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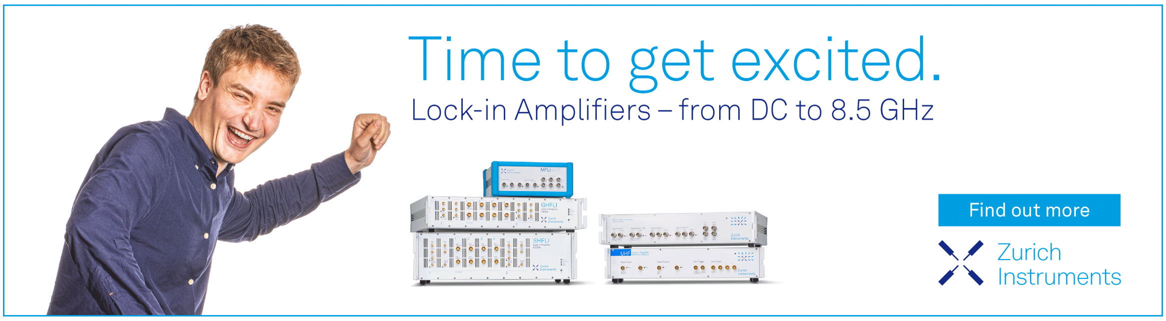

Biofuel Production from Palm Oil via Catalytic Hydrocracking over Modified-Zirconia Catalysts

Maisari Utami[1,a)], Resti Safitri[2,b)], M. Fajar Pradipta[2,c)], Karna Wijaya[2,d)]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia, Yogyakarta 55584, Indonesia*
[2]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia*

[d)]Corresponding author: karnawijaya@ugm.ac.id
[a)]maisariutami@uii.ac.id
[b)]restirerestiti@gmail.com
[c)]fajar@ugm.ac.id

Abstract. The hydrocracking process of palm oil using sulphated zirconia (ZrO_2-SO_4) and Cr-incorporated sulphated zirconia (Cr/ZrO_2-SO_4) catalyst has been conducted. The synthesis of ZrO_2-SO_4 was initiated by the activation process of zirconia acidification using H_2SO_4, followed by calcination process. Furthermore, the impregnation of Cr metal on ZrO_2-SO_4 was prepared by hydrothermal process, then calcined and reduced using H_2 gas. The FTIR instrument was utilized for confirmation of functional groups of the catalysts. The acidity values of catalysts were determined using the gravimetric method by studying NH_3 sorption. The XRD instrument was utilized to identify the crystalline structures of catalysts. The catalysts were then tested in a hydrocracking reactor. The GC-MS instrument was employed to analyze the liquid yields produced from the catalytic hydrocracking of palm oil. The results revealed that after the addition of Cr amounts, the Cr/ZrO_2-SO_4 acidity of catalyst was significantly increased. The catalysts contained monoclinic phase with high thermal stability and high crystallinity. The hydrocracking reaction of palm oil over Cr/ZrO_2-SO_4 effectively produced 35.852% gasoline fraction and 46.064% diesel fraction.

INTRODUCTION

Palm oil is one of the world's most produced in Indonesia. In addition, it becomes the largest potential as alternative energy source. Palm oil has a long hydrocarbon chain similar to petroleum. Therefore, palm oil can be processed to produce biofuel with gasoline (C_5-C_{12}) and diesel (C_{13}-C_{18}) fractions. It may replace the non-renewable fossil fuels, such as gasoline, kerosene, and diesel [1–2].

Palm oil contains of the unsaturated fatty acids of linoleic acid (11%), oleic acid (39%), and the saturated fatty acid of palmitic acid (44%) [3]. Palm oil can be used as a feedstock in hydrocracking reaction due to it has two reactive groups, namely a carbonyl group and a double bond. When palm oil is heated, the molecules will undergo polymerization. This high oleic acid composition can be used as a basis for consideration in the oleic acid hydrocracking process to produce the gasoline fraction [4]. The gas flow rate affects the catalytic conversion process of palm oil into biofuel. The cracking reaction involves hydrogen gas acting as a reactant and a carrier gas. The involving of hydrogen gas in the catalytic reaction can increase conversion [5].

Zirconia (ZrO_2) is a material that has high chemical stability and mechanical resistance. Zirconia is a metal oxide with high ion-exchange capacity and redox activity. Therefore, ZrO_2 is widely used in many catalytic reactions [6–7]. The activation process on solid ZrO_2 catalyst using sulfuric acid (H_2SO_4) aims to increase the reactivity and acidity of the catalyst. Sulfuric acid is strong mineral acid that affects the total acidity based on Lewis and Brønsted acid sites [8–9]. The impregnation of active metal component, such as chromium metal (Cr) into the carrier pore system of ZrO_2-SO_4 is necessary to initiate the hydrogenation reaction to enhance the catalytic activity [10].

