

Synthesis of free-standing chabazite-type films

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Abstract

An optimized synthesis procedure is reported for synthesis of free-standing chabazite-type films on walls of polypropylene reaction bottles. The optimum synthesis procedure involved a step heating procedure, in which the reaction composition is heated to 90°C for 40 h, followed by a rapid heating to 103°C, which is maintained for 2 h, and then the completion of the synthesis at 90°C for one more hour. The rapid heating to 103°C introduces thermally induced currents and particles from the settled gel move up from the bottom into solution by convection. This process promotes rapid film formation by releasing nuclei/aluminosilicate colloids into the solution. The films formed are typically 10 μm thick and made up of 4–5 μm spherical particles. It is malleable when wet and can be calcined. Relatively large pieces (cm²) can be readily peeled off from the walls of the polypropylene bottle. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Zeolites are porous, crystalline aluminosilicates, and find extensive applications in catalysis, gas separation and as ion-exchanging agents [1,2]. In general, they are synthesized in powder form. Recently, the synthesis of zeolite films has attracted considerable interest because of potential applications in separations, sensors and catalysts [3].

Several methods exist for preparation of zeolite films. The most commonly used method is direct synthesis on substrates under hydrothermal conditions. Substrates are typically immersed in the reaction mixture, and in some cases, the reaction

container itself can act as a substrate. Various zeolites have been grown on the surfaces of organic polymers [4–7], porous alumina [8,9], glasses [10–12], and metals [5,13] using direct film synthesis on substrates. The use of seeded substrates formed by depositing preformed crystals on substrates or laser ablation followed by further hydrothermal growth also allows for continuous film formation [14,15]. Nanocrystalline zeolites coated via a sol–gel method to make transparent films has been reported [16].

For many applications, free-standing zeolite films are of interest, and several examples have been reported [3]. ZSM films of thickness 20–250 μm have been grown on Teflon and silver surface, and can be readily removed from the substrate [4–6]. The preparation of one-crystal thick, free-standing gmelinite film was reported by Anderson et al. [6] with the (001) planes of the film oriented perpendicular to the substrate. Synthesis of

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self-supporting films of zeolite NaA on polyethylene has also been reported [7].

Chabazite is a small pore size zeolite (dehydrated chabazite has apertures of $0.38 \times 0.38 \text{ nm}^2$), with a Si/Al ratio of around 2 [17]. As anticipated from its high Al content, chabazite is hydrophilic. The aluminosilicate framework of chabazite consists of D6R units (double hexagonal rings) arranged in layers in the sequence of ABCABC [1]. Cation exchange properties of chabazite have been extensively studied [18]. Its preferential ion exchange towards cesium and strontium isotopes of, which are present in nuclear waste is of significant interest for nuclear remediation [19]. Chabazite has also been used as shape selective catalysts for methyl amine synthesis [20].

Despite numerous studies on chabazite, little is known about the films of chabazite except for examples of composite films with polymers or other zeolites. The preferential size-selective reactivity of ammonia (2.6 \AA) over tributyl amine (8.1 \AA) on acidic chabazite/silica films was reported by Bein and Brown [21]. Recently, Salomon et al. reported the synthesis of mordenite/ZSM-5/chabazite composite membrane on tubular α -alumina support [8]. Because of the high hydrophilicity, this composite membrane was used for the separation of water from ternary mixtures and showed a water/propanol selectivity as high as 149.

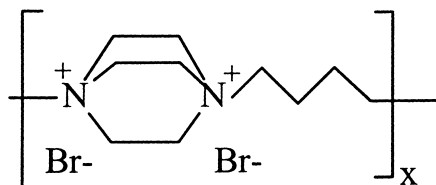
In this study, we present the hydrothermal synthesis of free-standing chabazite-type films grown on polypropylene surfaces. A novel hydrothermal treatment was developed to form the optimum zeolitic film. The influence of the synthesis parameters on the film formation and the mechanism of the crystal growth are discussed.

