Supporting Information

Heterogeneity of Polyoxometalates by Confining within Ordered Mesopores: Toward Efficient Oxidation of Benzene to Phenol

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Characterization

N_2 adsorption–desorption analysis was performed using a TriStar (Micromeritics Instrument Corp.; Norcross, GA, USA) at 77 K, equipped with automated surface area and pore size analyzer. All samples were degassed at 180 °C for 24 h before analysis. Fourier transform infrared spectrum (FTIR) was collected by PerkinElmer Frontier Fourier transform infrared spectrometer. TG analysis was carried out with a STA409 instrument in dry air at a heating rate of 5 °C/min. The electron spin resonance (ESR) spectra were measured on a Bruker EMX-10/12 spectrometer at X-band. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with Al Karadiation (1486.6 eV). Transmission electron microscopy (TEM) images were recorded with a Tecnai G2 F30 S-Twin electron microscope. STEM images were recorded on a Nion UltraSTEM 200 microscope operated at 200 kV. Powder X-ray diffraction (XRD) were measured on a Bruker D8 diffractometer equipped with scintillation counter. The adsorption kinetics experiments for benzene was determined by UV-visible spectrometer (Hitachi U-2900).

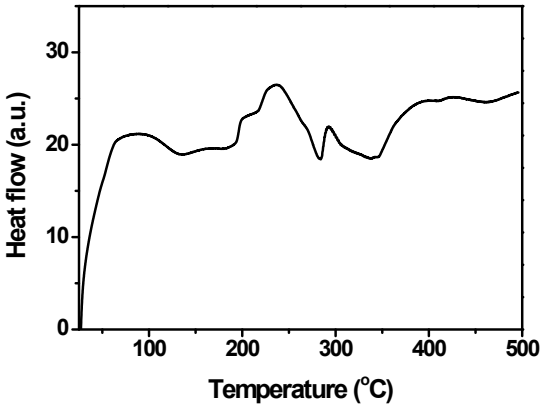

Figure S1. DSC analysis for PMo_1@OMP.

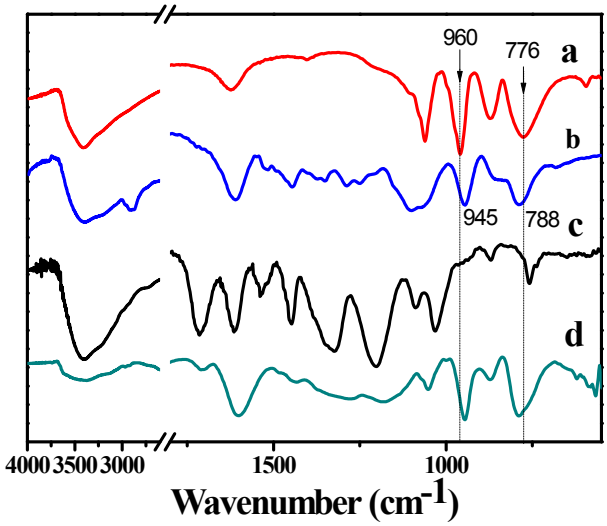

Figure S2. FT-IR spectra of (a) $H_3PMo_{12}O_{40}$, (b) PMo-AP-tannin-F127, (c) tannin and (d) PMo_1@OMP.

