

Supporting information

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

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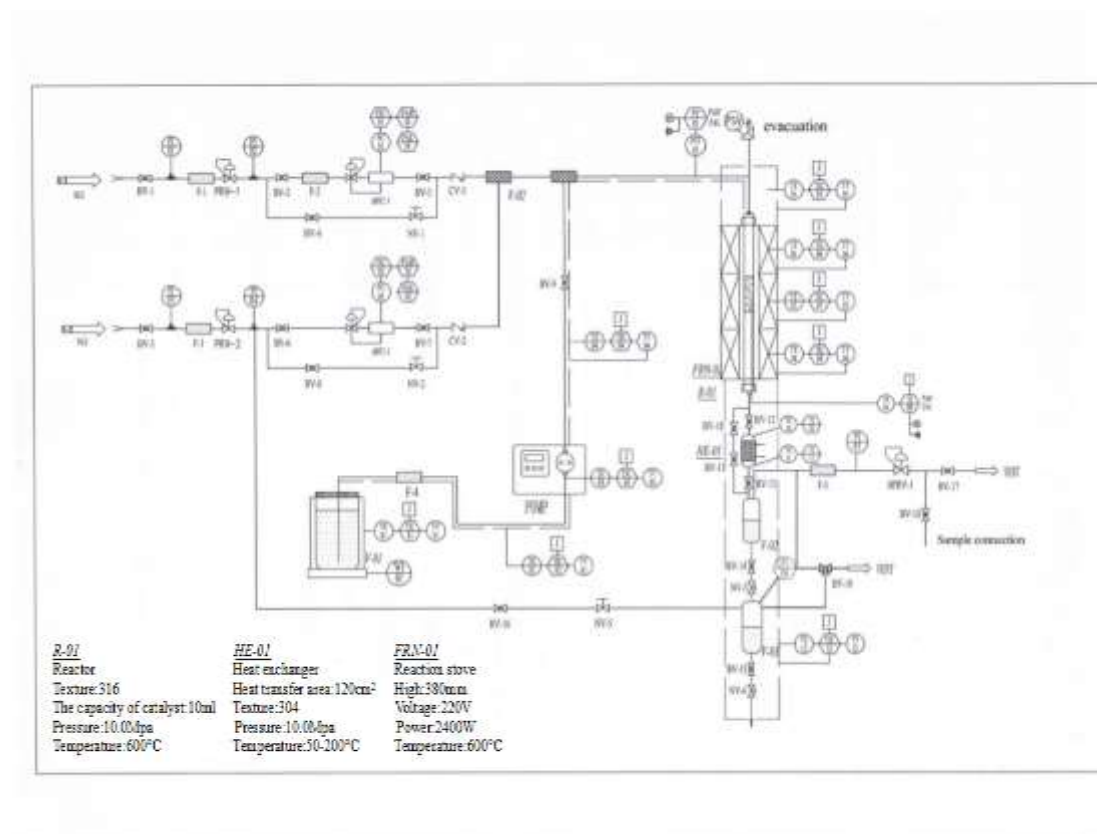


Figure S1. The reaction apparatus for catalytic activity test.

