

# Synthesis of *p*-cymene by electrocatalytic oxidation of $\alpha$ -terpinene and $\gamma$ -terpinene

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## Experimental

### *Procedures for synthesis of p-cymene*

Quantified matrix (including electrolyte of *n*-Bu<sub>4</sub>NClO<sub>4</sub>, catalyst of TEMPO, base), substrate ( $\alpha$ -TP or  $\gamma$ -TP) and solvents were added in an unsealed electrolytic reactor. Platinum sheet (1.0 cm × 1.0 cm) was used as the positive electrode and platinum net (1.0 cm × 1.0 cm) as the negative electrode. After a certain time of constant current electrolysis at room temperature under air condition, the products were collected. In this experiment, different base, substrate concentration, base concentration, TEMPO concentration, current and water addition on the effects of selectivity and yield of *p*-cymene were investigated successively.

### *Procedures for detection of p-cymene*

The contents of *p*-cymene were analyzed by gas chromatography method. Specifically, 0.1 mL of the product put into 1 mL MeCN and sufficient amount of anhydrous sodium sulfate used to dehydration, shake well and inject into GC (7890B, Agilent Technologies, Inc.). The GC was equipped with HP-5 column, FID detector. Both inlet temperature and detector temperature are 250°C. Air flow rate 400 mL/min, hydrogen flow rate 30 mL/min, nitrogen flow rate 1.0 mL/min, split ratio 5:1 and injection volume 1  $\mu$ L. Program heating: the initial temperature was 50°C and kept for 1 min, then increased to 320°C under the rate of 30°C/min, finally, kept for 1 min. The retention time was used for qualitative analysis and the standard curve method was used for quantitative analysis ( $C=1906.65A-67.82$ ,  $R^2=0.99965$ ).

### *Cyclic voltammetry experiments*

All cyclic voltammetry measurements were performed in an undivided reactor under air at room temperature by an electrochemical workstation (Interface 1010E, Gamry Instruments, USA). Acetonitrile (9.5 mL) and distilled water (0.5 mL) as solvent, 100 mM *n*-Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte. Glassy carbon electrode (diameter 5 mm) as the working electrode, platinum gauze (1.0 cm × 1.0 cm) as the counter electrode and saturated calomel electrode (SCE) as the reference electrode.

### *DFT calculations*

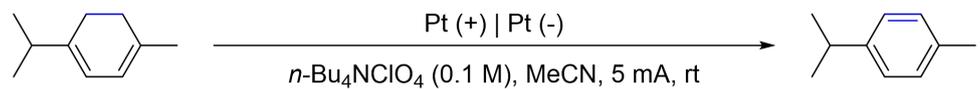
All calculations were processed by using Gaussian 16 program.<sup>1</sup> Structures were optimized in the gas phase at M06-2X/def2-SVP levels.<sup>2,3</sup> Subsequently, harmonic frequency analysis calculations were performed to verify the optimized geometries with the lowest energy conformation (no imaginary frequency) or transition states (TSs, with a unique imaginary frequency) and provided a thermal contribution of free energies at 298.15 K. The transition states were verified by the calculation of intrinsic reaction coordinate (IRC). In order to improve the energy accuracy, single-point energy was calculated at the level of M06-2X/def2-TZVP, and continuum solvation model of SMD was used to reflect the solvation effect.<sup>3,4</sup>

## Notes and references

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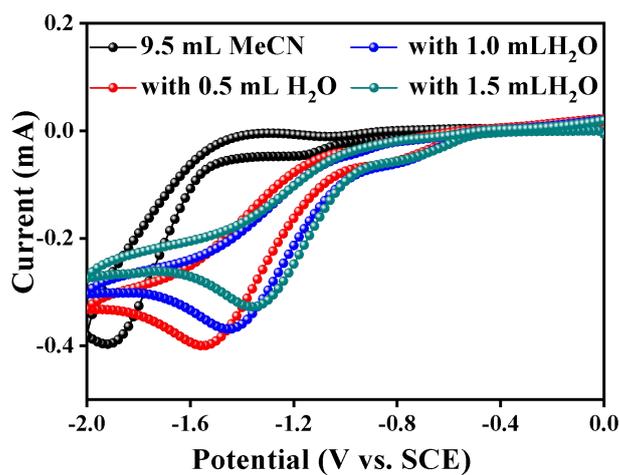
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**Table S1** The effect of different electrocatalysts.

