

## SUPPLEMENTAL INFORMATION

### **Insights into the Catalytic Mechanism of 5-Hydroxymethfurfural to Phthalic Anhydride with MoO<sub>3</sub>/Cu(NO<sub>3</sub>)<sub>2</sub> in One-pot**

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## EXPERIMENTAL PROCEDURES

**1. Materials.** HMF, potassium persulfate, cupric nitrate trihydrate, ferric nitrate nonahydrate, acetonitrile, DMSO, dioxane and other reagents were supplied by Sigma-Aldrich China Co. Ltd. (Shanghai, China). All reagents used in this study were analytical grade and not purified before using.

**2. Products Analyses.** The qualitative analysis of intermediates and products were determined by a thermo-Fisher Trace 1300 & ISQ LT GC-MS instrument equipped with a TR-5MS column (15.0 m × 250 μm × 0.25 μm). The following programmed temperature was used in the analysis: 40 °C (2 min)-10 °C/min - 260 °C (2 min). The carrier gas was He with a flow rate of 1.2 mLmin<sup>-1</sup> and the split ratio was 1:50. The mass spectra were obtained by electron impact ionization (EI), at an electron energy of 70 eV and with a 25 μA emission current.

The quantitative analysis of product was conducted on Agilent 7890 series GC equipped with a DB-Waxetr column (30 m × 0.25 mm × 0.25 mm, Agilent) and a flame ionization detector (FID) operating at 270 °C. The carrier gas was N<sub>2</sub>, with a flow rate of 1.0 mL/min. The following programmed temperature was applied: 40 °C (4 min) - 15 °C/min - 250 °C (5 min).

The quantitative analysis of acid product was performed on a Waters 2695 Separation Module HPLC equipped with a refractive index detector and a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm). The column oven temperature was 65°C, and the mobile phase was 5 mM H<sub>2</sub>SO<sub>4</sub> at a flow rate of 0.6 ml/min.

HMF conversion (conv. %) and DFF selectivity (Sele. %) before and after reaction are calculated according to the following equations:

$$\text{Conv.} = \left( 1 - \frac{\text{mol of HMF in products}}{\text{mol of HMF in substrate}} \right) \times 100\%$$
$$\text{Sele.} = \frac{\text{Mol of PA in productions}}{\text{Theoretical yield of PA from HMF}} \times 100\%$$

**3. Characterization.** X-ray diffraction (XRD) measurements were conducted by using a STADIP automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator and Cu Kα1 radiation, and operated at 40 kV and 150 mA. Data were collected in the 2θ range between 10° and 90° with a

step size of  $0.02^\circ$  at a scanning speed of  $10^\circ \text{ min}^{-1}$ .

The X-ray photoelectron spectroscopy (XPS) analysis was performed by using a Thermo Scientific ESCALAB 250Xi electron spectrometer under a base pressure less than  $2 \times 10^{-9}$  mbar. A monochromatic Al K $\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) excitation energy source was adopted.

The scanning electron microscopy (SEM) images were obtained by using a Hitachi S-4800 microscope operated at an accelerating voltage of 15 kV. The Energy dispersive X-ray spectrometer (EDS) and energy-dispersive X-ray (EDX) element mapping images were observed by using a ZEISS SUPRA 55 SAPPHIRE field emission scanning electron microscope (FE-SEM). The Field emission transmission electron microscopy (FE-TEM) with energy dispersive X-ray analysis (EDX) element mapping was carried out by using a FEI Tecnai G2 F20 at an accelerating voltage of 100 kV.

The H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) was measured by using a Micromeritics AutoChem II 2920 equipped with a thermal conductivity detector. In a typical experiment for H<sub>2</sub>-TPR, 30 mg sample was first loaded into a U-shaped, flow-through, and quartz sample tube. Prior to the measurement, the sample was preheated under a He flow (20 mL/min) at 550 °C for 1 h to remove adsorbed species on the surface of sample. The reactor was then cooled down to 100 °C, and H<sub>2</sub>/Ar (10 vol% H<sub>2</sub>) mixture was introduced. The TPR test was conducted under a H<sub>2</sub>/Ar flow by increasing the temperature to 800 °C with a heating rate of 20 °C/min.

