Synthesis and Characterization of Zeolite from Sodium Aluminosilicate Solution

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ABSTRACT
Zeolite was successfully synthesized from sodium aluminosilicate solution in this study. The synthesis process was performed at 80°C in closed reaction system for 2 weeks. The effect of the varying Si concentration in aluminosilicate solution from 1 to 8 towards zeolite crystallization was investigated. The surface morphology of lamellar structure with cubical edge was appeared under SEM investigation. The presence of FAU, LTA, SOD and GIS framework was detected via XRD .

Keywords: Zeolites, aluminosilicates, Si/Al ratio

INTRODUCTION

There are about 40 natural zeolites that have been identified during the past 200 years. The most common are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. There are also more than 150 zeolites that have been synthesized and the most common are zeolites A, X, Y, and ZMS-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

Typically, zeolite is synthesized by mixing together silicate and aluminate solutions or sols to form an aluminosilicate gels and later is treated hydrothermally to give the crystalline products (Harvey and Glasser, 1989). The product properties depend on reaction mixture composition, silica and alumina source that had been used, reaction time, pH of the system, operating temperature and pressure, synthesis condition such as the mixing order, aging, stirring and templates used (Marcus and Cormier, 1999).

EXPERIMENTAL METHODS

Sodium aluminate solution was prepared by dissolving sodium aluminate anhydrous with deionized water while sodium silicate solution was prepared from fumed silica and sodium hydroxide. Both solutions were then mixed together either by the addition of the excess alkali (A) into the silicate solution or (B) into the aluminate solution. Si/Al ratio varied from 1 to 8. The mixtures were then treated hydrothermally at temperature 80°C for two weeks. The product was filtered, washed until the supernatant liquid reached pH11 and dried into the oven for 24 hours. The synthesized product was characterized via SEM and XRD for its morphology and phase identification.

RESULTS AND DISCUSSION

XRD Analysis

Each synthesized product from aluminosilicate solution was analyzed via XRD and the result of phase identification was summarized in Table 1. As listed in the Table 1, via Method A, the LTAH (FAU) and Na-P1 (GIS) phases were able to be produce by using Si/A ratio of 1 in the sodium aluminosilicate composition while in Method B, only LTAH and Na=P1 zeolite were produced. However, samples AID3A, AID5A and AID7Afor both method did produce the same type of zeolite (Na-X and SOD) but at different peaks. Therefore, it can be conclude that there exists a correlation between the type of synthetic zeolite and the Si/Al ratio in the sodium aluminosilicate composition.

12 mls

Table 1: Summary of the phase identification of zeolite produced via Method A and B.

Si/Al ratio	Phase Identification	
	Method A	Method B
1	Na-X, LTAH, Na-P1	LTAH, Na-P1
3	Na-X, SOD	Na-X, SOD
5	Na-X, SOD	Na-X, SOD
7	Na-X, SOD	Na-X, SOD

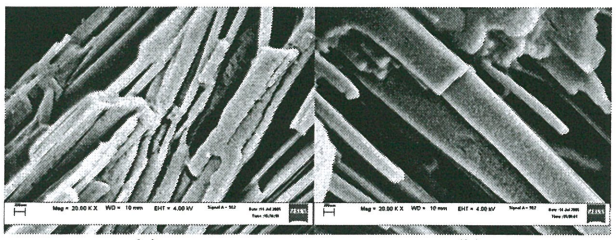
The estimation of crystallite sizes can be measured by applying Scherrer equation based on the XRD analysis. Table 2 shows the estimation of crystallite size of samples at ratio 1, 3, 5 and 7 respectively. It is found that the size of crystallite decreased with increasing of Si/Al ratio. This is due to the pores of the grains and generally it will be interconnected by surface and liquid forces for the grain growth (Rahaman, 1995).

Table 2. Crystallite size of zeolites with varying Si/Al ratio of 1, 3, 5 and 7.

