JURNAL KIMIA VALENSI
p-ISSN: 2460-6065; e-ISSN: 2548-3013
Journal homepage: https://journal.uinjkt.ac.id/index.php/valensi
Research Article

Modification of NiW/Al_2O_3 Bimetallic Catalysts by ZSM-5, HY Zeolite, and Amorphous Silica Additions for Heavy Gas Oil (HGO) Hydrotreating

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Article Info
Received: Dec 16, 2025
Revised: Marc 19, 2026
Accepted: Apr 06, 2026
Online: May 31, 2026

Citation:
Sarwan, Aziz, I., Rustyawan, W., Hanief, H., Nurhasni, Nurbayti, S., Azizah, Y. N. (2026). Modification of NiW/Al_2O_3 Bimetallic Catalysts by ZSM-5, HY Zeolite, and Amorphous Silica Additions for Heavy Gas Oil (HGO) Hydrotreating. *Jurnal Kimia Valensi*, 12(1), 26-34.

Doi: 10.15408/jkv.v12i1.49693

Abstract

The NiW/γ-Al_2O_3 bimetallic catalyst is widely used in the hydrotreating of heavy gas oil (HGO) fractions to remove impurities, particularly sulfur-containing compounds (hydrodesulfurization, HDS) and polycyclic aromatic hydrocarbons (hydrodearomatization, HDA). The incorporation of additives into the alumina support can enhance catalytic activity by increasing surface acidity and improving textural properties. This study aims to synthesize, characterize, and evaluate the performance of NiW/γ-Al_2O_3 catalysts modified with zeolitic (ZSM-5 and HY zeolite) and amorphous silica additives on HDS and HDA of HGO. Catalysts were prepared via the wet impregnation method using supports containing 3 wt% additive. Among the synthesized materials, the NiW/γ-Al_2O_3 catalyst incorporating ZSM-5 exhibited the highest crystallinity, with metal loadings of 4.960 wt% Ni and 16.269 wt% W. This catalyst showed a surface area of 153.415 m^2/g, a pore diameter of 116.643 Å, and a total acidity of 0.496 mmol/g. Hydrotreating evaluation demonstrated that the ZSM-5–modified NiW/γ-Al_2O_3 catalyst yielded a product with 4.50 ppm sulfur (99.96% HDS conversion) and 10.66% aromatics (54.10% HDA conversion) at 360 °C.

Keywords: Additive, hydrotreating, hydrodesulfurization, heavy gas oil, NiW/γ-Al_2O_3

1. INTRODUCTION

Heavy Gas Oil (HGO) is a by-product of petroleum processing that is utilised as a fuel for diesel engines. The ignition quality of diesel fuel is significantly influenced by its sulfur and aromatic content. It has been demonstrated that elevated levels of sulfur and polyaromatic hydrocarbons (PAHs) result in the emission of particulate matter containing SO_x. In addition, these compounds can reduce the efficiency of diesel combustion. Therefore, diesel fuel with low sulfur and aromatic content is required. According to Euro V standards, the required sulfur content is less than 10 ppm, and the aromatic content is less than 11% [1,2]. This fuel can be obtained through hydrotreating, such as hydrodesulfurization (HDS) and hydrodearomatization (HDA) reactions. HDS is a reaction that removes sulfur from compounds using hydrogen gas, whereas hydrodearomatization (HDA) is the removal of aromatic compounds [3].

Hydrotreating requires catalysts that can accelerate the HDS and HDA processes. Some of the catalysts that have been used include NiMo/ALOOH [4], CoMo/γ-Al_2O_3 [5], dan NiW/γ-Al_2O_3 [6]. Among these catalysts, Ni-W has an excellent ability to reduce sulfur (HDS) and aromatics (HDA) in petroleum raw materials. The Ni-W metal forms the Ni_3S_2–WS_2 pair, which is more reactive than the Ni_3S_2–MoS_2 pair. Tungsten (W) metal has a higher coefficient of thermal expansion than molybdenum, making it more thermally stable. The empty d orbitals of W are expected to bond with hydrogen and break double bonds. This means that tungsten metal acts as an active site provider in the catalyst, making the catalyst more acidic than Mo and more durable during the hydrodesulfurization and hydrodearomatization processes in the reactor. It also has increased catalyst temperature stability of >800 °C [7]. Nickel (Ni) metal, on the other hand, has the ability to break C-C and C-H bonds more effectively than cobalt (Co) due to its

face-centred cubic crystal structure. According to Fang et al [8], the optimal concentration ratio of Ni-W metal is 6–7% and 20–35.9%, respectively. This is because the NiW/γ-Al_2O_3 catalyst produced at these concentrations has the largest surface area (133.4 m^2/g), sufficient acidity, and high HDS (99.9%) and HDA (59.5%) abilities, as well as good impregnation stability [8].

