

Review



# **Recent Progress on Sulfated Nanozirconia as a Solid Acid Catalyst in the Hydrocracking Reaction**

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**Abstract:** Zirconia has advantageous thermal stability and acid–base properties. The acidity character of  $ZrO_2$  can be enhanced through the sulfation process forming sulfated zirconia ( $ZrO_2$ -SO<sub>4</sub>). An acidity test of the catalyst produced proved that the sulfate loading succeeded in increasing the acidity of  $ZrO_2$  as confirmed by the presence of characteristic absorptions of the sulfate group from the FTIR spectra of the catalyst. The  $ZrO_2$ -SO<sub>4</sub> catalyst can be further modified with transition metals, such as Platinum (Pt), Chromium (Cr), and Nickel (Ni) to increase catalytic activity and catalyst stability. It was observed that variations in the concentrations of Pt, Cr, and Ni produced a strong influence on the catalytic activity as the acidity and porosity of the catalyst increased with their addition. The activity, selectivity, and catalytic stability tests of Pt/ZrO<sub>2</sub>-SO<sub>4</sub>, Cr/ZrO<sub>2</sub>-SO<sub>4</sub> and Ni/ZrO<sub>2</sub>-SO<sub>4</sub> were carried out with their application in the hydrocracking reaction to produce liquid fuel. The percentage of liquid fractions produced using these catalysts were higher than the fraction produced using pure  $ZrO_2$  and  $ZrO_2$ -SO<sub>4</sub> catalyst.

Keywords: catalyst; zirconia; sulfated; acidity

# 1. Introduction

Zirconium dioxide, known as zirconia, is a crystalline oxide of zirconium that found form in the mineral baddeleyite. Zirconia is a white material that does not react with water or another solvent, and that has acid–base properties and excellent thermal dan chemical stabilization.  $ZrO_2$  materials are of wide interest and development in their application in various fields, such as heterogeneous catalyst, optics, electronics, magnetics, and ceramics owing to the high melting point ( $\geq$ 2700 °C), low thermal conductivity, corrosion resistance, and good thermal and mechanical strength [1–3].

Modification of zirconia to increase its catalytic activity has been developed. Many studies have showed that modification zirconia such as sulfated process or metal supported was effective during the chemical process [3–5]. Sulfated zirconia catalyst via hydrothermal treatment for hydrocracking of LDPE plastic waste into liquid fuels was examined by Utami et al. [6]. The total acidity of zirconia increased after the sulfation process, thus increasing the amount of liquid yield. However, the catalytic activity of sulfated zirconia catalyst during the hydrocracking reaction at high temperature decreases due to the deactivation catalyst. This process therefore requires an appropriate catalyst to increase the catalytic activity of sulfated zirconia, as well as the acidity and liquid yield [7,8].

Supported noble metals such as Platinum (Pt), Chromium (Cr), and Nickel (Ni) as a promoter have shown good catalytic activity in the hydrocracking reaction. The synthesis



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of Pt/sulfated zirconia [9], Cr/sulfated zirconia [10], and Ni/sulfated zirconia [11] catalyst in the hydrocracking reaction reported the enhance of acidity of sulfated zirconia and the liquid product of hydrocracking after the addition of promoter Pt, Cr, and Ni, respectively.

## 2. Zirconium Dioxide (ZrO<sub>2</sub>)

Zirconium dioxide (ZrO<sub>2</sub>) is a polymorphic material with three crystalline phases, namely the monoclinic, tetragonal, and cubic phases, as shown in Figure 1. The monoclinic and tetragonal phases are stable up to temperatures of 1170 and 2360 °C, respectively, while the cubic phase is stable at temperatures above 2680 °C. ZrO<sub>2</sub> as a catalyst is normally used in its monoclinic and metastable tetragonal crystalline phases [12–14]. Transformation of the crystalline phases of ZrO<sub>2</sub> is driven by changes in temperature. ZrO<sub>2</sub> calcined at <800 °C forms monoclinic and metastable tetragonal phases [15,16].

The transformations of one  $ZrO_2$  phase to another are accompanied by changes in lattice parameters. The rate of phase transformation of  $ZrO_2$  is also influenced by the particle size of the  $ZrO_2$  precursor used. The larger the  $ZrO_2$  particle size, the faster the phase transformation occurs. Nano-sized particles have a high surface area, allowing for more of the atoms of the particles to interact and form bonds [15,17,18]. Based on surface properties and polymorphic form,  $ZrO_2$  is also often used as a catalyst or carrier material because it has acidic and basic properties [19,20]. In addition,  $ZrO_2$  has a structure with vacant sites on its surface that can allow cations to easily enter [21,22].



Figure 1. Crystal structures of (a) monoclinic, (b) tetragonal, and (c) cubic ZrO<sub>2</sub>. Copyright Elsevier, reprinted from Ref. [23].

# 3. ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

Zirconia is a catalyst containing high Lewis acid sites. Ore [15] mentioned that  $ZrO_2$  can be modified with acid or base to achieve, based on the intended application, the appropriate and desired strong acid or base characteristics. Sulfation is a method that can increase the strength of  $ZrO_2$  acid through the formation of Brønsted acids on the zirconia substrate that consequently increases its catalytic activity.  $ZrO_2$ -SO<sub>4</sub> can be prepared from sulfate precursors such as H<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and (NH<sub>4</sub>)<sub>2</sub>S) [24–26].

The formation of  $ZrO_2$ -SO<sub>4</sub> occurs through the chelation of the zirconium cations ( $Zr^{4+}$ ) with sulfate ions. The SO<sub>4</sub><sup>2-</sup> ions acts as ligands that donate their lone pair of electrons from the O atom, thus forming a coordination bond with two  $Zr^{4+}$  as the central atoms and causing the acid molecule to release two protons simultaneously. After relaxation, adsorptive complex molecules are produced from the coordination of SO<sub>4</sub><sup>2-</sup> ions onto the  $ZrO_2$  surface through the sharing of two O atoms [27–29]. Saravan et al. [30] illustrate the surface model of  $ZrO_2$ -SO<sub>4</sub> with the Lewis and Brønsted acid sites shown as shown in Figure 2.



Figure 2. Brønsted and Lewis acid sites on ZrO<sub>2</sub>-SO<sub>4</sub>. Copyright MDPI, reprinted from Ref. [17].

Modification of zirconia to  $ZrO_2$ -SO<sub>4</sub> produces materials with high Lewis and Brønsted acid strengths. Wang et al. [29] presented an illustration of the  $ZrO_2$ -SO<sub>4</sub> surface as presented in Figure 3. The high acid strength of the Brønsted acid site is associated with the location of  $Zr^{4+}$  ions that are adjacent to the S=O bond which attracts electrons from the bisulfate to form the Brønsted acid site.