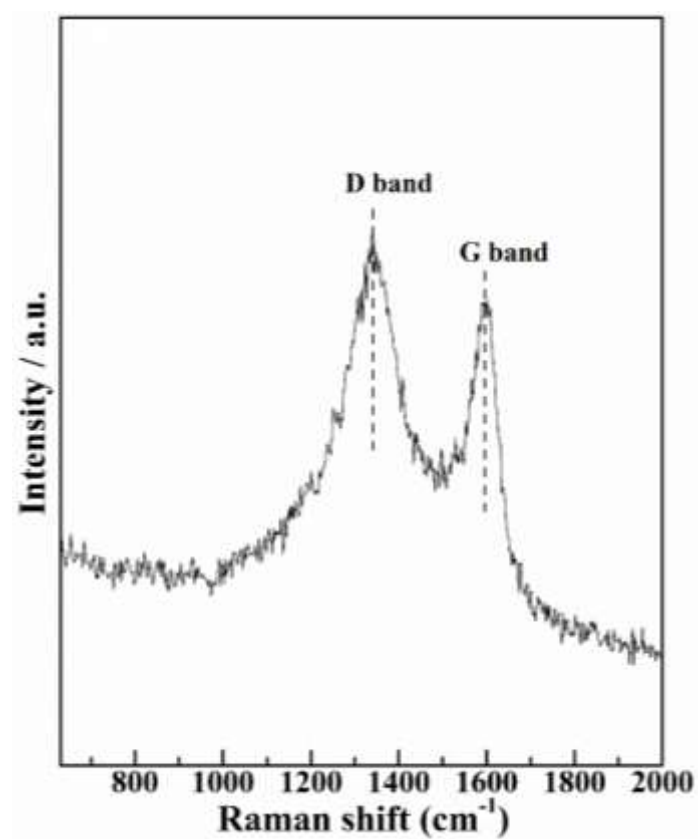


Figure S2. Raman spectra of the AC support.

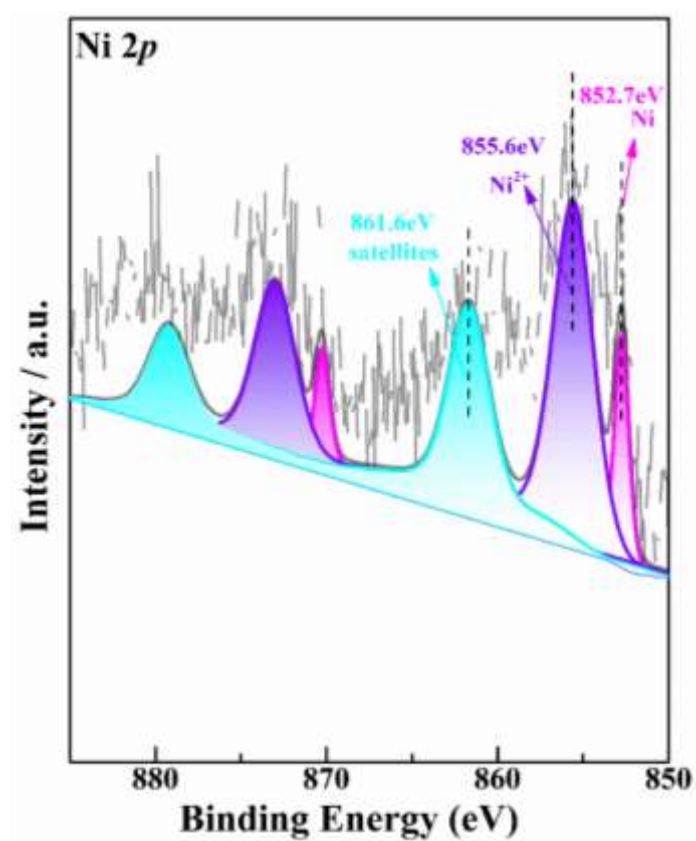


Figure S3. The XPS spectra of Ni 2*p* for the 10Ni10W precursor.

Figure S3 showed the X-ray photoelectron spectroscopy of the precursor. The peak appearing at 852.7 eV was attributed to metallic Ni, and the peak at 855.6 eV was ascribed to Ni²⁺ in NiO. The peak at 861.6 eV was ascribed to the shake-up satellites of nickel.

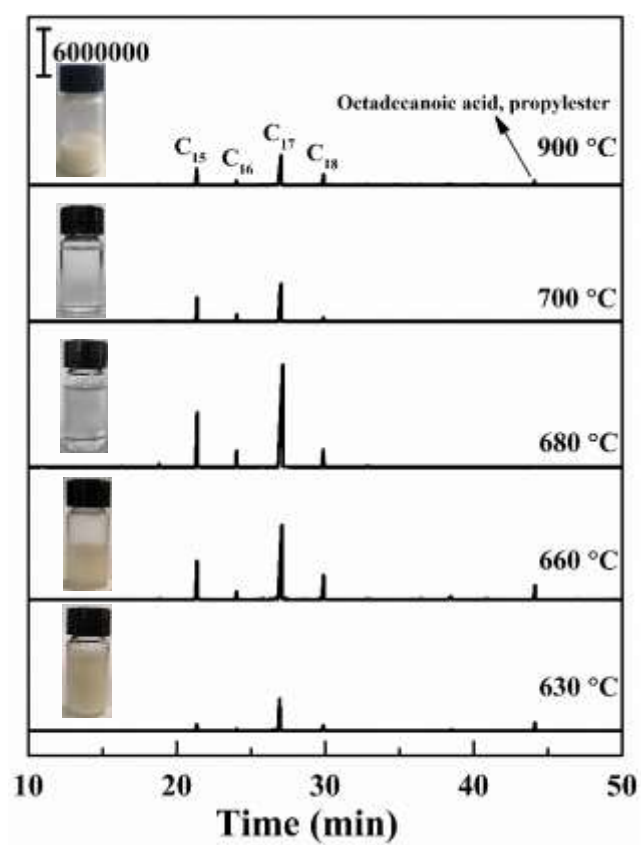


Figure S4. The GC-MS graphs of products on the 10Ni10W/AC catalysts reduced at different temperatures.