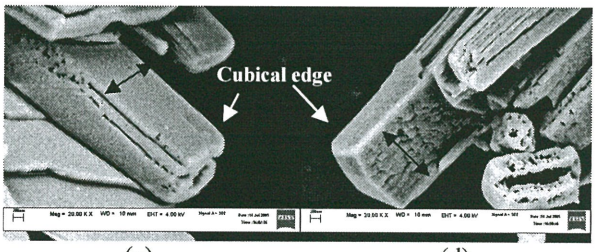
Si/Al ratio	Crystallite size	
	Method A	Method B
1	14.31	16.76
3	11.52	15.72
5	10.35	10.38
7	5.73	6.64

SEM Analysis

As ascribed in Figure 2(a)-(d), all samples portrayed a lamellar surface structure with cubical edge. However, the crystal size appeared to be decreased with the decreased of Si/Al ratio. This behavior is expected because a loss of yield with the decreased of Si/Al ratio happened due to the limited access of Si species in the liquid phases of synthesis process [Brar et al., (2001) and Armaroli et al. (2006)]



(a) (b)



(c) (d)

Figure 2: Scanning electron photomicrographs of zeolite product at 80°C with varying Si/Al ratio of (a) 1; (b) 3 ; (c) 5 and (d) 7, respectively. The arrowhead (◄►) indicates the size of the crystal in nanometer.

CONCLUSION

The synthesis of zeolite from sodium aluminosilicate solution has been successfully carried out. In the present investigation, the morphology and crystallite size are affected significantly by the Si/Al ratio. The type of material produced mostly have FAU framework structure with crystallite size ranging from 5 nm-17 nm.

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SYNTHESIS AND CHARACTERIZATION OF ZEOLITES FROM SODIUM ALUMINOSILICATE SOLUTION

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Abstract

A series of synthetic zeolites were successfully synthesized from sodium aluminosilicate solutions with varying Si concentration from 1 to 8 molar using fumed silica and sodium aluminate. The order of mixing and the effect of varying amount of Si in the sodium aluminosilicate solution towards surface morphology, structure and the type of material produced are reported. XRD results showed that the phases of zeolites synthesized are similar to FAU, LTA, SOD and GIS framework with crystallite size was varied from 3 to nearly 20 nm. Surface morphological studies obtained from SEM photomicrographs showed the powdered synthetic zeolite have a lamellar structure with cubical edge and the crystal size was estimated to be 1 to 1.2 micron while TEM analysis indicated the presence of pores with the pore sizes estimation at 13-23 nm (width) and 18-43 nm (length).

Keywords: Zeolites, aluminosilicates, Si/Al ratio,

Abstrak

Rangkaian siri sintetik zeolite telah berjaya disintesiskan daripada larutan natrium aluminosilikat dengan kepekatan Si dari 1 hingga 8 molar menggunakan habuk silika (fumed silica) dan natrium aluminat. Kesan daripada tertib pencampuran sumber sintesis dan penggunaan pelbagai kepekatan Si terhadap morfologi, struktur dan jenis bahan yang terhasil dilaporkan. Keputusan XRD menunjukkan kehadiran fasa zeolit dengan kerangka kerja sama seperti FAU, LTA, SOD dan GIS dengan saiz kristalit dianggarkan antara 3 hingga 20 nm. Kajian morfologi permukaan daripada fotomigrograf SEM menunjukkan serbuk sintetik zeolit yang terhasil mempunyai struktur berbentuk lamella dengan pinggir sisinya berbentuk kubik dengan anggaran saiz kristal antara 1 hingga 1.2 mikron manakala analisis TEM menunjukkan kehadiran liang-liang halus dengan anggaran saiz liang adalah 13 hingga 23nm (lebar) dan 18 hingga 43nm (panjang).

