# Highly efficient selective oxidation of benzyl alcohol to benzaldehyde on PCM-engineered heat-storage catalyst via *in-situ* thermal buffering and facilitated ROS yield

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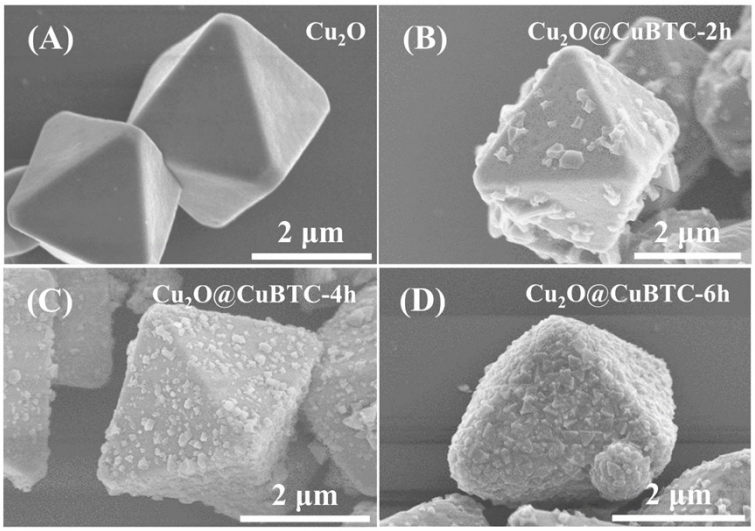



**Fig. S1** SEM images of synthesized samples: (A) $Cu_2O$, (B) $Cu_2O$@CuBTC-2h, (C) $Cu_2O$@CuBTC-4h and (D) $Cu_2O$@CuBTC-6h.

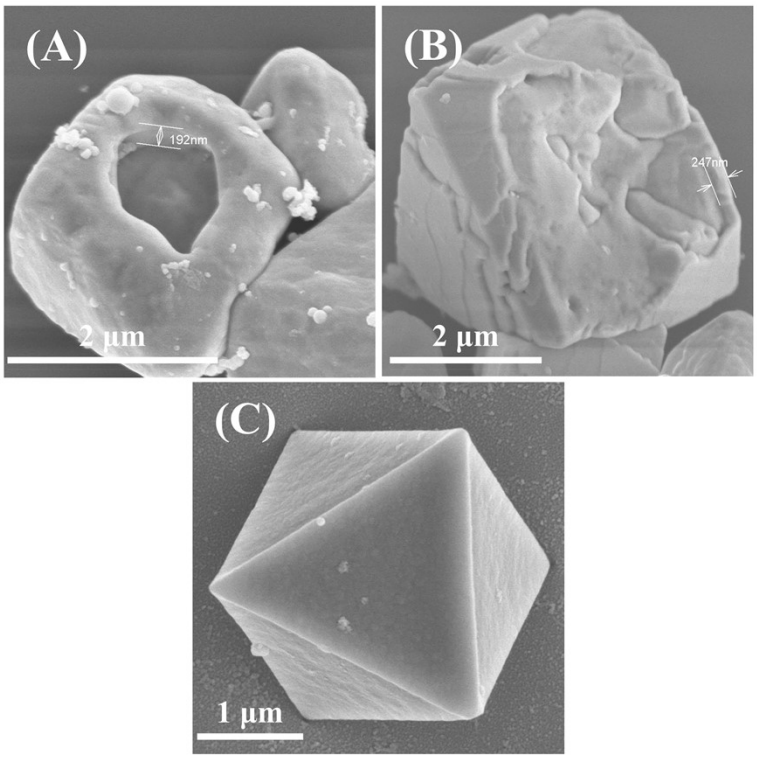



**Fig. S2** SEM images of (A, B) broken MEPCMs and (C) fabricated CuBTC.

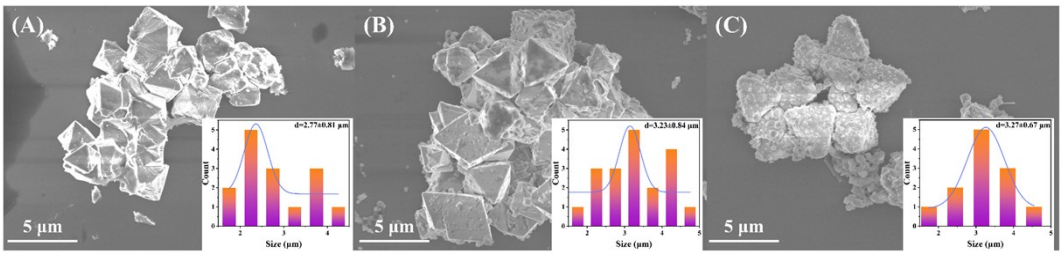



**Fig. S3** Low-magnification SEM images and size distribution of (A) MEPCM@CuBTC-2h, (B) MEPCM@CuBTC-4h and (C) MEPCM@CuBTC-6h.

