Copper-Containing POM-Based Hybrid $P_2Mo_{22}V_4Cu_4$ Nanocluster as Heterogeneous Catalyst for Light-Driven Hydroxylation of Benzene to Phenol

Qun Chen, Cheng-Yang Jiao, Hu Xu, Si-Man Li, Jian-Bo Yang, Hua Mei* and Yan Xu*
College of Chemical Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 211816, P.R. China.

Section 1. Crystal Structures

Figure. S1. The crystal image of $\mathbf{P_2Mo_{22}V_4Cu_4}$ under an optical microscope.

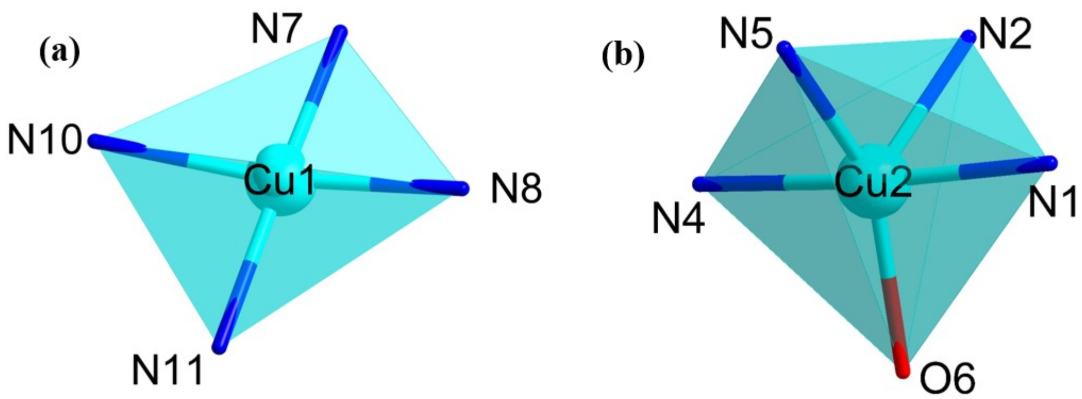


Figure. S2. Coordination modes of Cu1 (a) and Cu2 (b) ions in $\mathbf{P_2Mo_{22}V_4Cu_4}$.

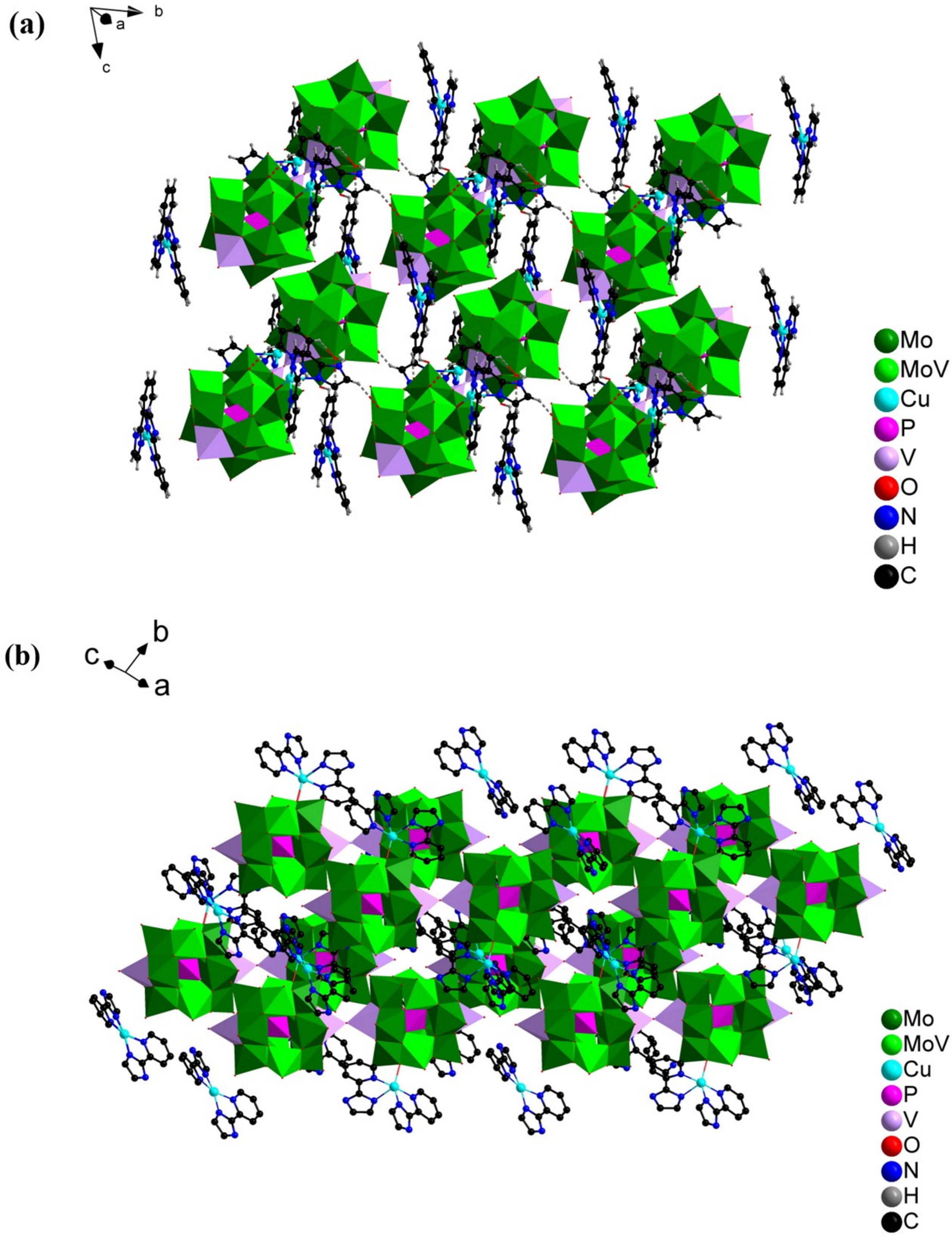


Figure. S3. 2D (a) and 3D (b) supramolecular architecture of $\mathbf{P_2Mo_{22}V_4Cu_4}$.

