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The Effect of HNO₃ and/or NaOH Treatments on Characteristics of Mordenite

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Abstract

Modification of mordenite had been performed by HNO₃ and/or NaOH treatments and used as a catalyst in the hydrotreating of pyrolyzed α -cellulose. The Si/Al ratio of mordenites was analyzed by Inductively Coupled Plasma (ICP), the acidity was gravimetrically determined using ammonium vapor adsorption, the crystallinity was identified by X-ray Diffraction (XRD), and pore characters of mordenites (BHM, BAM_{0.1}, and BAM_{0.5}) were analyzed using Gas Sorption Analyzed (GSA). Catalytic activity and selectivity of the mordenites were evaluated in the hydrotreating of pyrolyzed α -cellulose under 20 mL minute⁻¹ H₂ gas flow at 450 °C for 2 h with the weight ratio of catalyst:feed was 1:60. The liquid products were analyzed using Gas Chromatography-Mass Spectrometer (GC-MS). The acidity of mordenites decreased along with the increase of Si/Al ratio, except for the AM_{0.1} mordenite. The average pore diameter of BHM, BAM_{0.1} and BAM_{0.5} was 2.96; 3.34 and 4.53 nm, respectively. The BAM_{0.1} showed the highest catalytic activity in producing liquid fraction (64.04 wt%). The BAM_{0.5} showed the highest catalytic selectivity towards biofuels, i.e. 1-pentene 0.44 (wt%); 2-heptyne 2.75 (wt%) and 1-propanol 3.05 (wt%) from the hydrotreating process of pyrolyzed α -cellulose.

Keywords: modification, mordenite, HNO₃ treatment, NaOH treatment, hydrotreating

1. Introduction

Zeolite is a crystalline alumino-silicate material that has a micropore structure. The three-dimensional structure of the zeolite is composed of AlO₄ and SiO₄ which are related to each other by sharing electrons from oxygen and are arranged tetrahedral [1]. Zeolites have been widely used in industrial processes as environmentally friendly heterogeneous catalysts, ion exchange and adsorbents due to their high specific surface area, large pore volume, uniform micropore channels and excellent thermal and hydrothermal stability. The use of zeolite as a catalyst in various industries is limited due to its narrow pores. The reactant components that have a large molecular size will experience difficulties during the mass transfer process which

will affect the catalytic activity [2, 3]. Increasing the diffusion of the reactants on the catalyst can be done by increasing the pore size of the zeolite, or by creating a mesoporous structure on the zeolite. Therefore, the meso-sized catalyst structure is preferred by most industries, especially the petroleum processing industry because it can increase the effectiveness in the petroleum processing process [4].

Researchers [5] have synthesized mesoporous zeolite-Y using a mold in the form of pluronic F₁₂₇. In general, the mold used is a surfactant that has a long chain. This method has been effective in making of mesoporous zeolite-Y [6].

Mesoporous which is more practical and economical, namely the alkaline treatment known as desilication. This method has been used by many researchers, one of them is researchers [7] that have succeeded in synthesizing mesoporous mordenite using NaOH. Mesoporous distribution in the mordenite increased significantly after being treated with NaOH. This shows that NaOH treatment can produce mesoporous zeolites with a fairly practical and inexpensive process.

The Si/Al ratio in zeolite is one of the characteristics that is closely related to this method of mesoporosity recognition. Alkaline treatment can cause dominant desilication if the Si/Al ratio is above 25 [7]. The low Si/Al ratio value has a limited effect from the alkaline treatment, this is due to the high aluminum content in the zeolite framework, so to get the optimal Si/Al ratio for dominant desilication, the dealumination process needs to be done first. Researchers [8] have succeeded in dealing with H-mordenite, zeolite-Y and ZSM using nitric acid. The dealumination can increase the Si/Al ratio without significantly impairing the crystallinity. In addition, previous study [9] used nitric acid to alluminate zeolite HMCM-22. Nitric acid is considered a strong acid to increase the Si/Al ratio of the zeolite. The dealumination of mordenite with nitric acid showed an increase in the Si/Al ratio without destroying its crystallinity. This study was conducted by [10].

Mordenite is the most widely used catalyst in industrial processes, one of which is the petrochemical and petroleum process [11]. Mordenite has high thermal stability and is more resistant to acids. Mordenite is also a catalyst with a stronger acid site compared to zeolite-Y [12]. Therefore, mordenite can be used to produce biofuel. One of the raw materials in making biofuel is cellulose.

The research of [13] stated that 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 than fossil fuels. One type of cellulose polymer is α -cellulose. The α -cellulose polymer has a degree of polymerization above 200 [14]. This causes α -cellulose to be a carbon source that can be converted into biofuel. α -cellulose can be converted into fuel fractions in the form of hydrocarbons and alcohol by using a pyrolysis process.

However, the pyrolysis process is not effective in producing hydrocarbon and alcohol fractions, this is because bio-oil from pyrolysis is known to have acidic properties, is unstable for heating, and contains many oxygenated compounds [15]. Therefore, one effort that can be done to improve the quality of bio-oil from hydrolyzed α -cellulose is the hydrotreating process. The hydrotreating process can be applied to produce biofuels. This causes the hydrotreating process to become a major concern in the petroleum processing industry because it can produce products that have better selling power and usability [16].

