

Supporting Information (SI)

Water-assisted sonochemically-induced demethylenation of benzyl alcohol to phenol over a structurally stable cupric oxide catalyst

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1. CuO fresh catalyst characterization by dynamic light scattering (DLS)

Table S1. Particle Size Distribution (PSD) of the synthesized CuO-864 showing the mean radius in nm.

Sample Name	Average size (r.nm)	Size at the peak (r.nm)	Polydispersity
CuO-578	692	518	0.4
CuO-864	146	160	0.13
CuO-1140	1699	798	0.4

2. Hydrogen peroxide (H₂O₂) quantification

Reaction samples were taken directly in the solution from the ultrasound reactor and mixed with the titanium oxysulfate solution in 1/1 v/v (the same conditions as the standards solution). The absorbance is measured at the same wavelength as the one used for the calibration.

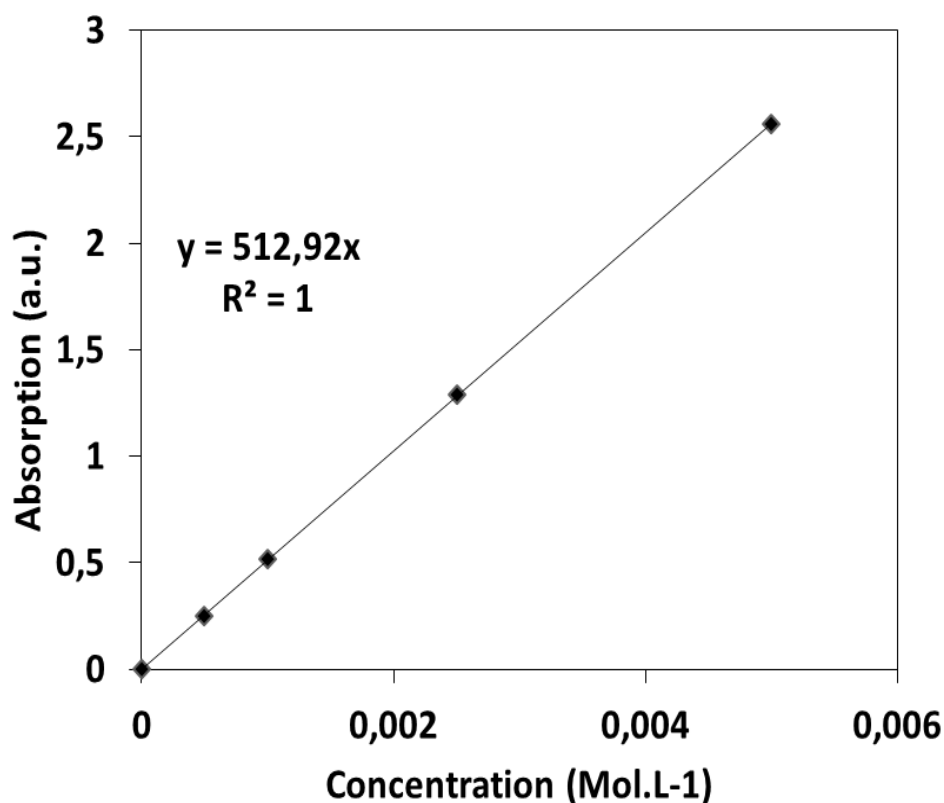
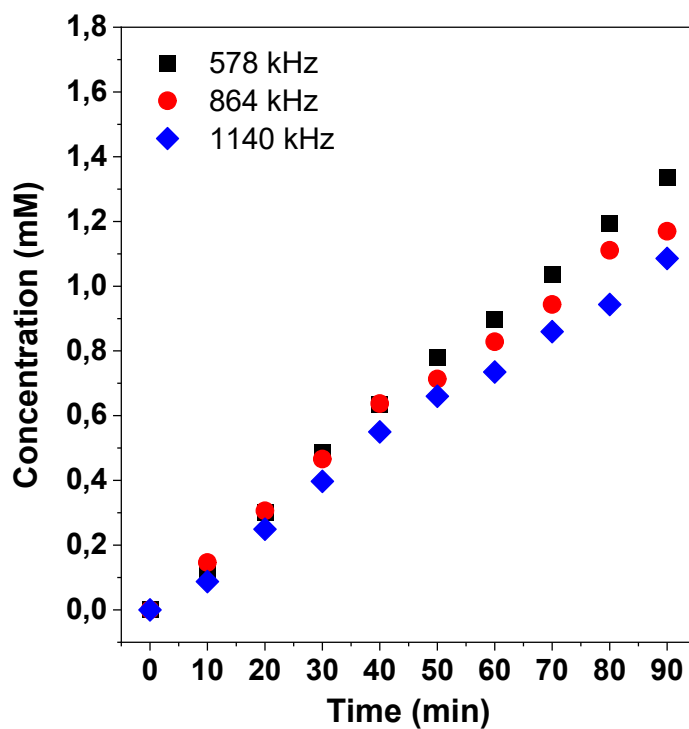


Figure S1. Hydrogen peroxide calibration curve

The H_2O_2 production rate under different ultrasound frequencies (864 and 1140 kHz) were also investigated. It was observed that after an irradiation time of 90 min, a maximum H_2O_2 concentration of 1.16 mmol. L^{-1} (production rate of 21.8×10^{-8} mol. $\text{L}^{-1} \cdot \text{s}^{-1}$) and 1.08 mmol. L^{-1} (production rate of 20.1×10^{-8} mol. $\text{L}^{-1} \cdot \text{s}^{-1}$) for 864 and 1140 kHz ultrasound frequencies, respectively. These production rates were lower than that obtained for the reactions performed under ultrasound frequency of 578 kHz (24.8×10^{-8} mol. $\text{L}^{-1} \cdot \text{s}^{-1}$). Hence all reactions reported in this investigation were performed at 578 kHz unless otherwise stated.



