

# Zeolite Synthesis from Natural Kaolin: The Effect of Metakaolin Heating and Transformation

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## Abstract

In this study, the effect of kaolin heating and metakaolin transformation on zeolite synthesis was investigated. Two different metakaolin temperatures at the early stage of transformation were chosen in determining the lowest temperature that was capable of synthesizing the zeolite structure from natural kaolin. The synthesis of zeolite materials from the transformation of natural kaolin to metakaolin was conducted through the hydrothermal method. Natural kaolin obtained from Ipoh, Perak, was calcined at two different calcination temperatures of 600°C and 650°C. Metakaolin was obtained after 2 hours of exposure at 600°C and 650°C, respectively, with slightly different FTIR peaks of quartz at both temperatures. The incomplete metakaolin formation at a slightly lower temperature revealed the unsuccessful zeolite formation. At slightly higher calcination temperatures, the metakoalin peak obviously existed and led to the formation of the complete zeolite phase. This experiment also proved the importance of accurate calcination temperature in converting to zeolite synthesis. Furthermore, this current work also revealed that the complete transformation of metakoalin that can be conducted slightly lower temperature as compared to the common metakoalin phase will minimize energy consumption during the zeolite synthesis as well as the metakoalin transformation.

## 1. Introduction

The heating process of kaolin to metakaolin involves the removal of the hydroxyl group under temperature control; in other words, the chemical change takes place as a result of the heating of the kaolin within a certain temperature range. The calcination involves restructuring the octahedral layer so that it can be oriented in a tetrahedral fashion. Temperature and time during the calcination phase are variables that may influence the arrangement structure and layer. In most cases, a temperature in the range of 550–700 °C is selected [1]. Several researchers have conducted studies on the process of metakaolinization; nevertheless, there are conflicting opinions regarding the conditions that must be met in order to manufacture metakaolin successfully [2,3].

Due to the fact that zeolite is widely used in many fields, such as the petroleum industry, fine-chemical synthesis, agriculture, and many more, the synthesis of zeolite from natural clay has become an active field of research. In zeolite synthesis, the hydrothermal technique is commonly used and normally conducted in the

primary aqueous solvent [1,4]. The synthesis of zeolites from kaolin consists of several steps, according to [3]: nucleation, aggregation, crystallization, and growth. There are two theories of zeolite synthesis: (i) the solid-solid transformation (nucleation process) and (ii) the mechanism of crystallization. Zeolite crystallization occurs through a solid-solid transition process directly from the amorphous gel in the crystalline phase [5,6]. Several parameters may affect zeolite synthesis, such as temperature, pH, and time for calcination and crystallization; alkalinity, nucleation, and growth; the Si/Al ratio; material impurities; and the composition of the slurry gel [4,5,7]. The composition is very crucial, especially when dealing with the synthesis of zeolite from natural sources. This is because kaolin from raw constituents has more impurities than chemically processed kaolin [4,8]. Therefore, this study was conducted to observe the effect of parameters in the calcination of kaolin in determining the appropriate composition for transforming the metakaolin into zeolite composition.

## 2. Methodology

### 2.1 Materials

The raw material, kaolin clay, was collected from Ipoh, Perak, and the clay mineral is kaolinite with a hydrous aluminosilicate structure. The sodium hydroxide (NaOH), QReC, used was from HmBG Chemical with an analytical grade.

### 2.2 Synthesis of Zeolites

Before any treatment, the raw kaolin clay samples were first sieved at 90  $\mu\text{m}$  to get a fine particle size and also to eliminate the larger particles and impurities present in the samples. After that, 4 g of kaolin powder was mixed with 6 g of sodium hydroxide before undergoing the calcination process. Calcination of the samples was done at temperatures of 600°C and 650°C, respectively, for 2 hours to convert the kaolin into metakaolin. The metakaolin powder was washed with deionized water five times to reduce the alkalinity of NaOH. This was followed by the hydrothermal method of zeolite, whereas the metakaolin powder was added to 75 mL of 2M NaOH solution. (The solution was labelled as sample A.) The mixtures were stirred using a magnetic stirrer for 30 minutes to give a homogeneous mixture. After the stirring process, the solution was crystallized in an oven at 100 °C for 12 hours. Then, the samples were filtered and washed with deionized water to reduce the alkalinity. The solution was transferred into the centrifuge tube and underwent the centrifugation process. The water in the centrifuge tube was changed every 10 minutes until the pH of the solution became neutral. The residue from the centrifugation process was placed in an oven and dried at 90 °C for 24 hours to get the zeolite powder. The dried powder was ground in a mortar with a pestle to obtain a fine powder for characterization. The steps above were repeated by using the solutions of sample B, as shown in Table 1.

