Supporting Information

Tungsten-based catalysts for lignin depolymerization: the role of tungsten species in C-O bond cleavage

Haiwei Guo,[a,c] Zaojuan Qi,[a] Yuxuan Liu,[a] Haian Xia,[b] Lin li,[a] Qitian Huang,[a] Aiqin Wang,[a,d] Changzhi Li[a,d*]

a. Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
b. Jiangsu provincial key lab for the chemistry and utilization of agro-forest biomass, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China
c. University of Chinese Academy of Sciences, Beijing, 100049, China.
d. Dalian National Laboratory for Clean Energy, 457 Zhongshan Road, Dalian, 116023, China.

Content

1. **General information and procedures** 1
2. **Supporting Figures and Tables** 3
3. **References** 15

1. General information and procedures

1. Preparation of the catalysts

The catalysts were prepared by wet impregnation of tungsten precursor on activated carbon (AC) support under different carbothermal heat treatment temperatures. For a typical preparation, 2 g of activated carbon (NORIT, AC) was impregnated with an aqueous solution containing 1.15 g of ammonium metatungstate (AMT), and the mixture was dried at 120 °C for 12 h. The sample was then carburized in N_2 flow under a two-stage heating ramp: from room temperature (RT) to 500 °C in 60 min, and then to certain temperatures (i.e., 500 °C to 1000 °C) at 1 °C/min and holding at that temperature for 3 h. Prior to exposure to air, the as-prepared carbide catalyst was passivated in a flow of 1 % O_2/N_2 at room temperature for 3 h to obtain the catalysts (labelled as N_2-500 to N_2-1000).

2. Characterization of the catalysts

2.1 X-ray diffraction (XRD) analysis

The X-ray diffraction (XRD) patterns of the samples were obtained with an X'pert Pro-1(19 dicp, PANalytical) diffractometer operatedat 40 kV and 40 mA, using Ni-filtered Cu-Kαradiation.

2.2 Raman spectroscopy

The Raman spectra were recorded on a high-resolution Raman spectrometer (LabRAM HR 800, France) acquired with a Jobin Yvon HR 800 Dispersive Raman Spectrometer and operated at a resolution better than 2 cm^{-1}. Approximately 25 mg of samples in the form of microcrystalline powder was pressed into a 10 mm diameter pellet. The Raman scattering was collected at room temperature in a static-scan mode in the 200-2000 cm^{-1} spectral region under excitation wavelength of 514 nm (He-Ne laser) with a power of 0.1 mW. The exposure time was 60 s.

2.3 Physical adsorption analysis

The specific surface area of the catalysts was determined from N_2 physical adsorption-desorption isotherms on an ASAP 2460 Quantachrome instrument and calculated by BET (Brunauer-Emmett-Teller) equation. Before analysis, the samples were treated at 100 °C for 1h and then degassed at 300 °C in vacuum for 3 h.

2.4 X-ray photoelectron spectroscopy (XPS)

XPS was performed on a Kratos AXIS ULTRA DLA X-ray photoelectron spectrometer equipped with an Al Kαradiation source (1486.6 eV, 15 kV). All binding energies were calibrated with the C1s peak at 284.8 eV for the adventitious carb.

2.5 Temperature-programmed desorption of ammonia

Temperature-programmed desorption of ammonia (NH_3-TPD) was conducted on a Micromeritics AutoChem II 2920 chemisorber. Before the measurement, the samples were swept in He stream at 500 °C for 30 min and then cooled down to 100 °C for NH_3 adsorption. After adsorption saturation, the samples were heated from 100 °C to 500 °C in He flow at a heating rate of 10 °C min^{-1}, while the desorbed NH_3 was monitored by a mass spectrometer system. Among various signals, m/e = 16 was monitored to analyze the desorbed NH_3 to avoid the interference of water.

2.6 H_2 Microcalorimetry

Microcalorimetric measurement was performed using a BT2.15 heat-flux calorimeter. Briefly, the calorimeter was connected to a gas handling and a volumetric system employing MKS Baratron Capacitance Manometers for precision pressure measurement ($\pm$ 0.5 $\times$ 10^{-4} Torr). The maximum apparent leak rate of the volumetric system was 10^{-6} Torr/min in a system volume of approximately 80 cm^{-3}. The ultimate dynamic vacuum of the system was *ca.* 10-7 Torr.

The procedures used in microcalorimetric measurement were briefly described as follows. First, sample was treated in a special treatment cell using a dynamic high pure He atmosphere at 500 ℃ for 1h. After that, the sample was transferred to a side-armed Pyrex and sealed with 300 Torr He in a Pyrex capsule. The capsule can minimize the possible contamination in the high vacuum system in the course of thermal equilibrium (6-8 h) with the calorimeter. After thermal equilibrium was reached, the capsule was broken by a vacuum feedthrough and 'fresh' catalyst was exposed. The microcalorimetric data were then collected by sequentially introducing small doses (1-10 μmol) of probe molecules onto the sample until it became saturated (5-6 Torr). The differential heat versus adsorbate coverage plots and adsorption isothermals can be obtained simultaneously after a typical microcalorimetric experiment.

2.7 Scanning Transmission Electron Microscopy (STEM)

HAADF-STEM images were obtained using a JEOL JEM-2100F at 200 kV. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

3. Catalytic conversion of model compounds and beech lignin over tungsten-based catalysts

Lignin dioxasolv extraction: as previous described.[1] In detail, to beech sawdust (70 g) was added 1,4-dioxane (504 mL) followed by 2 mol L^{-1} HCl (56 mL), and the mixture was heated with reflux at 100 °C for 1 h. The mixture was then cooled, and the lignin-containing liquor was collected by filtration. The collected liquor was concentrated in *vacuo* to give a gummy residue, and the residue was redissolved in 5mL acetone/H_2O (9:1) and then precipitated into H_2O (> 10 volumes) and stirred vigorously. The crude lignin was filtered and dried under vacuum for overnight. The dried crude lignin was dissolved in 5mL acetone/methanol (9:1) and precipitated into diethyl ether (> 10 volumes) by dropwise. The precipitated lignin was collected by filtration and dried in vacuum oven to get purified beech lignin. This lignin was used in subsequent experiments without further processing.

