The Deoxygenation of Jatropha Oil to High Quality Fuel via the Synergistic Catalytic Effect of Ni, W₂C and WC Species

Keyao Zhou, Xiangze Du, Linyuan Zhou, Huiru Yang, Xiaomei Lei, Yan Zeng, Dan Li * and Changwei Hu *

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China; 2018222030120@stu.scu.edu.cn (K.Z.); 2017141231225@stu.scu.edu.cn (L.Z.); 2019222030119@stu.scu.edu.cn (H.Y.); 2019222030152@stu.scu.edu.cn (X.L.); 2020222030048@stu.scu.edu.cn (Y.Z.)
* Correspondence: danli@scu.edu.cn (D.L.); changweihu@scu.edu.cn (C.H.); Tel.: +86-28-85411105 (C.H.)

Abstract: Tungsten carbide-based materials have good deoxygenation activity in the conversion of biomass. In this paper, catalysts with different nickel–tungsten carbide species were prepared by tuning the reduction temperature and Ni loading, and the effects of these different tungsten carbide species in the conversion of jatropha oil were studied. XRD, XPS, TEM, HRTEM, Raman, H₂-TPR, ICP-AES were used to characterize the catalysts. The results suggested that metallic W was gradually carburized to W₂C species, and W₂C species was further carburized to WC species with the increase in reduction temperature and Ni loading. The obtained 10Ni10W/AC-700 catalyst exhibited outstanding catalytic performance with 99.7% deoxygenation rate and 94.5% C₁₅₋₁₈ selectivity, which were attributed to the smallest particle size, the best dispersion, the most exposed active sites, and the synergistic effect of Ni, W₂C and WC species.

Keywords: deoxygenation; the synergistic effect; Ni–W₂C–WC catalyst; jatropha oil; bio-fuel

1. Introduction

The decline in fossil fuel reserves, increasing environmental problems such as global warming and environmental pollution are driving our society to seek new sustainable energy. Biomass energy has a wide range of sources and is an ideal substitute for fossil fuels. The development of biomass fuels not only promotes energy diversification, decreases the dependence on traditional fossil fuels, but also reduces greenhouse gas emissions and slows down the environmental pressure [1–11]. Fatty acids and their derivatives from natural vegetable oils and animal fats are important raw materials for the preparation of biofuels. Jatropha is a kind of large shrub distributed in the tropical and subtropical regions. They can grow well on the dry and semidry poor soil, and the jatropha curcas seeds contain 27%–40% inedible oil which can be easily converted into biodiesel that meets American and European standards. Jatropha oil (JO) has attracted great attention, since it is a cheap and ideal raw material and does not need to compete with cultivated land and food [12,13].

In order to obtain high-quality biofuel with high stability, high caloric value, and low viscosity, oxygen must be removed from fatty acids and their derivatives [14,15]. At present, the research on deoxygenation (DO) catalyst has made great progress. It was found that noble metal catalyst was very efficient for DO activity on fatty acids and their derivatives, and the product yield and selectivity of the reaction were fairly high [16,17]. Nevertheless, the limited availability of noble metals due to the high price motivated the exploration of alternative catalysts with low cost. Levy et.al discovered the platinumlike properties of transition metal carbides in hydrogenation performance, which gained great attention [18]. Transition metal carbides were formed by incorporating carbon atoms into the lattices of transition metals, which led to the formation of interstitial compounds via the interaction between the s-p orbitals of the carbon and the s-p-d band of the metal atoms [19,20].
The lattice carbon atom lengthened the metal–metal bond distance, and thus changed the D-band electron density of metals at Fermi level via electron transfer from the metal atom to the carbon atom [21], which brought about the distinct adsorption/desorption properties [22]. Owning to their unique properties, transition metal carbides have also been explored in biomass conversions, especially in the C–C, C–O and C–O–H bonds cleavage reactions [23–28]. Among those achievements, transition metal carbides have been proved to facilitate the DO for a variety of feedstocks, particularly for organic acid/ester [28]. Gosselink et al. [29] studied the performance of tungsten-based catalysts prepared at different treatment temperatures for the DO of stearic acid. The DO path on tungsten oxide species was decarboxylation (DCO$_2$) or decarbonylation (DCO), whereas the DO path on tungsten carbide species was hydrodeoxygenation (HDO). Guo et al. [26] studied the influence of tungsten species obtained at different calcination temperatures in the conversion of various β-O-4 model compounds and beech dioxasolv lignin (BL). It was found that the catalyst treated at a temperature of 1000 °C under nitrogen atmosphere mainly obtained WC species, showing a proper amount of both acidic sites and metallic sites. The catalytic performance of WC in C–O bond cleavage was better than WO$_3$ obtained at a temperature of 500 °C. Stellwagen et al. [30] demonstrated for the first time that carbide particle size was a critical factor for the activity and stability of tungsten carbide and molybdenum carbide catalysts in (hydro-)deoxygenation reactions. Studies have shown that when the particle size was greater than 10nm, it exhibited excellent hydrogenation performance. The abovementioned study mainly revealed that tungsten carbide exhibited excellent activity in selectively cleaving C–O bond in stearic acid, β–O–4 model compounds and lignin [26,29,30]. It was found that Ni as a promoter could significantly improve the catalytic performance of tungsten carbide, but the effect of nickel on the formation of tungsten carbide species also remained unclear.

