

Synthesis of Zeolite from Aluminium Etching By-Product: The Effect of Reaction Temperature on Crystallinity and Its CO₂ Adsorption Property

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Abstract: The synthesis of zeolite from the by-product of aluminium etching process was investigated. The starting by-product reactant had high aluminium content, 92.17% wt. as Al₂O₃. Si and Na compositions were adjusted by the addition of sodium metasilicate, in the hydrogel process. The reaction time was fixed at 1 h., while the stirring speed was controlled at 200 rpm. and the temperature varied in the range of 60-90°C. The mole ratio of the starting reactants were also fixed at 2 (SiO₂/Al₂O₃ = 2, Na₂O/ Al₂O₃ = 2). The product properties were found to depend on reaction temperature. The better zeolite product in the range of these experiments was found at 90°C, containing 75% crystallinity as referred to the commercial zeolite A. The percentage crystallinity of the synthesized zeolite was found to increase with increasing reaction temperature. Analysis of the X-Ray diffraction (XRF) and FT-IR spectra confirmed that the synthetic zeolite was of type A. The CO₂ (99.5% purity) absorption test was performed with the zeolite sample synthesized at 90°C, using N₂ (99.9% purity) as carrier at total flow rate of 15 cc min⁻¹, resulting in 0.00386 mole of CO₂ adsorption g⁻¹. The study showed the potential of developing the by-product of aluminium etching process into a higher value added product of zeolite A. Further economic study of the process was suggested.

Key words: Aluminium etching by product, hydrogel process, zeolite

INTRODUCTION

Zeolites are crystalline microporous solids containing regularity of cavities, with channels dimensions between 3-10 Å and the diverse framework chemical compositions allow tailoring^[1] of structure and properties, synonymously called molecular sieves. They are different from other adsorbent such as activated carbon, activated alumina and silica gel, by zeolites unique crystal structure while other materials do not have. Zeolites are crystalline hydrous aluminosilicate of alkali and alkali earth metals i.e., sodium, potassium, magnesium, calcium, strontium and barium, etc.,. The chemical formula of zeolite is M_{x/n}[(AlO₂)_x(SiO₂)_y] wH₂O^[2], where the charge-balancing non framework cation M (alkali or alkali earth cation) has valence n, y/x ratio is 1-5, w is amount of molecule water in the void. The typical zeolite properties that are determined during synthesis include: structure, silica-to-alumina ratio and pore size. The principal synthetic (aluminosilicate) zeolites in commercial use are Linde Type A (LTA) and Linde

Types X. The unique properties of low silica zeolites (zeolite NaA, zeolite NaX with SiO₂/Al₂O₃ ratios ~ 2 and ~ 3 respectively) such as ion exchange capacity, sorption and catalytic activity, make them ideal for various industrial applications^[3].

Zeolites are generally synthesized from sodium aluminosilicate gel prepared from various silica and alumina ratio^[4]. The factors that determine the type of synthetic zeolite are reaction time, temperature, pressure and synthesis conditions (like the order of mixing, gel aging and stirring). The by-product of aluminium etching process shall be used in this study for producing zeolite.

The etching process is the first step in aluminium profile surface treatment prior to anodizing and colourizing. It is etched by sodium hydroxide solution which produces aluminium hydroxide (Al(OH)₃) as by-product. The aluminium lost of the process is roughly found in the magnitude of 5% of the aluminium raw material. In some plants, the spent etching solution is disposed to the waste treatment facilities. In some other plants, which have the better waste management, the

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precipitate of aluminium hydroxide (Al (OH)₃) will be separated before the recycling of sodium hydroxide solution back to the etching tank. It produces a low wholesale price aluminium hydroxide (Al (OH)₃) normally further used for producing alum (Al₂(SO₄)₃). The quality of the aluminium hydroxide (Al (OH)₃) in this process is too purify to be wasted or used only in the alum (Al₂(SO₄)₃) production process. Thus, higher value added product such as zeolite should be considered as attempted in this study.

This study focuses on temperature as controlling factor for synthesis of zeolite A and also on its gas adsorbing capacity, using carbon dioxide as samples.

This study aims to achieve the following: (i) synthesis of zeolite A by hydrogel process using raw material from the by product of aluminium etching process, (ii) characterization of synthetic zeolite in comparison to the referenced commercial zeolite A by the following techniques; X-Ray Fluorescent spectroscopy (XRF), X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Nuclear Magnetic Resonance (NMR), Particle Size Distribution (PSD), Scanning Electron Microscopy (SEM) and surface area determination by N₂ gas adsorption-desorption, (iii) CO₂ adsorption capacity.

MATERIALS AND METHODS

Materials: Referenced commercial zeolite A was obtained from Thai Silicate Chemicals CO., LTD in the sodium ion form (Na-A zeolite, CODE: SMC-P). Synthetic zeolite was synthesized by hydrogel process, using sodium metasilicate (Ajax Finechem, lab grade), sodium hydroxide (Carlo Erba, lab grade) and by-product from aluminium etching process.