Katakunci: zeolite, aluminosilikat, nisbah Si/Al

1.0 Introduction

Zeolite are crystalline aluminosilicates containing pores and channels of molecular dimensions that are widely used in industry as ion exchange resins, molecular sieves, sorbents and catalysts. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. Many occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic, and are made commercially for specific uses, or produced by research scientist trying to understand their chemistry.

The zeolite history began with the discovery of stilbite by Crönstedt, a Swedish mineralogist in year 1756. Upon heating the zeolite released occluded water, which gave the materials their general name, zeolite, after the Greek words, "ξειν" (*zeo*) , to boil, and "λιθος" (*lithos)*, stone. A representative empirical formula of a zeolite is

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

where M represents the exchangeable cation of valence n. M is generally a Group I or II ion, although other metal, non-metal and organic cations may also balance the negative charge created by the presence of Al in the structure. The framework may contain cages and channels of discrete size, which are normally occupied by water (Ghobarkar et al., 1999).

There are about 40 natural zeolites that have been identified during the past 200 years. The most common are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. There are also more than 150 zeolites that have been synthesized and the most common are zeolites A, X, Y, and ZMS-5. Natural and synthetic zeolites are used commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.

Typically, zeolite is synthesized by mixing together silicate and aluminate solutions or sols to form an aluminosilicate gels and later is treated hydrothermally to give the crystalline products (Harvey and Glasser, 1989). The product properties depend on reaction mixture composition, silica and alumina source that had been used, reaction time, pH of the system, operating temperature and pressure, synthesis condition such as the mixing order, aging, stirring and templates used (Marcus and Cormier, 1999). Therefore, in this paper, the effects of the order of mixing and the varying amount of Si concentration in the sodium aluminosilicate solution were

investigated systematically from its morphology, crystal structure and the type of zeolite produced.

2.0 Experimental Methods

Sodium aluminate solution was prepared by dissolving sodium aluminate anhydrous with deionized water while sodium silicate solution was prepared from fumed silica and sodium hydroxide. Both solutions were then mixed together either by the addition of the excess alkali (A) into the silicate solution or (B) into the aluminate solution. The Si concentration in the solution is varied from 1 to 8 with Al remained constant. The mixtures were then treated hydrothermally at temperature 80°C for two weeks. The product was filtered, washed until the supernatant liquid reached pH11 and dried into the oven for 24 hours. The synthesized product was observed under Scanning Electron Microscope (Supra 50VP-23-57) and Transmission Electron Microscopy. The identification of product produced was identified by x-ray diffraction (Phillips, PW 1820).

3.0 Results and Discussion

3.1 XRD analysis

The results of phase identification from Si/Al ratio 1, 3, 5 and 7 for both Method A and B are shown in Table 1 and Table 2. Figure 1 illustrated the comparison of the XRD phases of the type of zeolite produced with varying Si/Al ratio of sodium aluminosilicate solution at temperature 80°C using Method A. As listed in the Table 1 and illustrated in Figure 1, the LTAH (FAU) and Na-P1 (GIS) phases were able to be produce by using Si/A ratio of 1 in the sodium aluminosilicate composition. Meanwhile, from Si/Al ratio 3, 5 and 7, only synthetic zeolite of type Na-X (FAU) and SOD (FAU) were synthesized. The illustration on Figure 2 shows the XRD phases of the type of synthetic zeolite produced with varying Si concentration using Method B. This figure shows that the sample AID1A (with Si/Al ratio = 1) produced LTAH and Na-P1 zeolite. However, samples AID3A, AID5A and AID7A did produce the same type of zeolite (Na-X and SOD) but at different peaks. Hence, there exists a correlation between the type of synthetic zeolite and the Si/Al ratio in the sodium aluminosilicate composition.

Table 1. Phase identification of zeolite produced through Method A.

Sample Code	Si/Al ratio	Framework Type
AID1A	1	Na-X, LTAH, Na-P1
AID3A	3	Na-X, SOD
AID5A	5	Na-X, SOD
AID7A	7	Na-X, SOD

Table 2. Phase identification of zeolite produced through Method B.

