Supporting Information

Electrocatalytic Upgrading of Model Lignin Monomers with Earth Abundant Metal Electrodes

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1. Condensed-phase heats of formation and combustion, and specific energies (fuel values) reported in higher heating value (HHV)

			Molecular	
Compound	$\Delta H_{\rm f} k J \ mol^{-1}$	$\Delta H_{c} \text{ kJ mol}^{-1}$	Weight	MJ/kg
Guaiacol ¹	-308.7 ± 1.8	-3589.1 ± 1.8	124.1	28.9 ± 0.02
Trans-2-methoxycyclohexanol ²	-494 ± 6	-4260.6 ± 6.0	130.2	32.7 ± 0.05
Cis-2-methoxycyclohexanol ²	-493 ± 6	-4261.9 ± 6.0	130.2	32.7 ± 0.05
Phenol ³	-165.1 ± 1.3	-3053.4 ± 1.3	94.1	32.5 ± 0.01
Cyclohexanol ³	-352.0 ± 0.67	-3723.9 ± 0.7	100.2	37.2 ± 0.01
Water ₍₁₎ ¹	-285.8 ± 0.04	-	18.0	-
Carbon Dioxide _(g)	-393.5 ± 0.13	-	44.0	-

2. Raney-Nickel cathode preparation

50 ml of plating solution⁴ (213 g of NiCl₂•6H₂O, 200 ml of 30% NH₄OH, and 30 g of NH₄Cl in 1 liter of deionized water) were mixed with 2.5 g Ni-Al powdered (50% Al Basis, 50% Ni Basis purum, Sigma Aldich). A 3 x 2.5 cm (only 2.5 x 2.5 cm was exposed to the solution) 314 stainless steel 50 mesh screen cathode and a flat nickel anode bar were placed oriented in parallel plane in the solution mixture. A total of 2 hours at 375 mA (60 mA cm⁻²) for the deposition constant current electrolysis was applied. The cathode was turned 180° every 30 minutes to ensure even deposition of Raney Nickel particles. The pH of the plating solution was monitored with pH paper after every plating and was maintained at pH 8 - 10 with NH₄OH solution.

The mass of the Ni-Al deposited could be calculated by weight difference, after subtracting the theoretical amount of plated nickel. Control experiments showed that the nickel plating efficiency in the absence of Ni-Al powder stirring was 95%.

Interestingly, the plating bath requires a pre-electrolysis process that takes approximately 4 - 5 hours before the Ni-Al alloy began to deposit on the surface of the stainless steel mesh. The pre-electrolysis is needed to "activate" the bath, and hence is not needed after the first successful plating.

A usable cathode, in general, looks black rather than grey, and has a roughened surface due to the Ni-Al powder deposition. Each electrode should have approximately 70 - 100 mg of Ni-Al embedded as shown in table S1 below:

	J		Before		Dif.	Ni-Al	Deposit Rate	
Current (A)	$(mA cm^{-2})$	Rxn Time (s)	(g)	After (g)	(g)	(g)	(µg s ⁻¹)	% Deviation
0.45	60.0	7680	0.8911	1.9978	1.107	0.107	13.99	12.4
0.45	60.0	7200	0.8569	1.8772	1.020	0.084	11.60	15.9
0.45	60.0	7260	0.8739	1.8951	1.021	0.077	10.55	17.4
0.45	60.0	7380	0.8970	1.9348	1.038	0.078	10.52	17.1
0.45	60.0	7260	0.8970	1.9366	1.040	0.095	13.09	14.0
0.45	60.0	7260	0.8720	1.9192	1.047	0.103	14.13	13.0
0.45	60.0	7380	0.8975	1.9330	1.036	0.075	10.20	17.7
0.45	60.0	9000	0.9033	2.1714	1.268	0.097	10.79	13.7

Table S1: Deposition rate and deviations on Ni-Al alloy deposition. Single- side physical area ($2.5 \times 2.5 \text{ cm}$) of the mesh was used for the *J* (current density) value calculation

