# Synthesis and characterization of mesoporous NaY zeolite from natural Blitar's kaolin

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# Synthesis and characterization of mesoporous NaY zeolite from natural Blitar's kaolin

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**Abstract**. Mesoporous NaY Zeolite has been synthesized from calcined natural Blitar's kaolin with the addition of NaOH and CTABr surfactant as mesoporous template by hydrothermal method. Natural kaolin was calcinated with different time and temperature to change kaolin to metakaolin. X-ray diffraction data showed that mesoporous NaY zeolite was formed with impurities compound of sodalite, kaolin and quartz phases. The BET analysis resulted that the pore of NaY Zeolite belongs to mesoporous type with pore size 9,421 nm. Characterization from FTIR confirmed about the functional group of zeolites (988, 776, 663, 464 $cm^{-1}$). Scanning electron microscopy characterization showed that the morphological of mesoporous NaY zeolites have uniform and crystalline particles formed.

## 1. Introduction

NaY zeolite is a material with regular architecture and micropores consist of cavities and channels [1]. Mesoporous NaY with larger specific surface area than micropores NaY zeolite has a wider application as catalyst [2,3], adsorption [4,5] and drug delivery system [6]. Mesoporous NaY zeolites can be synthesized using high-purity chemical reagent, but its relatively high cost. Natural Kaolin is an alternative raw material for low cost synthesis of mesoporous zeolite. This raw material is very cheap and exist abundantly in many areas in Indonesia, such as in Blitar. Kaolin is often used as the raw material for synthesis of low-silica zeolite such as zeolite X [7], zeolite P [8] and zeolite A [9,10], because the contents of $SiO_2$ and $Al_2O_3$ are relatively similar with the product. Zeolite with a higher Si/Al ratios, such as zeolit Y, can also be prepared using kaolin with additional sodium silicate solution [11,12] to increase the silica content. However, Blitar's kaolin has a high silica content, so the synthesis of zeolite NaY can be carried out from Blitar's kaolin without the addition of silica thus can lowering the zeolite production cost.

The synthesis of mesoporous NaY zeolites from natural kaolin involves two basics principle steps: (a) the conversion of kaolin to metakaolin with calcinations at high temperature to increase the reactivity of kaolin in the metastable phase [10, 13, 14, 15] and (b) the reaction of calcined kaolin with sodium hydroxide and surfactants in conventional hydrothermal method. The addition of surfactants serving as mesoporous templates. In this study, mesoporous NaY zeolite synthesized from Blitar's kaolin without the addition of silica by hydrothermal method using cationic surfactants of Cethyl Trimethyl Ammonium Bromide (CTABr) as mesoporous template.

## 2. Experimental

Kaolin was prepared by washing HCl 1M and calcination at 630 ˚C, 700 ˚C and 800 ˚C. The calcined kaolin reacted with aluminum oxide and sodium hydroxide at molar ratio $9Na_2O$: 2 $Al_2O_3$: $6SiO_2$: 249 $H_2O$. The mixture was stirred for 24 h and added by 18.73 g of CTABr. Stirring process continued until gel formed and aged at room temperature for 24 hours, then transferred into a hydrothermal reactor at 100 ° C for 48 hours. The obtained powder filtered, washed, dried and calcined at 550 ºC for 1 h.

Characterization of synthesized material were determined for the functional group, elemental analysis, structure, morphologycal characteristics and surface area using Fourier Transform Infra-Red (FT-IR), X-ray fluorescence (XRF), X-ray powder diffraction (XRD), Scanning Electron Microscopy (SEM) and BET analysis.

## 3. Result And Discussion

The element contents of Blitar's kaolin are given in Tabel 1. The Si/Al rasio found to be 5.45 and after washing HCl increased to 8.55. The other metals percentage decreased after washing with HCl.

**Table 1**. The element content of Blitar's kaolin

| Element | before washing HCl (%) | after washing HCl(%) |
|---|---|---|
| Al | 12 | 8.8 |
| Si | 65.4 | 75.2 |
| K | 8 | 5.83 |
| Ca | 2.68 | 2.38 |
| Ti | 3.68 | 3.18 |
| V | 0.08 | 0.06 |
| Mn | 0.22 | 0.19 |
| Fe | 8.61 | 2.50 |
| Ni | 0.19 | 1.11 |
| Cu | 0.12 | 0.18 |
| Eu | 0.11 | 0.05 |

Figure 1 shows the XRD pattern of Blitar's kaolin and calcined kaolin. The Blitar's kaolin in Figure 1 (c) contains kaolin structure and high impurities of quartz phase. Further calcinations until 800 ˚C for 24 hours did not show any significant differences in quartz content. It was previously reported that the major impurities in natural kaolin is the high content of quartz which can be removed by further alkali fusion treatment [16,17]. In this research, natural kaolin was only calcinated as physical treatment without additional treatment by alkali fusion, so the content of quartz was still high. The stucture of synthesized zeolite material show in Figure 2 indicated that crystalline stucture of NaY zeolite has been successfully synthesized according to IZA literature with some impurities were detected for sodalite, kaolin phase and quartz phase. The sodalite [16] and quartz phase [17] has reported as known impurities in zeolite which was synthesized from natural kaolin. The presence of impurities may caused by incompletely transformation of natural kaolin into metakaolin phase during physical treatment.