Section 2. Characterization

TG

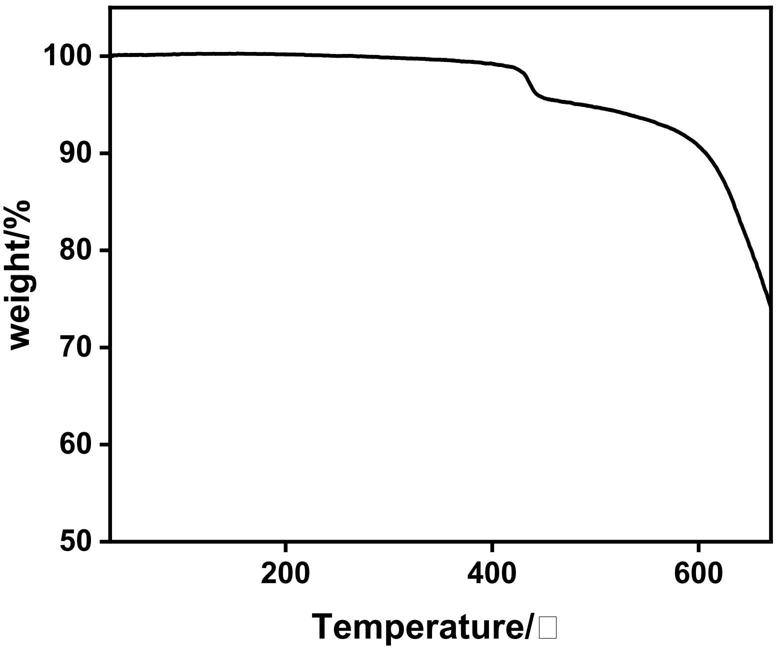


Figure. S3. The TG pattern of $\mathbf{P_2Mo_{22}V_4Cu_4}$.

XPS

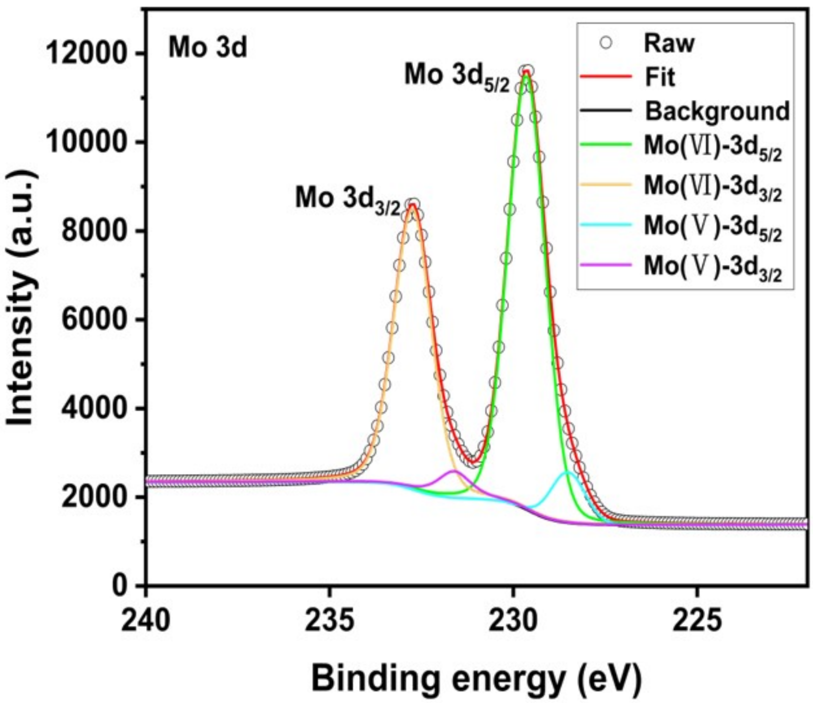


Figure. S4. The XPS binding energy of Mo 3d in the $\mathbf{P_2Mo_{22}V_4Cu_4}$.

As shown in Fig.S4, the characteristic binding energies of 232.8 eV and 229.7 eV belong to Mo^{6+}, while 231.8 eV and 228.5 eV belong to Mo^{5+}. In addition, the ratio of the peak area of Mo^{6+} $3d_{5/2}$ to the peak area of Mo^{5+} $3d_{3/2}$ in the XPS spectrum is approximately 11:1. This indicates that the ratio of Mo^{6+} to Mo^{5+} is 11:1, which is consistent with the theoretical calculation results.

UV-Vis

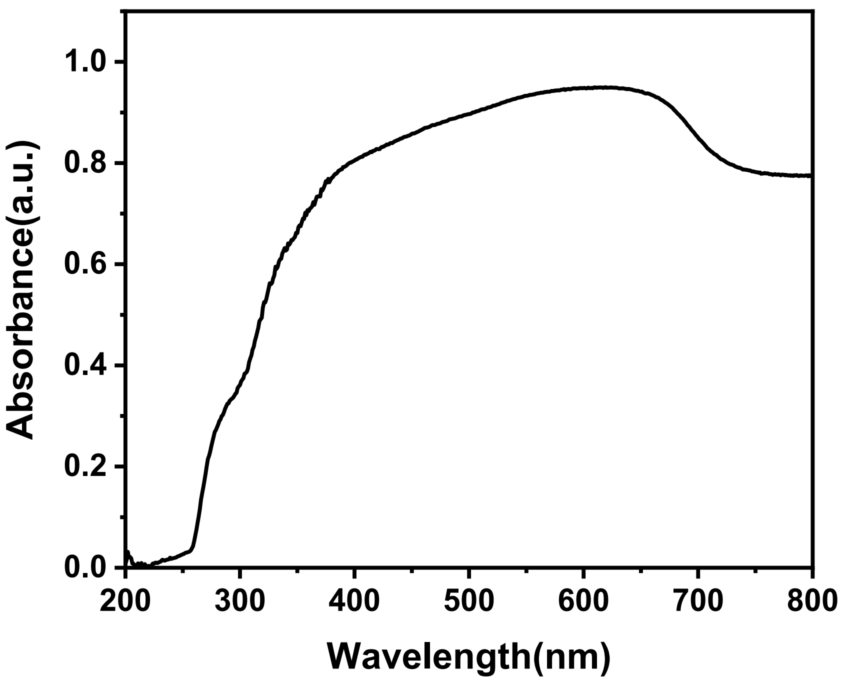


Figure. S5. The UV-vis diffuse reflectance spectra of $\mathbf{P_2Mo_{22}V_4Cu_4}$.