For NH<sub>3</sub>-TPD, 40 mg sample was first loaded into the quartz tube and preheated to 550 °C with a heating rate of 20 °C·min<sup>-1</sup> in helium gas flow for 1 h to remove adsorbed species on the surface of sample. The temperature was then reduced to 120 °C and NH<sub>3</sub>-He (10 Vol % NH<sub>3</sub>) mixture was introduced for 0.5 h. After NH<sub>3</sub> adsorption, the catalyst sample was treated at 120 °C for another 1 h in helium to remove the remaining or weakly adsorbed NH<sub>3</sub>. TPD test was conducted in helium flow by increasing the temperature to 800 °C with a heating rate of 20 °C·min<sup>-1</sup> and then keeping at 800 °C for 0.5 h.

For O<sub>2</sub>-TPD, 40 mg sample was first loaded into the quartz tube and preheated to 550 °C with a heating rate of 20 °C·min<sup>-1</sup> in helium gas flow for 1 h to remove adsorbed species on the surface of sample. The temperature was then reduced to 120 °C and O<sub>2</sub>-He (3 Vol % O<sub>2</sub>) mixture was introduced for 0.5 h. After O<sub>2</sub> adsorption, the catalyst sample was treated at 120 °C for another 1 h in helium to remove the remaining or weakly adsorbed O<sub>2</sub>. TPD test was conducted in helium flow by increasing the

## Supplemental information

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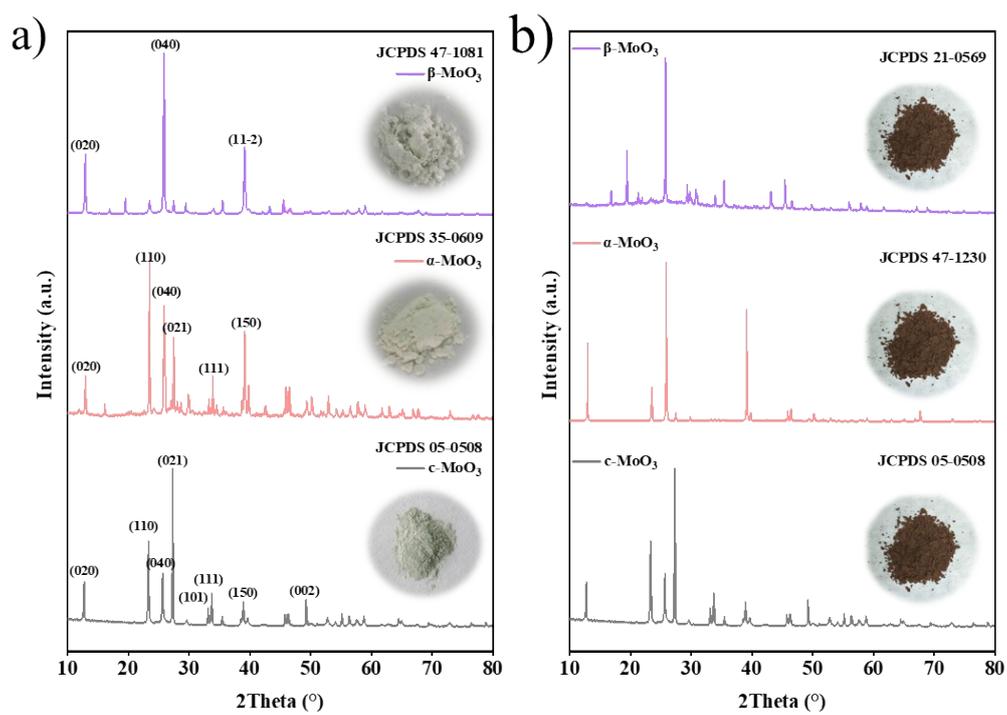
temperature to 800 °C with a heating rate of 20 °C·min<sup>-1</sup> and then keeping at 800 °C for 0.5 h.

