Journal of Metals, Materials and Minerals. Vol. 12 No. 2 pp. 41-50, 2003.

The Effect of Starting Material Ratio, Heating Temperature and Time on the Morphology of Na A zeolite

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ABSTRACT

1 μm crystal-size Na A zeolite (LTA) is successfully synthesized via the sol-gel process and microwave heating technique using alumatrane and silatrane as precursors. The optimal conditions to obtain LTA were 1:1:3:410 SiO_2:Al_2O_3:Na_2O:H_2O ratio, microwave heating temperature and a time of 110°C and 160 min, respectively. Under the same conditions, increasing the Na_2O concentration exponentially reduces the microwave heating time from 160 min at a Na_2O:SiO_2 ratio of 3:1 to 5 min at a Na_2O:SiO_2 ratio of 9:1. Increasing the Na_2O concentration strongly affects the particle size and particle size distribution, but does not affect the product composition. Increasing the amount of water increased the average particle size and also the number of irregular cubic shape crystals. Increasing the aging temperature from 90° to 150°C, everything else being the same (one hour heating time and the loading ratio of SiO_2:Al_2O_3:$5Na_2O$:$410H_2O$), only amorphous product was produced at 90°C and between 110°-150°C only LTA was produced.

Keywords : Alumatrane, Silatrane, Microwave technique, Sol-gel process, and Zeolite A

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INTRODUCTION

Zeolites are versatile materials, they can be used by continuous separation and purification of gas and liquid mixtures by both adsorption and molecular sieving (Weitkamp, *et al.* 1994). Most zeolites are also chemically and thermally stable (Yahiro, *et al.* 2000). Zeolites are used in many applications, such as household products, aquaculture, agriculture, water treatment, etc. The Na-A zeolite framework and pore size offer high selectivity and has been used as a selective gas separation membrane. Most membranes separate by molecular size and/or strength of adsorption. For 1,3 propanediol/glycerol separation using medium (MFI, MEL or mixture) or large (MOR or FAU) pores, the pores do not have much influence on membrane selectivity mainly due to preferential adsorption while 1,3 propanediol/glucose separation is mainly controlled by molecular sieving (Shiguang, *et al.* 2001).

Making Na A zeolite membrane by seeding the support with Na A zeolite crystals and followed by a one-time-only hydrothermal treatment yielded a dense inter-grown zeolite crystal layer on the outer surface (Ken-ichi, *et al.* 2001; Kita, 1995; and Wang, *et al.* 1994). The resulting membranes were hydrophilic and highly permeable to water vapor but impermeable to other gases unless dried completely. They performed excellent water perm-selective performance toward water/organic liquid mixtures. For gas permeation test, the permeation rate follows the order, ethylene > carbon dioxide > methane > nitrogen > oxygen. However, by using a Knudsen diffusion mechanism, the permeation tests indicated that noncondensable gases permeated through the membrane by passing mainly through the grain boundaries of the membrane. This process was dominated by a surface diffusion mechanism and not by molecular sieving diffusion through zeolite crystals. Thus, highly oriented LTA membrane was fabricated on a porous support with the faces parallel to the substrate surface (Hedlund, *et al.* 1997; Boudreau, *et al.* 1999; and Boudreau, *et al.* 1997). It was also highly useful for separating water from water/organic mixtures and suggested that the affinity between pore wall and permeates is more important than the pore size (Aorki, *et al.* 2000). However, the permeation still occurred through two types of pores, zeolitic pore and nonzeolitic pore (grain boundary) (Aoki, *et al.* 2000). A molecular size smaller than ethane is able to permeate through the zeolitic pore. Water can condense in both zeolitic and nonzeolitic pores, reducing the permeation of the hydrophobic and large permeates. Moreover, large molecules are able to diffuse through the nonzeolitic pores, making the permeation more complicated. ^{2}H-MNR and Monte Carlo Lattice Dynamics studies also indicated that 1-4 molecules of sorbates, ethane and ethylene can be adsorbed per cavity of zeolite Na A (Gladden, *et al.* 1997). Ethane has a higher mobility than ethylene within the zeolite cavity due to a dipole moment effect.

Since, the technique for fabricating defect-free-A-type zeolite membranes has not yet been accomplished it is desirable to explore new synthetic routes, which result in better crystallinity. Pore-filling techniques in the crystallization stage have been successfully used in siliceous zeolite synthesis and controlling the framework structure (Rollmann, *et al.* 1999; and Rollmann, *et al.* 2000). Our previous work successfully used atranes (metal trialkoxo amine) as precursors for ANA and GIS zeolite synthesis via the sol-gel process (Sathupanya, *et al.* (In press)). Both silatrane Piboonchaisit, *et al.* (1999) and alumatrane Opornsawad, *et al.* (2001) are directly synthsized via the Oxide-One-Pot-Synthesis (OOPS) process which is a cheap, simple and useful process from silicon dioxide and alumina in one step. The reaction is a condensation reaction, generating water as a by-product, which is removed to drive the reaction forward. Based on our previous work, (Sathupanya, *et al.* (In press)) both alumatrane and silatrane are successfully employed as precursors for a sol-gel process. It was found that the hydrolysis rate using NaOH aqueous solution as a hydrolytic agent was twice as fast than that of NaCl solution. It possibly resulted from OH^- being a stronger nucleophile than Cl^- (Robinovich and Klein, 1988). This study is further focused on Na A synthesis using the same method as the previous one with the expectation of a higher uniformity of crystallinity and narrower particle size distribution.

