

CHAPTER VIII

CONCLUSIONS

8.1 Conclusions

Crystalline aluminosilicates or zeolites are successfully one-step-synthesized using alumatrane and silatrane as starting materials via sol-gel process and hydrothermal treatment using microwave heating technique. These were the first time that crystalline aluminosilicate or zeolites can be synthesized directly from the mixture of alumatrane and silatrane and the first reports on sol-gel process of alumatrane and silatrane mixture. Products obtained from these new procurers have nicer and more uniform crystallinity and narrower particle size and distribution in a shorter time, which were suitable for making zeolite membrane. Moreover, the moisture of our own synthesized product can consume more moisture especially for Na A (LTA) zeolite that can absorb ~20% more moisture than the commercial. All synthesized products might be suitable to use as molecular sieve, in all drying purposes and humidity sensor.

The mixture of alumatrane and silatrane can undergo sol-gel process by using metal salt or metal hydroxide as hydrolytic agent. Using FTIR to follow the sol-gel reaction, the reduction of ν C-N peak at 1275 cm^{-1} indicating the cleavage and leave out of alkyl amine occurred. The hydrolysis rate of sodium hydroxide/water system is approximately two times faster than that of sodium chloride/water system due to higher nucleophilicity of hydroxyl group and larger radii of chloride ion. Changing type of metal hydroxide from sodium hydroxide to lithium or potassium hydroxide, the rate of gel formation was different. By fixing at $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:0.7\text{M}_2\text{O}:410\text{H}_2\text{O}$ ($\text{M} = \text{Li}, \text{Na}$ or K), the gel formation rate was $\text{KOH} > \text{NaOH} > \text{LiOH}$. Moreover, the morphologies of the resulting gels were also different. KOH system provided hard and cloudy gel, while NaOH system was soft and opaque and for LiOH system, it was liquid like.

Using high-pressure DSC cell, transformation temperatures of gel to aluminosilicate crystalline at the gel composition of $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:0.7\text{M}_2\text{O}:410\text{H}_2\text{O}$

were almost the same, which started to form at 103° C and the maximum transformation was at 106° C. The energy requirement of transformation to aluminosilicate of the KOH system was higher than that of the NaOH and LiOH systems, respectively. However, by treating gel using microwave-heating technique, the transformation temperature of each metal hydroxide was different. At $\text{SiO}_2:\text{Al}_2\text{O}_3:0.7\text{M}_2\text{O}:410\text{H}_2\text{O}$ (Si:Al = 2:1), for KOH system, the transformation to crystalline aluminosilicate was at 150° C for 5h which obtained product was zeolite K-H named as PPC-ZM-1. For NaOH system, the transformation to GIS type was found at 110° C for 3h while the LiOH system gave the transformation to lithium silicate at 90° C for 1h. The reason might be that the transformation under DSC caused only semi-oriented solid to occur due to a shorter reaction time while under hydrothermal condition using a longer period of time, the fully crystalline silicate or aluminosilicate were produced at different temperatures for different hydrolytic agent. Different radii size of each alkali, resulting in different alkalinity affects the dissolution rate of amorphous gel leading to different polymerization rate of silicate and aluminate anion.

By using sodium hydroxide as hydrolytic agent, varying the Si:Al loading ratio from 100:1 to 2:1 and fixing $\text{SiO}_2:3\text{Na}_2\text{O}:410\text{H}_2\text{O}$ ratio, ANA and GIS type zeolites were produced at 130° C for 8 h and 110° C for 3 h, respectively. The GIS zeolite was also formed at 130° C for 1.33 h or 80 min. before the ANA product occurred. Changing the Si:Al ratio from 2:1 to 1:1, the mixture of GIS and LTA was obtained even the microwave heating time was kept at 110° C for 15 h. Fully LTA product was produced at Si:Al ratio of 1:2 and microwave heating temperature of 110° to 150° C. The particle sizes and particle size distributions of all temperature conditions were the same. Increasing the $\text{Na}_2\text{O}:\text{SiO}_2$ ration form 3:1 to 10:1 and fixing at $\text{SiO}_2:\text{Al}_2\text{O}_3:410\text{H}_2\text{O}$ ratio, the microwave heating time was exponentially drop from 160 at 3:1 min to 5 min at 9:1 and the particle size and particle size distribution was dropped from ~ 5 to ~ 1 μm according to SEM results. Moreover, increasing $\text{Na}_2\text{O}:\text{SiO}_2$ ration also increased the small particle portion due to the formation of new nuclei. Increasing water ratio ($\text{H}_2\text{O}/\text{SiO}_2$) from 410:1 to 510:1, bigger and more irregular crystal structures were obtained.

