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PREPARATION AND CHARACTERIZATION OF SULFATED ZIRCONIA FOR BIODIESEL PRODUCTION

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Abstract

Sulfated zirconia has been prepared and characterized by X-ray diffraction, infrared spectroscopy, BET surface area, and BJH pore distribution methods. XRD patterns reveal that the sulfated zirconia mainly consists of tetragonal crystalline zirconia with average size of about 9.8 nm. N_2 adsorption data show that the nanosized sulfated zirconia has high surface area (109.4 m^2/g) and shows the uniform pore distribution aggregated by zirconia nanoparticles. Sulfated zirconias were used as catalysts in the alcoholysis of jatropha oil. The conversions of jatropha oil alcoholysis under good conditions (120^oC, 2 h, 3 wt% of catalyst and 1000 rpm agitation speed) were 79.65%.

Keywords: *biodiesel; characterization; solid catalyst; sulfated zirconia*

Abstrak

PREPARASI DAN KARAKTERISASI ZIRKONIA TERSULFATASI SEBAGAI KATALISATOR DALAM PEMBUATAN BIODIESEL. *Zirkonia tersulfatasi berhasil dibuat dan dikarakterisasi dengan difraksi sinar X, spektroskopi inframerah, pengukuran luas permukaan dengan metode BET dan dan pengukuran distribusi pori dengan metode BJH. Pola difraksi sinar X menunjukkan bahwa susunan utama zirkonia tersulfatasi terdiri atas kristal zirkonia tetragonal dengan ukuran pori rata-rata sekitar 9,8 nm. Data adsorpsi N_2 menunjukkan bahwa zirkonia tersulfatasi yang berukuran nano memiliki luas permukaan yang tinggi (109,4 m^2/g) dan memiliki distribusi ukuran pori yang seragam. Zirkonia tersulfatasi digunakan sebagai katalisator dalam reaksi alkoholisis minyak jarak pagar dengan konversi pada kondisi yang relatif baik (120^oC, 2 jam, 3% berat katalis dan kecepatan pengadukan 1000 rpm) sebesar 79,65%.*

Kata kunci: *biodiesel; karakterisasi; katalis padat; zirkonia tersulfatasi*

INTRODUCTION

Biodiesel is an environmentally friendly fuel as it is made from renewable resources and CO_2 neutral. It is usually derived from the esterification of free fatty acids or the transesterification of triglycerides with methanol or ethanol. In the industrial trans-esterification process, homogeneous base catalysts, such as sodium and potassium hydroxide, are often used. The base-catalyzed process suffers from some limitations of feedstock. The contents of free fatty acid in the feedstock need to be lower than 0.5% wt, otherwise soap formation seriously hinders the production of biodiesel (Jitputti *et al.*, 2006; Suwannakarn *et al.*, 2009). Transesterification is thus needed for converting long-chain triglycerides into esters. Esterifications are conventionally catalyzed homogeneously using concentrated sulfuric acid, which is however corrosive and poor for waste discharge. The use of heterogeneous acid catalyst in the manufacture of biodiesel was chosen to address the lack of a homogeneous base catalyst property such as soap formation, corrosion, excessive water use in laundering, and operating energy requirements on the separation (Suwannakarn *et al.*, 2009). This catalyst can be used to produce biodiesel from vegetable oil with high content of fatty acids esterified with trans-esterification and esterification simultaneously (Kulkarni *et al.*, 2006; Garcia *et al.*, 2009).

Ideal solid acid catalysts for biodiesel production must have high temperature stability, strong acid sites are numerous, large pores, surface hydrophobicity, and low price (Lotero *et al.*, 2005). According to Kawashima *et al.*, (2009) niobium-based heterogeneous acid catalyst and acidic zeolite catalyst

