Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Supporting Information

Selective hydrogenation of lignin-derived compounds under mild conditions

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SUPPORTING INFORMATION

Experimental

Synthesis of the catalysts

In a typical experiment, 2,4-dihydroxybenzoic acid (DA) (1.0 mmol), hexamethylentetramine 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 $RhCl_3 \cdot 3H_2O$ (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 H_2O (2.0 g) were introduced into a 20 mL glass vial and loaded in an autoclave (75 ml). After flushing the autoclave with H_2 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.

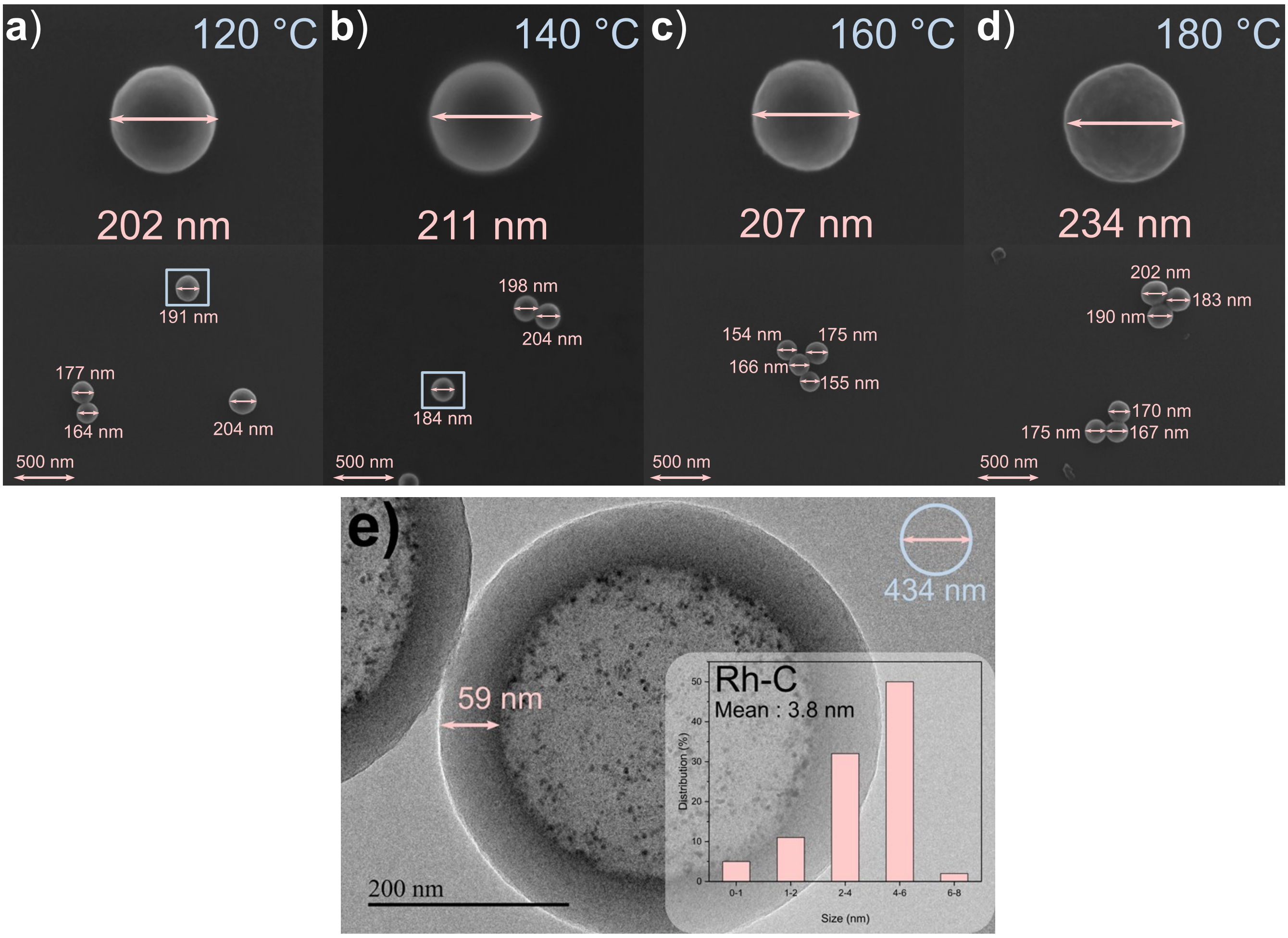


Figure S1. SEM images of the Rh-H catalysts obtained at different hydrothermal temperatures, (a) 120°C, (b) 140°C , (c) 160 °C, (d) 180 °C. (e) TEM characterization of Rh-C prepared at 160 °C. In the white insert, their corresponding size distribution, their mean diameter as well as the structure of 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.

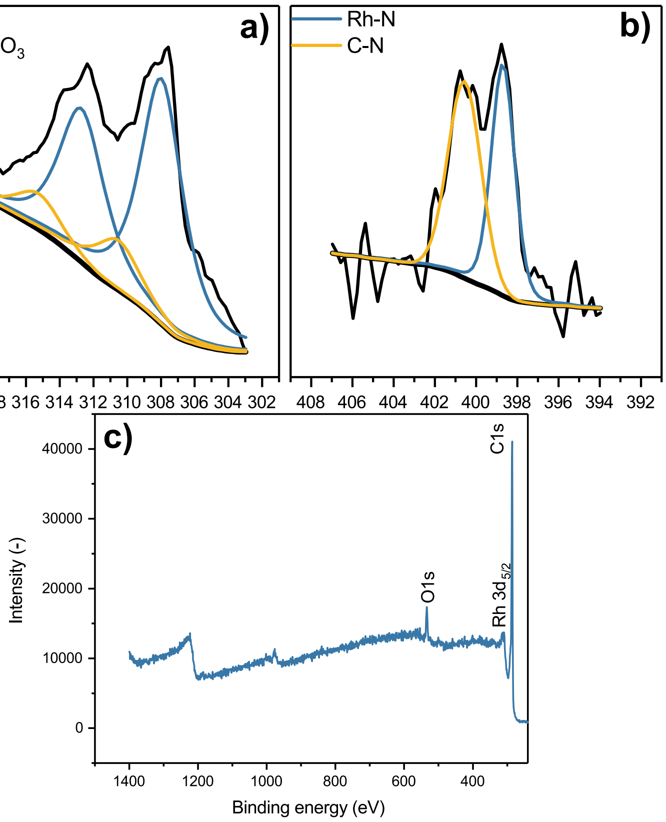


Figure S2. X-ray photoelectron spectroscopy (XPS) of the Rh-H catalyst. (a) Rh 3d5/2 region (b) N 1s region (c) Survey.

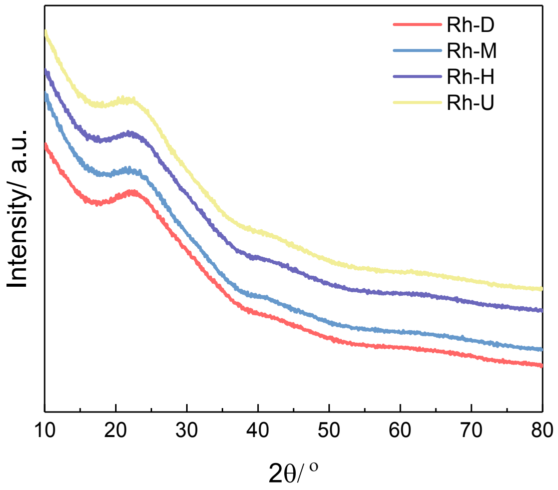


Figure S3. Powder X-ray diffraction (XRD) profiles of the catalysts with different N-doping agents.

