WCEJ

WORLD CHEMICAL ENGINEERING JOURNAL

Journal homepage: http://jurnal.untirta.ac.id/index.php/WCEJ

# Transformation of Natural Zeolites by the Fusion-Hydrothermal Method for Ammonium Adsorption

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*ARTICLE HISTORY*

Received 16 June 2023
Received in revised form 25 June 2023
Accepted 26 June 2023
Available online 30 June 2023

*ABSTRACT*

Zeolite application as an ammonium adsorbent has been widely studied. However, there is no previous research on transformation of Malang natural zeolite and its application as ammonium adsorbent. In this study, characterization of the zeolite was carried out by XRD, XRF, nitrogen adsorption-desorption, SEM and FTIR tests. With the addition of 18 g of NaOH and heated with temperature of 550 $^0$C for 2 h during the fusion, continued with aging for 18 h and temperature 100 $^0$C during hydrothermal stage, the fusion-hydrothermal method had transformed Malang natural zeolite which dominated by quartz and small amount of mordenite into transformed zeolite dominated by zeolite X. Malang natural zeolite best fitted the Elovich adsorption kinetics model with $\alpha$ 0.0096 and ß 11.93 and SSE 0.003 and Langmuir isotherm model with $q_{max}$ 32.38 mg/g and $K_L$ 0.01 L/mg with SSE 0.27, while the transformed zeolite best fitted the Intraparticle diffusion model with $k_i$ 0.0084 and C 0.017 with SSE 0.006 and Freundlich isotherm model with $K_F$ 0.00035 $L^{2.56}/(mg^{1.56}/g)$ and n 0.39 with SSE 1.17. Fusion-hydrothermal has changed the crystal shape from mostly the broken needle shape to round cube shapes, decreased the Si/Al ratio from 5.56 to 1.15, and increased the surface area from 43.5 $m^2/g$ to 89.8 $m^2/g$.

**Keywords:** *Ammonium, Fusion-hydrothermal, Malang natural zeolite, Transformation*

## 1. INTRODUCTION

Zeolites are rocky minerals those are composed of clusters of $Al_2O_3$ and $SiO_2$ which are tetrahedrally bound (Ngapa, 2016). These tetrahedral structures form cavities that, in nature, contain water and alkali metal or alkaline metal ions (Gougazeh et al., 2014). The porous structure gives zeolite an advantage as ion or molecular adsorbent. Ions or molecules that are fit with the zeolite cavity and zeolite composition could be diffused and distributed throughout the zeolite cavity system (Sumarlin et al., 2008).

Zeolite is available naturally and synthetically. Natural zeolite tends to have varied crystallinity and pore size, low catalytic activity, high Si/Al ratio and high impurities (Chaikittisilp et al., 2014). These factors overall reduce the application of natural zeolite (Wang et al., 2009). On the other hand, synthetic zeolite that made through controlled process have high crystallinity, less impurities, and high catalytic activity. However, the availability of the synthetic zeolite is not as abundant as the natural one (Syafi'i et al., 2011). Hence, methods developed to improve the natural zeolite characteristic to resembled with the synthetic zeolite. One of the methods is the hydrothermal transformation, which claimed to have increase the adsorption capacity of zeolite significantly compared to simple physics or chemical treatment (Ngapa, 2016).

One of the potential natural zeolite mining areas located in Malang, East Java, Indonesia. This research was intended to study the characterization along with the adsorption kinetic and isotherm of fusion-hydrothermal-transformed Malang natural zeolite.

## 2. MATERIALS AND METHODS

Parent sample, labelled as ZA, was the grinded Malang natural zeolite 80-100 mesh. 7.5 g of the parent sample then added to each 6, 12 and 18 g of powder NaOH. The mixture then heated to 550 $^0$C for 2 hours in a furnace. The fusion then labelled as Z6, Z12 and Z18. The fusions then manual grinded and sifted to get another 80-100 mesh of fused zeolite. Aging process conducted for 18 hours at room temperature after fused samples mixed with 75 ml aquadest. Hydrothermal process was done by heating the aged samples up to 100 $^0$C in an autoclave for 24 hours. The products then rinsed with aquadest until pH neutral and heated up to 100 $^0$C in an oven to dry for 16 hours. The dry products of the fusion-hydrothermal transformation then tested for characterization of XRD. The most potential transformed zeolite from the XRD result then characterized further with SEM, SEM-EDS, and BET Nitrogen Adsorption-Desorption Analysis.