During the hydrotreating process using conventional alumina-supported catalysts, polyaromatic compounds are also completely hydrogenated into saturated hydrocarbons, and the removal of sulfur and nitrogen compounds results in high hydrogen consumption [9]. Additionally, the hydrotreating process requires a large catalyst pore size to enhance reactant diffusion. Therefore, it is necessary to develop a specialized catalyst with high HDS activity and control the HDA activity that converts only polyaromatic compounds into monoaromatic compounds. Modifying the alumina support by adding additives such as HY zeolite and ZSM-5 can enhance the hydrotreating reaction [10].

The acid sites of these additives are used as additional active sites for hydrogenation and dehydrogenation reactions. Zeolite and amorphous silica can affect the properties of alumina, such as changing the surface area and increasing the acidity, because they are able to add Lewis and Brønsted acid sites. Lewis acid is required in the HDS process because it acts as an electron acceptor, attracting sulfur groups, while Brønsted acid functions in breaking double bonds in the HDA process [8,11]. According to Rahma, 3% addition of zeolite and amorphous silica to γ-Al_2O_3 support can increase the acidity up to 9.25%, which is sufficient for the HDS process. The limit of total acidity for the HDS and HDA processes to occur is 0.502 mmol/g [12].

This study will examine the impact of incorporating zeolite and silica additives into the synthesis of alumina supports on the catalyst's characteristics and activity. The resulting catalyst will be tested for various characteristics, including crystallinity using X-ray diffraction (XRD), elemental composition using X-ray fluorescence (XRF), total acidity using temperature-programmed desorption (TPD), and surface area using a surface area analyser (SAA). The catalyst with the best characteristics (large pore size) was then tested for activity in HDS and HDA of the HGO process by varying the reaction temperature to 320, 340 and 360 °C.

2. RESEARCH METHODS

Materials and Tools

The materials used in this study were Boehmite (AlOOH, USA), ammonium hydroxide (NH_4OH, pro analysis grade, Merck), nitric acid (HNO_3, pro analysis grade, Merck), nickel nitrate hexahydrate ($NiNO_3.6H_2O$, pro analysis grade, Sigma-Aldrich), ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$, pro analysis grade, Sigma-Aldrich), ZSM-5 (Zeolytst Internasional), HY zeolite, (Zeolytst Internasional) and amorphous silica (cabosil, high purity 96-99,8%).The instruments used in this study were Surface Area Analyzer (micromeritics ASAP 2400), degasser machine, X-ray Diffraction (Empyrean PANalytical), X-ray Flourescence (PANalytical), Temperature Programmed Desorption (Quantachrome TPRWin v4.0), Furnace (KSL-1100x), Pilot Plant NX1 reactor, densitymeter (VIDA), and hydraulic machine.

Synthesis of γ-Al_2O_3 Support [13]

A total of 100 g of boehmite (AlOOH) was mixed with 32 mL of distilled water in a bowl. Then, 68 mL of 4% HNO_3 and 10 mL of 24% NH_4OH were added and the mixture stirred for 15 minutes and 2 minutes, respectively until homogeneous. The mixture was then moulded using a hydraulic press and subsequently calcined at 550 °C for 5 hours.

Synthesis of γ-Al_2O_3 Support with Additives [14]

Using the previous method, a homogeneous boehmite mixture was prepared in the same ratio. Then, the mixture was moulded and calcined at 550 °C for 5 hours after the addition of 3% ZSM-5, HY zeolite and amorphous silica additives.

Synthesis of NiW/γ-Al_2O_3 Catalyst [13]

A total of 32 g of nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$) was dissolved in 100 mL of distilled water. Then, 30 g of $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$ was added to the solution and stirred until was homogeneous. The pre-formed support was placed in the solution and stirred until completely mixed, dried at 120 °C for two hours, and calcined at 450 °C for 3 hours.