IR

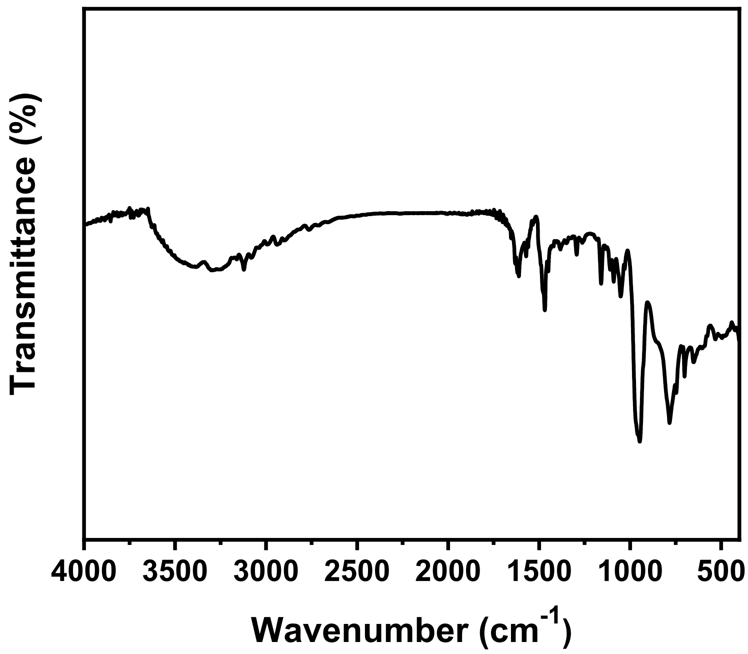


Figure. S6. FT-IR spectrum of $\mathbf{P_2Mo_{22}V_4Cu_4}$.

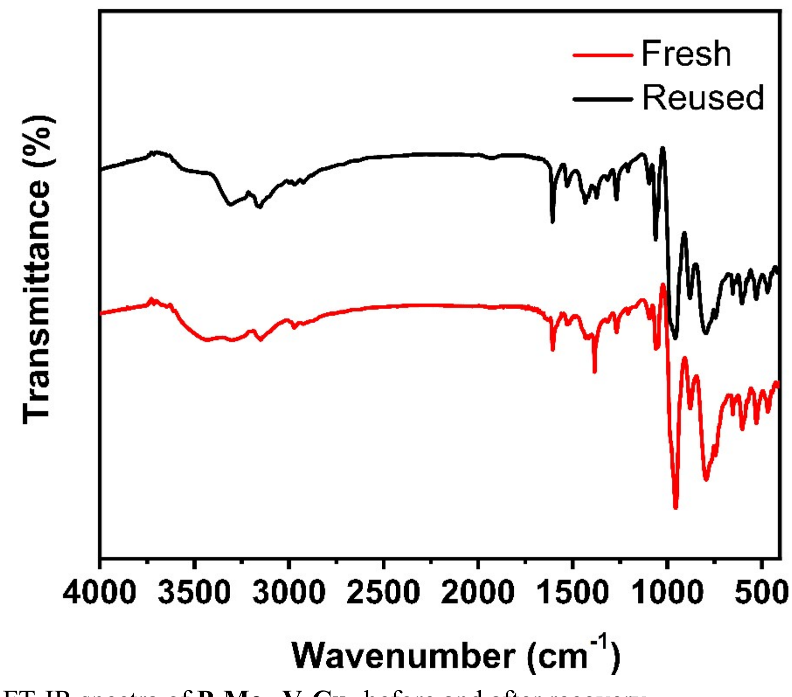


Figure. S7. FT-IR spectra of $\mathbf{P_2Mo_{22}V_4Cu_4}$ before and after recovery.

XRD

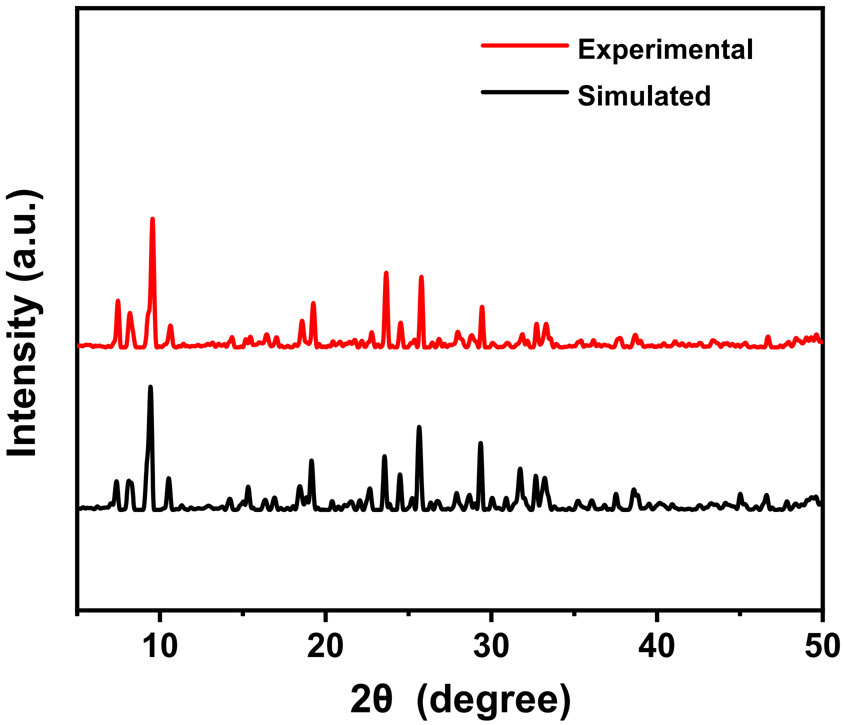


Figure. S8. The XRD patterns of $\mathbf{P_2Mo_{22}V_4Cu_4}$.

