Electronic Supporting Information

Selective lignin depolymerization via transfer hydrogenolysis using Pd/hydrotalcite catalysts: model compounds to whole biomass

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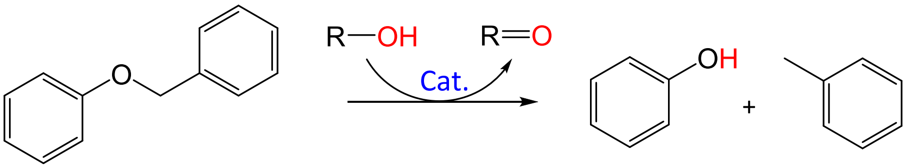
1. Related Work



Pd/Fe_3O_4
Mauriello et al. 2016

240 °C 1.5 hours
250 mg catalyst (5% Pd)
iPrOH
10 bar N_2
Recyclable for 7 runs

ReO_x/AC
Li et al. 2020

200 °C 3 hours
1.6 mol % Re
iPrOH
6.89 bar N_2
51 TON

Ni/Al_2O_3
Jiang and Guo 2019

150 °C 3 hours
20 mg catalyst (61 wt.% Ni)
iPrOH
4.7 TON

Pd-CuHT
Our system

150 °C 2 hours
2.5 mol % Pd
EtOH
At atmosphere
63 TON

Pd/C
Samec et al. 2014

80 °C 1 hours
2.5 mol % Pd
HCOOH
1 equiv. base (NH_3)
66 TON

Figure S1. Summary of related work on α-O-4 model compounds and relevant metrics.

2. Materials and Methods

2.1 General Considerations

Aluminum (III) nitrate nonahydrate (98%) and magnesium (II) nitrate hexahydrate (98%) were obtained from ACROS Organics, Palladium (II) nitrate hydrate (40% palladium basis) and palladium (II) acetate (98%) were purchased from Sigma Aldrich, γ-Alumina (150 mesh, 58 Å) was purchased from Aldrich Chemical Company. Sodium hydroxide (97%) was obtained from VWR AMRESCO® Life Sciences; sodium carbonate (99.5%) from Fisher Scientific. Compounds used to synthesize model compounds including acetophenone (>98 %), 2-phenoxyacetophenone (>98 %), 3,4-dimethoxyacetophenone (>98%), phenol (>99%), and guaiacol (>98%) were obtained from TCI chemicals. Formaldehyde solution (37 wt% in water) was acquired from Beantown Chemicals, sodium borohydride (99%, Venpure™ SF granules) was purchased from Acros Organics, and bromine (>98 %) was purchased from Aldrich Chemicals

2.2 Catalyst Preparation

Pd-Al_2O_3 was synthesized via wet impregnation as follows. γ-Alumina (Aldrich, 1 g) was calcined at 450 °C for 12 h and was then suspended in deionized (DI) water (10 mL). Palladium nitrate (0.2153 g, Aldrich) was dissolved in 100 mL DI water at room temperature, then added dropwise to the stirred alumina suspension. The slurry was stirred for a further 2 h, filtered through grade 410 filter paper, and the residue then dried for 12 h at 110 ^oC. The resulting solid was finally calcined at 450 ^oC for 12 h and stored in a desiccator.

Pd/HT was synthesized via a continuous flow method[1]. Briefly, a nitrate salt solution was prepared by dissolving $Mg(NO_3)_2{\cdot}6H_2O$ (3.590 g, 0.014 mol), $Al(NO_3)_3{\cdot}9H_2O$ $6H_2O$ (1.876 g, 0.005 mol), and $Pd(NO_3)_2{\cdot}xH_2O$ (0.230 g, 0.001 mol) into 70 mL of deionized (DI) water. A base solution was also prepared comprising NaOH (1.599 g, 0.040 mol) and Na_2CO_3 (0.265 g, 0.0025 mol) dissolved in 70 mL of DI water. Using a syringe pump equipped with a Y-connector, the two solutions were added at a rate of 4 mL/min to a beaker containing 100 mL of DI water, which was continuously stirred (200 rpm)(Figure S2). After addition, the mixture was aged at 65 ^oC for 2 h, allowed to cool to room temperature, filtered and washed with DI water until the pH of the filtrate was neutral. The resulting solid was dried at 110 °C for 12 h, ground to a powder with a mortar and pestle, and stored in a desiccator.

PdM/HT

Modified catalysts were synthesized through the same co-precipitation procedure. They were not formed via wet impregnation onto an already formed Pd/HT matrix. For transition metal modified Pd/HTs, the same procedure is followed with the addition of the appropriate metal nitrate (ie. $Cu(NO_3)_2 * 2.5\,H_2O$, $Fe(NO_3)_2 * 9\,H_2O$, etc.) to the original metal nitrate salt solution. In all cases for this publication, the metal modifier was added at a 15% mol ratio to all metals present. A total of 0.020 moles by metal is used in total. Therefore, if a +2 metal is used as a modifier it would replace the appropriate amount of Mg2+. For example, if Cu was introduced at 15% (0.003 moles), the metal nitrate salt solution would consist of $Mg(NO_3)_2{\cdot}6H_2O$ (0.011 mol), $Al(NO_3)_3{\cdot}9H_2O$ $6H_2O$ (0.005 mol), $Cu(NO_3)_2 * 2.5\,H_2O$ (0.003 mol), and $Pd(NO_3)_2{\cdot}xH_2O$ (0.001 mol). If a +3 metal modifier is used, this replaces that of Al^{3+}.

Pd/MgO was synthesized via wet impregnation using a modified protocol previously reported by Akuri *et al* [2]. In brief, a aqueous solution of $Mg(NO_3)_2{\cdot}6H_2O$ (10 mL, 1 M) was mixed with a solution of NaOH (10, mL 0.0312 M) in a continuous fashion using syringe pumps connected with a Y-connector at a flow rate of 4 mL/min. The solution mixture was dropped into a beaker containing 100 mL of DI water with stirring (200 rpm), as described above for Pd-HT. The pH was raised to 10 with the addition of aqueous NaOH and the mixture aged at 60 ^oC for 1 hour. The suspension was further stirred at room temperature for 12 h. The slurry was filtered, and the resulting solid then oven dried for 12 h at 110 ^oC before calcination at 450 ^oC for 12 h. The calcined solid was suspended in 10 mL of DI water. Palladium nitrate hydrate (0.069 g) was dissolved in 10 mL DI water at room temperature, then added dropwise to the stirred suspension. After completing the addition, the solution was stirred for 2 h. The slurry was then filtered, and the impregnated solid dried at 110 ^oC for 12 h, and finally calcined at 450 ^oC for 12 h.

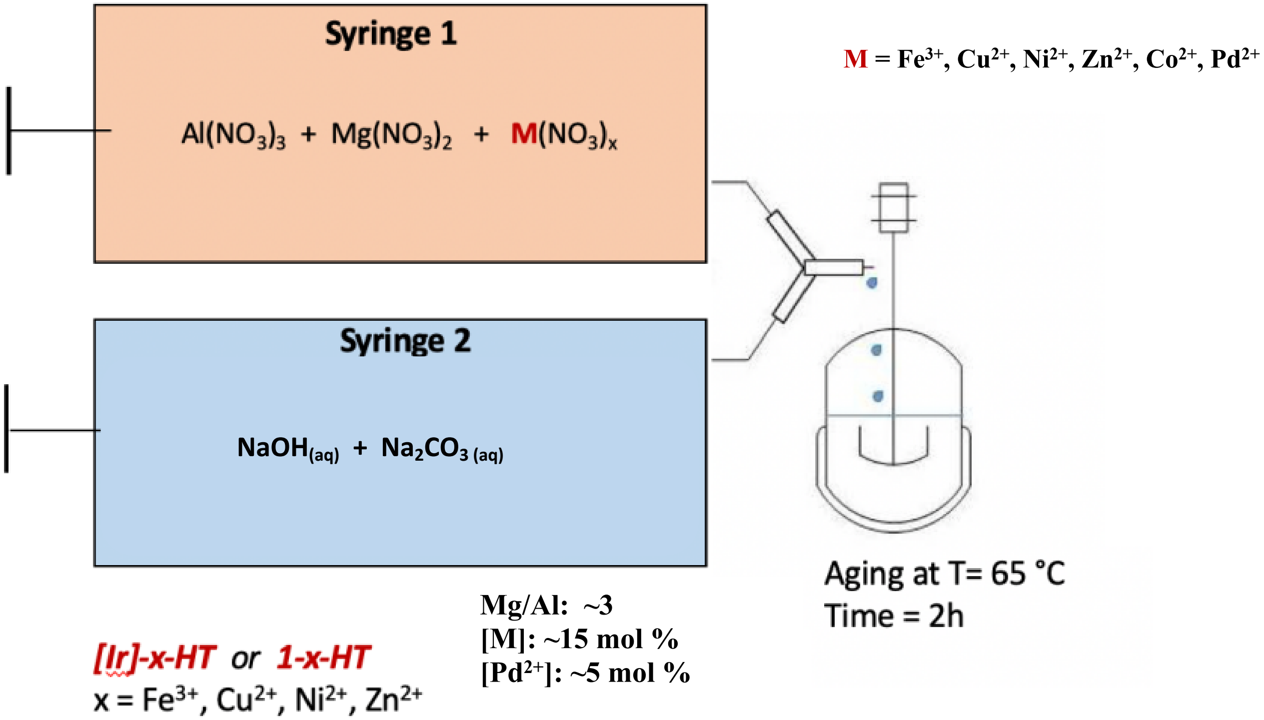


Figure S2. Schematic of the continuous flow synthesis of hydrotalcites.

2.3 Catalyst Characterization

Elemental analysis was carried out with inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Shimadzu ICPE-9820 Plasma Atomic Emission Spectrometer. Powder X-Ray Diffraction (PXRD) patterns were obtained using a Rigaku MiniFlex II X-Ray diffractometer, between 2θ of 0 - 70°. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo K-alpha spectrometer fitted with a charge neutralizer and a monochromated Al K α X-ray source. High resolution scans were recorded with a pass energy of 50 eV. Processing of spectra was performed using CASA-XPS V2.3.17, with binding energies corrected to adventitious carbon at 284.8 eV, and regions background subtracted and fitted with common line shapes and full-width half maxima. Surface compositions were determined by applying response factors from the Schofield library to correct spectral areas. Transmission Electron Microscope (TEM) images were collected on Talos F200X under 200kV FEG with Ceta 16M camera. Nitrogen porosimetry was performed on a Micrometric TriStar surface analyzer at 77 K. Samples were degassed under vacuum at 150 °C for 3 h prior to analysis. Surface areas were determined using the BET method, with pore sizes and volumes calculated using the BJH method applied to desorption isotherms. NMR spectra were recorded on an Agilent 400 MHz spectrometer ($CDCl_3$, 32 scan). GC-FID chromatograms were recorded on an Agilent 6890N GC System using a column with a DB-5 stationary phase. Thermogravometric analysis (TGA) was performed on a Perkin Elmer Pyris 1 TGA. Samples were heated from 30-650 °C at 20 °C min^{-1} in nitrogen.

Table S1. Structural properties of catalysts.

Sample	Ionic radius of 3rd /4th metal	Molar content[a,b], %				M^{2+}/M^{3+}	Crystallographic parameters[c]		
		Mg^{2+}	Al^{3+}	M^{2+} or M^{3+}	Pd^{2+}		*a* / Å	*c* / Å	L / nm
HT	-	75.12	24.88	-	-	3.02	3.06	23.31	10.4
Pd-Al_2O_3	-	-	-	-	1.95	-	-	-	9.9
Pd-MgO	-	-	-	-	2.30	-	-	-	5.5
Fe-HT	0.65	76.77	7.08	16.15	-	3.30	3.09	23.43	11.7
Cu-HT	0.73	61.97	23.91	14.12	-	3.18	3.06	23.23	9.8
Pd-HT	-	70.18	25.43	-	4.40	2.93	3.05	23.36	10.4
Pd-FeHT	0.65	70.34	10.79	14.66	4.21	2.93	3.09	23.31	11.3
Pd-CoHT	0.75	52.76	27.51	15.46	4.27	2.64	3.05	23.98	12.3
Pd-NiHT	0.69	51.18	26.07	18.42	4.33	2.84	3.07	23.62	9.6
Pd-CuHT	0.73	54.61	25.58	14.97	4.83	2.91	3.05	23.25	10.6
Pd-ZnHT	0.74	52.93	27.64	15.26	4.18	2.62	3.06	23.29	10.9

[a]ICP-AES; [b]mol% as fraction of all metals present (Mg, Al, Pd); [c]PXRD; *a* is average cation-cation distance; *c* is three times the distance from the center of one brucite-like layer to the next layer; *L* is the average crystallite size from peakwidth analysis using the Scherrer equation.

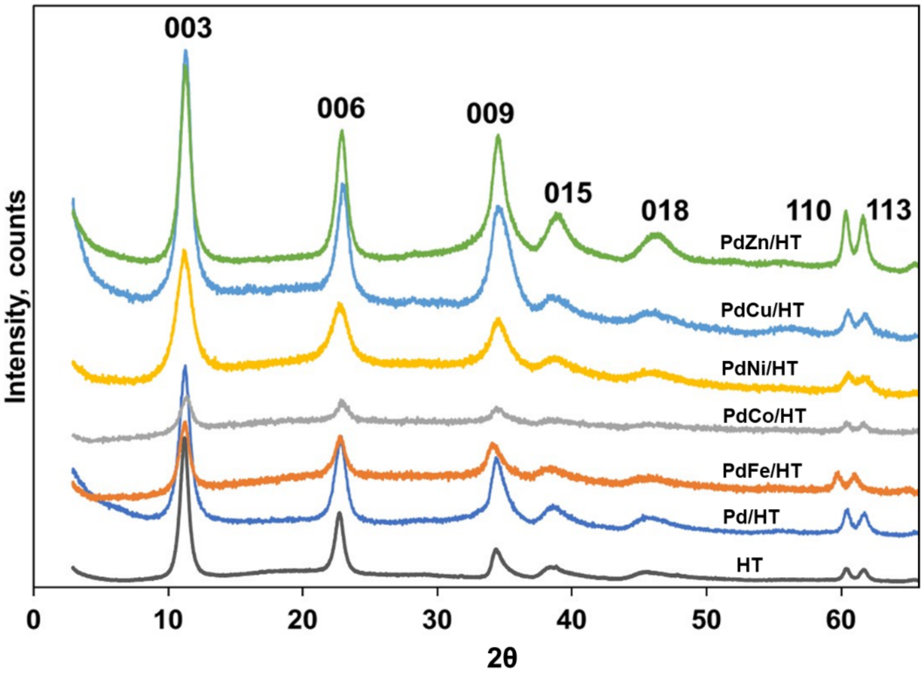


Figure S3. PXRD spectra of palladium doped HT's: 5% Pd-HT, 5% Pd-FeHT, 5% Pd-CoHT, 5% Pd-NiHT, 5% Pd-CuHT, and 5% Pd-ZnHT. Each Pd doped HT only show reflections characteristic of the Mg-Al hydrotalcite phase, indicating Pd is highly dispersed.

