Electronic Supplementary Material (ESI) for Catalysis Science & Technology. This journal is © The Royal Society of Chemistry 2015

# Supporting information

## Mechanistic Insights into Selective Hydrodeoxygenation of Lignin

### Derived β-O-4 Linkage to Aromatic Hydrocarbons in Water

Zhicheng Luo, Chen Zhao\*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Chemical Engineering, East China Normal University, Shanghai

200062, China

Email: czhao@chem.ecnu.edu.cn

#### **Experimental Section**

#### **Chemicals and materials**

All commercial chemicals were analytical reagents and used without further purification. RuCl<sub>3</sub>·3H<sub>2</sub>O, PdCl<sub>2</sub>, PtCl<sub>4</sub>, cyclooctene and (2-bromoethyl)-benzene were purchased from J&K. formaldehyde, phenol, activated carbon, Nafion and Amberlyst were purchased from sigma-aldrich. HCl, NaOH, hexadecyl trimethyl ammonium bromide, ethyl-benzene, ethyl acetate and diethyl ether anhydrous were purchased from Sinopharm. Sulfate zirconium powder was purchased from Changsha Jingkang Co., Ltd. Air, H<sub>2</sub> and N<sub>2</sub> gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of benzyl 2-phenylethyl ether ( $\beta$ -O-4 model compound): phenol (18.8 g, 0.2 mol) and hexadecyl trimethyl ammonium bromide (3.2 g, 0.10 mol) were firstly added into an aqueous NaOH solution (20 wt%, 500 mL) with stirring. The mixture was then heated to 60 °C with stirring for 1.0 h, and subsequently (2-bromoethyl)-benzene (18.5 g, 0.10 mol) was added. The suspension reacted at 80 °C for 24 h. After that, the organic phase was extracted by diethyl ether. The remaining liquid part was evaporated, and further reacted with an aqueous NaOH solution (10 wt%, 250 mL) at 60 °C for 24 h in order to remove the residual phenol. Followed by extraction by diethyl ether and sequential evaporation procedures, the final product was purified by distillation under vacuum. Purity: 99.5% (detected by GC), M<sub>w</sub>: 198 g·mol<sup>-1</sup>, formula: C<sub>14</sub>H<sub>14</sub>O.

#### **Catalyst preparation**

The supported Ru, Pt, Pd catalysts were synthesized by the method of liquid phase HCHO reduction. In a typical procedure for synthesizing of Ru/SZ, firstly a solution of RuCl<sub>3</sub>·H<sub>2</sub>O (6.35 mL, *conc*: 0.040 g/L) was added drop-wise to an aqueous suspension (150 mL H<sub>2</sub>O, 2.0 g support) with stirring at room temperature. After using NaOH to adjust the pH to 11, the reduction was carried out with formaldehyde (37 wt%, 10.0 mL) at 60 °C for 4 h. Finally the slurry was filtrated and washed with distilled water until no free chloride was detected.

#### **Catalytic testing**

Test the surface adsorbed H· species on Ru/SZ: Firstly, phenol or cyclohexanol (5.0 g), Ru/SZ (5 wt.%, 1.0 g), deionized water (100 mL) were charged into a batch autoclave (Parr Instrument, 300 mL). The reactor was firstly flushed with N<sub>2</sub> at ambient temperature for three times, and then heated up to 80 °C when 8 bar H<sub>2</sub> was purged, and the reaction started at a stirring speed of 650 rpm. After the reaction, H<sub>2</sub> was released and 100ul cyclooctene was charged into a batch autoclave, The reactor was flushed with N<sub>2</sub> at ambient temperature for three times, and then heated up to 80 °C, After the reaction, the organic products were extracted using ethyl acetate and analyzed by a gas chromatograph (GC) equipped with a mass spectrometer (MS, Shimadzu QP-2010 Ultra) with a Rtx-5Sil MS capillary column (30 m × 0.25 mm × 0.25 µm).

**Conversion with benzyl 2-phenylethyl ether** ( $\beta$ -O-4 model compound): A typical experiment was carried out as follows: benzyl 2-phenylethyl ether (1.0 g), Ru/C (5 wt.%, 0.1 g), deionized water (100 mL) were charged into a batch autoclave (Parr Instrument, 300 mL). The reactor was firstly flushed with N<sub>2</sub> at ambient temperature for three times, and then heated up to 240 °C when 8 bar H<sub>2</sub> was purged, and the reaction started at a stirring speed of 650 rpm. After the reaction, the organic products were extracted using ethyl acetate and analyzed by a gas chromatograph (GC) equipped with a mass spectrometer (MS, Shimadzu QP-2010 Ultra) with a Rtx-5Sil MS capillary column (30 m × 0.25 mm × 0.25 µm). An internal standard dodecane was added to calculate the carbon balance.