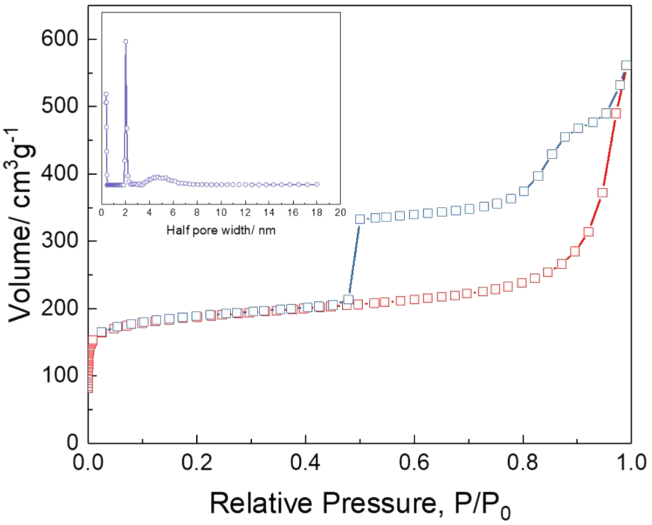


Figure S4. N_2 physisorption isotherms of Rh-H. The specific surface areas of 540 m^2/g, and the mean diameter of pores 4 nm. The pore size distribution curves were obtained by analysing the isotherm desorption branch using the Barrett–Joyner–Halenda (BJH) model.

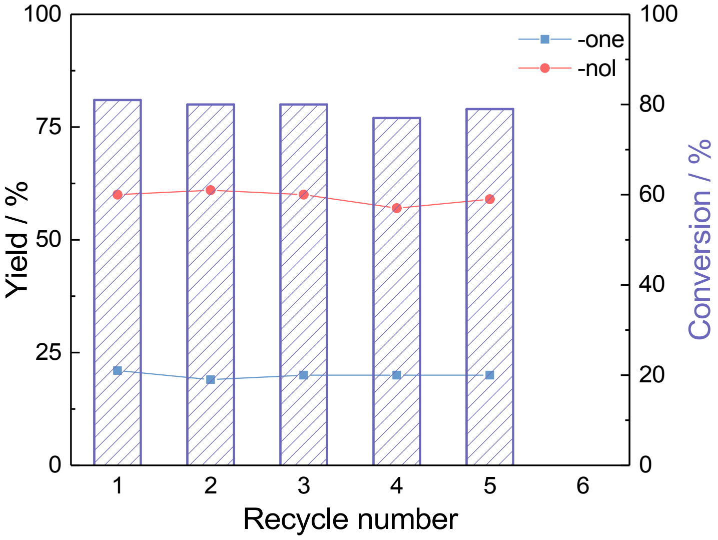


Figure S5. Recycling experiments. Reaction conditions: phenol (1.0 mmol), Rh-H (10 mg), H_2O (2.0 g) 5 bar H_2, 30 °C, 4 h.

