Acid-Alkaline Treatment of Mordenite and Its Catalytic Activity in the Hydrotreatment of Bio-Oil

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Abstract: *Acid-alkaline treatment using acetic acid and sodium hydroxide (NaOH) were applied on mordenite (MOR) to increase the Si/Al ratio and surface area properties. Various time treatment (3, 6, and 9 h) and concentration of acetic acid (6, 9, and 12 M) were used to treat MOR, and followed by the treatment with NaOH (0.1 M) under room temperature. The MOR and treated mordenite were applied as a catalyst for hydrotreatment of cellulose-derived bio-oil. The acetic acid treatment caused the increase of the Si/Al ratio of mordenite up to 27.03. The Si/Al ratio was determined using ICP-AES analysis which was also confirmed using FT-IR analysis. The acidity was determined using NH_3 vapors adsorption. The acidity test revealed that as the Si/Al ratio increased the acidity of mordenite decreased. The advantage of using acetic acid for acid treatment was that the XRD patterns of mordenite can be preserved with a little decrease of the intensity. On the other hand, the NaOH treatment under room temperature decreased the crystallinity down to 68%, which was calculated using XRD. The acid-alkaline treatment of mordenite succeeded to increase the surface area 2 times larger than the parent mordenite. The surface area was obtained from BET analysis. The acid-alkaline treated mordenite exhibited better catalytic activity upon hydrotreatment of biomass-derived bio-oil compared to the parent mordenite which corresponded to its highest surface area.*

Keywords: *acetic acid; bio-oil; dealumination; hydrotreatment; mordenite*

INTRODUCTION

Mordenite is a microporous aluminosilicate crystalline which belong to a large-pore zeolite family [1-2]. It consists of a 12-membered ring (MR) pore channels of 0.67 × 0.70 nm, interconnected by 8-MR pores of 0.34 × 0.48 nm [3-4]. Mordenite is one of the zeolites that can be employed as a catalyst in industrial processes such as alkylation and hydroisomerization [1,5-6]. The wide range application of mordenite is due to the mechanic and thermal stability of the mordenite structure [1]. High surface area, high Brønsted acidity, and flexible framework are unique properties of mordenite that also contributes to its extensive use [2,7-8]. Despite the immense use of mordenite as a catalyst, there are some drawback of mordenite. Mordenite has high aluminum content causing it to be undesired to be used as a catalyst. Aluminum can easily leach in the presence of water and acid which affects the chemical stability of mordenite as a catalyst [9-10]. In addition, it is reported that mordenite undergoes rapid deactivation due to the limited mass transfer between product and reactant [3,8].

Several ways to overcome the disadvantages of mordenite has been reported by many researchers. The most sought after method is post-synthesis treatment using acid and alkaline solution [11-12]. The acid and alkaline treatment can enhance the mordenite properties by magnifying mass transfer and catalytic activity [12-15]. Strong acid treatment affects the structure of mordenite. It is reported that employing strong acid on mordenite causes a partial loss in mordenite structure [8,13]. On the other hand, employing weak acids such as oxalic acid and acetic acid can preserve the structure of mordenite [4,8]. Throughout the acid treatment, the aluminum atoms are removed from the mordenite framework and extra-framework aluminum (EFAl) are formed [16]. The EFAl contributes to the addition of acid sites on the mordenite surface which increase the catalytic activity [16]. The utilization of strong acid and oxalic acid can completely remove the EFAl during the acid treatment, hence these acids are undesired to be used in treatment of mordenite.

Alkaline treatment is another way to increase zeolite properties such as mordenite. This treatment is mostly done using sodium hydroxide (NaOH). A low concentration of NaOH (0.1–0.5 M) can be used for alkaline treatment and can maintain the crystallinity of zeolite [17]. Alkaline treatment is mostly done at high temperature, however it can cause severe decrease in the crystallinity of zeolite. Interestingly, strong acid sites were formed during the alkaline treatment and the treated zeolite exhibited better catalytic activity than the parent zeolite [18]. A recent report on the low temperature of alkaline treatment caught attention of many researchers. This process removed the Si atom up to 78% from zeolite structure [19]. However, this caused the amorphization of zeolite. Therefore, controlling the concentration of NaOH is important to sustain mordenite structure.

