Effect of Pt and Ru-based catalysts on the electrochemical hydrodeoxygenation of phenol to cyclohexane

Jeffrey R. Page[1,2], Amol Pophali[3], Taejin Kim[3], Juan Ruiz-Lopez[4,5], Stoyan Bliznakov[1,2], Julia A. Valla[1,2]*

[1]Department of Chemical and Biomolecular Engineering. University of Connecticut, 191 Auditorium Rd, Unit 3222, Storrs, CT 06269, USA.
[2]Center for Clean Energy Engineering. University of Connecticut, 44 Weaver Rd, Unit 5233, Storrs, CT 06269, USA.
[3]Department of Materials Science and Chemical Engineering. Stony Brook University, Stony Brook, NY 11794, USA.
[4]Pacific Northwest National Laboratory, Institute for Integrated Catalysis, Energy and Environment Directorate, 902 Battelle Blvd., Richland, WA 99352, USA
[5] WSU-PNNL Bioproducts Institute

* Author to whom correspondence should be addressed, ioulia.valla@uconn.edu

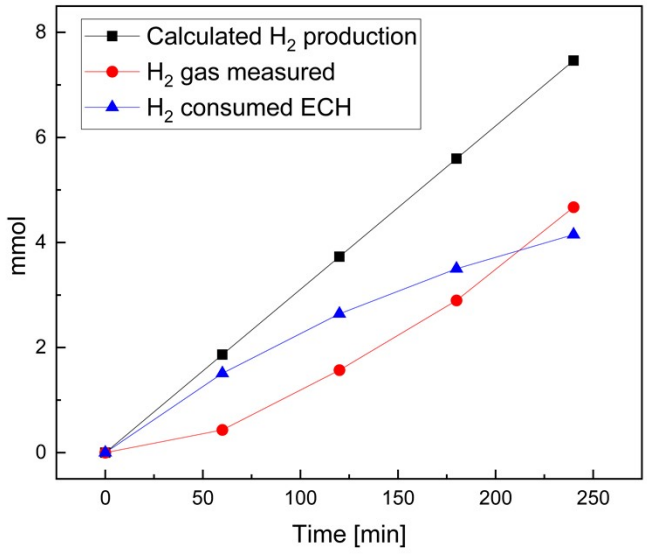

Figure S1. Hydrogen balance of phenol EC-HDO experiments using labPtRu-C at constant current 55 mA cm^{-2} electrolysis. Hydrogen was measured using an online mass spectrometer. Hydrogen consumed was calculated using the amount of hydrogen required to produce cyclohenane, cyclohexanol and cyclohexanone.

