

Supporting Information

Deep eutectic solvents coupled with polyoxometalate trigger aerobic oxidation of 5-hydroxymethylfurfural to 5-formyl-2-furancarboxylic acid

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Experimental Procedures

Chemicals

Butyl-3-methyl imidazolium chloride ([Bmim]Cl, 99%), 1-Butyl-3-methylimidazolium bromide ([Bmim]Br, 99%), 1-Octyl-3-methylimidazolium chloride ([Omim]Cl, 99%) and 1-Dodecyl-3-methylimidazolium chloride ([C₁₂-mim]Cl, 99%) were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Acetamide (ACE, 98.5%) and Dimethyl sulfoxide (DMSO, 99%) were obtained from Sinopharm Group Chemical Reagent Co. Ltd. 5-Formyl-2-furancarboxylic acid (FFCA, 98%), *N*-Methyl-2-pyrrolidone (NMP, 99%), and Caprolactam (CPL, 99%) were gotten from Shanghai Macklin Biochemical Technology Co., Ltd. 2,5-Furandicarboxylic acid (FDCA, 98%) and Butyrolactam (BYL, 99%) were received from Shanghai Aladdin Biochemical Technology Co., Ltd. 5-Hydroxymethyl-2-furancarboxylic acid (HMFCA, 97%) and 2,5-Diformylfuran (DFF, 98%) were purchased from Ark pharm Reagent (Shanghai, China). 5-Hydroxymethylfurfural (HMF, 99%) was received from Tianjin Heowns Biochemical Technology Co., Ltd. All chemicals were analytical grade and used as received without further purification.

Preparation of deep eutectic solvents and catalyst

The synthesis method of DESs was exhibited as follows: The HBD was mixed with the HBA at a certain molar ratio and stirred vigorously at 80 °C to form a homogeneous liquid¹. (NH₄)₃Co(OH)₆Mo₆O₁₈ was synthesized according to the literature^{2,3}. 30 mL of mixed aqueous solution of CoSO₄·7H₂O (0.015 mol) and 30% Aqueous H₂O₂ (2 g) was added to the boiling heptamolybdate aqueous solution (0.025 mol/260 mL water). The resulting solution was refluxed for 10 min and then filtered while hot. The filtrate is left to crystallize.

Characterization

Fourier transform infrared spectroscopy was conducted on a SHIMADZU IRAffinity-1S FT-IR spectrometer using KBr as a background. Ultraviolet-visible diffuse reflectance spectra were tested on a TU-1901 spectrophotometer in the region of 200–800 nm. Several substances in the test liquid UV were dissolved in acetonitrile (1 mmol/L), which was passed into the atmosphere at 60 °C for 1 h and then detected immediately. ¹H NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer at room temperature (400 MHz) and tetramethylsilane as the internal standard in C₂D₆SO. X-ray photoelectron spectroscopy analyses (XPS) were performed on an AXIS-ULTRA DLD-600W spectrometer equipped with a monochromatized aluminum X-ray source. Three mixed samples of XPS were prepared by grinding two components with equal mass in a glove box. Thermogravimetry was performed on a NETZSCH STA409PC thermal analyser on the conditions of 298–973 K at 10 °C min⁻¹ under N₂. Cyclic voltammogram (CV) was recorded on an CHI660e electrochemical potentiostat. Using glassy carbon electrode (GC) as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode, CV curves were determined by three-electrode method. An electrolyte was made by adding concentrated H₂SO₄ to a 1,4-dioxane/acetonitrile mixture solution (0.1 mol/L). The measurement was conducted in an electrolyte solution with a scan rate of 50 mV s⁻¹ after blowing O₂ or N₂ for 1 h. Electron spin resonance (ESR) spectra were obtained by JES-FA electron spin resonance spectrometer (JEOL, Tokyo, Japan) at -196 °C. Raman spectra of the specimen were detected from high-resolution Raman spectrometer (HOBIBA JY, LabRAM HR Evolution, France). The crystal structure of the catalyst was collected on X-ray diffraction (XRD, Rigaku, Smart Lab3) with Cu K α radiation.

