Modification of zeolite Y as a catalyst in the production of dimethyl ether from methanol dehydration

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ABSTRACT

Dimethyl ether is an eco-friendly alternative renewable energy that can be utilized in diesel engines to substitute fossil fuels and gas stoves as a household fuel. In the dimethyl ether synthesis process, a catalyst was used to assist the reaction. The catalyst used in this study was dealuminated zeolite Y. This study's objective was to determine the best-dealuminated zeolite Y as a catalyst for the synthesis of dimethyl ether. The zeolite Y catalyst was dealuminated by using sulfuric acid solution. In the preparation step, zeolite Y was dealuminated at different dealumination temperatures (40 to 60°C) and acid concentrations (7.5 to 9.5 N). The catalyst was characterized by using XRF, BET, and SEM-EDX methods. The acidity analysis of the catalyst was performed by the ammonia and pyridine absorption methods. The results showed that the best-dealuminated zeolite Y catalyst was achieved under conditions of dealumination temperature of 50°C and acid concentration of 8.5 N with total acidity of 37.665 mmol/g, Si/Al ratio of 69.42, and surface area of 41.310 m²/g, respectively. The result of catalyst performance test in the dimethyl ether synthesis through methanol dehydration showed that the dealuminated zeolite Y had higher activity than zeolite Y without dealumination. The obtained methanol conversion using dealuminated zeolite Y was 76.07%.

Keywords: Catalyst; Dealumination; Dimethyl ether; Si/Al ratio; Zeolite Y.

INTRODUCTION

Dimethyl ether (DME) is an eco-friendly alternative fuel that can be utilized to substitute fossil fuels. Dimethyl ether has better characteristics than other fuels, such as colorless, fragrant, non-toxic, biodegradable, non-corrosive, no contain sulfur and nitrogen so emissions are much lower than fossil diesel oil (Cai et al., 2016).

Dimethyl ether can be produced through 2 methods, the direct process and indirect process methods. The direct process method is the dimethyl ether formation process in one reactor that involves two processes, namely the synthesis of methanol (through hydrogenation of CO) and dehydration of methanol into dimethyl ether. Meanwhile, the indirect process is the dimethyl ether formation process consisting of 2 steps, including methanol synthesis from syngas using $Cu/ZnO/Al_2O_3$ catalyst and methanol dehydration producing dimethyl ether using an acid catalyst (Catizzone et al., 2015).

Zeolite is aluminosilicate micropore crystals with various structures. Moreover, zeolite has intrinsic properties such as high surface area and thermal stability, strong acidity, and good selectivity, so that it is suitable when applied to processes that require high temperatures (Verboekend et al., 2016) such as the methanol dehydration process to DME.

The use of synthetic zeolites in a synthesis process is sometimes not in accordance with the expected results. For this reason, the catalyst needs to be modified to change the properties of the catalyst to match the desired specifications. One of the modifications of zeolite is dealumination. The dealumination process is carried out using an acid solution to remove the aluminum metal in zeolites. The dealumination process of zeolite aims to increase the acidity of the zeolite by increasing the Si/Al ratio (Müller et al., 2015). The higher acidity of zeolite will improve the performance and efficiency of the zeolite itself (Catizzone et al., 2015).

Dehydration of methanol into dimethyl ether (DME) can use various types of catalysts from acidic solid materials such as γ-alumina, silica-alumina, copper-alumina, zeolites, etc. (Chiang and Lin, 2017). Some researchers used the γ-alumina catalyst in the experiment of methanol

dehydration to DME (Armenta et al., 2020; Kosova and Kurnia, 2011). The results show that the yield and selectivity of dimethyl ether obtained are relatively low.

The use of dealuminated zeolite Y in the methanol dehydration process to dimethyl ether has not been widely found in previous literature. The use of zeolites, such as zeolite Y, ZSM-5, Modernite, as a catalyst in the methanol dehydration process to DME, has been carried out by several researchers. However, the use of these catalysts has a drawback, namely the formation of other products than DME and coke deposition when the methanol dehydration process was conducted at high temperatures. In contrast, when the methanol dehydration process was carried out at low temperatures, it was difficult to achieve adequate methanol conversion (Hosseininejad et al., 2011). The use of the dealuminated Y zeolite was carried out by DeCanio et al. (1986) showed that the catalytic activity of dealuminated zeolite Y became relatively inactive at 750°C.