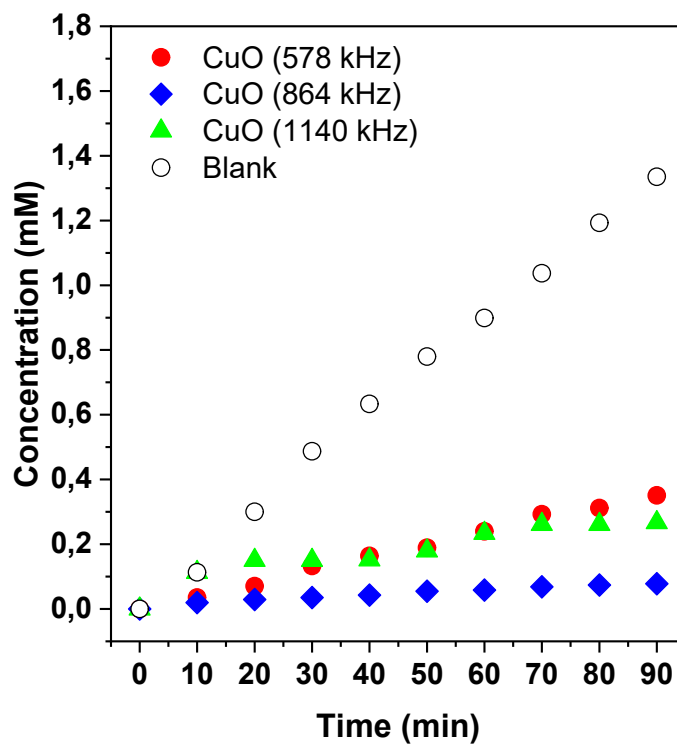


Figure S2. In-situ production of hydrogen peroxide (H_2O_2) under different reaction conditions: a) different ultrasound frequencies under argon $20\text{ mL}\cdot\text{min}^{-1}$ at controlled temperature $25\text{ }^\circ\text{C}$; b) CuO catalysts prepared at different ultrasound frequencies, 578 kHz ultrasound frequency, under argon $20\text{ mL}\cdot\text{min}^{-1}$ at controlled temperature $25\text{ }^\circ\text{C}$.