Meanwhile, the adsorption kinetics study conducted by soaking 10 g of 80-100 mesh transformed zeolite in a 100 ppm ammonium solution in a batch reactor without stirring. Sample then taken in a predetermined time range (0.5, 1, 2, 4, 8, 12, 24, and 32 h) to be measured with colorimeter. On the other hand, adsorption isotherm study conducted by soaking various mass of 80-100 mesh transformed zeolite (0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 10 g) in an ammonium solution in a batch reactor without stirring. Sample then taken after 72 h to be measured with colorimeter.

## 3. RESULT AND DISCUSSIONS

Diffraction pattern on Figure. 1 shows that Malang natural zeolite mainly consist of crystalline phase of quartz (Q), with some peaks that show mordenite (M), and clinoptilolite (C) zeolites. Along with the addition of NaOH during fusion stage, the quartz peaks gradually decreased without significant effect on the innate zeolite peaks. On the Z18, it shows that new peaks grow that indicates Faujasite family type of zeolites. After matching the XRD pattern with Match software, it was discovered that the Faujasite zeolite was zeolite X. Peaks on Figure. 1 were identified based on Collection of Simulated XRD Powder Patterns for Zeolites (Treacy et al., 2007).

Figure. 2A shows SEM image of Malang natural zeolite. It shows mostly the broken needle shape which indicates mordenite crystal shape (Hussain et al., 2019). Figure. 2B shows SEM image of Z18 transformed zeolite. Some round cube shapes were identified on the image. It was identical to faujasite crystal shape. Apart from the shape, the Figure. 2B also shows crystal structure with more cavity than the Figure. 2A. Figure. 2B showed zeolite crystal assembled unevenly in such a way that left some cavities with size approximately 0.5 µm to 1 µm while Figure. 2A showed zeolite crystal gather almost evenly left no gap or small gap in size approximately less than 0.2 µm.

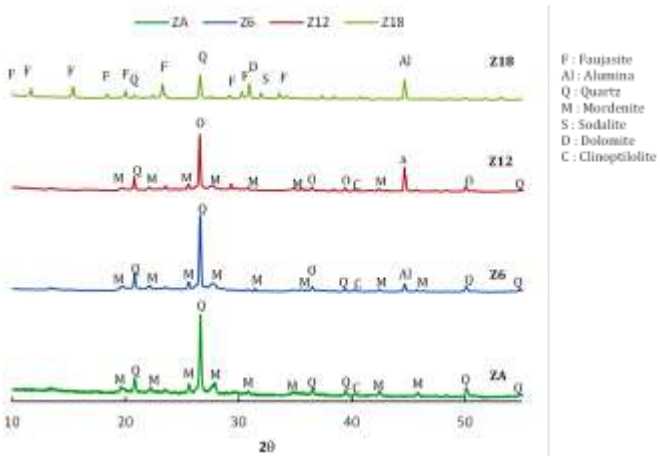
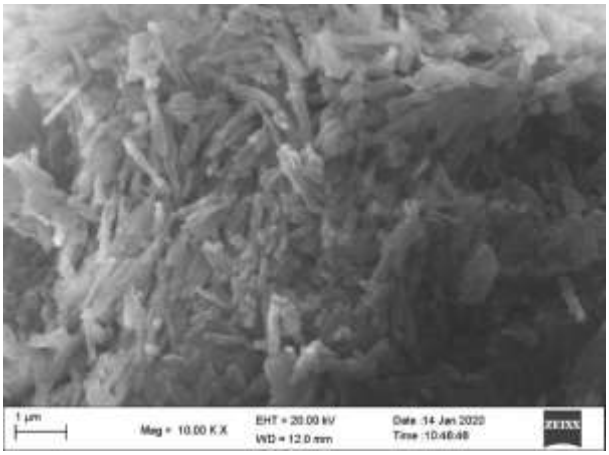
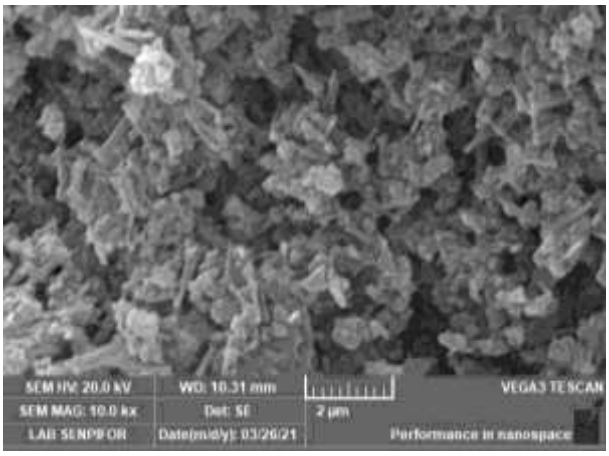



