

Characterisation of NaA Zeolite Made from Malaysian Kaolin

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In this study, as an alternative to the pure chemical used to prepare zeolite NaA, the clay mineral kaolinite was used as the source material for NaA-zeolite preparation. Kaolin as an alternative low cost material and as a potential precursor to zeolite A synthesis via metakaolinisation of kaolin at 900 °C to a reactive amorphous material called metakaolin and hydrothermal treatment of metakaolin with an aqueous alkali. Before this reaction takes place however, raw kaolin undergoes a pretreatment process to increase its purity through the removal of impurities. This research intends to prepare zeolite A from Malaysian kaolin. A series of composition and structural characterisations of both the starting material (kaolin) and the final product (zeolite A) were carried out using powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) to confirm the formation of NaA-zeolite. From the characterisation studies, it was found that high-purity NaA-zeolite can be produced from local kaolin. These findings enable us to answer the fundamental question regarding the structural characteristics of NaA-zeolites synthesised from Malaysian kaolin.

1. Introduction

Zeolites are crystalline, microporous, hydrated aluminosilicates of alkaline or alkaline Earth metals and are significantly more active than layered (clays) and mesoporous structures (whose walls are amorphous) (Rios et al., 2009). Zeolite framework is an assemblage of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra, which corner share to form different open structures. Zeolites unique properties have initiated a large number of research studies aimed at exploring potential new applications as sorbents and catalysts based on its unique adsorption, cation exchange, dehydration–rehydration and catalytic properties (Earl and Deem, 2006).

Traditionally, commercial production of zeolite is mainly conducted using the aluminosilicate hydrogel route of sodium silicate and sodium aluminate. The chemical sources of silica and alumina to prepare the synthetic zeolites is costly. Thus, kaolin which is more abundant and environmentally friendly materials has been used for the zeolite synthesis as an alternative low-cost raw material. Kaolin is clay mineral which has a structure assemblage of SiO_4 tetrahedral sheets and $\text{Al}(\text{O},\text{OH})_6$ octahedral sheets through shared oxygen (Rouquerol et al., 2013). In Malaysia, the main deposits of kaolin found in the states of Perak, Johor, Kelantan, Selangor, Pahang and Sarawak. There are several studies that have been done using Bulgarian kaolin (Georgiev et al., 2014) and Ethiopian kaolin (Ayele et al., 2015) mineral as the raw material to synthesis zeolite.

In general, kaolin is converted to highly active phase known as metakaolin by a method of calcination at high temperature and next, by the hydrothermal reaction of the reactive phase, metakaolin with an aqueous alkali medium (Corma et al., 1998). Consequently, only a small fraction of the AlO_6 octahedra is maintained, while the rest are transformed into the much more reactive tetra- and penta-coordinated units. The reactivity of the obtained solid is strongly influenced by the temperature used for the kaolin calcination. In the next step, the highly active metakaolin will be treated under a hydrothermal reaction with an aqueous alkali medium (Corma et al., 1998).

According to the Malaysian Department of Minerals and Geoscience, the country's annual production of kaolin was approximately 284,023 t in 2016; however, the exploitation of kaolin is limited to the papermaking industry and domestic ceramic factories. Thus, it is necessary to utilise the local kaolin in an environmentally friendly manner that has high commercial value. No research has been carried out previously, to produce zeolite type

A from Malaysian kaolin. Therefore, in this work, the potential of Malaysian kaolin as a raw material for NaA-zeolite preparation was explored. Zeolite A was hydrothermally synthesised from raw kaolin with NaOH used as the activator.

2. Experiment method

2.1 Preparation of Zeolite

In this study, commercial kaolin was purchased from Kaolin (M) Bhd. as the raw material for the synthesis of NaA zeolites. Kaolin was subjected to metakaolinisation in order to produce a metakaolin. Later, the metakaolin was zeolitised, to produce NaA zeolites. Prior to use, the kaolin was treated with 2.5 % sodium hexametaphosphate. One kilogram of kaolin was added to the reaction mix of 2.5 % of sodium hexametaphosphate and 5 L of distilled water while stirring the mixture homogenously at 4,000 rpm for 2 h by using an IKA mechanical stirrer. The supernatant was taken out after 1 h of settling time, and dried in an oven for 72 h. By calcined the treated kaolin at 900 °C for 2 h in a muffle furnace, metakaolin is produced. An alkaline hydrothermal synthesis was conducted by added 2.75 M of sodium hydroxide to the metakaolin while stirring the mixture at 200 rpm at 70 °C for 2 h. The mixture was left at 60 °C in the oven for 12 h for completion of the crystallisation process. After that, the zeolite was separated by vacuum filtration and was dried at 105 °C for 24 h in the oven.