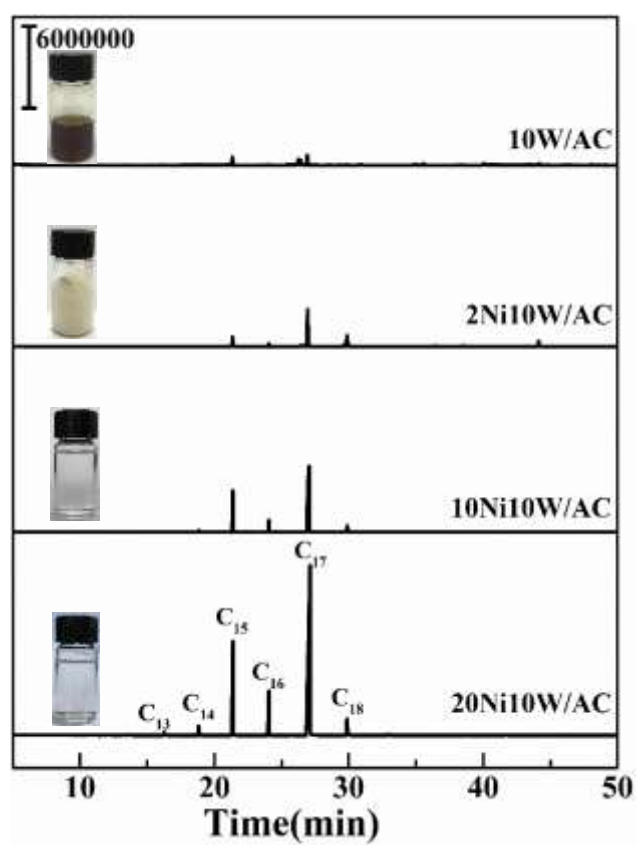


Figure S5. The GC-MS graphs of products on the xNi10W/AC (x=0, 2, 10, 20) catalysts.

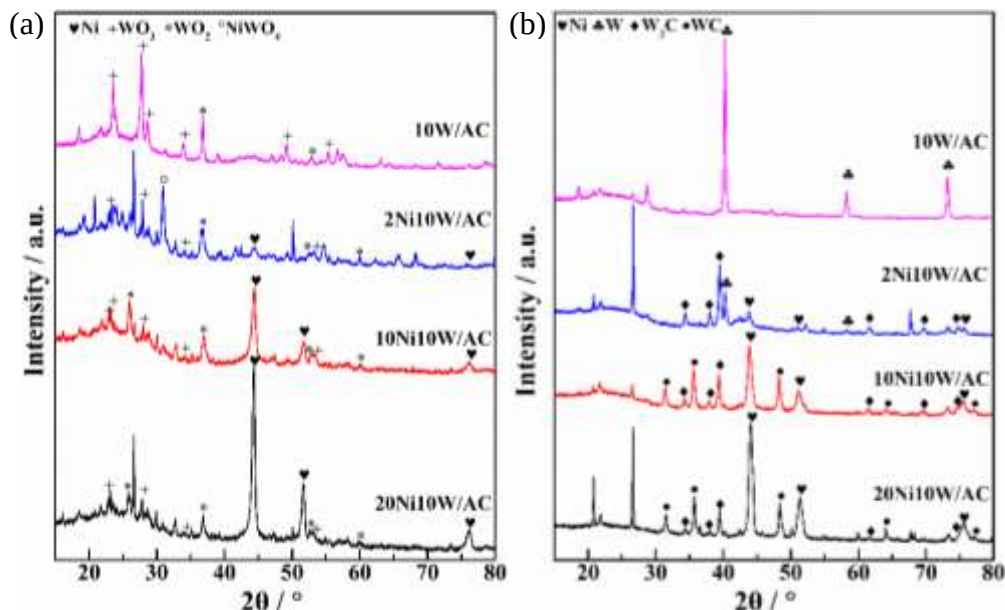


Figure S6. (a) XRD patterns of the nickel-tungsten precursors; (b) XRD patterns of the xNi10W/C (x=0, 2, 10, 20) catalysts.

