*Supporting Information*:

# Electrocatalytic hydrogenation of lignin monomer to methoxy-cyclohexanes with a high faradaic efficiency

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## Experimental Section

### Preparation of catalysts

In a typical procedure, RhPtRu working electrode was fabricated via an electro-deposition route onto a carbon felt (1 cm x 1 cm x 1mm), with graphite rod and SCE electrode (saturated calomel electrode) worked as counter and reference electrodes, respectively. The electrolyte consisted of an aqueous 0.5 M $Na_2SO_4$ solution (as supporting electrolyte) containing 8 mM of rhodium nitrate solution ($Rh(NO_3)_3$), 7 mM of chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), 4 mM of ruthenium (III) nitrosyl nitrate solution ($Ru(NO)(NO_3)_x(OH)_y$). Then we performed CV scans (50 cycles) in the potential range of -0.5 to 1.7 V at a scan rate of 0.1 $V \cdot s^{-1}$. The monometallic catalysts (i.e., Rh, Pt, Ru) and bimetallic catalysts (i.e., RhPt, PtRu, RhRu) as reference samples were also prepared by the aforementioned method using corresponding molar concentrations. After the electrodeposited process, the obtained working electrodes were washed by D.I. water, and then dried in the air for subsequent testing and characterizations.

### Materials characterization

X-ray diffraction (XRD) patterns collected using a Philips X'pert X-ray diffractometer (graphite-monochromatized Cu Ka radiation of wave lenth-1.5418Å). The images found from scanning electron microscopy (SEM) were examined by instrument JEOL-JSM-6700F field-emitting (FE) scanning electron microscope (acceleration voltage = 100 kV). In addition, transmission electron microscope (TEM), high-resolution TEM (HRTEM), and scanning transmission electron microscopy (STEM) with X-ray spectroscopy (EDX) mapping were collected using Hitachi HF-3300. Elemental ratios of prepared samples were analyzed from X-ray photoelectron spectroscopy (XPS), and it was performed on Thermo ESCALAB 250.

### Electrochemical performance and product analysis

The ECH experiments were conducted by CHI660E electrochemical workstation (CH Instruments, Inc., Shanghai, China) using a two-chambered H-cell system separated by a bipolar membrane (BPM). Ag/AgCl (saturated KCl solution), Pt mesh, and the catalyst-modified carbon felt were utilized as the reference electrode, counter electrode, and working

electrode, respectively. All potentials were measured against an Ag/AgCl reference electrode (saturated KCl, BASi) and converted to the RHE reference scale using:

$$E\ (vs\ \text{RHE}) = E\ (vs\ \text{Ag/AgCl}) + 0.059 \times \text{pH} + 0.197$$

In this work, all the used working electrodes have same geometric surface area (1 cm$^2$). 30 mL of 100 mM guaiacol solution containing corresponding supporting electrolyte (0.2 M HClO$_4$ solution) was used as both catholyte and anolyte in ECH test. Then liquid products were analyzed by gas chromatography-mass spectra GC-MS (Agilent 7890B+5977A) equipped with an Agilent Technologies DB-WAX UI column. An internal standard 4-propyl-cyclohexanone was used. Before the product analysis, electrolyte solution (800 uL) was accumulated from the anode compartment, and extracted with trichloromethane (800 uL) solution.

The yield, selectivity, conversion, and faradaic efficiency (F.E.) were calculated according to the following equations:

$$\text{Yield} = (\text{moles of target products})/(\text{initial moles of substrate}) \times 100\% \qquad (1)$$

$$\text{Selectivity} = (\text{moles of target products})/(\text{moles of all organic products}) \times 100\% \quad (2)$$

$$\text{Conversion} = (\text{moles of reactant consumed})/(\text{initial moles of substrate}) \times 100\% \qquad (3)$$

$$\text{F.E.} = (\text{n} \times \text{moles of target products})/(\text{total charge passed}/F) \times 100\% \qquad (4)$$

