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Research Article

Modification of Mordenite Characteristics by H₂C₂O₄ and/or NaOH Treatments and Its Catalytic Activity Test in Hydrotreating of Pyrolyzed α-Cellulose

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Abstract

The research about modification of mordenite characteristics has been performed by $H_2C_2O_4$ and/or NaOH treatments and catalytic activity tests in hydrotreating of pyrolyzed α -cellulose. Commercial mordenite (HSZ-604OA) as mordenite control (HM) immersed in 0.05, 0.5, and 1.0 M $H_2C_2O_4$ at 70 °C for three hours resulting in HM-0.05, HM-0.5, and HM-1. The four mordenites were immersed in 0.1 M NaOH for 15 minutes resulting in BHM, BHM-0.05, BHM-0.5, and BHM-1. The catalysts obtained were analyzed by XRD, SAA, ICP, and acidity test. The catalytic activity of the mordenites was evaluated in hydrotreating of pyrolyzed α -cellulose using stainless steel reactor with an H_2 gas flow rate of 20 mL.min⁻¹ at 450 °C for two hours with a catalyst: feed weight ratio of 1:60. The liquid products obtained from the hydrotreating were analyzed using GC-MS. The research results showed that the $H_2C_2O_4$ and/or NaOH treatment towards the mordenites increased Si/Al ratio and decreased crystallinity. The acidity of mordenites decreased along with the increase of the Si/Al ratio. The average pore diameter of BHM, BHM-0.05, BHM-0.5, and BHM-1 mordenites were 2.898; 3.005; 3.792; 7.429 nm, respectively. The BHM-0.5 mordenite showed the highest catalytic activity in generating liquid product (88.88 wt%) and selectivity toward propanol (4.87 wt%). The BHM-1 mordenite showed catalytic activity in generating liquid product (41.16 wt%) and selectivity toward ethanol (1.21 wt%) and 2-heptyne (4.36 wt%).

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Keywords: H₂C₂O₄ treatment; NaOH treatment; α-cellulose hydrotreating; mordenite; mesoporous structure

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1. Introduction

Zeolite is a crystalline aluminosilicate material that has micro-size pores (<2 nm) [1]. Zeolite has been widely used as a catalyst in various industrial processes such as oil refining, petrochemicals, hydrocarbon conversion, and as

an adsorbent in hydrocarbon refining [2]. There is currently an increasing interest in the industry, especially involving large molecules in the process. Zeolite has a faster diffusion rate of reactants and a higher conversion, but it has a weakness, namely the limitation of intracrystalline diffusion originating from a relatively smaller micropore network [3]. This limits the performance of zeolites in the catalyst industry. Therefore, the catalyst structure that has a pore

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diameter of meso-size is more desirable because it can increase the effectiveness of the petroleum processing process [1].

Great efforts for the formation of mesoporous zeolites have been carried out in the industry. Mesoporous zeolite synthesis can be carried out using a template. In general, the template used is a surfactant with a long chain. This method has been proven to produce mesoporous zeolites effectively [4]. However, the mass production of mesoporous zeolite materials using this method is always constrained due to the difficulty of the synthesis process with hydrophobic templates and the high price of templates [5]. Therefore, a more practical and economical method of mesoporous zeolite synthesis is needed, such as alkaline treatment (desilication) [6]. Researcher succeeded in synthesizing mesoporous beta zeolites using NaOH treatment. These mesoporous beta zeolites were shown to have higher catalytic activity than beta micropore zeolites in the α-pinene isomerization process [7].

This mesoporosity recognition method is related to the Si/Al zeolite ratio [8]. The low Si/Al ratio value has a limited effect from the alkaline treatment because it contains relatively high aluminum content which can prevent more dominant desilication. Among the various zeolites, mordenite is widely used in the hydrotreating process to produce biofuels [9]. The mordenite Si/Al ratio is in the range of 10 [10]. To achieve the Si/Al ratio within the optimal range for the dominant desilication, the dealumination needs to be done before. Dealumination using strong acids has the potential to produce amorphous debris on the zeolite surface so that it can clog the pores of the zeolite, therefore the effectiveness of the zeolite as a catalyst is reduced. Dealumination using a weak acid such as H₂C₂O₄ is still rarely done, but the dealumination process can increase the Si/Al ratio of zeolite without damaging the crystalline framework of the zeolite [11]. Acid and alkaline treatment sequentially for modification of mordenite into mesoporous mordenite using parent mordenite with Si/Al ratio 11.33. Acid treatment can increase the Si/Al ratio of mordenite to 21.65, then alkaline treatment causes mesoporosity in the mordenite [12].

Cellulose is a candidate biomass source with the most potential to replace fossil fuels in the next few years because it can reduce greenhouse gas emissions [13]. One type of cellulose polymer is α -cellulose. The α -cellulose polymer has a degree of polymerization above 300 [14]. This results in a large carbon source in α -

cellulose that can be converted into biofuel. The hydrotreating process is carried out on biooil produced from α -cellulose pyrolysis. This process can convert the compounds in bio-oil in the form of carboxylic acids, aldehydes, and ketones into fuel fractions such as hydrocarbons and alcohol [15].