has a small pore diameter (1.4 to 1.7 nm), making it less suitable for making biodiesel due to restriction of diffusion of large triglyceride molecules with molecular size of 2 nm up to 4 nm. Kiss *et al.* (2006) studied several solid acids (zeolites beta, zeolites gamma, H-ZSM-5, Nafion NR50, Amberlyst-15, $Nb_2O_5.5H_2O$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and sulfated zirconia) as catalysts for the esterification of dodecanoic acid with 2-ethylhexanol, 1-propanol and methanol at 130-180^oC, and sulfated zirconia was consider to be the best. Sulfated zirconia showed high activity and selectivity for the esterification of fatty acids with a variety of alcohols. Garcia *et al.* (2008) studied transesterification of soybean oil using sulfated zirconia catalyst that prepared by the precipitation methode, solvent-free method and conventional methode. The sulfated zirconia prepared by the solvent-free method was much more active than precipitation and conventional methode. It was very active in the transesterification of soybean oil and the esterification of fatty acids. This research aims to study the activity of sulfated zirconia catalyst prepared by solvent-free methode for transesterification reaction of jatropha oil.

MATERIALS AND METHOD

Reagents and Solvents

Refined Jatropha oil was obtained from Grobogan Market, Central Java. The oil density (0.911 g/cm^3), kinematic viscosity (44.47 cSt) and water content (0.1% v/v) were determined by ASTM official methods. The free fatty acid content (0.06 ± 0.001 mg KOH/g), the iodine value (132 ± 0,002 cg/g) of vegetable oil were determined by AOCS official methods (1998). Methanol (CH_3OH) that used has a purity of 99.99% and a density of 0.79 g/cm^3. Zirconia oxychloride (99.5%, Merck) and ammonium sulfate (99.9%, Merck) that used for the catalysts preparation were obtained from the Alfa Chemicals Inc., Yogyakarta.

Preparation of Sulfated Zirconia by the Solvent-Free Method

The solvent-free preparation of sulfated zirconia, designated as S–ZrO_2, was accomplished according to the procedure described by Sun *et al.* (2005) and Garcia *et al.* (2008). Zirconia oxychloride ($ZrOCl_2$ $8H_2O$) and ammonium sulfate, in a molar ratio of 1:6, were ground in an agate mortar for 20 minutes at room temperature (29^oC). After standing for 18 hours at room temperature in the air, the sample was calcined for 5 hours at 600^oC.

Characterization of the Catalysts

XRD analysis was performed using Rigaku diffractometer (Rigaku, Tokyo, Japan) using Cu Kα radiation at 40 kV and 130 mA in the scanning angle (2ɵ) of 5-70^o at a scanning speed of 10^o min^{-1}. FT-IR measurements were performed in a Bomem MB-Series spectrometer (ABB Bomem Inc., Quebec, Canada) using KBr pellet technique. Each spectrum was obtained in the transmission mode over 32 scans, in the range from 4000 to 400 cm^{-1} with a resolution of 4 cm. Background spectra were collected before every sampling. Data analyses were carried out using the Origin 7.5 program (OriginLab Corp. Northampton. MA). The nitrogen adsorption/desorption isotherms were obtained at -196^oC using a Micromeritics ASAP 2010 apparatus (Micromeritics Instrument Corp. Norcross, GA). Surface area was calculated using the BET equation and the pore volume was determined at a relative pressure of 0.98. The pore size was calculated using the Barrett-Joyner-Halenda (BJH) method.

Alcoholysis of Jatropha Curcas Oil

The alcoholysis of jatropha curcas oil were conducted in batch reactor equipped with heater, stirrer, thermocouple, a manometer and valves maker sample. Jatropha oil, methanol and a catalyst were inserted into the reactor and then it was closed. The temperature is set by rotating the pointer speed in accordance with the desired heating. After temperature reached, the stirring speed is set by rotating the pointing device in accordance with the stirrer speed as desired. The reaction is run for 120 minutes, followed by taking samples every 15 minutes. Glycerol analysis performed using iodometric-periodic acid titration (AOCS CA 14-56 or ASTM D-6584). This method is used to determine levels of total glycerol and free glycerol in the biodiesel. The conversion of oil into ethyl esters are calculated with initial glycerol mass balance in the oil and glycerol formed.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD)

Figure 1 shows XRD of sulfated zirconia prepared by the solvent-free method (S-ZrO_2). Figure 1 shows that S-ZrO_2 is a crystalline. The XRD diffractogram of S-ZrO_2 shows peaks assigned to the both tetragonal.