It could be seen from the XRD results (Figure S6) that on the precursors, metallic Ni crystal phase (PDF#04-0850), WO_3 crystal phase (PDF#20-1324) and WO_2 crystal phase (PDF#32-1393) were observed. Among them, on the 2Ni10W/AC precursor, the diffraction peak at 30.9° (PDF#15-0755) was corresponded to NiWO_4 . After reduced at 700°C , metallic W crystal phase (PDF#04-0806) was observed on the 10W/AC catalyst. Metallic W crystal phase and W_2C crystal phase (PDF#35-0776) were observed on the 2Ni10W/AC catalyst. W_2C crystal phase and WC crystal phase (PDF#51-0939) were observed on the 10Ni10W/AC and 20Ni10W/AC catalysts. With the increase of Ni loading, W species gradually carbonized into W_2C and WC species, indicating that Ni could reduce the carbonization temperature of tungsten species. However, when the loading amount of Ni exceeded 10%, the tungsten species generated on the AC no longer changed.

The crystal sizes of different species were calculated by the Scherrer equation and listed in Table S6. As the loading of Ni increased, the crystal size of the metallic W increased on the catalysts, but the metallic W disappeared when the loading of Ni was 10wt.%. The crystal size of W_2C decreased on the 2Ni10W/AC and 10Ni10W/AC catalysts. When the loading of Ni was 20wt.%, the crystal size of W_2C and WC had not changed much.

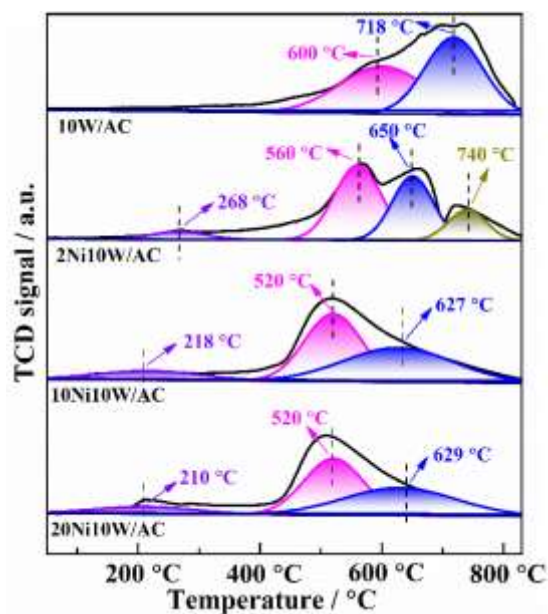


Figure S7. H₂-TPR curve of the xNi10W/AC (x=0, 2, 10, 20) catalysts.

It could be seen from H₂-TPR results (Figure S7) that the reduction peaks at 210 °C-268 °C, 520 °C-600 °C, 627 °C-718 °C, 740 °C were attributed to the reduction of NiO, WO₃, WO₂, NiWO₄ species, respectively. With the increase of Ni loading, the reduction temperature of WO₃ and WO₂ gradually decreased. When the loading of Ni exceeded 10%, the reduction temperature of WO₃ and WO₂ would no longer decrease.