Typical procedure for C-O cleavage of lignin model compounds: The catalytic conversion of lignin model compound was carried out in a stainless-steel autoclave (50 mL) with an initial H_2 pressure of 1MPa and 260 ^oC for 2 h. Typically, lignin model compound (100 mg), catalyst (300 mg), and n-hexane (30 mL) were added in a stainless-steel autoclave (50 mL), the autoclave was then charged with an initial H_2 pressure of 1 MPa and stirred (800 rpm) at 260 ^oC for 2 h. After reaction, the reaction mixture was cooled to room temperature and was filtered. The liquid phase was analyzed by GC-FID and was quantified by internal standard method (standard: mesitylene, HP-5 column, 30 m × 0.32 mm × 0.25 µm).

Typical procedure for W_2C/AC catalyzed depolymerization of lignin feedstocks: The catalytic conversion of lignin material was carried out in a stainless-steel autoclave (50 mL) with an initial H_2 pressure of 1 MPa and 200 ^oC for 6 h. Typically, lignin (100 mg), catalyst (100 mg), and methanol (30 mL) were charged in the autoclave and stirred at rate of 800 rpm. After reaction, the reaction mixture was cooled to room temperature and was filtered. The filtrate was concentrated under reduced pressure at 45 ^oC to obtain liquid oil and weighed. The liquid oil was then diluted to 1.5 mL with methanol, the monomer products in liquid oil were analyzed and quantified by internal standard method (standard: mesitylene) with HP 5973 GC–MS (HP-5 column, 30 m × 0.32 mm × 0.25 µm).

2. Supporting Figures and Tables

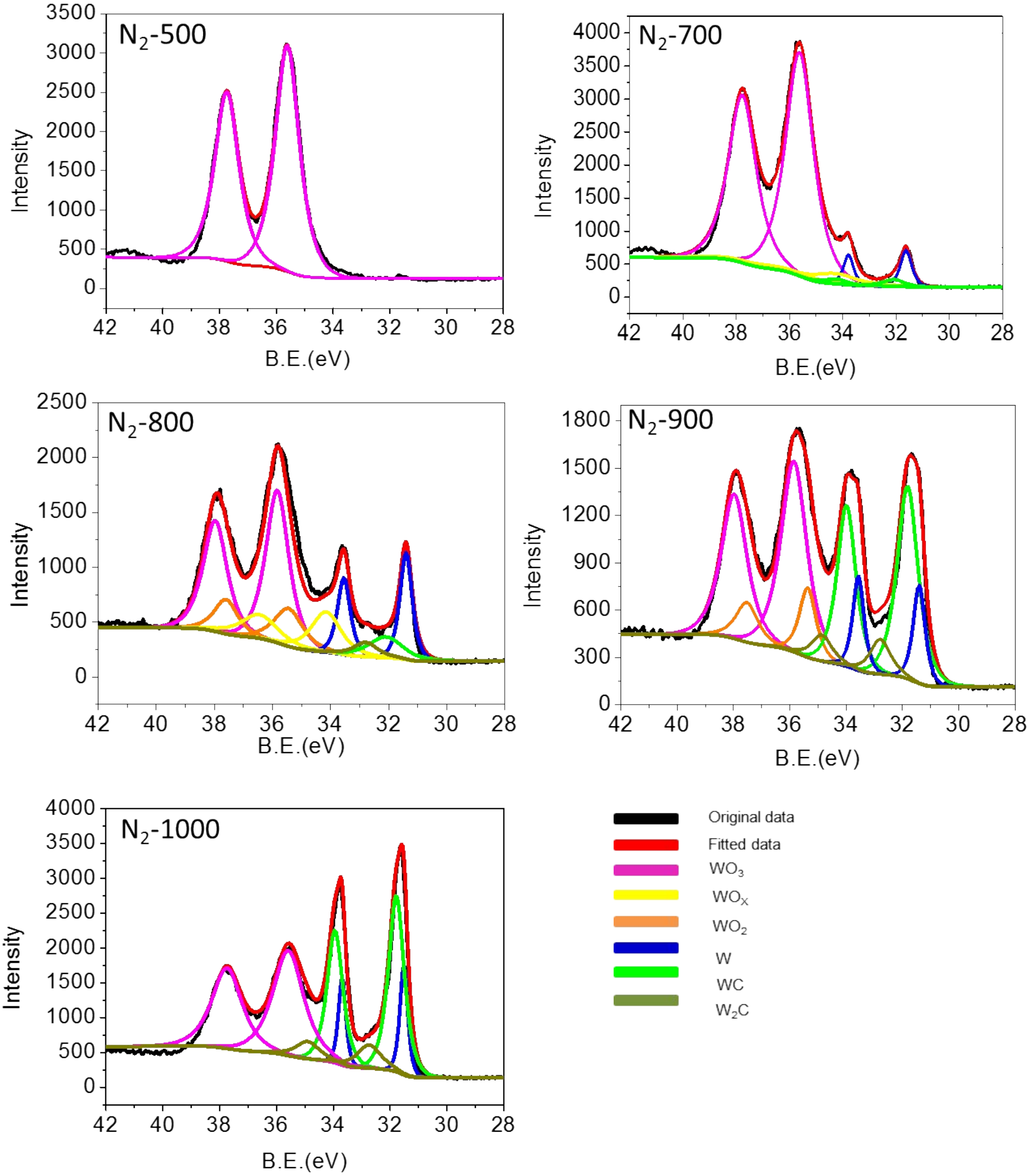


Figure S1. Curve-fitted W 4*f* XPS spectra for various tungsten-based catalysts.

Table S2. Percentage of each tungsten-based phases through XPS analysis.