EXPERIMENTAL

Materials

Fumed silica (SiO_2, surface area 473.5 m^2/g, average particle size of 0.007 μm) and aluminum hydroxide hydrate ($Al(OH)_3$, surface area 50.77 m^2/g), were purchased from the Sigma Chemical Co. and used as received. Triethanolamine (TEA, $N(CH_2CH_2OH)_3$), and triisopropanolamine (TIS, $N(CH_2CHCH_3OH)_3$) were supplied by Carlo Erba Reagenti and Fluka Chemical AG., respectively, and used as received. Ethylene glycol (EG, $HOCH_2CH_2OH$) was obtained from J.T. Baker Inc. and distilled using fractional distillation prior to use. Sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from EKA Chemicals and AJAX Chemicals, respectively. Both were used as received. Acetonitrile (CH_3CN) was obtained from Lab-Scan Co., Ltd. and distilled using standard purification methods prior to use.

Instrumentals

Fourier transform infrared (FTIR) spectroscopic analysis was conducted using a Bruker Instruments (EQUINOX55) specrometer with a resolution of 4 cm^{-1} to measure the absorbance by the functional groups. The solid samples were prepared by mixing 1% of sample with dried KBr, while the liquid samples were analyzed using a Zn-Se window cell. In measuring the molar mass of precursors, the mass spectra were obtained using a VG Autospec model 7070E from Fison Instruments with a VG data system, using the positive fast atomic bombardment (FAB^+-MS) mode and glycerol as a matrix. CsI was used as a reference, while a cesium gun was used as an initiator. The mass range used was from m/e = 20 to 3,000. Thermal properties and stability were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) mode. TGA was performed using a Perkin Elmer TGA7 analyzer while DSC was conducted with a Netzsch instrument: DSC200 Cell and TASC 414/3 controller at a heating rate of 10°C/min under a nitrogen atmosphere. Aluminum pans were used in the DSC analysis with sample sizes of 5-10 mg, while a platinum pan was used in the TGA with a sample size of 10-20 mg. For liquid and gel samples a high-pressure gold cell was used with the sample size of 10-20 mg. Simultaneous Thermal Analyzer (STA) was also employed for measuring the thermal stability and phase transformation of synthesized zeolite at a heating rate of 20°C/min under a nitrogen atmosphere. The testing was carried out with a Netzsch instrument: STA409 EP. The sample size for this measurement was in the range of 10-50 mg using an alumina-crucible as the sample cell. The crystallinity of the products was characterized by a Rigaku X-Ray Diffractometer at a scanning speed of 5 degrees/sec using CuKα as a source and CuKβ as a filter. The working range was 5°–50° theta/2 theta. SEM micrographs were obtained with a JEOL 5200-2AE scanning electron microscope. Electron Probe Microanalysis (EPMA) was used to analyze the sample in micro-scale for both qualitative and quantitative elemental analysis with the X-Ray mode detector (SEM/EDS; Energy Dispersive Spectroscopy) to obtain product compositions. Particle sizes and particle size distributions were determined using a Malvern Instruments Mastersize X Ver.2.15 analyzer. Water was used as a mobile phase. Hydrothermal treatment by a microwave heating technique was conducted using a MSP1000, CME Corporation (Spec. 1,000W and 2,450 MHz) oven. Samples were heated in a Teflon-lined digestion vessel sealed with a Teflon cap using an inorganic digestion mode with a time-to-temperature program.

Precursors Synthesis

Silatrane was synthesized by mixing 0.10 mol silicon dioxide and 0.125 mol triethanolamine in a simple distillation set using 100 mL. ethylene glycol as solvent (Piboonchaisit, *et al.* 1999). The reaction was carried out at the boiling point of ethylene glycol under a nitrogen atmosphere set for 10 h to remove water as a by-product and ethylene glycol from the system. Excess ethylene glycol was removed under vacuum (10^{-2} torr) at 110°C. The brownish white solid was washed with dried acetonitrile three times. Approximately 95% yield of white powder product was obtained and characterized using FTIR, TGA, DSC and FAB^+-MS. The product was named as SiTEA. FTIR: 3000-3700 cm^{-1} (w, intermolecular hydrogen bonding) 2860-2986 cm^{-1} (s, νC-H), 1244-1275 cm^{-1} (m, νC-N), 1170-1117 cm^{-1} (bs, νSi-O), 1093 and 915-940 cm^{-1} (s, νSi-O-C), 1073 cm^{-1} (s, νC-O), 1049 cm^{-1} (s, νSi-O), 1021 cm^{-1} (s, νC-O), 785 and 729 cm^{-1} (s, δSi-O-C) and 579 cm^{-1} (w, Si<---N). TGA: one mass loss transition at 390°C with 18.47 %ceramic yield corresponding to $Si((OCH_2CH_2)_3N)_2H_2$. DSC: 349°C (endothermic) and 380°C (exothermic). FAB$^+$-MS: approximately 3% of the highest m/e at 669 of $Si_3((OCH_2CH_2)_3N)_4H^+$ and 100% intensity at 323 of $Si((OCH_2CH_2)_3N)_2H_3^+$.

A similar process was used to synthesize alumatrane from 0.1 mol aluminum hydroxide and 0.125 mol triisopropanolamine (Opornsawad, *et al.* 2001). The crude product was washed with dried acetonitrile three times which ~90% yield product was obtained and characterized using FTIR, TGA, DSC and FAB$^+$-MS. The product was named as AlTIS. FTIR: 3000-3700 cm^{-1} (s, intermolecular hydrogen bonding) 2860-2986 cm^{-1} (m, νC-H), 1649 cm^{-1} (w, O-H overtone), 1244-1275 cm^{-1} (w, νC-N), 1037, 1130 cm^{-1} (m, νC-O), 1102 cm^{-1} (s, νAl-O-C), and 649 cm^{-1} (s, δAl-O). TGA: two mass loss transitions at 139° and 393°C with 23.97 %ceramic yield corresponding to $Al(OCHCH_3CH_2)N$. DSC: 145° and 196°C (endothermic) and 380°C (exothermic). FAB$^+$-MS: approximately 4% of the highest m/e at 1292 of $(Al(OCHCH_3CH_2)_3N)_6H^+$ and 100% intensity at 216 of $Al(OCHCH_3CH_2)_3NH^+$.