Catalyst Characterization

To analyse the diffraction pattern and crystallinity of the catalyst, an X-ray diffraction (XRD) instrument (ASTM D3906-03, ASTM D5758-01) was used. Analysis was performed using Cu radiation at a voltage of 40 kV and a current of 35 mA, with a 2θ measurement distance of 5–90°. The crystal size of the catalyst is determined the Debye-Scherrer equation (Equation 1).

$$D = \frac{K\gamma}{\beta.cos\theta} \quad \text{.....(1)}$$

Where:
D = crystal size, B = FWHM value,
θ = Bragg angle, **λ** = wavelength of X-ray light
K = constant shape factor (0.8-1)

X-ray fluorescence (XRF) was used to analyse the elemental composition of the catalyst. The ground catalyst was placed in an aluminium container and compacted using a press. The sample was analysed at 40 kV and 45 mA using a quantitative analysis programme (ASTM D7343). Sample acidity analysis was carried out using Chemisorb 2750 Temperature Programme Desorption (TPD-NH_3) and TPx System tools (ASTM D4824-13). The sample tube was cleaned, filled with sufficient glass wool, and weighed to determine its empty weight. Up to 0.102 g of the sample was inserted into the tube and installed on the device. Degassing was carried out by flowing helium gas at a temperature of 300 °C for 1 h, followed by flowing NH_3 gas at room temperature for 1 h. The helium gas was then reflowed at an increased temperature of 800 °C.

Analysis of the surface area, pore diameter and pore volume was performed using the ASAP 2400 tool (ASTM D3663, ASTM D4641 and ASTM D4222). The sample tube containing the filler was closed and weighed to determine the empty weight. 0.2 g of the sample was placed in the tube and installed in the degasser port. Degassing is carried out at 100 °C for 1 hour in a slow vacuum state. After this, the temperature is raised to 300 °C for 5 hours in a fast vacuum state. Once degassing is complete, the tube is weighed again to determine the mass after degassing. Helium gas is fed into the sample port and nitrogen gas is used in a vacuum to analyse it until N_2 adsorption-desorption isotherm curves are obtained. These curves can be used to determine the surface area (m^2/g), pore volume (cm^3/g) and pore diameter (Å).

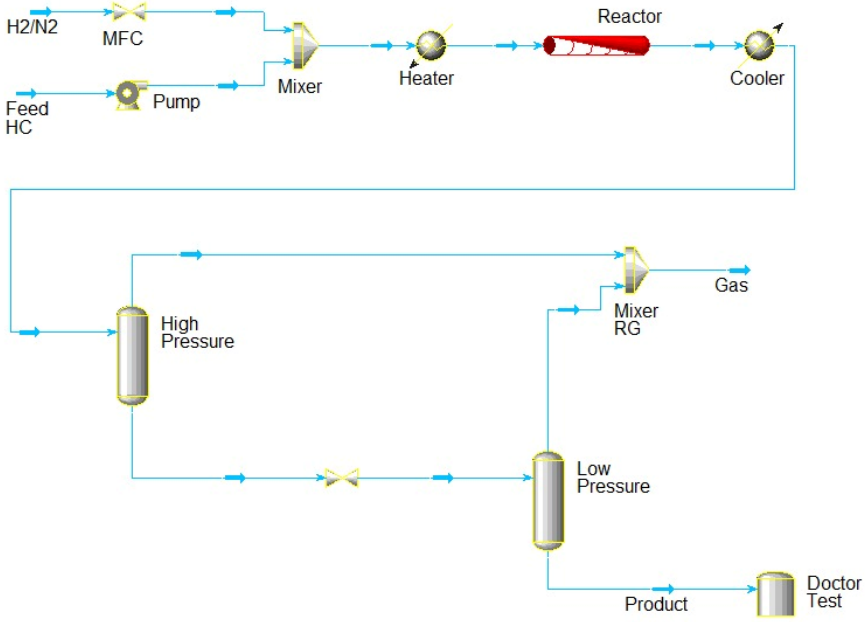

Figure 1. Working scheme of NX1 pilot plant reactor (Pertamina) [14]

Catalyst Activity Test

A series of hydrotreating processes are carried out in several stages: preparation, catalyst activation, and hydrotreating, which includes hydrodesulfurisation and hydrodearomatisation. These processes are carried out in the New Xytel 1 (NX1) Pilot Plant reactor, as shown in **Figure 1**. The line and reactor were purged of oxygen using streams of nitrogen and hydrogen gas. The catalyst was activated via sulfidation by flowing a mixture of hydrogen gas and dimethyl disulfide (DMDS) in naphtha. This process converts the catalyst from an inactive oxide form to an active metal form. The HGO feed (sulfur content 22,053,600 ppm) was introduced at an LHSV of 0.5, at a pressure of 100 bar and with an H_2/HC ratio of 320. The temperature varied between 320 and 360 °C.