The results of these studies indicate that the catalyst used in the methanol dehydration process to DME has several weaknesses and low activity. Therefore, the catalysts with good natures, including acidity, surface area, Si/Al ratio, crystallinity, pore size, and can be operated at moderate temperatures, are needed. The main objective of this research is to characterize the dealuminated zeolite Y prepared through acid treatment. The effect of dealumination temperature and acid concentration was studied. The best results from zeolite Y characterization were tested on the dimethyl ether synthesis from methanol dehydration. The utilization of dealuminated zeolite Y in DME production is supposed to enhance the methanol conversion so that it will increase the resulting DME product.

MATERIALS AND METHODS

Materials

Zeolite Y was used as raw material obtained from Surabaya, Indonesia. Chemicals including methanol (99.99%), sulfuric acid (95-97%), ammonia solution (25%), and pyridine for

analysis were obtained from Merck (Germany). Aquadest was obtained from the MeR-C (Membrane Research Centre) laboratory, Diponegoro University, Indonesia.

Dealuminated catalyst preparation

The zeolite Y dealumination process was carried out through several stages. The first stage was making the H_2SO_4 solution. The concentration of the acid solution was varied at 7.5; 8; 8.5; 9; and 9.5 N, respectively. Twenty-five grams of zeolite Y was then added into the H_2SO_4 solution. The dealumination process was carried out at a certain temperature according to the variable while stirring for 3 hours. The dealumination temperature was varied at 40, 45, 50, 55 and 60°C, respectively. Furthermore, the mixture was washed and filtered using a vacuum pump (Krisbow 1/3HP KW19-533). The filtered zeolite Y was then dried at 110°C in an oven (Memmert UN 55 B214.0281) for 1 hour. Subsequently, the dried zeolite Y was calcined in the Ney Vulcan furnace (D-550-240V) at 550°C for 3 h. The result of calcination was in the form of dealuminated zeolite Y.

Catalyst characterization

Testing and characterization of the catalyst were conducted through acidity test, X-Ray Fluorescence (XRF), surface area testing, and Scanning Electron Microscopy-Energy Dispersive of X-ray Spectroscopy (SEM-EDX).

The acidity test was carried out by flowing the pyridine and NH_3 gases into catalysts. Determination of the acid sites amount on zeolite Y was conducted by the gravimetric method using ammonia and pyridine vapors as the adsorbents. Total acidity, surface acidity, and cavity acidity were calculated using equations (1), (2), and (3),

$$TA\left(\frac{mmol}{g}\right) = \frac{W_{NH_3}(g)}{MW_{NH_3}\left(\frac{g}{mol}\right)xW_{sample}(g)} x1000\left(\frac{mmol}{mol}\right) \qquad (1)$$

$$SA\left(\frac{mmol}{g}\right) = \frac{W_{pyridine}(g)}{MW_{pyridine}\left(\frac{g}{mol}\right)xW_{sample}(g)} x1000\left(\frac{mmol}{mol}\right) \qquad (2)$$

$$CA\left(\frac{mmol}{g}\right) = TA\left(\frac{mmol}{g}\right) - SA\left(\frac{mmol}{g}\right) \qquad (3)$$

Where TA is Total Acidity; SA is Surface Acidity; CA is Cavity Acidity; W_{NH_3} is weight of NH$_3$; $W_{pyridine}$ is weight of pyridine; MW_{NH_3} is molecular weight of NH$_3$; $MW_{pyridine}$ is molecular weight of pyridine; and W_{sample} is weight of sample.

XRF analysis was carried out under vacuum using a Rigaku Supermini200 equipped with a Benchtop tube below sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. The zeolite Y surface area was analyzed by using the Brunauer-Emmett-Teller (BET) method. In this study, catalyst morphology was characterized by SEM JEOL JSM6510LA.

