Supporting Information

Efficient Electrocatalytic Hydrogenation of Cinnamaldehyde to Value-added Chemicals

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This file includes Figs. S1-S20 and Tables S1-S2.

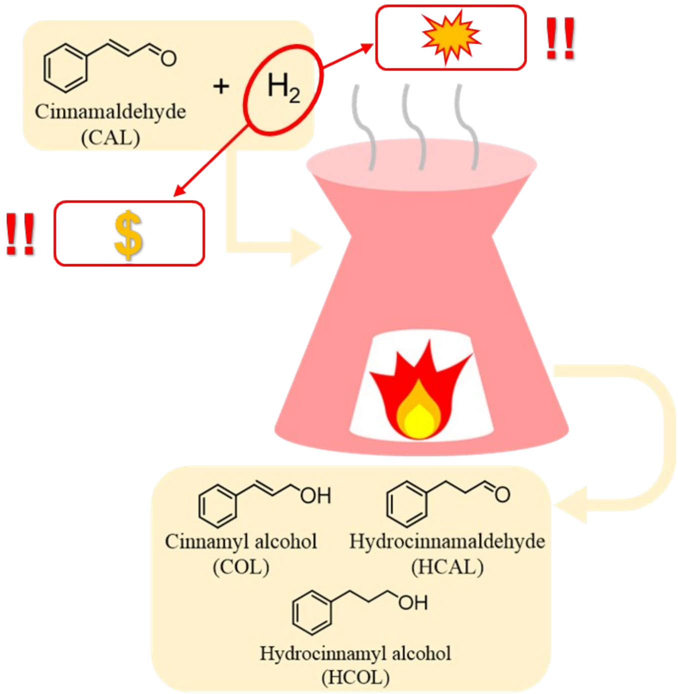

Fig. S1. Traditional thermocatalytic approach for CAL hydrogenation.

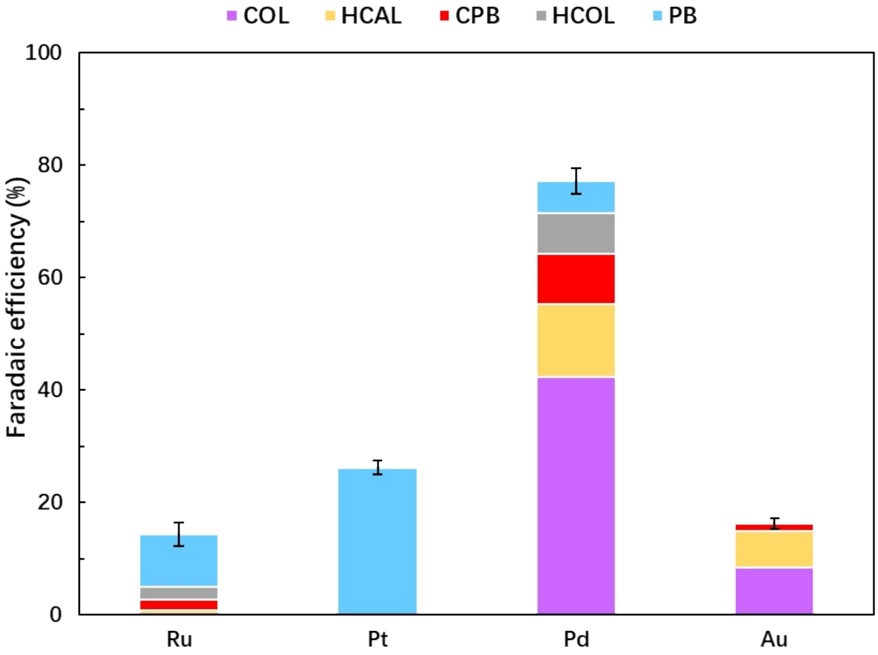

Fig. S2. FE for different metal catalysts. Each catalyst was prepared through electrodeposition onto carbon felt in an electrolyte containing 7 mM of the corresponding metal precursor.

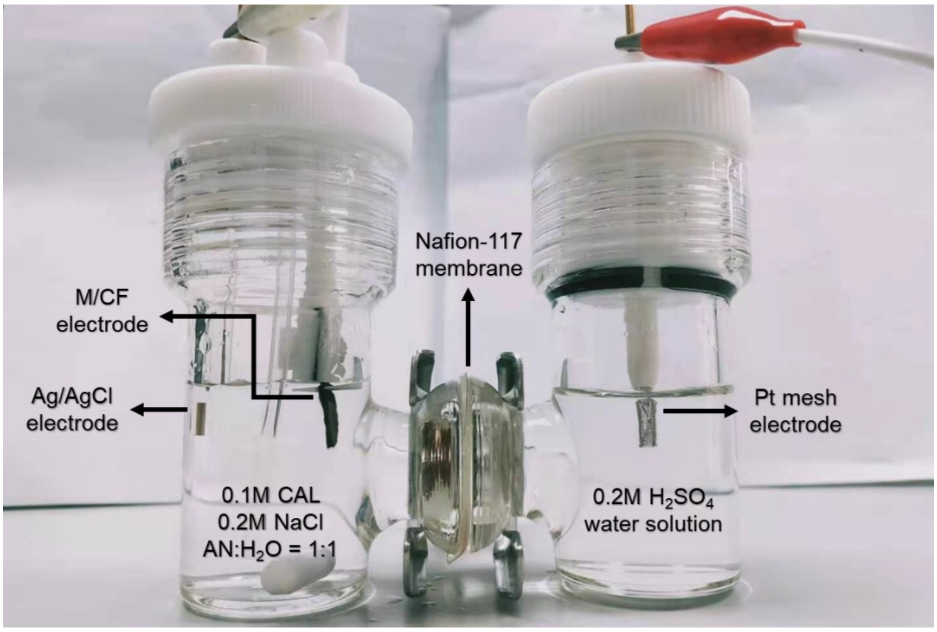

Fig. S3. Photograph of the H-cell reaction system.