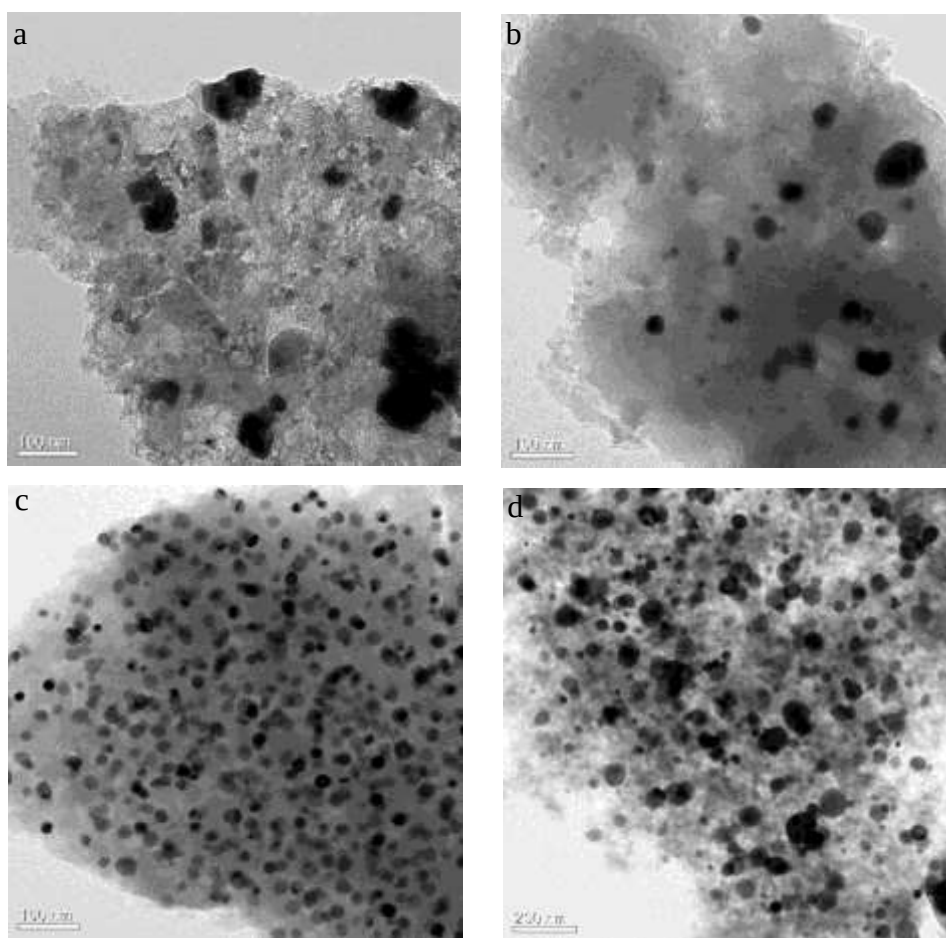


Figure S8. TEM images of (a) 10W/AC, (b) 2Ni10W/AC, (c) 10Ni10W/AC, (d) 20Ni10W/AC.

It could be seen from TEM results (Figure S8) that when the Ni loading was 0wt.%, the species on the catalyst was mainly metallic W with large particles. With the increase of Ni loading, the metallic W was gradually carbonized into tungsten carbide species with small particles. When the Ni loading was 10wt.%, the metallic W disappeared, and the particle size of the nickel and tungsten carbide components were almost the same and uniformly dispersed. When the Ni loading further increased to 20wt.%, the nickel and tungsten carbide species were easy to agglomerate, resulting in an increase in particle size. Therefore, Ni facilitated the dispersion of W species. And the optimum loading of Ni was 10wt.%.

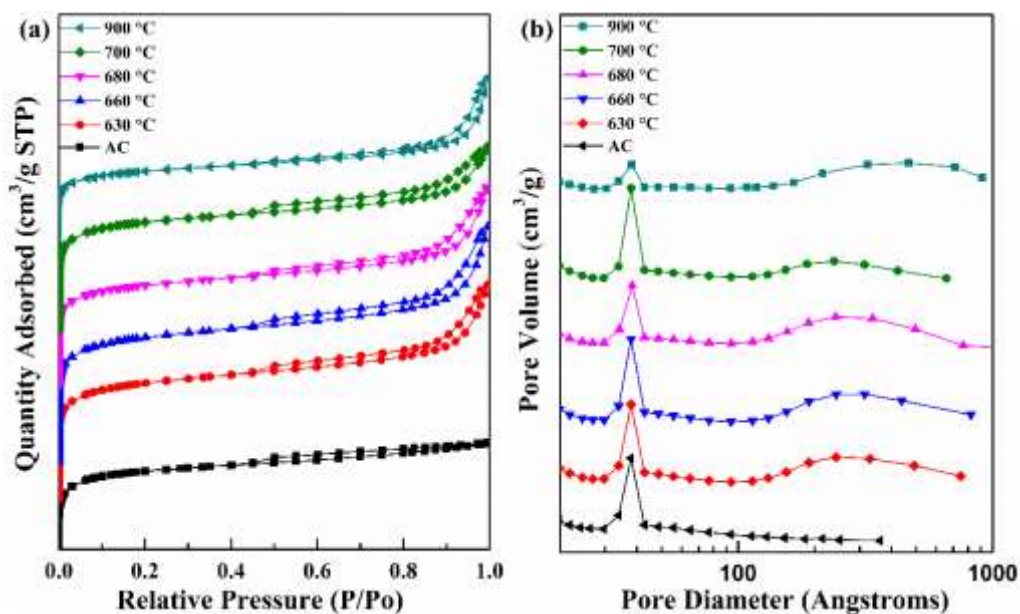


Figure S9. Nitrogen adsorption-desorption isotherms (a) and BJH pore-size distribution curves (b) of different catalysts.