3. CuO catalyst characterization after ultrasonic irradiation

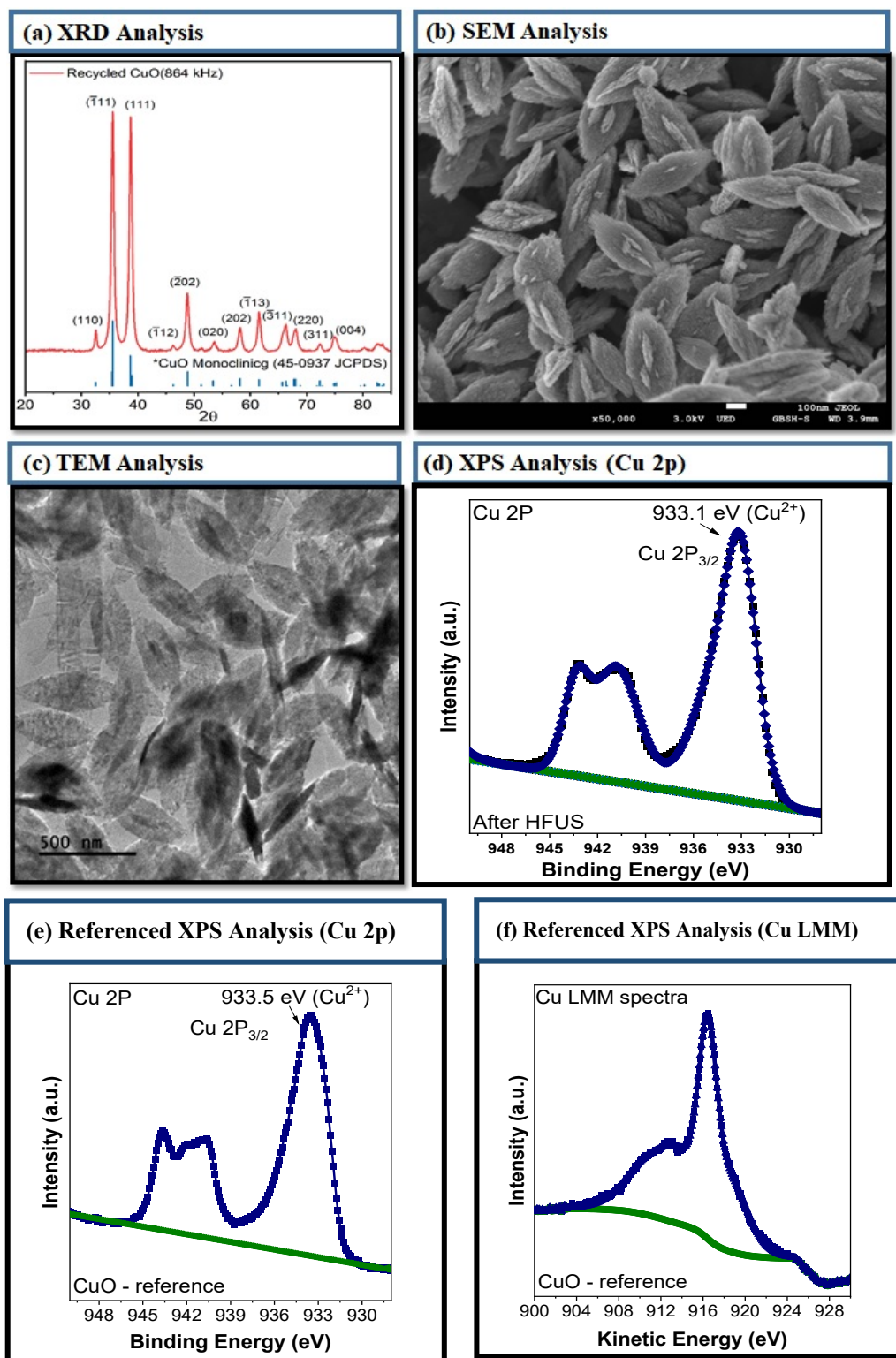


Figure S3. (a) XRD analysis (b) SEM analysis (c) TEM analysis (d) XPS Cu2p analysis of recovered CuO catalyst (e) XPS Cu2p analysis of referenced CuO and (f) XPS Cu LMM analysis of referenced CuO

4. Sonochemical oxidation of model substrates

Table S2. Product yields for the CuO catalyzed sonochemical oxidation of model substrates.

Substrate	Gas atmosphere	Reaction time (h)	Conversion (%)	Benzaldehyde	Phenol	Hydroxy-benzylalcohol	Benzoquinone	Hydroxy-benzaldehyde	Hydroquinone
Benzaldehyde	Argon	0.5	23	-	11	0	0	<1	0
		1	40	-	18	0	0	<1	0
		2	54	-	19	0	0	0	0
		2.5	66	-	23	0	0	0	0
Hydroxy-benzyl alcohol	Argon	1	26	0	0	-	2	2	8
		2	56	0	0	-	4	3	14
		3	72	0	0	-	4	2	15
		4	86	0	0	-	4	2	14

Reactions condition: 5 mmol.L⁻¹ of the substrate, 100 mL of H₂O, 10 wt.% of CuO-864 catalyst, 578 kHz, Ar bubbling (20 mL.min⁻¹), 25 °C, P_{acous.vol} = 0.11 W·mL⁻¹

5. Phenol yield for CuO catalyzed oxidation of benzyl alcohol under silent conditions

Table S3. Benzyl alcohol oxidation over CuO-864 under silent conditions. The reaction parameters are the following : 5 mmol.L⁻¹ of benzyl alcohol in 100 mL and 5.4 mg of catalyst under argon flow rate 20 mL.min⁻¹ and stirring 400 rpm

Entry	Gas atmosphere	Reaction temperature (°C)	Reaction time (h)	H ₂ O ₂ concentration (mmol.L ⁻¹)	Conversion (%)	Phenol (%)
1	Argon	25	6	-	0	0
2		100	6	-	0	0
3	Argon	62	1	5	9	1
			2	5	34.5	13.4
			3	5	34.7	15.7
			4	5	34.7	14.5
			5	5	34.7	14.5

Phenol yields for CuO catalyzed oxidation of benzyl alcohol

6. Sonochemical oxidation of Benzyl alcohol without adding a catalyst

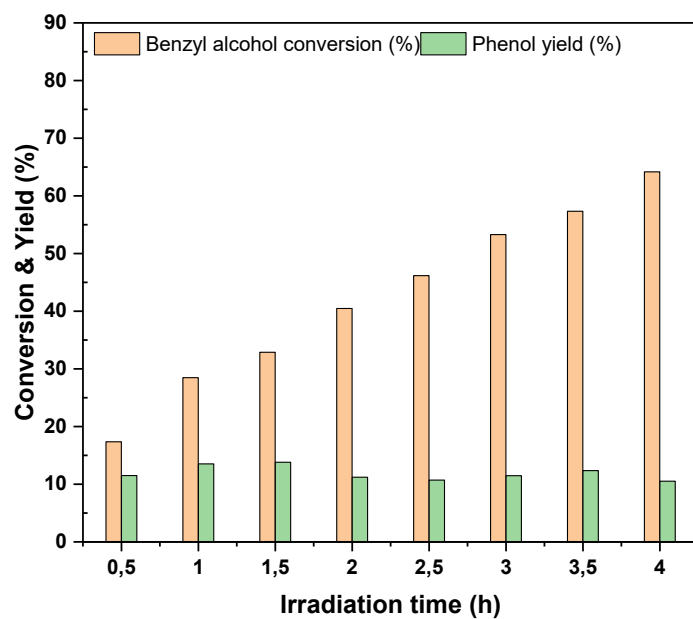


Figure S4a. Ultrasonic irradiation time course for benzyl alcohol oxidation. Reaction conditions: 5 mmol.L⁻¹ Benzyl alcohol, 578 kHz, 0.11 W.mL⁻¹, 25 °C