where n corresponds to the number of electrons involved in the intrinsic ECH of organic substrates; F denotes the faraday constant.
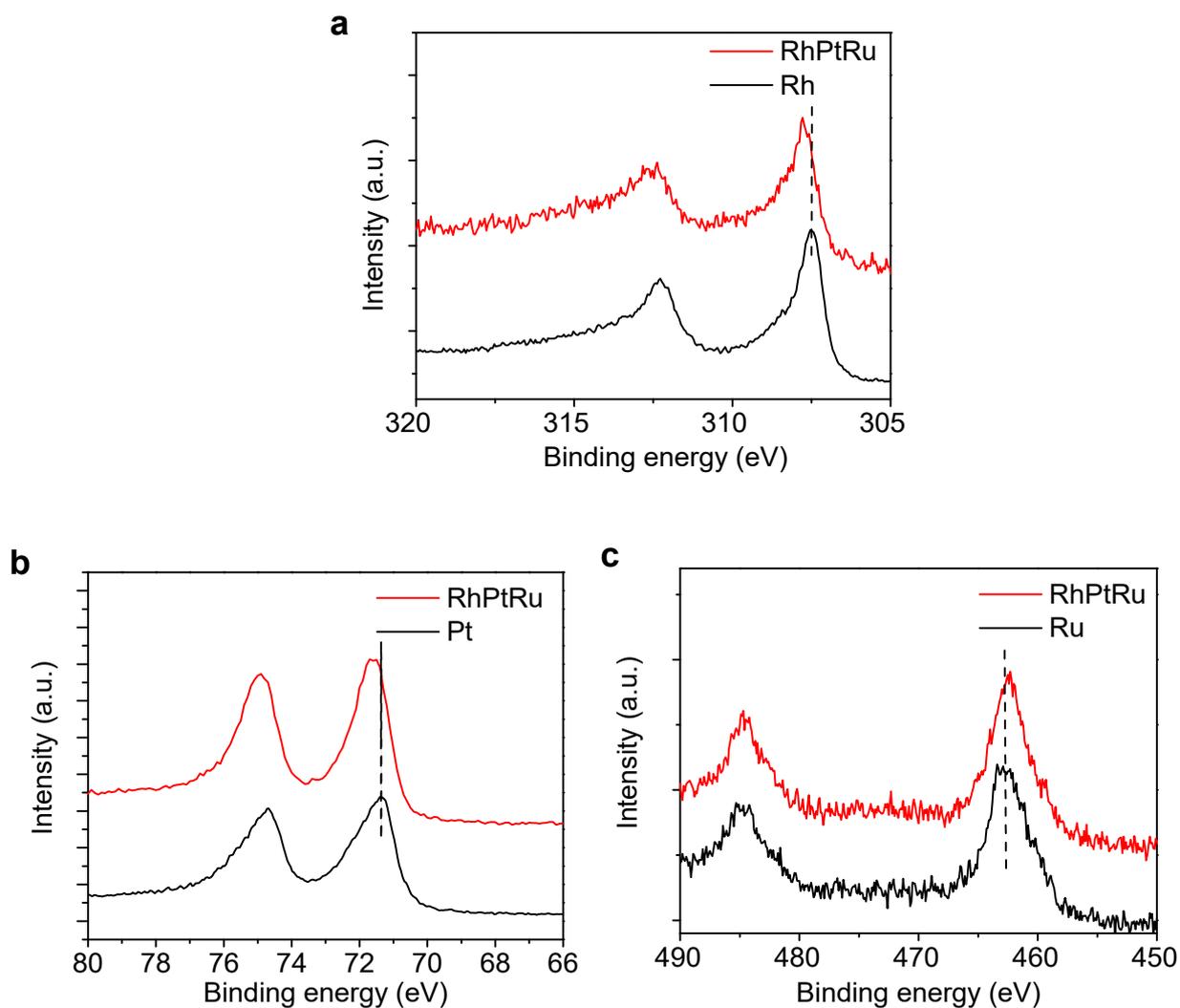
**Fig. S1** (a-c) XPS of (a) Rh 3d and (b) Pt 4f (c) Ru 3p levels of carbon felt-supported Rh, RhPt, and RhPtRu samples. XPS spectrum were calibrated using the adventitious C 1s at 284.8 eV. The binding energies of Rh 3d (by 0.3 eV) and Pt 4f (by 0.3 eV) increase, while the binding energy of Ru 3p decreases by 0.3 eV for RhPtRu catalyst. These core-level shifts are attributed to electron transfer from Rh and Pt to Ru upon alloying.[1]
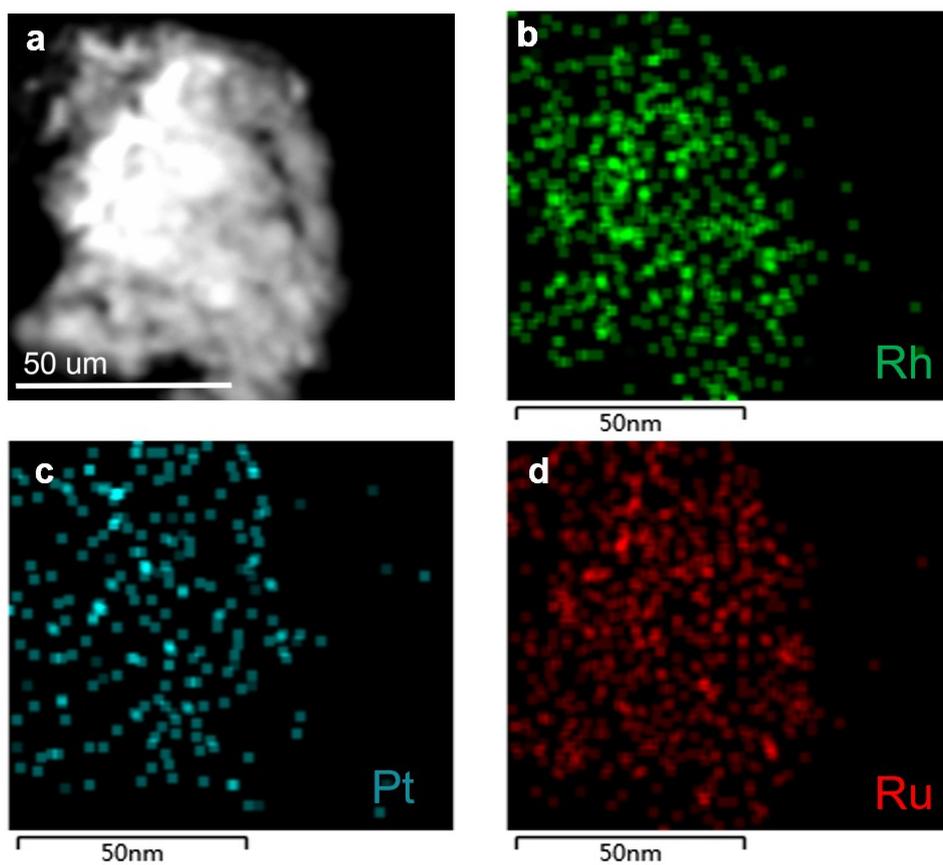
**Fig S2**. STEM and EDX mapping images of ternary RhPtRu alloy.
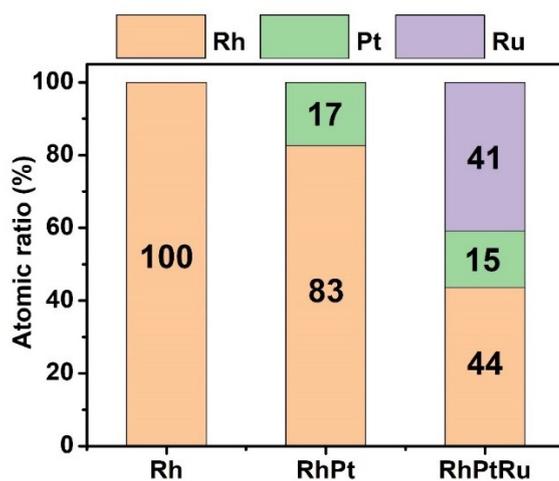