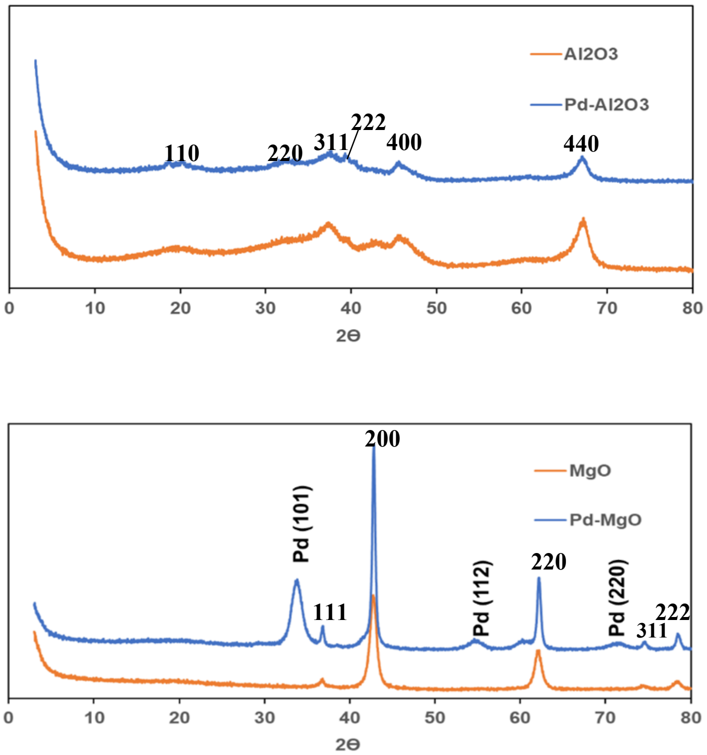


Figure S4. PXRD patterns of (a) 3% Pd/γAl_2O_3 and γ-Al_2O_3 and (b) 3% Pd/MgO and MgO. Pd/γAl_2O_3 shows diffraction features consistent with cubic γ-alumina only exhibits reflections characteristic of γ-Al_2O_3. No Pd phases can be resolved, either due to overlap with signals from alumina, small particle size or low crystallinity. Pd/MgO shows sharp reflections characteristic of large brucite nanocrystals, and weaker reflections associated with crystalline PdO phases.

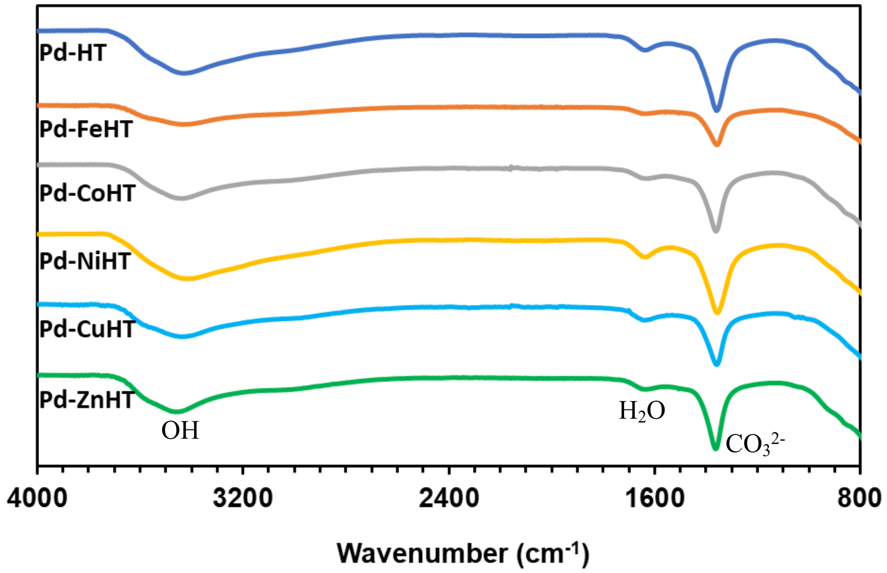


Figure S5. FT-IR of palladium doped hydrotalcites 5% Pd-HT, 5% Pd-FeHT, 5% Pd-CoHT, 5% Pd-NiHT, 5% Pd-CuHT, and 5% Pd-ZnHT.

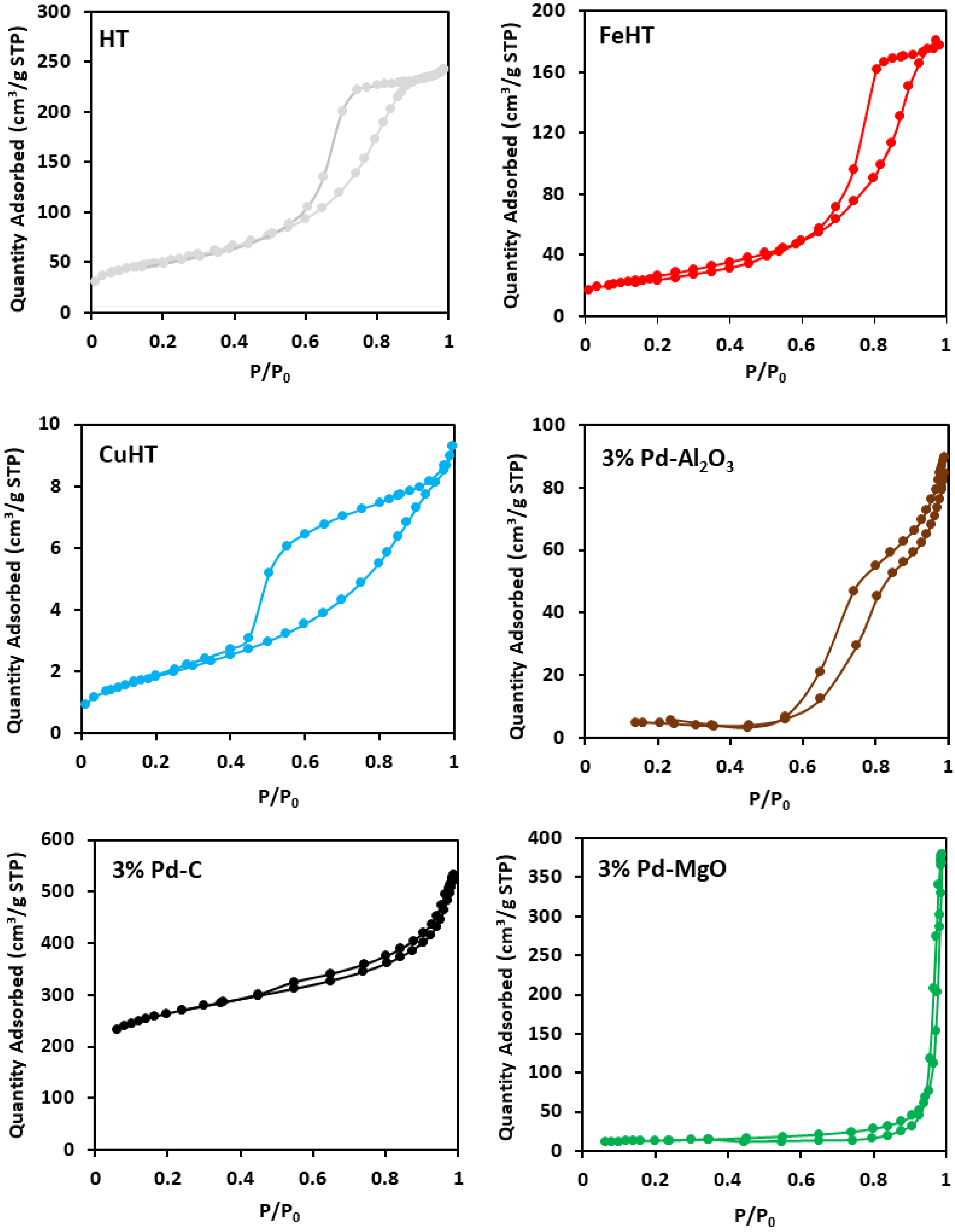


Figure S6. Nitrogen adsorption-desorption isotherms of HT, Fe/HT, Cu/HT, 3% Pd/Al_2O_3, 3% Pd/C and 3% Pd/MgO catalysts.

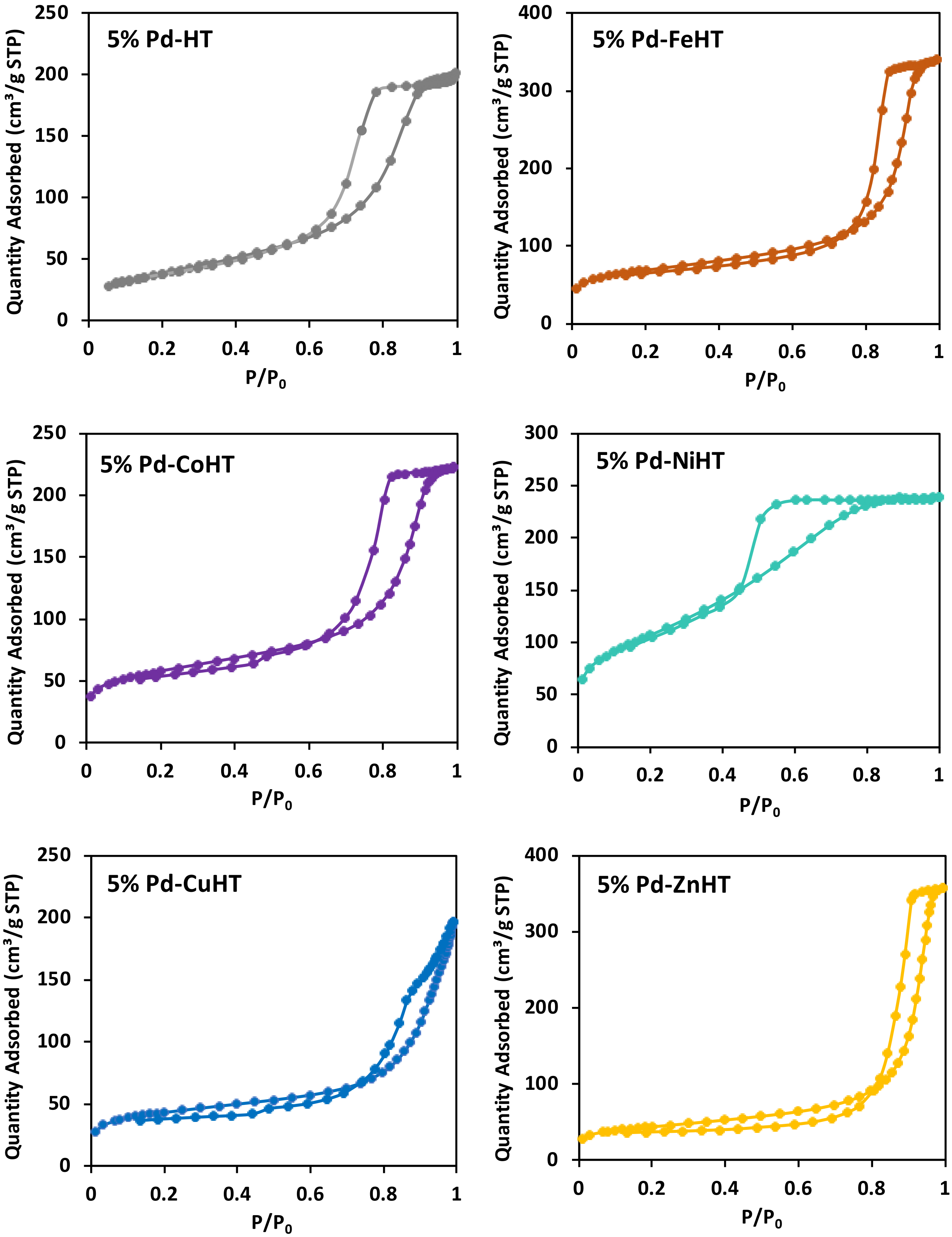


Figure S7. Nitrogen adsorption-desorption isotherms of 5% PdM/HT catalysts.

