

Hydrochloric Acid and/or Sodium Hydroxide-modified Zeolite Y for Catalytic Hydrotreating of α -Cellulose Bio-Oil

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Abstract: The zeolite Y had been successfully modified by HCl and/or NaOH treatment. The modification of zeolite Y was performed by leaching the protonated zeolite Y (HY) in HCl solution (0.1 and 0.5 M) at 70 °C for 3 h resulting in DY_{0.1} and DY_{0.5}. Subsequently, HY, DY_{0.1}, and DY_{0.5} zeolites were immersed in 0.1 M NaOH for 15 min at room temperature resulting in AHY, ADY_{0.1}, and ADY_{0.5}. All samples were analyzed for acidity, crystallinity, Si/Al ratio, morphology, and textural properties. The catalytic performance of all samples was investigated in hydrotreating of α -cellulose bio-oil with a catalyst/feed weight ratio of 1/30. The HCl and NaOH treatment led to the decrease of the zeolite Y crystallinity and the increase of the zeolite Y average pore diameter (i.e., the mesopore distribution). The ADY_{0.5} gave the highest mesopore distribution, which was 43.7%, with an average pore diameter of 4.59 nm. Moreover, both of the treatments were found to increase the Si/Al ratio that caused the decrease of zeolites Y acidity. All the zeolite Y samples gave better catalytic activity to produce liquid products after being treated by NaOH. The sample ADY_{0.5} managed to produce 6.12% of 1-isopropyl-2,4-dimethylbenzene that has good potential to be processed into fuel.

Keywords: HCl treatment; mesoporous structure; NaOH treatment; pyrolyzed α -cellulose hydrotreatment

■ INTRODUCTION

Zeolite Y is crystalline microporous aluminosilicate material that widely used as a catalyst, especially in the petroleum industry [1]. However, in a reaction involving large molecules, these microporous structures reduce the catalytic activity due to the limited diffusion of the large molecules [2]. Si/Al ratio of zeolite is one of the many important factors that determine the zeolite properties, especially its catalytic properties. The higher the Si/Al ratio of zeolite, the higher the thermal stability. On the other hand, higher Si/Al decreases zeolite acidity due to the removal of aluminum from its framework [3]. Consequently, the Si/Al ratio should be optimal to get suitable catalytic properties.

Zeolite Y is only possible to be directly synthesized with a maximum Si/Al ratio of 3 [4]. Therefore, post-synthetic treatment must be performed to increase its

Si/Al ratio. Acid leaching is one of many treatments that are capable of increasing the Si/Al ratio of the zeolites. A weak acid, such as oxalate acid, has been proved to effectively increase the Si/Al ratio of zeolite [5-6]. However, it is not sufficient to increase the Si/Al ratio of zeolite Y due to the low Si/Al ratio; thus, a strong acid is required [7-8].

A mesoporous structure should be introduced to enhance the performance of zeolite Y as a catalyst. The mesoporous structure was generated using a surfactant as a soft template or polymer composite as a hard template [2,9]. However, this method is not suitable for mass production due to its complicated synthesis procedure and the hydrophobicity of the template [6]. On the other hand, post-synthetic treatments such as acid leaching and alkaline treatment were proven to be simpler and more effective. Alkaline treatment was

found to be a promising procedure to generate a mesoporous structure on the zeolite surface [5-6,10-12].

Mesoporous zeolite Y was found to be an effective catalyst because of its acidity and high conversion percentage due to its mesoporous structure [2]. Therefore, mesoporous zeolite Y is highly possible to be used as a catalyst in the hydrotreatment process to enhance the quality of α -cellulose bio-oil. In the hydrotreatment process, numbers of reactions occur, such as hydrocracking, hydrodeoxygenation, hydrogenation, etc. Cellulose is the most promising biomass to be used to generate biofuel due to its availability on the earth [13]. Cellulose can be converted into bio-oil by using the pyrolysis method [14-16]. However, cellulose bio-oil contains a significant amount of oxidized products that are not suitable enough to be used as a fuel [17]. Consequently, catalytic hydrotreatment should be performed to enhance the quality of cellulose bio-oil.

In this work, the effect of HCl and/or NaOH treatments toward zeolite Y characters were investigated. The concentration of HCl and NaOH solution used in this work was according to the previous study to maintain the crystallinity of the zeolite Y [8,11]. Those treatments were carried out to increase the mesopore distribution of zeolite Y. Then, the catalytic activities and selectivities of the modified zeolites Y were investigated in the hydrotreating of α -cellulose bio-oil.