Synthesis of zeolites: Preparing of the reactant sodium silicate solution; weigh sodium metasilicate about 42 g, dissolve in water at temperature 50°C to make the mole ratio of reactants of 2 (SiO₂/Al₂O₃ = 2, Na₂O/Al₂O₃ = 2). Preparing of sodium aluminates solution, weigh by-product from aluminium etching process about 10.7525 g to make the mole ratio of reactants of 2 (SiO₂/Al₂O₃ = 2, Na₂O/Al₂O₃ = 2), dissolve into water 240 cm⁻³ and add 30 cm⁻³ of 50% NaOH at temperature 60°C for 30 min before filtrating. The hydrogel process for zeolite synthesis was carried out between sodium silicate solution and sodium aluminates solution in the range of temperature of 60-90°C in stirrer tank reactor, temperature controlled by water bath with stirring speed fixed at 200 rpm for 1 h. The experimental design was reported in Table 1, with the crystallized products

Table 1: List of experimental design, the mole ratio of reactants, temperature, and reaction time

Samples	SiO ₂ / Al ₂ O ₃	Na ₂ O/ Al ₂ O ₃	H ₂ O/ SiO ₂	temp. (°C)	time (h)
ZA1	2	2	85	90	1
ZA2	2	2	85	80	1
ZA3	2	2	85	70	1
ZA4	2	2	85	60	1

obtained by filtrating, washed with deionized water and dried in an air oven at 100°C for 16 h.

Characterization: X-ray fluorescent spectroscopy (Philips PW-2404, XRF) was used to determine the chemical compositions of the by-product from the aluminium etching process, referenced commercial zeolite A (ZA) and synthetic zeolites (ZA1-ZA4).

Infrared transmission spectra (FT-IR) of the synthetic zeolites were obtained by the KBr wafer technique. The spectra were recorded on a FTIR-Spectrometer (Perkin Elmer) in the region of 370-4000 cm⁻¹ (Middle rang IR).

X-Ray diffraction (JEOL JDX 3530, XRD) technique was used for identification and quantification of crystalline phases. The Cu radiation at 30 kV and 40 mA was used. The samples were scanned from 0-40° (2θ where θ is the angle of diffraction).

The surface areas of various samples were determined by gas adsorption and desorption (Micromeritics ASAP 2010). Approximately 0.01-0.03 g of the sample was placed in the sample cell, heated to 623 K and held at that temperature for 6 h., under a N₂/He flow. The sample was then cooled to room temperature and dipped into liquid nitrogen. After the adsorption of nitrogen reached equilibrium, the sample cell was then dipped into a water bath at room temperature. The amount of nitrogen desorped was measured by a gas chromatograph.

Nuclear Magnetic Resonance spectroscopy (NMR) was one of the most important techniques for the determination of chemical structures, determining the nature and chemical environment of the atoms. This technique was found to be very useful in understanding the structural and physicochemical properties of the zeolites. Attention had been focused mainly on ²⁷Al NMR and ²⁹Si NMR spectra which provided information on Si/Al ordering, such as crystallographic equivalent and non-equivalent Si and Al ions in various sites, framework silica to alumina ratio, coordination of Si and Al, spectral correlation with Si-O-T bond angles (T stands for tetrahedral) and Si-O bond lengths. NMR spectroscopy for ²⁹Si and ²⁷Al confirm tetrahedral coordinated atoms in the zeolite lattice and also indicate octahedral aluminum which may be present in the pores of the zeolites.

Particle Size Distribution (PSD) and mean particle size were determined with a laser scattering particle size distribution analyzer using water as the medium for dispersion of the zeolite samples. The solution was ultrasonicated for 2 min to break down the flocculates before the measurement.

Scanning Electron Microscopy (SEM) was the study of the surface topography of the samples. Electrically conductive materials may require a thin conductive coating to prevent electrical charging of the specimens. Sample size was limited to specimens less than about 10 cm in diameter. SEM pictures were obtained on a Quanta 200 Scanning electron microscope.

The CO₂ adsorption using small column test equipment was conducted on the adsorbents of the synthesized zeolite. Adsorbent (1g) of the synthesized zeolite was placed in a u-tube stainless steel column 1 cm diameter, using CO₂ (99.5%) as test gas with N₂ as carrier with the total flow rate 15 cm³ min⁻¹. A gas chromatograph (GC) was used to analyze the concentration of CO₂ in the inlet and outlet gases.

RESULTS AND DISCUSSION

Chemical characterization: The chemical composition of the aluminium etching by-product consisted of the following oxides expressed as percentage by weight, Al₂O₃, 92.17%, Na₂O, 6.03%, SiO₂, 0.47%. It carried a large amount of Al₂O₃ content which was useable as raw materials for synthesis of zeolites. Si and Na compositions could be adjusted by the addition of sodium metasilicate. The results of the mole ratio and the chemical composition in the referenced commercial Zeolite A (ZA) and synthetic zeolites (ZA1-ZA4) were reported in Table 2 and 3 respectively. These results showed that the mole ratio of Na₂O/Al₂O₃ and SiO₂/Al₂O₃ of ZA and synthetic zeolites (ZA1-ZA4) were affected by temperature in the range between 60 - 90°C. The above results indicated that the highest reaction temperature in the range (ZA1, 90°C) resulted in the successful synthesis of zeolite A. The compositions were compared with the reference in Table 2. The increasing reaction temperature ensured the better value of the mole ratio of Na₂O/Al₂O₃ (ZA = 1.15, ZA1 = 1.17) and SiO₂/Al₂O₃ (ZA = 2, ZA1 = 2.48), which is the indices of the zeolite A framework.