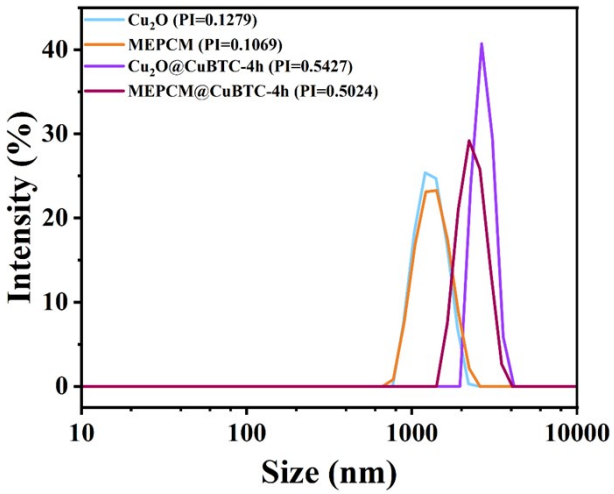



**Fig. S4** Dynamic Light Scattering (DLS) analysis and PI data of $Cu_2O$, $Cu_2O$@CuBTC-4h, MEPCM and MEPCM@CuBTC-4h.

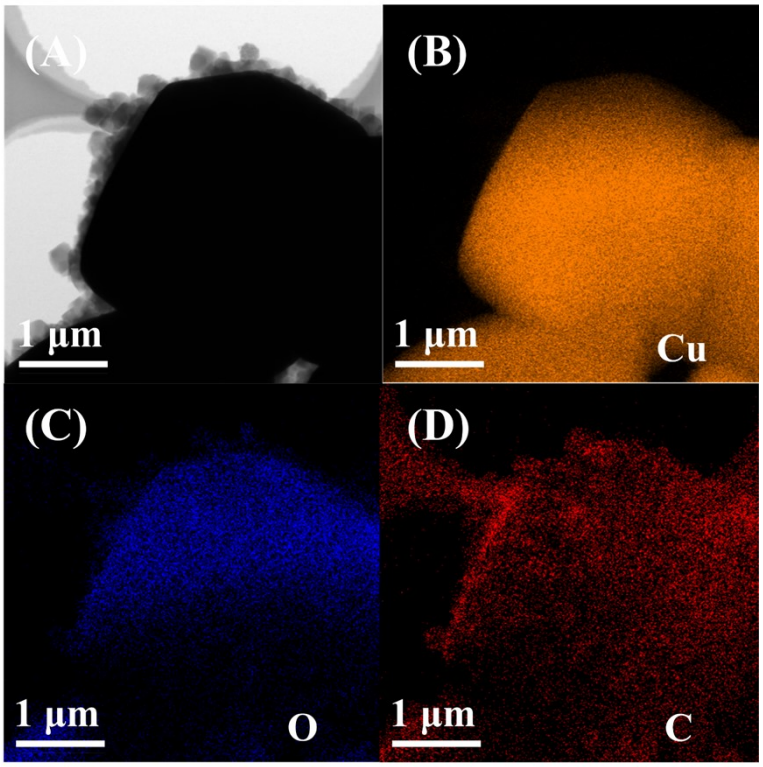



**Fig. S5** (A) EDX mapping images of MEPCM@CuBTC-4h: (B) Cu, (C) O and (D) C elements.

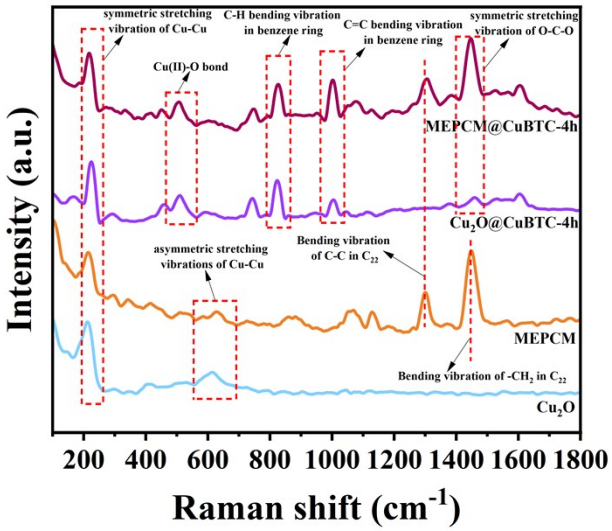



**Fig. S6** Raman spectra of $Cu_2O$, $Cu_2O$@CuBTC-4h, MEPCM and MEPCM@CuBTC-4h.

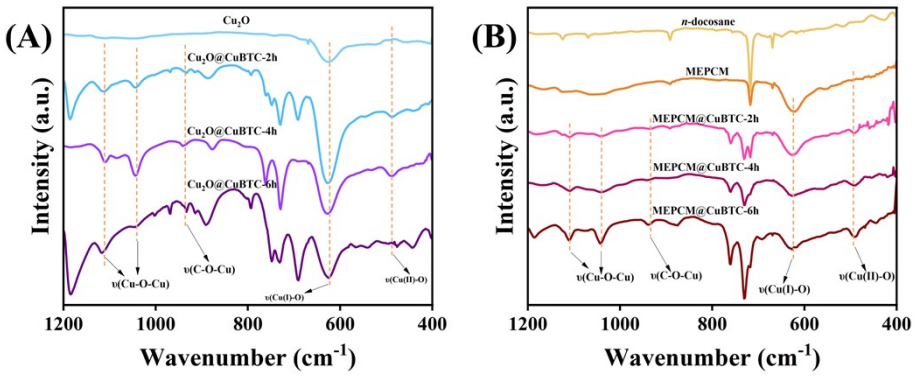



**Fig. S7** FT-IR spectra in the range of 400-1200 $cm^{-1}$ over synthesized samples: (A) $Cu_2O$ and $Cu_2O$@CuBTC-xh; (B) *n*-docosane, MEPCM and MEPCM@CuBTC-xh.