7. Catalyst recycling tests

Product selectivity was calculated according to the equation;

$$\text{Products selectivity (\%)} = \frac{\text{Product Yield}}{\text{Benzyl alcohol conversion}}$$

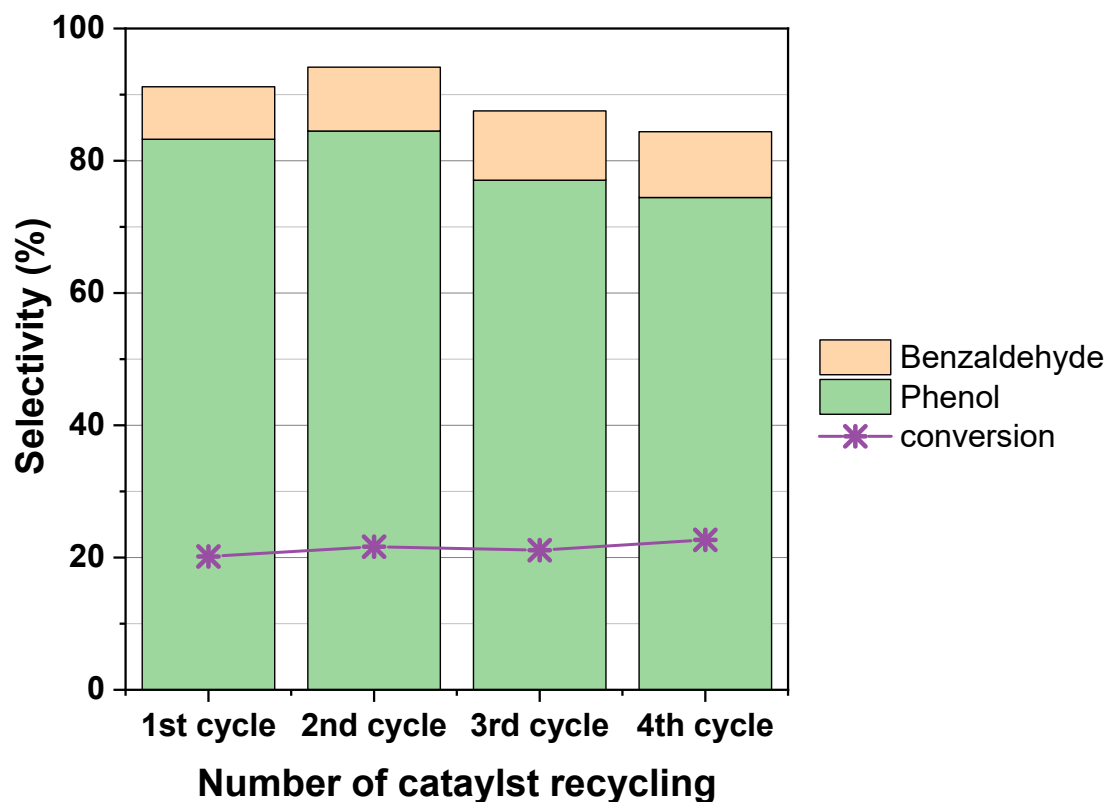
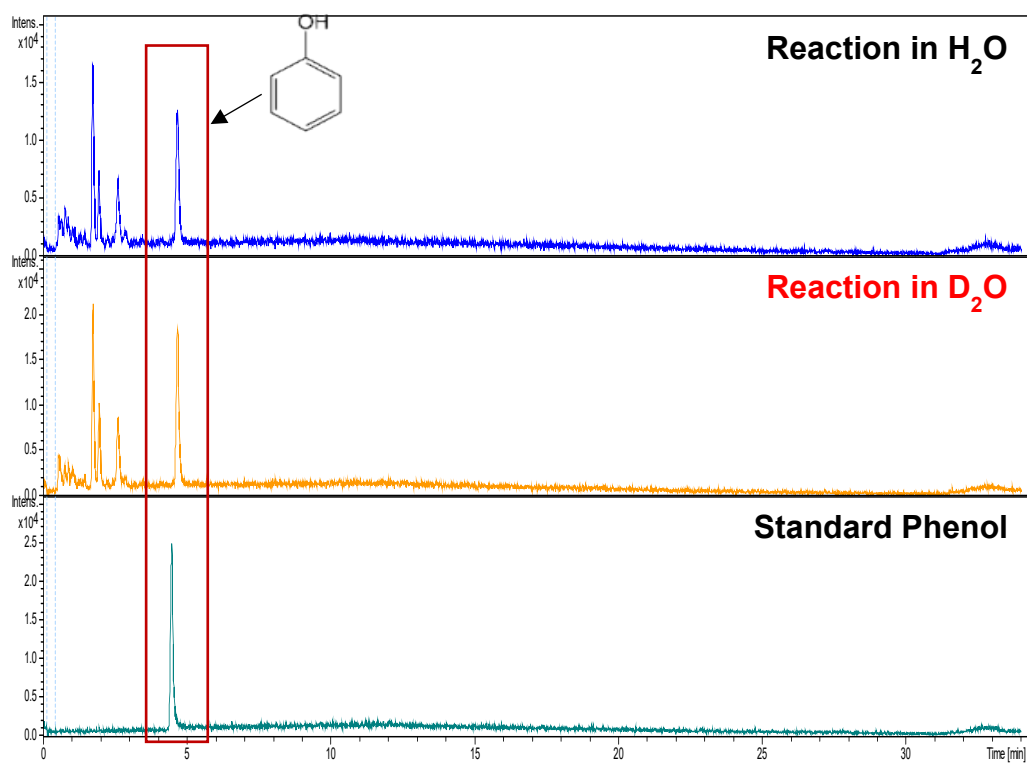


Figure S4b. Benzyl alcohol oxidation over 4 cycles of 10% wt of CuO catalyst. Reaction conditions: 578 kHz, 0.11 W.mL⁻¹, 25 °C.

