Supplementary Information

Hydrodeoxygenation of lignin related phenolic monomers in polar organic electrolyte via electrocatalysis in a stirred slurry catalytic reactor

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Materials and reagents

All materials and reagents used in this study were purchased from various suppliers as listed below.

Table S1. List of materials and reagents used in this work.

Material	Supplier	Reagent	Supplier
Pt gauze (100 mesh) Nafion-117 membrane Ag/AgCl reference electrode Pt/C (5 wt.% metal loading) Ru/C (5 wt.% metal loading) Pd/C (5 wt.% metal loading)	Sigma-Aldrich	Guaiacol ($\geq$99%), Phenol ($\geq$99%), 4-Propylguaiacol ($\geq$99%), Creosol ($\geq$98%), Potassium chloride (KCl, 99%), Methanesulfonic acid ($\geq$99%), Acetone ($\geq$99.7%), 2-Propanol (>70%), 1,4-Dioxane ($\geq$99.9%), Acetonitrile ($\geq$99.7%), THF ($\geq$99.9%), Ethanol (reagent grade)	Sigma-Aldrich
Pt wire Magnetic stirrer bar	Alfa Aesar VWR	1-Butanol (99%), Acetic acid ($\geq$99.7%) Sodium chloride (NaCl, 99.8%)	Alfa Aesar Fisher Chemical

Catalyst characterizations

The characterization methods of carbon-supported metal catalysts used in this study including N_2 physisorption measurements (i.e., to determine surface area, pore volume, and the average pore diameter of the catalysts) and CO chemisorption (i.e., to measure the metal dispersion and the metal surface area) were described in our previous works.[1,2] The results are presented in Table S2.

Table S2. Characteristics of the carbon-supported metal catalysts used in this study.[2]

Catalyst	S_{BET}[a] (m^2/g)	V_{pore}[b] (cm^3/g)	D_{pore}[c] (nm)	φ (%)	S_{metal} (m^2/g)	d_p (nm)
Pt/C	1487	1.4	4.4	28.9	71.5	3.9
Ru/C	777	0.9	6.2	22.0	80.4	6.0
Pd/C	762	0.8	5.2	25.1	111.8	4.5

[a] BET surface area

[b] Single point adsorption total pore volume ($P/P_0 = 0.99$)

[c] Average pore diameter by BJH desorption

φ = metal dispersion

S_{metal} = metallic surface area

d_p = active particle diameter

Thermodynamic analysis for ECHDO of cerulignol, creosol, guaiacol, and phenol

The model compound study indicates that demethoxylation occurred easily in electrocatalytic reduction of cerulignol and creosol (including guaiacol, which has been previously discussed[1,2]), producing methanol as the by-product. Dehydration of cyclic alcohols, which occurred in the guaiacol ECH, was also observed in the ECHDO of cerulignol and creosol under the experimental conditions. All the reactions in ECHDO of cerulignol to propylcyclohexane, creosol to methylcyclohexane, and guaiacol (or phenol) to cyclohexane are thermodynamically favorable ($\Delta G_R^0 < 0$) and exothermic ($\Delta H_R^0 < 0$), thus can proceed at low temperatures. Note that the standard reduction potentials for all the reactions are above that of the H_2 evolution reaction ($E_{red}^0 = 0$ V_{SHE}). Thermodynamic analysis for ECHDO of all the phenolic compounds (cerulignol, creosol, guaiacol, and phenol) is presented in Table S3.

Table S3. Thermodynamic data for ECHDO of bio-oil-relevant phenolic compounds into the identified major products in this study.

Reaction	Equation	ΔG_R^0 (kJ mol^{-1})	ΔH_R^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	E_{red}^0 (V$_{SHE}$)	$\frac{\partial E_T^0}{\partial T}$ (mV K^{-1})
ECHDO of cerulignol						
4-Propylguaiacol to 4-Propylphenol	$C_{10}H_{14}O_2 + 2H^+ + 2e^- \rightarrow C_9H_{12}O + CH_4O$	-73.1	-68.8	14.4	0.38	0.08
4-Propylphenol to 4-Propylcyclohexanone	$C_9H_{12}O + 4H^+ + 4e^- \rightarrow C_9H_{16}O$	-55.9	-132.0	-255.2	0.14	-0.66
4-Propylcyclohexanone to 3-Propylcyclohexene	$C_9H_{16}O + 2H^+ + 2e^- \rightarrow C_9H_{16} + H_2O$	-154.1	-86.4	227.3	0.80	1.18
3-Propylcyclohexene to Propylcyclohexane	$C_9H_{16} + 2H^+ + 2e^- \rightarrow C_9H_{18}$	-30.0	-81.9	-174.2	0.16	-0.90

Reaction	Equation	ΔG_R^0 (kJ mol^{-1})	ΔH_R^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	E_{red}^0 (V$_{SHE}$)	$\dfrac{\partial E_T^0}{\partial T}$ (mV K^{-1})
ECHDO of creosol						
Creosol to *p*-Cresol	$C_8H_{10}O_2 + 2H^+ + 2e^- \rightarrow C_7H_8O + CH_4O$	-73.1	-68.6	15.0	0.38	0.08
p-Cresol to 4-Methylcyclohexanone	$C_7H_8O + 4H^+ + 4e^- \rightarrow C_7H_{12}O$	-55.9	-114.0	-195.0	0.14	-0.51
4-Methylcyclohexanone to 4-Methylcyclohexanol	$C_7H_{12}O + 2H^+ + 2e^- \rightarrow C_7H_{14}O$	-21.9	-64.9	-144.2	0.11	-0.75
4-Methylcyclohexanol to Methylcyclohexane	$C_7H_{14}O + 2H^+ + 2e^- \rightarrow C_7H_{14} + H_2O$	-162.2	-104.1	194.8	0.84	1.01
ECHDO of guaiacol (and phenol)						
Guaiacol to 2-Methoxy-cyclohexanone	$C_7H_8O_2 + 4H^+ + 4e^- \rightarrow C_7H_{12}O_2$	-55.9	-118.3	-209.2	0.15	-0.54
2-Methoxy-cyclohexanone to 2-Methoxy-cyclohexanol	$C_7H_{12}O_2 + 2H^+ + 2e^- \rightarrow C_7H_{14}O_2$	-34.9	-47.0	-40.7	0.18	-0.21
2-Methoxy-cyclohexanol to Cyclohexanol	$C_7H_{14}O_2 + 2H^+ + 2e^- \rightarrow C_6H_{12}O + CH_4O$	-75.0	-101.7	-89.7	0.39	-0.47
Guaiacol to Phenol	$C_7H_8O_2 + 2H^+ + 2e^- \rightarrow C_6H_6O + CH_4O$	-73.1	-70.2	9.8	0.38	0.05
Phenol to Cyclohexanone	$C_6H_6O + 4H^+ + 4e^- \rightarrow C_6H_{10}O$	-57.9	-120.9	-211.7	0.15	-0.55
Cyclohexanone to Cyclohexanol	$C_6H_6O + 2H^+ + 2e^- \rightarrow C_6H_{12}O$	-21.9	-75.9	-181.1	0.11	-0.94
Cyclohexanol to Cyclohexane	$C_6H_{12}O + 2H^+ + 2e^- \rightarrow C_6H_{12} + H_2O$	-162.2	-91.5	237.0	0.84	1.23

ΔG_R^0 = standard Gibbs free energy of the reaction; ΔH_R^0 = standard enthalpy of the reaction; ΔS^0 = standard entropy of the reaction; E_{red}^0 = standard reduction potential of the reaction; $\dfrac{\partial E_T^0}{\partial T}$ = temperature coefficient of the standard equilibrium electrode potential. All the thermodynamic data were obtained based on NIST and Joback method at standard condition (298 K and 1 atm).