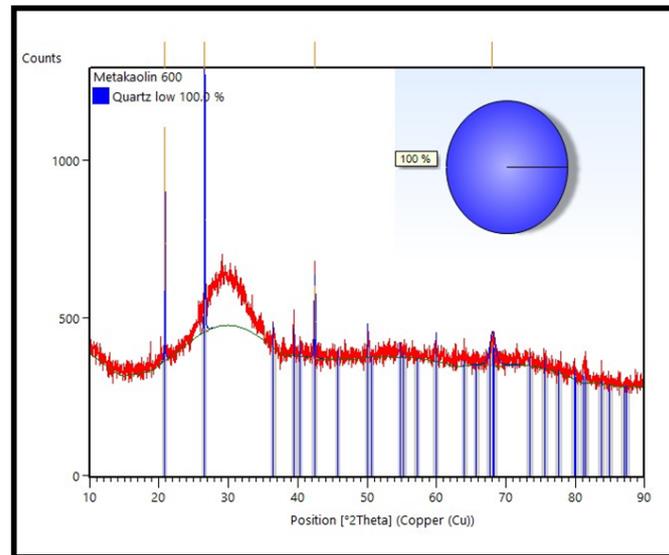
**Table 1** Solution used in synthesized of zeolite

Sample	Solution
A	4g of 600 °C metakaolin powder + 75 mL of 2M NaOH solution
B	4g of 650 °C metakaolin powder + 75 mL of 2M NaOH solution

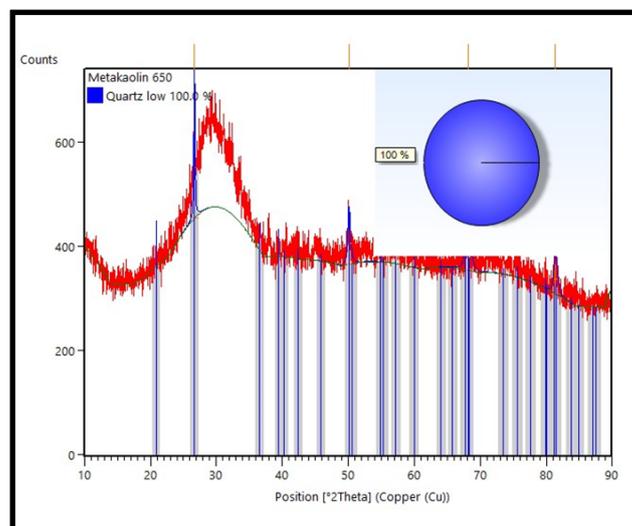
## 3. Result and Discussion

### 3.1 X-ray Diffraction (XRD)

XRD analysis was conducted on both metakaolin that produced form powders fused at 600°C and 650°C and revealed the existence of the silica quartz phase. The XRD pattern of the metakaolin at 600 °C in Fig. 1 shows an intense peak position at  $2\theta = 26.644^\circ$  with the diffraction of the (011) plane. While for metakaolin 650°C, the XRD pattern shows slightly sharp peak of silica existence with position at  $2\theta = 26.641^\circ$  with plane of (011) indicating the complete transformation to quartz silica. Both peaks representing the quartz of silica 100% patterns. The position of metakaolin phase is related to existence of silica phase in the range of  $2\theta = 25-26^\circ$  is in agreement with range of peak as reported elsewhere [9,10].