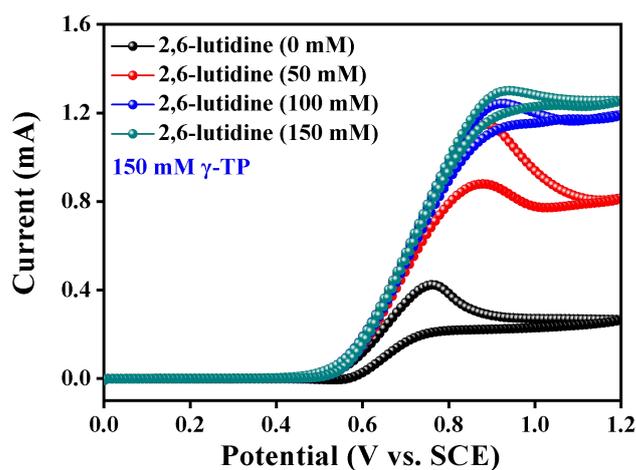


Entry <sup>a</sup>	Electrocatalysts	Yield/% <sup>b</sup>
1	None	35
3	Cp <sub>2</sub> Fe	20
4	Ar <sub>3</sub> N	41
2	TEMPO	46

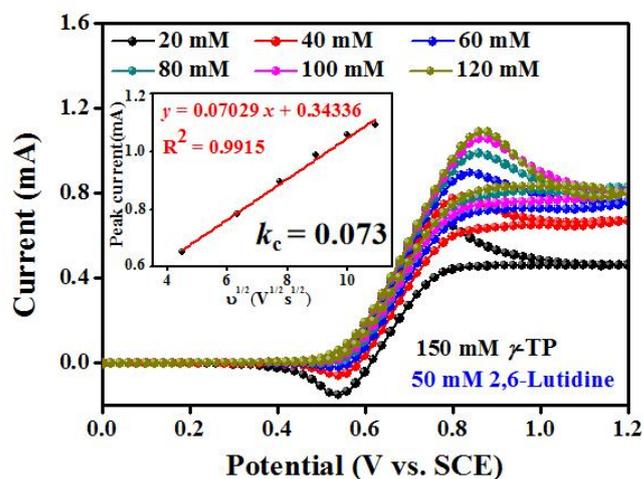
Other conditions:  $\alpha$ -TP (1.5 mmol),  $n$ -Bu<sub>4</sub>NClO<sub>4</sub> (1.0 mmol), MeCN (10 mL), Pt as working electrode and counter electrode, 5 mA, 18 h, room temperature.



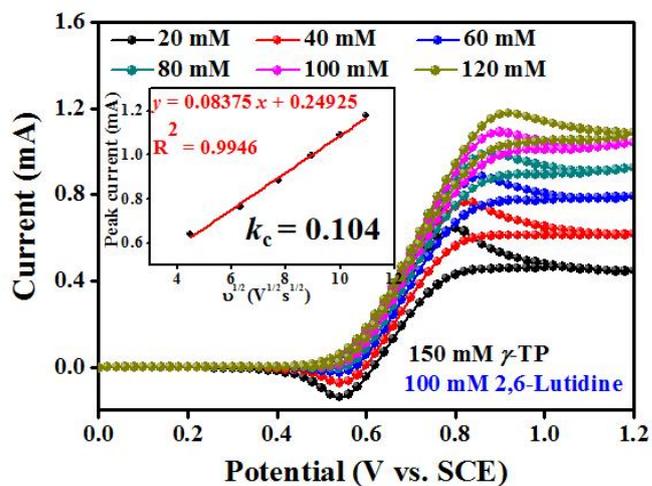
**Fig.S1.** CVs of water quantity in the electrolyte. Other conditions: 30 mM TEMPO, 150 mM  $\gamma$ -TP, scan rate 50 mV/s.



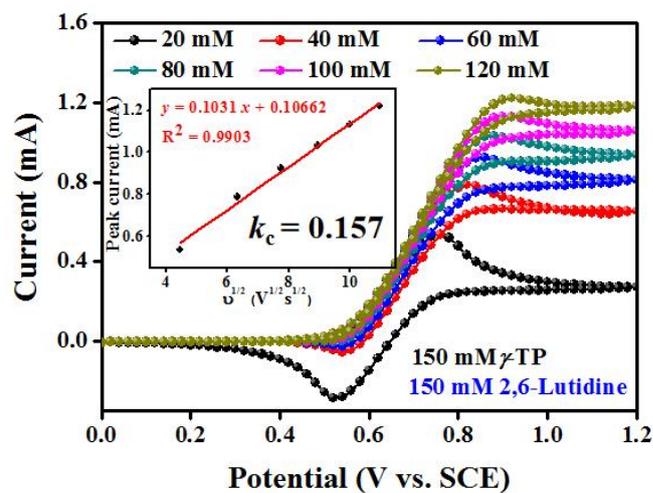
**Fig.S2.** CVs of base concentration in the electrolyte. Other conditions: 30 mM TEMPO, 150 mM  $\gamma$ -TP, scan rate 50 mV/s.



