by heating the samples at 500°C with a dwell time of 1 h in a programmable electric furnace in air atmosphere.

To examine the performance of the membranes, single gas N₂ permeation experiments were carried out (Xu *et al* 2001; Chen *et al* 2002; Lee and Shantz 2005; Yin *et al* 2007; Zah *et al* 2007). The membrane was sealed in a custom-made gas permeation reactor with the membrane side facing the feed. Single gas N₂ permeation was measured using a soap-film bubble flow-meter at ambient temperature (30°C) keeping a pressure difference of 3 kg/cm² between feed and permeate side of the membrane. The results are summarized in table 2.

3. Results and discussion

3.1 Stabilization of the aqueous zeolitic droplets

In w/o type emulsions, as in the present investigation, dispersion of the water phase (aqueous solution of zeolitic composition) in the oil phase (*n*-heptane) as small droplets under agitation causes an increase in the surface area of the dispersed phase. Thermodynamically, the increase in surface area 'Δ*A*' of the dispersed phase associated with a free energy change (Δ*G*) of the system can be represented as (Dickinson 1994)

$$\Delta G = \gamma \Delta A, \quad (1)$$

where γ is the interfacial tension. The equation indicates that a low interfacial tension favours droplet disruption. This is accomplished by the addition of a system compatible amphiphilic surface active agent or surfactant which gets adsorbed on the dispersed aqueous droplets and lowers the interfacial tension of the emulsion system. The droplet size is controlled with the type of the surfactant, synthesis temperature, time, etc (Dutta *et al* 1995; Chatterjee *et al* 2000; Guo *et al* 2005; Naskar and Chat-

terjee 2005; Naskar *et al* 2006). In the present work, Span 80, Span 20, Igepal CO-520 and Tween 80 with HLB values of 4.3, 8.6, 10 and 15 respectively were used for the preparation of emulsions. Figure 2 presents the molecular structures of the amphiphilic surfactants used in the present study.

The non-ionic surfactants are characterized by their HLB values. A high HLB value indicates strongly hydrophilic nature, while a low value is an indication of a strong hydrophobic nature. Considering these points, non-ionic surfactants, e.g. Span 80, Span 20, Igepal CO-520 and Tween 80 with HLB values of 4.3, 8.6, 10 and 15 respectively have been selected for understanding their role in zeolite particle formation. The sorbitan group in figures 2a and b, the phenylethoxylate group in figure 2c and the polyoxyethylene sorbitan group in figure 2d act as the hydrophilic 'polar head', while the oleic acid group in figures 2a and d, lauric acid in figure 2b and the nonyl group in figure 2c act as the hydrophobic 'non-polar tail'.

3.2 Formation of zeolite nanoparticles

Free-standing zeolite nanoparticles were obtained by the addition of methanol to the surfactant-stabilized reverse emulsion system. In the emulsified aqueous microdroplets, the surfactant molecules get adsorb on the surface of zeolite nanoparticles and remain in the dispersed state. However, the solubility of surfactant molecules in methanol, added to the system, destabilizes the emulsion system, leading to the flocculation of NaA particles.

The zeolite nanoparticles in the emulsified aqueous microdroplets crystallized at 65 ± 1°C with an ageing time of 2 h during hydrothermal treatment. It is obvious that an increase in the reaction temperature and ageing period over 65 ± 1°C and 2 h, respectively resulted in the crystallization of large agglomerated zeolite particles, irrespective of the nature of the surfactants used. The particle size was tailored by using surfactants of different HLB values, keeping other parameters unaltered. Considering the HLB values and structures of the surfactants (figure 2) used in the present study, it is to be noted that the HLB value decreases with increase in the hydrophobic chain length and decrease in the number of polyoxyethylene groups attached to the molecules. Figure 3

shows the XRD patterns of NaA particles crystallized in presence of (a) Span 80, (b) Span 20, (c) Igepal CO-520 and (d) Tween 80. It is to be noted that under the stipulated reaction temperature and time, all the surfactants, crystallized with NaA zeolite particles. TEM images show the nature of the NaA zeolite particles formed in presence of different surfactants (figure 4). It was noticed that for all the surfactants the crystals were almost

Figure 2. Molecular structures of amphiphilic non-ionic surfactants: (a) Span 80 (HLB: 4.3); (b) Span 20 (HLB: 8.6); (c) Igepal CO-520 (HLB: 10) and (d) Tween 80 (HLB: 15).

Figure 3. XRD patterns of the emulsion-derived NaA particles crystallized at $65 \pm 1^\circ\text{C}/2\text{ h}$ in presence of different non-ionic surfactants: (a) Span 80; (b) Span 20; (c) Igepal CO-520 and (d) Tween 80.

spherical in shape which is different from large NaA crystals having typical cubic morphology. The round crystals produced act as builders (Kumakiri *et al* 1999). It was observed that irregular shaped large agglomerated particles were obtained with Span 80 (figure 4a). Since the Span 80 derived particles were highly agglomerated and irregular in shape, assessment of particle size could not be made. For the surfactants, Span 20 and Igepal CO-520 with higher HLB values than Span 80, the particle size became smaller with narrow size distribution (50–65 nm). However, in presence of Tween 80, agglomerated particles with a size range of 65–105 nm were obtained.