2.2 Characterization techniques

Structural and relative crystallinity for all samples were analysed using powder XRD using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of $2\theta = 3-80$ at a scanning speed of $1^\circ/\text{min}$. By using XRF, the chemical composition of the raw kaolin and synthesised zeolite were analysed. The morphologies of the samples were investigated by an electron dispersive spectroscopy (EDS) system attached to field-emission scanning electron microscope (FESEM) at 30 kV with a resolution of 5 nm. The FTIR analysis of synthesised zeolite was collected from 64 scans and wave number range of 400 cm^{-1} and $4,000 \text{ cm}^{-1}$ with 4 cm^{-1} resolution to study their structural features infrared. The surface area and pore size of synthesised zeolite were carried out at 77 K (liquid nitrogen temperature with accompanying software from Micromeritics (Micro Active 4.00)).

3. Results and discussion

3.1 Synthesized of Zeolite from kaolin

Sedimentation method was carried for pre-treatment of the raw kaolin. The difference in the settling times of the kaolin and the associated impurities forms the basis of a simple mechanism to separate the impurities from the raw kaolin. Sodium hexametaphosphate was used as the soluble dispersing agent. The dispersing agent ionises to produce cations that are attracted to the negative charges on the clay particles. The settling process during sedimentation allowed the coarse grit particles to settle to the bottom of the beaker. Minerals such as mica, particles of which are flake shaped, do not settle as rapidly as the quartz and heavy minerals. Once the settling product was removed and the supernatant was taken, kaolinite was separated from the major impurities. After the pre-treatment process, fine kaolin powder with a high kaolin concentration was produced. However, impurities made of quartz and very small quantities of clay mineral (Johnson et al., 2014) were present in the refined kaolin. The X-ray fluorescence (XRF) results for the chemical composition of both the raw and refined kaolin are shown in Table 1.

Table 1: XRF data of kaolin before and after sedimentation treatment

Chemical constituent	wt% in raw kaolin	wt% in refined kaolin
Aluminium (Al ₂ O ₃)	21.41	33.83
Silica (SiO ₂)	70.08	53.44
Iron (Fe ₂ O ₃)	0.55	1.28
Potassium (K ₂ O)	2.72	3.44
Magnesium (MgO)	4.74	5.99
TiO	0.29	0.47
Trace Metals	0.19	1.55

In the XRF analysis, the chemical compounds present in the kaolin and their concentrations were obtained, with the major elements present expressed in the form of their oxides. Figure 1 demonstrates the XRD patterns of the refined kaolin samples. The kaolin clay undergoes metakaolinisation, called dehydroxylation, transforming it into an amorphous, but highly reactive and metastable, phase that a very suitable source for

zeolite synthesis (Kovo et al., 2009). According to Chandrasekhar (1996), kaolin was found to have maximum reactivity in terms of zeolite formation when it is calcined at 900 °C for 1 h. After the metakaolinisation process, the phase change in the sample was verified by using XRD. Formation of metakaolin due to the dehydroxylation reaction was confirmed in the XRD pattern, where the refined kaolin in Figure 2 shows the disappearance of kaolinite peaks. The metakaolinisation of kaolin by heating the refined kaolin for 2 h at 900 °C reassembled all the kaolinite peaks, except for the peaks due to the admixed impurities. Thermal treatment of kaolin causes the kaolinite crystal lattice to collapse and form a highly disordered and amorphous structure. The only crystalline phase in the metakaolin was quartz, because quartz is not affected by the thermal treatment during calcination. The activation of kaolin produces structural changes to this mineral, promoting its reactivity for synthesising zeolitic materials (Kovo et al., 2009).