2. Experimental

2.1. Synthesis

Dab-4Br, a polymer formed from 1,4-diazabicyclo [2.2.2] octane (Dabco, Aldrich) and 1,4-dibromobutane (Aldrich), was used as structure directing agents for the present work. Dab-4Br has previously been utilized for a structure-directing

agent for a number of zeolites including chabazite and gmelinite [6,22]. The polymers had a molecular weight estimated to be $\sim 10,000$ and were synthesized according to the procedure outlined by Daniels et al. [22]. Proton chemical shifts of the synthesized polymer were measured on a Bruker DRX 500 MHz NMR spectrometer. In addition to Dabco protons at about 4.1 ppm, the protons on the α and β carbons linking these Dabco units were observed at 3.8 and 2.0 ppm, respectively. Dab-4Br polymer has the following structure:



The primary composition of the reaction mixture used in this study was $\text{SiO}_2:\text{Al}_2\text{O}_3 = 15$, $\text{Na}:\text{SiO}_2 = 1.2$, $\text{R}:\text{SiO}_2 = 0.16$, $\text{H}_2\text{O}:\text{SiO}_2 = 26$, where R represents the Dab-4 unit. Crystallization experiments with various amounts of Dab-4Br polymer as well as varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have been performed to investigate the effects of these parameters on film formation. Gels were prepared by mixing colloidal silica (Ludox HS-40, Du Pont) with aqueous solutions of Dab-4Br polymer in a 125 ml of polypropylene or Teflon bottle followed by the addition of NaOH (Mallinckrodt) and NaAlO_2 (Strem Chemicals) aqueous solutions. The bottles were cleaned with 49% hydrofluoric acid for 12 h prior to use.

Three temperature profiles were followed for the crystallization, 90°C , 103°C and a 'step heating' procedure. The 'step heating' involved 40 h of heating at 90°C followed by 2 h of heating at 103°C (obtained via a heating rate of $1^\circ\text{C}/10 \text{ min}$). The oil bath was then cooled to 90°C and maintained for 1 h.

Zeolitic films and crystals were formed simultaneously on the walls and on the bottom of the bottle, respectively. Both were collected and washed with distilled water for analysis. The membranes were calcined at 500°C for 18 h to remove trapped structure-directing agent.

2.2. Analytical procedures

X-ray diffraction (XRD) patterns for membranes and crystals were obtained using RigakuD-Max-2B X-ray diffractometer with nickel-filtered CuK_α ($\lambda = 1.5405 \text{ \AA}$) radiation. The morphology of the zeolite was characterized by scanning electron microscopic method (SEM), using a Jeol JSM-820 electron microscope. Prior to the examination, the samples were mounted with double-sided carbon paste tape on copper pegs and coated with a film of evaporated gold.

3. Results

In order to investigate the effect of the synthesis temperature on the zeolite film formation, three different hydrothermal treatments were examined, constant heating at 90°C , constant heating at 103°C and a step heating procedure (described in experimental section).

In all cases, the initial reaction mixture was cloudy and thick, but became homogeneous after mixing and a solid started to settle down 1–2 h after heating. A film became visible on the polypropylene wall surrounding the solution after about 45 h and became continuous around the bottle after 90 h. The XRD patterns of the film and crystals formed in the same reaction are presented in Fig. 1(a)–(c). Fig. 1(a) corresponds to the diffraction pattern of the film. Comparing with the data in the literature [22,23], the film is mainly chabazite with traces of gmelinite intergrowths. (The three most characteristic lines (2θ values) of gmelinite are 21.7° , 27.7° and 7.4°). Fig. 1(b) corresponds to the XRD pattern of the powdered film and is identical to the intact film in Fig. 1(a). This indicates no preferred orientation of the crystals in the film. The XRD pattern of the powder recovered from the bottom of the reaction bottle is shown in Fig. 1(c). The peaks from chabazite are marked as C, and those from gmelinite are marked as G. The crystals on the bottom are mainly gmelinite, while the membrane is dominantly chabazite.

From the SEM of the film shown in Fig. 2(a), it appears that the film consists of spherical ag-

glomerates of almond-shaped crystals made up of a collection of smaller crystallites, often present as interpenetrating twins. Aggregates were also reported for Al-enriched chabazite [24]. Near-chabazite zeolite K-G [25] and the gmelinite films [6] have very similar morphology as in the present case. The sizes of the spherical crystals were about 7–9 μm . Fig. 3 is a side view of the film and shows that it consists of a dense layer followed by several layers of loosely packed particles.

Upon synthesis at 103°C , the film formation is complete after 30–40 h of heating, and is not thick enough to be detached from the wall of the bottle. For SEM analysis, the bottle with the film was cut and the surface of the film was coated with gold. As shown in Fig. 2(b), the size of spherical crystals in the film is 1–2 μm , less than the 7–9 μm size observed at 90°C . The XRD pattern of the film was that of chabazite (similar to Fig. 1(a)), while the powder obtained at 103°C indicate the formation of mainly gmelinite.

