Supporting Information

In Situ Preparation of Ru@N-Doped Carbon Catalyst for the Hydrogenolysis of Lignin To Produce Aromatic Monomers

Tianjin Li[†], Hongfei Lin[‡], Xinping Ouyang^{*†}, Xueqing Qiu^{*†}, Zechen Wan[†]

[†]School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P.R China

‡Voiland School of Chemical Engineering and Bioengineering, Washington State

University, Pullman, Washington 99164, United States

*Corresponding author: Xinping Ouyang, E-mail: ceouyang@scut.edu.cn

Xueqing Qiu, E-mail: cexqqiu@scut.edu.cn

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1. General information

Reagents and Feedstocks

Birch wood was purchased from Shandong dongxing wood Co., LTd. China. All agents and solvents were purchased from Aladdin Co., China and used without further purification.

Characterization

The BET surface area measurements were performed with N₂ adsorption isotherms at 77 K (model Tristar II 3020, USA). Before the analysis, the samples were evacuated at 250 °C for 6 h. The element analyzer (model Vario EL cube, Germany) was used to measure the C, H and N content of the sample. Powder X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku diffractometer (D/MAX-IIIA, 3kW) using Cu K α radiation (40 kV, 30 mA, λ =0.1543 nm) (Bruker, Germany). The size and the elemental distribution were determined using a high resolution transmission electron microscope (TEM, JEOL, JEM-2100F) and scanning transmission electron high-angle annular dark-field microscopy (HAADF-STEM) with an EDX analysis system (Bruker Xflash 5030T) operated at 200 kV. The samples were suspended in ethanol and deposited straightaway on a copper grid prior to analysis. X-ray photoelectron spectroscopy (XPS) was conducted by using a Kratos Axis Ultra DLD system with a base pressure of 10-9 Torr (Thermo K-Alpha⁺ USA). Inductively coupled plasma emission spectroscopy (ICP-AES) was executed on Perkin-Elmer TJA RADIAL IRIS 1000. The graphite degree was measured by a Raman spectrometer (model LabR AMA Ramis, France). Gel permeation chromatography (GPC) using a Waters 1515/2414 liquid chromatography

system (Waters 1515/2414, Waters Co., USA) was used to measure the molecular weight of lignin samples and depolymerized products. Before analysis, lignin samples and the depolymerized products were dissolved in tetrahydrofuran. Calibration was made using polystyrene standards. Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) was carried out on a maxis impact (Bruker Co., Germany). The structural characteristics of lignin samples and depolymerized products were studied using a 2D HSQC method (Bruker AVIII 600 MHz spectrometer, Germany). Before analysis, 100 mg sample was dissolved on 0.5mL of DMSO- d_6 . The gas chromatography-mass spectrometry (GC/MS) was used to analyze the hydrogenolysis products. The instrument (5975C-7890A, Agilent Co., USA) was equipped with a capillary column (HP-5MS 30 m×mm×0.25 µm) and EI ion source (70 eV). Helium (1 mL min⁻¹) was used as the carrier gas, with a split ratio set to 1:30. The oven temperature program started at 50 °C (held for 3 min). The temperature was raised to 150 °C (7 °C min⁻¹, held for 10 min), then to 170 °C (7 °C min⁻¹) and finally to 300 °C (20 °C min⁻¹, held for 20 min). Decane was used as an internal standard for the quantification of the depolymerized products.

2. Lignin extraction and isolation

Birch organosolv lignin (BOSL) was extracted according to reported works¹. 60 g of the dried Birch wood and 430 ml 1,4-dioxane with the 50 ml solution of HCl (2mol L⁻¹) were added to a 1 L round-bottom flask. The mixture was refluxed for 90 min under a nitrogen atmosphere, and cooled to room temperature. The residue was removed by filtration and the filtrate was concentrated. The resulting concentrate was then added into 2 L water to get precipitate. The precipitate was collected by filtration and washed with a large number of water until the filtrate was neutral. The yield of crude birch lignin with dried was 9 g (15 wt%). The resulting crude birch lignin was dissolved in 60 ml solvent (acetone : water = 9:1) and the precipitated with 1.5 L of ice-cold water. The final lignin was collected by filtration, washed and dried under vacuum at 60 °C. The yield of purified birch lignin was 6 g (10 wt%).