Product Quality Analysis

The XRF instrument (ASTM D7343-07) was used to analyse the sulfur levels in the product after hydrotreating. A total of 5 g of the product solution was analysed every 20 minutes using the SuperQ Manager programme until the ppm of sulfur was obtained. The HDS reaction conversion is calculated using Equation (2). To test the product density, a density meter that had been optimised using toluene (ASTM D4052-96) was employed. An aniline point analysis was performed by adding 10 ml of aniline and the product to an aniline point tester tube (ASTM D611).

Meanwhile, the number of aromatics in the diesel product is determined by the presence of density and AP values. The density value was measured at 15 °C, with the diesel AP value measured in the range of 70–85 °C. The aromatic content is based on the percentage of aromatic carbon, as shown in equations (3) and (4), where A is aromaticity (%), H is hydrogen weight (%), SG15 is specific gravity at 15 °C, and AP is aniline point temperature (K)[15]. The HDA reaction conversion is calculated based on Equation (5).

$$\text{HDS conversion} = \frac{\text{Sulfur content in HGO (ppm)}}{\text{Sulfur content after reaction (ppm)}} \text{ x } 100\% \quad (2)$$

$$\%\,H = 11.17 - 12.89\,SG_{15} + 0.0389\,AP \quad (3)$$

$$\%\,A = 233.54 - 15.67\,\%H \quad (4)$$

$$HDA\ conversion = \frac{PAH\ content\ in\ HGO\ (\%)}{PAH\ content\ after\ reaction\ (\%)}\ x\ 100\% \quad (5)$$

3. RESULTS AND DISCUSSION

The synthesis of γ-Al_2O_3 using the sol-gel method begins with the dissolution of boehmite in distilled water to produce aluminium hydroxide. Adding nitric acid triggers the formation of crystal nuclei (nucleation) in the sol-gel phase, resulting in small, homogeneous crystals. Aluminium hydroxide powder is obtained by adding NH_4OH to the sol-gel solid. Equations i-v explain the reaction for the formation of γ-Al_2O_3.

$$AlOOH_{(s)} + H_2O_{(aq)} \rightarrow AlOOH.H_2O_{(s)} \quad (i)$$

$$AlOOH.H_2O_{(s)} + 3HNO_{3\,(aq)} \rightarrow Al(NO_3)_{3\,(s)} + 3H_2O_{(aq)} \quad (ii)$$

$$Al(NO_3)_{3\,(s)} + 3NH_4OH_{(aq)} \rightarrow Al(OH)_{3\,(s)} + 3NH_4NO_{3\,(aq)} \quad (iii)$$

$$NH_4NO_{3\,(aq)} \rightarrow NH_4NO_{3\,(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(g)} \quad (iv)$$

$$2Al(OH)_{3\,(s)} \rightarrow Al_2O_{3\,(s)} + 3H_2O_{(g)} \quad (v)$$

The aim of calcination is to decompose impurities bound to the crystal structure in the form of volatile gases, such as nitrous oxide and water. In this study, calcination was carried out at 550 °C for 3–5 hours, with the temperature being increased gradually, in order to form oxides and increase the physical strength of the catalyst [16]. The release of the -OH group to H_2O on the aluminium atom causes the aluminium atom to act as a Lewis acid, accompanied by a change in structure from octahedral to tetrahedral, as seen in **Figure 2**.

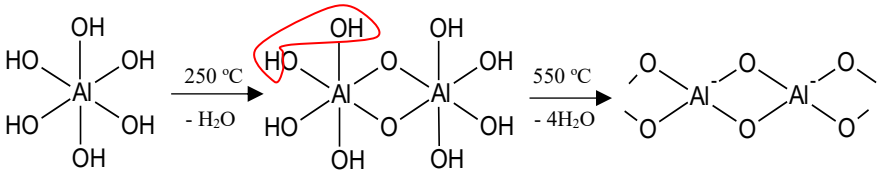

Figure 2. The process of changing the structure from octahedral aluminium to aluminium tetrahedral during calcination [16]

γ-Al_2O_3 modified with zeolite and silica, with NiW metal impregnated onto its surface, is then calcined which makes the dispersion of the active metals on the support surface more even. The formation of the WO_4^{2-} anion, which interacts weakly with Al_2O_3, causes fast transport of W in the support pore and an even distribution of the WO_4^{2-} anion on the support surface, resulting in higher catalyst activity. However, if the $W_6O_{21}^{6-}$ anion is formed, it interacts strongly with the positively charged Al_2O_3. This results in the slow transport of W along the support pore because the $W_6O_{21}^{6-}$ molecule is quite large. The synthesised catalyst is then characterised to determine its crystallinity, active metal composition, surface area, and total acidity [17].