The experimental work on synthesis of dimethyl ether

The experimental work was used to evaluate the catalytic activity of zeolite Y catalyst. The experimental work on synthesis of dimethyl ether was carried out in a fixed bed stainless steel column reactor. The reactor has 1 in (2.54 cm) inner diameter and 15.0 g catalyst loading. Liquid methanol (purity > 99.99%) is put into a three-neck flask and evaporated. After that, the methanol which has changed in the gas phase flows to the reactor which has contained the dealuminated zeolite Y catalyst. The methanol dehydration process to DME is conducted in a reactor at 250°C and atmospheric pressure. The product obtained from the reactor is taken after the methanol dehydration process lasts for 1 hour. Next, the product is analyzed using Gas Chromatography-Mass Spectrometry (GCMS) (SHIMADZU, Restex RTX1-MS column). Experimental setup for the methanol dehydration process is shown in Figure 1.
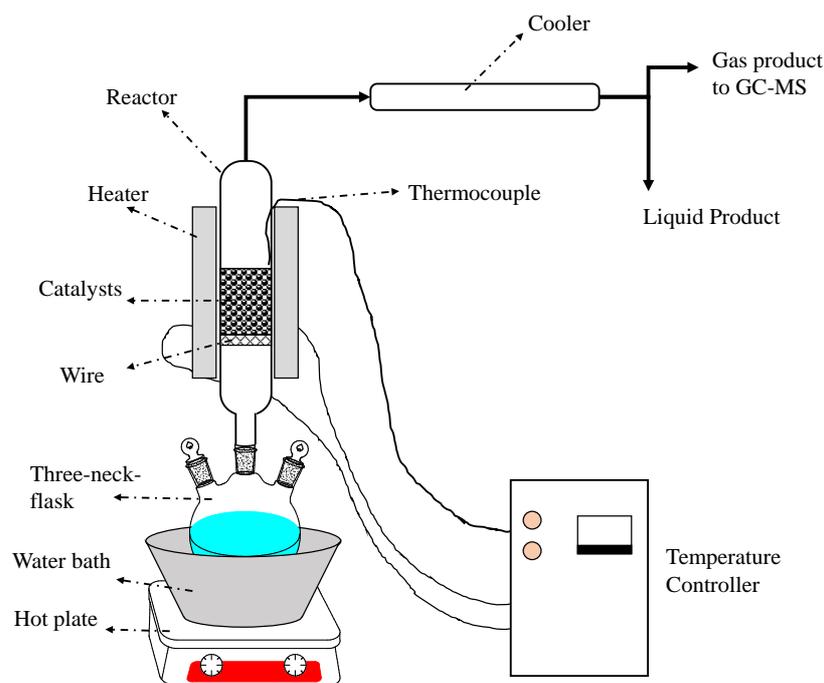
Figure 1. Experimental set up for methanol dehydration

RESULTS AND DISCUSSIONS

Effect of dealumination on the acidity of zeolite Y

The ammonia and pyridine absorption tests were performed to establish the acid sites amount

or acidity of the zeolite Y (Sulistyowati et al., 2018). The acidity of zeolites can be expressed

in mmol ammonia and mmol pyridine per gram of catalyst. The acidity values of zeolite Y

without dealumination are presented in Table 1, while the acidity test results of dealuminated

zeolite Y are shown in Table 2 and Table 3.

Table 1. The acidity values of zeolite Y without dealumination.

Treatment of zeolite Y	Total acidity (mmol/g)	Surface acidity (mmol/g)	Cavity acidity (mmol/g)
Without Dealumination	25.167	12.585	12.582

Based on the acidity analysis results shown in Table 1, it indicates that the value of total

acidity, surface acidity, and cavity acidity of zeolite Y without dealumination is smaller than

the acidity value of dealuminated zeolite Y (Tables 2 and 3). This difference is due to the

dealumination process in zeolite Y reduce alumina so that the dealuminated zeolite Y catalyst has more active sites (Dias and Dias, 2018).

Table 2. The analysis results of the dealuminated zeolite Y acidity at an acid solution concentration of 8.5 N.

Dealumination temperature (ºC)	Total acidity (mmol/g)	Surface acidity (mmol/g)	Cavity acidity (mmol/g)
40	33.099	13.148	19.951
45	35.953	13.654	22.299
50	37.665	13.401	24.264
55	33.099	13.401	19.698
60	34.811	14.159	20.652

Table 2 shows the acidity analysis results of the dealuminated zeolite Y at various dealumination temperatures. It shows that the dealumination temperature of 50ºC is the best. The temperature of the dealumination process affects catalyst crystallinity. The higher the dealumination temperature, the higher the catalyst crystallinity. However, at higher temperatures, the framework begins to be a failure; therefore, the zeolite structure changes lead to a reduction in the zeolite Y crystallinity (Borges and de Macedo, 2016). As a result, the zeolite acidity decreases.