Based on the description above, mordenite modification is carried out by treating HNO₃ and/or NaOH. This study examines the effect of HNO₃ and/or NaOH treatment on Si/Al ratio, crystallinity and acidity of mordenite and the effect of NaOH treatment on mordenite pore character. Then the activity and selectivity of the catalyst were tested in the hydrolyzed α -cellulose hydrotreating process.

2. Experimental methods

2.1 Materials and methods

2.1.1 Materials

The materials used in this study were synthetic mordenite type zeolite (HSZ-640HOA, Tosoh Corporation Japan®), NH₄Cl, 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 gas (PT. Samator Gas) were utilized.

2.1.2 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).

2.2 Procedures

2.2.1 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 HNO₃ (0.1 and 0.5) at a temperature of 70 °C for 2 hours, then washed with bi-distilled water until it was neutral, dried overnight at 110 °C, then calcined in a furnace 550 °C for 5 hours to form AM-0.1 and AM-0.5.

2.2.2 Alkaline treatment on mordenite

The HM; AM-0.1; and AM-0.5 were stirred respectively in 0.1 M NaOH for 15 minutes at room temperature (27°C), then ion exchange was carried out with 1 M NH₄Cl solution at 70 °C for 2 hours, washed with bi-distilled 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; BAM-0.1, and BAM-0.5 were obtained.

2.2.3 Pyrolysis of α -cellulose

A total of 25 grams of α -cellulose is put into the pyrolysis reactor which is made of stainless steel. Pyrolysis was carried out with N₂ 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 α -cellulose was then analyzed using a Gas Chromatography–Mass Spectrometer (GC–MS) to determine its compound content.

2.2.4 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 formula:

$$\text{Liquid product (wt.\%)} = \frac{M_{j1} - M_{j0}}{M_s - (M_{u1} - M_{u0})} \times 100\% \quad (1)$$

$$\text{Coke (wt.\%)} = \frac{M_{k1} - M_{k0}}{M_s - (M_{u1} - M_{u0})} \times 100\% \quad (2)$$

$$\text{Gas (wt.\%)} = 100\% - (\text{liquid product} + \text{coke}) \quad (3)$$

Where M_s = mass of α -cellulose; M_{j0} = mass of an empty flask; M_{j1} = flask mass after hydrotreating; M_{u0} = mass of the feed container before hydrotreating; M_{u1} = mass of the feed container after hydrotreating; M_{k0} = mass of catalyst before hydrotreating; M_{k1} = mass of catalyst after hydrotreating.

3. Results and discussion

3.1 The effect of HNO₃ and/or NaOH treatment on Si/Al ratio and acidity of mordenite

The Si/Al mol ratio in zeolites is one of the most important character which affected the acidity, thermal stability, and activity in catalytic reactions. The dealumination process towards zeolite generally increases activity and thermal stability [17].

Based on the ICP measurement results, there was a change in the Si/Al ratio in the mordenite before and after the NaOH treatment (**Table 1**). The change in the Si/Al ratio indicates that the dealumination and desilication processes of mordenite are going well.

Based on **Table 1**, it shows an increase in Si/Al ratio of mordenite with the higher concentration of HNO₃. The increase in Si/Al ratio is due to the dealumination process in mordenite. In the dealumination process, previous experiment [18] stated

Mordenite code	Si/Al ratio	Total acid sites (mmol NH ₃ g ⁻¹)
HM	9.8	3.67
AM _{0.1}	13.8	3.84
AM _{0.5}	14.1	2.27
BHM	8.8	4.24
BAM _{0.1}	14.8	4.19
BAM _{0.5}	15.3	2.85

Table 1.

The Si-Al ratio and acidity of mordenite after HNO₃ and or NaOH treatment.

that the presence of H⁺ ions resulting from the ionization of HNO₃ in water will cause H⁺ ions to tend to be bound by O atoms that have bound Si and Al. This causes the O atom to have three unstable bonds. The stability of the O atom will be achieved if it breaks a bond that has the lowest dissociation energy. It can be seen that the dissociation energy of Al-O (116 kcal/mol) is much lower when it compared to the dissociation energy of Si-O (190 kcal/mol) so that the Al-O bond will be broken more easily than Si-O [19]. Therefore, the number of Al atoms in the framework will be reduced to non-framework Al due to the bond between Al atoms and NO₃⁻ ions.

The NaOH treatment was then carried out on mordenite HM, AM_{0.1} and AM_{0.5}. This treatment can cause desilication which results in a decrease in the Si/Al ratio. In **Table 1**, it is shown that after NaOH treatment, Si/Al ratio of mordenite (AM) has decreased compared to that of mordenite (HM). The mordenite is in contact with NaOH which causes the silicon to be extracted from the mordenite framework, causing the Si/Al ratio decreased.