In this work, mordenite was treated using acetic acid and NaOH. Various concentrations and condition time of acetic acid treatment were performed to obtain the effective condition to remove the Al atom from mordenite. The treated mordenite was used as a catalyst in the hydrotreatment of bio-oil to investigate its catalytic activity.

■ EXPERIMENTAL SECTION

Materials

Ca-Mordenite (HSZ-642NAA) was purchased from Tosoh Co. Glacial acetic acid (CH_3COOH), sodium hydroxide (NaOH), ammonium chloride (NH_4Cl), silver nitrate ($AgNO_3$), nitric acid 65% (HNO_3), hydrochloric acid 37% (HCl), hydrofluoric acid 40% (HF) and ammonia solution 25% (NH_3) were purchased from Merck. All chemicals were of analytical grade. N_2 gas and H_2 gas were purchased from Samator Ltd., and distilled water was used during the experiments.

Instrumentation

Inductively coupled plasma-atomic emission spectrometer (ICP-AES) Shimadzu model ICPE-9820, Fourier transform-infrared (FTIR) spectrophotometer Thermo Nicolet iS10, X-Ray Diffractometer (XRD) Rigaku Miniflex 600, Gas Sorption Analyzer Quantachrome Touchwin Series, Gas Chromatography-Mass Spectroscopy (GC-MS) Shimadzu QP2010S, and other supporting instrumentations, were used in this research.

Procedure

Preparation of H-mordenite

Ca-mordenite (denoted as MOR) was calcined at a temperature of 550 °C for 5 h. Afterwards, the Ca-MOR was introduced into 1 M of NH_4Cl solution accompanied by stirring at 70–75 °C for 2 h. The mixture was then filtered and the solid phase was washed until there was no chloride ion in the liquid phase which was confirmed using $AgNO_3$ solution. The solid phase was then dried at 100 °C and calcined at 550 °C for 5 h. The obtained solid from this process was named H-mordenite (denoted as HMOR).

Acid-alkaline treatment of HMOR

This procedure followed the procedures done by Chung [8] and Yusniyanti [9]. H-MOR was treated using 6 M of CH_3COOH solution (1 g of HMOR in 30 mL of CH_3COOH solution) for 3, 6 and 9 h at 90–95 °C. The solid phase was then filtered, washed and dried. Afterwards, the solid material was subsequently calcined at 550 °C for 5 h (with a temperature rate of 10 °C min^{-1}) to produce acid treated mordenite. The solids obtained from this step were denoted as HMOR(6-x), in which x stood for reflux time variation. In addition, the optimum concentration of CH_3COOH solution was also investigated using the same procedures under 9 h of reflux. The concentrations of CH_3COOH solution used in this step were 6, 9 and 12 M. The solids obtained from this step were denoted as HMOR(y-9), in which y stood for acid concentration variation.

The acid treatment of mordenite was then followed by alkaline treatment. The acid-treated mordenite was added into 0.1 M of NaOH solution for 30 min at room temperature under constant stirring. Afterwards, the mixture was filtered, dried at 100 °C for 3 h and later refluxed using 1 M of NH_4Cl. The solid obtained was calcined at 550 °C for 5 h and denoted as DHMOR(y-x).

All the samples were destructed using concentrated HNO_3, HCl and HF. Afterwards, the samples were characterized using ICP-AES to measure the Si/Al ratio. Further analysis is needed to confirm the effect of acid-alkaline treatment. The samples were characterized using XRD to determine the change of the structure and the crystallinity of the mordenites. The crystallinity of the samples was measured using Eq. (1). HMOR, HMOR(6-9) and DHMOR(6-9) was further investigated to determine the surface area using a Gas Sorption Analyzer which is also well known as the N_2 adsorption-desorption.

$$\%\text{Crystallinity} = \frac{\text{Area under } 2\theta : 5-40° \text{ of Samples}}{\text{Area under } 2\theta : 5-40° \text{ of MOR}} \times 100\% \quad (1)$$