**Fig. S3** Atomic ratios of Rh, RhPt, and RhPtRu samples analyzed by XPS results.
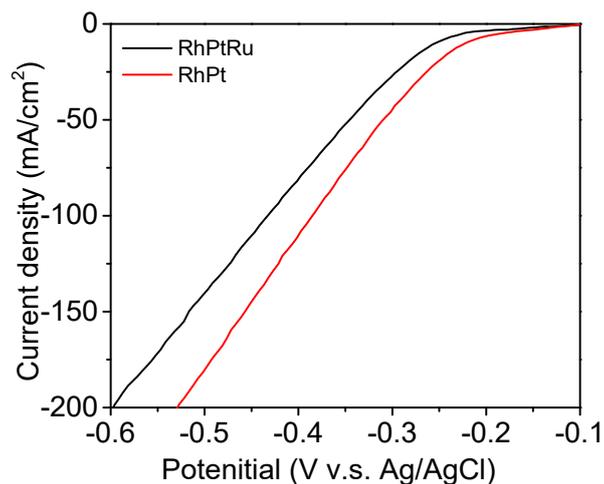
**Fig. S4** Linear sweep voltammetry plots of RhPt and RhPtRu in 0.2 M HClO$_4$, indicating the decreased HER activity on RhPtRu compared to RhPt.
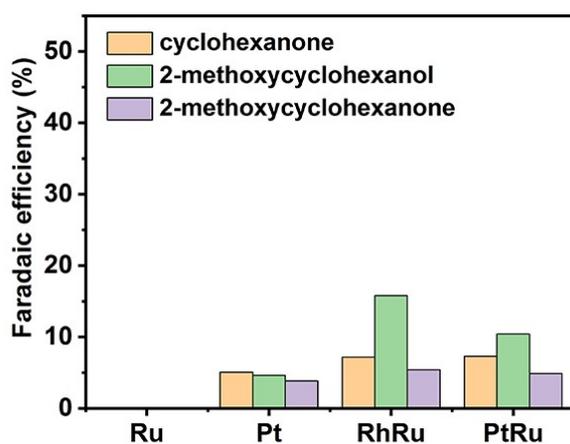


