

Improved natural mordenite- solketal

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Improved Natural Mordenite as Low-Cost Catalyst for Glycerol Acetalization Into Solketal - An Effective Fuel Additive

Teguh Kurniawan^{1,2,a*}, Nuryoto Nuryoto^{1,b}, Natasya Diwa Milenia^{1,c},
Kirana Dian Lestari^{1,d}, Asep Bayu Dani Nandiyanto^{3,e},
Muhammad Roil Bilad^{4,f}, Hairus Abdullah^{5,6,g},
and Teuku Meurah Indra Mahlia^{7,h}

¹Chemical Engineering Department, Universitas Sultan Ageng Tirtayasa, Serang 42122, Indonesia

²Biomass Valorization Laboratory, Center of Excellence Faculty of Engineering,
Universitas Sultan Ageng Tirtayasa, Cilegon 42435, Indonesia

³Department of Chemistry, Universitas Pendidikan Indonesia, Bandung, 40154, Indonesia

⁴Faculty of Integrated Technologies, Universiti Brunei Darussalam, Jalan Tungku Link, Gadong
BE1410, Brunei

⁵Department of Industrial Engineering, Universitas Prima Indonesia, Medan, Indonesia

⁶Department of Materials Science and Engineering, National Taiwan University of Science and
Technology, No. 43, Sec. 4, Keelung Road, Taipei 10607, Taiwan

⁷Centre for Green Technology, School of Civil and Environmental Engineering, University of
Technology, Sydney, NSW 2007, Australia

*^ateguh@untirta.ac.id, ^bnuryoto@untirta.ac.id, ^cnatasyadiwamilenia@gmail.com,
^dkiranasinurat@gmail.com, ^enandiyanto@upi.edu, ^froil.bilad@ubd.edu.bn,
^ghairus@mail.ntust.edu.tw, ^hTMIndra.Mahlia@uts.edu.au

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Abstract. The increase in biodiesel production results in an excessive amount of crude glycerol by-product. Therefore, production of solketal –an effective additive of gasoline fuel- from glycerol and acetone via catalytic acetalization could improve the added value of glycerol. This study investigates enhancement of natural mordenite catalytic properties through the hydrothermal recrystallization method for glycerol acetalization. The hydrothermal temperature was varied at 150, 170 and 190 °C to form ZT 150, ZT 170 and ZT 190, respectively. The samples were characterized by using the x-ray diffraction and the scanning electron microscope-Energy dispersive X-Ray. They were later used as catalysts for glycerol acetalization with acetone. The best obtained catalyst was further studied to explore the effect of acetone to glycerol ratio. The glycerol conversion was determined using the ASTM D7637-10 titration method. Solketal product was identified by using the Fourier transform infrared spectroscopy. The results showed that the recrystallization temperature affected the intensity of the mordenite phase and quartz impurity phase in the modified zeolites. A high recrystallization temperature led to a higher phase of mordenite, peaking at 170 °C, beyond which the quartz impurity phase increased. Glycerol acetalization conversions over zeolite parent, ZT 150, ZT 170 and ZT190 with acetone to glycerol ratio of 3 were 16.1, 30.4, 33.9 and 32.5%, respectively. When the ratio of acetone to glycerol was increased to 12, the glycerol conversion over ZT 170 catalyst reached 59%, a good starting point for further modifications. Overall finding demonstrated a straight-forward fabrication of catalyst from natural resource to enhance glycerol as the biodiesel production by-product into a higher value end-product of solketal.

1. Introduction

The engine has been developed since eighteen century and since then it has never been changed so much. Only the fuel has been changed from biofuel to fossil fuel, and now the trend is to biofuel

again. These biofuels have been produced from many feedstocks such as edible plants that grow on land [1]. However, some countries try to ban these feedstocks due to its conflicting with food [2]. Therefore, scientists attempt to find the feedstocks that are not conflicting with food such as *Jatropha* sp., *Calophyllum* sp. and *Ceiba pentandra* [3–5]. Some other scientists tried to extract feedstock from plant that grows in water such as microalgae to avoid using precious land that can be used for agriculture [6]. However, most of the feedstocks in the biodiesel industry are processed via transesterification with alcohol pathway, that produce enormous glycerol as the by-product. The amount of glycerol produced in the biodiesel manufacturing process is 10% by weight [7], resulting in the total glycerol by-product in the world in 2012 was 1.2 million tons. If the use of glycerol is still limited to the resin and the nitroglycerin industries, it soon could be oversupplied with minimum economic value. The abundance of glycerol by-products of biodiesel plummets the price of glycerol [8]. By converting it to solketal, the use of glycerol will be wider, because solketal can be used as a fuel additive to increase the octane number and reduce gum in gasoline, lower the freezing point of biodiesel or diesel fuel, improve the properties of lubricants, polymer additives and suspending materials, as well as pharmaceutical materials [8–10].

The conversion of glycerol into solketal can take place effectively with the help of catalysts. Homogeneous catalysts such as strong acid H_2SO_4 and iron(III) complex is well-known to pose high glycerol conversion to solketal [11–13]. However, the reaction system conducted under homogeneous acid suffers in the separation of the reaction products, the unreacted reactants, and the catalyst. The acetalization over heterogeneous catalysts offers advantageous in catalyst separation. There are various heterogeneous catalysts for glycerol acetalization, including heteropolyacid, resin, meso- SiO_2 and zeolites [11,14].