Catalytic activity test on the hydrotreatment of bio-oil

The bio-oil used in this research was produced from the pyrolysis of α-cellulose. The pyrolysis of α-cellulose was done in a semi-batch reactor at temperature of 600 °C under N_2 gas flow (flow rate was 20 mL min^{-1}) for 2 h. The liquid obtained from this process was characterized by GC-MS to determine its composition. The hydrotreatment of bio-oil was done to improve the bio-oil properties. The process was carried out in a semi-batch reactor under H_2 gas flow (flow rate was 20 mL min^{-1}) for 2 h at temperature of 450 °C in the presence of a catalyst. The catalysts used in this process were HMOR, HMOR(6-9), and DHMOR(6-9). The weight ratio between catalyst and bio-oil as the feed was 1:30. The thermal treatment of bio-oil was also done in the same condition without a catalyst. The liquid produced from the hydrotreatment and thermal treatment processes was characterized by GC-MS.

Acidity test

The acidity of the samples were tested by the gravimetric method using adsorption of ammonia vapor. In porcelain crucible, 0.002 g of the sample was added and placed in a desiccator. The weight of the porcelain crucible before and after the addition of the samples were measured. The desiccator was vacuumed and NH_3 vapor was flowed into the desiccator for 30 min by heating the 25% ammonia solution until bubbles were formed. Afterwards, the samples were settled for 24 h in the desiccator. After 24 h, the samples were taken out from the desiccator and the weight of the porcelain crucible with the sample after ammonia adsorption was measured. The acidity of the samples were calculated using Eq. (2).

$$\text{Acidity}\left(\text{mmol/g}\right) = \frac{W_2 - W_1}{\left(W_1 - W_0\right) \times \text{MW}} \times 1000 \quad (2)$$

where, W_0: the weight of the empty porcelain crucible (g); W_1: the weight of the porcelain crucible + sample before adsorption (g); W_2: the weight of the porcelain crucible + sample after adsorption (g); MW: molecular weight of NH_3 (mmol/g)

■ RESULTS AND DISCUSSION

Characterization of the Acid-Alkaline Treated Mordenite

Acid-treated mordenite

In the acid treatment of zeolite, the acid removes aluminum atoms from the zeolite framework causing an increase in the Si/Al ratio of the zeolite. This process is well known as the dealumination process. This process hydrolyzes Si–O–Al bonds, resulting in –Si–OH and –Al–OH, and initiates the formation of vacant sites in the zeolite framework [7]. It is reported that mordenites with Si/Al ratio between 25 and 50 exhibit higher stability than mordenites with Si/Al ratio below that range (25–50) [3]. Moreover, this Si/Al ratio range is also needed to carry out effective silicon removal in alkaline treatment [15].

Since the use of acetic acid is rarely reported for acid treatment of mordenite, it is necessary to evaluate the optimum time and acetic acid concentration required for the treatment. The Si/Al ratios of the mordenites are listed in Table 1. The highest Si/Al ratio was obtained using 6 M of acetic acid for 9 h of treatment. This condition is required to effectively remove silicon from mordenite. The change in Si/Al ratio can also be proven using FT-IR characteristics. When the Si/Al ratio increases, the T–O–T band (T=Si or Al) tends to shift to a higher wavenumber. This is due to the difference in bond strength between Al–O and Si–O.

The infrared spectra of acid-treated mordenite are depicted in Fig. 1(a) and (b). The band assigned to the T–O asymmetric stretching shifted to higher wavenumbers of 1075, 1088, 1087 and 1089 cm^{-1} for

Table 1. The Si/Al ratio of acid-alkaline treated mordenite

Sample	Conc. Si (mmol/L)	Conc. Al (mmol/L)	Si/Al Ratio	Acidity (mmol/g)
HMOR	1.31	0.21	11.33	25.88
HMOR(6-3)	3.30	0.25	13.02	20.01
HMOR(6-6)	1.94	0.11	17.87	14.17
HMOR(6-9)	2.88	0.11	27.05	16.59
HMOR(9-9)	1.49	0.08	19.08	17.65
HMOR(12-9)	1.58	0.08	18.58	10.94
DHMOR(6-9)	1.48	0.07	21.65	12.03
DHMOR(9-9)	1.47	0.08	18.94	10.87
DHMOR(12-9)	1.38	0.07	20.37	9.25