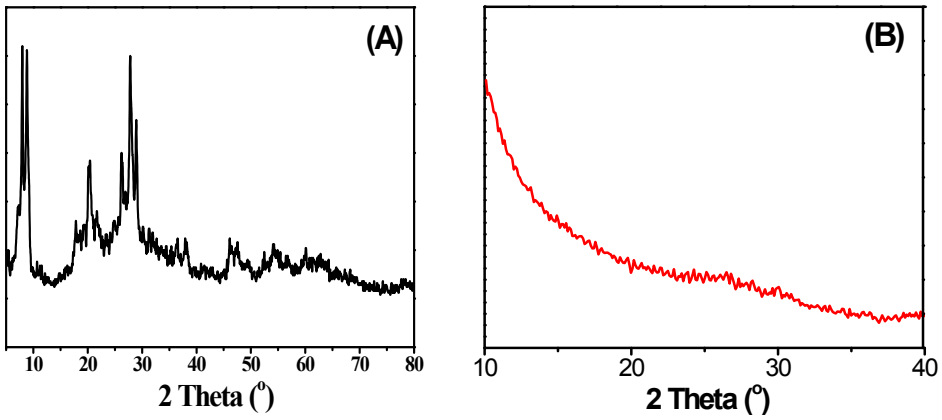

Figure S3. XRD patterns of (A) $H_3PMo_{12}O_{40}$ and (B) PMo_1@OMP.

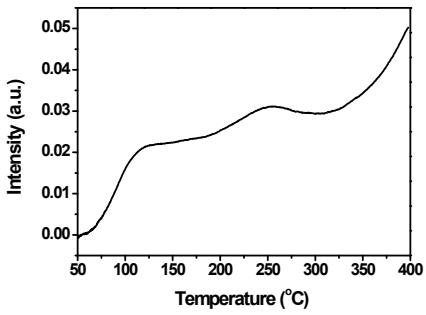

Figure S4. NH_3-TPD analysis for PMo_1@OMP.

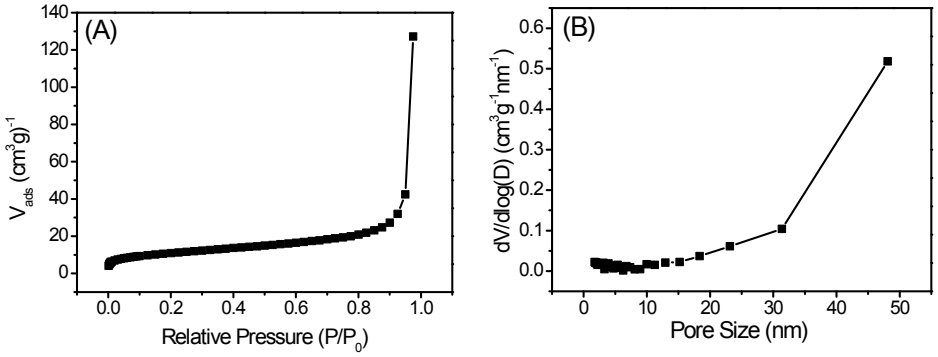

Figure S5. (A) N_2 adsorption isotherm and (B) BJH pore-size distribution of $PMo_1@C_{no\text{-}AP}$.

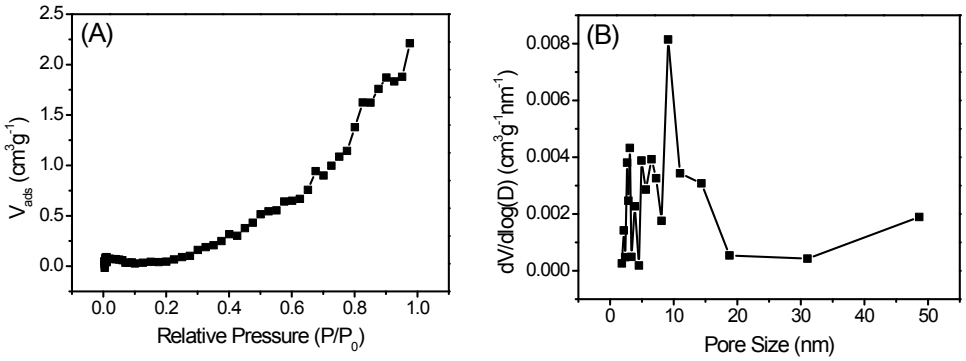

Figure S6. N_2 adsorption isotherm and BJH pore-size distribution of $PMo_1@C_{no\text{-}tannin}$.