By using KOH as hydrolytic agent, vary the Si:Al ration from 2:1 to 100:1 and fixing $\text{SiO}_2:3\text{K}_2\text{O}:410\text{H}_2\text{O}$, the crystalline aluminosilicate was found at 150°C and the microwave heating time are the same for all conditions. The synthesized product was closely matched with zeolite K-H, which was the unknown structure type and named as PCC-ZM-1. The morphology was needle-like aggregated into flower-petal-like. Increasing microwave-heating temperature to 170°C , the assembly morphology was changed to bundle. Increasing the Si:Al ratio also affected the product morphology. When silica content was higher, the product was first changed from flower-petals to bundle and the size was then reduced. Increasing the $\text{K}_2\text{O}/\text{SiO}_2$ ratio from 2:1 to 4:1 has mostly influenced microwave heating time, which dropped from 360 to 180 min, respectively. However, the heating time increased up to 240 min at the ratio 6:1. The morphology of the products was smaller, more agglomerate and more irregular when increasing the microwave heating time longer due to dissolution and recrystallization effects.

By using lithium hydroxide as hydrolytic agent and changing Si:Al ratio, $\text{Li}_2\text{O}/\text{SiO}_2$ ratio or microwave heating temperature affected the type and morphology of synthesized products. By fixing $\text{SiO}_2:0.5\text{Al}_2\text{O}_3:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and microwave heating time at 300 min, different microwave heating temperature provided different type of products. At temperature of 110°C or higher, the ABW type zeolite was produced while at temperature range of $70^\circ - 90^\circ\text{C}$, EDI type zeolite was found. Both EDI and ABW were not stable at temperature higher than 200°C . EDI was changed to amorphous first and then to lithium aluminate silicate while ABW was changed directly to lithium aluminate silicate. At microwave heating temperature of 90°C , only EDI type was generated while at 110°C , the mixture of EDI and ABW were formed at various time. At temperature higher than 110°C and heating time at 300 min, ABW product was smaller and more agglomerate. Varying Si:Al ration by fixing $\text{SiO}_2:3\text{Li}_2\text{O}:410\text{H}_2\text{O}$ and microwave heating temperature of 110°C for 300 min, at Si/Al ratio of 2 and higher, only lithium silicate product was produced. At Si/Al ratio of 1 to 0.2, ABW was obtained but the morphologies of these two conditions were totally different, higher alumina loading content, higher irregular product was found. For various $\text{Li}_2\text{O}:\text{SiO}_2$ ratio from 1:1 to 5:1, silicon nitride was

resulted at $\text{Li}_2\text{O}:\text{SiO}_2$ of 5:1 while EDI mixed with silicon nitride and EDI mixed with FAU were found at 4:1 and 2:1, respectively. ABW was made at 3:1 while FAU and LZ-200 were produced at 1:1. From SEM and XRD results at $\text{LiO}_2:\text{SiO}_2$ ratio of 1:1, FAU was the major product and was stable up to 600°C , as measured by STA.

Both Na-LTA and Li-FAU can absorb moisture for ~16% by weight while PPC-ZM-01 can absorb up to ~25% by weight. Comparing the moisture absorption ability of synthesized Na-LTA with the commercial, the absorption ability of our synthesized product is ~20% more. Due to high moisture absorption ability of our synthesized zeolites, especially for PPC-ZM-01, it might be suitable to use as molecular sieve, in all purposes of drying, especially for air drying in refinery industry and humidity sensor. Most of products obtained from these precursors have nicer and more uniform crystallinity and more uniform particle size and narrow particle size distribution that are suitable properties for making zeolite membrane.

8.2 Suggestion for Future Work

Based on all good properties studied, our synthesized products seem to be suitable for using as molecular sieve and zeolite membrane. The suggestions for future work thus are;

1. Making zeolite membrane directly from aluminatane and silicatane via sol-gel process and microwave heating technique.
2. Making humidity sensor from zeolite: microwave-preparing zeolite directly from aluminatane and silatane by sol-gel process and microwave technique.

Since Li-FAU was made at only one condition and mixed with LZ-200, it's very interesting to study;

3. Preparation of Li-FAU zeolite directly from aluminatane and silatane by sol-gel process and microwave technique.

Moreover, there are many types of atranes, such as titanatane, germatane, zirconatane, cerianatane and etc. that have potential in using as precursors for zeolite synthesis, another future work should also be;

4. Preparation of zeolite directly from different atranes by sol-gel process and microwave technique.