■ EXPERIMENTAL SECTION

Materials

Zeolite Y, in the form of $\text{NH}_4\text{-Y}$ (TSZ-310NHA), was supplied by Tosoh Corporation Japan. Meanwhile, NH_4Cl , HCl 37%, NaOH, NH_3 25%, and AgNO_3 were purchased from Merck, α -cellulose was provided by Sigma-Aldrich, and demineralized water was purchased from a local supplier. All of the chemicals were analytical grade. The N_2 and H_2 gas were supplied by Samator Ltd.

Instrumentation

Si/Al ratio of all samples was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES) Shimadzu ICPE-9820. The functional group of all samples was recorded on the Shimadzu Prestige-21 FT-IR

spectrometer with a data station in the range of 400–4000 cm^{-1} with the KBr disc technique. The sample acidity was calculated gravimetrically based on ammonia vapor adsorbed. Acidity calculation was conducted using the formula:

$$\text{Acidity} = \frac{W_{\text{NH}_3}}{W_Y \times M_{\text{NH}_3}} \times 1000 \frac{\text{mmol}}{\text{g}}$$

where W_{NH_3} is the weight of ammonia vapor adsorbed (g), W_Y is the weight of zeolite Y, and M_{NH_3} is the molecular weight of ammonia (17.03 g/mol). Pore size and volume were analyzed using N_2 gas sorption analysis, which was carried out by Quantachrome NOVAtouch. Adsorption and desorption isotherm were measured by the multipoint method. The total surface areas were calculated by the BET method. BJH desorption model was used to provide mesoporous size distribution. The micropore surface areas were obtained using the t-plot method. X-ray diffraction (XRD) analysis was performed using Rigaku Miniflex 600 with Cu K α monochromatized radiation source ($\lambda = 0.154$ nm), operated at 40 kV, 15 mA, at a scan rate of 10°/min between 2–80°. The pore image was taken by transmission electron microscope (TEM) JEOL JEM-1400 with 120 kV acceleration voltage.

Procedure

Acid treatment of zeolite Y

First, $\text{NH}_4\text{-Y}$ was transformed into a protonated form. In this experiment, 12 g of $\text{NH}_4\text{-Y}$ was calcined at 10 °C/min rate to 550 °C and kept at this temperature for 5 h. This protonated zeolite Y was designated as HY. Acid treatment of zeolite Y was carried out using HCl solution. In this experiment, 4 g of HY were immersed into 80 mL of 0.1 M HCl solution at 70 °C stirring for 3 h. The slurry was filtered, washed with demineralized water until it was free of chlorine ion then dried at 110 °C overnight. The product was then calcined at a 10 °C/min rate to 550 °C and kept at this temperature for 5 h. The consequent sample was designated as $\text{DY}_{0.1}$. Sample $\text{DY}_{0.5}$ was acquired by the same procedures except for the concentration of HCl solution, which is 0.5 M.

Alkaline treatment of zeolite Y

The protonated zeolite Y (HY) and the dealuminated

zeolite Y (DY_{0.1} and DY_{0.5}) were treated by NaOH solution. In this experiment, 2 g of zeolite Y was immersed into 60 mL of 0.1 M NaOH solution at room temperature under stirring for 15 min. Then, the slurry was filtered, washed with demineralized water, and dried at 110 °C. Subsequently, the product was transformed into protonated form by an ion-exchange process in 40 mL of 1 M NH₄Cl solution at 70 °C for 2 h and then calcined at 10 °C/min rate to 550 °C and kept on this temperature for 5 h. The consequent samples were designated as AHY, ADY_{0.1}, and ADY_{0.5}.

Zeolite Y catalytic test in hydrotreating of α -cellulose bio-oil

The α -cellulose bio-oil was produced by the pyrolysis method. Solid α -cellulose was heated at 600 °C for 3 h under the N₂ gas stream with a 20 mL/min flow rate to produce α -cellulose bio-oil. The resulting bio-oil was analyzed for its content using gas chromatography-mass spectrometer (GC-MS) Shimadzu QP2010S with a column length of 30 m, a diameter of 0.25 mm, the thickness of 0.25 μ m, temperature 50–300 °C, and helium as a carrier gas with an acceleration voltage of 70 eV. The catalytic hydrotreatment of α -cellulose bio-oil was then carried out in a semi-batch stainless steel reactor at 450 °C under the H₂ gas stream with a 20 mL/min flow rate for 2 h using the obtained zeolite Y catalysts (HY, DY_{0.1}, DY_{0.5}, AHY, ADY_{0.1}, and ADY_{0.5}). The catalyst and the α -cellulose bio-oil were placed into the reactor with a ratio of 1:30. Subsequently, the liquid product from the catalytic hydrotreatment was analyzed by GC-MS.

