

Investigating (pseudo)-heterogeneous Pd-catalysts for Kraft lignin depolymerization under mild aqueous basic conditions

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Supporting information

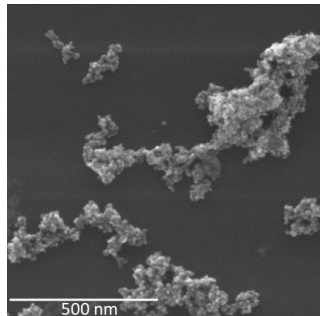
- Scanning electron microscopy (SEM) of materials of Family 2
- X-ray diffraction (XRD) of materials of Family 2
- Plane indexing of materials of Family 2
- NMR spectroscopy and elemental analysis of Kraft lignin
- MS Spectra (from GCMS analysis) from unknown compound found in Organic fraction in certain conditions

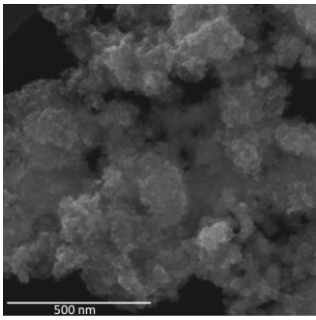
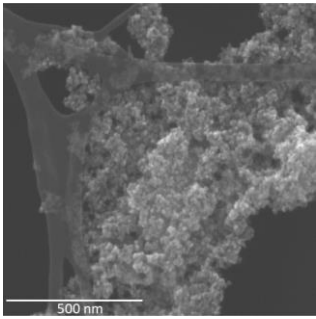
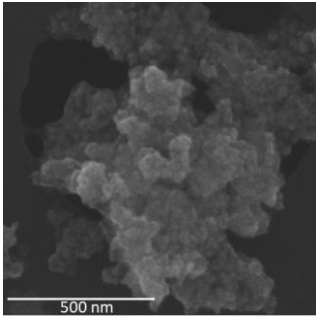
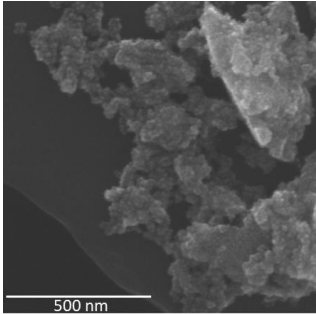
Scanning electron microscopy (SEM) of materials of Family 2

About twenty materials of Family 2 were synthesized by supercritical flow and initially characterized using scanning electron microscopy (SEM). A FEI XL30 ESEM-FEG apparatus (Thermo Fisher Scientific Materials & Structural Analysis, Hillsboro, Oregon, USA) was used under high vacuum mode (SE and BSE 4 dial detectors) with a 30 kV voltage and WD = 5. Materials were first dispersed in ethanol and then deposited on standard holey carbon-covered copper TEM grids. The use of TEM grids for SEM analysis was to improve the analysis conditions.

SEM characterizations conducted on **2a₁**, **2b₁**, **2a₂**, **2a₃** and **2a₄** materials have demonstrated that working with Pd(acac)₂ and Pd(hfacac)₂ precursors led to aggregated particles in both cases but with better definition and homogeneity from Pd(acac)₂ at 300 °C. When formic acid was present, the formation mechanism of NPs was different and led to small NPs with polyhedral morphology, whereas in the absence of formic acid NPs are smaller with irregular morphology. Among the around twenty synthesized these five materials were chosen since the most representative of the modified key parameters (precursor, temperature, formic acid addition) to further characterizations by TEM and application as catalytic systems (see Main text).

Table S1. Synthesis parameters for some materials of Family 2.

Catalyst	Precursor	Pd (mmol.L ⁻¹)	Temp. (°C)	Time (s)	Formic acid (mmol.L ⁻¹)	SEM pictures
2a₁	Pd(acac) ₂	10	250	50	-	

2b	Pd(hfacac) ₂	10	250	50	-	
2a2	Pd(acac) ₂	10	300	124	-	
2a3	Pd(acac) ₂	10	300	83	100	
2a4	Pd(acac) ₂	5	300	10	20	

X-ray diffraction (XRD) of materials of Family 2

XRD analysis was conducted on Bruker D8 Advance A25 diffractometer (Bruker France SAS, Champs-sur-Marne, France) using a CuK α radiation ($\lambda=0.154184$ nm). A Ni filter eliminates the K β line from the anticathode.