Zeolites are heterogeneous catalysts that are known to facilitate the conversion of glycerol to solketals. Zeolite pores are generally small between 3–10 Å, so that they are in the category of micropores (<20). Zeolites with hierarchical pores, i.e., having both micropores and mesopores (2–50 nm) are useful in providing access for large molecules to and from the active site of the catalyst [15–17]. The crystal size and acidity of beta zeolite also affect the acetalization [18]. Synthetic H-beta zeolite with a small crystal size showed high glycerol conversion of up to 86% and solketal selectivity of 98.5%. Glycerol conversion tends to decrease with decreasing total acidity of beta zeolite. Similarly, the high ratio between the strong acid sites to the weak acid sites also enhances the conversion and the selectivity of the acetalization.

Recent study reported the effect of transition metal ions such as Fe, Co, Ni, Cu, Zn with mordenite as the support on the glycerol catalysis reaction using a microwave radiation as heat source [19]. The findings showed that the Cu-MOR catalyst offered the highest conversion and selectivity. One of the catalytic products of glycerol with acetone is water which reduced the effectiveness of the zeolite catalyst. Other researchers impregnated niobium oxide Nb_2O_5 to increase the hydrophobic properties of synthetic HUSY zeolite. They reported an increase in glycerol conversion after the impregnation from 20 to 60% [20]. Recently, several types of synthetic zeolites, i.e., zeolite beta, mordenite, ZSM-5, SAPO-34, SAPO-11, and Y-zeolite were also investigated for conversion of glycerol to solketal [21]. The reaction was performed in a batch reactor at 60°C for 3 h. The highest glycerol conversion was observed over zeolite mordenite catalyst because it posed the highest Bronsted acidity [21].

Most of the reported studies employed synthetic zeolite as acetalization catalyst with limited report on utilization of natural zeolite. Mordenite is one of the zeolite types that occurred in nature along with chabazite and clinoptilolite, and was reported to successfully improve oilsands bitumen via catalytic reaction [22]. Natural mordenite is low-cost and abundantly available throughout the world. However, natural mordenite needs to be improved in terms of their physical and chemical properties to optimize its catalytic performances. Application of low-cost natural zeolite as catalyst can offer economic benefit to replace synthetic catalyst that often significantly contributed to operational expenditure of a chemical reactor.

The objective of this study was to enhance the performance of natural zeolite by modification through hydrothermal recrystallization. After modification, the performance of the prepared

catalysts was evaluated for catalyzing the glycerol acetalization. The effect of hydrothermal temperature on the properties and performance of the modified zeolite as catalysts were studied. Furthermore, the effect of glycerol to acetone ratio during acetalization was also investigated.

2. Experimental

2.1 Materials

Natural zeolites were obtained from Bayah, Banten Province, Indonesia (Figure 1), henceforth referred to as Bayah natural zeolite. Bayah natural zeolite particles were crushed and sieved to reduce particles size to -60+80 mesh. The grounded zeolites as-received sample was labelled as "parent". Modified natural zeolite samples were prepared by the hydrothermal recrystallization method. Afterward, the H-protonated form of the recrystallized natural zeolite samples were prepared by using NH_4NO_3 .

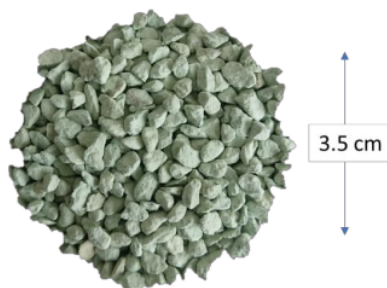


Fig.1 Bayah natural zeolites sample as-received.

2.2 Methods

Experimental steps are presented in Figure 2. There are 4 steps in this investigation which are pre-treatment of Bayah natural zeolites, hydrothermal recrystallization, ion-exchange, and acetalization of glycerol with acetone. The pre-treatment of Bayah natural zeolites is described in Section 2.1. After that, sample was recrystallized in an autoclave as explained in Section 2.2.1. The recrystallized samples - still in Na-zeolites form- were required to convert them into H-zeolites by following ion-exchange procedure (Section 2.2.3). The catalyst samples were tested in an acetalization batch reactor for converting glycerol and acetone into solketal as described in Section 2.2.5.