RESULTS AND DISCUSSION

Effect of HCl and/or NaOH Treatments towards Zeolite Y Characters

Si/Al ratio and acidity analysis

The effect of different HCl concentration treatments toward the Si/Al ratio of zeolites Y is displayed in Table 1. As can be seen, the Si/Al ratio of the consequent zeolite Y increases along with the increase of HCl concentration, giving the values of 6.71 and 8.59 for DY_{0.1} and DY_{0.5}, respectively. The increase of the Si/Al ratio indicated the removal of the aluminum atom from the zeolite Y framework. Moreover, this phenomenon resulted in a

decrease in the acidity of zeolite Y since the aluminum atoms act as acid sites on the zeolites. As shown in Table 1, DY_{0.1} and DY_{0.5} had lower acidity value than HY.

The effect of NaOH treatment towards the Si/Al ratio of zeolites Y is summarized in Table 1. The NaOH treated samples, which are AHY and ADY_{0.5}, show a higher Si/Al ratio compared to the untreated one. The increase of the Si/Al ratio was caused by the removal of extra-framework aluminum (EFAL) throughout the NaOH treatment [18]. Moreover, this can occur because the initial Si/Al ratio of the zeolites (before NaOH treatment) was lower than 15, which led to the inhibition of the desilication process [10]. As a result, the acidity of the NaOH treated zeolites Y decreased. On the other hand, the Si/Al ratio of DY_{0.1} remained the same after NaOH treatment, possibly due to the simultaneous process of the EFAL removal and desilication.

The skeletal IR vibration of the samples is shown in Fig. 1. The wavenumber between 1040–1100 cm⁻¹ represents the asymmetric O–T–O (T = Si or Al) stretching shifts linearly with the amount of aluminum framework in the zeolite. The wavenumber increases along with the decrease of the aluminum framework content [6]. As shown in Fig. 1, the higher Si/Al ratio of the samples, the higher the asymmetric O–T–O stretching wavenumbers. The asymmetric O–T–O stretching vibration of the HY sample (1042 cm⁻¹) was found to be lower than those observed on AHY, DY_{0.1}, ADY_{0.1}, DY_{0.5}, and ADY_{0.5}, which are 1049, 1065, 1080, 1088, and 1096 cm⁻¹, respectively.

Crystallinity analysis

The XRD patterns of zeolites Y before and after treatments are shown in Fig. 2. As can be seen, the HCl

Table 1. Si/Al ratio and acidity of zeolite Y with various Si/Al ratio before and after treatments

Catalyst	Si/Al ^a	Acidity (mmol NH ₃ /g)
HY	5.00	10.10
AHY	6.00	10.80
DY _{0.1}	6.71	7.70
ADY _{0.1}	6.70	6.80
DY _{0.5}	8.59	4.90
ADY _{0.5}	14.5	4.80

^a Measured by ICP-AES

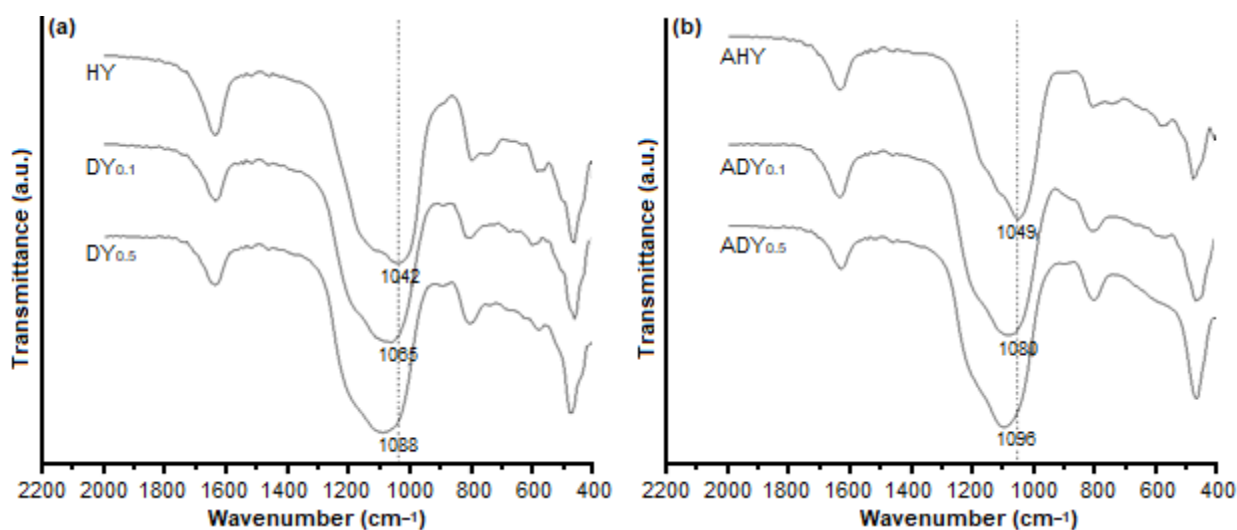


Fig 1. FT-IR spectra of zeolites Y with various Si/Al ratio (a) before and (b) after NaOH treatment