Figure 3. ZrO<sub>2</sub>-SO<sub>4</sub> surface model of bidentate chelate type. Reprinted from ref. [29].

# 3.1. Functional Group Characterization for ZrO<sub>2</sub>-SO<sub>4</sub>

Research conducted by Utami et al. [31] reported the preparation of sulfated zirconia catalysts with various  $H_2SO_4$  concentrations and calcination temperatures. Figure 4 shows the same absorption peak at wave number 424–741 cm<sup>-1</sup>, indicating the Zr–O–Zr bond [32]. Absorptions at 3426–3449 and 1636 cm<sup>-1</sup> refer to the O-H stretching and bending vibrations of the water molecules adsorbed on the material [33]. In addition, according to Ore et al. [15], the broadband in the absorption region of 3400 cm<sup>-1</sup> signifies the bridge between the hydroxyl group with two or three Zr atoms.



**Figure 4.** FTIR spectra of SZ catalyst at various sulfate concentrations and calcination temperatures. Reprinted with permission from Dr. Utami, Ref. [31]. Copyright 2019 Trans Tech Publication.

The presence of  $SO_4^{2-}$  ions on the surface of  $ZrO_2$  can be confirmed by the formation of a new peak at 995-1404 cm<sup>-1</sup> which is typical of the bidentate  $SO_4^{2-}$  chelate ion covalently bonded to the  $Zr^{4+}$  cation [7,27]. The absorption peaks at 995–1003, 1049–1096, 1134–1157, and 1227 cm<sup>-1</sup> are S–O symmetric vibrations, S–O asymmetric vibrations, S=O symmetry vibrations, and S=O asymmetric vibrations [34–36]. The peak with low intensity in the area of 1404 cm<sup>-1</sup> is the stretching vibration of S=O, indicating the formation of SO<sub>3</sub> species on the surface of  $ZrO_2$  [37]. The presence of characteristic bands of  $ZrO_2$ -SO<sub>4</sub> proves that the impregnation of H<sub>2</sub>SO<sub>4</sub> on  $ZrO_2$  has been successfully carried out.

The use of too high a concentration of H<sub>2</sub>SO<sub>4</sub> can lead to loss of several absorption bands of the SO<sub>4</sub><sup>2-</sup> ion which is covalently bonded to Zr<sup>4+</sup> cations as the ZrO<sub>2</sub> structure is degraded [9,37]. Such a case implies that an appropriate or optimum concentration of H<sub>2</sub>SO<sub>4</sub> is needed for the ZrO<sub>2</sub> activation process. The absorption intensity of ZrO<sub>2</sub>-SO<sub>4</sub> increased at a temperature range of 500–600 °C but decreased at temperatures of 700–800 °C. Calcination treatment at 600 °C (SZ-0.8-600) was found to be optimum resulting in the highest SO<sub>4</sub><sup>2-</sup> dispersion. According to Ore [15], the maximum calcination temperature in the sulfation process is 650 °C. Temperatures above 650 °C cause the decomposition of SO<sub>4</sub><sup>2-</sup> ions, thereby reducing the acidity and reactivity of the catalyst.

The acidity test of the catalyst was carried out by the gravimetric method based on the amount of NH<sub>3</sub> vapor absorbed by the catalyst. Table 1 shows the results of the catalyst acidity test.  $ZrO_2$  has a total acidity of 0.18 mmol/g. The acidity of  $ZrO_2$  comes from the  $Zr^{4+}$  cations that act as Lewis acid sites [7,8]. After modification with H<sub>2</sub>SO<sub>4</sub>, the acidity of  $ZrO_2$  increased. SZ-0.8-600 catalyst showed the highest acidity value of 1.06 mmol/g. Ore et al. [15] reported that the number of Brønsted and Lewis acid sites depends on the SO<sub>4</sub><sup>2–</sup> concentration present on the catalyst surface. Sulfation with optimum sulfate concentration can increase the catalytic activity of the catalyst, while the decrease in catalyst acidity with increasing temperature occurs due to dehydration of protonic sites and loss of SO<sub>4</sub><sup>2–</sup> groups on the surface of the catalyst [38–40].

Catalant		Acidity (	(mmol/g)	
Catalyst	600 °C	700 °C	800 °C	900 °C
ZrO <sub>2</sub>	0.18	-	-	-
SZ-0.2	0.39	0.32	0.29	0.26
SZ-0.5	0.83	0.33	0.30	0.28
SZ-0.8	1.06	0.56	0.53	0.33

Table 1. Acidity test for the SZ catalyst at various sulfate concentrations and calcination temperatures [31].

Qualitatively, the number of Brønsted and Lewis acid sites can be observed absorption spectra intensity that denotes the interaction between the catalyst acid sites and NH<sub>3</sub> [41]. Figure 5 presents the FTIR spectra of the catalyst after the acidity test. The absorption peak at 1119-1126 cm<sup>-1</sup> indicates the presence of NH<sub>3</sub> coordinated to the Lewis acid site. The peak at 1404 cm<sup>-1</sup> confirmed the presence of NH<sup>4+</sup> ions formed by proton transfer from the Brønsted acid site to NH<sub>3</sub> [42,43]. The higher the intensity of the absorption band, the higher the number of Brønsted and Lewis acid sites. It was found that the SZ-0.8-600 catalyst had the highest acid site intensities. The absorption intensities of the acid sites decreased with the increase in calcination temperature. Calcination treatment at high temperature decreases the acidity of the catalyst due to the decrease in the number of acid sites on the surface of the catalyst [44,45].



**Figure 5.** FTIR spectra of SZ catalyst at various sulfate concentrations and calcination temperatures after acidity test. Reprinted with permission from Dr. Utami, Ref. [31]. Copyright 2019 Trans Tech Publication.

# 3.2. ZrO<sub>2</sub>-SO<sub>4</sub> Crystal Structure Characterization

Figure 6 presents the diffraction pattern of the SZ catalyst at various sulfate concentrations and calcination temperatures. The main diffraction peaks appear at  $2\theta = 28.34^{\circ}$  (d-111) and  $31.64^{\circ}$  (d111), referring to the ZrO<sub>2</sub> monoclinic crystalline phase [6,15]. In general, the diffraction pattern showed stable crystallinity even after the addition of acid and calcination treatment. However, the intensity of the ZrO<sub>2</sub> monoclinic diffraction peak decreased after acid treatment. SZ-0.8-600 catalyst with the highest total acidity showed the lowest monoclinic peak intensity. The addition of a high concentration of H<sub>2</sub>SO<sub>4</sub> causes a large number of SO<sub>4</sub><sup>2-</sup> ions to cover the surface of ZrO<sub>2</sub>, decreasing crystallinity [37,38]. The intensities of the monoclinic peaks at temperatures of 800 and 900 °C were higher than those at 600 and 700 °C. This occurred because the high calcination temperature caused SO<sub>4</sub><sup>2-</sup> ions to decompose from the catalyst surface, increasing the crystallinity of the catalyst.



