Supporting Information

Precise Oxygen Scission of Lignin Derived Aryl Ethers to Quantitatively Produce Aromatic Hydrocarbons in Water

Zhicheng Luo,^a Yimeng Wang,^a Mingyuan He,^a Chen Zhao^{*a}

^a Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

Email: czhao@chem.ecnu.edu.cn

Experiment Section

Chemicals: RuCl₃·3H₂O (J&K, \geq 59.5 wt%), PdCl₂ (J&K, > 59.5 wt%), PtCl₄ (J&K, \geq 58 wt%), activated carbon (Aldrich, powder, 200 mush), sulfate zirconium powder (Changsha Jingkang Co., Ltd), HBeta (SiO₂:Al₂O₃ = 20, The Catalyst Plant of Nankai University), HZSM-5 (SiO₂:Al₂O₃ = 5, The Catalyst Plant of Nankai University), HZSM-5 (SiO₂:Al₂O₃ = 5, The Catalyst Plant of Nankai University), Nafion (Aldrich, powder, 35-60 mush), Amberlyst (Aldrich, wet), Al₂O₃ (J&K), ZrO₂ (J&K), formaldehyde (Sinopharm, AR), cyclooctene (J&K, > 95 wt%), benzyl phenyl ether (TCI, > 98% GC assay), diphenyl ether (Sinopharm, AR), guaiacol (Sinopharm, > 98% GC assay), anisole (Sinopharm, CP), 4-methylguaiacol (J&K, > 99% GC assay), 4-ethylguaiacol (TCI, > 97% GC assay), 2,6-dimethoxyphenol (Alfa Aesar, > 97% GC assay), eugenol (J&K, > 98% GC assay), (2-bromoethyl)-benzene (J&K, > 98% GC assay), phenol (Sinopharm, AR), HCI (Sinopharm, > 36%), NaOH (Sinopharm, AR), hexadecyl trimethyl ammonium bromide (Sinopharm, AR), ethyl-benzene (Sinopharm, AR), diethyl ether anhydrous (Sinopharm, AR), Air, H₂ and N₂ gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of phenethoxybenzene (β -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_w: 198 g·mol⁻¹, formula: C₁₄H₁₄O. The ¹H and ¹³C NMR spectra are displayed in Fig. S1.

Synthesis of supported Ru, Pt, Pd catalysts by the method of liquid-phase HCHO reduction: 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 RuCl₃·H₂O (6.35 mL, *conc*: 0.040 g/L) was added drop-wise to an aqueous suspension (150 mL H₂O, 2.0 g support) with stirring at room temperature. After using NaOH to adjust the pH value to 11, the reduction of RuCl₃ was carried out with formaldehyde (37 wt%, 10.0 mL) at 60 °C for 4 h. Finally the solid was filtrated and washed with distilled water until no free chloride was detected.

Catalyst characterization

The Ru 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⁻¹ H₂ at 200 $^{\circ}$ C for 2 h and then flushed in a flow of 90 mL·min⁻¹ He for 1 h. After cooled to 35 $^{\circ}$ C temperature in He, the CO gas pulses (5 vol% in He) were introduced in a flow of 90 mL·min⁻¹. The changes in the CO gas phase concentration were tracked by a thermal conductor detector (TCD). The measurement of temperature programmed desorption of NH₃ (NH₃-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⁻¹) at 823 K for 2 h. Subsequently NH₃ was adsorbed at 323 K for 20 min., and the catalyst was flushed with helium at 373 K for 2 h to remove physisorbed NH₃ from the catalyst surface. The TPD profile was recorded at a heating rate of 10 K min⁻¹ from 373 to 823 K.

Catalytic testing

Test the surface adsorbed H· species on Ru/SZ monitored by a mass spectrometry: Firstly, a Ru/SZ (5 wt.%, 2.0 g) catalyst was reacted with 8 bar H₂ in the deionized water (100 mL) in a batch autoclave (Parr Instrument, 300 mL) at 120 or 240 °C for 1 h, at a stirring speed of 650 rpm. Then the Ru/SZ was separate from the aqueous phase by decantation, and dried at ambient temperature for 24 h. Subsequently, the desorption of the surface adsorbed H· on the Ru/SZ catalyst (100 mg) was carried out in a He flow (flow rate: 25 mL·min⁻¹), initially at 80 °C for 0.5 h, and then heated from 80 °C to 350 °C with a ramp of 10 °C·min⁻¹. The H₂ signal was monitored by temperature programmed desorption of the surface H· species on a mass spectrometry.

Conversion with phenethoxybenzene (PEB, β -O-4 model compound): A typical experiment was carried out as follows: PEB (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 N₂ at ambient temperature for three times, and then heated up to 240 °C when 8 bar H₂ 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 GC and GC-MS. An internal standard dodecane was added to calculate the carbon balance.

Kinetics of phenethoxybenzene (PEB, β **-O-4 model compound) conversion:** The typical reaction was carried out as follows: PEB (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 N₂ at ambient temperature for three times, the autoclave was charged with 8 bar H₂ 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.