Impact of different polar organic solvents

<u>Potentiostatic ECH of guaiacol</u>

Five different polar organic solvents (acetone, isopropanol, acetonitrile, ethanol, and acetic acid) were used as electrolyte mixed with the MSA solution (0.5 M) with 10% volume ratio in the potentiostatic ECH of guaiacol. Overall, the presence of organic solvent suppressed guaiacol ECH, as shown by the lower conversions (<54%) and F.E.s (<38%) after 4 h (Figure S1a). Based on polarization tests, the organic electrolyte current density decreased as: acetonitrile > acetone > isopropanol > acetic acid > ethanol (Figure S1b), which correspond to the conductivity measurement results (Table S4) at the room temperature. However, it was counter-intuitive that acetonitrile, despite the highest conductivity, had the most undesirable effect in the guaiacol ECH, resulting in zero products. As a polar aprotic solvent, acetonitrile is known to have Lewis base characteristic (an electron-pair donor), hence the presence of acetonitrile could presumably interfere the adsorption chemistry of guaiacol and proton reduction on the catalyst surface and block the adsorption sites for H_{ads} as reported elsewhere.[3] Isopropanol and acetic acid showed the least detrimental effect, resulting in moderate guaiacol conversions (51–54%) and F.E. (35–38%), while ethanol and acetone were similarly suppressive, resulting in the lower guaiacol conversions (30–34%) and F.E. (22–29%). Hence, the reactivity of guaiacol ECH over the same catalyst (5 wt.%-Pt/C) was not proportionally related to the organic electrolyte conductivity. In all cases, cyclohexanol was the most selective product (32–46%) and the presence of organic solvent did not appear to influence guaiacol ECH product distribution.

In the absence of organic solvent, higher guaiacol conversion (~75%) was achieved at reasonable F.E. (~50%). The suppressive effect of organic solvent was further investigated by

varying the acetone concentration (5–40 vol.%). Guaiacol conversion decreased with the increasing acetone concentration (Figure S1c). With only 5 vol.% acetone added, guaiacol conversion was over 40% suppressed and the conversion further dropped to 15% in the presence of 40 vol.% acetone. This negative effect was likely attributed to: (i) the increased ohmic resistance by the higher acetone concentration (shown by the decreasing current density), (ii) the competitive catalyst surface active sites occupancy (indicated by the formation of isopropanol from acetone hydrogenation), (iii) unfavorable desorption of organic solvent molecules from the catalyst at low temperatures (27–45 °C). It is estimated that acetone converted in the catholyte was about 15% and acetone diffused to the anolyte was 3–9% forming acetic acid via electrooxidation. The acetone inhibition effect was also clearly observed at the different cathode potentials. With the increasing potential (from -1.25 V to -2.25 V), guaiacol conversion was not significantly improved (13–16%) and, consequently, F.E. decreased further (from 24% to 9%) because HER predominated over ECH as the current density increased (Figure S1d). Similarly, the suppressive effect can also be seen in the potentiostatic ECH of guaiacol using IPA-mixed MSA electrolyte (Figure S2). Recently, the negative impact of alcohols (methanol, ethanol, and isopropanol) on benzaldehyde ECH rates was also reported by Lopez-Ruiz et al. using a fixed-bed continuous flow electrocatalytic cell with Pd supported on carbon felt electrode.[4] The presence of alcohols diluted the H_3O^+ concentration (i.e., decreased the activity of H_3O^+ ions), thereby slowing down the ECH rates. Consequently, the higher alcohol concentrations resulted in the lower F.E. Increasing half-cell cathodic potentials also decreased F.E. due to the HER rates enhancement to a greater extent than ECH rates.

These results indicate another challenge in ECH processes using organic electrolyte, albeit the benefit of improved substrate solubility. Competitive adsorption of organic solute and solvent

molecules on the catalyst is inevitable under mild conditions (low temperatures). High temperature conditions may promote product desorption and facilitate hydrodeoxygenation and/or dehydration rates. For this reason, an improved reactor design for a robust, high-temperature electrolysis will be worth investigating for the future development of this area. Meanwhile, the use of organic electrolyte in mild ECH process seems more reasonable if the solvent becomes the desired product along with the upgraded substrates. For instance, conversion of acetone to IPA via ECH can be competitive with the conventional hydrogenation routes (100–300 °C). Hydrogenation of acetone to IPA, an industrially important commodity chemical, represents the reduction of ketones to the corresponding alcohols, which is very valuable in organic synthesis.[5] Importantly, these results demonstrate the applicability of polar organic solvent in the ECH process. Future studies will focus on ECHDO of material substrates (e.g., pyrolysis oil) using polar organic electrolyte.

Table S4. Summary of physical properties of the organic solvents used in this work.

Solvent	Acetone	Isopropanol	Acetonitrile	Ethanol	Acetic acid
Formula	C_3H_6O	C_3H_8O	C_2H_3N	C_2H_6O	$C_2H_4O_2$
BP (°C)	56.05	82.5	81.65	78.5	118
MW (g mol^{-1})	58.08	60.10	41.05	46.07	60.05
ρ (kg m^{-3})	784	786	786	789	1045
pKa	20	17.1	-4.3	15.9	4.76
ε	21.01	18.30	36.64	24.60	6.20
κ (mS cm^{-1})	140.5	132.7	147.4	113.8	128.7