In this paper, the bimetallic nickel–tungsten catalysts supported on activated carbon (AC) were prepared by carbothermal hydrogen reduction (CHR) method [31]. Different tungsten carbide species were obtained by tuning the reduction temperature [32] and Ni loading. The DO reaction of JO on the bimetallic nickel–tungsten catalyst was evaluated, and related physical and chemical characterization experiments were used to further explore the bimetallic nickel–tungsten catalysts. The promotion effect of nickel on the formation of tungsten carbide and the effect of nickel and tungsten carbide species on DO performance were explored.

2. Results and Discussion
2.1. Catalyst Structures and Properties
2.1.1. XRD Results

The AC, the nickel–tungsten precursor and catalysts reduced at different temperatures were characterized by X-ray diffraction. The results were shown in Figure 1 and Table 1. As shown in Figure 1a, for the AC, there were only diffraction peaks of carbon species. For the nickel–tungsten precursor, the diffraction peaks at 2θ = 44.4°, 51.7° and 76.2° (PDF#04-0850) were attributed to metallic Ni. Metallic Ni appeared directly on the precursor due to the reduction capacity of the AC. Meanwhile, WO$_3$ and WO$_2$ crystal phase diffraction peaks were observed at 2θ = 22.9°, 23.2°,28.0°, 34.1°, 53.3° (PDF#20-1324), and 2θ = 26.0°, 36.9°, 52.7°, 60.0° (PDF#32-1393), respectively.

Figure 1b showed the powder X-ray diffraction pattern of the nickel–tungsten catalysts reduced at different temperatures. It could be seen that the diffraction peaks at 2θ = 44.4°, 51.7°, 76.2° (PDF#04-0850) on all catalysts were those of metallic Ni. For the 10Ni10W/AC-630 catalyst, the peaks at 2θ = 44.4°, 51.7°, 76.2° (PDF#04-0850) were corresponded to metallic W. For the 10Ni10W/AC-660 catalyst, in addition to the peak of metallic W, the new diffraction peaks of W$_2$C and WC were observed at 2θ = 34.4°, 38.0°, 39.5°, 75.1° (PDF#51-0939) and 2θ = 31.5°, 35.6°, 48.3° (PDF#51-0939) were detected, respectively. For the 10Ni10W/AC-680 catalyst, the diffraction peaks of W, W$_2$C and WC were also observed. For the 10Ni10W/AC-700 catalyst, the diffraction peak of W disappeared, and W$_2$C crystal
Phase diffraction peaks were observed at $2\theta = 34.4^\circ$, $38.0^\circ$, $39.5^\circ$, $61.6^\circ$, $69.5^\circ$ and $75.1^\circ$, and WC crystal phase diffraction peaks were observed at $2\theta = 31.5^\circ$, $35.6^\circ$, $48.3^\circ$, $64.2^\circ$, $73.2^\circ$ and $77.0^\circ$. For the 10Ni10W/AC-900 catalyst, the diffraction peaks of W$_2$C disappeared, and the diffraction peaks of WC were observed. The above analysis suggested that the metallic W was gradually carburized to W$_2$C phase, and W$_2$C phase was further carburized to WC phase with the increase in reduction temperature. Accordingly, the growth process of the catalysts was proposed in Figure 2. It should be noted that Figure 2 was just a schematic diagram to describe the formation of different species on the catalysts reduced at different temperatures.

Table 1. The crystal size of different phases for the catalysts reduced at different temperatures.

| Catalysts          | Ni     | W     | W$_2$C | WC    |
|-------------------|--------|-------|--------|-------|
| 10Ni10W/AC-900    | 16.6   | —     | —      | 24.3  |
| 10Ni10W/AC-700    | 14.5   | —     | 23.7   | 21.4  |
| 10Ni10W/AC-680    | 13.7   | 35.3  | 26.7   | 22.7  |
| 10Ni10W/AC-660    | 12.0   | 31.8  | 39.1   | 22.8  |
| 10Ni10W/AC-630    | 12.5   | 24.4  | —      | —     |

—: not detected.

Figure 1. (a) XRD patterns of the AC and the nickel–tungsten precursor; (b) XRD patterns of the 10Ni10W/AC catalysts reduced at different temperatures: 900 °C corresponded to the 10Ni10W/AC-900 catalyst; 700 °C corresponded to the 10Ni10W/AC-700 catalyst; 680 °C corresponded to the 10Ni10W/AC-680 catalyst; 660 °C corresponded to the 10Ni10W/AC-660 catalyst; 630 °C corresponded to the 10Ni10W/AC-630 catalyst. It was the same afterwards.

The crystal size of different species was calculated by the Scherrer equation and listed in Table 1. As the reduction temperature increased, the crystal size of the metallic Ni and W increased on the catalysts, but the metallic W disappeared at 700 °C. The crystal size of W$_2$C decreased with increasing reduction temperature on the 10Ni10W/AC-660, 10Ni10W/AC-680 and 10Ni10W/AC-700 catalysts. As the reduction temperature rose from 660 °C to 700 °C, the crystal size of WC decreased, while when the temperature further rose to 900 °C, the crystal size of WC increased, which presented an inverted volcano-like trend. The crystal size of W$_2$C and WC at 23.7 nm and 21.4 nm were the smallest on the 10Ni10W/AC-700 catalyst, respectively.
Figure 2. The schematic growth process of the species on the catalyst.