Infrared (IR) Spectroscopy

Figure 2 shows IR spectra of the sulfated zirconia. Figure 2 shows a strong and broad band in the 3600-3000 cm^{-1} region, assigned to physisorbed and coordinated water, accompanied by a broad band in 1631.7 cm^{-1}, assigned to the bending mode (δ HOH) of coordinated water (Garcia *et al.*, 2008). The bands at 1203.6, 1139, 1043.5, and 997.2 cm are typical for sulfate ions coordinated to the zirconium cation (Sun *et al.*, 2005. The S–ZrO_2 spectrum also shows a weak band at 1400 cm^{-1}, due to the stretching vibrations of the S=O bond.

N_2 Adsorption Desorption Isotherms

Figure 3 shows N_2 adsorption desorption isotherms of S-ZrO_2. A hysteresis loop at high relative pressure is observed, which is generally due to the capillary condensation associated with mesopores.

Correspondingly, BJH pore size distribution for S-ZrO_2 is narrow and gives a mean value at 9.8 nm (Figure 4). Possibly, the mesoporosity may be assigned to the aggregation of nanoparticles with each other. Multi-point BET plot of sulfated zirconia was shown Figure 5. Interestingly, a high BET surface area of 109.4 m^2/g and a large pore volume of 0.359 cm^3/g are observed for S-ZrO_2. The sample of S-ZrO_2 exhibits high BET surface area and more uniform pore distribution. Table 1 presents some of physical properties of the catalyst used in this study.

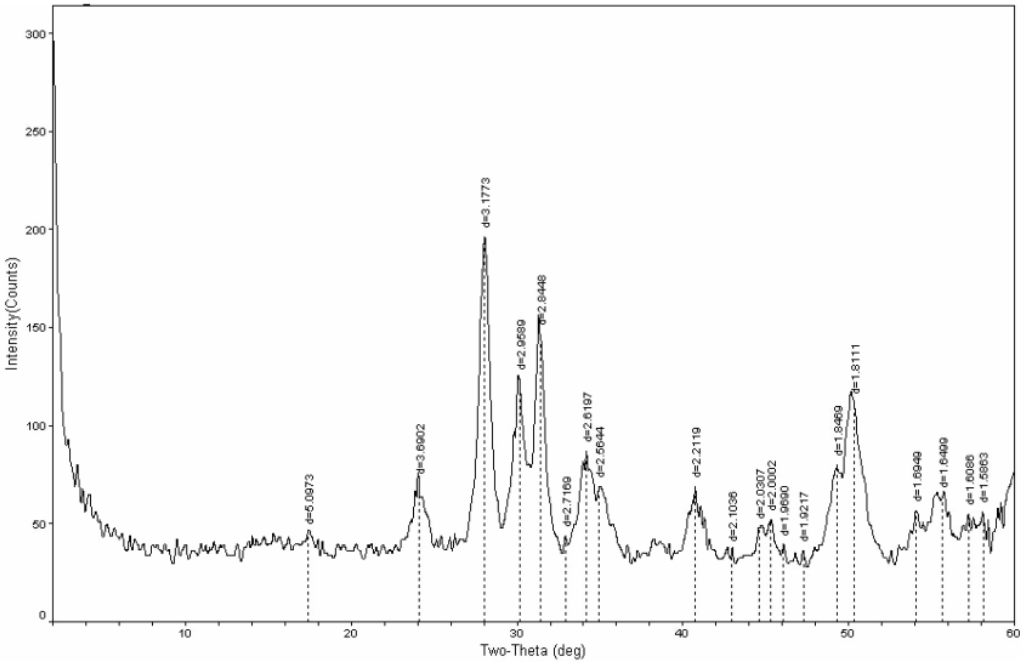

Figure 1. XRD patterns of sulfated zirconia (S–ZrO_2)