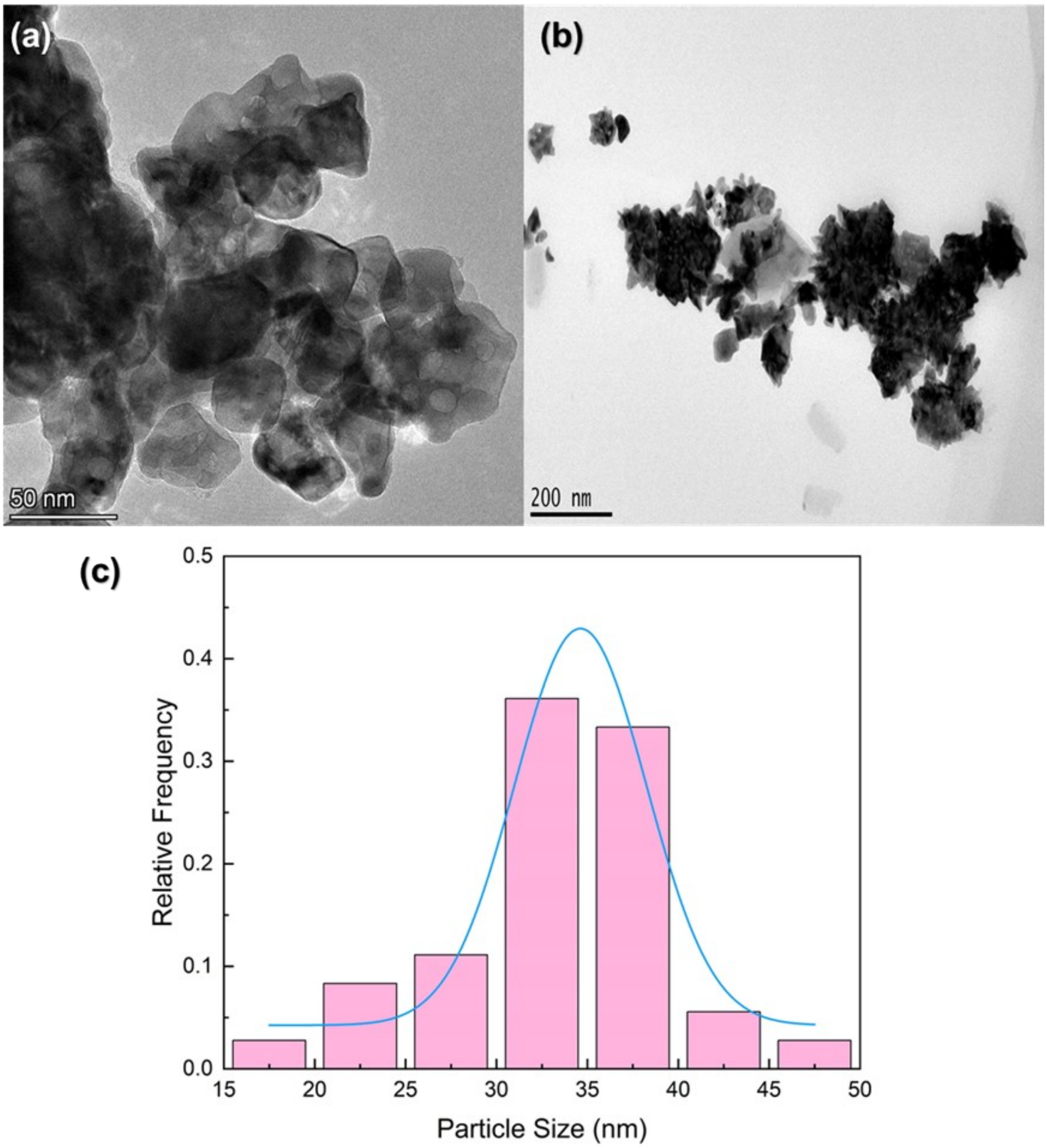

Fig. S4. (a,b) HRTEM patterns of the Pd catalyst. (c) Particle sizes distribution of Pd in the CF.