Catalysts	WO_3	WO_X	WO_2	W	WC	W_2C	WO_3: WC
N2-500	100%	0%	0%	0%	0%	0%	1/0
N2-700	85%	7%	0%	6%	2%	0%	1/0.02
N2-800	44%	13%	15%	16%	8%	4%	1/0.18
N2-900	41%	0%	10%	10%	33%	6%	1/0.80
N2-1000	44%	0%	0%	11%	37%	8%	1/0.84

Note: All the values were calculated through the integrated area of each peaks in $W4f_{7/2.}$

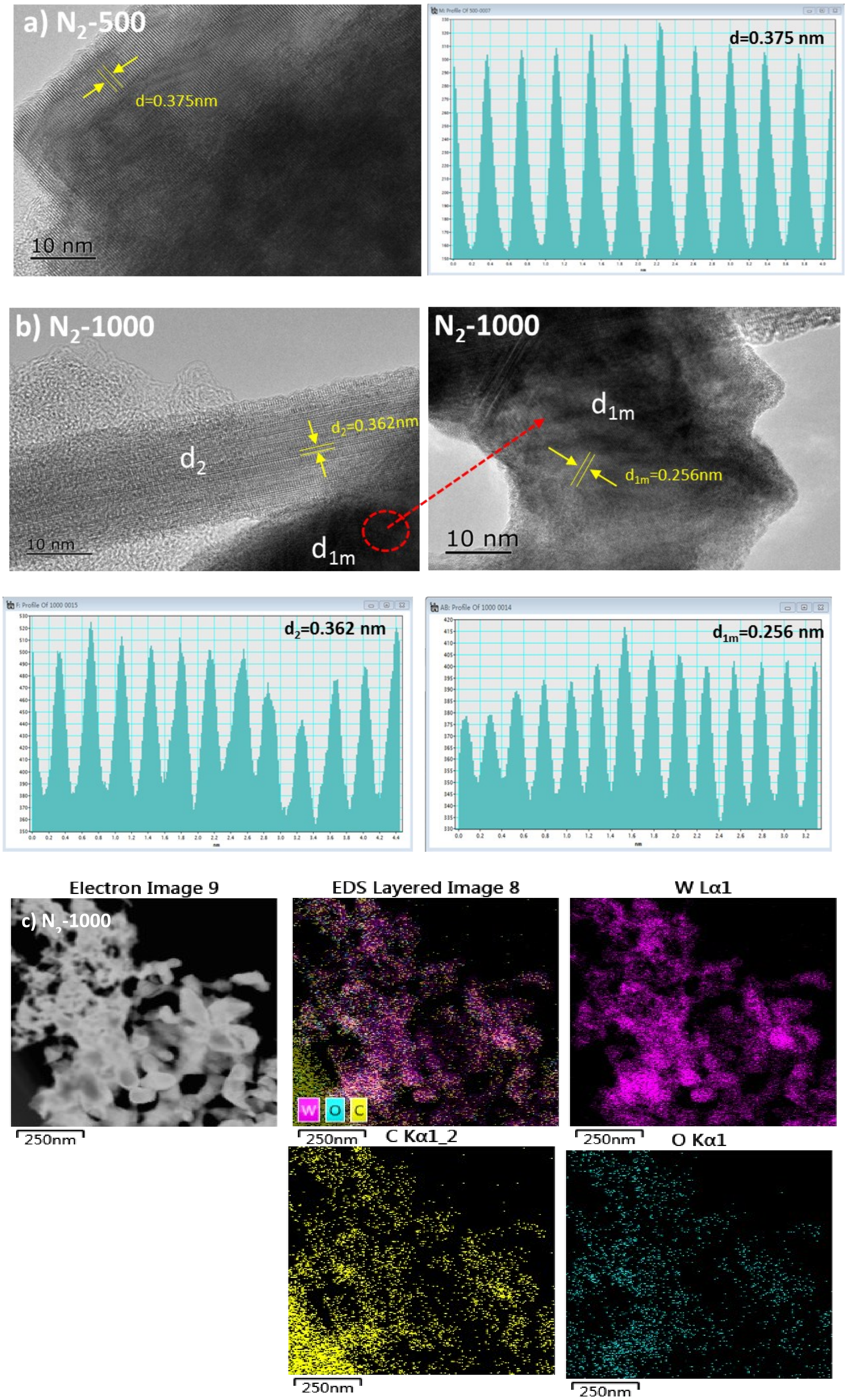
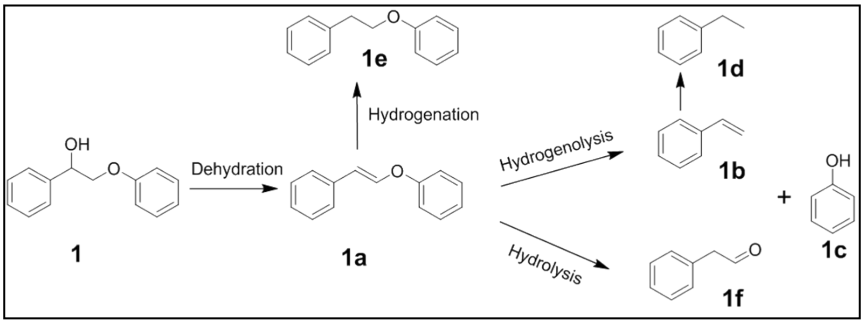


