One Shot of the Hydrothermal Route for the Synthesis of Zeolite LTA Using Kaolin

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Abstract
The zeolite LTA (Z-LTA) was successfully produced from the synthesis of kaolin and well-crystallized using a hydrothermal method. The main purpose of the synthesis Z-LTA from kaolin was to illustrate the transformation Z-LTA with different molarity of alkaline solution and crystallization time. The kaolin was heated in the furnace for 4 h at 500, 600, 700, and 800 °C, resulting in a metakaolinization process that transformed it into an amorphous state. The Z-LTA mixture was obtained by dissolving metakaolin in a sodium hydroxide (NaOH) solution without adding other silica or alumina sources. Before going through the hydrothermal synthesis process, the solution mixture was aged for 24 h. The crystal morphology and degree crystallinity (%) of Z-LTA were evaluated using the various molarity (M) of sodium hydroxide (NaOH) and crystallization time (h). The degree crystallinity of the Z-LTA increases from 62.83 to 86.8% when the molarity of NaOH is increased from 0.5 to 1 M but does not increase when the molarity of NaOH is increased to 1 M and 2 M (80.77% and 67.78%), respectively. The degree crystallinity (%) Z-LTA based on molarity proceeded with the various crystallization time (h) factors. 1 M NaOH with 9 h give highest degree crystallinity (88.45%) compared to other time, 12 h (86.16%), 16 h (87.11%), 24 h (86.80%) and 30 h (86.59%) respectively. The crystal morphology structure with Na, Al, O, and Si was seen in SEM images of the Z-LTA at a 1 M NaOH, 9 h crystallization time (Z-LTA, 1 M 9 h). The particle size of (Z-LTA, 1 M 9 h) is smaller, 0.329 µm, than kaolin, 0.497 µm. Under low alkali conditions and crystallization time, the hydrothermal process successfully generates high crystallinity from natural kaolin. As a result, low-grade Malaysian kaolin can be successfully transformed into Z-LTA using the traditional hydrothermal process when the composition parameters are carefully controlled. The hydrothermal synthesis from natural kaolin was the most cost-effective and efficient method, with comparable product quality to zeolite synthesized with conventional raw materials.

Keywords Zeolite LTA · Hydrothermal · Kaolin · Crystallinity

1 Introduction
Zeolites are aluminosilicates with a three-dimensional (3D) network that forms an open framework structure with molecular-sized pores and cavities [1]. Z-LTA is a low silica zeolite with Si/Al molar ratio = one that has a high ion-exchange capacity [2, 3] and adsorption properties [4]. Since Z-LTA is used for a wide range of applications, including petroleum refining [5, 6], water treatment [7, 8], gas adsorption [9], agriculture [10], animal feed additives [11], and ecofriendly [12, 13], they are now prevalent in our modern lifestyle. There are approximately 234 different framework types of zeolites, which can be found naturally [14, 15] or synthesized [16]. Most zeolites are aluminosilicate materials; however, zeolites made up of different framework elements, such as titanosilicates, are now common [17]. The market for synthetic zeolite materials is now worth $5.2 billion per year, and it is expected to grow to $5.9 billion by 2023 [18].

The most popularly used zeolites are Z-LTA, X, Y, USY, and ZSM-5. In terms of volume and value, Z-LTA is one of the most widely used zeolites. Commercially, Z-LTA is primarily used as a laundry detergent additive [19]. Zeolite Linde Type A (Z-LTA or Zeolite A) was the first synthetic zeolite to be commercialized in 1956, according to Milton and colleagues [20]. It is also known as Zeolite 3A, 4A,
or 5 Å, depending on the exchangeable cation in the zeolite structure and whether the material is potassium, sodium, or calcium ion-exchanged [21]. Na$_{12}$(AlO$_2$)$_{12}$(SiO$_2$)$_{12}$·27H$_2$O is the general formula for sodium exchanged Z-LTA, where the framework silicon to aluminium (Si/Al) mole ratio is one and sodium ions are the exchangeable extra-framework cations. In terms of structure, the lattice of zeolite LTA (Z-LTA) has two cage types: -cage (sodalite cage) and -cage [22]. In the centre of eight-membered rings, eight sodalite cages are linked by double four-membered rings to form a homonuclear -super cage. The Si/Al ratio of about 1 in the most common form of Z-LTA indicates that it has a high cation exchange capacity. Thermal stability [23], high selectivity, non-toxicity, and superior mechanical strength [24, 25] are some of the other commercial advantages. Z-LTA is used in industry for ethanol dehydration in addition to being used in laundry detergents [26].