BP = boiling point, MW = molecular weight, ρ = density (at 25 °C), pKa = acidity, ε = dielectric constant, κ = measured conductivity (specific conductance) of the solvent mixed with 0.5 M MSA solution (volume ratio = 1:9). Physical properties data (except κ and pKa) were adapted from Division of Organic Chemistry, American Chemical Society: https://organicchemistrydata.org/solvents/; pKa data are adapted from National Library of Medicine: https://pubchem.ncbi.nlm.nih.gov
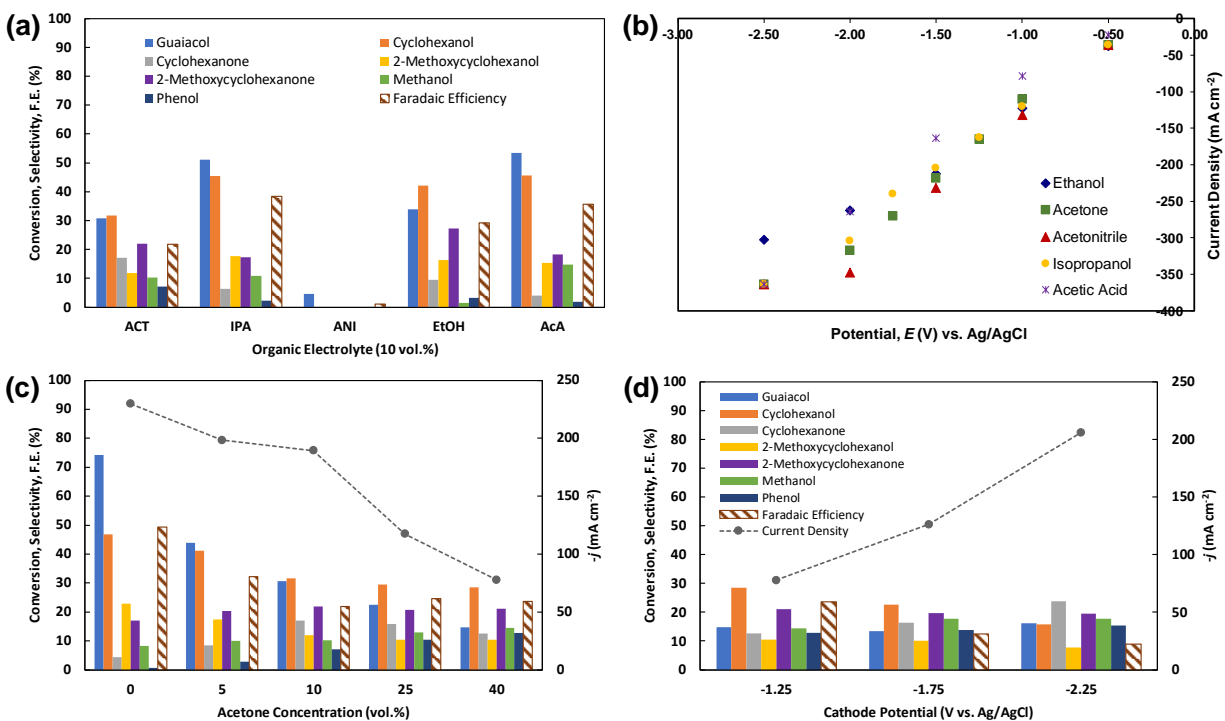
Figure S1. Impact of different polar organic solvents in the ECH of guaiacol under potentiostatic conditions. (a) Conversion, product selectivity, and Faradaic efficiency after 4 h, (b) Polarization test results for the different solvents mixed with MSA (0.5 M) electrolyte, (c) Effect of acetone volumetric concentration, (d) Effect of cathode potential in the ECH of guaiacol in the presence of acetone (40 vol.%). Typical conditions: E = -1.25 V (vs. Ag/AgCl), C_{MSA} = 0.5 M, C_{GUA} = 0.1 M, Temperature (T): (a) 32–35 ℃, (b) room T, (c) 27–36 ℃, (d) 27–45 ℃. Catalyst: 5 wt.%-Pt/C (0.125 g, R/M = 314, equivalent to 0.5 wt.% Pt or 9.1 wt.% Pt/C), R_d = 350 rpm (Stirrer A). Notation: ACT = acetone, IPA = isopropanol, ANI = acetonitrile, EtOH = ethanol, AcA = acetic acid.
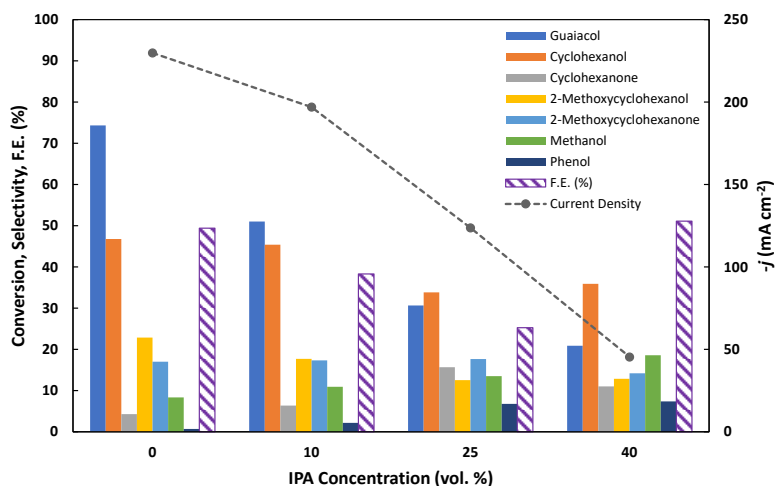
Figure S2. Impact of isopropanol in the ECH of guaiacol under potentiostatic conditions. Conversion, product selectivity, Faradaic efficiency, and current density profiles after 4 h. Conditions: E = -1.25 V (vs. Ag/AgCl), C_{MSA} = 0.5 M, C_{GUA} = 0.1 M, T = 27–36 ℃. Catalyst: 5 wt.%-Pt/C (0.125 g, R/M = 314, equivalent to 0.5 wt.% Pt or 9.1 wt.% Pt/C concentration).

Galvanostatic ECHDO of cerulignol

In this work, different polar organic solvents including polar protic (2-propanol, ethanol) and polar aprotic (acetone, THF, and 1,4-dioxane) were tested in the electrocatalytic reduction of cerulignol under identical conditions (Table S5). The experimental results clearly indicated that the different solvents give different reactivities, possibly due to the different proton and substrate solvation effects. The cerulignol conversion in IPA was much higher (>70%) than those in the other solvents, with also significantly higher degrees of hydrogenation (~50%) and oxygenation (69%). After 4 h reaction, deoxygenation was dominant as indicated by the high selectivity of the major products, such as 3-propylcyclohexene (61%) and propylcyclohexane (22%). At low conversions (8–13%), the demethoxylation product, i.e., 4-propylphenol was dominant, as shown by the results using ethanol and acetone. The low conversions might be attributed to the competitive adsorption of the organic solvent molecules on the catalyst surface, which interrupted the adsorption, reaction, and desorption of the reactant. In case of acetone, the occurrence of competitive reaction on the catalyst surface was also evidenced by the formation of IPA from acetone hydrogenation, which was observed in the ECH of guaiacol as well (see Figures S1–S2). Meanwhile, the presence of THF could promote the deoxygenation steps to propylcyclohexane (via 3-propylcyclohexene dehydration), resulting in nearly 60% selectivity at 20% conversion. However, experimentally, a phase separation was noticed when THF was used, thus most of the organics were presumably dissolved in the organic (upper) layer. In all other cases, the substrates were well miscible as visually indicated by the phase homogeneity. Interestingly, the use of 1,4-dioxane resulted in no conversion whatsoever, suggesting that it is not a good solvent for this mild hydrogenation purpose. Compared to THF, 1,4-dioxane has one extra oxygen atom, which makes it strongly Lewis-basic (i.e., electron-rich, or able to donate electron). Moreover, 1,4-dioxane is aprotic