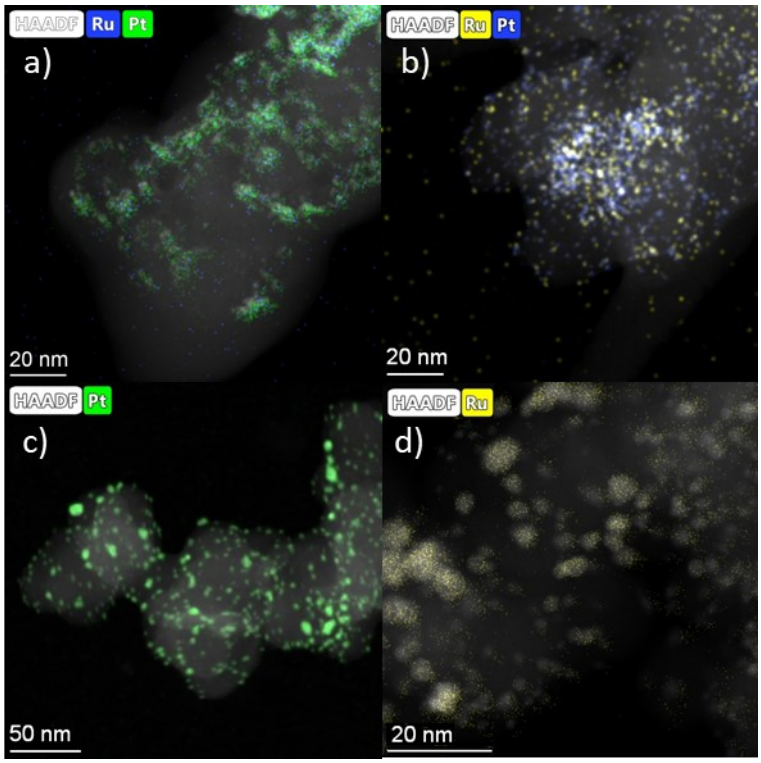

Figure S2. HAADF EDS mapping of Pt and Ru for a) comPtRu-C, b) labPtRu-C, c) Pt-C, and d) Ru-C catalysts and e) Ru-C at higher magnification.

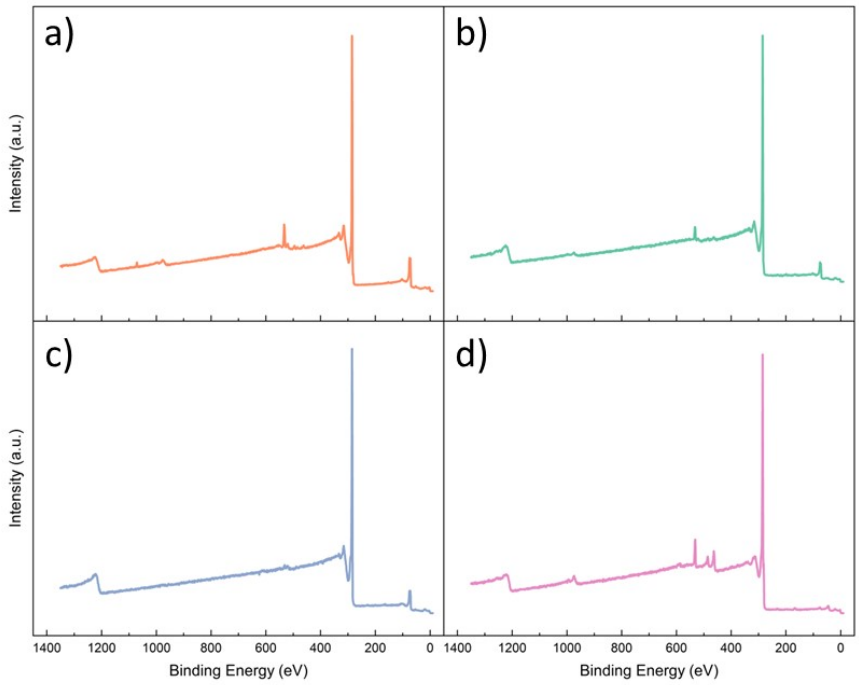

Figure S3. XPS binding energy surveys from 1350 eV to 0 eV of a) comPtRu-C, b) labPtRu-C, c) Pt-C, and d) Ru-C catalysts.

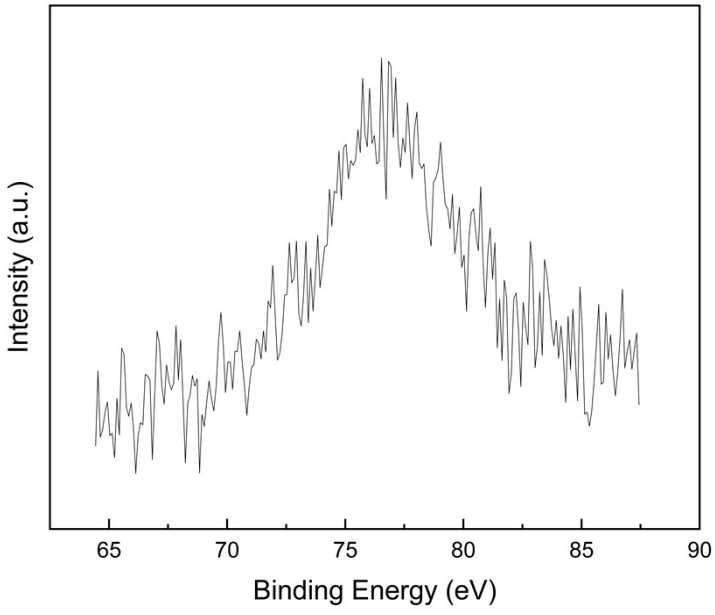

Figure S4. XPS Pt 4f scan from 64 eV to 87 eV for the Ru-C catalyst. Ru 4s signal at 75.0 eV for Ru(0) and 75.7 eV for Ru oxide