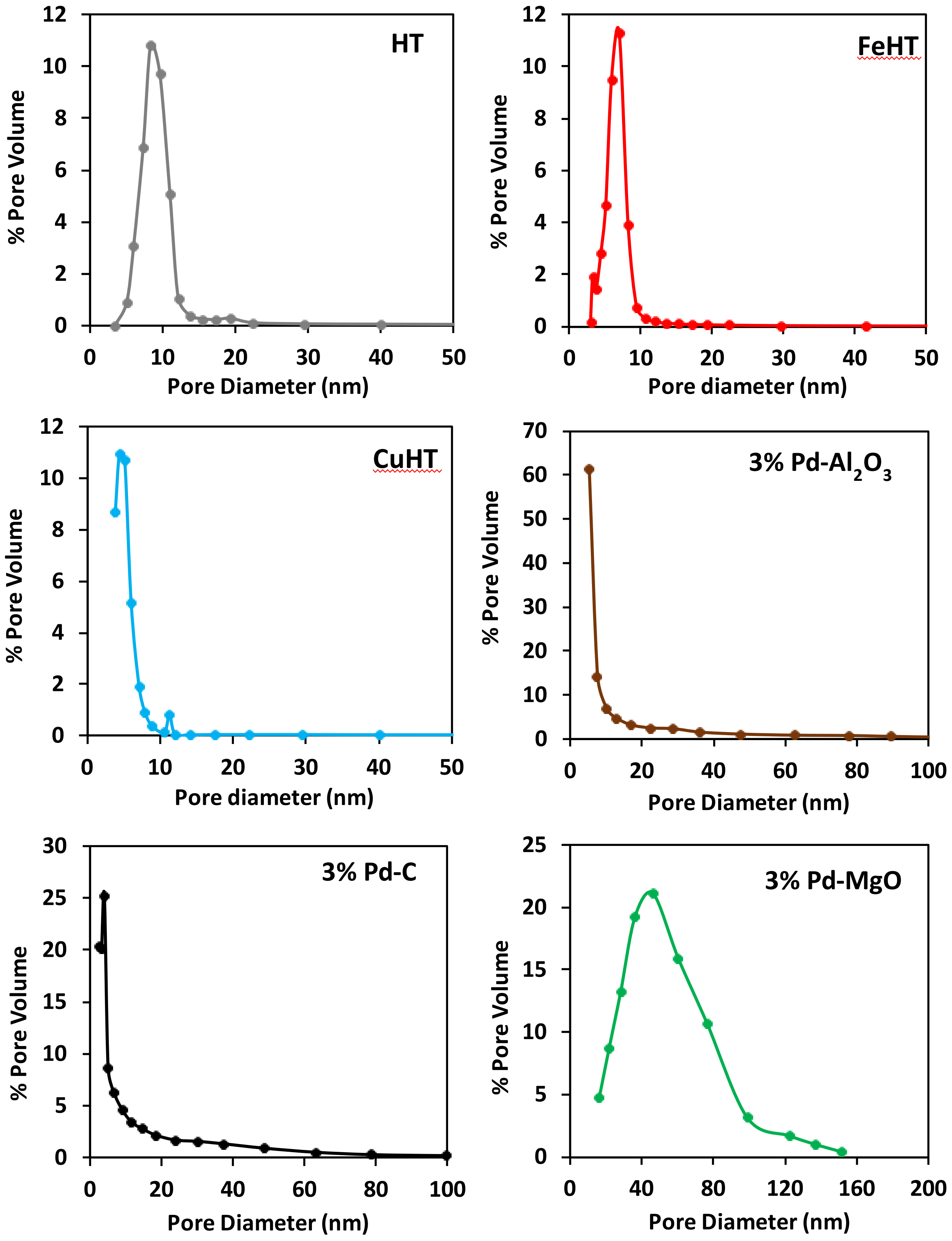


Figure S8. BJH pore size distributions of HT, Fe/HT, Cu/HT, 3% Pd/Al$_2$O$_3$, 3% Pd/C, and 3% Pd/MgO catalysts.

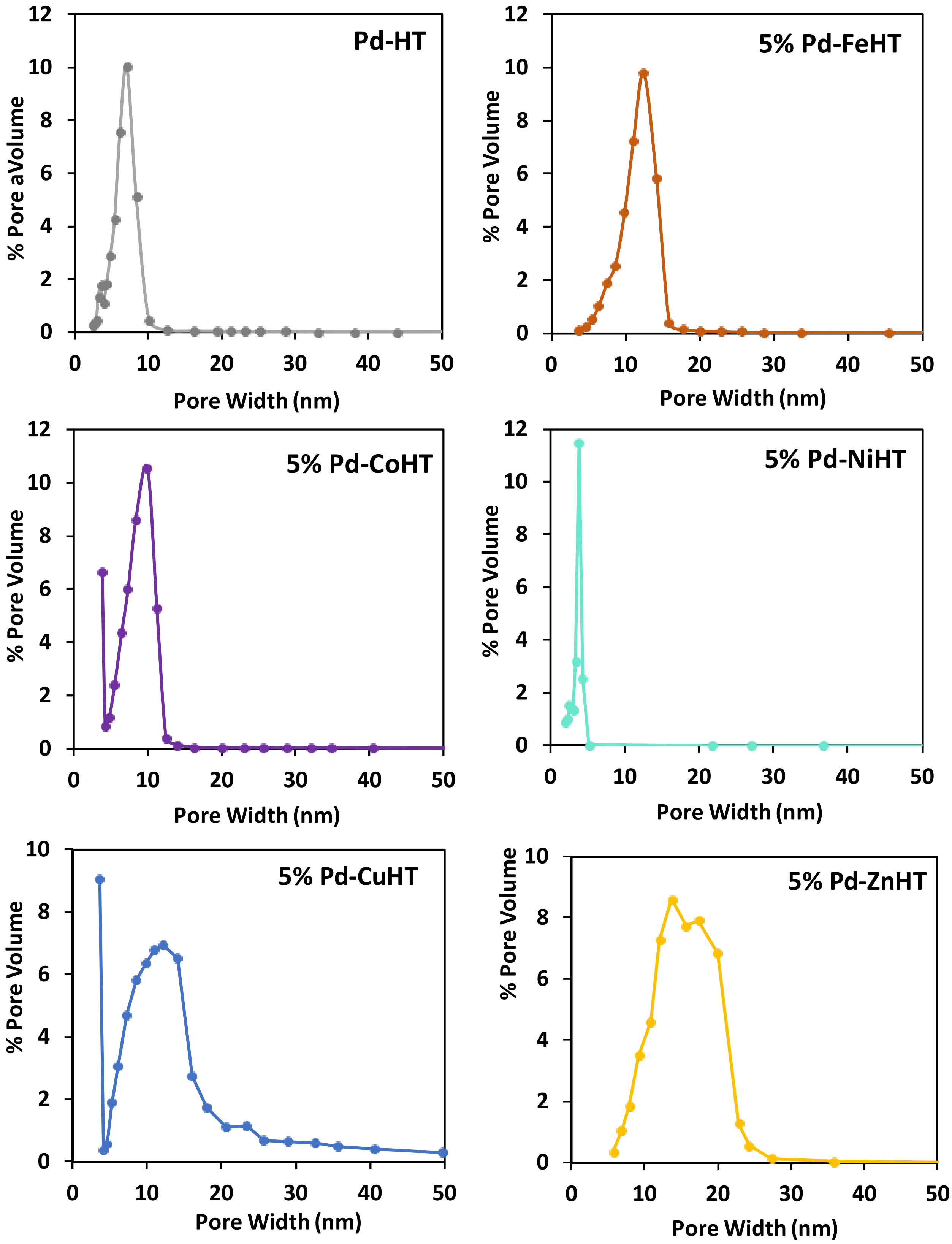


Figure S9. BJH pore size distributions of 5% PdM/HT catalysts.

Table S2. Textural properties of parent and metal modified supports.

Sample	S_{BET} ^{a} (m^2/g)	BJH Pore Volume ^{b} (cm^3/g)	Pore Width ^{b} (nm)
HT	148	0.26	3.6
FeHT	126	0.34	6.6
CuHT	140	0.27	3.6
PdHT	53	0.13	6.6
Pd-FeHT	242	0.53	8.7
Pd-CoHT	203	0.33	8.5
Pd-NiHT	385	0.39	4.1
Pd-CuHT	152	0.29	7.6
Pd-ZnHT	155	0.54	11.7
Pd-Al_2O_3	83	0.12	8.8
Pd-MgO	45	0.59	46.5

^{a}BET determined for relative pressures p/p_0 = 0.05-0.25; ^{b}Determined using the BJH method applied to the desorption branch of the isotherm.

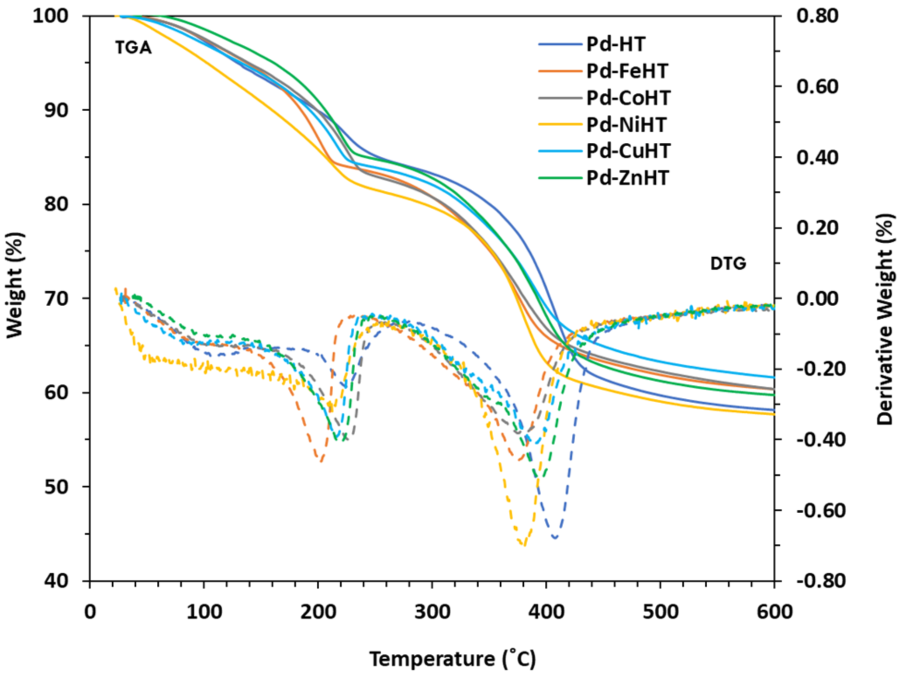


Figure S10. Thermogravimetric analysis and differential thermal gravimetry (DTG) of 5% PdM/HT catalysts.

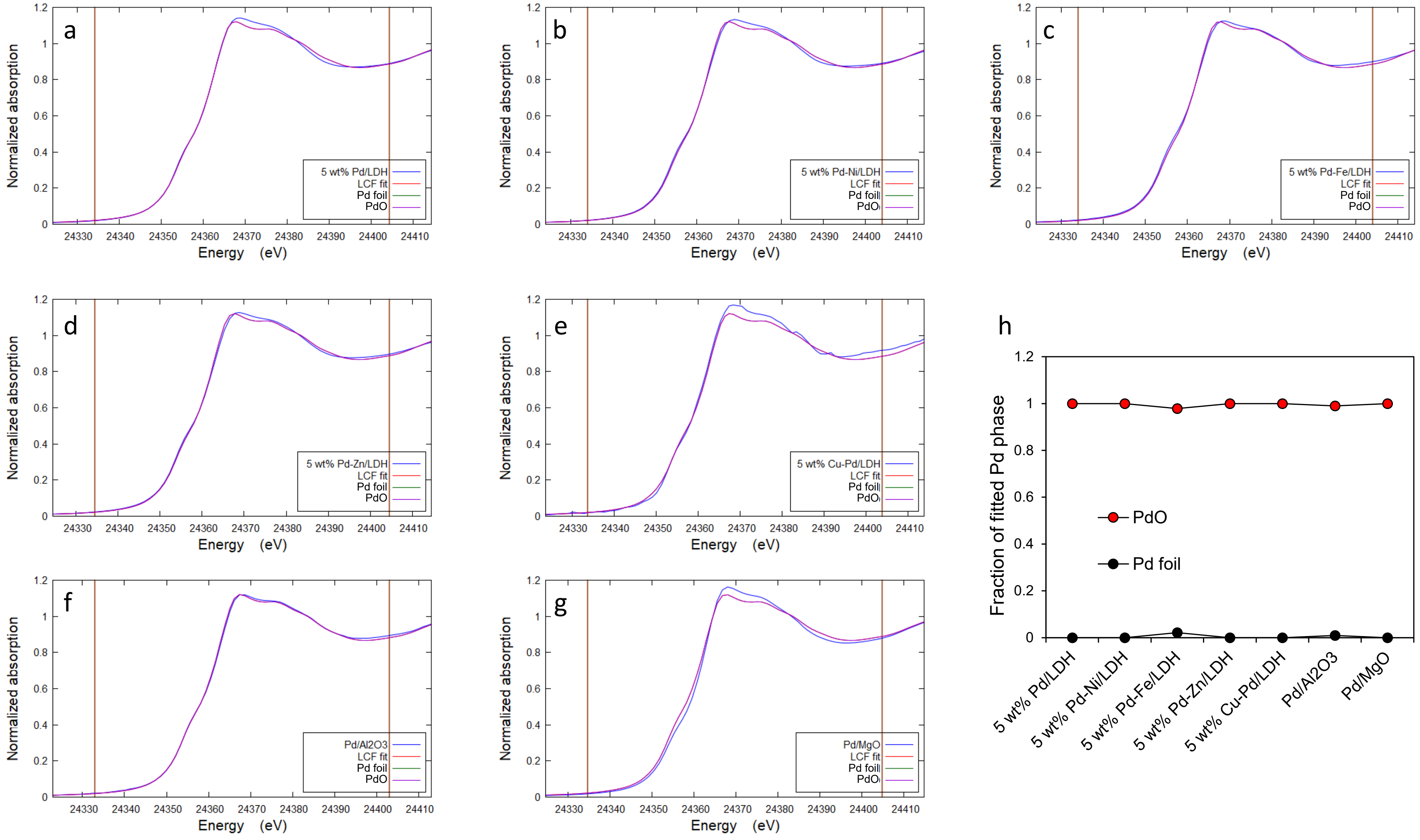


Figure S11. (a-g) Pd K-edge transmission XANES spectra and least squares fits (to Pd foil and PdO reference materials), and (h) corresponding Pd phase quantification for 5% PdM/HT catalysts.