solvent (i.e., the opposite of protic solvent like alcohols which may donate proton), therefore these properties might be undesirable under the ECH conditions. Acetonitrile (which is also a Lewis-base solvent) also gave poor results (no activity) in the ECH of guaiacol (Figure S1). This detrimental effect was attributed to the aforementioned solvent characteristics, which could interfere the adsorption chemistry of the phenolic reactant and the proton reduction on the catalyst surface, blocking the adsorption sites for H_{ads}, as reported elsewhere.[3] Considering its superior performance and stability, only IPA was then used in the subsequent experiments in this study. Detailed evaluation of organic solvent effect on the ECH chemistry and reaction mechanism is subject to further investigation.

Table S5. Solvent screening results for ECHDO of cerulignol over Pt/C slurry catalyst.

	IPA	Ethanol	Acetone	THF	Dioxane
X (%)	70.58	8.02	12.62	20.32	0.00
S_1 (%)	0.91	40.04	29.90	13.12	0.00
S_2 (%)	0.17	0.00	2.60	0.36	0.00
S_3 (%)	60.55	41.58	40.98	0.00	0.00
S_4 (%)	21.50	2.59	8.37	59.99	0.00
S_5 (%)	8.59	15.80	14.68	24.52	0.00
S_6 (%)	8.28	0.00	3.47	2.01	0.00
$F.E.$ (%)	36.08	2.62	4.59	9.62	0.00
DOH (%)	49.87	5.61	8.90	17.34	0.00
DOD (%)	68.70	6.24	10.23	18.70	0.00
pH (c)	0.92	0.91	0.80	0.82	0.75
E ($V_{Ag/AgCl}$)	-2.71	-2.25	-2.23	-2.81	-2.11

Conditions: Solvent ratio = 1:1 v/v, [MSA] = 0.5 M (catholyte), 1 M (anolyte); I = -0.5 A (j = -182 mA cm^{-2}), T = 50 °C, t = 4 h. Catalyst: 5 wt.%-Pt/C (0.5 g, equivalent with 2.8 wt.% Pt or 36.7 wt.% Pt/C concentration). Cerulignol concentration = 50 mM. Notation: X = cerulignol conversion, S = normalized selectivity (C mol%) of the major products: (1) 4-propylphenol, (2) 4-propylcyclohexanone, (3) 3-propylcyclohexene, (4) propylcyclohexane, (5) methanol, (6) others. $F.E.$ = Faradaic efficiency, DOH = degree of hydrogenation, DOD = degree of deoxygenation; pH (c) = pH of catholyte, measured after the reaction, E = average cathode potential (vs. Ag/AgCl).

Complementary results: ECHDO of cerulignol under other conditions and control experiments

In our previous work, different electrolyte pairs were investigated for ECH of guaiacol (and phenol) whereby acid-acid and neutral-acid combinations were found to be the most effective, resulting in high conversion and F.E.[1,2] Here, comparable cerulignol conversion (68%) was achieved in a neutral-acid catholyte-anolyte pair (Table S6, Entry 1) with reasonable selectivities to 3-propylcyclohexene (53%) and propylcyclohexane (9%) over Pt/C, with the high proton concentration supply from the anolyte (i.e., 1 mol L^{-1} MSA).

This neutral-acid catholyte-anolyte pair configuration was then applied for ECHDO of cerulignol using Ru/C, and the catalytic activity was dramatically enhanced as compared to the reaction in the acid-acid pair (Table S6, Entry 2 vs. 3). When neutral catholyte (e.g., KCl or NaCl) was used, the solution pH increased to the alkaline regime (pH >10) due to water reduction into H$_2$ and OH$^-$, consistent with our previous observation in ECH of guaiacol (or phenol) using NaCl (catholyte) and H$_2$SO$_4$ (anolyte) pair.[2] These results again confirmed that Ru/C activity is inhibited in acidic media, but improved in alkaline solutions.[2] However, the overall activity of Ru/C is still lower than that of Pt/C as indicated by the lower conversion (27% vs. 68%) and F.E. (25% vs. 36%) and the absence of fully HDO product (i.e., propylcyclohexane). Meanwhile, Pd/C showed extremely low activity for ECHDO of cerulignol (X < 2%) regardless of the pH of electrolyte (Table S6, Entries 4–5). Both Ru/C and Pd/C were also applied for ECHDO of phenolic mixtures, resulting in low conversions and no HDO products (Figures S5–S6). These results confirmed the superior performance of Pt/C for HDO pathways.

In order to decouple the role (or function) of each specific substance in the reaction, a series of control experiments was conducted (Table S6, Entries 6–7), including: (i) electrolysis without

Pt/C catalyst in IPA mixed-acidic electrolyte (MSA), (ii) electrolysis in IPA-mixed KCl electrolyte over Pt/C without the presence of acid. In both cases, no conversions were obtained after 4–20 h, which clearly shows the essential roles of hydrogenation catalytic sites (Pt/C) and acidic protons (H^+) for an effective ECHDO.

**Table S6.** Summary of the complementary ECHDO results at other conditions, including control experiments.

Entry	Catholyte (M)	Anolyte (M)	Catalyst (g)	E (V)	t (h)	pH (c)	pH (a)	X (%)	S_1 (%)	S_2 (%)	S_3 (%)	S_4 (%)	S_5 (%)	S_6 (%)	C.B. (%)	F.E. (%)
1	KCl (0.2)	MSA (1)	Pt/C (0.25)	-4.5	4	5.41	0.04	67.74	5.59	10.51	53.05	9.35	4.56	16.94	96.7	35.5
2	MSA (0.2)	MSA (1)	Ru/C (0.5)	-3.1	4	1.29	0.12	0.28	68.77	0.00	0.00	0.00	31.23	0.00	98.3	0.10
3	KCl (1)	MSA (1)	Ru/C (0.5)	-2.7	4	11.07	0.09	26.50	8.30	0.00	56.16	0.00	2.41	33.12	96.8	24.6
4	MSA (0.2)	MSA (1)	Pd/C (0.5)	-2.1	4	1.09	0.04	1.56	28.60	0.00	0.00	0.00	12.23	59.17	91.0	0.27
5	KCl (1)	MSA (1)	Pd/C (0.5)	-2.8	4	10.83	0.06	0.14	76.78	0.00	0.00	0.00	23.22	0.00	78.3	0.05
6	MSA (0.5)	MSA (1)	-	-2.9	20	0.88	0.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	87.3	0.00
7	KCl (1)	KCl (1)	Pt/C (0.25)	-2.3	4	13.75	0.79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	74.7	0.00

