



# Enhanced catalytic conversion of palm oil into biofuels by Cr-incorporated sulphated zirconia

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## ABSTRACT

The conversion of palm oil into biofuels using commercial zirconia ( $\text{ZrO}_2$ ) modified sulfuric acid ( $\text{H}_2\text{SO}_4$ ) incorporated with Cr metal has been systematically studied. Sulphated zirconia ( $\text{ZrO}_2\text{-SO}_4$ ) was prepared by dispersing  $\text{ZrO}_2$  in  $\text{H}_2\text{SO}_4$  solution via wet impregnation method. Cr-incorporated sulphated zirconia ( $\text{Cr/ZrO}_2\text{-SO}_4$ ) were prepared hydrothermally through wet impregnation of  $\text{ZrO}_2\text{-SO}_4$  and chromium (III) nitrate non-hydrate ( $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ) solution. The results showed that reduction step with pure hydrogen gas ( $\text{H}_2$ ) over non-calcined catalyst ( $\text{Cr/ZrO}_2\text{-SO}_4$  (NC)) resulted in higher activity and selectivity than calcined catalyst ( $\text{Cr/ZrO}_2\text{-SO}_4$  (C600)). A maximum acidity test result was obtained on  $\text{Cr/ZrO}_2\text{-SO}_4$  (NC) of  $2.33 \text{ mmol g}^{-1}$ , increasing from  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600) of  $1.32 \text{ mmol g}^{-1}$ . The selectivity of gasoline fraction demonstrated by  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600) and  $\text{Cr/ZrO}_2\text{-SO}_4$  (NC) was observed to contain 35.85% and 36.51%, respectively.

## 1. Introduction

Fossil fuels are classified as non-renewable resource of energy. An existing alternative to replace the fossil fuels is biofuels. Biofuels can be broadly defined as solids, liquids or combustible gases that are derived from biomass [1]. Vegetable oils, commonly used in biofuel production, are triglycerides that contain oleic acid and linoleic acid. Hydrocracking is a conversion process in which simultaneous successive breaking of the carbon bonds and hydrogenation of larger hydrocarbon molecules occur, so that they turn into smaller molecules [2,3].

The thermal hydrocracking process, self-evidently, requires extreme temperatures. Alternatively, hydrocracking carried out using catalyst are generally carried out at relatively lower temperatures [4,5]. In catalytic hydrocracking, metal oxides in zirconia ( $\text{ZrO}_2$ ) are widely explored in the field of catalyst due to their unique properties [6–10]. The high acidity of  $\text{ZrO}_2\text{-SO}_4$  consequential of its performance can be attributed to the presence of Brønsted and Lewis acid sites [11,12]. The

properties of  $\text{ZrO}_2\text{-SO}_4$  are dependent upon the modification method, sulphating agent, temperature, and  $\text{ZrO}_2$  precursor [13]. It is known that  $\text{ZrO}_2$  has three crystalline phases, encompassing the monoclinic, tetragonal, and cubic phases. The composition of phases in  $\text{ZrO}_2$  product is influenced by calcination temperature [14]. However, very high temperatures can cause removal of sulphate groups from  $\text{ZrO}_2\text{-SO}_4$  [15].

Recently, the preparation of  $\text{Cr/ZrO}_2\text{-SO}_4$  using hydrothermal method was studied. To the best of our knowledge, the investigation of comparison between calcined and non-calcined  $\text{Cr/ZrO}_2\text{-SO}_4$  on the catalytic activity has not yet been reported. Therefore, in this work, the performance of calcined and non-calcined  $\text{Cr/ZrO}_2\text{-SO}_4$  were compared to evaluate the effect of the calcination temperature of catalyst on the conversion of palm oil into biofuels.

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## 2. Experimental

### 2.1. Preparation of Cr/ZrO<sub>2</sub>-SO<sub>4</sub>

ZrO<sub>2</sub>-SO<sub>4</sub> was prepared using wet impregnation method [10]. ZrO<sub>2</sub> (36.4 g) was added into 546 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub>, then stirred for 24 h at room temperature. The sample was dried in an oven at 100 °C for 24 h and then calcined at 600 °C for 4 h [16].

Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O salt (0.38 g) was dissolved into 100 mL of distilled water. ZrO<sub>2</sub>-SO<sub>4</sub> (5 g) was added into the solution in a hydrothermal autoclave. The solution was dried in an oven at 150 °C for 5 h. The impregnated ZrO<sub>2</sub>-SO<sub>4</sub> obtained was dried in an oven at 100 °C for 24 h. The dry solids with and without calcination treatment at 600 °C for 4 h were reduced under H<sub>2</sub> gas stream (20 mL/min) at 400 °C for 2 h. The materials were characterized using FTIR (Shimadzu 8210 PC), XRD (Shimadzu 6000), GSA (Quantachrome Instrument Version 11.0), TEM (JEOL JEM-1400), and AAS (ContraAA 300 Analytic Jena).

### 2.2. Catalytic cracking of palm oil

Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (C600) and Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC) were applied in the hydrocracking of palm oil into biofuels. The catalytic reaction was carried out in a hydrocracking reactor with a catalyst-to-palm oil ratio of 1:100 at 300 °C and the feed at 350 °C for 40 min under H<sub>2</sub> gas stream (20 mL/min). The liquid products were analyzed using GC-MS (Shimadzu QP 2010S).

## 3. Results and discussion

Fig. 1 shows that ZrO<sub>2</sub> had absorption peaks at 424–741 cm<sup>-1</sup> indicating Zr-O-Zr vibration. After the activation and calcination process, characteristic peaks of the sulphate group appeared at 1033–1118 cm<sup>-1</sup> denoting the asymmetrical vibration of S=O and the bonding between S—O with ZrO<sub>2</sub>. Absorption peaks found in the wavenumber around 1033–1404 cm<sup>-1</sup> was attributed to the stretching vibration of S=O bond. A peak found in the wavenumber of 1627–1635 cm<sup>-1</sup> indicated the bending vibration of H—O—H. In addition, a peak that widened at 3417–3448 cm<sup>-1</sup> of the O—H stretching vibration of water [13,15]. Moreover, upon the loading of Cr metal, the FTIR spectrum of Cr/ZrO<sub>2</sub>-SO<sub>4</sub> had the same vibrations as ZrO<sub>2</sub> and ZrO<sub>2</sub>-SO<sub>4</sub>. Table 1 shows that ZrO<sub>2</sub> had a low level of total acidity obtained from Zr<sup>4+</sup> acting as Lewis acid site. The SO<sub>4</sub><sup>2-</sup> ions on the surface of ZrO<sub>2</sub> increased

**Table 1**

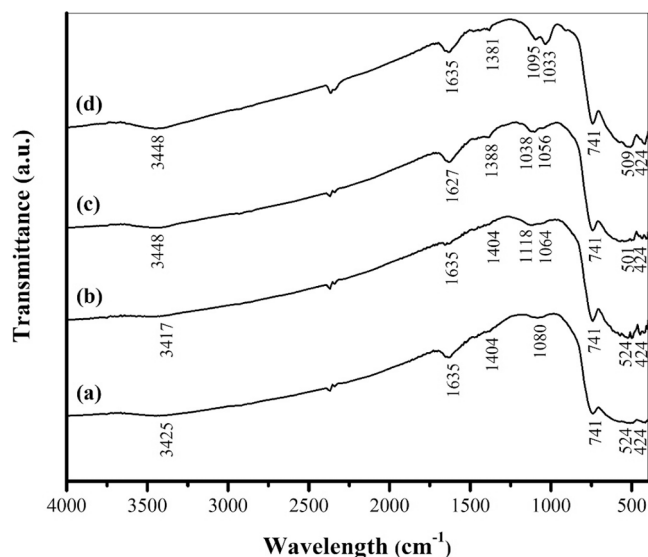
Acidity value of catalysts.

