

New SUZ-4 Zeolite Membrane from Sol-Gel Technique

P. Worathanakul, and P. Kongkachuichay

Abstract—A new SUZ-4 zeolite membrane with tetraethylammonium hydroxide as the template was fabricated on mullite tube via hydrothermal sol-gel synthesis in a rotating autoclave reactor. The suitable synthesis condition was $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 21.2 for 4 days at 155 °C crystallization under autogenous pressure. The obtained SUZ-4 possessed a high BET surface area of 396.4 m^2/g , total pore volume at 2.611 cm^3/g , and narrow pore size distribution with 97 nm mean diameter and 760 nm long of needle crystal shape. The SUZ-4 layer obtained from seeding crystallization was thicker than that of without seeds or in situ crystallization.

Keywords—Membrane, seeding, sol-gel, SUZ-4 Zeolite.

I. INTRODUCTION

ZEOLITES are routinely used in heterogeneous catalytic reaction, ion exchange and gas separation. The regular nanoporous networks of zeolites and other crystalline molecular sieves have been put to extensive and increasing use in separations. SUZ-4 is a new type of synthetic zeolite [1-5]. There are some researches demonstrated and claimed that it has an excellent catalytic properties, high thermal stability as well as high organic solvents resistance [6-13]. There are approximately 150 different zeolite structures reported by the International Zeolites Association (IZA). Among them, only 15 structures have been tried to fabricate as a zeolite membrane [14]. However, SUZ-4 zeolite as membrane form has not been found yet. Therefore, it is very interesting to synthesize and prepare this membrane for potential applications. In this work, seeding and in situ crystallization or without seeds of SUZ-4 zeolite membranes were fabricated and characterized using X-ray powder diffraction, BET N_2 -adsorption, Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Zeta potential.

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II. EXPERIMENTAL

SUZ-4 zeolite membrane was prepared by a sol-gel hydrothermal technique carried out in 390 ml Teflon-lined stainless steel autoclave that was placed in a circulating air drying oven under optimal conditions previously determined by our laboratory and others [8], [15-17].

A. Chemical Preparation for Zeolite Membrane

An appropriate chemical composition of materials used to successfully synthesize SUZ-4 zeolite membrane was prepared. Tetraethylammonium hydroxide (TEAOH, 35 wt. % in water, Aldrich) was used as a structure directing agent accompanied with 3 main chemicals: LUDOX AS-40 colloidal silica (40 wt. % SiO_2 , Aldrich) as the silica source, aluminum powder (99.7% Al, Hi Media) as the aluminum source, and potassium hydroxide (85% KOH pellet, Carlo Erba) as the potassium source. Gel preparation for one of several batches is described here: 5.88 g KOH was dissolved in 140 g of distilled water and 0.6 g of aluminum powder was added with the bottle loosely capped (H_2 gas was evolved) and stirred continuously until the aluminum was completely dissolved to form a clear solution. A second solution containing 35.37 g of LUDOX, 12.18 g of TEAOH aqueous solution, and 70 g of water was prepared and stirred for 1 hour and then added successively under stirring to the dissolved aluminum solution and stirred for 3 hours. A white gel was formed and mixed thoroughly until an even consistency was achieved. The resulting gel had composition of $3.98\text{K}_2\text{O}:\text{Al}_2\text{O}_3:21.22\text{SiO}_2:1.30\text{TEA}_2\text{O}:1.202\text{H}_2\text{O}$. The gel was then transferred to a rotating stainless steel bomb at 30 rpm for crystallization at 155°C under autogenous pressure. In order to retard the homogeneous nucleation of zeolite in the liquid phase, the starting concentrations of the reactants were decreased as compared to those for the usual synthesis of powder zeolites [8], [15-17]. The $\text{H}_2\text{O}:\text{Al}_2\text{O}_3$ was varied in the range of 1,198-2,554. The suitable condition of $\text{H}_2\text{O}:\text{Al}_2\text{O}_3$ zeolite membrane was reproduced with different crystallization time at 3.9, 4 and 4.9 days with and without seeding.