(a)

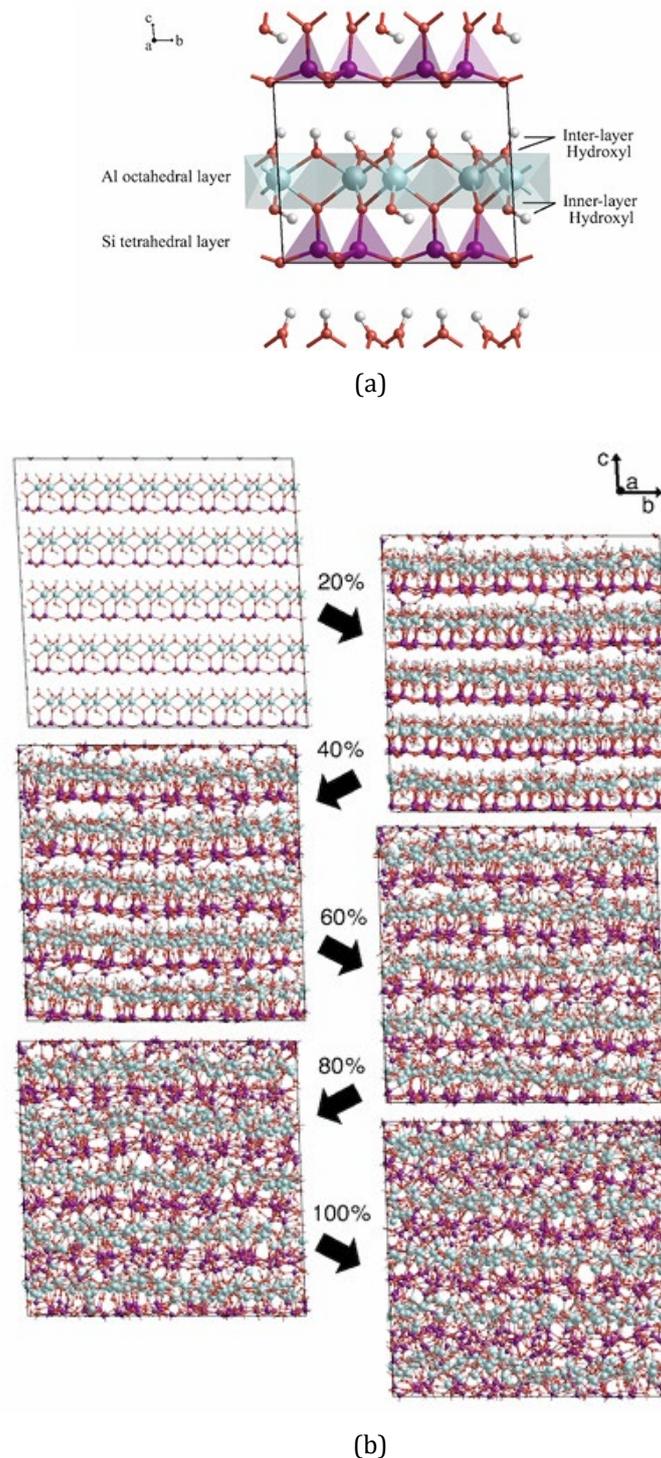


(b)