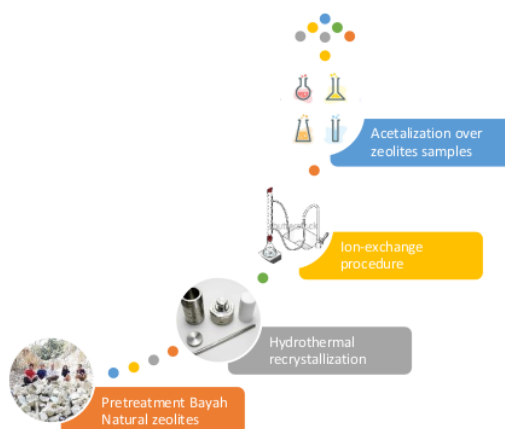


Fig.2 Experimental process flow diagram

2.2.1. Recrystallization Procedure

The hydrothermal recrystallization of Na-Parent was conducted by using sodium silicate solution with a molar ratio of 18 SiO₂ :12 NaOH: 720 H₂O. A 1.5 g of NaOH was dissolved in 40 mL of distilled water. Afterward, 3.4 g of fumed silica was added into the solution. The mixture was then stirred at 300 rpm using a magnetic stirrer until homogeneous. After that, 1.0 g of Na-Parent sample was added into the mixture and stirred at 300 rpm for a minute. A PTFE-lined autoclave was used to perform the hydrothermal recrystallization for 8 h under autogenous pressure. The temperature was varied at 150, 170 and 190°C. The hydrothermally treated zeolites were washed using distilled water for several times until reaching a pH of around 7. After that, the sample was heated in an oven for 2 h at 90 °C. The recrystallized samples were labelled as ZT-150, ZT-170 and ZT-190 for hydrothermal treating temperatures of 150, 170 and 190 °C, respectively.

2.2.3. Ion-Exchange Procedure

The ion exchange procedure was conducted by mixing 400 g of 2 M NH₄NO₃ and 20 g of zeolite sample into a three-neck rounded flask. After that, the mixture was re-fluxed for 1 h at constant temperature of 75°C. The ion exchange was carried out twice. Solid particles were separated and washed using distilled water several times, then dried in an oven for 6 h at 110°C. Afterward, the dried samples were calcined under a static air at 550°C for 8 h to obtain the H-protonated zeolites.

2.2.4. Material Characterization

Zeolite characterizations were carried out using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM-EDS). XRD (Pan Analytic) was performed to identify the crystal phase structure. SEM-EDS (JEOL) was used to study the morphology of the samples and their surface elemental composition.

2.2.5. Glycerol Acetalization

The zeolite samples were tested in a lab-scale acetalization batch reactor. The reaction was performed in a glass tube by mixing glycerol and acetone reactants with a mol ratio of 1:6, then stirred at 600 rpm. 1 g of methanol was added to improve the miscibility between reactants. Afterward, the zeolite was added to the reaction tube as a catalyst. The reaction was carried out for 90 min and the temperature was maintained at 50°C. The glycerol to acetone ratio was also varied at 1:3, 1:6, 1:9, 1:12 to investigate the effect of glycerol/acetone ratio on the acetalization performances.

The glycerol conversion was analysed using the ASTM D7637-10 titration method. 400 mg of sample from analytical balance were transferred into a 600 mL beaker and diluted with 50 mL of distilled water. An amount of 3 mL bromothymol blue indicator was added, and the solution was acidified carefully with 0.2 N sulfuric acid to a definite green or greenish yellow colour. The solution was then neutralized with 0.04 N sodium hydroxide to a definite blue and free from green colour endpoint. Afterward, sodium metaperiodate solution 50 mL was pipetted into the beaker and the solution was stirred at 300 rpm on a magnetic stirrer while the beaker was covered with a watch glass. 10 mL of ethylene glycol was added and mixed into the solution and stirred at 300 rpm while the beaker was covered with a watch glass. The solution was then diluted with 300 mL of distilled water and stirred further at 300 rpm. The final solution was then slowly titrated as the endpoint was approached by using 0.1 sodium hydroxide to a pH of 8.1 for the specimen under assay.

Solketal products and glycerol were analysed by using FTIR (Type-4600, Jasco Corp., Japan). Solketal with high purity was analysed for standard in comparison with the solketal product from the acetalization experiment. In addition, high purity glycerol was obtained by heating 99.5%-v of glycerol (Merck) at 100 °C for 2 h, which later used as the standard in the FTIR analysis.

The acetalization reaction was carried out by reacting acetone and glycerol by employing the modified zeolites as the catalyst. However, the low miscibility of acetone and glycerol resulted in an initial two-phase mixture and considerable interfacial transfer limitation between the liquid phase

and the active site of the catalyst. To overcome the limitations of interfacial mass transfer, methanol was added during the reaction

3. Results and Discussion

3.1 Characteristics of Bayah natural zeolites

According to diffraction pattern presented in Figure 3, Bayah natural zeolites were identified as mordenite, clinoptilolite and quartz. The dominant phase of zeolite type was mordenite. This is in agreement with previous literature that reported Bayah natural zeolites comprised of those three crystalline phases with mordenite as the dominant phase [23]. However, in another report, the dominant zeolite phase of Bayah natural zeolites was clinoptilolite [24]. Despite the zeolites were obtained from the same district, i.e., Bayah, the zeolite mining sites could be different, which caused the different in composition of the zeolites.