When Z-LTA is exchanged with silver ions, it can be used as an antibacterial material [27, 28]. While medical devices, such as umbilical catheters, are impregnated with silver-Z-LTA, the incidence of catheter-related bloodstream infections is dramatically reduced [29]. This growing trend is highlighted by the following factors: (1) novel synthesis methods; (2) expansion of applications beyond detergents and ethanol dehydration; and (3) conversion of aluminium and silicon-containing waste materials to Z-LTA. Regrettably, it appears that the use of novel Z-LTA technologies in the industry has not progressed. In terms of manufacturing cost and market development, one justification is a compelling business case for the commercialization of next-generation Z-LTA materials. Another reason could be that no comprehensive analysis of Z-LTA synthesis and applications has been published which integrates data in a way that demonstrates cutting-edge achievements in this field. Furthermore, no extensive analysis has been conducted to determine the best path forward for turning exciting Z-LTA discoveries into commercially viable applications.

Clay minerals are prevalent in kaolin. The most important is kaolinite, which is made up of clay minerals as well as non-clay minerals. Kaolinite (Al$_2$O$_3$·2SiO$_2$·2H$_2$O) with Si/Al molar ratio=1, which is similar to zeolite 4Å, is considered the most suitable source to be used as a starting material for its production among all raw materials in the universe [30–34]. The framework structure of kaolinite is made up of a 1:1 ratio of one layer of alumina octahedron sheet and one layer of silica tetrahedron sheet. The crystalline phase of kaolinite should be metakaolinized into an amorphous and reactive phase in order to properly exploit kaolin as a feedstock for zeolite synthesis. Kaolinite minerals are highly valued as low-cost raw materials because they are abundant around the world. But even so, established procedures using kaolin as a raw material after thermal activation and synthesis steps are currently being researched due to differences in the conditions required to create metakaolin. In comparison to other countries, China was the first to develop and use kaolin resources on the planet, and it is also the world's largest source of kaolin [35]. China has six large kaolin mines, and there are also high-quality kaolin resources in the US, the UK, Brazil, India, and other countries [36]. The composition and structure of kaolin, on the other hand, vary depending on geological and weather conditions, which may affect its chemical reactivity [37, 38]. The higher the kaolinite content in kaolin, the closer the chemical composition is to the theoretical one.

Metakaolinization is a process of requiring thermal activation at high temperatures, typically in the 600–1100 °C range [39, 40]. The hydrothermal synthesis stage begins with the involvement of metakaolin mix with an aqueous alkali medium at suitable reaction temperatures. Kaolinite minerals are highly valued as low-cost raw materials because they are abundant around the world. However, established procedures using kaolin as a raw material after thermal activation and synthesis steps are currently being researched due to disagreements over the conditions required to create metakaolin. Depending on the origin of the raw material, these conflicts may be related to the activation temperature [41, 42], impurity, particularly iron content [43, 44], Si/Al molar ratio [45–47], quartz content [39, 48], and initial crystallinity of raw material [49].

The hydrothermal synthesis method was the first and most widely used method for synthesizing zeolite, and it has continued to play a significant role. It’s a common ingredient in the production of zeolites from kaolin. Based on the reaction temperature, the hydrothermal synthesis method is divided into subcritical and supercritical reactions. The hydrothermal synthesis method has several advantages, including high reactivity of the reactants, low energy consumption, and low air pollution [50]. Researchers have used this approach to conduct extensive research on the synthesis of zeolite using kaolin as a result of these benefits. The whiteness and ion exchange capacity of zeolite A have been greatly improved when compared to the old method of synthesis. This technique also has the advantage of being able to remove or transform impurities in the kaolin into chemical elements of the desired product. The writers use alkaline kaolin initiation to reduce pollution caused by traditional calcination processes, as well as to eliminate impurities in kaolin or convert them into components of the target product, allowing for more efficient use of natural resources.