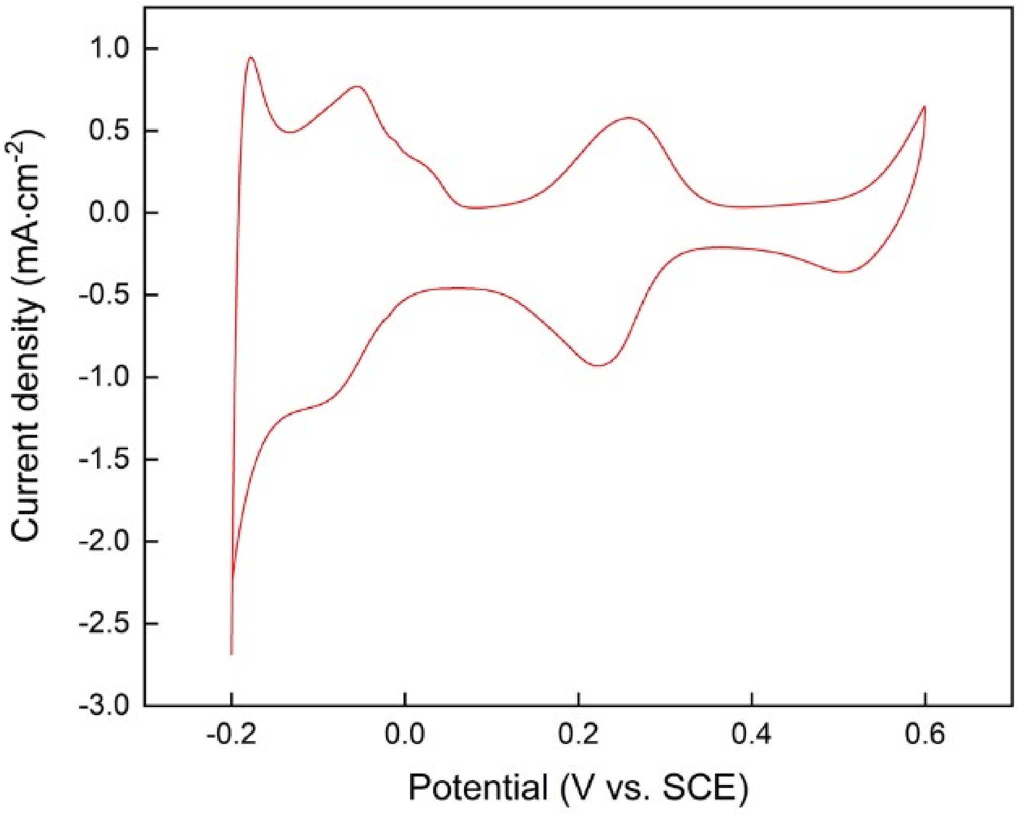

Fig. S5. CV diagram for underpotential deposition of Cu on Pd/CF cathode. The charge density is about 708.2 μC·cm^{-2}.

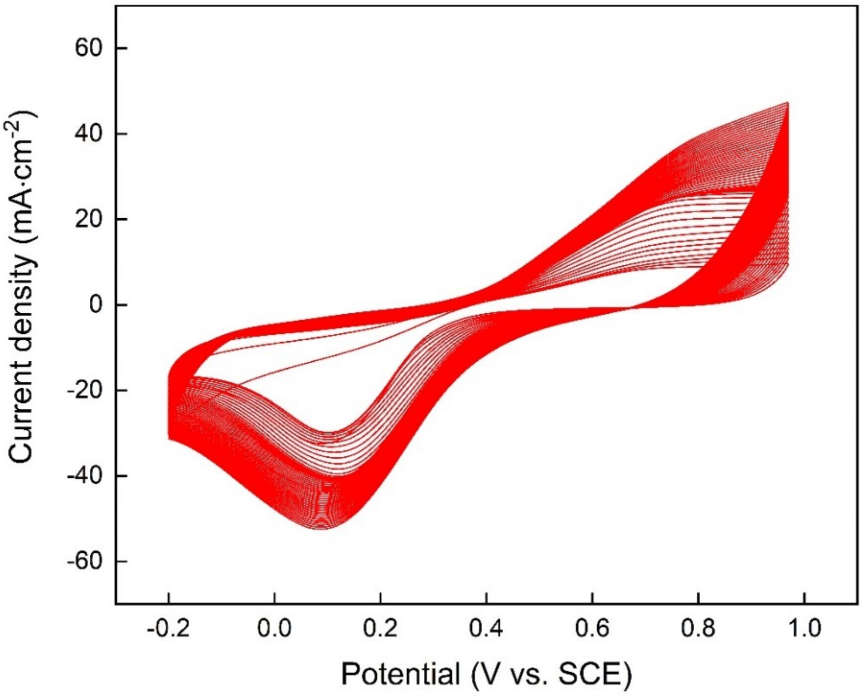

Fig. S6. Cyclic voltammetry curves for electrodepositing nano Pd on the surface of CF.

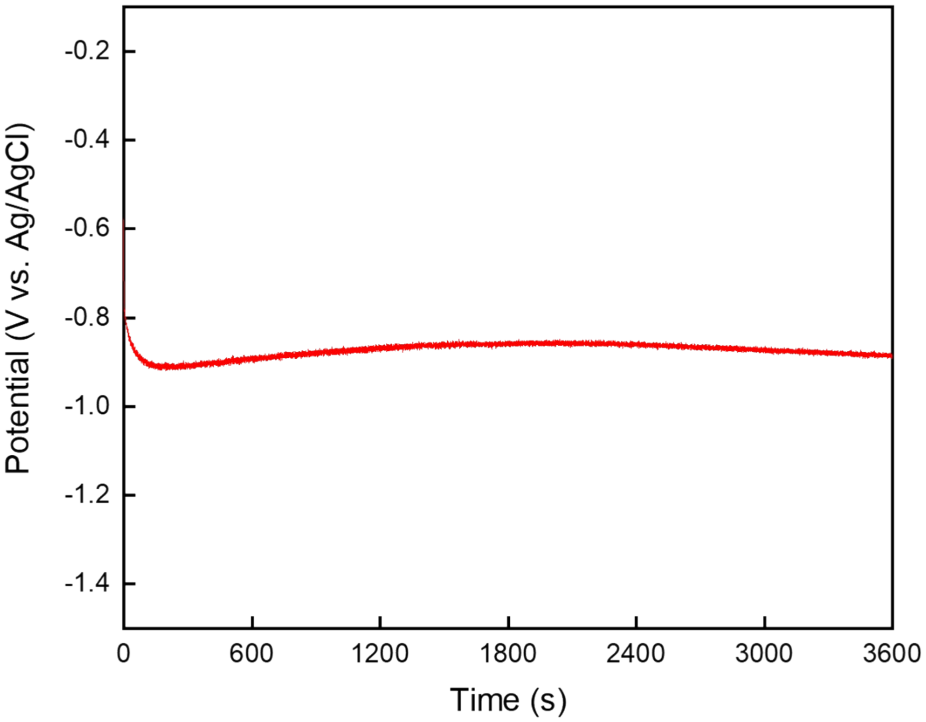

Fig. S7. I-t curve for ECH of CAL over Pd/CF electrode (cathode) for 1 h at a current density of 50 mA·cm^{-2}.