Sol-Gel Process and Microwave Technique

SiTEA and AlTIS were mixed with NaOH or NaCl solution at room temperature at a ratio of $SiO_2:Al_2O_3:xNa_2O:yH_2O$ (where $0 \leq x \leq 10$ and $63 \leq y \leq 1000$). The solution mixture was aged for at least 12 h to obtain full gel formation and then placed into a Teflon vessel for further hydrothermal treatment using a microwave technique. The solution mixtures containing different ratios of $SiO_2:Al_2O_3$: $xNa_2O:yH_2O$ were treated for various times and the resulting white powder products were washed three times using distilled water. The products were finally dried at 75°C for 15 h. There was no carbon component in the pores or the framework of synthesized products, as confirmed by SEM/EDS and STA.

RESULTS AND DISCUSSION

Gels started to form at the $SiO_2:Na_2O$ of 1:0.0063 and the ratio of $SiO_2:H_2O$ had to be at most 1:63 to obtain a better heat transfer and homogeneous dispersion of particle in solution. However, a better condition for microwave heating technique was $SiO_2:H_2O$ ratios in the range of 1:410–1:510. In this work, $SiO_2:Na_2O$ ratios were 1:3 to 1:10 with the NaOH system. The solution mixture started from a clear solution due to the Na-atranes complex formation Aoki, *et al.* (2000), a form of organic-inorganic composite and dissolution of partial metal-oxide network by NaOH (Bell, 1999). The Si:Al loading ratio for synthesizing LTA or Na A zeolite was at ~ 1:2. A white precipitated product was obtained after the hydrothermal treatment, during which the polycondensation of amorphous gel was transformed to crystalline aluminosilicate (Sehmachtl, *et al.* 2000; and Caputo, *et al.* 2000). In the case of the $NaCl/H_2O$ system, the solution mixture became cloudy at the start due to the slow dissolution of metal-oxide network.

Gel Transformation to Aluminosilicate

The crystal formation under hydrothermal condition was next studied by fixing $SiO_2:Al_2O_3:xNa_2O:yH_2O$ at the loading ratio of 1:1:3:410 and the microwave heating temperature at 110°C for 3 h using either NaOH or NaCl as a hydrolytic agent. XRD results indicated that only NaOH solution could provide crystalline aluminosilicate, as illustrated in Figure 1. The reason is the ability of NaOH to dissolve the metal-oxide network, which accelerates the organic-inorganic micelle formation leading to the formation of meso-structured material. The XRD results of synthesized product were matched with the Linde (A-LTA) structure type or Na A zeolite having PDF# 39-0222 and

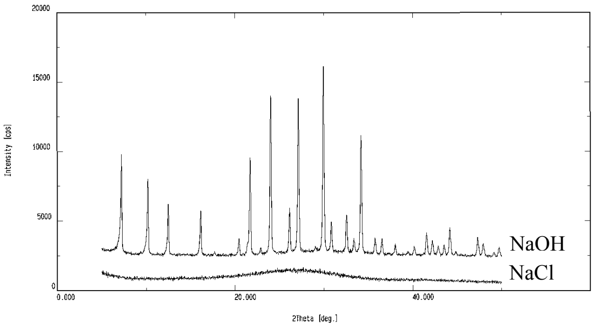


Figure 1 XRD spectra of aluminosilicate synthesized from $SiO_2:Al_2O_3:3Na_2O: 410H_2O$. Conditions 110°C for 180 min in $NaCl/H_2O$ + $NaOH/H_2O$ system

$Na_{96}Al_{96}Si_{96}O_{384}.216H_2O$ ~ Si:Al:Na = 1:1:1 in which the building unit was in cubic form, as confirmed by SEM in Figure 2. Though our synthesized products turned out to be mostly uniform in crystal structure and size, there also was some irregular crystal morphology and size indicating the formation of secondary nuclei. The EDS-SEM results show that the synthesized product contained only Si, Al and Na atoms, and the ratio of Si:Al:Na ratio was 1:1:1.25. The excess of Na atoms is due to the interaction of OH^- anions with a zeolite framework to form the siloxy groups ($\equiv SiO^-$), which must be accommodated with extra Na^+ cations. (Shen, *et al.* 1997) The STA results of synthesized zeolite also indicate (not given) no mass loss of residue carbon and no phase-transformation in the range of 150°-600°C. The thermal stability of synthesized product was at 600°C similar to those obtained from XRD results. Even at 700°C LTA was found as a major product, however the XRD baseline started to exhibit curvature and the signal to noise ratio was higher indicating the morphology change of LTA in Figure 3. The structural transformation occurred very slowly and changed from LTA to sodium aluminum silicate (PDF#11-0220, $NaSiAlO_4$) due to the collapse of LTA.