Based on this description, mordenite modification was carried out by treating H₂C₂O₄ and/or NaOH. Treatment of zeolite in acid solution can extract Al from the structure and consequently the overall Si/Al ratio will increase [1]. In addition, during the dealumination process, the number of zeolite acid sites will make the decrease was due to the extraction of aluminum atoms from the zeolite framework [16]. The higher the Si/Al zeolite ratio, the higher thermal and chemical stability. Hence, zeolites with a high Si/Al ratio are suitable for using as a catalyst in the hydrotreating process [17]. Previous researcher [18] reported on his research in the formation mesoporosity to mordenite with a Si/Al ratio of 20 and 30 with treatment NaOH, the result is a zeolite with a Si/Al ratio of 20, no desilication occurs dominant, because in addition to desilication, dealumination also occurs. Other research [1] reported that desilication only occurs naturally dominant only in the Si/Al mordenite ratio above 25. Mesoporous formation can increase the internal transport of large molecules, which results in an increase in the catalytic activity of the desilicated zeolite. HZSM1-5 micropore zeolite treated with alkaline has been reported by previous other researcher [19] that significantly produce high catalytic activity for the gas phase in hydrotreating cumene and liquid phase in the α -pinene isomeration.

This study examines the effect of $H_2C_2O_4$ and/or NaOH treatment on Si/Al ratio, crystal-linity, and acidity of mordenite and also the effect of NaOH treatment on mordenite pore characteristics. Besides, the activity and selectivity of the catalyst were tested in the α -cellulose hydrotreating process.

2. Materials and Methods

2.1 Materials

The materials used in this study were synthetic mordenite type zeolite (HSZ-640HOA, Tosoh Corporation Japan®), NH₄Cl, H₂C₂O₄, NaOH, 37% HCl, 40% HF, 65% HNO₃, and 25% NH₃ (Merck®). Besides, cellulose (Sigma-Aldrich #C8002), Whatman filter paper No.42, bi-distilled water, N₂ and H₂ gases (PT. Samator Gas) were utilized.

2.2 Instrumentations

The instruments used for analysis are X-ray Diffraction (Rigaku® Miniflex 600), Inductively Coupled Plasma (Shimadzu® ICPE-9820), Surface Area Analyzer (Quantachrome® NOVAtouch), and Gas Chromatography–Mass Spectrometer (Shimadzu® QP 2010S).

2.3 Experimental Procedures

2.3.1 Acid treatment on mordenite

Ion exchange of zeolite type mordenite (HSZ-604HOA) was carried out with 1 M NH₄Cl for 3 hours at 70 °C and calcined in a furnace at 550 °C for 5 hours as HM. Zeolite HM formed was refluxed in a solution of $\rm H_2C_2O_4$ (0.05; 0.50; and 1.00 M) at a temperature of 70 °C for 2 hours, then washed with bidistilled water until it was neutral, dried overnight at 110 °C, then calcined in a furnace 550 °C for 5 hours to form HM-0.05; HM-0.5; and HM-1.

2.3.2 Alkaline treatment on mordenite

The HM; HM-0.05; HM-0.5; and HM-1 was stirred respectively in 0.1 M NaOH for 15 minutes at room temperature (29 °C), then ion exchange was carried out with 1 M NH₄Cl solution at 70 °C for 2 hours, washed with bidistilled water until it was neutral, dried overnight, then calcined in a furnace at a temperature of 550 °C for 5 hours. In the end, the zeolite BHM, BHM-0.05, BHM-0.5, and BHM-1 were obtained.

2.3.3 Determination of the Si/Al ratio

Determination of the Si/Al ratio was carried out by mixing each 0.1 gram of the digestible mordenite sample with 2 ml of aquaregia (HCl:HNO₃ = 3:1) and 1 mL of HF in a plastic volumetric flask. The solution was stirred until homogeneous (all zeolite dissolves). Furthermore, it was diluted with aquabidest until 100 mL (main solution). Then a 10X dilution of the main solution was made, and this solution was analyzed as a sample. The Si standard solution used was dissolved in aquabidest to obtain a concentration variations of 20, 40, 60, 80, and 100 ppm. The standard Al solution used was dissolved in aquabidest to obtain variations in the concentration of 2.4, 6, 8, and 10 ppm. Each solution was measured by ICP.

2.3.4 Crystallinity Analysis Using X-Ray Diffraction

The structure of zeolites of HM, HM-0.05,

HM-0.5, HM-1, BHM, BHM 0.05, BHM-0.5, and BHM-1 were analyzed for their crystallinity using X-Ray Diffraction (XRD) at 2θ in the range $2-80^{\circ}$. Analysis with XRD instrument to determine how much effect the dealumination has on the crystallinity of mordenite samples. From XRD, it can be seen what percentage of damage to mordenite crystals after dealumination. The percentage of zeolite crystallinity was obtained from the ratio between the mordenite intensity after $H_2C_2O_4$ and/or NaOH treatment to mordenite (HM) as written in Equation (1).

$$\% Crystallinity = \frac{\sum mordenite\ intensity\ after\ treatment}{\sum mordenite\ HM\ intensity} \times 100\% \quad (1)$$

