Synthesis, Characterization, and Hydrotreating Activity of NiW Presulfurized Catalysts Prepared via a Tetrathiotungstate-Intercalated NiAl LDH

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ABSTRACT: A tetrathiotungstate-intercalated NiAl layered double hydroxide (LDH) was synthesized and then calcined under N₂ at various temperatures to prepare a series of NiW presulfurized hydrotreating catalysts. Upon calcination, WS₄²⁻ in the interlayer decomposes into WS₃ and then WS₂, releasing sulfur to sulfurize nickel in the sheets. The property and activities of catalysts for hydrosulfurization (HDS) of dibenzothiophene and hydrodearomatization (HDA) of tetralin are dependent on the calcination temperature. At 300 °C, WS₃ can be well maintained, offering highly active hydrogenation sites S₂²⁻ and superior HDA activity. As the temperature increases up to 500 °C, WS₃ converts into WS₂, while nickel sulfides migrate to the edge of WS₂ to form NiWS phases with high HDS activity. LDH-based presulfurized catalysts can achieve fully sulfurized and well-dispersed tungsten species even at high tungsten loadings and can retain more WS₃ even at high temperatures because of the peculiar properties of LDHs. Therefore, they show better HDS and superior HDA activities over an oxidic NiW LDH-based catalyst (LDO) and an alumina-supported NiWS presulfurized catalyst (NiWS/Al₂O₃). The optimized catalyst shows 1.59 and 1.05 times higher HDS activity than LDO and NiWS/Al₂O₃ while 2.05 and 1.77 times higher HDA activity than LDO and NiWS/Al₂O₃, respectively. It also shows better HDS and HDA activity for a real diesel than a NiCoMoW/Al₂O₃ commercial catalyst.

1. INTRODUCTION

Recent 20 years have witnessed ever-stringent emission regulations of vehicles, forcing refineries to further reduce sulfur and polyaromatic contents of the diesel fuel. Hydrotreating over transition-metal sulfide catalysts is a major technique to reduce sulfur and polyaromatics in diesel. To fulfill the stricter quality standards of diesel, it is necessary to advance the activity of hydrotreating catalysts, particularly the hydrogenation (HYD) activity because upgrading of diesel mostly focuses on hydrodearomatization (HDA) nowadays in China.

Hydrotreating catalysts generally consist of tungsten or molybdenum sulfides promoted with nickel or cobalt. The most widely used approach to prepare hydrotreating catalysts starts from oxidative metal sulfates, which have to be sulfurized with sulfurizing agents under 3–8 MPa at 300–400 °C for a long duration of more than 24 h. This process suffers from high cost, time consumption, and toxic sulfurizing agents. Moreover, oxidative catalysts are hard to be fully sulfurized under industrial conditions, especially tungsten, which needs to be sulfurized above 650 °C for complete sulfidation because of the stronger W–O bond than Mo–O.¹

Recently, the preparation of hydrotreating catalysts in the sulfuric form, that is, presulfurized catalysts, has been of interest to researchers.²,³ It could overcome the disadvantages of oxidative hydrotreating catalysts.⁴,⁵ Unsupported bulk MoS₂, WS₂, CoMoS, and NiMoS presulfurized catalysts have been synthesized by various methods including the decomposition of thiosalts⁶,⁷ and the hydrothermal route.⁸ However, bulk catalysts normally suffer from high metal content, poor activity per metal atom, low specific surface area, and dispersion.⁹,¹⁰ Supported presulfurized catalysts are normally prepared via impregnation of thiosalts onto various porous supports such as SBA-15,¹¹ Al₂O₃,¹² carbon fiber,¹³ and N-doped mesoporous carbon.¹⁴ However, the active Mo or W metal contents of supported catalysts might still be maintained at a low level in order to achieve high dispersion.¹⁵

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Layered double hydroxides (LDHs) are anionic lamellar clays, which could be represented by the formula $[\text{M}^{2+}\text{x}^{2}\text{M}^{3+}\text{(OH)}_{2}]^{y}\text{A}^{z-}\text{nH}_{2}\text{O}$, where $\text{M}^{2+}$ and $\text{M}^{3+}$ are divalent and trivalent metal cations in host layers, respectively, $\text{A}^{z-}$ is interlayer guest anion, and $x$ is the ratio of $\text{M}^{3+}/(\text{M}^{3+} + \text{M}^{2+})$. The versatility of metal cations in the sheets and exchangeability of anions in the interlayer result in a huge variety of host–guest assemblies and nanoarchitectures with tunable physical and chemical properties. Therefore, LDHs have been applied in heterogeneous catalysis as catalysts, catalyst precursors, and catalyst supports. In the past decade, molybdate or tungstate anions are intercalated into the interlayer of nickel or cobalt cations are incorporated onto the sheets of LDHs, acting as catalyst precursors or catalysts for hydrotreating. Li’s group prepared hydrodesulfurization (HDS) catalysts derived from $(\text{MoO}_{3})^{6-}$ and $(\text{H}_{2}\text{W}_{2}\text{O}_{13})^{6-}$-intercalated NiAl and NiZnAl LDHs. Faro’s group introduced $(\text{MoO}_{3})^{6-}$ and/or $(\text{H}_{2}\text{W}_{2}\text{O}_{13})^{6-}$ into the interlayer of NiAl and CoMgAl LDHs as precursors of dibenzothiophene (DBT) HDS catalysts. Our group synthesized $(\text{WO}_{4})^{2-}$-intercalated NiAl and NiAlZr LDHs as precursors to prepare catalysts for HDS of DBT and diesel. Researchers revealed that the hydrotreating catalysts from LDHs might combine the advantages of bulk and supported catalysts because of the easiness of preparation and distinctive properties such as large surface area, well-dispersed active metal species even at high loadings, good thermal stability, and mechanical strength.