XANES spectra were obtained at the XAS beamline of the Australian Synchrotron in fluorescence mode using a 36 element Ge detector. Samples were diluted with boron nitride and mounted inside a He purged cell sealed by using Kapton tape at room temperature. Spectra were collected up to k =15 Å^{-1}, with simultaneous collection of Pd foil reference spectra. Data analysis was performed using the IFEFFIT software package Athena.[3]

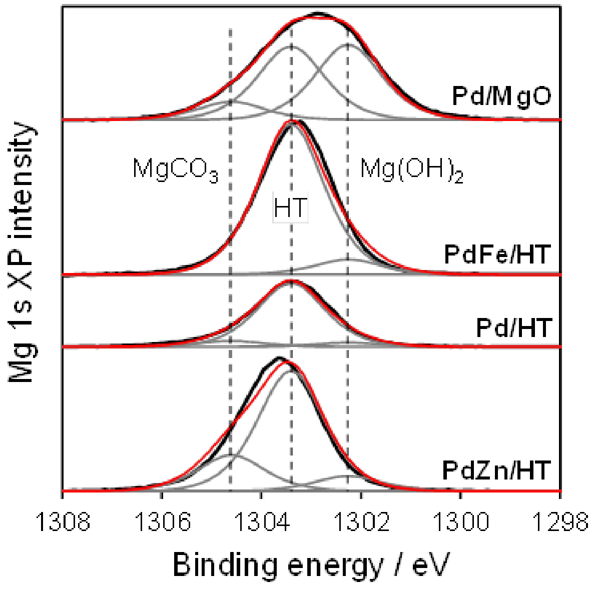


Figure S12. Mg 1s XPS spectra of Pd/MgO, PdFe/HT, Pd/HT, and PdZn/HT.

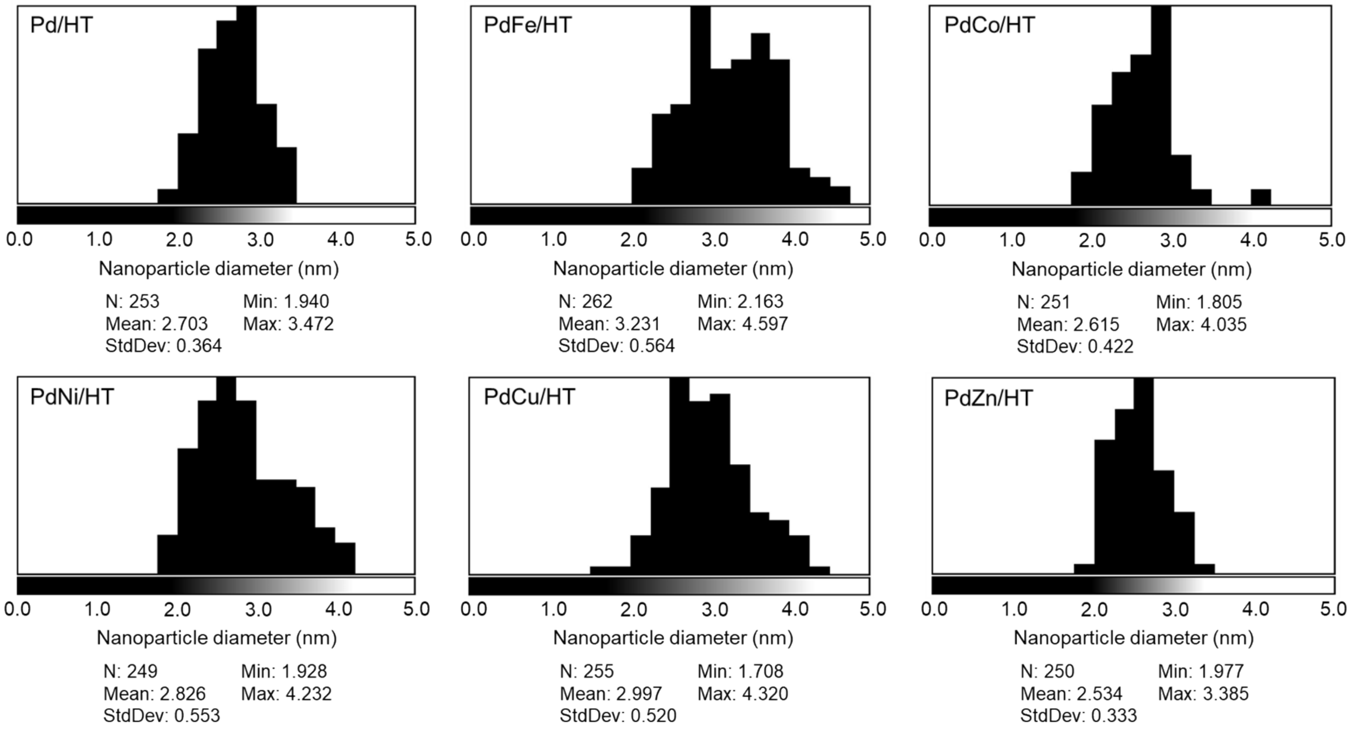


Figure S13. Particle size distribution histograms of PdM/HTs. Particle size (diameter) was determined through analysis of TEM images using ImageJ software.

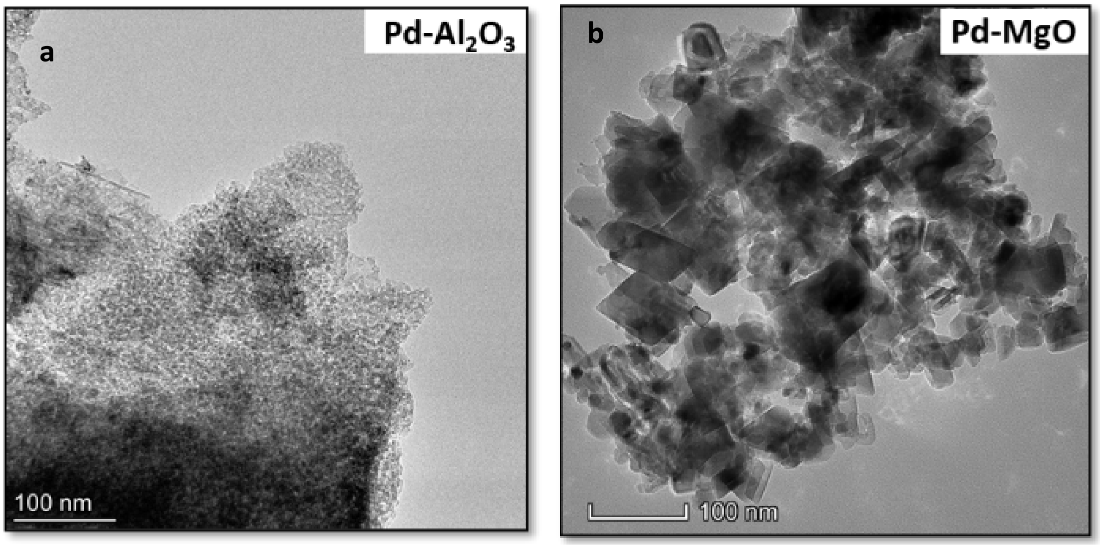
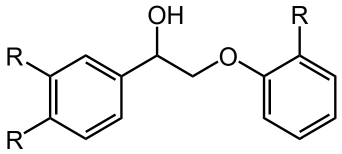
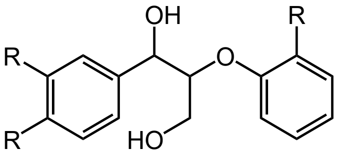


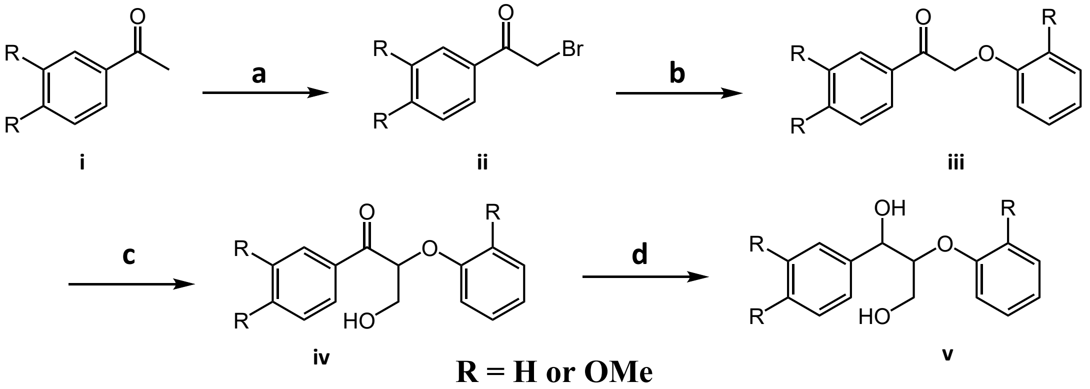
Figure S14. Bright-field TEM images of (a) 3% Pd-Al_2O_3, and (b) 3% Pd-MgO.

3. Model Compounds

3.1 Synthesis


C2 Type
(lack of γ-hydroxymethyl group)

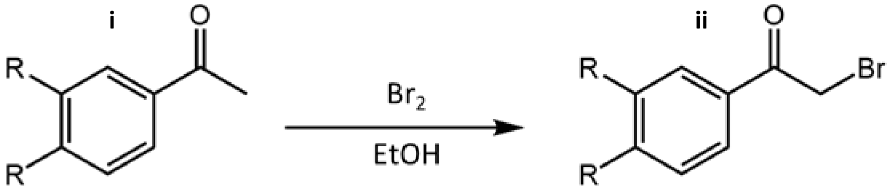

C3 Type
(presence of γ-hydroxymethyl group)



Scheme S1. General steps in the optimized synthesis of C3 type lignin model compounds

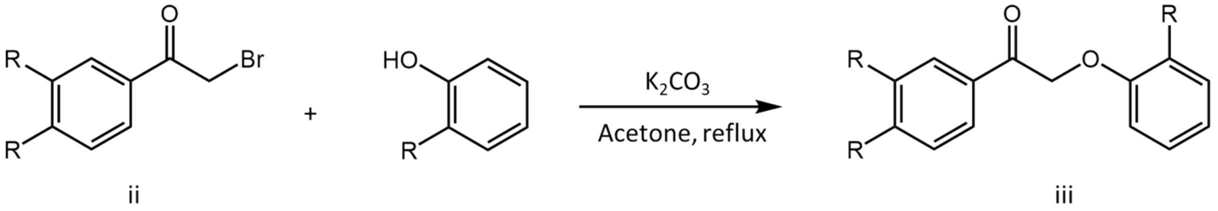
- The following procedures can be followed to obtain the desired type of substitution on the final model compound. The compounds outlined in the procedure can be substituted with the corresponding substituted compound.
- Additionally, the C2 type model compounds can be achieved by skipping step c and going directly to step d (reduction using $NaBH_4$). See following image for distinction between C3 and C2 type model compounds.

(a) Bromination of Acetophenones



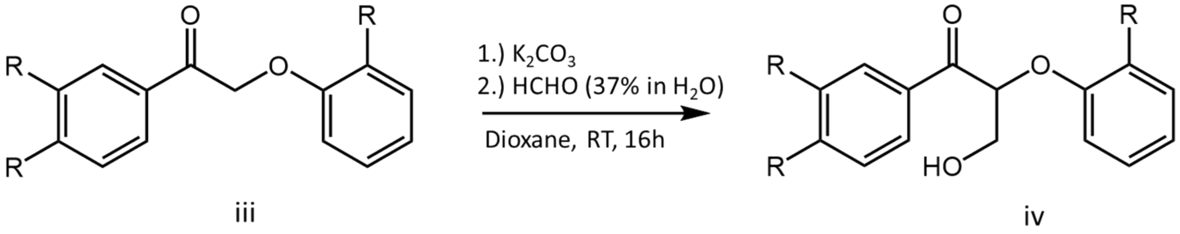
Bromine (15.10g, 94.6mmol, 1.14eq.) was added dropwise to a solution of acetophenone (i) (15.0 g, 83.2 mmol, 1 eq.) in ethanol (150 mL) at room temperature. After 2 hours, the red color of the bromine had faded and a white precipitate had spontaneously formed. The mixture was then stoppered and cooled on ice for 3 hours. The precipitate was isolated by filtration, washed with cold ethanol and dried in air to yield the title compound as white crystals[4].