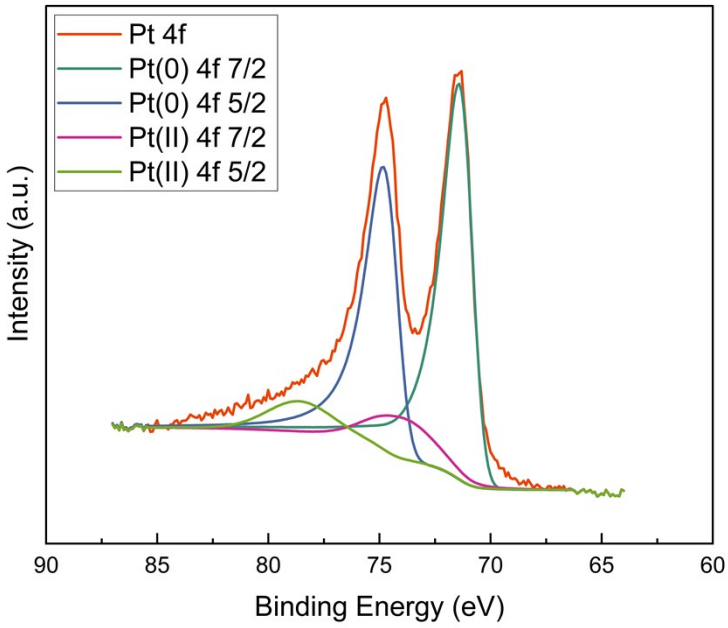

Figure S5. XPS Pt 4f scan from 64 eV to 87 eV and peak fitting for the monometallic Pt-C.