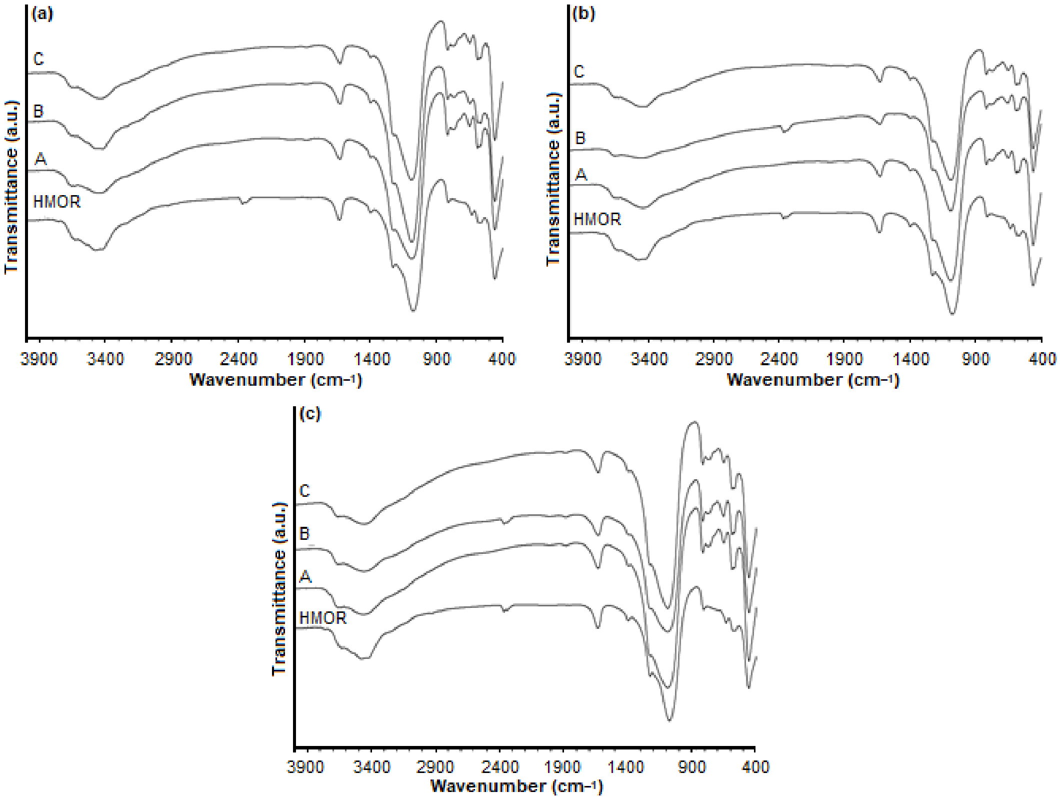

Fig 1. Infrared spectra treated mordenite (a) Treated mordenite using acetic acid 6 M in various treatment time (A. HMOR(6-3), B. HMOR(6-6) and C. HMOR(6-9)), (b) Treated mordenite using the various concentration of acetic acid in 9 h, (A. HMOR(6-9), B. HMOR(9-9 and C. HMOR(9-12)) and (c) Acid-alkaline treated mordenite for various acetic acid concentration (A. DHMOR(6-9), B. DHMOR(9-9) and C. DHMOR(12-9))

Table 2. Interpretation of infrared spectra of mordenites

Type of vibration	Wavenumber (cm^{-1})								
	HMOR	HMOR (6-3)	HMOR (6-6)	HMOR (6-9)	HMOR (9-9)	HMOR (12-9)	DHMOR (6-9)	DHMOR (9-9)	DHMOR (12-9)
T-O bending	458	457	457	457	482	457	457	457	457
T-O Sym. stretching	632	650	648	649	649	649	652	652	651
T-O Asym. stretching	1075	1088	1087	1089	1089	1088	1089	1089	1090
O-H bending	1635	1630	1628	1629	1630	1628	1631	1631	1630
O-H stretching	3474	3454	3421	3437	3453	3426	3455	3453	3453
EFAl	3650	3654	3653	3654	3654	3654	3654	3655	3655

HMOR, HMOR(6-3), HMOR(6-6) and HMOR(6-9) respectively (Table 2). This result is in good agreement with Sandoval-Díaz and co-workers [20].