## 2 Materials and Methods

### 2.1 Reagents and Materials

Delta Kaolin Sdn. Bhd, based in Selangor, Malaysia, provided the raw kaolin used in this study. The beneficiation
of raw kaolin was insignificant progress. In one week, a 15 l container was filled with 10 l of distilled water and 3 kg of crushed kaolin. The soaking kaolin was stirred on a regular basis. The beneficiation had a positive effect in that the kaolin settled after stirring, the floating dirt was decanted with the supernatant, and all solid particles were removed by handpicking during decantation. This was ensured that this process would continue until there was no solid layer left at the bottom of the container. The fine particles suspended in water were dried for one day at room temperature before sieving with a 63-μm mesh. The sieve particle was then dried for 12 h in an oven. Bg Oil Chem Sdn Bhd provided the sodium hydroxide used in the experiments (Malaysia). These are analytical-grade reagents. In a laboratory, distilled water was created. In the laboratory, Z-LTA with various molarities and crystallization times was prepared from kaolin.

### Table 1  Chemical composition (wt%) of the kaolin and metakaolin by XRF

| Material     | Chemical compositions | SiO₂  | Al₂O₃  | TiO₂  | Fe₂O₃ | CaO  | MgO  |
|--------------|-----------------------|------|-------|-------|-------|------|------|
| Kaolin       |                       | 48.72| 37.63 | 1.35  | 0.59  | 0.34 | 0.25 |
| Metakaolin   |                       | 50.73| 36.34 | 1.21  | 0.42  | -    | -    |

2.2 Zeolite Preparation and Hydrothermal Synthesis

The production of several zeolites from kaolin has relied heavily on hydrothermal synthesis [51, 52]. The calcination of kaolin to form metakaolin was the first step in the synthesis of zeolite. After 4 h of calcination at 500, 600, 700, and 800 °C, metakaolin was obtained. Table 1 shows the chemical compositions of raw kaolin and metakaolin. The hydrothermal technique was used in the experiment, as shown in Fig. 1. 3 g of metakaolin were mixed with 0.5, 1, 2, and 3 M of NaOH, respectively. Then, the kaolin was dispersed in 80 mL of distilled water and aged for 24 h at 40 °C with stirring. The mixture was placed in a 100 mL stainless-steel autoclave with a Teflon coating and hydrothermal at 100 °C for 9, 12, 16, 24, and 30 h, depending on the crystallization time. The heated product was then filtered with a pump, washed several times with distilled water to remove any remaining NaOH, and dried in a 60 °C oven for 12 h.

![Fig. 1](image) The flowchart procedure of kaolin, metakaolin, and hydrothermal synthesis with various molarity NaOH (0.5, 1, 2, and 3 M) and crystallization time (9, 12, 16, 24, 30 h)
2.3 Characterization

SEM, FTIR, XRD, PSA, and TGA were used to characterize the crystallization and chemical properties of raw kaolin and Z-LTA: X-ray diffraction was used to identify the crystalline phases of the samples in this study (XRD, D8-Advance, Bruker, Germany). Cu K radiations can be used to determine the crystallinity of zeolite. XRD (Ultima IV, Rigaku, UK) analyses with Cu K radiation, a fixed power source, and a diffraction angle (2) of 10–90 were used to determine the crystal phase and mineral compositions of the samples. The sample was evaluated structurally, and Rietveld fitted using specialized software (XPert High score). Using Origin Pro software, the degree of crystallinity (%) was calculated as follows:

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\text{Crystallinity} = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks (crystalline + amorphous)}} \times 100.
\]

A Fourier transform infrared (FTIR) spectrometer (Nicolet iS50, Thermo Fisher, America) was used to analyze the samples' infrared spectra in the range 4000–400 cm\(^{-1}\). Prior to FTIR characterization, the samples were ground with dried KBr powder and pressed into small discs. An X-ray fluorescence spectrometer (AXIOS-mAX, PANalytical B. V., Holland) was used to examine the samples' major chemical compositions while Scanning electron microscopy was used to examine the surface morphologies (SEM, SU8010, Hitachi, Japan). A thermogravimetric differential thermal analyzer was used to measure thermal stability (TG–DSC, STA 409 PC, Netzsch, Germany). Malvern Mastersizer 2000 used a particle size analyzer to measure the particle size of raw kaolin and synthesize zeolite.