8. LCMS analysis of benzyl alcohol oxidation at the optimal condition:



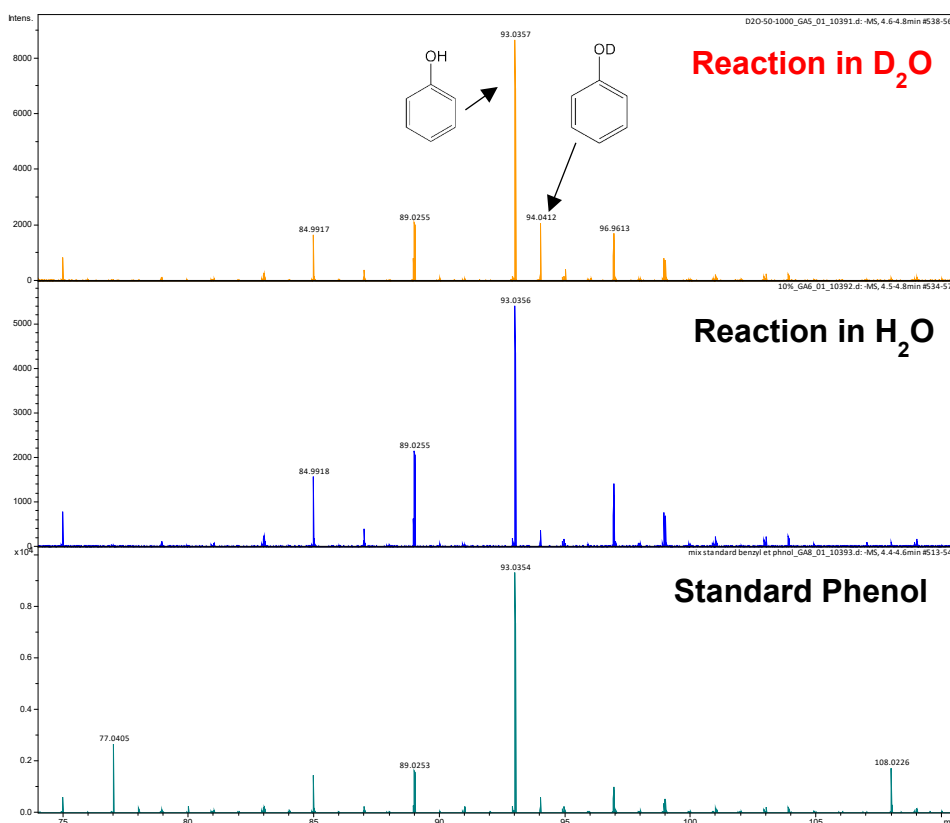


Figure S5. LC-MS analysis of the reaction in water and deuterated water: A) LC-MS chromatograms of benzyl alcohol oxidation over CuO catalyst, benzyl alcohol oxidation over CuO catalyst in D_2O and Standard phenol. B) ESI-MS Spectra of benzyl alcohol oxidation over CuO catalyst, benzyl alcohol oxidation over CuO catalyst in D_2O and Standard phenol. Reaction conditions: 5 mmol.L^{-1} Benzyl alcohol, 5.4 mg CuO , 578 kHz , 0.11 W.mL^{-1} , $25 \text{ }^\circ\text{C}$.

Table S4. Peak ratio between the m/z monoisotopic (93.035) and m/z of the isotope (94.041)

	Standard Phenol	Reaction in H_2O	Reaction in D_2O
Peak 93,035	8524	5079	5264
Peak 94,04	532	338	1022
Ratio	6%	6%	20%

9. Optimization of CuO-catalyzed oxidation of Benzyl alcohol

Experiments were carried out focusing on the optimization of the reaction conditions. For this purpose, several reaction parameters were investigated such as reaction temperature, the amounts of catalyst loading and the concentration of benzyl alcohol. The oxidative conversion of benzyl alcohol was carried out at higher temperatures ($60 \text{ }^\circ\text{C}$), higher concentration (50 mmol.L^{-1}) and over a range of catalyst loading (20-100%).