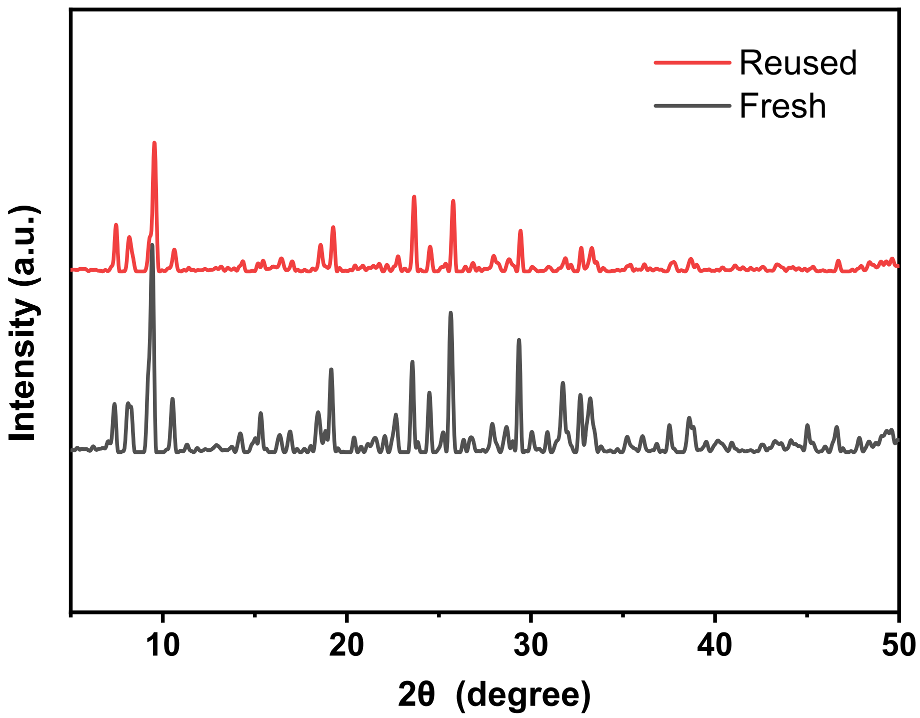


Figure. S9. The XRD patterns of $\mathbf{P_2Mo_{22}V_4Cu_4}$ after benzene hydroxylation.

Section 3. Materials and Physical property studies

The heteropolyacid ($H_5PMo_{10}V_2O_{40}$) were prepared according to a previously documented process and other chemicals were purchased and used without further purification. Powder X-ray diffraction PXRD tests were performed at room temperature using a Bruker D8X diffractometer equipped with monochromatic Cu Kα radiation (λ=1.5418 Å). Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) were obtained using a Hitachi S-4800 scanning electron microscope. Nicolet Impact 410 FT-IR spectrometer was used to analyze the infrared spectrum in the range of 4000~400 cm^{-1}. TG analysis was performed using a diamond thermogravimetric analyzer in a nitrogen atmosphere (25~800 °C, 10 °C min^{-1}). X-ray photoelectron spectroscopy (XPS) was used to analyze the catalyst. Ultraviolet-visible (UV-vis) diffuse reflectance spectra in the range of 200~800 nm (barium sulfate as reference) was collected on Shimadzu UV-2600 spectrophotometer.

Synthesis of $H_5PMo_{10}V_2O_{40}$: MoO_3 (7.20 g, 0.050 mol) and V_2O_5 (0.91 g, 0.005 mol) were added into 100 mL highly puried water and heated to boiling with stirring. Then, 0.58 g of 85 % phosphoric acid (0.005 mmol) was diluted with 10 mL; water, titrated into the above-mentioned solution within 30 min, and heated to reux for 24 hours. The product was collected via centrifugation and dried in a vacuum oven at 50 ℃. The crude product was recrystallized from water to get orange solid powder.[1]

Section 4. Investigation of benzene oxidation

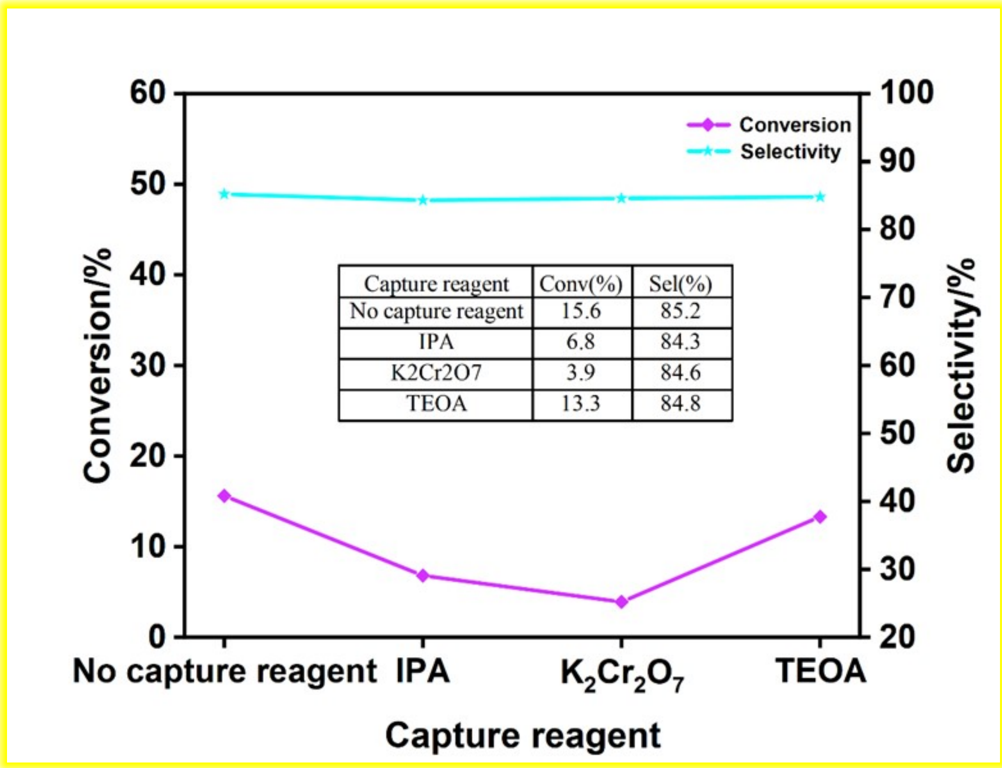
After each reaction, the catalyst was recovered by centrifugation, washed several times with C_2H_5OH, followed by drying at 60 °C for 12 h before the next reaction. The conversion and selectivity were calculated according to the following equations:

$$Conversion = \frac{n_2 + n_3}{n1} \times 100\%$$

$$Phenol\ selectivity = \frac{n_2}{n_2 + n_3} \times 100\%$$

$$Phenol\ yield\ =\ Conversion \times Selectivity$$

Note: n_1= amount of benzene added, n_2= amount of phenol formed, n_3= amount of benzoquinone formed