**Fig. S5** Faradaic efficiency toward hydrogenated products from guaiacol using various control catalysts at 50 mA·cm$^{-2}$ for 1 h electrocatalytic reaction.
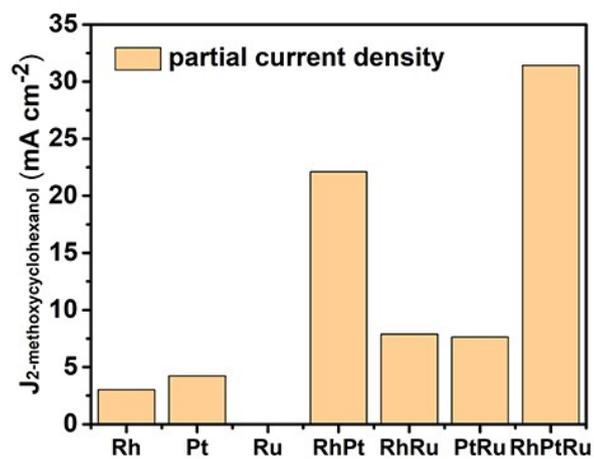
**Fig. S6** Partial current density toward methoxylated cyclohexanes on all electrocatalysts screened in this work. The total current density of 50 mA·cm$^{-2}$ was applied for the electrocatalytic hydrogenation of guaiacol.

**Table S1** Summary of catalysts that aiming to preserve the methoxy group via electrocatalytic hydrogenation (ECH). S: selectivity; I: current density applied; FE: faradaic efficiency.