However, most LDH-based hydrotreating catalysts are prepared in the oxidic form, which need to be sulfurized prior to reactions. Thiometallate anions can be intercalated into the interlayer of LDHs. Most recently, thiomolybdate-intercalated MgAl, MgAlFe, MgMnAl, and CoFe LDHs were synthesized as adsorbents to remove heavy metal ions from wastewater or fuel gas. Therefore, an idea is generated to prepare presulfurized hydrotreating catalysts based on thiomolybdate- or thiotungstate-intercalated LDHs, which could take advantages of the favorable characteristics of LDHs to solve the problems of bulk and supported presulfurized catalysts. In our previous study, a thiotrienediyldicarboxylate-intercalated NiAl LDH was synthesized as a precursor and calcined at various temperatures to prepare a series of presulfurized catalysts with high HDS activity and superior HDA activity. It is generally accepted that tungsten-based hydrotreating catalysts have better HYD activity than Mo-based catalysts because of the modifier ability of tungsten sulfides to lose sulfur ions under $\text{H}_{2}$ and thus are easier to form anion vacancies as active sites when compared to molybdenum sulfides. However, tungsten oxides are much more difficult to be sulfurized than molybdenum oxides, which limit the application of tungsten-based hydrotreating catalysts. In the present investigation, a novel thiotungstate-intercalated NiAl LDH is synthesized as a precursor and calcined at various temperatures to prepare a series LDH-based NiW presulfurized hydrotreating catalysts. The properties of the LDH and catalysts are characterized. Their HDS activity for DBT and HDA activity for tetralin (THN) are evaluated. The effects of calcination temperature on the property and activity of catalysts are discussed. To the best of our knowledge, such thiotungstate LDH and its derivative hydrotreating catalysts have not been reported yet.

2. RESULTS AND DISCUSSION

2.1. Characterization of Tetrathiotungstate LDHs.

2.1.1. X-ray Diffraction. X-ray diffraction (XRD) patterns of the tetrathiotungstate NiAl LDH (NiAl–$\text{WS}_{4}$), nitrate NiAl LDH (NiAl–$\text{NO}_{3}$) and tungstate NiAl LDH (NiAl–$\text{WO}_{4}$) are shown in Figure 1. For NiAl–$\text{WS}_{4}$, a series of reflections at 8.5, 18.2, 27.8, 34.7, 36.9, and 61.5° are observed, which are assigned to the (003), (006), (009), (012), (015), and (110) crystal planes of LDHs, respectively. The basal distances of the (003), (006), and (009) crystal planes are 1.04 $(d_{003})$, 0.49 $(d_{006})$, and 0.34 $(d_{009})$ nm, respectively. They follow the relationship of $d_{003}/d_{006}/d_{009} = 6.3:2$, suggesting the ordered stacking of brucite-like layers. Compared to that of NiAl–$\text{NO}_{3}$, the (003) reflection of NiAl–$\text{WS}_{4}$ shifts toward lower 2$\theta$ angles, and $d_{003}$ increases from 0.89 to 1.04 nm because of the replacement of nitrate in the interlayer by bigger-sized $\text{WS}_{4}^{2-}$. The $d_{003}$ of NiAl–$\text{WS}_{4}$ is close to that of MoS$_{2}$-$^{2-}$-intercalated LDHs reported in the literature.

Figure 1. XRD patterns of (a) NiAl–$\text{WS}_{4}$, (b) NiAl–$\text{NO}_{3}$, and (c) NiAl–$\text{WO}_{4}$.
and 405 cm
attenuation in the interlayer, the two vibrations red-shift to 472 and attributed it to the interaction between MoS₄ symmetric stretching and M through H-bonding or the bridge structure. The bands of W vibrations of W and positively charged layers, and the barrier e...s. The decomposition and conversion of WS₃ into WS₂. The second step might be ascribed to the conversion of WS₃ into WS₂. The decomposition and conversion of WS₄ occur at higher temperatures than those of ATT. It may be associated to the formation of H-bonding between WS₄ and hydroxyl groups in sheets, the stronger Coulombic interaction between WS₄ and positively charged layers, and the barrier effect of LDH platelets, which may inhibit the emission of produced degradation gases and transmission of heat. The multistep thermal decompositions of WS₄ and LDHs are mixed together, resulting in the counteracting thermal behaviors; therefore, no obvious endothermal or exothermal peak is observed in the DSC curve of NiAlWS₄. NiAlLDH reported previously. In addition, the complete decomposition of NiAl–WS₄ occurs above 650 °C, which is close to that of a tetrathiomolybdate-intercalated MgAlFe LDH and CaAl LDH. It is noted that the mass loss of second steps for NiAl–WS₄ is much less than

100–300 °C accompanied by an endothermal peak centered around 255 °C is caused by the decomposition of ATT into amorphous WS₂. The other in 300–500 °C is due to the decomposition of WS₂ into crystalline WS₂, which is accompanied by an exothermal peak centered around 360 °C due to the crystallization of WS₂. The mass loss percentage is 18.7% for the first step and 8.7% for the second step. The main route of thermal decomposition of ATT in the inert gas can be represented by reactions 1 and 2. For NiAl–NO₃, the mass loss below 200 °C is attributed to the release of H₂O adsorbed on LDHs, while the mass loss centered around 340 °C is caused by the dehydroxylation of layers and the decomposition of nitrate in the interlayer. The mass loss of these two steps is 5.7 and 30.2%, respectively. For NiAl–WS₄, besides the mass loss (8.9%) below 250 °C attributed to water removal, the mass loss (10.8%) in 300–500 °C is composed of two steps with the maximum mass loss rate at 370 and 410 °C, respectively, as shown in the DTG curve. The first step could be ascribed to the dehydroxylation of layers and the decomposition of WS₄ into WS₃. The second step might be ascribed to the conversion of WS₃ into WS₂. The multistep thermal decompositions of WS₄ and LDHs are mixed together, resulting in the counteracting thermal behaviors; therefore, no obvious endothermal or exothermal peak is observed in the DSC curve of NiAl–WS₄. The decomposition behavior of NiAl–WS₄ is similar to that of a tetrathiomolybdate-intercalated NiAl LDH reported previously. In addition, the complete decomposition of NiAl–WS₄ occurs above 650 °C, which is close to that of a tetrathiomolybdate-intercalated MgAlFe LDH and CaAl LDH. It is noted that the mass loss of second steps for NiAl–WS₄ is much less than