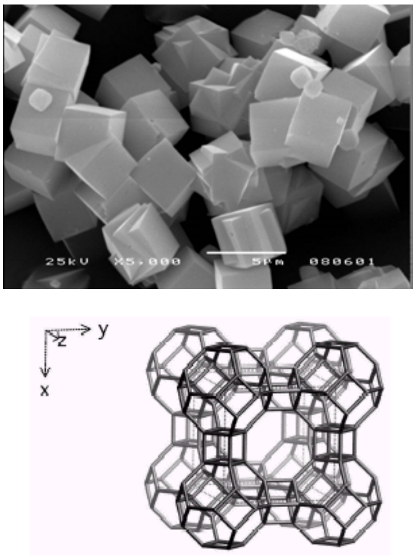


Figure 2 Unit cell structure and crystal morphology of Na A zeolite synthesized from Sio_2: Al_2O_3:3No_2 O: 410H_2O at 110°C for 180 min in Na:OH/H_2O

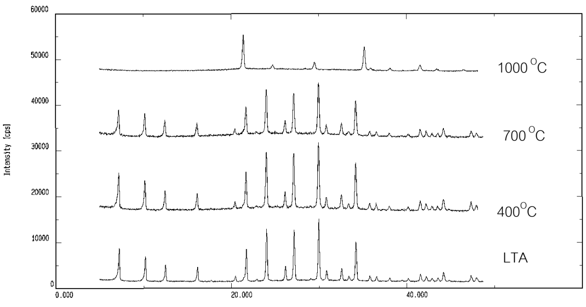


Figure 3 XRD spectra of calcined Na A zeolite at various temperature

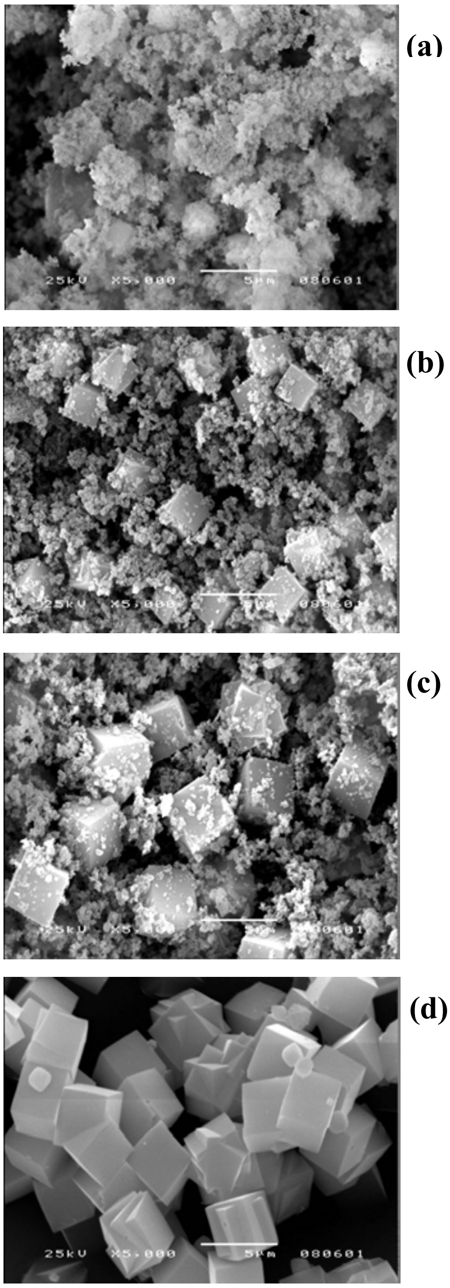


Figure 4 SEM micrographs of Na A zeolite synthesized from SiO_2:Al_2O_3:3Na_2O: 410H_2O and 110°C for (a) 60, (b) 100, (c) 140 and (d) 160 min

Effect of Microwave Heating Time

Using SEM in Figure 4 to follow the changing of amorphous gel to crystalline product LTA product was firstly found at 60 min and become fully crystalline at 160 min. The observed Na A zeolite was in a sharp edge cubic shape indicating that pre-nuclei might not be formed due to the organic-inorganic micelle formation during the sol-gel process (Shen, *et al.* 1997; Kresge, *et al.* 1997; Corma, 1997; Ying, *et al.* 1999; Monnier, *et al.* 1993; and Antonelli, *et al.* 1995). The complex formation not only prevented the precipitation to occur, but also retarded the nucleophilic attack of water, which enhanced the metal-oxide-metal formation, allowing a three-dimensional network to form. Additionally, the formation of complexes also helped in dissolving the amorphous aluminosilicate gel and slowly precipitating crystalline aluminosilicate resulting in low defect crystallization. However, we also observed some irregular cubic crystallites and smaller crystal size of Na A zeolite, most likely due to the growing of new nuclei after the initial nucleation and precipitation.

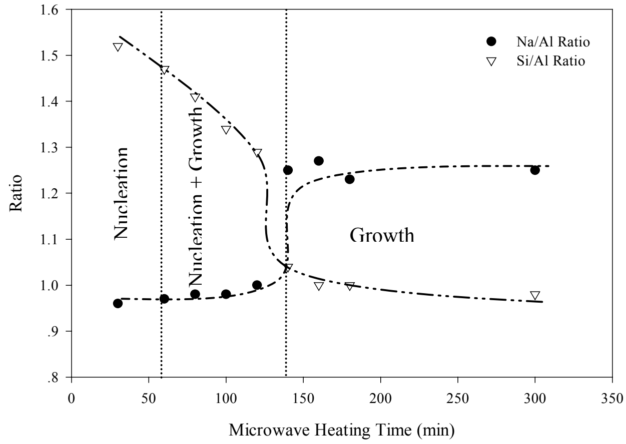


Figure 5 Na/Al and Si/Al ratios of synthesized zeolites at SiO_2:Al_2O_3:$3Na_2O$: $410H_2O$ and 110°C for varying heating times (30-180 min)

The Si/Al ratio of synthesized products versus microwave heating time showed that it was reduced from 1.53 to ~1.00, as shown in Figure 5. Even we load the Si/Al ratio less than 1, some aluminum would become sodium aluminate dissolved in NaOH solution. The Si/Al ratio was mostly dropped at 140 mins at which almost all of the crystalline products were formed, as confirmed by the SEM results in Figure 4. After crystalline formation, Si/Al ratios approached unity while the Na/Al ratios were greater than one, ~1.25. This indicated that the nucleation period might take place from 0-50 min and the growth period might start from 60 min onward. The use of alumatrane and silatrane can prolong growth period with good particle size distribution due to the complex formation.