Oxidation of HMF and analytical method

Oxidation of HMF was studied in a 25 mL three-neck round bottom flask with a reflux condenser. Typically, 0.4 mmol HMF and 40 mg catalyst were dissolved into deep eutectic solvents, and then the reaction was carried out for a certain period of time at a suitable temperature. During the reaction, atmospheric molecular oxygen

was continuously passed through the reaction system. Recycling experiments of the CoMo₆ were carried out under similar condition. To test the activity and stability of CoMo₆ under high product concentrations, the experiments were performed without FFCA separation. New HMF was added to the reaction solution after the recycle test, and no product was separated from the solution.

After the reaction, the products were diluted with pure water and tested. Analysis of HMF, HMFCA, and FFCA was made on a Shimadzu LC-20A HPLC system with a SPD-20A UV detector and a reversed-phase ZORBAX Eclipse XDB-C18 column (4.6 × 250 mm). Acetonitrile and 0.1 wt% acetic acid with a volume ratio of 50: 950 were used as mobile phase at a flow rate of 1.0 mL/min. The content of HMF, HMFCA, and FFCA in the product solution was directly obtained by the calibration curve of external standard constructed by pure substance, and the conversion and yield were calculated. HMF conversion and FFCA yield were defined as follows:

$$\text{Conversion} = \frac{n_{\text{HMF,initial}} - n_{\text{HMF,final}}}{n_{\text{HMF,initial}}} \times 100\%$$

$$\text{Yield} = \frac{n_{\text{FFCA}}}{n_{\text{HMF,initial}}} \times 100\%$$

Recyclability of the CoMo₆-DESs system

Recycling experiments were carried out in a similar process. In order to test the activity, selectivity, and stability of the CoMo₆-DES system at high FFCA concentrations, the stability test was performed without separating FFCA. In brief, a new HMF (0.4 mmol) was added to the reaction solution after the cycle test, and the product FFCA was not separated from the reaction system.

Results and Discussion

Table S1. Contents of Mo species and corresponding experiment results

Entry	Samples	Mo ⁵⁺ /(Mo ⁵⁺ +Mo ⁶⁺)	Conversion (%)	Y _{FFCA} (%)
1	CoMo ₆	0	---	---
2 ^{a, b}	CoMo ₆ +CPL	0	98	0
3 ^{a, c}	CoMo ₆ + [Bmim]Cl	54.93	98	4
4 ^{a, d}	CoMo ₆ +DES	63.21	100	93

(a) Reaction conditions: 40 mg CoMo₆, 130 °C, 6 h, Flow rate of O₂ 20 mL/min, 600 rpm, 0.4 mmol HMF, (b) 1.5726 g CPL, (c) 2.4274 g [Bmim]Cl, (d) 4 g [Bmim]Cl/CPL 1/1