**Figure 6.** Diffraction patterns of SZ catalyst at various sulfate concentrations and calcination temperatures. Reprinted with permission from Dr. Utami, Ref. [31]. Copyright 2019 Trans Tech Publication.

 $ZrO_2$ -SO<sub>4</sub> calcined at a temperature of <800 °C can exist in a metastable tetragonal phase and a monoclinic phase. Similar results were reported by Ore et al. [15] which stated that  $ZrO_2$ -SO<sub>4</sub> calcined at a temperature of 600 °C consists of a mixture of metastable tetragonal and monoclinic phases. The  $ZrOCl_2 \cdot 8H_2O$  amorphous precursor used made

it possible for transformation to a metastable tetragonal structure to occur. However, the  $ZrO_2$  used in this study is commercial  $ZrO_2$ , which contains the monoclinic structure of high stability and crystallinity, hindering it from undergoing phase transformation [46]. The catalyst diffraction pattern in the research by Utami et al. [6] demonstrated the  $ZrO_2$  catalyst and its modifications consisting only of monoclinic structure.

# 4. Platinum/Sulfated Zirconia (Pt/ZrO<sub>2</sub>-SO<sub>4</sub>) Catalyst

A heterogeneous catalyst is a catalyst material composed of two components, namely the doping and carrier components. The metal catalyst, when used in its pure form, has low thermal stability and tends to sinter that can leading to a decrease in surface area and deactivation [47–49]. Appropriate distribution of metal catalysts on the carrier material having acid–base sites and a large surface area is necessary to avoid sintering [50,51]. The ZrO<sub>2</sub>-SO<sub>4</sub> material has many Brønsted and Lewis acid sites in which, despite its high acidity, this catalyst can be rapidly deactivated. The addition of Pt metal can increase the stability of the catalyst with the simultaneous presence of hydrogen gas (H<sub>2</sub>) [52–54].

The distribution mechanism of H<sub>2</sub> through the Pt surface on the  $ZrO_2$ -SO<sub>4</sub> carrier is illustrated in Figure 7. The H<sub>2</sub> molecule dissociates on the surface of the Pt particle homolytically to form two H radicals which then bind to the unpaired electrons in the 5d orbitals. The H<sup>+</sup> ions released from Pt are distributed on the  $ZrO_2$ -SO<sub>4</sub> carrier and migrate to the electron-rich O atomic sites, forming Brønsted acid sites [55,56]. Figure 8 shows the physical appearance of  $ZrO_2$ -SO<sub>4</sub> catalyst which a white powder and after the impregnation with Pt metal as a Pt/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst, solid powder which is darker in color is formed due to the presence of the Pt metal that impregnated to the  $ZrO_2$ -SO<sub>4</sub> catalyst [6,9].



**Figure 7.** Mechanism of H<sub>2</sub> distribution through the Pt surface on ZrO<sub>2</sub>-SO<sub>4</sub>. Reprinted and modified with permission from Dr. Utami, Ref. [9]. Copyright 2019 The Royal Society of Chemistry.



Figure 8.  $ZrO_2$ -SO<sub>4</sub> (right) and Pt/ZrO<sub>2</sub>-SO<sub>4</sub> (left) catalyst. Reprinted with permission from Dr. Utami, Ref. [42].

# 4.1. FTIR and Acidity Characterization of Pt/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

Utami et al. [6] researched the synthesis of Pt-promoted zirconia (Pt/SZ) catalyst and its application in hydrocracking LDPE plastic into liquid fuel. The FTIR spectra of the sulfated zirconia impregnated with Pt metal can be seen in Figure 9. Overall, the Pt1/SZ, Pt2/SZ, and Pt3/SZ spectra showed the same absorption peaks as ZrO<sub>2</sub> and SZ. Pt metal impregnated catalysts had characteristic peaks of  $ZrO_2$ -SO<sub>4</sub> at wave number 1065–1126 cm<sup>-1</sup>. The addition of Pt metal caused some of the absorption peaks of  $ZrO_2$ -SO<sub>4</sub> to disappear. This is an early indication that Pt metal had been impregnated on nanoSZ [9].





Table 2 shows the total acidity of the catalysts of the present study. Pt metal impregnation on sulfated zirconia was proven to increase the total acidity of the catalyst significantly (from 1.06 to 10.75 mmol/g). Pt1/SZ, Pt2/SZ, and Pt3/SZ catalysts showed increasing acidity values with increasing concentrations of Pt metal. The increase in the acidity of the catalyst occurs because the Pt metal provides vacant orbitals that can act as electron-pair acceptors (Lewis acid sites) and the presence of unpaired electrons in the d orbitals that form Brønsted acid sites [57,58].

 Sample	Acidity (mmol/g)
ZrO <sub>2</sub>	0.18
SZ	1.06
Pt1/SZ	10.75
Pt2/SZ	11.05
Pt3/SZ	11.14

Table 2. Acidity test results of ZrO<sub>2</sub>, SZ, Pt1/SZ, Pt2/SZ, and Pt3/SZ [6].

FTIR spectra interpretations of  $ZrO_2$ , SZ, Pt1/SZ, Pt2/SZ, and Pt3/SZ are shown in Figure 10. Increasing concentration of Pt metal produced increased adsorption of NH<sub>3</sub> bound to the Brønsted and Lewis acid sites as shown at wavenumbers of 1396–1404 and 1119 cm<sup>-1</sup>, indicating that the higher the concentration of Pt metal, the higher the number of acid sites contained in the catalyst. The Pt3/SZ catalyst showed the highest intensity of Brønsted and Lewis acid absorptions. Based on the results of the acidity test of the catalyst, the Pt3/SZ catalyst was confirmed to have the highest acidity value.



**Figure 10.** FTIR spectra of ZrO<sub>2</sub>, SZ, Pt1/SZ, Pt2/SZ, and Pt3/SZ after acidity test. Reprinted with permission from Dr. Utami, Ref. [6]. Copyright 2019 Elsevier.