496 cm⁻¹ could be assigned to M–O–M and M–O stretching in brucite-like sheets, respectively, while an intense band at 717 cm⁻¹ is assigned to the asymmetric stretching of NO₃. For ATT, an intense band at 481 cm⁻¹ and a weak band at 455 cm⁻¹ are assigned to the symmetric and asymmetric stretching vibrations of W–S in WS₄, respectively. After WS₂ being introduced in the interlayer, the two vibrations red-shift to 472 and 405 cm⁻¹, respectively. Ma et al. and Jawad et al. found the red shift of Mo–S vibrations in MoS₂-intercalated LDHs and attributed it to the interaction between MoS₂ layers and through H-bonding or the bridge structure. The bands of W–S symmetric stretching and M–O stretching in the sheets may overlap and thus lead to a broad band at 472 cm⁻¹. The weak band at 565 cm⁻¹ is attributed to the M–O–M stretching in brucite-like sheets of LDHs.

2.1.4. Thermogravimetry–Differential Scanning Calorimetry. Thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry (DSC) curves of NiAl–WS₄, NiAl–NO₃, and ATT are shown in Figure 4. The decomposition of ATT undergoes two primary steps. One in

Figure 2. FT-IR spectra of (a) NiAl–WS₄, (b) NiAl–NO₃, and (c) ATT.

Figure 3. Raman spectra of (a) NiAl–WS₄, (b) NiAl–NO₃, and (c) ATT.
that for NiAl—NO₃ because of the complete gasification of NO₃⁻.

2.2. Characterization of Presulfurized Catalysts. 2.2.1. XRD and Compositions. XRD patterns of presulfurized catalysts calcined at 300, 400, 500, and 600 °C (WLDS-300, WLDS-400, WLDS-500, and WLDS-600) are shown in Figure 5. WLDS-300 exhibits similar characters to NiAl—WS₄ (Figure 5).

Table 1. Composition and Textual Properties of the Presulfurized Catalysts

| Sample    | S   | Ni  | Al  | W   | Ni/W/S molar ratio | Specific surface area (m²g⁻¹) | Pore size (nm) | Pore volume (cm³g⁻¹) |
|-----------|-----|-----|-----|-----|-------------------|-------------------------------|-----------------|----------------------|
| NiAl—WS₄  | 15.5| 26.7| 6.4 | 22.3| Ni₅₋ₓWSₓₐₓ,ₚₓ     | 30.0                         | 3.74            | 0.08                 |
| WLDS-300  | 16.7| 32.2| 7.6 | 26.7| Ni₃₋ₓWSₓₐₓ,ₚₓ     | 88.2                         | 3.40            | 0.22                 |
| WLDS-400  | 11.8| 32.5| 7.6 | 27.1| Ni₅₋ₓWSₓₐₓ,ₚₓ     | 99.1                         | 3.81            | 0.24                 |
| WLDS-500  | 11.4| 32.8| 7.8 | 27.7| Ni₅₋ₓWSₓₐₓ,ₚₓ     | 78.0                         | 3.79            | 0.12                 |
| WLDS-600  | 11.3| 34.0| 8.1 | 28.7| Ni₅₋ₓWSₓₐₓ,ₚₓ     | 15.5                         | 26.7            | 6.4                  |

Figure 6. Raman spectra of (a) NiAl—WS₄ (b) WLDS-300, (c) WLDS-400, (d) WLDS-500, and (e) WLDS-600.

2.2.2. Raman Spectroscopy. The catalysts were further characterized by Raman spectroscopy, and the spectra are shown in Figure 6. Four bands are observed in the spectrum of WLDS-300. The band at 225 cm⁻¹ is assigned to the deformation vibration of O—W—S in WO₂S₂, probably owing to the oxidation of tungsten sulfides by exposure to air and heat generated in situ by the laser. The bands at 290 and 470 cm⁻¹ are attributed to the characteristic vibration of NiS and symmetric stretching of W—S in WS₄, respectively. The band at 511 cm⁻¹ is assigned to terminal S—S stretching of WS₄. As the temperature increases to 400 °C, the
band of WS$_3$ weakens, whereas two bands at 411 and 350 cm$^{-1}$, respectively, attributed to the A$_{1g}$ vibration of S and the E$_{2g}^1$ vibration of W$-$Si NW S$_2$ are observed. A weak band around 175 cm$^{-1}$ can also be assigned to NiS. After being calcined at 600 °C, the bands of NiS fade out, while a band around 280 cm$^{-1}$ assigned to Ni$_3$S$_2$ is present.

2.2.3. N$_2$ Adsorption and Desorption. The N$_2$ adsorption$-$desorption isotherms of catalysts are given in Figure S1 (Supporting Information). These isotherms exhibit typical type IV curves with a clear hysteresis loop, indicative of mesoporous characteristics in the catalysts. With the increasing temperature, the surface area and pore volume increase significantly because of the removal of interlayer water and the delamination of layers. They reach a maximum at 500 °C and then decrease, probably because of the densification and grain growth upon annealing.