Catalyst characteristics

This study involved analysing the crystal phase of γ-Al_2O_3 and NiW/γ-Al_2O_3 catalysts containing ZSM-5, HY zeolite and amorphous silica additives using XRD instruments. The main peaks in the diffractogram of γ-alumina appear at diffraction angles of 40–50° and 60–70°, as referred to ICDD No. 98-009-9836, the diffraction pattern of γ-Al_2O_3 appeared at 2θ angles of: 39.52°; 45.38°; and 67.37°. As shown in **Figure 3**, the addition of additives to the catalyst reduces the intensity of the γ-Al_2O_3 peak, which indirectly increased the amorphous phase of alumina in the 2θ of 10–40°. The catalyst containing ZSM-5 additives exhibits intensity in the diffraction pattern at 2θ: 7.83°; 9.37°; 11.07°; 13.22°; 15.9°; 23.04°; 23.91°; 24.37°; 29.5° and 45.6°, as determined by ICDD No. 98-006-1010. According to Tye [18], the higher the crystallinity of the catalyst, the higher the acidity of the catalyst due to the addition of acid sites.

Based on **Table 1**, it is known that the smaller FWHM (Full Width at Half Maximum) value indicates a larger crystal size. The crystal size of the catalyst NiW/γ-Al_2O_3-ZSM-5 is the smallest, due to its highest diffraction peak. Smaller crystal sizes provide a greater number of active sites, ensuring an even distribution of atoms on the surface [19]. The peak of NiO was detected based on ICDD no. 00-004-0850, with Face Centered Cubic (FCC) crystal structure that formed at 2θ 37.21 °, 43.23 °, and 62.75°. The absence of tungsten peaks in its oxide form indicates that the metal is largely evenly dispersed in its support, and reduces agglomeration [8].

It has been observed that the surface area of synthesized catalysts decreases following the

deposition of NiW and zeolite/silica additives. The surface area of the synthesis catalyst was found to have reduced by 33.6%, due to the active metal covering its surface. As shown in **Table 2**, the average pore volume and diameter of the oxide phase catalysts are reduced in comparison to alumina supports, with the exception of ZSM-5. Nevertheless, the surface area, pore volume and pore diameter of the synthesis catalyst are preferable to the reference catalyst. The addition of amorphous silica additives results in the highest surface area of all synthesised catalysts: up to 164.149 m²/g. This can be advantageous due to the large contact area between the catalyst and reactant molecules. However, the pore size of the amorphous silica additive (86.817 Å) is smaller than that of the catalyst containing the ZSM-5 additive (116.643 Å). Larger pore sizes facilitate the diffusion of long-chain hydrocarbon molecules into the pores. In addition to reducing the percentage of aromatics, the catalyst is expected to have a longer lifespan due to the minimal diffusion barriers for large molecules.