E = average cathode potential (vs. Ag/AgCl), t = reaction time, X = cerulignol conversion, S = normalized selectivity (C mol%) of the major products: (1) 4-propylphenol, (2) 4-propylcyclohexanone, (3) 3-propylcyclohexene, (4) propylcyclohexane, (5) methanol, (6) others (including 1-methoxy-3-propylbenzene, propylbenzene, and unknown), *C.B.* = carbon balance, *F.E.* = Faradaic efficiency. Conditions: I = -0.4 A or j = -146 mA cm^{-2} (except Entry 6: I = -0.5 A or j = -182 mA cm^{-2}), T = 50 °C (for Entries 2–6), 60 °C (for Entries 1, 7). [Cerulignol] = 50 mM. Solvent: IPA (all cases). Solvent-to-catholyte ratio = 1:1 (v/v); pH of catholyte (c) and anolyte (a) measured at the end of reaction.
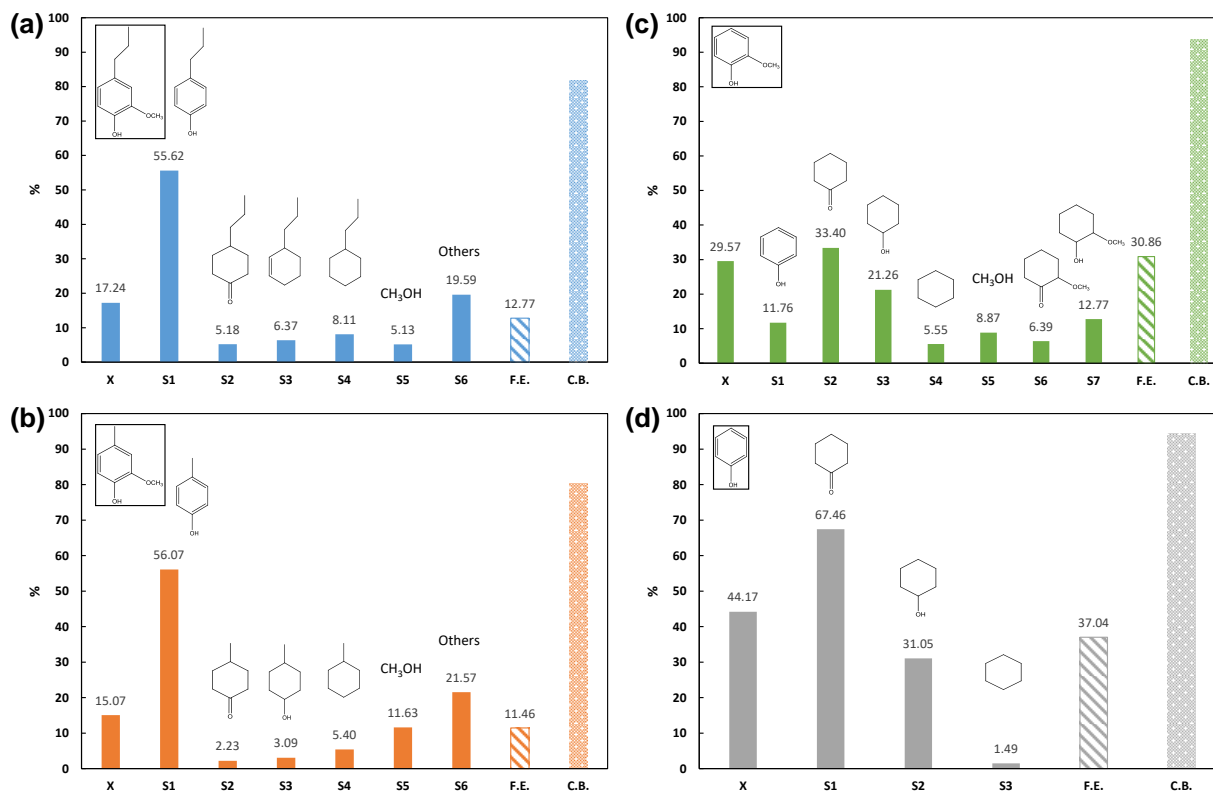
ECHDO of phenolic reactant mixtures