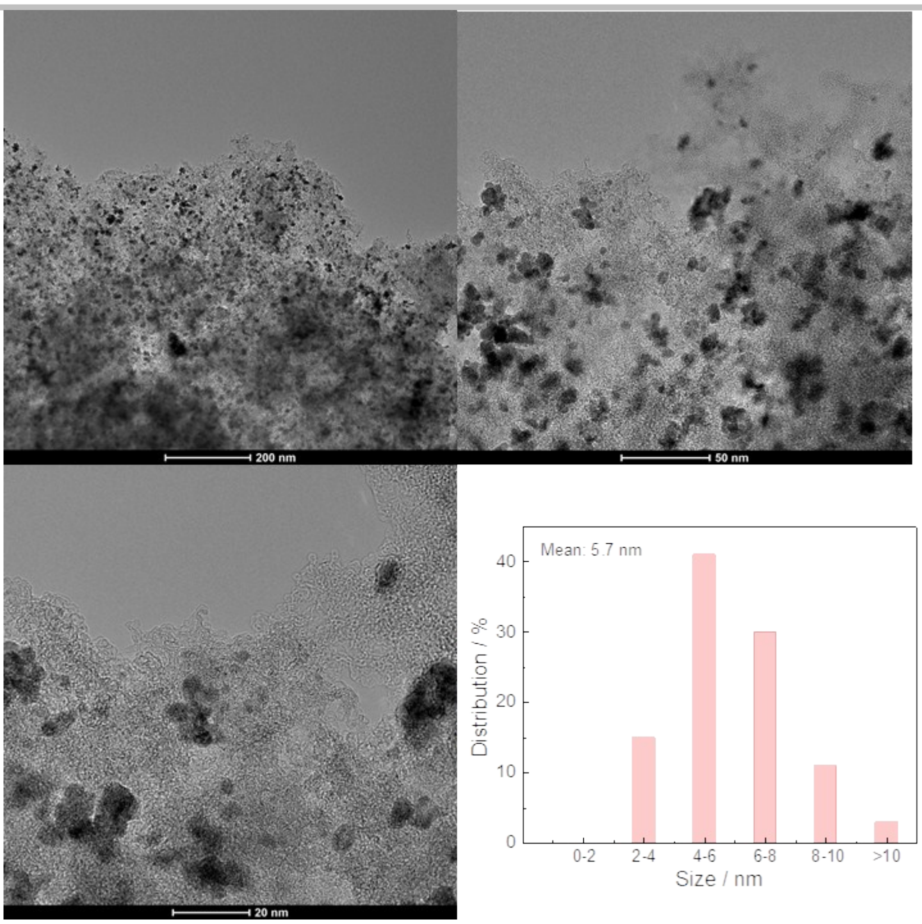


Figure S6. TEM images and size distribution of the Rh/C.

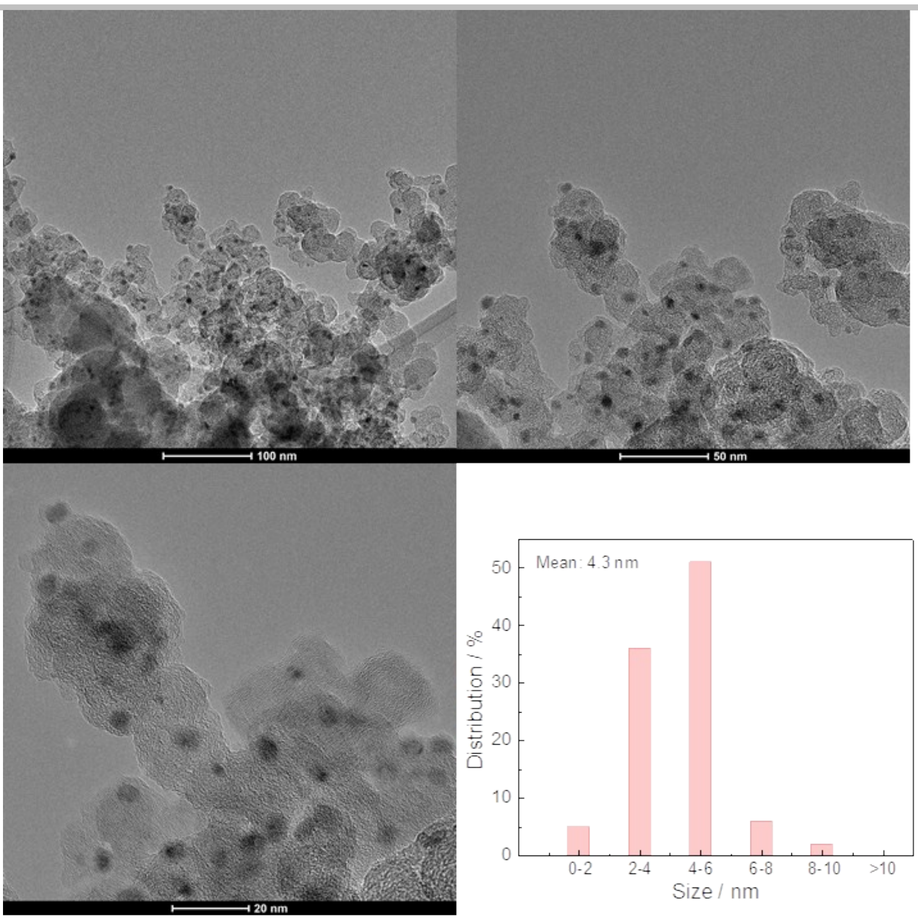


Figure S7. TEM images and size distribution of the Ni/C.