3. Preparation and characterization of catalysts

Preparation of catalysts

Ru@N-doped carbon catalysts were synthesized as follows: first, the carbon precursor (1 g GC or 1 g GAH) and 20 g melamine was added into 40 ml water with vigorous stirring for 2 h, and then 4 ml solution RuCl₃ (4 mg mL⁻¹) was added. The mixture was heated at 150 °C for 1 h under microwave-assisted. After that, the mixture was collected by filtration and dried under vacuum for 6 h. The resulting solid was grounded to power and then transferred into a tubular furnace for pyrolyzing under N₂ flow (100 mL min⁻¹). The sample was heated at a heating rate of 2 °C/min, maintained at 600 °C for 1 h, and then heated to 800 °C and calcined for 1 h. The prepared samples were denoted as Ru@CM-800 and Ru@NCM-800, respectively. The synthesis of Ru@C-800 and Ru@NC-800 was similar, except for not adding melamine. The synthesis of Ru@NCM-x (x represents the final pyrolysis temperature) was similar to that of Ru@NCM-800, except that at the second stage, the samples were calcined at 700 °C, 900 °C and 1000 °C for 1h, respectively. The Ru@g-C₃N₄ composite was obtained by pyrolyzing the mixture of GAH and melamine (weight ratio of 1:20) at 600 °C for 1 h, which was denoted as Ru@M.



Figure S1. Preparation of Ru@N-doped carbon catalysts.

Characterization of catalysts



Figure S2. The picture of various catalysts with the same mass (0.2 g). (a) Ru@C-800, (b) Ru@CM-800 (c) Ru@NC-800, (d) Ru@NCM-800.



Figure S3. The content of three nitrogen species (Pyridine N, Pyrrolic N, Graphite N) of various

catalysts.



Figure S4. The Ru 3p XPS analysis of various catalysts.



Figure S5. Microstructure and morphology characterization of Ru@CM-800. (a) TEM image. (b) HADDF-STEM image. Inset shows the size distribution of Ru NPs. (c) HRTEM image.



Figure S6. Characterizations of Ru@C-800 and Ru@NC-800. (a, b) TEM images of Ru@C-800.
(c) HAADF-STEM image of Ru@C-800. (d, e) TEM images of Ru@NC-800. (f) HAADF-STEM image of Ru@NC-800. Inset shows the size distribution of Ru NPs.



Figure S7. Raman spectra of various catalysts.



Figure S8. SEM images of Ru@N-doped carbon catalysts prepared at various pyrolysis temperature. (a) Ru@NCM-700. (b) Ru@NCM-800. (c) Ru@NCM-900. (d) Ru@NCM-1000.



Figure S9. TEM images of Ru@NCM-700. (a) TEM image. (b) HAADF-STEM image.



Figure S10. TEM images of Ru@NCM-900. (a) TEM image. (b) HAADF-STEM image. (c) The

size distribution of Ru NPs.



Figure S11. TEM images of Ru@NCM-1000. (a) TEM image. (b) HAADF-STEM image. (c) The

size distribution of Ru NPs.



Figure S12. MALDI-TOF-MS spectrum of depolymerized products. (a) without a catalysts; (b) with Ru@NCM-800 (Reaction conditions: BOSL 0.3 g, catalyst 0.06 g, H₂O 10 ml, Ethanol 10 ml, 300 °C, 120 min, H₂ 1.0 MPa, 400 rpm).

Catalysts	ICP-AES analysis (wt%)		
	Ru		
Ru@C-800	1.49		
Ru@CM-800	1.47		
Ru@NC-800	1.50		
Ru@NCM-800	1.51		

Table S1. ICP-AES analysis for the Ru@ N-doped carbon catalysts.

 Table S2. Element analysis of the prepared Catalysts.