Infrared spectra of ZA and ZA1-ZA4 were reported in Fig. 1. The results indicated that the spectra of synthetic zeolite agreed well the spectra of reference zeolite A. The comparison of IR spectra of ZA, ZA1 showed the better matching with fingerprints of wave number values. The first class of spectra consists of the

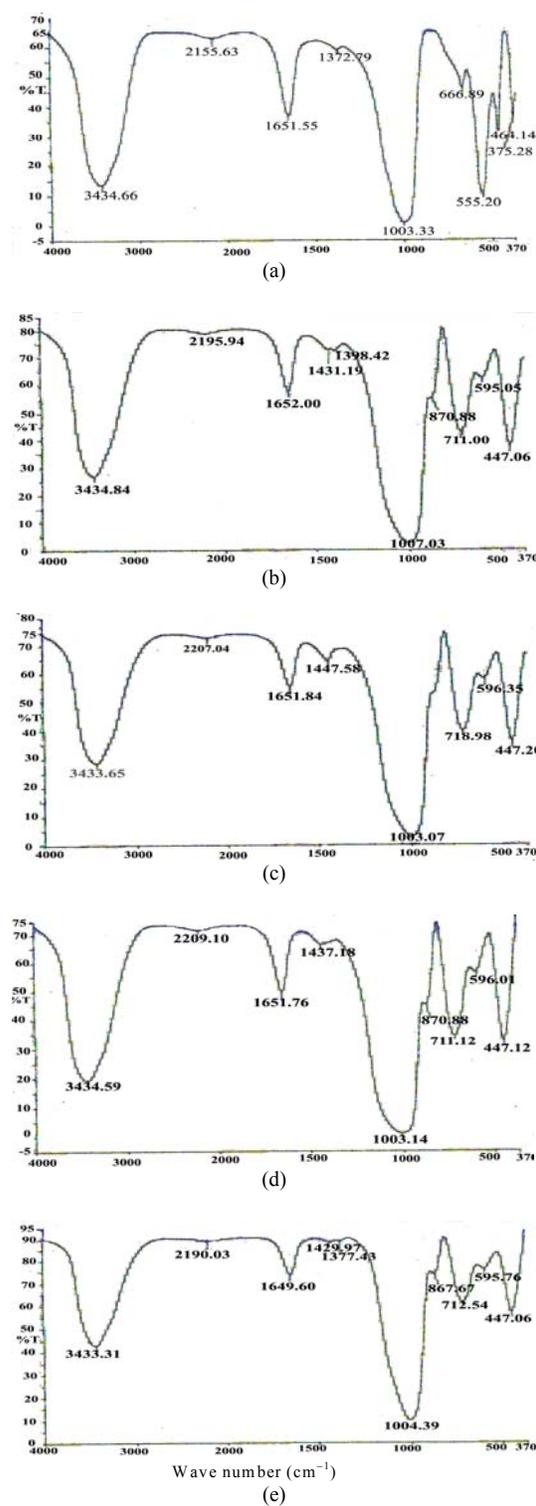


Fig. 1: FT- IR spectra of (a): Reference zeolite A, ZA and synthetic zeolite; (b): ZA1 (90°C); (c): ZA2 (80°C); (d): ZA3 (70°C); (e): ZA4 (60°C)

Table 2: The mole ratio of reference zeolite A (ZA) and synthetic zeolites (ZA1-ZA4)

Samples	Temp.(°C)	Mole ratio of reactant		Mole of products				
		SiO ₂ /Al ₂ O ₃	Na ₂ O/ Al ₂ O ₃	SiO ₂	Al ₂ O ₃	Na ₂ O	Na ₂ O/Al ₂ O ₃	SiO ₂ /Al ₂ O ₃
ZA	-	-	-	0.6522	0.3511	0.4040	1.15	2.0
ZA1	90	2	2	0.7650	0.3082	0.3623	1.17	2.48
ZA2	80	2	2	0.7927	0.2975	0.3515	1.18	2.66
ZA3	70	2	2	0.7742	0.2936	0.3776	1.28	2.63
ZA4	60	2	2	0.7812	0.2931	0.3690	1.26	2.66

Table 3: The chemical composition of reference Zeolite A (ZA) and synthetic Zeolites (ZA1-ZA4)

Element	The chemical composition of the samples (% wt)				
	ZA	ZA1	ZA2	ZA3	ZA4
Na	24.64	23.44	22.78	24.42	23.88
Al	33.91	29.63	28.56	28.29	28.18
Si	41.45	46.54	48.08	46.91	47.26
Oxide	ZA	ZA1	ZA2	ZA3	ZA4
Na ₂ O	25.02	22.46	21.79	23.41	22.88
Al ₂ O ₃	35.82	31.44	30.35	29.95	29.90
SiO ₂	39.13	45.90	47.56	46.45	46.87

strongest vibration found in all zeolites which were assigned to the internal tetrahedron vibrations and were found at 1003/1007 cm⁻¹ (ZA/ZA1). The next strongest band was in the 464/447 cm⁻¹ region. Stretching modes involving mainly the tetrahedral atoms were assigned in the region of 666/712 cm⁻¹ for ZA/ZA1. These results indicated that ZA1 shift to a higher frequency (wave number) more than ZA, since the stretching modes were sensitive to the Si-Al composition of the framework and shift to a higher frequency with increasing number of tetrahedral silica atom.