# 4.2. XRD and GSA Characterizations of Pt/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

SZ catalysts are shown in Figure 11. Based on crystal identification, all samples showed the presence of the monoclinic phase. According to Ore [15],  $SO_4^{2-}$  species can be thermally crystallized through the calcination process and undergo a crystalline phase transformation, further stabilizing the  $ZrO_2$  crystalline phase. The addition of Pt metal to SZ would not have caused changes in the crystal structure of the material. A decrease in the intensity of the diffraction peak after the addition of Pt metal was observed. This phenomenon indicated that Pt metal had been successfully impregnated on the SZ surface, where a higher concentration of the impregnated Pt metal would cause the intensity of the monoclinic peak to decrease [6,9].



**Figure 11.** Diffraction patterns of ZrO<sub>2</sub>, SZ, Pt1/SZ, Pt2/SZ, and Pt3/SZ. Reprinted with permission from Dr. Utami, Ref. [6]. Copyright 2019 Elsevier.

Based on the catalyst diffraction pattern, Pt metal characteristic peaks were not detected. This is because the concentration of impregnated Pt metal was relatively low. This is by research conducted by Aboul-Gheit et al. [59] that showed similar results whereby the diffraction peak of Pt metal was not identified after the addition of 0.6% Pt metal to ZrO<sub>2</sub>-SO<sub>4</sub>. A relatively low concentration of Pt metal was used in the present study to prevent agglomeration of Pt particles on the ZrO<sub>2</sub>-SO<sub>4</sub> surface, which could cause a decrease in catalytic activity.

Characterization carried out by GSA (Table 3) showed an increase in surface area and pore volume along with the increasing concentration of Pt metal impregnated onto SZ. The Pt1/SZ catalyst had a surface area and pore volume of  $13.49 \text{ m}^2/\text{g}$  and  $0.05 \text{ cm}^3/\text{g}$ , respectively, which saw an increase to  $20.23 \text{ m}^2/\text{g}$  and  $0.06 \text{ cm}^3/\text{g}$  for Pt2/SZ and  $29.48 \text{ m}^2/\text{g}$  and  $0.08 \text{ cm}^3/\text{g}$  for Pt3/SZ. Based on the data reported in the study by Utami et al. [9], the increase in the surface area and pore volume of the SZ catalyst can be attributed to the inhibition of the agglomeration process related to the high presence of Pt metal.

Sample	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Diameter (nm)
ZrO <sub>2</sub>	22.05	0.08	3.49
SZ	12.49	0.05	3.82
Pt1/SZ	13.49	0.05	3.83
Pt2/SZ	20.23	0.06	3.84
Pt3/SZ	29.48	0.08	3.86

Table 3. Textural characteristics of ZrO<sub>2</sub>, SZ, Pt1/SZ, Pt2/SZ, and Pt3/SZ [6].

The increase in the surface area of the catalyst can also be attributed to the smaller crystal size dimensions. Crystal size results of ZrO<sub>2</sub>, SZ, Pt1/SZ, Pt2/SZ, and Pt3/SZ (Table 4) presented a decrease in size after metal impregnation of Pt. This indicated that the Pt metal impregnated by the reflux technique was evenly dispersed on the surface and pores of SZ [9]. In contrast, Aboul-Gheit et al. [59] impregnated Pt metal on ZrO<sub>2</sub>-SO<sub>4</sub> through the wet impregnation method and reported an increase in the concentration of Pt metal causing the surface area and pore volume to increase due to the Pt metal being not evenly distributed and covering most of the ZrO<sub>2</sub>-SO<sub>4</sub> pores.

Table 4. Crystal sizes of ZrO<sub>2</sub>, SZ, Pt1/SZ, Pt3/SZ Pt2/SZ and Pt3/SZ [6].

Sample	Crystal Size (nm)
ZrO <sub>2</sub>	31.54
SZ	34.06
Pt1/SZ	32.80
Pt2/SZ	31.54
Pt3/SZ	31.53

#### 4.3. Elemental Composition Characterization Using EDXRF

Table 5 shows the concentrations of elements contained in the catalysts. The concentrations of Pt metals identified in the Pt1/SZ, Pt2/SZ, and Pt3/SZ samples were 0.35, 0.90, and 1.19%. The metal content of Pt in SZ was strongly influenced by the dispersion ability on the surface and pores of the carrier material. The reduction treatment with  $H_2$  gas flow was carried out after the calcination step which aimed to obtain Pt<sup>0</sup> particles that would result in dispersion [14].

Committee	Elemen	tal Compositions (	% w/w)	
Sample	Zr	Pt	0	S
ZrO <sub>2</sub>	64.08	-	35.46	0.46
SZ	60.51	-	37.42	2.07
Pt1/SZ	75.24	0.35	24.02	0.74
Pt2/SZ	74.37	0.90	25.02	0.61
Pt3/SZ	75.34	1.19	24.40	0.26

Table 5. Elemental compositions of ZrO<sub>2</sub>, SZ, Pt1/SZ, Pt2/SZ dan Pt3/SZ [6].

Based on the elemental compositions above, the concentrations of Pt that were observed were lower than the theoretical concentration of Pt metal by the addition of  $PtCl_4$ solution used in the impregnation process. This discrepancy occurred due to competition between impregnated Pt metals, causing the formation of multilayer stacking of the active metal in the pore mouth area of the carrier material [60,61]. The active Pt metal that sat at the top position would have weak interaction and would experience easier desorption [62]. Because of this, the amount of active metal in the pore area of the carrier material was observed to be less.

## 4.4. Pt metal Composition Identification Using XPS

Subsequent research related to the synthesis of platinum-loaded sulfated zirconia catalysts using the hydrothermal method was reported by Utami et al. [9]. XPS spectra were used to determine the composition of Pt in the samples based on a comparison of binding energy values. The peaks generated from XPS are not single peaks, so that deconvolution of the peaks was needed to identify the multiple peaks that made up each peak. Figure 12 presents the XPS spectra along with the deconvolution of Pt 4f peaks from Pt/nano ZrO<sub>2</sub>-SO<sub>4</sub> consisting of Pt<sup>0</sup> 4f<sub>7/2</sub>, Pt<sup>0</sup> 4f<sub>5/2</sub>, and Pt<sup>2+</sup> 4f<sub>7/2</sub>. The spectra indicated the interaction of electrons between the Pt particles and the nanoZS surface. Table 6 shows the relative area of the deconvoluted peaks of Pt<sup>0</sup> 4f<sub>7/2</sub>, Pt<sup>0</sup> 4f<sub>5/2</sub>, and Pt<sup>2+</sup> 4f<sub>7/2</sub> in the Pt/nano ZrO<sub>2</sub>-SO<sub>4</sub> sample. The data obtained showed that the detected Pt<sup>0</sup> composition was 81.82%. The results indicated that the reduction treatment with H<sub>2</sub> gas flow at the metal impregnation stage succeeded in forming Pt<sup>0</sup> particles.