**Supplemental information**

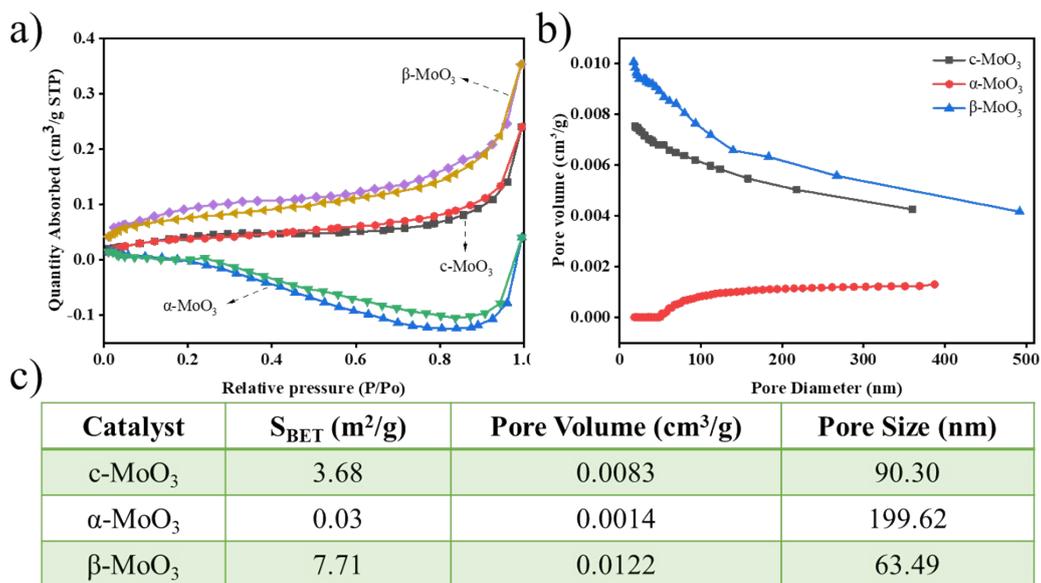
**Table S1** Effect of catalyst and oxidant on the conversion of HMF to PA <sup>[a]</sup>

Entry	Catalyst	Conv. (%)	Sele. (%)		
			DFE	MA	PA
1	Cu(NO <sub>3</sub> ) <sub>2</sub>	100	53	29	10
2	<i>c</i> -MoO <sub>3</sub>	100	0	37	30
3	TBN	64	75	14	0
4	CuSO <sub>4</sub>	100	26	31	0
5 <sup>b</sup>	CuSO <sub>4</sub>	0	0	0	0
6 <sup>b</sup>	HNO <sub>3</sub>	82	28	54	0
7 <sup>b</sup>	TBN	73	54	42	0
8 <sup>[c]</sup>	<i>c</i> -MoO <sub>3</sub>	100	15	73	6
9 <sup>[c]</sup>	CuSO <sub>4</sub>	8	0	0	0

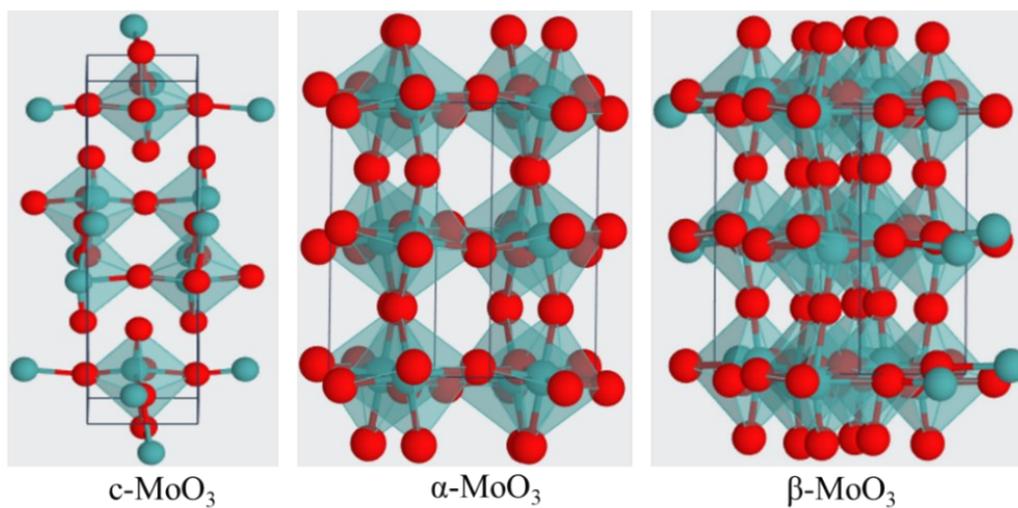
[a] Reaction conditions: 5 mmol HMF, 10 wt% catalyst, 40 ml mixed solvent of water and acetonitrile (33:7), 5 mmol K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 7 h, 90 °C, without purging air in the reactor. [b] Substituting K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> with 1 Mpa O<sub>2</sub>; [c] Substituting K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> with 5 mmol H<sub>2</sub>SO<sub>4</sub>.