Completely crystalline LTA was formed at a Si:Al loading ratio of 1:2 and microwave heating temperature of 110 °C for 3 h, while a Si:Al ratio of 1:1 provided a mixture of LTA and GIS type zeolite. However, higher Al content, and a Si:Al ratio of 1:3, resulted in a mixture of LTA and amorphous solid due to more formation of octahedral alumina atoms at high concentrations, leading to high amorphous solid fraction.

Effect of NaOH Concentration

Previously, we had found out that the Na_2O concentration and temperature affected the microwave heating time. (Sathupanya, *et al.* (In press) In this investigation, we fixed the microwave heating temperature at 110°C and the ratios of silica, alumina and water at 1:1:410. The Na_2O concentration was varied from 3 to 10 times of SiO_2. It was found that as the Na_2O concentration increased, the microwave heating time was reduced dramatically in the Na_2O:SiO_2 ratio range from 3:1 to 5:1, as illustrated in Figure 6. We speculate that this is due to the fact that the increase in Na_2O concentration increased the hydroxyl concentration, which in turn enhanced the dissolution of the amorphous gel

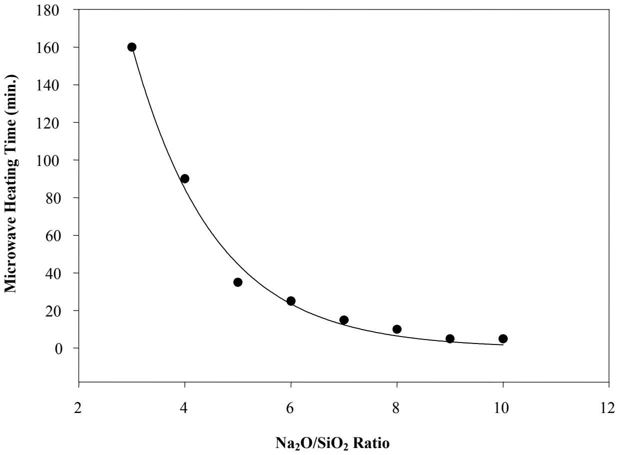


Figure 6 Effect of NaOH concentration on Na A zeolite synthesis using SiO_2:Al_2O_3:xNa_2O:$410H_2O$ (x =3 - 10)and 110°C

and the nucleation rate leading to the growth of more crystals. At $Na_2O:SiO_2$ ratios higher than 5:1, the reaction time decreased slightly and at the $Na_2O:SiO_2$ ratios of 9:1 and 10:1, the microwave heating time was reduced to 5 min. Moreover, a high concentration of Na_2O did affect the particle size and particle size distribution, as shown in Figure 7. For $Na_2O:SiO_2$ ratios of 3:1 to 5:1, the particle size distribution was bimodal with peaks at 2.16 and 7.84 μm, respectively. As the $Na_2O:SiO_2$ ratio increased to 6:1 and 7:1, the average particle size of each modal was shifted to lower-sizes, 1.62 and 7.08 μm, respectively, whereas at the $Na_2O:SiO_2$ ratios higher than 7:1, the particle size distribution was changed to mono-modal with smaller particle size (less than 4 μm). For $Na_2O:SiO_2$ ratios equal to 9:1 and 10:1, the particle size distributions were the same. However, from SEM results in Figure 8, we observed that the crystal size was different. It was found that the crystals agglomerated due to the presence of much more nuclei in the system. As compared to the $Na_2O:SiO_2$ ratio of 3:1, the average crystal size was ~ 4.5 μm which was twice smaller than the result obtained from the particle size analyzer. Indicating that the particles tended to agglomerate. Increasing the Na_2O concentration did not affect the product composition. All synthesized Na A zeolites have the Si:Al:Na ratio of ~1:1:1.25.

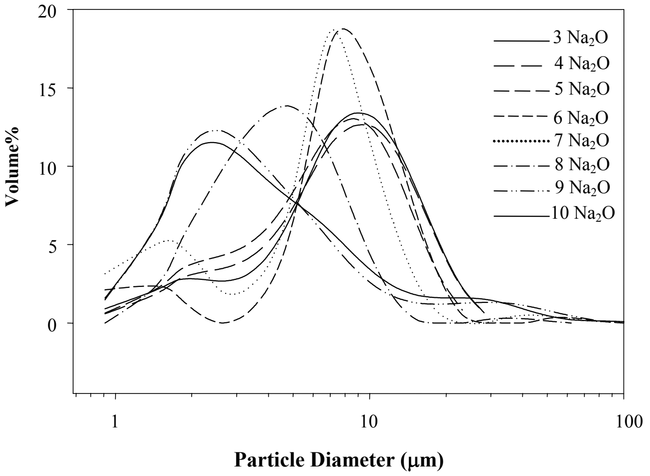


Figure 7 Agglomerated particle size distribution of Na A zeolite synthesized at various Na_2O concentration at $SiO_2:Al_2O_3:xNa_2O:410H_2O$ (x = 3-10) and 110°C/180 min