The step heating method involved heating at 90°C for 40 h, followed by a temperature increase to 103°C with a heating rate of $1^\circ\text{C}/10 \text{ min}$ and maintained for 2 h. Upon temperature increase, a portion of the deposits floated up and the solution became cloudy. Rapid film formation on the wall could be visually observed during the 2-h heating period. The oil bath was cooled to 90°C , and maintained for 1 h. A continuous film covering the walls of the reaction bottle was formed. Pieces of film could be readily removed and an optical micrograph of such a piece is shown in Fig. 4. If the heating was continued at 90°C , the films fell apart after total heating period of 90–100 h.

The XRD pattern of the film is identical to those shown in Fig. 1(a), indicating that the chabazite-type film is produced. The ground-up powder of the membrane resulted in the same pattern as the intact membrane. It was also observed from the XRD that the deposits at the bottom of the reaction vessel included substantial amounts of amorphous material after 45 h of heating even though the membrane is completely crystalline. In case the heating was continued at 90°C , the film fell apart, but the deposits became more crystalline and were predominantly gmelinite.

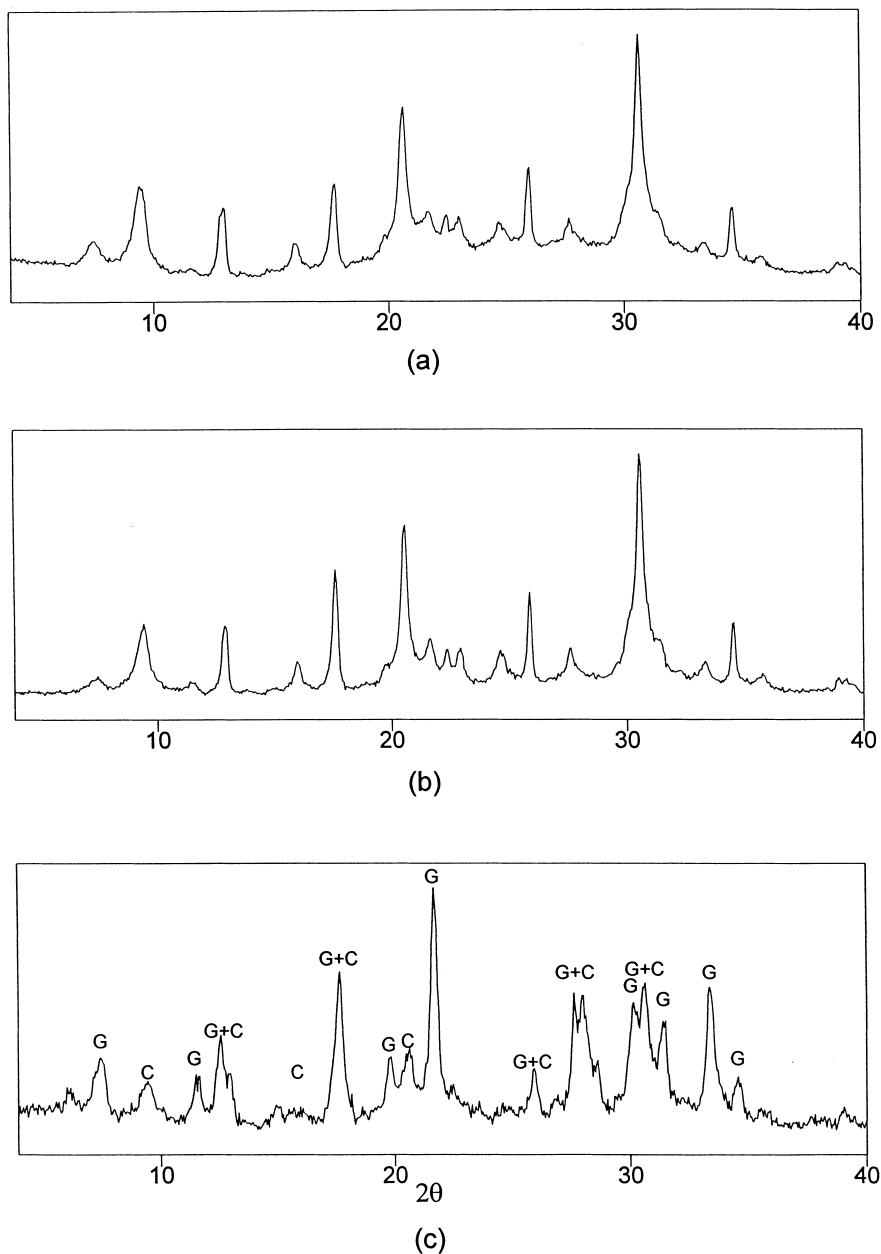
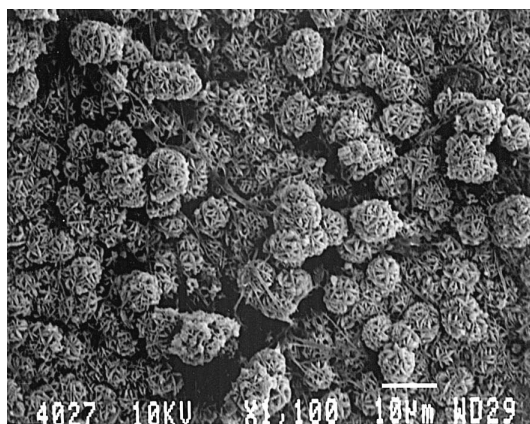