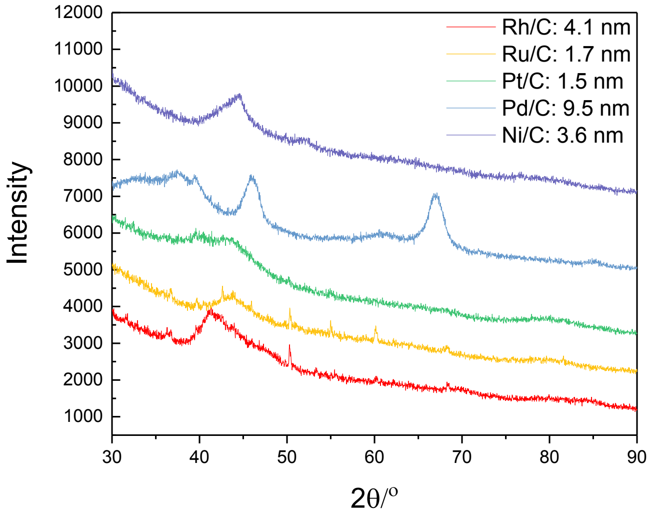
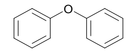
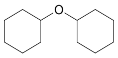
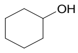
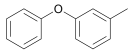
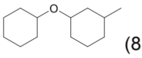
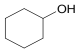
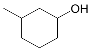
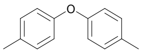
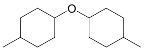
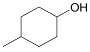
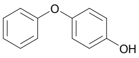
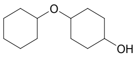
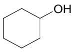
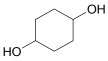
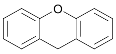
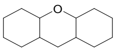
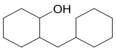
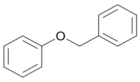
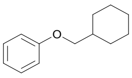
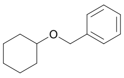
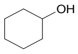
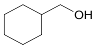
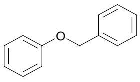
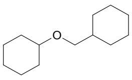
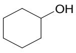
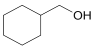
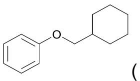
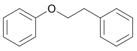
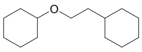
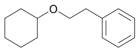
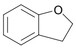
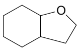
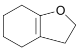
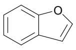
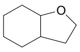
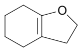
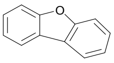
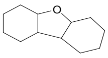
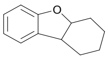
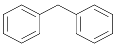
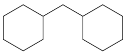
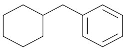
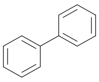
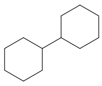
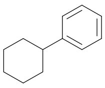


Figure S8. XRD of the Rh/C, Ru/C, Pt/C, Pd/C and Ni/C.

Table S1. Hydrogenations of lignin dimer model compounds using Rh-H in H_2O.

Entry	Substrate	Conversion %	Products (Yield %)			
1	 4-O-5	100	 (82)	 (18)	-	-
2		100	 (85)	 (7.5)	 (7.5)	
3		100	 (85)	 (15)	-	-
4		95	 (90)	 (5)	 (5)	-
5		100	 (98)	 (2)	-	-
6	 α-O-4	83	 (21)	 (15)	 (24)	 (23)
7[a]	 α-O-4	98	 (45)	 (26)	 (25)	 (2)
8	 β-O-4	84	 (67)	 (17)	-	-
9[a]	 β-5	80	 (77)	 (3)	-	-
10[a]		79	 (76)	 (3)	-	-
11[a]	 β-5	100	 (75)	 (25)	-	-
12	 α-1	100	 (98)	 (2)	-	-
13	 5-5	100	 (98)	 (2)	-	-

Reaction conditions: phenol (1.0 mmol), Rh-H (20 mg), H_2O (2.0 g) 15 bar H_2, 80 °C, 24 h. Conversion and yields determined by GC.

[a] 100 °C.