**Figure 12.** XPS spectra of  $Pt/nano ZrO_2$ -SO<sub>4</sub> in the 4*f* region and the catalyst model. Reprinted and modified with permission from Dr. Utami, Ref. [9]. Copyright 2019 The Royal Society of Chemistry.

Table 6.	Percentage of	relative areas of Pt 4 <i>f</i>	deconvoluted	peaks [4].

Pt 4f Peak	Peak Position (eV)	Relative Area (%)
$Pt^0 4f_{7/2}$	71.45	36.36
$Pt^0 4f_{5/2}$	74.75	45.46
$Pt^{2+}4f_{7/2}$	73.08	18.18

## 4.5. Thermal Stability Characterization with TG/DTA

The TG/DTA curve provides information about changes in thermal conditions with mass changes in the sample. Figure 13 shows the TGA curves for nano  $ZrO_2$ , nano  $ZrO_2$ -SO<sub>4</sub>, and Pt/nano  $ZrO_2$ -SO<sub>4</sub> samples analyzed at temperatures of 30–900 °C. The TGA curve of nano  $ZrO_2$  did not indicate mass decrease indicating that nano Z had good thermal stability [63]. Mass decrease in nano  $ZrO_2$ -SO<sub>4</sub> and Pt/nano  $ZrO_2$ -SO<sub>4</sub> in the range of 50–200 °C by 2.41 and 1.24% were associated with the elimination of water molecules physically adsorbed on the material. At 500–700 °C, decreases in a mass of 5.69 and 2.48%, indicating the decomposition of SO<sub>4</sub><sup>2–</sup> ions bound to the  $ZrO_2$  surface. The decomposition of SO<sub>4</sub><sup>2–</sup> ions at 600–1000 °C affected the structural changes of  $ZrO_2$ -SO<sub>4</sub>, causing a decrease in catalytic activity [64]. The decomposition of H<sub>2</sub>SO<sub>4</sub> occurs through a two-stage endothermic process at high temperatures according to Equations (1) and (2).

$$H_2SO_4_{(aq)} \to H_2O_{(l)} + SO_3_{(g)}$$
 (1)

$$SO_{3(g)} \to SO_{2(g)} + \frac{1}{2}O_{2(g)}$$
 (2)



**Figure 13.** TGA curves of (a) nano ZrO<sub>2</sub>, (b) nano ZrO<sub>2</sub>-SO<sub>4</sub>, (c) Pt/nano ZrO<sub>2</sub>-SO<sub>4</sub>. Reprinted and modified with permission from Dr. Utami, Ref. [9]. Copyright 2019 The Royal Society of Chemistry.

# 4.6. Activity and Selectivity of Pt/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst in LPDE Hydrocracking Application

Utami et al. [6] reported the activity and selectivity of the Pt/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst applied in LPDE hydrocracking. The hydrocracking liquid fraction of the LDPE plastic waste thermal cracking is shown in Figure 14. Physically, the hydrocracking liquid fraction has a yellow color and pungent odor, which indicate the success of the hydrocracking process. The percentages of liquid fractions produced using the Pt1/SZ, Pt2/SZ, and Pt3/SZ catalysts were higher than that of the SZ catalyst. The percentage of liquid fraction obtained with the SZ catalyst was 57.92%, while with Pt1/SZ, Pt2/SZ, and Pt3/SZ the liquid fractions were 70.58, 71.15, and 74.60%, respectively. Through MS data, it was found that the hydrocarbon compounds in the gasoline range (C<sub>5</sub>–C<sub>12</sub>) were more commonly found in the liquid fraction samples that had used Pt3/SZ (catalyst with the highest acidity). Table 7 shows the gasoline fraction percentages from the hydrocracking reaction using Pt1/SZ, Pt2/SZ, and Pt3/SZ catalysts, which were 48.76, 64.22, and 67.51 w/w%, respectively. This cased that besides affecting the amount of hydrocracking liquid fraction produced, the addition of Pt metal can also increase selectivity towards the gasoline fraction [65].





**Figure 14.** The physical appearance of the hydrocracking liquid fraction (**a**) without catalyst, and with catalyst (**b**) ZrO<sub>2</sub>, (**c**) SZ, (**d**) Pt1/SZ, (**e**) Pt2/SZ3, (**f**) Pt3/SZ. Reprinted with permission from Dr. Utami, Ref. [14].

**Table 7.** Distribution of hydrocracking products using different catalysts (T = 250 °C, t = 60 m, catalyst to feed ratio = 1% w/w) [6].

		Hydrocracking F	Product (% <i>w/w</i> )	
Sample	Liq	luid	Solid	Gas
	C <sub>5</sub> -C <sub>12</sub>	C <sub>13</sub> -C <sub>20</sub>		
SZ	42.95	14.97	0.35	41.73
Pt1/SZ	48.76	21.82	0.15	29.27
Pt2/SZ	64.22	6.93	0.16	28.69
Pt3/SZ	67.51	7.09	0.15	25.25

The percentage of hydrocarbon compounds in the  $C_5-C_{12}$  range can be seen to be greater than that of  $C_{13}-C_{20}$  hydrocarbons. This shows that the hydrocracking liquid fraction of LDPE plastic waste had a higher gasoline fraction than the diesel fraction and that the four types of catalysts used had good selectivity towards the hydrocracking reaction that produces liquid fuel fraction (gasoline fraction).

Figure 15 shows the proportion of hydrocarbon compounds contained in the hydrocracked liquid fraction in the gasoline range, namely olefins, paraffin, isoparaffins, and naphthenes, with a total composition of 56.36 and respective amounts of 20.07, 14.60, and 6.81% w/w with use of the Pt3/SZ catalyst. Aromatic compounds in small amounts were also produced with a composition of 0.70% w/w, and only 1.46% w/w was indicated to be non-hydrocarbon compounds. Overall, olefin (unsaturated/double-bonded compound) was dominantly produced from the hydrocracking. This is because LDPE, as the plastic feed used, consists of olefin in which, during the hydrocracking reaction, not all olefins react with the hydride to become paraffin (saturated/single bond compound) [6,9].

#### 4.7. Stability Test of Pt/ZrO<sub>2</sub>-SO<sub>4</sub>

A stability test of the Pt/nano  $ZrO_2$ -SO<sub>4</sub> catalyst, along with nano  $ZrO_2$  and nano  $ZrO_2$ -SO<sub>4</sub> for comparison, was carried out by Utami et al. [9] through a hydrocracking reaction of LDPE plastic waste with a catalyst/feed ratio 1% w/w and a temperature of 250 °C for 60 min. The catalyst stability test was carried out for six cycles with the same reaction conditions. Figure 16 shows that  $ZrO_2$ , SZ, and Pt3/SZ had good catalytic performances when first used. The hydrocracking reaction with the  $ZrO_2$  catalyst showed a significant decrease in the percentage of liquid fraction produced in the fourth cycle, while in SZ this significant reduction occurred in the second cycle.