Catalytic tests of hydrodeoxygenation of diverse phenolic monomers and dimers: In a typical procedure, phenolic monomers or dimers (5 mmol), Ru/SZ (5 wt.%, 0.1 g), and deionized water (100 mL) were mixed and charged into a batch autoclave (Parr, 300 mL). After flushing the reactor with N₂ by three times, the reaction was carried out at 240 °C in presence of 2 bar H₂ and 6 bar N₂ for 5 h. After reaction, 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. Analysis for gaseous products was performed on a GC (Techcomp 7900) equipped with a thermal conductivity detector (TCD) and (TDX-01: 30 cm × 3 mm, TDX-01: 2 m × 3 mm) columns, as well as a flame ionization detector (FID) and a HP-PLOT Q capillary column (50 m × 0.53 mm × 25 μ m). In the gas phase, only trace methane was found in the gas phase, therefore, in this work only the change in the liquid phase was considered. The carbon balance in the liquid phase attains 95 ± 3%. The calculations of conversion and selectivity were based on carbon mole basis. Conversion = (changes of raw material / total amount of raw phenolic compounds) × 100%. Selectivity = (C atoms in each product / total C atoms in the products) × 100%.

Density functional theory (DFT) calculation: The quantum chemical calculations of compounds in water and gas phase were performed using Gaussian09 program. The DFT/B3LYP functional with 6-311++G(d,p) basis set were applied. The accuracy of the B3LYP functional was checked by comparing with the second-order Möller-Plesset perturbation theory (MP2). The solvation effects on water were described by the polarizable continuum model (PCM) model with dielectric constants of 78.3553 for water.

Catalyst	Initial hydrogenolysis rate (mmol·g ⁻¹ ·h ⁻¹)	Initial hydrogenation rate (mmol·g ⁻¹ ·h ⁻¹)	Hydrogenolysis/hydrogenation rate ratio
Pd/C	270	47	5.7
Pt/C	47	26	1.8
Ru/C	165	3.3	55

 Table S1. Data for Pd, Pt, Ru catalyzed individual rates in PEB conversion.

General condition: PEB (1.0 g), metal catalyst (5 wt%, 0.020 g), H₂O (100 mL), 240 °C, 8 bar H₂, stirring at 650 rpm.

 Table S2. Hydrogenation of toluene and ethyl-benzene over Ru/SZ in water.



Reaction conditions: toluene or ethyl-benzene (0.10 mol), Ru/SZ (5 wt%, 0.10 g), H₂O (100 mL), 240 °C, 8 bar H₂, 1 h, stirring at 650 rpm.

 Table S3. Alkylation of substituted phenols with methanol over SZ in water.



Reaction conditions: substituted phenols (0.10 mol), methanol (0.10 mol), SZ (0.10 g), H_2O (100 mL), 240 °C, 8 bar H_2 ,

1 h, stirring at 650 rpm.



Scheme S1. The reaction network for PEB conversion with bifunctional catalysts in presence of H₂ in water.



Scheme S2. Reaction pathways for conversion of PEB with variations of temperatures and hydrogen pressures.



Figure S1. ¹H NMR spectra (a) and ¹³C NMR spectra (b) of PEB.



Figure S2. Comparison of hydrogenolysis and hydrogenation of PEB over Ru/C, Pt/C, and Pd/C (5 wt.%, 0.020 g). General conditions: PEB (1.0 g), H₂O (100 mL), 240 °C, 8 bar H₂, stirring at 650 rpm.



Figure S3. Comparison of rates for phenol and ethyl-benzene hydrogenation over Ru/C in aqueous phase. General condition: phenol (0.5 g), ethyl-benzene (0.5 g), Ru/C (5 wt.%, 0.10 g), H₂O (100 mL), 240 °C, 8 bar H₂, stirring at 650 rpm.

Figure S4. Characterization of Ru/SZ catalyst by (a) TEM, (b) HR-TEM, (c) SEM, (d) NH₃-TPD measurements.

Figure S5. Product distributions of PEB conversion over Ru/SZ in water as a function of (a) H_2 pressure and (b) temperature. Reaction conditions: PEB (1.0 g), Ru/SZ (5 wt%, 0.10 g), H_2O (100 mL), 1 h, stirring at 650 rpm, (a) 240 °C, and (b) 8 bar H_2 .

Figure S6. DFT modelling of adsorbed PEB on the Ru (0001) surface, with an adsorption energy of 262 kJ·mol⁻¹.

Figure S7. GC spectrum of aromatic hydrocarbon products after hydrodeoxygenation of a phenolic dimer mixture (phenethoxybenzene, benzyl phenyl ether, and diphenyl ether). Reaction conditions: each reactant (2.5 mmol), Ru/SZ (5 wt%, 0.15 g), H₂O (100 mL), 240 °C, 8 bar H₂, 2 h, stirring at 650 rpm. After reaction, ethyl acetate was used as solvent to extract the organic products.

Figure S8. GC spectra of (a) liquid aromatic hydrocarbon products and (b) gaseous products after hydrodeoxygenation of a phenolic monomer mixture (anisole, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 2,6-dimethoxyphenol, 2,6-dimethoxy-4-methyl-phenol, and eugenol). Reaction conditions: each reactant (0.3125 mmol), Ru/SZ (5 wt%, 0.30 g), H₂O (100 mL), 240 °C, 2 bar H₂ and 6 bar N₂, 5 h, stirring at 650 rpm. After reaction, ethyl acetate was used as solvent to extract the organic products.