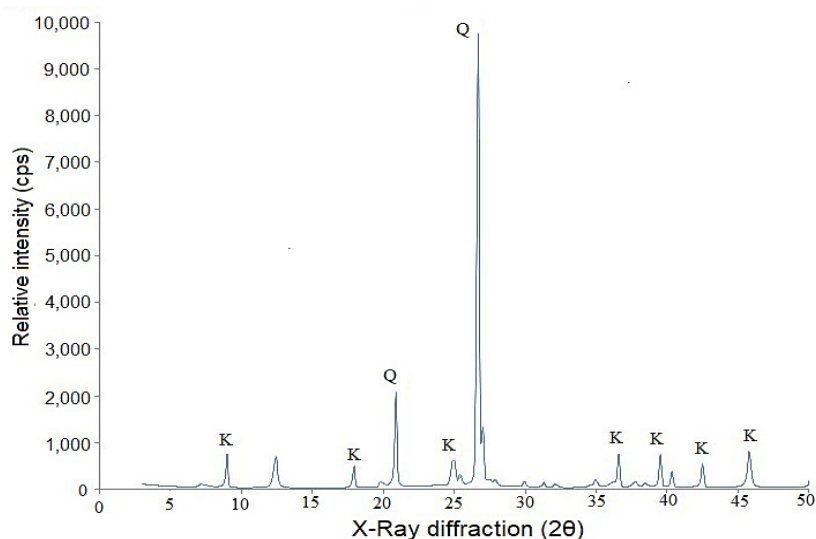


Figure 1: XRD pattern of refined kaolin (quartz and kaolin peaks are identified)

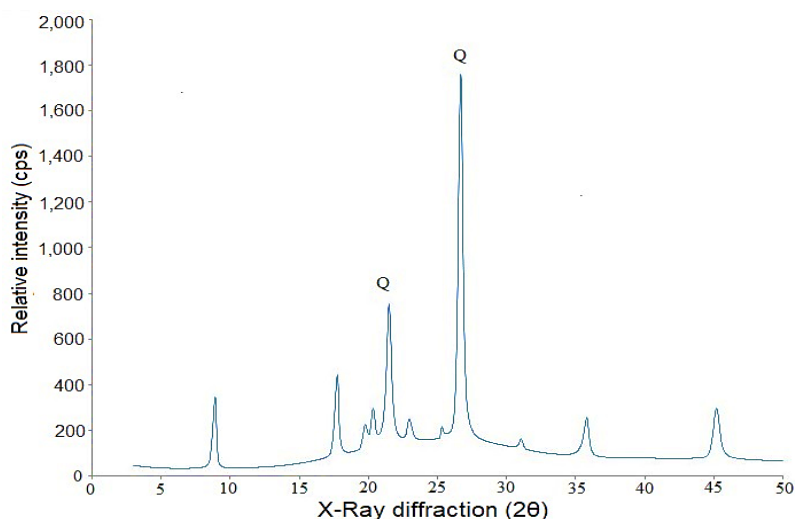


Figure 2: XRD pattern of kaolinite after heating at 900 °C

3.2 Synthesis of zeolite A

For the synthesis of zeolite A, the metakaolin produced by calcination at 900 °C for 120 min was utilised as a preliminary material. Zeolite A was obtained by using the hydrothermal synthesis of metakaolin with 2.5 M NaOH at 70 °C. Crystallisation of zeolite A was carried out at 60 °C for 12 h. XRD was used to confirm the phase change for the kaolin transformation to zeolite A (Figure 3). The XRD analysis of the synthesised zeolite A showed a similar pattern to commercial zeolite A.

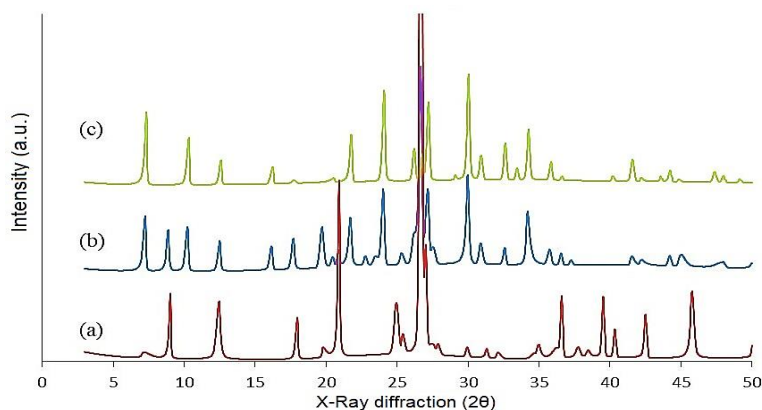


Figure 3: XRD results for (a) kaolin; (b) synthesised zeolite; and (c) commercial zeolite

The SEM images of the kaolin and synthesised zeolite are presented in Figure 4a and Figure 4b. The observed morphologies are similar to those reported in previous studies (Johnson et al., 2014). The SEM images (Figure 4a) show that the flake-like structure of kaolin was transformed into well-defined cubic crystals, as expected for highly crystalline zeolite A (Figure 4b). The SEM image (Figure 4b) shows well-developed cubes of zeolite Na-A co-existing with metakaolin debris. The data obtained by SEM agreed with the mineralogical composition of the zeolite products, which was supported by XRD analysis of the synthesised zeolite (Figure 3).

