

Catalytic acetalization

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Catalytic acetalization of glycerol waste over alkali-treated natural clinoptilolite

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ABSTRACT

One of the most potential byproducts of transesterification that has been produced in a large amount is glycerol. Converting glycerol into Solketal via catalytic acetalization using natural zeolites is an interesting route to improve its economic value. Natural zeolites are abundant and inexpensive catalysts with low crystallinity and surface area. Thus, modification of its properties is required to improve material characteristics and alter the transesterification reaction. Investigation of the effect of NaOH concentration treatment on the Bayah natural zeolite was performed from 0.1 to 0.4 M NaOH at 65 °C and 30 min of mixing. Physical characteristic analysis, such as X-ray diffraction, proves that natural zeolite from Bayah was identified predominantly as clinoptilolite. The crystallinity significantly improved after NaOH treatment and could reach a high crystallinity material at 0.4 M NaOH. The textural properties using nitrogen physisorption are also shown by a high surface area of 164 m²/g (from parent Z-0.4; 19 m²/g). In addition, the mesopore volume also improved after alkali treatment, increasing the mass transfer of molecules. The application of modified natural zeolite for glycerol acetalization was tested in a glass tube reactor at a temperature of 50 °C for 90 min showing a significant alteration in conversion from 3.5 % (parent zeolite) to 90.4 % (modified zeolite).

1. Introduction

Indonesia has been implementing the policy of the Mandatory B30 Program, a blend of 30% biodiesel with 70% diesel oil, since January 2020. It makes Indonesia the first country to apply the B30. The biodiesel production in Indonesia was 9.4 million kilo liter in 2021. Commercially, biodiesel produces via transesterification with glycerol as the byproduct. The glycerol byproduct is approximately 10%-wt. from its total converted product. Hence glycerol production will surge as the glycerol supply increases, leading to the decreasing price of glycerol. Nonetheless, it is urged to valorize glycerol by converting it into higher-value chemical products.

The conversions of glycerol to chemicals could be performed by different routes such as acetalization, acetylation, dehydration, and oxidation with various products, i.e., Solketal, aromatics, acrolein, and

glycerol carbonate [1–3]. Among these reactions, only a few experiments have been done for the acetalization of glycerol to solketal. Solketal functions as a bio additive of gasoline, which can improve octane number and reduce the gum formation [4]. Solketal has a better value than glycerol. A study of the technical and economic feasibility of Solketal production reported that solketal could be sold at 2,250 USD/t by small-scale plants with a minimum capacity of 10,000 glycerol t/y [5]. Production Solketal via acetalization glycerol can also be experimented on a low temperature and pressure, giving advantages to its simple procedure.

Glycerol conversion to Solketal via acetalization was reported to be highly active over homogeneous acid catalysts. The most active homogeneous catalyst was the sulfuric acid [6]. However, the sulfuric acid catalyst has drawbacks such as being hard to separate and very corrosive chemical. The heterogeneous catalyst is easy to separate and can be

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reused several times. Various types of heterogeneous catalysts are reported to be active for glycerol acetalization, such as zeolites and tin-based catalyst [7]. Glycerol conversion into Solketal over acid zeolites has been explored for various types, such as H-BEA, H-MOR, H-MFI, and H-FER [7–9]. One of the modifications to improve the mass transfer within the pore zeolites is by introducing the mesopore characteristic for various synthetic zeolite types, such as H-ZSM5, H-BEA, H-FAU, and H-MOR [10–11]. Chemical treatment over a synthetic mordenite was reported to improve the acid sites and create a mesoporous feature that resulted in high glycerol conversion into Solketal [12].

Synthetic zeolites are relatively expensive compared to natural zeolites. Synthetic zeolites require various chemicals to produce, such as silica, NaOH, and aluminum, such as silica, NaOH, and aluminum, require various chemicals to produce, making them expensive [13]. Natural zeolites are abundant and low-cost natural minerals. However, the quality of natural zeolites is generally poor, as the natural zeolites contain impurities and low crystallinity. There are various modifications, physical and chemical which were reported to improve the quality of natural zeolites. The chemical modification using NaOH has been reported to improve the natural zeolites' properties [14–16].

The clinoptilolite phase in the zeolites is not stable after 1 M NaOH treatment at 90 °C for 1h and a mixing rate of 500 rpm [14]. Ates and his team found that the treatment leads to the disappearance of clinoptilolite and clay phases. However, Jha and Hayashi reported that the natural clinoptilolite remained intact after 4 M NaOH treatment at room temperature with time variation from 24 to 72h [17]. The treatment successfully enhanced NH_4^+ retention capacity as the alkaline metal cations increased in the alkali-treated natural clinoptilolite.

The investigation aims to study the effect of NaOH concentration in soft conditions on the properties of natural clinoptilolite and testing as a catalyst for glycerol acetalization. The soft conditions are a low concentration of 0.1 – 0.4 M NaOH with 30 min and a low temperature of 65 °C. To the best of our knowledge, the present investigation is rarely reported.