(b) Ether bond Formation between Bromoacetophenone and Phenol Derivatives



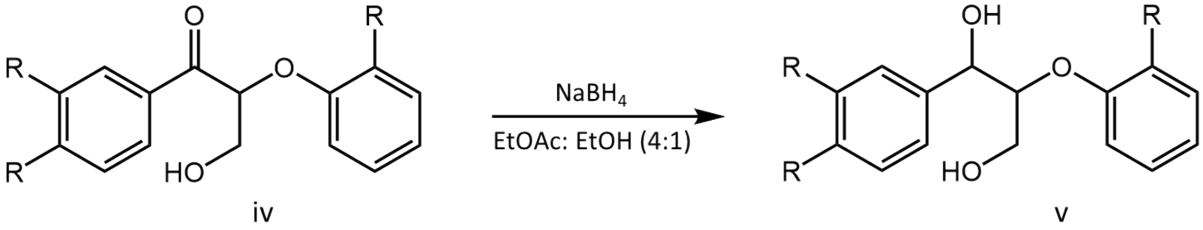
To a solution of (ii) (6.02 g, 23.3 mmol, 1 eq.) in acetone (60 mL) was added phenol (2.88 g, 23.2 mmol, 1 eq.) followed by anhydrous K_2CO_3 (6.41 g, 46.4 mmol, 2 eq.). The mixture was then heated to reflux for 2 h, allowed to cool to room temperature, filtered and concentrated in vacuo. The resulting yellow solid was manually broken up with a spatula, suspended in ethanol and stirred for 30 mins. The resulting solid was collected by filtration and allowed to dry to give the desired product (iii).[4]

(c) Addition of γ-Hydroxy Methyl Group



To a solution of (iii) (3.32 g, 10.9 mmol, 1 eq.) in 1,4-dioxane (30 mL) was added formaldehyde (37% in H_2O, 0.36 g, 12.1 mmol, 1.1 eq.) followed by K_2CO_3 (6.08 g, 44.0 mmol, 4 eq.). The mixture was stoppered and vigorously stirred overnight. TLC indicated full consumption of starting material. The mixture was then filtered and concentrated in vacuo. The resulting oil was dissolved in methanol (30mL) and left in the fridge overnight resulting in the formation of a white precipitate. The precipitate was collected by filtration, washed with methanol and air dried to give the title compound (iv).[4]

(d) Reduction of Carbonyl Group



To a suspension of (iv) (1.98 g, 6.0 mmol, 1 eq.) in ethyl acetate:ethanol (4:1, 20 mL), $NaBH_4$ (0.11 g, 3.0 mmol, 0.5 eq.) was added portion-wise. The mixture was stirred for 1 hour forming a homogeneous solution. The reaction was quenched by addition of a saturated solution of NH_4Cl (20 mL) and vigorously stirred for 10 mins. The organic layer was separated, washed with water, brine, dried ($MgSO_4$) and concentrated in vacuo to give the title compound (v) (1:1 mixture diastereoisomers).[4]

3.2 NMR Spectra of Model Compounds

2-Phenoxyacetophenone (L-2)

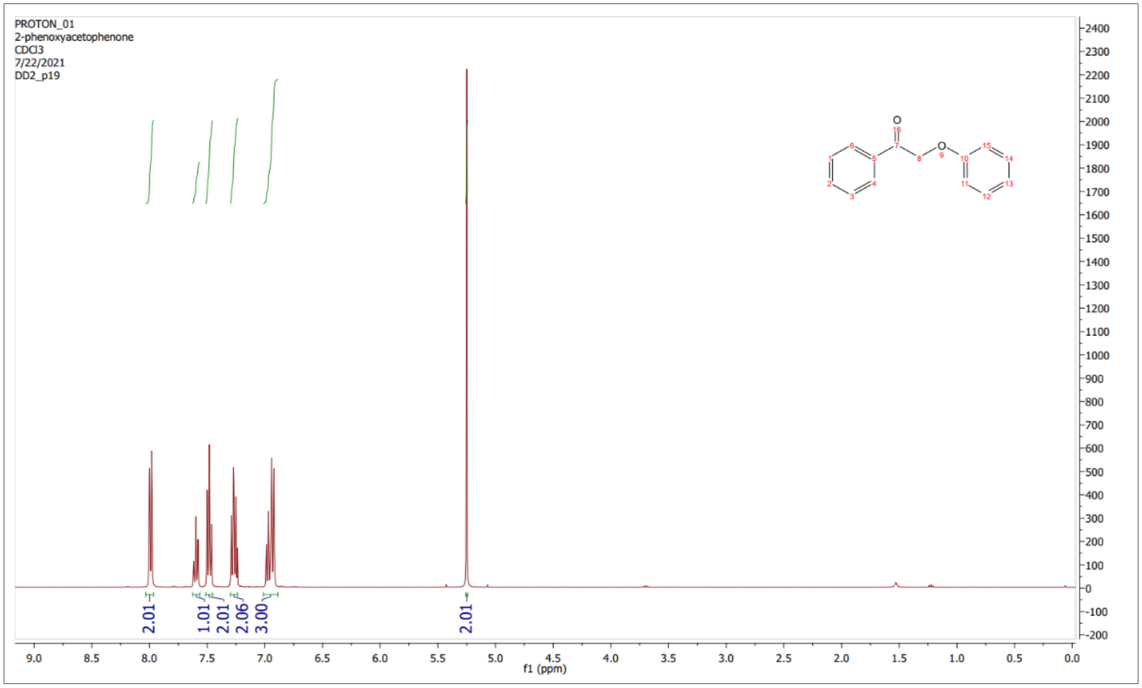


Figure S15. NMR Spectrum of 2-phenoxyacetophenone (L2) (Agilent, 400 MHz, $CDCl_3$)

2-Phenoxy-1-phenethanol (L-3a)

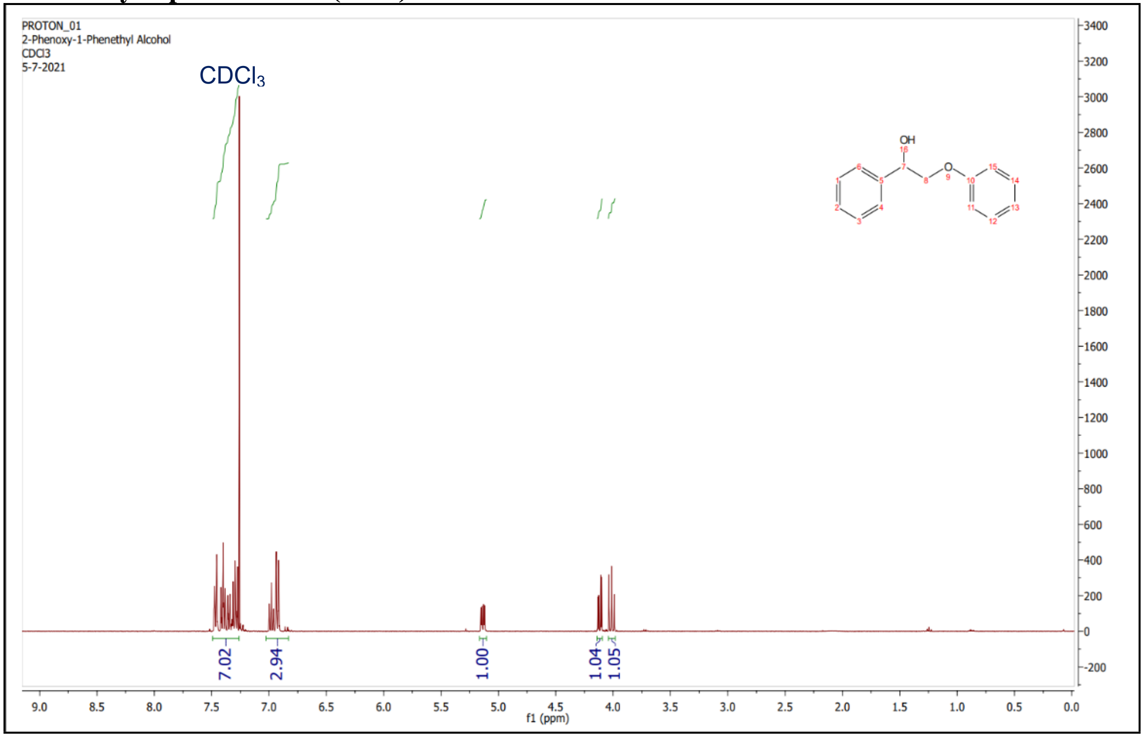


Figure S16. NMR Spectrum of 2-phenoxy-1-phenethanol (L3a) (Agilent, 400 MHz, $CDCl_3$)

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanol (L-3b)

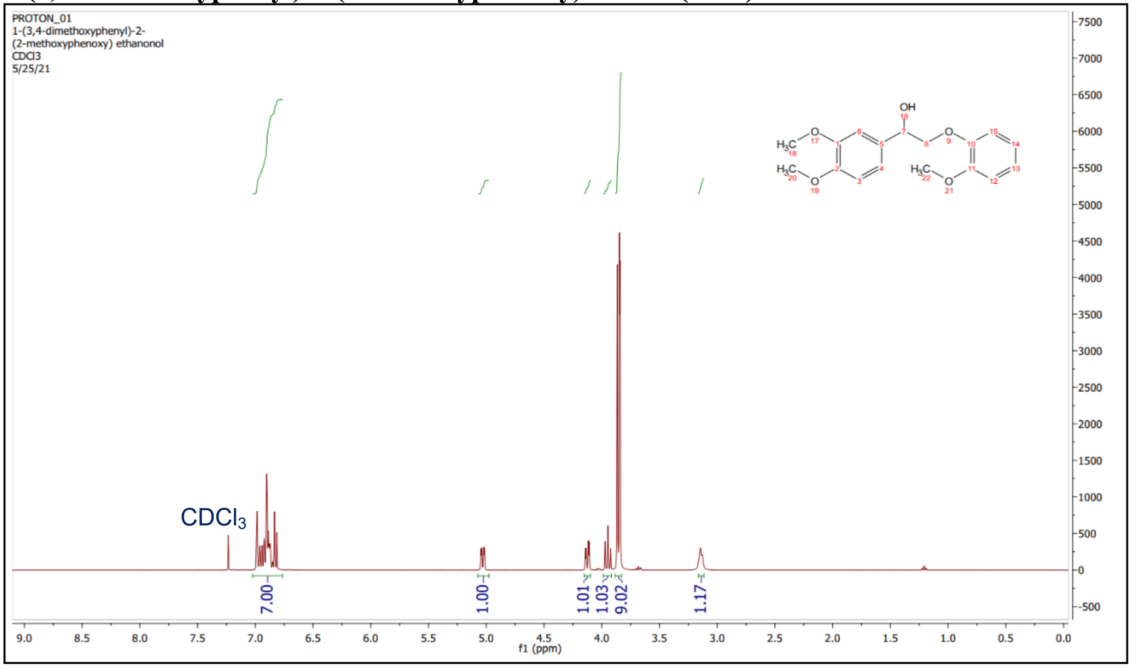


Figure S17. NMR Spectrum of 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy) ethanol (L-**3b**) (Agilent, 400 MHz, $CDCl_3$)

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propandiol (L4)

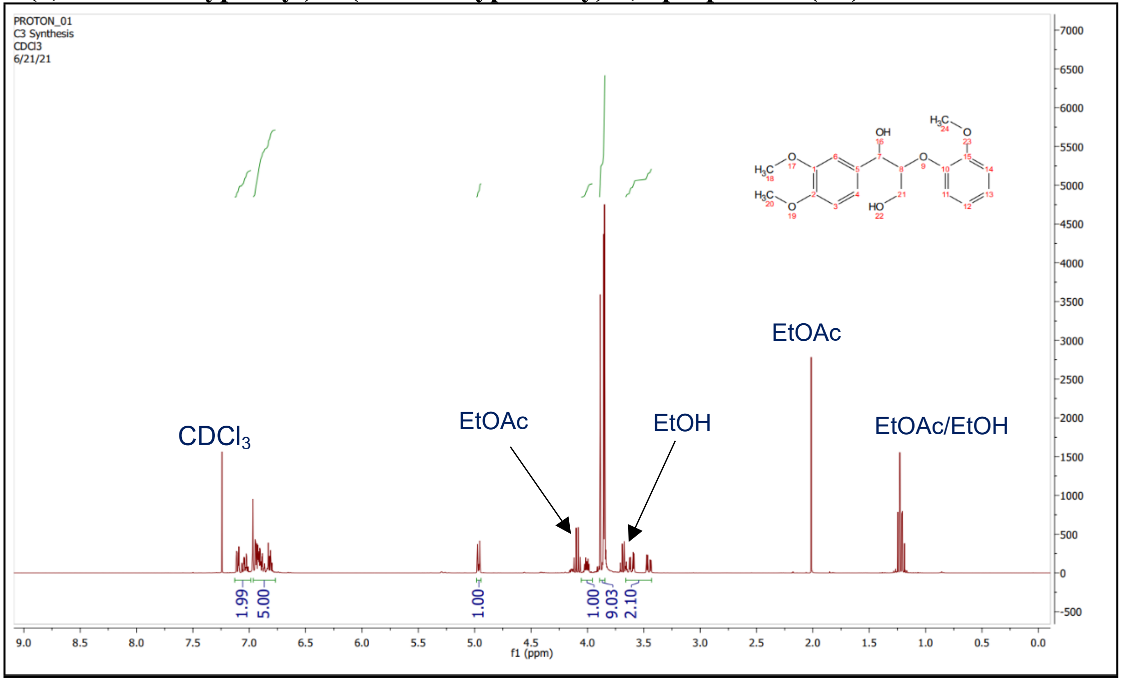


Figure S18. NMR Spectrum of 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (L4) (Agilent, 400 MHz, $CDCl_3$)

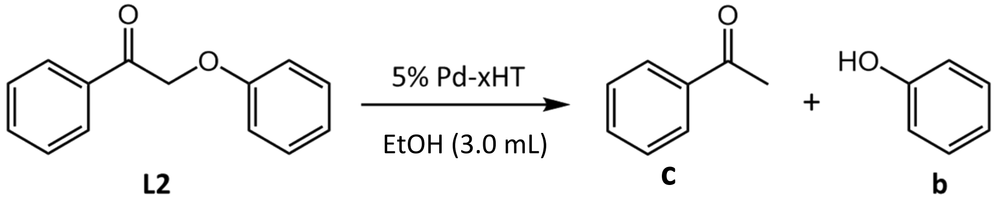
4 Catalytic Reactions

4.1 Model Compound Reactions

Reactions were carried out under microwave conditions using an Anton Parr Monowave 450. Lignin model compounds (**Figure 1**) (0.1 mmol) were placed in a G10 Anton Parr glass microwave vial with a magnetic stir bar. Solvent (3.0 mL) and catalyst (5.0 mol % Pd) was added and agitated for dispersion. The vial was sealed, placed in the microwave system, and carried out for the specified time and temperature with a stir rate of 600 rpm. The catalyst was separated by filtration after the reaction. Gas chromatography-mass spectrometry (GC-MS) was used to identify the chemicals in the product mixture. Products were then quantitatively analyzed via gas chromatography – flame ionization detection (GC-FID)

4.2 Hydrogenolysis Reaction with 2-Phenoxyacetophenone (L2)

Table S3. Catalytic transfer hydrogenolysis of 2-phenoxyacetophenone (β-O-4 C2 model) (L-**2**).