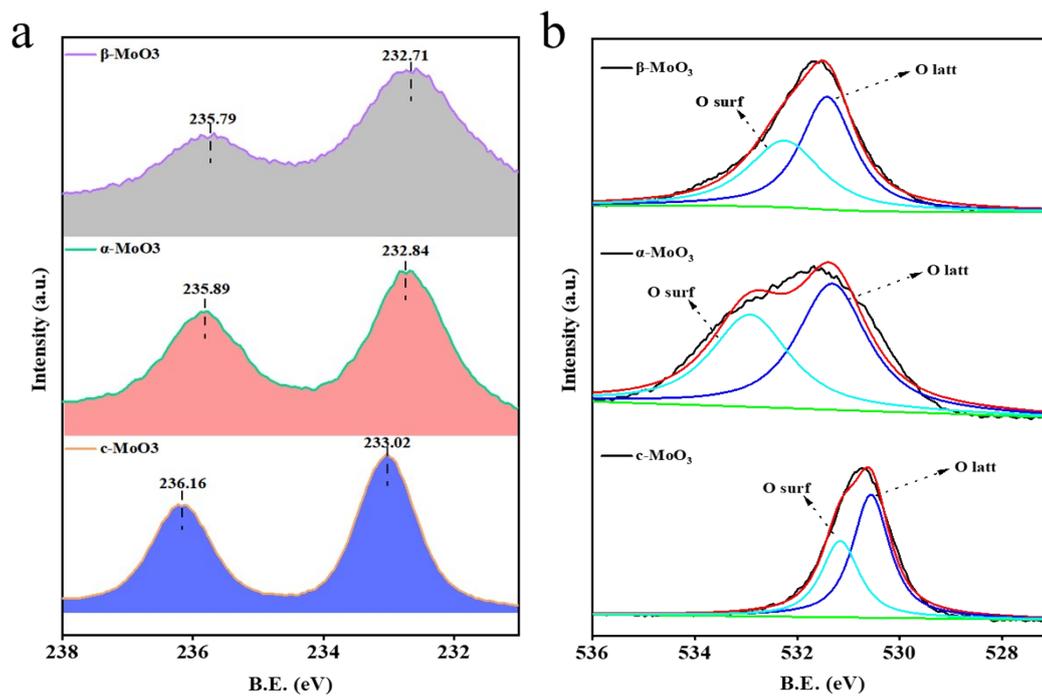
**Fig. S1** XRD spectra of the fresh (a) and recycled catalysts (b) ( $\alpha$ - $\text{MoO}_3$  (JCPDS 35-0609),  $\beta$ - $\text{MoO}_3$  (JCPDS 47-1081) and  $c$ - $\text{MoO}_3$  (JCPDS 05-0508)).