Kinetics of benzyl 2-phenylethyl ether ( $\beta$ -O-4 model compound) conversion: The typical reaction was carried out as follows: benzyl 2-phenylethyl ether (1.0 g), Ru/SZ (5 wt.%, 0.050 g), and deionized water (100 mL) were charged into a batch autoclave (Parr Instrument, 300 mL). After the reactor was flushed with N<sub>2</sub> at ambient temperature for three times, the autoclave was charged with 8 bar H<sub>2</sub> and the reaction was conducted at 240 °C with a stirring speed of 650 rpm. As it is a two-phase reaction, the kinetic data were collected at different time durations. The liquid

products were extracted using ethyl acetate and analyzed by GC and GC-MS. For analysis, an internal standard dodecane was added to calculate the carbon balance.

### **Catalyst characterization**

The Ru, Pd, Pt content was quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission. The crystal morphology and size were determined by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) was performed on a Tecnai G2 f30 microscope. For determination of metal dispersion, pulse CO chemisorption was measured by a Micromeritics AutoChem 2910. Prior to test, 50 mg catalyst was reduced in a flow of 50 mL·min<sup>-1</sup> H<sub>2</sub> at 200 °C for 2 h and then flushed in a flow of 90 mL·min<sup>-1</sup> He for 1 h. After cooled to 35 °C temperature in He, the CO gas pulses (5 vol% in He) were introduced in a flow of 90 mL·min<sup>-1</sup>. The changes in the CO gas phase concentration were tracked by a thermal conductor detector (TCD). The measurement of temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) was detected by with a Micrometritics tp5080 apparatus equipped with a TCD. The procedures are conducted as followed: 80 mg of sample was pre-treated in helium stream (25 mL min<sup>-1</sup>) at 550 °C for 2 h. Subsequently NH<sub>3</sub> was adsorbed at 50 °C for 20 min., and the catalyst was flushed with helium at 100 °C for 2 h to remove physisorbed NH<sub>3</sub> from the catalyst surface. The TPD profile was recorded at a heating rate of 10 °C min<sup>-1</sup> from 100 to 550 °C.



**Figure S1.** Characterization of Ru/SZ catalyst by (a) TEM, (b) HR-TEM, (c) SEM, and Characterization of Ru/SZ, Pd/SZ and Pt/SZ catalysts respectively by (d), (e) and (f) NH<sub>3</sub>-TPD measurements.



Figure S2. Characterization of Ru/SZ, Pd/SZ, Pt/SZ catalysts measured by TEM images.



**Figure S3**. Product distributions on BPE conversion over two metal catalysts (a) Pd/C, and (b) Pt/C in aqueous phase as a function of temperature. Conditions: BPE (1.0 g), Pd/C, and Pt/C (5 wt%, 0.10 g), H<sub>2</sub>O (100 mL), 8 bar H<sub>2</sub>, stirring at 650 rpm.

Ũ	OO Beta-O-4	$\bigcirc$		$\rightarrow \qquad \qquad$									
9 10											11		
Cat.	t (min)	1	2	3	4	<u> </u>	1010 (C9	%) 7	8	9	10	11	
Ru/C	0	0	0	0	0	0	0	0	0	0	0	0	
	20	0.4	0	0.2	0	11	0	0	7.3	1.3	0.1	0.3	
	40	0.8	0.4	0	0	24	0	0.3	23	2.2	0.1	0.4	
	0	0	0	0	0	0	0	0	0	0	0	0	
Pd/C	20	0	0	0.4	0	14	0.2	2.7	12	3.8	1	4.7	
	40	0	0	0.6	0	22	0.2	2.7	19	2.7	0.7	3.7	
Pt/C	0	0	0	0	0	0	0	0	0	0	0	0	
	20	0.3	0	0	0	1.8	0	0.5	1.5	1.7	1.5	1.7	
	40	0.3	0	0	0	2	0	0.2	1.7	1.1	0.7	0.9	

Table	<b>S1.</b>	Product	distributions	on	PEB	conversion	over	Ru/C,	Pd/C,	and	Pt/C	catalysts	in
water.													

General condition: PEB (1.0 g), metal catalyst (5 wt%, 0.02 g), H<sub>2</sub>O (100 mL), 240 °C, 8 bar H<sub>2</sub>, stirring at 650 rpm.

Hydrogenolysis Yield % =  $\sum 1 + 2 + 3 + 4 + 5 + 6 + 7 + 8 + 9$ Hydrogenation Yield % =  $\sum 10 + 11$