Throughout the acid treatment, the EFAl can be formed as the result of incomplete removal of Al atom [16]. The EFAl on the mordenite framework can be detected in FTIR spectra at wavenumbers around 3650 cm^{-1} which corresponds to the OH group attached to EFAl species [21]. It is shown in Fig. 1(a) that the band around 3650 cm^{-1} can be seen in the HMOR and after acid treatment. The wavenumber corresponds to the EFAl listed in Table 2.

The XRD patterns of the acid-treated mordenites were found to be almost identical (Fig. 2). However, the peak intensities slightly decreased which correspond to the crystallinity of the acid-treated mordenites. The crystallinity of the acid-treated mordenites changed from 100% to 68%, 74% and 88% for acid-treatment using acetic acid 6 M (Fig. 2(c)), 9 M (Fig. 2(d)) and 12 M (Fig. 2(e)) respectively. It clearly shows that acetic acid

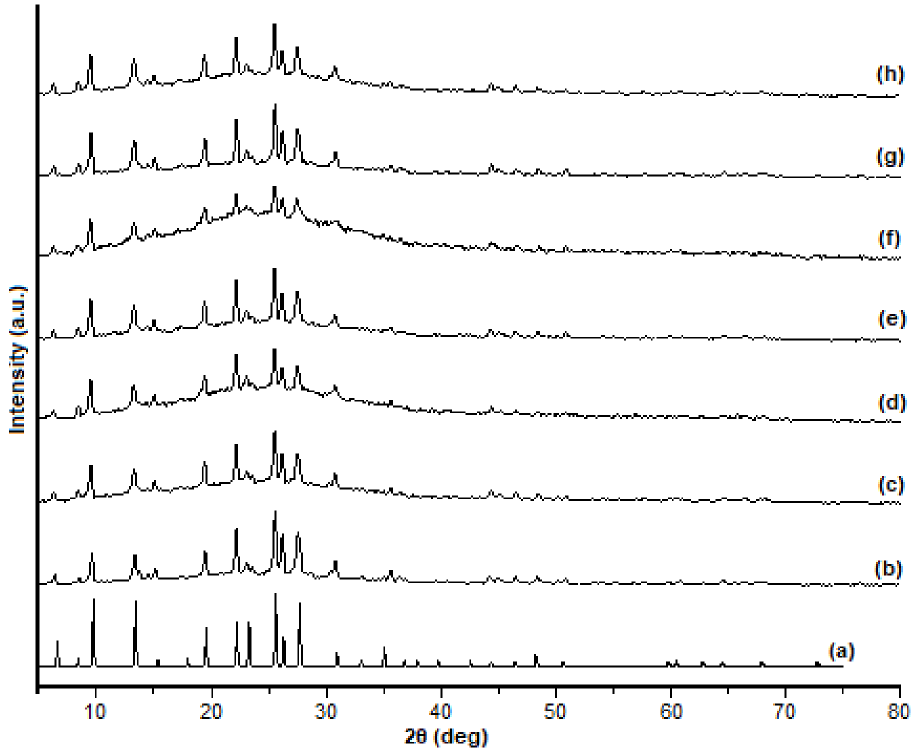

Fig 2. The diffractogram of acid-alkaline treated mordenite (a) JCPDS card 011-0155, (b) HMOR, (c) HMOR(6-9), (d) HMOR(9-9), (e) HMOR(12-9), (f) DHMOR(6-9), (g) DHMOR(9-9) and (h) DHMOR(12-9)

12 M does not cause more damage than acetic acid 9 M. It can be suggested that acetic acid 12 M removed the Al atoms from the mordenite framework, hence the EFAl was not completely formed during the acid treatment process. The EFAl species contributes to the amorphous nature of zeolites hence it can decrease the crystallinity of zeolites.