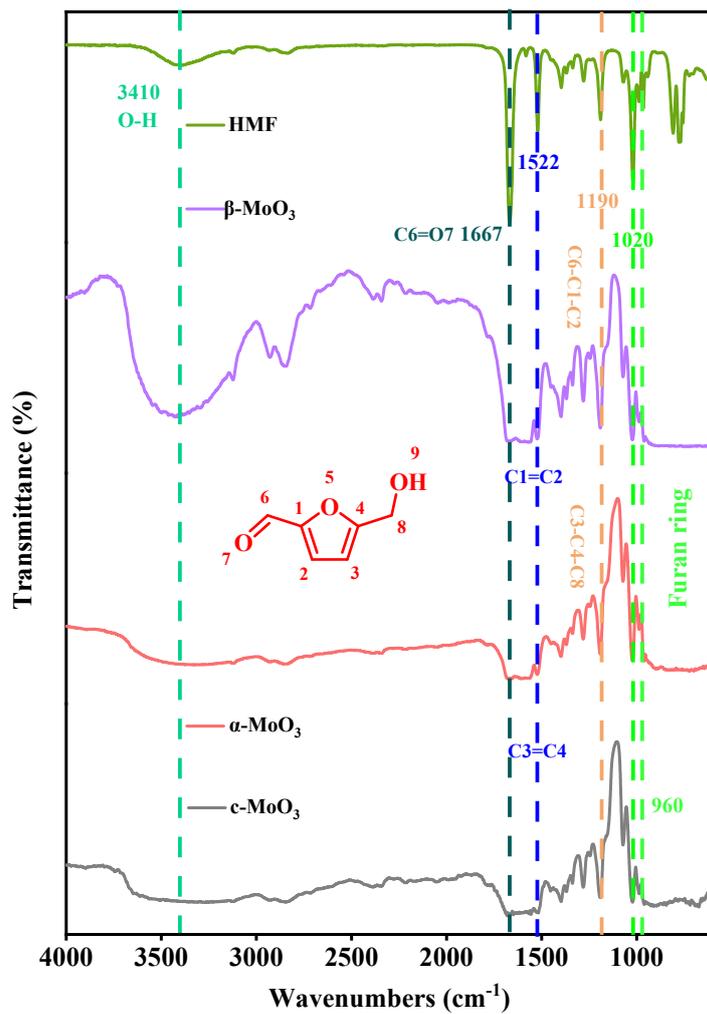
**Fig. S2** Low-temperature N<sub>2</sub> adsorption-desorption isotherms (a), corresponding pore size distributions (b) and the structural and textural data (c) of the MoO<sub>3</sub> catalysts



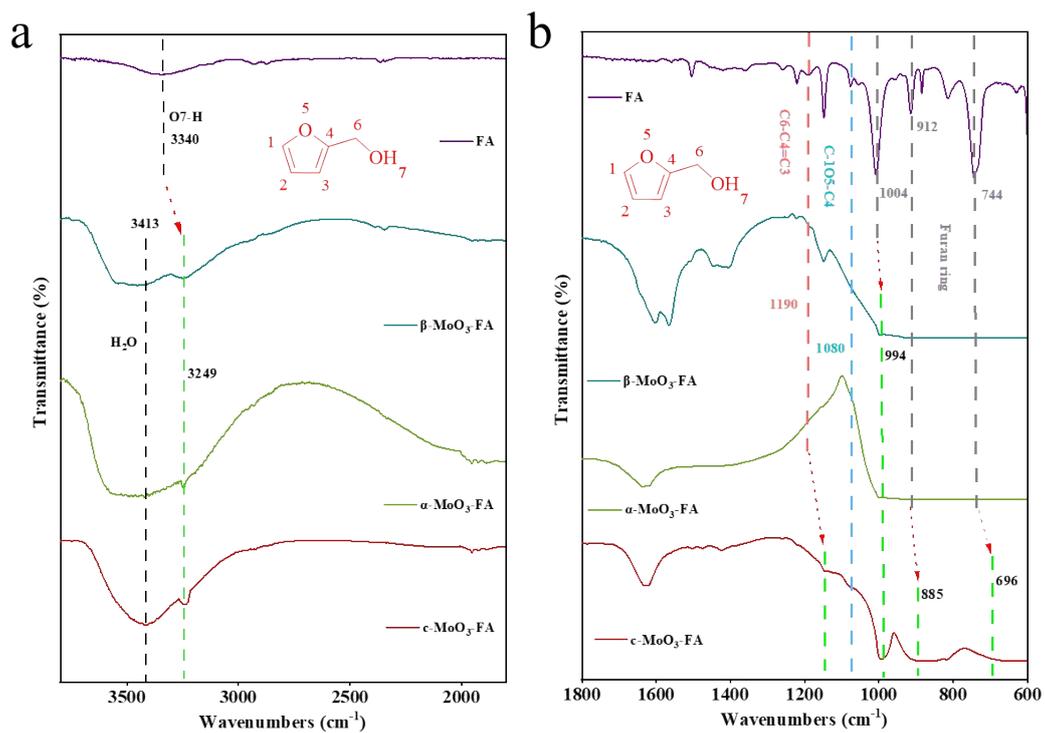
**Fig. S3** Unit cell structure of three kind of MoO<sub>3</sub> catalysts