Table 3. The analysis results of the dealuminated zeolite Y acidity at a dealumination temperature of 50ºC

Acid concentration (N)	Total acidity (mmol/g)	Surface acidity (mmol/g)	Cavity acidity (mmol/g)
7.5	33.099	13.401	19.698
8	32.529	13.401	19.128
8.5	37.665	13.401	24.264
9	33.670	13.654	20.016
9.5	33.099	13.401	19.698

Table 3 shows the acidity analysis results of the dealuminated zeolite Y at various acid concentrations. It shows that the concentration of 8.5 N is the best. The addition of acid aims to exchange the cations present; consequently, the zeolite will form zeolite-H. An exchange occurs between cations in zeolites and H^+. These cations can be exchanged with other cations

so that all the cations will be exchanged for H^+. The higher the acid solution concentration, the more Al is released from its bonds. However, higher concentrations of sulfuric acid solution cause an ineffective exchange of H^+ ions with base ions contained in the zeolite structure due to the limitation of the base ion lattice in the zeolite structure (Sulistyowati et al., 2018).

Effect of dealumination on the Si/Al composition of zeolite Y

In the dealumination process, zeolite acidity is also decided based on the Si/Al ratio. Thus, the purpose of XRF analysis on zeolite is to find out the composition of Si and Al in zeolite Y before and after dealumination process. The results of the XRF test on the zeolite Y catalysts are shown in Tables 4, 5, and 6.

Table 4. The XRF analysis results of the zeolite Y without dealumination.

Treatment of zeolite Y	Composition of Si (% mass)	Composition of Al (% mass)	Ratio of Si/Al
Without Dealumination	10.2	3.320	3.07

In the dealumination process, Al atoms are released from zeolites. This dealumination is conducted to increase the Si/Al ratio. Changes in the Si/Al ratio of material will affect the nature of the material. As the Si/Al ratio of a zeolite material increases, the acid sites on the zeolite itself increase (Dias and Dias, 2018). Dealumination will also cause the material to be more hydrophobic (Borges and de Macedo, 2016). Tables 4 shows that the Si/Al ratio of zeolite Y which has not been dealuminated is 3.07. Meanwhile, zeolite that has been dealuminated has a higher Si/Al ratio (Tables 5 and 6). This shows that the dealumination of zeolite Y by H_2SO_4 influences the Si/Al ratio in zeolite Y so that the Si/Al ratio in zeolite Y increases after dealumination process.

Table 5. The XRF analysis results of the dealuminated zeolite Y at an acid solution concentration of 8.5 N.

Dealumination	Composition of Si	Composition of Al	Ratio of Si/Al

temperature (°C)	(% mass)	(% mass)	
40	17.5	0.331	52.87
45	18.9	0.367	51.49
50	19.3	0.278	69.42
55	18.0	0.330	54.54
60	15.7	0.291	53.95

Table 6. The XRF analysis results of the dealuminated zeolite Y at a dealumination temperature of 50°C

Acid concentration (N)	Composition of Si (% mass)	Composition of Al (% mass)	Ratio of Si/Al
7.5	73.2	2.000	36.60
8	70.8	2.390	29.62
8.5	19.3	0.278	69.42
9	74.6	1.580	47.22
9.5	73.2	1.720	42.56

The XRF analysis results in Table 5 show that the zeolite Y dealumination process with the variation of the dealumination temperature shows that the highest Si/Al ratio obtained occurs at 50°C. These results are in accordance with the acidity analysis which shows that the acidity of zeolite has the highest value at a dealumination temperature of 50°C.

Table 6 shows that the highest Si/Al ratio is obtained at a concentration of 8.5 N. These results are in accordance with the acidity analysis of zeolite which shows the highest value at a concentration of 8.5 N. Therefore, based on the results of acidity analysis and XRF analysis, it is suggested that the best concentration conditions were obtained at 8.5 N.

Effect of dealumination on the surface area of zeolite Y

The zeolite surface area can be established using the Brunauer-Emmett-Teller (BET) analysis and the results are presented in Tables 7, 8, and 9.