2.3.5 Test the acidity of the catalyst

The acidity of the catalyst was tested using the gravimetric method with ammonia gas as the adsorbate base. The porcelain crucibles were heated at 100 °C for 1 hour then weighed and the mass obtained was recorded as M_0 . The mordenite catalyst was inserted into each porcelain crucible and the mass obtained was recorded as M_1 . The porcelain crucible containing the sample was put into a desiccator then vacuumed and then flowed with the adsorbate alkaline steam and then left for 24 hours. After the adsorption process, each sample was weighed and the mass obtained was recorded as M_2 . The catalysts before and after base adsorption were analyzed by FTIR. The acidity of the catalyst is determined by the following Equation (2):

$$Acidity = \frac{M_2 - M_1}{M_1 - M_0} \times \frac{1000}{Mr} \quad (mmol \ g^{-1})$$
 (2)

where, M_0 is empty porcelain crucible mass (g), M_1 is porcelain crucible mass + initial sample before adsorption (g), M_2 is porcelain crucible mass + final sample after adsorption mass (g), Mr is molecular relative mass of base adsorbate (g.mol⁻¹).

2.3.6 Pore Properties Analysis by Nitrogen Gas Adsorption

Zeolites, treated with NaOH, namely: BHM, BHM $_{0.05}$, BHM $_{0.5}$, and BHM $_{1}$, were analyzed for their pore characteristics using adsorption and desorption of N $_{2}$ gas. The analysis was carried out at a temperature of 77.35 K. The Brunauer – Emmet – Teller (BET) theory was used to determine the surface area of zeolites. Then for the pore size distribution the Barrett – Joyner – Halenda (BJH) theory was used. The distribution of micropores and mesopores was determined using the t-plot method using the

Harkins-Jura formula. The thickness (t) of the zeolite was calculated using the equation for silica-based materials. Equation (3) was written as follows:

$$t(\text{Å}) = \left[\frac{13.99}{\log\left(\frac{p}{p_0}\right) + 0.034}\right]^{0.5}$$
(3)

Then the t-plot was made using the data adsorbed volume as the Y axis and thickness as the X axis. The slope of the t-plot linear line represents the amount of external surface area with mesoporous calculated by the following Equation (4):

$$S_t(m^2g^{-1}) = s \times 15.47$$
 (4)

where S_t is external surface area, s is slope of linear t-plot line.

The intercept from linear *t*-plot line describes micropore volume that it is been calculated with Equation (5):

$$V_{micro}\left(cm^{3}g^{-1}\right) = i \times 0.001547$$
 (5)

where V_{micro} is micropore volume, i is intercept of linear t-plot line.

2.3.7 Pyrolysis of α-cellulose

A total of 25 grams of $\alpha\text{-cellulose}$ is put into the pyrolysis reactor which is made of stainless steel. Pyrolysis was carried out with N_2 gas with a flow rate of 20 mL.min $^{-1}$ at a temperature of 600 °C for 3 hours. The resulting liquid product is cooled by a condenser and collected in a flask. The pyrolysis product of $\alpha\text{-cellulose}$ was then analyzed using a Gas Chromatography–Mass Spectrometer (GC–MS) to determine its compound content.

2.3.8 Catalyst activity test

Hydrotreating reaction of α-cellulose in three variations of conditions, namely thermal hydrotreating, catalytic hydrotreating with mordenite catalyst before and after NaOH alkaline treatment. The hydrotreating reaction with a mordenite catalyst was carried out on cellulose with a catalyst / feed ratio of 1/60 (w/w). The feed and catalyst are put into the sleeve with the feed position under the catalyst, then the sleeve is inserted into the reactor. The hydrotreating reaction was carried out with hydrogen gas with a flow rate of 20 mL.min⁻¹ at a temperature of 450 °C for 2 hours. In comparison, a thermal hydrotreating reaction is also carried out. The product formed is flowed through a condenser (cooler) to a flask which is cooled with an ice bath.

The percentage (%) conversion of the hydrotreating reaction results is determined by the following Equations (6), (7), and (8):

Liquid product (wt%) =
$$\frac{M_{j1} - M_{j0}}{M_s - (M_{u1} - M_{u0})} \times 100\%$$
 (6)

$$Coke(wt\%) = \frac{M_{k1} - M_{k0}}{M_s - (M_{u1} - M_{u0})} \times 100\%$$
 (7)

$$Gas(wt\%) = 100\% - (liquid\ product - coke)$$
 (8)

where M_s is mass of α -cellulose, $M_{j\theta}$ is mass of an empty flask, M_{jI} is flask mass after hydrotreating, $M_{u\theta}$ is mass of the feed container before hydrotreating, M_{uI} is mass of the feed container after hydrotreating, $M_{k\theta}$ is mass of catalyst before hydrotreating, M_{kI} is mass of catalyst after hydrotreating.

3. Results and Discussion

In the formation of mesoporosity in a zeolite, the Si/Al ratio is an important thing to consider because it affects the activity and

Table 1. Si/Al ratio, acidity, and crystallinity of catalyst.