Sample Code	Si/Al ratio	Framework Type
AID1B	1	LTAH, Na-P1
AID3B	3	Na-X, SOD
AID5B	5	Na-X, SOD
AID7B	7	Na-X, SOD

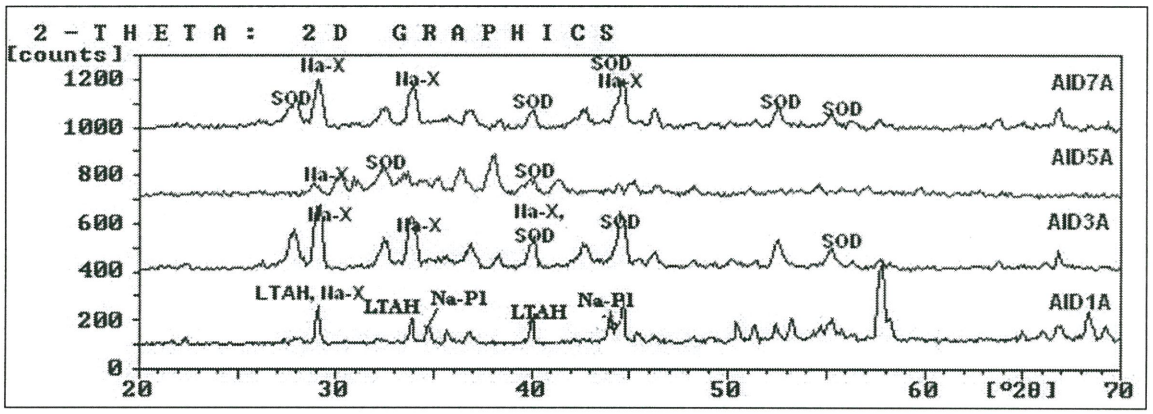


Figure 1. Comparison of synthetic zeolite from varying Si concentration of 1, 3, 5 and 7 using Method A. *With reference to simulated XRD pattern (Treacy and Higgins, 2001)*

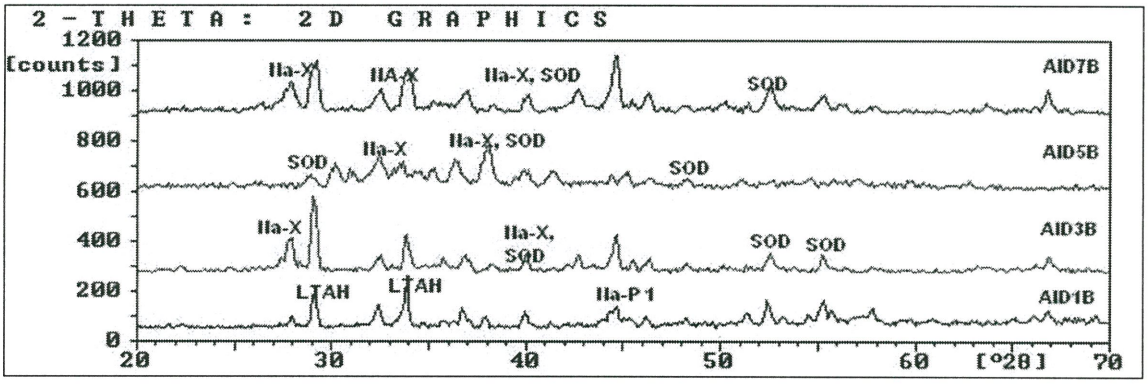


Figure 2. Comparison of synthetic zeolite from varying Si concentration of 1, 3, 5 and 7 using Method B. *With reference to simulated XRD pattern (Treacy and Higgins, 2001)*

From Scherrer equation, the size of crystallite is calculated and it is found that the crystallite size of zeolite that was produced is varied from 3 to nearly 20 nm. Figure 3 shows the results of crystallite size of zeolite produced at a temperature of 80°C with varying Si concentration for method A and method B. As ascribed in Figure 3, it can be seen that the crystallite size is correlated with Si/Al ratio. The higher the Si/Al ratio, the smaller will be the crystallite size.