**Figure 15.** The composition of liquid yield in the gasoline fraction from the hydrocracking reaction of LDPE plastic waste using Pt3/SZ at 250 °C. Reprinted with permission from Dr. Utami, Ref. [6]. Copyright 2019 Elsevier.



**Figure 16.** Hydrocracking liquid fraction graphs of (a) nano ZrO<sub>2</sub>, (b) nano ZrO<sub>2</sub>-SO<sub>4</sub>, and (c) Pt/nano ZS3 Pt/nanoZS3-600. Reprinted and modified with permission from Dr. Utami, Ref. [9]. Copyright 2019 The Royal Society of Chemistry.

The catalytic activity of Pt3/SZ showed very good stability up to the sixth cycle. Aboul-Gheit et al. [59] reported that the catalytic activity of  $ZrO_2$ -SO<sub>4</sub> in the n-pentane isomerization reaction decreased in the fourth cycle and became inactive in the eighth cycle. In contrast, the Pt/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst showed stable activity until the tenth cycle. The Pt/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst showed high resistance to the deactivation related to the removal of coke from the catalyst surface, thus increasing the stability of the catalyst [36,37].

Figure 16 illustrates the proposed origin of the catalytic stability of  $ZrO_2$ -SO<sub>4</sub> and Pt/nanoZS3-600 nanoscales. Based on the activity and catalytic selectivity data, the conversion of LDPE using nano  $ZrO_2$ -SO<sub>4</sub> produced the highest amount of coke. In addition, this material had a high initial activity but low resistance to the deactivation process as its catalytic properties decreased rapidly in its consequent cycle of use. The formation of a coke can causes the pores and the active sites of the catalyst to be closed and thus reduce activity [44], i.e., the deactivation process that occurred in the  $ZrO_2$ -SO<sub>4</sub> nanocatalyst would have been difficult to control. To restore the activity of nanoZS3-600, catalyst regeneration, i.e., coke removal, is indispensable, especially in large-scale industrial applications. Promisingly, the Pt/nanoZS3-600 catalyst showed good activity, selectivity, and stability even after repeated use.

# 5. Cr/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

The metals that are widely used for bifunctional catalysts are usually transition metals with have incomplete orbitals that function as Lewis acid sites. One of the said transition metals is chromium (Cr) [66]. Cr can be doped on a carrier to enhance the catalytic activity of the host [67,68]. The addition of Cr metal to sulfated zirconia can also increase the acidity of the catalyst as the metal would contribute to the presence of Lewis acid sites [69]. The presence of Cr metal on sulfated zirconia also affects increasing the surface area of the catalyst [70,71]. Figure 17 illustrates the reaction mechanism of sulfated zirconia impregnated with Cr metal when interacting with ammonia during an acidity test. Hauli et al. [71] stated that the addition of chromium metal to sulfated zirconia not only increases the surface area of the catalyst but also stabilizes pure zirconia at high calcination temperatures. Increased temperature can thus remove sulfate groups and damage the porosity of the structure, causing the catalyst to deactivate. The physical appearance of the  $ZrO_2$ -SO<sub>4</sub> and  $Cr/ZrO_2$ -SO<sub>4</sub> catalyst (Figure 18) shows solid particle color change after the impregnation of Cr metal.



**Figure 17.** Proposed model of ammonia interaction on metal-embedded sulfated zirconia. Reprinted from Ref. [68]. Copyright Elsevier.



**Figure 18.** ZrO<sub>2</sub>-SO<sub>4</sub> (**left**) and Cr/ZrO<sub>2</sub>-SO<sub>4</sub> (**right**) catalyst. Reprinted with permissission from Dr. Hauli, Ref. [71].

#### 5.1. FITR and Acidity Characterizations of Cr/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

Research on Cr/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst has been reported by Hauli et al. [72]. FTIR results of ZrO<sub>2</sub>, SZ 0.8-600 (SZ), 0.5% Cr/SZ (Cr1/SZ), 1.0% Cr/SZ (Cr2/SZ), and 1.5% Cr/SZ (Cr3/SZ) are shown in Figure 19. The spectra showed no specific differences between the spectra of Cr-embedded zirconia catalyst and sulfated zirconia. However, the specific absorption peak of the sulfate group at 1053–1224 cm<sup>-1</sup>, decreased with the presence of Cr. This is because the heating process involved in the loading of the metal had allowed sulfates to be released from the ZrO<sub>2</sub> surface. The presence of metal produced not sulfate decomposition but rather the release of the sulfate groups from the surface of ZrO<sub>2</sub> during the heating process [72]. Hanifah et al. [38] reported similar phenomena, namely that the presence of monometals and bimetals on ZrO<sub>2</sub>-SO<sub>4</sub> release of sulfate group materialized whilst its decomposition did not.





The presence of empty orbitals in Cr metal allows electrons from other atoms to take their place in the orbital in what would then contribute to higher acidity of the Cr-containing material. Acidity test results of Cr-containing catalysts are presented in Table 8 confirming this. The acidity of the catalyst increased after the addition of Cr metal. The Cr1/SZ catalyst was the catalyst with the highest acidity value with 8.22 mmol/g. The low acidity value at high Cr-metal concentration was caused by the presence of metal particle aggregates that had covered the active metal sites on the carrier material. The more Cr metal that was embedded, the greater the amount of metal not accommodated in the pores of the carrier material, leading to the formation of aggregates.

Table 8. Acidity values of the catalysts [	72	l.
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Sample	Acidity (mmol/g)
SZ	3.81
Cr1/SZ	6.24
Cr2/SZ	8.22
Cr3/SZ	6.75

The acidity test of the catalyst was carried out to determine the total acidity value of each catalyst. The FTIR spectra after the acidity test results for the  $ZrO_2$ , SZ, Cr1/SZ, Cr2/SZ, and Cr3/SZ catalysts are shown in Figure 20. The results show the same absorption peaks at wave numbers 1119 and 1404 cm<sup>-1</sup>, confirming the presence of the Lewis and Brønsted acid sites on each catalyst. Cr-embedded sulfated zirconia catalyst showed a higher intensity of Lewis and Brønsted acid sites than before Cr metal was added. The spectra of the Cr/SZ catalyst had the highest acid site intensity, indicating that Cr2/SZ had a high acidity value. The results of the acidity test of the catalysts confirmed that Cr2/SZ had the highest acidity value of 8.22 mmol/g.