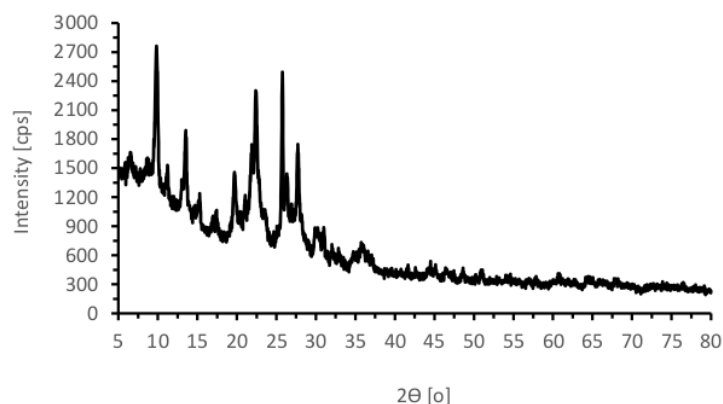


Fig. 3 Diffraction pattern of Bayah natural zeolite as received

Figure 4 presents the isotherm nitrogen physisorption of Bayah natural zeolites. It shows a low nitrogen adsorption in the lower relative pressure, which was an indication of low micropore area of the sample. In the range of relative pressure 0.5 – 1.0, the adsorption curve was lower than the one in the same point of relative pressure called as hysteresis. It suggested that the mesopore surface area was relatively high in the Bayah natural zeolites. The hysteresis in the hierarchical synthetic zeolite after NaOH treatment was also obvious from the isotherms of the treated samples [25]. The pattern of isotherm Bayah natural zeolites was similar to Bayah natural zeolites in our previous work, despite of taken from different mining locations [26].

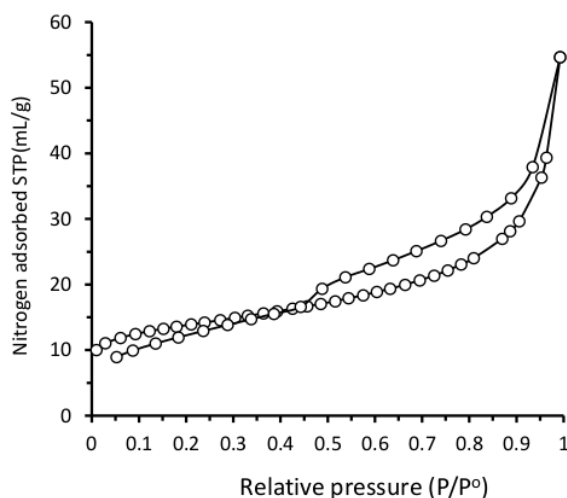


Fig. 4 Isotherm of nitrogen physisorption of Bayah natural zeolites

From the isotherm curve, one may predict qualitatively the textural properties of sample. Various models can be utilized to determine some important textural properties as presented in Table 1. Total specific surface area of Bayah zeolites was $46 \text{ m}^2/\text{g}$, much lower than synthetic mordenite with specific surface area of $> 300 \text{ m}^2/\text{g}$ [27]. The mesopore area was relatively higher than the micropore area, which could be beneficial in enhancing molecular diffusion within the pores. Hierarchical pores of zeolites were reported can improve the performance of various reactions such as catalytic cracking [28], aromatization of alkanes [29] dehydration of glycerol to acrolein [30], glycerol acetalization [15,31].

Table 1 Textural properties of Bayah natural zeolite as received

Textural properties	Quantity	Unit
Total Surface area	46	m^2/g
Micropore surface area	20	m^2/g
Mesopore surface area	26	m^2/g
Micropore volume	0.01	mL/g
Mesopore volume	0.07	mL/g
Total volume	0.08	mL/g

3.2 Effect of hydrothermal treatment temperature on the resulting modified zeolite crystallinity

Zeolite crystallinity is one indicator of how hydrothermal temperature affect the quality of recrystallized zeolite. We performed XRD analysis of parent Bayah natural zeolites to identify the initial phase and intensity peaks before hydrothermal recrystallization. The recrystallized samples of ZT 150, ZT 170, and ZT 190 were analyzed by XRD to determine the effect of temperature on the zeolite crystallinity.

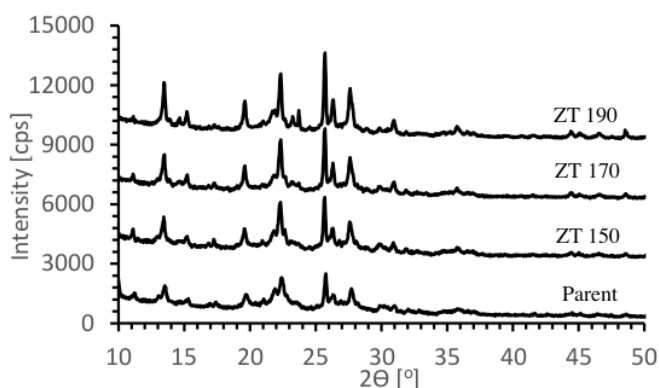


Fig. 5 XRD Analysis result of recrystallized zeolites.