2. Material and method

2.1. Catalyst preparation

Natural zeolites were obtained from local mining PT. Minerindo Trifa Buana at Pasir Gombong, Bayah, Indonesia. The natural zeolite was dried at 110 °C for 8h. A weight of 1 g of natural zeolites was diluted in 40 mL NaOH solution of 0.1, 0.2, 0.3, and 0.4 M. The solution was mixed at 400 rpm for 30 min at 65 °C. 1 g natural zeolites were ion exchanged using 50 mL NH_4Cl 2 M for 4h and temperature 70 °C. The sample was rinsed 3 times using distilled water. Afterward, the sample was dried at 110 °C for 8h. Calcination of zeolite was performed at 550 °C for 6h. The samples were labeled Z-0.1, Z-0.2, Z-0.3, and Z-0.4 for different NaOH treatments.

2.2. Characterization

The natural zeolites were characterized by X-ray diffraction (XRD), nitrogen physisorption, Scanning Electron Microscope (SEM)- Energy Dispersive X-ray (EDX), and Fourier-Transform Infrared (FTIR). The natural zeolite diffraction was examined using Shimadzu 7000 (Shimadzu Corporation Kyoto, Japan) to study the crystallinity of natural zeolites. The scanning range was 5 – 50° with a sampling pitch of 0.02° and scan speed at 2°/min. Zeolite morphology and elemental composition were studied by SEM-EDX using a Zeiss. FTIR spectroscopy was performed using a Shimadzu to evaluate the functional groups of the zeolites with range spectra from 4000 to 400 cm^{-1} . We used the attenuated total reflectance (ATR) mode with powder samples for the FTIR analysis. Textural properties were examined by nitrogen physisorption technique (Quantachrome TouchWin v1.22) using liquid nitrogen at a temperature of –196 °C. Prior to adsorption-desorption

analysis, degassing was performed by heating to 200 °C at 5 °C/min and dwelled for 10 min, followed by heating to 300 °C at 10 °C/min and dwelled for 60 min.

2.3. Catalysts testing

The catalytic reaction process was performed in a batch glass reactor. The first step was mixing acetone and glycerol with a mole ratio of 6:1. A mass of 7.568 g of acetone and 2 g of glycerol were added to a glass tube reactor. The solution was stirred using a magnetic stirrer at 600 rpm. Afterward, 0.2 g zeolite catalyst was added to the glass tube at a temperature of 50 °C for 90 min.

Glycerol concentration was examined using a titration method following the ASTM D7637-10. A weight of 0.4 g liquid sample from the glass tube reactor was transferred into a 600 mL beaker glass and diluted with 50 mL distilled water. An amount of 3 mL bromothymol blue was added as an indicator, and the solution was acidified slowly with 0.2N sulfuric acid to a definite green or greenish yellow. The solution was added with 0.04N NaOH to a definite blue and free from the green color endpoint. Subsequently, 50 mL of sodium metaperiodate solution was transferred into the beaker, and the solution was stirred at 300 rpm on a magnetic stirrer. 10 mL of ethylene glycol was added to the solution and stirred at 300 rpm while the beaker was covered with a watch glass. The solution was diluted with 300 mL of distilled water and stirred at 300 rpm. The final solution was titrated using 0.1 sodium hydroxide to a pH of 8.1 bit by bit.

3. Result and discussion

3.1. Natural zeolites type identification

The diffraction pattern of the as-received natural zeolite compared with the clinoptilolite from the reference [18] is presented in Fig. 1. As one may see, the natural zeolite diffraction pattern is almost like the clinoptilolite. However, the impurities were observed as indicated by the alphabets, which belong to mordenite (m) at 2 θ 19.61, 22.02, 27.79°, and quartz (q) at 2 θ 21.10, 26.65°. Hence, we identified that the natural zeolite is clinoptilolite dominant phase. This finding contradicts our previous work using the zeolites from Bayah, which showed that the zeolite was mordenite dominant phase [19–20]. This most likely occurred because the zeolites were obtained from the different mining areas. The mining location determines the zeolite phase, crystallinity, and impurities, even in the same region or district. From other research experiments, the Bayah natural zeolite was also reported as a mordenite dominant phase and clinoptilolite dominant phase [2].

3.2. Effect of NaOH concentration on zeolites crystallinity

Diffraction patterns of zeolite samples with different NaOH concentration treatments were presented in Fig. 2. As NaOH concentration increased, the peaks of subjected material increased. Furthermore, no significant difference is observed at low NaOH concentration (Z-0.1) compared to parent zeolites. The highest peaks showed when the natural zeolites were treated with 0.4 M NaOH (Z-0.4). The high peak intensity indicated that the Z-0.4 has high crystallinity compared to other samples. The NaOH solution seems to remove the amorphous silica phase in the natural zeolites while maintaining the remaining silicon of the zeolite framework. Amorphous silica contributes to no peaks at diffraction result. However, from this experiment, the zeolite samples after NaOH treatment showed high peak intensity as the concentration increased. From our previous work, high concentration of NaOH solutions (0.8 M and 1.0 M NaOH) led to a decrease in peak intensity which suggested that the crystallinity of zeolite was decrease [21]. Ates et al. reported the vanishing of zeolite crystallinity after 1 M NaOH treatment 90 °C for 1h and mixing at 500 rpm [14]. Softening the alkaline environment presumably would not destroy the crystallinity. As a result, it

