# **Supporting Information**

# Performance of base and noble metals for electrocatalytic hydrogenation of

## bio-oil-derived oxygenated compounds

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#### S1. Catalyst synthesis and characterization

**Table S1.** Description of metal precursors and thermal treatment temperatures used for the synthesis of all the catalyst supported on carbon felt (CF). Inductively coupled plasma analysis of the catalysts was done before and after reaction to confirm metal loading and are reported elsewhere.<sup>1</sup> H<sub>2</sub>-chemisorption, and N<sub>2</sub>O titration was done to estimate the metal fractional exposure and are reported elsewhere.<sup>1</sup>

		Temperature, °C	
Catalyst	Precursor	N <sub>2</sub> treatment	H <sub>2</sub> Treatment
0.5 wt% Pd/CF	Pd(NO <sub>3</sub> ) <sub>2</sub> (Sigma Aldrich, 10 wt% in 10 wt% HNO <sub>3</sub> , 99.999% trace metals basis)	180	250
0.5 wt% Rh/CF	Rh(NO <sub>3</sub> ) <sub>3</sub> (Sigma Aldrich, 10 wt% in >5 wt% HNO <sub>3</sub> )	400	400
0.5 wt% Ru/CF	Ru(NO)(NO <sub>3</sub> ) <sub>3</sub> (Sigma Aldrich, 1.5% Ru in dilute HNO <sub>3</sub> )	350	250
0.3 wt% Cu/CF	Cu(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O (Sigma Aldrich, 99.999% trace metals basis)	260	200
0.3 wt% Ni/CF	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O (Sigma Aldrich, 99.999% trace metals basis)	320	350
0.3 wt% Zn/CF	Zn(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O (Sigma Aldrich, reagent grade, 98%)	300	550
0.3 wt% Co/CF	Co(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O (Sigma Aldrich, 99.999% trace metals basis)	260	200

#### Thermogravimetric analysis

Thermogravimetric analysis of the metal nitrate precursors was used to determine the decomposition temperatures. The metal precursor was first loaded ( $\sim$ 5–10 mg) in an alumina crucible and heated from room temperature to 600°C at a heating rate of 5 K min<sup>-1</sup> under a N<sub>2</sub> flow of 25 scm<sup>3</sup> min<sup>-1</sup>.



**Figure S1.** Thermogravimetric analysis of different metal nitrates that were used as precursors to prepare the corresponding metal catalysts where a) is  $Pd(NO_3)_2$ · $3H_2O$ , b) is  $Cu(NO_3)_2$ · $2.5H_2O$ , c) is  $Ru(NO)(NO_3)_3$ · $3H_2O$ , d) is  $Ni(NO_3)_2$ · $6H_2O$ , e) is  $Rh(NO_3)_3$ · $2H_2O$ , f) is  $Zn(NO_3)_2$ · $6H_2O$ , and g) is  $Co(NO_3)_2$ · $6H_2O$ .

Catalyst characterization after thermal treatment



**Figure S2.** BET surface area and pore volume of selected samples as determined from N<sub>2</sub> physisorption. As-received CF refers to the carbon felt received from the manufacturer. Blank CF refers to CF after the HNO<sub>3</sub>-treatment. Pd/CF and Cu/CF are the catalyst prepared by wet-impregnation of the metal precursor followed by thermal treatment. The  $\square$  bar represents the surface area and the  $\square$  symbol represents the pore volume. The metal precursors and temperatures of the treatment are summarized in Table S1.

The as-received carbon felt (CF) has negligible surface area and pore volume. Upon treatment with  $HNO_3$ , the CF developed microporosity (average pore size of 1.3 nm), which increased the surface area to 45 m<sup>2</sup> g<sup>-1</sup>. The deposition of Pd or Cu slightly decreased the surface area and pore volume without changing the average pore size of the micropores. Thus, the metal particles form on the external surface of the CF without further impacting the textural properties.



**Figure S3.** Scanning transmission electron microscopy (STEM) images of the catalysts after thermal treatment where a) is Ru/CF, b) is Rh/CF, c) is Pd/CF, d) is Co/CF, e) is Ni/CNT, f) is Cu/CF, and g) is Zn/CF. The thermal treatment conditions and metal weight loadings are outlined in Table S1 and further described in the catalyst synthesis and characterization section.

#### S2. Quantification of dimer using <sup>1</sup>H- NMR. Hydrofuroin identification

<sup>1</sup>H-NMR analysis with a Varian 500 MHz NMR spectrometer was used to detect the presence of the dimer products. As shown by Chadderdon et al.,<sup>2</sup> hydrofuroin is characterized by a doublet at ~4.87 ppm, two doublets of doublets between ~6.25 and ~6.41 ppm and another doublet of doublets at ~7.41 ppm. Unfortunately, the doublets of doublets are obscured by furfural and furfuryl alcohol, which have peaks at similar shifts. However, the presence of the doublet at ~4.87 ppm is indicative of the dimer and not of other furfural species, because it is generated by the protons on the coupled carbons. Spectra were taken for all furfural experiments run over the different catalyst samples (example shown in Figure S1).