(i) Effect of bulk liquid temperature

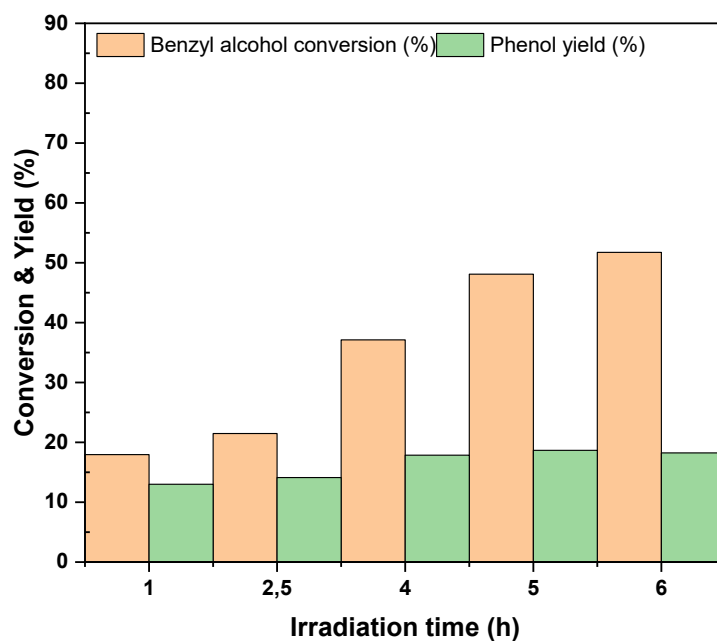


Figure S6. Ultrasonic irradiation time course for benzyl alcohol oxidation over CuO catalyst. Reaction conditions: 5 mmol.L⁻¹ Benzyl alcohol, 5.4 mg CuO, 578 kHz, 0.24 W.mL⁻¹, 60 °C.

(ii) Effect of substrate concentration

The effect of benzyl alcohol substrate concentration was next investigated while keeping the catalyst weight loading constant (10 wt. %). It was observed that at higher substrate concentration, the rate of benzyl alcohol conversion was significantly impacted. Even after extending the reaction irradiation time to 6 h, benzyl alcohol conversion was only ~ 20 %, with a phenol yield of ~ 10 %.

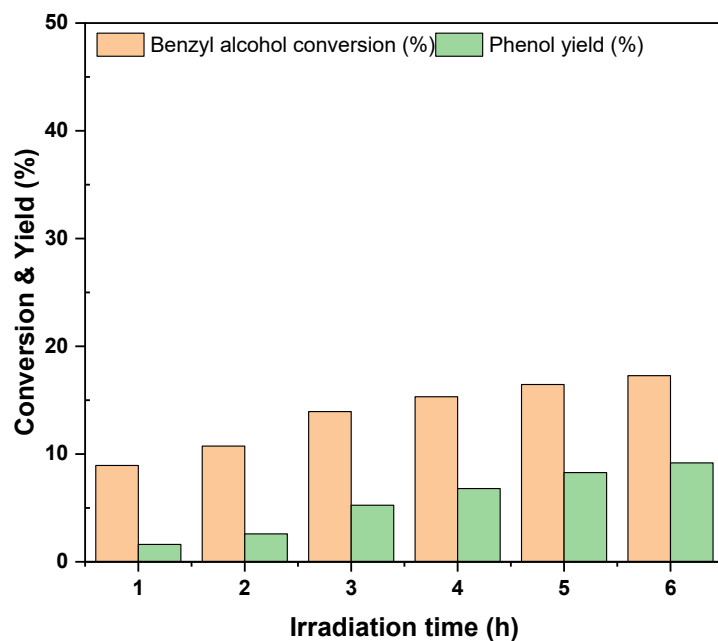


Figure S7. Ultrasonic irradiation time course for benzyl alcohol oxidation over CuO catalyst. Reaction conditions: 50 mmol.L⁻¹ Benzyl alcohol, 54 mg CuO, 578 kHz, 0.11 W.mL⁻¹, 25 °C.

(iii) Effect of catalyst loading

Increasing the catalyst loading amount in the reaction media negatively impacted the conversion rate of benzyl alcohol and the yield of phenol. At higher catalyst loading, the reaction medium tends to be viscous, which could potentially negatively impact cavitation and consequently the efficient generation and collapse of cavitation bubbles.

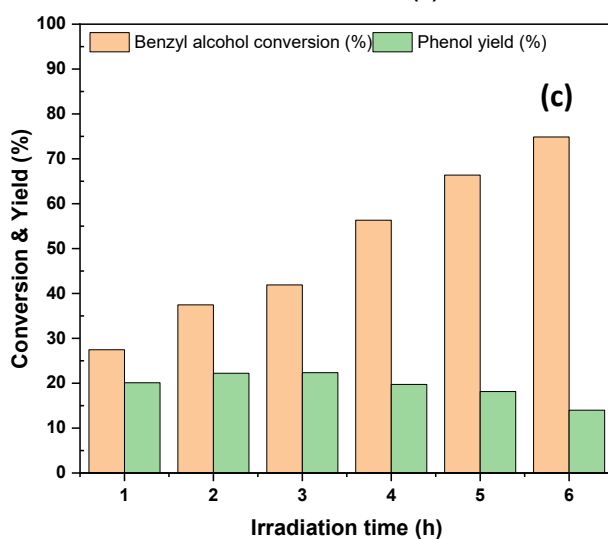
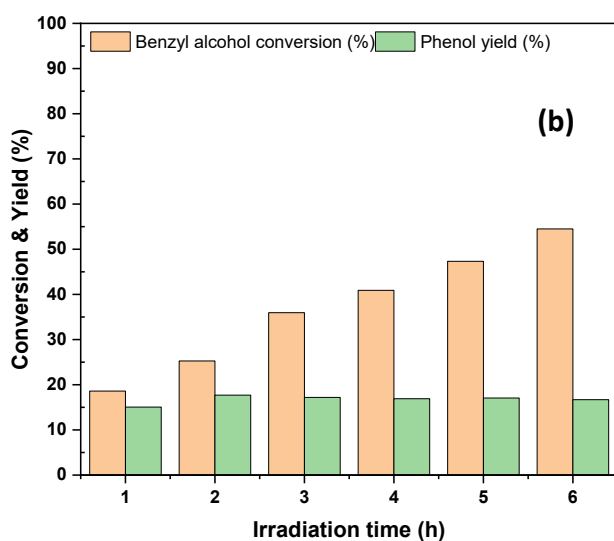
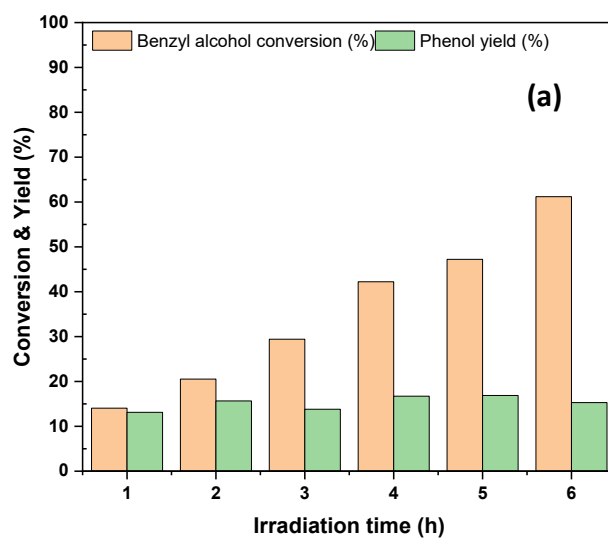