Sample	Si/Al ratio	Acidity (mmol.g ⁻¹)	Crystallinity (%)
HM	9	4.85	100
HM-0.05	15	3.98	79
HM-0.5	62	2.80	76
HM-1.0	92	1.65	80
BHM-0	11	5.08	76
BHM-0.05	20	4.97	96
BHM-0.5	47	4.65	76
BHM-1.0	56	2.35	78

thermal stability of the zeolite. Dealumination process in zeolites can generally increase the activity and thermal stability of these zeolites [20]. Dealumination is carried out by adding an acid solution. This dealumination process can cause the Si–O–Al bonds of the zeolite to be damaged, causing the release of aluminum from the zeolite framework [21]. Therefore, to increase the Si/Al ratio of mordenite, the dealumination process needs to be carried out using oxalic acid before alkaline treatment (the desilication process). From the results of measurements using ICP (Table 1), it can be seen that there was a change in the Si/Al ratio both in mordenite before and after NaOH treatment.

Table 1 shows that the Si/Al ratio of mordenite has quite significantly increased as the concentration of H₂C₂O₄. The increase in the Si/Al ratio was due to the dealumination process of the mordenite which resulted in the release of Al from the zeolite framework [22]. During the dealumination process, the H⁺ ion generated from the ionization of oxalic acid in water will break the Al bond in the zeolite framework and is attacked by oxygen atoms bound to Si and Al. The H+ ions break more easily Al-O bonds than Si-O. This is because the dissociation energy of the Al-O bond (116 kcal/mol) is lower than Si-O (190 kcal/mol). The $C_2O_4^{2-}$ ion from the acid ionization will affect the strength of the Al-O and Si-O bonds. The C₂O₄²⁻ ions will bind with Al atoms which have a smaller electronegativity value (1.61) than Si (1.90). Breaking of Al-O bond by H⁺ ions and binding of C₂O₄²⁻ ions to Al cause Al to be isolated from the zeolite framework to the Si/Al ratio increases [23].

In contrast to the dealumination process, the desilication process through NaOH treatment on the mordenite catalyst causes a decrease in the Si/Al ratio as shown in Table 1.

Figure 1. Desilication reaction using NaOH [23].

This occurs because during the alkaline treatment NaOH causes silicon to be extracted from the zeolite framework. The mechanism of the process in Figure 1.

However, the BHM and BHM-0.05 catalysts experienced an increase in the Si/Al ratio after NaOH treatment towards HM and HM-0.05. This happens because the low Si/Al ratio results in desilication which is followed by the dealumination process. If the Si/Al ratio is low, the distance between Si and Al is close together. When the silicon is extracted, aluminum also accompanies it because of the amphoteric nature of aluminum [16]. At a low Si/Al ratio, the desilication process is limited by the repulsion between OH- and the negative charge of the zeolite lattice, whereas at high Si/Al ratio can lead to loss of crystallinity. Generally, the alkaline treatment requirement was successful when the Si/Al ratio had above 25 [25]. Dealumination was more dominant than desilication for mordenite with a Si/Al ratio of 20 [26].

Zeolites that have been given NaOH base treatment are then subjected to ion exchange process with ammonium ions. The exchange between the cations in the zeolite and NH₄⁺ aims to replace all impurities in the form of cations in the zeolite because in the zeolite there may still be alkaline or alkaline earth cations, such as: K⁺, Na⁺, Ca²⁺, Mg²⁺ which act as a zeolite balancer, which can be exchanged with other cations, so that all these cations will be exchanged into NH₄⁺ by pressing the metal ions, followed by calcination, because at high temperature heating can remove water molecules bound to the zeolite so that the surface area increases.

Measurement of the acidity of the catalyst was carried out using a gravimetric method based on the difference in weight of the zeolite after and before adsorbing ammonia gas (NH₃). Ammonia base was chosen as the adsorbate because of the small molecular size so that it can be adsorbed into all zeolite pores. The more ammonia base is absorbed, the more acid sites the catalyst has. Therefore, acidity is measured based on the amount of NH3 (mmol) adsorbed on the surface of the catalyst in each weight of the catalyst to be measured for acidity. Ammonia base was chosen as the adsorbate because its molecular size is small enough so that it can be adsorbed into all zeolite pores. The acidity of the catalyst reflects the large number of Bronsted and Lewis acid sites. Gravimetrically, the number of acid sites can be determined by measuring the amount of base reacting with the acid catalyst. The amount of base adsorbed will be proportional to the acid sites present in

the catalyst. The acidity test of the catalyst was carried out to determine the effect of acid and/ or alkaline treatment on mordenite on both the Bronsted acid and Lewis acid sites. Based on the data from the determination of the total acid site in Figure 2, it shows that the increasing Si/Al ratio of mordenite catalyst, the total acid site number of the catalyst has decreased. This decrease in acidity is due to the reduced number of Bronsted acid sites contained in the zeolite. Bronsted acid sites will decrease along with the reduction of aluminum content in a zeolite [1] in the dealumination process. The Bronsted zeolite acid site comes from protons (H+) that are covalently bonded to oxygen atoms that bridge the skeletons of silicon and aluminum atoms.