2.2.4. X-ray Photoelectron Spectroscopy. To determine the chemical state of S, W, and Ni on the surface of catalysts, WLDS-300 and WLDS-500 were characterized by X-ray photoelectron spectroscopy (XPS). The spectra of S 2p, W 4f, and Ni 2p$_{3/2}$ consist of a number of partially overlapping peaks; therefore, the spectra were deconvoluted as shown in Figure 7. Table 2 summarizes the binding energies and the percentages of the S, W, and Ni species with various states. For the fitting, the full width at half-maximum (fwhm) values of peaks assigned to each species are kept similar. Each S 2p spectrum can be deconvoluted into two spin$-$orbit doublets containing 2p$_{3/2}$ and 2p$_{1/2}$ with a fixed area ratio of 2:1 and a doublet separation around 1.1 eV, among which the peaks around 162.1 and 163.2 eV are assigned to 2p$_{3/2}$ and 2p$_{1/2}$ of S$^{2-}$, respectively, and the others around 163.5 and 164.5 eV are assigned to 2p$_{3/2}$ and 2p$_{1/2}$ of S$^{2-}$, respectively. S$^{2-}$ ligands are present in metal sulfides including WS$_4$$^{2-}$, WS$_2$, NiS$_x$, and

![XPS spectra of (a) S 2p, (b) W 4f, and (c) Ni 2p$_{3/2}$ of WLDS-300 and WLDS-500.](https://pubs.acs.org/doi/10.1021/acsomega.0c03105/fig/si/7)

**Table 2. Deconvolution Results of S 2p, W 4f, and Ni 2p$_{3/2}$ XPS Spectra**

| sample    | binding energy (eV) | percentage of moieties (%)$^d$ |
|-----------|---------------------|-------------------------------|
|           | $S^{2-}$ $S^{2-}$   |                               |
| WLDS-300  | 2p$_{1/2}$ 2p$_{3/2}$ | 163.2 162.1 164.6 163.5       |
| WLDS-500  | 2p$_{1/2}$ 2p$_{3/2}$ | 163.2 162.1 164.5 163.5       |
|           | $W^{6+}$ $W^{5+}$ $W^{4+}$ |
| WLDS-300  | 4f$_{5/2}$ 4f$_{7/2}$ | 35.4 33.4 34.9 32.8 34.3 32.2 |
| WLDS-500  | 4f$_{5/2}$ 4f$_{7/2}$ | 38.3 36.2 35.0 32.9 34.4 32.3 |
|           | Ni$^{2+}$ |
| WLDS-300  | 852.8 853.8 856.5 862.0 | 8.1 3.6 88.3 |
| WLDS-500  | 852.9 853.7 856.4 861.7 | 14.8 21.3 63.9 |

$^a$Ni$^{2+}$ in NiS$_x$. $^b$Ni$^{2+}$ in NiWS. $^c$Ni$^{2+}$ in NiO. $^d$Peak area of each moiety in percentage of the total area.
Scheme 1. Structure of WS$_4^{2−}$, WS$_3$, and WS$_2$

WS$_2$, while S$_2^{−}$ ligands are characteristics of bridging disulfide anions in WS$_x$. Martin et al. indicated that the S 2p XPS spectrum of WS$_3$ showed two overlapping doublets attributed to S$_2^{−}$ and S$^{2−}$ in a 1:2 proportion. Alsabban et al. suggested that both WS$_3$ and WS$_2$ contained S$^{2−}$, but only WS$_2$ possessed S$_2^{−}$. The percentage of S$_2^{−}$ in WLDS-300 is 3 times higher than that in WLDS-500, suggesting more WS$_3$ in the former, which is consistent with the Raman results.

The W 4f spectrum of WLDS-300 can be deconvoluted into three doublets arising from the 4f$_{7/2}$ and 4f$_{5/2}$ lines of W$^{6+}$, W$^{5+}$, and W$^{4+}$. For the fitting, the area ratio of 4f$_{7/2}$ to 4f$_{5/2}$ is kept at 4.3 and the doublet separation is around 2.1 eV. The W$^{4+}$ state with a binding energy around 32.2 (4f$_{7/2}$) and 34.3 eV (4f$_{5/2}$) relates to WS$_2$. The peaks at 32.8 and 34.9 eV are indicative of 4f$_{7/2}$ and 4f$_{5/2}$ of the W$^{5+}$ species in WS$_3$, respectively. Researchers proposed tungsten centers in satellite, the fwhm values of Ni$^{2+}$ species in sulffides, respectively. For WLDS-500, its W 4f spectrum also showed two overlapping doublets attributed to the 4f$_{7/2}$ and 4f$_{5/2}$ lines of WS$_3$, and another doublet around 2.1 eV. The doublet separation is therefore 2.1 eV.

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migrate to the edge of WS$_2$. Hensen et al.\textsuperscript{67} indicated that the percentage of peak III could be attributed to the decomposition of NiS into Ni$_3$S$_2$ and WS$_2$ to generate CUS at the edges of WS$_2$. However, such a promotion effect differs with various NiS$_x$ crystallites. Amaya et al.\textsuperscript{68} reported that NiS favored DBT HDS, whereas Ni$_3$S$_2$ depressed the HDS activity. Ni$_3$S$_2$ crystallites are formed in WLDS-600, whereas NiS crystallites dominate in WLDS-400 and WLDS-500, which are responsible for the lower HDS activity of WLDS-600.

An exception is observed that WLDS-300 has more NiWS phases but lower HDS activity than WLDS-600. It might be related to the latter’s 2.6 times higher specific surface area than the former’s.

In contrast to HDS activity, the HYD selectivity decreases with the raised temperature. It is known that DBT with no sulfur is converted into NiS.

Table 3. Positions and Contributions of Reduction Peaks Obtained by the Deconvolution of TPR-S Profiles

| Samples     | Peak I (°C) | Peak II (°C) | Peak III (°C) | Peak IV (°C) | Peak V (°C) |
|-------------|-------------|--------------|---------------|--------------|-------------|
| WLDS-300    | 347/15.1    | 431/31.6     | 525/11.7      | 622/20.3     | 745/21.3    |
| WLDS-400    | 338/11.6    | 443/33.9     | 548/14.9      | 640/15.5     | 756/24.1    |
| WLDS-500    | 336/8.4     | 465/43.8     | 569/15.7      | 652/11.5     | 771/20.6    |
| WLDS-600    | 330/6.3     | 448/28.0     | 530/19.9      | 638/23.6     | 782/22.2    |