**Fig. 1.** XRD characterization of Malang natural zeolite and transformed zeolite



**(A)**




**(B)**

**Fig. 2.** Comparison of SEM image of (A) Malang natural zeolite (B) Z18 transformed zeolite.

Table. 1 shows the SEM EDS characterization comparison result of Malang natural zeolite and Z18. It shows that the Si/Al ratio was decreased from 5.56 on Malang natural zeolite to 1.15 on the transformed zeolite. This reduced Si/Al ratio also indicates that the transformed zeolite will affiliate with anion better than its parent zeolite.

**Table 1**. SEM EDS characterization comparison result of Malang natural zeolite and Z18 transformed zeolite

| Element | Normalized concentration % weight | |
|---|---|---|
| | Malang natural zeolite | Z18 transformed zeolite |
| Oxygen | 54.4 | 50.4 |
| Silicon | 31.7 | 16.1 |
| Sodium | 1.7 | 15.1 |
| Aluminium | 5.7 | 14.0 |
| Iron | | 2.0 |
| Calcium | 2.2 | 1.7 |
| Magnesium | 0.3 | 0.7 |
| Carbon | 3.7 | |
| Potassium | 0.3 | |

Source: laboratory analyzing

Figure. 3 shows comparison of nitrogen adsorption-desorption isotherm profiles and BJH desorption profiles of Malang natural zeolite and Z18 transformed zeolite. Both Figure. 3A and 3B show type IV nitrogen adsorption-desorption isotherm profiles based on IUPAC classification (Sing, 1982). This profile describes the mesopore characteristic of both zeolites. BJH desorption profiles showed on Figure. 3C and 3D also support the result that both zeolites are mesopore with most pore width between 30-50 Å. Based on previous study, mesopore width is between 20-500 Å (Sing, 1991).