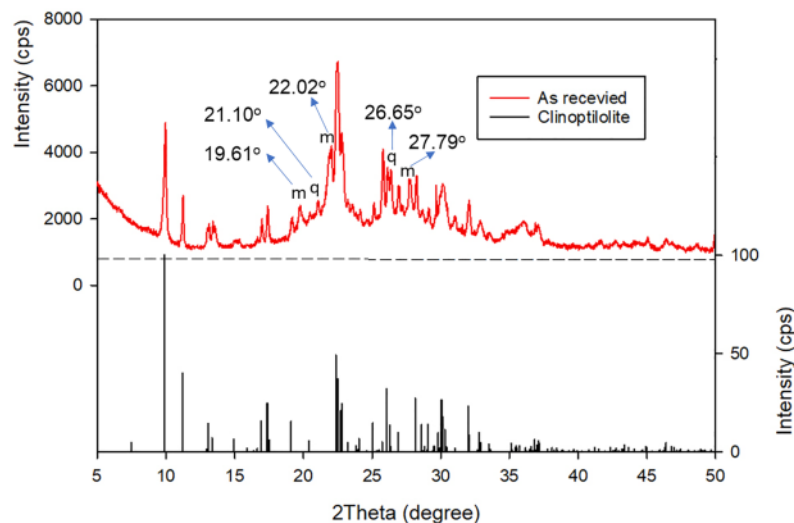


Fig. 1. Diffraction pattern of natural zeolites from Bayah compared with clinoptilolite reference.

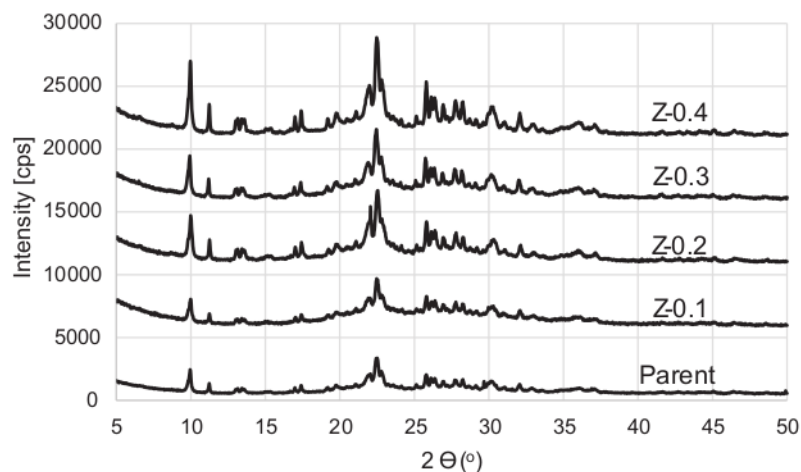


Fig. 2. Effect of NaOH concentration on the crystallinity of the natural zeolites.

was proven that lowering NaOH from the previous experiment could enhance material crystallinity instead. The harsh condition of alkali treatment highly leached out the silicon in the framework zeolites, which could diminish the silica framework within the zeolite crystal and decrease its peak intensity.

Wang and his team reported that the NaOH treatment reduced the crystallinity of natural zeolites by performing the alkali treatment with stirring at 60 °C for 24h. The experiment caused the silica on the framework to be extracted [22]. In the present work, another finding has been discovered, such that other zeolite phases, mordenite, and silica crystalline, were observed high in all diffraction patterns after alkali treatments. This suggested that soft alkaline treatment is effective in carry-over silica amorphous.

3.3. Effect of NaOH concentration on textural properties

Soft conditions of various NaOH concentration treatments enhanced the textural properties while preserving the framework of zeolites, as

presented in Fig. 3. The nitrogen isotherm of all alkali-treated zeolites showed higher nitrogen adsorbed. The highest volume adsorbed of isotherm was at zeolite after being treated with 0.4 M NaOH solution. The increment of nitrogen adsorbed was enormous from the parent to the treated zeolite. At the same time, the increment from 0.1 to 0.4 M was not significant. Hence most silica in the amorphous phase has been reacted and dissolved into NaOH solution at 0.1 M solution. In contrary, the positive change was not observed after 0.1 M NaOH treatment at room temperature for 1h as reported in literature [23]. In our work the NaOH treatment was performed at higher temperature, i.e. 65 °C increasing the dissolution rate of the amorphous silica. Before alkali treatment, the isotherm type follows Type 2 with low nitrogen sorption at lower pressure and high nitrogen adsorption at high relative pressure. This result is an indication of low micropore and high mesopore or macropore. On the contrary, the isotherms shifting to Type 1 and 4 simultaneously indicated after soft alkali treatment proved by high nitrogen adsorbed at a low relative pressure (P/P^0), and the hysteresis was observed while at high P/P^0 (Fig. 3).