These results were explained by the theory of Breck^[4]. The second group of frequencies which were sensitive to the linkages between tetrahedron and the topology and mode of arrangement of the secondary units of structure in the zeolite occurred in 555/595 cm⁻¹ for ZA/ZA1. A band in the 500-650 regions in related to the presence of the double rings in the framework structures and was observed in all of the zeolite A structures.

X-Ray Diffraction (XRD) patterns of ZA and ZA1-ZA4 were shown in Fig. 2. From the XRD pattern, ZA1-ZA3 and ZA showed 9 strong main peaks at 2θ = 7.1, 10.1, 12.4, 16.0, 21.6, 23.9, 27.0, 29.9 and 34.1°. It could be seen that, no XRD peaks could be detected for ZA4 (Fig. 2e), which was the result of the complete amorphous stage. When the reaction temperature was increased in the range from 70°C-80°C, XRD patterns ascribed to zeolite A of the resulting products could be observed (Fig. 2c-d, ZA3-ZA2), but they were weaker than ZA, indicating that the crystallization of the samples were not completed. When the reaction temperature was increased to 90°C

Table 4: The XRD intensity and percentage crystallinity of the samples Characteristic

2θ	Intensity for the samples				
	ZA	ZA1	ZA2	ZA3	ZA4
7.1	4164	2757	2252	1952	-
10.1	3143	2173	1753	1566	-
12.4	2108	1464	1247	1082	-
16.0	1460	1095	911	749	-
21.6	2208	1685	1484	1174	-
23.9	3391	2661	2337	1875	-
27.1	2871	2355	2157	1634	-
29.9	3696	3023	2789	2049	-
34.1	2195	1924	1695	1257	-
Total	25234	19137	16625	13338	-
% C*	100	75.83	65.87	52.85	-

Note: * : % crystallinity

(ZA1), the peaks became stronger (Fig. 2b), showed strong XRD patterns matched closer to ZA (Fig. 2a).

The percentage crystallinity of ZA and ZA1-ZA4 was presented in Table 4, taking ZA as reference of 100% crystallinity. It could be seen that, the percentage of crystallinity increased with increasing reaction temperature (ZA1>ZA2>ZA3). These results reaffirmed the important role of reaction temperature in the successful synthesis of zeolite A.

Analysis of surface area was performed by standard BET technique for analysis of gas adsorption-desorption using nitrogen. Adsorption-desorption isotherms and BET Specific Surface Area (SSA) were determined using 1 g of the samples.

Figure 3 shows a typical nitrogen adsorption/desorption isotherm for ZA, ZA1 and ZA3 observed with hysteresis which can be classified as type III^[5]. But, the results of all samples showed very high value of the BET C (more than 300, shown in Table 5) which is outside the accuracy range of BET method and suggests that other model should also be examined.

The results of Surface Area (SA) are reported in Table 5, several methods have been introduced for normalization. It can be seen that, the SA of ZA1 for all methods were higher than ZA3 and the SA of ZA3 is close to ZA than those of ZA1. These results indicated that the SA of synthetic zeolites increases progressively with increases reaction temperature (SA of ZA1>ZA3) this could be the results of more perfect structure of ZA1 as compared to ZA3 (refer to XRD pattern).