2.1.2. XPS Results

Figure 3 showed the X-ray photoelectron spectroscopy of the catalysts, which provided the chemical states of nickel and tungsten on the catalyst’s surface. As shown in Figure 3a, for the 10Ni10W/AC catalysts reduced at different temperatures, the peaks appearing at the Ni 2p$_{3/2}$ binding energy of 852.7–852.9 eV were attributed to the peaks of metallic Ni [33], and those at 855.5–855.8 eV were ascribed to Ni$^{2+}$ in NiO [34], with the shake-up satellites of nickel at 861.3–861.7 eV caused by the multielectron effect [35]. As shown in Figure 3b, for the 10Ni10W/AC catalysts reduced at different temperatures, the peaks at 35.4–35.6 eV of W4f$_{7/2}$ corresponded to W$^{6+}$ in WO$_3$. The peaks at 31.7–31.8 eV of W4f$_{7/2}$ region on the 10Ni10W/AC-700, 10Ni10W/AC-700, 10Ni10W/AC-680 and 10Ni10W/AC-660 catalysts were ascribed to WC. The peaks at 32.3 eV of W4f$_{7/2}$ region on the 10Ni10W/AC-700, 10Ni10W/AC-680 and 10Ni10W/AC-660 catalysts were ascribed to W$_2$C. The peaks at 31.5 eV of W4f$_{7/2}$ region on the 10Ni10W/AC-700, 10Ni10W/AC-680 and 10Ni10W/AC-660 catalysts were ascribed to metallic W [26,36–41]. As shown in Figure 3c, for the 10Ni10W/AC catalysts reduced at different temperatures, the peaks at the C 1s binding energy of 282.8 eV, 283.8 eV, 284.6 eV, 285.7 eV, and 289.3 eV were ascribed to carbon in WC, carbon in W$_2$C, C–C, C–O, and C=O accordingly [39,42]. The XPS results were in agreement with the above XRD analysis.

![Figure 3](image-url)

Figure 3. (a) The XPS spectra of Ni 2p for the catalysts reduced at different temperatures; (b) the XPS spectra of W 4f for the catalysts reduced at different temperatures; (c) the XPS spectra of C 1s for the catalysts reduced at different temperatures.

| Temperature (℃) | Ni (wt.%) | W (wt.%) | C (wt.%) |
|-----------------|-----------|----------|----------|
| 630             | 81.0      | 18.9     | 0.1      |
| 660             | 79.6      | 20.4     | 0.1      |
| 680             | 79.9      | 20.1     | 0.1      |
| 700             | 79.5      | 20.5     | 0.1      |
| 730             | 79.2      | 20.8     | 0.1      |
| 760             | 78.9      | 21.1     | 0.1      |
| 790             | 78.6      | 21.4     | 0.1      |
| 820             | 78.3      | 21.7     | 0.1      |
| 850             | 78.0      | 22.0     | 0.1      |
| 880             | 77.7      | 22.3     | 0.1      |

Table 3. The percentage content of several species on different catalysts. The data were calculated according to the XPS results.
Semi-quantification of the percentage of the surface element content and the percentage content of several species on the above catalysts were shown in Tables 2 and 3, respectively. It could be seen from Table 2 that as the reduction temperature increased, the content of C was almost unchanged (the impact of contaminant carbon was considered as systematic error), and the content of Ni gradually increased. Combined with the XRD results, it could be seen that as the reduction temperature increased from 630 °C to 700 °C, the crystal size of tungsten carbide species gradually decreased, and the amount of surface Ni covered by tungsten species gradually decreased, resulting in an increase in the surface Ni content [43]. The ratio of [C]/[W] exhibited a volcano-like trend, with the highest point on the 10Ni10W/AC-700 catalyst. It could be seen from Table 3 that as the reduction temperature increased, the percentage of metallic Ni gradually decreased, while the percentage of Ni\(^{2+}\) gradually increased. During the passivation process, as the surface Ni content increased, the content of oxidized Ni increased. While no NiO crystal phase was detected on all catalysts according to the XRD results. At first, the metallic Ni on the surface of the catalyst was oxidized during the passivation process. Second, the oxide materials such as CO\(_2\) and H\(_2\)O might be adsorbed on the Ni\(^{0}\) site [44]. As the reduction temperature rose from 630 °C to 900 °C, the percentage of WC species increased from 0 to 36.2%. From 630 °C to 700 °C, the percentage of metallic W decreased from 23.2% to 0, and the percentage of W\(_2\)C species increased from 0 to 17.4%. On the 10Ni10W/AC-660, 10Ni10W/AC-680 and 10Ni10W/AC-700 catalysts, the ratio of the percentage of W\(_2\)C species to WC species was 2.0, 1.6 and 1.0, respectively.

Table 2. The surface element content on different catalysts.

| Catalysts         | C (wt.%) | Ni (wt.%) | W (wt.%) | [C]/[W] |
|-------------------|----------|-----------|----------|---------|
| 10Ni10W/AC-900    | 79.9     | 5.6       | 4.1      | 19.5    |
| 10Ni10W/AC-700    | 78.9     | 5.3       | 3.7      | 21.3    |
| 10Ni10W/AC-680    | 79.6     | 5.1       | 3.8      | 20.9    |
| 10Ni10W/AC-660    | 80.9     | 4.9       | 4.4      | 18.4    |
| 10Ni10W/AC-630    | 81.0     | 3.5       | 5.7      | 14.2    |

\(^a\) The ratio of the percentage of C species to W species.