Capture reagent	Conv(%)	Sel(%)
No capture reagent	15.6	85.2
IPA	6.8	84.3
K2Cr2O7	3.9	84.6
TEOA	13.3	84.8

Figure. S10. Effect of different scavengers on the photocatalytic hydroxylation reaction of benzene.

Section 5. Other Tables

Table S1 Selected bond lengths (Å) and bond angles (˚) for catalyst.

Mo(1)-O(38)	1.670(6)	Mo(6)-O(14)	1.848(6)
Mo(1)-O(17)	1.862(6)	Mo(6)-O(40)	1.981(5)
Mo(1)-O(35)	1.871(5)	Mo(6)-O(33)	1.989(6)
Mo(1)-O(15)	1.990(5)	Mo(6)-O(32)	2.436(5)
Mo(1)-O(33)	2.028(6)	Mo(7)-O(36)	1.681(6)
Mo(1)-O(32)	2.444(6)	Mo(7)-O(16)	1.851(6)
Mo(2)-O(12)	1.686(6)	Mo(7)-O(28)	1.875(6)
Mo(2)-O(4)	1.856(6)	Mo(7)-O(40)	1.994(6)
Mo(2)-O(9)	1.863(6)	Mo(7)-O(23)	2.003(6)
Mo(2)-O(37)	1.969(6)	Mo(7)-O(13)	2.476(5)
Mo(2)-O(29)	2.022(6)	Mo(8)-O(25)	1.674(6)
Mo(2)-O(11)	2.447(5)	Mo(8)-O(5)	1.902(5)
Mo(3)-O(8)	1.678(6)	Mo(8)-O(3)	1.925(6)
Mo(3)-O(5)	1.873(5)	Mo(8)-O(35)	1.930(6)
Mo(3)-O(24)	1.882(6)	Mo(8)-O(14)	1.983(6)
Mo(3)-O(7)	1.986(6)	Mo(8)-O(32)	2.517(5)
Mo(3)-O(37)	2.011(6)	Mo(9)-O(22)	1.669(6)
Mo(3)-O(11)	2.461(5)	Mo(9)-O(24)	1.912(5)
Mo(4)-O(20)	1.671(5)	Mo(9)-O(17)	1.916(6)
Mo(4)-O(3)	1.878(6)	Mo(9)-O(10)	1.953(6)
Mo(4)-O(2)	1.880(6)	Mo(9)-O(4)	1.957(5)
Mo(4)-O(7)	1.957(5)	Mo(9)-O(11)	2.462(5)
Mo(4)-O(30)	1.978(6)	Mo(10)-O(21)	1.666(6)
Mo(4)-O(26)	2.468(5)	Mo(10)-O(18)	1.896(6)
Mo(5)-O(39)	1.669(6)	Mo(10)-O(28)	1.916(6)
Mo(5)-O(10)	1.836(6)	Mo(10)-O(2)	1.937(6)
Mo(5)-O(6)	1.906(6)	Mo(10)-O(19)	1.944(6)
Mo(5)-O(15)	1.971(6)	Mo(10)-O(26)	2.461(5)
Mo(5)-O(23)	2.015(6)	Mo(11)-O(1)	1.679(6)
Mo(5)-O(13)	2.429(5)	Mo(11)-O(27)	1.876(6)
Mo(6)-O(34)	1.686(6)	Mo(11)-O(18)	1.895(6)

Mo(6)-O(19)	1.838(6)	O(21)-Fe(6)-O(46)	80.6(3)
Mo(11)-O(29)	1.956(6)	O(17)-Mo(1)-O(33)	154.3(2)
Mo(11)-O(30)	1.983(6)	O(35)-Mo(1)-O(33)	89.9(2)
Mo(11)-O(26)	2.461(5)	O(15)-Mo(1)-O(33)	80.6(2)
Mo(12)-O(31)	1.651(6)	O(38)-Mo(1)-O(32)	169.5(3)
Mo(12)-O(27)	1.886(6)	O(17)-Mo(1)-O(32)	85.6(2)
Mo(12)-O(9)	1.911(6)	O(35)-Mo(1)-O(32)	74.4(2)
Mo(12)-O(16)	1.932(6)	O(15)-Mo(1)-O(32)	81.9(2)
Mo(12)-O(6)	2.037(6)	O(33)-Mo(1)-O(32)	71.2(2)
Mo(12)-O(13)	2.435(5)	O(12)-Mo(2)-O(4)	102.4(3)
Cu(1)-N(7)	1.985(8)	O(12)-Mo(2)-O(9)	103.1(3)
Cu(1)-N(8)	1.995(8)	O(4)-Mo(2)-O(9)	94.3(3)
Cu(1)-N(11)	2.013(7)	O(12)-Mo(2)-O(37)	101.3(3)
Cu(1)-N(10)	2.018(8)	O(4)-Mo(2)-O(37)	90.5(3)
Cu(2)-N(5)	1.969(7)	O(9)-Mo(2)-O(37)	153.5(2)
Cu(2)-N(1)	1.991(8)	O(12)-Mo(2)-O(29)	99.5(3)
Cu(2)-N(4)	2.011(7)	O(4)-Mo(2)-O(29)	157.6(2)
Cu(2)-O(6)	2.032(5)	O(9)-Mo(2)-O(29)	84.9(2)
Cu(2)-N(2)	2.238(8)	O(37)-Mo(2)-O(29)	80.9(3)
V(1)-O(42)	1.576(10)	O(12)-Mo(2)-O(11)	171.8(2)
V(1)-O(29)	1.908(6)	O(4)-Mo(2)-O(11)	74.4(2)
V(1)-O(7)	1.931(6)	O(9)-Mo(2)-O(11)	84.9(2)
V(1)-O(30)	2.071(7)	O(37)-Mo(2)-O(11)	71.4(2)
V(1)-O(37)	2.119(7)	O(29)-Mo(2)-O(11)	83.3(2)
V(2)-O(41)	1.497(3)	O(8)-Mo(3)-O(5)	104.7(3)
V(2)-O(40)	1.918(7)	O(8)-Mo(3)-O(24)	100.7(3)
V(2)-O(15)	1.994(7)	O(5)-Mo(3)-O(24)	93.6(2)
V(2)-O(23)	2.080(7)	O(8)-Mo(3)-O(7)	102.6(3)
V(2)-O(33)	2.109(7)	O(5)-Mo(3)-O(7)	85.4(2)
O(38)-Mo(1)-O(17)	104.1(3)	O(24)-Mo(3)-O(7)	156.1(2)
O(38)-Mo(1)-O(35)	100.5(3)	O(8)-Mo(3)-O(37)	100.6(3)
O(17)-Mo(1)-O(35)	94.5(2)	O(5)-Mo(3)-O(37)	153.6(2)
O(38)-Mo(1)-O(15)	102.6(3)	O(24)-Mo(3)-O(37)	89.0(3)
O(17)-Mo(1)-O(15)	85.4(2)	O(7)-Mo(3)-O(37)	81.7(2)
O(35)-Mo(1)-O(15)	156.2(3)	O(8)-Mo(3)-O(11)	168.8(2)