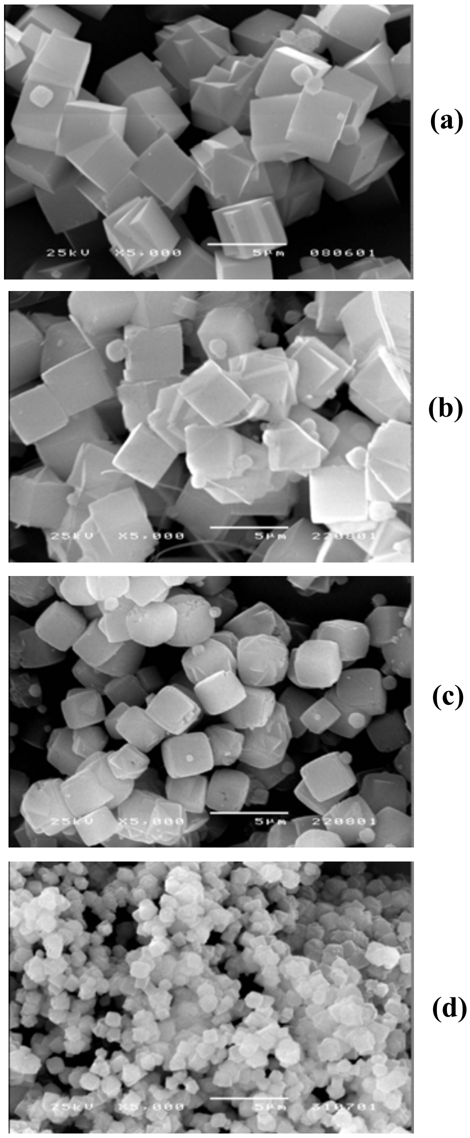
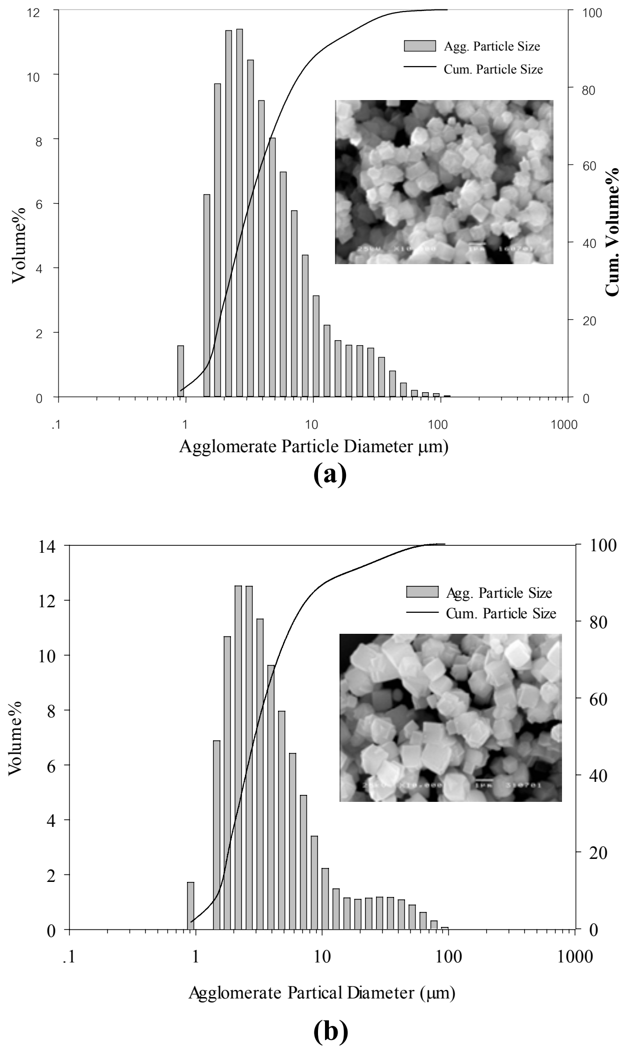


Figure 8 SEM micrographs of Na A zeolite synthesized using $SiO_2:Al_2O_3:xNa_2O$: $410H_2O$ and 110°C, with x = (a) 3, (b) 7, (c) 8 and (d) 10

Since the Na_2O concentration and hydroxyl group concentration were proportional, increasing the Na_2O concentration increased the HO^- concentration resulting in a higher pH for the system. When we fixed the pH by controlling OH^- loading, and adding NaCl to increase the Na_2O concentration, the results came out to be the same as those having the same OH^- concentration, meaning that the major influence on crystalline formation was OH^- concentration.

Reducing OH^- concentration by increasing the amount of water from 410 to 510 at the $SiO_2:Al_2O_3:10Na_2O$ ratio and microwave heating temperature of 110°C for 5 min, the agglomerate particle size distribution of synthesized Na A zeolite was almost the same, however, the results from SEM were slightly different, as shown in Figure 9. The higher water quantity provided a slightly bigger particle size (~1.5 µm for 510 H_2O and ~1 µm for 410 H_2O), and also more irregular cubic particles. There are two reasons for this. Higher water concentration lowered the Na_2O concentration, which led to a decreased rate of nucleation resulting in larger particles. Secondly, increasing the amount of water increased the pressure in the hydrothermal system, as a result, accelerating the crystallization process. Higher crystallization rate leads to less time to reach the most thermodynamically favored lattice positions in irregular particle sizes and shapes.