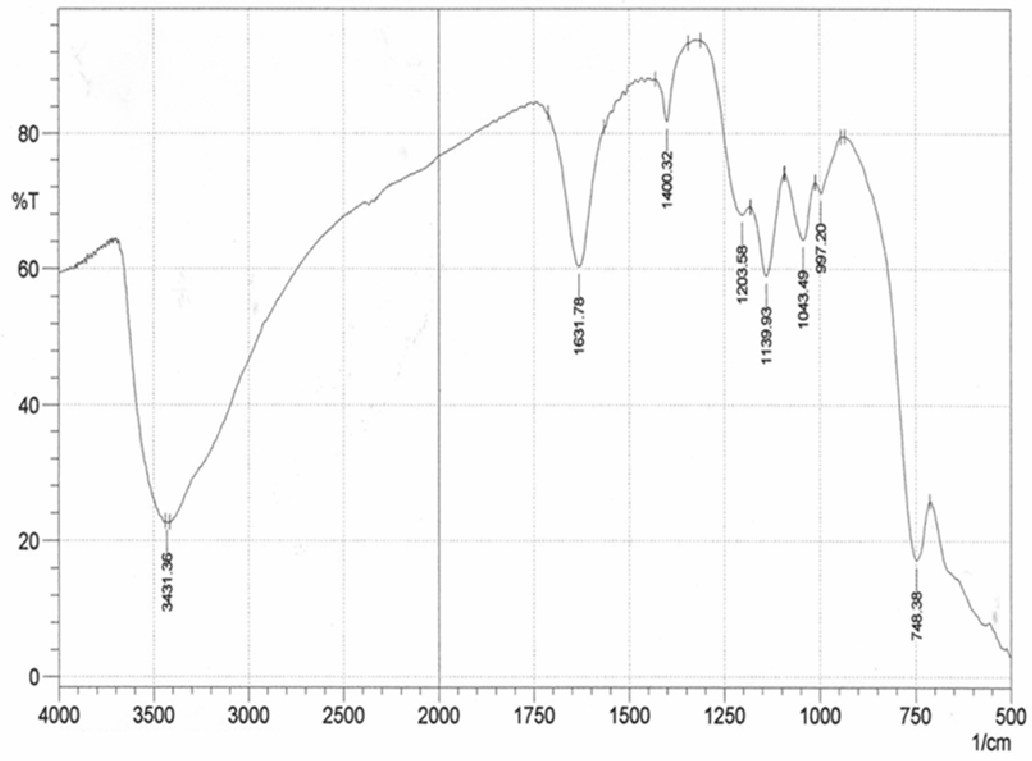

Figure 2. Infrared spectra of the sulfated zirconia

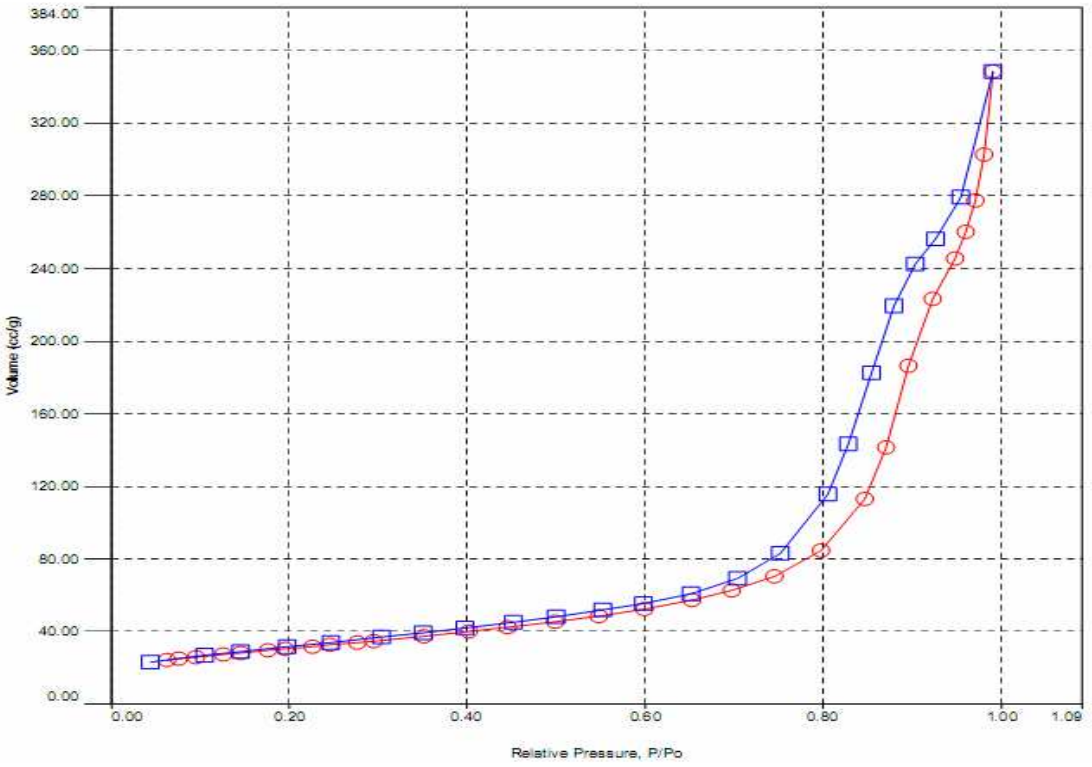

Figure 3. N_2 adsorption/desorption isotherm of sulfated zirconia

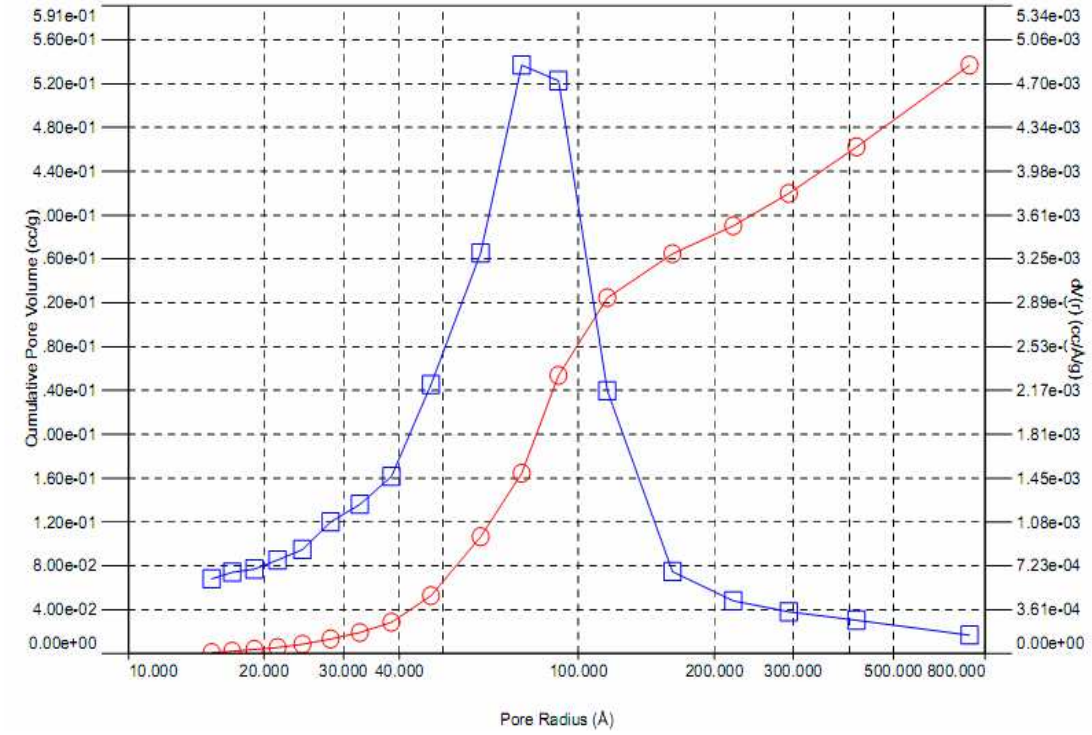

Figure 4. BJH pore distribution plots of sulfated zirconia

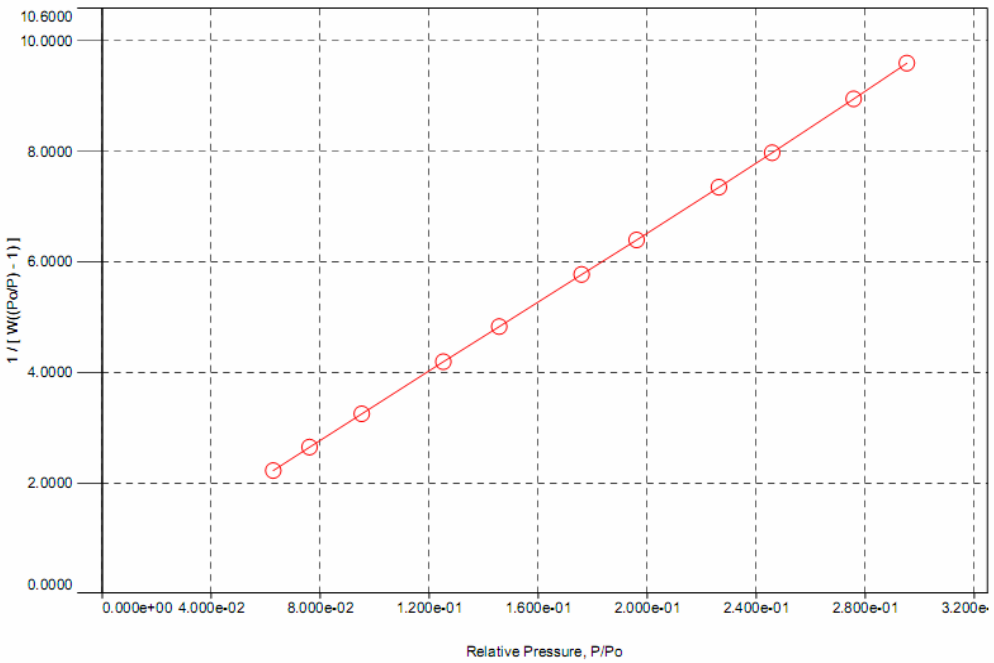

Figure 5. Multi-point BET plot of sulfated zirconia (S-ZrO_2)

Table 1. Physical property of catalyst

Physical property	Unit	S-ZrO_2
shape		powder
BET surface area	m^2/g	109. 397
pore volume	cm^3/g	0.359
average pore radius	nm	9.856
sulfate content	%	2.5
acidity	(meq/g)	0.26
thermal stability	^oC	600
size	µm	88
particle density	g/cm^3	3.125

Catalytic Activity