B. Membrane Preparation

For zeolite membrane preparation, cylindrical mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) tube having 15 mm outer diameter and 2 mm thickness was cut in 130 mm length by a low speed diamond saw. It was then polished with fine sand paper, washed in ultrasonic bath for 15 minutes and heated at 550 °C for 1 hour.

Subsequently, it was used as supporter for the zeolite membrane. With seeding crystallization, grounded SUZ-4 zeolite crystals were kneaded with water and then were rubbed on outer surface of the supporter. The inner space of the supporter was filled with quartz glass wool to prevent the formation of the zeolite layer on the inner surface. The supporter was then placed axially in the autoclave under the crystallization conditions.

III. RESULTS AND DISCUSSION

A. Effect of H_2O/Al_2O_3

Fig. 1 shows XRD patterns from reproducible synthesis under controlled conditions with different H_2O/Al_2O_3 [1]. SUZ-4 zeolite crystal was obtained under $H_2O/Al_2O_3 = 1,198$ -1,351 and Si/Al (by weight) of 6.8-7.7. However, at high H_2O/Al_2O_3 ratio of 2,554 SUZ-4 zeolite could not be produced. This indicates that H_2O/Al_2O_3 ratio is also one of key factors for zeolite membrane synthesis.

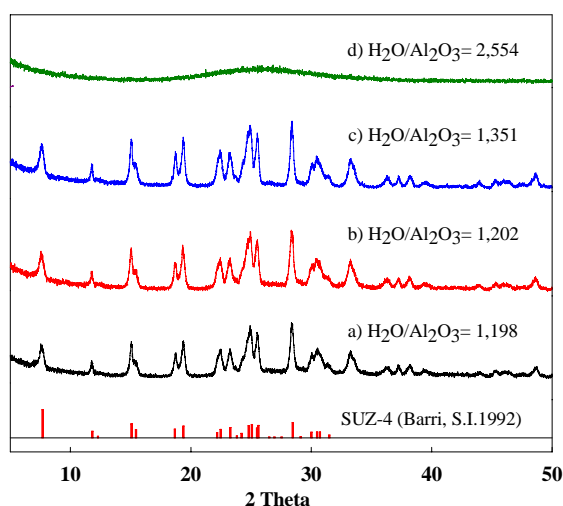


Fig. 1 XRD patterns of reproducible SUZ-4 zeolite powder synthesis prepared with different H_2O/Al_2O_3 ratios

Subsequently, specific surface area, pore volume and pore diameter for reproducible SUZ-4 synthesis at $SiO_2/Al_2O_3 = 21.2$ conditions were determined by BET N_2 -adsorption/desorption isotherms as shown in Table I. It should be noted that crystallization with seeding yields larger surface than that of without seeding.

TABLE I
BET SURFACE AREA AND PORE VOLUME OF REPRODUCIBLE ZEOLITE AT $SiO_2/Al_2O_3 = 21.2$ WITH DIFFERENT H_2O/Al_2O_3 RATIOS

No.	H_2O/Al_2O_3	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Pore diameter ¹ (\AA)
M2*	1,202	390.6	1.910	5.8 ± 1.4
M2S	1,202	407.5	2.368	5.4 ± 1.3
M4*	1,198	378.6	1.766	4.7 ± 1.1
M4S	1,198	430.2	0.4469	5.8 ± 1.4
M5*	1,351	391.5	1.684	5.7 ± 1.2
M5S	1,351	396.4	2.611	4.8 ± 0.6

¹ SF micropore analysis method

* without SUZ-4 seeding

B. Effect of SUZ-4 Seeding

Before coating with zeolite the porosity of the mullite tube was determined by a mercury intrusion porosimetry and it was found to have the porosity of 21% with average pore diameter of 90 μm . Then, it was coated with SUZ-4 membrane via in situ hydrothermal crystallization with and without SUZ-4 seeding. The results show that SUZ-4 zeolite layer with seeding is thicker than that of without seeding. As shown in Fig. 2c, the thickness of SUZ-4 zeolite layer with seeding is about 14 μm while the thickness of layer without seeding (Fig. 2a) is about 4 μm . It implies that seeding can enhance the secondary nucleation growth. The SEM top view images (Fig. 2b and 2d) show the stack of SUZ-4 needle crystals and confirm the formation of the SUZ-4 zeolite membrane on the supporter. In addition, it is observed that the membrane with seeding composes of smaller SUZ-4 crystals than that of without seeding.