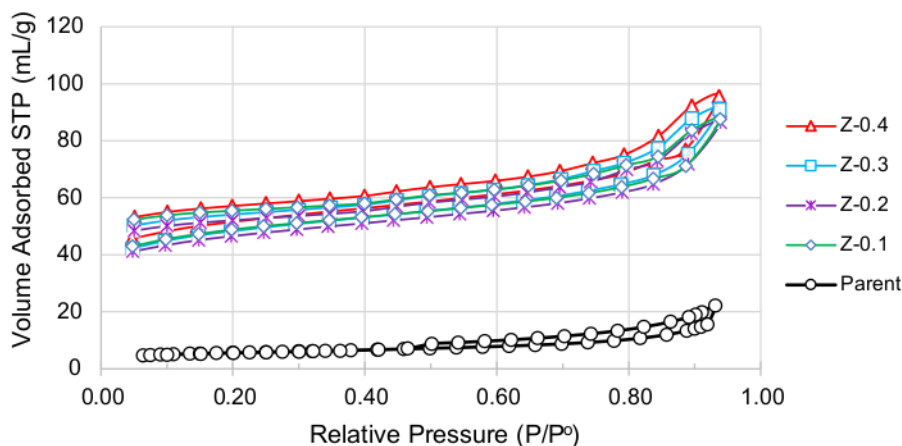


Fig. 3. Effect of NaOH concentration on the nitrogen isotherm.

The textural properties of the parent and alkali-treated samples are present in Table 1. The total surface area of the parent was $19 \text{ m}^2/\text{g}$ and increased to $156 \text{ m}^2/\text{g}$ at Z-0.1, equal to eight times higher than its original form. The total pore volume increased significantly improved from 0.0030 to 0.1357 mL/g . The increment of micropore and mesopore were 18 and 3.6 times, respectively. This suggested that the increase of micropore mainly contributes to the pore surface area increment. Meanwhile, the increment of the surface area after NaOH treatment from 0.1 to 0.4 M was insignificant due to the low range concentration of NaOH to extract the silica from the extra zeolite framework. Verboekend et al. performed $0.2\text{--}1 \text{ M}$ NaOH treatment using a high purity of clinoptilolite ($>97\%$ purity) at temperature $65 \text{ }^\circ\text{C}$ with the results no significant change on the pore properties [24]. However, when we use the clinoptilolite with some impurities in the present work, the micropore and mesopore volume increase significantly.

Clinoptilolite has a theoretical pore that can diffuse a molecule with a diameter of 3.67 \AA through the c-axis (IZA, 2022). This small pore aperture hinders large molecules from diffusing in and reaching the acid sites inside the pore. The clinoptilolite is excluded molecule with a diameter of more than 0.4 nm [25], and after treatment with NH_4Cl followed by steaming and calcination at a temperature of $500 \text{ }^\circ\text{C}$, the pore enlarges while at a higher temperature at $600 \text{ }^\circ\text{C}$ the pore contraction to smaller pore. In our case, the mesopore diameter shifted to a larger pore size, as shown in Fig. 4. Sample Z-0.4 show a higher portion of large pore diameter.

3.4. Effect of NaOH concentration on FTIR spectra

The IR spectra for parent and modified zeolite samples were presented in supplementary file. Generally, there are no significant differences between the parent and modified samples. The spectra between 3000 and 3700 cm^{-1} are attributed to the adsorbed water amount, at which 3389.8 cm^{-1} is attributed to the characteristic hydrogen-bonded

Table 1
Textural properties of catalysts according to nitrogen physisorption analysis.

Sample	BET total surface area (m^2/g)	t-plot micropore area (m^2/g)	t-plot mesopore area (m^2/g)	Total pore volume (mL/g)
Parent	19	6	13	0.0030
Z-0.1	156	109	47	0.1357
Z-0.2	149	101	48	0.1340
Z-0.3	155	104	51	0.1412
Z-0.4	164	113	51	0.1482

OH to oxygen ions broadband, the sharp band typical of isolated OH stretching vibration of water at $\sim 3620 \text{ cm}^{-1}$. The bending vibration of H_2O was also observed at 1626.7 cm^{-1} . The vibrational bands at $780\text{--}820 \text{ cm}^{-1}$ are attributed to the vibration of the Al–O. The main vibrational bands at about $960\text{--}1250 \text{ cm}^{-1}$ conformed to the asymmetric stretch mode of SiO_4 and AlO_4 . This is in agreement with the analysis FTIR of natural clinoptilolite and mordenite [26–27]. The FTIR analysis suggested that the alkali-treated zeolite has all the functional groups of the parent zeolite.

3.4. Effect of NaOH concentration on morphology and elemental composition

Fig. 5 presents the SEM images of the parent and NaOH-treated zeolites. The Bayah natural zeolite's parent morphology was irregular and had no specific shape. There is no significant morphology change after the NaOH treatment. According to SEM EDX analysis (Table 2), silicon was the major component with 18.46% -mol followed by aluminum with 4.37% -mol. Thus, the mol ratio of Si to Al of Bayah natural zeolites is 4.22 . Minor components detected were Fe, K, and Mg. Most likely, the bath at lanced cations within the zeolite framework was K^+ and Mg^{2+} . Hence, those cations are easily exchanged with other cations via an ion-exchanged mechanism. The NaOH treatment decreased the ratio Si to Al from 4.22 to 3.76 . This is suggested that the desilication occurred after NaOH treatment, leading to the amorphous silica removal from the zeolite framework.