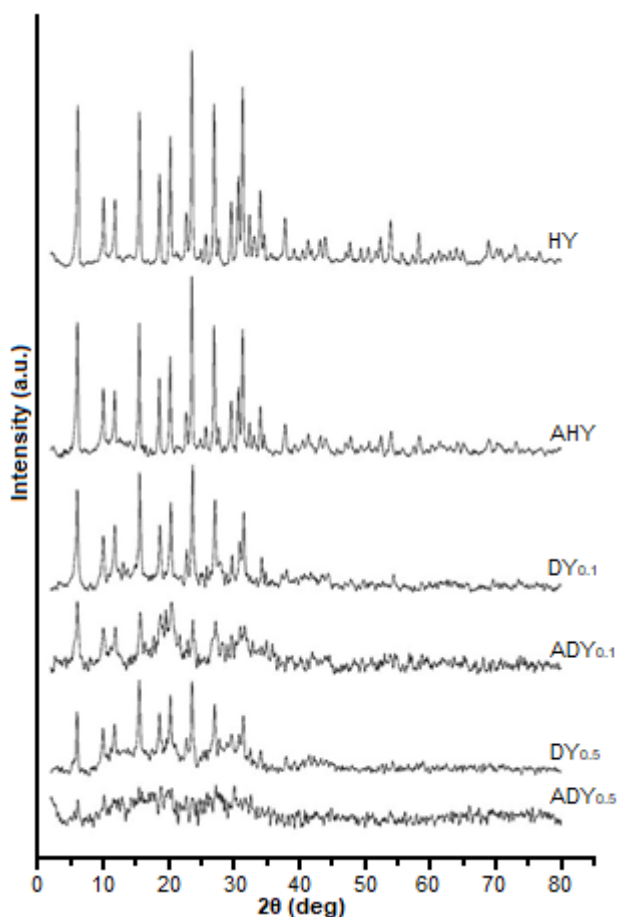


Fig 2. Powder XRD pattern of zeolites Y with various Si/Al ratio before and after treatments

and/or NaOH treatments reduced the crystallinity of zeolite Y. The XRD pattern of AHY showed that NaOH

treatment without HCl treatment only slightly reduced the crystallinity of zeolite Y, but insufficient to generate enough mesoporous structure (as shown in Table 2, the composition of the mesoporous surface area in AHY samples was only 7.08%). On the other hand, the zeolite Y managed to maintain its crystallinity after being treated with 0.5 M HCl, as indicated by the XRD pattern of $DY_{0.5}$. However, after treated with NaOH, the $DY_{0.5}$ completely lost its crystallinity (see XRD pattern of $ADY_{0.5}$). The $ADY_{0.5}$ had the highest percentage of the mesoporous structure (as shown in Table 2). The loss of crystallinity was caused by the removal of aluminum and silicon framework throughout the HCl and NaOH treatments. Higher Al and Si atoms removal from the zeolite Y framework resulted in more pores as a defect in the zeolite structure. Therefore, the higher the concentration of HCl used, which is further treated with NaOH, will increase the Si/Al ratio, decrease the crystallinity of zeolites, and increase the mesoporous region.

Morphology analysis

The morphology of HY and NaOH treated samples (AHY , $ADY_{0.1}$, and $ADY_{0.5}$) was investigated by TEM analysis (Fig. 3). According to TEM analysis, the particle size of HY was around 400 nm. The TEM image of AHY , $ADY_{0.1}$, and $ADY_{0.5}$ showed that NaOH treated sample had a smaller particle size, which was around 200 nm. This indicates that NaOH treatment decreased the particle size of zeolite Y. The TEM image of AHY did not