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Hydrothermal is a suitable method for for preparation of well-crystallized materials. Furthermore, the hydrothermal is simple preparation method which effectively produce high purity materials [11]. So far, the use of metal modified sulphated zirconia as a catalyst in the production of biofuel from palm oil has not yet been examined. The present study developed Cr-incorporated sulphated zirconia (Cr/ZrO_2-SO_4) using a hydrothermal technique. This catalyst can be effectively used in converting palm oil into gasoline and diesel fractions.

MATERIALS AND METHODS

Materials

The materials used in this study were commercial nanozirconia supplied from China (ZrO_2 99.9%) and sulfuric acid (H_2SO_4 97%), chromium(III) nitrate nanohydrate ($Cr(NO_3)_3{\cdot}9H_2O$ 99%), and ammonium hydroxide (NH_4OH 25%) from Merck. Palm oil was purchased from PT Tunas Baru Lampung Tbk, Indonesia.

Synthesis of Cr/ZrO_2-SO_4 Catalyst

Sulfated zirconia (ZrO_2-SO_4) was synthesized by dispersing commercial ZrO_2 and 0.5 M H_2SO_4 then stirred at room temperature for 24 hours. The mixture was then centrifuged at 1500 rpm for 10 minutes. The material was dried at temperature of 100 °C for 24 hours and calcined at temperature of 600 °C for 4 hours.

A total amount of ZrO_2-SO_4 was dispersed in an aqueous solution of $Cr(NO_3)_3{\cdot}9H_2O$ in a hydrothermal autoclave, heated at temperature of 150 °C for 5 hours, and then dried at temperature of 100 °C for 24 hours. The dried solid was calcined at temperature of 600 °C for 4 hours, and followed by reduction with H_2 gas flow of 20 mL/minutes at temperature of 400 °C for 2 hours. [11–12]. The obtained material was labelled as Cr/ZrO_2-SO_4. The synthesized catalysts (ZrO_2-SO_4 and Cr/ZrO_2-SO_4) were analyzed by Fourier transform infrared spectrophotometer (FTIR, Shimadzu 8210 PC) and X-ray diffractometer (XRD, Shimadzu 6000).

The acidity of ZrO_2-SO_4 and Cr/ZrO_2-SO_4 catalysts were determined by flowing the ammonia (NH_3) vapor toward the sample at room temperature for 24 hours in vacuum condition. The acidity values of catalysts were calculated using the following equation:

$$\text{Acidity value (mmol/g)} = \frac{W_2 - W_1}{(W_1 - W_0) \text{ x Mr } NH_3} \text{ x } 1000$$

W_2 = sample weight after adsorption
W_1 = sample weight before adsorption
W_0 = crucible weight

Hydrocracking of Palm Oil

The application of synthesized catalyst was carried out on hydrocracking of palm oil into biofuel fraction. The hydrocracking reaction was carried out in a mini reactor with a catalyst-to-palm oil ratio of 1:100 at temperature of 300 °C for the catalyst (ZrO_2-SO_4 and Cr/ZrO_2-SO_4) and 350 °C for the feed (palm oil) for 40 minutes with a H_2 gas rate of 20 mL/min [11]. The gas chromatograph-mass spectrometer (GC-MS, Shimadzu QP 2010S) was used to characterize the liquid product from hydrocracking reaction.

RESULTS AND DISCUSSION

Characterization of Cr/ZrO_2-SO_4 Catalyst

The catalysts was characterized by FTIR spectrophotometer to determine the presence of functional groups in the structure. FIGURE 1 depicts the FTIR spectra of ZrO_2-SO_4 and Cr/ZrO_2-SO_4 at wavenumber of 400-4000 cm^{-1}. The FTIR spectra shows absorption peaks at a wave number of 408-740 cm^{-1} which correspond to Zr-O-Zr vibration. After the activation of sulphate and calcination process at high temperature, the peaks of the sulfate group appears at wave number of 1056-1118 cm^{-1} which indicate S-O and S=O asymmetric vibrations in ZrO_2 [13].

The peaks at wave numbers around 1388 cm^{-1} correspond to S=O stretching vibration by the formation of SO_3 species on ZrO_2 surface [14]. Moreover, absorption peaks at wave number of 1627-1635 cm^{-1} which indicate H-O-H bending vibration. while wide peaks at 3417-3448 cm^{-1} indicate O-H stretching vibration of water [14–15].

Determination of the surface acidity of the material was carried out using acidity test method with NH_3 absorption in a vacuum condition using gravimetric method. The NH_3 can effectively enter the pores of the catalysts and absorp in active site of catalyst due to its small particle size. The total number of acid sites can be determined by measuring the amount of base adsorbate that reacts with an acid catalyst. Therefore, total acidity is the number of Lewis and Brønsted acid sites based on the amount of NH_3 adsorbed by the catalyst.