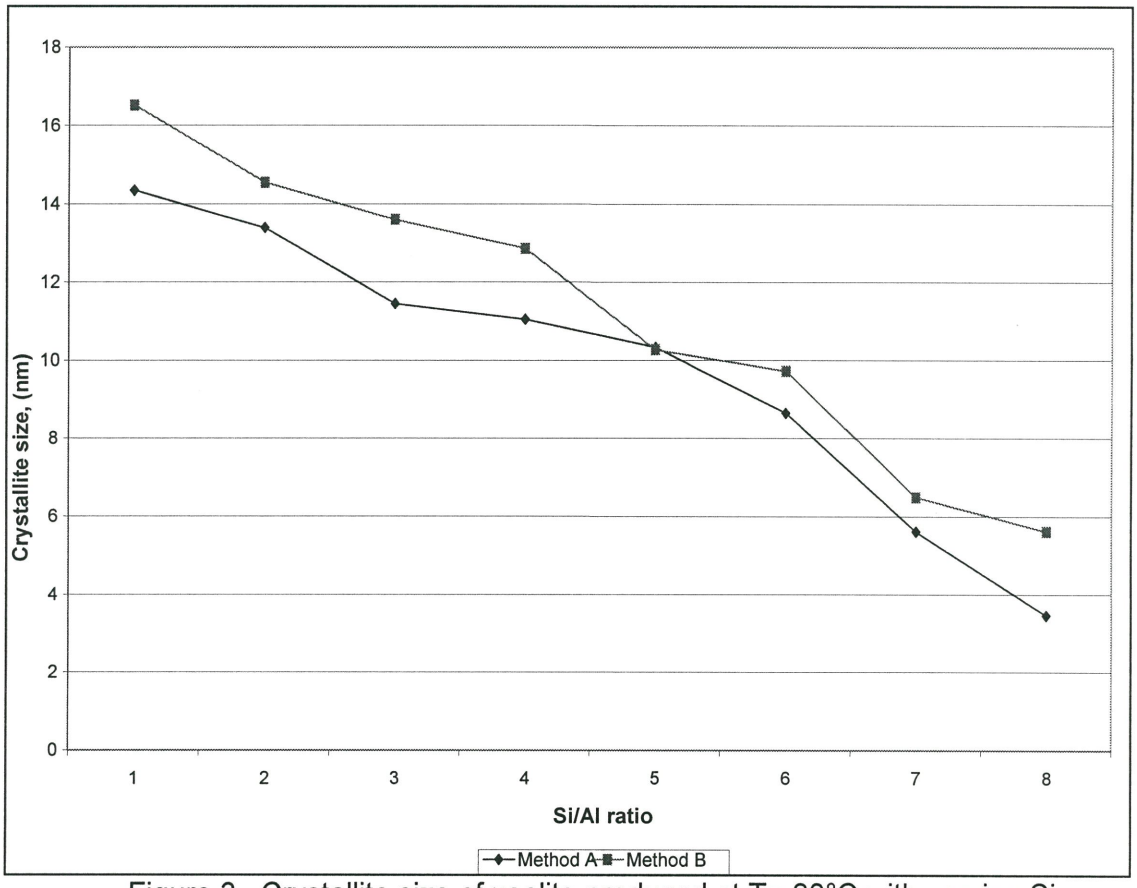


Figure 3. Crystallite size of zeolite produced at T= 80°C with varying Si concentration.

3.2 Scanning Electron Microscope

The morphology of the zeolite crystal has been examined by using a scanning microscope with magnification of 20K. Figure 4 shows the photomicrographs of zeolite synthesized at temperature 80°C for two weeks with Si/Al ratio of 1, 3, 5 and 7 respectively. The SEM photomicrograph shows that the zeolite particles have a lamellar surface structure with cubical edge.