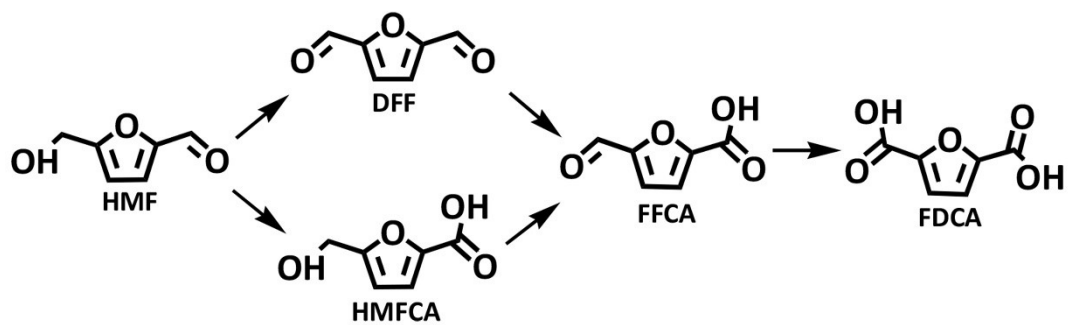


Fig. S1 Oxidation paths and products of HMF

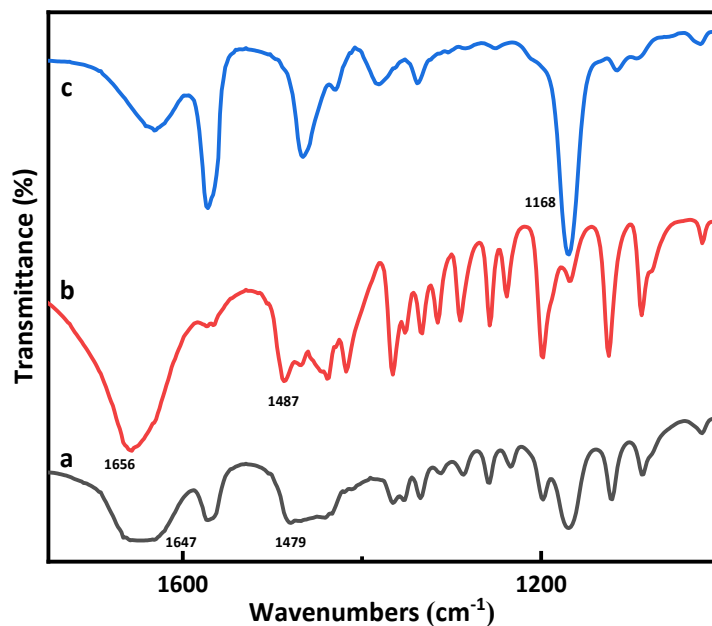


Fig. S2 FT-IR spectra of [Bmim]Cl/CPL (a), CPL (b) and [Bmim]Cl (c).

Note: DES was synthesized from imidazolyl ionic liquid with caprolactam at the molar ratio of 1/1. The interaction between [Bmim]Cl and CPL in DES was characterized by FT-IR, ¹H NMR and TG-DTA. The bands at 1656 cm⁻¹ and 1487 cm⁻¹ of CPL belonged to C=O stretching vibration and N-H bending vibration, which redshifted to 1647 cm⁻¹ and 1479 cm⁻¹, respectively (Fig. S1). In comparison with [Bmim]Cl and DES, it was found that the peak intensity at 1168 cm⁻¹ was weakened, which peak was attributed to C-H bending vibration on the imidazole ring^{4,5}.

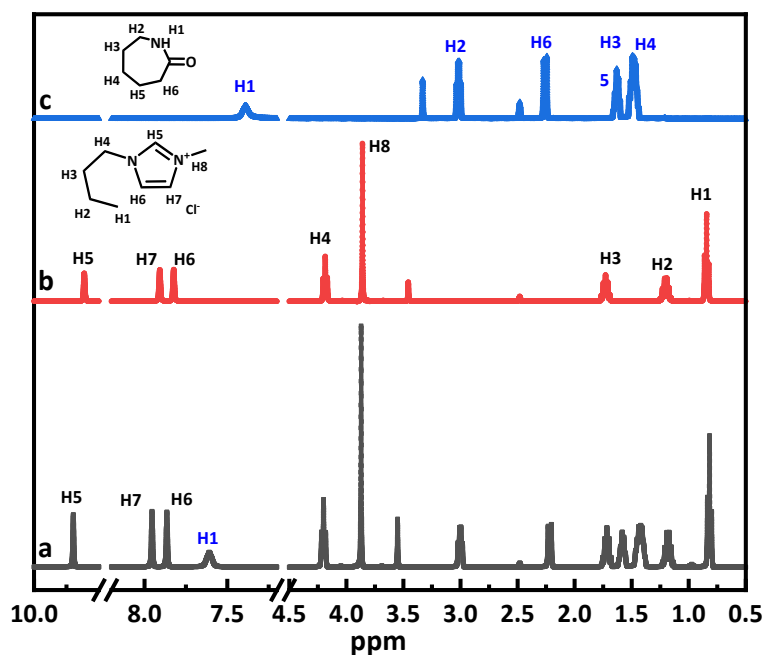


Fig. S3 ¹H NMR spectra of [Bmim]Cl/CPL (a), CPL (b) and [Bmim]Cl (c).