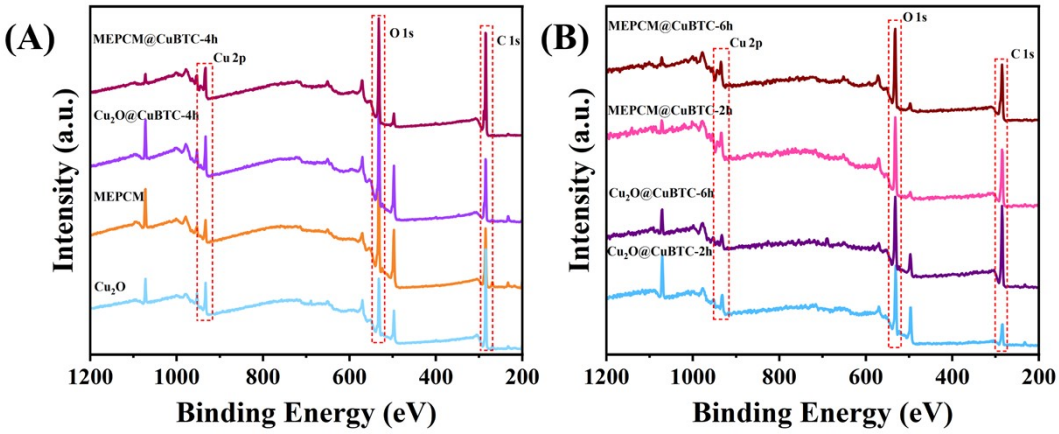



**Fig. S8** XPS survey spectra of prepared samples.

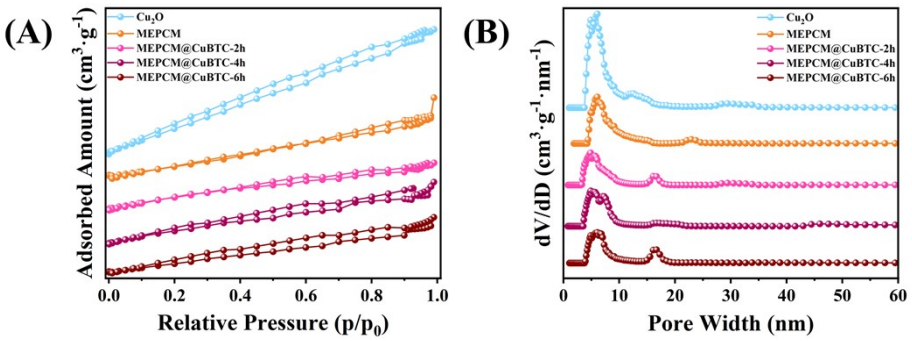



**Fig. S9** (A) 77 K $N_2$ adsorption-desorption isotherms and (B) pore size distribution curves of $Cu_2O$, MEPCM and MEPCM@CuBTC-xh.

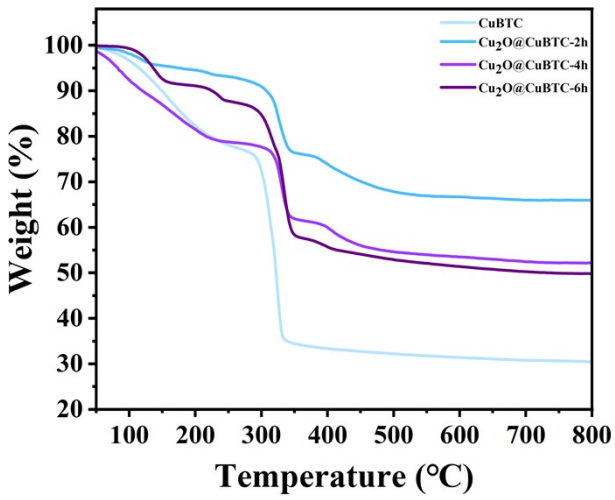



**Fig. S10** TGA curves of CuBTC and $Cu_2O$@CuBTC-Xh.

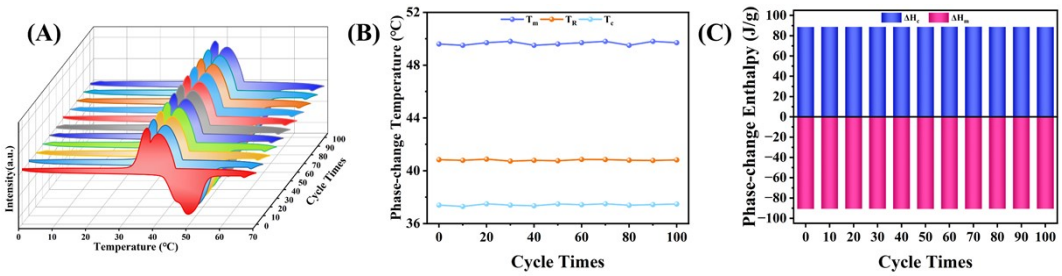



**Fig. S11** (A) Multicycle DSC diagrams, (B) phase-change temperatures and (C) phase-change enthalpies of MEPCM@CuBTC-4h.