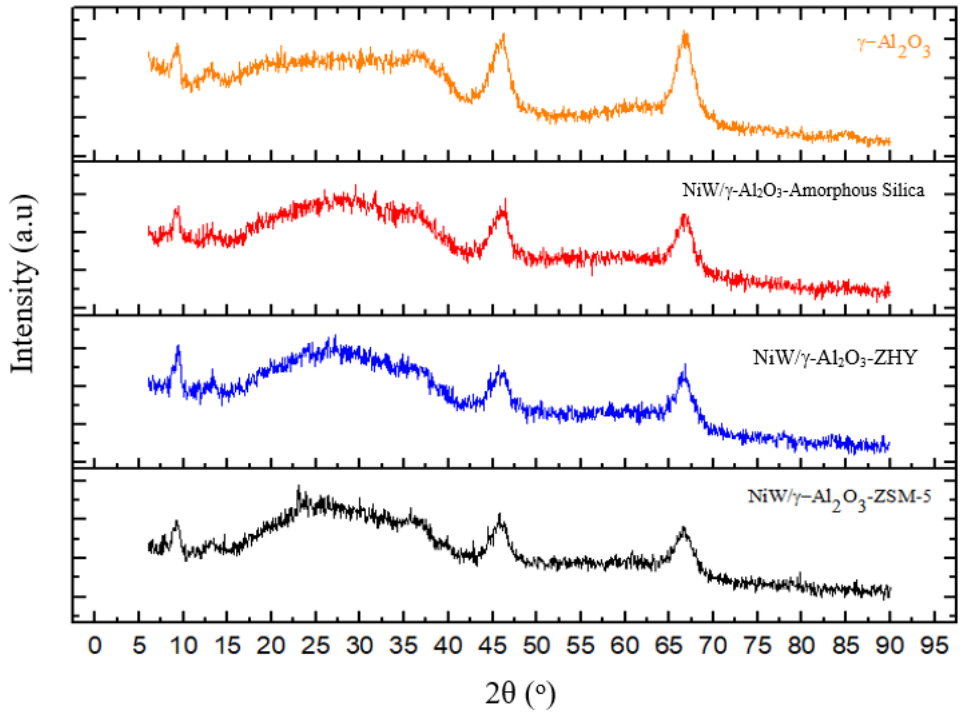

Figure 3. XRD pattern for support and catalysts NiW/γ-Al_2O_3

Table 1. Crystal size of catalysts

Sample	2θ (°)	FWHM (rad)	D (nm)
γ-Al_2O_3 standar	45.211	3.091 x 10^{-3}	50.937
NiW/γ-Al_2O_3-ZSM-5	45.748	4.122 x 10^{-3}	38.135
NiW/γ-Al_2O_3-ZHY	45.546	3.091 x 10^{-3}	50.812
NiW/γ-Al_2O_3-Amorphous Silica	46.042	0.785 x 10^{-3}	200.341

Table 2. Physical and chemical properties of the catalysts and support

Catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (Å)	Ni (%)	W (%)	Atomic Ratio	Acid Site Strength (mmol/g)		
							Weak	Medium	Strong
γ-Al_2O_3	231.080	0.580	100.430	-	-	-	0.106	0.315	-
Reference catalyst	119.040	0.140	46.620	3.807	15.699	0.195	-	-	-
NiW/γ-Al_2O_3-ZSM-5	153.415	0.425	116.643	4.960	16.269	0.234	0.317	-	0.179
NiW/γ-Al_2O_3-HY-zeolite	149.247	0.434	76.721	5.071	16.638	0.234	0.302	-	0.135
NiW/γ-Al_2O_3-Amorphous Silica	164.149	0.452	86.817	4.629	15.428	0.231	0.317	-	0.203

Ni-W metal composition of 4.960% (Ni) and 16.269% (W), with an atomic ratio of Ni/(Ni + W) 0.4885. Each catalyst was analysed using XRF to determine the levels of nickel (Ni) and tungsten (W) that had been successfully deposited on the support surface. These values used to determine the atomic ratio of the catalyst and its elemental composition, which was found to be 6% Ni and 20% W. Based on **Table 2**, the atomic ratios in descending order were found to be: NiW/γ-Al_2O_3-ZSM-5 > NiW/γ-Al_2O_3-HY zeolite > NiW/γ-Al_2O_3-Amorphous Silica > Reference. In addition, based on previous research, the size of the metal molecules, the impregnant solution atmosphere, and the metal distribution process in the support affect the levels of impregnated metals in the catalyst[8]. The atomic ratio of synthesis catalysts is slightly greater than that of reference catalysts. This ratio is within the maximum range for HDA reactions (0.2–0.3).

Based on the acidity value, there are more Brønsted acid sites (weak acids) than Lewis acid sites (strong acids) on each catalyst. Brønsted acids play a role in the process of carbocation formation for the HDA reaction. The catalyst with the highest number of Brønsted acid sites is the NiW/γ-Al_2O_3-ZSM-5 catalyst, while the catalyst with the highest number of Lewis acid sites is NiW/γ-Al_2O_3-Amorphous Silica. Lewis acids are useful as electron acceptors and have the ability to remove sulfur (HDS). Additionally, each catalyst had more Brønsted acid sites than Lewis acid sites. Based on this analysis, NiW/γ-Al_2O_3-ZSM-5 catalysts are most suitable for HDS and HDA reactions. This is because the total acidity of the NiW/γ-Al_2O_3-ZSM-5 catalyst does not exceed the limit of 0.502 mmol/g [8,20].

Catalyst Activity Test Results

Based on the results of the characterisation, the NiW/γ-Al_2O_3-ZSM-5 catalyst is used for the activity tests in the HDS and HDA processes for the HGO fraction because it has a large pore diameter and suitable acidity. As can be seen from **Table 3**, higher temperatures and greater conversions were obtained under optimal reaction conditions for the HDS and HDA HGO fractions to meet Euro V standards, at an LHSV of 0.5 h^{-1} and a temperature of 360 °C, with conversions of 99.958% and 54.097% for HDS and HDA, respectively.

