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Preparation of Zirconium Nitride supported on SiO_2 Catalyst for Vegetable Oil Conversion

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Abstract

Hydrocracking of crude palm oil (CPO) to produce biofuels was conducted over zirconium nitride supported on SiO_2 (SiO_2/ZrN) catalyst. SiO_2/ZrN was prepared by nitriding the SiO_2/Zr at 600 °C for 3 hrs under NH_3 gas on the cylindrical reactor. SiO_2/ZrN exhibited a surface acidity of 0.7132 mmol pyridine g^{-1} with a surface area of 96 m2 g^{-1}, forming predominant mesopores on the catalyst. EDS-mapping analysis showed that the ZrN species exhibited a highly distributed on the SiO_2 surface. CPO hydrocracking was conducted at a temperature of 500 °C for 1 hr, with a CPO flow rate of 0.02 L min^{-1} and H_2 flow rate of 0.03 L min^{-1}. The study revealed that the SiO_2/ZrN successfully afforded a CPO conversion up to 94.98 wt.%, a liquid yield of 50.40 wt.%, with a low residue and coke formation. This catalyst promoted high selectivity towards bio-jet up to 72.95 wt.%.

Keywords: SiO_2/ZrN, vegetable oil, hydrocracking, SiO_2, ZrN, catalyst

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Hidrorengkah minyak sawit mentah untuk memproduksi bahan bakar nabati telah dilakukan menggunakan katalis zirkonium nitrida dengan pengemban SiO_2 (SiO_2/ZrN). SiO_2/ZrN telah dipreparasi melalui nitridasi SiO_2/Zr pada temperatur 600 °C selama 3 jam dengan atmosfer gas NH_3 dalam reaktor silindris. Keasaman permukaan SiO_2/ZrN dilaporkan sebesar 0.7132 mmol pyridine g^{-1} dengan luas permukaan 96 m^2 g^{-1}, didominasi oleh ukuran pori skala meso. Analisis EDS-mapping menunjukkan bahwa konstituen ZrN terdistribusi secara baik pada permukaan SiO_2. Hidrorengkah minyak sawit mentah dilakukan pada temperatur 500 °C selama 1 jam, dengan laju alir minyak sebesar 0.02 L $menit^{-1}$ dan laju alir gas H_2 0.03 L $menit^{-1}$. Studi mengungkapkan bahwa SiO_2/ZrN berhasil mengonversi minyak sawit mentah mencapai 94.98 b/b%, perolehan rendemen minyak 50.40 b/b%, dengan pembentukan residu dan kokas yang rendah. Katalis ini mampu mempromosikan selektivitas bio-jet mencapai 72.95 b/b%

Kata kunci: SiO_2/ZrN, minyak nabati, hidrorengkah, SiO_2, ZrN, katalis

INTRODUCTION

Catalytic hydrocracking remains an innovative method for producing biofuel from triglyceride-containing feedstock. This method offers the advantages of high conversion rates and high heating value products [1]. The demand for higher quantities of biofuels is increasing worldwide. On the other hand, process optimization studies to get high-quality biofuel remain challenging and continue to evolve [2].

The use and selection of the appropriate catalyst in the hydrocracking process are the critical parameters that intrinsically affect conversion performance and biofuel selectivity [3]. Currently, numerous catalysts with diverse varieties have been employed for producing biofuels from vegetable oil through oil hydrocracking [4]. Noble mono metal-based catalyst is commonly used for catalytic cracking-hydrogenation process due to high catalytic activity. However, this

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catalyst has various limitations, including being easily deactivated and unaffordable for long-term and sustainable consumption [5]. The tendency for carbon deposition during the reaction impairs the stability of the catalytic performance. In this context, an essential role in increasing the efficiency of the conversion process can profoundly be enhanced by the presence of a supported catalyst.

numerous metal-supported based catalysts have been continuously reported and synthesized for hydrocracking applications [6-7]. Silica is one of the prospective supported catalysts that provide advantages such as high surface area, thermally stable, and non-toxic. This material can be comfortably modified and functionalized by other compounds to increase catalytic activity [8]. NiMo/SiO_2 modified induced by $NaHCO_3$ has been successfully prepared, affording 68.57 wt% of a liquid product at an optimum condition of 475 °C with a catalyst-to-oil ratio of 1% [9]. SiO_2/Zr assisted by EDTA as chelate agent profitably provided a CPO conversion up to 87.37% with 66.29% of liquid yield at 500 °C for 1 h with a feed flow rate of 20 mL h^{-1} [10].