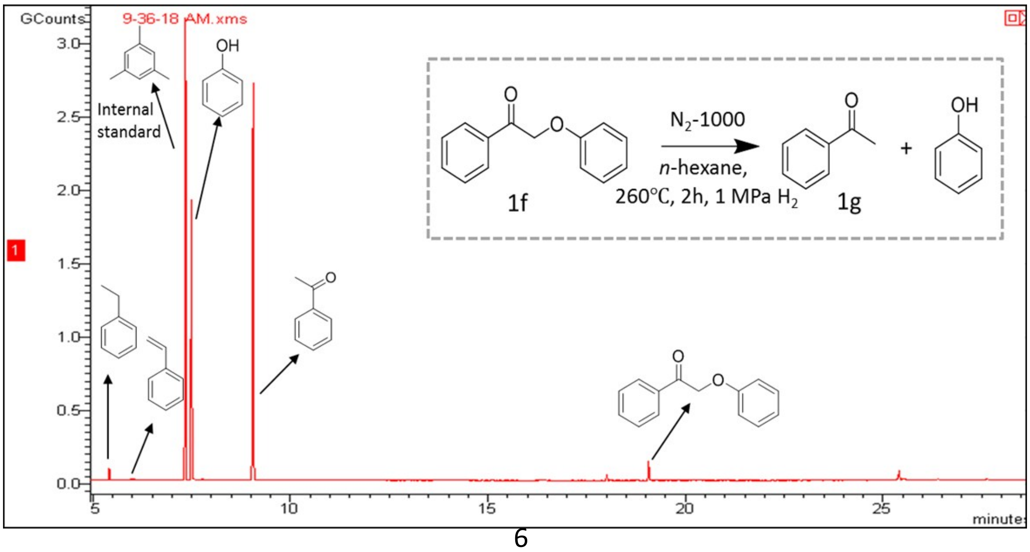
Figure S2. HRTEM and lattice distance of a) N_2-500 and b) N_2-1000; c) EDS of N_2-1000.

Table S3. The catalytic activity of model compounds over various tungsten-based catalysts.



		Yield %						
Catalysts	Conversion%	**1a**	**1b**	**1d**	**1d: 1b**	**1f**	**1c**	**1e**
AC	48	9	8	2	20:80	0	18	4
N_2-500	60	18	19	2	10:90	0	14	4
N_2-700	62	17	17	3	15:85	2.0	14	4
N2-800	79	15	13	2	13:87	6.4	20	4
N2-900	100	12	25	15	38:62	6.5	37	6
N_2-1000	100	10	29	15	34:66	6.5	47	6
N_2-500[a]	65	22	8	0	0:100	14	21	3
N_2-1000[a]	70	15	6	0	0:100	21	27	4
N_2-700[b]	96	33	30	3	9:81	0	29	4
N_2-1000[b]	100	10	12	43	78:12	0	39	22

Reaction conditions: substrate: 100 mg, catalyst :30 mg, *n*-hexane: 30 mL, 260 °C, 2 h, 1 MPa H_2 (RT). [a] Performed in 1MPa N_2; [b] 100 mg catalysts were employed.