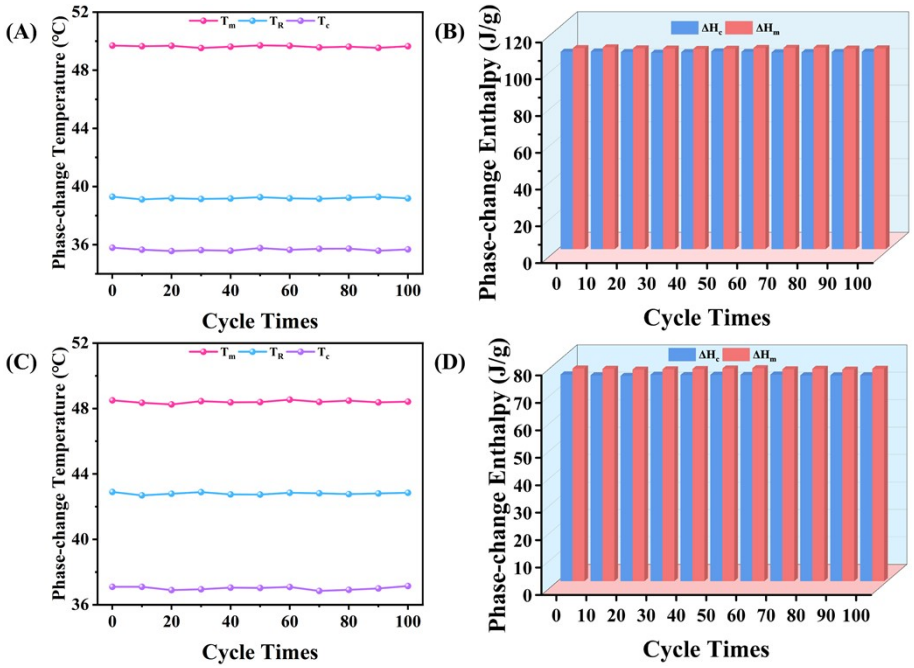



**Fig. S12** (A) phase-change temperatures and (B) phase-change enthalpies of MEPCM@CuBTC-2h, (C) phase-change temperatures and (D) phase-change enthalpies of MEPCM@CuBTC-6h.

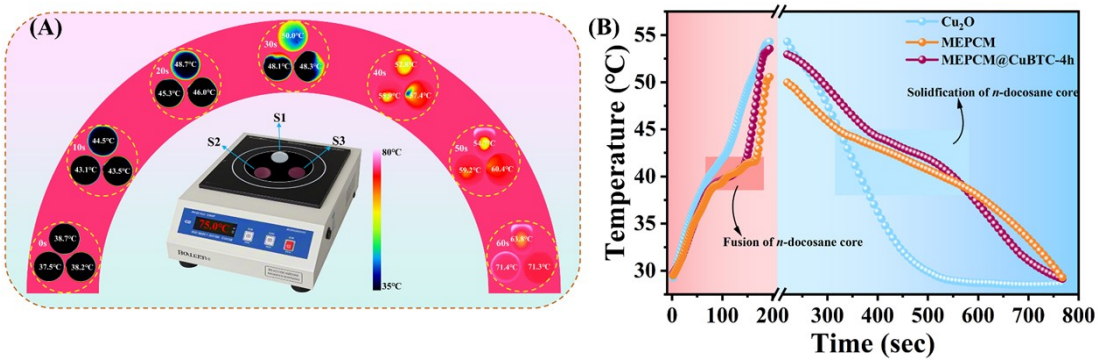



**Fig. S13** (A) Infrared thermal images of (S1) *n*-docosane, (S2) MEPCM and (S3) MEPCM@CuBTC-4h. (B) Curves of time vs. temperature obtained from heating and cooling process for pure $Cu_2O$, MEPCM and MEPCM@CuBTC-4h.

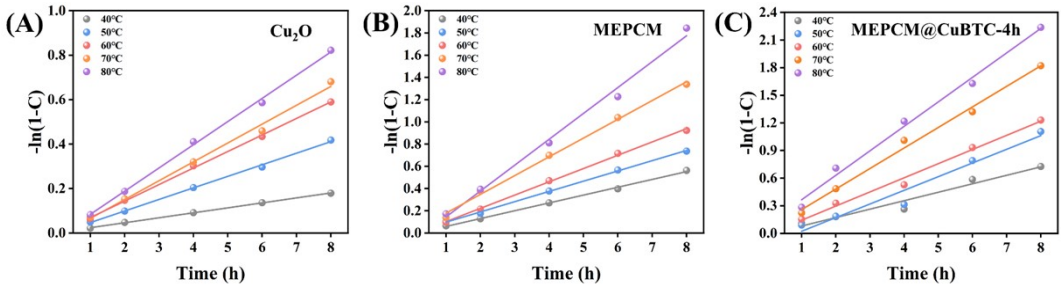



**Fig. S14** Time-conversion plots under various temperatures for (A) $Cu_2O$, (B) MEPCM and (C) MEPCM@CuBTC-4h. Reaction conditions: 15 mL toluene, 1 mmol benzyl alcohol, 5 mmol TBHP, 0.28 mmol Cu-catalyst, reaction temperature 40-80 ℃, reaction time 1-8 h, air.