O(38)-Mo(1)-O(33)	99.9(3)	O(5)-Mo(3)-O(11)	85.1(2)
O(24)-Mo(3)-O(11)	73.0(2)	O(19)-Mo(6)-O(14)	94.7(3)
O(7)-Mo(3)-O(11)	83.2(2)	O(34)-Mo(6)-O(40)	101.0(3)
O(37)-Mo(3)-O(11)	70.5(2)	O(19)-Mo(6)-O(40)	86.2(2)
O(20)-Mo(4)-O(3)	101.8(3)	O(14)-Mo(6)-O(40)	157.8(2)
O(20)-Mo(4)-O(2)	99.9(3)	O(34)-Mo(6)-O(33)	99.8(3)
O(3)-Mo(4)-O(2)	90.8(2)	O(19)-Mo(6)-O(33)	155.2(2)
O(20)-Mo(4)-O(7)	103.1(3)	O(14)-Mo(6)-O(33)	89.8(3)
O(3)-Mo(4)-O(7)	87.3(2)	O(40)-Mo(6)-O(33)	80.8(2)
O(2)-Mo(4)-O(7)	156.8(2)	O(34)-Mo(6)-O(32)	170.6(3)
O(20)-Mo(4)-O(30)	101.6(3)	O(19)-Mo(6)-O(32)	85.6(2)
O(3)-Mo(4)-O(30)	156.2(2)	O(14)-Mo(6)-O(32)	75.4(2)
O(2)-Mo(4)-O(30)	89.6(3)	O(40)-Mo(6)-O(32)	82.6(2)
O(7)-Mo(4)-O(30)	83.1(2)	O(33)-Mo(6)-O(32)	72.0(2)
O(20)-Mo(4)-O(26)	170.3(3)	O(36)-Mo(7)-O(16)	102.1(3)
O(3)-Mo(4)-O(26)	85.5(2)	O(36)-Mo(7)-O(28)	102.8(3)
O(2)-Mo(4)-O(26)	73.4(2)	O(16)-Mo(7)-O(28)	93.5(3)
O(7)-Mo(4)-O(26)	83.4(2)	O(36)-Mo(7)-O(40)	101.9(3)
O(30)-Mo(4)-O(26)	71.8(2)	O(16)-Mo(7)-O(40)	155.6(2)
O(39)-Mo(5)-O(10)	102.7(3)	O(28)-Mo(7)-O(40)	85.3(2)
O(39)-Mo(5)-O(6)	100.1(3)	O(36)-Mo(7)-O(23)	101.1(3)
O(10)-Mo(5)-O(6)	94.7(2)	O(16)-Mo(7)-O(23)	90.4(3)
O(39)-Mo(5)-O(15)	100.6(3)	O(28)-Mo(7)-O(23)	154.4(2)
O(10)-Mo(5)-O(15)	87.5(2)	O(40)-Mo(7)-O(23)	80.9(2)
O(6)-Mo(5)-O(15)	158.2(2)	O(36)-Mo(7)-O(13)	170.7(2)
O(39)-Mo(5)-O(23)	100.1(3)	O(16)-Mo(7)-O(13)	73.3(2)
O(10)-Mo(5)-O(23)	156.0(2)	O(28)-Mo(7)-O(13)	85.8(2)
O(6)-Mo(5)-O(23)	88.9(2)	O(40)-Mo(7)-O(13)	82.2(2)
O(15)-Mo(5)-O(23)	80.7(2)	O(23)-Mo(7)-O(13)	71.2(2)
O(39)-Mo(5)-O(13)	170.6(3)	O(25)-Mo(8)-O(5)	104.3(3)
O(10)-Mo(5)-O(13)	85.9(2)	O(25)-Mo(8)-O(3)	104.0(3)
O(6)-Mo(5)-O(13)	75.1(2)	O(5)-Mo(8)-O(3)	86.7(2)
O(15)-Mo(5)-O(13)	83.4(2)	O(25)-Mo(8)-O(35)	101.9(3)
O(23)-Mo(5)-O(13)	72.0(2)	O(5)-Mo(8)-O(35)	89.8(2)
O(34)-Mo(6)-O(19)	103.3(3)	O(3)-Mo(8)-O(35)	153.9(2)