**Figure 20.** FTIR spectra of SZ, Cr1/SZ, Cr2/SZ, and Cr3/SZ after acidity test. Reprinted with permission from Dr. Hauli, Ref. [72]. Copyright 2019 Trans Tech Publication.

# 5.2. XRD Characterization of Cr/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

The diffraction patterns of ZrO<sub>2</sub>, SZ, Cr1/SZ, Cr2/SZ, and Cr3/SZ catalysts are presented in Figure 21. The bearing of Cr metal on sulfated zirconia provided no change in the crystal phase structure of ZrO<sub>2</sub>. The main peaks were found in the 2 $\theta$  region around 28°, 31°, and 50° denoting plane distances of d<sub>-111</sub> (3,2 Å), d<sub>111</sub> (2,8 Å), d<sub>220</sub> (1,8 Å) with the highest intensity in the 28° region. Sulfate and Cr impregnation on ZrO<sub>2</sub> have a lower intensity peak than ZrO<sub>2</sub>. This is due to the presence of sulfate on ZrO<sub>2</sub> and to Cr metal covering the surface of SZ, inhibiting the growth of ZrO<sub>2</sub> crystals and thereby decreasing the crystallinity of the materials [73,74].



**Figure 21.** Diffraction patterns of ZrO<sub>2</sub>, SZ, Cr1/SZ, Cr2/SZ, Cr3/SZ. Reprinted with permission from Dr. Hauli, Ref. [72]. Copyright 2019 Trans Tech Publication.

## 5.3. SAA Characterization of Cr/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

Characterization of pore characteristics including surface area, pore diameter, and pore volume was carried out by SAA analysis. The results of the SAA measurements of the catalysts are shown in Table 9. As can be seen, the addition of Cr metal to sulfated zirconia increased the surface area, pore diameter, and pore volume of the catalyst. This can be attributed to the uniform distribution of Cr metal on the catalyst surface [69,70]. The surface area of the catalyst, however, decreased upon the addition of higher concentrations of Cr metal, namely at Cr3/ZS, due to the entry of Cr metal into the catalyst pores causing agglomeration of metal atoms that covered the catalyst pores [74].

Sample	Surface Area (m <sup>2</sup> /g)	Pore Diameter (nm)	Pore Volume (cm <sup>3</sup> /g)
ZrO <sub>2</sub>	12.27	3.70	0.07
SZ	7.79	3.68	0.08
Cr1/SZ	12.62	3.70	0.12
Cr2/SZ	14.56	3.70	0.08
Cr3/SZ	11.91	9.04	0.04

Table 9. Pore characteristics of the catalysts [72].

The adsorption and desorption isotherm patterns for ZrO<sub>2</sub>, SZ, Cr1/SZ, Cr2/SZ, and Cr3/SZ catalysts are shown in Figure 22. Based on the IUPAC classification, all catalysts showed a type IV isotherm pattern, which is characteristic of the isotherm pattern for mesoporous materials with pore diameter sizes of 2–50 nm. The adsorption–desorption isotherm patterns of the Cr1/SZ and Cr2/SZ catalysts demonstrated monolayer absorption of nitrogen gas on the surface when  $P/P_0 < 0.2$ . At a relative pressure of  $0.2 < P/P_0 < 1$ , the isotherm curve experienced a sharp increase in volume representing a multilayer arrangement. In the Cr3/SZ catalyst, the absorption of a monolayer of nitrogen gas on the surface occurred when  $P/P_0 < 0.4$  and experienced a sharp increase in volume at  $0.4 < P/P_0 < 1$ . The ZrO<sub>2</sub>, Cr2/SZ, and Cr3/SZ catalyst had a type H4 hysteresis, while SZ and Cr1/SZ had type H3. Type H3 hysteresis showed no absorption limit at high  $P/P_0$ . Type H4 hysteresis is associated with narrow slit pores [4,72]. These three types of catalysts exhibit the characteristics of porous materials. This form of porous material is composed of aggregates of particles such as plates that form pore gaps [10].



**Figure 22.** Adsorption desorption isotherm patterns of ZrO<sub>2</sub>, SZ, Cr1/SZ, Cr2/SZ, and Cr3/SZ. Reprinted with permission from Dr. Hauli, Ref. [72]. Copyright 2019 Trans Tech Publication.

# 5.4. Activity and Selectivity Tests of Cr/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

A catalytic activity test of the  $Cr/ZrO_2$ -SO<sub>4</sub> catalyst in the hydrocracking reaction of LDPE into liquid fuel has been carried out by Hauli et al. [72]. The hydrocracking reaction was carried out at a temperature of 250 °C using  $ZrO_2$ , SZ, Cr1/SZ, Cr2/SZ, and Cr3/SZ catalysts. The percentages of conversion yields of the hydrocracking of each catalyst are presented in Table 10. The presence of sulfate and Cr metal in  $ZrO_2$  can increase the yield of liquid products from the hydrocracking reaction. The liquid product increased along with the increase in the amount of Cr metal deposited on  $ZrO_2$ . This can be attributed to the role of acid sites in the catalyst (from sulfate and metal Cr) which contribute to the active sites of the catalyst, thereby increasing its catalytic activity [50].

Catalant	Pr	oduct Conversion (% b/	b)
Catalyst	Liquid	Coke	Gas
ZrO <sub>2</sub>	17.39	0.36	32.23
SZ	28.72	0.34	29.51
Cr1/SZ	33.48	0.01	25.78
Cr2/SZ	40.99	0.01	24.84
Cr3/SZ	37.51	0.01	26.77

Table 10. Distribution of LDPE plastic hydrocrack products on various catalysts [72].

The highest conversion of liquid product was produced using the Cr2/SZ catalyst, which was 40.99%, with a lesser amount of 37.51% with the use of the Cr3/SZ catalyst. Moreover, the Cr2/SZ catalyst had a higher acidity value than Cr3/SZ. In addition, the surface area of the catalyst also affects the catalytic activity of the catalyst in the hydrocracking of LDPE plastics [75,76]. Accordingly, the Cr2/SZ had a larger surface area, resulting in greater conversion. The modification of Cr on sulfated zirconia demonstrated a reduction in coke formation, thereby increasing the feed interaction on the active sites of the catalysts.

The selectivity of the catalysts towards liquid products in the hydrocracking reaction are shown in Figure 23. All the catalysts showed higher selectivity in the gasoline fraction than the diesel fraction. The presence of sulfate and Cr in sulfated zirconia increased the selectivity towards the gasoline fraction ( $C_5$ – $C_{12}$ ) and decreased the selectivity towards the diesel fraction ( $C_{13}$ – $C_{20}$ ), as expected. The highest selectivity of the gasoline fraction was obtained from the use of the Cr2/SZ catalyst, which was at 93.42%.