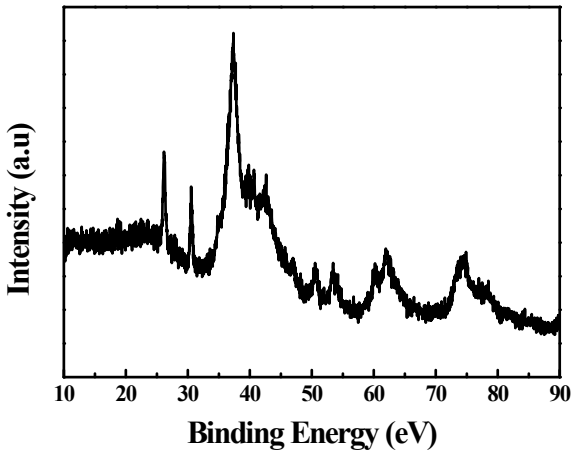

Figure S7. XRD pattern of PMo_1@OMC.

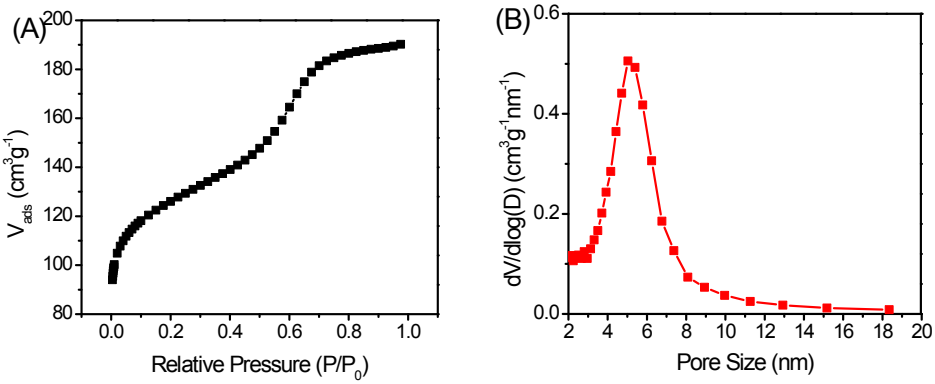

Figure S8. N_2 adsorption isotherm and BJH pore-size distribution of PMo_1@OMC.

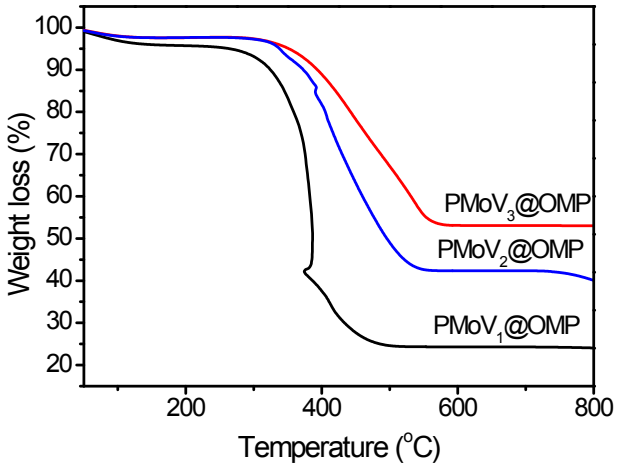

Figure S9. TG curves of $PMoV_1$@OMP, $PMoV_2$@OMP and $PMoV_3$@OMP.