Based on Euro V standards, the maximum allowable amounts of aromatics and sulfur are 11% and 10 ppm, respectively, for ULSD catalysts. The amount of sulfur and aromatics decreases as the temperature increases. An increase in reaction temperature increases the availability of energy for contact with reactant molecules. This contact increases the number of reactant collisions on the catalyst surface and accelerates the reaction of double bond breaking and sulfur removal.

The hydrodesulfurization (HDS) and HDA processes of dibenzothiophene (DBT) compounds begin with the interaction between hydrogen and the benzene ring with the active sites of the NiW catalyst. This interaction results in the formation of two adsorbed hydrogen atoms, where the benzene ring is then adsorbed at two active sites through the formation of C-Ni and C-W bonds, resulting in the opening of the double bond. The d orbitals of the active Ni-W metal are not fully occupied, so the adjacent d and s orbitals degenerate to the same energy level. This degenerate state increases the probability of the electron orbitals providing Lewis acid sites capable of adsorbing the feedstock onto the metal catalyst surface. Meanwhile, ZSM-5, as an additive, contributes both Lewis acid and Brønsted acid sites. The Brønsted acid sites play a role in forming carbocations that break the double bonds in aromatic compounds.

Table 3. Catalytic properties of NiW/γ-Al_2O_3 catalyst in hydrotreating HGO

Sample	Temperature (ºC)	Compounds in Hydrotreating Process		Conversion Capabilities (%)	
		Sulfur (ppm)	PAH (%)	HDS	HDA
Feed HGO	-	22,053.600	23.233	-	-
Product	320	3,514.125	17.804	84.07	23.37
	340	619.950	14.058	97.19	39.49
	360	4.500	10.665	99.96	54.10

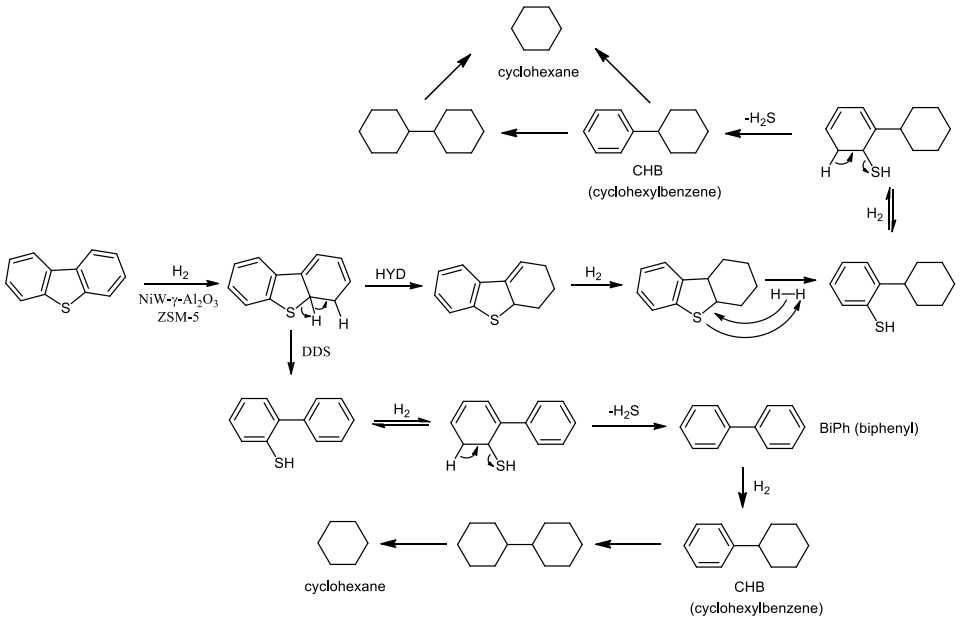

Figure 4. HDS and HDA mechanisms from DBT (sulfur modeling inside PAH) [21]

Table 4. Comparison of the NiW/-ZSM-5 catalyst with other catalysts

Catalyst	Process	Sulfur model compound	Conversion HDS	Conversion HDA	Reference
NiW/γ- Al_2O_3-ZSM-5	HDS and HDA	HGO, 22,053.6 ppm S, 23.2 PAH	99.97	54.10	This work
ZFMoCo	HDS, pressure 55 bar, temperature 300 °C and catalyst (0.6 g)	DBT, initial concentration of 550 S-ppm	98	-	[25]
CoMo/Ti-SBA-15	HDS and HAD, temperature 320 C, pressure 5 MPa, WHSV 39 h−1	4,6-DMDBT and Phenanthrene	71.7	49	[9]
Fe-Co/ZSM-5	Oxidative Desulfurization (ODS), temperature 45 oC, time 45 minutes, catalyst 0.2 g	Dibenzothiophene (DBT), 500 ppm	37.13	-	[26]