The Bronsted acid site acts as a proton donor. Although there is a decrease in the number of acid sites, an increase in the Si/Al ratio can lead to an increase in acid strength. This is due to changes in the distribution of aluminum atoms in the zeolite framework. However, although there is a decrease in the number of mordenite acid sites, it can increase the strength of the acid, because the farther the distance between the aluminum atoms in the zeolite framework, the less interference between the aluminum atoms so that the Bronsted acid sites possessed by the aluminum atoms experience an increase in acid strength [27]. Based on the data in Table 1 shows that the increasing Si/Al ratio of the mordenite catalyst, the total acid site number of the catalyst has decreased. This decrease in acidity is due to the reduction in the number of Bronsted acid sites contained in zeolites after the dealumination process. The Bronsted acid site of zeolite comes from protons (H⁺) covalently bonded to oxygen atoms that bridge the skeletal silicon and aluminum atoms. Bronsted acid sites will decrease as the aluminum content in a zeolite decreases [1].

Based on Table 1, the total number of acid sites in mordenite after alkaline treatment has increased compared to mordenite before alkaline treatment. This is due to the emergence of Lewis acid sites due to the presence of Al in the extra framework position. The role of an extra aluminum framework (EFAL) can be generated through a series of mordenite realization processes, namely the desilication processes, namely the desilication process produced due to the presence of Al in a non-skeletal position [7]. This phenomenon also occurs in a study conducted by Tian *et al.* [5] which showed an increase in the number of acid sites on zeolites after the alkaline treatment was carried out [5].

The crystallinity of zeolite as a catalyst is very important because it is related to the stability of the zeolite at high temperatures and its activity. The crystallinity test on the mordenite catalyst used X-ray diffraction (XRD) to determine the effect of dealumination with acids and/or desilication with bases on mordenite on crystallinity (peak intensity). In Figures 2 and 3, it can be seen that H₂C₂O₄ and/or NaOH treatment does not damage the crystalline framework of mordenite. This is evidenced by the 3 highest peaks in mordenite at $2\theta = 22$, 25, and 27° where the peaks were still visible on zeolites but decreased in intensity after H₂C₂O₄ and/or NaOH treatment. This is due to the presence of Al and/or Si atoms extracted

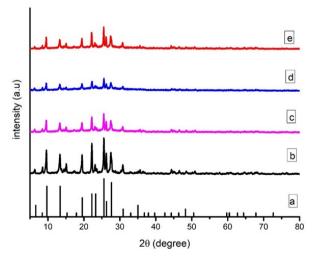


Figure 2. Diffractogram of mordenite before alkaline treatment (a) JCPDS card 11-0155, (b) HM, (c) HM-0.05, (d) HM-0.5, (e) HM-1.

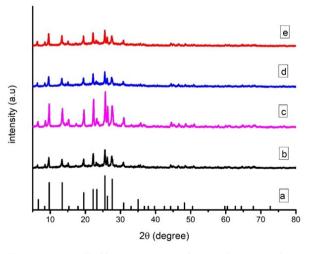


Figure 3. Diffractogram of mordenite after alkaline treatment (a) JCPDS card 11-0155, (b) BHM, (c) BHM-0.05, (d) BHM-0.5, (e) BHM-1.

from the zeolite framework and match with JCPDS card 11-0155.

Analysis of the pore characteristics of the catalyst was carried out using a Gas Sorption Analyzer (GSA) which aims to determine the impact of alkaline treatment on the pore characteristics of the mordenite catalyst. The surface area of the catalyst is defined as the number of surfaces (contact areas) contained in the weight units of the catalyst. If the surface of the catalyst is wide, the probability of the reactants being adsorbed on the surface of the catalyst will be higher so that it can increase the activity of the catalyst. The determination of the surface area of the catalyst was measured using the Branauer-Emmet-Teller method. Figure 4 shows that all mordenite catalysts after alkaline treatment show a type IV isotherm graph which is characteristic of mesoporous materials from the presence of a hysteresis loop [27].

However in BHM-1, it can be seen that the hysteresis loop does not close. Usually, the loop that does not close is well known as low-pressure. However, in this case, the loop that does not close is not because of the low-pressure hysteresis loop. In the low-pressure

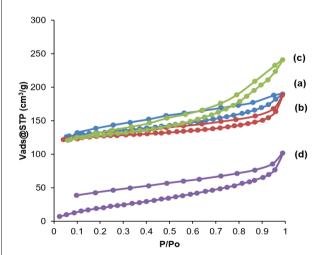


Figure 4. N₂ isotherm adsorption of mordenite after alkaline treatment (a) BHM, (b) BHM-0.05, (c) BHM-0.5, (d) BHM-1.

hysteresis loop, in the desorption process, the amount of adsorbate decreases as the relative pressure decreases. In this case, as the relative pressure decreases, the amount of the adsorbate increases. This shows that the desorption process releases more gases than the amount of gases in the adsorption process. This can be due to the incomplete degassing process [12].

The pore size distribution gives an overview of the number of pores in the micropore, mesoporous, or macropore regions of the catalyst. The pore size is desirable because it is related to the feed compound that will interact and diffuse with the surface of the catalyst. The pore distribution in this study was carried out using the Barret–Joyner–Halenda (BJH) method.