Note: To further understand the nature of interaction, the ¹H NMR spectra of [Bmim]Cl, CPL and [Bmim]Cl/CPL DES were recorded (Fig. S2). Three H signals on the imidazole ring at 7.82 ppm, 7.90 ppm and 9.61 ppm downshifted to 7.86 ppm, 7.95 ppm and 9.69 ppm respectively after the formation of DES. In terms of the principle of chemical shift, the electron density of hydrogen atom decreased when hydrogen bond was formed, resulting in downshift of the chemical shift⁶. In addition, the N-H hydrogen signal of CPL had a chemical shift from 7.38 to 7.60 ppm, which may also be due to the formation of hydrogen bond^{4,7,8}

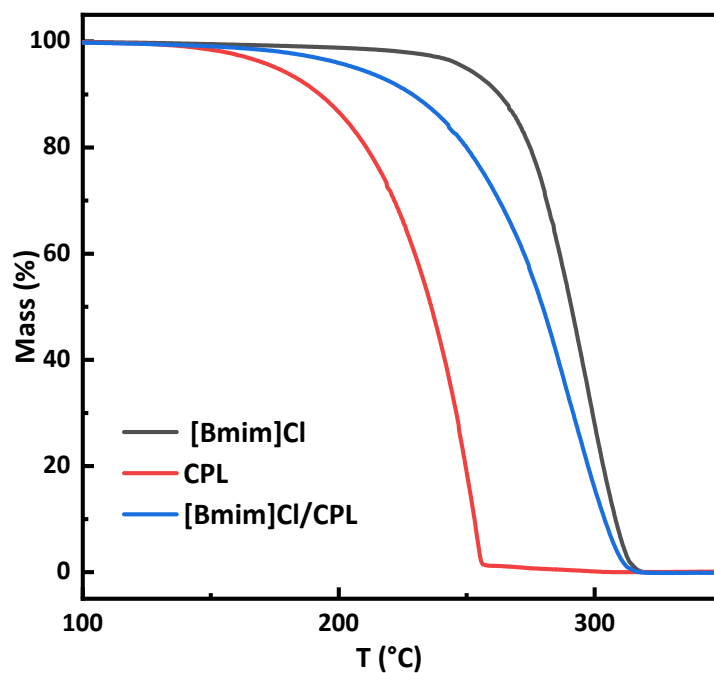


Fig. S4 TG curves of [Bmim]Cl/CPL, CPL and [Bmim]Cl.

Note: To design a novel DES for HMF oxidation and to understand the interaction HBD and HBA, TG analysis of DES and its components was performed. As can be seen from Fig. S3, when the temperature is lower than 200 °C, the samples exhibited favorable thermodynamic stability. Obvious weight loss of DES occurred between 200-300 °C. In addition, the thermal stability of DES was between the two initial components, which can be inferred that the two substances formed weaker hydrogen-bonding interaction⁹. In conclusion, DES was successfully formed between [Bmim]Cl and CPL by hydrogen bond.

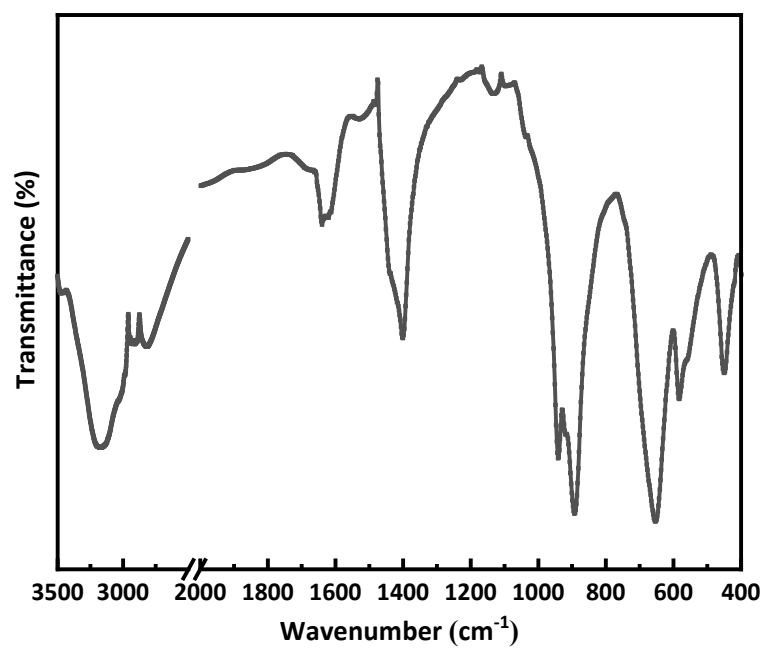


Fig. S5 The FT-IR spectrum of $(\text{NH}_4)_3\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}$