Table 4. HDS and HDA Activities of the Presulfided Catalysts and Reference Catalysts

| Samples     | $k_{HDS}$ (mmol g$^{-1}$ h$^{-1}$) | HYD/DDS | TOF$_{HDS}$ (h$^{-1}$) | $k_{HDA}$ (mmol g$^{-1}$ h$^{-1}$) | TOF$_{HDA}$ (h$^{-1}$) |
|-------------|----------------------------------|---------|------------------------|-----------------------------------|------------------------|
| WLDS-300    | 0.81                             | 0.93    | 0.34                   | 2.21                              | 1.24                   |
| WLDS-400    | 0.92                             | 0.76    | 0.35                   | 1.75                              | 0.91                   |
| WLDS-500    | 1.01                             | 0.61    | 0.39                   | 1.59                              | 0.86                   |
| WLDS-600    | 0.87                             | 0.52    | 0.32                   | 0.99                              | 0.55                   |
| LDO         | 0.51                             | 0.43    | 0.22                   | 1.08                              | 0.58                   |
| NiWS/Al$_2$O$_3$ | 0.77                        | 0.51    | 0.31                   | 1.25                              | 0.71                   |

As seen from Table 3, WLDS-300 has the highest percentage of peak I among the samples, suggesting the presence of more S$_2^{2-}$ because of the incomplete decomposition of WS$_4^{2-}$ into WS$_2$. With the raised temperature, peak I shows a declined percentage and a lower maximum reduction temperature because of the further conversion of WS$_4$ into WS$_2$ and the better promotion of Ni upon higher temperature.\textsuperscript{59} The percentage of peak II increases with the raised temperature up to 500 °C because the high temperature facilitates Ni atoms to migrate to the edge of WS$_2$.\textsuperscript{66} Hensen et al.\textsuperscript{67} indicated that sulfate at higher temperatures allowed the redisposition of Ni sulfides to small ones over the formed WS$_2$ edges, inducing more NiWS phases. The maximum reduction temperature of peak II moves up owing to the strengthened interaction between the metal and aluminum with the raised calcination temperature.\textsuperscript{60} As the temperature increases to 500 °C, the percentage of peak III increases, while the percentage of peak IV decreases because more sulfur species released by the complete decomposition of WS$_4^{2-}$ could sulfurize oxidic nickel. The change in the maximum reduction temperature of peak III could be attributed to the different reducibility of various NiS$_x$ species. Among all samples, WLDS-600 seems to be an exception, for which the percentage of peak II decreases, whereas the percentage of peak IV increases. The former could be related to the sintering of NiWS phases which are converted into Ni$_3$S$_2$ and WS$_2$ at higher temperatures,\textsuperscript{60} while the latter is due to the loss of sulfur.

Based on the above characterization results, the conversion of NiAl–WS$_2$ upon calcination could be proposed. At 300 °C, some interlayer WS$_4^{2-}$ anions decompose into amorphous WS$_2$ well dispersed on the catalyst, while some WS$_4^{2-}$ anions are still retained in the interlayer. The sulfur released during the decomposition of WS$_4^{2-}$ can sulfurize a part of nickel ions in the sheets to produce NiS which does not yet grow into crystallites and thus is invisible to XRD. With the raised temperature, both WS$_4^{2-}$ and WS$_2$ decompose completely; therefore, WS$_2$ nanocrystallines are dominant and well dispersed on catalysts. In the case of nickel, the dehydroxylation of sheets leads to poorly crystallized NiO, some of which are sulfurized to small NiS crystallites and some of which still remain in the oxidic form because of the inadequate sulfur. The higher temperature could improve the mobility of nickel sulfides which move to the edge of WS$_2$ slabs and thus participate in the formation of NiWS phases. At 600 °C, NiS is transformed into Ni$_3$S$_2$.

2.3. Catalytic Activity. 2.3.1. HDS Activity. The catalytic reactions were performed for more than 30 h to ensure the stable activity. The variations of HDS conversion and HYD selectivity with time on stream over each catalyst are shown in Figures S2 and S3 (Supporting Information). It is found that the activity and selectivity reach a stable state after 24 h, and therefore, the rate constant, turnover frequency (TOF), and HYD/direct desulfurization (DDS) selectivity are calculated from the stable data. The results are given in Table 4.

With the raised calcination temperature, both $k_{HDS}$ and TOF$_{HDS}$ increase up to 500 °C. Based on the above characterization results, it is found that HDS activity is highly dependent on the amount of NiWS phases. The decoration of nickel on the edges of WS$_2$ slabs leads to the formation of NiWS phases, through which the electron cloud density of the neighboring W atoms increases, which will increase the mobility of S atoms to induce the formation of the active CUS.\textsuperscript{55} Because of a Lewis acid character, CUS could act as adsorption sites for sulfur-containing molecules via the unpaired electrons of sulfur; therefore, these sites are assigned to the direct removal of sulfur, that is, to the C−S bond scission.\textsuperscript{68} WLDS-500 has a larger number of NiWS phases and thus higher HDS activity and efficiency.

In addition, the role of segregated NiS$_x$ crystallites on HDS activity cannot be ruled out. According to the remote-control model,\textsuperscript{68} NiS$_x$ clusters might help to adsorb and dissociate H$_2$ molecules to generate spillover hydrogen, which could attack WS$_2$ to generate CUS at the edges of WS$_2$. However, such a promotion effect differs with various NiS$_x$ crystallites. Amaya et al.\textsuperscript{68} reported that NiS favored DBT HDS, whereas Ni$_3$S$_2$ depressed the HDS activity. Ni$_3$S$_2$ crystallites are formed in WLDS-600, whereas NiS crystallites dominate in WLDS-400 and WLDS-500, which are responsible for the lower HDS activity of WLDS-600.

An exception is observed that WLDS-300 has more NiWS phases but lower HDS activity than WLDS-600. It might be related to the latter’s 2.6 times higher specific surface area than the former’s.

In contrast to HDS activity, the HYD selectivity decreases with the raised temperature. It is known that DBT with no significant steric constraints is preferentially converted via
DDS, however, WLDS-300 shows a HYD/DDS close to 1, implying the enhanced HYD activity. Therefore, THN, which is a typical polyaromatic in diesel and hardly to be fully saturated, was used as a model compound to further investigate the HDA activity of catalysts.