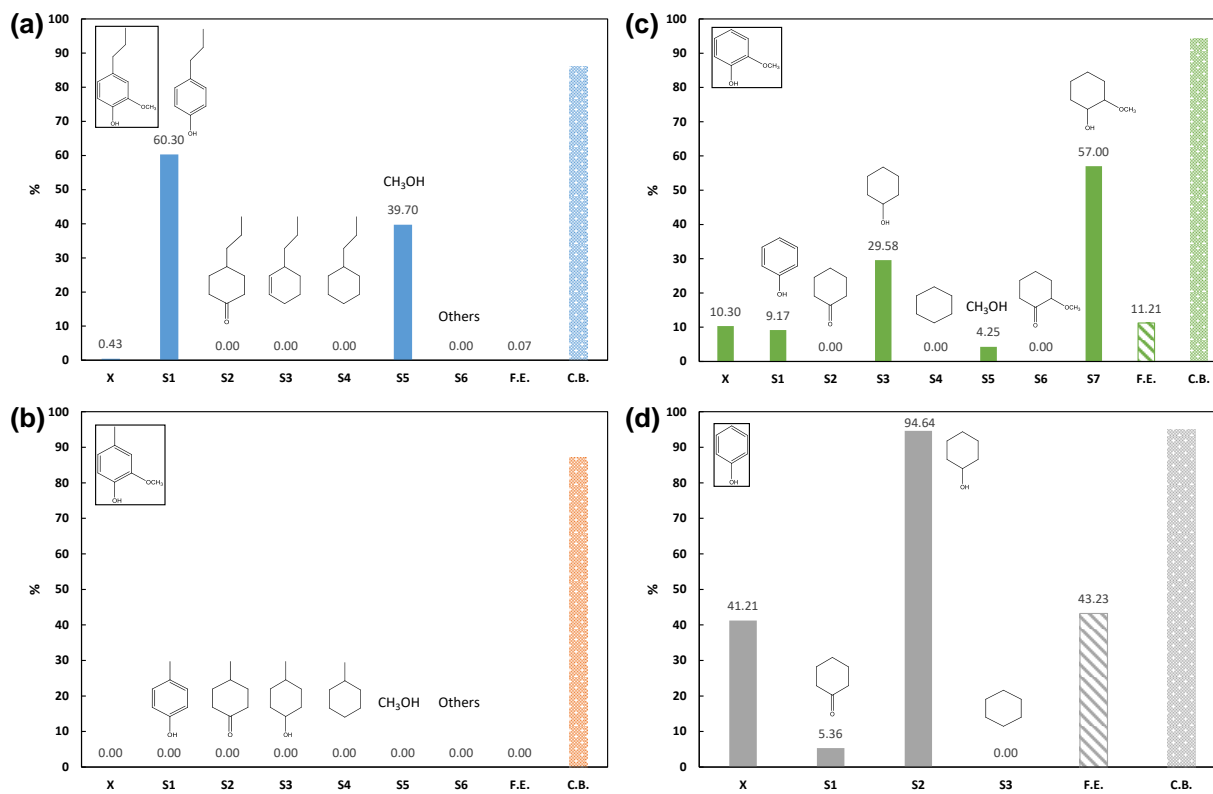## In acid-acid catholyte-anolyte pair using Pt/C
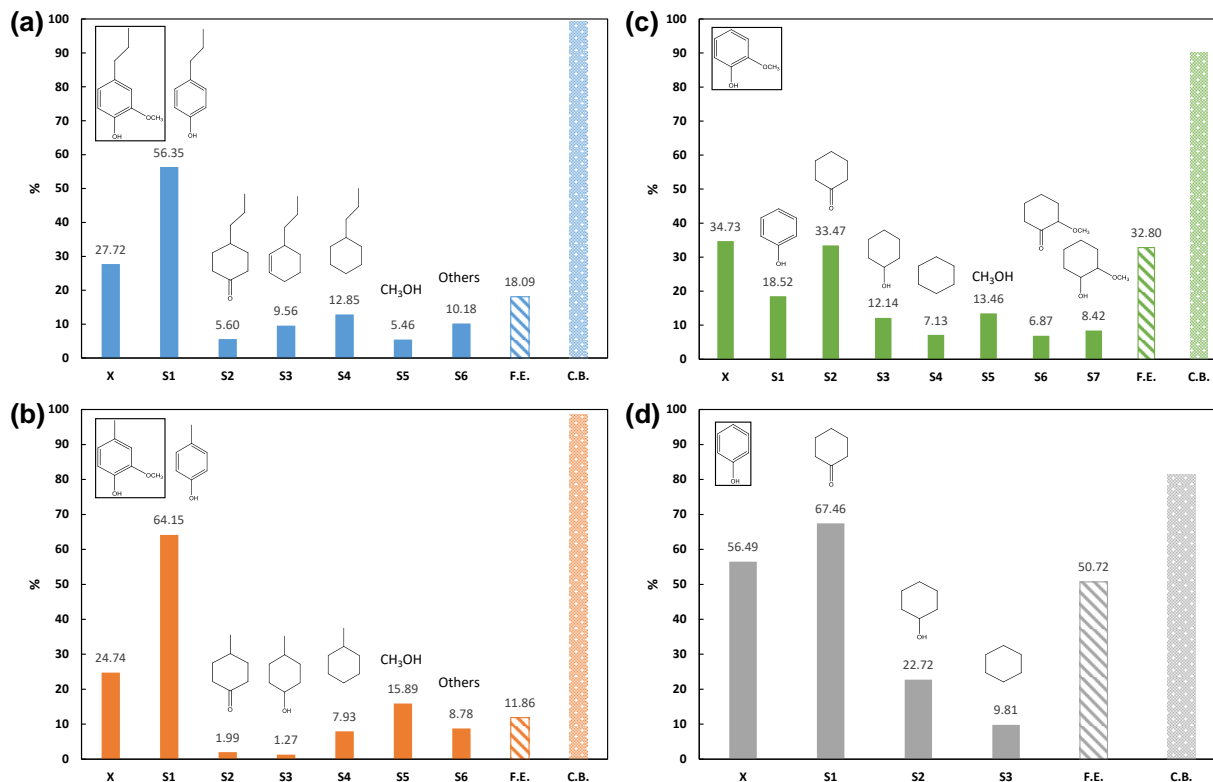
Figure S3. Product distributions from the ECH of mixed phenolic reactants, including cerulignol, creosol, and guaiacol (or phenol). Conditions: I = -0.4 A (j = -146 mA cm^{-2}), T = 50 °C, t = 4 h, R_d = 240 rpm. Catholyte: MSA (0.2 M)–IPA (1:1, v/v), Anolyte: MSA (1 M). Catalyst: 5 wt.%-Pt/C (1 g, equivalent to 1.2 wt.% Pt or 18.9 wt.% Pt/C concentration relative to the total reactant). Reactant concentration = 0.1 M (for each reactant, with respect to the catholyte volume). Catholyte pH ≈ 1.3 (after 4 h). Notation: X = conversion (mol-%), S = product selectivity (mol-%), F.E. = Faradaic efficiency (%), C.B. = carbon balance (mol-%).

