

Electronic Supporting Information

Boosting catalysis of cesium phosphomolybdate encapsulated in hierarchical porous UiO-66 by microenvironment modulation for epoxidation of alkenes

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Materials and Instrumentation information

N,N'-dimethylformamide (DMF), tetrachloromethane, methanol, ethanol, acetone, 1,4-dioxane, 1,2-dichloroethane, acetonitrile, lauric acid (LA), potassium bromide (KBr), barium sulfate (BaSO₄) and phosphomolybdic acid (HPM) were purchased from Energy Chemical. ZrCl₄, terephthalic acid (BDC), 2,5-dimethylterephthalic acid styrene (2,5-2CH₃-BDC), 2,5-2,5-dihydroxyterephthalic acid (2,5-2OH-BDC), styrene, 1-octene, 1-decene, cyclooctene, cyclododecene, and 5.5 mol·L⁻¹ *tert*-butyl hydroperoxide (*t*-BuOOH) were purchased from Sigma-Aldrich. All the chemicals were obtained commercially and used without further purification.

Elemental quantity was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) using iCAP 7400. X-ray diffraction (XRD) was performed on a Bruker AXS D8 ADVANCE diffractometer with Cu *K*α radiation ($\lambda = 1.54178 \text{ \AA}$). N₂ adsorption-desorption isotherms were measured at 77 K with Quantachrome iQ automated adsorption analyzer. The Brunauer-Emmett-Teller (BET) surface area and total pore volume were calculated from the N₂ sorption isotherms, and the pore size distribution was calculated based on the N₂ sorption isotherm by using Non Local Density Functional Theory (NLDFT) model. Scanning electron microscopy (SEM) images were recorded on a Hitachi SU-8020 scanning electron microscopy. Transmission electron microscopy (TEM) was carried out using a Tecnai G2 F20 S-TWIN transmission electron microscope. Fourier transform infrared (FT-IR) spectra were collected from KBr pellets on a Nicolet Nexus 870 spectrometry in the range of 400 to 4000 cm⁻¹. UV-visible (UV-Vis) spectra were carried out on a Shimadzu UV-

2600 spectrometer with the reference of BaSO₄. Raman experiments were carried out using a Renishaw inVia Raman microscope. ³¹P MAS NMR spectra were recorded on a Bruker DSX-300 spectrometer. The chemical shifts are given relative to external 85% H₃PO₄. X-ray photoelectron spectroscopy (XPS) was measured on a Thermo ESCALAB 250Xi with Al K α irradiation (1486.6 eV), and the binding energies were calibrated using the C1s peak at 284.8 eV. Electron spin resonance (ESR) spectra were obtained on Bruker A300 spectrometer at room temperature. Water contact angle measurement was carried on Dataphysics OCA20.

Table S1 The element compositions determined by ICP-OES analyses of various materials.

Sample	HPM loading (mmol·g ⁻¹ / wt.%)	Mo loading (mmol·g ⁻¹ / wt.%)	Cs loading (mmol·g ⁻¹ / wt.%)
HPM@HP-UiO-66	0.038 / 6.7	0.418 / 4.0	—
HPM@HP-UiO-66-2CH ₃	0.032 / 5.9	0.384 / 3.7	—
HPM@HP-UiO-66-2OH	0.037 / 6.6	0.407 / 3.9	—
CsPM@HP-UiO-66	0.038 / 6.7	0.418 / 4.0	0.105 / 2.8
CsPM@HP-UiO-66-2CH ₃	0.032 / 5.9	0.384 / 3.7	0.083 / 2.2
CsPM@HP-UiO-66-2OH	0.037 / 6.6	0.407 / 3.9	0.081 / 2.2

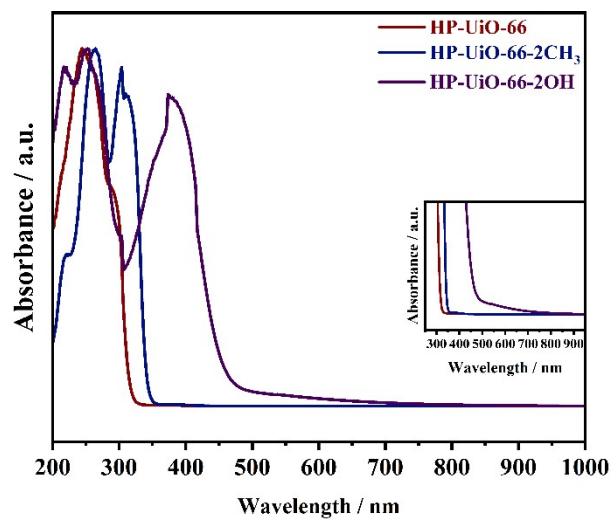


Fig. S1 DR-UV-vis spectra of HP-UiO-66-X.

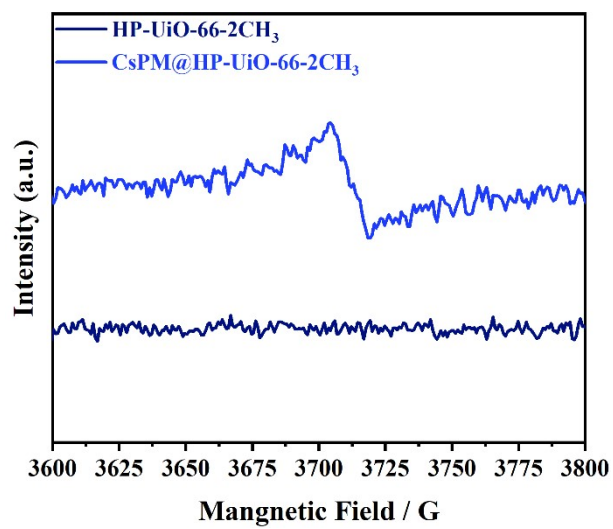


Fig.S2 EPR spectra of HP-UiO-66-2CH₃ and CsPM@HP-UiO-66-2CH₃ measured at room temperature.