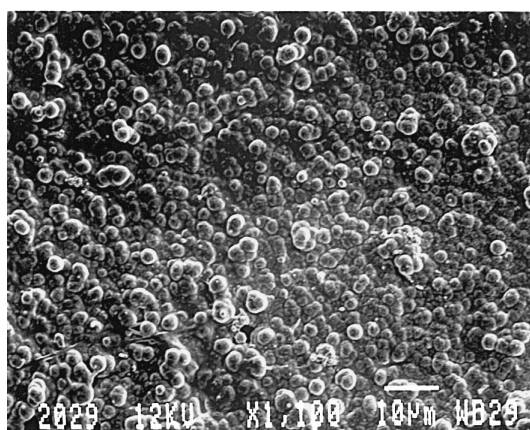
Fig. 1. XRD patterns of products formed from 90°C synthesis: (a) films from walls of bottle; (b) films ground to powder; (c) powder recovered from bottom of the reaction bottle.

The step heating treatment produced continuous, uniform and one to two crystal thick (about 10 μm) zeolitic film. The SEM images of the top and side views of the resulting film are shown in Fig. 5. The size of the spherical crystals in the film

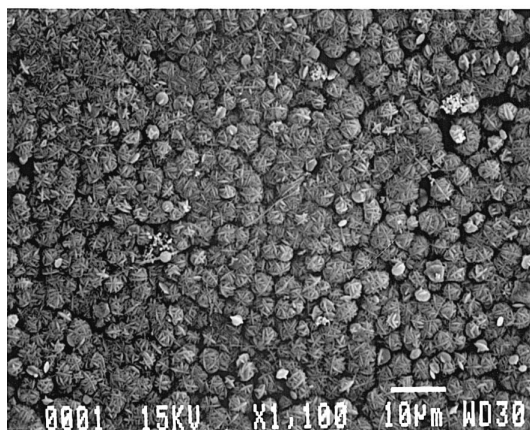
is about 4–6 μm in this case. Because the film is thin and crystalline, it is fragile when dried, but malleable when it is wet. The films can be stored for a long period of time (more than 2 months). The structure-directing agent can be removed by



(a)



(b)



(c)

Fig. 2. SEM pictures of films formed upon (a) 90°C; (b) 103°C, and (c) step-heating procedures.

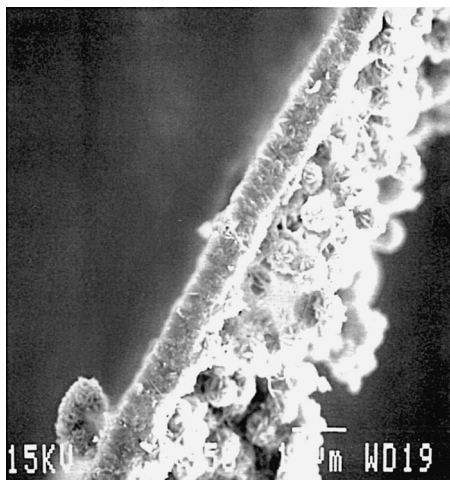


Fig. 3. Side view of films formed at 90°C.