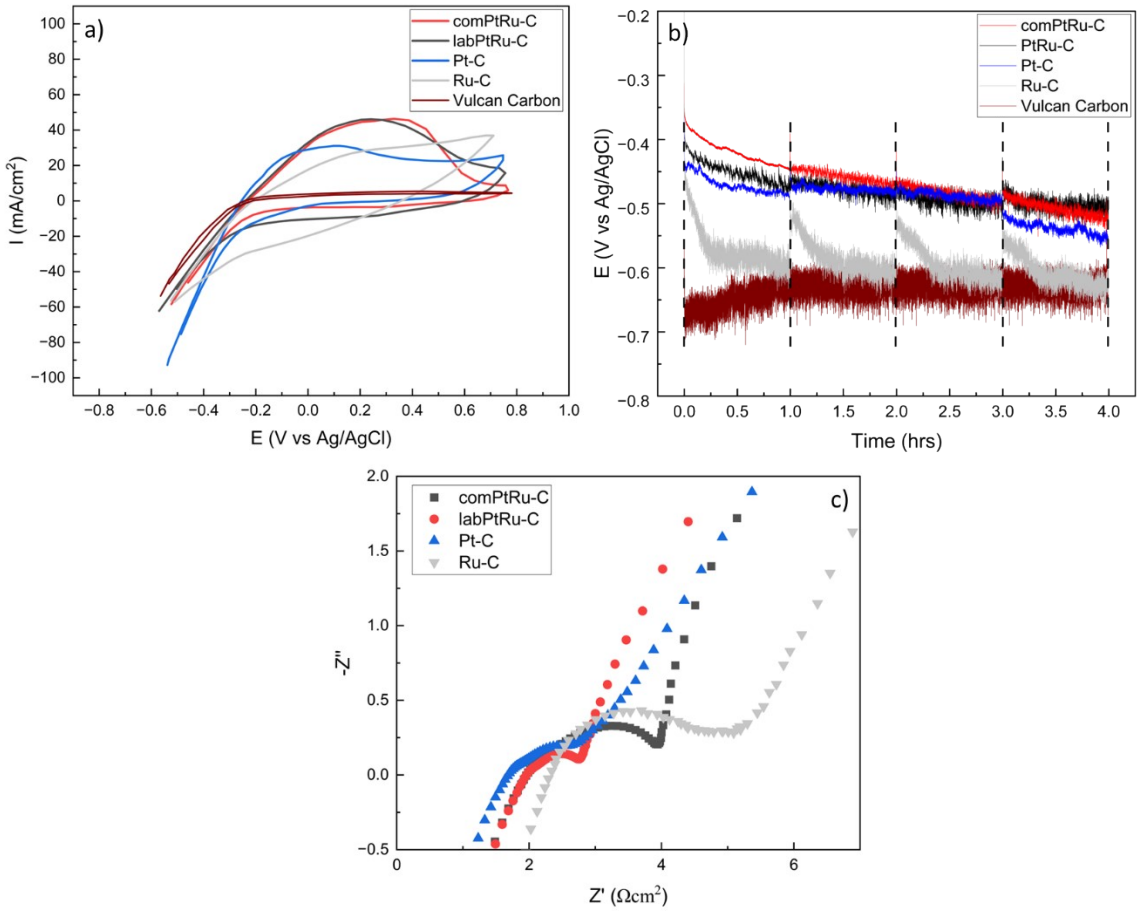

Figure S6. a) cyclic voltammogram and b) cathodic potential vs time for the comPtRu-C, labPtRu-C, Pt-C, Ru-C and Vulcan Carbon experiments. Dashed black line represents time point when samples were taken from the catholyte and solvent trap. c) Representative Nyquist plots collected at -0.2 V vs Ag/AgCl for the comPtRu-C, labPtRu-C, Pt-C, and Ru-C experiments.

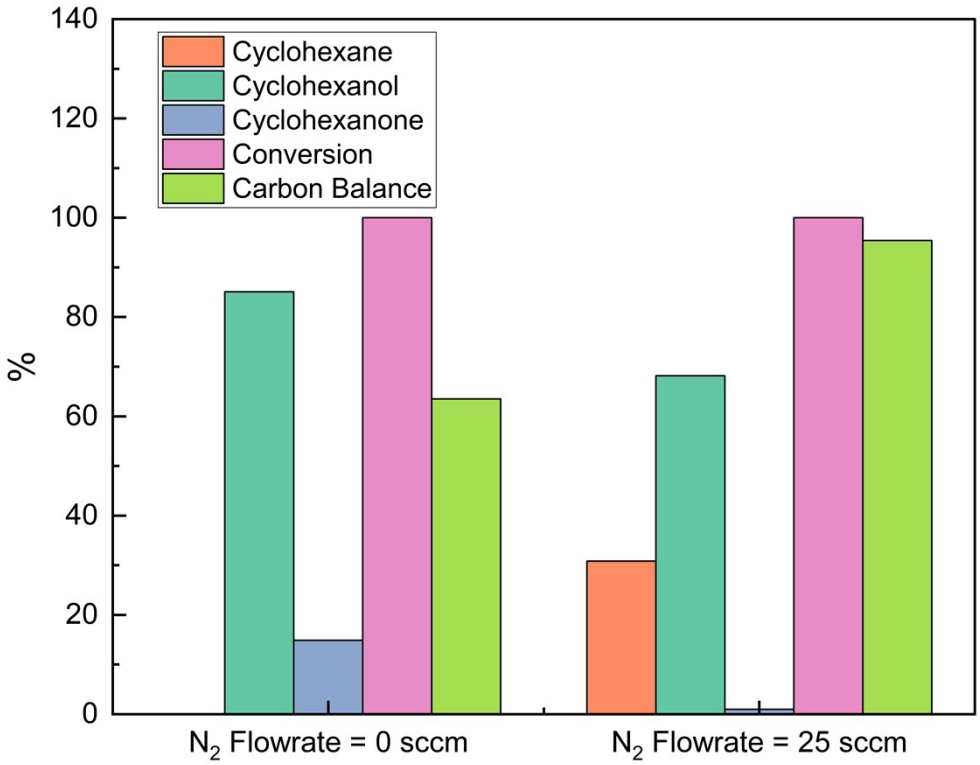

Figure S7. Cyclohexane, cyclohexanol, cyclohexanone selectivity, phenol conversion and carbon balance for an EC-HDO experiment of phenol performed in the absence of nitrogen gas flow and with 25 sccm of nitrogen flow through the system. Reaction conditions: N_2 flowrate = 0 mL min^{-1} and 25 mL min^{-1}, labPtRu-C catalyst, 60 ºC, constant current 55 mA cm^{-2}, initial phenol concentration 30 mM, electrolyte 0.2 M perchloric acid.