Figure 5 shows X-ray diffraction patterns of zeolites recrystallized at 150, 170, and 190°C. There is an increase in the intensity at diffraction angles of 2θ 13.45°; 15.25°; 19.69°; 22.2°; 23.15°; 25.63°; 26.25°; 27.67°; and 30.89° with increasing recrystallization temperature. The recrystallization temperature correlated positively to the mordenite crystallinity judging from the increasing intensity of the diffraction peaks. However, there was a decrease in intensity at diffraction 2θ angles of 9.77°; 17.26° and 29.93° as the temperature increased, which indicated a decrease in the clinoptilolite phase. The peak intensity at 2θ of 21.8° belongs to the quartz phase of the zeolite ZT 170, which was lower than ZT 150. However, there was an increase in the quartz phase in ZT 190 sample.

The high crystallinity of recrystallized zeolites could be achieved thanks to the new mordenite crystal growth during the hydrothermal process, as also reported earlier [17]. The mordenite phase grew due to the addition of fumed silica and NaOH during the hydrothermal process. The increase of the XRD peaks intensity indicated a higher quantity of the mordenite phase, which was found positively correlated with the recrystallization temperature up to 170°C. However, quartz -the impurity phase- increased with higher intensity at recrystallization temperature of 190 °C. The mordenite might be unstable and acted as precursors for quartz phase growth in alkaline conditions, as also reported earlier [32]. A prolonged hydrothermal process might also completely convert the initial mordenite phase into other unwanted phases. Conversion of the mordenite phase into other phases is also affected by temperature and NaOH concentration [33,34].

3.3 Morphology and elemental compositions of hydrothermally modified zeolites

Microstructure images of the Na-parent sample and ZT 170 were captured using SEM to identify the morphology and growth of new crystals after hydrothermal treatment. Elemental compositions of the samples were analysed using EDS.

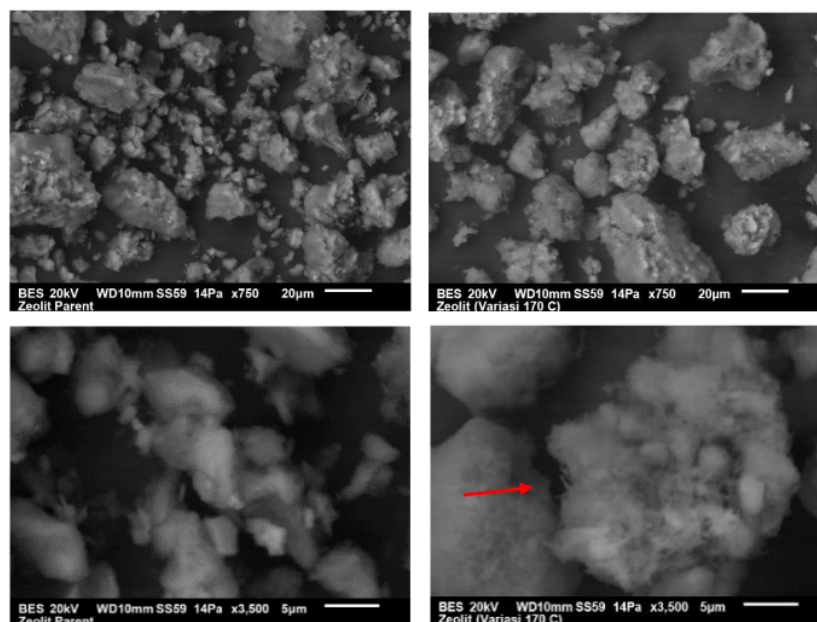


Fig.6 SEM images with different magnifications of (a) the Na-parent zeolite and (b) the modified zeolite hydrotreated at 170 °C (ZT 170 sample).

Figure 6 presents the SEM images of the parent and recrystallized samples at 170°C. At the magnification of 3500 \times , the needle-like sharp fibres appeared and increased in numbers in the ZT 170 (pointed by the arrow) when compared to the Na-parent zeolite. The typical form of natural zeolite mordenite is a needle [34], and the SEM images clearly demonstrate the increasing amount of zeolite mordenite for the recrystallized samples (ZT 170). The H-Parent sample did not clearly show a needle-shaped crystal shape like the typical form of recrystallized natural zeolites. The crystal growth of mordenite was in accordance with XRD results (Figure 5), which revealed a gradual increase in the intensity of the peaks associated with mordenite with increasing hydrothermal treatment temperature. Non-needle morphological forms were also still observed according to the results of the SEM analysis.

Table 2. Elemental compositions of H-parent and recrystallized natural zeolites ZT 170.

Element	Atom (%)	
	H-Parent	ZT 170
O	47.04	61.31
Si	15.66	21.50
C	32.15	12.25
Al	3.94	3.70
K	0.63	0.44
Total	100	100