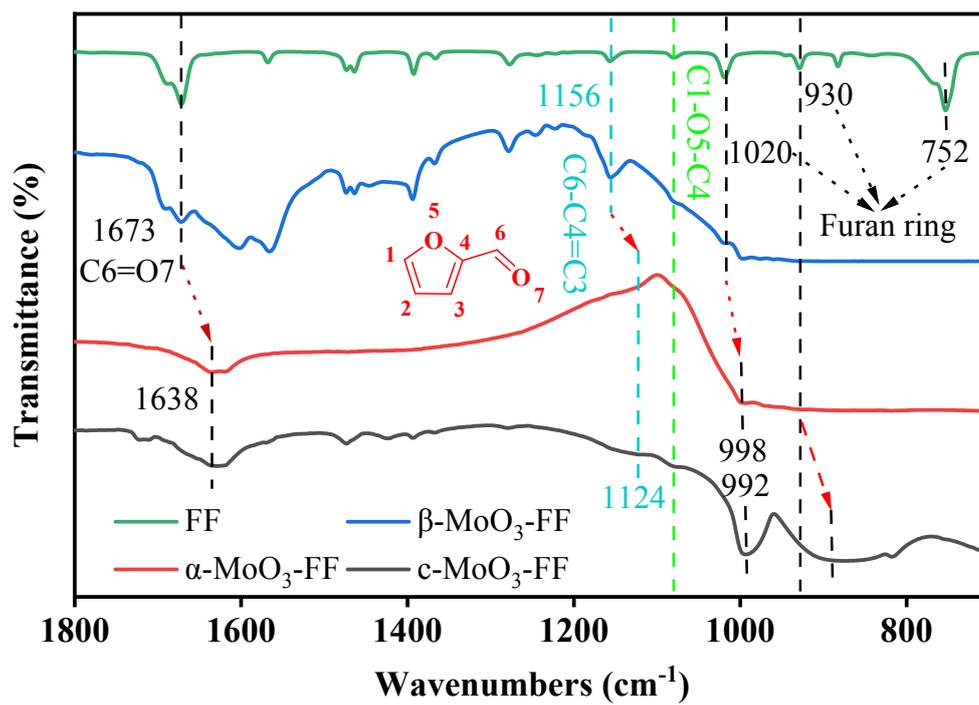
**Fig. S4** XPS of three kinds of MoO<sub>3</sub> catalysts ( $c$ -MoO<sub>3</sub>,  $\alpha$ -MoO<sub>3</sub> and  $\beta$ -MoO<sub>3</sub>; a: Mo 3d, b: O 1s)



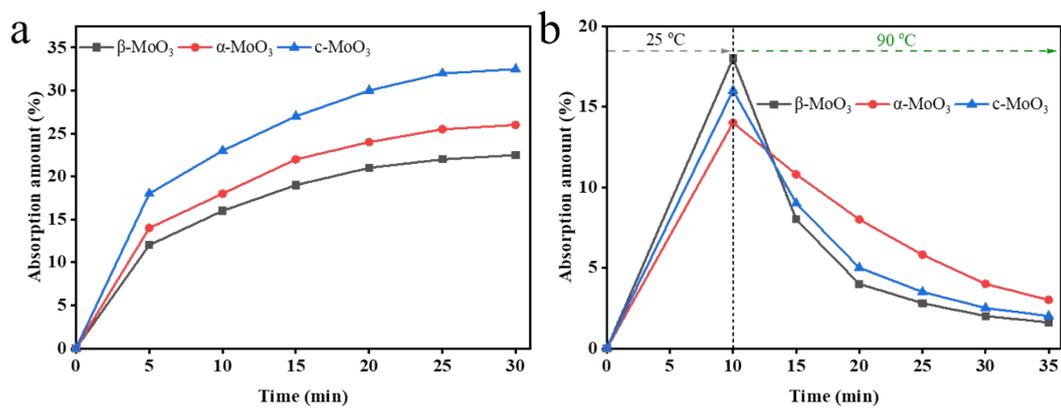
**Fig. S5** ATR- IR of HMF adsorbed on the  $\text{MoO}_3$  catalysts ( $\alpha$ -,  $\beta$ - and  $\gamma$ - $\text{MoO}_3$ ).