The influence of catalyst quantity and reaction time on the methanolysis conversion of soybean oil was evaluated and the results are shown in Figure 6. The catalytic activity of the sulfated zirconia (S–ZrO_2) was highly dependent on the catalyst quality. From Figure 6 shows that the conversion of triglyceride increased with increasing of the percentage of catalyst, this is due to an increasing in active surface area and the total number of acid sites so that the collision between reactant substances becoming more frequently. Catalysts also contribute to direct the collision of the reactant molecules and decrease the activation energy of reaction, so the reaction runs faster. However, after reaction for 90 minutes the reaction conversions are nearly constant. This may be due to the decreasing of the catalyst activity or catalyst deactivation, so the ability of catalyst to activate the reactant molecules also decreased. Lopez *et al.* (2005) explained that the deactivation of solid catalysts in the transesterification reaction of vegetable oils was due to the blockage of active sites by adsorption of intermediate molecules or products.

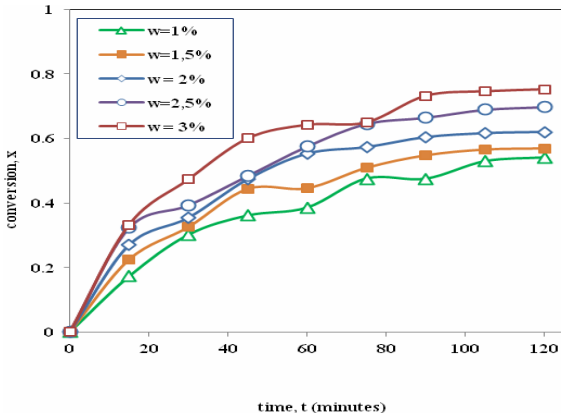

Figure 6. The relationship between the conversion versus time at methanol-oil molar ratio of 9, agitation speed of 1000 rpm and temperature of 120^{o}C

CONCLUSIONS

Sulfated zirconia that was prepared by a solvent-free method (S-ZrO_2) is very active in the transesterification of jatropha oil. The conversions in the alcoholysis catalyzed by S-ZrO_2 obtained under relatively good conditions (120^{o}C, 2 h, 3% of catalyst (w/w)) were 79.65%. However, S-ZrO_2 is rapidly deactivated and this aspect must be evaluated further.

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