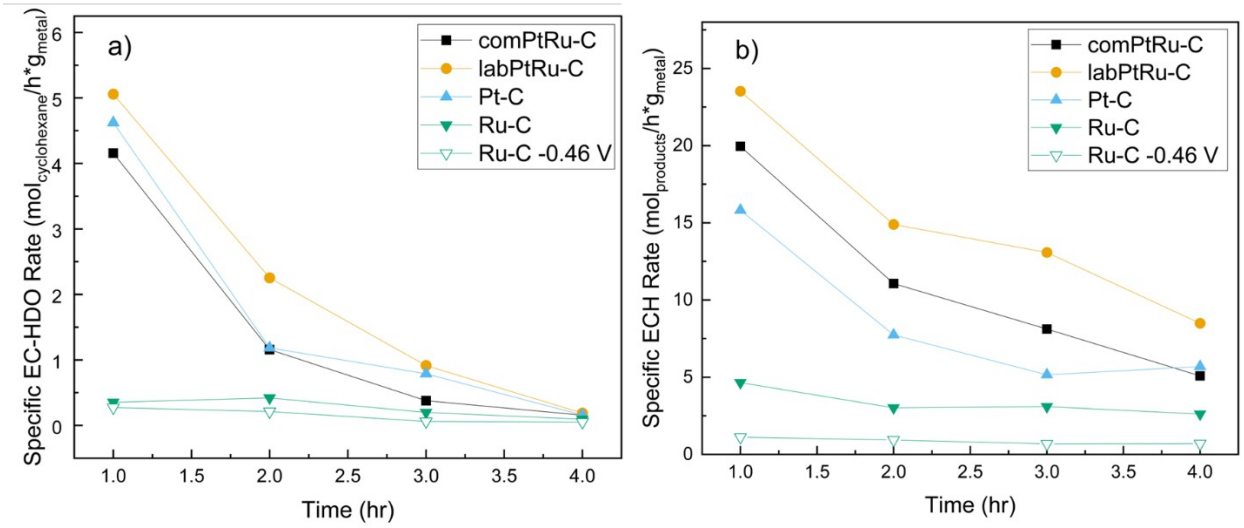

Figure S8. a) specific EC-HDO rate and b) specific ECH rate during phenol electrolysis as a function of time for the comPtRu-C, labPtRu-C, Pt-C, and Ru-C catalysts. (Reaction conditions: 50 mL min^{-1} N_2, 60 °C, 0.2 M perchloric acid, 0.2 mg cm^{-2}, constant current 55 mA/cm^2)

Table 1. Conversion (X), Selectivity (S) where A = cyclohexane B = cyclohexanol C = cyclohexanone, specific ECH rate (at t = 1 hour), Faradaic efficiency (FE), carbon balance (CB) and average cathodic potential (E) bimetallic lab synthesized PtRu at varying ruthenium to Pt ratios. (Reaction conditions: 50 mL min^{-1} N_2, 60 °C, 0.2 M perchloric acid, 0.2 mg cm^{-2}, constant current 55 mA/cm^2) $^+$Reported potentials were iR correct post-experiment.