**Fig. S6** ATR-IR spectra of furfur-alcohol (FA) adsorbed on the different catalysts ( $\alpha$ -MoO<sub>3</sub>,  $\beta$ -MoO<sub>3</sub> and  $c$ -MoO<sub>3</sub>)



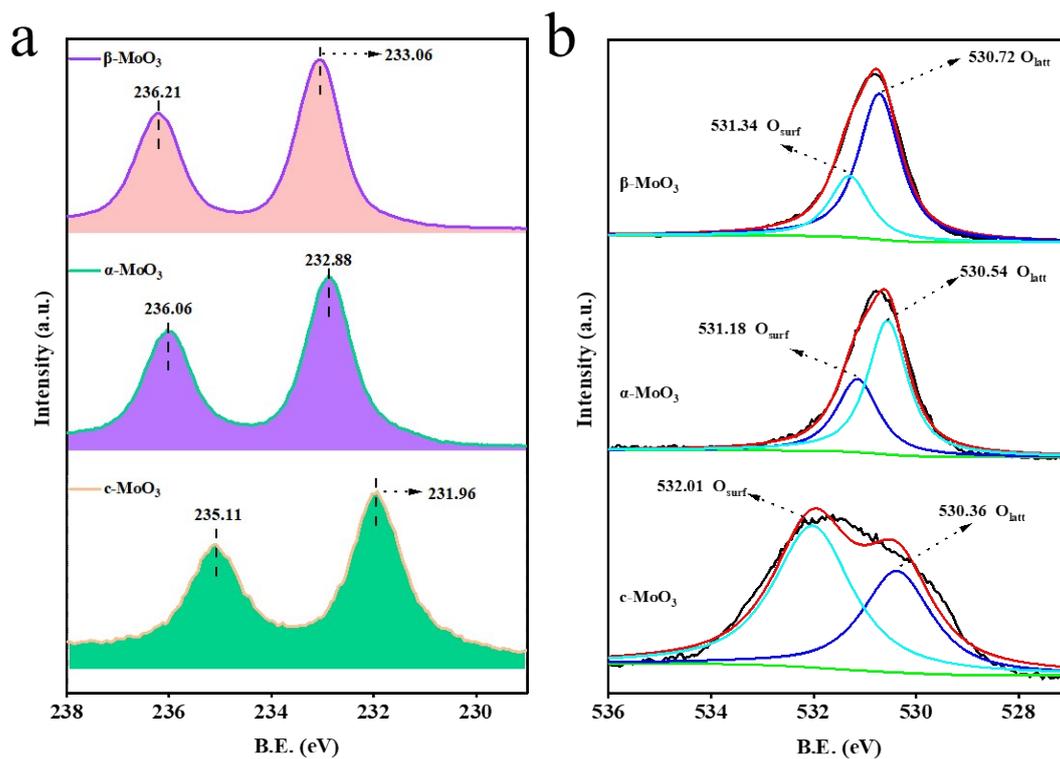
**Fig. S7** ATR-IR spectra of FF adsorbed on the different catalysts ( $\alpha$ - $\text{MoO}_3$ ,  $\beta$ - $\text{MoO}_3$  and  $c$ - $\text{MoO}_3$ )



**Fig. S8** Adsorption kinetics of HMF (a) and desorption kinetics of PA (b) on the surface of  $\alpha$ -MoO<sub>3</sub>,  $\beta$ -MoO<sub>3</sub> and c-MoO<sub>3</sub>.

a: Reaction conditions: HMF (0.1 mmol), catalyst (10 wt%), solvent (33 ml H<sub>2</sub>O and 7 ml MeCN), 25 °C, stirring.

b: Reaction condition: PA (0.1 mmol), catalyst (10 wt%), solvent (33 ml H<sub>2</sub>O and 7 ml MeCN), stirring.



**Fig. S9** XPS spectra of the recovered catalysts ( $\alpha$ -MoO<sub>3</sub>,  $\beta$ -MoO<sub>3</sub> and  $c$ -MoO<sub>3</sub>; a: Mo 3d, b: O 1s).