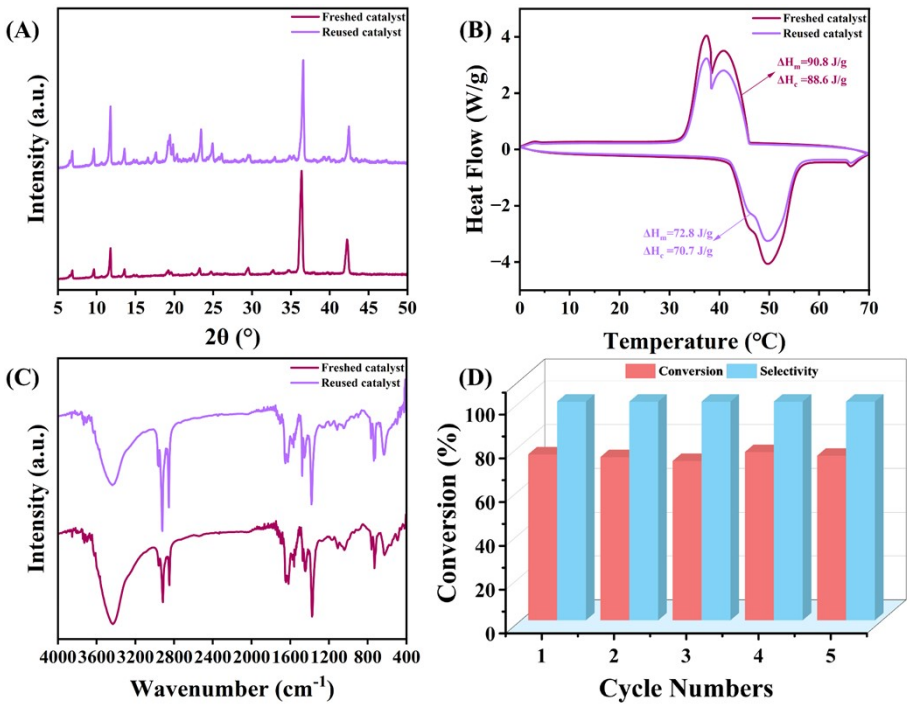



**Fig. S15** (A) XRD patterns, (B) DSC curves and (C) FT-IR spectra of fresh and reused MEPCM@CuBTC-4h. (D) The cycling performance of MEPCM@CuBTC-4h for benzyl alcohol oxidation.

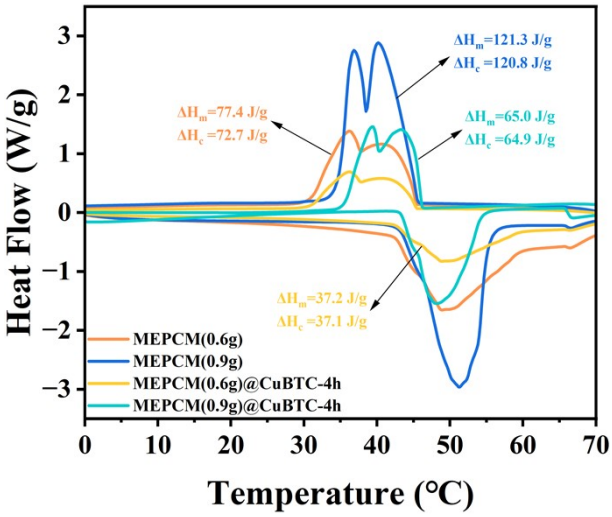



**Fig. S16** DSC curves of MEPCM(0.6g), MEPCM(0.9g), MEPCM(0.6g)@CuBTC-4h and MEPCM(0.9g)@CuBTC-4h.

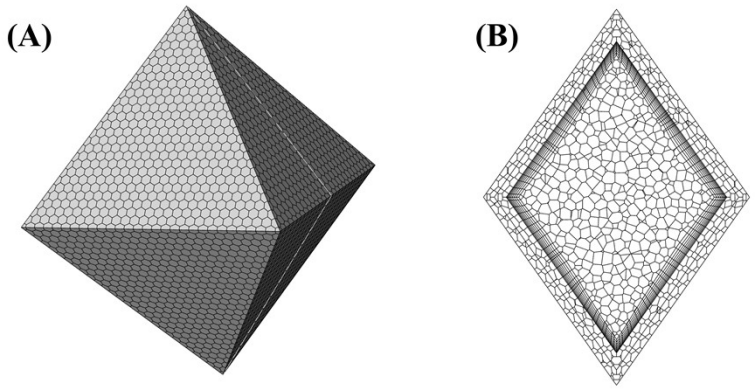



**Fig. S17** (A) Geometric model and (B) mesh refinement based on finite element analysis.

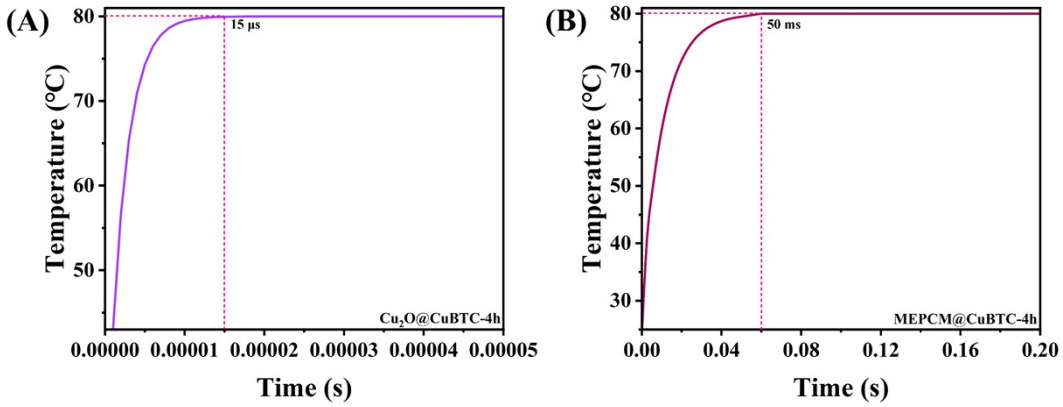



**Fig. S18** Finite element simulation of the central temperature curve of (A) $Cu_2O$@CuBTC-4h and (B) MEPCM@CuBTC-4h under surface loading of 80 ℃ boundary conditions.