However, there were differences in mordenite BAM_{0.1} and BAM_{0.5}, where there were an increase in Si/Al ratio compared to Si/Al ratio before being treated with NaOH as shown in **Table 1**. This is due to the low Si/Al ratio in mordenite before being treated with NaOH. The low Si/Al ratio causes of Si and Al distance to be close, so that when silicon is extracted, aluminum is also extracted due to its amphoteric nature [17].

The mordenite that has been treated with NaOH, then the ion exchange process is carried out with the ammonium ion. The exchange of cations in mordenite with NH₄⁺ aims to remove impurities in the form of alkaline or cations such as K⁺, Na⁺, Ca²⁺, Mg²⁺ which act as a counterweight to mordenite which can be exchanged with other cations so that the cations will be exchanged into NH₄⁺ by pushing the cations. Then, the calcination process is carried out at high temperatures which aims to remove water molecules bound to the mordenite so that the surface area increases.

Besides the Si/Al ratio, another aspect that must be considered in mordenite is acidity. The calculation of the acid centre on the surface of a solid relates to the theory of Brønsted and Lewis acids, namely Brønsted acid (proton giver) and Lewis acid (an empty orbital capable of accepting an electron pair) present on the solid surface.

A simple method that can be used to determine acidity in solids or catalysts is by average of gravimetry, namely by weighing the solids before and after adsorbing the base. One of the bases that can be used as adsorbed substances is ammonia [20]. Ammonia base was chosen as the adsorbate because it has small molecular size so that it can be adsorbed into all mordenite pores.

Based on **Table 1**, it shows a decrease in the number of total acid sites (acidity) along with the increase in the Si/Al ratio of mordenite. The decrease in the total number of acid sites is due to a reduction in the number of Brønsted acid sites which present in the mordenite. The Brønsted acid site will decrease as the aluminum content in a zeolite decreases [4].

Increasing Si/Al ratio can lead the increase of acid strength. This is due to changes in the distribution of aluminum atoms in the zeolite framework. The farther of distance between the aluminum atoms, the less interference between the aluminum atoms, which causes an increase in the acid strength of the Brønsted acid sites possessed by aluminum atoms [21].

However, mordenite AM_{0.1} was found to increase the number of acid sites when compared to mordenite HM. This could be due to the appearance of Lewis acid sites on the mordenite AM_{0.1} framework. Lewis acid sites can occur if there are aluminum atoms bonded outside the main zeolite framework which is known as extra-framework aluminum (EFAL). This phenomenon also occurs in a study conducted by [6] who showed an increase in the number of acid sites on zeolites.

3.2 Effect of HNO₃ and/or NaOH treatment on the crystallinity of mordenite

Crystallinity of a sample solid can be analyzed using X-ray diffraction (XRD) which aims to determine and compare the crystallinity of mordenite either before or after treatment of HNO₃ and/or NaOH. The level of crystallinity of the catalyst can be seen from the peak intensity, while the type of mineral can be seen from the position of the diffraction angle (2θ) and the distance between planes. The crystallinity of a mordenite is very important, because it will be related to the stability of the mordenite. The results of mordenite analysis after HNO₃ treatment are shown in **Figure 1** and Intensity data of mordenite HM, AM_{0.1} and AM_{0.5} peaks in **Table 2**.

Table 2 shows a decrease in the crystallinity of mordenite in line with the increasing concentration of HNO₃, which can be seen in the decrease in mordenite intensity of AM_{0.1} and AM_{0.5} at 25.55°; 22.19°; and 27.51°. This was also confirmed by the percentage of crystallinity data of mordenite HM, AM_{0.1} and AM_{0.5} which were 100%, 91%, and 89%. This decrease in crystallinity was caused by the increasing amount of aluminum extracted from the mordenite (HM) framework [22].

The crystallinity test was also carried out on mordenite BHM, BAM_{0.1} and BAM_{0.5}. The diffractograms of the three mordenites are shown in **Figure 2**. NaOH treatment has less effect on crystallinity than mordenite, where there was still a peak at 2θ 25.54°; 22.18°; and 27.50° and strengthened by mordenite intensity data BHM, BAM_{0.1}, and BAM_{0.5} in **Table 3**.

Table 3 shows the intensity data possessed by the three mordenite catalysts at the 3 highest peaks. Based on these results, it can be seen that overall there is no significant change at the 2θ peak after NaOH treatment, this is also evidenced by the percentage data of mordenite crystallinity of 94%, 95%, and 94%.

Overall the crystallinity of mordenite treated with HNO₃ and/or NaOH did not change significantly. Therefore, this mordenite can be used further in the hydrolyzed α -cellulose hydrotreating process. This is because the hydrotreating process is carried out at high temperatures so that a catalyst with good crystallinity is needed or is maintained so that the stability of mordenite as a catalyst will also be maintained and will produce good activity.