3. Cobalt-Phosphate anode preparation

The stainless steel anode was prepared separately and in advance of the reaction of interest. A stainless steel mesh 8 anode 4 x 12 cm (wire area 39.8 %) stainless steel screen was rolled into a cone shape and placed in a freshly prepared solution made of 0.5 mM $Co(NO_3)_2 \cdot 6H_2O$ in 0.1 M pH 7.0 phosphate buffer. A constant current electrolysis to deposit catalyst was carried out at 50 mA using a stainless steel wire as a cathode for at least 3-6 hours prior to use in the ECH reaction.

4. Reaction Procedure

Reactions were conducted in a divided cell, in which the compartments were separated by a Nafion 117 membrane. 30 ml of catholyte (0.1 M pH 8.0 borate buffer with 0.5 mM CTAB) and 30 ml of anolyte (0.1 M pH 7.0 phosphate buffer with 0.5 mM Co(NO₃)₂) were added to the respective compartments. The filled cell was preheated to $75(\pm 3)$ ⁰C in a water bath before a 60-minute pre-electrolysis at 50 mA. Substrate was added immediately after the pre-electrolysis. During the reaction, the cathode compartment was covered with rubber stopper, and the anode compartment was left open to allow oxygen to escape. The sampling port was loosely covered with a glass stopper to prevent pressure built up in the cell. The anode compartment volume was maintained at approximately a 30 ml volume by occasional addition of anolyte solution to correct for evaporative losses. At various time intervals, 0.25 ml samples were taken from the cathode compartment and saturated with 0.1 g sodium chloride. They were then extracted into 1.0 ml of diethyl ether, which was separated and dried over 0.05 g of oven-dried magnesium sulfate. The ether extracts were analyzed with a 30 m DB-5 column in a Perkin-Elmer 8500 GC-FID using *p*-dioxane as internal standard reference and response factors derived from standard external references mixtures treated with the same extraction procedures as experimental samples. The 3-methoxycyclohexanol and 4-methoxycyclohexanol were assumed to have the same FID response as 2-methoxycyclohexanol.

CTAB mM	Guaiacol	Phenol	2-methoxy cyclohexanol	Cyclohexanol	Coulombs passed (C)	Mass Balance (%)
0.25	12.4	0.63	0.39	3.2	363.8	83
0.50	10.6	0.66	0.52	5.3	374.6	85
0.75	15.1	0.59	0.37	3.6	376.5	98
1.50	14.2	0.05	0.19	0.66	364.5	75

5. Optimal CTAB Determination

Table S2: Reduction of 20 mM of guaiacol in 0.1 M pH 8.2 borate buffer at $82 \pm 2^{\circ}$ C, and Current density, J = 8 mA cm⁻²

After 1 hour of pre-electrolysis, reduction of 30 ml of 20 mM guaiacol was performed at 50 mA (8 mA cm⁻²) in 0.1 M pH 8.2 borate buffer at 82 °C for 6 hours, only traces of 2-methoxycyclohexanol was detected at this higher temperature setting

compared to the standard 75 ^oC reported in the manuscript. 0.5 mM concentration of CTAB was shown to give the largest yield of cyclohexanol and hence was chosen to be the optimal condition for the rest of the investigation.

6. Raney-Cobalt electrode Preparation

A 50:50 (atomic %) mixture of metallic cobalt powder and aluminum powder, both of which were mesh 325, was mixed by tumbling in a rotary evaporator flask in a nitrogen atmosphere for 6 hours, placed in a tube furnace purged with ultra-high purity argon gas and heated to 1000 °C at a rate of approximately 1 °C/min over 16 hours, then held at 1000 °C for 6 hours. The furnace was then switched off and allowed to cool to room temperature overnight. The flow of the argon gas was maintained at approximately 1 bubble per second in the solution trap. The product alloy Co-Al was ground to powder with a mortar and pestle, and was examined with XRD to verify that the lattice structure agreed with the International Center for Diffraction Data (ICDD) 2009 data base.