A previous study revealed that choosing a suitable metal Lewis site on the metal-supported system catalyst affects catalytic performance during hydrocracking reactions [11]. This specific active site will prominently catalyze the conversion process and thus transform the triglyceride molecules into biofuel. Transition metal nitride (TMN) catalytic systems are increasingly being explored due to their distinct features [12-14]. The synergetic interaction between the metal and nitrogen promotes higher electron density, thus significantly enhancing the catalytic performance [15]. Among numerous TMN that have been explored, zirconium nitride (ZrN) is one of the materials that provide high surface area, stability and also revealed high acidity features. Their robustness characteristics, when combined with a properly supported catalyst, appear promising for hydrocracking purposes. Several studies have attempted to prepare ZrN for various applications and modifications [16-18]. Up to this point, the potential of SiO_2/ZrN for hydrocracking vegetable oils has not been addressed in the literature.

In this research, a SiO_2/ZrN catalyst will be synthesized and evaluated for the hydrocracking of vegetable oils. Crude palm oil (CPO) was used as a triglycerides feedstock because of its abundance, high long-chain hydrocarbon content, and low sulfur and nitrogen content, thus offering environmentally friendly features and sustainability [19]. The catalyst will be assessed using several techniques. It is projected that as a result of this work, high catalytic performance SiO_2/ZrN catalysts can be employed to provide an effectual route to generate biofuels from crude palm through the hydrocracking process.

MATERIALS AND METHOD

SiO_2/ZrN Preparation

SiO_2 was prepared using the sol-gel method with TEOS as a precursor, whereas $ZrOCl_2{\cdot}8H_2O$ salt was utilized as a Zr precursor. All chemicals involved were analytical grade purchased from Sigma-Aldrich. Prior to nitridation, SiO_2/Zr was synthesized using the wet impregnation method, as previously reported elsewhere [10]. Afterward, SiO_2/Zr (1 g) was heated at 600 °C for 3 hrs on the cylindrical reactor and subsequently nitridated the catalyst by flowing the ammonia gas (50 mL) into the reactor. The as-synthesized SiO_2/ZrN was later characterized using XRD, FTIR, SEM-EDS, N_2 adsorption-desorption, PSA and FTIR-pyridine. The acidity features of SiO_2/ZrN was also analyzed using the gravimetric method by pyridine as reported in the previous work [20].

Hydrocracking of CPO

The as-synthesized SiO_2/ZrN was tested for its catalytic activity on CPO hydrocracking on a continuous flow cylindrical reactor [10]. In this test, 0.5 g of SiO_2/ZrN was utilized, and the temperature was controlled to 500 °C. The reaction was conducted for 1 hr with a hydrogen flow of 0.03 L min^{-1} and a CPO flow rate of 0.02 L min^{-1}. The liquid was subsequently analyzed using GC-MS with TG-5MS columns.

The catalytic activity of the CPO hydrocracking was calculated with the equations (1-6) as follows:

$$\text{Conversion (\%.wt)} = \frac{X_o(g) - X(g)}{X_o(g)} \times 100\% \tag{1}$$

$$X_{liquid}\ \text{(\%.wt)} = \frac{\text{liquid product (g)}}{X_o(g)} \times 100\% \tag{2}$$

$$X_{coke}\ \text{(\%.wt)} = \frac{\text{coke (g)}}{X_o(g)} \times 100\% \tag{3}$$

$$X_{residue}\ \text{(\%.wt)} = \frac{X(g)}{X_o(g)} \times 100\% \tag{4}$$

$$X_{gas}\ \text{(\%.wt)} = 100\% - (X_{liquid} + X_{coke} + X_{gas})\ \text{\%.wt} \tag{5}$$

$$Y\ (\%) = \frac{\text{\% GCMS HC fraction area}}{\text{\% GCMS total area}} \times 100\% \tag{6}$$

X_o and X are denoted as CPO feed and residue, respectively, whereas X_{liquid}, X_{coke}, $X_{residue}$, and X_{gas} are denoted as yield of liquid, coke, residue, and gas products. The selectivity of biofuel is denoted as Y.