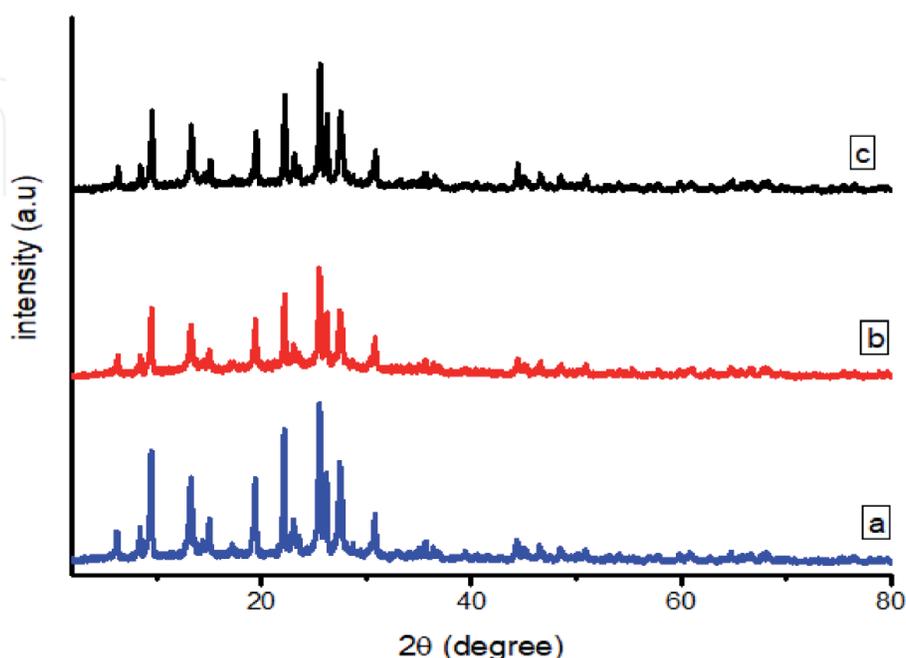


Figure 1.
Diffractogram HM (a), AM_{0.1} (b) and AM_{0.5} (c).

2θ (°)	Relative intensity		
	HM	AM _{0.1}	AM _{0.5}
25.55	1105	778	767
22.19	929	518	507
27.51	712	534	442

Table 2.
 Intensity data of mordenite HM, AM_{0.1} and AM_{0.5} peaks.

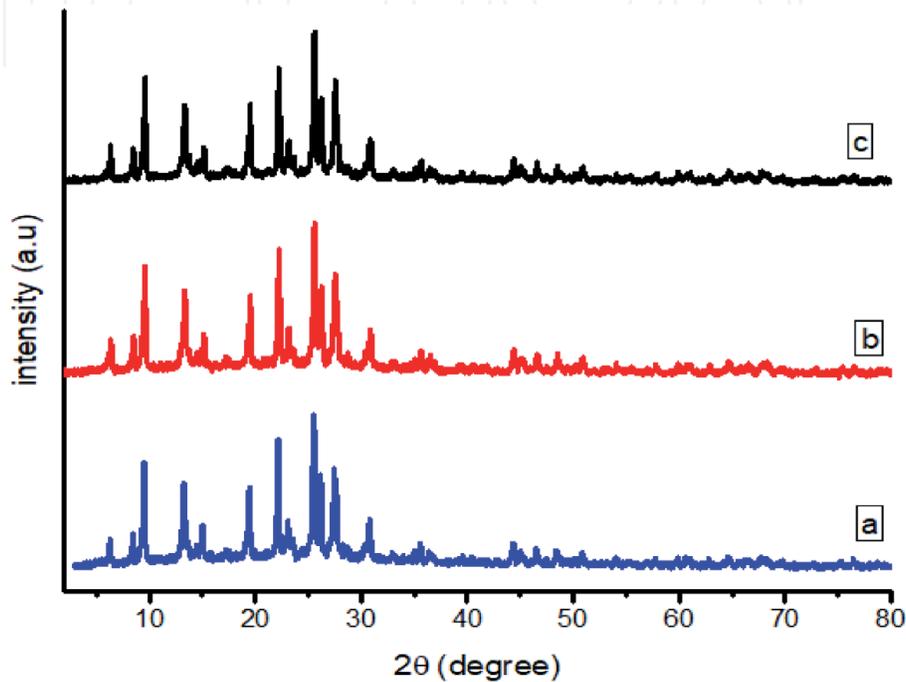


Figure 2.
 Diffractograms of BHM (a), BAM_{0.1} (b) and BAM_{0.5} (c).

2θ (°)	Relative intensity		
	BHM	BAM _{0.1}	BAM _{0.5}
25.54	906	966	789
22.18	629	647	576
27.50	586	590	572

Table 3.
 Intensity data of mordenite BHM, BAM_{0.1} and BAM_{0.5} peaks.

3.3 Effect of HNO₃ and/or NaOH treatment on mordenite pore character

The mordenite pore character analysis was performed using a Gas Sorption Analyzer (GSA). This pore character was carried out in order to determine the impact of the HNO₃ and/or NaOH treatment on the pore character of mordenite. The mordenite analyzed is mordenite that has been given alkaline treatment in order to determine the pore distribution of the mordenite. In addition, analysis by GSA provides information regarding the distribution of pore size (diameter), pore volume and specific surface area of mordenite. The specific surface area analysis of mordenite was carried out using the N₂ gas adsorption–desorption isotherm data

on the mordenite surface based on the Branauer-Emmett-Teller (BET) method. The BET method describes the phenomenon of gas molecular adsorption on the surface of solids. N₂ gas is the most gas often used for analysis of the pore character of a material. The pore character in this study was carried out at a temperature of 77.35 K which is the boiling point of N₂.