3 Results and Discussion

3.1 Characterization of Raw Kaolin

The raw kaolin's XRD pattern corresponded to kaolinite, which has a layered structure with diffraction planes (0 0 1) and (0 0 2) at 2 Theta (2θ) = 12.398 and 24.944, respectively, which are the kaolinite characteristic peaks (Fig. 2). The ICSD pattern number 98–0,037,558 was found to match the sharp peak. The XRF was used to determine the chemical composition of the kaolin, which is listed in Table 1. The kaolin contained SiO\(_2\) (48.72%) and Al\(_2\)O\(_3\) (37.63%), which were used as Si and Al sources in the synthesis of zeolite. To synthesize, the various Z-LTA from the kaolin, silica, and alumina composition was used without adjustment based on the XRF analysis.

3.2 Phase Transformation of Kaolin to Metakaolin

After calcination, the metakaolin XRD pattern changes, with shifts and changes in peak intensities occurring between 2θ = 20.861 and 26.644 at 600, 700, and 800 °C, but not at 500 °C (Fig. 3). The temperatures of 600, 700, and 800 °C indicate that quartz is the primary component. Figure 4 also includes SEM images of the kaolin and metakaolin morphologies. Raw kaolin morphologies show lamellar structure (Fig. 4a). The metakaolin morphology, on the other hand, indicates newly formed tiny crystals on the kaolin particle surfaces (Fig. 4b–e). The calcination treatment has resulted in a highly disordered metakaolin with a sheet-like...
morphology and a highly disordered and amorphous structure. This result is consistent with Chandrasekhar [53], Feng et al. [54], and El-Diadamy et al. [55]. As shown in Fig. 4a [56], kaolin comprises a morphological assemblage of plate-like hexagonal structures or book-like stacks. The raw kaolin clay appears to have a layered crystalline morphology, which supports earlier research [57, 58] on a variation of mineralogy in kaolin Malaysia. Further examination of the micrograph revealed irregular platelets and a poorly defined flake containing sub-rounded particles.

The kaolinite molecular structure is committed to the 400–1300 cm$^{-1}$ band region of the kaolin clay spectrum (Fig. 5) [59, 60]. At 436 to 700 cm$^{-1}$, Si–O stretching is described, which is likely the same as the previous study [61], which found a sharp peak at 700 cm$^{-1}$ as Si–O. Furthermore, the bands at 700 cm$^{-1}$ and 1033 cm$^{-1}$ are described by Kovo and Holmes [62] as Si–O stretching, whereas bands due to hydroxyl groups are found between 3610 and 3695 cm$^{-1}$ [59]. The bands depicting the hydroxyl groups for the kaolin samples, on the other hand, were identified at 3620 to 3690 cm$^{-1}$, indicating that most kaolin is hydrophilic [59]. After calcination, the two typical kaolinite vibration absorption peaks at 478 and 530 cm$^{-1}$ disappear, and new characteristic vibrational bands appear at 1080, 790, and 470 cm$^{-1}$.

**Fig. 4** SEM image a kaolin, b metakaolin (500 °C), c metakaolin (600 °C), d metakaolin (700 °C), and e metakaolin (800 °C)
The metakaolin shows the effect of metakaolinization treatment on kaolin samples when heated to 500–800 °C for 240 min. Because there is still kaolinite peat at 2θ = 12.376 and 24.899, the obtained X-ray diffraction pattern for treatment at 500 °C does not reveal a complete transformation of the kaolin to amorphous SiO2. However, due to a decrease in kaolinite peak intensity at 2θ = 12.398 and 24.944, the XRD treatment for 600 to 800 °C gradually shows a complete transformation of kaolin to amorphous SiO2.

The complete absence of a kaolinite peak at 2θ = 12.398 and 24.944 positions indicated that this parameter is suitable for calcination. According to TGA data, when the heating temperature was increased to 350 °C, the sample’s initial weight decreased by 1.5% (Fig. 6). The decomposition and loss of crystallization water become noticeable as the heating temperature rises. The crystallization water is distinct from the “pore water” typically lost during the drying process. Crystallization water combines chemically to form a fundamental unit of the crystal structure of kaolin. Temperatures above 400 °C affect kaolin crystallization water [63].

The loss of crystallization water was sparked at around 570 °C, as shown in the kaolin thermograms, indicating the start of the dehydroxylation reaction. When the heating temperature was increased to 570 °C, a weight reduction of 10.5% was observed, attributed to the structural loss of the hydroxyl group present in the kaolinite layers [64]. From the TGA curves of kaolin samples, a dehydroxylation reaction of about 650 to 750 °C appears to have been achieved. As the heat temperature begins to rise, another event that could lead to an exothermic reaction is expected. Still, this research is limited to the response that could lead to metakaolin (dehydroxylation). At 710 °C, the mineral kaolinite disintegrates into free alumina, silica, and water [64]. Kaolin had lost 13% of its weight at this point.