2.3.2. HDA Activity. The THN HDA conversion with time on stream is shown in Figure S4 (Supporting Information). The stable HDA activity is achieved after 24 h. The rate constant and TOF calculated from the stable data are listed in Table 4. The HDA activity decreases with the raised temperature. WLDS-300 is the most active catalyst, whose \( k_{\text{HDA}} \) is 1.4 and 2.2 times higher than those of WLDS-500 and WLDS-600, respectively. This suggests that the property–activity relation of HDA differs from that of HDS. The above characterization results reveal that \( S_2^{2−} \) in catalysts could be the predominant property determining HDA activity. Low-valence sulfur (\( S_2^{2−} \)) species located on the edge of WS\(_2\) slabs are regarded to be involved in H\(_2\) activation. Homolytic hydrogen adsorption occurs on \( S_2^{2−} \) and thus forms \( −SH \) groups. Starsev\(^{70}\) demonstrated that bridged S atoms (\( S_2^{2−} \)) in the Mo–S–S–Mo structure could serve as probable sites for hydrogen activation because of the electronic charge transfer between S atoms with an excess negative charge and the H\(_2\) antibonding \( \sigma^* \) orbital. Such transfer may facilitate the homolytic H\(_2\) dissociation and form \( −SH \) groups. However, the Mo–S–Mo (\( S_2^{2−} \)) bridge is not suitable for the dissociation of H\(_2\) because of saturation of both valence bonds in sulfur atoms. Sierralta and Ruette\(^{71}\) also found that a four-center model involving \( S_2^{2−} \) (Mo–S–S–Mo) and H\(_2\) molecules was favorable for breaking H\(_2\) and giving two \( −SH \) groups, whereas a three-center model involving one \( S_2^{2−} \) (Mo–S–Mo) and H\(_2\) molecule was not. Accordingly, \( S_2^{2−} \) could favor the formation of \( −SH \) groups rather than \( S_2^{2−} \). The hydrogen needed for HYD is provided by \( −SH \).\(^{72}\) At higher temperatures, the decomposition of \( S_2^{2−} \) accelerates, leading to the decreased HYD activity. WLDS-300 has the largest amount of \( S_2^{2−} \) and thus the highest HYD activity, which is also responsible for the highest HYD selectivity for DBT HDS because the HYD pathway is more demanding for \( −SH \) than DDS.\(^{63}\)

2.3.3. Comparison with Reference Catalysts. The DBT HDS and THN HDA activities of reference catalysts (an oxidic NiW LDH-based catalyst referred to as LDO and an alumina-supported NiW presulfided catalyst referred to as NiW/SiO\(_x\)) were tested, and the results are listed in Table 4. The activities with time on stream are shown in Figures S5–S7 (Supporting Information). The HDS and HDA activities of LDO are much lower than those of WLDS-300, WLDS-400, and WLDS-500. This could be explained by the poor sulfuration ability of oxidic W species which are normally fully sulfurized above 650 °C.\(^{4}\) Conversely, W species in presulfurized catalysts are almost fully sulfurized. Additionally, WLDS-300 exhibits 2.05 times \( k_{\text{HDA}} \) enhancement over LDO because of the absence of \( S_2^{2−} \) in the latter. As reported previously,\(^{25}\) \( S_2^{2−} \) species are hard to be formed on oxidic catalysts because the sulfuration of MoO\(_3\) or WO\(_3\) undergoes oxygen–sulfur exchange to form Mo oxysulfide (MoO\(_x\)S\(_y\)) containing \( S_2^{2−} \) ligands at the sulfuration temperature around 100–150 °C; however, such an oxysulfide will decompose with the raised sulfuration temperature and disappear completely around 200–250 °C. Nevertheless, oxidic catalysts have to be sulfurized above 300 °C.

For NiW/SiO\(_x\), its HDS and HDA activities are lower than those of WLDS-300, WLDS-400, and WLDS-500. This could be related to the following reasons: First, tungsten sulfides are poorly dispersed on NiW/SiO\(_x\). The XRD pattern of NiW/SiO\(_x\) (Figure S8, Supporting Information) shows strong reflections assigned to WS\(_x\), indicating poorly dispersed WS\(_x\) crystallites. This is unfavorable for the formation of NiW phases because of the less exposed edge sites of WS\(_x\) slabs.\(^{63}\) In contrast, all tungsten sulfides are well dispersed on LDH-based catalysts. The peculiar properties of LDHs facilitate preparing homogeneous mixtures containing well-dispersed elements in both the layer and the interlayer in a wide range of compositions.\(^{13}\) After being calcined below a certain temperature, the cleaved layers (Figure S9, Supporting Information) can act as both supports to enable active metal species well dispersed on catalysts and separators to prevent active metal species from aggregation.\(^{19,20}\) Second, the formation of highly active HYD sites \( S_2^{2−} \) is less favorable for NiW/SiO\(_x\). The TPR-S profile of NiW/SiO\(_x\) (Figure S10, Supporting Information) shows no distinct reduction peak below 400 °C, suggesting the absence of \( S_2^{2−} \) species. For NiW/SiO\(_x\), tungsten and nickel are sequentially loaded on alumina by impregnation of ATT and nickel nitrate, followed by calcination. The calcination temperature in the step for loading nickel should be above 300 °C to ensure the complete decomposition of nickel nitrate into NiO.\(^{73}\) However, WS\(_x\) from the decomposition of ATT will be converted into WS\(_x\) because of the higher calcination temperature in the nickel loading process. In contrast, \( S_2^{2−} \) can be well retained in LDH-based catalysts even upon high calcination temperatures because of the interaction between interlayer anions and sheets as well as the barrier effect of sheets. Therefore, WLDS-300, respectively, shows 1.82, 1.77, and 1.75 times higher HYD/DSS selectivity, \( k_{\text{HDA}} \) and T\( \text{OF}_{\text{HDA}} \) than NiW/SiO\(_x\).