Catalyst	Total acidity (mmol g <sup>-1</sup> )
ZrO <sub>2</sub>	0.47
ZrO <sub>2</sub> -SO <sub>4</sub>	0.57
Cr/ZrO <sub>2</sub> -SO <sub>4</sub> (C600)	1.32
Cr/ZrO <sub>2</sub> -SO <sub>4</sub> (NC)	2.33

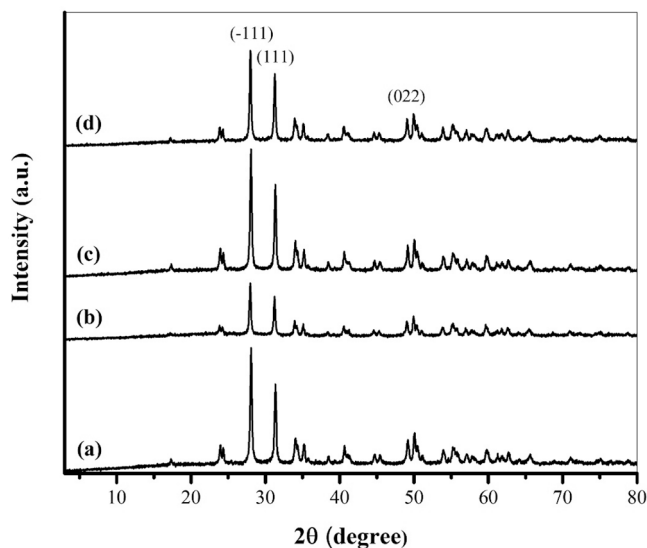
the acidity of catalyst by the formation of higher amount of Brønsted and Lewis acid sites [10]. Cr metal played a role to enhance the acidity of catalyst by providing strong Lewis acid site from unoccupied 3d orbital to initiate the hydrogenation reaction. It was found that Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC) had the higher acidity value of 2.33 mmol g<sup>-1</sup> than Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (C600) of 1.32 mmol g<sup>-1</sup>. The calcination process led to loss of active sites in catalyst.

Fig. 2 depicts that the three highest peaks present at 2θ = 28, 31, and 50° with hkl values of (−111), (111), and (022) depicting the monoclinic phase of ZrO<sub>2</sub> crystal [11]. Moreover, the intensity of Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (C600) was found to be higher than the intensity of Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC). This calcination process caused the material to have a better crystal structure, and thus increasing its crystallinity. Fig. 3 indicates that there were no visible Cr metal aggregates. The black areas were thought to represent groups of accumulated particles [17]. Furthermore, this observation also observed different sizes and disordered shapes morphology of catalyst [18]. The average particle size of ZrO<sub>2</sub>, ZrO<sub>2</sub>-SO<sub>4</sub>, Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (C600), and Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC) was 70.37; 96.29; 94.44; and 84.82 nm, respectively. It observed that the presence of particle agglomeration after the addition of Cr metal most likely caused by heat treatment [11].

Fig. 4 shows the isotherms for catalyst, which conform to the formation of a mesoporous material. Table 2 summarizes that Cr metal loaded onto ZrO<sub>2</sub>-SO<sub>4</sub> increased the surface area of catalyst. Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC) exhibited higher surface area than Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (C600). It was attributed to highly dispersion of Cr species on Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC) and inhibition of the agglomeration process. Fig. 5 presents that the highest liquid product conversion of 36.51% gasoline fraction and 45.81% diesel fraction was obtained from the hydrocracking reaction using Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC). Accordingly, Cr metal loading had an effect in increasing the adsorption capability of catalyst in the hydrocracking process as Cr metal content on Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC) was higher than Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (C600). Cr metal has d orbitals that can be filled with free electron pair and thus functioning as Lewis acid site that can help in the cracking



**Fig. 1.** FTIR spectra of a) ZrO<sub>2</sub>, b) ZrO<sub>2</sub>-SO<sub>4</sub>, c) Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (C600), and d) Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC).



**Fig. 2.** Diffractogram of XRD a) ZrO<sub>2</sub>, b) ZrO<sub>2</sub>-SO<sub>4</sub>, c) Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (C600), and d) Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (NC).