3.3 Hydrothermal Synthesis of Zeolite

Z-LTA 0.5 M, Z-LTA 1 M, Z-LTA 2 M, Z-LTA 3 M, Z-LTA 1 M, 9 h, Z-LTA 1 M, 12 h, Z-LTA 1 M, 16 h, and Z-LTA 1 M, 30 h were synthesized from the kaolin using the hydrothermal method. To confirm the structure of the Z-LTA, their XRD patterns, and SEM images were compared with that of the raw kaolin and metakaolin. The XRD is used to determine the phase of Z-LTA. For the XRD pattern of Z-LTA (Fig. 7), there are different zeolite formations at different molarities of sodium hydroxide (0.5–3 M NaOH), with zeolite A formation at 0.5 M NaOH, Z-LTA formation at 1 and 2 M NaOH, and sodalite formation at 3 M NaOH.

There are ten characteristic peaks of zeolite formation, at 2θ = 10.158, 12.449, 16.093, 20.397, 20.857, 21.649, 23.966, 26.089, 26.637, 27.092, 29.916, 30.804, 32.515, 34.150. These peaks are almost identical to the XRD patterns of single-phase Z-LTA and zeolite A. The crystallinity percentage of Z-LTA at 1 M NaOH is 86.80%, followed by 2 M NaOH (80.77%), 3 M NaOH (67.78%), and 0.5 M NaOH.
NaOH (67.78%, 62.83%, Table 2; Fig. 8). The molarity of 1 M NaOH increased the rate of dissolution of Si and Al ions, which helped form suitable Z-LTA crystal nuclei. The crystallization of the LTA zeolite is influenced by the formation of suitable nuclei.

High supersaturation and steric stabilization of the nuclei are critical factors for minimizing the final zeolite crystal sizes [65]. Meanwhile, Reyes et al. [66] found that the Z-LTA could be synthesized less time using a lower concentration of NaOH (1.33 M). The crystallinity of the synthesis product was high, and the crystal size distribution was uniform (1.0 µm). Gougazeh and Buhl [67] made Na-A zeolite by heating kaolin with 1.0–4.0 M NaOH for 20 h at 100 °C. The crystallinity increased from 70.2 to 74.6% as the NaOH concentration increased, according to their findings (from 1.5 to 3.5 M). The crystallinity decreased from 68.2 to 50.8% when the NaOH concentration was increased from 3.5 to 4.0 M.

**Table 2** Crystallinity (%) for different alkali solutions and crystallization time

| Zeolite | Aging parameter | Molarity (M) | Crystallization time (h) | Crystallinity (%) |
|---------|-----------------|--------------|-------------------------|-------------------|
|         | Reaction parameter |            |                         |                   |
| 24      | 0.5             | 24           | 62.83                   |                   |
| 1       | 24              | 24           | 86.80                   |                   |
| 2       | 24              | 24           | 80.77                   |                   |
| 3       | 24              | 24           | 67.78                   |                   |
| 1       | 9               | 24           | 88.45                   |                   |
| 1       | 12              | 24           | 86.16                   |                   |
| 1       | 24              | 24           | 86.80                   |                   |
| 1       | 16              | 24           | 87.11                   |                   |
| 1       | 30              | 24           | 86.59                   |                   |
1 M NaOH was chosen for further study on the formation of higher crystallinity percentages of different crystallization times (9–30 h). Figure 9 shows a higher intensity peak of Z-LTA at 9 h when compared to other times. The crystallinity percentage of Z-LTA at 1 M NaOH is higher at 9 h (88.45%), 12 h (86.16%), 16 h (87.11%), 24 h (86.80%), and 30 h (86.59%) than at other times (Table 2; Fig. 10). At the conclusion of the analysis, the mean diameter of Z-LTA 1 M, 9 h final product was 329 nm or 0.329 µm. Jawor and Jeong [68] confirmed this finding and found it to be almost identical to conventional zeolite, 0.427 µm. In addition, the mean diameter recorded at the end of the result for kaolin was 497 ± 0.4 nm which is equivalent to 0.497 µm. The result agreed with Yahaya et al. [69], the size of the kaolin is 0.4–0.75 µm. This finding indicates that varying the synthesis time resulted in the production of different zeolite types and purity [70]. This phenomenon can also be explained by the fact that zeolite is a thermodynamically metastable phase, which means that the synthesis process was overwhelmed by Ostwald’s step rule of successive reactions. Because of the replacement of phases that occurred at varying crystallization times, this finding confirmed the earlier assertion that zeolites are thermodynamically metastable phases [71]. At 3 M NaOH, 24 h crystallization time, there was a zeolite crystallization failure for synthesis zeolite.