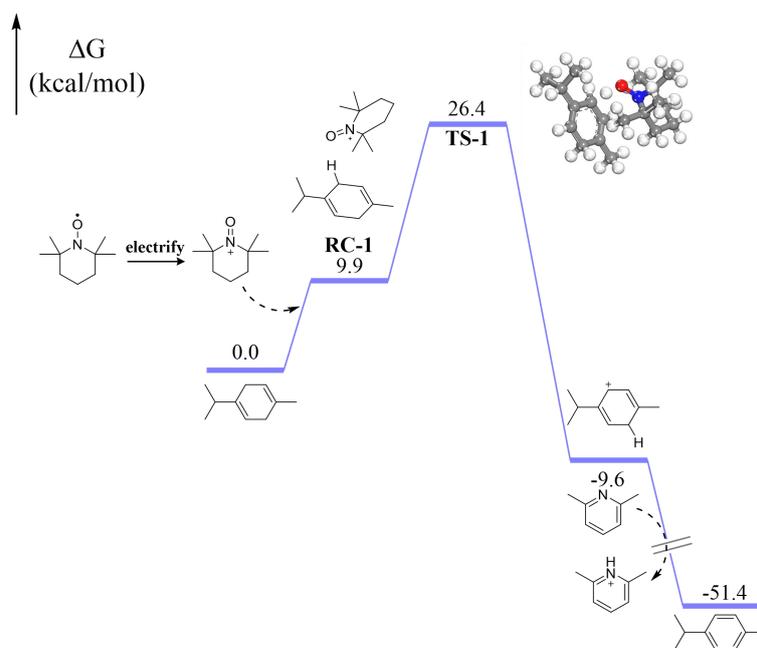
**Fig.S3.** CVs for various concentrations of  $\gamma$ -TP with 30 mM TEMPO in 50 mM 2,6-lutidine. Other conditions: glassy carbon working electrode, scan rate = 100 mV/s, 0.1 M  $n$ -Bu<sub>4</sub>NClO<sub>4</sub> in MeCN/H<sub>2</sub>O (19:1).



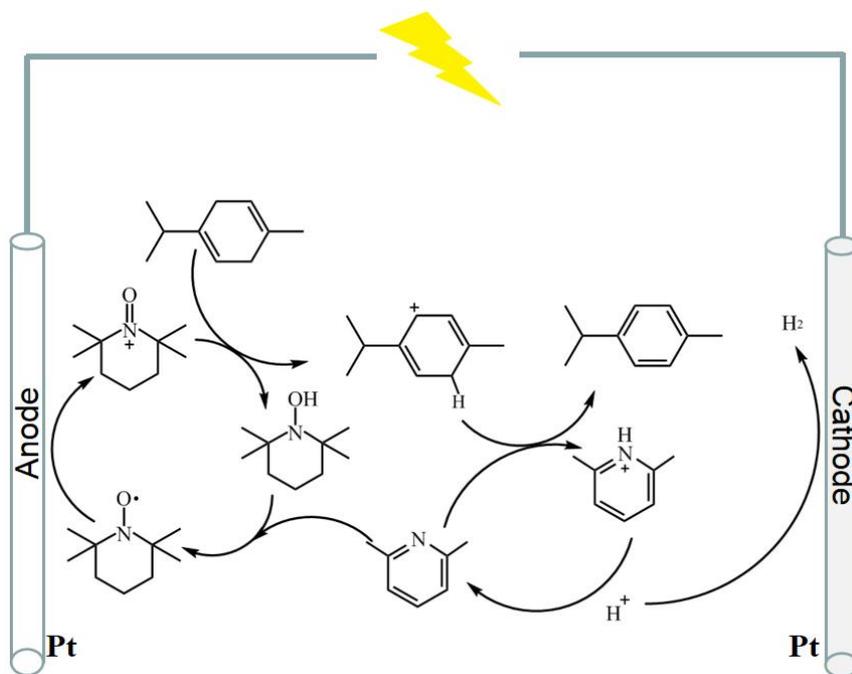
**Fig.S4.** CVs for various concentrations of  $\gamma$ -TP with 30 mM TEMPO in 100 mM 2,6-lutidine. Other conditions: glassy carbon working electrode, scan rate = 100 mV/s, 0.1 M  $n$ -Bu<sub>4</sub>NClO<sub>4</sub> in MeCN/H<sub>2</sub>O (19:1).



**Fig.S5.** CVs for various concentrations of  $\gamma$ -TP with 30 mM TEMPO in 150 mM 2,6-lutidine. Other conditions: glassy carbon working electrode, scan rate = 100 mV/s, 0.1 M  $n$ -Bu<sub>4</sub>NClO<sub>4</sub> in MeCN/H<sub>2</sub>O (19:1).



**Fig. S6.** DFT calculation of  $\gamma$ -TP electrocatalytic oxidation reaction pathway.



**Fig. S7.** Mechanism of TEMPO-mediated  $\gamma$ -TP electrocatalytic oxidation reaction assisted by 2,6-lutidine.