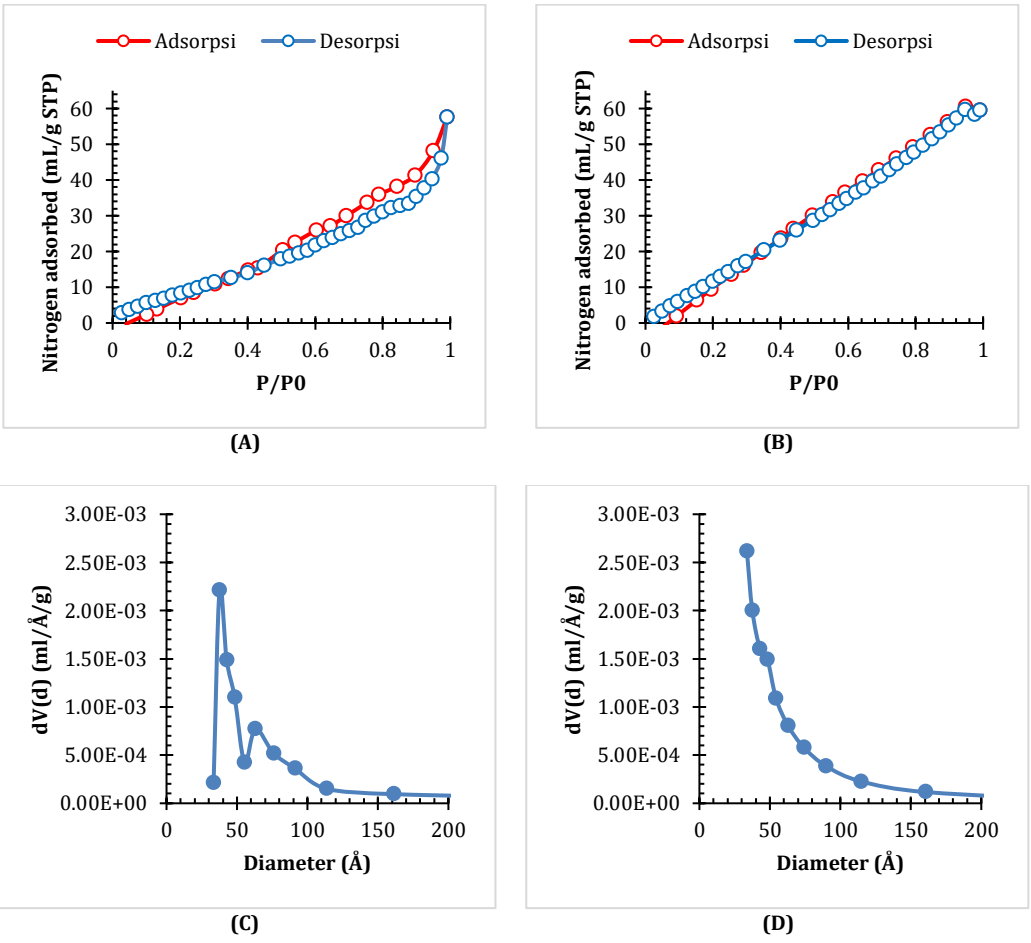



**Fig. 3.** Comparison of nitrogen adsorption-desorption characterization (A) Malang natural zeolite nitrogen adsorption-desorption isotherm profile (B) Z18 transformed zeolite nitrogen adsorption-desorption isotherm profile (C) Malang natural zeolite BJH desorption profile (D) Z18 transformed zeolite BJH desorption profile

Table. 2 shows numerical result of the BET nitrogen adsorption-desorption characterization. In general, Z18 transformed zeolite has increased its surface area compared to its parent natural zeolite. This surface area increase indicates that the Z18 transformed zeolites has better adsorption performance compared to its parent natural zeolite. On the other hand, the average pores diameter of the Z18 transformed zeolite was reduced compared to its parent natural zeolite. This result indicates that the transformed zeolites was more selective than its parent natural zeolite.

**Table 2.** Comparison of nitrogen adsorption-desorption characterization of Malang natural zeolite and Z18 transformed zeolite.

| Method | Parameter | Malang natural zeolite | Z18 transformed zeolite |
|---|---|---|---|
| BJH desorption | Surface area ($m^2/g$) | 46.0 | 57.2 |
| | Pore volume (ml/g) | 0.09 | 0.09 |
| | Average pores diameter (Å) | 37.7 | 33.7 |
| t-plot | Surface area ($m^2/g$) | 43.5 | 89.8 |
| Multi point BET | Surface area ($m^2/g$) | 43.5 | 89.8 |
| Area-Volume summary | Pore volume (ml/g) | 0.09 | 0.09 |
| | Average pores diameter (Å) | 81.9 | 41.1 |

Source: laboratory analyzing

Table. 3 shows specific parameters and Sum of Squared Error (SSE) of each of the adsorption kinetics model of both Malang natural zeolite and Z18 transformed zeolite. On the natural zeolite, Elovich model gives smallest SSE with 0.003. This model assumed that the adsorption rate decreases exponentially with the increase of the adsorbed solution. The matching of the adsorption kinetics profile with the Elovich model shows that the ammonium adsorption into the zeolite is chemisorption (William et al., 2018).

Meanwhile for the transformed zeolite, Diffusion Intraparticle model gives smallest SSE with 0.006. This model shows that there is a complex adsorption process of ammonium into the zeolite (William et al., 2018). This matching is in line with the BET characterization that shows that the zeolite pore become smaller.