**Fig. 1** XRD spectra of metakaolin at (a) 600 °C and (b) 650 °C

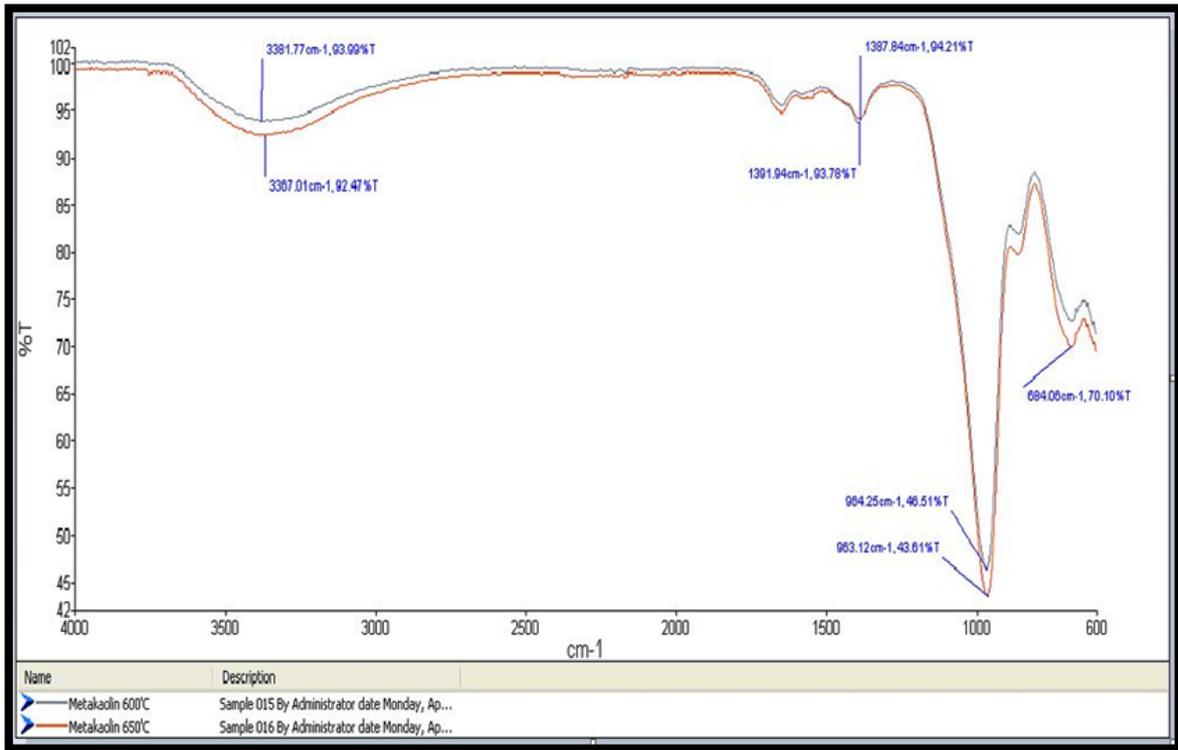
The transformation of compositional materials that commonly appear in Malaysia is in the range of 40–60% silica and 20–40% alumina, which has led to the formation of the quartz phase during calcination at a temperature of 600–800 °C. The transformation of metakaolin will preferably occur at temperatures above 600 °C and will form the quartz phase. This was proven by referring to the binary phase diagram of  $\text{SiO}_2\text{-Al}_2\text{O}_3$ , which revealed this transformation of composition is always associated with the formation of quartz phase of metakaolin. This process transformation involves the changes of the aluminosilicate structure to the amorphous quartz phase, as also reported elsewhere [10,11].

This quartz phase is in the form of a hydrated aluminosilicate structure (as can be seen in Fig. 2(a) that is produced due to the removal of water molecules or dehydroxylation during the calcination process. The dehydroxylation of kaolin to metakaolin is an endothermic process due to the large amount of energy required to remove the chemically bonded hydroxyl ions [13]. Therefore, in the temperature range of dehydroxylation, kaolinite transforms into metakaolin, a complex amorphous structure that retains some long-range order due to layer stacking, as shown in Fig. 2 [12].