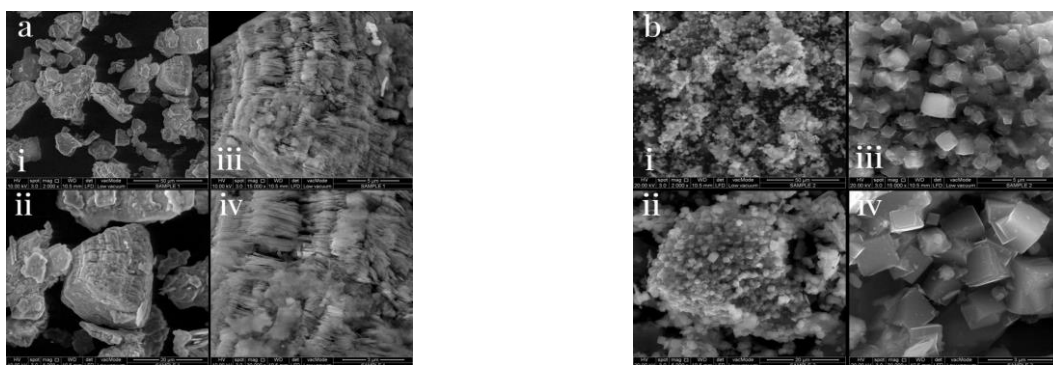


Figure 4: SEM images of (a) kaolin and (b) synthesised zeolite at different magnifications (i) 2,000; (ii) 5,000; (iii) 15,000; and (iv) 30,000

3.3 Properties of synthesized zeolite

For each crystalline material of the unique XRD pattern makes it suitable for sample identification by comparing the XRD pattern of the samples with standard material. In addition, the simulated patterns collected by the International Zeolite Association Structure Commission (IZA-SC) are used to confirm the structural framework type of the samples. The XRD patterns of the synthesised zeolite and commercial zeolite A are shown in Figure 3. Diffraction patterns of the synthesised zeolites in comparison to the commercial zeolites indicated that the samples were similar to Linde Type A (zeolite A). The peak positions of the synthesised and commercial zeolites are in good agreement with those reported by the IZA-Structure Commission (Table 2). It was found that both synthesised and commercial samples exhibit a low background signal and sharp reflection, but with a minor change in peak positions.

The presence of a polyhedral building unit in the zeolite framework can be detected by the use of IR spectroscopy. In this region, the infrared spectrum of zeolite consists of internal vibrations which are insensitive to variations in the framework and vibrations related to external linkages between tetrahedra which are sensitive to the framework structure. In addition, the presence of some secondary building units (SBUs) and building block polyhedra, such as double rings and large pore openings, can also be detected (Mozgawa et al., 2011). Zeolites of the same structural type and group usually have a similar infrared pattern. The FTIR spectrum of the synthesised zeolite is similar to the FTIR spectrum of commercial zeolite A as illustrates in Figure 5.

Table 2: The peak positions and intensities of the synthesised zeolite and commercial zeolites A obtained from XRD data.

hkl	Linde Type A, Hydrated (LTA) (IZA-SC)	Zeolite A (Synthesised)		Zeolite A (Commercial)	
	2 θ	2 θ	I(cps)	2 θ	I(cps)
222	12.66	12.52	385.432	12.60	317.330
420	16.38	16.16	328.738	16.24	238.697
442	21.68	21.70	654.452	21.76	610.533
620	23.16	24.02	989.216	24.10	1,116.781
642	27.34	27.18	988.438	27.22	988.056
644	30.16	29.98	1,148.45	30.04	1,310.496

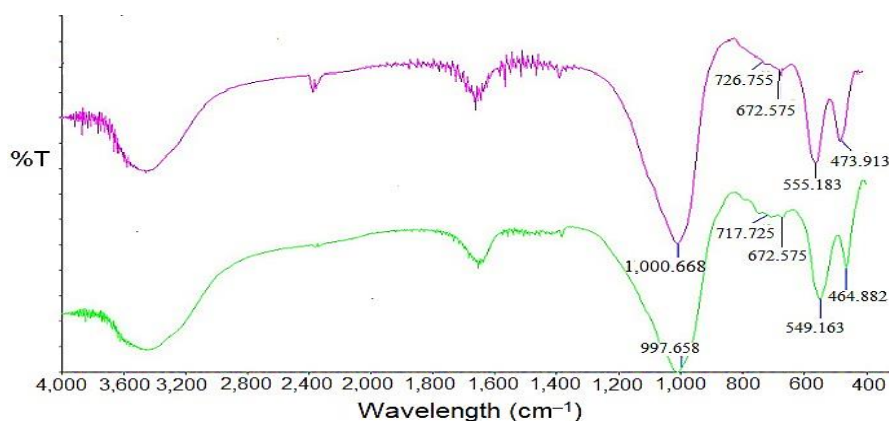


Figure 5: The FTIR spectrum of zeolite: (a) synthesised zeolite and (b) commercial zeolite A