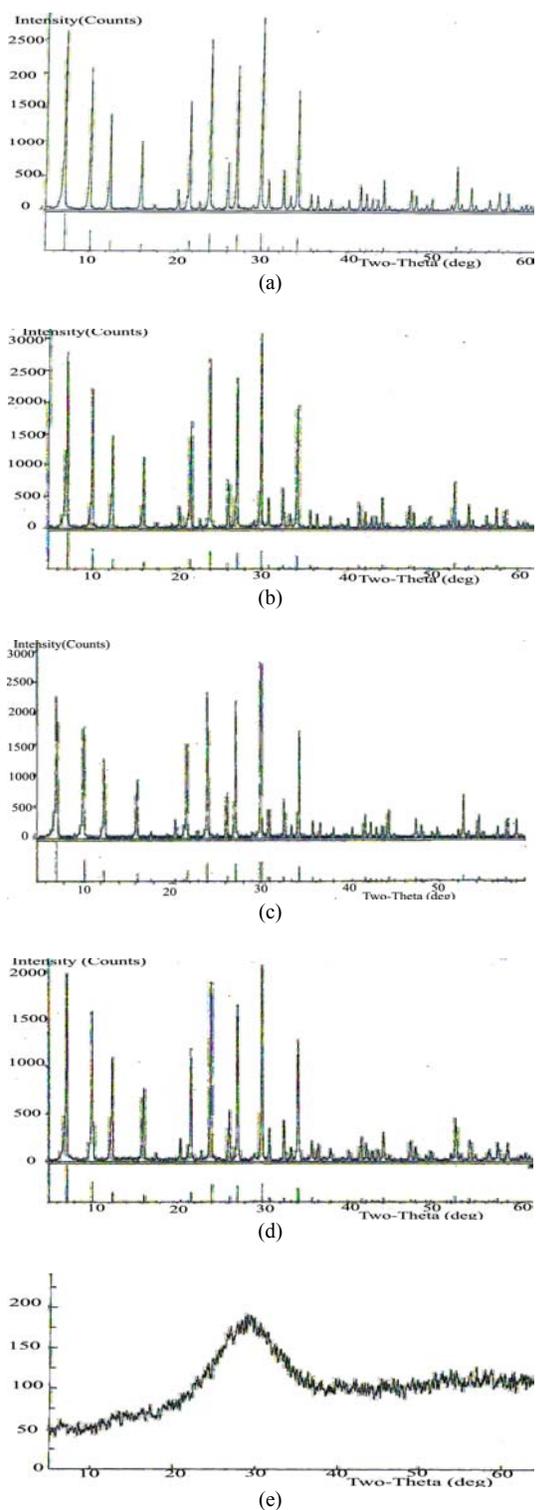


Fig. 2: The XRD pattern for (a): Reference zeolite A, ZA and synthetic zeolite; (b): ZA1 (90°C); (c): ZA2 (80°C); (d): ZA3 (70°C); (e): ZA4 (60°C)

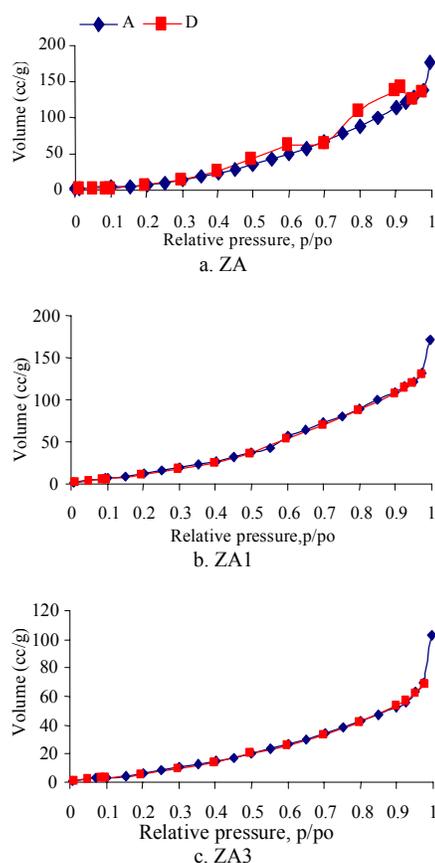


Fig. 3: Isotherm curves for (a) reference zeolite A, ZA and synthetic zeolite; (b) ZA1 (90 °C), (c) ZA3 (70°C)

However, the BJH and DH method measured cumulative adsorption surface area; combination of mesopore volume and microporosity. While the results from BET and the DR methods were closely agreed these could be due to the fact that both were the analysis for microporosity. The approved higher value of ZA1 surface area in all method could be the result of the external surface area of the crystal which would be further discussed.

NMR spectrum determined the nature and chemical environment of the atoms. Figure 4 showed the ²⁷Al NMR spectra of ZA1-ZA3 and ZA, in which one signal was observed. There was one sharp line 64.9-65.3 ppm. These spectra occurred on Al(2Si), confirmed with the data from Gillian^[6]. These results were closely resembled spectral of zeolite A. Which consisted of Al only in AlO₄ form in the tetra hedral structure thus only one narrow NMR line was observed.

Figure 5 shows the ²⁹Si NMR spectra line of ZA1-ZA3 and ZA. In the all samples, there was a strong

Table 5: Specific surface area of the samples

Samples	The BET C Value ¹	BET surface area (m ² g ⁻¹)	BJH method ² (m ² g ⁻¹)	D.H. method ³ (m ² g ⁻¹)	DR method micro pore ⁴ (m ² g ⁻¹)
ZA	1089	8.326E+00	31.25E+00	39.62E+00	8.291E+00
ZA1	723.6	11.46 E+00	52.57 E+00	58.14 E+00	12.46E+00
ZA3	765.5	6.169 E+00	29.62 E+00	32.21E+00	7.149E+00

Note: ¹: dominate of accuracy BET surface area is suggested between 50-300^[5] due to some approximate in the solution the BET method, ²: the model for mesopore volume and microporosity, ³: is quite similar to BJH method, ⁴: is developing mainly for micropore surface area

