Supporting Information

Selective hydrogenation of lignin-derived compounds under mild conditions

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Table Contents

Experimental ..............................................................................................................................................2
Figure S1. SEM and TEM images of the Rh-H catalysts ...........................................................................3
Figure S2. X-ray photoelectron spectroscopy (XPS) of the Rh-H catalyst. ...............................................4
Figure S3. Powder X-ray diffraction (XRD) profiles of the catalysts with different N-doping agents.....5
Figure S4. N\textsubscript{2} physisorption isotherms of Rh-H .........................................................................5
Figure S5. Recycling experiments. ............................................................................................................6
Figure S6. TEM images and size distribution of the Rh/C .........................................................................7
Figure S7. TEM images and size distribution of the Ni/C..........................................................................8
Figure S8. XRD of the Rh/C, Ru/C, Pt/C, Pd/C and Ni/C............................................................................9
Table S1. Hydrogenations of lignin dimer model compounds using Rh-H in H\textsubscript{2}O .........................10
Experimental

Synthesis of the catalysts

In a typical experiment, 2,4-dihydroxybenzoic acid (DA) (1.0 mmol), hexamethylenetetramine HMT (0.5 mmol) and the N-dopant (0.5 mmol) were dissolved in deionized water (60 ml) to form Solution 1. EO20-PO70-EO20 Pluronic (P123) (0.01 mmol), sodium oleate (SO) (0.25 mmol) and RhCl₃·3H₂O (0.05 mmol) were dissolved in deionized (DI) water (20 mL), to form Solution 2. Next, Solution 2 was added to Solution 1 dropwise, and then the mixture was transferred into a Teflon-lined cell, and loaded into a stainless steel autoclave (120 ml). The autoclave was heated from 30 °C to 160 °C with a heating rate of 1 °C min⁻¹ and maintained at 160 °C for 4 h. After cooling to room temperature, the solid was separated by centrifugation and washed three times with DI water. The obtained solid was dried under vacuum at 60 °C. The resulting powder was heated from 30 °C to 600 °C at a heating rate of 2 °C min⁻¹ under an argon atmosphere and maintained at 600 °C for 3 h.

Characterizations of catalysts

Transmission electron microscopy (TEM): The catalysts were dispersed in ethanol and ultra-sonicated for 1 h. Subsequently, the ethanol suspension of nanoparticles was deposited on a carbon film coated copper grid and then examined by TEM. (FEI Talos, operated at 200 keV).

Inductively coupled plasma optical emission spectrometry (ICP-OES): The catalyst (5 mg) was digested in aqua regia and then diluted. The ICP-OES test was conducted on an ICP-OES 5110 instrument (Agilent) using standard metal solutions as reference for each measurement. Result: Rh (35225.8 mg/kg)

Catalyst Testing

The substrate (1 mmol), catalyst (10 mg), and H₂O (2.0 g) were introduced into a 20 mL glass vial and loaded in an autoclave (75 ml). After flushing the autoclave with H₂ three times, the autoclave was pressurized to the desired pressure and placed in a heating block maintained at the desired temperature with stirring at 800 rpm. After reaction, the products were extracted with diethyl ether and analysed by gas chromatography-mass spectrometry (GC-MS).

Recycling Experiment

The recycling experiments followed the same procedure except a reaction time of 5 h was used. An additional washing step with diethyl ether (3 × 5 mL) was also added. Before each experiment, the solution was ultra-sonicated for 30 s to disperse the catalyst.
Figure S1. SEM images of the Rh-H catalysts obtained at different hydrothermal temperatures, (a) 120°C, (b) 140°C, (c) 160°C, (d) 180°C. (e) TEM characterization of Rh-C prepared at 160°C. In the white insert, their corresponding size distribution, their mean diameter as well as the structure of the N-dopant used during the synthesis. The blue circle represents the average outer diameter of the carbon support. The pink scale represents the average thickness of the shell.
Figure S2. X-ray photoelectron spectroscopy (XPS) of the Rh-H catalyst. (a) Rh 3d5/2 region (b) N 1s region (c) Survey.
**Figure S3.** Powder X-ray diffraction (XRD) profiles of the catalysts with different N-doping agents.

**Figure S4.** N$_2$ physisorption isotherms of Rh-H. The specific surface areas of 540 m$^2$/g, and the mean diameter of pores 4 nm. The pore size distribution curves were obtained by analysing the isotherm desorption branch using the Barrett–Joyner–Halenda (BJH) model.
Figure S5. Recycling experiments. Reaction conditions: phenol (1.0 mmol), Rh-H (10 mg), H₂O (2.0 g) 5 bar H₂, 30 °C, 4 h.
Figure S6. TEM images and size distribution of the Rh/C.
Figure S7. TEM images and size distribution of the Ni/C.
**Figure S8.** XRD of the Rh/C, Ru/C, Pt/C, Pd/C and Ni/C.
Table S1. Hydrogenations of lignin dimer model compounds using Rh-H in H₂O.

<table>
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<th>Entry</th>
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<td>(21) (15) (24) (23)</td>
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<td>(45) (28) (25) 2)</td>
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</table>

Reaction conditions: phenol (1.0 mmol), Rh-H (20 mg), H₂O (2.0 g) 15 bar H₂, 80 °C, 24 h. Conversion and yields determined by GC.

[a] 100 °C.