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To cite this article: S K Wahono *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **251** 012009

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Transformation of Mordenite-Clinoptilolite Natural Zeolite at Different Calcination Temperatures

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Abstract. Natural zeolite is one of prospective material with various applications. The material has low-cost provisioning and abundant availability in the world. Mordenite-clinoptilolite is one of the common types of natural zeolite; one of the deposits are located in Gunungkidul, Yogyakarta, Indonesia. For optimizing the utilization, some treatment is needed, calcination being one of the possible treatments. The dealuminated natural zeolite was used as the base material for understanding the transformation effect, then calcinated the zeolite in various temperature range between 400 °C and 1000 °C. Some characterization was conducted after the treatment, such as XRD, SEM-EDX, and BET to explore the structure, morphology, composition, and specific surface area. Drastic structure changes were demonstrated at the calcination of 1000 °C which eliminating the zeolite structure into cristobalite as one of the silica structures. The specific surface area decreased after 600 °C, even elapsed after the structure change. Calcination has the ability to transform the zeolite structures and also affected the specific surface area properties. This transformation provides critical information for further application of natural zeolite in the various treatment of calcination.

Keywords: natural zeolite, mordenite-clinoptilolite, calcination, crystal structure, specific surface area

1. Introduction

Zeolites are one of the essential materials used in various applications such as catalyst, adsorbent and porous carrier material. It is available as a natural resource and synthetic structures from manufacturing of alumina and silica. The synthetic products provide uniform structures and purity of phases but have some drawback of complex processing, waste production, and high-cost. In comparison, natural zeolites are available in an abundant quantity which spread out over the world [1-3] and low-cost production [4]. Utilization of the natural zeolite resources is needed to overcome the drawback of synthetic product.

Indonesia has abundant natural zeolites with the high silica concentration of around 60% [5], which are found in various areas, one specific location being Gunungkidul, Yogyakarta [6, 7]. Indonesian natural zeolite is categorized as mordenite and clinoptilolite [3, 8, 9]. By activation and



modification, this natural zeolite has good properties of Si/Al ratio, surface area, crystallinity, and functional groups [10-12]. It provides several prospective applications such as in catalyst [5, 13-15], wastewater treatment [16-19], radioactive waste treatment [20, 21], drug delivery [22], bio-ethanol dehydration [10, 11, 23], and biogas purification [7, 24-26].

The various applications of natural zeolites provide room for improvement by activation and modification. One of the standard treatments for the natural zeolite is calcination which is conducted to remove water and impurity gases that are trapped in the crystal pores. This treatment also affects the natural zeolite properties of crystallinity, surface area and porosity [21, 27-31]. Therefore, this study is conducted to understand the characteristic transformation of mordenite-clinoptilolite natural zeolite at different temperatures of calcination.

2. Methods

2.1. Natural Zeolite Modification

CV Mountain Stones supplied Mordenite-Clinoptilolite Natural Zeolite from Gunungkidul, Yogyakarta, Indonesia. It was supplied in powder size of under 40 mesh (425 microns) which is assigned as A0 zeolite in further. A0 zeolite was dealuminated by submerging in 3N HCl (Merck with purity of 37-38%) with a volume ratio of 1:1 for 24 hours which assigned in further as CT1-0 zeolite as the base material. The material was washed and calcinated at a different temperature of 400, 600, 800, and 1000 °C for 3 hours which assigned further as CT1, CT2, CT3, and CT4 zeolite, respectively.

2.2. Natural Zeolite Characterization

For understanding the structural transformation caused by these treatments, the initial characterization of the crystal structure is the XRD analysis. The supporting study of the specific surface area, Si/Al ratio and morphology were conducted to complement the structure transformation results. All of the investigations were performed on all of the modified and pristine natural zeolites. PANalytical Empyrean XRD determined the crystal structure analysis in high angle analysis of 5° – 80° and the scan rate of 0.02 °/sec. The type of crystal was assessed using the High Score Plus Software which complementing the XRD instrument by the Search-Match method.

Micromeritics ASAP 2420 analyzer was utilized to determine the specific surface area (Brunauer–Emmett–Teller/BET Model) and porosity (Barrett-Joyner-Halenda/BJH Model) which carried out in isotherm nitrogen adsorption-desorption at -196 °C. For pre-analysis treatment, the samples were degassed at 350 °C for 24 hours for cleaning the pores from water and impurities [32, 33]. Particularly for non-calcination treatment, the degassing treatment was conducted at 120 °C for removing the water only.