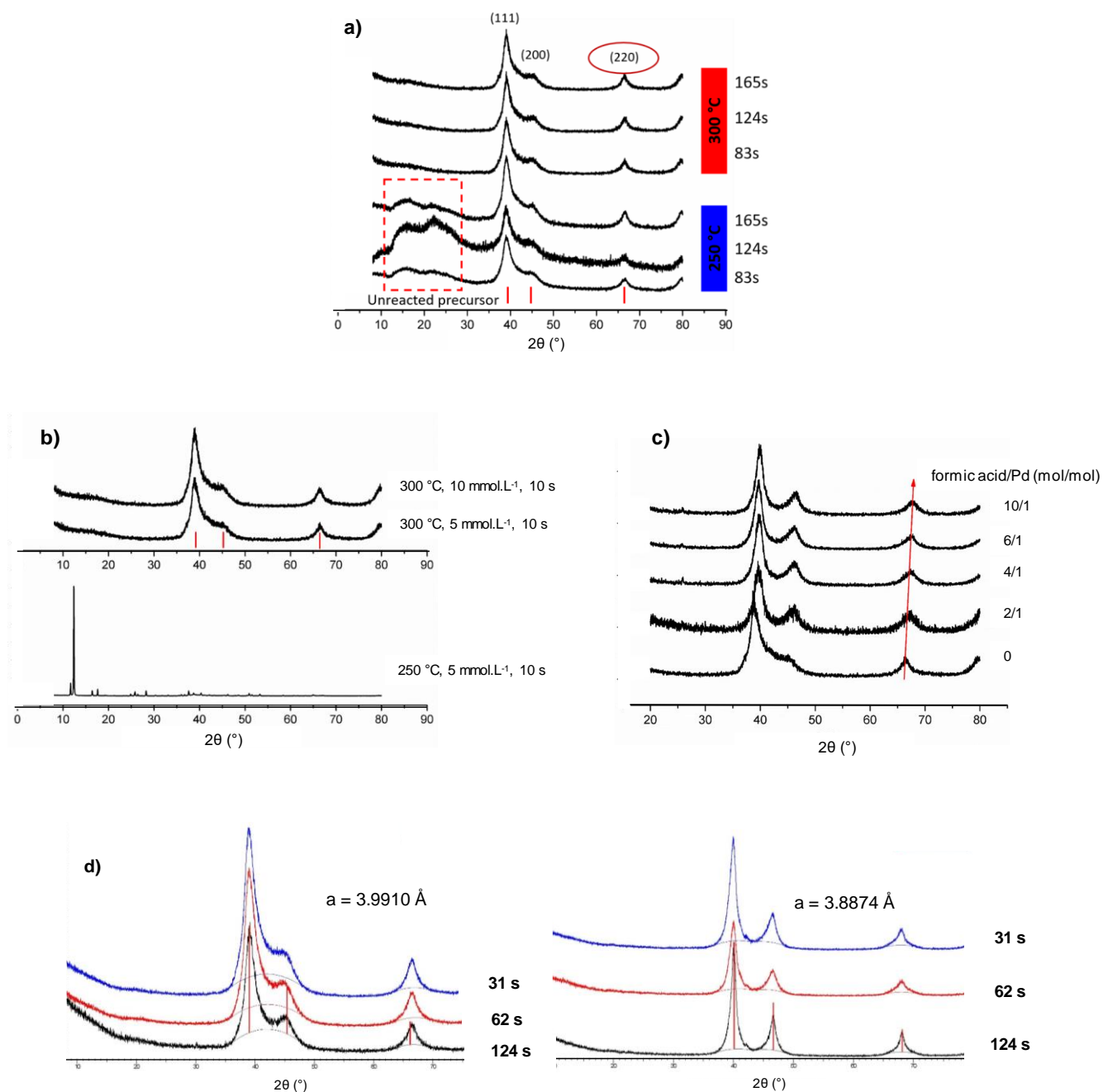
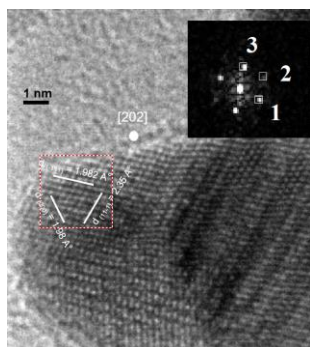