**Table 3.** Ammonium adsorption kinetics parameters

| Kinetics model | Malang natural zeolite Parameter | | SSE | Z18 transformed zeolite Parameter | | SSE |
|---|---|---|---|---|---|---|
| Lagergren's first order | $k_L$ | $q_e$ [mg/g] | | $k_L$ | $q_e$ [mg/g] | |
| | 0.0078 | 0.39 | 0.011 | 0.00195 | 0.37 | 0.010 |
| Pseudo second order | $k_S$ | $q_e$ [mg/g] | | $k_S$ | $q_e$ [mg/g] | |
| | -0.02 | 0.44 | 0.004 | -0.0044 | 0.46 | 0.009 |
| Elovich | $\alpha$ | ß | | $\alpha$ | ß | |
| | 0.0096 | 11.93 | 0.003 | 0.0013 | 8.57 | 0.007 |
| Intraparticle diffusion | $k_i$ | C | | $k_i$ | C | |
| | 0.0081 | 0.125 | 0.013 | 0.0084 | 0.017 | 0.006 |

Source: MATLAB analyzing

Table. 4 shows specific parameters and Sum of Squared Error (SSE) of each of the adsorption isotherm model of both Malang natural zeolite and Z18 transformed zeolite. On Malang natural zeolite, the fittest model showed by Langmuir with SSE of 0.27. This shows that the adsorption mechanism was chemisorption, and the adsorption sites were homogenous.

Meanwhile, the fittest isotherm model for the transformed zeolite was Freundlich with SSE of 1.17. This shows that the adsorption sites were more heterogenous compared to the natural ones. This result also in line with the XRD characterization that shows the transformed zeolite mainly consist of zeolite X which has three-dimensional cage crystal. The matching with the Freundlich model also suggests that the transformed zeolite is rougher compared to the natural ones. This is also supported by the SEM images result.

**Table 4**. Ammonium adsorption isotherm parameters

| Isotherm model | Malang natural zeolite Parameter | | SSE |
|---|---|---|---|
| Langmuir | $q_{max}$ [mg/g] | $K_L$ [L/mg] | |
| | 32.38 | 0.01 | 0.27 |
| Freundlich | $K_F$ [$L^{0.93}.mg^{0.07}/g$] | n [-] | |
| | 0.30 | 1.07 | 0.28 |
| Temkin | B [mg/g] | $K_t$ [L/mg] | |
| | 2.00 | 0.41 | 0.39 |
| **Isotherm model** | **Z18 transformed zeolite Parameter** | | **SSE** |
| Langmuir | $q_{max}$ [mg/g] | $K_L$ [L/mg] | |
| | 1586.46 | 5.35x10-05 | 6.66 |
| Freundlich | $K_F$ [$L^{2.56}/(mg^{1.56}.g)$] | n [-] | |
| | 0.00035 | 0.39 | 1.17 |
| Temkin | B [mg/g] | $K_t$ [L/mg] | |
| | 3.76 | 0.068 | 2.72 |

## 4. CONCLUSION

With the addition of 18 g of NaOH and heated with temperature of 550 $^0$C for 2 h during the fusion, continued with aging for 18 hours and temperature 100 $^0$C during hydrothermal stage, the fusion-hydrothermal method had transformed Malang natural zeolite which dominated by quartz and small amount of mordenite into transformed zeolite dominated by zeolite X. Based on the characterization and the adsorption study, this transformation had improved the ammonium adsorption profile. Malang natural zeolite best fitted the Elovich adsorption kinetics model with $\alpha$ 0.0096 and ß 11.93 and SSE 0.003 and Langmuir isotherm model with $q_{max}$ 32.38 mg/g and $K_L$ 0.01 L/mg with SSE 0.27, while the transformed zeolite best fitted the Intraparticle diffusion model with $k_i$ 0.0084 and C 0.017 with SSE 0.006 and Freundlich isotherm model with $K_F$ 0.00035 $L^{2.56}/(mg^{1.56}/g)$ and n 0.39 with SSE 1.17. Fusion-hydrothermal has changed the crystal shape from mostly the broken needle shape to round cube shapes, decreased the Si/Al ratio from 5.56 to 1.15, and increased the surface area from 43.5 $m^2/g$ to 89.8 $m^2/g$.

## 5. ACKNOWLEDGMENTS

Author would like to thank DIKTI for funding the research through project number B/03/UN43.9/PT.00.03/2020 scheme of Penelitian Dasar Unggulan Perguruan Tinggi.

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