The textural properties of all catalysts were determined by BET and BJH methods, as shown in Figure S9 and Table S9. The isotherms with a hysteresis loop were identified as a type IV characteristic of mesoporous materials. It was disclosed that the support and all catalysts belonged to mesoporous materials[1]. Compared with the AC support, the BET surface area of 10Ni10W/AC catalysts was decreased, which indicated that the nickel-tungsten active components were supported on the surface of the support and in the pores of the support. The pore volume and pore size were all increased because the small particles accumulated into pores after loading the nickel-tungsten active component. The pore volume and pore size of different catalysts were not different.

Table S1. The CO uptake on the 10Ni10W/AC catalysts reduced at different temperatures.

Catalysts	10Ni10W/AC- 900	10Ni10W/AC- 700	10Ni10W/AC- 680	10Ni10W/AC- 660	10Ni10W/AC- 630
CO uptake (mmol/g)	2.97×10^{-2}	3.16×10^{-2}	3.15×10^{-2}	3.06×10^{-2}	2.81×10^{-2}

Table S2. The activity results on the 10Ni10W/AC catalysts reduced at different temperatures.

catalyst	Yield (%)	DO rate (%)	C₁₂ (%)	C₁₃ (%)	C₁₄ (%)	C₁₅ (%)	C₁₆ (%)	C₁₇ (%)	C₁₈ (%)	C₁₅-C₁₈ (%)	C₁₅+C₁₇/ C₁₆+C₁₈
10Ni10W/AC -900	60.8	75.0	0.04	0.06	0.10	6.81	1.49	35.03	6.38	49.71	5.3
10Ni10W/AC -700	67.1	99.7	0.11	0.25	0.72	14.81	4.06	72.29	3.34	94.5	11.8
10Ni10W/AC -680	63.2	97.4	0.07	0.17	0.44	11.54	2.49	60.06	3.37	77.46	12.2
10Ni10W/AC -660	60.0	88.0	0.05	0.08	0.14	8.23	1.54	42.30	5.92	57.99	6.8
10Ni10W/AC -630	68.3	66.0	0.03	0.05	0.08	4.70	0.97	25.02	4.21	34.90	5.7

Table S3. The concentration of the gas products on the 10Ni10W/AC catalysts reduced at different temperatures.

Catalyst Gas content (%)	10Ni10W/AC	10Ni10W/AC	10Ni10W/AC	10Ni10W/AC	10Ni10W/AC
	-900	-700	-680	-660	-630
Methane	0.16	1.49	1.55	0.76	0.11
Ethane	0.13	---	0.72	0.49	---
Ethylene	---	0.18	---	---	0.03
Propane	---	0.28	0.88	0.94	0.37
Cyclopropane	---	---	---	---	---
Isobutane	---	---	0.06	0.03	---
N-butane	---	---	0.30	0.20	---
Butene	---	---	0.08	0.05	---
Carbon dioxide	0.08	---	---	0.05	0.06
Carbon monoxide	0.25	---	---	0.02	0.25

---: not detected.

The gas products were mixed with H₂ and N₂.

Table S4. The activity results on the xNi10W/AC (x=0, 2, 10, 20) catalysts.

catalyst	Yield (%)	DO rate (%)	C₁₂ (%)	C₁₃ (%)	C₁₄ (%)	C₁₅ (%)	C₁₆ (%)	C₁₇ (%)	C₁₈ (%)	C₁₅-C₁₈ (%)	C₁₅+C₁₇/ C₁₆+C₁₈
10W/AC	57.8	19.7	0.04	0.03	0.01	1.00	0.11	1.64	0.05	2.80	16.5
2Ni10W/AC	74.5	26.2	0.03	0.02	0.04	1.57	0.02	6.29	0.68	8.56	11.2
10Ni10W/AC	67.1	99.7	0.11	0.25	0.72	14.81	4.06	72.29	3.34	94.50	11.8
20Ni10W/AC	67.1	96.2	0.18	0.42	1.17	13.46	5.82	64.99	2.89	87.17	9.0

Table S5. The concentration of the gas products on the xNi10W/C (x=0, 2, 10, 20) catalysts.