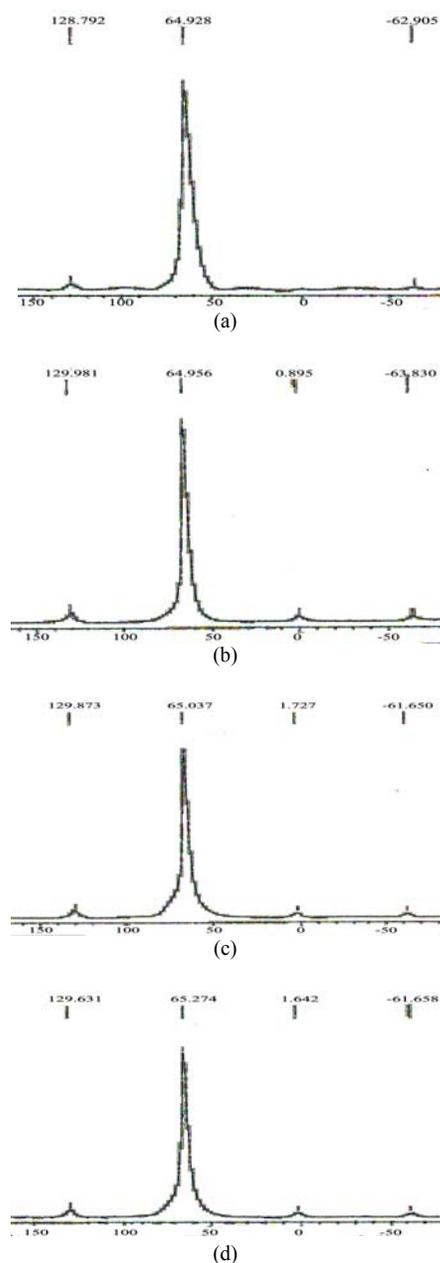


Fig. 4: The ²⁷Al NMR spectra of (a): Reference zeolite A, ZA and synthetic zeolite; (b): ZA1 (90°C); (c): ZA2 (80°C); (d): ZA3 (70°C)

the results in the mean particle size of synthetic zeolites (ZA1-ZA3 sample), it could be seen that the mean particle size of ZA1 was, respectively, bigger than ZA2 and ZA3. This confirmed that when higher temperature was applied, the rate of crystal growth was increased, which results in the formation of bigger crystals. From the above results and by comparing the results of the mean particle sizes in reference Zeolite A (ZA) and synthetic zeolites showed that ZA1 and ZA2 had bigger crystal size than ZA, while ZA3 was smaller than ZA. This result with the combination of Table 5, it could be concluded that the higher surface area as reported in Table 5 was the contribution from the external surface of the crystal rather than the pore internal surface area.

This result is in agreement with increase in the percentages of crystallinity the significant with increasing reaction temperature. The relationships between the percent crystallinity and the mean particle size of synthetic zeolites, showed that the percent crystallinity increased with increasing particle sizes and the maximum percent crystallinity of 75% was observed for the mean particle size of 1.85 μm.

The SEM pictures of the samples were shown in Fig. 7 the morphology of synthetic zeolites was mostly cubic shape, similar to the morphology of the referenced Zeolite A (ZA). The micrograph for ZA3 (Fig.7d) was somewhat different, the crystal faces were still quite rounded in cubic shape with scattered minor particles. This suggested the presence of the short chain structure of molecules which were the amorphous parts of the zeolite A, at lower reaction temperature, agreed with the PSD and XRD results.

The results of gas adsorption studies conducted utilizing a gas of 99.5% CO₂ with 99.9% N₂ carrier on samples were shown in Fig. 8 and Table 6. Carbon dioxide (CO₂) adsorption for ZA1-ZA3 showed that the amount of CO₂ adsorbed increased progressively with reaction temperature of synthesis zeolite. The total amount of CO₂ adsorbed followed the order of ZA1>ZA2>ZA3.

The capacity of CO₂ adsorbed by ZA was 0.1183cc g⁻¹. While that of ZA1 was 0.0943 cc g⁻¹, which was better agreed with ZA as compared with other sample. From these results, it showed that the synthetic zeolite

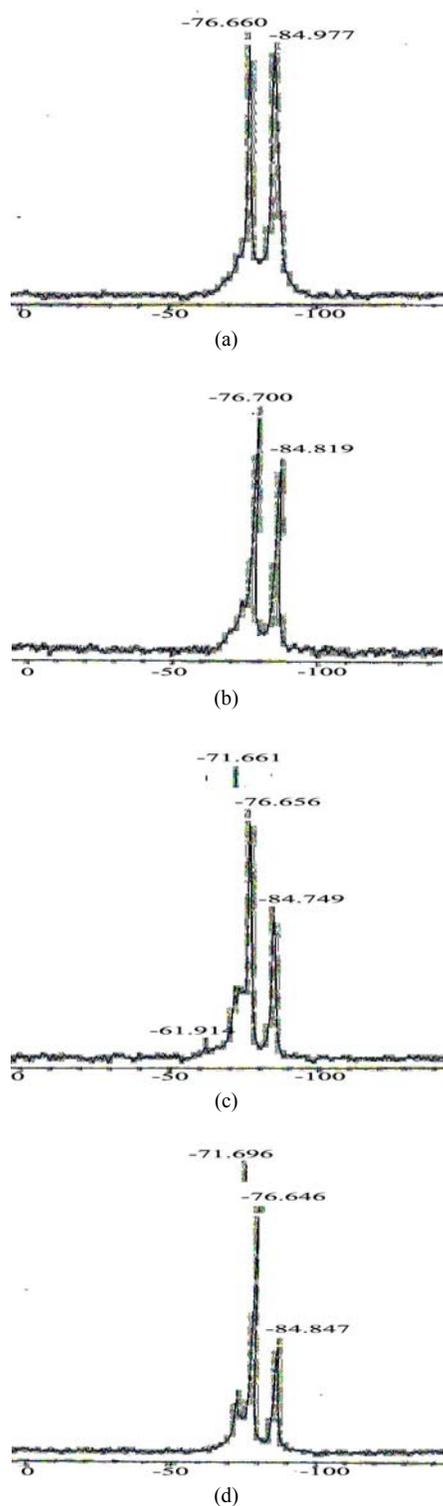


Fig. 5: The ^{29}Si NMR spectra line of (a): Reference zeolite A, ZA and synthetic zeolite; (b): ZA1 (90°C); (c): ZA2 (80°C); (d) ZA3 (70°C)