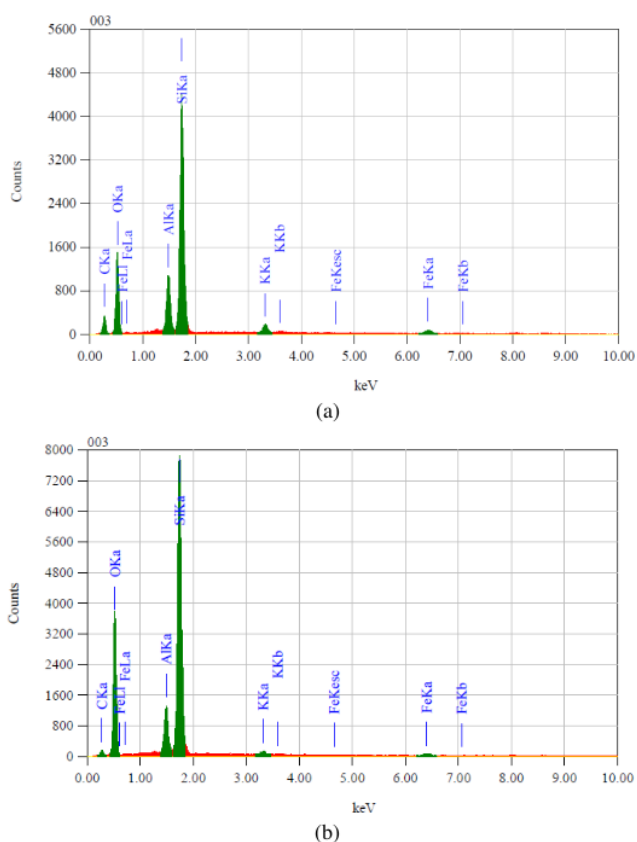


Fig. 7 Elemental composition of (a) parent and (b) ZT 170 on SEM-EDS analysis.

The results of the EDS analysis are summarized in Table 2. It shows that the constituent elements of the zeolite samples mainly consisted of O, Si, C, Al, and K. It showed that the hydrothermal process significantly affected the Si/Al ratio in the zeolite. The ratio of Si/Al for H-Parent and ZT 170 were 4 and 6 respectively (Figure 7). The increase in the Si/Al ratio in ZT 170 occurred due to the addition of fumed silica during the hydrothermal process that reacted with the aluminium on the surface of the zeolite framework. Increasing the Si/Al ratio after the hydrothermal recrystallization process enlarged the Brønsted acid site in the zeolite, turned it more acidic [17]. In our case, the addition of silica incorporated within the framework of mordenite also increased the numbers of the acid sites. The stronger the acidity of the active sites of a zeolite catalyst, the greater the protonation power of the catalyst, and could trigger a more reaction [35].

3.4 Glycerol acetalization on prepared catalysts

Catalysts testing for the reaction between glycerol and acetone were evaluated for 5 samples. We started the reaction without catalysts as the baseline. The protonated parent zeolites were first evaluated, followed by testing the hydrothermally recrystallized samples.

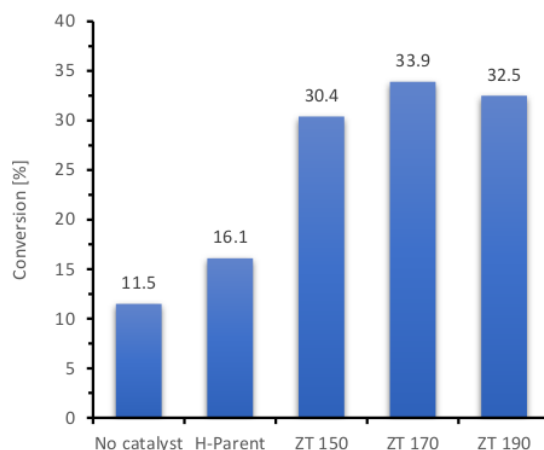


Fig. 8 Glycerol conversion over various zeolite catalysts.

Figure 8 shows that the type of catalyst affects the conversion of glycerol. The catalytic reaction on ZT 150 resulted in a glycerol conversion of 30.4%. The catalytic reaction on ZT 170 catalyst increased the glycerol conversion to 33.9%. The increasing conversion trend can be explained as follow. The increase of the zeolite recrystallization temperature resulted in the growth of the mordenite crystal phase which replaced the quartz phase on the ZT 170 catalyst as discussed earlier. The growth of the new mordenite crystal phase increased the acid sites numbers that facilitated more reaction. The higher the crystallinity of the zeolite is, the higher the Brønsted acid site [14]. The stronger the acidity of the active site of a zeolite catalyst is, the greater the protonation power of the catalyst [35].

The conversion using ZT 190 catalyst of 32.5% was slightly lower than ZT170 because of the formation of quartz as proved from the XRD (Figure 5). The increase in the quartz crystal phase resulted in a decrease in the Brønsted acid site because quartz does not have an acid active site for acetalization. Therefore, the decrease in Brønsted acid sites in the catalyst resulted in fewer acetalization reactions, as well as a decrease in glycerol conversion in the reaction using a ZT 190 when compared to the reaction using a ZT 170 catalyst. It is widely reported that Brønsted acidity played important role in the conversion of glycerol to aromatics over zeolite catalysts [36]. Hence, increasing Brønsted acid sites in zeolites strengthens the acidity as well as the activity of the catalyst, which eventually enhances the glycerol conversion as also demonstrated by our results.

3.5 Solketal characterization by FTIR

The titration method ASTM D7637-10 was performed to determine glycerol conversion. The solketal product was identified by using the FTIR. Glycerol was also analyzed by using FTIR to confirm its conversion during the acetalization.