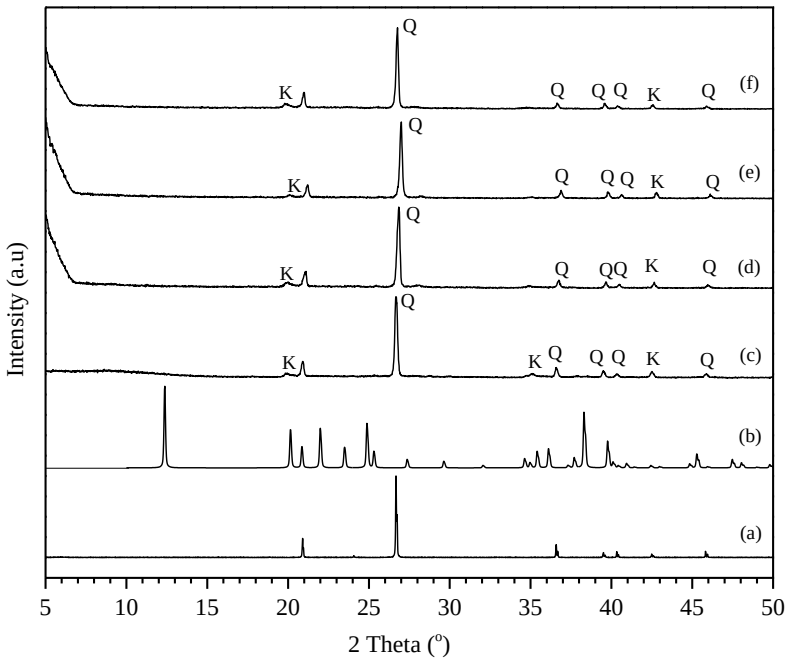


**Figure 1**. XRD pattern of quartz standard (ICPDS) (a), kaolin standard (ICPDS) (b), Blitar's kaolin (c), calcined kaolin 630 °C 3 h (d), calcined kaolin 700 °C 3 h (e), calcined kaolin 800 °C, 24 h (f). Peaks marked with letter are: Q- quartz, K-kaolin.

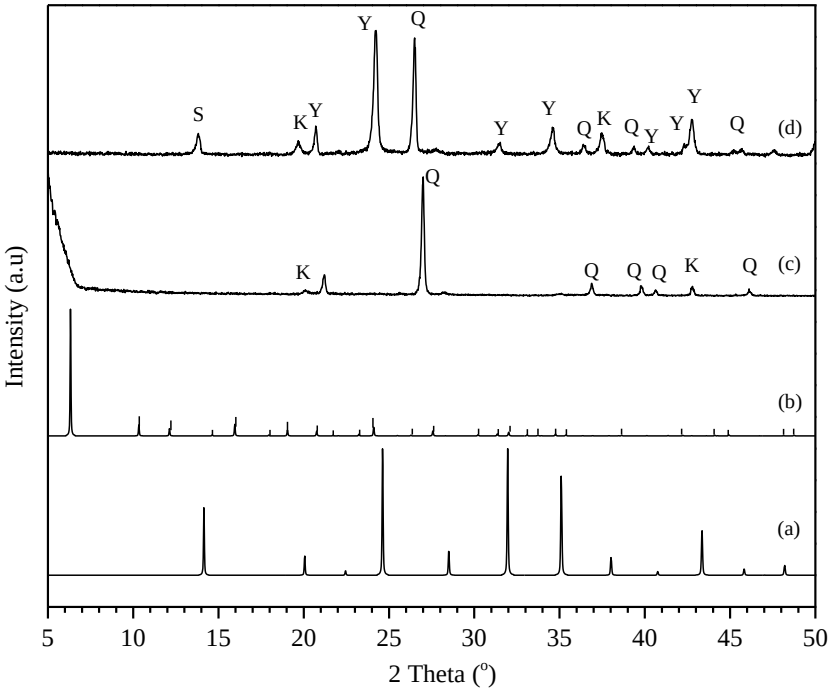


**Figure 2**. XRD pattern of sodalit standard (IZA) (a), zeolit Y standard (IZA) (b), calcined kaolin 700 °C 3 h (c), Mesoporous NaY zeolite by conventional hydrothermal (d). Peaks marked with letters are: Q- quartz, K-kaolin, S-sodalit, Y-NaY zeolite