Table 3. The percentage content of several species on different catalysts. The data were calculated through the integrated area of each peaks in Ni 2p and W 4f in XPS in Figure 3.

| Catalysts         | Ni (wt.%) | W (wt.%) | [W\(_2\)C]/[WC] |
|-------------------|-----------|----------|-----------------|
| 10Ni10W/AC-900    | Ni 21.4   | Ni\(^{2+}\) 78.6 | WC 63.8 | W 36.2 | — |
|                   | 10Ni10W/AC-700 | Ni\(^{2+}\) 23.8 | WC 64.8 | W 17.8 | WC 17.4 | — | 1.0 |
|                   | 10Ni10W/AC-680 | Ni\(^{2+}\) 26.2 | WC 65.8 | W 8.7 | WC 14.0 | W 11.5 | 1.6 |
|                   | 10Ni10W/AC-660 | Ni\(^{2+}\) 27.2 | WC 70.3 | W 4.3 | WC 8.5 | W 16.9 | 2.0 |
|                   | 10Ni10W/AC-630 | Ni\(^{2+}\) 33.3 | WC 76.8 | — — | — — | WC 23.2 | — |

\(^b\) The ratio of the percentage of W\(_2\)C species to WC species. —: not detected.

2.1.3. Raman Results

As shown in Figure 4a, the scattering peaks located at 700 cm\(^{-1}\) and 790 cm\(^{-1}\) were ascribed to the stretching vibration of W–C [36,37,45–48], which further confirmed the existence of WC or W\(_2\)C species on the catalysts. However, when the reduction temperature was 630 °C, there were no scattering peaks ascribed to the stretching vibration of W–C. The results were in agreement with the XRD results. The featured Raman peaks assigned to the stretching mode of the terminal W=O bonds of tungsten oxide appeared clearly
at 894 cm\(^{-1}\) [37], which might be due to passivation. The scattering peaks located at 1345 cm\(^{-1}\) and 1599 cm\(^{-1}\) were observed for the D band and the G band of carbon, which were also observed on the AC support (Figure S2) [36,37,45–48]. The intensity ratio of the G band to the D band (\(I_G/I_D\)) of the catalysts reduced at different temperatures was shown in Figure 4b, and the \(I_G/I_D\) value of the catalysts was higher than that of the AC support (0.80). As the reduction temperature increased, the \(I_G/I_D\) value first increased and then decreased, showing a volcano-like trend, which was in agreement with the [C]/[W] value of XPS results. Among them, the 10Ni10W/AC-700 catalyst had the highest \(I_G/I_D\) value (0.97), implying the partial graphitization, which might facilitate the electron transfer of the catalyst, thereby improving the catalytic performance [36].

![Figure 4. (a) Raman spectra; (b) the intensity ratio of G band to D band (\(I_G/I_D\)) for catalysts reduced at different temperatures.](image)

### 2.1.4. H\(_2\)-TPR Results

H\(_2\)-temperature-programmed reduction (H\(_2\)-TPR) experiments were carried out for the precursor to determine the reducibility of Ni and W species on the AC. As shown in Figure 5, the reduction peak at 218 °C was attributed to the reduction of NiO species on the 10Ni10W/AC precursor [49]. The NiO reduction peak was very weak, and it should be attributed to a small amount of the highly dispersed oxidized nickel, which was consistent with the XPS result of the precursor (Figure S3). The peaks at 520 °C and 627 °C might be ascribed to the reduction of WO\(_3\) and WO\(_2\), respectively [50].

![Figure 5. H\(_2\)-TPR curve of 10Ni10W precursor supported on the AC.](image)
2.1.5. TEM and HRTEM Results

In order to further explore the surface morphology of the catalysts and the degree of dispersion of active species, the transmission electron microscopy (TEM) and the high-resolution TEM (HRTEM) were performed on the 10Ni10W/AC catalysts reduced at different temperatures. As shown in Figure 6, as the reduction temperature increased, the particle size gradually decreased and then increased, and presented a volcano-like trend. The smallest particle size of $21 \pm 7$ nm was obtained on the 10Ni10W/AC-700 catalyst. The results of XRD and TEM were consistent. When the reduction temperature was 630 °C and 900 °C, the 10Ni10W/AC catalyst had a wide particle size distribution, respectively $33 \pm 24$ nm and $45 \pm 19$ nm. The HRTEM inset of the 10Ni10W/AC-900 catalyst displayed the lattice fringes with a space of 0.25 nm, which corresponded to the (100) plane of WC [51]. On the 10Ni10W/AC-700 catalyst, in addition to the lattice fringes of WC, the lattice fringes of W$_2$C could be seen, and the distance of 0.23 nm was ascribed to the (102) plane of W$_2$C [38,45,51]. The lattice fringes of WC and W$_2$C could be also seen on the 10Ni10W/AC-680 catalyst. When the reduction temperature was 630 °C, the species on the catalyst were mainly metallic Ni and W with large particles. As the reduction temperature gradually increased, the metallic W was gradually carbonized into tungsten carbide species with small particles. When the reduction temperature was 700 °C, the metallic W disappeared, and the particle size of the nickel and tungsten carbide components were almost the same and uniformly dispersed. However, when the reduction temperature further increased to 900 °C, the nickel and tungsten carbide species were easy to agglomerate, resulting in an increase in particle size. In addition, the CO uptake results were consistent with the above results, which also attested that the 10Ni10W/AC-700 catalyst had higher dispersion and more active sites (Table S1).