**Figure S4.** <sup>1</sup>H-NMR spectrum of the reaction products during electrocatalytic hydrogenation (ECH) of furfural on the 0.30 wt% Co electrocatalysts. The catholyte composition was 80 mM furfural in an electrolyte composed of 47.5 wt% isopropanol, 47.5 wt% DI water, and 5 wt% acetic acid. The anolyte was composed of 1 M KOH in an electrolyte composed of 50 wt% methanol and 50 wt% DI water. The spectrum is cropped to show peaks of interest for hydrofuroin identification.

#### **S3.** Tafel plots



**Figure S5.** Tafel plots of the benzaldehyde ECH as a function of applied potentials on the different catalysts where a) is Pd/CF, b) is Ru/CF, c) is Rh/CF, d) is blank CF, e) is Cu/CF, f) is Ni/CF, g) is Zn/CF, and h) is Co/CF. The symbols represent the different electrochemical reactions, where  $\blacksquare$  is alcohol formation,  $\bullet$  is dimer formation,  $\blacktriangle$  is hydrogen evolution and  $\clubsuit$  is all the products combined. The experiments were carried out galvanostatically at atmospheric pressure and room temperature. The catholyte was 80 mM benzaldehyde in an electrolyte composed of 47.5 wt% isopropanol, 47.5 wt% DI water, and 5 wt% acetic acid. The anolyte was 1 M KOH in an electrolyte composed of 50 wt% DI water and 50 wt% methanol.

S4. Benzaldehyde conversion and Faradaic efficiency as a function of applied half-cell potential



**Figure S6.** Conversions of benzaldehyde ECH as a function of WvR potentials on noble and base metals. The experiments were carried out galvanostatically at atmospheric pressure and room temperature. The catholyte was composed of 80 mM benzaldehyde in an electrolyte composed of 47.5 wt% isopropanol, 47.5 wt% DI water, and 5 wt% acetic acid. The experiments were performed in an open-loop, single-pass continuous flow cell at a LHSV of 20 h<sup>-1</sup>. The anolyte was composed of 1 M KOH in an electrolyte composed of 50 wt% DI water and 50 wt% methanol. The conversion calculations are discussed elsewhere.<sup>3</sup>



**Figure S7.** Faradaic efficiencies of benzaldehyde ECH as a function of WvR potentials on (a) noble and (b) base metals. The experiments were carried out galvanostatically at atmospheric pressure and room temperature. The catholyte was composed of 47.5 wt% isopropanol, 47.5 wt% DI water, and 5 wt% acetic acid. The anolyte was composed of 1 M KOH solution composed of 50 wt% DI water and 50 wt% methanol.

### S5. Cathode performance during the electrocatalytic upgrading of bio-oil containing feeds

Table S2. Electrocatalytic performance during the upgrading of electrolytes with different bio-oil concentrations under galvanostatic operation conditions at -150 mA.

				Pd						Cu		
wt% Bio-oil Content.	ECH	HER	Benzyl Alcohol	Benz- aldehyde ECH	Full-Cell Potential	Half- Cell Potential	ECH	HER	Benzyl Alcohol	Benz- aldehyde ECH	Full- Cell Potential	Half- Cell Potential
%	mA	mA	wt%	mA	mV	mV	mA	mA	wt%	mV	mV	mV
0	-78.43	-71.57	0.280	-78.43	-2540	-1110	-89.98	-60.02	0.290	-89.98	-1300	-1096
1	-78.75	-71.25	0.161	-45.10	-2640	-1113	-90.37	-59.63	0.160	-50.89	-1480	-1176
10	-87.94	-62.06	0.046	-12.89	-2680	-1112	-109.1	-40.91	0.050	-14.27	-1610	-1306
0	-76.47	-73.53	0.290	-79.20	-2700	-1090	-68.86	-81.14	0.120	-29.21	-2260	-1956

Table S3. Electrocatalytic performance of Pd during the upgrading of the electrolyte containing 10 wt% bio-oil at different currents.

Current	Half-Cell Potential	CAN	PhAN	CON	ЕСН	HER	FE
mA	mV	mg KOH g sample <sup>-1</sup>	mg KOH g sample <sup>-1</sup>	mmol g <sub>sample</sub> <sup>-1</sup>	mA	mA	%
0 (Feed)	-	54.5	9.10	0.721	-	-	-
-50	-700	52.5	9.80	0.722	-50	0	53.3
-150	-1100	55.2	9.50	0.539	-80	-70	21.4
-450	-1300	53.3	10.2	0.476	-90.5	-360	8.08
-700	-1400	53.9	9.00	0.345	-105	-595	6.69
-50	-700	52.7	9.80	0.724	-49.8	-0.200	53.2

## S6. Composition of bio-oil containing feeds before and after electrocatalytic upgrading

**Table S4.** Composition of the feed with 10 wt% bio-oil in the catholyte before electrocatalytic hydrogenation characterized by gas chromatography-mass spectrometry (GC-MS).