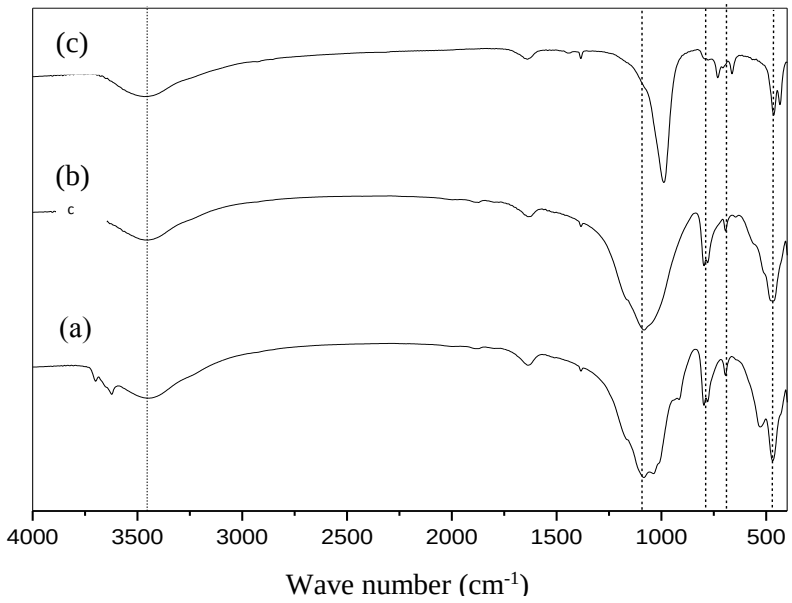


**Figure 3.** FTIR spectra of Blitar's kaolin (a), Calcined kaolin 700 °C for 3 h (b) Mesoporous NaY zeolite by conventional hydrothermal (c)

The transformation from kaolin to metakaolin (calcined kaolin) and NaY zeolite can be analyzed from its functional group by infrared spectroscopy in Figure 3. Blitar's kaolin showed characteristic bands at 3623 $cm^{-1}$ which is assigned as stetching vibration of –OH and at 529 assigned as vibrations Al-O in octahedral alumina structure. The bands at 1037.811 $cm^{-1}$ is assigned as stretched vibrations of Si-O, while the bands at 796 $cm^{-1}$ is assigned as vibrations of O-Si-O, and the bands at 468 $cm^{-1}$ is assigned as bending vibrations Si-O. The bands at 3623 $cm^{-1}$ and 529 $cm^{-1}$ were dissapeared for the calcined kaolin spectra in Figure 3(b). Its indicated that octahedral alumina structure of kaolin was destroyed during calcination step. The spectra of NaY zeolite in Figure 3(c) contains new vibration bands at 988 $cm^{-1}$ assigned to the characteristics vibration of $SiO_4$ or $AlO_4$ tetrahedral units in zeolite structure. Thus can be concluded that synthesis product was zeolite material.

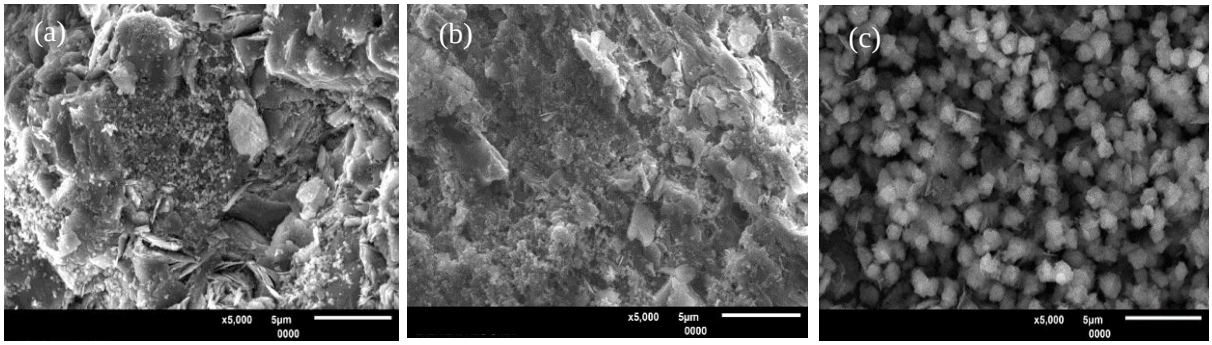


**Figure 4.** SEM morphologies of Blitar's kaolin (a), Calcined kaolin 700 °C for 3 h (b), Mesoporous NaY zeolite by conventional hydrothermal (c).

Figure 4 showed the morphological transformation of kaolin, calcined kaolin and NaY zeolite. Figure 4 (a) showed that the kaolin morphology is a coated sheet while the calcined kaolin in Figure 4(b) showed a damaged layered sheets (began to form amorphous). NaY zeolites in Figure 6 (c) shows the uniform morphology which is indicated that crystalline particles of zeolite has formed from natural kaolin as raw material.