| Catalyst | T (ºC) | Proton source | Reactant | Product | S (%) | I (mA·cm$^{-2}$) | F.E. (%) | Reference |
|---|---|---|---|---|---|---|---|---|
| RhPtRu | 25 | $H_2O$ | Guaiacol | 2-Methoxycyclohexanol/-none | 91.2 | 50 | 62.8 | This work |
| Raney Ni | 75 | $H_2O$ | Mequinol | 4-Methoxycyclohexanol | 48 | 8 | 15.2 | *Green Chem.* **17**, 601-609 (2015) |
| Ru/ACC | 50 | $H_2O$ | Guaiacol | 2-Methoxycyclohexanol | 62 | 25 | 31 | *Green Chem.* **14**, 2540-2549 (2012) |
| Ru/ACC-1 | 80 | $H_2O$ | Guaiacol | 2-Methoxycyclohexanol | 48 | 24 | 19.4 | *ACS Sustain. Chem. Eng.* **7**, 8375-8386 (2019) |
| PtNiB/C | 60 | $H_2O$ | Guaiacol | 2-Methoxycyclohexanone | 7 | 20 | 7 | *Adv. Funct. Mater.* **29**, 1807651 (2019) |
| Pt/C | 35 | $H_2O$ | Guaiacol | 2-Methoxycyclohexanol/-none | 14.5 | 100 | 18.2 | *Energy Environ.Sci.* **13**, 917-927 (2020) |