3.5. Alkali treatment mechanism in soft condition

According to all catalyst characterization performed, alkali treatment with soft conditions significantly improved the quality of natural zeolites. The possible mechanism is depicted in Fig. 6. A lot of amorphous silica debris could block the pore of natural zeolites. The NaOH solution reacts with amorphous silica into sodium silicate and dissolves it. As a result, the crystallinity and surface area significantly increased. Further ion exchange with NH_4Cl and rinsing the samples with distilled water removed the rest of the sodium silicate. The sample after alkali soft treatment became high in crystallinity and open-pore of zeolite, as suggested by the X-ray diffraction and nitrogen physisorption analysis. At harsh NaOH treatment, the crystallinity decreases as more silica from the zeolite framework extracted. It also creating the mesopore and at the same time demolishing the micropore. The total surface area would decrease significantly as reported in our previous work [21].

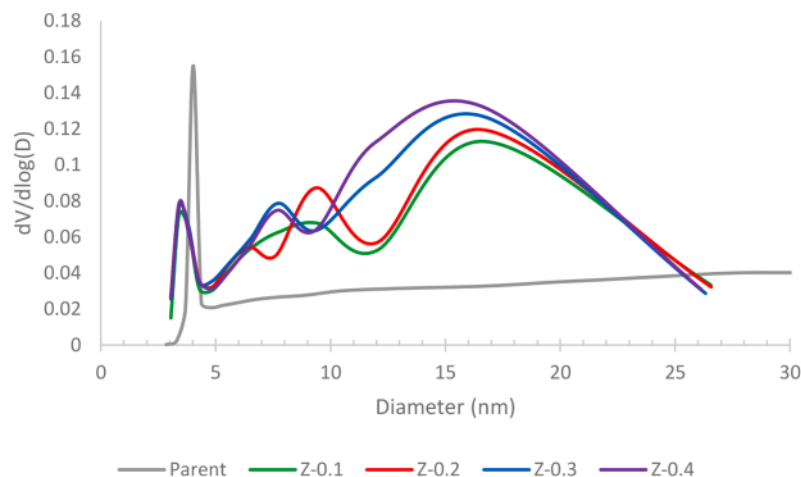


Fig. 4. Pore diameter distribution based on BJH desorption.

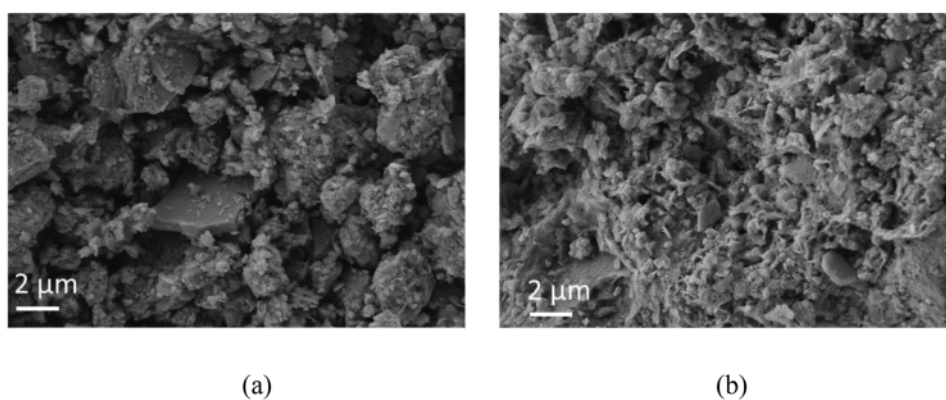


Fig. 5. SEM pictures of (a) parent (b) Z-0.4.

Table 2
Elemental composition of natural zeolites based on SEM-EDX.

Element	Parent	Z-0.4
	%mol	
Si	18.46	17.35
Al	4.37	4.61
K	2.05	2.77
Fe	0.33	0.15
Mg	0.27	0.41
Si/Al	4.22	3.76

3.6. Glycerol acetalization

Glycerol conversion over alkali-treated natural zeolites increased, as presented in Fig. 7. Several factors improved the conversion. First, the crystallinity of alkali-treated natural zeolites was higher than the parent as the amorphous part of the material, particularly amorphous silica removed. This makes the glycerol acetalization occurs in a much higher part of the zeolite phase in the alkali-treated zeolite samples. The high crystallinity of zeolites after hydrothermal improved the glycerol acetalization as the active side provided higher in the high crystalline sample [19]. Secondly, the alkali-treated natural zeolites altered the textural properties. The high mesopore and external volume over the

alkali-treated natural zeolites reduced the diffusional limitation improving the overall reaction rate. Glycerol kinetic diameter is 0.61 nm [28] which was higher than clinoptilolite pore, 0.4 nm. However, the mordenite pore size is 0.65 x nm. The small particle size, which has a higher external surface area, improves the glycerol conversion, as reported in our previous work [29]. The alkali-treated zeolites also improve the micropore and mesopore volume (Table 1), which can be a verdict of high acid sites within the zeolite framework. Kowalska et al. reported that the desilication of MFI, MOR and BEA zeolites using 0.2 M NaOH at 80 °C resulted in the increase of both total acidity and strong acidity using pyridine probe [10]. The pyridine has diameter kinetic about 0.533 nm. The increase in total acidity of the zeolites contributed by Brønsted acidity and Lewis acidity which could be more accessed by the pyridine after the NaOH treatment. The other groups reported that tandem acid-base created the mesopore while preserved the total acidity by NH₃-TPD analysis [24].