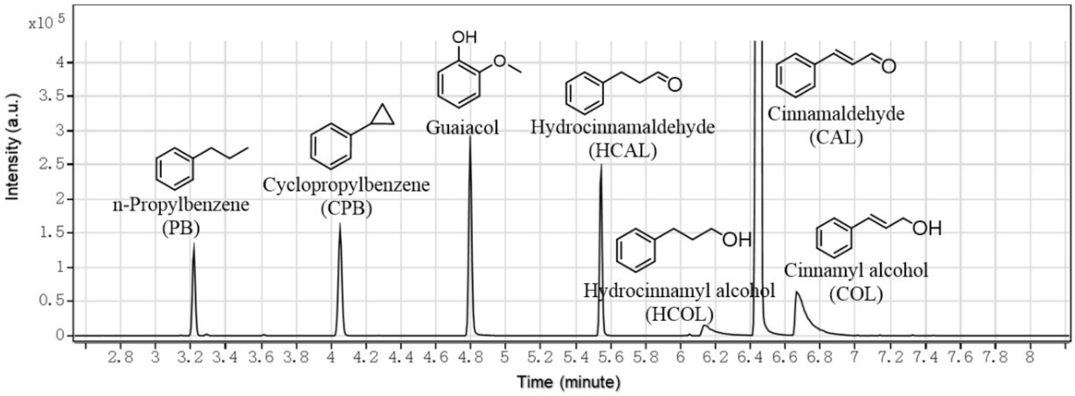

Fig. S8. (a) Gas chromatogram spectrum of the products *via* ECH of CAL over Pd/CF electrode by GC-MS.

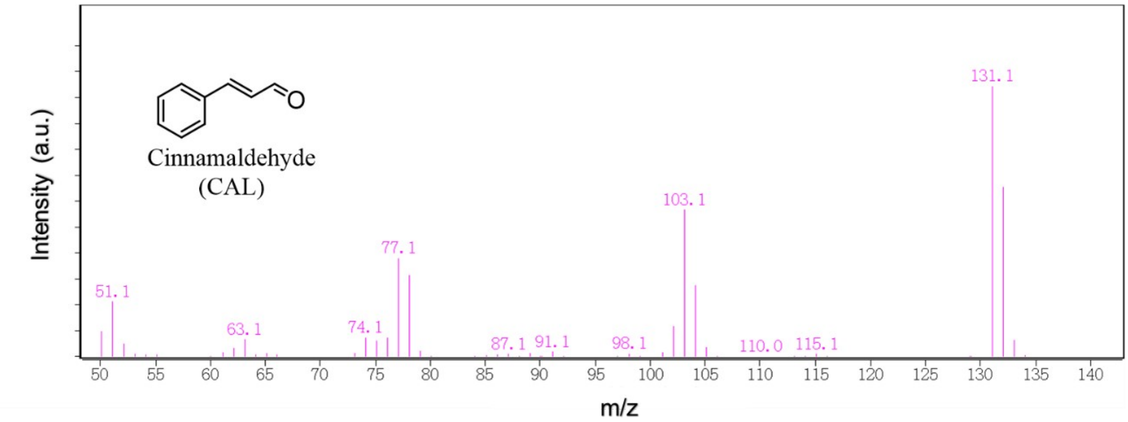

Fig. S9. Mass spectrum and identification result of CAL.

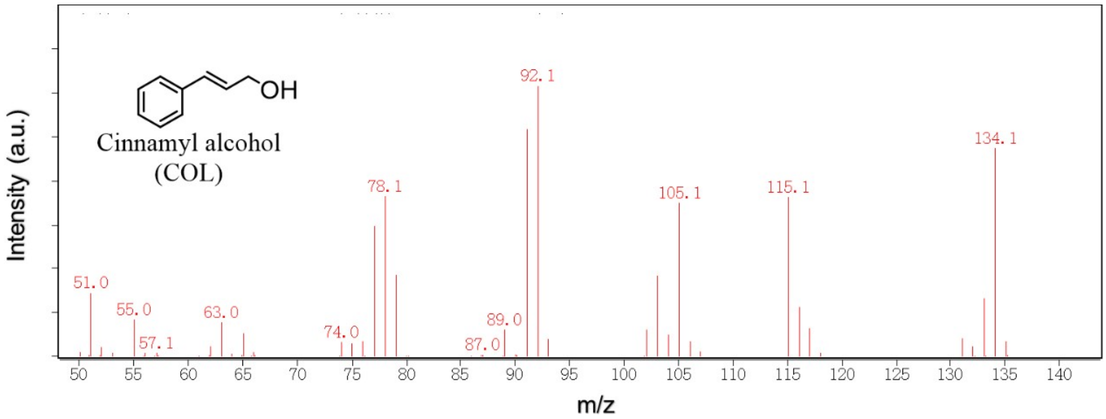

Fig. S10. Mass spectrum and identification result of COL.