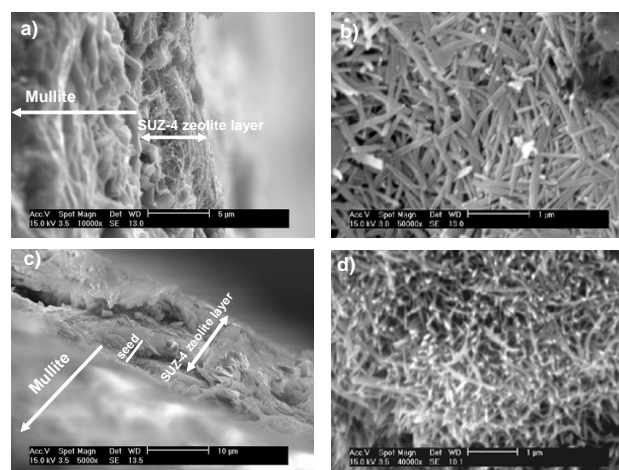


Fig. 2 SEM images of SUZ-4 zeolite membrane prepared for $H_2O/Al_2O_3 = 1,202$ without seeding (a) M2 cross-section (b) M2 top view and with seeding (c) M2S cross-section and (d) M2S top view

The synthesis of SUZ-4 zeolite membrane with seeding still has more thickness than without seeding when H_2O/Al_2O_3 is decreased and increased to 1,198 and 1,351, respectively (Fig. 3 and Fig. 4). However, top view images of $H_2O/Al_2O_3 =$

1,198 show that SUZ-4 crystals are not in perfect order arrangement and they have not been stacked together under these conditions.

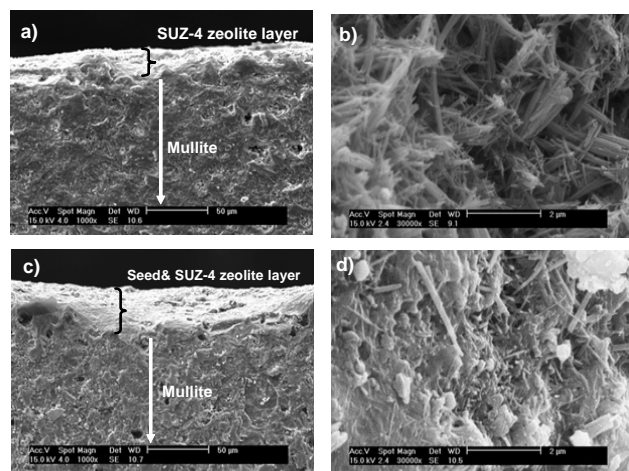


Fig. 3 SEM images of SUZ-4 zeolite membrane prepared for $\text{H}_2\text{O}/\text{Al}_2\text{O}_3=1,198$ without seeding (a) M4 cross-section (b) M4 top view and with seeding (c) M4S cross-section and (d) M4S top view