The SEM-EDX analysis was carried out on the powder material analysis for morphology observation and Si/Al ratio determination by the Hitachi SU3500 which equipped with EDX analyzer by EDAX Element. As sample preparation, the sample was dried then a small quantity of powder was splashed on the carbon tape surface. For EDX analysis, the minimum voltage acceleration requirement was set to 3 kV then adjusted with the material conductivity.

3. Results and Discussions

3.1. Mordenite-Clinoptilolite Natural Zeolite from Gunungkidul, Yogyakarta-Indonesia

First, characterizations of crystal structure, surface area and porosity, morphology and Si/Al ratio was carried out to the pristine natural zeolite. The crystal structure of this natural zeolite is implied as mordenite-clinoptilolite and is supported in published studies [3, 8, 9, 26]. Figure 1 shows the calcite peak between 30-60°, whereas the mordenite-clinoptilolite or the zeolite structure between 10-30° which is supported by the search match analysis shown in table 1. The specific surface area of the pristine natural zeolite is 25.95 m²/g as shown in Table 2. It is consistent with published studies of natural zeolite which report surface area between 14-30 m²/g [10, 34-36]. The morphology of the pristine natural zeolite is shown in figure 2.a which indicates as the porous material. The Si/Al ratio of the pristine natural zeolite was 4.4 as shown in table 3.

3.2. Crystal structure transformation of mordenite-clinoptilolite natural zeolite

Figure 1 and table 1 show the results of XRD analysis of the natural zeolite crystal structure transformation as a result of high-temperature calcination. The 400 °C was selected as the starting calcination temperature since the organic compound decomposition still occurs under that temperature [32, 37]. Moreover, this temperature was referred to the previous study of the calcination treatment of this natural zeolite which using 400 °C for biogas purification [7, 38].

Figure 1 shows the graph of XRD transformation of the pristine natural zeolite into the dealuminated natural zeolite, then into various high temperatures treatment of calcination. The calcite is visible in the spectrum of the pristine material (A0) and showed a lower peak intensity between 30°-60° in the spectrum of the dealuminated natural zeolite (CT1-0). After calcination of the CT1-CT4, the calcite elapsed and transformed into anorthite (calcium silicate structure) which indicates an interaction between calcium and silica during the treatment.

On the other hand, the zeolite structure remains without transformation. The substantial change of zeolite occurs at CT4 which shows the appearance of a high peak at 21° and the loss of peaks between 10-30° as the zeolite structure indicator in the previous material treatment. The combination of various peaks transformation indicates the shifting of zeolite structure into cristobalite structure as the solid silica structure.

