

Electronic Supporting Information

Modulated synthesis of cesium phosphomolybdate encapsulated in hierarchical porous UiO-66 for catalysing alkene epoxidation

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Materials and Instrumentation information

N,N'-dimethylformamide (DMF), tetrachloromethane, ethanol, acetone, toluene, 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), 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. Diffuse reflectance UV-visible (DR-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. ^{31}P MAS NMR spectra were recorded on a Bruker DSX-300 spectrometer. The chemical shifts are given relative to external 85% H_3PO_4 . X-ray photoelectron spectroscopy (XPS) was measured on a Thermo ESCALAB 250Xi with Al $K\alpha$ 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.

Reference catalyst preparation

Synthesis of microporous UiO-66

Typically, 0.36 g ZrCl_4 and 0.24 g BDC were dissolved in 60 mL DMF. After stirring for 2 h, the mixture was transferred to a Teflon-lined autoclave and kept at 393 K for 24 h. After cooling down to room temperature, the precipitate was washed several times with DMF and acetone. Finally, the precipitate was dried overnight under a vacuum at 373 K.

Synthesis of microporous HPM@UiO-66

Typically, 0.36 g ZrCl_4 , 0.24 g BDC and 0.06 g HPM were dissolved in 60 mL DMF. After stirring for 2 h, the mixture was transferred to a Teflon-lined autoclave and kept at 393 K for 24 h. After cooling down to room temperature, the precipitate was washed several times with DMF and acetone. Finally, the precipitate was dried overnight under a vacuum at 373 K. The loading amount of HPM in the hybrid composite was determined by ICP-OES spectrometer as shown in Table S1.

Synthesis of microporous CsPM@UiO-66

CsPM@UiO-66 composite was carried out by cation exchange. Firstly, twice synthetic equivalent HPM@UiO-66 was added to 10 mL of a methanol solution of cesium acetate ($12 \text{ mg}\cdot\text{mL}^{-1}$) at 333 K. After stirring for 3 h, the solids were separated by vacuum rotary evaporation method, Soxhlet-extracted with methanol and dried overnight under vacuum at 373 K to obtain the CsPM@UiO-66 composite, respectively. The loading amount of CsPM in the hybrid composite was determined by ICP-OES spectrometer as shown in Table S1.

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	0.040 / 7.4	0.480 / 4.7	—
CsPM@HP-UiO-66	0.040 / 7.4	0.480 / 4.7	0.105 / 2.8
HPM@UiO-66	0.016 / 2.9	0.192 / 1.8	—
CsPM@UiO-66	0.016 / 2.9	0.192 / 1.8	0.030 / 0.8

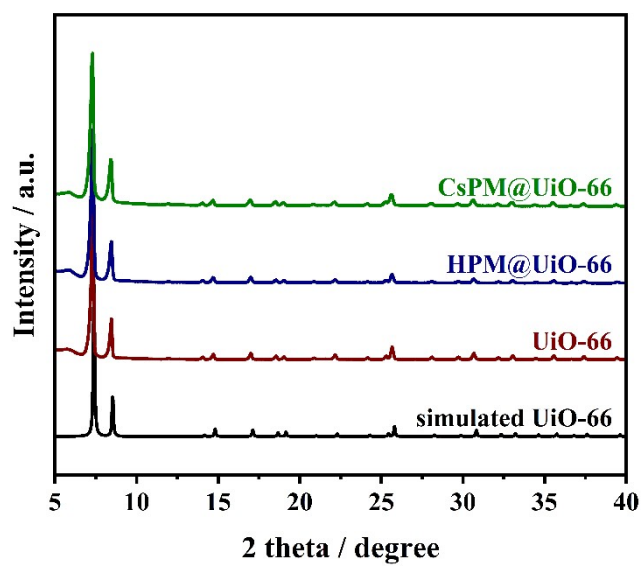


Fig. S1 XRD patterns of simulated UiO-66, UiO-66, HPM@UiO-66 and CsPM@UiO-66 composites.

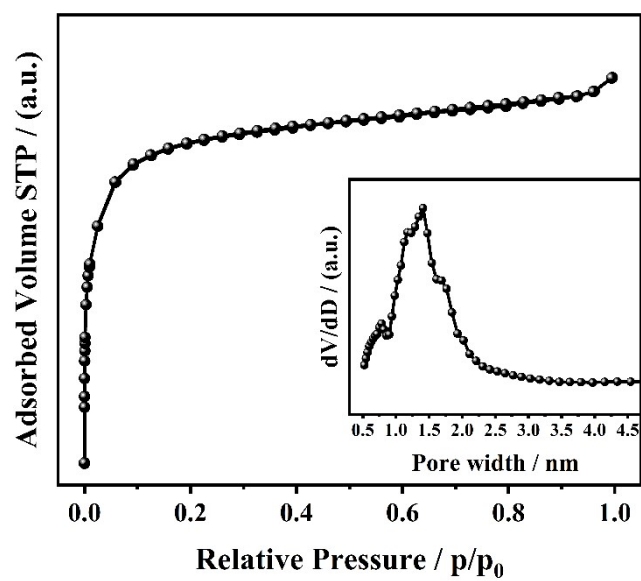


Fig. S2 N₂ adsorption-desorption isotherms and pore size distribution (insert) of CsPM@UiO-66 composites.