Besides the catalyst material aspect, the ratio of glycerol to acetone and operating conditions also affect the reaction, such as reaction temperature, time, and mixing speed. Table 3 presents a comparison between the present work and the literature. From our previous work, the recrystallization of natural mordenite via the hydrothermal method improved the glycerol conversion from 16% to 59% [19]. In the present work, the glycerol conversion reached 90%, which is higher than the previous work. The morphology of natural mordenite is observed as

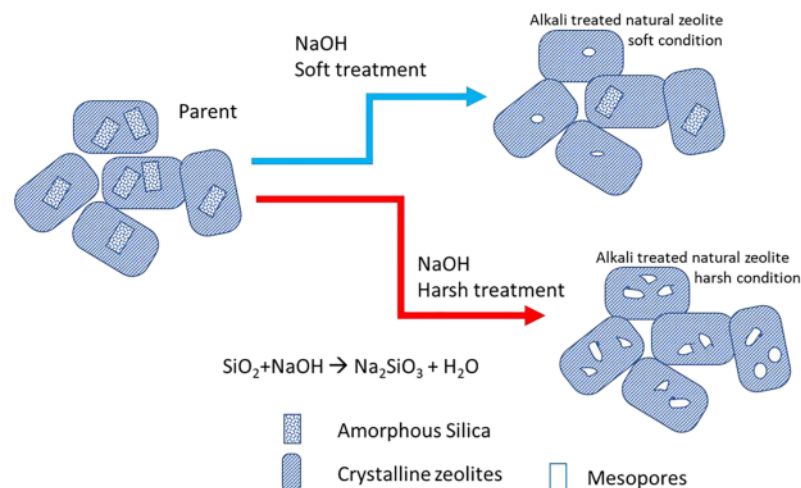


Fig. 6. Soft and harsh alkali scheme upon Bayah natural zeolites.

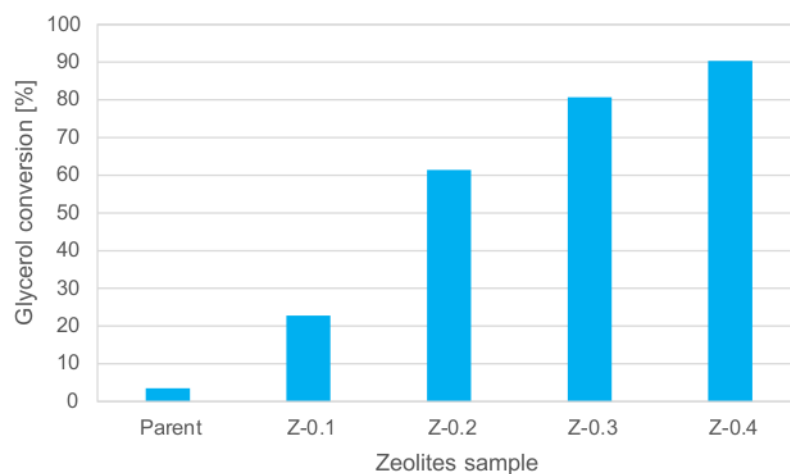


Fig. 7. Glycerol conversion over alkali-treated natural zeolites.

Table 3

Glycerol acetalization over zeolites presents work and literature.

Catalyst	Catalyst Loading to glycerol [%]	Temperature [°C]	Time [min]	Glycerol to Acetone [mol/mol]	Glycerol conversion	Ref.
Alkali treated natural clinoptilolite	10	50	90	1:6	90	Present work
Hydrothermal treated Natural mordenite	10	50	90	1:12	59	[19]
Alkali treated natural mordenite-clinoptilolite	0.5 – 3	60	300	1:2	98	[16]
Synthetic Mordenite	1	70	–	1:1	65	[10]
Alkali treatment Synthetic Mordenite	1	70	–	1:1	80	[10]
H-Beta nanoparticle	5	28	60	1:2	86	[30]

needles that make the diffusion obstacles of molecules transport.

In contrast, the natural clinoptilolite has a platelet shape with a higher mass transfer than the mordenite. The glycerol conversion increased from 65% to 80% after NaOH treatment of the synthetic mordenite [10]. The mesopore created after NaOH treatment improved the mass transfer of molecules. The crystal size of H-Beta also significantly affected the glycerol conversion and solketal selectivity [30].

Acetalization over H-Beta with an average crystal size of 450 nm showed a conversion of 38%, while over the smaller crystal size of 135 nm, the glycerol conversion increased to 86%. The small crystal size shortened the diffusion path of molecules while improving the mass transfer during acetalization.

4. Conclusion

The Bayah natural zeolites properties have successfully improved by NaOH treatment in soft conditions. The crystallinity improved significantly after NaOH treatment and reached high crystallinity at 0.4 M NaOH. The alkali treatment yielded a positive result on the textural properties, as showed by the high surface area of 164 m²/g in the sample Z-0.4 from only 19 m²/g in the parent. The hierarchical pore zeolite was also created after NaOH treatment. The glycerol conversion over alkali-treated zeolites was higher over the parent natural clinoptilolite. The NaOH treatment is a simple method to improve natural clinoptilolite's crystallinity and textural properties, which results in high glycerol conversion.