Compounds	Retention Time (min)	Start Time (min)	End Time (min)	Area (%)
Acetic acid	1.171	1.025	1.192	55.72
Benzaldehyde dimethyl acetal	6.198	6.117	6.25	15.16
Benzaldehyde	3.849	3.792	3.875	13.63
2-Propanone, 1-hydroxy-	1.208	1.192	1.267	3.26
Phenol, 2-methoxy-4-methyl-	7.405	7.367	7.45	1.19
Propanoic acid, 2-oxo-, ethyl ester	1.425	1.392	1.45	0.93
1,2-Benzenediol	7.505	7.475	7.567	0.92
Phenol, 2-methoxy-	5.839	5.808	5.883	0.85
2(5H)-Furanone	3.168	3.083	3.217	0.76
1H-Pyrazole, 3,5-dimethyl-	2.176	2.142	2.225	0.53
2-Cyclopenten-1-one, 2-hydroxy-	3.316	3.217	3.358	0.43
Propylene carbonate	1.629	1.592	1.667	0.42
1,2-Benzenediol, 4-methyl-	8.791	8.767	8.85	0.39
Benzaldehyde	3.767	3.75	3.792	0.38
Phenol	4.183	4.158	4.225	0.35
4-Methyl-5H-furan-2-one	5.117	5.083	5.175	0.34
Phenol, 4-methyl-	5.64	5.608	5.675	0.32
Phenol, 4-ethyl-2-methoxy-	8.643	8.608	8.683	0.32
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	4.857	4.833	4.892	0.31
Furo[3,4-b]furan-2,6(3H,4H)-dione, 4-ethyldihydro-3- methylene-, [3aR-(3a.alpha.,4.beta.,6a.alpha.)]-	3.892	3.875	3.933	0.29
Vanillin	10.251	10.225	10.3	0.29
N-Methoxydiacetamide	2.342	2.325	2.367	0.27
Phenol, 2-methoxy-3-(2-propenyl)-	9.717	9.683	9.75	0.26
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	11.361	11.325	11.383	0.24
Phenol, 2-methyl-	5.315	5.175	5.35	0.23
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	7.924	7.9	7.983	0.23
Ethanol, 2-nitro-, propionate (ester)	1.299	1.267	1.325	0.22
2-Propanone, 1-(acetyloxy)-	2.582	2.558	2.625	0.21
Phenol, 2,4-dimethyl-	6.74	6.717	6.783	0.2
Phenol, 2-methoxy-4-(1-propenyl)-	10.38	10.35	10.408	0.14
4-Hydroxy-2-methoxycinnamaldehyde	14.209	14.183	14.242	0.14
2-Cyclopenten-1-one, 2-methyl-	3.057	3.025	3.083	0.13
2-Propanone, 1-hydroxy-	3.725	3.7	3.75	0.13
2(5H)-Furanone, 3-methyl-	4.117	4.092	4.158	0.13
1,2-Benzenediol, 3-methyl-	8.383	8.358	8.425	0.13
5-(Hydroxymethyl)-2-(dimethoxymethyl)furan	8.912	8.85	8.942	0.13
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	10.908	10.883	10.942	0.12
Benzeneacetic acid, 4-hydroxy-3-methoxy-	13.27	13.242	13.3	0.11
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	11.917	11.892	11.967	0.1
Phenol, 2-methoxy-4-propyl-	11.027	11	11.058	0.09