In neutral-acid catholyte-anolyte pair using Pt/C

Figure S4. Product distributions from the ECH of mixed phenolic reactants, including cerulignol, creosol, and guaiacol (or phenol). Conditions: I = -0.4 A (j = -146 mA cm^{-2}), T = 50 $^{\circ}$C, t = 4 h, R$_d$ = 240 rpm. Catholyte: KCl (1 M)–IPA (1:1, v/v), Anolyte: MSA (1 M). Catalyst: 5 wt.%-Pt/C (0.5 g, equivalent to 0.6 wt.% Pt or 10.5 wt.% Pt/C concentration relative to the total reactant). Reactant concentration = 0.1 M (for each reactant, with respect to the catholyte volume). Catholyte pH ≈ 10 (after 4 h). Notation: X = conversion (mol-%), S = product selectivity (mol-%), F.E. = Faradaic efficiency (%), C.B. = carbon balance (mol-%). The lower carbon balances were attributed to deprotonation of the phenolics due to the pH changes to alkaline regime, as evidenced by the color changes of the solution; this was also previously observed in the ECH of guaiacol.[1]
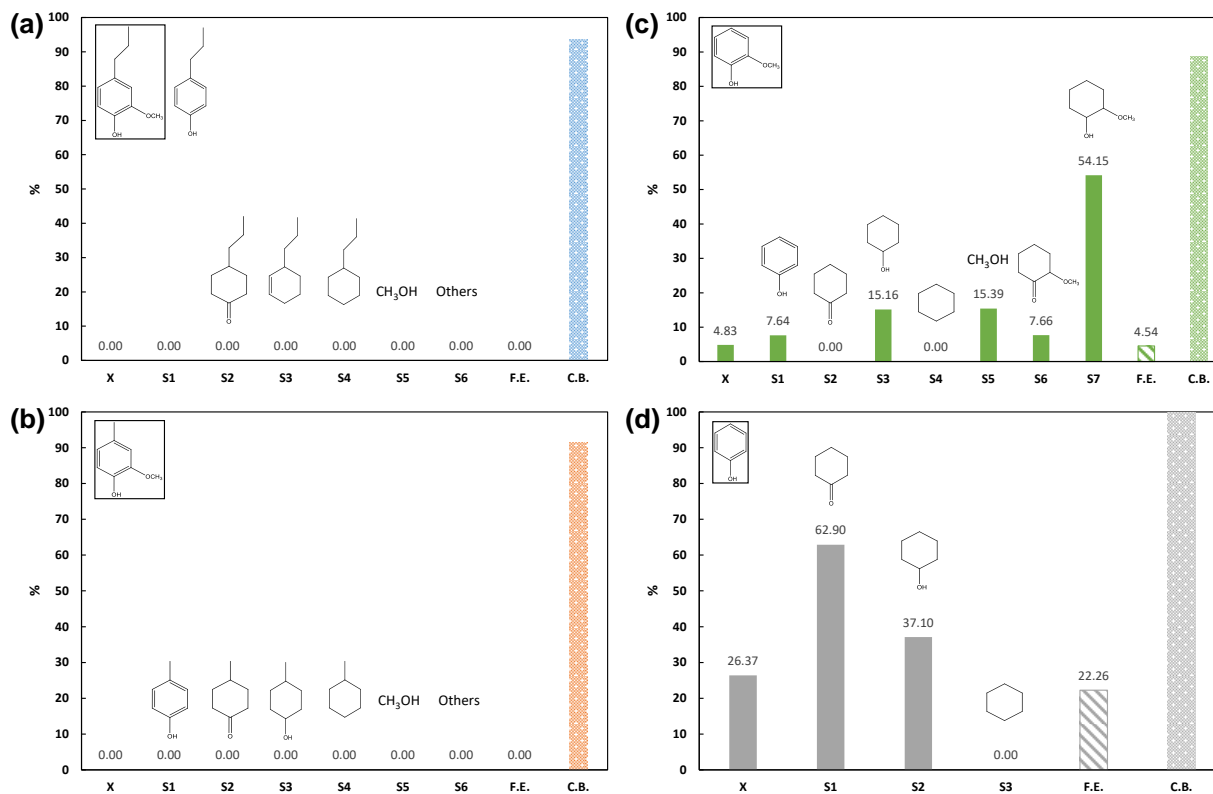
In neutral-acid catholyte-anolyte pair using Ru/C

Figure S5. Product distributions from the ECH of mixed phenolic reactants, including cerulignol, creosol, and guaiacol (or phenol). Conditions: I = -0.4 A (j = -146 mA cm^{-2}), T = 50 $^{\circ}$C, t = 4 h, R$_d$ = 240 rpm. Catholyte: KCl (1 M)–IPA (1:1, v/v), Anolyte: MSA (1 M). Catalyst: 5 wt.%-Ru/C (0.5 g, equivalent to 0.7 wt.% Ru or 12.5 wt.% Ru/C concentration relative to the total reactant). Reactant concentration = 0.05 M (for each reactant, with respect to the catholyte volume). Catholyte pH ≈ 10 (after 4 h). Notation: X = conversion (mol-%), S = product selectivity (mol-%), F.E. = Faradaic efficiency (%), C.B. = carbon balance (mol-%).
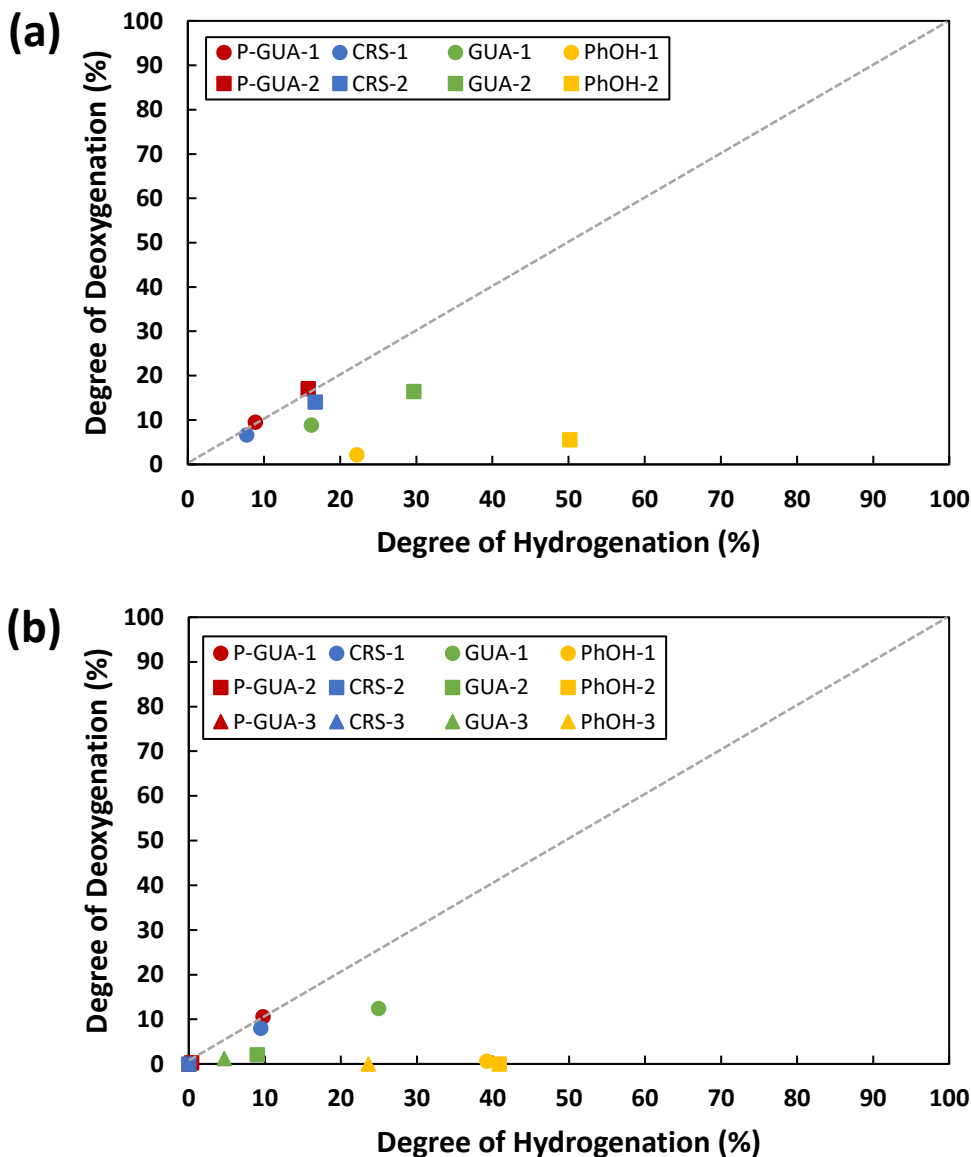
## In neutral-acid catholyte-anolyte pair using Pd/C