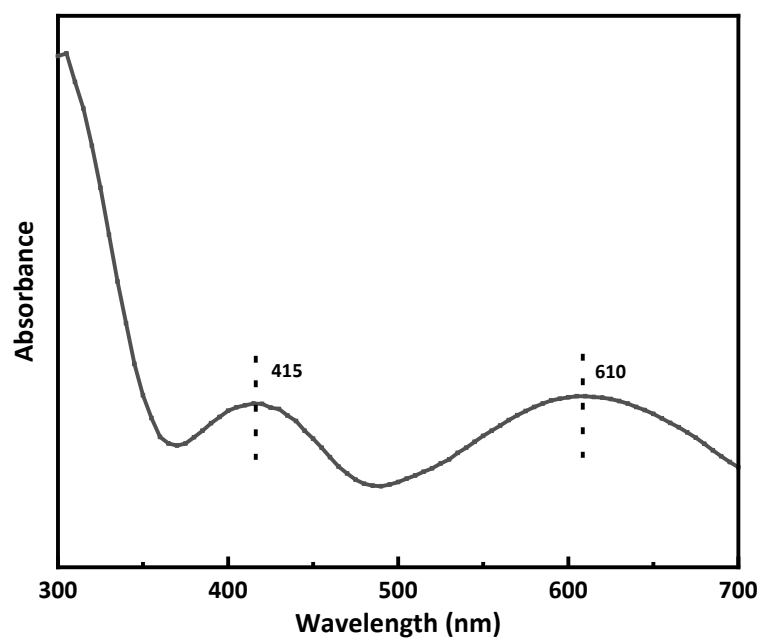


Fig. S6 UV-vis spectrum of $(\text{NH}_4)_3\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}$

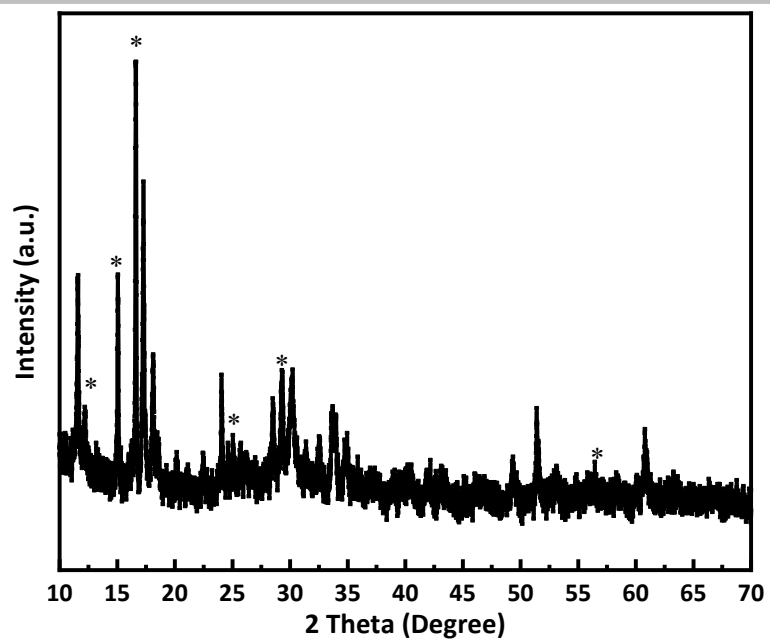


Fig. S7 The XRD pattern of $(\text{NH}_4)_3\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}$