It is interesting to point out that the surfactants with low HLB (Span 80, HLB: 4.3) and high HLB (Tween 80, HLB: 15) resulted in agglomerated NaA particles with large size distribution while the surfactants with intermediate HLB (Span 20 and Igepal CO-520) rendered smaller NaA particles with narrow size distribution. Because of more hydrophobic character of Span 80, the interfacial tension between the aqueous zeolitic solution and organic solvent molecules (*n*-heptane) became relatively high (Chatterjee *et al* 2000; Naskar *et al* 2006). It failed to stabilize the emulsion up to an optimum level, resulting in the formation of highly agglomerated NaA particles during hydrothermal reaction. On increasing the HLB values of the surfactants (Span 20 and Igepal CO-520), their hydrophilicity increased. It caused a progressive decrease in the interfacial tension between zeolitic solution and organic

Figure 4. TEM images of the emulsion-derived NaA particles crystallized at $65 \pm 1^\circ\text{C}/2\text{ h}$ in presence of different non-ionic surfactants: (a) Span 80; (b) Span 20; (c) Igepal CO-520 and (d) Tween 80.

solvent, stabilizing the emulsion with the formation of smaller droplets which led to the generation of smaller particles with narrow size distribution. With further increase in the hydrophilicity of the surfactant (Tween 80, HLB: 15), it is believed that the smaller droplets formed tend to coalesce each other resulting in the agglomeration (Guo *et al* 2005; Kim *et al* 2006) of NaA particles under the above hydrothermal condition. Therefore, from the above results it can be inferred that the intermediate HLB values (8–10) of non-ionic surfactants are suitable for the preparation of well dispersed nano-sized NaA zeolites.

The surface area and ignition loss of the particles derived from Span 80-, Span 20-, Igepal CO-520- and Tween 80-stabilized emulsions were 11.1, 14.2, 13.9 and 12.3 m²/g and 7.8, 9.2, 9.9 and 8.8 wt.% respectively.

3.3 Coating of the supports with the NaA seed particles

For controlled growth of NaA films on the support, the nucleation seeds should be small, well dispersed in the

dispersion medium and homogeneously distributed on the support (Xu *et al* 2001). In addition, for rapid pore closure of voids between seeds, a good surface coverage (Naskar *et al* 2009) with small sized seeds is necessary. Keeping these points in mind, the NaA nanoparticles obtained from Span 20 (agglomerate-free) and Tween 80 (highly agglomerated) were used as seeds to understand the characteristics of the membranes prepared from the expected different seed layers. The 4 wt% aqueous dispersions of particles exhibited good wettability with the support. Figures 5a and b show the SEM of top surface view of the Span 20 and Tween 80 derived seed layers respectively. It is evident from figure 5a that the Span 20 derived nanoparticles could produce homogeneous seed layer with good surface coverage, while in figure 5b the seed layer became inhomogeneous. This happened because the Tween 80 derived nanoparticles formed agglomerates which could not be effectively broken down during ultrasonic treatment of the aqueous dispersion.

Figure 5. SEM images of top surfaces of seed layers generated from NaA nano-particles obtained via (a) Span 20 and (b) Tween 80-stabilized emulsions.

Figure 6. FESEM images of top surfaces of as-prepared NaA membranes grown hydrothermally on the (a) Span 20 (A-4) and (b) Tween 80-derived (A-4*) seed-coated supports in single-step (4 h).

3.4 Formation of NaA zeolite membrane on seed-coated supports

Figures 6a and b show the FESEM images of top surfaces of the membranes prepared at $65 \pm 1^\circ\text{C}$ for 4 h in single step with Span 20 and Tween 80 derived seed-coated supports respectively. It is clear that in Span 20 derived seed-coated support, a better interlocking of the NaA crystals were obtained (figure 6a) which could be effective for a continuous membrane on the support surface (Xu *et al* 2001; Chen *et al* 2002; Yin *et al* 2007; Zah *et al* 2007). Under identical conditions, the Tween 80 derived agglomerated particles, however, failed to develop interlocked zeolite crystals (figure 6b). On increase in treatment time to 6 h in a single step, formation of cracks developed (shown by arrow in figure 7) in the microstructure of the membranes prepared with both Span 20 (figure 7a) and Tween 80 (figure 7b) derived seed-coated supports. It is observed that in the membranes prepared from Tween 80 (figure 7b) derived seed-coated support a mixture of spherical and cubic shaped particles

could hinder a better interlocking in the membrane formation. Therefore, the Tween 80 derived seed-coated membrane was not taken into consideration for further study.