The Co-Al powder was deposited on the stainless steel using the Raney-nickel electrode preparation procedure.

7. Devarda's Copper Electrode

Devarda's Copper precursor was purchased from a commercial vendor (Alfa Aesar), and was ground to powder (ca. mesh 325) prior to deposition. Deposition was run as for the Raney-Nickel electrode, using the nickel plating solution.

8. Control Experiments – Study of organic substrate diffusion across Nafion membrane



Figure S1: Diffusion tests on guaiacol and phenol under experimental condition. Raney nickel electrode is replaced with a plain nickel bar to prevent the hydrogenation of the substrates. Note: No phenol was detected in the anode compartment after the 1st sample

A plain nickel bar was use to mimic the electrocatalytic reactions but to prevent aromatic hydrogenation. The results revealed that guaiacol and phenol were vulnerable to diffusion across the Nafion membrane at 75 °C. After 5 hours of electrolysis of 20 mM (30 ml in volume) guaiacol and 10 mM phenol, only 14 mM guaiacol and 9 mM phenol remained in the cathode compartment. In the anode compartment, 0.6 mM of guaiacol, and 1 mM of phenol were found at the beginning of the ECH but disappeared by the end. This suggests that both guaiacol and phenol diffused across the membrane in the beginning and were then electrochemically oxidized on the anode surface. These diffusion studies account for the loss of materials in the cathode compartment, and suggested that the Nafion membrane as a compartment separator should be reconsidered. Search for other compartment separators is currently underway to improve the material balance by preventing diffusion.

9. Mechanistic Study – H¹-NMR spectrum for the ECH of 30 mM of Guaiacol in D₂O, 0.1 M pH 8.0 Borate Buffer



Figure S2: ¹H-NMR analysis on the 6th hour sample from the guaiacol ECH in pH 8 borate buffer in D_2O . Methanol peak is observed at 3.47 ppm. Sample was extracted in a 5 to 1 ratio to ensure that the organic portion was concentrated to maximize signal to noise ratio



Figure S3: ¹H-NMR spectrum of the sample from figure S2 above after methanol sample spiking, note the enlarged peak at 3.47 ppm.



Figure S4: ¹H-NMR spectrum of the sample from figure S2 above after methanol and 2-methoxycyclohexanol sample spiking, note the enlarged peaks at 3.47 for methanol and 3.38 ppm for the methoxy group on 2-methoxycyclohexanol

10. Mechanistic Study - ECH of 20 mM of Syringaldehyde in 0.1 M pH 8.0 Borate Buffer



Figure S5: GC-MS results of 20mM Syringaldehyde in 0.1M pH 8.0 Borate Buffer after 4 hours at 8 mA cm⁻² at 75 ^oC. Sample was extracted with 5 ml of aqueous reaction solution into ~1.5 ml of chloroform to ensure saturation of the organic samples.

ECH of syringaldehyde forms a series of products shown on the GC-MS trace above. Syringaldehyde undergoes hydrogenation to form syringyl alcohol which then is hydro-dehydroxymethylated to form syringol and formaldehyde. The latter is then hydrogenated to methanol. Syringol then follows the known path to cyclohexanol as shown in figure 3 in the

manuscript. A small amount of syringyl alcohol, however, undergoes dehydroxylation, followed by reduction of the resulting quinone methide, to form p-methyl syringol, which is then demethoxylated in steps to creosol and cresol. Related reactions have been reported for syringyl alcohol upon treatment under base conditions.⁵ The absence of 4-methyl cyclohexanol from the GC-MS chromatogram was probably due to the modest reaction time; under the reaction conditions, cresol does undergo ring saturation as shown in the competition study (figure 5 in the manuscript). This reduction sequence is depicted in Scheme S1below:

Scheme S1: Mechanistic sequences for conversion of syringaldehyde to cyclohexanol and p-cresol



References and Notes:

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