RESULTS AND DISCUSSION

Characterization of SiO_2/ZrN

XRD pattern of SiO_2/ZrN is presented in **Figure** 1. Several major phases are observed in SiO_2/ZrN. It is apparent that a prominent broad diffraction peak at 2θ of ~22° is noticed, corresponding to the presence of amorphous silica in nature [21]. Similar results were also consistent with other reported [22-23]. The diffraction peaks at 2θ of 29.74°, 34.72°, 50.3°, and 60.32° are assigned to predominant zirconia with tetrahedral phase (ICDD No. 80-2155) [24]. The zirconium nitride phase is reasonably difficult to perceive, presumably due to high dispersion particles with a low concentration [25].

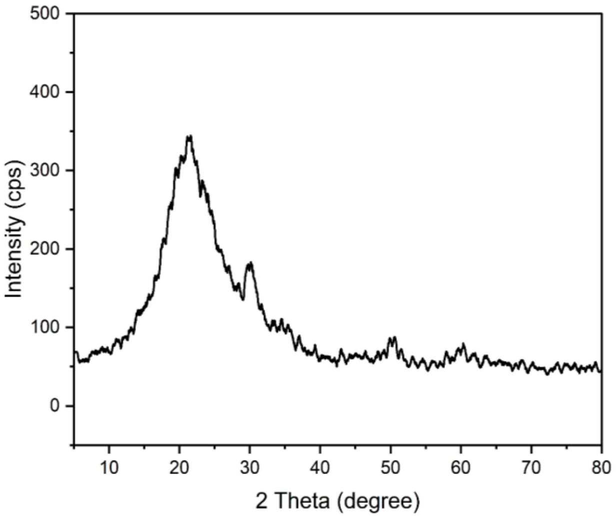

Figure 1. Diffractogram of SiO_2/ZrN catalysts

Figure 2 shows the SEM micrograph and EDS spectrum of as-synthesized SiO_2/ZrN. The catalyst exhibits an agglomeration presumably due to ZrN species dispersion on the SiO_2 surface. Similar conditions were also consistently reported elsewhere when preparing different catalysts of chromium supported on sulfated zirconia using the impregnation method [26].

EDS semi-quantitative analysis was conducted in order to confirm the corresponding constituent of the as-prepared catalysts. The EDS spectrum of SiO_2/ZrN catalyst (**Figure** 2b) shows peaks without appreciable impurities consisting of Si, O, Zr, and N, indicating that the SiO_2/ZrN catalyst was successfully prepared without appreciable impurities.