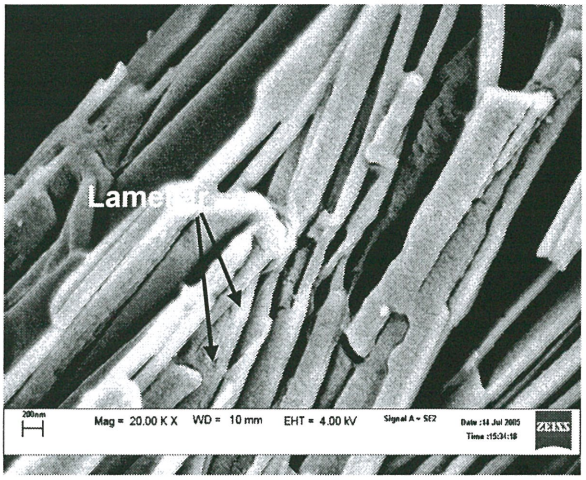


Figure 4(a)

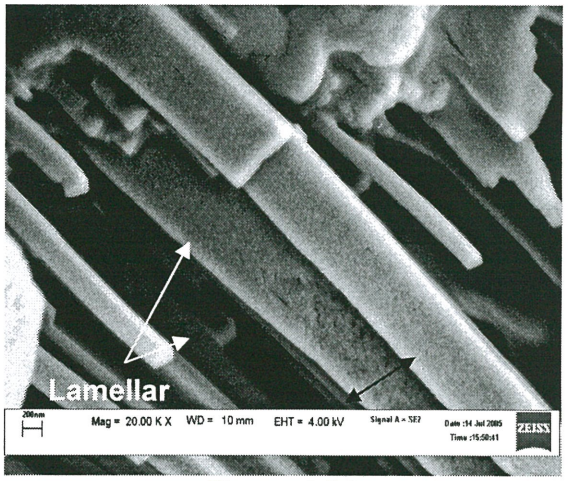


Figure 4 (b)

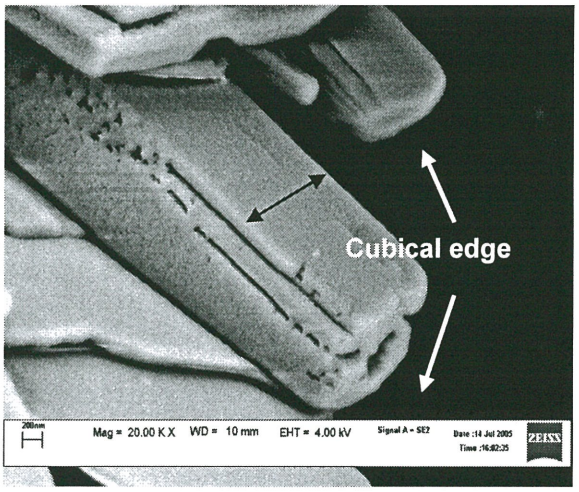


Figure 4(c)

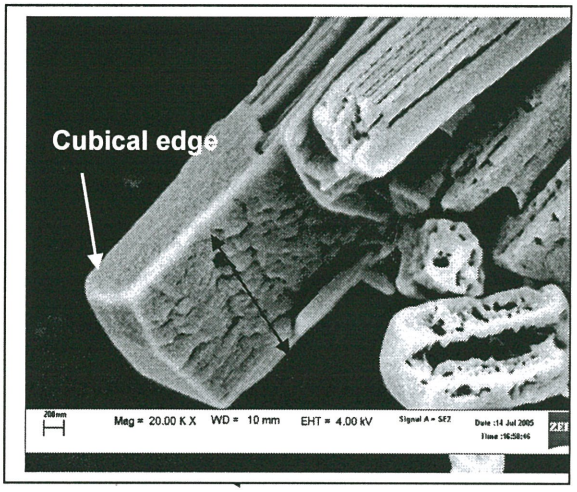


Figure 4(d)

Figure 4 (a to d). Scanning electron photomicrographs of zeolite product at 80°C with varying Si/Al ratio of (a) 1; (b) 3 ; (c) 5 and (d) 7, respectively. The arrowhead (⟷) indicates the size of the crystal in nanometer.