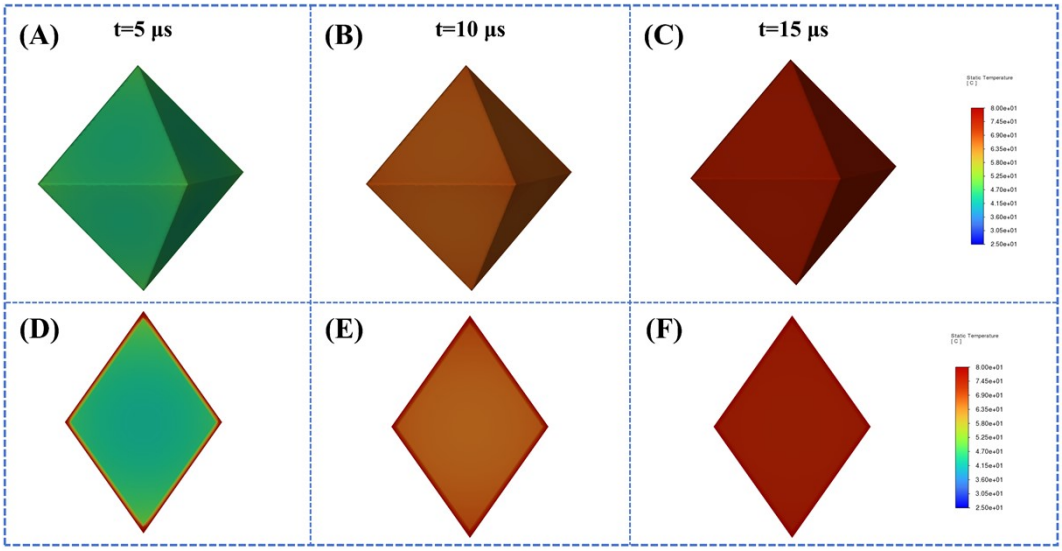



**Fig. S19** 3D surface and cross-sectional temperature-distribution contours of $Cu_2O$@CuBTC-4h under heating: (A, D) t=5 μs, (B, E) t=10 μs and (C, F) t=15 μs.

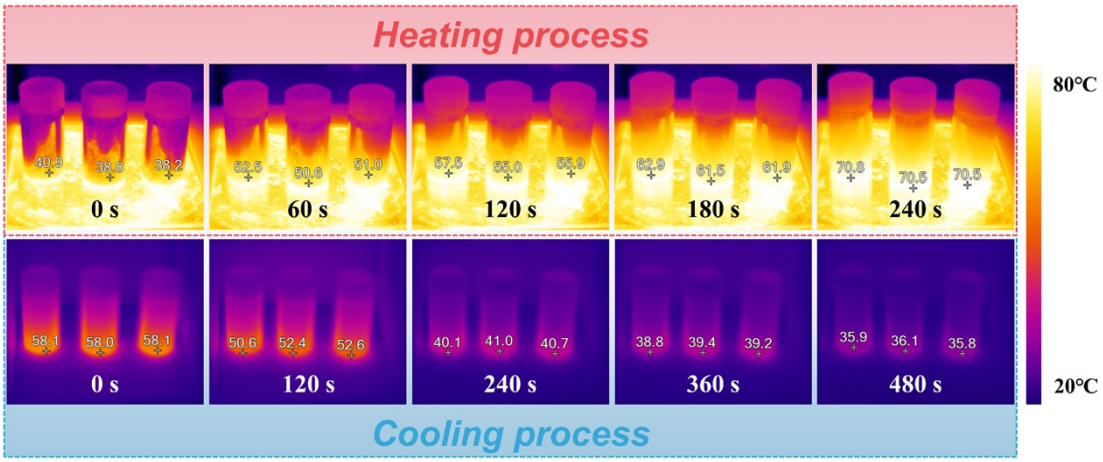



**Fig. S20** Infrared thermal images of three samples during the heating-cooling process in the catalytic system: $Cu_2O$, MEPCM and MEPCM@CuBTC-4h from left to right.

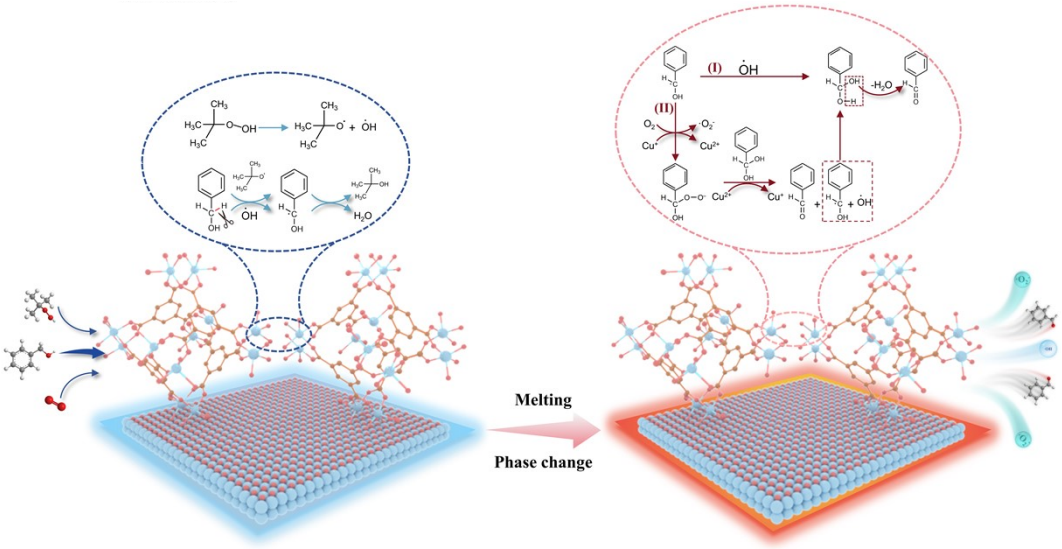



**Fig. S21** Proposed reaction mechanism for benzyl alcohol on the surface of MEPCM@CuBTC-4h catalyst: (I) ·OH oxidation pathway, (II) $\cdot O_2^-$ oxidation pathway.