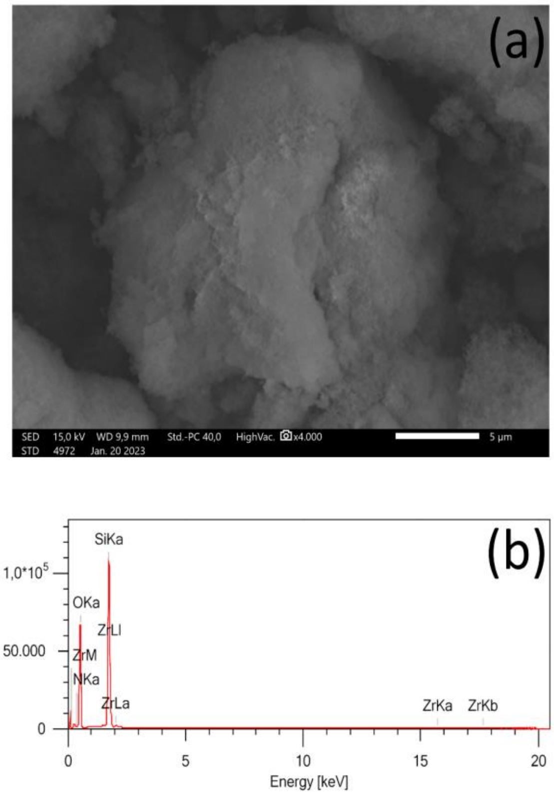

Figure 2. (a) SEM micrographs and (b) EDS spectrum of SiO_2/ZrN catalyst

Figure 3 reveals an EDS mapping of the SiO_2/ZrN catalyst. The ZrN species appear well distributed on the silica surface, suggesting an excellent metal-supported interaction. This result corroborates the accomplishment of the impregnation process.

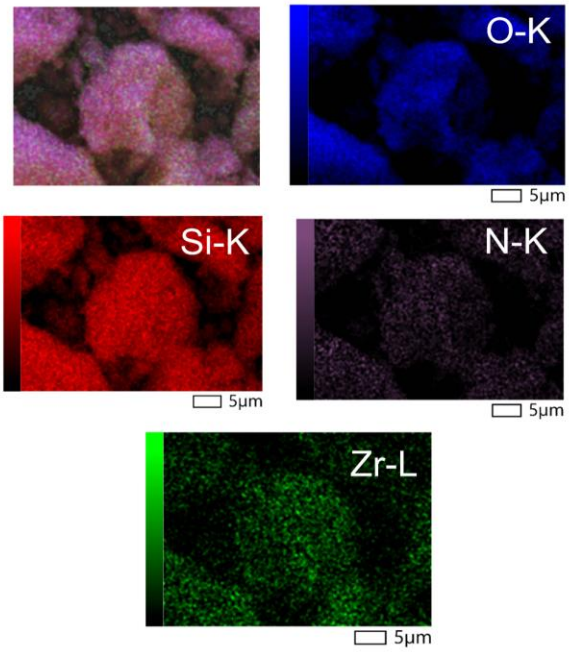

Figure 3. SEM-mapping of SiO_2/ZrN catalyst

FTIR spectrum of SiO_2/ZrN is shown in **Figure** 4. The considerable absorption band of the SiO_2/Zr catalyst is found to be between 2000 and 450 cm^{-1}. Absorption bands at 1850-1600 cm^{-1} are attributed to the OH groups adsorbed onto the silica surface as well as the presence of Si-OH groups [27]. Moreover, a strong band at 954 cm^{-1} suggests the characteristic of Si-O-Si vibration groups [28]. The Si-O-Zr group is observed presumably at an absorption band of 755 cm^{-1}. Another study reported that the stretching vibration of Zr-O-Zr can be observed at 750-500 cm^{-1} [29].

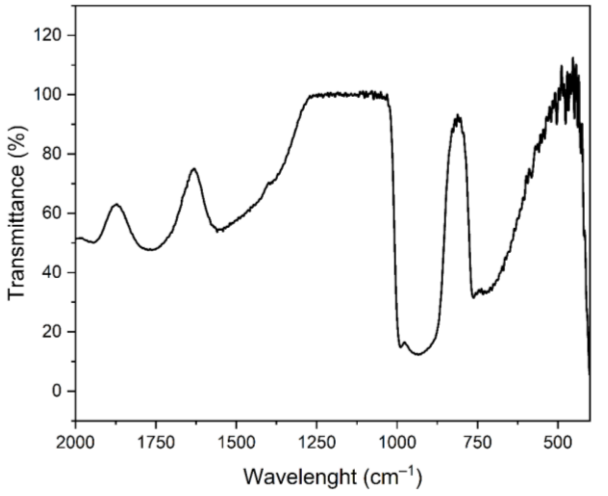

Figure 4. FTIR spectrum of SiO_2/ZrN catalyst

The particle size distribution of SiO_2/ZrN can be discerned in **Figure** 5. It is evident that the SiO_2/ZrN catalyst exhibits narrow particle size distribution. The particle size of SiO_2/ZrN was found to be 11.51±0.29 µm, showing higher particle size compared with the SiO_2/Zr prepared catalyst [10].