It can be seen in Figure 5 that the pore distribution of mordenite after alkaline treatment shows the pore diameter with the meso-size (3-30 nm). This pore diameter increases with increasing Si/Al ratio. The highest mesopore distribution is owned by the BHM-1 catalyst which illustrates that this catalyst has the largest mesopore compared to other catalysts. This is because this catalyst has the highest Si/Al ratio before the alkaline treatment so that the desilication process is more optimal.

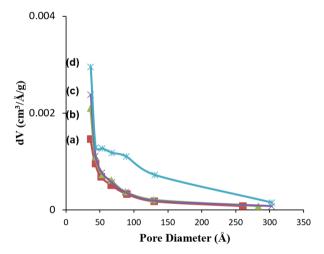


Figure 5. Pore distribution of mordenite after alkaline treatment (a) BHM, (b) BHM-0.05, (c) BHM-0.5, (d) BHM-1.

Table 2. Pore volume properties of mordenite.

Catalyst	Total pore volume (cm³/g)	$V_{ m micro} \ m (cm^3/g)$	$V_{ m meso} \ m (cm^3/g)$	$V_{ m micro} \ (\%)^{ m a}$	$V_{ m meso} \ (\%)^{ m b}$
BHM	0.294	0.168	0.126	57.04	42.96
BHM-0.05	0.290	0.175	0.115	60.17	39.81
BHM-0.5	0.373	0.156	0.217	41.78	58.22
BHM-1	0.157	0.003	0.154	2.10	97.90

Note: ${}^{a}V_{micro\;(\%)} = (V_{micro\;(cm^{3}/g)}/Total\;pore\;volume\;_{(cm^{3}/g)})\;x\;100\%$ ${}^{b}V_{meso\;(\%)} = (V_{meso\;(cm^{3}/g)}/Total\;pore\;volume\;_{(cm^{3}/g)})\;x\;100\%$

The distribution of micropores and mesopores was measured using the *t*-plot method. The intercepts obtained from the *t*-plot method illustrate the composition of the pore volume in mordenite as presented in Table 2. Based on Table 2, it shows an increase in the percentage volume of meso in mordenite after alkaline treatment as the Si/Al ratio of the mordenite increases. The phenomenon that occurs for BHM-0.05 is due to the Si/Al ratio before the base treatment is less than 25 so that the mesoporosity formed is not optimal.

The total surface area (S_{BET}) of the zeolite was calculated by the multi-point BET method. Mesoporous surface area can be calculated using the t-plot method. Mesoporous surface area calculations are performed using the slope of the mordenite t-plot chart. The results of the calculations from the t-plot method on the surface area are presented in Table 3. Table 3 shows that the percentage of the surface area of the meso after alkaline treatment has generally increased as the Si/Al ratio of the mordenite increases. Based on the data, it shows that alkaline treatment on mordenite can produce mordenite with a meso pore diameter, the higher the Si/Al ratio of mesoporosity mordenite produced also increases, this is because alkaline treatment can cause desilication, which can enlarge pores. Compared to catalysts, the higher the Si/Al desilication ratio is more optimal, so that the mesoporosity formed is also more optimal. In compared to catalysts with low Si/Al ratios, the BHM-1 has the highest average pore diameter because BHM-1 has the highest Si/Al ratio compared to other cata-

The catalyst activity test was used to determine the ability of the catalyst to convert α -cellulose through a hydrotreating reaction into a shorter hydrocarbon product [28]. The α -cellulose powder used is a synthetic product so it is expected that it does not contain impurity components. Before hydrotreating,

α-cellulose pyrolysis is carried out, which aims to obtain α-cellulose in the form of a yellow liquid (bio-oil). α-Cellulose bio-oil will change color to brown when allowed to stand at room temperature and open conditions. This indicates that α-cellulose is not sufficiently stable so that it is easily oxidized. The conversion value of α-cellulose pyrolysis in this study is around 45 wt%. The content of α-cellulose bio-oil was analyzed using GC-MS. The results of the GC-MS analysis are shown in Table 4.

Table 4 shows that the content of the pyrolyzed α -cellulose contains ketones and carboxylic acids. These results are consistent with the research conducted by Huber *et al.* [29]. The compound content in the pyrolyzed α -cellulose still has low quality as a fuel due to the presence of oxygen atoms. Therefore, the hydrotreating process needs to be done.

Hydrotreating of pyrolyzed α -cellulose produces the brighter yellow liquid. The α -cellulose hydrotreating reaction was carried out with and without using a catalyst. Hydrotreating is carried out to test the activity between catalysts. The distribution of products from the hydrotreating process is shown in Table 5. The hydrotreating results indicate that catalytic hydrotreating produces more liquid

Table 4. The compound containing in bio-oil α -cellulose based on GC-MS result.