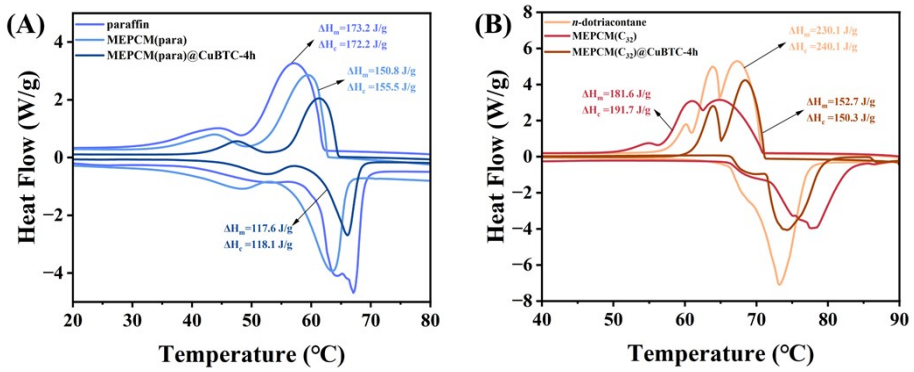
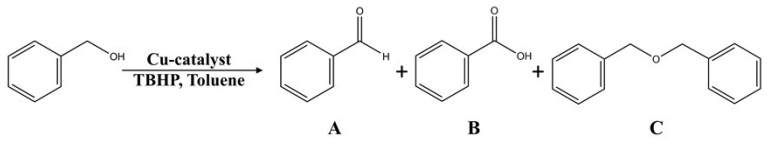



**Fig. S22** DSC curves of (A) paraffin, MEPCM(para) and MEPCM(para)@CuBTC-4h; (B) *n*-dotriacontane, MEPCM($C_{32}$) and MEPCM($C_{32}$)@CuBTC-4h.

**Table S1** Cell parameters, microstructural properties, mass fraction and $Cu^{2+}/Cu^{+}$ content of synthesized samples.

| Samples | *a=b=c* (Å) | Volume (Å$^3$) | Cu (wt%) | $Cu^{2+}/(Cu^{2+}+Cu^{+})$ (%) | $S_{BET}$ ($m^2 g^{-1}$) | Total Volume ($cm^3 g^{-1}$) |
|---|---|---|---|---|---|---|
| $Cu_2O$ | 4.269 | 77.79 | 88.80% | 15.7% | 68.6 | 0.124 |
| $Cu_2O$@CuBTC-2h | 4.270 | 77.85 | 58.63% | 21.9% | —— | —— |
| $Cu_2O$@CuBTC-4h | 4.272 | 77.96 | 46.08% | 35.2% | —— | —— |
| $Cu_2O$@CuBTC-6h | 4.275 | 78.13 | 36.68% | 45.2% | —— | —— |
| MEPCM | 4.243 | 76.39 | 30.00% | 25.1% | 31.6 | 0.066 |
| MEPCM@CuBTC-2h | 4.252 | 76.85 | 21.40% | 33.2% | 54.7 | 0.045 |
| MEPCM@CuBTC-4h | 4.256 | 77.09 | 19.36% | 67.1% | 54.9 | 0.059 |
| MEPCM@CuBTC-6h | 4.263 | 77.45 | 17.58% | 70.7% | 52.5 | 0.050 |
| CuBTC | 26.303 | 18197.67 | | — | | |

**Table S2** Catalytic activity of samples for benzyl alcohol oxidation to aldehydes [a]




A B C

| Entry | Samples | Conv. (%) | Sel. (%) | | |
|---|---|---|---|---|---|
| | | Benzyl alcohol | A | B | C |
| 1 | $Cu_2O$ | 33.7 | 90.8 | 6.4 | 2.8 |
| 2 | $Cu_2O$@CuBTC-2h | 46.3 | 98.3 | 0.8 | 0.9 |
| 3 | $Cu_2O$@CuBTC-4h | 45.0 | 94.4 | 5.6 | 0 |
| 4 | $Cu_2O$@CuBTC-6h | 51.0 | 99.2 | 0.8 | 0 |
| 5 | MEPCM | 55.6 | 100.0 | 0 | 0 |
| 6 | MEPCM@CuBTC-2h | 65.9 | 100.0 | 0 | 0 |
| 7 | MEPCM@CuBTC-4h | 75.8 | 100.0 | 0 | 0 |
| 8 | MEPCM@CuBTC-6h | 71.5 | 100.0 | 0 | 0 |
| 9 | $Cu_2O$@CuBTC-4h+PCMs | 50.2 | 96.3 | 3.7 | 0 |
| 10 | CuBTC | 40.9 | 100.0 | 0 | 0 |
| 11 | MEPCM@CuBTC-4h [b] | 31.9 | 100.0 | 0 | 0 |
| 12 | MEPCM@CuBTC-4h [c] | —— | | —— | |

[a] Reaction conditions: 15 mL toluene, 1 mmol benzyl alcohol, 5 mmol TBHP, 0.28 mmol Cu-catalyst, reaction temperature 80 ℃, reaction time 4 h, air.

[b] Reaction conditions: 15 mL toluene, 1 mmol benzyl alcohol, 5 mmol TBHP, 0.28 mmol Cu-catalyst, reaction temperature 80 ℃, reaction time 4 h, argon.

[c] Reaction conditions: 15 mL toluene, 1 mmol benzyl alcohol, 0.28 mmol Cu-catalyst, reaction temperature 80 ℃, reaction time 4 h, air.