(a)

(b)

Figure 9 Effect of water amount on the Na A zeolite synthesized from SiO_2:Al_2O_3: $10Na_2O$:xH_2O (x = 410(a) and 510(b)) and 110°C/5 min

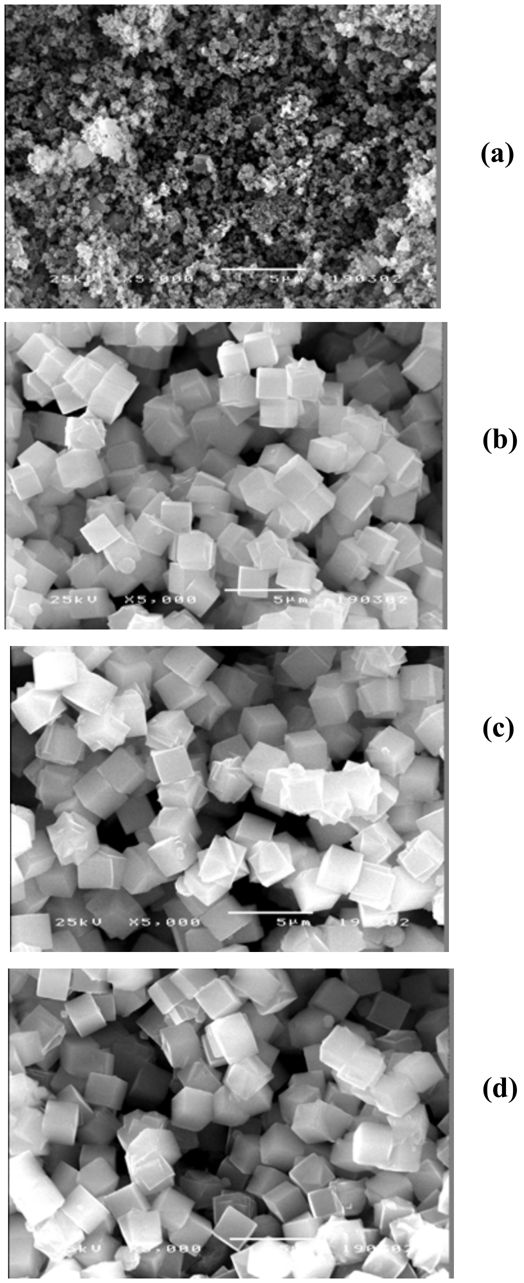


Figure 10 SEM micrographs of Na A zeolite synthesized using SiO_2:Al_2O_3:$5Na_2O$: $410H_2O$ and varying temperatures/60 min (a) 90, (b) 110, (c) 130 and (d) 150

Effect of Microwave Heating Temperature

Based on the effect of the Na_2O concentration study, the crystallization time decreased exponentially with increasing Na_2O concentration. By fixing the SiO_2:Al_2O_3 ratio at

1:1, the Na_2O/SiO_2 ratio at 5:1, the microwave heating time at 60 min and varying the heating temperature from 90° to 150°C, it was found that only at 90°C, a mixture of LTA and amorphous solid was produced. At temperatures higher than 90°C, the LTA product was obtained, and the particle size and the particle size distribution, as evidenced by SEM and particle size analyzer (Figures 10–11), did not change with temperature.

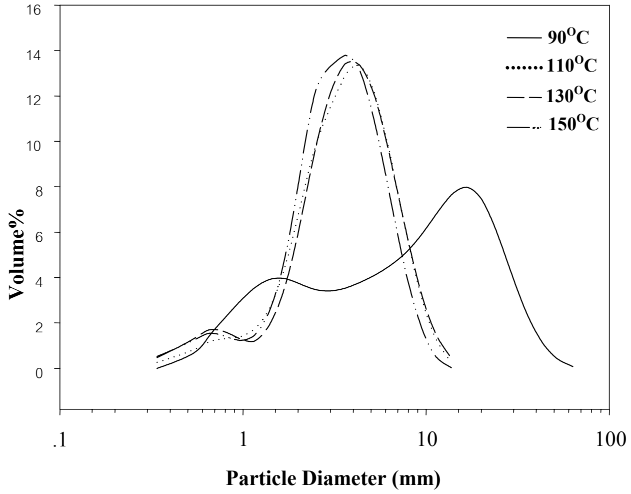


Figure 11 Agglomerated particle size distribution of Na A zeolite synthesized at various microwave temperatures for SiO_2:Al_2O_3:$5Na_2O$:$410H_2O$ and various heating temperatures

CONCLUSIONS

Uniform particle size Na A zeolite was successfully synthesized using alumatrane and silatrane as precursors. At a fixed silica to alumina to sodium oxide and to water ratio of 1,1,3,410 respectively and microwave heating temperature of 110°C, the product changed from amorphous to fully crystalline at 160 min with an average particle size of ~4.5 μm. Due to organic-inorganic micelle formation, sharp edged crystals were formed which indicated a better crystallization. Moreover, the organic-inorganic self-assembly depended on the NaOH concentration, increasing the Na_2O concentration by increasing the NaOH component decreased the microwave heating time and reduced the particle size. The shortest microwave heating time was 5 min. When the Na_2O:SiO_2 ratios of 9:1 – 10:1 were used, the smallest particle size obtained was ~1 μm. Increasing the water quantity and microwave heating temperature (>90 °C) slightly influenced the particle size and particle size distribution. Even synthesis Na A zeolite using silatrane and alumatrane as precursors behaved like conventional synthesis, the nucleation period was longer and perfect crystal was obtained with a narrow particle size distribution.

ACKNOWLEDGEMENT

This research work was fully supported by the Thailand Research Fund (TRF).

REFERENCES

Antonelli, D. and Ying, J. 1995. Synthesis of Hexagonally Packed Mesoporous TiO_2 by a modified Sol-gel Method. *Angew. Chem. Int. Ed. Engl.* **34** : 2014.

Aoki, K., Kusakabe, K. and Morooka, S. 2000. Preparation of oriented A-type zeolite membranes. *AIChE J.* **46** : 211.

Aoki, K., Kusakabe, K. and Morooka, S. 2000. Separation of gases with an A-type zeolite membrane. *Ind. Eng. Chem. Res.* **39** : 2245.