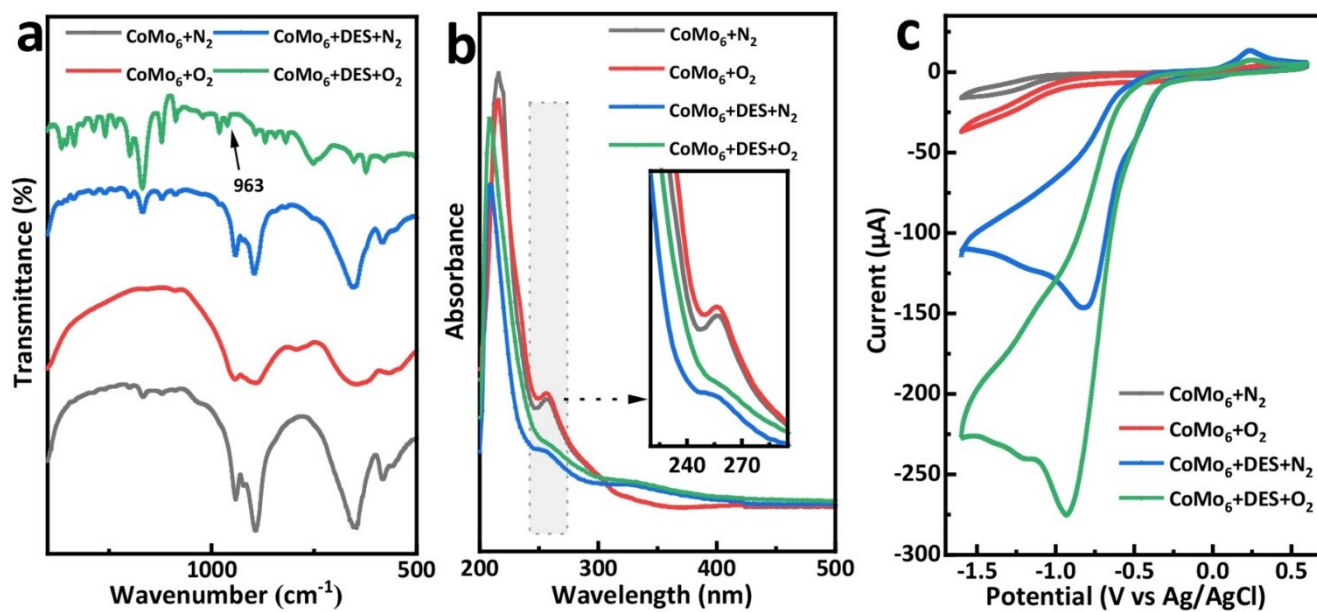
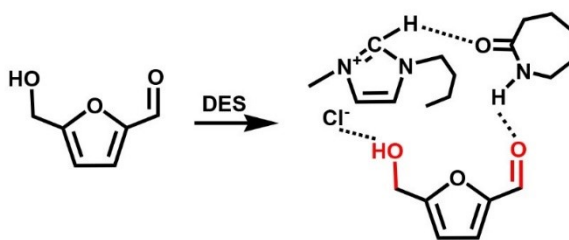
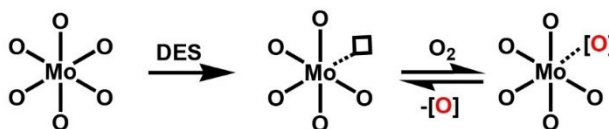


Fig. S8 (a) FT-IR spectra, (b) UV-vis spectra, (c) Cyclic voltammograms curves of POM and POM+DES purged with O₂ or N₂