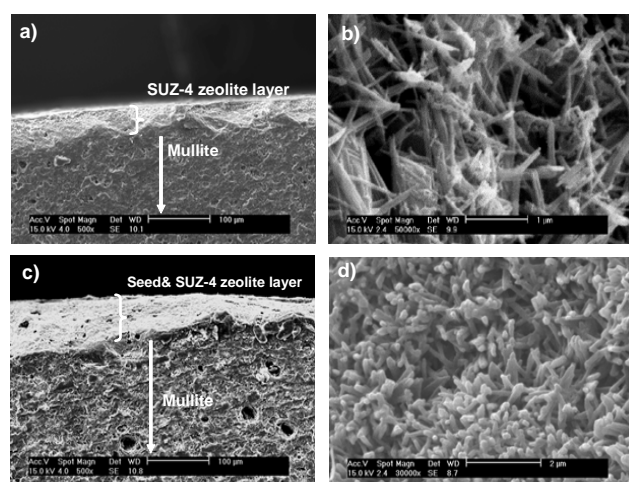


Fig. 4 SEM images of SUZ-4 zeolite membrane prepared for $\text{H}_2\text{O}/\text{Al}_2\text{O}_3=1,351$ without seeding (a) M5 cross-section (b) M5 top view and with seeding (c) M5S cross-section and (d) M5S top view

C. Effect of Crystallization Time

Table II shows zeolite layer thickness and crystal size of at $\text{SiO}_2/\text{Al}_2\text{O}_3=21.2$ with different crystallization time. The results from increasing crystallization time of SUZ-4 zeolite membrane up to 4.9 days show that longer synthesis time under the same conditions can give thicker layer having larger SUZ-4 crystals. When crystallization time is decreased to 3.9 days, they still show that SUZ-4 zeolite layer having thicker than that of 4 days crystallization. It is implied that SUZ-4 crystals are not in perfect order arrangement for 3.9 days. However, the crystal sizes of SUZ-4 were not much different in each experiment.

TABLE II
ZEOLITE LAYER THICKNESS AND CRYSTAL SIZE OF REPRODUCIBLE ZEOLITE AT $\text{SiO}_2/\text{Al}_2\text{O}_3=21.2$ WITH DIFFERENT CRYSTALLIZATION TIME

Crystallization time (day)	Samples	Thickness (μm)	Crystal size (μm)
3.9	M4*	17	0.07 μm dia. x 0.73 μm long
	M4S	24.8	0.07 μm dia. x 0.71 μm long
4	M2*	4	0.08 μm dia. x 0.60 μm long
	M2S	14	0.07 μm dia. x 0.50 μm long
4.9	M5*	41	0.10 μm dia. x 0.88 μm long
	M5S	54	0.10 μm dia. x 0.76 μm long

* without SUZ-4 seeding

D. Bonding Analysis from FTIR of SUZ-4 Zeolite

Fig. 5 shows FTIR spectrum in the region of $4000-400\text{ cm}^{-1}$ for the powder sample under 155°C hydrothermal for 4 days with $\text{SiO}_2/\text{Al}_2\text{O}_3=21.2$ (No. M2S). As it is well known that the thermal stability of zeolite is related to the defect sites, i.e., the number of silanol groups, within zeolite crystal, thus the FTIR spectra of uncalcined and calcined SUZ-4 zeolites synthesized were observed. The peaks at 3741 and 3603 cm^{-1} are assigned to isolated silanol groups and acidic bridged OH of $\text{Si}(\text{OH})\text{Al}$, respectively [6], [13]. Frequencies of $\text{Si}(\text{OH})\text{Al}$ group vibration in zeolites depend generally on local structure and composition. There is IR spectroscopic evidence for the presence of different peaks between before and after calcinations. Absorbed water bonding at 3000 cm^{-1} still shows for uncalcined while no peak for calcined SUZ-4. Moreover, the vibration bonding results clearly show that some position disappeared for calcined sample when compared to uncalcined one that still have TEOAH in the sample.