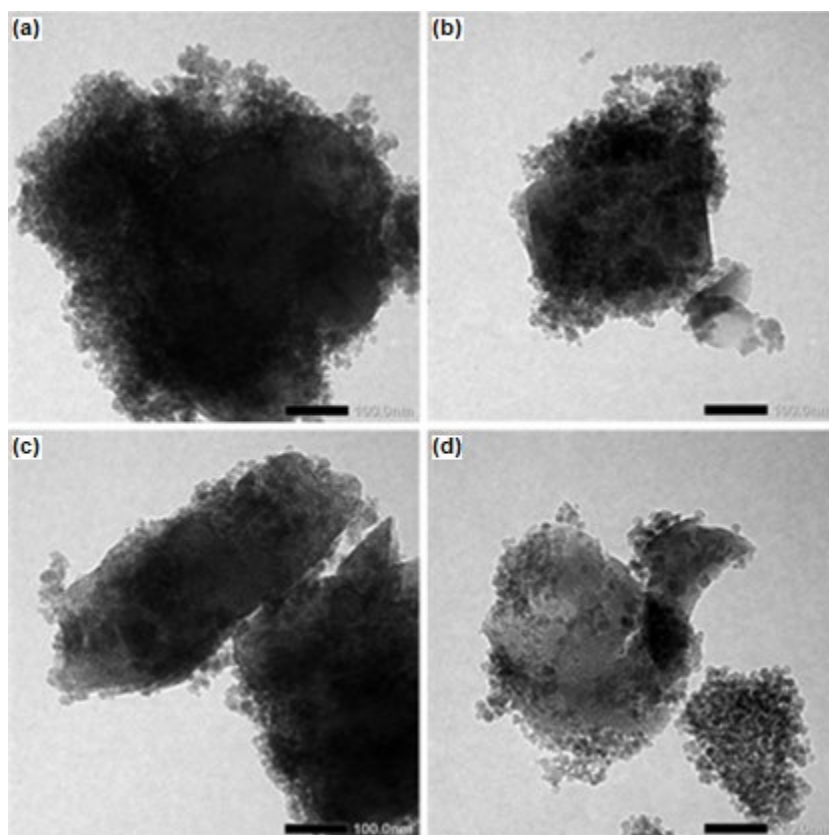


Fig 3. TEM images of (a) HY, (b) AHY, (c) ADY_{0.1}, (d) ADY_{0.5}

Table 2. Textural properties of zeolites Y before and after treatments

Catalyst	Average Pore Diameter (nm)	S_{BET} (m ² /g)	$S_{\text{micro}}^{\text{a}}$ (m ² /g)	$S_{\text{meso}}^{\text{b}}$ (m ² /g)	S_{micro} (%)	S_{meso} (%)	V_{total} (cc/g)	$V_{\text{micro}}^{\text{a}}$ (cc/g)	$V_{\text{meso}}^{\text{c}}$ (cc/g)	V_{micro} (%)	V_{meso} (%)
HY	2.52	549	517	32.0	94.3	5.75	0.35	0.27	0.07	78.5	21.5
AHY	2.63	414	385	29.0	92.9	7.08	0.27	0.20	0.07	73.9	26.1
DY _{0.1}	3.03	278	249	29.0	89.6	10.4	0.21	0.14	0.07	67.5	32.5
ADY _{0.1}	3.62	157	137	20.0	87.5	12.5	0.14	0.09	0.05	66.5	33.5
DY _{0.5}	3.42	182	156	26.0	85.5	14.6	0.16	0.09	0.06	59.9	40.1
ADY _{0.5}	4.60	119	95.0	24.0	79.7	20.3	0.14	0.08	0.06	56.3	43.7

^a t-plot method; ^b $S_{\text{meso}} = S_{\text{BET}} - S_{\text{micro}}$; ^c $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$

reveal any mesoporosity. On the other hand, the TEM image of ADY_{0.1} and ADY_{0.5} revealed a significant mesoporosity that was shown by the lighter zone on the zeolite Y particles.

Textural properties analysis

The N₂ adsorption-desorption isotherms of zeolite Y samples are shown in Fig. 4, and the corresponding textural properties are summarized in Table 2. All the samples showed the adsorption isotherm type IV with hysteresis loops at $P/P_0 > 0.4$. This indicates that all the

zeolite Y samples already had a mesoporous structure in their framework. The hysteresis loops, which became wider after the HCl and/or NaOH treatments, were introduced to the zeolite Y. This confirms that HCl and/or NaOH treatment increased the composition of the mesoporous structure of zeolite Y by removing aluminum and silicon atom from its framework.

As can be seen in Table 2, the reduction of total specific surface area (S_{BET}) and total pore volume (V_{total}) occurred because of the formation of mesoporous

structure in the zeolites Y structure. Therefore, the discussion with pore size composition (in percentage) became more convenient. The mesoporous percentage (whether the specific surface area or the pore volume) of samples increased along with the increase of the Si/Al ratio before NaOH treatment. After NaOH treatment, the percentage of mesoporous volume (V_{meso}) of HY increased from 21.51% to 26.14%, which gave a higher increase than $DY_{0.1}$ (from 32.54% to 33.52%) and $DY_{0.5}$ (from 40.07% to 43.68%). This indicates that HCl treatment was more effective in increasing the pore volume of zeolite Y with a lower Si/Al ratio and higher crystallinity.