2.2. The Conversion of JO over Nickel–tungsten Carbide Catalysts

The catalytic activity evaluation of JO was carried out on nickel–tungsten catalysts, as shown in Figure 7. As the reduction temperature rose from 630 °C to 900 °C, the DO rate first increased and then decreased, which were 66.0%, 88.0%, 97.4%, 99.7% and 75.0%, respectively. The total C$_{15-18}$ selectivity and C$_{17}$ selectivity first increased and then decreased, showing a volcano-like trend. The 10Ni10W/AC-700 catalyst had the highest DO rate of JO, which reached 99.7%, and the total C$_{15-18}$ selectivity reached 94.5%, while the C$_{17}$ selectivity reached 72.3%, and the yield of fuel was 67.1%. As shown in Figure S4, the products obtained on the 10Ni10W/AC-700 and 10Ni10W/AC-680 catalysts were clear and transparent liquid oil. However, the DO rate on the 10Ni10W/AC-680 catalyst was 97.4%, and the total C$_{15-18}$ selectivity was 77.5%, which were lower than those obtained on the 10Ni10W/AC-700 catalyst. The DO rate on 10Ni10W/AC-900, 10Ni10W/AC-660, and 10Ni10W/AC-630 catalysts were obviously lower than that on the above two catalysts, and the products obtained were white solids, as shown in Figure S4, which mainly contained octadecanoic acid propyl ester. Combined with the XRD and XPS results, it was found that the species on the 10Ni10W/AC-630 and 10Ni10W/AC-900 catalysts were mainly Ni + W and Ni + WC, respectively, and the two catalysts had poor DO capability. There were Ni + W + WC species on the 10Ni10W/AC-660, 10Ni10W/AC-680 and 10Ni10W/AC-700 catalysts, and the ratio of the percentage of W$_2$C species to WC species was 2.0, 1.6 and 1.0, respectively. When the value of [W$_2$C]/[WC] was 1, the DO capability of the 10Ni10W/AC-700 catalyst was the best.

JO was mainly composed of C$_{16}$ and C$_{18}$ fatty acids [12,52]. As shown in Tables S2 and S3, the ratio of C$_{15}$+C$_{17}$/C$_{16}$+C$_{18}$ was greater than 1, and the gas products contained carbon dioxide and carbon monoxide, indicating that the main DO path on the five catalysts was DCO$_2$ or DCO. The carbon monoxide might also come from the reaction of Dry reforming of methane (DRM) and Reversed water–gas shift reaction (RWGS) [53,54]. The 10Ni10W/AC-700 catalyst had the highest DO rate, the total C$_{15-18}$ selectivity, especially C$_{17}$ selectivity, indicating that the catalyst had the best DO capacity.
Figure 6. TEM images of: (A) 10Ni10W/AC-900; (B) 10Ni10W/AC-700; (C) 10Ni10W/AC-680; (D) 10Ni10W/AC-660; (E) 10Ni10W/AC-630, the bottom right corner was the distribution of particle size of the corresponding catalyst; (a) HRTEM image of 10Ni10W/AC-900; (b) HRTEM image of 10Ni10W/AC-700; (c) HRTEM image of 10Ni10W/AC-680.
2.2. The Conversion of JO over Nickel–tungsten Carbide Catalysts

From the above results, it could be seen that the different tungsten carbide species were formed by tuning the reduction temperature, and the 10Ni10W/AC-700 catalyst had the best catalytic activity. Therefore, the effects of the loading of Ni on the catalyst were explored by keeping the reduction temperature at 700 °C and the loading of W at 10 wt.%. The catalytic activity evaluation experiments of JO were also carried out on the xNi10W/AC (x = 0, 2, 10, 20) catalysts. The results were shown in Figure 8a, Figure S5, Tables S4 and S5. As shown in Figure 8a, with the Ni loading increased, the DO rate on the catalysts were: 19.7%, 26.2%, 99.7%, 96.2%, respectively, and the total C_{15-18} selectivity and C_{17} selectivity on the catalysts first increased and then decreased, showing a volcano-like trend. The DO rate of the 10W/AC catalyst without Ni was 19.7%, and the product obtained on the catalyst was brown liquid. The DO rate of the 2Ni10W/AC catalyst was 26.2%, and the product obtained on the catalyst was white solid. When the loading of Ni was 10 wt.% and 20 wt.%, the DO rate of the two catalysts was 99.7% and 96.2%, respectively, and the products obtained on the two catalysts were clear and transparent liquid oil. Figure 8b revealed that the C_{15} and C_{17} were the main components in the products, while the ratio of C_{15} + C_{17}/C_{16} + C_{18} was greater than 1, and the gas products contained carbon dioxide and carbon monoxide, indicating that the DO path on these four catalysts was DCO or DCO, which was the same as that on the 10Ni10W/AC catalysts reduced at different temperatures. The characterization results of the catalysts were shown in Figures S6–S8, Tables S6 and S7. According to the results, it could be found that the addition of Ni was beneficial to increase the loading of W (Table S7), lower the reduction temperature of tungsten oxide (Figure S7) [31] and increase the dispersion of tungsten carbide species (Figure S8), further control the species of tungsten carbide generated on the AC (Figure S6) and affect the activity of the catalysts. However, when the loading amount of Ni exceeded 10 wt.%, the particles agglomerated again, and the activity of the catalyst decreased instead. The aggregation of the active species would lead to the decrease in catalyst activity [55,56]. Therefore, the optimum loading of Ni was 10 wt.%.
Figure 8. (a) The activity performance of JO on the xNi10W/AC (x = 0, 2, 10, 20) catalysts; (b) the variation trend of C_{15}-C_{18} selectivity on the xNi10W/AC (x = 0, 2, 10, 20) catalysts. Reaction conditions: T = 340 °C, P = 3 MPa, t = 5 h, WHSV = 55.2 h\(^{-1}\), \(\text{H}_2/\text{N}_2 = 1\), \(F = 200 \text{ mL/min}\). Before the reaction, the catalyst was pretreated in \(\text{H}_2\) at 360 °C for 30 min to remove the surface oxides resulting from passivation process.