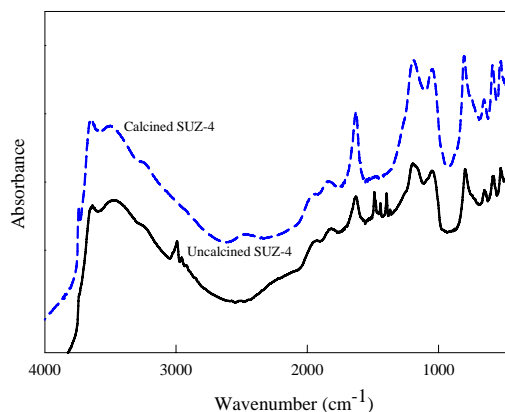


Fig. 5 FTIR spectra of as-synthesized SUZ-4 zeolite obtained from M2S powder for uncalcined and calcined SUZ-4 zeolites

E. Zeta Potential Studies of SUZ-4 Zeolite

Fig. 6 shows zeta potential values as a function of pH for mullite supporter and synthesized SUZ-4 zeolite. It is observed that there is no iso-electric point (IEP) of SUZ-4 zeolite powder at pH 2-12. The powder has negative charge

on its surface in this pH range. It reveals that the SUZ-4 powder will suspend well in water under these pHs. On the other hand, Mullite supporter has an IEP at pH about 5.9, while at the other pH it has negative surface charge.

Since both mullite and SUZ-4 have the same negative surface charge under crystallization condition (pH=13.2), the deposition of SUZ-4 crystals on the mullite surface will be retarded from the repulsive force. Therefore, the mullite surface should be modified its charge to be positive in order to enhance the membrane formation.

Generally, synthesis zeolite in the membrane form is more difficult than in the powder form. Moreover, the needle shape structure makes the SUZ-4 membrane synthesis much more complicated than simple shape such as cubic or spherical structure. Therefore, the systematic experiments of synthesis in crystal orientation, plane deposition and surface charge between supporter and zeolite layer should be investigated in more details.

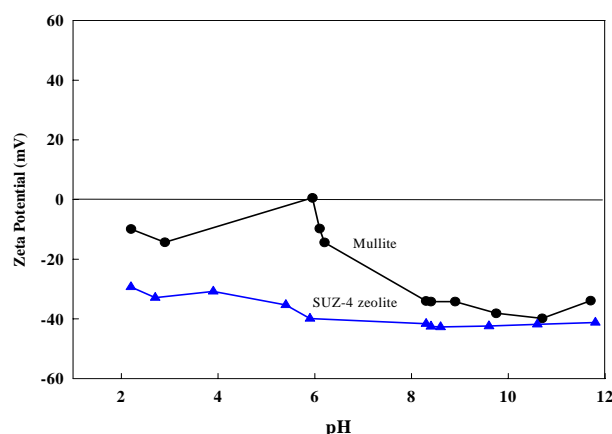


Fig. 6 Zeta potential of mullite supporter and as-synthesized SUZ-4 zeolite powder as a function of pH

IV. CONCLUSION

Hydrothermal sol-gel process with TEOH as structure directing agent has been used to successfully synthesize novel SUZ-4 zeolite membrane. Specific surface area, pore volume and pore size distribution has been reported. Novel SUZ-4 zeolite membrane has been produced under this condition in the home-made design rotating autoclave reactor. The results also show the negative zeta potential values both SUZ-4 zeolite powder and mullite. The experiments were needed to control and adjust the conditions to get good characteristic of SUZ-4 zeolite membrane. Moreover, it was found that with seeding the obtained zeolite membrane has more thickness than without one. Thus, the results indicate that the new SUZ-4 zeolite membrane has potential from unusual shape-selective and catalytic properties.