On the other hand, the percentage of mesoporous specific surface area (S_{meso}) of HY only slightly increased

from 5.75% to 7.08% after treated by NaOH, which was lower than the increasing value of S_{meso} of $DY_{0.1}$ (from 10.40% to 12.49%) and $DY_{0.5}$ (from 14.55% to 20.32%). This phenomenon showed that a combination of HCl and NaOH treatment was more effective in increasing the percentage of the mesoporous surface area of zeolite Y with higher Si/Al ratio and lower crystallinity. The highest increase of S_{meso} occurred in $DY_{0.5}$ because its framework had already been destroyed by the 0.5 M HCl treatment; thus, the removal of aluminum and silicon from the framework throughout NaOH treatment became easier.

The results of the textural properties of zeolites Y were then confirmed by the BJH pore size distribution analysis shown in Fig. 5. It indicates that the mesoporous

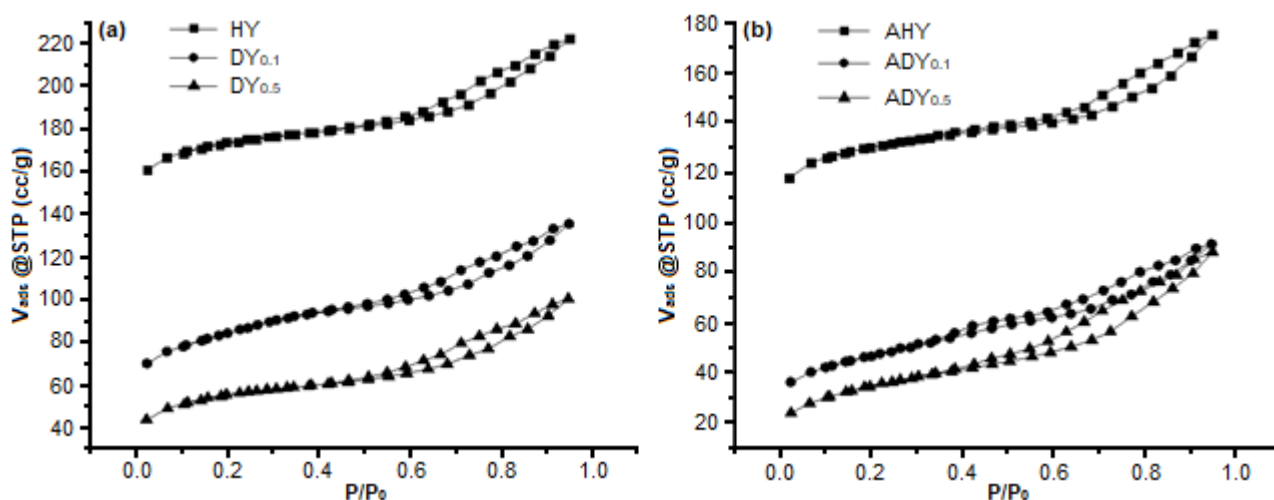


Fig 4. Isotherm adsorption-desorption of zeolites Y with various Si/Al ratio (a) before and (b) after NaOH treatment

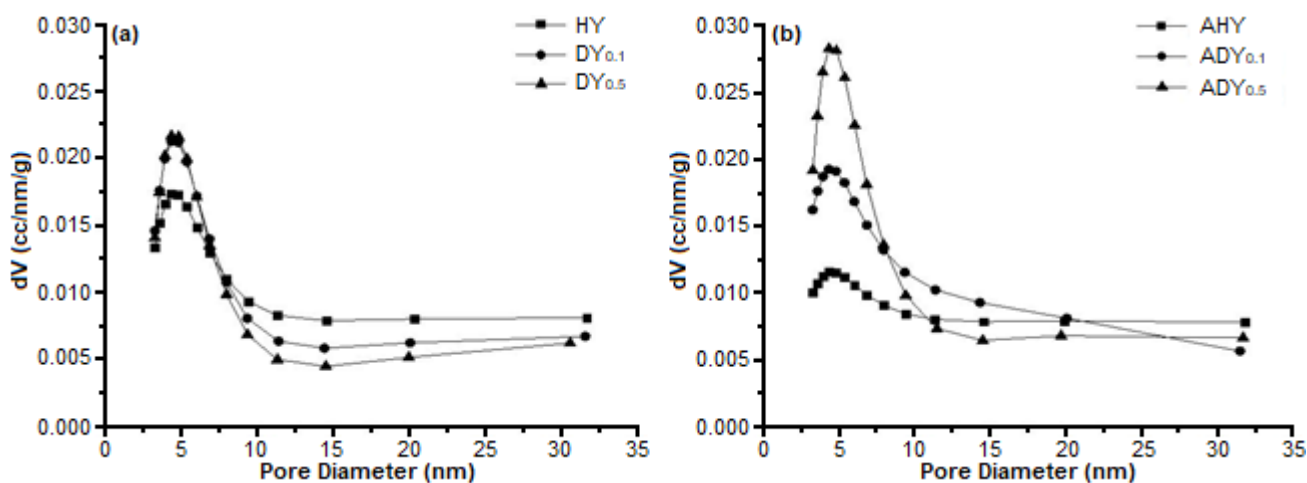


Fig 5. BJH pore distribution with various Si/Al ratio (a) before and (b) after NaOH treatment