Table 7. The BET analysis results of the zeolite Y without dealumination.

Treatment of zeolite Y	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Radius ($\dot{A}$)
Without Dealumination	668.694	0.027	15.301

Table 8. The BET analysis results of the dealuminated zeolite Y at an acid solution concentration of 8.5 N.

Dealumination temperature (°C)	Surface Area (m²/g)	Pore Volume (cc/g)	Pore Radius ($\dot{A}$)
40	21.432	0.032	15.306
45	9.162	0.015	17.050
50	41.310	0.074	15.295
55	20.400	0.030	21.589
60	20.387	0.034	15.305

Table 9. The BET analysis results of the dealuminated Zeolite Y at a dealumination temperature of 50°C

Acid concentration (N)	Surface Area (m²/g)	Pore Volume (cc/g)	Pore Radius ($\dot{A}$)
7.5	13.044	0.024	17.353
8	9.582	0.021	16.088
8.5	41.310	0.074	15.295
9	7.041	0.017	18.859
9.5	13.175	0.028	16.022

Tables 8 and 9 show that the zeolite Y surface area that has been dealuminated decreased compared to zeolite Y without dealumination (Table 7). This change in the surface area proves that the zeolite Y structure also changes. The change in zeolite structure is due to the change in the zeolite Y catalyst pore size as a result of the dealumination process.

Tables 8 and 9 indicate that the dealuminated zeolite Y surface area is smaller than the zeolite Y surface area without dealumination (Table 7). These results are following the results of the study conducted by Peron et al. (2019). This phenomenon indicates that the dealumination process can damage the structure of alumina and silica from zeolites so that it can reduce the surface area of zeolites. High calcination temperature (550°C) causes the zeolite surface area to get smaller.

The zeolite dealumination process using acids can improve the character of zeolites, including increasing acidity, crystallinity, specific surface area, Si/Al ratio and loss of impurity (Borges and de Macedo, 2016). In addition, in the dealumination process, Si can substitute for Al which is lost due to the dealumination process (Dias and Dias, 2018; Lutz, 2014).

In Tables 8 and 9, the highest zeolite surface area after dealumination was acquired at a dealumination temperature of 50°C and an acid solution concentration of 8.5 N, namely 41.310 m^2/g. Based on the XRF analysis shown in Tables 5 and 6, it was discovered that the highest Si/Al ratio was obtained at dealumination temperature and acid solution concentration of 50°C and 8.5 N, namely 69.42. In the dealumination process, the Si atom replaces the place left by the Al atom so that the Si content in the zeolite sample increases (Lutz, 2014). The insertion of Si atoms in the pores of the catalyst causes a reduction in pore size so that the zeolite surface area increases. Particles with smaller pores have a higher specific area.

Effect of dealumination on surface morphology of zeolite Y

The surface morphology of zeolite Y can be observed by microstructure analysis using Scanning Electron Microscopy (SEM). The results of the SEM analysis are shown in Figure 2.
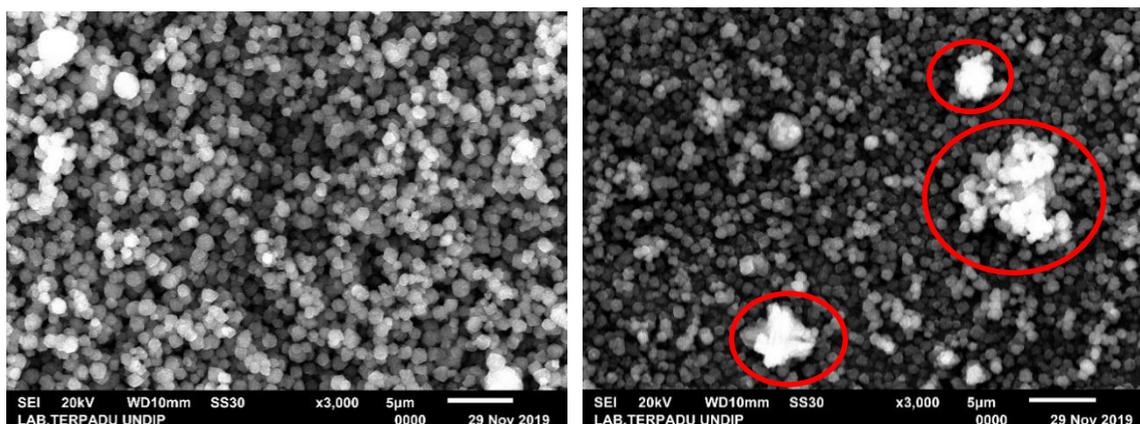
Figure 2. The results of SEM analysis of zeolite Y with a magnification of 3000x: (a) Without-dealumination; (b) Dealumination.