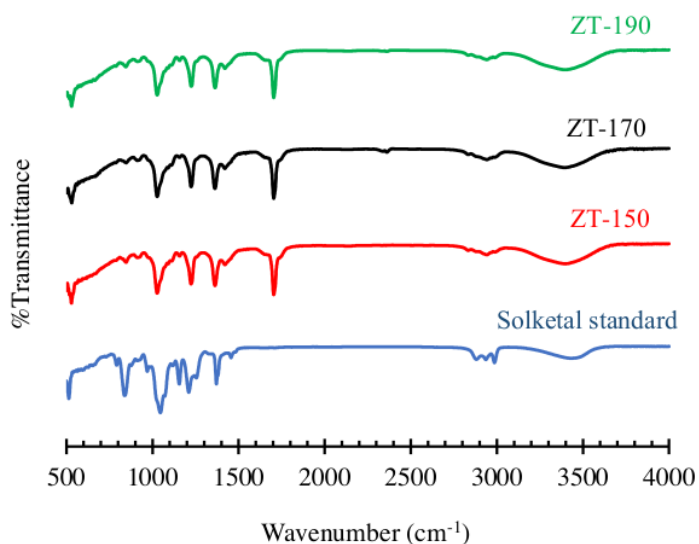
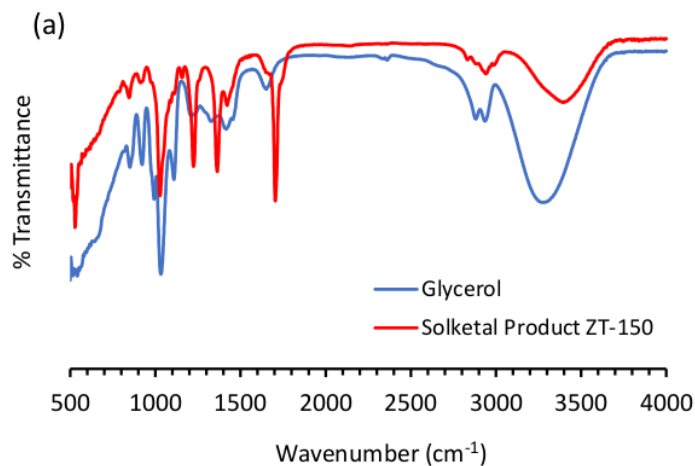


Fig. 9 FTIR spectra of acetalization products over modified zeolites

Figure 9 presents the FTIR spectra of the reaction mixture over various prepared catalysts. They show that the three variations presented the same wavenumber but with different intensities. Peaks at the wavenumber of 3100 cm⁻¹ to 3500 cm⁻¹ were associated with the variation of O-H functional group [37], in which the ZT 190 intensity was greater. It depicts that more glycerol presented in the reaction mixture, indicating a lower conversion when compared to the ZT 150 and ZT 170 catalysts. The peak was more intense at the wavenumber of 1362 cm⁻¹ associated with the methyl group in the ZT 170, if compared with the ZT 150 and ZT 190 catalysts, which indicated the presence of more solketal.



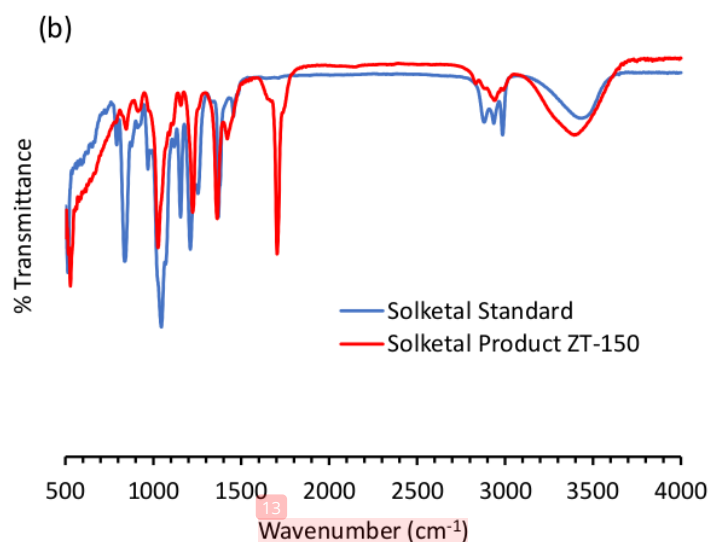


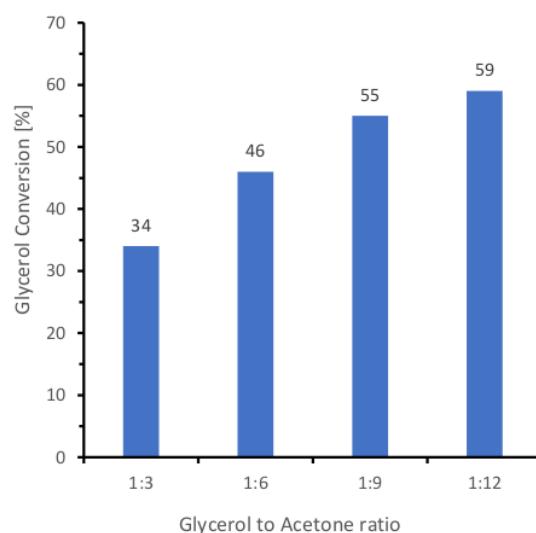
Fig. 10 FTIR spectra of (a) glycerol feed and (b) solketal products