Vibrations in the following bands can be assigned based on the analysis of the theoretical Linde Type A (LTA) zeolite unit spectra (Mozgawa et al., 2011):

- 995-1005 cm^{-1} – asymmetric stretching vibrations of bridge bonds of Si-O(Si) and Si-O(Al).
- 720-730 cm^{-1} – symmetric stretching vibrations of bridge bonds of Si-O-Si.
- 665-675 cm^{-1} – symmetric stretching vibrations of bridge bonds of Si-O-Al.
- 545-555 cm^{-1} – (complex band) symmetric stretching vibrations of bridge bonds of Si-O-Si and bending vibrations of O-Si-O.
- 465-475 cm^{-1} – bending vibrations of O-Si-O, occurring in “antiphase”.

The bands in the region of 545-555 cm^{-1} correspond to symmetric stretching vibrations of 4-membered rings in the LTA structure. Its complex envelope denotes that it is a superposition of several component bands. The bands positioned at the lowest wave numbers, i.e. at less than 460 cm^{-1} , correspond to the characteristic bending vibrations carried out in the 4-membered rings.

The behaviour of a gas-solid adsorption system can be evaluated based on the adsorption isotherms which have been classified by International Union of Pure and Applied Chemists (IUPAC). Identification of isotherm type is the important step in the behaviour of the adsorption system and the nature of the adsorption process (Rouquerol et al., 2013). Figure 6 shows the N_2 adsorption-desorption isotherm of synthesized zeolite. A textural analysis suggests that nitrogen was not accessible to the synthesised zeolite pore system. Keerthana et al. (2014) reported that due to sodium cations which occupy positions near the micropore aperture, NaA zeolite does not adsorb N_2 at 77 K while minimizing their size and hence preventing access of N_2 molecules.

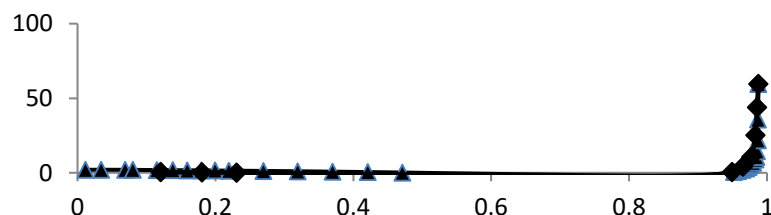


Figure 6: Nitrogen adsorption and desorption isotherms of synthesized zeolites

Besides, the zeolite relative crystallinity and unit cell parameter were calculated based on the LTA group of zeolites using the XRD data presented in Figure 3 following ASTM D5357-03. The crystallinity value and the unit cell dimension of the synthesised zeolite is 98% and 24.347 Å. It was found that the crystallinity value and the unit cell dimension of the synthesised zeolite is 98% and 24.347 Å. The calculated unit cell dimension of the synthesised zeolite is not much different from the data published by IZA, in which the unit cell dimension for Linde Type A, (hydrated) is 24.61 Å. According to Armaroli et al. (2006) an increase of the Si/Al ratio will reduce the unit cell dimension as both are related to each other. The high content of silica in the kaolin might be the reason for the high Si/Al ratio. Based on the elemental analysis the synthesised zeolite, the Si/Al ratio is 1.5.

4. Conclusion

The formation of zeolite Na-A from pretreated Malaysian kaolinites with sodium hexametaphosphate (to remove quartz and impurities) has been studied. Amorphous metakaolin was obtained at a calcination temperature of 900°C. Through an alkaline hydrothermal reaction of calcined metakaolin with 2.75 M NaOH, high purity Na-A zeolite was successfully synthesised. Based on XRD, FTIR and SEM results, it was clear that Na-A zeolite can be synthesised using local kaolin. The results specified that the zeolite A as the major constituent phase, while hydroxysodalite (HS) and quartz were found as minor phases in obtained zeolite products. Highly crystalline phases present in the synthesised zeolite were shown by the high intensity of the peak observed in the XRD pattern. In addition, SEM showed that the synthesised zeolite has a cubic crystalline structure. By using FTIR, the changes due to the conversion process were observed. To summarise, this study demonstrates that local kaolin is a feasible and economically viable raw material for the production of NaA zeolite for industrial applications.

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