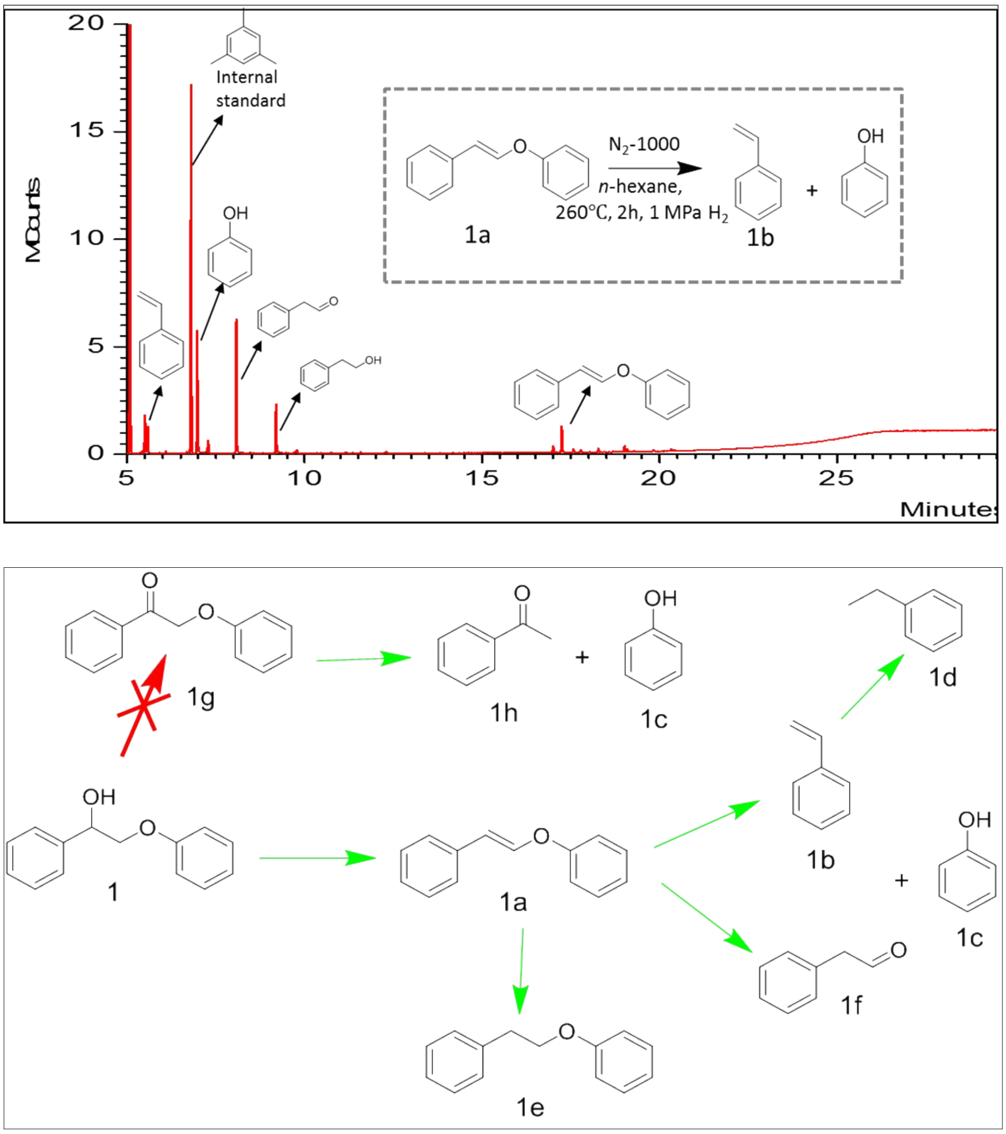
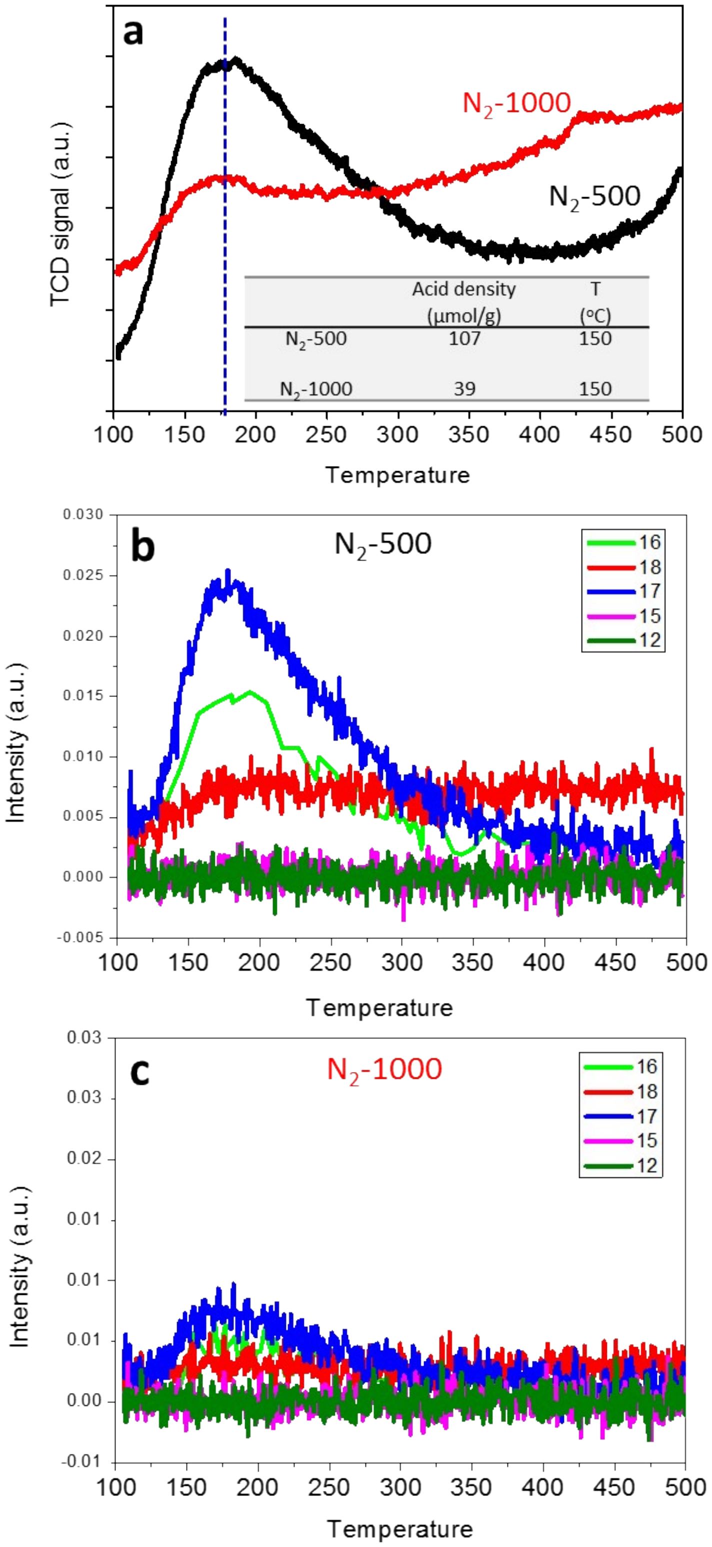


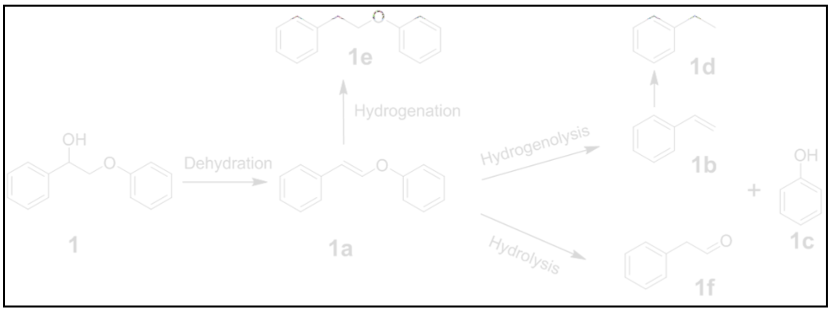
Figure S3. Proof study for the reaction route.



	Acid density (μmol/g)	T (°C)
N_2-500	107	150
N_2-1000	39	150

Figure S4. NH3-TPD profile **(a)** and corresponding MS spectra **(b & c**) of tungsten-based catalysts.