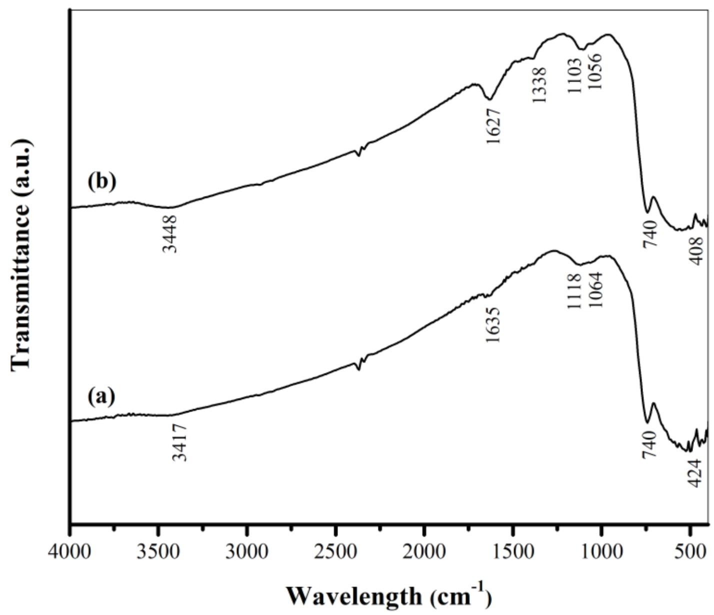

FIGURE 1. FTIR data of (a) ZrO_2-SO_4 and (b) Cr/ZrO_2-SO_4

TABLE 1 shows that the acidity value of ZrO_2-SO_4 and Cr/ZrO_2-SO_4. These data summarize that ZrO_2 had a very low total acidity by the presence of Lewis acid site (Zr^{4+}) in ZrO_2. The activation of ZrO_2 using H_2SO_4 increased the total acidity of ZrO_2 (0.578 mmol/g). The SO_4^{2-} ion on the zirconia surface plays a role in increasing the acid sites of the catalyst [16–17]. ZrO_2-SO_4 was modified by Cr metal using hydrothermal method. After Cr metal deposition on ZrO_2-SO_4, the total number of acid sites in the catalyst increased (1.318 mmol/g). The increase in acidity value of Cr/ZrO_2-SO_4 is due to the presence of unoccupied 3*d* orbital which acts as a Lewis acid.

TABLE 1. Acidity value of catalysts

Catalyst	Total acidity (mmol/g)
ZrO_2-SO_4	0.578
Cr/ZrO_2-SO_4 (C600)	1.318

FIGURE 2 shows the X-ray diffraction patterns of ZrO_2, ZrO_2-SO_4, and Cr/ZrO_2-SO_4. Base on the series of XRD data, there are 3 highest peaks at 2θ around 27.976-28.194° (-111) 31.221-31.484° (-111), and 50.300-50.285° (022), which correspond to monoclinic crystal phase of ZrO_2 [18]. There are three phases of crystalline zirconia, namely cubic (stable temperature ≥2370 °C), tetragonal (stable temperature = 1170-2370 °C), and monoclinic (stable temperature ≤1170 °C) [19].

Based on TABLE 2, the addition of sulphate can be stabilized the crystal phase of ZrO_2. The diffractogram of Cr/ZrO_2-SO_4 shows a peak shifting in typical monoclinic peaks when compared to ZrO_2-SO_4 due to the impregnation and calcination process. The presence of Cr metal on ZrO_2-SO_4 tends to form crystals so that there is a change in peak intensity. The increase in the peak intensity after Cr impregnation can be caused by the contribution of crystals from Cr metal. However, Cr peaks are not detected because the total amount of Cr used in this research was relatively low.

