

Electronic Supplementary Information

**In situ synthesis of Molybdenum oxide @ N-doped Carbon
from biomass for selective vapor phase
hydrodeoxygenation of Lignin-derived phenols under
atmosphere H₂**

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Method for analyzing products and processing data

The liquid products were analyzed by GC-MS (Thermo Trace GC Ultra with an ISQ i mass spectrometer) equipped with a TR-35MS capillary column (30 m × 0.25 mm × 0.25 mm). Split injection was performed at a split ratio of 50 using helium (99.999%) as carrier gas. The GC heating ramp was: 1) hold at 40 °C for 3 min, 2) heat to 180 °C at 5 °C /min, 3) heat to 280 °C at 10 °C /min, and 4) hold at 280 °C for 5 min.

The total amount of liquid products was determined by the weight difference of the condensation tube before and after the experiment. The coke at the end of the run was measured after the reaction by weighing the solids and subtracting the weight of the catalyst.

The major liquid products were quantitatively determined by gas chromatography (GC 1690, Kexiao, China) employing a 30 m × 0.25 mm × 0.25 μm fused-silica capillary column (HP-Innowax, Agilent). The liquid sample was mixed with bi-cyclohexane as the internal standard and diluted by ethanol. The GC operating conditions were as follows: carrier gas: nitrogen; injection port: 250 °C in a split mode; detector (FID): 250 °C; column temperature: 40 °C; oven temperature program: heating up to 250 °C at a rate of 10 °C/min, and holding at a final temperature for 5.0 min.

The gas products were collected in gas bags. The gas bags were weighed before and after reaction and their contents were analyzed using gas chromatography (GC-SP6890, Shandong Lu-nan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China) with two detectors, a TCD for analysis of H₂, CO, CH₄, and CO₂ separated on TDX-01 column, and a FID (flame ionization detector) for gas hydrocarbons separated on Porapak Q column. The moles of gas products were determined by the normalization method with standard gas.

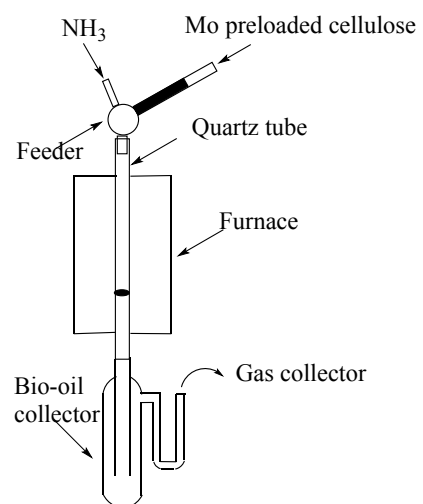


Figure S1. Pyrolysis reactor for preparing MoO_x@NC catalysts.

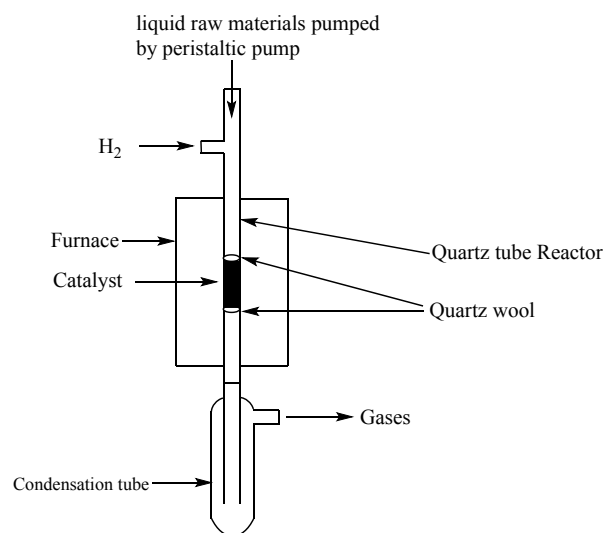


Figure S2. Bench-top reactor for vapor phase HDO of lignin-derived phenols.

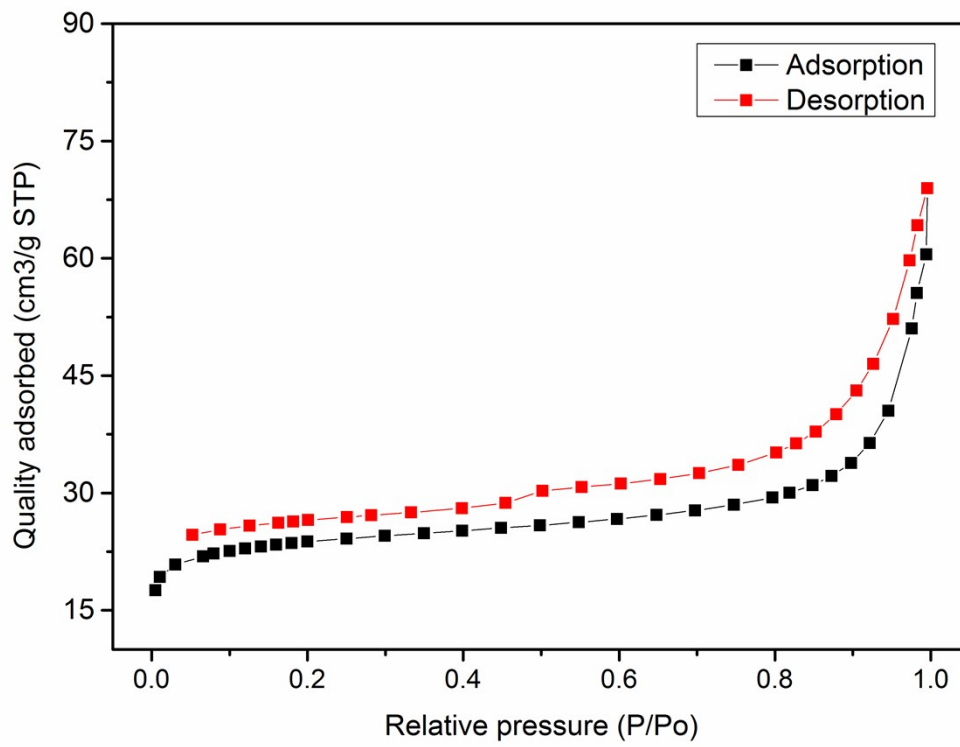


Figure S3. N₂ adsorption–desorption isotherms of MoO_x@NC-600 catalyst.