Bell, A. T. 1999. NMR applied to zeolite synthesis. *Colloids Surf. A: Phys. Chem. Eng. Asp.* **158** : 221.

Boudreau, L. C. and Tsapatsis, M. A. 1997. Highly oriented thin film of zeolite A. *Chem. Mater.* **9** : 1705.

Boudreau, L. C., Kuck, J. A. and Tsapatsis, M. 1999. Deposition of oriented zeolite A films: in situ and secondary growth. *J. Membr. Sci.* **152** : 41.

Caputo, D., De Gennaro, B., Liguori, B., Resta, F., Carotenuto, L. and Piccolo, C. 2000. A preliminary investigation on kinetics of zeolite A crystallization using optical diagnostics. *Mat. Chem. Phys.* **66** : 120.

Corma, A. 1997. From Microporous to Mesoporous Molecular sieve Materials and their Use in Catalyst. *Chem. Rev.* **97** : 2373.

Gladden, L. F., Sousa-Goncalves, J. A. and Alexander, P. 1997. Adsorption and transportation of ethane and ethene in zeolite Na A: 2H-NMR and Monte Carlo Lattice dynamics studies. *J. Phys. Chem. B.* **101** : 10121.

Hedlund, J., Schoeman, B., and Sterte, J. 1997. Ultrathin oriented zeolite LTA films. *J. Chem. Soc., Chem. Commun.* : 1193.

Ken-ichi, O., Hidetoshi, K., Kohji, H. and Kazuhiro, T. 2001. Zeolite NaA membrane: Preparation, single-gas permeation and pervaporation and vapor permeation of water/organic liquid mixtures. *Ind. Eng. Chem. Res.* **40** : 163.

Kita, H., 1995. Prevaporation through zeolite membranes. *Membrane (Tokyo).* **20** : 169.

Kresge, C., Leonowicz, M., Roth, M., Vartuli, J. and Beck, J. 1992. Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Trmplate Mechnism. *Nature*. **359** : 710.

Monnier, A., Schuth, F., Huo, Q., Kumar, D., Margolese, D., Maxwell, R., Stucky, G., Krishnamurty, M., Petroff, P., Firouzi, A., Janiche, J. and Chmelka, B. 1993. Cooperative Formation of Inorganic-organic Interfaces in the Synthesis of Silicate Mesostructure. *Science.* **261** : 1290.

Opornsawad, Y., Ksapabutr, B., Wongkasemjit, S. and Laine, R. 2001. Formation and Structure of Tris(alumatranyloxy-*I*-propyl)amine Directly from Alumina and Triiospropanolamine. *Eur. Polym. J.* **37(9)** : 1877.

Piboonchaisit, P. Wongkasemjit, S. and Laine, R. 1999. A Novel Route to Tris(silatranyloxy-*I*-propyl)amine Directly from Silica and Triiospropanolamine, Part I. *Sci. Asia.* **25** : 113.

Rabinovich, E. M. and Klein, L.C. 1988. *Particulate silica gels and glasses from the sol-gel process, Sol-Gel Technology for Thin Filmes, Fibers, Electronic and Specially Shapes*. New Jersey, Nayes Publication. : 260

Rollmann, L. D., Schlenker, J. L., Kennedy, C. L., Kennedy, G. J. and Doren, D. 2000. On the role of small amines in zeolite synthesis: 2. *J. Phys. Chem. B.* **104** : 721.

Rollmann, L. D., Schlenker, J. L., Lawton, S. L., Kennedy, C. L., Kennedy, G. J. and Doren, D. 1999. On the role of small amines in zeolite synthesis. *J. Phys. Chem. B.* **103** : 7175.

Sathupunya, M., Gulari, E. and Wongkasemjit, S. ANA and GIS Zeolites Synthesis Directly from Alumatrane and Silatrane by Sol-Gel Process and Microwave Technique. *J. Eur. Cer. Soc.* (In Press).

Schmachtl, M., Kim, T. J., Gill, W., Herrmann, R., Scharf, O., Schwieger, W., Schertlen, R. and Stenzel, C. 2000. Ultrasonic monitoring of zeolite synthesis in real time. *Ultrasonic*, **38** : 809.

Shen, V., Watanabe, K. and Bell, A. T. 1997. Theoretical analysis of the thermodynamics of ZSM-11 zeolites synthesis. *J. Phys. Chem. B.* **101** : 2207.

Shiguang, L., Tuan, V. A., Falconer, J. L., and Nobel, R. D. 2001. Effect of zeolite membrane structure on the separation of 1,3 propanediol from glycerol and glucose by prevaporation. *Chem. Mater.* **13** : 1865.

Wang, J., Wang, Y., Fan, S. and Shi, X. 1994. Preparation and gas permeabilities of zeolite A membrane. *Proceeding of the 3rd International Conference on Inorganic Membranes*, Worcester, MA.

Weitkamp, J., Jansen, J. C. and Karge, H. G. 1994. Application of molecular sieves in view of cleaner technology. Gas and liqiud phase separation, In : Jensen, J.C. (eds.) *Advanced Zeolite Science and Application,Amsterdam,Elsevier Science*. : 632.

Yahiro, H., Lund, A., Aasa, R., Benetis, N. P. and Shiotani, M. 2000. Association forms of NO in sodium ion-exchanged A-type zeolite:Temperature-dependent Q-band EPR spectra. *J. Phys. Chem. A.***104** : 7950.

Ying, J., Mehnert, C. and Wong, M. 1999. Synthesis and Applications of Supramolecular Templated Mesoporous Materials. *Angew. Chem. Int. Ed. Engl.* **38** : 56.

(Revised version accepted January 22, 2003)