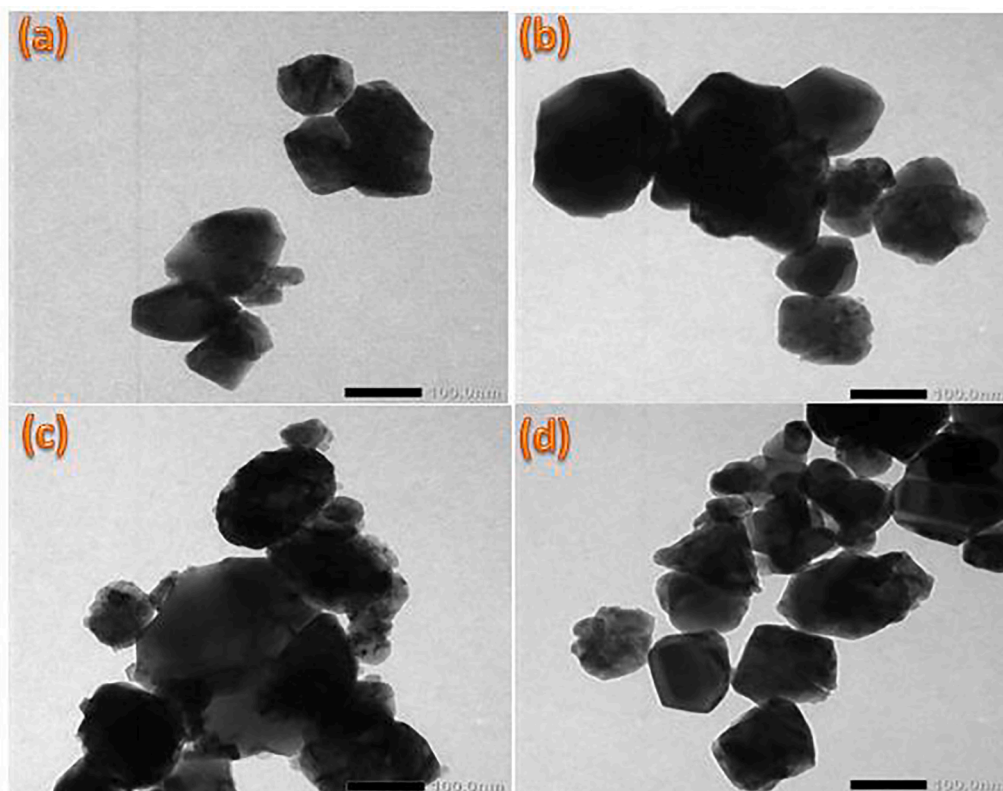


Fig. 3. TEM images of a)  $\text{ZrO}_2$ , b)  $\text{ZrO}_2\text{-SO}_4$ , c)  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600), and d)  $\text{Cr/ZrO}_2\text{-SO}_4$  (NC).

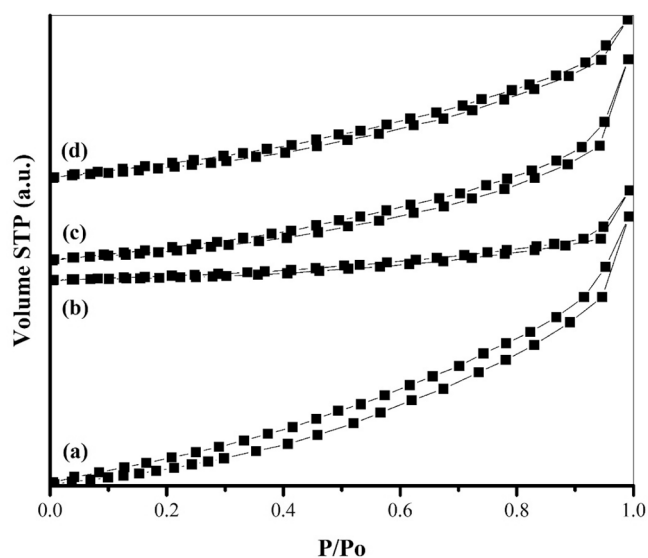


Fig. 4.  $\text{N}_2$  gas adsorption isotherm of a)  $\text{ZrO}_2$ , b)  $\text{ZrO}_2\text{-SO}_4$ , c)  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600), and d)  $\text{Cr/ZrO}_2\text{-SO}_4$  (NC).

process of hydrocarbons with longer chains into shorter hydrocarbons. The active sites capture H atoms from the hydrogen gas which was later transferred into the compound to be cracked. The H atom would be substituted onto the hydrocarbon compound cracked by Brønsted acid site on catalyst. The concentration of Cr metal measured on  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600) and  $\text{Cr/ZrO}_2\text{-SO}_4$  (NC) was 4605.30 ppm (0.46%) and 5930.16 ppm (0.59%), respectively. The higher Cr metal content in  $\text{Cr/ZrO}_2\text{-SO}_4$  (NC) was what caused the increase in the acid sites of catalyst. The higher the acidity, the more liquid products are produced.