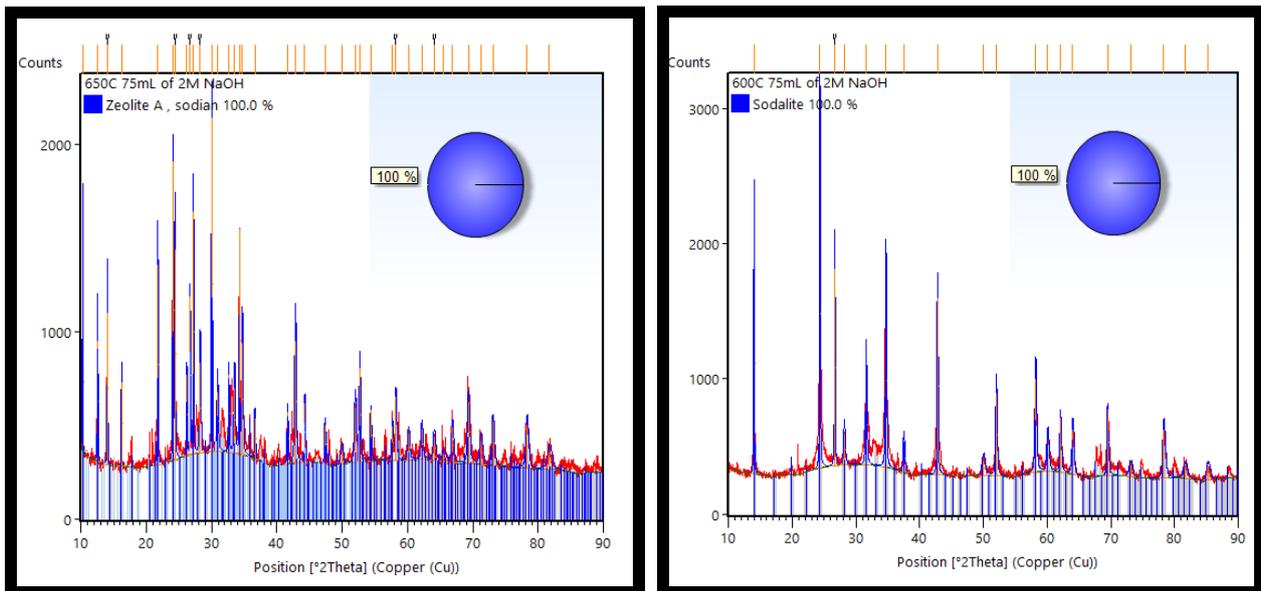


**Fig. 2** (a) Initially layered structure of kaolinite, (b) Dehydroxylation mechanism of kaolin(kaolinite) to metakaolin via calcination [12]

The removal of hydroxyl ions changes the physical and chemical properties of the material, making metakaolin more reactive and hydrophilic than kaolin [14,15]. Due to this condition, metakaolin will have an amorphous structure that may assist and benefit the next synthesizing process. Thus, further observation was conducted to determine the hydrophilicity effect of both metakaolins that were heated at different temperatures using FTIR by comparing the peak at  $3500\text{--}3000\text{ cm}^{-1}$ . As can be seen from Fig. 3, samples heated at a slightly higher temperature show a slightly broader and deeper peak, indicating a strong hydrophilicity property as compared to metakaolin heated at a lower temperature. This may be due to the uncompleted transformation of kaolin to metakaolin that is able to affect the hydrophilicity property, resulting in the formation of a slightly lower peak of existence.



**Fig. 3** FTIR of metakaolin powder fused at 600 °C and 650 °C respectively



**Fig. 4** XRD pattern for synthesized zeolite from metakaolin heated at 600 °C and 650 °C

As shown in Fig. 4, the effect of the calcination temperature of metakaolin seems to have slightly influenced the effect of final zeolite formation. As expected, the incomplete transformation of metakaolin leads to the formation of the undesired dense zeolite structure. Meanwhile, the metakaolin heated at a slightly higher temperature showed complete transformation to the desired mesoporous structure of zeolite A. This is probably due to the effect of the existence of impurities that easily disturb the formation of the zeolite mesoporous structure, as reported previously [16]. As reported previously, the transformation of quartz metakaolin to zeolite involves the polymerization of an aluminosilicate structure that initially took the form of an amorphous phase. This polymerization process will lead to zeolite structure formation as well as the growth of zeolite structure, as shown in Fig. 5 [10,13,17].



**Fig. 5** The polymerization of aluminosilicate layer to the final zeolite structure

#### 4. Conclusion

In this present work, the effect of calcination temperature was obviously affected by the final zeolite formation. The effect of a slightly different temperature range within the appropriate calcination temperature of kaolin has resulted in a different zeolite formation. As natural kaolin consists of various compositions such as silica, alumina, and others, the selection of an appropriate calcination temperature may also vary. As proven in this work, with a slightly higher temperature of calcination, it was revealed that the complete transformation of kaolin to amorphous metakaolin has resulted in better zeolite formation, which may be due to the complete formation of hydrated aluminosilicate structure as well as a better reduction of impurities effect.

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#### Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

#### Author Contribution

The authors confirm contribution to the paper as follows: **study conception and design:** Zawati Harun, Norsuhailizah Sazali; **data collection:** Faiz Hafeez Azhar, Anuar Ismail; **analysis and interpretation of results:** Rosniza Hussin, Zakiah Kamdi, Ainun Rahmahwati Ainuddin, Muhamad Zaini Yunos; **draft manuscript preparation:** Faiz Hafeez Azhar, Wan Nur Farah Atikah Hanafi. All authors reviewed the results and approved the final version of the manuscript.

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