**Figure 23.** Liquid product selectivity of ZrO<sub>2</sub>, SZ, Cr1/SZ, Cr2/SZ, and Cr3/SZ catalysts. Reprinted with permission from Dr. Hauli, Ref. [72]. Copyright 2019 Trans Tech Publication.

# 6. Ni/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

# 6.1. FITR Characterization of Ni/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

Research on the  $ZrO_2$ -SO<sub>4</sub> catalyst was also carried out about its application in the hydrocracking of used cooking oil into liquid fuel. Modification of  $ZrO_2$ -SO<sub>4</sub> with Ni metal has been reported by Aziz et al. [73]. Figure 24 show the FTIR spectra of Ni-SZ 1, Ni-SZ 2, and Ni-SZ 3. Impregnated Cr metal to SZ caused the presence of a new peak in the area of 1103 and 1141 cm<sup>-1</sup>, confirming the S-O-S stretching of from SO<sub>4</sub> ion from SZ coordinated with Ni metal [76,77]. However, the sulfate spectra at 1002–1219 cm<sup>-1</sup> disappear due to the Ni metal coverage on the SZ surface and the higher calcination temperature.



**Figure 24.** FTIR spectra of SZ (a), Ni-SZ 1 (b), Ni-SZ 2 (c), and Ni-SZ 3 (d) catalysts. Reprinted with permission from Aziz, Ref. [73]. Copyright 2020 Budapest University.

# 6.2. Acidity and SAA Analysis of Ni/ZrO<sub>2</sub>-SO<sub>4</sub> Catalyst

The total acidity and pore characteristic of Ni-SZ catalysts is shown in Table 11. It can be seen that the sulfation of  $ZrO_2$  (SZ catalyst) and Ni metal impregnated to SZ catalysts successfully increase the total acidity of the catalyst. Ni metal has a vacant p orbital that will accepting electron pair and acts as a Lewis acid site [78]. The Ni-SZ 3 catalyst was the catalyst with the highest total acidity of 4.235 mmol/g.

Sample	Acidity	Surface Area (m²/g)	Pore Diameter (nm)	Pore Volume (cm <sup>3</sup> /g)
ZrO <sub>2</sub>	0.355	5.63	30.72	0.04
SZ	2.004	4.04	35.84	0.04
Ni-SZ 1	3.905	7.09	3.82	0.06
Ni-SZ 2	4.061	8.75	3.82	0.05
Ni-SZ 3	4.235	11.68	3.82	0.05

Table 11. The acidity and pore characteristics of the Ni-SZ catalysts [73].

The pore characteristic of the catalyst shows the increase in surface area after the impregnation of Cr metal onto the SZ catalyst due to the highly dispersion of Ni metal on the pore and surface of the SZ catalyst [79]. However, the presence of Ni causing the form of pore-blocking that significantly decreases the pore diameter of Ni-SZ catalysts [72].

The selectivity of the Ni- $ZrO_2$ -SO<sub>4</sub> catalyst is shown in Table 12.  $ZrO_2$  and SZ catalysts were observed to have lower activity and selectivity than Ni-SZ due to the lowest acidity and surface area that will produce considerable amounts of coke (block the active site)

and decreases the amount of liquid product [80,81]. The addition of Ni metal (Ni-SZ 3 catalyst) increased the acidity (4.23 mmol/g) and surface area (11.68 m<sup>2</sup>/g) of ZrO<sub>2</sub>, thereby increasing its activity and selectivity in the hydrocracking process [82,83]. The largest amount of liquid product produced was gasoline with the highest selectivity was produced by the Ni-SZ 3 catalyst with the diesel fraction ( $C_5$ – $C_{12}$ ) reached 100%.

**Table 12.** Selectivity of ZrO<sub>2</sub>, SZ, Ni-SZ 1, Ni-SZ 2, and Ni-SZ 3 catalysts in the hydrocracking reaction of used cooking oil into liquid fuel [73].

Catalyst -	Selectivity (wt%)				
	(C <sub>1</sub> –C <sub>4</sub> )	(C <sub>5</sub> –C <sub>12</sub> )	$(C_{13}-C_{20})$	Non-Hydrocarbon	
ZrO <sub>2</sub>	1.86	77.31	19.26	1.57	
SZ	1.93	67.83	28.15	2.54	
Ni-SZ 1	0.00	51.59	15.16	33.25	
Ni-SZ 2	0.00	87.01	12.99	0.00	
Ni-SZ 3	0.00	100.00	0.00	0.00	

## 7. Conclusions

Zirconia and its modified heterogeneous catalyst forms hold great potential in hydrocracking reaction applications to convert LDPE waste into liquid fuels with their excellent activity, selectivity, and stability. The sulfation process on  $ZrO_2$  with various concentrations of sulfuric acid and calcination temperatures succeeded in increasing the acidity of  $ZrO_2$ . The  $ZrO_2$ -SO<sub>4</sub> catalyst treated with Platinum (Pt) and Chrome (Cr) transition metals had significantly increased acidity. Characterization analyses confirmed that Pt and Cr metals had been successfully impregnated on the SZ surface. The percentage of liquid fraction obtained with the use of the Pt/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst proofed better activity, selectivity, and stability than Cr/ZrO<sub>2</sub>-SO<sub>4</sub> and ZrO<sub>2</sub>-SO<sub>4</sub>. The optimum amount of liquid fraction produced from the hydrocracking reaction LDPE plastic waste with the Pt/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst was 67.515%, while that from the Cr/ZrO<sub>2</sub>-SO<sub>4</sub> catalyst was 40.99%. The development of Ni on the ZrO<sub>2</sub>-SO<sub>4</sub> catalyst also demonstrated an increase in selectivity in the hydrocracking reaction of used cooking oil into liquid fuel. The selectivity of the Ni-SZ catalyst was found to be better than that of SZ. The percentages of gasoline fractions produced were 100%.

#### 8. Future Suggestion

Zirconia-based nanocatalysts have bright prospects for application in various industrial areas such as petroleum cracking, biofuel synthesis, pharmaceutical, and the synthesis of various organic materials. The potential application of sulfated nanozirconia catalysts is shown in the Figure 25. Due to characteristics such as being non-toxic and easy to regenerate, as well as having a large surface area and high thermal and structural resistance, nanozirconia catalysts also have the potential to be used in the pharmaceutical industry. Preliminary studies in our laboratory have shown that this catalyst has the potential to be used as a solid acid catalyst in the synthesis of nitrobenzene from benzene.



Figure 25. Potential application of sulfated nanozirconia catalysts.

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