CRedit authorship contribution statement

Teguh Kurniawan: Conceptualization, Methodology, Writing – original draft. **N. Nuryoto:** Methodology, Formal analysis. **Nava Syahbana Fitri:** Investigation, Formal analysis. **Hilma Siti Sofiyah:** Investigation, Formal analysis. **Muhammad Roil Bilad:** Writing – review & editing. **Kajornsak Faungnawakij:** Validation. **Sutarat Thongratkaew:** Validation.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rechem.2022.100584>.

References

- J. Kowalska-Kus, A. Held, K. Nowinska, A continuous-flow process for the acetalization of crude glycerol with acetone on zeolite catalysts, *Chem. Eng. J.* 401 (2020), 126143. <https://doi.org/10.1016/j.cej.2020.126143>.
- H.I. Mahdi, E. Irawan, N. Nuryoto, J. Jayanudin, H. Sulisty, W.B. Sediawan, O. Muraza, Glycerol carbonate production from biodiesel waste over modified natural clinoptilolite, *Waste Biomass Valorization* (2016), <https://doi.org/10.1007/s12649-016-9495-3>.
- O. Muraza, Peculiarities of glycerol conversion to chemicals over zeolite-based catalysts, *Front. Chem.* 7 (2019) 233.
- C.J.A. Mota, C.X.A. da Silva, N. Rosenbach, J. Costa, F. da Silva, Glycerin derivatives as fuel additives: the addition of glycerol/acetone ketal (Solketal) in gasolines, *Energy Fuels* 24 (4) (2010) 2733–2736, <https://doi.org/10.1021/ef9015735>.
- J.A. Vannucci, M.N. Gatti, N. Cardaci, N.N. Nichio, Economic feasibility of a solketal production process from glycerol at small industrial scale, *Renewable Energy* 190 (2022) 540–547. <https://doi.org/10.1016/j.renene.2022.03.125>.
- G.S. Dmitriev, A.V. Terekhov, L.N. Zhanavskina, A.L. Maksimov, S.N. Khadzhiev, Kinetics of the formation of solketal in the presence of sulfuric acid, *Kinet. Catal.* 59 (4) (2018) 504–508, <https://doi.org/10.1134/S002315841804002X>.
- G.L. Catuzo, C.V. Santilli, L. Martins, Hydrophobic-hydrophilic balance of ZSM-5 zeolites on the two-phase ketalization of glycerol with acetone, *Catal. Today* (2020), <https://doi.org/10.1016/j.cattod.2020.07.008>.
- M.S. Rahaman, T.K. Phung, M.A. Hossain, E. Chowdhury, S. Tulaphol, S.B. Lalvani, M. O'Toole, G.A. Willing, J.B. Jasinski, M. Crocker, N. Sathitsuksano, Hydrophobic functionalization of HY zeolites for efficient conversion of glycerol to solketal, *Appl. Catal. A* 592 (2020), 117369. <https://doi.org/10.1016/j.apcata.2019.117369>.
- V. Rossa, *Production of Solketal Using Acid Zeolites as Catalysts* (G. C. Diaz (ed.); p. Ch. 3). IntechOpen. 2019. <https://doi.org/10.5772/intechopen.85817>.
- J. Kowalska-Kus, A. Held, M. Frankowski, K. Nowinska, Solketal formation from glycerol and acetone over hierarchical zeolites of different structure as catalysts, *J. Mol. Catal. A: Chem.* 426 (2017) 205–212. <https://doi.org/10.1016/j.molcata.2016.11.018>.
- A. Talebian-Kiakalaieh, S. Tarighi, Hierarchical faujasite zeolite-supported heteropoly acid catalyst for acetalization of crude-glycerol to fuel additives, *J. Ind. Eng. Chem.* 79 (2019) 452–464. <https://doi.org/10.1016/j.jiec.2019.07.021>.
- B. Saini, A.P. Tathod, S.K. Saxena, S. Arumugam, N. Viswanadham, Sustainable upgrade of bioderived glycerol to solketal through acetalization over metal-free mordenite catalysts, *ACS Sustainable Chem. Eng.* 10 (3) (2022) 1172–1181, <https://doi.org/10.1021/acssuschemeng.1c06330>.
- T. Kurniawan, D. Satria, J.B. Saputra, M.R. Bilad, N.A.H.M. Nordin, H. Abdullah, Conversion of Green Silica from Corn Leaf into Zeolites Na A-X, *Indonesian J. Sci. Technol.* 7 (2) (2022), <https://doi.org/10.17509/ijost.v7i2.45831>.
- A. Ates, Effect of alkali-treatment on the characteristics of natural zeolites with different compositions, *J. Colloid Interface Sci.* 523 (2018) 266–281. <https://doi.org/10.1016/j.jcis.2018.03.115>.
- A. Ates, G. Akgül, Modification of natural zeolite with NaOH for removal of manganese in drinking water, *Powder Technol.* 287 (2016) 285–291. <https://doi.org/10.1016/j.powtec.2015.10.021>.