Figure S1. XRD diffractograms of some materials prepared under fluidic conditions from Pd(acac)₂. a) influence of temperature and time (Pd(acac)₂ 10 mmol.L⁻¹, 200 bar). b) influence of Pd concentration (Pd(acac)₂ 10 mmol.L⁻¹, 300 °C, 200 bar 10 s). c) influence of formic acid/Pd ratio (Pd(acac)₂ 5 mmol.L⁻¹, 300 °C, 200 bar, 10 s), difference in lattice constant: 3.991 Å (no formic acid) *vs* 3.879 Å (with formic acid). d) lattice parameters in the absence, and presence of formic acid (Pd(acac)₂ 10 mmol.L⁻¹, 300 °C, 200 bar), lattice constant (no formic acid, left; with formic acid, right).

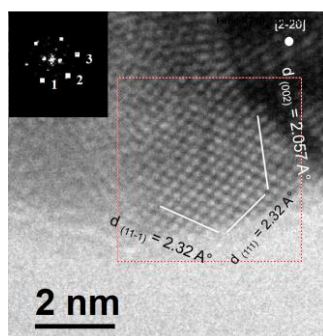
Plane indexing of materials of Family 2



Pd-SC-300 **2a₂**

Pd JCPDF 00-046-1043

Spot	d-spacing (Å) observed	Degrees to Spot 1	d-spacing (Å) theoretical	Angle between HKL planes theoretical	HKL
1	2.353	0	2.246	0	11-1
2	1.982	55.82	1.945	54.74	200
3	2.288	110.42	2.246	109.47	-111



Pd-SC-250 **2b**

Pd JCPDF 89-4897

Spot	d-spacing (Å) observed	Degrees to Spot 1	d-spacing (Å) theoretical	Angle between HKL planes theoretical	HKL
1	2.32	0	2.312	0	11-1
2	2.32	69.37	2.312	70.53	111
3	2.057	125.21	2.5227	125.26	002

Figure S2. Plane indexing of Pd nanoparticles for **2a₂** and **2b** materials.

NMR spectroscopy and elemental analysis of Kraft lignin

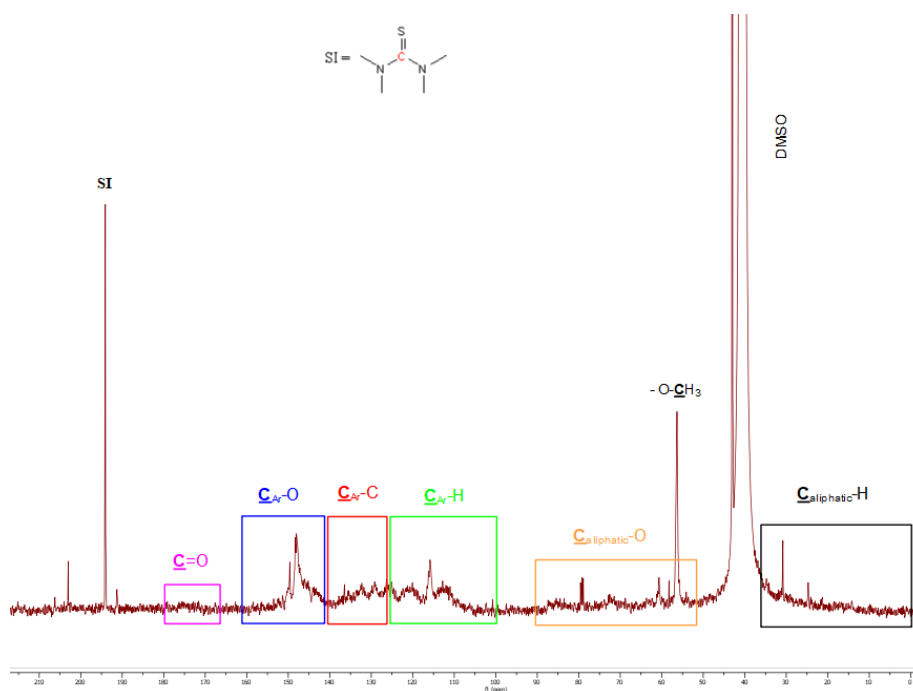


Figure S3. ¹³C NMR spectrum of initial Kraft lignin (11000 scans).