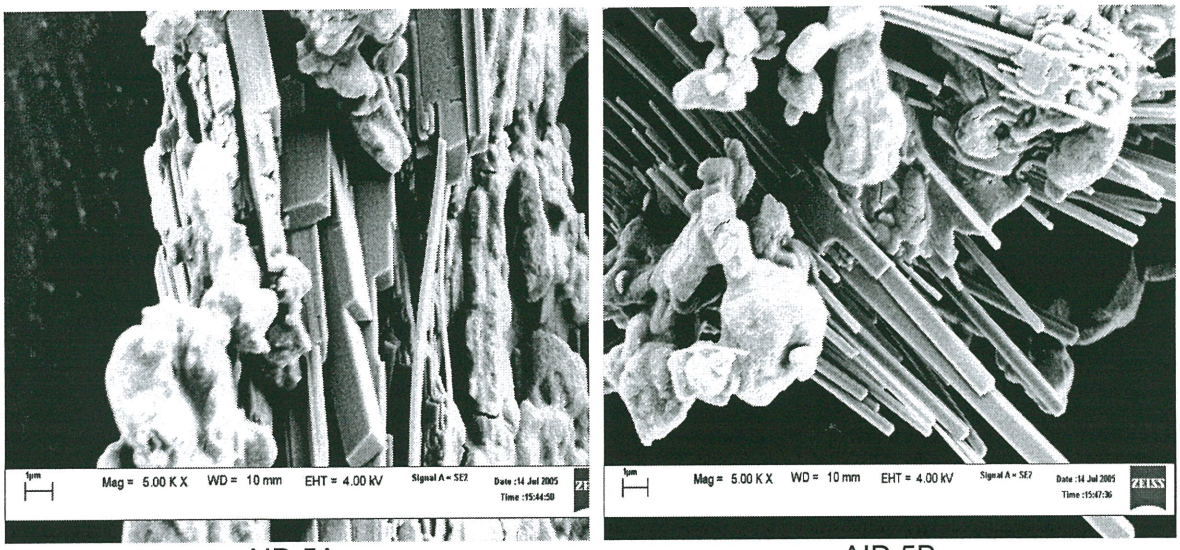
As seen from the SEM micrograph (Figure 4), it is postulated that there is a correlation between Si/Al ratio and the size of the crystal. In this case, the size of the crystal decreased with the decreased of Si/Al ratio. This behavior is expected because a loss of yield with the decreased of Si/Al ratio happened due to the limited access of Si species in the liquid phases of synthesis process. Table 3 shows the comparison of crystal size between those four samples. In comparison among those samples in Figure 4 (a) to Figure 4 (d), the crystal size of sample AID7A is 2 times higher compared to sample AID5A while sample AID3A is 1.3 times lower than sample B. However, sample AID1A shows an agglomerate cluster. Several studies were found to support the idea that the crystal size of zeolite was related to Si/Al ratio in the synthesis. According to Brar (2001), the particle size of zeolite is decreased when

silica/alumina ratio is decreased. This is also can be found in the studies by Armaroli et al (2005).

Table 3. The Relationship between Crystal Size and Si/Al Ratio

Sample Code	Si/Al ratio	Crystal size (nm)
AID1A	1	Agglomerate
AID3A	3	733
AID5A	5	933
AID7A	7	1533

The SEM micrograph displayed in Figure 5 indicated that the size of crystal did not change much in comparison for both Method A and Method B. The size of crystal for both methods was estimated to be 1 to 1.2 μm. As seen in the Figure, both methods had a similar morphology with nearly cubic and lamellar structure. Therefore, it can be concluded that the sequence of mixing order between aluminate and silicate solution in the process does not show considerable influence towards the morphology of the samples.