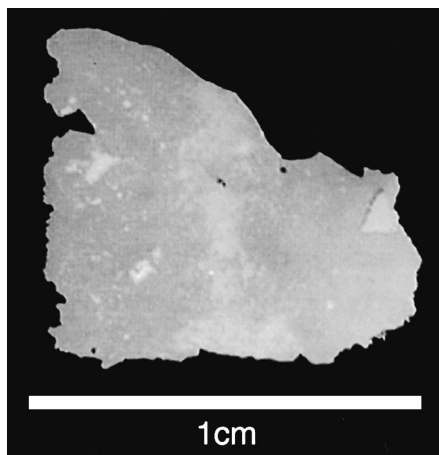
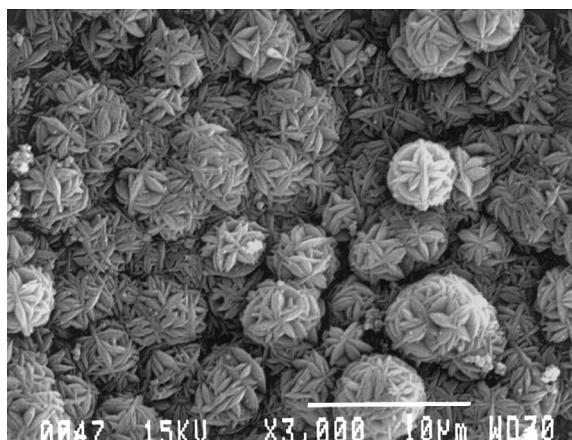


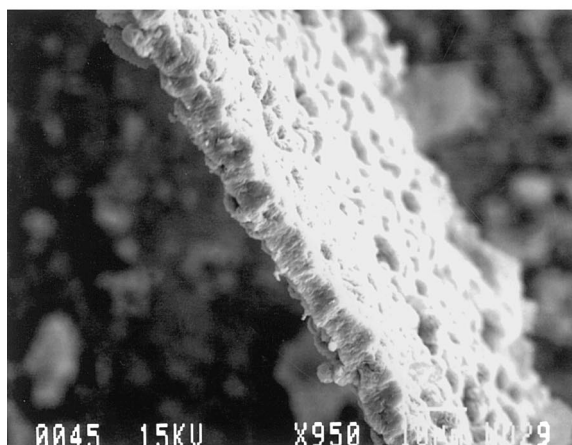
Fig. 4. Optical micrograph of a piece of films recovered from the step-heating procedure.

calcination at 500°C for 18 h. By inspecting the SEM image, we observed no cracks generated by the calcination process.

In order to evaluate the range of compositions from which the chabazite-type films could be formed, a series of experiments with varying $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (5–15) at a fixed Dab4-Br concentration as well as varying the Dab4-Br/ SiO_2 ratio (0–0.24) at fixed $\text{SiO}_2/\text{Al}_2\text{O}_3$ were done. Table 1 shows the results of these experiments. At a fixed



(a)



(b)

Fig. 5. (a) Top and (b) side views of films from the step-heating procedure.

concentration of Dab4-Br, good quality chabazite-type films were only formed with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 15. At this $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, good quality chabazite-type films were obtained as long as the Dab4-Br/ SiO_2 was kept within the range of 0.08–0.16. No differences in the detachable films are observed via powder diffraction. At the lower Dab4-Br/ SiO_2 ratio, the zeolite powders formed were zeolites Y and P along with gmelinite and chabazite, whereas at the high Dab4-Br/ SiO_2 of 0.16, the powder was mainly gmelinite, along with chabazite as the secondary phase.

4. Discussion

There are three issues that form the basis of the discussion section. First, our results appear to be different from an earlier report [6] for a similar reaction system. Second, the role of the step heating in producing the optimum uniform thickness film provides clues to the film formation process. Third, the difference between the framework formed on the walls (primarily chabazite) with that formed on the bottom of the reaction vessel is discussed.

4.1. Comparison with previous study [6]

Anderson et al. reported the formation of an aligned gmelinite film from a reaction gel of similar composition as in this study and hydrothermal treatment at 90–95°C for 90 h [6]. They used Teflon bottles and polysulfonated styrene discs as substrates. We repeated our experiments with Teflon bottles and the resulting films show the same XRD pattern and SEM image as those of films grown on polypropylene surface. Therefore, the difference between substrates is not responsible for chabazite versus gmelinite film formation. Anderson et al. reported that the XRD peaks corresponding to $(h0l)$ and $(0kl)$ are absent or considerably reduced in intensity for the synthesized films and suggested that this was indicative of the (001) planes of gmelinite crystals being preferentially oriented perpendicular to the film plane. In our experiments, the XRD pattern of gmelinite peaks appeared to be changed in intensity by the overlap with chabazite peaks. However, comparison of the XRD patterns of the ground film and the film clearly shows that the crystallites are randomly oriented. It is unclear why our results do not agree with that of Anderson et al.