Ru Content (%)	X (%)	S_A (%)	S_B (%)	S_C (%)	Specific ECH rate (mol hr^{-1} g$^{-1}_{metal}$)	FE (%)	CB (%)	E (V vs Ag/AgCl)$^+$
0	84.5	24.9	60.8	14.3	15.84	32.6	87.0	-0.47
8	77.7	27.2	65.0	7.8	15.7	23.3	82.0	-0.52
16	100.0	30.8	68.2	1.0	23.52	34.9	95.4	-0.47
33	80.7	22.2	72.8	9.7	14.83	27.5	90.4	-0.48
50	46.9	22.8	69.6	10.5	11.04	15.3	93.1	-0.48
100	41.9	10.5	84.2	2.3	4.65	11.0	91.5	-0.59

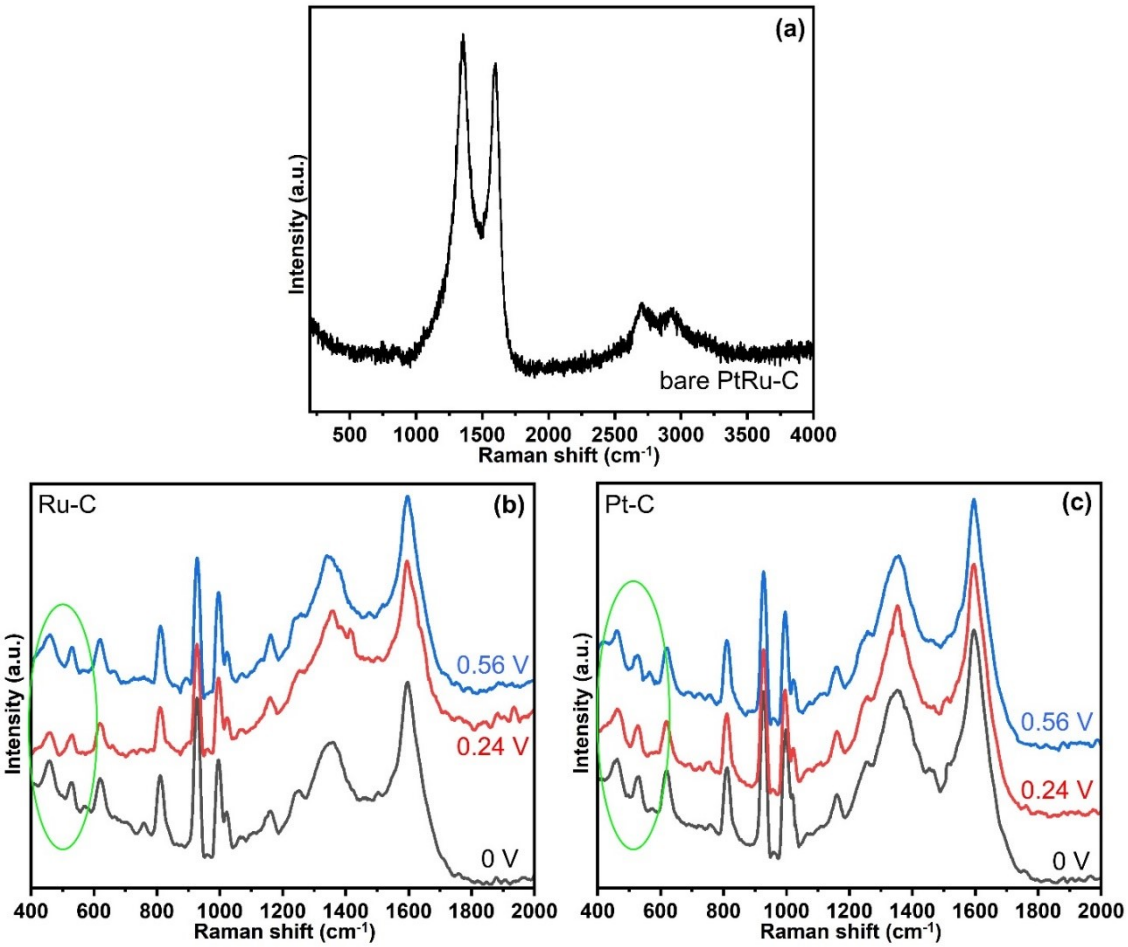

Figure S9. Raman spectra for: (a) bare labPtRu-C fresh catalyst; (b) EC-HDO on Ru-C catalyst at varying voltage; and (c) EC-HDO on Pt-C catalyst at varying voltage.