Figure S8. Effect of catalyst loading on the oxidation benzyl alcohol: CuO loading (wt. %) a) 20; b) 40; c) 100. Reaction conditions: 5 mmol.L⁻¹ Benzyl alcohol, 578 kHz, 0.11 W.mL⁻¹, 25 °C.

10. Structures of reaction intermediates and transition states in the catalytic conversion of benzyl alcohol to phenol

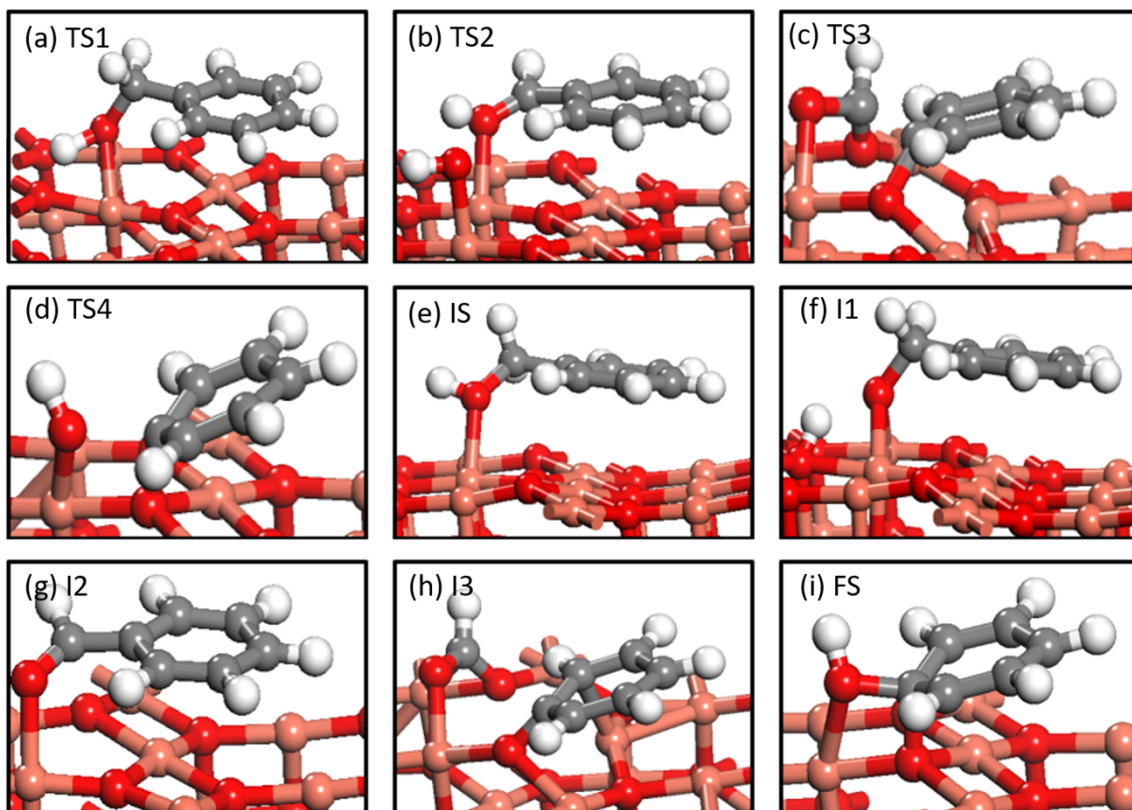


Figure S9. (a) transition state for initial O-H activation (*TS1); (b) transition state for subsequent C-H activation to form benzaldehyde (*TS2); (c) transition state for C-C cleavage from benzaldehyde (*TS3); (d) transition state for hydroxylation to phenyl ring(*TS4); (e) adsorbed benzyl alcohol (IS), (f) intermediate after initial O-H activation (IS), (g) key intermediate of benzaldehyde (I2), (h) intermediate after C-C cleavage from benzaldehyde (I3) and (i) adsorbed phenol (FS) on CuO (111) surface. Activation free energy barriers and reaction free energies are in kJ/mol. Salmon, red, grey, and white balls represent copper (Cu), oxygen (O), carbon (C) and hydrogen (H) atoms, respectively.