It can be seen in Figure 2 that zeolite Y structure has been changed after dealumination process. These changes are shown with the agglomerate formation of several particles after dealumination (Figure 2b, red circle). This fact occurs because of the magnetic properties of the particles, especially Si and O atoms (Rüscher et al., 2006). Zeolites that have been dealuminated do not contain Al, so Si which substitutes Al on the surface structure of zeolites reacts with O atoms to form SiO_4.

Performance test of the dealuminated zeolite Y in dimethyl ether synthesis

The performance test of zeolite Y was performed by comparing the performance of zeolite Y without dealumination and dealuminated zeolite Y in dimethyl ether synthesis. The dealuminated zeolite Y used in the performance test is the dealuminated zeolite Y that has the highest acidity which is obtained at dealumination temperature of 50°C and sulfuric acid solution concentration of 8.5 N. The results of the zeolite Y performance tests are presented in Table 10.

Table 10. Methanol conversion to dimethyl ether in the performance test of zeolite Y

Treatment of zeolit Y	Methanol conversion (%)
Without Dealumination	46.25
Dealumination	76.07

As can be seen in Table 10, methanol conversion to dimethyl ether obtained by dealuminated zeolite Y is higher than obtained by zeolite Y without dealumination. These results prove that the dealuminated zeolite Y has greater activity compared to zeolite Y without dealumination. The methanol conversion obtained in this study is greater than the methanol conversion obtained by other catalysts reported in several previous studies such as $CuO-Al_2O_3$ (Chiang and Lin, 2017), $\gamma-Al_2O_3$ (Kosova and Kurnia, 2011), $Fe_3O_4/\gamma-\chi-Al_2O_3$ (Armenta et al., 2020). This proves that the zeolite Y catalyst which was dealuminated by using acid solution has a higher activity compared to other catalysts so that it can produce a higher conversion.

The reaction mechanism in this study adopts the reaction mechanism proposed by Lu et al. (2004). Lu et al. (2004) used HZSM-5 as a catalyst in the methanol dehydration to dimethyl ether. The reaction mechanism is as follows,

$$CH_3OH(a) + HY \Leftrightarrow HYCH_3OH \tag{1}$$

$$HYCH_3OH \Leftrightarrow CH_3^+Y^- + H_2O(a) \tag{2}$$

$$CH_3^+Y^- + HYCH_3OH \Leftrightarrow HYCH_3OCH_3^+H + Y^- \tag{3}$$

$$HYCH_3OCH_3^+H \Leftrightarrow HYCH_3OCH_3H^+ \tag{4}$$

$$HYCH_3OCH_3H^+ \Leftrightarrow HYCH_3OCH_3 + H^+ \tag{5}$$

$$HYCH_3OCH_3 \Leftrightarrow CH_3OCH_3 + HY \qquad (6)$$

$$H^+ + Y^- \Leftrightarrow HY \qquad (7)$$

CONCLUSIONS

The dealumination process has a very significant effect on zeolite acidity. The zeolite acidity is determined by the acidity of the cavity in the zeolite where the dealuminated zeolite has a higher cavity acidity than the zeolite without dealumination. The dealumination process also causes the enlargement of the zeolite pores which is causing in the decrease of the dealuminated zeolite surface area. Dealuminated zeolites have structural changes wherein the agglomerate of several particles is formed. The best dealumination results are obtained at dealumination temperature of 50°C and H_2SO_4 solution concentration of 8.5 N with the total acidity and Si/Al ratio obtained are 37.665 mmol/g and 69.4, respectively. The performance test of zeolite Y catalysts in dimethyl ether synthesis proves that the dealuminated zeolite Y can produce greater results compared to zeolite Y without dealumination.

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