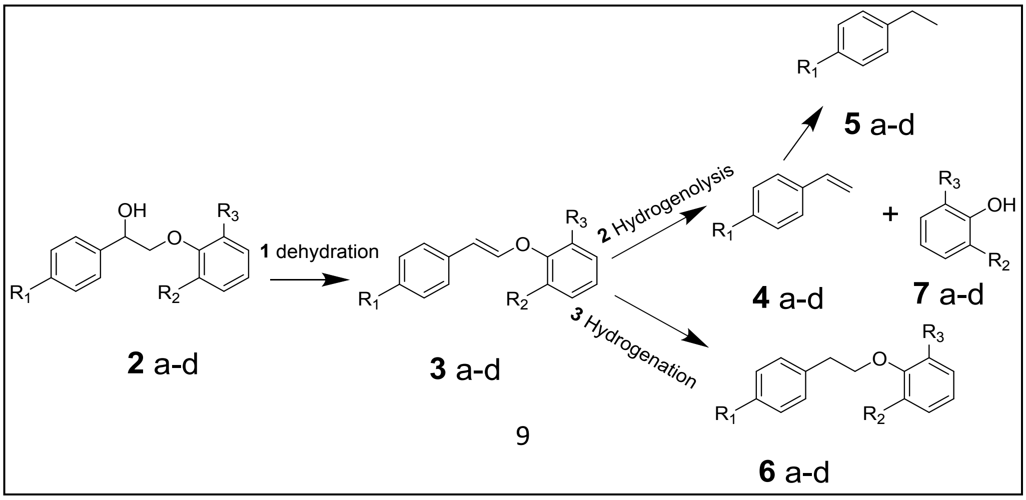
Table S4. Composition of the reaction mixture over time for N_2-1000



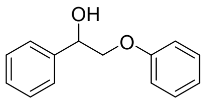
		Yield %					
Time (min)	Conversion %	**1a**	**1b**	**1d**	**1c**	**1e**	**1f**
0	49	9	5	1	12	3	0
15	55	10	7	1	10	3	0
30	83	24	9	0	14	4	0
60	86	10	12	4	19	5	0
90	89	11	12	3	20	4	0
120	100	10	29	15	47	6	6.4

Reaction conditions: substrate: 100 mg, catalyst :30 mg, *n*-hexane: 30 mL, 260 °C, 0-120 min, 1 MPa H_2 (RT).

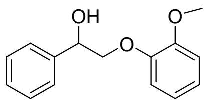
Table S5. The catalytic activity of various model compounds over N_2-500 and N_2-1000.



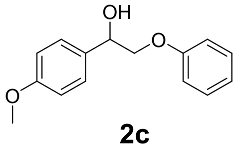
[a] Dehydration to Hydrogenation = compound **3**: compound **7**



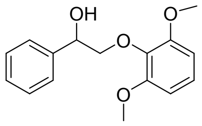
2a



2b



2c



2d

Feeds	Catalysts	Conversion %	Yield %					Dehydration /hydrogenation[a]
			3	**4**	**5**	**6**	**7**	3:7
2a	N_2-500	60	17	19	2	4	14	55:45
	N_2-1000	100	10	29	15	6	47	17:83
2b	N_2-500	68	18	13	0	0	31	37:63
	N_2-1000	94	8	44	2	0	57	12:88
2c	N_2-500	100	47	5	7	0	10	82:18
	N_2-1000	100	27	6	7	0	20	57:43
2d	N_2-500	62	8	7	1	0	6	57:43
	N_2-1000	100	0	38	5	0	32	0:100

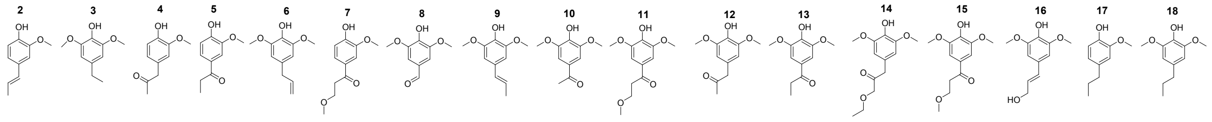
Table S6. The Catalytic activity various tungsten-based catalysts for beech lignin.

Product	N_2-1000	N_2-500
2	1.0	0.4
3	0.3	0.0
4	0.4	0.3
5	0.3	0.3
6	0.2	0.1
7	0.2	0.2

8	0.0	0.2
9	4.4	1.7
10	0.1	0.2
11	0.9	0.7
12	0.2	0.1
13	0.3	0.2
14	0.7	0.9
15	0.0	0.4
16	0.3	0.4
17	0.4	0.0
18	1.3	0.2
Total Monomers yield (wt%)	10.8	6.3
Total oil yield (wt%)	56.4	52.3
Ratio of monomer to oil[a]	0.19	0.12
Hydrogenation ability[b]	0.31	0.11

[a] Ratio of monomer to oil = total monomer yield/total oil yield.

[b] Hydrogenation ability was calculated through the yield ratio of products with saturated alkyl linkage (e.g., products **17** or **18**) to products with unsaturated alkyl linkage (e.g., products **2, 6** or **9**). I.e., Hydrogenation ability = (**17**+**18**)/ (**2**+**6**+**9**).



Reaction conditions: substrate: 100 mg, catalyst: 100 mg, methanol: 30 mL, 200 °C, 6 h, 1 MPa H_2 (RT).