Fig. S9 shows the transition states, initial states, and final states for the catalytic conversion of benzyl alcohol to phenol on the CuO (111) surface. These structures correspond to the reaction pathway shown in Fig. 5.

11. Water dissociation on CuO (111)

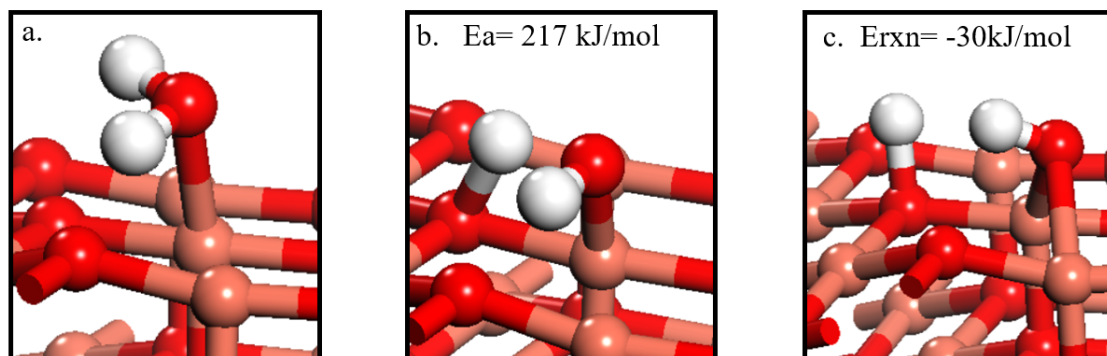


Figure S10. The configurations for a) water molecule adsorbed on CuO (111); b) transition state for Activation free energy barriers and reaction free energies are indicated in kJ/mol. Salmon, red, and white balls represent copper (Cu), oxygen (O), and hydrogen (H) atoms, respectively

Fig. S10 shows the adsorbed water molecule dissociation on CuO (111). The activation energy barrier and reaction energy for water dissociation on CuO are 218 kJ/mol and -30 kJ/mol, respectively.

12. Hydroxy-benzyl alcohol adsorption configurations on CuO (111) surface

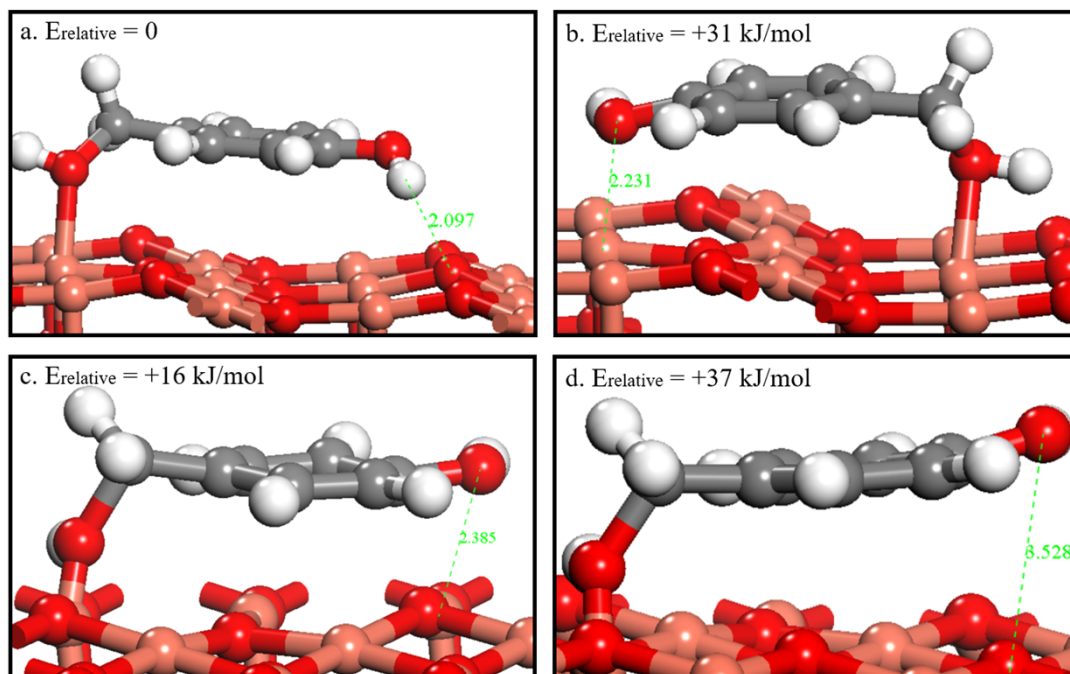


Figure S11. hydroxy-benzyl alcohol adsorption configurations on CuO (111) surface, as the relative energy reported compared to the most stable configuration as a., in kJ/mol. Salmon, red, grey, and white balls represent copper (Cu), oxygen (O), carbon (C) and hydrogen (H) atoms, respectively.

Fig. S11 shows different hydroxy-benzyl alcohol adsorption configurations on CuO (111) surface. The most stable adsorption configuration is similar to the adsorption configuration for benzyl alcohol on CuO (111) via the alcohol group. The distance between the hydroxyl group and catalyst surface are also labelled, as the distance is at least 2Å which further confirms the hypothesis that the hydroxyl group on the aromatic ring does not interact with the catalyst surface and hence it would not affect the reaction mechanism.