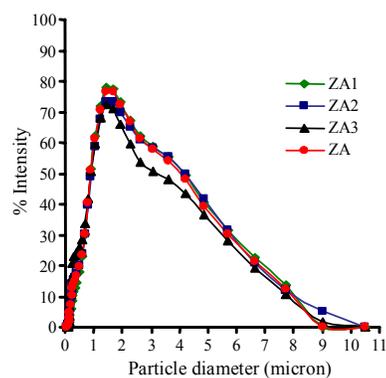


Fig. 6: Particle size distribution of synthetic eolites (ZA1-ZA3) and reference zeolite A (ZA)

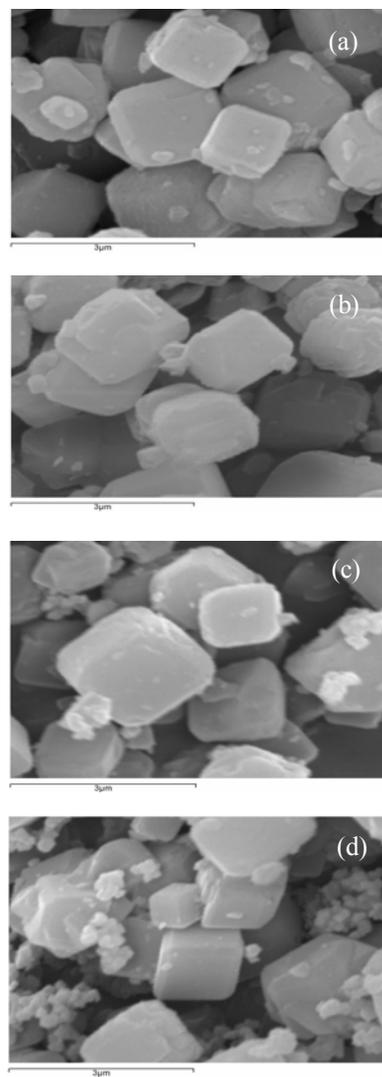


Fig. 7: The SEM pictures of (a) ZA, (b) ZA1, (c) ZA2 and (d) ZA3

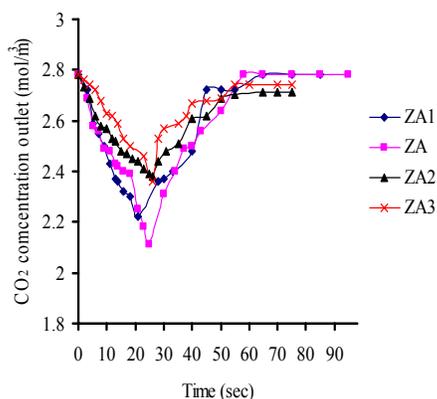


Fig. 8: The CO₂ concentration-time profiles of the adsorption

Table 6: The CO₂ adsorbed capacity and the total amount of CO₂ adsorbed

Samples	CO ₂ adsorbed capacity (mol g ⁻¹)	The total amount of CO ₂ adsorbed (cc/g) at NTP
ZA	4.84 E-03	0.1183
ZA1	3.86E-03	0.0943
ZA2	3.32 E-03	0.0811
ZA3	1.78 E-03	0.0436

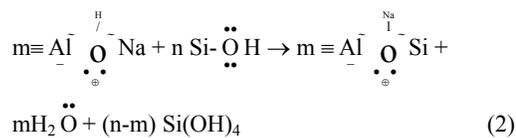
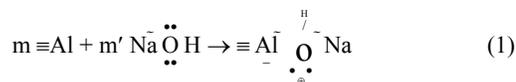
could adsorb the CO₂, but the adsorption capacity of synthetic zeolite decreased with decreasing synthesis temperature these result confirmed by surface area analysis, showing the increased surface area with increasing reaction temperature.

The chemical composition of by-product of aluminium etching process showed that it could be utilized as a very proper raw material for synthesis zeolites. There was a large amount of Al₂O₃ content, which is one of the main compositions of synthetic zeolites; namely, Al and Si (chemical formular is Na_{x/n}[(AlO₂)_x(SiO₂)_y]wH₂O). While, Si and Na composition can be adjusted by sodium metasilicate.

The chemical composition analysis performed for reference zeolite A and synthetic zeolites indicated that higher synthesis reaction temperature resulted in the more successful synthesis of zeolite A (at 90°C). It was reasoned that at higher temperatures the reaction yielded more condensed phase species and that at lower temperature (such as 60-80°C); there were the short chain molecule of ≡Si-O⁻ which contributes to parts of the amorphous zeolite.

