Preparation of Zirconium Nitride supported on SiO₂ 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 SiO₂ (SiO₂/ZrN) catalyst. SiO₂/ZrN was prepared by nitriding the SiO₂/Zr at 600 °C for 3 hrs under NH₃ gas on the cylindrical reactor. SiO₂/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 SiO₂ 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 H₂ flow rate of 0.03 L min⁻¹. The study revealed that the SiO₂/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: SiO₂/ZrN, vegetable oil, hydrocracking, SiO₂, ZrN, catalyst

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
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/SiO₂ modified induced by NaHCO₃ 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]. SiO₂/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 SiO₂/ZrN for hydrocracking vegetable oils has not been addressed in the literature.

In this research, a SiO₂/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 SiO₂/ZrN catalysts can be employed to provide an effectual route to generate biofuels from crude palm through the hydrocracking process.

**MATERIALS AND METHOD**

**SiO₂/ZrN Preparation**

SiO₂ was prepared using the sol-gel method with TEOS as a precursor, whereas ZrOCl₂·8H₂O salt was utilized as a Zr precursor. All chemicals involved were analytical grade purchased from Sigma-Aldrich. Prior to nitridation, SiO₂/Zr was synthesized using the wet impregnation method, as previously reported elsewhere [10]. Afterward, SiO₂/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 SiO₂/ZrN was later characterized using XRD, FTIR, SEM-EDS, N₂ adsorption-desorption, PSA and FTIR-pyridine. The acidity features of SiO₂/ZrN was also analyzed using the gravimetric method by pyridine as reported in the previous work [20].

**Hydrocracking of CPO**

The as-synthesized SiO₂/ZrN was tested for its catalytic activity on CPO hydrocracking on a continuous flow cylindrical reactor [10]. In this test, 0.5 g of SiO₂/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:

\[
\text{Conversion (\% wt)} = \frac{X_o(g) - X(g)}{X_o(g)} \times 100\% \quad (1)
\]

\[
X_{\text{liquid}} (\% \text{ wt}) = \frac{\text{liquid product (g)}}{X_o(g)} \times 100\% \quad (2)
\]

\[
X_{\text{coke}} (\% \text{ wt}) = \frac{\text{coke (g)}}{X_o(g)} \times 100\% \quad (3)
\]

\[
X_{\text{residue}} (\% \text{ wt}) = \frac{X(g)}{X_o(g)} \times 100\% \quad (4)
\]

\[
X_{\text{gas}} (\% \text{ wt}) = 100\% - (X_{\text{liquid}} + X_{\text{coke}} + X_{\text{gas}}) \text{ \% wt} \quad (5)
\]

\[
Y (%) = \frac{\% \text{ GCMS HC fraction area}}{\% \text{ GCMS total area}} \times 100\% \quad (6)
\]

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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](image)

**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](image)

**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](image)
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$_2$/Zr 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].
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 SiO2/ZrN was found to be 96 m² 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 SiO2/Zr catalyst (76.43 m² g⁻¹) [10].

Hydrocracking Test

Hydrocracking of CPO was tested at a continuous flow cylindrical reactor using 0.5 g of SiO2/ZrN catalyst. The catalytic performance is presented in Table 1. It can be seen that the SiO2/ZrN catalyst exhibit relatively high conversion, up to 94.98 wt.%, with a liquid yield of 50.40 wt.%, compared with previous SiO2 and SiO2/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 SiO2/ZrN promotes high catalytic activity towards CPO conversion. Further analysis by GCMS shows that the SiO2/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 SiO2/ZrN on CPO hydrocracking

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction condition</th>
<th>Results</th>
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<tbody>
<tr>
<td>SiO2/ZrN</td>
<td>T= 500 °C for 1 hr, CPO flow rate= 0.02 L min⁻¹, H2 flow rate= 0.03 L min⁻¹</td>
<td>Conversion= 94.98 wt.%, Xliquid= 50.40 wt.%, Xgas= 44.54 wt.%, Xcoker= 0.04 wt.%, Xresidue= 5.02</td>
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<tr>
<td>SiO2/Zr [10]</td>
<td>T= 500 °C for 1 hr, CPO flow rate= 0.02 L min⁻¹, H2 flow rate= 0.03 L min⁻¹</td>
<td>Conversion= 82.75 wt.%, Xliquid= 45.93 wt.%, Xgas= 40.23 wt.%, Xcoker= 0.21 wt.%, Xresidue= 13.63</td>
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<tr>
<td>SiO2 [10]</td>
<td>T= 500 °C for 1 hr, CPO flow rate= 0.02 L min⁻¹, H2 flow rate= 0.03 L min⁻¹</td>
<td>Conversion= 77.10 wt.%, Xliquid= 53.44 wt.%, Xgas= 17.97 wt.%, Xcoker= 0.09 wt.%, Xresidue= 28.58</td>
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<tr>
<td>Bentonite/ZrN [16]</td>
<td>T= 450 °C for 0.12 hr, CPO flow rate= 11.94 g min⁻¹, H2 flow rate= 2 mL s⁻¹</td>
<td>Conversion= 87.93 wt.%,</td>
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</table>

CONCLUSION

The as-prepared SiO2/ZrN was successfully synthesized by nitriding the SiO2/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 SiO2/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. SiO2 catalyst also promoted high selectivity towards biofuel in the order bio-jet > bio-gasoline > bio-diesel.

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REFERENCES