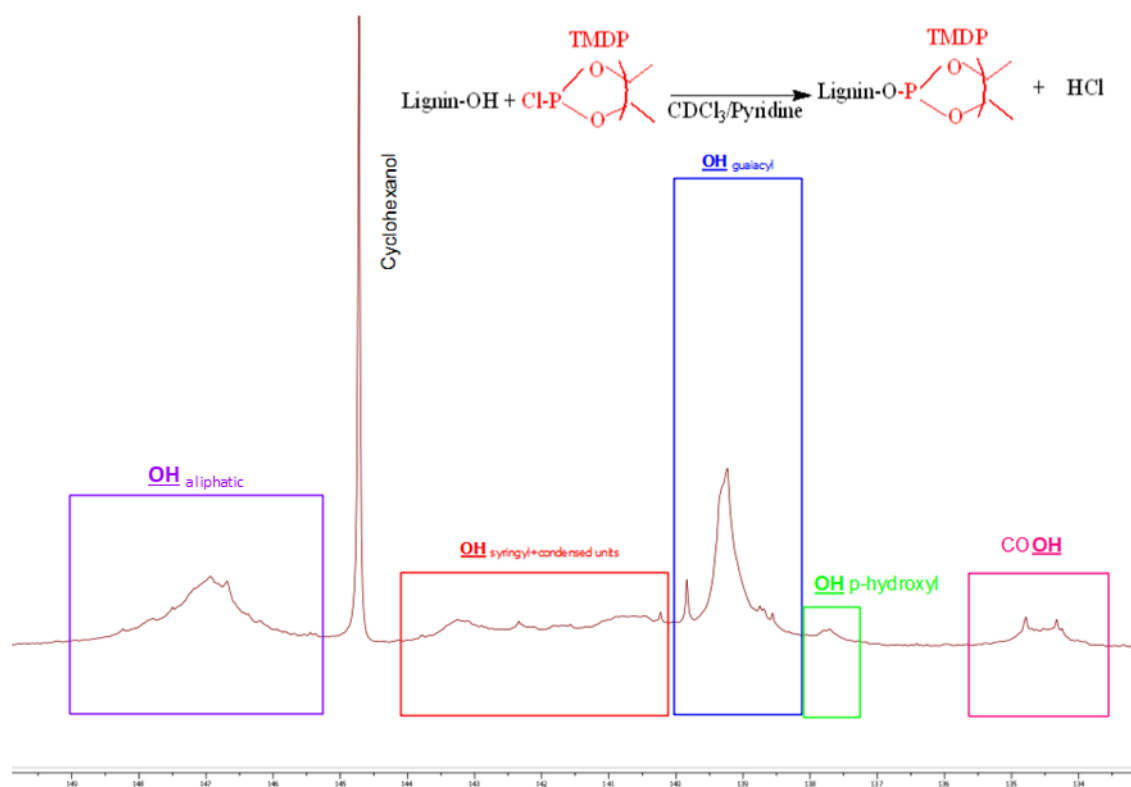


Figure S4. ^{31}P NMR spectra of Kraft lignin after derivatization with TMDP.

Table S2. Quantitative data concerning C in the initial lignin, obtained by ^{13}C NMR and classified by nature (see Figure S2). Comparison with elemental analysis data.