In another set of experiments, multi-steps membrane preparation were adopted to examine the quality of the membrane. For this purpose, a stepwise hydrothermal treatment was followed with the membrane prepared at $65 \pm 1^\circ\text{C}$ for 4 h using zeolitic solution of molar composition $50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 1000\text{H}_2\text{O}$ (initial step) and Span 20 derived seed-coated supports. Further in each step, 2 h reaction time was given at $65 \pm 1^\circ\text{C}$ with the zeolitic solution of molar composition $50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 2300\text{H}_2\text{O}$. Figures 8a and b show respectively the top surface and cross-sectional views of FESEM images for the membrane prepared in a third-step (B-4-2-2) synthesis condition. The thickness of the NaA coating was about $3\text{ }\mu\text{m}$ (figure 8b). Membranes prepared in fourth-step hydrothermal treatment (B-4-2-2-2), however, generated cracks in the microstructure. It is to be noted that compared to the treatment temperature of $65 \pm 1^\circ\text{C}$, when the synthesis was performed

Figure 7. FESEM images of top surfaces of as-prepared NaA membranes grown hydrothermally on the (a) Span 20 (A-6) and (b) Tween 80-derived (A-6*) seed-coated supports in single-step (6 h).

Figure 8. FESEM images of (a) the top surface view of as-prepared NaA membrane grown hydrothermally on the Span 20-derived seed-coated support in third-step (B-4-2-2) and (b) the cross-sectional view of (a) (inset shows the magnified view of the membrane).

Figure 9. XRD pattern of NaA zeolite membrane grown hydrothermally on the Span 20-derived seed-coated support in different synthesis steps (a) first-step (A-4); (b) second-step (B-4-2) and (c) third-step (B-4-2-2). 'S' represents the peaks due to 'substrate'.

at $55 \pm 1^\circ\text{C}$ or $75 \pm 1^\circ\text{C}$, the developed membrane failed to exhibit the desired characteristics. Therefore, the synthesis temperature, $65 \pm 1^\circ\text{C}$ was considered as optimum.

Figure 9 shows the XRD patterns for the membranes prepared from the Span 20 derived seed crystals under different hydrothermal conditions. All the peaks characteristic of NaA were present in the samples. The intensity of NaA peaks in figure 9 increases with increase in treatment time in different steps. Therefore, growth of NaA crystals on the substrate with increase in treatment time is obvious.

Membranes developed under different experimental conditions were evaluated by single gas N_2 permeation at ambient temperature (30°C) and under a pressure difference of 3 kg/cm^2 (table 2). It is to be noted that although the membranes prepared in first step (A-4) and second step (B-4-2) synthesis conditions exhibited no crack formation under SEM, the N_2 gas permeation values were not satisfactory, which proves the presence of some defects in the membrane. However, the membrane prepared after third-step (B-4-2-2) treatment exhibited low permeance for nitrogen gas while that obtained under fourth-step (B-4-2-2-2) synthesis condition showed a higher permeance value. Formation of defects/microcracks in the zeolite layer is the reason for the low performance of the membrane after fourth-step treatment. Therefore, it can be inferred that the NaA nanoparticles derived from Span-20 stabilized w/o emulsions are highly suitable for preparation of high quality NaA zeolite membranes.

As compared to literature reports (Kumakiri *et al* 1999; Aoki *et al* 2000), in the present study, we have developed

NaA zeolite membranes at a relatively lower temperature of $65 \pm 1^\circ\text{C}$ by a stepwise hydrothermal treatment. The nitrogen permeation through the developed NaA membrane is comparable to the literature data (Aoki *et al* 2000; Okamoto *et al* 2001; Xu *et al* 2001).

4. Conclusions

NaA zeolite nanoparticles of size 50–65 nm could be successfully synthesized at a considerably low temperature of $65 \pm 1^\circ\text{C}$ and a short duration of 2 h via the developed w/o emulsion technique in presence of non-ionic surfactants, Span 20 (HLB value: 8.6) and Igepal CO-520 (HLB value: 10). Highly agglomerated NaA crystals were formed while using the surfactants, Span 80 with the lower HLB value of 4.3 and Tween 80 with the higher HLB value of 15, under identical conditions. The highly dispersible NaA zeolite particles were effective in the formation of seed-layer on porous support with good surface coverage. The membrane prepared hydrothermally in three-steps (B-4-2-2) at $65 \pm 1^\circ\text{C}$ from the Span 20-derived seeds exhibited the formation of high quality interlocked coating on the support. Single nitrogen gas permeation proved the formation of high quality NaA membrane by exhibiting a permeance value of $1.01 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at ambient temperature and under a pressure difference of 3 kg/cm^2 . This enables us to infer that a good surface coverage of seed layer with the nano-sized NaA zeolites helps in developing high quality membrane via secondary growth mechanism.

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