4.2. Film formation

The film formation was investigated by SEM and the data contrasting the 90°C heating with the step heating procedure is shown in Fig. 6. The SEM micrographs are those of the material on the polypropylene wall (cut out from different reaction

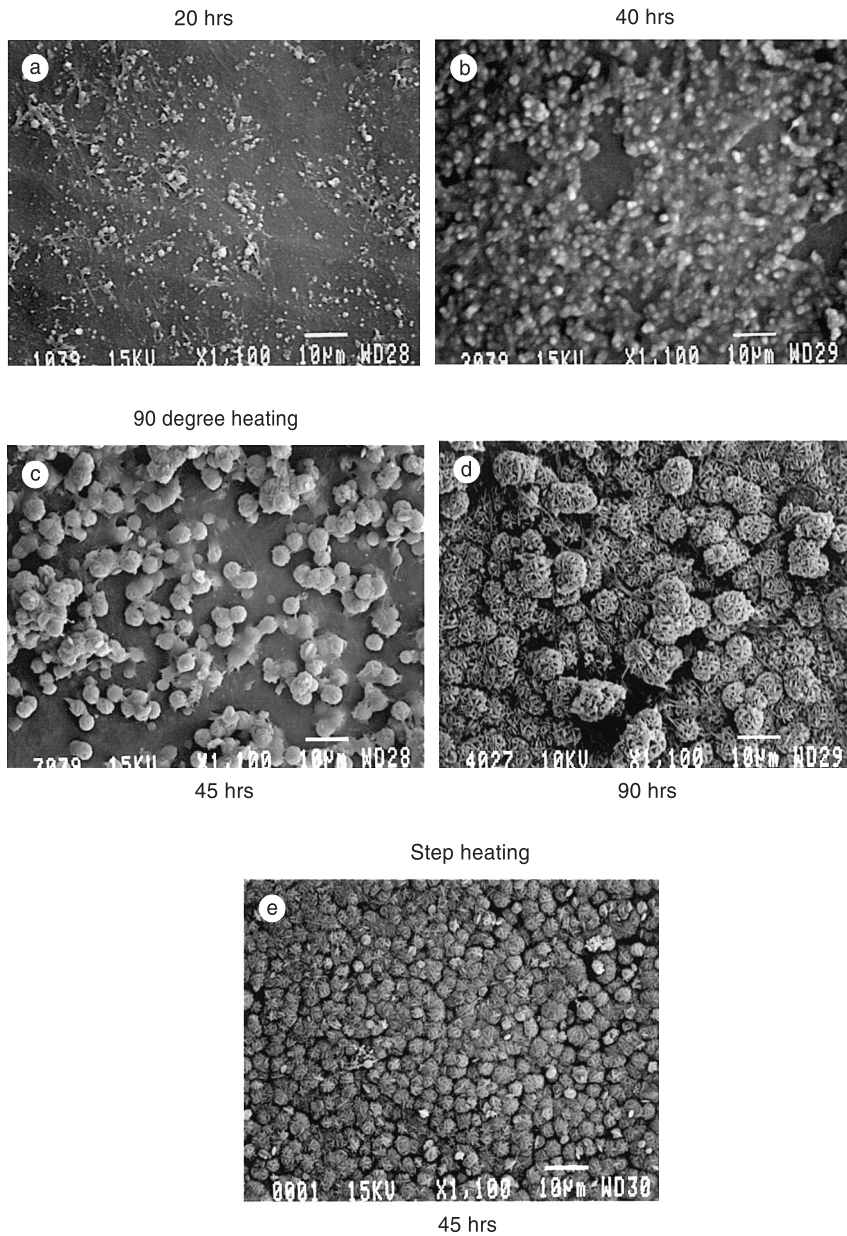


Fig. 6. SEM pictures during synthesis. Results of heating at 90°C for (a) 20 h; (b) 40 h; (c) 45 h; and (d) 90 h; (e) after 40 h at 90°C, sample heated to 103°C for 2 h and synthesis completed at 90°C by 45 h.

vessels) after the specified heating period. For the sample heated for 20 h (Fig. 6(a)), the polypropylene substrate appeared coated with an amorphous gel layer, with small particles embedded in them. The formation of a gel layer during zeolitic

film synthesis has been reported. Nakazawa et al. reported a gel layer in the early stages of the MFI film synthesis [12]. Mintova et al. also observed a gel-like layer on a quartz plate during the ZSM-5 film synthesis [11].