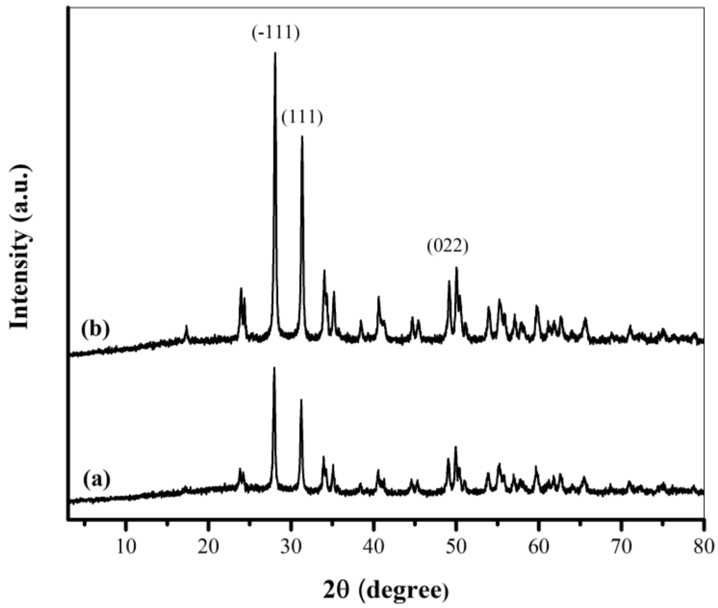

FIGURE 2. XRD patterns of (a) ZrO_2-SO_4 and (b) Cr/ZrO_2-SO_4

TABLE 2. Comparison of standard and observed XRD data

Standard		**ZrO_2**		**ZrO_2-SO_4**		**Cr/ZrO_2-SO_4**	
2θ (degree)	**d (Å)**	**2θ (degree)**	**d (Å)**	**2θ (degree)**	**d (Å)**	**2θ (degree)**	**d (Å)**
28.194	3.163	28.077	3.176	27.976	3.187	28.077	3.176
31.484	2.839	31.330	2.853	31.221	2.863	31.330	2.853
50.585	1.803	50.430	1.808	50.300	1.813	50.430	1.808

Hydrocracking of Palm Oil

TABLE 3 shows that a high conversion of gasoline and diesel fractions was produced by hydrocracking reaction over Cr/ZrO_2-SO_4. Cr metal has Lewis acid site with unpaired electrons in *d* orbital which can initiate the hydrocracking process of longer chains. This site will bind H atom of hydrogen gas. The H atom will be substituted in the compound that has been cracked by the Brønsted acid site on the catalyst [20]. The addition of Cr metal content in catalyst leads to increase the selectivity for gasoline fraction. Data derived from GC-MS analysis indicate that the compounds produced were hydrocarbon compounds in the gasoline and diesel fractions.

TABLE 3. Product distributions of standard and observed GC-MS data

Sample	**Yield (%)**		
	Gasoline	**Diesel**	**Others**
Biofuel over ZrO_2-SO_4	27.834	56.083	16.083
Biofuel over Cr/ZrO_2-SO_4	35.852	46.064	18.084
Commercial gasoline	93.923	-	6.077
Commercial diesel	12.780	59.431	27.789

Hydrocracking products are expected to have carbon compounds that are similar to the compounds formed in the gasoline and diesel fractions. According to TABLE 4, the five highest peaks are confirmed as dominant compounds in biofuel from palm oil and compared with commercial gasoline and diesel. The dominant compounds in commercial gasoline and diesel are hydrocarbon compounds with shorter chains than biofuel. Based on the results, it can be confirmed that hydrocracking of palm oil over Cr/ZrO_2-SO_4 contained gasoline and diesel fractions with a conversion of 35.852% and 46.064%, respectively. The liquid yield consisted of hydrocarbon compounds indicated fuel chemical structures, such as 1-decene, 1-undecene, tridecane, 1-nonene, and 1-dodecene.

TABLE 4. GC-MS of commercial gasoline and diesel

Sample	Retention time (min)	Area (%)	Predicted compound
Biofuel over ZrO_2-SO_4	16.502	3.33	1-nonene
	23.224	3.21	Tridecane
	26.101	3.14	Tetradecane
	28.600	3.73	1-undecene
	28.847	1.52	1-decene
Biofuel over Cr/ZrO_2-SO_4	9.021	2.93	1-nonene
	16.499	4.75	1-undecene
	19.854	2.49	1-dodecene
	23.219	3.75	Tridecane
	28.842	14.40	1-decene
Gasoline	2.171	5.91	2-methyl butane
	2.226	6.91	Pentane
	2.454	5.82	2-methyl pentane
	4.944	8.95	Methyl benzene
	8.277	8.61	Ethyl benzene
Diesel	24.190	5.03	Tridecane
	27.040	6.11	Tetradecane
	29.698	6.52	1-decene
	32.201	6.06	1-undecene
	34.718	4.36	5,10-dimethyl undecene

CONCLUSIONS

The synthesis of Cr/ZrO_2-SO_4 catalyst through the impregnation process was carried out using the hydrothermal technique. The addition of Cr on ZrO_2-SO_4 was increased the acidity of catalyst which indicated the increment of active sites. The hydrocracking of palm oil over Cr/ZrO_2-SO_4 contained 35.852% gasoline fraction and 46.064% diesel fraction. The liquid yield contained of hydrocarbon-range compounds of 1-decene, 1-undecene, tridecane, 1-nonene, and 1-dodecene. Therefore, Cr/ZrO_2-SO_4 showed the ability to convert palm oil into biofuel through hydrocracking reaction over Cr/ZrO_2-SO_4.

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