According to the studies above, NaOH concentrations less than 2 M are best for synthesizing Z-LTA because higher concentrations can produce impurities like hydroxy sodalite, which prevent crystallization (Fig. 11) [72]. When NaOH concentrations of over 3 M are used, previous studies [73] have also shown the presence of hydroxy sodalite. With a decrease in degree crystallinity, higher alkalinity promotes the formation of impurities and the decomposition of zeolite [74].

With a range of 400–4000 cm⁻¹, FTIR spectroscopy is used to specify the structure of zeolites and to monitor reactions in the zeolite framework. The different bands are illustrated by the IR spectra of raw kaolin, metakaolin (700 °C, 4 h, Fig. 5), and Z-LTA (1 M, 9 h, Fig. 12). After calcination, the two typical kaolinite vibration absorption peaks at 478 and 530 cm⁻¹ disappear, and new characteristic vibrational bands show up at 1080, 790, and 470 cm⁻¹ (Fig. 5b). Meanwhile, at 790 cm⁻¹, the vibration band appears, indicating that the kaolinite structure has been broken, resulting in amorphous aluminosilicate. The broadband appointed to Al–O bonds in Al₂O₃ in the spectral range from about 930 cm⁻¹ to about 700 cm⁻¹ does not appear in zeolitic materials (Fig. 5a).

There was an occurrence of the same width bands of kaolin (Fig. 5b) after 240 min of exposure time that had never been seen before and was located at around 790 cm⁻¹. This was applied to the Al–O bond in Al₂O₃, implying that free alumina is formed and that coordinated octahedral Al is converted to Al with tetrahedral coordination [75]. At 1080 cm⁻¹, the shoulder was also wide. The stretching bands in SiO₂ are responsible for this. The broad shoulder peak in metakaolinite is clearly not seen as the Si–O bond percentages of low quartz. As reported by Brindley and Nakahira [76], it again suggests the formation of free silica. The 4-coordinated Al–O stretching was also assigned to the 470 cm⁻¹ bands in a metakaolinite structure [77]. This necessitated the development of a highly reactive substance capable of converting into zeolites. After rapid kaolin heating at 700 °C, the obtained bands generally show the conversion of kaolinite to metakaolinite.

In aluminosilicates with zeolite structure, the 1030 cm⁻¹ band of kaolin was shifted to 995 cm⁻¹, which could be attributed to antisymmetric stretching of T–O bonds (T = Si or Al) (Fig. 12). During the reaction between raw kaolin and NaOH, SiO₂ and Al₂O₃ are transformed into aluminosilicates. There is an important assignment in the literature for the characteristic bands between 995 cm⁻¹ asymmetric stretching vibrations for all zeolitic materials in the range
of 1000–970 cm⁻¹. Zeolitic water is responsible for the broad band around 3430 cm⁻¹ and a band around 1650 cm⁻¹ (Fig. 12). Stretching vibrations of Si–O and Al–O groups could be assigned to the strongest vibration at 995 cm⁻¹. Bending vibration of Al–O groups in the zeolite structure could be responsible for the vibration at 452 cm⁻¹. Furthermore, FTIR analysis of the zeolite structure reveals that the potassium ions added during the reaction enter the pores or cages of zeolite and do not alter the zeolite’s original framework structure. Table 3 shows the summary of the FTIR wavelength number for kaolin, metakaolin and Z-LTA 1M, 9h.

The detailed microstructure of zeolitic materials with sheet structure was revealed using the SEM technique. In the Z-LTA 0.5 M, Z-LTA 1 M, and Z-LTA 2 M, changes in the morphological structure of the kaolin surfaces and the formation of euhedral cubic crystals were observed. Z-LTA 3 M, Z-LTA 1 M, 9 h, Z-LTA 1 M, 12 h, Z-LTA 1 M, 16 h, Z-LTA 1 M, 24 h, and Z-LTA 1 M, 30 h (Fig. 13a–h). The crystalline particles with lattice frames could also have the LTA zeolite cubic structure, as shown in Fig. 13. Sodalite has a spherical form with an array of long fibres surrounding it, whereas zeolite A and LTA are cubic.