| Pd/C | 55 | $H_2O$ | Guaiacol | 2-Methoxycyclohexanone | 43.7 | 100 | 41.2 | *Energy Environ.Sci.* **13**, 917-927 (2020) |
| Rh/C | 55 | $H_2O$ | Guaiacol | 2-Methoxycyclohexanol/-none | 45.9 | 100 | 41.8 | *Energy Environ.Sci.* **13**, 917-927 (2020) |
| Pt/Al$_2$O$_3$ | 55 | $H_2O$ | Guaiacol | 2-Methoxycyclohexanol/-none | 8.2 | 100 | 7.3 | *Energy Environ.Sci.* **13**, 917-927 (2020) |
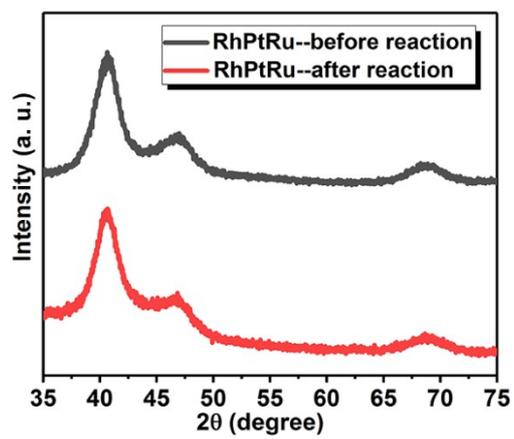
**Fig. S7** XRD patterns of RhPtRu catalyst before and after electrocatalytic hydrogenation reaction.
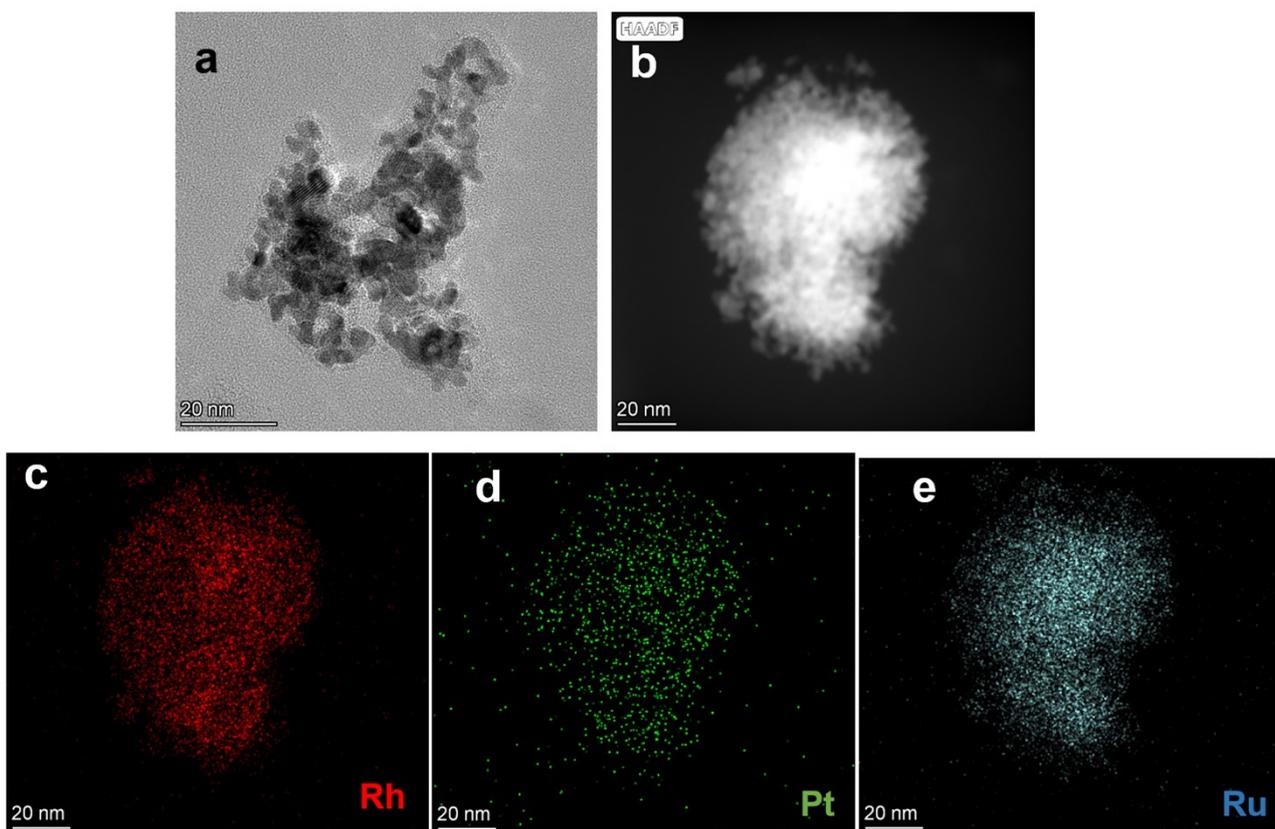
**Fig. S8** TEM (a), HAADF (b) with EDX mapping (c-e) images for carbon felt-supported RhPtRu catalyst before and after 40h ECH.
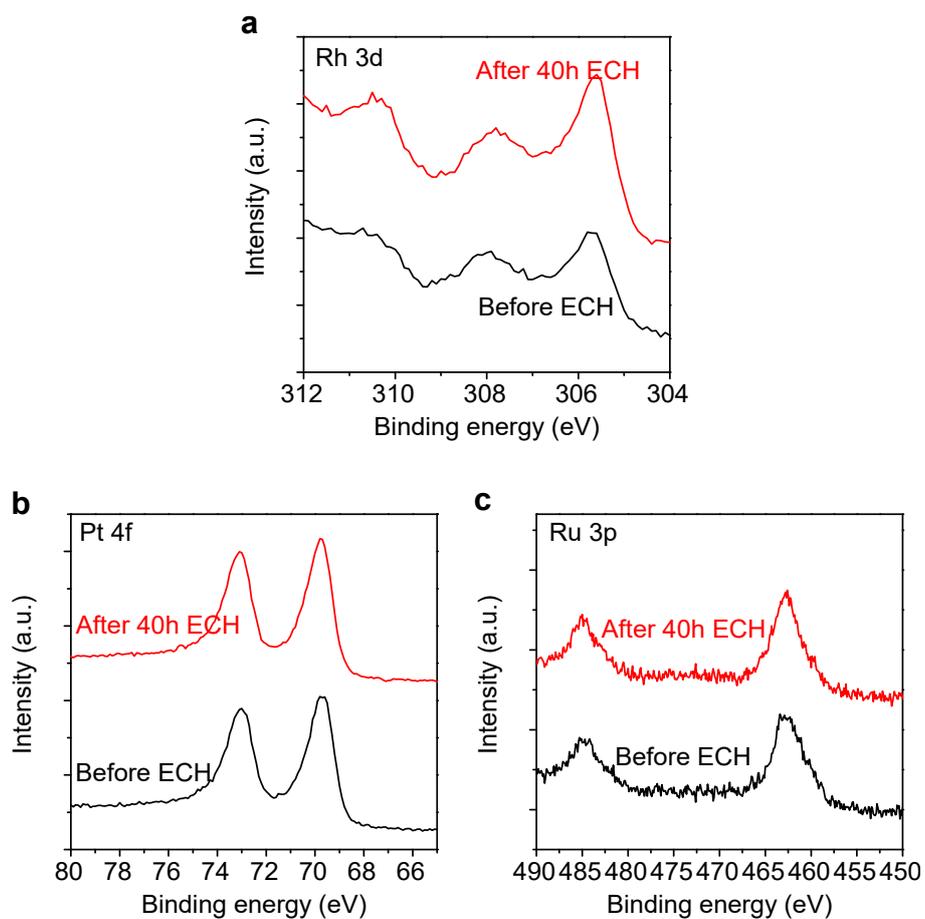
**Fig. S9** X-Ray photoelectron spectral regions for (a) Rh 3d (b) Pt 4f and (c) Ru 3p levels of carbon felt-supported RhPtRu catalyst before and after 40h ECH.