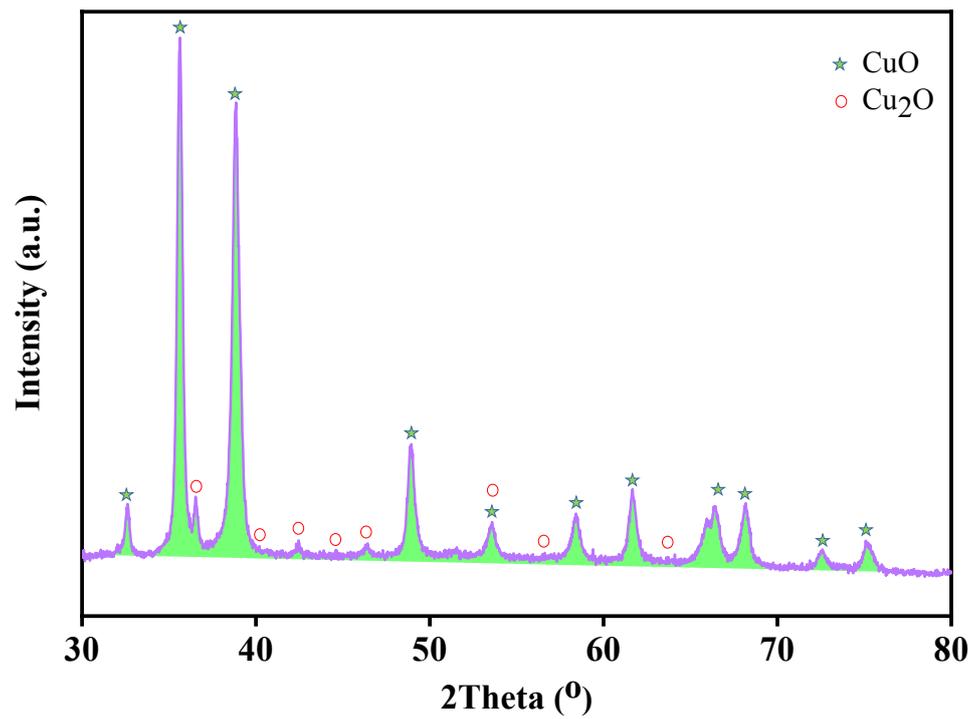
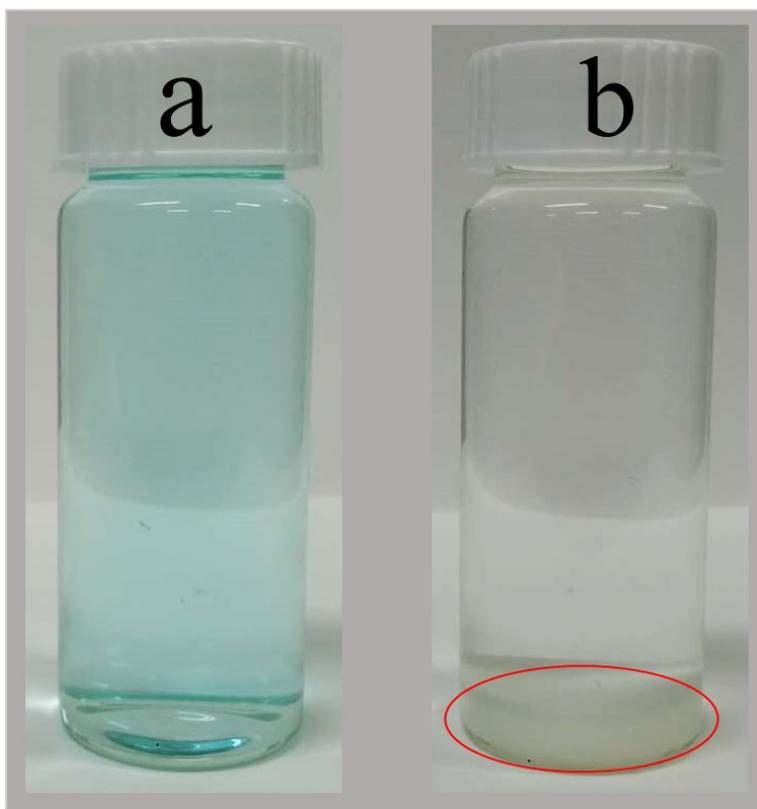


Fig. S10 XRD spectrum of the recovered Cu-based catalyst.



**Fig. S11** Effect of Copper Nitrate on the decomposition of  $\text{K}_2\text{S}_2\text{O}_8$  (a: adding 1 mmol  $\text{CuSO}_4$ ; b: without  $\text{Cu}(\text{NO}_3)_2$ ).

Reaction conditions: 10 mmol  $\text{K}_2\text{S}_2\text{O}_8$ , 40 ml solvent (7 mL acetonitrile and 33 ml water), 0.5 h, 90 °C, purging air with  $\text{N}_2$ .