Group	Product description	wt%
	Acetone	6.59
Ketone	1-hydroxy-2- propanone	7.13
	2-hexyne-2-one	6.52
Carboxylic acid	Acetate acid	10.72
	14.04	
	45	

Table 3. Surface area and average pore diameter of mordenite

Catalyst	Total surface area (m²/g)	$S_{ m meso} \ (m m^2/g)$	$S_{ m micro} \ (m m^2/g)$	$S_{ m meso} \ (\%)^{ m a}$	$S_{ m micro} \ (\%)^{ m b}$	Average pore diameter (nm)
ВНМ	405.6	85.30	320.3	21.03	78.97	2.898
BHM-0.05	386.4	47.46	339.6	12.28	87.88	3.005
BHM-0.5	393.5	96.71	296.8	24.58	75.43	3.792
BHM-1	84.36	80.56	3.815	95.49	4.522	7.429

Note: ${}^{a}S_{meso} \, {}^{(\%)}_{(\%)} = (S_{meso} \, {}^{(m^2/g)}_{g}) / \text{Total surface } area_{(m^2/g)}) \times 100\%$ ${}^{b}S_{micro} \, {}^{(\%)}_{(\%)} = (S_{micro} \, {}^{(m^2/g)}_{g}) / \text{Total surface } area_{(m^2/g)}) \times 100\%$

than thermal products. This phenomenon follows the statement of Vogt and Weckhuysen [30] that the use of catalysts in the hydrotreating process can increase the percentage of liquid fraction and product quality [30]. Thermal hydrotreating occurs through a free radical mechanism so that it tends to produce shorter carbon chains (gas products). On the other hand, catalytic hydrotreating occurs by the mechanism of carbonium ions which are more likely to produce liquid products containing long-chain hydrocarbons [31]. In overall, the al-

Table 5. The product distribution of α -cellulose hydrotreating.

Catalant	Product Distribution (wt%)					
Catalyst	Liquid	Coke	Gas			
Thermal	23.16	_	76.84			
$_{ m HM}$	31.74	1.720	66.54			
HM-0.05	37.19	0.010	62.80			
HM-0.5	82.62	0.030	17.35			
HM-1	29.58	3.010	67.41			
BHM	60.48	1.080	38.44			
BHM-0.05	73.50	1.050	25.45			
BHM-0.5	88.88	0.450	10.67			
BHM-1	41.16	0.030	58.81			

kaline treatment caused a significant increase in the liquid product fraction compared to before the alkaline treatment. The liquid product from: HM to BHM was 28.74%, HM-0.05 to BHM-0.05 was 36.31%, HM-0.5 to BHM-0.5 was 6.26%, and HM-1 to BHM-1 was 11.58%. In most of results, after being treated with NaOH, the catalysts produced the more liquid product, indicating that the increase in average pore size, pore volume, and surface area improve the catalyst performance to give better activities in producing a liquid product.

Sample BHM-0.5 had the best activity as a catalyst due to the highest liquid product yield (88.88%). This indicated that BHM-0.5 had the most optimal state between a combination of acidity, pore size, pore volume, and surface area to yield liquid products among the other samples effectively. In the BHM-1 catalyst, there was a decrease in the liquid product even though it had a higher mesopore diameter, surface area, pore-volume, compared to other catalysts, but it had a significant reduction in the number of acid sites at high Si/Al ratios. The same phenomenon also occurred in the study of Paixão [32]. In their study, there was a decrease in m-xylene conversion in the use of replicated mordenite due to a decrease in the concentration of acid sites.

The majority of product selectivity produced in the pyrolyzed α-cellulose hydrotreating pro-

Table 6. Liquid product selectivity of α -cellulose hydrotreating using mordenite before alkaline treatment.

C	Product Description	Selectivity (wt%)*				
Group		Thermal	HM	HM-0.05	HM-0.5	HM-1
	5-hexyne-2-one	=	-	2.61	-	0.44
Ketone	2-hexyne-2-one	-	1.08	-	-	-
	1-Hydroxy-2-Propanone	0.66	-	-	-	3.25
	Formaldehyde	-	-	-	-	1.71
	Propanal	-	-	-	6.57	0.81
Aldehyde	2-furancarbosaldehyde	1.13	-	-	-	-
	Acetaldehyde	1.40	1.62	2.36	5.27	-
G 1 1: .1	Formic acid	-	0.63	1.79	5.09	0.73
Carboxylic acid	Acetic acid	-	2.06	2.54	12.48	0.97
Hydrocarbon	2,3-dihydroxy-1,3- butadiene	-	0.76	-	-	-
Ester	Methyl Acetate	-	2.17	3.09	14.79	1.17
Others		19.97	23.42	24.80	38.42	20.50
Liquid product		23.16	31.74	37.19	82.62	29.58

Note: *selectivity (wt.%) = (%area compound : %total GC-MS) x liquid product

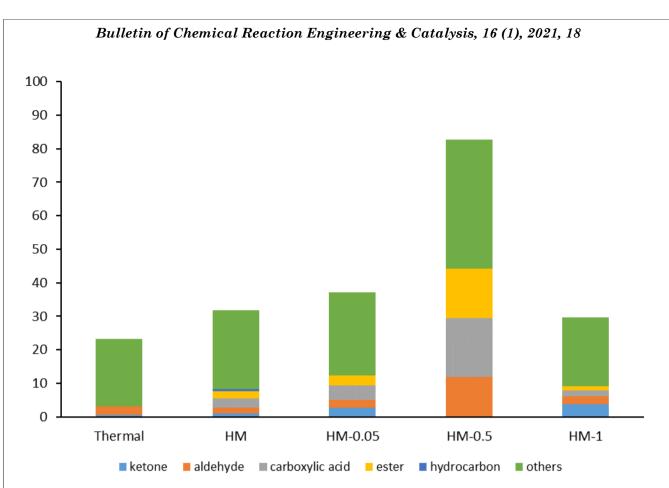


Figure 6. Stem diagram of liquid product selectivity of α -cellulose hydrotreating using mordenite before alkaline treatment.