distribution of all samples was mainly obtained at 4 nm. As indicated in Fig. 5, there was an increase in mesoporous distribution on DY_{0.1} and DY_{0.5} after NaOH treatment. Such a phenomenon was not observed on HY. This indicated that NaOH treatment was more effective for increasing the mesoporous distribution of the HCl-treated zeolite Y, as also supported by the TEM images of NaOH treated samples in Fig. 3.

Catalytic Performance in Hydrotreating α -Cellulose Bio-Oil

The α -cellulose bio-oil appearance was yellowish and thick liquid. The α -cellulose bio-oil easily changed its appearance into a dark brownish and thick liquid when exposed into the open air at room temperature due to its chemical instability, oxidation, and a strong tendency to re-polymerize. This phenomenon was caused by the high oxygen content in the bio-oil [19]. The pyrolysis process in this work managed to convert solid α -cellulose into α -cellulose bio-oil with 40–45% of the conversion value. The α -cellulose bio-oil mainly contains furans, ketones, aldehydes, carboxylic acid, etc. The major contents of the α -cellulose bio-oil are listed in Table 3.

The hydrotreatment of the α -cellulose bio-oil resulted in a yellowish liquid that clearer and thinner than the α -cellulose bio-oil. Moreover, the hydrotreated α -cellulose bio-oil did not change its appearance if it was exposed to open air and room temperature. This phenomenon suggests that hydrotreated α -cellulose bio-oil was more stable than the untreated α -cellulose bio-oil.

In this work, the hydrotreatment was conducted with HCl and/or NaOH treated zeolites Y to investigate the zeolites Y catalytic performance. The distribution of hydrotreated α -cellulose bio-oil products is shown in Fig. 6. The liquid product in the thermal hydrotreatment of α -cellulose bio-oil (i.e., hydrotreatment without catalyst) was lower than the catalytic hydrotreatment. This is caused by the radical mechanism reaction in thermal hydrotreatment resulted in excess of the gas product [20]. Sample ADY_{0.1} had the best activity as a catalyst due to the highest liquid product yield (74.1%). This indicated that ADY_{0.1} 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. The liquid product increase

Table 3. Major product contents of untreated α -cellulose bio-oil

Contents (% ^a)	Product Description	Molecular Formula
9.77	1,3-Dioxolane-4,5-dione	C ₂ H ₄ O
7.15	Acetone	C ₃ H ₆ O
4.12	Acetaldehyde	C ₂ H ₄ O ₂
6.48	2,3-Butanedione	C ₄ H ₆ O ₂
15.13	Acetic acid	C ₂ H ₄ O ₂
19.28	2-Propanone-1-hydroxy	C ₃ H ₆ O ₂
1.28	3-Buten-2-one	C ₅ H ₈ O
1.01	2-Butanone	C ₅ H ₁₀ O
2.66	2,3-Pentanedione	C ₅ H ₈ O ₂
1.94	Propanoic acid	C ₃ H ₆ O ₂
1.14	1,4-Dioxin	C ₄ H ₆ O ₂
3.74	1-Hydroxy-2-butanone	C ₄ H ₈ O ₂
1.26	Propanal	C ₃ H ₆ O
1.91	2-Propanone	C ₃ H ₆ O ₂
11.41	2-Furancarboxaldehyde	C ₅ H ₄ O ₂
3.18	2-Furanmethanol	C ₅ H ₆ O ₂
1.21	Vinyl acetate	C ₄ H ₆ O ₂
2.20	Vinyl propionate 1-Hydroxy-2-butanone	C ₅ H ₈ O ₂
1.23	acetate	C ₆ H ₁₀ O ₃

^a % area of GC-MS

of HY to AHY was 6.3%, $DY_{0.1}$ to $ADY_{0.1}$ was 24.4%, and $DY_{0.5}$ to $ADY_{0.5}$ was 15.3%. In most of the 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.