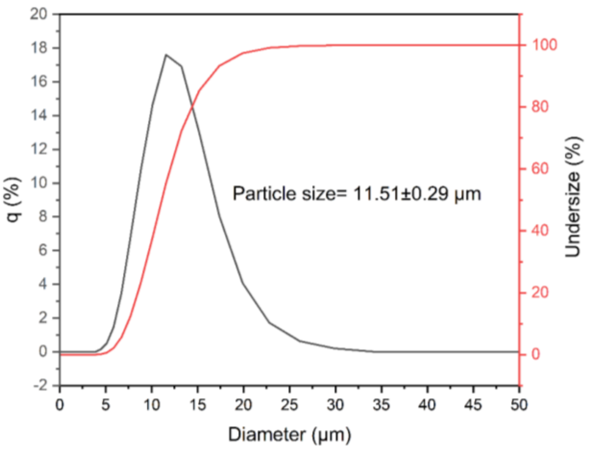

Figure 5. Particle size distribution of SiO_2/ZrN catalyst

FTIR-pyridine spectra and the surface acidity of SiO_2/ZrN are shown in **Figure** 6. FTIR spectra of the catalyst after pyridine adsorbed exhibit two prominent absorption bands ranging from 1750-1400 cm^{-1}. An absorption at ~1450 cm^{-1} is ascribed to the attachment of the pyridine that coordinately interacts with the Lewis acid sites [30]. The Brønsted acid site can be noticed at ~1630 cm^{-1}, which originated from the pyridinium ion [31].

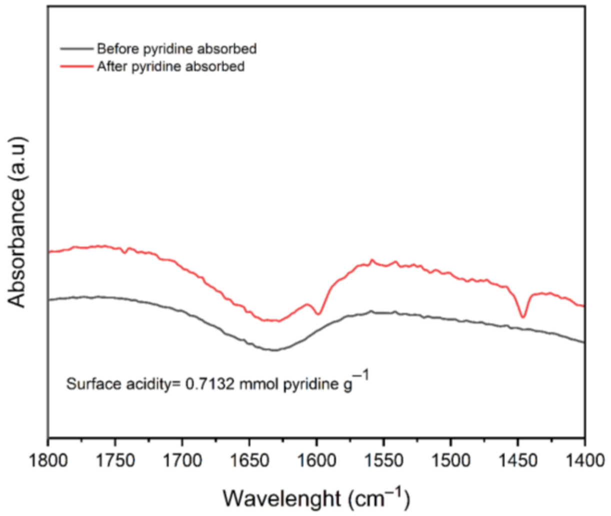

Figure 6. FTIR-pyridine spectra and calculated surface acidity of SiO_2/ZrN catalyst

The surface acidity of SiO_2/ZrN found to be 0.7132 mmol pyridine g^{-1}. This result was relatively higher than the parent SiO_2 and SiO_2/Zr, as previously prepared [10], suggesting that the nitridation process successfully escalated the surface acidity of the catalyst. The incorporation of nitrogen towards the Zr lattices presumably changed the metal structure, thus providing a better acidic catalyst active site [16].

Figure 7 depicts the N_2 adsorption-desorption and pore size distribution of SiO_2/ZrN. SiO_2/ZrN catalyst displays a typical of type IV isotherm coexisting with type H3 hysteresis loop, suggesting the formation of dominant mesopores in the catalyst [32].