The uncompleted formation of EFAl on the mordenite framework is also supported by the Si/Al ratio and the acidity of mordenite after acid treatment (Table 1). Table 1 shows that the acidity of HMOR(12-9) is the lowest for acid-treated mordenite. However, the Si/Al ratio is not the highest. This indicates that EFAL in acid-treated mordenite using 12 M of acetic acid is not completely formed during the acid treatment. When the acetic acid concentration is raised, it is expected that the Si/Al ratio will increase. However the result shows that the Si/Al ratio cannot exceed 25 (Table 1). The possible explanation for this is that a large number of aluminum atoms were extracted from the mordenite framework causing the framework to collapse (Fig. 2(c-e)). Hence, the silicon atoms were also removed from the mordenite framework and resulted in the lowering of the Si/Al ratio.

Acid-alkaline treated mordenite

Alkaline treatment of zeolites cause the removal of Si sites on the mordenite framework. This process is well known as desilication. It can lead to the decrease of the Si/Al molar ratio of mordenite. Zeolite framework contains more silicon than aluminum atom. Hence it would be easy to create mesopores upon alkaline treatment. However, it is reported that there is an optimal Si/Al ratio to create the mesoporosity of zeolite after alkaline treatment [15]. Above the optimum ratio, the Al atoms prevented the removal of Si from mordenite. This resulted in the limitation of mesopore formation. The optimal Si/Al ratio was 25. When the Si/Al molar ratio > 25, the alkaline treatment caused a decrease in the Si/Al molar ratio (as seen in the case of the alkaline treatment of HMOR(6-9)). However, when the Si/Al molar ratio < 25, the Si/Al molar ratio increased after alkaline treatment (as seen in the case of the alkaline treatment of HMOR(12-9)). When HMOR(9-9) (Si/Al = 19.08) was treated with alkaline, the Si/Al molar ratio decreased. This is due to the removal of EFAl or maybe further dealumination that occurred on the mordenite framework, that caused the decrease of Al content on DHMOR(9-9).

We can see that the alkaline treatment of HMOR(6-9) decreased the crystallinity of mordenite down to 65%. However, the characteristic peak of HMOR still appeared on the XRD pattern of DHMOR(6-9). When HMOR(9-9) was treated with sodium hydroxide, there was no significant change in the diffractogram of the mordenite (Fig. 2(d) and 2(g)). The crystallinity of HMOR(9-9) increased after alkaline treatment (DHMOR(9-9)) from 74 to 97%. This indicates that the EFAl was removed from HMOR(9-9). However, the removal of Si atoms is more likely to occur than the removal of EFAl. This is supported by the Si/Al molar ratio and the acidity of DHMOR(9-9) (Table 1).

The increase of mordenite crystallinity after alkaline treatment also occurred on the DHMOR(12-9). The crystallinity of HMOR(12-9) was 88%. After alkaline treatment, the crystallinity increased up to 93% (DHMOR(12-9)). This shows that the existence of EFAl or Al atoms prevents the removal of silicon atoms from HMOR(12-9). This result is in good agreement with the previous work of Shilagi et al. [15]. This result is also supported by the Si/Al molar ratio of HMOR(12-9) after the alkaline treatment. There was an increase in the Si/Al molar ratio (Table 1), which indicates that there was the removal of Al atoms either in the mordenite framework or EFAl. This result is also supported by the acidity of DHMOR(12-9).

N_2 Adsorption-Desorption

Fig. 3 depicts the adsorption-desorption isotherm curve of mordenite. In general, the hysteresis loop of adsorption-desorption isotherm curve should close. However in Fig. 3, it can be seen that the hysteresis loop does not close. Usually, the loop that does not close is well known as low-pressure hysteresis loop. The low-pressure hysteresis loop could occur because of the swelling of the adsorbent during the adsorption process or when there is a chemisorption process together with physical adsorption [22]. However, in this case, the loop that does not close is not because of the low-pressure hysteresis loop. In the low-pressure hysteresis loop, in the