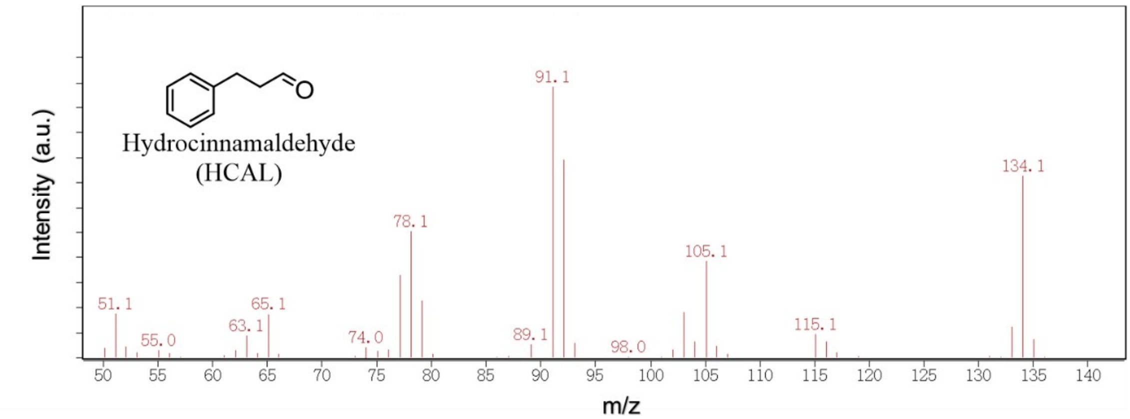

Fig. S11. Mass spectrum and identification result of HCAL.

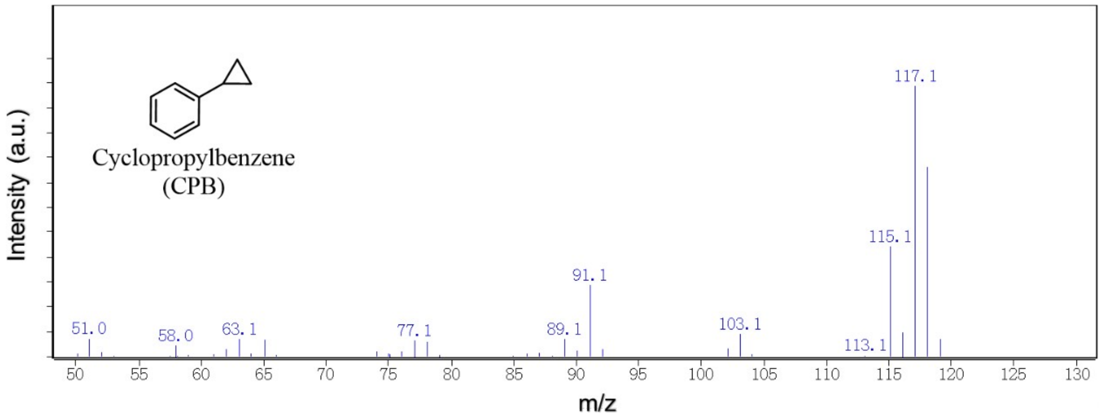

Fig. S12. Mass spectrum and identification result of CPB.

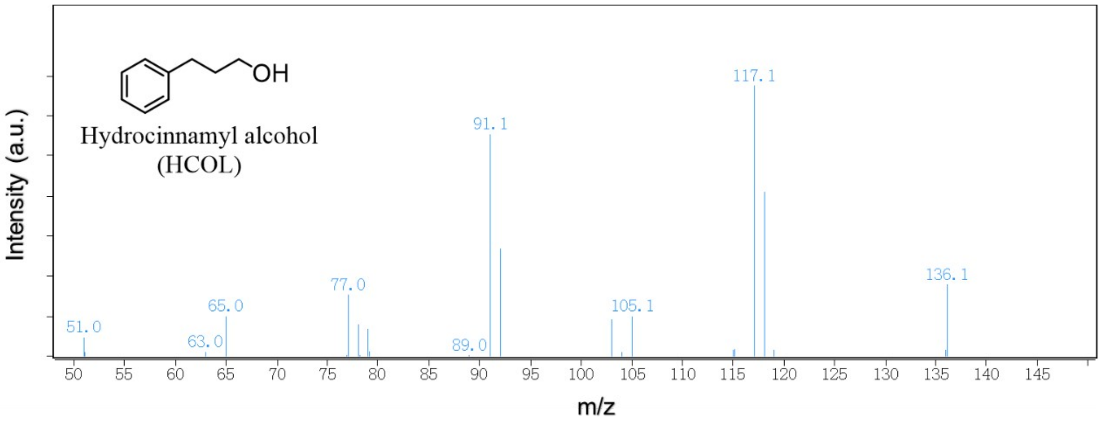

Fig. S13. Mass spectrum and identification result of HCOL.