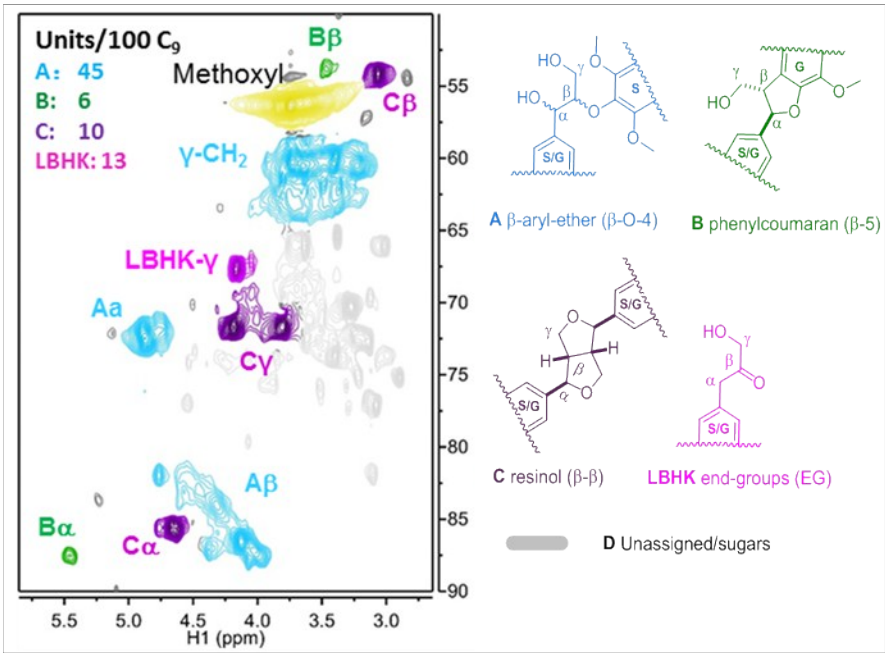
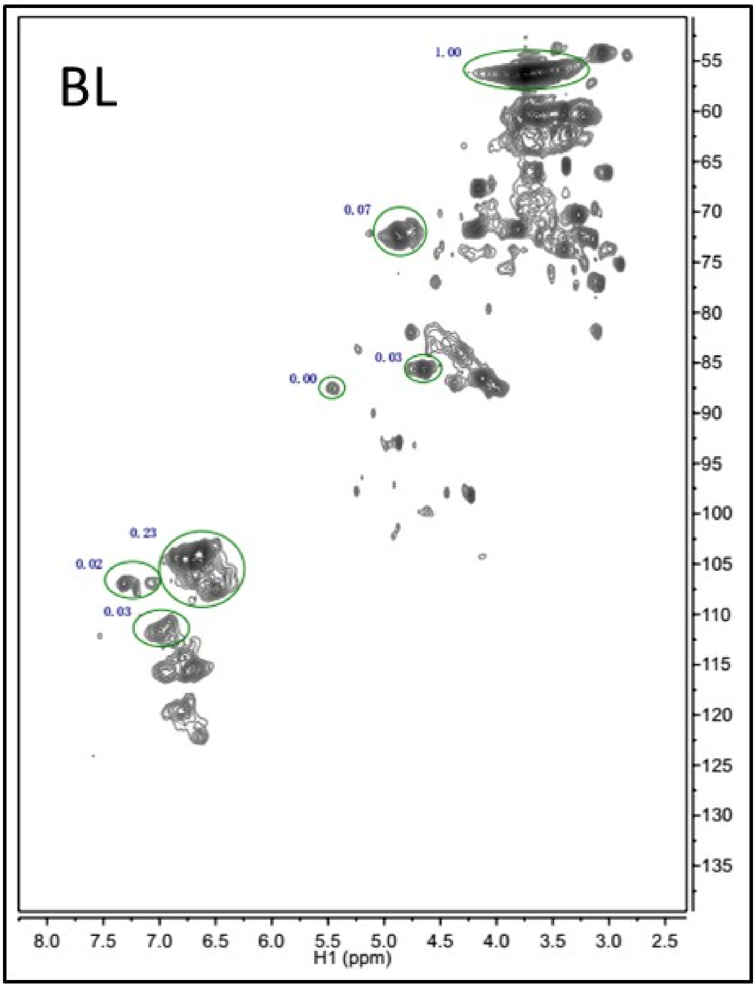
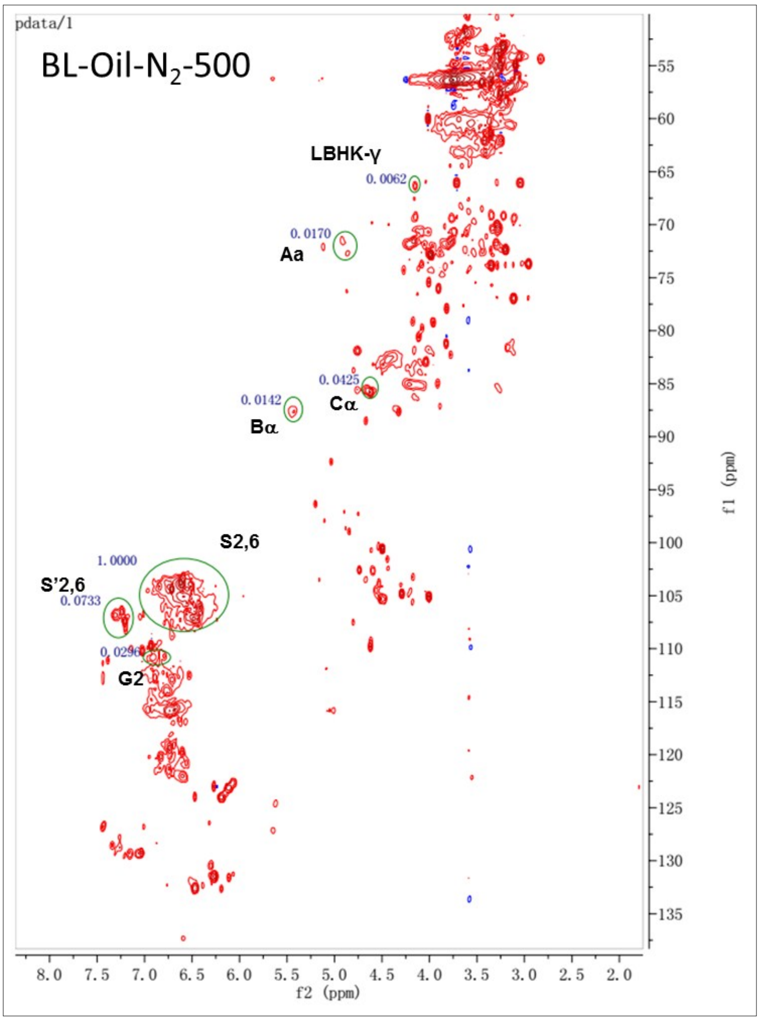


Figure S5. 2D HSQC NMR spectrum of beech lignin (BL) which was repeated in this work based on our previous isolated lignin[1] and the corresponding linkages per 100 C_9 (i.e., Units per C_9) was revisited.