Entry	Catalyst	Conversion (%)	Yield (%)	
			c	**b**
1	HT **(A)**	0	0	0
2	5% Pd/HT **(B)**	75	71	75
3	5% PdFe/HT **(C)**	99	97	98
4	5% PdNi/HT **(D)**	55	48	55
5	5% PdCo/HT **(E)**	88	84	88
6	5% PdCu/HT **(F)**	99	95	96
7	5% PdZn/HT **(G)**	85	64	71

Reaction conditions: 0.1 mmol L-**2**, 3.0 mL ethanol, 5 mol% catalyst, µW heating at 150 °C, 2 h. Majority of the unaccounted yield is a result of aldol condensation between acetaldehyde and acetophenone forming ethyl benzoate and to a lesser extent, hydrogenation of acetophenone (c) to the secondary alcohol.

4.3 Catalyst stability (reuse)

After an initial cycle with compound L-**3a**, the catalyst was separated from the reaction mixture by centrifugation (5000 rpm, 10 min). The reaction mixture was removed and sampled for product analysis while the catalyst remained in the G10 microwave vial. Fresh L-**3a** (0.1 mmol) and ethanol (3.0 mmol) were then added to the vial and heated for 2 hours at 150 °C. This process was repeated for five cycles where the cleavage yield was determined after each. This methodology is beneficial as it minimizes errors due to catalyst loss during filtration and/or washing steps. After the final cycle, the catalyst was separated by filtration and washed with fresh ethanol to rid the catalyst of remaining organics. The catalyst was then washed with an aqueous solution of Na_2CO_3 followed by DI H_2O. Finally, the catalyst was dried for 12 hours at 110 °C. The used catalyst was fully characterized the same as the fresh catalysts.

Table S4. Elemental composition data of fresh PdCu/HT vs. used PdCu/HT (measured by ICP-OES)

Sample	**Molar composition[a] / %**				**M^{2+}/M^{3+}**
	Mg^{2+}	**Al^{3+}**	**Cu^{2+}**	**Pd^{2+}**	
Pd-Cu/HT	54.61	25.59	14.97	4.83	2.91
Pd-Cu/HT after 5 reaction cycles	54.84	26.33	14.20	4.63	2.80

[a] ICP-OES.

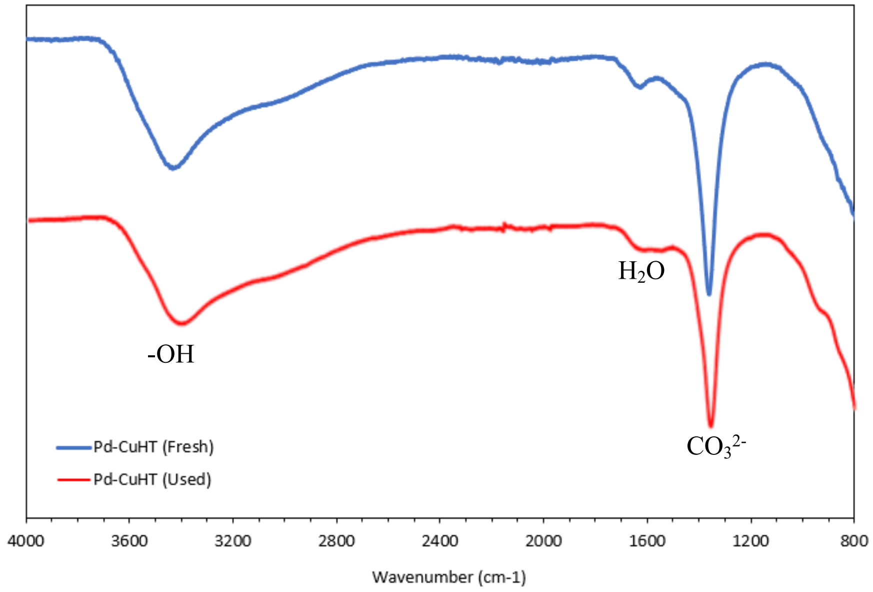


Figure S19. FT-IR spectra comparing fresh Pd-CuHT and Pd-CuHT after 5 reaction cycles.

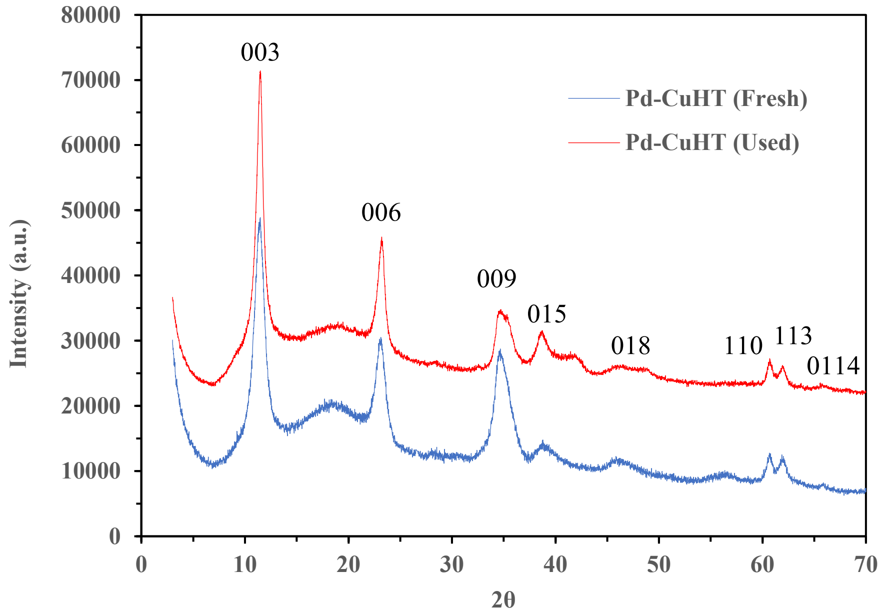


Figure S20. PXRD spectra comparing fresh PdCu/HT and PdCuHT after 5 reaction cycles.

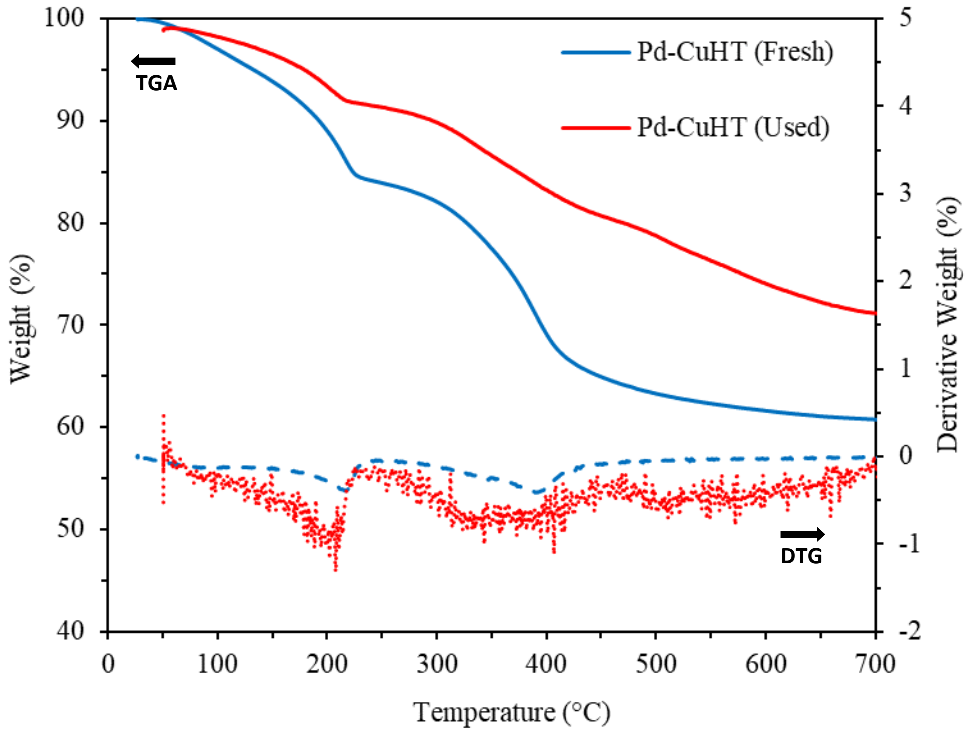


Figure S21. Thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG) for fresh PdCu/HT and PdCu/HT after 5 reaction cycles.

4.4 Whole pine wood sawdust Reductive Catalytic Fractionation

Pine sawdust (5.0 g), ethanol (50 mL), and 5% Pd/HT or 5% PdCu/HT (0.60 g) were loaded in a 100 mL borosilicate liner in a Parr autoclave reactor. The reactor was sealed, stirring started, and allowed to come to temperature (200-225 °C) before starting the reaction time (3 h). Upon completion, the reaction was allowed to cool to 50 °C before filtering. The residual pulp was washed with ethanol (3 x 20 mL), acetone (3 x 20 mL), and water (20 mL). The filtrate was concentrated in *vacuo* and the crude product mass was determined. The filtered cellulose pulp residue was dried under vacuum overnight at 70 °C and weighed. Lignin and small molecules were extracted from the crude product using ethyl acetate (3 x 150 mL) and sonication for 20 minutes after each addition. The ethyl acetate layers were combined and filtered over celite before removing the solvent in *vacuo*. The lignin oil was weighed to determine the yield, and subsequently characterized by ^{1}H-NMR and GC-MS to analyze monomer formation.

Determination of moisture content in pine wood

The moisture content was determined using previously described methods.[5] Pine dust (10.00 g) was dried in a furnace at 105 °C for 24 h. Moisture content (7 %) was determined by weight loss.

Determination of lignin content in pine wood.

The lignin content was determined using previously described methods.[5] Pine dust (5.00 g) was placed in a Soxhlet extractor with ethanol/benzene mixture (1:2 v/v, 100 mL) for 4 h to remove extractables such as resin, wax and fat. The pine dust was then washed with ethanol (4x 20 mL), dried in a vacuum oven at 70 °C for 4 h, and the weight loss determined (extractables, 8 %). Dried pine dust (1.00 g) was placed in a round bottom flask over an ice bath and 72 wt % H_2SO_4 (15 mL) was added slowly under magnetic stirring. The flask was allowed to sit at room temperature for 2.5 h with periodic swirling. Deionized water (200 mL) was added to the flask and was allowed to reflux for 4 h. The reaction was cooled to room temperature and placed in a refrigerator overnight. The solid residue was filtered and washed with deionized water until the filtrate was a neutral pH. The solid was dried under vacuum overnight. The lignin content was calculated using **Equation S1** below. The content of lignin in 'wet' pine dust was 32%.

$$Lignin, \% = \frac{S}{P}$$

Equation S1

where S = solid residue recovered (g) and P = pine dust mass corrected for moisture and extractables (g).

Delignification determination after one-pot extraction/depolymerization of whole pine dust

Delignification refers to the amount of lignin removed from whole biomass. The liquid fraction obtained by RCF was concentrated in vacuo to afford a crude oil consisting of monomers, oligomers, and hemicellulose. The hemicellulose and larger lignin-derived components were precipitated and separated from the oil fraction through a workup described by Galkin and Samec,[5] leaving an oil enriched in monomers, dimer, and small oligomers. The residual solid was subjected to a water wash to remove hemicellulose and dried overnight in vacuo; the remaining solid was weighed and considered unfractionated or insoluble lignin. Thus, delignification is the sum of insoluble lignin and the remaining oil. Based on Klason lignin [5], this sum will have a maximum and the ratio between the sum and the theoretical maximum provides the %delignification.

$$\%Delignification = \frac{g\ lignin\ oil + g\ insoluble\ lignin}{gtheoretical\ lignin\ content} \times 100$$

Equation S2

Note that only solid product was obtained by RCF in the absence of any catalyst.

B-O-4 Content and Theoretical Maximum Monomer Yield

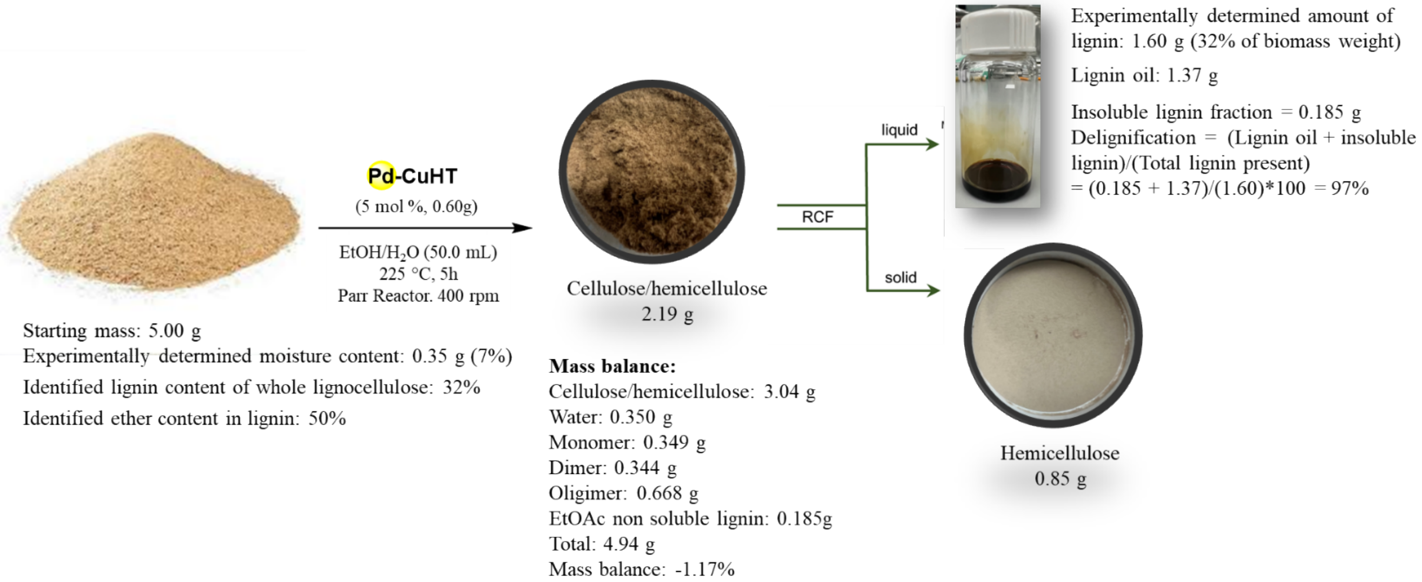
Lignin is a complex 3-dimensional irregular polymer with randomly cross-linked phenolic building blocks. To estimate the theoretical maximum monomer yield for a certain substrate, a simplified linear lignin polymer is imagined, in which each building block is linked to two other units, either by a C-C bond or an ether-bond. In a hydrogenolysis reaction, the ether bonds are cleaved to depolymerize the lignin structure. When a unit is connected on both sides by ether bonds, cleavage of both ether bonds will result in a monomer. The maximum monomer amount is related to the square of the fraction of ether bonds in the lignin structure. Literature values for the β-ether content of pine lignin are typically ~50%, which implies a theoretical maximum monomer yield of ~25%.[5] In this work, the β-ether content was first determined by the semi-quantitative HSQC (^1H-^{13}C) 2D correlation NMR method reported by Deuss et al,[6] and indicated a β-O-4 content of 50% consistent with the preceding literature. The monomer yield was also quantitatively determined by nitrobenzene oxidation (NBO) following literature methods.[7, 8] NBO affords aldehyde monolignols, which can be quantified via NMR using a 5-iodovanillin internal standard. Whole pine biomass (1.0 g) was added to a solution of 4.8 mL nitrobenzene and 80 mL 2 M sodium hydroxide, and heated at 170 °C for 1 h in a stainless steel Parr reactor. On cooling to room temperature, the resulting solution was filtered to remove solids, and the filtrate acidified with 1 M HCl to reach pH 2-3. The aqueous component of this solution was then removed by washing three times with ethyl acetate, and the organic component then washed with brine and dried over $MgSO_4$. The organic component was then concentrated in vacuo, to which 50 mg 5-iodovanillin and 10.0 mL of $CDCl_3$ were added. Subsequent triplicate analysis of the organic component by $^1H/^{13}C$ NMR revealed a total monolignol yield of 22 ±1.2%, equating to a β-ether content of 48% (consistent with the HMQC analysis).