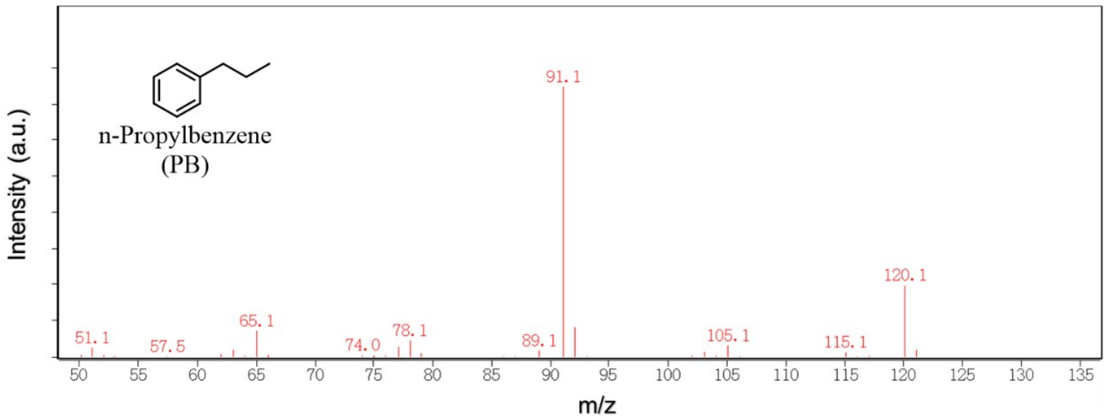

Fig. S14. Mass spectrum and identification result of PB.

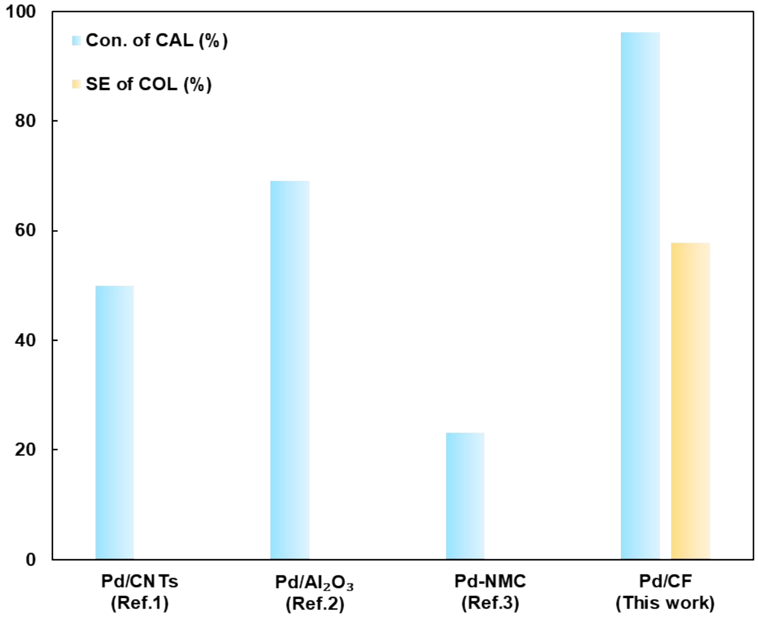

Fig. S15. Comparison of conversion (Con.) of CAL and selectivity (SE) of COL from the CAL hydrogenation by various Pd catalysts.[1-3] Ref. 1-3 reported TCH of CAL using Pd-based catalysts.

Table S1. Conversion (Con.) of CAL and selectivity (SE) of COL from the CAL hydrogenation by various Pd catalysts.

Catalyst	Con. of COL (%)	SE of COL (%)
Pd/CNTs (Ref.1)	50.00	0
Pd/Al_2O_3 (Ref.2)	69.00	0
Pd-NMC (Ref.3)	23.20	0
Pd/CF (This work)	96.21	57.88

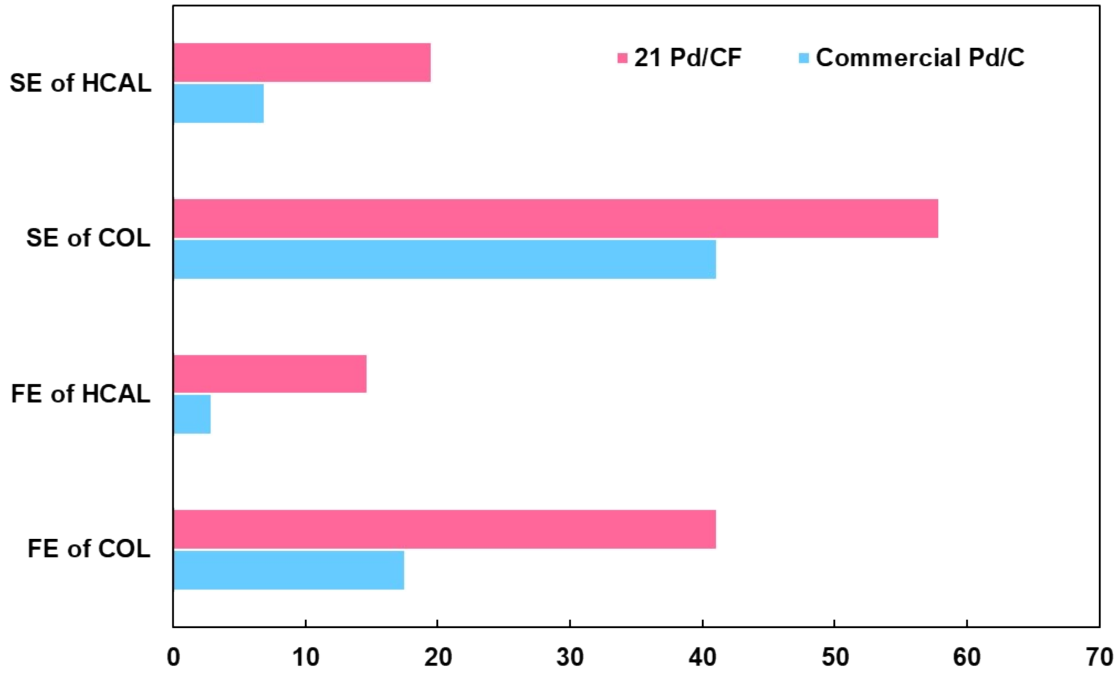

Fig. S16. FE and selectivity of COL and HCAL via 21 Pd/CF and a commercial Pd/C (Average particles ~5 nm, Macklin), indicating the preference of COL production for both electrocatalysts.