AID 5A AID 5B

Figure 5. Scanning electron photomicrographs of zeolite product at 80°C with Si/Al ratio of 5 (Method A and Method B)

3.3 Transmission Electron Microscope

From TEM photomicrograph this sample exhibits the presence of pores as indicate in Figures 6. For further analysis, the measurements of the pores are taken and the estimation of the pore sizes is shown in Table 4. These pores are estimated to be between 13nm to 23nm in width and 18nm to 43nm in length. As suggested by Depmeier (2002), these materials can be classified as mesoporous materials according to the IUPAC rules. However, due to the lamellar structure of the crystal, there could be some pores on the upper layer overlapping with the underneath pores.

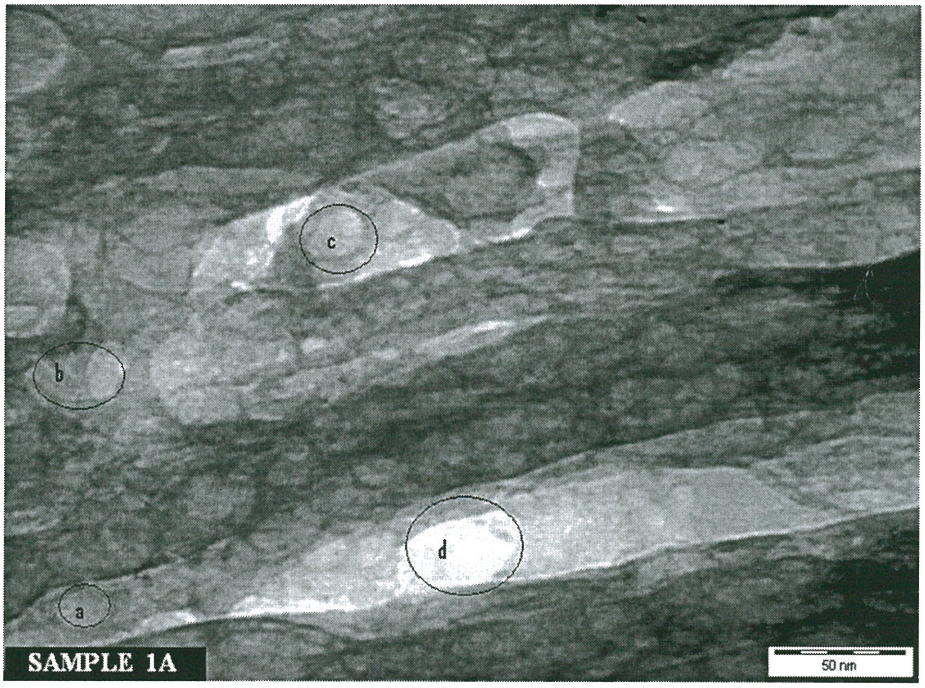


Figure 6. TEM photomicrograph of mesoporous zeolite obtained with Si/Al ratio of 1.

Table 4.. Pore size of zeolite produced with Si/Al ratio of 1

Pore Number	Width (nm)	Length (nm)
a	22.29	42.90
b	14.75	21.19
c	13.42	18.94
d	16.24	22.17

4.0 CONCLUSION

The synthesis of zeolite from aluminosilicate solution has been successfully carried out. In the present investigation, the morphology and crystallite size are affected significantly by the Si/Al ratio. However, the sequence mixing order (Method A and Method B of mixing) did not give much effect in the crystal size and morphology. TEM result showed that this material is mesoporous with pore sizes estimated between 13nm to 23 nm in width and 18nm to 43 nm in length. The type of material produced mostly have FAU structure with crystallite size ranging from 3nm-20nm.

5.0 REFERENCES

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