A real diesel fraction was used to test the hydrotreating performance of WLDS-300, which shows the best HYD activity among the presulfurized catalysts. Moreover, a commercial oxidic diesel hydrotreating catalyst NiCoMoW/Al\(_x\)O\(_y\) (W: 14.9 wt %, Mo: 6.7 wt %, Ni: 2.6 wt %, and Co: 2.5 wt %; a specific surface area of 239.6 m\(^2\) g\(^-1\); a pore volume of 0.31 cm\(^3\) g\(^-1\); and a pore size of 4.99 nm) from PetroChina is chosen as a reference. Before reaction, the commercial catalyst was sulfurized under the same conditions as LDO. The reaction was performed for 72 h to ensure the stable activity data (Table 5). The conversion with time on stream curves are shown in Figure S11 (Supporting Information). It is noted that the sulfur level of the feed is not very high because it is from the straight run fraction of a sweet crude oil with a sulfur content less than 5000 mg kg\(^{-1}\). It is found that the catalysts show stable activity. WLDS-300 is more active in the HDS of diesel than the commercial catalyst. In addition, WLDS-300

| Table 5. Sulfur and Aromatic Contents of Diesel before and after Hydrotreating over WLDS-300 and a Commercial Catalyst |
|-------------------------------|-----------------|-----------------|-----------------|
|                              | feed            | WLDS-300        | commercial catalyst |
| sulfur (mg kg\(^{-1}\))       | 2346            | 1246            | 1390            |
| naphthenes (wt %)             | 216             | 33.1            | 27.8            |
| aromatics (wt %)              | 19.5            | 15.3            | 19.4            |
| mono                          | 11.6            | 10.6            | 13.1            |
| di                            | 7.3             | 4.5             | 6.1             |
| tri                           | 0.6             | 0.2             | 0.2             |

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A tetrathiotungstate-intercalated NiAl LDH was successfully synthesized via an ion-exchange method. It was further calcined at various temperatures to prepare a series of NiW presulfurized hydrotreating catalysts. Upon calcination, interlayer WS$_2$$^-$$^-$ anions can decompose into WS$_5$ and subsequently WS$_5$ releasing sulfur to sulfurize nickel in the sheets.

The formation of S$_2$$^2$- and NiWS active species is dependent on the calcination temperature. At 300 °C, WS$_5$ containing S$_2$$^2$- can be well preserved, whereas more NiWS phases are formed at 500 °C. The DBT HDS activity and THN HDA activity are determined by NiWS and S$_2$$^2$-. Tungsten sulfides are well dispersed on catalysts because of the peculiar layered structure, which is a prerequisite for forming NiWS phases. Moreover, the interaction between interlayer WS$_5$$^-$$^-$ and sheets and the barrier effect of sheets allow S$_2$$^2$- to be well maintained in catalysts at higher temperatures. Therefore, such catalysts show higher HDS and HDA activities than an alumina-supported conventional presulfurized catalyst and a commercial catalyst, especially much higher in HDA. This work may offer a convenient one-step approach to prepare NiW presulfurized hydrotreating catalysts with superior HYD activity.

### 4. Experimental Section

#### 4.1. Catalyst Preparation

A nitrate NiAl LDH with a Ni/Al ratio of 2 referred to as NiAl–NO$_3$ was synthesized via a coprecipitation method as reported previously. A tetrathiotungstate-intercalated NiAl LDH denoted as NiAl–WS$_5$ was synthesized through an ion-exchange method using NiAl–NO$_3$ as a precursor and ammonium tetrathiotungstate [(NH$_4$)$_2$WS$_4$, ATT] as a tungsten resource. ATT is traditionally prepared by bubbling H$_2$S in an aqueous ammonia solution of ammonium metatungstate. However, H$_2$S is poisonous and unsafe, while ammonium metatungstate is more expensive than Na$_2$WO$_4$. Therefore, ATT was synthesized by Na$_2$WO$_4$ and (NH$_4$)$_2$S. Typically, 10 g of Na$_2$WO$_4$·2H$_2$O (Kelon, China) was added to 45 mL of (NH$_4$)$_2$S solution (40–48 wt %, Aladdin, China), and then, 10 mL of ammonia solution (25–28 wt %, Kelong, China) was added under stirring. The mixture was refluxed at 60 °C for 12 h. The yellow crystal products are collected as described in the reference. Their XRD pattern is shown in Figure S12 (Supporting Information).

For a typical ion-exchange process, 1.2 g of ATT was dissolved in 50 mL of water and then 1.0 g of NiAl–NO$_3$ was dispersed in the solution, in which the molar ratio of WS$_5$$^-$$^-$ to NO$_3$ was set at 2 in order to ensure a complete exchange. The pH of the suspension was adjusted to 8 by the ammonia solution. Afterward, the mixture was stirred vigorously under N$_2$ at 60 °C for 24 h. The resulting solid was filtered, successively washed with water, CCl$_4$ (Kelon, China), and anhydrous ethanol (Kelon, China), and then dried under vacuum at 60 °C for 4 h. Herein, CCl$_4$ is used as a solvent to remove a small amount of elemental sulfur, which floats on the surface of the suspension and might be produced from the excessive hydrolysis of thiometallate. It is noted that the ion-exchange conditions are chosen based on a series of experiments which were performed to optimize the exchange pH, time, and temperature. The corresponding results are shown in Figures S13–S16 (Supporting Information).

NiAl–WS$_5$ was activated under a N$_2$ flow of 10 mL min$^{-1}$ at various temperatures (300, 400, 500, and 600 °C) for 3 h to prepare presulfurized catalysts, which were referred to as WLDS-300, WLDS-400, WLDS-500, and WLDS-600, respectively.

For the purpose of comparison, a tungstate-intercalated NiAl LDH referred to as NiAl–WO$_4$ was synthesized by an ion-exchange method using NiAl–NO$_3$ as a precursor. It was further calcined under air at 450 °C for 3 h to prepare a reference oxidic LDH-based catalyst with similar Ni and W contents to WLDS-500. Such a catalyst was referred to as LDO. In addition, an alumina-supported NiW presulfurized catalyst referred to as NiWS/Al$_2$O$_3$ was prepared by a sequential incipient wetness impregnation method according to the reference.