The DBT hydrodesulfurization (HDS) and hydrodearomatization (HDA) mechanisms proceed via two main pathways: the direct desulfurization (DDS) pathway and the hydrogenation (HYD) pathway (**Figure 4**)**.** In the DDS pathway, one of the bonds between a carbon (C) and sulfur (S) atom is broken, producing a biphenyl compound with a thiol group (-SH) on one side. After partial hydrogenation, this group is released as H_2S, resulting in the formation of biphenyl (BiPh). If the hydrogenation reaction continues, one of the rings in the biphenyl will become saturated and form cyclohexylbenzene (CHB). The final stage of this pathway is the total hydrogenation of CHB, accompanied by the breaking of the C-C bond to produce the final product, cyclohexane. On the other hand, the HYD pathway begins with hydrogenation until one of the benzene rings in DBT becomes saturated. This saturated state weakens the C–S bond, making it easier for hydrogen to break it. The breaking of this C-S bond produces a thiol group (-SH), which if it reacts further with hydrogen, will be released as H_2S gas and form the CHB compound. Just

like in the previous pathway, the resulting cyclohexylbenzene (CHB) will undergo further hydrogenation and C-C bond cleavage to produce the final product, cyclohexane.

Activation by the sulfuring method produces the active species NiWS, NiS, Ni^{2+}, WS_2, WS_xO_y and W^{6+}[8]. In the calcination process, WO_3, WO_4 or $Al_2(WO_4)_3$ can form, and if these are activated through sulfidation, they form the active phase WS_2 [21,22], as shown in equation vi-vii.

$$3WO_3 + Al_2O_3 \rightarrow Al_2(WO_4)_3 \quad \text{(vi)}$$

$$3WO_3 + 6H_2S + 3H_2 \rightarrow 3WS_2 + 9H_2O \quad \text{(vii)}$$

These active phases facilitate sulfur adsorption through the formation of Ni and W cationic sites. Due to the greater availability of vacant d-orbitals, tungsten (W) plays a more significant role in the desulfurization process compared to nickel (Ni). Tungsten primarily contributes to the weakening of the C–S bond in thiophene, while nickel promotes the activation and cleavage of the C=C bonds within the thiophene ring.

The reaction mechanisms of hydrodesulfurization (HDS) and hydrodearomatization (HDA) over NiW/γ-Al_2O_3 catalysts in the heavy gas oil (HGO) fraction remain unclear, particularly regarding whether the process predominantly follows the hydrogenation (HYD) or direct desulfurization (DDS) pathway. The competition between HYD and DDS routes is influenced by the electronic structure and composition of the sulfur-containing compounds analyzed [23]. Although NiMo and CoMo catalysts are widely recognized for their high HDS activity, NiW-based catalysts are often preferred due to their ability to achieve nearly complete desulfurization.

Hur et al [24] reported that the use of the NiWS catalyst could only achieve a 86.5% sulfur reduction, whereas the addition of additives to the NiW catalyst in this study enabled a 99.958% sulfur removal. However, improvements are still needed to optimize the HDA process. **Table 4** presents a comparison of the performance of this catalyst with that of other reported systems [9,25,26]. The NiW/ZSM-5 catalyst exhibited superior activity in both hydrodesulfurization (HDS) and hydrodearomatization (HDA) processes. Compared to oxidative desulfurization (ODS) [24], this catalyst also demonstrated enhanced performance, although it operates under relatively higher temperature and pressure conditions than those typically required for ODS.

4. CONCLUSIONS

The best catalyst obtained was the NiW/γ-Al_2O_3 with 3% ZSM-5 additive, which had the best crystallinity and crystal size. It had a sufficient Ni-W metal composition of 4.960% (Ni) and 16.269% (W). It also had a surface area and pore diameter of 153.415 m^2/g and 116.643 Å, respectively. The NiW/γ-Al_2O_3-ZSM-5 catalyst exhibits maximum HDA and HDS activity, meeting Euro V standards at 360 °C with sulfur and aromatic content of 4.50 ppm and 10.655%, respectively.

ACKNOWLEDGMENTS

The authors acknowledge Technology Innovation & Implementation PT Pertamina for supporting this research project.

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