Catalysts		Content (wt %)	
	С	Н	Ν
Ru@C-800	80.96	0.74	0
Ru@NC-800	76.37	1.47	6.98
Ru@CM-800	60.94	1.47	19.11
Ru@NCM-800	66.83	1.09	22.67

Catalysts	$\frac{S_{BET}}{(m^2g^{-1})}$	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
Ru@C-800	76	0.15	2.01
Ru@CM-800	293	0.60	8.67
Ru@NC-800	80	0.09	3.32
Ru@NCM-800	274	0.53	7.72

Table S3. BET surface area (S_{BET}), Pore volume and Pore diameter of catalysts.

Table S4. Element analysis of the prepared Catalysts.				
Catabata		Content (wt %)		
Catalysts —	С	Н	Ν	
Ru@NCM-700	58.44	1.63	26.53	
Ru@NCM-800	66.83	1.09	22.67	
Ru@NCM-900	71.71	0.93	10.53	
Ru@NCM-1000	78.64	1.10	5.17	

4. Catalytic hydrogenolysis of lignin

The detailed reaction conditions are described in the figure captions and table footnotes. In a typical reaction, 0.3 g of BOSL, 0.06 g catalyst and 20 ml of water/ethanol (1:1) were added into a 100 mL stainless steel autoclave (Beijing Century Senlang experimental apparatus Co., Ltd., China). The vessel was purged three times with H₂ and charged with 1.0 MPa H₂. The hydrogenolysis reaction was carried out under 240-340 °C with reaction time was 30-180 min with mechanical stirring of 400 rpm. After reaction, the reaction vessel was cooled down to room with ice water and the organic products were extracted three time using ethyl acetate. The yield of the aromatic monomers was calculated using the following equation (1):

Yield monomer (%) =
$$(W_{\text{monomer}}/W_{\text{initial lignin}}) \times 100\%$$
 (1)

Where W_{monomer} and $W_{\text{initial lignin}}$ were the weight of the aromatic monomers after the hydrogenolysis and the initial lignin.

No	Ret. time (min)	Compound	Yield (%)
1	9.341	MeOOH	0.19
2	11.293	MeOOH	0.32
3	12.832	MeOOH	0.52
4	14.142	MeO OMe OH	2.45
5	14.365	MeOOH	3.60
6	15.349	O MeO OH	1.30
7	15.664	MeO OMe OH	1.20

hydrogenolysis of BOSL with Ru@NCM-800. Reaction condition: BOSL 0.3 g, Ru@NCM-800 0.06 g, H₂O 10 ml, Ethanol 10 ml, 300 °C, 120 min, H₂ 1.0 MPa, 400 rpm.

Table S5. The GC-MS identified liquid products, their retention time and yield after the



Table S6. The distribution of aromatic monomers after hydrogenolysis of BOSL over various catalysts.



Entury	Catalyst	Yield of aromatic monomers (%)				Total	Total				
Entry	Catalyst	G1	G2	G3	G4	S 1	S2	S3	S4	S (%)	G (%)
1	Ru@NCM-800	0.19	0.32	0.52	3.60	2.45	1.20	1.73	13.25	24.82	5.68
2	Ru@CM-800	0.31	0.27	0.87	2.75	1.63	0.58	2.61	8.23	21.23	5.07
3	Ru@NC-800	0.09	0.15	0.62	0.97	2.27	0.83	2.95	4.46	13.64	2.66
4	Ru@C-800	0.16	0.19	1.22	0.80	2.52	0.87	4.39	2.65	12.79	3.81
5	Ru@NCM-700	0.07	0.17	0.61	1.60	0.97	0.71	2.49	4.94	11.84	4.86
6	Ru@NCM-900	ND	0.18	0.64	2.86	1.62	0.78	2.13	9.96	19.13	4.37
7	Ru@NCM-1000	0.18	0.24	0.92	2.35	1.51	0.57	3.32	7.29	16.53	4.57
8	Ru/C*	0.28	0.22	1.18	0.61	1.75	0.82	3.46	1.90	10.41	5.29
9	Pd/C^*	0.40	0.33	0.59	0.78	2.13	0.88	1.33	1.52	9.94	4.86
10	Blank	0	0.16	0.01	0.15	1.05	1.17	0.89	1.68	6.39	2.31

Reaction conditions: 0.3 g BOSL, 0.06 g catalyst, 10 ml H₂O, 10 ml Ethanol,1 MPa H₂, 300 °C,

120 min, 400 rpm. ND: No detected. Ru/C* and Pd/C* were commercial purchased and the loading

amount of metal was 5 wt%.