O(34)-Mo(6)-O(14)	100.4(3)	O(25)-Mo(8)-O(14)	101.7(3)
O(5)-Mo(8)-O(14)	154.1(2)	O(29)-Mo(11)-O(26)	82.6(2)
O(3)-Mo(8)-O(14)	87.4(2)	O(30)-Mo(11)-O(26)	71.9(2)
O(35)-Mo(8)-O(14)	84.5(2)	O(31)-Mo(12)-O(27)	103.5(3)
O(25)-Mo(8)-O(32)	170.7(3)	O(31)-Mo(12)-O(9)	102.4(3)
O(5)-Mo(8)-O(32)	82.8(2)	O(27)-Mo(12)-O(9)	87.8(2)
O(3)-Mo(8)-O(32)	82.2(2)	O(31)-Mo(12)-O(16)	101.5(3)
O(35)-Mo(8)-O(32)	71.7(2)	O(27)-Mo(12)-O(16)	91.5(2)
O(14)-Mo(8)-O(32)	71.37(19)	O(9)-Mo(12)-O(16)	155.6(2)
O(22)-Mo(9)-O(24)	101.5(3)	O(31)-Mo(12)-O(6)	97.7(3)
O(22)-Mo(9)-O(17)	102.1(3)	O(27)-Mo(12)-O(6)	158.8(2)
O(24)-Mo(9)-O(17)	90.5(2)	O(9)-Mo(12)-O(6)	88.4(2)
O(22)-Mo(9)-O(10)	103.6(3)	O(16)-Mo(12)-O(6)	83.5(2)
O(24)-Mo(9)-O(10)	154.9(2)	O(31)-Mo(12)-O(13)	169.4(3)
O(17)-Mo(9)-O(10)	84.9(2)	O(27)-Mo(12)-O(13)	86.0(2)
O(22)-Mo(9)-O(4)	102.6(3)	O(9)-Mo(12)-O(13)	82.5(2)
O(24)-Mo(9)-O(4)	86.1(2)	O(16)-Mo(12)-O(13)	73.1(2)
O(17)-Mo(9)-O(4)	155.2(2)	O(6)-Mo(12)-O(13)	72.86(19)
O(10)-Mo(9)-O(4)	87.9(2)	N(7)-Cu(1)-N(8)	83.0(3)
O(22)-Mo(9)-O(11)	172.3(2)	N(7)-Cu(1)-N(11)	167.7(3)
O(24)-Mo(9)-O(11)	72.5(2)	N(8)-Cu(1)-N(11)	100.3(3)
O(17)-Mo(9)-O(11)	83.1(2)	N(7)-Cu(1)-N(10)	97.9(4)
O(10)-Mo(9)-O(11)	82.4(2)	N(8)-Cu(1)-N(10)	163.1(3)
O(4)-Mo(9)-O(11)	72.5(2)	N(11)-Cu(1)-N(10)	82.3(3)
O(21)-Mo(10)-O(18)	102.0(3)	N(5)-Cu(2)-N(1)	97.5(3)
O(21)-Mo(10)-O(28)	101.9(3)	N(5)-Cu(2)-N(4)	82.0(3)
O(18)-Mo(10)-O(28)	90.9(2)	N(1)-Cu(2)-N(4)	174.2(3)
O(21)-Mo(10)-O(2)	101.3(3)	N(5)-Cu(2)-O(6)	149.9(3)
O(18)-Mo(10)-O(2)	87.6(2)	N(1)-Cu(2)-O(6)	93.0(3)
O(28)-Mo(10)-O(2)	156.5(2)	N(4)-Cu(2)-O(6)	90.2(3)
O(21)-Mo(10)-O(19)	101.8(3)	N(5)-Cu(2)-N(2)	95.1(3)
O(18)-Mo(10)-O(19)	156.2(2)	N(1)-Cu(2)-N(2)	78.2(3)
O(28)-Mo(10)-O(19)	85.3(2)	N(4)-Cu(2)-N(2)	96.1(3)
O(2)-Mo(10)-O(19)	86.6(2)	O(6)-Cu(2)-N(2)	114.7(3)
O(21)-Mo(10)-O(26)	172.7(3)	O(42)-V(1)-O(29)	118.5(5)

O(18)-Mo(10)-O(26)	73.9(2)	O(42)-V(1)-O(7)	125.1(5)
O(29)-V(1)-O(7)	116.2(3)	Mo(12)-O(13)-Mo(7)	86.92(17)
O(42)-V(1)-O(30)	109.9(4)	Mo(6)-O(14)-Mo(8)	126.0(3)
O(29)-V(1)-O(30)	81.8(3)	Mo(5)-O(15)-Mo(1)	146.4(3)
O(7)-V(1)-O(30)	81.3(3)	Mo(5)-O(15)-V(2)	102.4(3)
O(42)-V(1)-O(37)	105.3(4)	Mo(1)-O(15)-V(2)	102.9(3)
O(29)-V(1)-O(37)	79.9(3)	Mo(7)-O(16)-Mo(12)	126.5(3)
O(7)-V(1)-O(37)	80.3(3)	Mo(1)-O(17)-Mo(9)	154.3(3)
O(30)-V(1)-O(37)	144.8(3)	Mo(11)-O(18)-Mo(10)	125.7(3)
O(41)-V(2)-O(40)	129.0(3)	Mo(6)-O(19)-Mo(10)	153.1(3)
O(41)-V(2)-O(15)	119.8(3)	Mo(7)-O(23)-Mo(5)	123.0(3)
O(40)-V(2)-O(15)	111.2(3)	Mo(7)-O(23)-V(2)	95.9(3)
O(41)-V(2)-O(23)	108.6(2)	Mo(5)-O(23)-V(2)	98.0(3)
O(40)-V(2)-O(23)	80.8(3)	Mo(3)-O(24)-Mo(9)	127.2(3)
O(15)-V(2)-O(23)	78.6(3)	Mo(10)-O(26)-Mo(11)	86.55(17)
O(41)-V(2)-O(33)	109.5(2)	Mo(10)-O(26)-Mo(4)	87.45(17)
O(40)-V(2)-O(33)	79.2(3)	Mo(11)-O(26)-Mo(4)	90.59(18)
O(15)-V(2)-O(33)	78.5(3)	Mo(11)-O(27)-Mo(12)	150.7(3)
O(23)-V(2)-O(33)	141.5(3)	Mo(7)-O(28)-Mo(10)	152.7(3)
Mo(4)-O(2)-Mo(10)	126.4(3)	V(1)-O(29)-Mo(11)	100.6(3)
Mo(4)-O(3)-Mo(8)	151.0(3)	V(1)-O(29)-Mo(2)	102.2(3)
Mo(2)-O(4)-Mo(9)	125.7(3)	Mo(11)-O(29)-Mo(2)	147.5(3)
Mo(3)-O(5)-Mo(8)	153.8(3)	Mo(4)-O(30)-Mo(11)	124.4(3)
Mo(5)-O(6)-Cu(2)	125.4(3)	Mo(4)-O(30)-V(1)	95.1(3)
Mo(5)-O(6)-Mo(12)	121.8(3)	Mo(11)-O(30)-V(1)	94.4(3)
Cu(2)-O(6)-Mo(12)	111.6(3)	Mo(6)-O(32)-Mo(1)	92.32(18)
V(1)-O(7)-Mo(4)	100.4(3)	Mo(6)-O(32)-Mo(8)	87.17(16)
V(1)-O(7)-Mo(3)	102.4(3)	Mo(1)-O(32)-Mo(8)	86.66(17)
Mo(4)-O(7)-Mo(3)	147.5(3)	Mo(6)-O(33)-Mo(1)	122.4(3)
Mo(2)-O(9)-Mo(12)	153.0(3)	Mo(6)-O(33)-V(2)	96.4(3)
Mo(5)-O(10)-Mo(9)	152.0(3)	Mo(1)-O(33)-V(2)	97.7(3)
Mo(2)-O(11)-Mo(3)	91.77(17)	Mo(1)-O(35)-Mo(8)	127.2(3)
Mo(2)-O(11)-Mo(9)	87.45(16)	Mo(2)-O(37)-Mo(3)	124.5(3)
Mo(3)-O(11)-Mo(9)	87.32(17)	Mo(2)-O(37)-V(1)	96.9(3)
Mo(5)-O(13)-Mo(12)	90.20(17)	Mo(3)-O(37)-V(1)	95.3(3)