Experimentally Determined Monomer Yield for Whole Biomass Reactions

Approximately 0.500 g of crude ethyl acetate extracted lignin oil, was subjected to silica gel column chromatography. The compounds were eluted with a mobile phase hexane/ethyl acetate from 3:1 to 1:1 (v/v). The yield of each pure compound was determined using **Equation S3**.[5] The major product identified was 4-(3-hydroxypropyl)-2-methoxyphenol **(**hydroconiferyl alcohol, HA)(**Figure S23-S24**.) The highest yield of HA was determined to be 14 wt% using PdCu/HT as catalyst.

$$\text{Monomer yield / \%} = \left(\frac{\frac{m\,(isolated\ product)}{m\,(loaded\ on\ column)} x\ m(oil\ obtained)}{Mw\,(product)} \middle/ \frac{m(total\ \ lignin\ in\ biomass)}{Mw\,(lignin\ monomer)} \right) \times\ 100$$

Equation S3



Starting mass: 5.00 g
Experimentally determined moisture content: 0.35 g (7%)
Identified lignin content of whole lignocellulose: 32%
Identified ether content in lignin: 50%

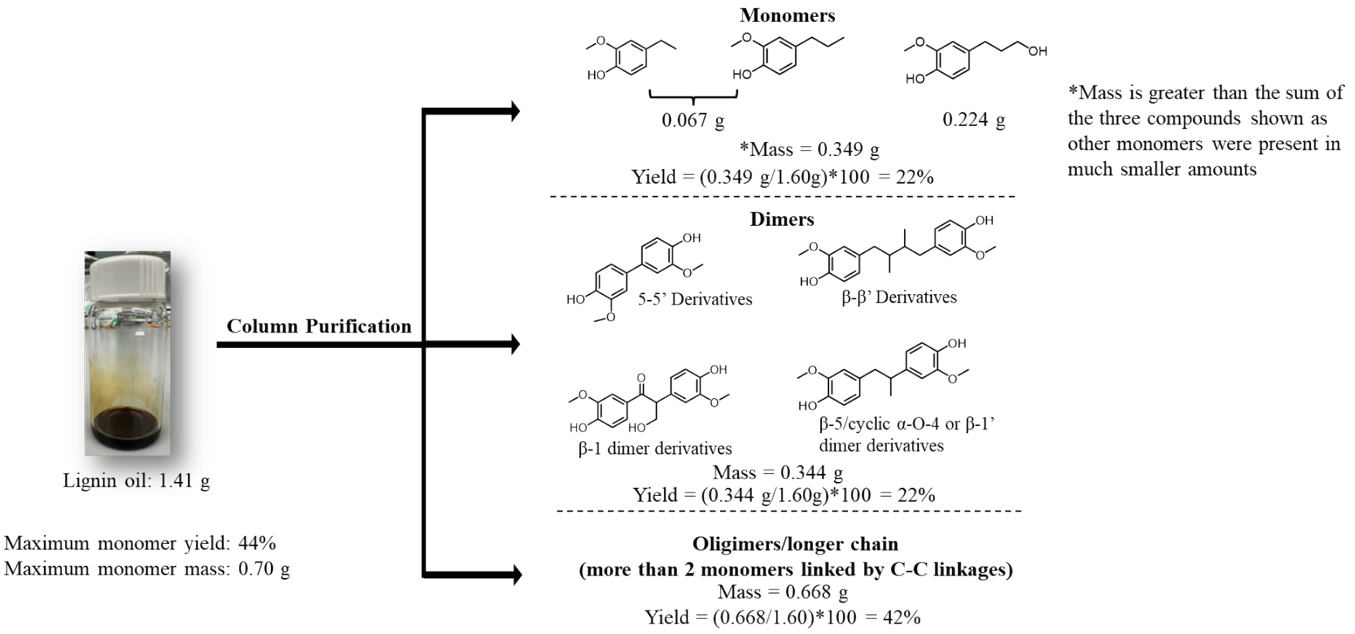
Mass balance:
Cellulose/hemicellulose: 3.04 g
Water: 0.350 g
Monomer: 0.349 g
Dimer: 0.344 g
Oligimer: 0.668 g
EtOAc non soluble lignin: 0.185g
Total: 4.94 g
Mass balance: -1.17%

Experimentally determined amount of lignin: 1.60 g (32% of biomass weight)

Lignin oil: 1.37 g

Insoluble lignin fraction = 0.185 g
Delignification = (Lignin oil + insoluble lignin)/(Total lignin present)
= (0.185 + 1.37)/(1.60)*100 = 97%

Figure S22. Schematic depicting the RCF process and corresponding mass balance.



*Yield is based on the total amount of lignin present in the biomass prior to the reaction (ie. 1.60g).
** Maximum monomer yield is based on the amount of ether linkages present in the lignin as a percentage. Experimentally, we determined pine to consist of 50% ether linkages. The square of the percentage of ether linkages provides the maximum monomer yield as only C-O bonds are cleaved and no C-C linkages. Based on 50% ether linkages, the maximum monomer yield is 25%. Thus, we are obtaining approximately 87% of the theoretical maximum amount of monomers to be obtained. Based on the amount of unfractionated lignin (0.185g), if we were to say that 25% of this could also be broken down to monomer, it would account for the missing 13%.
^The yields of monomers, dimers, and oligomers comes to 85% and since delignification is 97% (1.55g) the unaccounted mass is due to insoluble fractions of lignin that are not EtOAc soluble.

Figure S23. Identification and yield determination of monomers, dimers, and longer chain compounds from the breakdown of lignin.

Whole pine biomass product identification

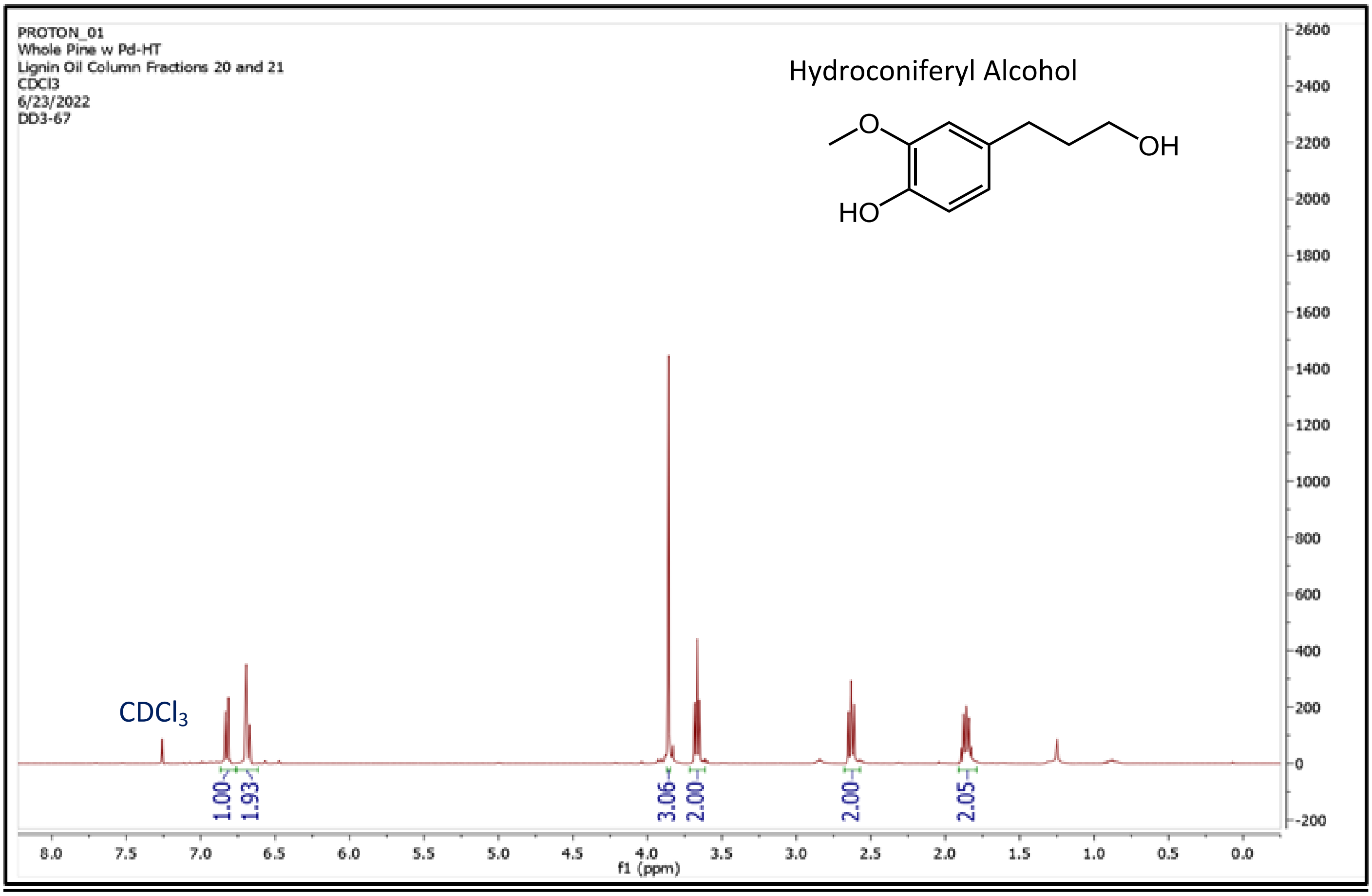


Figure S24. ^{1}H NMR spectrum of major isolate of the lignin fraction after RCF of whole pine biomass using Pd/HT as catalyst.

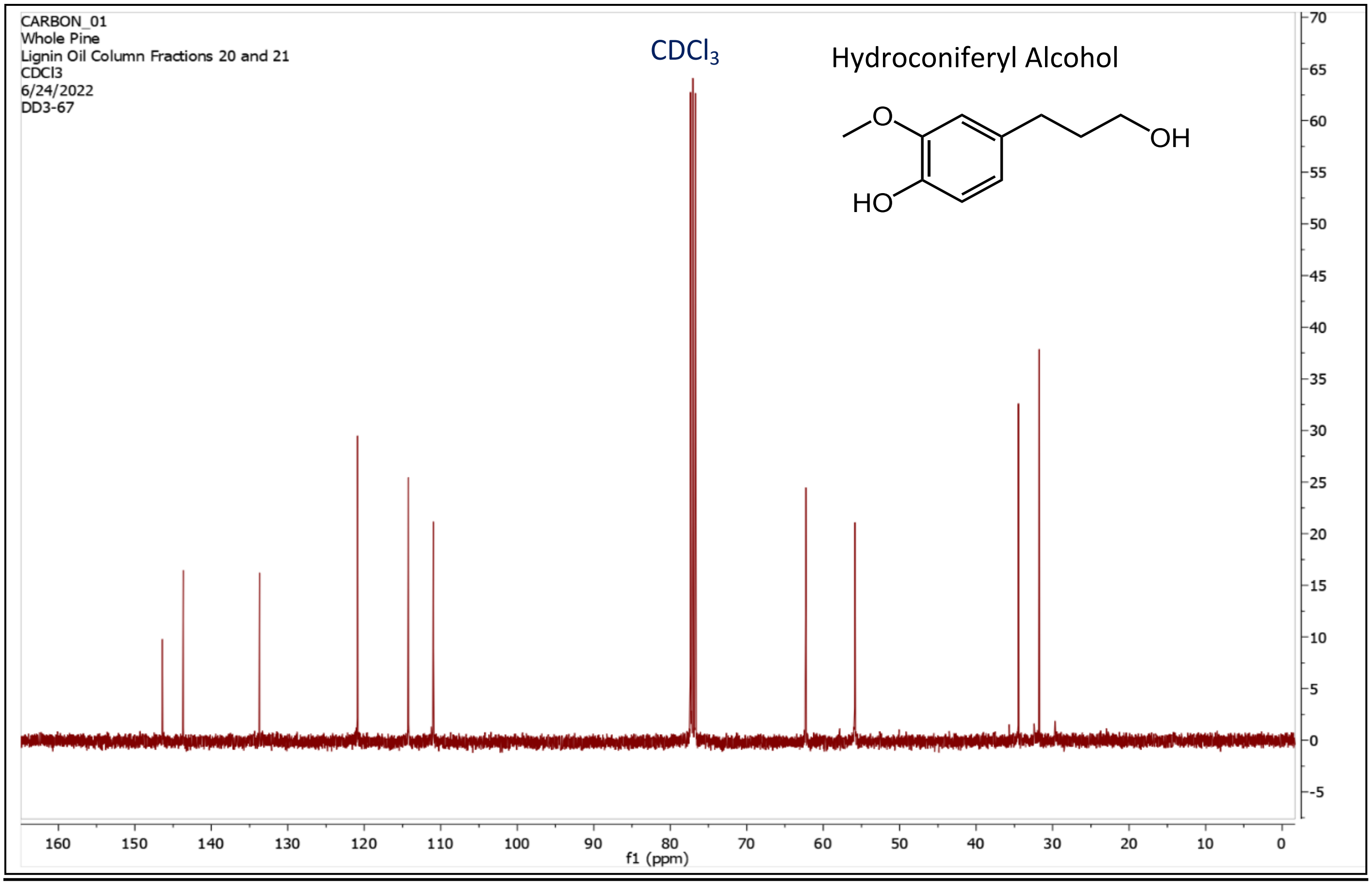


Figure S25. ^{13}C NMR spectrum of major isolate of the lignin fraction after RCF of whole pine biomass using Pd/HT as catalyst.