Table S1. Physicochemical properties of catalysts

Catalyst	BET surface area m ² /g	Composition (wt %)			
		C ^a	H ^a	N ^a	Mo ^b
C-600	43.1	78.2	3.1	-	-
NC-600	110.2	79.5	2.7	6.9	-
MoOx@C-600	26.9	55.5	3.2	0.7	25.6
MoOx@NC-500	20.7	51.3	2.6	7.8	23.5
MoOx@NC-550	46.0	53.8	2.3	6.4	26.1
MoOx@NC-600	81.0	51.0	1.8	6.9	28.7
MoOx@NC-650	75.2	43.2	1.6	7.5	37.4

a: Analyzed by elemental analysis; b: Analyzed by AAS.

Table S2.Elemental content analyzed by XPS

Catalysts	C	O	N	Mo
C-600	83.2	16.8	-	-
NC-600	87.0	5.1	7.9	-
MoOx@C-600	80.9	15.0	0.9	3.2
MoOx@NC-500	83.5	7.9	7.3	1.4
MoOx@NC-550	83.8	6.8	8.2	1.2
MoOx@NC-600	85.7	6.5	6.1	1.7
MoOx@NC-650	87.3	5.6	5.6	1.5
Analyzed by XPS.				

Table S3. The effect of HDO reaction temperature.

Entry	1	2	3	4	5	6
Reaction temperature (°C)	300	350	400	450	500	600
Guaiacol conversion (%)	80.7	96.0	100	100	100	100
Gases	4.2	7.2	9.3	13.4	15.1	16.2
Coke	19.5	14.4	10.3	6.9	6.3	4.8
Aromatic hydrocarbons	2.1	6.1	68.8	70.2	57.4	50.7
Phenolic products	45.6	63.9	6.7	1.8	9.6	14.8
	Aromatic hydrocarbons					
Benzene	2.1	4.6	46.1	51.8	34.7	33.9
Tolunene	0	1.5	19.8	15.0	18.2	13.8
Other alkylbenzenes	0	0	2.9	3.4	4.5	3.0
	Phenolic products					
Phenol	30.6	50.9	3.3	0.7	2.9	5.4
anisole	5.5	8.3	1.7	0.6	2.1	1.8
cresol	9.2	4.7	1.4	0.5	3.4	5.8
other alkylphenols	0.3	0	0.3	0	1.2	1.8

The catalytic test condition: the guaiacol/ mesitylene=1:1, catalyst is MoOx@NC-600, catalyst usage is 1g, WHSV of the mixture is 1 h⁻¹, H₂ flow rate is 70 ml/min; c: The yield in this study is carbon yield.

Table S4. Catalyst stability test.

Entry	1	2	3	4	5	6	7	8	9	10	11
Time on stream (h)	0.5	1	1.5	2	2.5	5	7.5	10	12.5	15	20
Conversion (%)	100	100	100	100	100	100	100	100	100	100	100
Aromatics	83.3	81.8	81.6	81.6	82.0	83.9	82.7	71.0	67.6	60.4	42.7
Phenols	0	3.1	5.2	6	5.6	5.4	6.1	8.8	15.3	19	25.8
	Aromatics										
Benzene	65.7	61.9	64.6	63.0	58.8	66.2	64.3	56.1	53.8	48.1	35.8
Tolunene	15.5	17.6	14.8	16.8	21.9	15.3	16.7	13.0	12.3	10.5	5.6
Other alkylbenzenes	2.1	2.3	2.2	1.8	1.3	2.4	1.7	1.9	1.5	1.8	1.3
	Phenols										
Phenol	0	0	0	0	0	0	0	0	4.6	9.5	18.2
Anisole	0	3.1	5.2	6.0	5.6	5.4	6.1	3.4	4.3	3.8	2.6
Cresol	0	0	0	0	0	0	0	4.8	6.1	5.2	4.3
other alkylphenols	0	0	0	0	0	0	0	0.6	0.3	0.5	0.7

The catalytic test condition: reaction temperature for HDO is 450 °C, catalyst dosage is 1.5g, WHSV of the mixture is 1 h⁻¹, H₂ flow rate is 70 ml/min; c: The yield in this study is carbon yield.

Table S5. Physicochemical properties of MoOx@NC-600 before and after reaction.

	Elemental contents (wt %) ^a					Surface Elemental contents (wt %) ^b				BET surface area (m ² /g)	Pore volume (cm ³ /g)
	C	H	N	Mo	O	C	N	Mo	O		
MoOx@NC-600 before reaction	47.2	1.7	4.5	26.1	20.5	85.7	6.1	1.7	6.5	81.0	0.085
MoOx@NC-600 after reaction	52.0	2.0	4.1	22.7	19.2	92.6	1.4	0.4	5.5	2.6	0.012

a: The content of C, H, and N was determined by elemental analyzer. The content of molybdenum in MoOx@NC-600 was measured by atomic absorption spectrum (Escalab 250Xi, Thermo Fisher). b: The elemental content of the catalyst surface was determined by XPS.