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REFERENCES

- [1] S. A. Barri. "Crystalline (metallo) silicates and germanates-SUZ-4," United States 5,118, 483, 1992.
- [2] S. L. Lawton, J. M. Bennett, J. L. Schlenker and M. K. Rubin. "Synthesis and proposed framework topology of zeolite SUZ-4," *J. Chem. Soc., Chem. Commun.* vol. 11, pp. 894-896, 1993.
- [3] K. G. Strohmaier, M. Afeworki and D. L. Dorset. "The crystal structures of polymorphic SUZ-4," *Z. Kristallogr.*, vol. 221, pp. 689-698, 2006.
- [4] W. C. Paik, C. H. Shin and S. B. Hong. "Synthesis of zeolites P1 and SUZ-4 through a synergy of organic N,N,N',N',N' hexaethylpentanediammonium and inorganic cations," *J. Chem. Soc., Chem. Commun.*, pp. 1609-1610, 2000.
- [5] W. C. Paik, C. H. Shin, J. M. Lee, B. J. Ahn and S. B. Hong. "Host-guest interactions in P1, SUZ-4, and ZSM-57 zeolites containing N,N,N',N',N' hexaethylpentanediammonium ion as a guest molecule," *J. Phys. Chem. B*, vol.105, pp. 9994-10000, 2001.
- [6] D. B. Lukyanov, V. L. Zholobenko, J. Dwyer, S. A. I. Barri and W. J. Smith. "On the structural, acidic and catalytic properties of zeolite SUZ-4," *J. Phys. Chem.* vol. 103, pp. 197-202, 1999.
- [7] H. Choo, S. B. Hong and L. Keven. "Comparative ESR and catalytic studies of ethylene dimerization on Pd(II)-exchanged clinoptilolite, mordenite, ferrierite, and SUZ-4," *J. Phys. Chem. B*, vol. 105, pp. 7730-7738, 2001.
- [8] M. A. Asensi, M. A. Cambor and A. Martinez. "Zeolite SUZ-4: Reproducible synthesis, physicochemical characterization and catalytic evaluation for the skeletal isomerization of n-butenes," *Micropor. Mesopor. Mater.* vol. 28, pp. 427-436, 1999.
- [9] A. Subbiah, B. K. Cho, R. J. Blint, A. C. Gujar, G. L. Price and J. E. Yie. "NO_x reduction over metal-ion exchanged novel zeolite under lean conditions: activity and hydrothermal stability," *Applied Catalysis B: Environmental*, vol.42, pp. 155-178, 2003.
- [10] S. Jiang, Y. K. Hwang, S. H. Jhung, J.-S. Chang and J.-S. Hwang. "Zeolite SUZ-4 as selective dehydration catalyst for methanol conversion to dimethyl ether," *Chemistry Letters*, vol.33, pp. 1048-1049, 2004.
- [11] S.-H. Lee, C.-H. Shin, G. J. Choi, T.-J. Park, I.-S. Nam, B. Han and S. B. Hong. Zeolite synthesis in the presence of flexible diquaternary alkylammonium ions (C₂H₅)₃N⁺(CH₂)_nN⁺(C₂H₅)₃ with n = 3-10 as structure-directing agents. *Micropor. Mesopor. Mater.*, vol. 60, pp. 237-249, 2003.
- [12] A. C. Gujar, A. A. Moye, P. A. Coghill, D. C. Teeters, K. P. Roberts and G. L. Price. "Raman investigation of the SUZ-4 zeolite," *Micropor. Mesopor. Mater.* vol.78, pp. 131-137, 2005.
- [13] V. L. Zholobenko, D. B. Lukyanov and J. Dwyer. "Ferrierite and SUZ-4 Zeolites: Characterization of Acid Sites," *J. Phys. Chem.* vol. 102, pp. 2715-2721, 1998.
- [14] J. Caro, M. Noack, P. Kolsch and R. Schafer. "Zeolite membranes-state of their development and perspective," *Micropor. Mesopor. Mater.* vol. 38, pp. 3-24, 2000.
- [15] A. C. Gujar and G. L. Price. "Synthesis of SUZ-4 in the K⁺/TEA⁺ system," *Micropor. Mesopor. Mater.* vol. 54, pp. 201-205, 2002.
- [16] D.-K. Kim, Y. H. Kim, Y. K. Kwang, J.-S. Chang and S.-E. Park. "Effect of synthesis conditions on physicochemical properties of zeolite SUZ-4 (in Korean, English abstract)," *J. the Korean Chemical Society* vol. 48, pp. 623-628, 2004.
- [17] S.-H. Lee, C.-H. Shin and S. B. Hong. "Investigations into the origin of the remarkable catalytic performance of aged H-ferrierite for the skeletal isomerization of 1-butene to isobutene," *J. Catalysis*, vol.223, pp. 200-211, 2004.

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