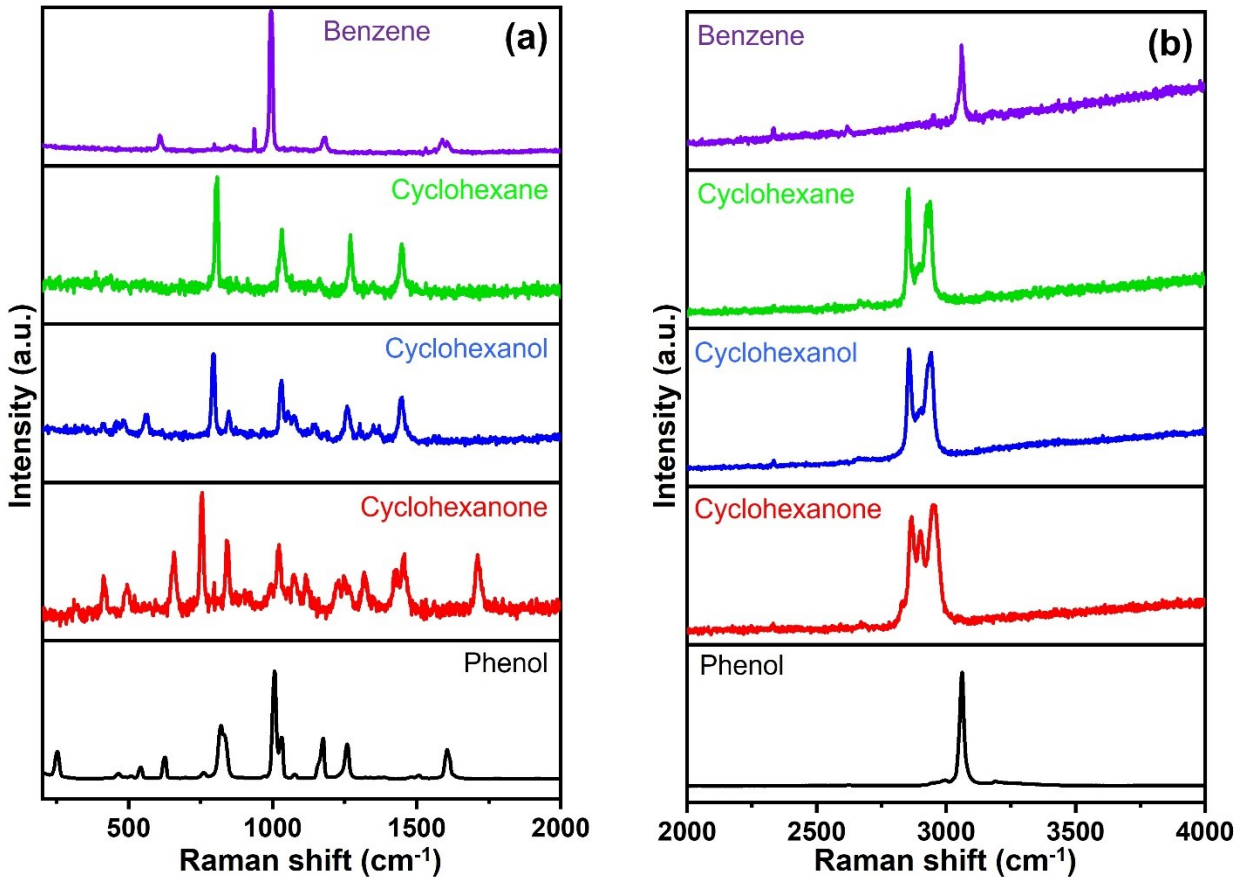

Figure S10. Raman spectra for reactants, intermediates and product compounds tested separately for (a) 200 – 2000 cm^{-1}; and (b) 2000 – 4000 cm^{-1} Raman shifts.