Figure 3 below shows that the three mordenites have a type IV adsorption isotherm pattern. This type IV adsorption isotherm pattern indicates the formation of mesoporous characters in the three mordenites as indicated by the presence of loop hysteresis on the mordenite after being treated with NaOH. However, BAM_{0.5} shows a wide and open hysteresis loop, it is presumed that in BAM_{0.5} has pore diameter with the highest meso size compared to other mordenites and is followed by partial collapse of the mordenite framework, which is indicated by the presence of decrease in surface area drastically. Based on the shape of the hysteresis loop, it can be seen that the pore size formed in the three mordenites is homogeneous. This is supported by the pore distribution data obtained.

The pore distribution graph shows a relationship between dV (r) and pore diameter. Dv (r) (Differential volume radius) shows the pore distribution in mesoporous materials. The pore distribution in this study used the BJH method. Based on **Figure 4**, it can be seen that the pore distribution in the three materials

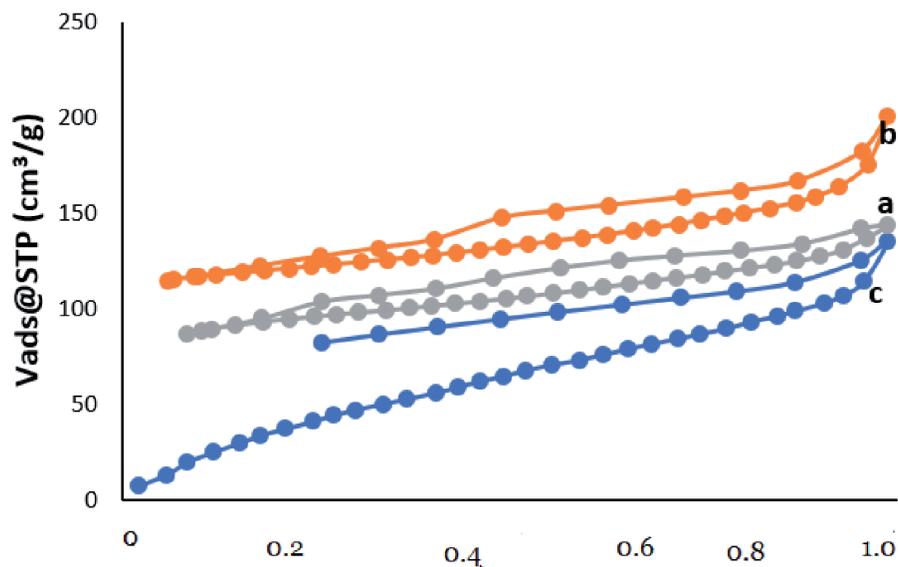


Figure 3.
Adsorption and desorption of isothermal gases N₂ BHM (a), BAM_{0.1} (b) and BAM 0.5 (c).

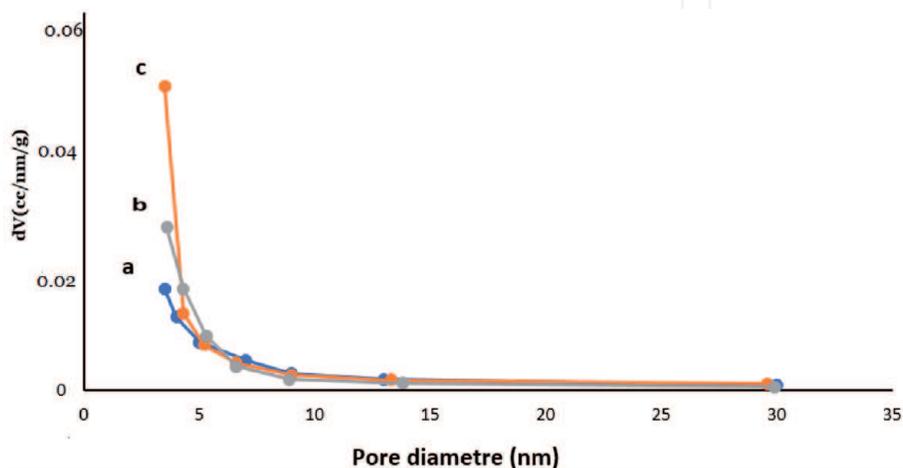


Figure 4.
Distribution of the desorption mordenite BJH BHM (a), BAM_{0.1} (b) and BAM_{0.5} (c).

is homogeneous. In addition, **Figure 4** also shows that all the pore distributions of the mordenite material are found in the mesoporous region, namely in the 3–30 nm range.