C nature (^{13}C NMR chemical shift)	C content ± 0.05 (mmol.g _{lignin} ⁻¹)
aliphatic (10 - 34 ppm)	3.0
CH ₃ -O (55 - 58 ppm)	2.0
aliphatic-O (58 - 90 ppm)	3.5
aromatic-H (102 - 125 ppm)	5.0
aromatic -C (125 - 142 ppm)	4.5
aromatic -O (142 - 162 ppm)	4.5
total aromatic (102 - 162 ppm)	14
COOR (R=H or alkyls)	0.5
Total	23

Analytical method	C content (% _{wt})
¹³ C NMR	28 ± 0.5
elemental analysis	62 ± 0.5
ratio of C analyzed by ¹³ C NMR	45%

MS Spectra (from GCMS analysis) from unknown compound found in Organic fraction in certain conditions

The mass spectra were obtained using a Shimadzu GC-MS-QP2010S (Shimadzu Europa GmbH, Duisburg, Nordrhein-Westfalen, Germany) equipped with a AOC-20i+ autosampler and a Macherey-Nagel Optima 5 MS Accent column (5 % diphenyl-95 % dimethylpolysiloxane 30 m, 0.25 mm, 0.25 μm) (Macherey-Nagel SAS, 1 Rue Gutenberg - BP 135, 67720 Hoerd, France). Helium was used as carrier gas. The GC program was 60 $^{\circ}\text{C}$ for 2 h, up to 150 $^{\circ}\text{C}$ (30 $^{\circ}\text{C}\cdot\text{min}^{-1}$), up to 200 $^{\circ}\text{C}$ (2 $^{\circ}\text{C}\cdot\text{min}^{-1}$), up to 260 $^{\circ}\text{C}$ (10 $^{\circ}\text{C}\cdot\text{min}^{-1}$) for 2 min.

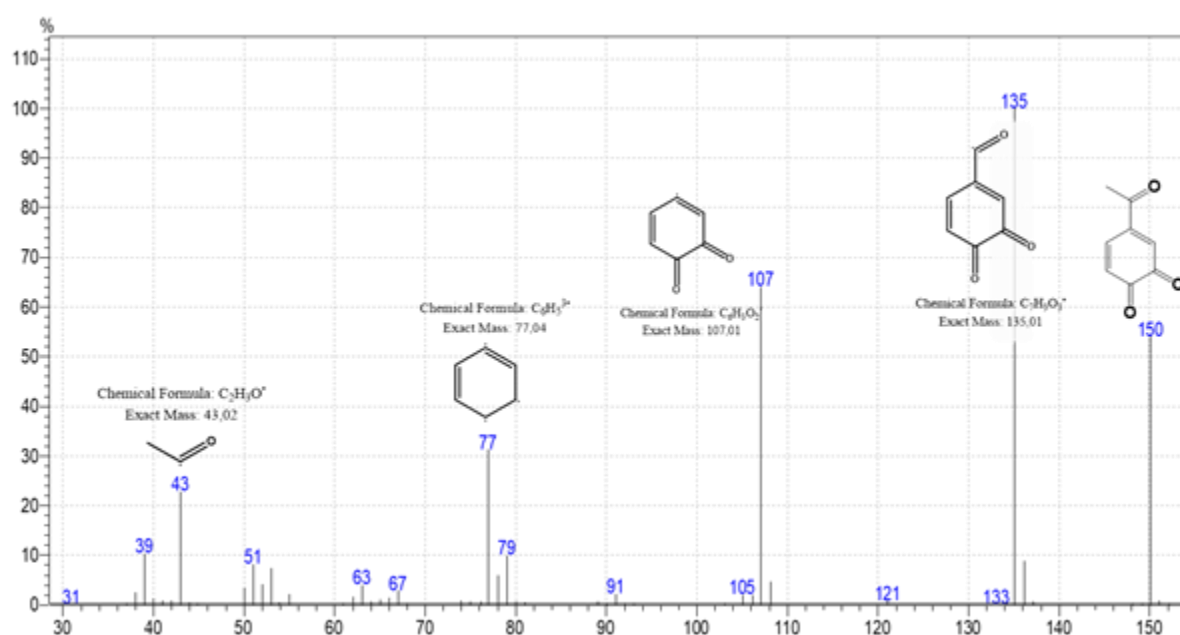


Figure S5. MS spectra of identified orthodiquinone reaction product formed in acetone in the presence of **2a₅**.