Table 1
Composition examined for forming chabazite-type film

| Run | Composition | Film quality | Film composition | Crystals on the bottom |
|-----------------|--|-------------------------|------------------|-------------------------------------|
| 1 ^a | SiO ₂ /Al ₂ O ₃ = 5 | No membrane | | Zeolite Y |
| 2 | SiO ₂ /Al ₂ O ₃ = 7.5 | No membrane | | Zeolite Y |
| 3 | SiO ₂ /Al ₂ O ₃ = 10 | No membrane | | Zeolite Y + chabazite |
| 4 | SiO ₂ /Al ₂ O ₃ = 15 | Good yield, detachable | Chabazite-type | Gmelinite + chabazite |
| 5 ^b | R/SiO ₂ = 0.00 | No membrane | | Zeolite Y |
| 6 | R/SiO ₂ = 0.08 | Good yield, detachable | Chabazite-type | Zeolite Y,P + Gmelinite + chabazite |
| 7 | R/SiO ₂ = 0.10 | Good yield, detachable | Chabazite-type | Zeolite Y,P + Gmelinite + chabazite |
| 8 | R/SiO ₂ = 0.12 | Good yield, detachable | Chabazite-type | Zeolite Y,P + Gmelinite + chabazite |
| 9 | R/SiO ₂ = 0.16 | Good yield, detachable | Chabazite-type | Gmelinite + chabazite |
| 10 | R/SiO ₂ = 0.18 | Small yield, detachable | Chabazite-type | Gmelinite + chabazite |
| 11 | R/SiO ₂ = 0.20 | Small yield, detachable | Chabazite-type | Gmelinite + chabazite |
| 12 ^c | R/SiO ₂ = 0.16 | Small yield, detachable | Amorphous | Gmelinite + chabazite |
| 13 | R/SiO ₂ = 0.24 | Small yield, detachable | Amorphous | Gmelinite |

^aRuns 1–4 were done at a fixed concentration of Dab-4Br(R)/H₂O of 0.006.

^bRuns 5–11 were done at a fixed SiO₂/Al₂O₃ of 15.

^cRuns 12–13 were done at a fixed SiO₂/Al₂O₃ of 30.

After the reaction mixture had been heated for 40 h (Fig. 6(b)), spherical particles 1–2 μm in diameter are observed in the layer on the substrate. This layer on the polypropylene support was investigated by XRD and no peaks were observed, indicating that the particles were amorphous at this stage. After 45 h of heating at 90°C, spherical crystals 4–5 μm in diameter were formed (Fig. 6(c)). These particles were crystalline and bigger than the particles in Fig. 6(b). The crystalline spheres consist of small, almond-shaped crystals. These particles eventually grow to form a continuous multilayer after 90 h of heating at 90°C. If the synthesis is carried out at 103°C, the process of film formation is speeded up, but smaller crystals are produced, and the film is not stable enough mechanically.

The step heating method provides an optimum procedure, with the first 40 h at 90°C producing nuclei in the gel. The rapid temperature rise to 103°C after 40 h results in thermal convective forces that release nuclei and nutrients from the gel into solution, which diffuse and grow at a rapid rate on the walls of the reaction container. This process can actually be observed visually, the solution gets cloudy and the membrane begins to form, and is evident from Fig. 6(e). As pointed out by Myatt et al. in their study on zeolite NaA membrane [7], nuclei/colloidal aluminosili-

cate particles diffuse to the substrate and initiate growth of the film.

If the step heating procedure is continued, the film becomes thicker and it falls off from the wall. The arrival of nuclei at different times on the wall is consistent with the fact that there is no orientational relationship between the crystallites.

4.3. Film versus powder composition

From Table 1, it is clear that the presence of Dab4-Br is required to form the chabazite-type film. In its absence, not only the film is not formed, but also no gmelinite or chabazite powder is formed. Also, the composition of the film as measured by powder diffraction appears to be quite invariant even though the types of zeolite formed as powder at the bottom of the bottle varies. Dab4-Br is a templating agent for gmelinite [22] and in most cases, gmelinite is the primary powder product. Gmelinite is a member of the chabazite zeolite group. It consists of the same secondary building units as that of chabazite, but the framework is slightly different. In gmelinite, the D6R units are stacked in the sequence of ABAB instead of ABCABC [23]. Chabazite-gmelinite intergrowths have been reported by several researchers [22,23,26,27], indicating that

these two frameworks may share similarly structured nuclei. Moreover, Daniels et al. [22] observed that with increase in the Si/Al ratio of the composition, chabazite is the preferred product. For the compositions under which the chabazite-type membrane is formed (Table 1), the solutions are always more siliceous and could explain why chabazite is the primary constituent of the film. The formation of the film is closely connected with the presence of the Dab4-Br. An amorphous film is observed at the early stages of film growth (Fig. 6(a)). Anderson et al. [6] have proposed that Dab-4 attaches to the walls of the bottle via electrostatic interactions and would be consistent with the present observations. However, with increasing concentrations of Dab4-Br, the yield of the film decreases. This could result from the film becoming too thick and therefore the crystals formed may collapse into solution. Thus, an optimum amount of Dab4-Br is required for adequate film formation.