2.4. The Structure-activity Relationship of Nickel–Tungsten Carbide Catalysts

According to the above results, we found that the tungsten carbide species could be controlled by tuning the reduction temperature and the loading of Ni during the preparation process. With the increase in reduction temperature or Ni loading, tungsten species on the catalyst were gradually carbonized into \(\text{W}_2\text{C}\) species, and then further carbonized into WC species. Nickel was beneficial to increase the loading and dispersion of tungsten species, and reduce the carbonization temperature of tungsten species. In the conversion of JO, compared with the catalyst with only metallic W species, the catalyst with Ni + W species had higher deoxygenation capability, indicating that Ni species had a certain deoxygenation capability. However, compared with the catalyst with Ni + W species, the catalyst with Ni + W + \(\text{W}_2\text{C}\) + WC species had higher deoxygenation capability, indicating that \(\text{W}_2\text{C} + \text{WC}\) species had deoxygenation capability. Moreover, when the reduction temperature was 700 °C and the Ni loading was 10 wt.%, the species were Ni, \(\text{W}_2\text{C}\) and WC on the 10Ni10W/AC-700 catalyst and the ratio of the percentage of \(\text{W}_2\text{C}\) species to WC species was 1. Compared with other catalysts, the 10Ni10W/AC-700 catalyst had the smallest particle size, the highest graphitization degree, and the highest CO uptake; at the same time the active phase of nickel and tungsten carbide components on the catalyst was more dispersed. Therefore, the 10Ni10W/AC-700 catalyst exhibited the best catalytic performance in the deoxygenation of JO. Compared with other reports [57–61], the catalytic performance of Ni–\(\text{W}_2\text{C}–\text{WC}\) catalyst was close to or even better than that of precious metal catalyst, sulfided catalysts, and most nonprecious metal catalysts reported, as shown in Table 4. The Ni–\(\text{W}_2\text{C}–\text{WC}\) catalyst could obtain a high deoxygenation rate and \(\text{C}_{15-18}\) selectivity at a relatively low temperature and pressure (340 °C and 3 MPa). Duan et al. found that Ni had the ability of deoxygenation and it went through the DCO method in the conversion of octanoic acid [62]. Gosselink et al. found that pure \(\text{W}_2\text{C}\) was selective towards HDO products in the conversion of Stearic acid [29]. Li et al. found that \(\text{W}_2\text{C}\) and WC species could selectively break C–O in the conversion of biomass, such as lignin and cellulose [26,27,63]. In the present work, compared with the HDO deoxygenation path of tungsten carbide species, after Ni species were added, the deoxygenation path of the nickel–tungsten carbide catalyst was DCO/DCO₂. Compared with the catalytic performance of the 10Ni/AC catalyst (Table S8), with the addition of tungsten carbide species, the deoxygenation rate, the total \(\text{C}_{15-18}\) selectivity, the \(\text{C}_{17}\) selectivity and the product yield were improved. Therefore, there was a synergistic effect among Ni, \(\text{W}_2\text{C}\)
and WC species in the deoxygenation of JO. The ratio of C₁₅ + C₁₇/C₁₆ + C₁₈ was greater than 1 on all the catalysts. Therefore, the deoxygenation reactions were mainly through DCO/DCO₂ reaction pathway, which suggested that the synergistic effect of Ni–W₂C–WC was conducive to C–C bond cleavage in the conversion of JO. The deoxygenation path diagram was shown in Figure 9, where R represented a hydrocarbyl group.

Table 4. The activity performance over various catalysts in the conversion of vegetable oil.

| Catalyst          | Reactor                  | Raw Material       | Reaction Conditions | Activity Performance               | Ref.  |
|-------------------|--------------------------|--------------------|---------------------|-----------------------------------|-------|
| WO₃-Pt/TiO₂       | fixed-bed reactor        | crude Jatropha fatty acid | T = 360 °C, P = 4 MPa, LHSV = 1.33 h⁻¹ | A degree of deoxygenation of 86% | [57]  |
| NiMoLa/Al₂O₃      | fixed-bed reactor        | jatropha oil       | T = 370 °C, P = 3.5 MPa, LHSV = 0.9 h⁻¹ | 83% conversion, 94.5% C₁₅₋₁₈ selectivity | [58]  |
| NiMoS/titania     | bench-top micro-reactor  | jatropha oil       | T = 360 °C, P = 8 MPa, WHSV = 2 h⁻¹ | near 100% conversion, 97.2% C₁₅₋₁₈ selectivity | [59]  |
| NiMoCe/Al₂O₃      | fixed-bed reactor        | jatropha oil       | T = 370 °C, P = 3.5 MPa, LHSV = 0.9 h⁻¹ | 89% conversion, 90.0% C₁₅₋₁₈ selectivity | [60]  |
| Pt/SAPO-11        | fixed-bed flow microreactor | jatropha oil | T = 350 °C, P = 3 MPa, LHSV = 1 h⁻¹ | 100% conversion, 75.0–80.0% C₁₅₋₁₈ selectivity | [61]  |
| Ni–W₂C–WC/AC      | fixed-bed reactor        | jatropha oil       | T = 340 °C, P = 3.0 MPa, WHSV = 55.2 h⁻¹ | 99.7% DO rate, 94.5% C₁₅₋₁₈ selectivity | This work |

Figure 9. The deoxygenation path diagram.