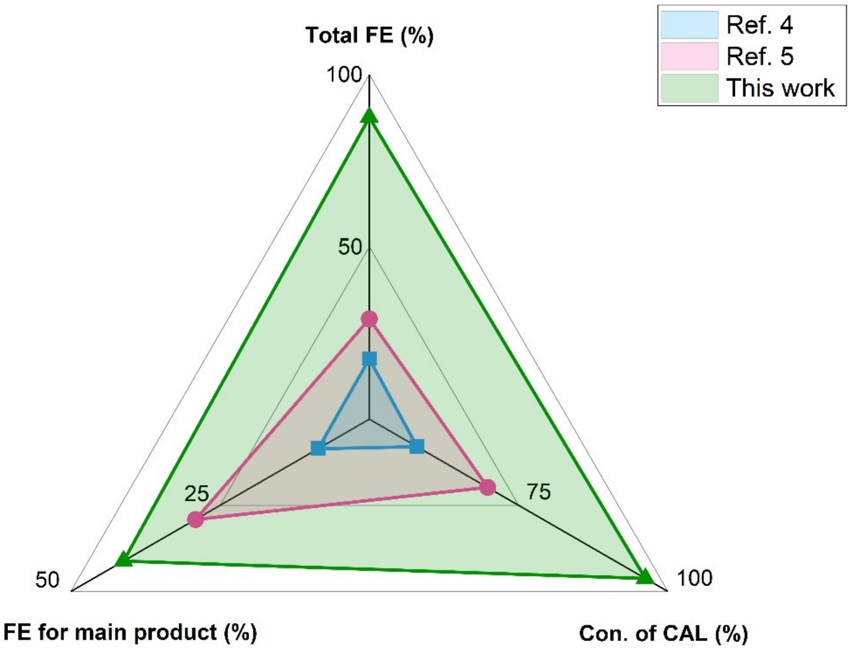

Fig. S17. The performance of this work for the ECH of CAL compared with other electrochemical-based reports.[4, 5]

Table S2: Performance comparison for the ECH of CAL. Data with a symbol * means that it was recalculated from the corresponding paper.

	Total FE (%)	Con. of CAL (%)	FE for main product (%)
Ref. 4	17.47	58.00	8.59*
Ref. 5	29.10	69.80	29.10
This Work	87.54	96.21	41.15

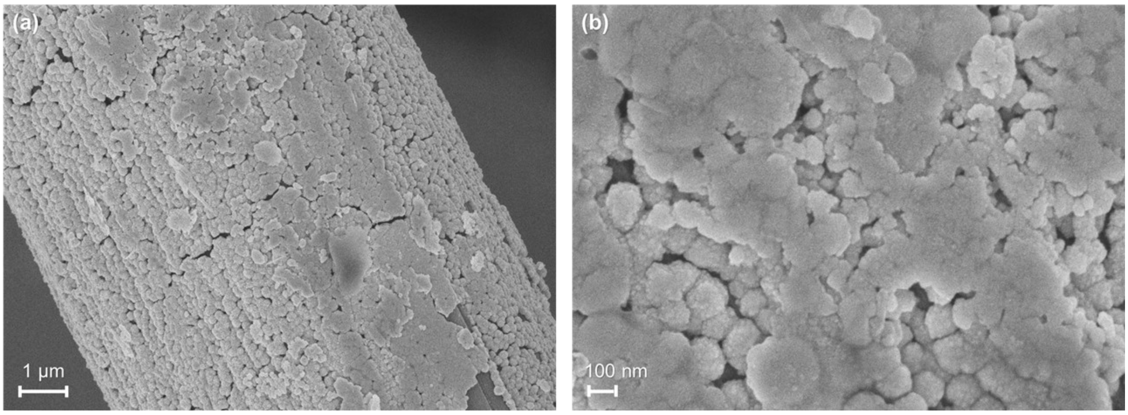

Fig. S18. (a-b) SEM images of the Pd/CF after stability test

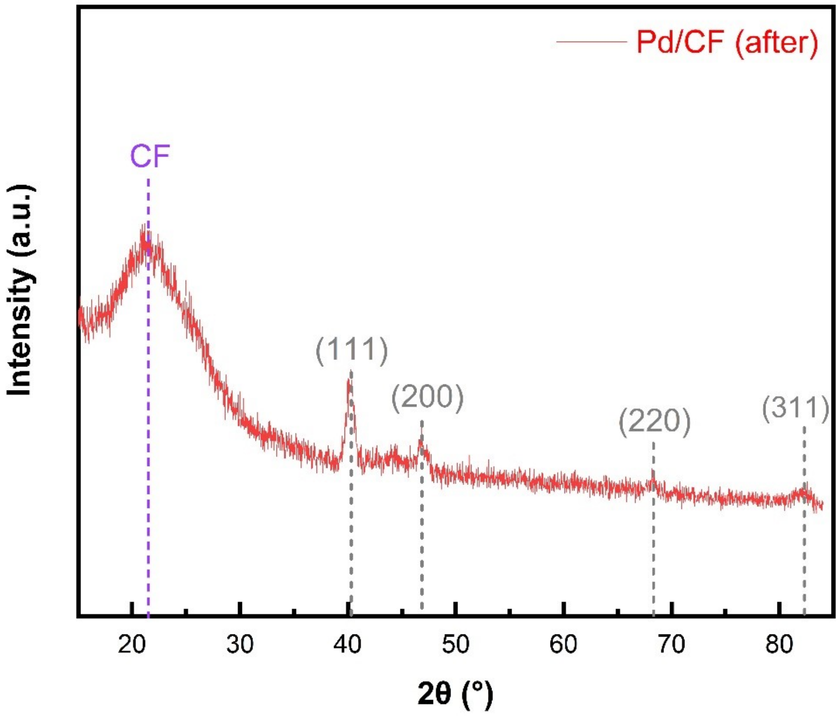

Fig. S19. XRD pattern of Pd/CF electrode after stability test.