Labe	$\delta_{\rm C}/\delta_{\rm H}({\rm ppm})^{\rm a}$	$\delta_{\rm C}/\delta_{\rm H}({\rm ppm})^{\rm b}$	Assignments
OCH ₃	55.6/3.8	55.6/3.8	C-H in methoxyls
$\mathbf{B}_{\!\alpha}$	87.5/5.5	87.5/5.5	C_{α} -H _{α} in β -5 structures (B)
$\mathbf{B}_{\!\beta}$	53.7/3.1	53.7/3.1	C_{β} -H _{β} in β -5 structures (B)
$\mathbf{B}_{\!\gamma}$	62.9/3.7	63.0/3.7	C_{γ} -H _{γ} in β -5 structures (B)
C_{α}	85.6/4.7	85.4/4.7	C_{α} -H _{α} in β - β structures (C)
C_{β}	54.5/2.8	54.5/2.9	C_{β} -H _{β} in β - β structures (C)
\mathbf{C}_{γ}	72/3.8-4.2	72.0/3.8-4.2	C_{γ} - H_{γ} in β - β structures (C)
Aα	85.5/4.7	85.5/4.7	C_{α} -H _{α} in β -O-4 structures (A)
$A_{\beta}(G)$	84/4.3	84.0/4.3	$C_{\beta}\text{-}H_{\beta}$ in $\beta\text{-}O\text{-}4$ structures linked to a G-unit (A)
$A_{\beta}(S)$	87/4.1	87.0/4.1	$C_\beta\text{-}H_\beta$ in $\beta\text{-}O\text{-}4$ structures linked to a S-unit (A)
Aγ	59.6/3.7	60.0/3.4	C_{γ} -H _{γ} in β -O-4 structures (A)

Table S7. Assignments of $peaks^2$ in 2D HSQC NMR spectra of BOSL and its depolymerized

a : The peaks assigned in 2D HSQC NMR spectra of BOSL.

products after the hydrogenolysis over Ru@NCM-800.

b: The peaks assigned in 2D HSQC NMR spectra of the depolymerized products after the hydrogenolysis over Ru@NCM-800.

Table S8. Weight average M_W , number average M_n of BOSL and its depolymerized products after the hydrogenolysis over Ru@NC-800 and Ru@NCM-800.

Sample	M_{W}	M _n
BOSL	4051	2439
Depolymerized products 1	1098	1530
Depolymerized products 2	525	479

Reaction conditions: 0.3 g BOSL, 0.06 g Ru@NC-800, 10 ml H₂O, 10 ml Ethanol,1 MPa H₂, 300 °C, 120 min, 400 rpm. Depolymerized products 1: After catalytic hydrogenolysis reaction over Ru@NC-800. Reaction conditions: 0.3 g BOSL, 0.06 g Ru@NCM-800, 10 ml H₂O, 10 ml Ethanol, 1 MPa H₂, 300 °C, 120 min, 400 rpm. Depolymerized products 2: After catalytic hydrogenolysis reaction over Ru@NCM-800. Reaction conditions: 0.3 g BOSL, 0.06 g Ru@NCM-800, 10 ml H₂O, 10 ml Ethanol, 1 MPa H₂, 300 °C, 120 min, 400 rpm.

5. References

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(2) Zhao, L.; Ouyang, X.; Ma, G.; Qian, Y.; Qiu, X.; Ruan, T. Improving Antioxidant Activity of Lignin by Hydrogenolysis. *Ind. Crop. Prod.* **2018**, *125*, 228-235.