- D. Kurniawati, J. Jumaeri, S. Tursiloadi, O. Arutanti, M. Safaat, Modification of Indonesian Natural Zeolite (Clinoptilolite-Mordenite) for Synthesis of Solketal, *Iran. J. Catal.* 11 (3) (2021) 295–302. http://ijc.iaush.ac.ir/article_685586.html.
- V.K. Jha, S. Hayashi, Modification on natural clinoptilolite zeolite for its NH₄⁺ retention capacity, *J. Hazard. Mater.* 169 (1) (2009) 29–35. <https://doi.org/10.1016/j.jhazmat.2009.03.052>.
- M.M.J. Treacy, J.B. Higgins, *HEU - Clinoptilolite* (M. M. J. Treacy & J. B. B. T. C. of S. X. R. D. P. P. for Z. (Fifth E. Higgins (eds.); pp. 206–207). Elsevier Science B.V. . 2007.
- T. Kurniawan, N. Nuryoto, N.D. Milenia, K.D. Lestari, A.B.D. Nandiyo, M. R. Bilad, H. Abdullah, T.M.I. Mahlia, Improved natural mordenite as low-cost catalyst for glycerol acetalization into solketal – An effective fuel additive, *Mater. Sci. Forum* 1057 (2022) 71–87, <https://doi.org/10.4028/p-gwf9>.
- T. Kurniawan, Nuryoto, Rahmayetty, Characterization and application of bayah natural zeolites for ammonium capture: isotherm and kinetic, *Mater. Sci. Forum* 988 (2020) 51–64, <https://doi.org/10.4028/www.scientific.net/MSF.988.51>.
- A. Irawan, Y. Bindar, T. Kurniawan, H. Alwan, R. Rosid, N.A. Fauziah, Bayah natural zeolites to upgrade the quality of bio crude oil from empty fruit bunch pyrolysis, *J. Eng. Technol. Sci.* 53 (3) (2021) 210308, <https://doi.org/10.5614/j.eng.technol.sci.2021.53.3.8>.
- C. Wang, S. Leng, H. Guo, L. Cao, J. Huang, Acid and alkali treatments for regulation of hydrophilicity/hydrophobicity of natural zeolite, *Appl. Surf. Sci.* 478 (2019) 319–326. <https://doi.org/10.1016/j.apsusc.2019.01.263>.
- Y. Çalışkan, S. Harbeck, N. Bektaş, Adsorptive removal of basic yellow dye using bigadic zeolites: FTIR analysis, kinetics, and isotherms modeling, *Environ. Prog. Sustainable Energy* 38 (s1) (2019) S185–S195. <https://doi.org/10.1002/ep.12969>.
- D. Verboekend, T.C. Keller, M. Milina, R. Hauer, J. Pérez-Ramírez, Hierarchy brings function: mesoporous Clinoptilolite and L Zeolite catalysts synthesized by tandem acid-base treatments, *Chem. Mater.* 25 (9) (2013) 1947–1959, <https://doi.org/10.1021/cm4006103>.
- A. Farjoo, J.A. Sawada, S.M. Kuznicki, Manipulation of the pore size of clinoptilolite for separation of ethane from ethylene, *Chem. Eng. Sci.* 138 (2015) 685–688. <https://doi.org/10.1016/j.ces.2015.08.044>.
- E.P. Favvas, C.G. Tsanaktsidis, A.A. Sapalidis, G.T. Tzilantonis, S.K. Papageorgiou, A.C. Mitropoulos, Clinoptilolite, a natural zeolite material: Structural characterization and performance evaluation on its dehydration properties of hydrocarbon-based fuels, *Microporous Mesoporous Mater.* 225 (2016) 385–391. <https://doi.org/10.1016/j.micromeso.2016.01.021>.
- T. Kurniawan, O. Muraza, A.S. Hakeem, A.M. Al-Amer, Mechanochemical route and recrystallization strategy to fabricate mordenite nanoparticles from natural zeolites, *Cryst. Growth Des.* 17 (6) (2017) 3313–3320.
- S. Li, V.A. Tuan, J.L. Falconer, R.D. Noble, Separation of 1,3-propanediol from aqueous solutions using pervaporation through an X-type zeolite membrane, *Ind. Eng. Chem. Res.* 40 (8) (2001) 1952–1959, <https://doi.org/10.1021/ie000905i>.
- N. Nuryoto, H. Sulisty, W. Budi Sediawan, I. Perdana, Peningkatan Unjuk Kerja Katalisator Zeolit Alam Bayah pada Reaksi Ketalisasi Glycerol, *Reaktor; Volume 17 No.1 Maret 2017DO - 10.14710/Reaktor.17.1.9.16 - 2017*.
- P. Manjunathan, S.P. Maradur, A.B. Halgeri, G.V. Shanbhag, Room temperature synthesis of solketal from acetalization of glycerol with acetone: effect of crystallite size and the role of acidity of beta zeolite, *J. Mol. Catal. A: Chem.* 396 (2015) 47–54. <https://doi.org/10.1016/j.molcata.2014.09.028>.

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