This is also supported by the average pore diameter data in **Table 4**. Based on the data in **Table 4**, it shows that alkaline treatment on mordenite can produce mordenite with a meso pore diameter. The higher the Si/Al ratio of mordenite, the resulting mesoporosity will also increase, this is because NaOH treatment can enlarge the pores than mordenite. The highest average pore diameter is owned by BAM_{0.5}, this is because the Si/Al ratio of BAM_{0.5} is the highest compared to other mordenites.

The distribution of micropores and mesopores can be measured using a t-plot. This method can calculate the micropore volume and surface area of mesoporous rather than mordenite. The intercepts obtained from the t-plot method were 71.92 (BHM), 96.94 (BAM_{0.1}) and 13.03 (BAM_{0.5}). Through the intercept of the t-plot method, data on the pore volume composition of the mordenite will be obtained which are presented in **Table 5**.

Table 5 shows a decrease in the percentage of micro volume in mordenite after being treated with NaOH and followed by an increase in the percentage of volume of meso in the mordenite, along with the increase in the Si/Al ratio. This shows that the higher the Si/Al ratio of mordenite, the resulting mesoporosity will also increase.

The total surface area (S_{BET}) of mordenite was calculated using the multi-point BET method. Mesoporous surface area can also be calculated using the t-plot method. Mesoporous surface area calculations were performed using the slope of the mordenite t-plot chart. This calculation can produce data in the form of mesoporous surface area. The slopes obtained from the t-plot method are 5.259 (BHM), 5.445 (BAM_{0.1}) and 8.174 (BAM_{0.5}). Total surface area, micropore and mesoporous data are shown in **Table 6**.

Table 6 shows an increase in the percentage of the mesoporous surface area (S_{meso}) along with the increase in the Si/Al ratio of the mordenite. In addition, it was found a decrease in the total surface area of mordenite, but an increase in the percentage of S_{meso}. This is due to an increase in the surface area of the mesoporous structure compared to the micropore structure.

Mordenite code	Average pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)	S _{BET} (m ² g ⁻¹)
BHM	2.96	0.2223	371.5
BAM _{0.1}	3.34	0.3105	300.7
BAM _{0.5}	4.53	0.2101	185.6

Table 4.
 Data of average pore diameter. Total pore volume and SBET.

Mordenite code	Total pore volume (cm ³ g ⁻¹)	V _{mikro} (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)	V _{mikro} (%)	V _{meso} (%)
BHM	0.2223	0.1113	0.1110	50.07	49.93
BAM _{0.1}	0.3105	0.1500	0.1605	48.31	51.69
BAM _{0.5}	0.2101	0.0202	0.1900	9.61	90.43

Table 5.
 Data of Mordenite pore volume composition.

Mordenite code	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{mikro} ($\text{m}^2 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)	S_{mikro} (%)	S_{meso} (%)
BHM	371.5	290.1	81.36	78.09	21.90
BAM _{0.1}	300.7	216.5	84.23	72.00	28.01
BAM _{0.5}	185.6	59.64	126.0	32.13	67.89

Table 6.
Data on mordenite surface area composition.

3.4 Pyrolysis of α -cellulose (bio-oil)

Pyrolysis of α -cellulose in the form of a white powder produces a liquid product that has physical characteristics, dark brown, thick and has a strong odor. In addition, the oil resulting from α -cellulose pyrolysis can easily change color when left to stand at room temperature and open conditions. This change is possible due to the oxidation process. Experiment of [5] explained that bio-oil obtained from biomass pyrolysis is a multi-component mixture that has high acidity, high water content and is unstable in storage. The instability characteristic of the pyrolysis bio-oil is indicated by the easy color change of the α -cellulose pyrolysis bio-oil.

The liquid product resulting from α -cellulose pyrolysis was analyzed by GC-MS to determine the approximate compounds contained in the liquid product using data detected by MS after the liquid components were separated by the GC method. In addition, analysis of the content of the liquid product from α -cellulose pyrolysis by GC-MS is useful for knowing the main components of the liquid product from α -cellulose pyrolysis itself using area data from GC results. The results of the analysis of the liquid product content of α -cellulose pyrolysis are used as a reference in assessing the success of the hydrotreating process using a catalyst that has been synthesized. The conversion value of α -cellulose pyrolysis in this study was around 40–50% and the results of α -cellulose pyrolysis are shown in **Table 7**.

Table 7 shows that the liquid product resulting from α -cellulose is pyrolyzed containing furan, ketone, aldehyde, and carboxylic acid group compounds. Based on regional data, the five main components of the liquid product resulting from α -cellulose pyrolysis are 2-furancarboxaldehyde (21.21%), 1-hydroxy-2-propanone (20.96%), formic acid (9.15%), acetic acid (7.66%) and ethanal (7.27%). These results are the same as those of researchers [5] in their research report where the

Compound name	Molecular formula	Contains (%)
2-Furancarboxaldehyde	$\text{C}_5\text{H}_4\text{O}_2$	21.21
1-Hidroxy-2-Propanone	$\text{C}_3\text{H}_6\text{O}_2$	20.96
Formic acid	CH_2O_2	9.15
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2$	7.66
Ethanal	$\text{C}_2\text{H}_4\text{O}$	7.27
5-Methyl-2-Furancarboxaldehyde	$\text{C}_6\text{H}_6\text{O}_2$	7.18
2-Propanone	$\text{C}_3\text{H}_6\text{O}$	5.73
1-Acetoxyethylene	$\text{C}_4\text{H}_6\text{O}_2$	3.22
2,3-Pentandione	$\text{C}_5\text{H}_8\text{O}_2$	2.92

Table 7.
Analysis results of the main product of α -cellulose by GC-MS.

liquid products from the hydrolyzed α -cellulose contained the main components in the form of furan compounds, ketones, carboxylic acids and aldehydes.