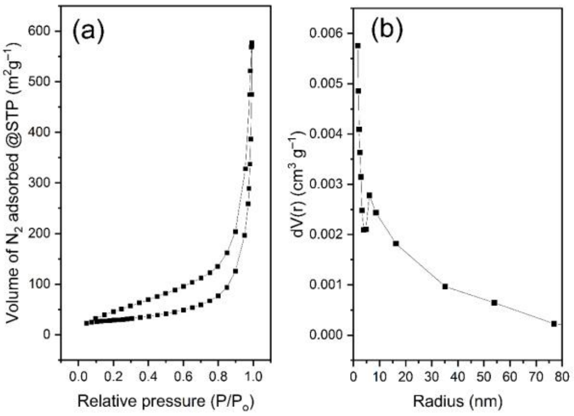

Figure 7. (a) N_2 adsorption-desorption and (b) pore size distribution of SiO_2/ZrN catalyst

The pore size distributions (**Figure** 7) corroborate the presence of meso and macropores ranging from 2-80 nm. According to the BET multi-points method, the surface area of SiO_2/ZrN was found to be 96 $m^2 g^{-1}$, with a total pore volume and average pore radius was 0.88 cc g^{-1} and 18.22 nm, respectively, which reveals higher surface area compared with SiO_2/Zr catalyst (76.43 $m^2 g^{-1}$) [10].

Hydrocracking Test

Hydrocracking of CPO was tested at a continuous flow cylindrical reactor using 0.5 g of SiO_2/ZrN catalyst. The catalytic performance is presented in **Table** 1. It can be seen that the SiO_2/ZrN catalyst exhibit relatively high conversion, up to 94.98 wt.% with a liquid yield of 50.40 wt.%, compared with previous SiO_2 and SiO_2/Zr reported catalyst [10], due to high acidic site provide by the ZrN species. This catalyst also shows a low coke formation as well as residue, suggesting the SiO_2/ZrN promotes high catalytic activity towards CPO conversion. Further analysis by GCMS shows that the SiO_2/ZrN affords 72.95% selectivity towards bio-jet, followed by 24.2% of bio-gasoline and 2.85% of bio-diesel. High selectivity towards bio-jet presumably due to the presence of predominantly mesopores on the silica, thus facilitating adequate accessibility of the triglyceride towards the acidic sites. Consequently, increased the bio-jet selectivity [33].

Table 1. Catalytic performance of SiO_2/ZrN on CPO hydrocracking

Catalyst	Reaction condition	Results
SiO_2/ZrN	T= 500 °C for 1 hr, CPO flow rate= 0.02 L min^{-1}, H_2 flow rate= 0.03 L min^{-1}	Conversion= 94.98 wt.%, X_{liquid}= 50.40 wt.%, X_{gas}= 44.54 wt.%, X_{coke}= 0.04 wt.%, $X_{residue}$= 5.02
SiO_2/Zr [10]	T= 500 °C for 1 hr, CPO flow rate= 0.02 L min^{-1}, H_2 flow rate= 0.03 L min^{-1}	Conversion= 82.75 wt.%, X_{liquid}= 45.93 wt.%, X_{gas}= 40.23 wt.%, X_{coke}= 0.21 wt.%, $X_{residue}$= 13.63
SiO_2 [10]	T= 500 °C for 1 hr, CPO flow rate= 0.02 L min^{-1}, H_2 flow rate= 0.03 L min^{-1}	Conversion= 77.10 wt.%, X_{liquid}= 53.44 wt.%, X_{gas}= 17.97 wt.%, X_{coke}= 0.09 wt.%, $X_{residue}$= 28.58
Bentonite/ZrN [16]	T= 450 °C for 0.12 hr, CPO flow rate= 11.94 g min^{-1}, H_2 flow rate= 2 mL s^{-1}	Conversion= 87.93 wt.%,

CONCLUSION

The as-prepared SiO_2/ZrN was successfully synthesized by nitriding the SiO_2/Zr at 600 °C for 3 hrs under ammonia gas. This catalyst possesses a high surface acidity with predominantly mesopores appearing on the catalyst. The hydrocracking test showed that SiO_2/Zr adequately afforded a CPO conversion up to 94.98 wt.% and a liquid yield of 45.93 wt.%, showing a higher catalytic activity than the previously prepared catalyst. SiO_2 catalyst also promoted high selectivity towards biofuel in the order bio-jet > bio-gasoline > bio-diesel.

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