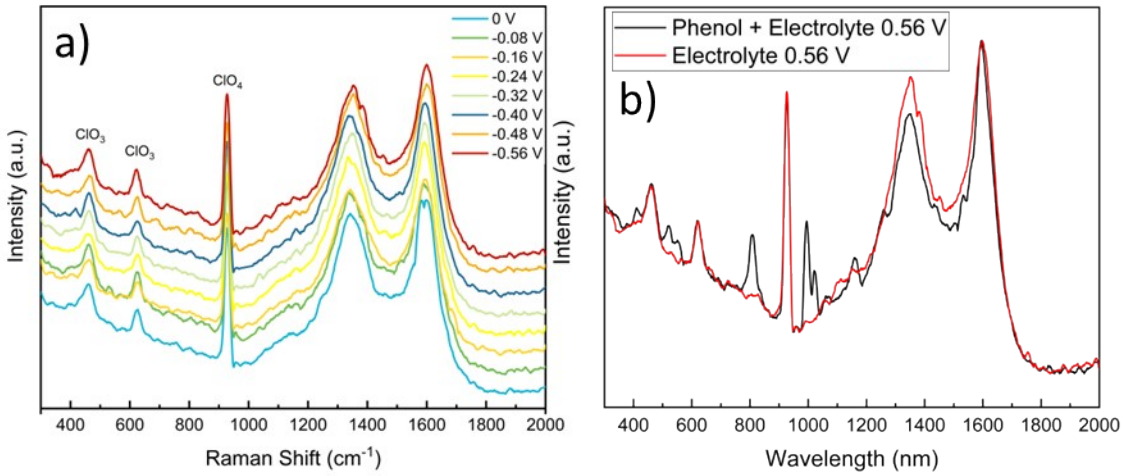

Figure S11. a) Operando Raman spectra for electrolysis in the absence of phenol using labPtRu-C catalyst at potentials from 0.0 V to -0.56 V vs Ag/AgCl. b) PtRu-C with phenol present and without at 0.56 V Ag/AgCl.

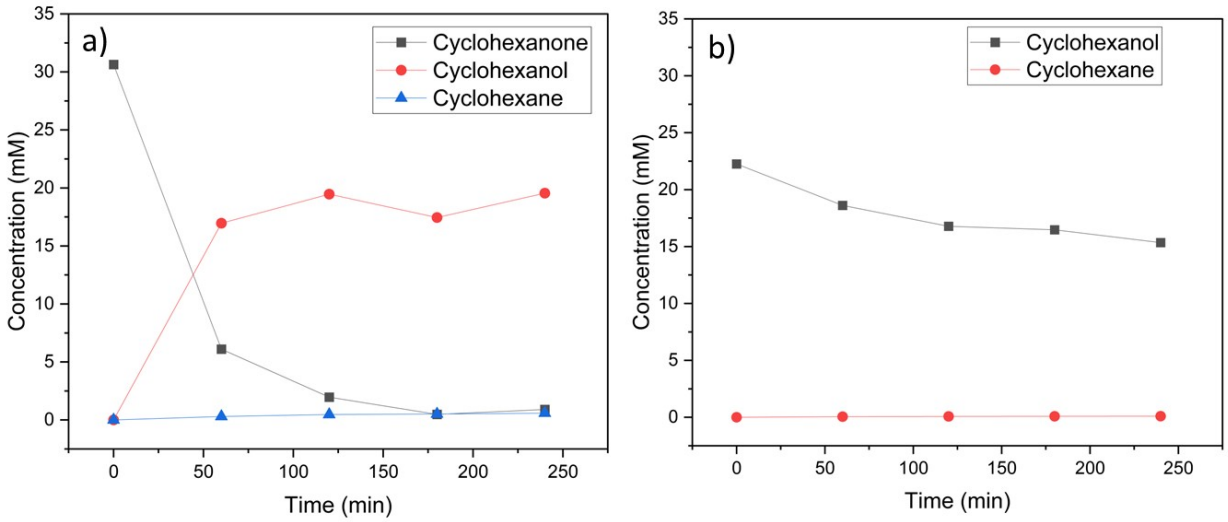

Figure S12. Concentration profile of EC-HDO of a) cyclohexanone and b) cyclohexanol. (Reaction conditions: constant potential -0.46 V vs Ag/AgCl, labPtRu-C catalyst, 0.2 M perchloric acid, 60 ºC, average current 57 mA cm^2)