3.5 Catalyst activity

The catalyst activity test was carried out through the hydrotreating process. The hydrotreating process was carried out to determine the ability of the catalyst to convert the resulting α -cellulose from pyrolysis into a liquid fraction in the form of a more functional chemical. The analysis was carried out by determining the percentage of the liquid fraction produced as the main target, as well as the gas and coke fractions. The results of product distribution through the hydrotreating process can be seen in **Table 8**.

Based on **Table 8**, the catalytic hydrotreating process produces a higher liquid fraction than the liquid fraction without a catalyst (thermal). This is in accordance with the statement of [23] that the use of a catalyst in the hydrotreating process can increase the percentage of liquid fraction and product quality. Thermal hydrotreating and catalytic hydrotreating occur via different mechanisms. Thermal hydrotreating occurs through a free radical mechanism so that it is easier to produce products with short carbon chains and are gaseous in form. On the other hand, catalytic hydrotreating occurs through the carbonium ion mechanism which is easier to produce a liquid fraction with a long enough carbon chain.

The hydrotreating catalytic data in **Table 8** shows that the catalyst after being treated with a base produces a higher liquid fraction than the catalyst before being treated with a base. This is due to an increase in the pore distribution of higher meso size after alkaline treatment along with the increase in the Si/Al ratio of mordeinite catalyst. However, the BAM_{0.5} catalyst has a high mean pore diameter of meso compared to other catalysts, but produces a lower liquid fraction, this is due to a significant decrease in the number of acid sites at high Si/Al ratios. Therefore, the activity of a catalyst is not only determined by the pore diameter but also by the number of acid sites possessed by the catalyst. Increased activity in dealumination of mordeinite was observed by [24], as well as [25], in a study using mordeinite to convert m-xylene, where there was a decrease in m-xylene conversion in replicated mordeinite due to a decrease in the concentration of the acid site.

3.6 Selectivity of liquid fraction

The liquid fraction resulting from the hydrolyzed α -cellulose hydrotreating was analyzed using a Gas Chromatography-Mass Spectrometer (GC-MS) to

Catalyst code	Product distribution% (b/b)		
	Liquid fraction	Gas fraction	Coke fraction
Thermal	23.16	76.48	—
HM	42.69	55.02	2.29
AM _{0.1}	59.73	36.62	3.65
AM _{0.5}	33.22	64.37	1.81
BHM	53.01	45.13	1.86
BAM _{0.1}	64.04	32.69	3.28
BAM _{0.5}	37.57	59.65	2.78

Table 8.
The results of product distribution through the hydrotreating process.

determine the selectivity of the catalyst. GC-MS analysis provides information from the hydrolyzed α -cellulose hydrotreating process. Selectivity is the tendency of a catalyst to produce certain components. The trends in the types of products produced in this study are functional chemicals.

The data in **Table 9** below can be used to explain the selectivity of catalyst use in the hydrolyzed α -cellulose hydrotreating process. The selectivity of the catalyst for the hydrotreating reaction can be seen based on the percentage of the main components of the resulting liquid fraction. The hydrotreating process both thermally and with a catalyst produces the main components of the same liquid fraction, namely acetic acid, 1-hydroxy-2-propanone, and ethanal, but with different liquid fraction percentages. But overall the hydrotreating products with mordenite after HNO_3 treatment still have the same compound as the pyrolyzed α -cellulose, these compounds are thought to be compounds from pyrolysis that do not convert to other compounds after hydrotreating.

Acetic acid, 1-hydroxy-2-propanone, and ethanal were produced with the highest product percentages of 11.03% (w/w), 11.49% (w/w), and 9.26% (w/w) on the use of an $\text{AM}_{0.1}$ catalyst. The main components of the hydrolyzed α -cellulose hydrotreating liquid product in the form of acetic acid, 1-hydroxy-2-propanone (dihydroxyacetone) and ethanal are functional compounds that are widely used. Acetic acid is widely used as a food additive and is a very important chemical in various chemical industries. Acetic acid is an important industrial chemical used in the production of polyethylene terephthalate, cellulose acetate, polyvinyl acetate, and so on [26]. Study of [27] produced a 1-hydroxy-2-propanone compound which is used as a spice in food, colorants and additives in cosmetics. Ethanal is a compound that can be used as a solvent in the production of rubber, in tanning leather, in the paper industry, as a preservative for fruit and fish, and as an additive in flavorings in food.