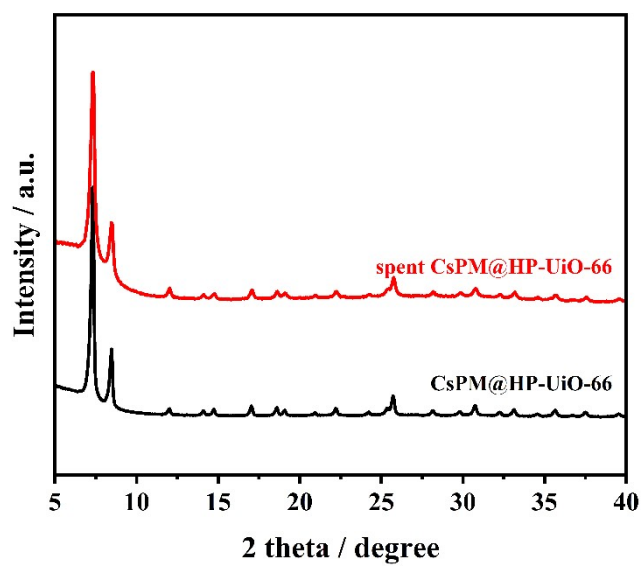


Fig. S3 XRD patterns of CsPM@HP-UiO-66 and the spent CsPM@HP-UiO-66 composite.

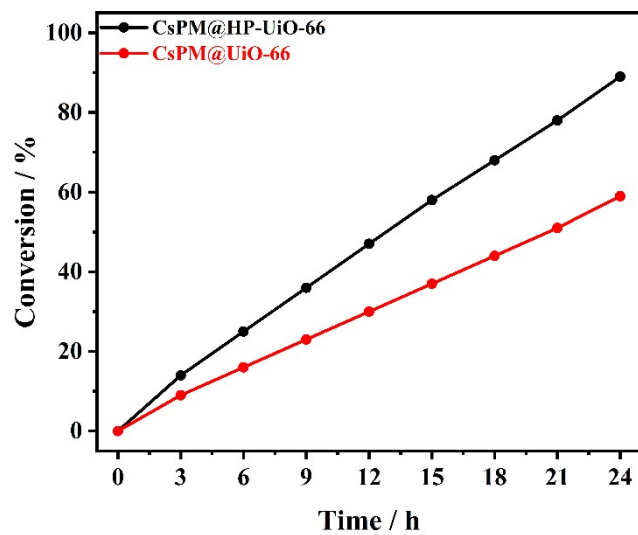
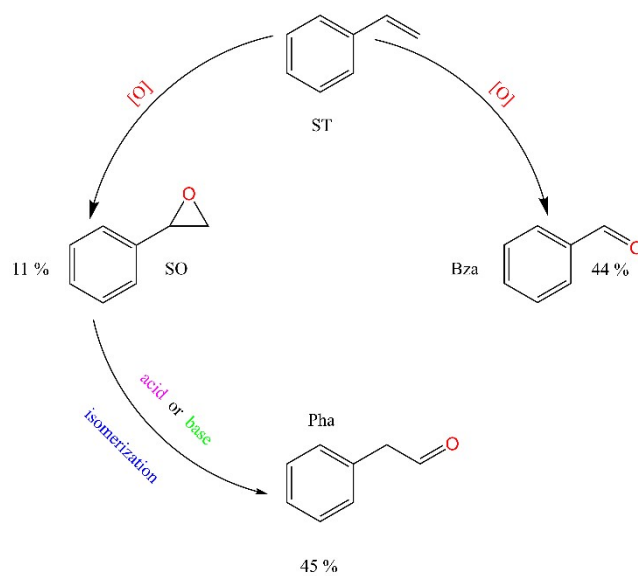
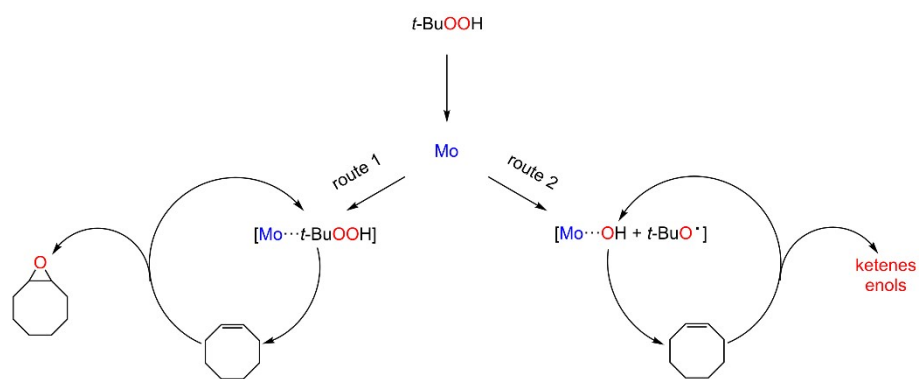


Fig. S4 Kinetic profile of cyclooctene epoxidation over CsPM@UiO-66 and CsPM@UiO-66 composites. Reaction condition: cyclooctene 1.0 mmol, *t*-BuOOH 2.0 mmol, tetrachloromethane 2.5 mL, catalyst 10 mg, reaction temperature 353 K.



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



Scheme S2 Proposed tentative mechanism of cyclooctene epoxidation over CsPM@HP-UiO-66 composite.