### Techno-economic analysis (TEA)

We assume the production capacity of the plant is fixed at 100 kg per day. The prices of guaiacol and methoxy-cyclohexanes are $10/kg and $431/kg (ChemicalBook), respectively. We calculated the total current need to hydrogenate the guaiacol using the following equation:

$$Total\ Current\ needed\ (A) = \frac{Plant\ capacity\left(\frac{kg}{day}\right) \times No.\ of\ electron\ ransfered\ \times 96485\ (\frac{C}{mol})}{Product\ molecular\ weight\left(\frac{kg}{mol}\right) \times 86400\left(\frac{second}{day}\right) \times FE\ (\%)}$$

**(5)**

The cost of the electrolyzer is $920/m² [2]. The surface area needed and total cost for electrolyzer are calculated based on the current density (note 1 mA·cm$^{-2}$ = 10 A·m$^{-2}$) as follows:

$$Tatal\ Surface\ area\ needed\ (m^2) = \frac{Total\ current\ needed\ (A)}{Current\ density\ (\frac{A}{m^2})}$$

**(6)**

$$Tatal\ electrolyzer\ cost\ (\$) = Tatal\ Surface\ area\ needed\ (m^2) \times 920\ (\frac{\$}{m^2})$$

**(7)**

$$Electrolyzer\ cost\left(\frac{\$}{kg}\right) = \frac{Total\ electrolyzer\ cost\ (\$) \times Capital\ recovery\ factor}{Capitcity\ factor\ \times Production\ (\frac{kg}{day})}$$

**(8)**

We assume the membrane cost is 5 % of the total electrolyzer cost.

$$Membrane\ cost\left(\frac{\$}{kg}\right) = \frac{Total\ cost\ of\ electrolyzer\ (\$)\ \times 5\%}{Electrolyzer\ lifetime\ (year)\ \times 365\ day\ \times production\ (\frac{kg}{day})}$$

**(9)**

Next, the total catalyst cost is calculated based on the total surface area of the electrolyzer, catalyst loading, metal precursor cost, and electrode preparation cost:

$$Total\ catalyst\ cost\ (\$)$$
$$= Tatal\ Surface\ area\ needed\ (m^2) \times Catalyst\ loading\left(\frac{mg}{cm^2}\right) \times (\sum_{1}^{3}\frac{n\ weight\ ratio\ \times n\ precusor\ molar\ mass\left(\frac{g}{mol}\right) \times n\ pre}{n\ molar\ mass\ (\frac{g}{mol})}$$

**(10)**

Where the electrode preparation cost includes carbon felt cost (from Longshenbao, China), electrolyte cost, electrolyzer cost, and electricity cost base on the method mentioned in the Experimental Section. We assume the price of renewable electricity is 13.4 ¢/kWh (2x the average price of industrial electricity 6.7 ¢/kWh in 2020 in the United States). The FE toward methoxy-cyclohexanes and the full-cell potential are 62.8% and 3.5 V, respectively, at an operating current density of 50 mA·cm$^{-2}$ using an H-cell system. The electricity cost is calculated using following equations:

$$Power\ consumed\ (kW) = \frac{Power\ consumed\ (kW) \times 24\left(\frac{hour}{day}\right) \times Electricity\ cost\ \left(\frac{\$}{kwh}\right)}{Plant\ capacity\ \left(\frac{kg}{day}\right)} \tag{11}$$

$$Electricity\ cost\ \left(\frac{\$}{kg}\right) = \frac{Power\ consumed\ (KW) \times 24\left(\frac{hour}{day}\right) \times Electricity\ cost\ \left(\frac{\$}{kwh}\right)}{Plant\ capacity\ \left(\frac{kg}{day}\right)} \tag{12}$$

Extractive distillation has been widely applied to extract the methoxy-cyclohexanes in an aqueous solution[3], indicating a cost of 14.5 ¢/kg (200% of the reported maximum cost of 9.6 $/k mol)[3]. We assume that other operation costs as 10% of the electricity cost and that the capacity factor is 0.67 associated with an operational 16 hours a day for the plant.

$$Captical\ recovery\ factor = \frac{Discount\ rate \times (1 + Discount\ rate)^{lifetime}}{(1 + Discount\ rate)^{lifetime} - 1} \tag{13}$$

$$Maintenance\ cost\ \left(\frac{\$}{day}\right) = Maintenance\ frequency \times Maintenance\ factor\ (\%\ of\ Capital\ cost) \times Total\ capital\ cost\ \left(\frac{\$}{kg}\right) \tag{14}$$

$$Balance\ of\ plant\ \left(\frac{\$}{kg}\right) = Balance\ of\ plant\ factor\ (\%) \times Captital\ cost\ \left(\frac{\$}{kg}\right) \tag{15}$$

$$Installation\left(\frac{\$}{kg}\right) = Lang\ factor\ (\%) \times Captital\ cost\ \left(\frac{\$}{kg}\right) \tag{16}$$

## References

1 Q. Wang, Y.-W. Zhou, Z. Jin, C. Chen, H. Li and W.-B. Cai, *Catalysts 2021,* **11**.

2 M. Jouny, W. Luc and F. Jiao, *Industrial & Engineering Chemistry Research 2018,* **57**, 2165-2177.

3 C. Yin and G. Liu, *Processes 2021,* **9**, 565.