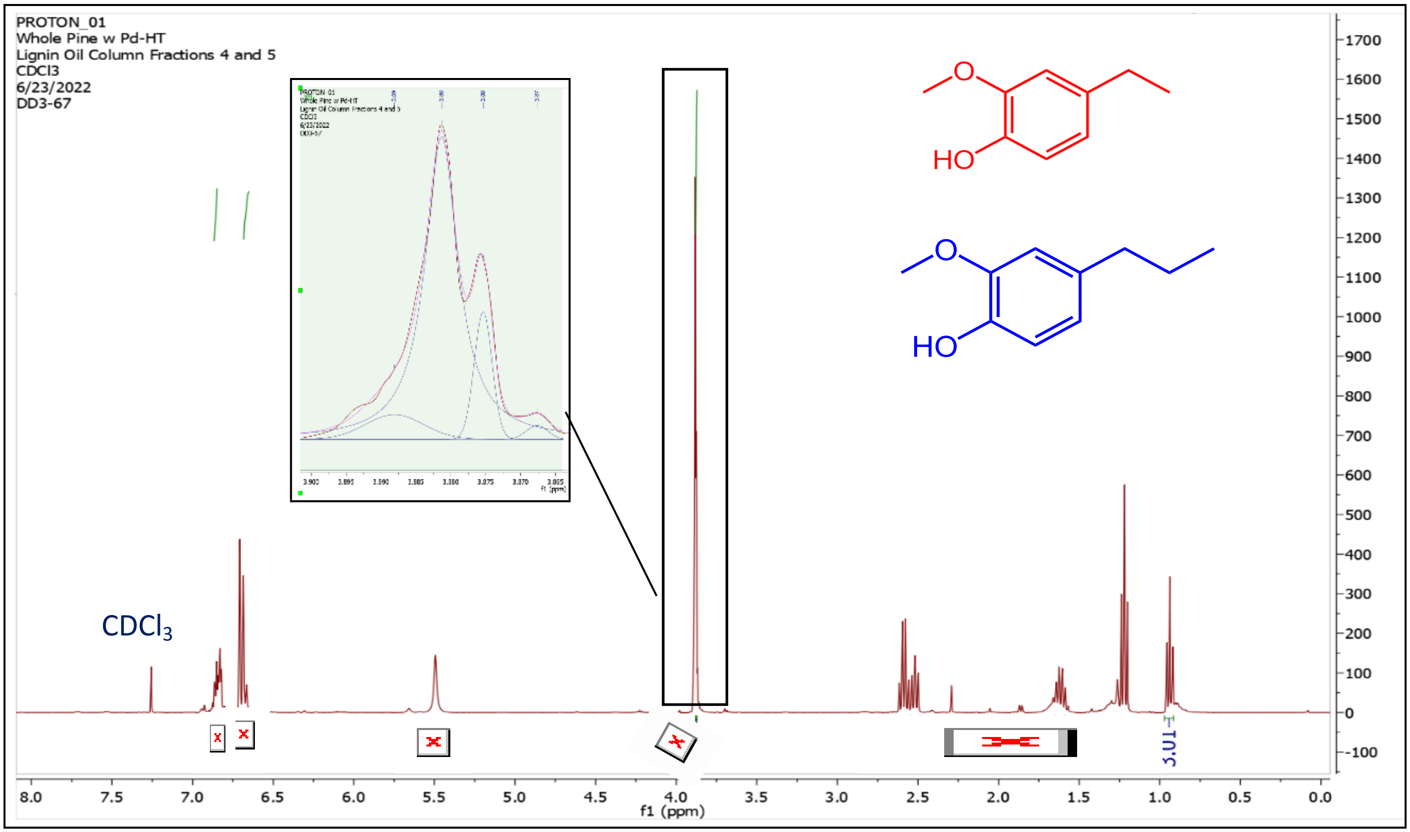


Figure S26. ^{1}H NMR spectrum of minor isolates from the lignin fraction after RCF of whole pine biomass using PdCu/HT as catalyst. Due to the similarity of ethyl- and propylguaiacol, separation through silica gel chromatography was not possible and hence this spectrum reflects both products. Inset shows the overlap and deconvolution of the methoxy methyl peaks of both ethyl and propyl guiacol.

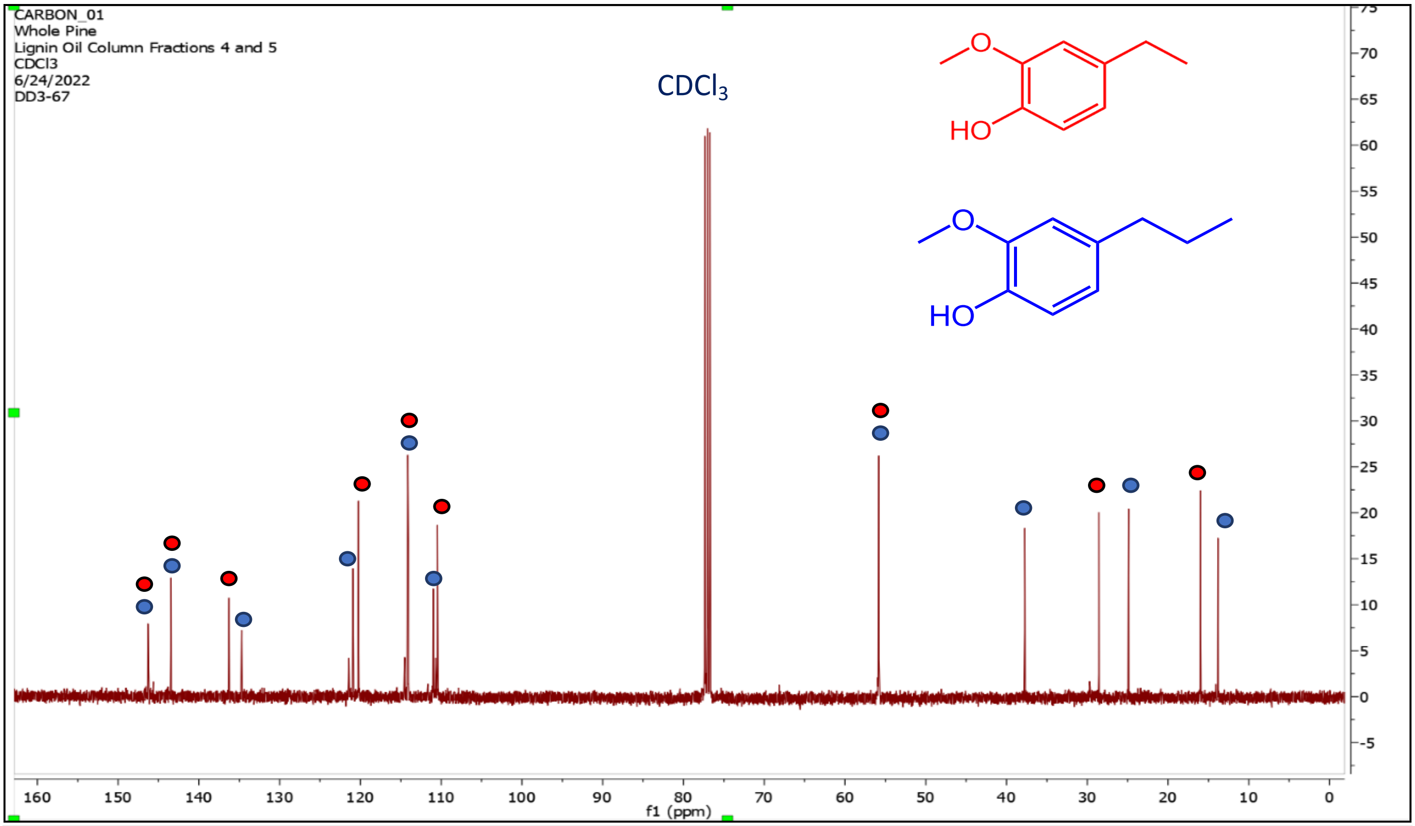


Figure S27. ^{13}C NMR spectrum of minor isolates from the lignin fraction after RCF of whole pine biomass using PdCu/HT as catalyst. Due to the similarity of ethyl- and propylguaiacol, separation through silica gel chromatography was not possible and hence this spectrum reflects both products.

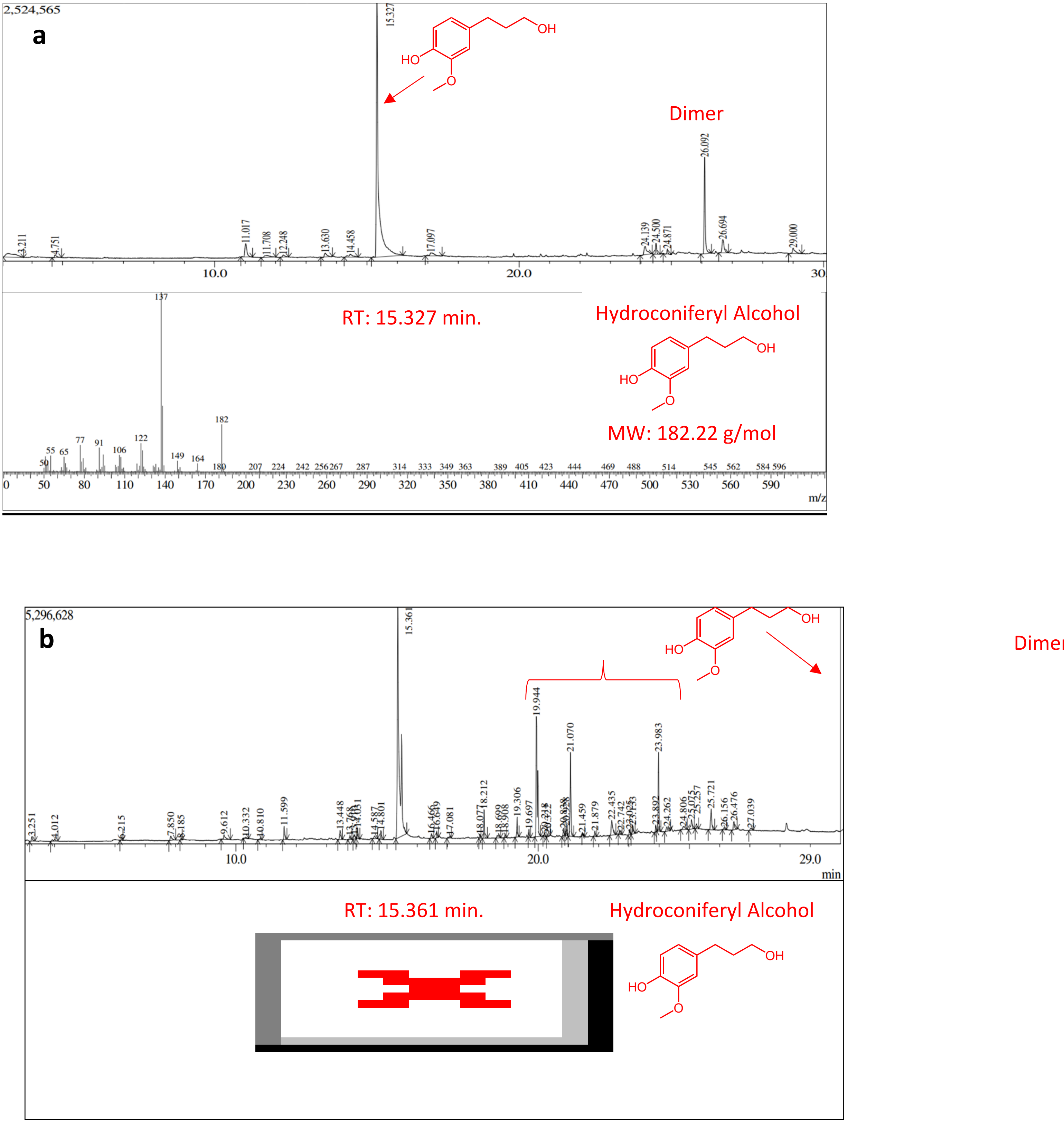


Figure S28. GC-MS chromatograms and mass spectra of crude lignin oil obtained by RCF of whole pine biomass using (a) Pd/HT or (b) PdCu/HT as a catalyst. Labelled peaks correspond to 5-hydroxy coniferyl alcohol major product. Rection conditions: 5 g whole pine sawdust, 50 mL EtOH, 5 mol% catalyst, stirred Parr reactor at 225 °C, 5 h.

5. References

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