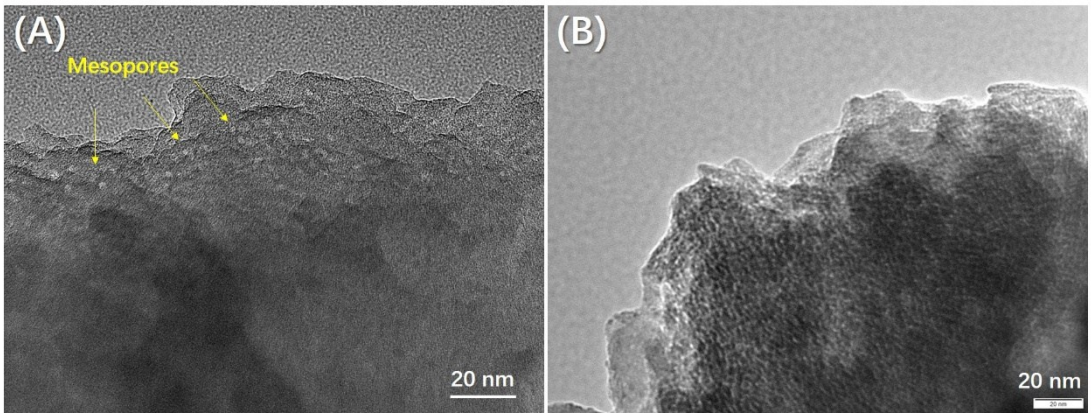

Figure S10. TEM images of (A) $PMoV_2$@OMP and (B) $PMoV_3$@OMP.

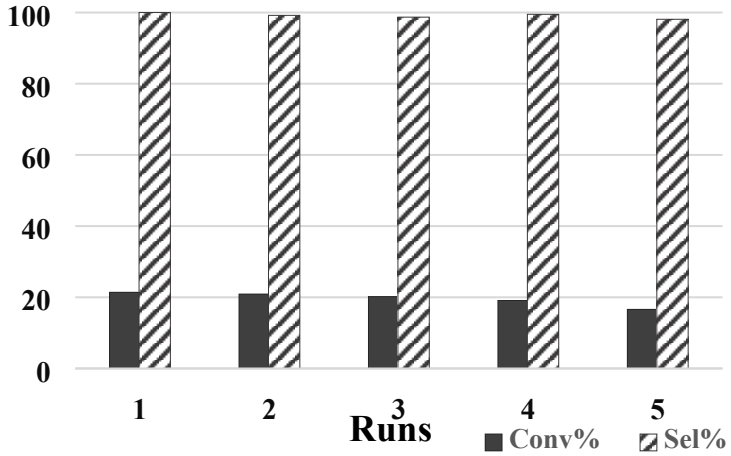

Figure S11. A five-run recycling test for hydroxylation of benzene over $PMoV_1$@OMP. Reaction conditions: benzene (6 mmol), H_2O_2 (18 mmol), acetonitrile (5 mL), acetic acid (1 mL), catalyst $PMoV_1$@OMP (0.05 g), 80 °C, 3 h.

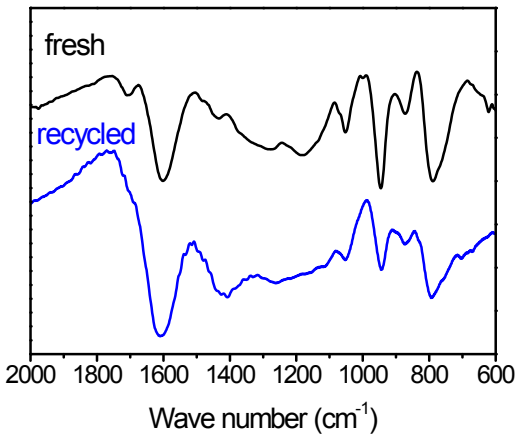

Figure S12. FT-IR spectra for the fresh and recovered catalyst $PMoV_1$@OMP.

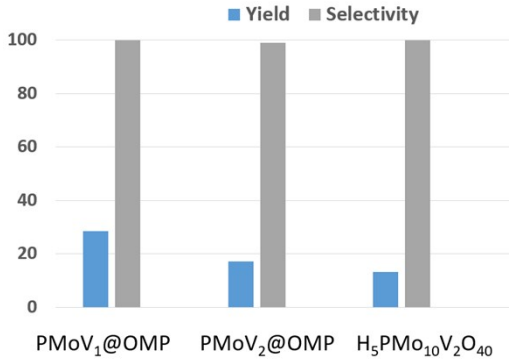

Figure S13. Hydroxylation of benzene over $PMoV_1$@OMP, $PMoV_2$@OMP, and $H_5PMo_{10}V_2O_{40}$ with fixed active sites. Reaction conditions: benzene (6 mmol), H_2O_2 (18 mmol), acetonitrile (5 mL), acetic acid (1 mL), $PMoV_1$@OMP (0.05 g) (or $PMoV_2$@OMP 0.03 g, $H_5PMo_{10}V_2O_{40}$ 0.015 g), 80 °C, 8 h.