Table 2

Pore characteristics of catalysts.

Catalyst	Surface area ( $\text{m}^2\text{g}^{-1}$ )	Pore volume ( $\text{mLg}^{-1}$ )	Average pore diameter (nm)
$\text{ZrO}_2$	84.79	0.18	8.35
$\text{ZrO}_2\text{-SO}_4$	10.64	0.06	23.59
$\text{Cr/ZrO}_2\text{-SO}_4$ (C600)	40.62	0.13	13.04
$\text{Cr/ZrO}_2\text{-SO}_4$ (NC)	42.88	0.10	9.75

#### 4. Conclusions

The synthesis of Cr-incorporated  $\text{ZrO}_2\text{-SO}_4$  with and without calcination treatment was conducted successfully as proved by catalytic activity and selectivity on the conversion of palm oil into biofuels. The acidity test showed that the addition of Cr metal on  $\text{ZrO}_2\text{-SO}_4$  increased the acidity of catalyst upon increasing of active sites. The non-calcined  $\text{Cr/ZrO}_2\text{-SO}_4$  showed higher acidity of  $2.33\text{ mmol g}^{-1}$  than calcined  $\text{Cr/ZrO}_2\text{-SO}_4$  of  $1.32\text{ mmol g}^{-1}$ . The heat treatment caused loss of active sites. The GSA and TEM results revealed that  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600) had smaller surface area with larger particle size than  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600) due to particle agglomeration caused by calcination process. The biofuel contents produced were 35.85% gasoline and 46.06% diesel for  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600), and 36.51% gasoline and 45.81% diesel for  $\text{Cr/ZrO}_2\text{-SO}_4$  (NC). The hydrocarbons contained in liquid fuels had insufficient application as transportation fuel, however, it can be employed as refinery feedstock in oil industry.

*CRedit authorship contribution statement*

**Maisari Utami:** Conceptualization, Data curation, Writing – original draft, Visualization, Investigation, Software, Validation, Writing –

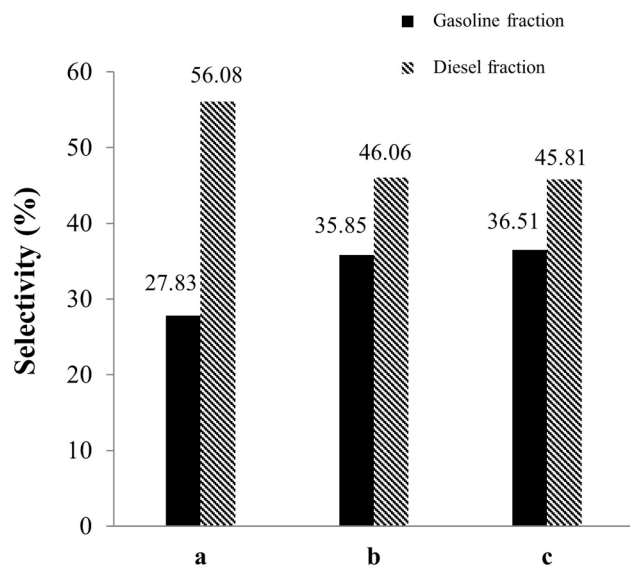


Fig. 5. Selectivity in liquid products with use of a)  $\text{ZrO}_2\text{-SO}_4$ , b)  $\text{Cr/ZrO}_2\text{-SO}_4$  (C600) and c)  $\text{Cr/ZrO}_2\text{-SO}_4$  (NC).

review & editing. **Resti Safitri**: Writing – review & editing. **M. Fajar Pradipta**: Writing – review & editing. **Karna Wijaya**: Conceptualization, Data curation, Writing – original draft, Data curation, Writing – original draft, Visualization, Investigation, Software, Validation, Writing – review & editing. **Soon Woong Chang**: Writing – review & editing. **Balasubramani Ravindran**: Writing – review & editing. **Debnath Ovi**: Writing – review & editing. **R. Jothi Ramalingam**: Writing – review & editing. **Neda Poudineh**: Writing – review & editing. **Robert Moonsamy Gengan**: Conceptualization, Data curation, Writing – original draft, Visualization, Investigation, Software, Validation, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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