Catalyst Gas content (%)	10W/AC	2Ni10W/AC	10Ni10W/AC	20Ni10W/AC
Methane	0.04	0.10	1.49	2.57
Ethane	---	0.07	---	---
Ethylene	---	---	0.18	0.19
Propane	---	0.04	0.28	0.17
Cyclopropane	---	---	---	
Isobutane	---	0.17	---	0.03
N-butane	---	---	---	0.11
Butene	---	---	---	0.03
Carbon dioxide	6.33	0.22	---	0.05
Carbon monoxide	---	0.12	---	---

---: not detected.

The gas products were mixed with H₂ and N₂.

Table S6. The crystal size of different phases for the xNi10W/C (x=0, 2, 10, 20) catalysts.

Catalysts	Crystal size (nm)			
	Ni	W	W ₂ C	WC
10W/C	---	33.0	---	---
2Ni10W/AC	18.4	37.3	29.4	---
10Ni10W/AC	14.5	---	23.7	21.4
20Ni10W/AC	15.4	---	24.2	20.3

---: not detected.

Table S7. The Ni and W mass fraction of the xNi10W/C (x=0, 2, 10, 20) catalysts.

Catalyst	Ni (controlled content) (wt.%)	W (controlled content) (wt.%)	Ni (actual content) (wt.%)	W (actual content) (wt.%)
10W/AC	---	10.0	---	1.5
2Ni10W/AC	2.0	10.0	1.5	6.0
10Ni10W/AC	10.0	10.0	7.8	6.8
20Ni10W/AC	20.0	10.0	17.7	7.4

The actual content of nickel and tungsten on all catalysts were tested by inductively coupled plasma atomic emission spectrometry (ICP-AES) (seen in Table S7), and it was found that with the loading of Ni increased, the loading of W increased from 1.5% to 7.4%. Ni was beneficial to the loading of W. However, when the controlled loading amount of Ni exceeded 10wt.%, the actual loading of W no longer increased.

Table S8. The activity results on the 10Ni/AC catalyst. Reaction conditions: T=340 °C, P=3 MPa, t=5 h, WHSV=55.2 h⁻¹, H₂/N₂=1, F=200 mL/min. Before the reaction, the catalyst was pretreated in H₂ at 360 °C for 30min to remove the surface oxides resulting from passivation process.

catalyst	Yield (%)	DO rate (%)	C₁₂ (%)	C₁₃ (%)	C₁₄ (%)	C₁₅ (%)	C₁₆ (%)	C₁₇ (%)	C₁₈ (%)	C₁₅-C₁₈ (%)	C₁₅+C₁₇/ C₁₆+C₁₈
10Ni/AC	60.7	95.6	1.06	1.89	3.83	15.35	10.42	54.04	1.09	80.90	6.0

The 10Ni/AC catalyst was prepared by carbothermal hydrogen reduction (CHR) method. The controlled loading of Ni was 10wt.%, and the final reduction temperature was 700 °C. The DO reaction of JO on the 10Ni/AC catalyst was evaluated, and the results were shown in Table S8. The DO rate of the 10Ni/AC catalyst was 95.6%, the total C₁₅₋₁₈ selectivity was 80.9%, the C₁₇ selectivity was 54.0% and the yield of fuel was 60.7%, which were lower than that on the 10Ni10W/AC-700 catalyst.

Table S9. Physicochemical Properties of 10Ni10W/AC catalysts reduced at different temperatures.

Catalysts	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
10Ni 10W/C-900	333	0.36	4.36
10Ni 10W/C-700	526	0.42	3.17
10Ni 10W/C-680	483	0.45	3.73
10Ni 10W/C-660	595	0.53	3.56
10Ni 10W/C-630	557	0.48	3.49
AC	649	0.38	2.33

References

1. Lee, S.-U.; Lee, Y.-J.; Kim, J.-R.; Jeong, S.-Y. Rational synthesis of silylated Beta zeolites and selective ring opening of 1-methylnaphthalene over the NiW-supported catalysts. *Applied Catalysis B: Environmental* **2017**, *219*, 1-9.