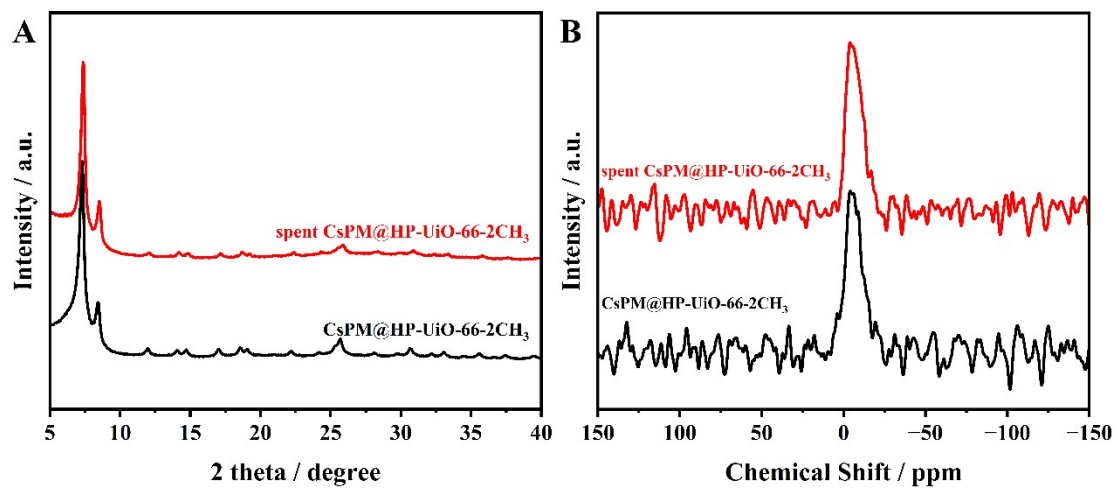


Fig.S3 Characterizations of CsPM@HP-UiO-66-2CH₃ and the spent CsPM@HP-UiO-66-2CH₃ composite (A) XRD and (B) MAS ³¹P solid state NMR.

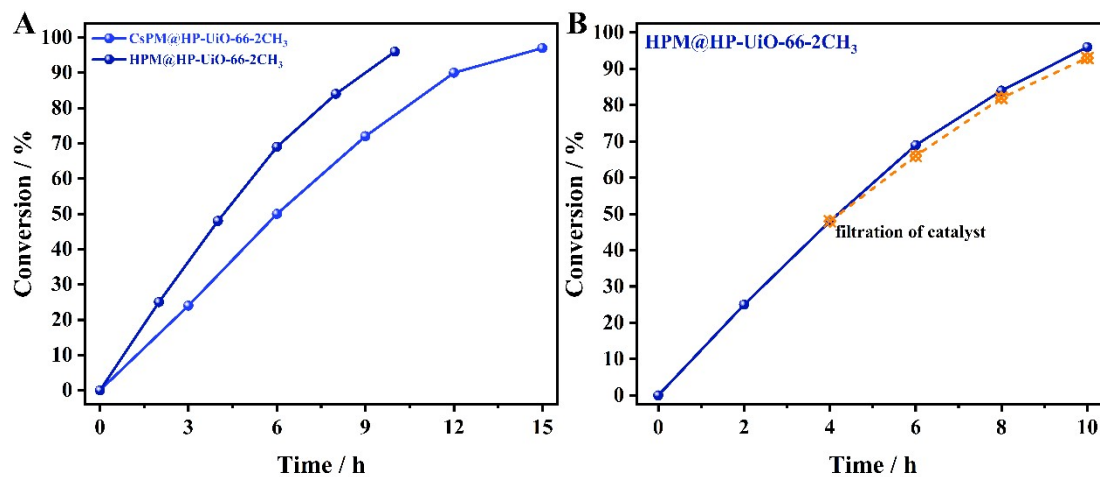
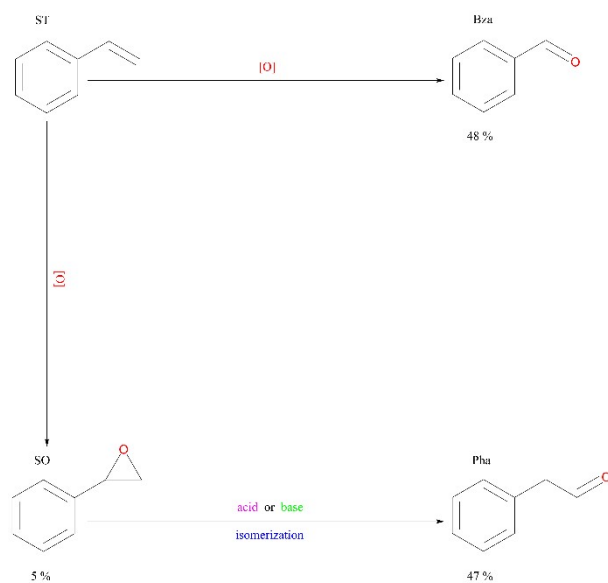


Fig.S4 (A) Kinetic profile and (B) Leaching. experiment of cyclooctene epoxidation over HPM@HP-UiO-66-2CH₃ composites Reaction condition: cyclooctene 1.0 mmol, *t*-BuOOH 3.0 mmol, tetrachloromethane 2.5 mL, catalyst 10 mg, reaction temperature 353 K.



Scheme S1 Oxidation products distribution of styrene over CsPM@HP-UiO-66-2CH₃ composite.