3. Materials and Methods

3.1. Raw Materials

The reactant JO was purchased from Shenyu company in Yunnan Province, China. JO were obtained from the wild seeds collecting at the south-west region of China. The oil was produced by hot pressing method. It mainly contained C₁₅ and C₁₈ fatty acids. The AC support was purchased from Jiangsu Nantong Activated Carbon Cooperation (China). It was calcined at 600 °C under nitrogen atmosphere for 4 h to remove some impurities and make the pores completely exposed.

3.2. Synthesis of the Catalysts

The catalysts were all prepared by the CHR method. Firstly, the AC was impregnated with aqueous solution, which was obtained by dissolving certain amount of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and ammonium metatungstate (AMT) in deionized water. After being stirred for 4 h, the mixture was kept static for 24 h, and then dried by oil bath at 80 °C. Secondly, the obtained samples were calcined at 600 °C under N₂ (40 mL/min) and kept for 4 h. Finally, the precursors were reduced from room temperature to 450 °C at 5 °C/min in a flow of H₂ (40 mL/min), then to 630 °C (660 °C/680 °C/700 °C/900 °C) at 1 °C/min and maintained for 2 h. Subsequently, the catalysts were cooled to room temperature in H₂ (40 mL/min) flow, and then passivated in 5% O₂/N₂ (20 mL/min) flow for 10 h. Two groups of catalysts were prepared. In the first group, the loading of Ni and W were both 10 wt.%, whereas the final reduction temperatures were varied (630 °C or 660 °C or 680 °C or 700 °C or 900 °C). The obtained catalysts were recorded as 10Ni10W/AC-630, 10Ni10W/AC-660, 10Ni10W/AC-680, 10Ni10W/AC-700, 10Ni10W/AC-900. In the second group, the loading of W was fixed at 10 wt.%, and the reduction temperature was fixed at 700 °C, while the loading of Ni was changed. The obtained catalysts were recorded as xNi10W/AC (x = 0, 2, 10, 20), where x represented the loading of Ni. For example, 2Ni10W/AC corresponded to the catalyst with the Ni loading of 2 wt.%.
10 wt.% and the reduction temperature of 700 °C. The active component nickel loading and tungsten loading were calculated by Equation (1).

\[
\text{Wt. \%M} = \left( \frac{m_{\text{mental}}}{m_{\text{support}}} \right) \times 100\%, \quad (1)
\]

where \( m_{\text{mental}} \) and \( m_{\text{support}} \) were the mass of the supported metals and the support, respectively.

### 3.3. Catalyst Characterizations

X-ray diffraction (XRD) was conducted on a diffractometer (Shimadzu XRD-6100, Kyoto, Japan) by using Cu Kα radiation (\( \lambda = 0.1542 \text{ nm} \)). The X-ray tube was operated at 40 kV and 30 mA. XRD patterns for all samples were collected over the 2θ range from 5° to 80° with 0.06° step size. Scherrer equation was used for the calculation of crystal size.

X-ray photoelectron spectroscopy (XPS) measurements were taken by an AXIS Ultra DLD (KRATOS, England) spectrometer using monochromatic Al Kα radiation at 80 eV pass energy. The binding energy of the samples was referenced to the C1s peak at 284.6 eV.

Raman spectrum was operated by HORIBA-XploRA PLUS (HORIBA Scientific, Paris, France) with an excitation wavelength of 532 nm. Before the experiment, Raman shift was calibrated by a silicon wafer. Each sample was scanned twenty times. The Raman spectrum was collected at grating of 1800 gr/mm with an average of 5 scans in the range of 100–3000 cm\(^{-1}\).

Hydrogen temperature-programmed reduction (H\(_2\)-TPR) was tested on a Micromeritics Autochem II 2920 instrument (Norcross, GA, USA). Approximately 0.1 g of each sample was put into the U tube. Before a TPR run, the samples were pretreated in Ar at 150 °C for 1 h and then cooled to 50 °C. The pretreated samples were heated from 50 °C to 950 °C at a rate of 5 °C/min under a flow of a 10%H\(_2\)/Ar mixture (50 mL/min).

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed by Tecnai G2 F20 S-TWIN (Hillsboro, OR, USA) instrument with an acceleration voltage of 200 kV. The powder sample was ultrasonically dispersed in alcohol and then directly dripped onto holey-carbon-coated copper grids.

CO pulse chemisorption was tested on a Micromeritics Autochem II 2920 instrument. Approximately 0.1 g of each sample was put into the U tube. The samples were pretreated at reduction temperature for 2 h. After being treated in 3% CO/Ar until it was saturated, the sample was heated to 600 °C at a rate of 10 °C/min for desorption.

Inductively coupled plasma atomic emission spectrometry was used to determine the actual content of nickel and tungsten in the catalyst. Before the test, all catalysts were dissolved by a mixed solution of hydrofluoric acid (48%) and aqua regia.