First, γ-Al$_2$O$_3$ (Sasol, Germany) particles were impregnated in a solution of ATT and ethylene diamine (Kelon, China) at ambient temperature for 12 h, followed by drying at 60 °C for 3 h under vacuum and calcination at 250 °C for 3 h under N$_2$ flow. Second, the corresponding solid was impregnated in a solution of Ni(NO$_3$)$_2$·6H$_2$O (Kelon, China) and acetone at ambient temperature for 12 h, followed by calcination at 450 °C for 3 h under N$_2$ flow. Its W and Ni contents are 28.2 and 9.2 wt %, respectively. It has a similar W content but a lower Ni content than WLDS-500 because a lot of NiO crystallites are formed at the high Ni/W ratio. Therefore, the ratio of Ni/(Ni + W) in NiWS/Al$_2$O$_3$ is set at 0.5, which is normally regarded as an optimal Ni/(Ni + W) ratio for alumina-supported hydrotreating catalysts. All water used is degassed and deionized. All chemicals are used as received.

#### 4.2. Characterization Techniques

XRD patterns of samples were collected on an X’pert Pro MPD diffractometer (PANalytical, Netherlands) using a Cu Kα radiation source operated at 40 kV and 40 mA in the 2θ region of 5°–70° with a step size of 0.02° and a counting time of 12 s per step. FT-IR spectra of samples were recorded on a WQ520 spectrophotometer (Beifen, China) at ambient temperature using the KBr pellet method in the region of 400–4000 cm$^{-1}$. A total of 32 scans were taken for each sample with a resolution of 2 cm$^{-1}$. Raman spectra of samples were recorded on an InVia Raman microscopic confocal spectrometer (Renishaw, UK) with a
He–Cd laser as the excitation source operating at 514.5 nm and a laser power of 0.17 mW. Thermal analyses including TG, DSC, and DTG were performed on an STA-449F3 (NETZSCH, Germany) instrument. Typically, 10 mg of the sample was loaded in an alumina crucible and heated from 40 to 700 °C with a ramping temperature of 10 °C min⁻¹ in an Ar flow of 60 mL min⁻¹. The metal contents of samples were measured by inductively coupled plasma atomic emission spectroscopy on an Optima 7300 V spectrometer (PerkinElmer, USA). Carbon, hydrogen, nitrogen, and sulfur elemental analyses of samples were carried out using a Vario EL cube elemental analyzer (Elementary, Germany). The texture property of samples was measured on a QUADRA SORB Si analyzer (Quantachrome, USA). Prior to measurement, the sample was degassed under vacuum at 200 °C for 6 h. X-ray photoelectron spectra were recorded using a K-alpha spectrometer (Thermo Fisher Scientific, USA) equipped with a monochromatic Al Kα X-ray source. The binding energies were referenced to the C 1s peak at 284.7 eV. The peak deconvolution was obtained by the software XPSPeak 4.1 with the Shirley background. TPR was performed on a ChemBET chemisorption analyzer (Quantachrome, USA) equipped with a thermal conductivity detector. The sample (0.1 g) was pretreated in Argon at 350 °C for 0.5 h, cooled down to ambient temperature, and then heated to 900 °C with a ramping rate of 10 °C min⁻¹ in 10 vol % H₂/Ar. Scanning electron microscopy (SEM) images were obtained on an EVOMA-15 (Zeiss, Germany) instrument. The sample was dispersed in cyclohexane by sonication, and then, a drop of the suspension was deposited on the sample platform and dried before testing.

4.3. Catalytic Activity Tests. Catalytic activity tests were performed in a tubular flow fixed-bed microreactor operated in a continuous mode, whose size and catalyst packing were reported previously. A 1 wt % DBT (98%, J&K, China)/cyclohexane (AR, Kelong, China) and 5 wt % THN (99%, J&K, China)/heptane (AR, Kelong, China) were used as HDS and HDA feeds, respectively. For the presulfurized catalysts, the reaction was carried out at 300 °C, 4 MPa H₂ pressure, a liquid hourly space velocity of 16.5 h⁻¹, and a hydrogen/hydrocarbon ratio 400. For the oxidative catalyst LDO, it was presulfurized in 3 wt % CS₂/cyclohexane at 300 °C and 4 MPa for 4 h, and then, the feed was switched. It is noted that the present reaction conditions had been proved to be able to eliminate the external and internal diffusion. The reactions over all catalysts were kept for more than 24 h to reach a steady state. Liquid products were collected each 4 h and analyzed using a 9790 II gas chromatograph (Fuli, China) equipped with an FID detector and a KB-5 capillary column (30 m × 0.32 mm × 0.25 μm, Kromat, USA).

The HDS and HDA activities were expressed by the reaction rate constant (kHDS or kHDA) and TOF. HDS of DBT occurs in two parallel pathways. One is DDS, for which sulfur elimination takes place via hydrogenolysis of C–S bonds and yields a main product of biphenyl (BP). The other is HYD, for which sulfur extrusion occurs after HYD of one of the aromatic rings in DBT and mainly yields cyclohexylbenzene (CHB). Therefore, the HYD selectivity can be obtained by analyzing the contents of BP and CHB in products. A straight run diesel fraction from a refinery was also used to evaluate the hydrotreating activity and stability of the catalysts. The reaction was performed on the microreactor under the same conditions as described above. The sulfur content was determined using a TSN-3000 fluorescence analyzer (Jiangfen, China) according to ASTM-D5453. The aromatic content was determined using a 7890 A gas chromatograph and a 5975C mass spectrometry instrument (Agilent, USA) according to ASTM-D2425.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03105.

N₂ adsorption–desorption isotherms; plots of HDS and HDA conversion with time on stream; XRD pattern and TPR-S curve of NiWS/Al₂O₃; SEM micrographs of LDH and catalysts; XRD pattern of ATT; and XRD patterns and FTIR spectra of tetrathiotungstate-intercalated NiAl LDHs synthesized under various pH, temperatures, and times (PDF)

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Notes
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