Mo(5)-O(13)-Mo(7)	92.05(17)	V(2)-O(40)-Mo(6)	103.2(3)
V(2)-O(40)-Mo(7)	101.6(3)	Mo(6)-O(40)-Mo(7)	147.4(3)
V(2)-O(41)-V(2)$^{\#1}$	180.0		

Table S2 Hydrogen bonds for catalyst [Å and °].

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···O34	0.86	2.44	3.045(13)	128
N6—H6A···O2	0.86	2.34	3.076(10)	143
N6—H6A···O3	0.86	2.40	3.160(9)	148
N9—H9B···O42	0.86	1.84	2.694(14)	173
N12—H12A···O31	0.86	2.10	2.939(11)	163
C1—H1A···O16	0.93	2.46	3.105(13)	126
C2—H2A···O16	0.93	2.57	3.217(19)	127
C4—H4A···O34	0.93	2.57	3.319(16)	138
C7—H7A···O18	0.93	2.50	3.327(15)	149
C11—H11A···O20	0.93	2.51	3.393(14)	159
C16—H16A···O21	0.93	2.59	3.159(11)	120
C16—H16A···O28	0.93	2.60	3.434(11)	150
C18—H18A···O34	0.93	2.44	3.222(13)	142
C19—H19A···O36	0.93	2.58	3.221(15)	126
C23—H23A···O12	0.93	2.45	3.369(12)	169
C25—H25A···O24	0.93	2.56	3.192(14)	125
C26—H26A···O5	0.93	2.51	3.178(14)	129
C26—H26A···O17	0.93	2.48	3.300(14)	147
C26—H26A···O35	0.93	2.52	3.211(13)	131
C27—H27A···O1	0.93	2.33	3.055(17)	134

Table S3 BVS analysis of compound for molybdenum atoms.

Catalyst	Mo1	Mo2	Mo3	Mo4	Mo5	Mo6	Mo7
value	5.77	5.79	5.70	5.85	5.83	5.94	5.76

Catalyst	Mo8	Mo9	Mo10	Mo11	Mo12
value	5.35	5.73	5.86	5.77	5.81

Table S4. The comparison of benzene hydroxylation of the reported POM-based catalysts.

Catalyst	**Time/h**	**T/°C**	**Phenol yield/%**	**Ref**
NH_2-MIL-88/$PMo_{10}V_2$	3	60	24	1
$H_5PMo_{10}V_2O_{40}$/UiO-66-NH_2	4	60	14.08	2
$PMo_{10}V_2$/DMA16-CMPS	9	65	21.9	3
$\{[Cu(pyim)_2(PMo_{10}^{VI}Mo^{V}V_2)]_2\cdot[Cu(pyim)_2]_2\}$	5	65	13.29	This work
$[DiBimCN]_2HPMoV_2$@NC- 580	17	140	10.5	4
$([(CH_3)_4N]_6[PMo_9V_3O_{40}][Cu_2(C_6H_3O_6)_{4/3}]_6)$	1.33	80	9.93	5
POM@MOF-199@SBA-15	0.33	80	6	6

Reference

1. P. P. Xu, L. X. Zhang, X. Jia, H. Wen, X. L. Wang, S. Q. Yang and J. X. Hui, Catal. Sci. Technol., 2021, **11**, 6507-6515.
2. X. Jia, F. Y. Wang, H. Wen, L. X. Zhang, S. Y. Jiao, X. L. Wang, X. Y. Pei and S. Z. Xing, RSC Adv., 2022, **12**, 29433-29439.
3. H. Wang, L. Fang, Y. Yang, L. Zhang and Y. Wang, Catal. Sci. Technol., 2016, **6**, 8005-8015.
4. X. Cai, Q. Wang, Y. Liu, J. Xie, Z. Long, Y. Zhou and J. Wang, ACS Sustain. Chem. Eng., 2016, **4**, 4986-4996.
5. H. Yang, J. Li, L. Wang, W. Dai, Y. Lv and S. Gao, Catal. Commun., 2013, **35**, 101-104.
6. H. Yang, J. Li, H. Zhang, Y. Lv and S. Gao, Microporous and Mesoporous Materials., 2014, **195**, 87-91.