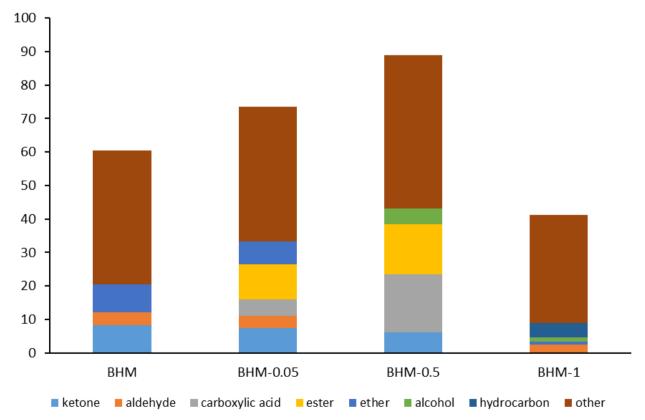


Figure 7. Liquid product selectivity of α -cellulose hydrotreating using mordenite after alkaline treatment.

cess is shown in Tables 6 and 7 and Figures 6 and 7. Table 6 and Figure 6 show that most of the hydrotreating products using catalyst before NaOH treatment still have the same compound as the pyrolysis product. The compound is thought to have originated from pyrolysis, which was not converted into other compounds after hydrotreating. Although there are new compounds in the form of hydrocarbon (0.76 wt%) from HM catalyst, but the largest content of this product still contains oxygen groups such as ketones, carboxylic acids, esters, and aldehydes.

The selectivity of the liquid product resulting from α-cellulose hydrotreating after NaOH treatment is shown in Table 7 and Figure 7. The hydrotreating produces the liquid product containing ether and alcohol which is not produced in hydrotreating before NaOH treatment. Table 7 and Figure 7 also shows that hydrotreating is capable of producing hydrocarbon compounds with a content of 4.36 wt%. This is due to the highest pore diameter of the catalyst after NaOH treatment. From Table 7, the process using a BHM-0.5 catalyst produces propanol (4.87 wt%) and BHM-1 produces ethanol (1.21 wt%) and 2-heptyne (4.36 wt%). Alcohol has been shown to increase the octane value and can be used as diesel and diesel fuel. Ethanol has a high octane value, namely 109 RON (Research Octane Number) and 90 MON (Motor Octane Number) [33]. This is because BHM-1 has a highest mesopore diameter of 7.429 nm which allows large molecules to diffuse. The higher the chance of reactants to enter the pore, the higher also the chance of a catalytic reaction between reactant with the catalyst surface. Besides, the high Si/Al ratio results in better thermal stability.

4. Conclusion

The $\rm H_2C_2O_4$ treatment on mordenite caused a dealumination effect which increased the Si/Al ratio. Desilication with NaOH treatment occurred in mordenite with a Si/Al ratio above 25, which was followed by a decrease in the Si/Al ratio compared to before the alkaline treatment. Moreover, it can produce a mesoporous structure in mordenite. Of all the catalysts, the BHM-1 catalyst had best selectivity to ethanol of 1.21 wt% and 2-heptyne of 4.36 wt%, meanwhile, BHM-0.5 had selectivity to propanol of 4.87 wt% of α -cellulose hydrotreating products.

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Table 7. Liquid product selectivity of α -cellulose hydrotreating using mordenite after alkaline treatment.

C	Due de et De serietie	Selectivity (wt%)				
Group	Product Description	BHM	BHM-0.05	BHM-0.5	BHM-1	
Hydrocarbon	2-heptyne	-	-	-	4.36	
Ester	Methyl acetate	-	10.58	14.84	-	
0 1 1: :1	Formic acid	-	4.89	9.24	-	
Carboxylic acid	Acetic acid	-	-	8.13	-	
Aldehyde	Acetaldehyde	3.80	3.58		2.40	
	2,3-butanedione	-	7.50	-	-	
T7 ·	Acetone	4.71	-	-	-	
Ketone	5-hexyne-3-one	-	-	6.16	-	
	2-hydroxy-1-butene-3-one	3.57	-	-	-	
Alcohol	Ethanol	-	-	-	1.21	
	Propanol	-	-	4.87	-	
Ether	1-ethenoxypropane	8.41	-	-	0.94	
	Methoxyethane	-	6.79	-	-	
	Others	39.99	40.16	45.64	32.25	
Li	quid product	60.48	73.50	88.88	41.16	

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