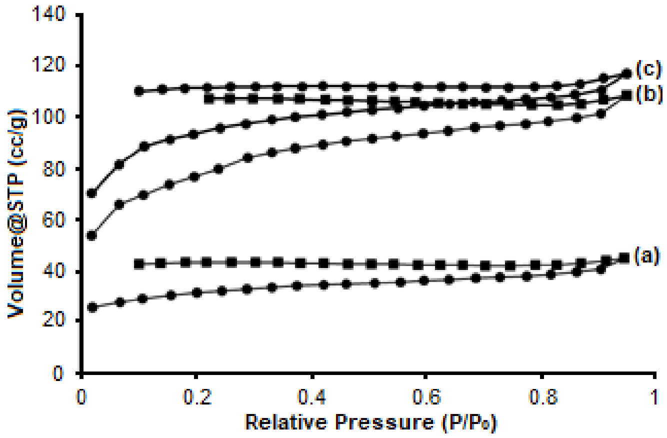

Fig 3. N_2 Adsorption-desorption of (a) HMOR, (b) HMOR(6-9), and (c) DHMOR(6-9)

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 [23].

Mordenite is well known as a porous material. Acid and Alkaline treatment would change the porosity of mordenite. Table 3 shows the pore characteristic of mordenite before and after the treatments. It can be seen that after acid and alkaline treatment, the BET surface area increased. This increase indicates the removal of Al atoms and Si atoms from the mordenite framework. The acid treatment removed Al atoms from the mordenite and rose the uniformity of the Si atoms in the mordenite. Zeolites with high Si/Al ratio would have higher surface area than zeolites with low Si/Al ratio [24]. In accordance to Stefanidis et al., it was also reported that acid treatment of mordenite caused the increase of pore volume [14]. It was also reported that the combination of acid and alkaline treatment of mordenite caused the increase of surface area [25].

The Catalytic Activity of Treated Mordenite

Based on Table 4, it can be seen that a catalyst can increase the liquid fraction on the hydrotreatment product. The liquid fraction of HMOR(6-9) was lower than HMOR. Even though the specific surface area of HMOR(6-9) was higher than HMOR, the acidity of HMOR(6-9) was lower than that of HMOR. This result is in good agreement with Boveri et al. [13]. Boveri reported that mordenite after acid treatment showed less catalytic activity due to the elimination of the acid sites [13]. In the case of DHMOR(6-9), the result shows that DHMOR(6-9) had the highest liquid fraction of hydrotreatment product among all of the catalysts. Although the acidity of DHMOR(6-9) was lower than HMOR(6-9) and HMOR, the high specific surface area

Table 3. The pore characteristic of parent mordenite, acid-treated and acid-alkaline treated mordenite

Parameter	Sample		
	HMOR	HMOR (6-9)	DHMOR (6-9)
Average pore size (nm)	2.72	2.56	2.37
Surface area ($m^2\ g^{-1}$)[a]	102.31	262.07	306.14
Total pore volume ($mL\ g^{-1}$)[b]	0.07	0.17	0.18

Note: [a]BET surface area determined using BET method
[b]Pore volume determined at $P/P_0 = 0.95$

Table 4. The distribution of hydrotreatment product

Catalyst	Surface Area ($m^2\ g^{-1}$)	Acidity ($mmol\ g^{-1}$)	Hydrotreatment product	
			Liquid Fraction (wt.%)	Gas Fraction (wt.%)
Thermal	-	-	47.08	52.92
HMOR	102.31	25.88	74.40	25.60
HMOR(6-9)	262.07	16.59	66.66	33.16
DHMOR(6-9)	306.14	12.03	81.00	19.00

of DHMOR(6-9) (Table 4) caused the liquid product to be improved. It clearly shows that the activity of the catalyst toward hydrotreatment was affected by the acidity and the surface area of the catalyst.

■ CONCLUSION

Acetic acid as a weak acid can be applied for acid treatment of mordenite which is proven by the increase of Si/Al ratio. The optimum condition for acid treatment of mordenite using acetic acid is 9 h using 6 M of acetic acid under reflux method. On the other hand, alkaline treatment can be carried out at room to temperature, using a low concentration of NaOH. The acid-alkaline treatment was able increase the surface area of mordenite and also increase the catalytic activity upon hydrotreatment of biomass-derived bio-oil.

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