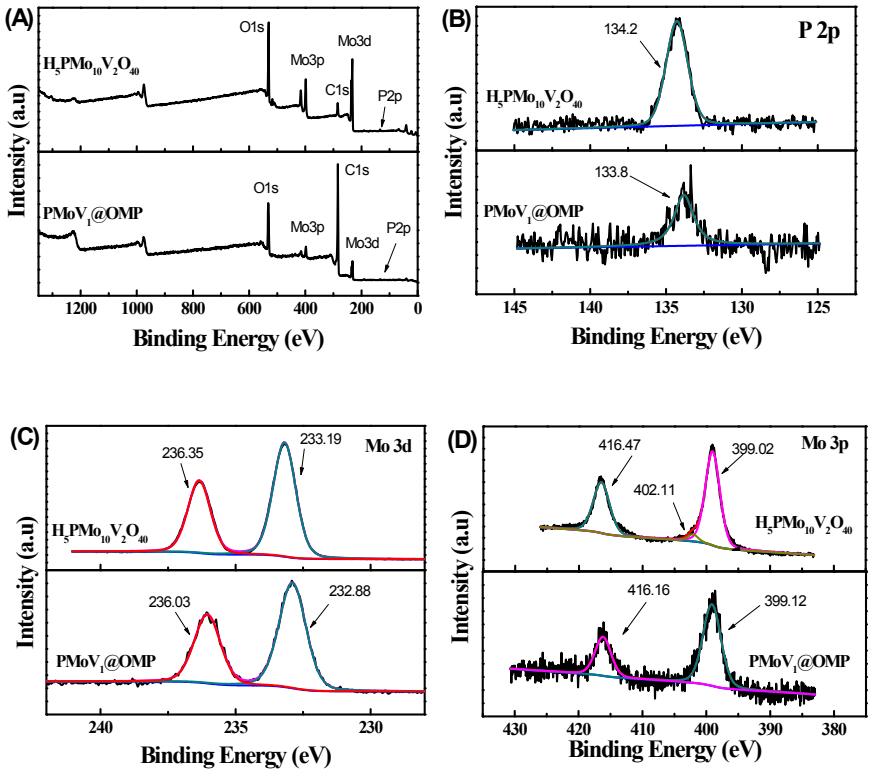

Figure S14. (A) XPS spectra, (B) P 2p spectra, (C) Mo 3d spectra, (D) Mo 3p spectra of $H_5PMo_{10}V_2O_{40}$ and $PMoV_1$@OMP.

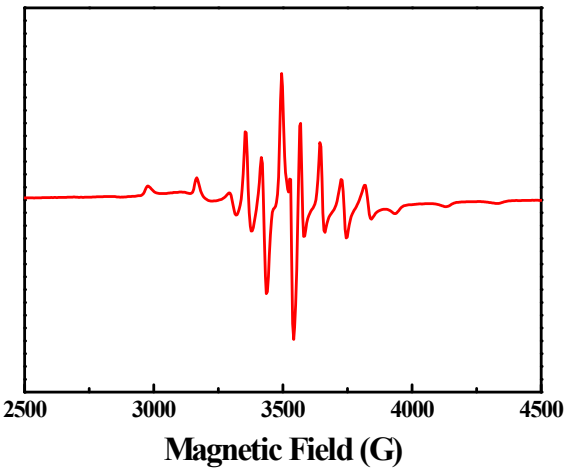

Figure S15. ESR pattern of recovered catalyst $PMoV_1$@OMP.