The selectivity of the liquid fraction resulting from hydrotreating α -cellulose hydrolyzed using mordenite after NaOH treatment is shown in **Table 10**. **Table 10** shows that hydrotreating α -cellulose is hydrolyzed using mordenite after NaOH treatment to produce the main liquid fractions, namely ethanal and 1-hydroxy-2-propanone. Hydrotreating after NaOH treatment can produce hydrocarbon and alcohol group compounds that are not produced in hydrotreating by using mordenite after HNO_3 treatment. This is due to the formation of a mesoporous structure on the catalyst after NaOH treatment.

Group	Product description	Bio-oil (%area)	Product contains % (b/b)			
			Thermal	HM	$\text{AM}_{0.1}$	$\text{AM}_{0.5}$
Carboxylic acid	Acetic acid	7.66	3.50	7.19	11.03	4.59
	Formic acid	9.15	3.50	5.31		2.15
Ketone	1-Hidroxy-2-Propanone	20.96	4.67	10.43	11.49	6.89
Aldehyde	Ethanal	7.27	4.09	2.76	9.26	3.04
	2-Furancarboxaldehyde	21.21		2.63	5.25	2.45
Others		33.75	7.40	14.38	22.7	14.1
Total contains % (b/b)		100	23.16	42.69	42.69	33.22

Table 9. Selectivity of hydrolyzed α -cellulose hydrotreating liquid fraction using mordenite after HNO_3 treatment.

Group	Product description	Bio-oil (%area)	Product contains % (b/b)		
			BHM	BAM _{0.1}	BAM _{0.5}
Carboxylic acid	Acetic acid	7.66	8.33	9.56	
	Formic acid	9.15	2.44	5.33	
Ketone	1-Hidroxy- 2-Propanone	20.96	11.38	15.50	7.40
Aldehyde	Ethanal	7.27	6.72	7.05	4.26
	2-Furancarboxaldehyde	21.21	3.23		
Hydrocarbon	1-Pentene				0.44
	2-Heptyne				2.75
Alcohol	1-Propanol				3.05
Others		33.75	20.9	26.6	19.68
Total contain% (b/b)		100	53.01	64.04	37.57

Table 10.
 Selectivity of hydrotreating α -cellulose liquid fraction by using mordenite after NaOH treatment.

Table 10 shows that the use of the BAM_{0.5} catalyst in the hydrolyzed α -cellulose hydrotreating reaction gives the percentage of components of the hydrocarbon group, namely 1-pentene 0.44% (w/w) and 2-heptuna 2.75% (w/w) which is the fraction C5 and C7. The C5 and C7 fractions are included in the gasoline fraction where the gasoline fraction is a hydrocarbon that has a carbon chain range from C5-C12 [28], and produces an alcohol group compound, namely 1-propanol 3.05% (w/w). Joshi [29] stated that alcoholic fuels have been shown to increase the octane value and can be used as diesel and diesel fuel. Other catalysts as a whole only produce carboxylic acids, ketones, aldehydes and esters. This shows that BAM_{0.5} has a Si/Al ratio, pore size, surface area, acidity, and has a good crystal structure and can work optimally in producing gasoline and alcohol fractions through the hydrolyzed α -cellulose hydrotreating process.

4. Conclusions

HNO₃ and/or NaOH treatments caused an increasing Si/Al ratio of mordenite HM with Si/Al ratio of 9.8 to 13.8; 14.1; 8.8; 14.8 and 15.3 which are AM_{0.1}, AM_{0.5}, BHM, BAM_{0.1} and BAM_{0.5}, respectively. HNO₃ and NaOH treatments decreased the total acid sites from 3.67 to 3.84; 2.27; 4.24; 4.19 and 2.85 mmol NH₃ g⁻¹ were AM_{0.1}, AM_{0.5}, BHM, BAM_{0.1} and BAM_{0.5}, respectively and the treatments did not cause damage to the crystalline structure of the mordenite. NaOH treatment can produce mesoporosity in mordenite, which respectively have an average pore diameter of 2.96; 3.34 and 4.53 nm as BHM; BAM_{0.1} and BAM_{0.5}. Catalyst BAM_{0.5} has selectivity to 1-pentene 0.44% (w/w); 2-heptyne 2.75% (w/w) and 1-propanol 3.05% (w/w) from the hydrolyzed α -cellulose hydrotreating product.

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Appendices and nomenclature

Appendices

AM _{0.1}	HM treated with HNO ₃ 0.1 M
AM _{0.5}	HM treated with HNO ₃ 0.5 M
BAM	acid treatment of mordenite
BAM _{0.1}	acid treatment of mordenite with HNO ₃ 0.1 M
BAM _{0.5}	acid treatment of mordenite with HNO ₃ 0.5 M
BHM	base/alkaline treatment of mordenite
HM	zeolite type mordenite (HSZ-604HOA)

Nomenclature

GC-MS	Gas Chromatography-Mass Spectrometer
GSA	Gas Sorption Analyzed
ICP	Inductively Coupled Plasma
XRD	X-Ray Diffraction

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