**Table S3** Catalytic performance of samples for benzyl alcohol oxidation at different temperatures.

| Samples | Conv. & Sel. (%) | | | |
|---|---|---|---|---|
| Temperature(°C) | 50 | 60 | 70 | 80 |
| $Cu_2O$ | 18.5, 100.0 | 26.1, 100.0 | 27.4, 95.6 | 33.7, 90.8 |
| $Cu_2O$@CuBTC-4h | 19.7, 100.0 | 30.5, 100.0 | 40.9, 97.5 | 45.0, 94.4 |
| MEPCM | 31.5, 100.0 | 37.6, 100.0 | 51.3, 100.0 | 55.6, 100.0 |
| MEPCM@CuBTC-4h | 24.0, 100.0 | 41.0, 100.0 | 63.6, 100.0 | 75.8, 100.0 |

[a] Reaction conditions: 15 mL toluene, 1 mmol benzyl alcohol, 5 mmol TBHP, 0.28 mmol Cu-catalyst, reaction time 4 h, air.

**Table S4** Detailed catalytic performance of $Cu_2O$, MEPCM and MEPCM@CuBTC-4h under different temperature and time for kinetic study.

| Samples | Temperature | Conversion (%) | | | | | *k* | $R^2$ | Slope in Arrhenius plot |
|---|---|---|---|---|---|---|---|---|---|
| | | 1h | 2h | 4h | 6h | 8h | | | |
| $Cu_2O$ | 40℃ | 2.2% | 4.9% | 6.1% | 7.0% | 7.9% | 0.0223 | 0.99941 | -3.9641 |
| | 50℃ | 4.7% | 9.4% | 13.7% | 14.2% | 17.1% | 0.0520 | 0.99811 | |
| | 60℃ | 8.8% | 18.5% | 26.1% | 27.4% | 33.7% | 0.0743 | 0.99886 | |
| | 70℃ | 12.8% | 25.7% | 35.2% | 36.9% | 44.4% | 0.0848 | 0.99407 | |
| | 80℃ | 16.4% | 34.2% | 44.6% | 49.4% | 56.1% | 0.1043 | 0.99824 | |
| MEPCM | 40℃ | 6.4% | 9.9% | 9.3% | 13.1% | 15.9% | 0.0704 | 0.99781 | -3.3000 |
| | 50℃ | 12.1% | 16.3% | 19.4% | 31.6% | 32.6% | 0.0922 | 0.99890 | |
| | 60℃ | 23.8% | 31.5% | 37.6% | 50.3% | 55.6% | 0.1194 | 0.99846 | |
| | 70℃ | 32.8% | 43.3% | 51.2% | 64.6% | 70.7% | 0.1688 | 0.99628 | |
| | 80℃ | 43.1% | 52.2% | 60.3% | 73.8% | 84.2% | 0.2327 | 0.99246 | |
| MEPCM@ CuBTC-4h | 40℃ | 10.5% | 8.6% | 14.3% | 20.0% | 24.8% | 0.0918 | 0.95971 | -2.5206 |
| | 50℃ | 16.6% | 17.0% | 27.9% | 38.4% | 50.8% | 0.1484 | 0.95876 | |
| | 60℃ | 23.2% | 27.0% | 41.0% | 63.6% | 75.8% | 0.1536 | 0.99032 | |
| | 70℃ | 44.3% | 54.6% | 60.7% | 73.3% | 80.4% | 0.2231 | 0.99337 | |
| | 80℃ | 51.7% | 66.9% | 70.8% | 83.8% | 89.3% | 0.2658 | 0.99132 | |

Reaction conditions: 15 mL toluene, 1 mmol benzyl alcohol, 5 mmol TBHP, 0.28 mmol Cu-catalyst, reaction temperature 40-80 ℃, reaction time 1-8 h, air.

**Table S5** Catalytic performance comparison for BA oxidation of MEPCM@CuBTC-4h catalyst in this work with other reported catalysts.

| Entry | Samples | $n_{oxidant}/n_{substrate}$ | Time (h) | Temperature (℃) | Conversion (%) | Selectivity (%) | Reference |
|---|---|---|---|---|---|---|---|
| 1 | MEPCM@CuBTC-4h | 5 | 4 | 80 | 75.8 | 100 | This work |
| 2 | Fe-UiO-66 | 2 | 9 | 90 | 32.0 | 100 | 1 |
| 3 | $Cu_2O$@HKUST-1@Au | 5 | 9 | 90 | 63.0 | 100 | 2 |
| 4 | MIL-100(Fe) | 4.5 | 6 | 100 | 38.0 | 99 | 3 |
| 5 | $PW_4$/DAIL/MIL-100(Fe) | 4.5 | 6 | 100 | 58.0 | 99 | 3 |
| 6 | Au/$TiO_2$ | 1.5 | 2 | 95 | 63.1 | 79.2 | 4 |

**Table S6** The catalytic performance of MEPCM($C_{22}$)@CuBTC-4h, MEPCM(para)@CuBTC-4h and MEPCM($C_{32}$)@CuBTC-4h for benzyl alcohol oxidation at different temperatures.

| Samples | Conversion (%) | | | | |
|---|---|---|---|---|---|
| Temperature(℃) | 50 | 60 | 70 | 80 | 90 |
| MEPCM($C_{22}$)@CuBTC-4h | 24.0 | 41.0 | 63.6 | 75.8 | 82.8 |
| MEPCM(para)@CuBTC-4h | 25.6 | 39.2 | 66.1 | 71.4 | 77.6 |
| MEPCM($C_{32}$)@CuBTC-4h | 27.3 | 40.8 | 61.7 | 66.0 | 69.2 |

Reaction conditions: 15 mL toluene, 1 mmol benzyl alcohol, 5 mmol TBHP, 0.28 mmol Cu-catalyst, reaction time 4 h, air.

## References

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