pdata/1
BL-Oil-N$_2$-500
LBHK-γ
0.0062
0.0170
Aa
0.0425
Cα
0.0142
Bα
S2,6
1.0000
S'2,6
0.0733
0.0296
G2
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)

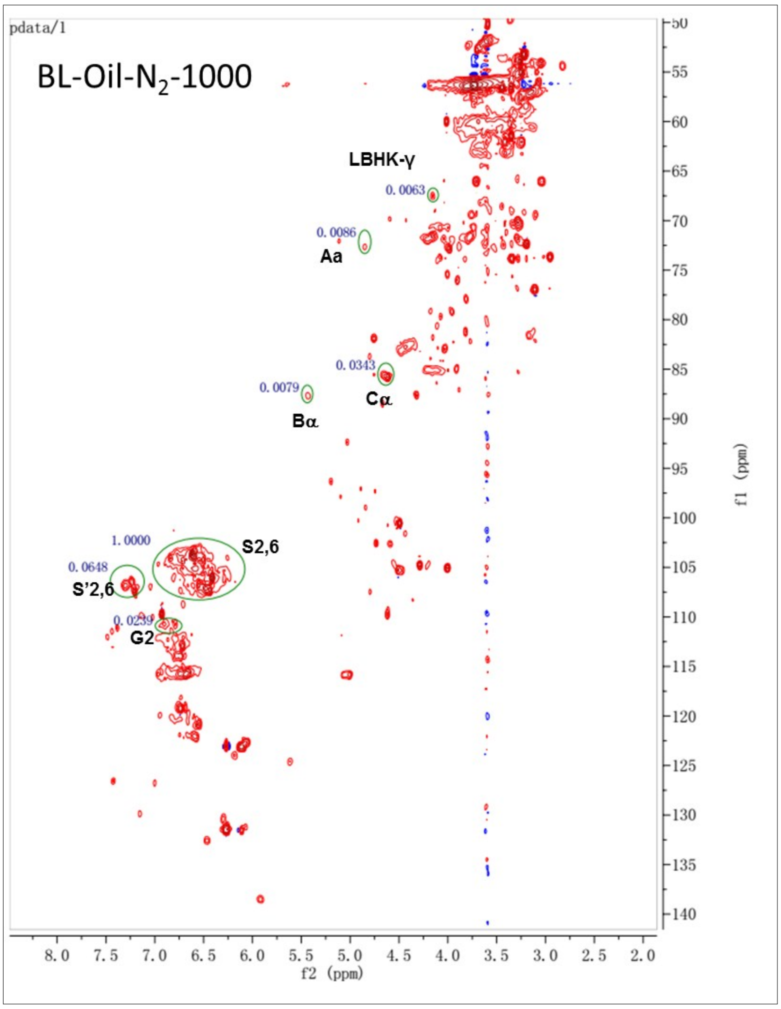


Figure S6. Full spectra of of BL and BL oil over N_2-500 and N_2-1000 and the corresponding integration of corresponding integration of linkages.

Calculation process of **Units per C9**:

$$\mathbf{A}\text{ (or }\mathbf{B}\text{ / }\mathbf{LBHK}\text{) /100 C9} = \mathbf{A_{\alpha}}\text{ (or }\mathbf{B_{\alpha}}\text{ /}\mathbf{LBHK\text{-}\gamma}\text{) *100/ }[(\mathbf{S_{2,6}} + \mathbf{S'_{2,6}})/2 + \mathbf{G_2}]$$

$$\mathbf{C}\text{ /100C9} = \mathbf{C_{\alpha}}/2*100/\ [(\mathbf{S_{2,6}} + \mathbf{S'_{2,6}})/2 + \mathbf{G_2}]$$

For example: **Figure 6**: BL-Oil-N_2-500:

$$\text{A /100 C9} = 0.0086*100/\ [(1+0.0648)/2+0.0239] = 3$$

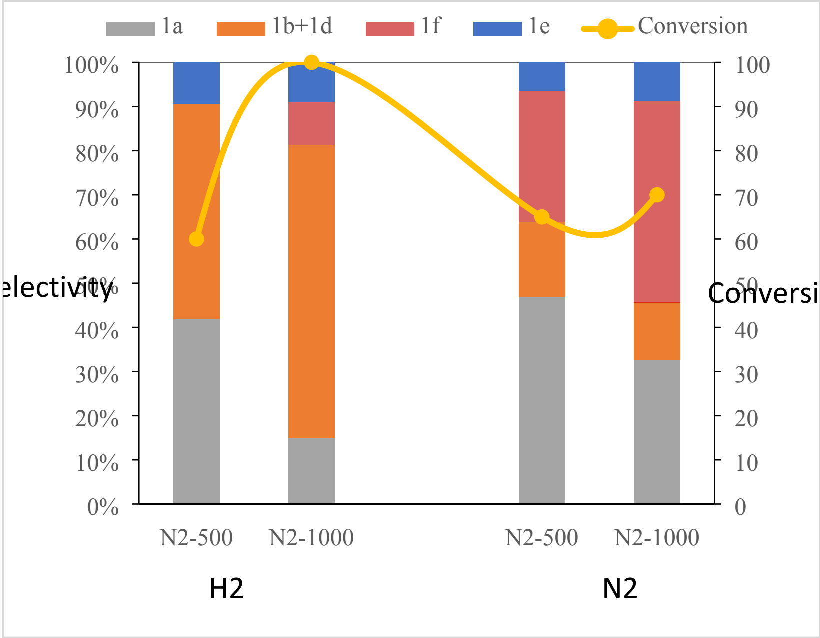


Figure S7 Catalytic activity comparison of N_2-500 and N_2-1000 under difference atmosphere.

3. References

1. Guo, H.; Miles-Barrett, Daniel M.; Neal, A. R.; Zhang, T.; Li, C.; Westwood, N. J., *Chem. Sci.* **2018,** *9* (3), 702.