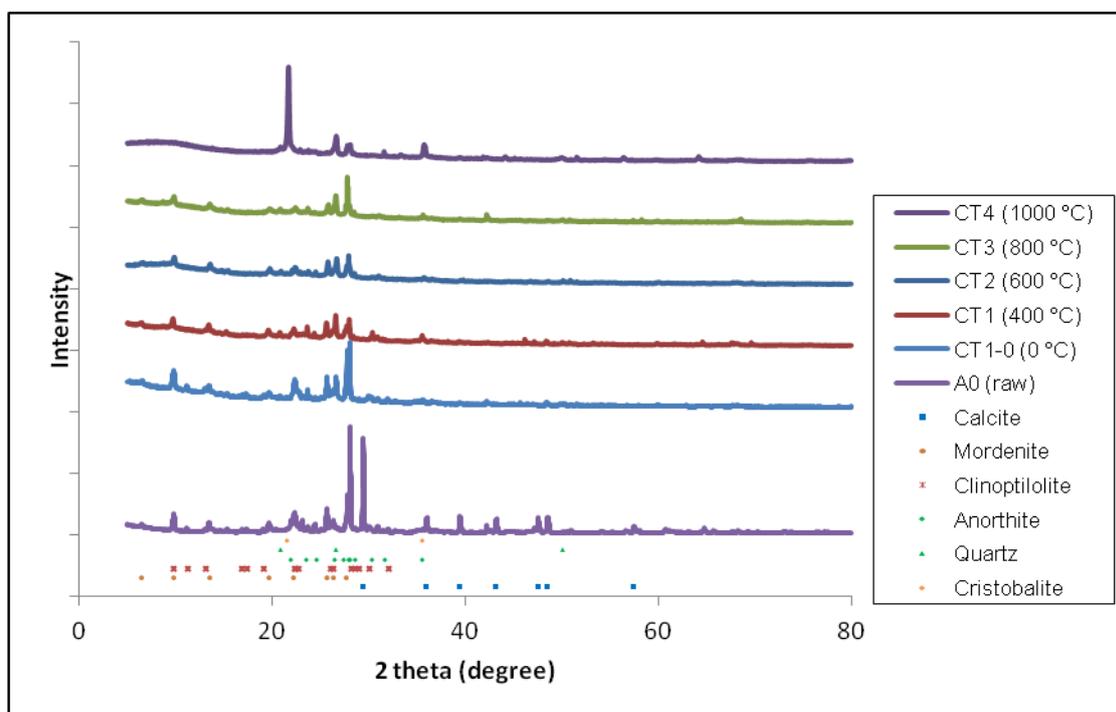


Figure 1. XRD graph of mordenite-clinoptilolite natural zeolite in various treatments

The structural changes are also supported by further analysis using the search-match method from High Score plus software shown in table 1. The match score of the crystal structure in table 1 shows the calcite and zeolite structure in the pristine natural zeolite. The calcium crystal changes after calcination in CT1-CT4, while a zeolite structure change indicates only CT4.

Detail information can be obtained from this search-match analysis about the existence of the quartz structure and the decreasing match score of clinoptilolite and anorthite. The quartz structure pulls out after dealumination treatment and in the further calcination treatment, even increase the match score after calcination. This result indicates that the treatments remove some mineral interaction with silica on the natural structure since the acid reaction or the high-temperature heating, then purifying the silica or quartz structure. CT1-CT4 also shows the decreasing match score of the clinoptilolite and anorthite. It indicates that the high temperature destructs both crystal structure. Moreover, the results also show the mordenite and quartz structure do not affect by high-temperature treatment.

Table 1. Crystal structure match score of mordenite-clinoptilolite natural zeolite in various treatments

Code	A0	CT1-0	CT1	CT2	CT3	CT4
Temp. (°C)	0	0	400	600	800	1000
Structure	Match Score					
Calcite	63	56	-	-	-	-
Mordenite	48	51	52	54	52	-
Clinoptilolite	31	26	21	21	17	-
Anorthite	-	-	37	30	25	25
Quartz	-	41	51	59	53	55
Cristobalite	-	-	-	-	-	51

3.3. Surface area and porosity transformation of mordenite-clinoptilolite natural zeolite

Table 2 shows the change in surface area and porosity properties of the various high-temperature calcination treatment of mordenite-clinoptilolite natural zeolite. Calcination treatments effect on the surface area and porosity as one of the aims of calcination, mainly to clean the pores from the impurities [21, 27-31]. This function is appointed at CT1 and CT2 zeolite which increase the surface area until four times from the pristine. Although it is less than the surface area of CT1-0 as the dealumination treatment only, the anorthite structure which presented after calcination is more stable in heating temperature than calcite as mentioned in previous discussion part.

However, the high-temperature calcination does not always produce improvement in the surface area and porosity, especially at too high temperatures. CT3 and CT4 displayed these conditions; even the CT4 shows the lost porosity. It indicates that the material converts from porous material into a solid or compact material which destructs the pore [29, 31]. This condition is supported by the published studies of zeolite calcination treatment above 500 °C which state that the zeolite change into siliceous phase (quartz or cristobalite) or a compact aluminosilicate (labradorite) or amorphous crystal [39-44].

Table 2. Surface area and porosity of mordenite-clinoptilolite natural zeolite in various treatment

Code	Calcination Temperature (°C)	Specific Surface Area (m ² /g)	Pore Volume (x 10 ⁻² cm ³ /g)	Average Pore Size (nm)
A0	0	25.95	5.31	8.18
CT1-0	0	146.91	10.97	2.99
CT1	400	103.82	8.87	3.42
CT2	600	107.95	9.40	3.48
CT3	800	35.27	6.22	7.05
CT4	1000	0.61	0.18	11.52

3.4. Morphology and Si/Al ratio transformation of mordenite-clinoptilolite natural zeolite

The morphology and Si/Al ratio were determined by SEM-EDX which shown the results in figure 2 and table 3 respectively. For the morphology, the various treatments of mordenite-clinoptilolite natural zeolite do not provide the extraordinary change from the SEM results, except for the figure 2.f (CT4 zeolite) as the most considerable transformation. The morphology of CT4 zeolite shows the melting structure configures the compact structure which is different from others morphology. This condition is supported by the XRD result on the previous section about CT4 properties that the new crystal structure of cristobalite constructs and the loss of surface area after the calcination of 1000 °C.