A. Interaction between HMF and DES.



B. Formation of pentavalent molybdenum, oxygen vacancy and active oxygen species.



C. Selective oxidation of 5-hydroxymethylfurfural.

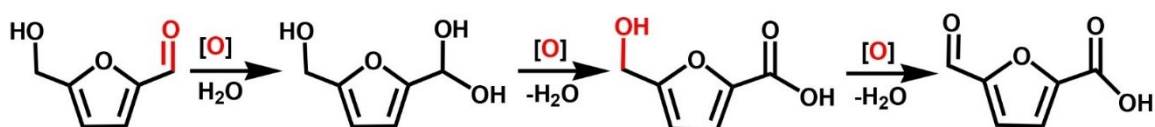


Fig. S9 Proposed dual activation mechanism for the HMF oxidation

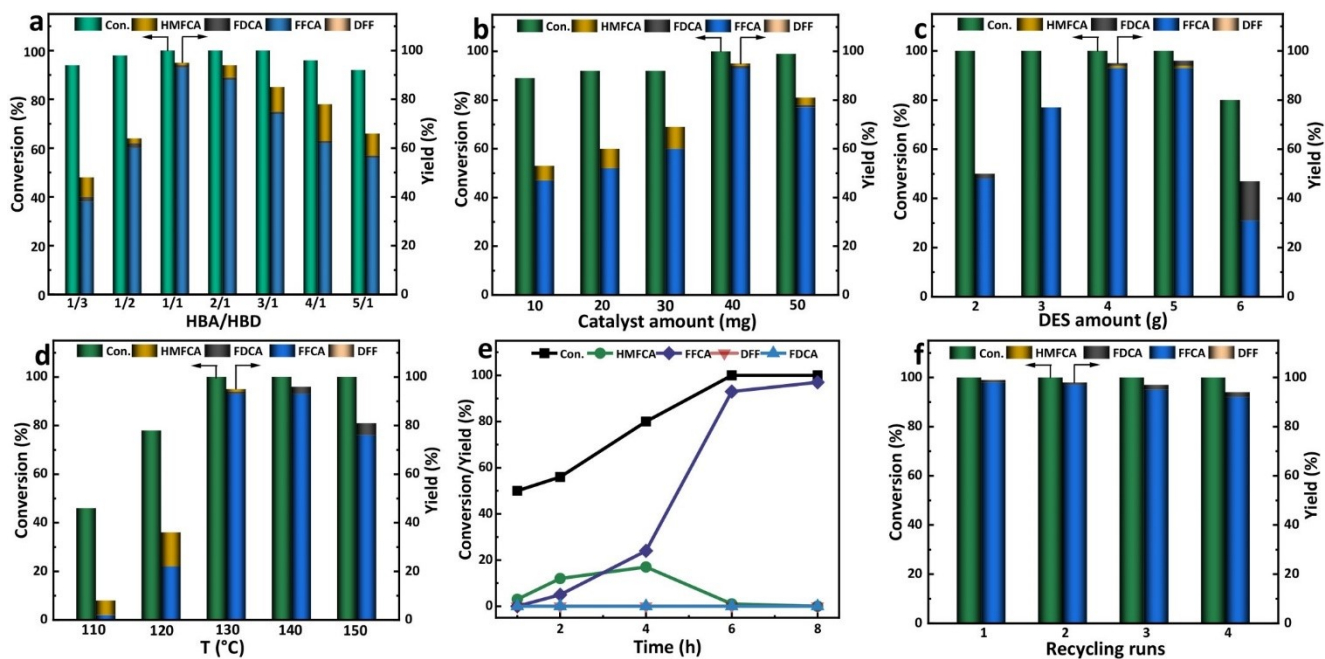


Fig. S10 Influence of reaction conditions on the oxidative behavior. (a) HBA/HBD, (b) catalyst dosage, (c) DES dosage, (d) temperature, (e) time, (f) recycling runs. Reaction conditions of (a-e): 0.4 mmol HMF, 4 g DES, [Bmim]Cl/CPL 1/1, 40 mg Co Mo₆, 130 °C, Flow rate of O₂ 20 mL/min, 6 h. Reaction conditions of (f): 0.4 mmol HMF, 4 g DES, [Bmim]Cl/CPL 1/1, 40 mg CoMo₆, 130 °C, Flow rate of O₂ 20 mL/min, 8 h, no product separation.

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Author Contributions

Hongying Lü designed experiments; Yanbin Sun carried out experiments; Hongying Lü, Yanbin Sun, Kaixuan Yang, Zhiguo Zhu, Ting Su, and Wanzhong Ren analyzed experimental results; Yanbin Sun and Hongying Lü wrote the manuscript.