The major composition of hydrotreated α -cellulose bio-oil is shown in Table 4. The composition distribution

of hydrotreated α -cellulose bio-oil was slightly different than the untreated α -cellulose bio-oil (Table 3). The hydrotreated α -cellulose bio-oil mainly contained furans, ketones, aldehydes, and carboxylic acid, which was remained the same as the untreated α -cellulose bio-oil. However, in catalytic hydrotreatment using $ADY_{0.5}$ as the catalyst, there was 6.12% of 1-isopropyl-2,4-dimethylbenzene that managed to be produced. This compound is a deoxygenated branched aromatic that has

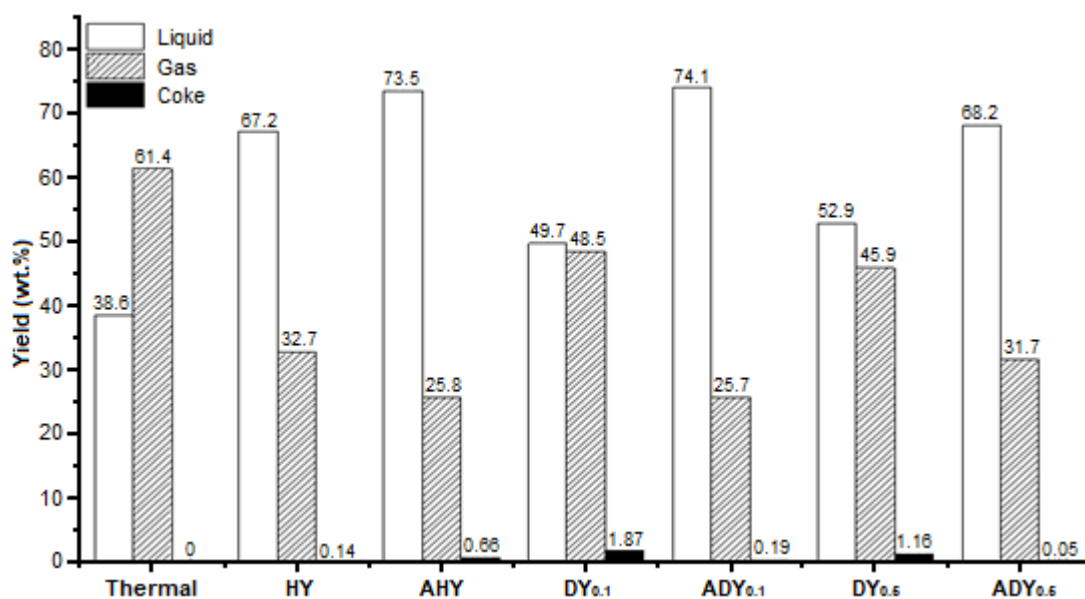


Fig 6. Product distribution of hydrotreated α -cellulose bio-oil

Table 4. Major product of hydrotreated α -cellulose bio-oil

Group	Product Description	Contents (% area of GC-MS)						
		Thermal	HY	$DY_{0.1}$	$DY_{0.5}$	AHY	$ADY_{0.1}$	$ADY_{0.5}$
Carboxylic Acid	Formic acid			6.34	7.72			
	Acetic acid	16.4	12.6	28.4	29.3	19.9	25.4	
	Propionic acid	5.47				6.78	7.17	7.16
	Hexadecanoic acid		6.76					
	Linoleic acid		5.81					
Ketone	1-Hydroxy-2-propanone	29.2	13.2	22.7	18.9	14.0	23.0	16.7
	2-Methyl-3-pentanone			3.95				
	4-Octen-3-one	13.9						
	1-Hydroxy-2-butanone	8.03					5.30	
Aldehyde	Acetone		28.6		7.45	21.9	10.7	6.56
	2-Furancarboxaldehyde	5.27		14.2	7.15	15.3		
	Acetaldehyde		7.91	12.5	16.2	7.97	11.2	17.2
Ester	Vinyl propionate							22.9
Aromatic	1-Isopropyl-2,4-dimethylbenzene							6.12

good potential to be processed into fuel. This indicated that ADY_{0.5} had the best selectivity and properties in producing gasoline-potential compounds among the other samples.

■ CONCLUSION

The HCl and NaOH treatment of zeolites Y managed to increase the mesopore distribution of all zeolites Y. On the other hand, the acidity and crystallinity of zeolite Y samples decreased after the treatments. The sample ADY_{0.5} gave the highest mesopore distribution at 43.7% and the highest average pore diameter at 4.59 nm. The initial Si/Al ratio that was proven to be the most crucial parameter to generate a mesopore structure in zeolite Y. The higher the Si/Al ratio before NaOH treatment, the higher mesopore managed to be generated on the zeolite Y surface. Catalytic performance in hydrotreating α -cellulose bio-oil showed that HY, AHY, DY_{0.1}, ADY_{0.1}, DY_{0.5}, and ADY_{0.5} gave a similar result of product selectivity. However, ADY_{0.5} managed to generate 6.12% of 1-isopropyl-2,4-dimethylbenzene that had the potential to be processed into fuel because it has the largest pore size of 4.6 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.

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