5. Conclusion

Free-standing chabazite-type zeolite films were synthesized on the walls of polypropylene bottles. By following a step heating method, which results in a burst of nuclei and nutrients into solution during the synthesis, uniformly thick self-standing films could be produced.

Acknowledgements

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References

- [1] D.W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974 (Chapters 1 and 2).
- [2] J.M. Newsam, *Science* 231 (1986) 1093.
- [3] T. Bein, *Chem. Mater.* 8 (1996) 1636.
- [4] T. Sano, Y. Kiyozumi, M. Kawamura, F. Mizukami, H. Takaya, T. Mouri, W. Inaoka, M. Watanabe, Y. Toida, K. Toyada, *Zeolites* 11 (1991) 842.
- [5] J.G. Tsikoyiannis, W.O. Haag, *Zeolites* 12 (1992) 126.
- [6] M.W. Anderson, K.S. Pachis, J. Shi, S.W. Carr, *J. Mater. Chem.* 2 (1992) 255.
- [7] G.J. Myatt, P.M. Budd, C. Price, S.W. Carr, *J. Mater. Chem.* 2 (1992) 1103.
- [8] M.A. Salomon, J. Coronas, M. Merendez, J. Santamaria, *Chem. Commun.* (1998) 125.
- [9] Z.A.E.P. Vroon, K. Keizer, A.J. Burggraaf, H. Verweij, *J. Membr. Sci.* 144 (1998) 65.
- [10] S. Yamazaki, K. Tsutsumi, *Microporous Materials* 4 (1995) 205.
- [11] S. Mintova, J. Hedlund, V. Valtchev, B.J. Schoeman, J. Sterte, *J. Mater. Chem.* 8 (1998) 2217.
- [12] T. Nakazawa, M. Sadakata, T. Okubo, *Microporous Mesoporous Mater.* 21 (1998) 325.
- [13] G. Clet, J.C. Jansen, H. van Bekkum, *Chem. Mater.* 7 (1999) 1696.
- [14] G. Xomeritakis, A. Gouzens, S. Nair, T. Okubo, M. He, R.M. Overney, M. Tsapatsis, *Chem. Engng. Sci.* 54 (1999) 3521.
- [15] K.J. Balkus Jr., T. Munoz Jr., M.E. Giman-Kinsel, *Chem. Mater.* 10 (1998) 464.
- [16] K.T. Jung, Y.G. Shul, *Chem. Mater.* 9 (1997) 420.
- [17] W.M. Meier, D.H. Olson, *Atlas of Zeolite Structure Types*, Butterworth, Storeham, 1992.
- [18] A. Dyer, M. Zubair, *Microporous Mesoporous Mater.* 22 (1998) 135.
- [19] B.W. Mercer, L.L. Ames, in: L.B. Sand, F.A. Mumpton (Eds.), *Natural Zeolites: Occurrence, Properties, Use*, Pergamon Press, Oxford, 1978, p. 451.
- [20] M.C. Ilaio, H. Yamamoto, K. Segawa, *J. Catal.* 161 (1996) 20.
- [21] T. Bein, K. Brown, *J. Am. Chem. Soc.* 111 (1989) 7640.
- [22] R.H. Daniels, G.T. Kerr, L.D. Rollmann, *J. Am. Chem. Soc.* 100 (1978) 3097.
- [23] M. Chatterjee, D. Ganguli, P. Saha, *Indian Ceram. Soc. Transactions* 35 (1976) 99.
- [24] K.A. Thrush, S.M. Kaznicki, *Chem. Soc. Faraday Trans.* 87 (1991) 1031.
- [25] R.M. Barrer, D.E. Mainwaring, *J. Chem. Soc. Dalton Trans.* (1972) 1254.
- [26] G.R. Millward, S. Ramdas, J.M. Thomas, *Proc. R. Soc. Lond. A* 399 (1985) 57.
- [27] R.M. Barrer, J.W. Baynham, *J. Chem. Soc. (Lond.)* (1959) 195.