### 3.4. Catalytic Performance Evaluation

JO was selected as the raw material for the catalytic activity evaluation. The activity tests of JO conversion into hydrocarbons were operated by a triple channel fixed-bed reactor (\( \Phi = 13 \text{ mm}, \ 14 \text{ cm of isothermal zone} \)). Each channel was independent of the others. The schematic diagram of the reaction device was shown in Figure S1. For a typical experiment, approximate 33 g inert silicate filling was put into the bottom of the reactor. The mixture of 3 g catalyst and about 12 g inert silicate filling was placed into the isothermal zone. Before the activity test, the catalyst was pretreated in H\(_2\) (40 mL/min) flow at 360 °C for 30 min. Then, it was cooled down to reaction temperature (340 °C). The reaction system was pressurized to 3 MPa with N\(_2\) and H\(_2\). After the temperature and pressure were stable, JO was added to the reactor by a Series III pump (305SFD02eV). The reaction was carried out in continuous mode for 5 h under a 50% H\(_2\)/N\(_2\) flow.

### 3.5. Product Analysis

After being dried by anhydrous calcium chloride, the liquid products were quantitatively analyzed by using a gas chromatograph (GC, PANNA A91, Zhejiang, China) equipped with a flame ionization detector (FID) and HP-5 column (30 m × 0.25 mm × 0.25 μm) and
identified qualitatively by using gas chromatography-mass spectrometry (GC–MS, Agilent 5973, Santa Clara, CA, USA) equipped with a capillary column (HP-INNOWAX, 30 m × 0.25 mm × 0.25 µm). The oxygen content of the product was measured by Element analyzer (Flash EA 1112). The compositions of the gaseous products were identified with a gas chromatograph (GC, PANNA A91, Zhejiang, China) equipped with EC-1 column (30 m × 0.53 mm × 0.5 µm). The deoxygenation (DO) rate of JO was calculated according to Equation (2).

\[
\text{DO rate} \% = \frac{(O_1 - O_2)}{O_1} \times 100\% ,
\]

The selectivity was calculated according to Equation (3).

\[
\text{Selectivity} \% = \frac{W_{\text{products (C}_{12-18}}} {W_{\text{total organic products}}} \times 100\% ,
\]

The yield was calculated according to Equation (4).

\[
\text{Yield} \% = \frac{W_{\text{product}}} {W} \times 100\% ,
\]

where \(O_1\) and \(O_2\) were the oxygen content of JO and product, respectively. \(W_{\text{products (C}_{12-18}}\) and \(W_{\text{total organic liquid products}}\) were the weight of \(C_{12-18}\) obtained and the weight of total organic products obtained, respectively. \(W\) and \(W_{\text{product}}\) were the weight of the added JO and the weight of total oil products obtained, respectively.

4. Conclusions

In summary, we successfully prepared a high-performance nickel-promoted tungsten carbide catalyst for the deoxygenation of JO by tuning the reduction temperature and the loading of Ni. With the increase in reduction temperature or Ni loading, the tungsten species on the catalyst were gradually carbonized into \(W_2C\) species, and then further carbonized into WC species. Nickel was beneficial to increase the loading and dispersion of tungsten species, and reduce the carbonization temperature of the tungsten species. When the reduction temperature was 700 °C and the Ni loading was 10 wt.%, the obtained 10Ni10W/AC-700 catalyst exhibited the best catalytic performance due to having the smallest particle size, the highest graphitization degree, the best dispersion and the synergistic effect of the Ni, \(W_2C\) and WC species. Ni–\(W_2C–WC\) was conducive to the breaking of C–C bond, but not to the breaking of the C–O bond in the conversion of JO. Therefore, on all the catalysts, the deoxygenation reactions proceeded mainly through DCO/DCO\(_2\) pathway.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11040469/s1, Figure S1. The reaction apparatus for catalytic activity test. Figure S2. Raman spectra of the AC support. Figure S3. The XPS spectra of Ni 2p for the 10Ni10W precursor. Figure S4. The GC-MS graphs of products on the 10Ni10W/AC catalysts reduced at different temperatures. Figure S5. The GC-MS graphs of products on the xNi10W/AC (x=0, 2, 10, 20) catalysts. Figure S6. (a) XRD patterns of the nickel-tungsten precursors; (b) XRD patterns of the xNi10W/C (x=0, 2, 10, 20) catalysts. Figure S7. \(H_2\)-TPR curve of the xNi10W/AC (x=0, 2, 10, 20) catalysts. Figure S8. TEM images of (a) 10W/AC, (b) 2Ni10W/AC, (c) 10Ni10W/AC, (d) 20Ni10W/AC. Figure S9. Nitrogen adsorption-desorption isotherms (a) and BJH pore-size distribution curves (b) of different catalysts. Table S1. The CO uptake on the 10Ni10W/AC catalysts reduced at different temperatures. Table S2. The activity results on the 10Ni10W/AC catalysts reduced at different temperatures. Table S3. The concentration of the gas products on the 10Ni10W/AC catalysts reduced at different temperatures. Table S4. The activity results on the xNi10W/AC (x=0, 2, 10, 20) catalysts. Table S5. The concentration of the gas products on the xNi10W/C (x=0, 2, 10, 20) catalysts. Table S6. The crystal size of different phases for the xNi10W/C (x=0, 2, 10, 20) catalysts. Table S7. The Ni and W mass fraction of the xNi10W/C (x=0, 2, 10, 20) catalysts. Table S8. The activity results on the 10Ni/AC catalyst. Reaction conditions: \(T=340\ ^\circ C, P=3\ MPa, t=5\ h, WHSV=55.2\ h^{-1}, H_2/N_2=1, F=200\ mL/min\). Before the reaction, the catalyst was pretreated in \(H_2\) at 360 °C for 30 min to remove the surface oxides resulting from passivation process. Table S9. Physicochemical Properties of 10Ni10W/AC catalysts reduced at different temperatures.
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