This can be explained by the following process. The first step is the dissolution of the solid until a concentration of specie Al(OH)₃ and Si(OH)₄ are reached. At this point the system is constituted of these species plus the initial components of the solution, NaOH and the formation process of three dimensional silicoaluminated begins. The second step involves the

interaction of the species formed in first step, according to Lewis mechanism in Eq. 1 and Brønsted mechanism in Eq. 2^[8]:



where m, m' and n are stiocheometric coefficients of the reaction. The new formed specie of m ≡ Al ^{Na} O Si gives

rise to the growth of the crystal specie through the further condensation mechanism, which requires both proper ratio of Si and high enough temperature to enhance this latter propagation of the polymeric skeleton of the zeolite^[8]. It can be seen, the XRF and FTIR results demonstrated that chemical composition and wave number of ZA1 was closed to ZA and that the percentage of crystallinity were in the order of ZA1>ZA2>ZA3.

In term of NMR results, there was line on Si(OAl) in the structure of ZA2 and ZA3 (ZA3 stronger than ZA2) which is a part of amorphous zeolite A (it is a part of -O-Si ≡ in Eq. 2), except ZA1 which was different. Furthermore, from surface area results, all methods showed that ZA1 had higher surface area than the other samples. The mean Particle Size Distribution (PSD) results showed that lower reaction temperature (lower crystal growth rate) resulted in smaller zeolite crystals. A similar result was reported by Zhdanov^[9] for the synthesis of Na-A zeolite. Typically, the particle size of zeolites depends on the relative rates of the two competing phenomena occurring during synthesis, namely, nucleation and crystal growth. Both rates decrease with decreasing temperature. However, the impact of decreasing temperature is more pronounced on the crystal growth rate than on the nucleation rate, resulting in smaller particle size at lower temperature. Finally, ZA1 had a high CO₂ adsorbed capacity than ZA2-ZA3; observed results confirmed all the previous.

In addition to the sieving phenomena, the adsorption of a gas on a zeolite depends on polarizability and polarity of a guest adsorbate molecule. In general, a large or more polarizability gas molecule will be more strongly and selectively adsorbed on zeolites having smaller pores. In comparison between CO₂ and N₂, the larger polarizability of CO₂ creates a stronger interaction energy with the zeolites (polaizability: CO₂ = 26.5 × 10⁻²⁵ cm⁻³, N₂ = 17.60 ×

10^{-25} cm^{-3} ; diameter: $\text{CO}_2 = 3.3\text{-}3.94 \text{ \AA}$, $\text{N}_2 = 3.64\text{-}3.8 \text{ \AA}$)^[10]. Then, CO_2 was selectively adsorbed on synthetic zeolites.

CONCLUSION

Based on the present study, it can be concluded that the by-product of aluminium etching process can be used to produce zeolites by the hydrogel process. It carries a large amount of Al_2O_3 content which is usable as raw materials for zeolites synthesis and it was found that the insufficient content of Si and Na in the By-product needed to be compensated by the addition of sodium metasilicate. In the process, the reaction was conducted between the sodium silicate solution and sodium aluminate solution with the mole ratio of reactants about 2 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 2$), in the range of temperature $60^\circ\text{C}\text{-}90^\circ\text{C}$ for 1 h. The synthetic zeolites were characterized using various techniques included X-Ray Fluorescent spectroscopy (XRF), X-Ray Diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy, Nuclear Magnetic Resonance (NMR), surface area by N_2 gas adsorption-desorption, Particle Size Distribution (PSD), Scanning Electron Microscopy (SEM). In addition, the adsorption using CO_2 was also tested.

Zeolites of different values of surface area, silica/alumina ratio and crystallinity were obtained by changing the reaction temperatures. The crystallinity of the prepared zeolite was found to change with reaction temperature and a better value was obtained at 90°C for 1 h. The best quality zeolite within the range of this experiment was obtained at the following conditions: $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ reaction ratios of 2, reaction temperature, 90°C for 1 h., by hydrogel process. The chemical composition confirmed that the main product was zeolite A. The synthetic zeolite had the mole ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.17 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 2.48 while the reference zeolite A had the mole ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 1.15 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 2.00. The surface area of synthetic zeolite also increased with temperature of reaction. The bigger mean particle size was observed as $1.85 \mu\text{m}$ at 90°C and was mostly of cubic shape. These samples had 75% crystallinity as referred to the reference ZA (taken as 100%). While the zeolite synthesized at lower reaction temperature (70°C), showed lower mean particle size of $1.61 \mu\text{m}$ and the micrograph was somewhat different. As the crystal faces were still quite rounded in cubic shape, the existences of scattered amorphous parts were clearly observed.

Therefore, it could be concluded that zeolite synthesis of by product from alkaline etching of the aluminum industry had the major analysis agree well with those of reference commercial zeolite A.

Adsorption test with CO_2 , yielded the best result with ZA1 which was the zeolite synthesis at 90°C , with the capacity of $0.00386 \text{ mole g}^{-1}$ (0.0943 cc g^{-1} at NTP) It is recommended that selection sieving of other gases, such as SO_2 and O_2 be further study, followed by the economic study of the process for better decision in adopting this process as part of the aluminium profiles plants.

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