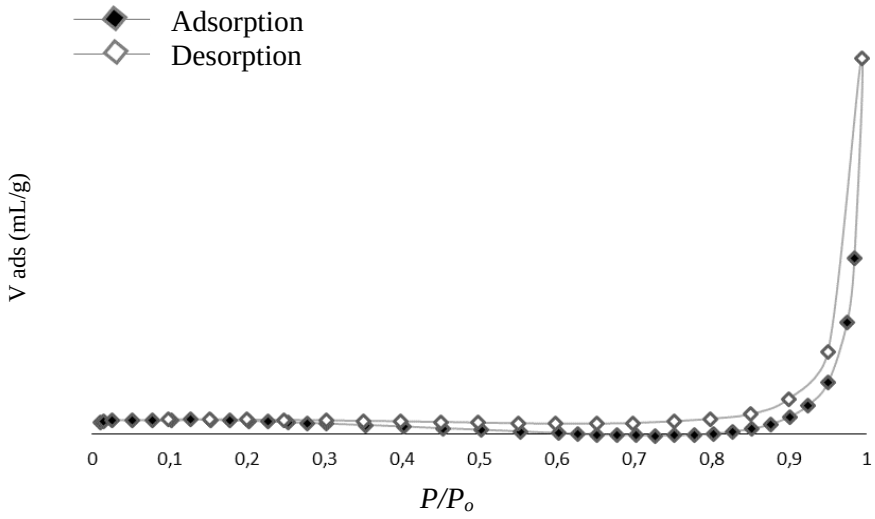


**Figure 5**. $N_2$ adsorption-desorption isotherm of mesoporous NaY zeolite

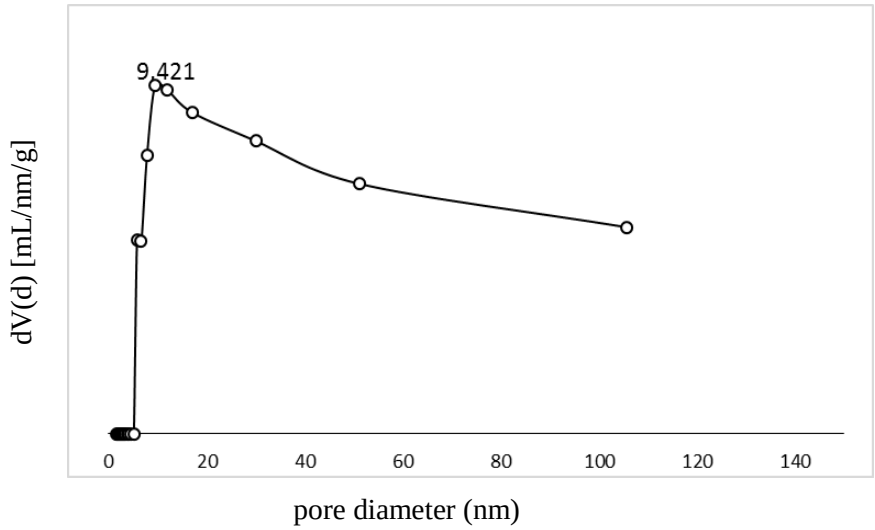


**Figure 6.** BJH pore size of mesoporous NaY zeolite

Figure 5 showed the $N_2$ adsorption-desorption isotherm of NaY zeolite. The NaY zeolite exhibited the type IV curve with H3-type hysteresis loop which indicated as mesoporous zeolite. The Brunauer-Emmett-Teller ($S_{BET}$) of the synthesized mesoporous NaY zeolite was measured to be 434.2 $m^2/g$. This result showed significant enhancement of specific surface area than the Blitar's kaolin which only has $S_{BET}$ 16,16 $m^2/g$. However this result is still lower than commercial NaY zeolite ($S_{BET}$ 626 $m^2/g$) [18] which may contributed by incompletely transformation of the raw material. The mesopore size according to Barrett-Joyner-Halenda (BJH) algorithm in Figure 6 showed the pore diameter of mesoporous NaY zeolite is 9.421 nm. This pore diameter was larger than the pore of raw material for Blitar's kaolin which is 1,72 nm.

## 4. Conclusion

Mesoporous NaY zeolite has been successfully synthesized from Blitar's kaolin with sodalite, quartz and kaolin impurities. The NaY zeolite has uniform morphology and crystalline particle with the vibration of $SiO_4$ or $AlO_4$ tetrahedral units detected at 988 $cm^{-1}$. The synthesized zeolite was the mesoporous material with type IV of isotherm curve, 434.2 $m^2/g$ of surface area and 9.421 nm of pore diameter.

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