Figure 13 shows an SEM micrograph demonstrating that the synthesized Z-LTA perfectly fits the cubic crystalline system family. The presence of well-crystalline zeolite crystals with the same cubic morphology and uniform sizes was revealed in Fig. 13. The cubic morphology of the zeolite crystals became very pronounced, with an average length of ± 2 µm. From 1 to 2 M and 9–30 h, it can be deduced that no significant amount of amorphous materials is detected at the end of the synthesis process. Indicating that low-grade Malaysian kaolin can be successfully transformed into Z-LTA using the traditional hydrothermal method when the composition parameters are carefully controlled. Water treatment, membrane separation and water softening are widely used for these Z-LTA.

Sodalite is a spherical mineral with a ring of long fibres surrounding it (see Fig. 13d). Due to the faster and more uniform heating, the 3 M produced more diminutive and homogeneous grain sizes of zeolite A and sodalite. Inadequate mixing was blamed for the formation of sodalite as a byproduct of the Z-LTA synthesis. When a Z-LTA mixture moved into the HS range, the dissolution and regrowth of crystal composition occurred. For example, when a Z-LTA mixture moved into the HS range, all of the LTA was eventually transformed into sodalite. The only sodalite that nucleated

| Vibration | Wavelength number kaolin (cm⁻¹) | Wavelength number metakaolin (cm⁻¹) | Wavelength number Z-LTA 1 M, 9 h (cm⁻¹) |
|-----------|-------------------------------|-------------------------------------|------------------------------------------|
| Si–O      | 436                           | –                                   | –                                        |
| Si–O      | 478                           | 470                                 | –                                        |
| Si–O–Al   | 530                           | –                                   | –                                        |
| Si–O      | 700                           | –                                   | –                                        |
| Si–O–Al   | 760                           | –                                   | –                                        |
| Al–OH     | 800                           | 790                                 | 452                                      |
| Al–OH     | 930                           | –                                   | 580 (Vibration within the external linkage of zeolite-LTA structure tetrahedral building units) |
| Si–O      | 1030                          | 1080                                | 995                                      |
| Si–O      | 1110                          | –                                   | –                                        |
| ––OH      | 1650                          | –                                   | 1650                                     |
| ––OH      | 3620                          | –                                   | 3430                                     |
| ––OH      | 3690                          | –                                   | –                                        |
Fig. 13  SEM image a Z-LTA 0.5 M b Z-LTA 1 M c Z-LTA 2 M d Z-LTA 3 M e Z-LTA 9 hr f Z-LTA 12 hr g Z-LTA 16 hr h Z-LTA 30 hr
4 Conclusion

Z-LTA 1 M, 9 h with good crystallization, was hydrothermally synthesized using raw kaolin from the Delta Kaolin, Selangor, Malaysia. Z-LTA was obtained under optimal conditions, 1 M NaOH and 9 h crystallization time. XRD analysis confirmed that Z-LTA 1 M, 9 h is zeolite type LTA with ICSD pattern number 98-0037558. The crystallinity percentage of Z-LTA at 1 M NaOH gives a higher reading which is 86.80%, followed by 2 M NaOH (80.77%), 3 M NaOH (67.78%) and 0.5 M (62.83%). The crystallinity percentage of Z-LTA at 1 M NaOH, 9 h give higher percentage compared to other time with 9 h (88.45%), 12 h (86.16%), 16 h (87.11%), 24 h (86.80%) and 30 h (86.59%). The mean diameter recorded at the end of the analysis of Z-LTA 1 M, 9 h is 329 nm, equivalent to 0.329 μm. Using FTIR spectroscopy, the strongest vibration at 995 cm$^{-1}$ could be assigned to the stretching vibration of Si–O and Al–O groups. The vibration recorded at the end of the analysis of Z-LTA 1 M, 9 h is 3518–3520 cm$^{-1}$ could be assigned to the bending stretching vibration of Si–O and Al–O groups. The vibration recorded at the end of the analysis of Z-LTA 1 M, 9 h is 3518–3520 cm$^{-1}$ could be assigned to the bending stretching vibration of Si–O and Al–O groups.

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Data Availability Data will be made on request.

Code Availability Not applicable.
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