The results of FTIR analysis on solketal, glycerol and reaction products were compared to determine the functional groups formed in the reaction products. Figure 10 confirms that solketal was formed as the main reaction product. A peak at a wavenumber of 1362 cm^{-1} (in Figure 10a) corresponded to the formation of a methyl group in the reaction product, which was the same as the standard solketal. It is worth noting that the methyl group in the reaction was also originated from methanol. When compared with the standard solketal, the FTIR spectra of the reaction products showed a stronger peak at the wavenumber of 3100 cm^{-1} than at 3500 cm^{-1} , which was associated with the O-H functional group. It means that the reaction products had more hydroxyl functional groups than the standard solketal, which probably came from unreacted glycerol. In addition, a peak at a wavenumber of 1705 cm^{-1} showed a C=O bond, which indicated that there was unreacted acetone.

Figure 10b compares FTIR spectra of the reaction product and glycerol. At the wavenumber range of 3100 cm^{-1} to 3500 cm^{-1} (associated with the O-H group), the intensity of the reaction was smaller than that of standard glycerol. It suggests that the glycerol from reactant was reduced in the reaction product because it had partly been converted to solketal.

3.6 Effect of glycerol to acetone ratio on glycerol acetalization

The ratio of reactants affects the collisions frequency and intensity between reactants. Higher collisions lead to an increase of the reaction rate. The tests on the effect of the ratio of reactants were carried out at 1:3, 1:6, 1:9 and 1:12 mole ratio of glycerol to acetone.



7 Fig. 11 Effect of glycerol to acetone ratio to glycerol conversion over ZT-170

Figure 11 presents glycerol conversion with various glycerol to acetone ratio. It shows that an increase in the ratio of reactants caused an increase in glycerol conversion. This is in accordance with the kinetic theory that the number of collisions between reactants is higher at higher reactant concentration which eventually increases the conversion of the reaction achieved. In this study, the most optimum ratio of reactants was 1:6 mole of glycerol/mole of acetone as the increment of glycerol conversion was the highest when the ratio of glycerol to acetone change from 1:3 to 1:9. The ratio of acetone to glycerol is significantly affected the rate of reaction was also reported elsewhere [38].

Table 3 compares catalyst's performance between the modified zeolites prepared in this study and the ones reported in the literature. In our work, recrystallized of Bayah natural mordenite showed the highest glycerol conversion of 59%. Despite of the recrystallized process to improve the crystallinity, acid site, and textural properties, the performance was still inferior to synthetic zeolites. The synthetic mordenite resulted in glycerol conversion of 65% [15]. The glycerol conversion increased to 80% after alkaline treatment of the synthetic mordenite. The mesopore created through the desilication process during alkaline treatment improved the mass transfer of reactants into the active sites as well as a product out of the active sites. Particle size also affects significantly glycerol conversion and solketal selectivity [18]. Acetalization over H-Beta nanoparticles with an average crystal size of 135 nm showed the highest glycerol conversion of 86% over the larger crystal size of 450 nm with a conversion of 38%. The small crystal size shortened the diffusion path, hence improving the mass transfer during acetalization. Besides improving the mass transfer aspect, acetalization over zeolite was improved by creating hydrophobicity as reported by [39,40]. Glycerol and acetone are immiscible which the immiscibility could be improved by using hydrophobic zeolites.

Table 3 Comparison of the performance of modified natural zeolites prepared in this work with synthetic zeolites reported in the literature

Catalyst	Catalyst Loading to glycerol (%)	Temperature (°C)	Time (min)	Glycerol to Acetone ratio (-)	Glycerol conversion (%)	Ref.
Bayah Natural Zeolites	10	50	90	1:12	59	This work
MOR synthetic	1	70	-	1:1	65	[15]
MOR-Hierarchical	1	70	-	1:1	80	[15]
H-Beta (crystal size 135 nm)	5	28	60	1:2	86	[18]
H-Beta microparticle (450 nm)	5	28	60	1:2	38	[18]
H-Beta	8.3	50	60	1:3	85	[41]
HY-Hydrophobic (OTS)	5	30	480	1:12	85	[39]

4. Conclusion

This work demonstrated that natural mordenite could be improved through the hydrothermal process by showing a higher conversion of glycerol acetalization when used as the catalyst. The hydrothermal temperature affected the intensity of diffraction peaks associated with the mordenite phase. The hydrothermal temperature of 170°C showed a mordenite phase with high intensity peaks and a low quartz impurity phase. Glycerol conversions over recrystallized mordenite ZT 170 with acetone to glycerol ratio of 3 and 12 were 33.9 and 59%, respectively. The higher ratio of acetone to glycerol led to high glycerol conversion. Products identification by FTIR analysis showed that the solketal was the main component of the reaction. The simple recrystallization process reported in this study increased the glycerol conversion from 11.5% (without catalyst), 16.5% (with Bayah natural zeolite catalyst) and to 59% (with ZT 170 catalyst). The results are very promising considering that further modifications can still be done to improve the catalyst performance

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