Compounds	Retention Time (min)	Start Time (min)	End Time (min)	<b>Area</b> (%)
Acetic acid	1.147	1.025	1.258	56.8
Benzaldehyde	3.84	3.783	3.875	16
Benzaldehyde dimethyl acetal	6.184	6.125	6.25	15.23
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	11.361	11.325	11.583	1.83
Phenol, 2-methoxy-4-methyl-	7.399	7.367	7.45	1.06
n-Propyl acetate	1.417	1.392	1.45	1.04
Tetradecanoic acid, 2-hydroxyphenyl ester	7.508	7.45	7.567	0.95
Propanal, 2,3-dihydroxy-, (S)-	1.3	1.258	1.35	0.83
Phenol, 2-methoxy-	5.832	5.8	5.875	0.76
Propylamine, N,N,2,2-tetramethyl-, N-oxide	1.617	1.567	1.658	0.58
1H-Pyrazole, 3,5-dimethyl-	2.171	2.133	2.217	0.57
Benzyl alcohol	4.968	4.883	5.017	0.46
1,3-Octanediol	3.892	3.875	3.933	0.42
2(5H)-Furanone	3.159	3.125	3.208	0.41
1,2-Benzenediol, 4-methyl-	8.785	8.767	8.833	0.36
Benzaldehyde	3.766	3.742	3.783	0.32
Phenol, 4-methyl-	5.629	5.6	5.675	0.29
1-Butanol, 2-methyl-, acetate	11.979	11.942	12.033	0.29
Propane, 2,2',2"-[methylidynetris(oxy)]tris-	2.335	2.317	2.358	0.28
Acetic acid ethenyl ester	2.576	2.55	2.617	0.27
Phenol	4.174	4.15	4.217	0.27
Phenol, 4-ethyl-2-methoxy-	8.641	8.608	8.683	0.26
1,2-Cyclopentanedione, 3-methyl-	4.848	4.825	4.883	0.25
Vanillin	10.247	10.225	10.292	0.25
Phenol, 2-methoxy-3-(2-propenyl)-	9.715	9.692	9.75	0.22

**Table S5**. Composition of 10 wt% bio-oil after galvanostatic ECH at -150 mA and single pass reactor configuration characterized by gas chromatography-mass spectrometry (GC-MS).

Compounds	Retention Time (min)	Start Time (min)	End Time (min)	Area (%)
Acetic acid	1.147	1.025	1.183	50.66
Benzaldehyde	3.841	3.783	3.875	15.51
Benzaldehyde dimethyl acetal	6.185	6.125	6.25	14.97
2-Propanone, 1-hydroxy-	1.2	1.183	1.258	5.11
1,6-AnhydrobetaD-glucopyranose (levoglucosan)	11.5	11.392	11.575	1.74
Phenol, 2-methoxy-4-methyl-	7.401	7.367	7.458	1.13
Benzyl alcohol	4.969	4.892	5.017	1.06
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	11.36	11.283	11.392	1.06
Tetradecanoic acid, 2-hydroxyphenyl ester	7.506	7.467	7.567	1.04
Ethanol, 2-nitro-, propionate (ester)	1.291	1.258	1.358	1.02
n-Propyl acetate	1.421	1.392	1.45	0.95
Phenol, 2-methoxy-	5.833	5.808	5.875	0.82
Propylamine, N,N,2,2-tetramethyl-, N-oxide	1.623	1.567	1.658	0.69
1H-Pyrazole, 3,5-dimethyl-	2.173	2.133	2.225	0.55
2(5H)-Furanone	3.161	3.125	3.208	0.47
Z-10-Pentadecenol,trimethylsilyl ether	3.89	3.875	3.933	0.42
1,2-Benzenediol, 4-methyl-	8.785	8.767	8.833	0.4
4-Methyl-5H-furan-2-one	5.108	5.017	5.292	0.38
Phenol, 4-methyl-	5.629	5.6	5.675	0.3
Phenol, 4-ethyl-2-methoxy-	8.641	8.608	8.683	0.3
1-Butanol, 2-methyl-, acetate	11.98	11.942	12.042	0.3
1,2-Cyclopentanedione, 3-methyl-	4.851	4.833	4.892	0.29
2-Cyclopenten-1-one, 2-hydroxy-	3.308	3.208	3.35	0.28
Vanillin	10.247	10.225	10.292	0.28
Propane, 2,2',2"-[methylidynetris(oxy)]tris-	2.339	2.325	2.358	0.27

**Table S6.** Composition of 10 wt% bio-oil after galvanostatic ECH at -450 mA and single pass reactor configuration characterized by gas chromatography-mass spectrometry (GC-MS).

S7. Electrocatalytic upgrading of 10 wt% bio-oil-containing samples using full-recycle configuration



**Figure S8.** Schematic of the reaction system used for the full-recycle experiment. The reactor cross-sectional area was 30 cm<sup>2</sup> with and catalyst volume of 18 cm<sup>3</sup>. The electrolyte flow rate was 1.0 cm<sup>3</sup> min<sup>-1</sup>, and the LHSV was 3.33 h<sup>-1</sup>. Peristaltic pump photo<sup>©</sup> Cole-Parmer. VersaSTAT 4 Potentiostat photo <sup>©</sup> AMETEK. Schematic adapted from Lopez-Ruiz et al.<sup>3</sup>



**Figure S9.** Effect of residence time on the electrocatalytic upgrading of a sample containing 10 wt% bio-oil at -150 mA and -1100 mV vs. Ag/AgCl. The electrolyte was composed of 80 mM benzaldehyde in 47.5 wt% IPA, 47.5 wt% DI water, and 5.0 wt% acetic acid. The experiments were performed in a close-loop, full-recycle continuous flow cell at a LHSV but, the gases (H<sub>2</sub>) generated were evacuated.

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