Fig. S20. Photograph of the flow reactor experiment for further stability test. The 200 mL of electrolyte was circulated through the H-cell at 70 mL/min using peristaltic pumps (Lead Fluid BT100S-1).

Preliminary Technoeconomic analysis (TEA):

We performed a preliminary TEA to evaluate the economic potential of ECH of CAL using a modified reported model[6, 7]. Plant-gate levelized cost consists of 7 parts: operational cost, cost of input chemicals, balance of plant, capital cost, maintenance cost, electricity cost, and installation cost. All units are in US dollars per ton during calculation.

Assumption for TEA:

1. The electrolyzer cost is set as 920 $\$/m^2$ based on Matthew Jouny *et al.*'s report.[8]
2. The electricity cost per KWh is calculated as 14.04 c/KWh, which is 2 times as the industrial electricity price of 7.02 c/KWh in 2022.[9] (Data was obtained from U.S. Energy Information Administration)
3. Separation cost of products and solvent is assumed to be 20% of electricity cost, which is 2 times of the literature reports.[7, 9, 10] The solvent is assumed to be recyclable after separation.
4. Other operational cost of is assumed to be 20% of electricity cost, which is 2 times of the previous research work.[6, 7]
5. The capacity factor is assumed to be 0.8, which means the plant will work for 19.2 hours per day.[7]
6. The Faradaic efficiency of ECH to COL is 42.06%, same as that in the 20-hour stability test. The cell voltage is 8.70 V at a current density of 50 $mA\cdot cm^{-2}$.

7. The current market price of CAL and COL are assumed to be 890.0 \$/ton and 8955.2 \$/ton. (Data was obtained from Alibaba)
8. The production of COL is assumed to base on the input amount of CAL, which is set as 1 ton/day. The yield of COL is set as 60.52% according to our experimental results.
9. The loading of Pd on the carbon felt is assumed to be 6.9 wt% based on the ICP-OES result. Considering the cost of catalyst synthesis in actual production, the cost of Pd/CF catalyst is assumed to be same as the price of commercial Pd powder catalyst about 12000.0 \$/kg, while the cost of Pt mesh is assumed to be 8000 \$/kg. (Data was obtained from Alibaba)
10. The cost of Dupont nafion-117 membrane is assumed to be 2084.4 \$/m^2 (Data was obtained from Alibaba)
11. The lifetime of catalyst and membrane is assumed to be 4 months.

Formulas for TEA:

1. Catalyst and membrane:

$$Total\ cost\ of\ catalyst\ (\$) = \Sigma mass\ of\ catalyst\ (kg) \times Price\ of\ catalyst\ (\$/kg)$$

$$Total\ cost\ of\ membrane\ (\$) = Area\ of\ membrane\ \left(m^2\right) \times Price\ of\ membrane\ (\$/m^2)$$

$$Catalyst\ and\ membrane\ cost\ (\$) = Total\ cost\ of\ catalyst\ (\$) + Total\ cost\ of\ membrane\ (\$)$$

2. Electrolyzer and electricity

$$Total\ current\ needed\ (A) = \frac{Plant\ capacity(ton/day) \times numbers\ of\ electron\ transferred\ in\ reactic}{Molecular\ weight\ of\ product\ (ton/mol) \times 86400\ (s/day) \times Fa}$$

$$Total\ eletrolyzer\ area\ needed\ \left(m^2\right) = \frac{Total\ current\ needed\ (A)}{Current\ density\ \left(A/m^2\right)}$$

$$Total\ cost\ of\ electrolyzer\ (\$) = Total\ electrolyzer\ area\ needed\ (m^2) \times Electrolyzer\ price\ per\ \ (\$/m^2)$$

$$Electrolyzer\ cost\ (\$/ton) = \frac{Capital\ recovery\ factor \times Total\ cost\ of\ electrolyzer\ (\$)}{365\ (day/year) \times capacity\ factor \times Production\ (ton/day)}$$

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

$$Power\ consumed\ (kW) = \frac{Total\ current\ needed\ (A) \times Voltage\ of\ reaction\ cell\ (V)}{1000 (W/kW)}$$

$$Electricity\ cost\ per\ ton\ of\ product\ (\$/ton) = \frac{Power\ consumed\ (kW) \times Electricity\ cost\ (\$/kWh) \times 24 (hour/day)}{Plant\ capacity\ (ton/day)}$$

3. Maintenance

$$Maintenance\ cost\ (\$/ton) = 20\% \times Maintenance\ frequency \times Total\ capital\ cost\ (\$/ton)$$

4. Balance of plant

$$Balance\ of\ plant\ (\$/ton) = Balance\ of\ plant\ factor\ (\%) \times Total\ Capital\ cost\ (\$/ton)$$

5. Installation

$$Installation\ cost\ (\$/ton) = Lang\ factor\ (\%) \times Capital\ cost\ (\$/ton)$$

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