Figure S6. Product distributions from the ECH of mixed phenolic reactants, including cerulignol, creosol, and guaiacol (or phenol). Conditions: I = -0.4 A (j = -146 mA cm^{-2}), T = 50 °C, t = 4 h, R$_d$ = 240 rpm. Catholyte: KCl (1 M)–IPA (1:1, v/v), Anolyte: MSA (1 M). Catalyst: 5 wt.%-Pd/C (0.5 g, equivalent to 0.7 wt.% Pd or 12.5 wt.% Pd/C concentration relative to the total reactant). Reactant concentration = 0.05 M (for each reactant, with respect to the catholyte volume). Catholyte pH ≈ 10 (after 4 h). Notation: X = conversion (mol-%), S = product selectivity (mol-%), F.E. = Faradaic efficiency (%), C.B. = carbon balance (mol-%).

Degrees of hydrogenation and deoxygenation of phenolic mixtures ECHDO

Figure S7. Correlations between degree of hydrogenation (DOH) and degree of deoxygenation (DOD) from: (a) the ECHDO of phenolic reactant mixtures in acid-acid catholyte-anolyte pairs using different Pt/C catalyst concentration: (●) 0.2 wt.% Pt, (■) 1.2 wt.% Pt. Catholyte: MSA (0.2 M)-IPA (1:1, v/v), anolyte: MSA (1 M). These data correspond to Figures 6 and S3. (b) the ECHDO of phenolic reactant mixtures in neutral-acid catholyte-anolyte pairs using different catalysts: (●) Pt/C, (■) Ru/C, (▲) Pd/C. Catholyte: KCl (1 M)-IPA (1:1, v/v), Anolyte: MSA (1 M). Catalyst loading = 0.5 g. These data correspond to Figures S4, S5, S6, showing the superior performance of Pt/C. Notation: P-GUA = cerulignol, CRS = creosol, GUA = guaiacol, PhOH = phenol.

GC-MS chromatograms from ECH of cerulignol in IPA-mixed MSA electrolyte
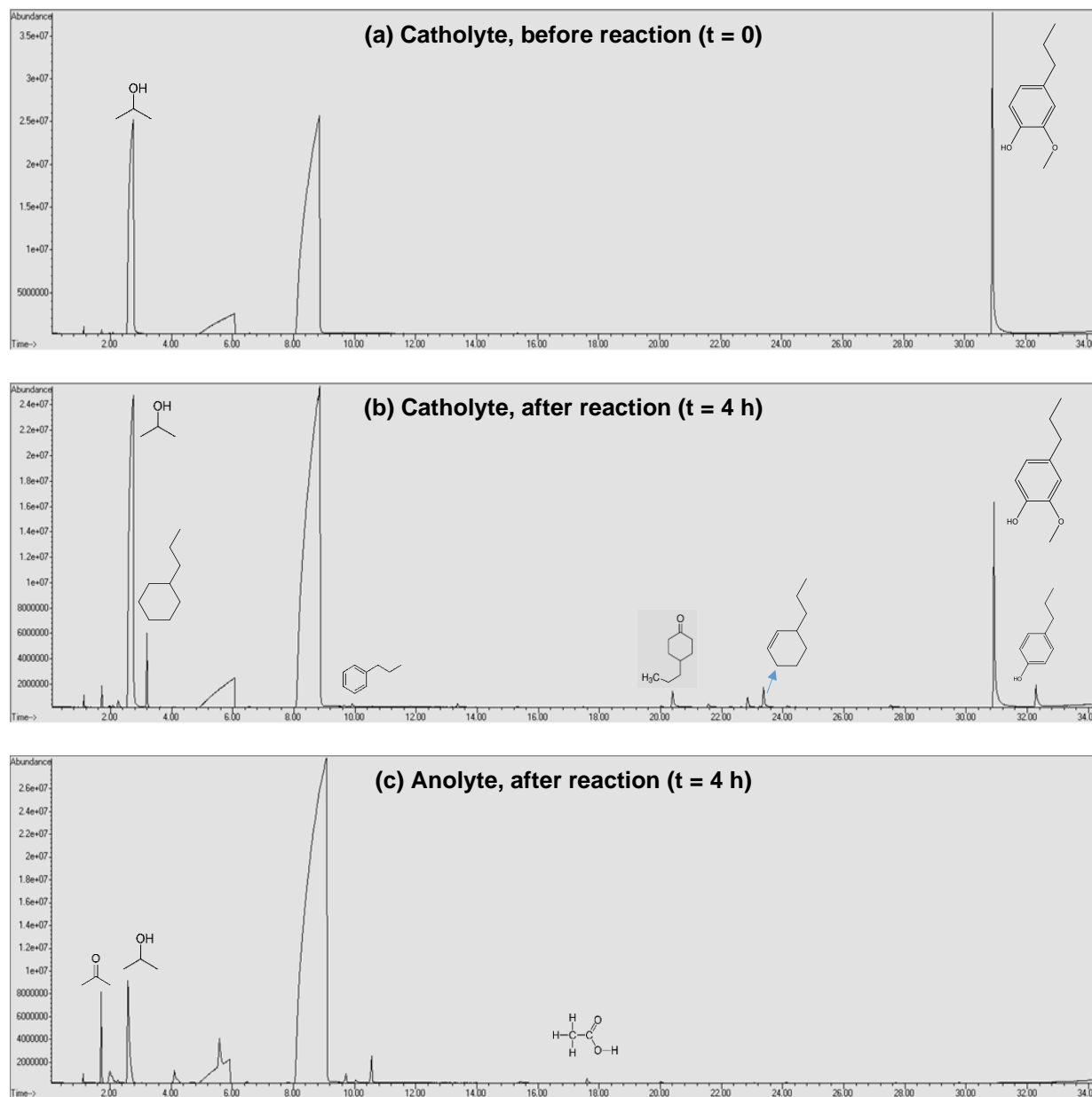
Figure S8. GC-MS chromatograms from the ECH of cerulignol in the isopropanol-mixed MSA (0.2 M) catholyte over 5 wt.% Pt/C catalyst: (a) before reaction, (b) after 4 h reaction. Major product peaks were identified, such as propylcyclohexane (3.2 min), propylbenzene (9.9 min), 3-propyl-cyclohexene (23.5 min), 4-propylcyclohexanone (20.5 min), 4-propylphenol (32.4 min) from the cerulignol reactant (31 min). GC analysis was performed using HP-INNOWax column. Anolyte sample after reaction (c) shows no products of interest cross-over, only acetone (1.6 min) and acetic acid (18 min) as IPA oxidation products, which indicates good membrane performance.

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