For the Si/Al ratio, the different value finds in the pristine natural zeolite only (A0 zeolite). After the dealumination, Si/Al ratio increases up to 7.1 for the base material (CT1-0 zeolite) which indicates the effectiveness of Al removal. The calcination in various high temperatures provides the similar Si/Al ratio value between 6.3-6.9. These ratio values close to the ratio of the base material and indicate no effect of calcination which supported the previous studies [45, 46].

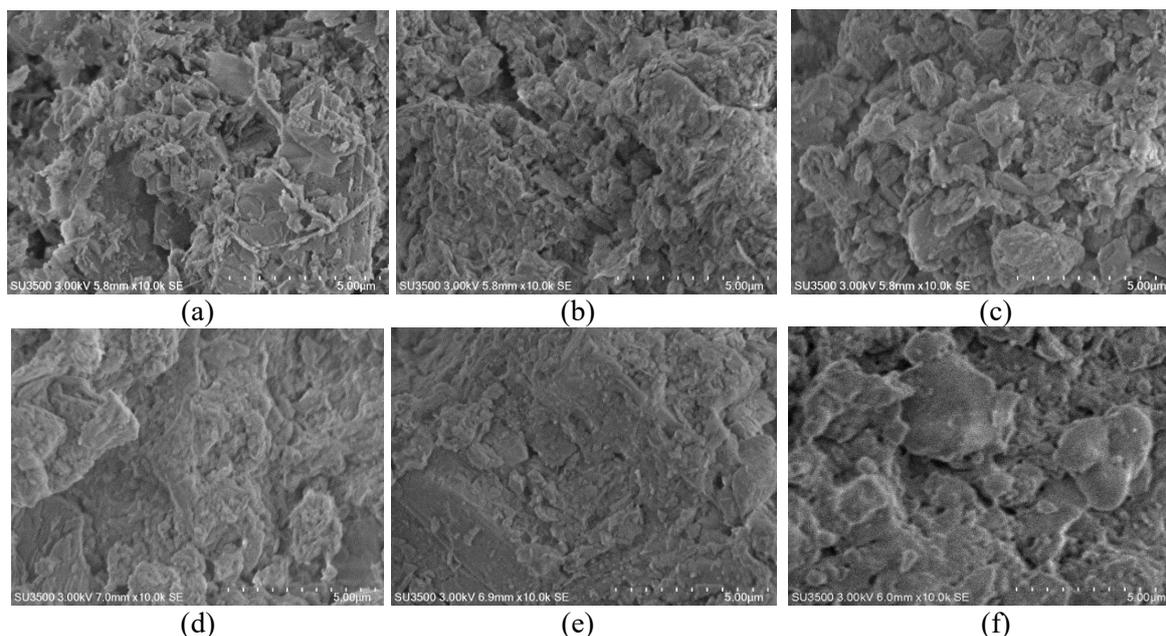


Figure 2. The morphology of mordenite-clinoptilolite natural zeolite in various treatments: (a) A0 zeolite; (b) CT1-0 zeolite; (c) CT1 zeolite; (d) CT2 zeolite; (e) CT3 zeolite; (f) CT4 zeolite

Table 3. Si/Al ratio of mordenite-clinoptilolite natural zeolite in various treatments

Code	A0	CT1-0	CT1	CT2	CT3	CT4
Si/Al ratio	4.6	7.1	6.4	6.3	6.9	6.7

4. Conclusions

In this work, transformational changes in the mordenite-clinoptilolite zeolite, as one of the typical structure of natural zeolite, were carried out. The characterization of mordenite-clinoptilolite natural zeolite at different temperatures of calcination demonstrates the primary effect on the crystal structure and surface area, particularly in the high temperature of above 600 °C. The calcium crystal transforms from calcite into anorthite, while the zeolite crystal transforms from mordenite-clinoptilolite into cristobalite. The crystal transformation into cristobalite destructs the pores of the structure which is also detected in the morphological characterization. However, the Si/Al ratio did not change much with an increase of the calcination temperature. The results of this study guide the appropriate calcination temperature treatments of mordenite-clinoptilolite natural zeolite to enhance its properties for applications in various fields.

5. Acknowledgment

The authors would like to acknowledge the scholarship support from Riset-PRO Project, Ministry of Research, Technology and Higher Education, Republic of Indonesia; also for the research facilities support from Future Industries Institute-School of Engineering, Div. ITEE, University of South Australia and BPTBA LIPI-Indonesia.

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