Electronic Supplementary Information

Self-confinement synthesis of POMs decorated MOFs thin film for actively hydrolyzing ethyl acetate

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Experimental section

Materials and chemicals

Zinc nitrate ($Zn(NO_3)_2·6H_2O$), copper nitrate ($Cu(NO_3)_2·3H_2O$), and 2-aminoethanol (NH_2-CH_2CH_2OH) were purchased from ACROS Chemicals. 2-methylimidazole (2-Hmim) ($C_4H_6N_2$) was purchased from Sigma-Aldrich. 1,3,5-benzenetricarboxylic acid (trimesic acid, H_3BTC) was purchased from ALDRICH. Sodium phosphomolybdate hydrate was purchased from Nanjing Caobenyuan Biotechnology Company. Sodium phosphotungstate octadecahydrate was purchased from MACKLIN. Ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. Ethyl acetate, ethanol and acetic acid standards for GC were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd.

The substrates were polyvinylidene fluoride filter thin film (PVDF, Millipore) with an average pore size of ca. 0.22 mm and diameter of 47 mm. The ultrapure water of 18.2 MΩ used throughout the experiments was produced by a Millipore direct-Q system (Millipore).

All materials used in this work were purchased from commercial sources and used without further purification.

Synthesis of PW_{12}@ZIF-8 and PMo_{12}@ZIF-8

PW_{12}@ZIF-8: the positively charged zinc hydroxide nanostrands (ZHNs) were prepared by vigorous stirring equal volume 4 mM zinc nitrate ($Zn(NO_3)_2$) water–ethanol solution (water/ethanol volume ratio 3:2) and 1.6 mM 2-aminoethanol (AE) water–ethanol solution (water/ethanol volume ratio 3:2) for 5 minutes at room temperature and aging for about 30 minutes. Subsequently, moderate sodium phosphotungstate (PW_{12}) solution was added into ZHNs solution and quickly blend for 5 min to make sure the negatively charged PW_{12} fully absorbed on the surface of ZHNs films because of electrostatic attraction. The PW_{12}@ZHNs thin film was obtained by filtering the solution onto a porous PVDF membrane. After that, thin film was took out and washed with deionized water for 3 times. The PW_{12}@ZIF-8 thin film was successfully achieved by immersing the PW_{12}/ZHNs thin film into 25 mM 2-methylimidazole (2-Hmim) water - ethanol (water/ethanol volume ratio 4:1) mixed solution at room temperature for 24 h. To investigate the PW_{12} amount effect, 0.05, 0.1, 0.25, 0.5 and 1 mL 5.25 $mg \cdot L^{-1}$ PW_{12} solutions were used, respectively, and resulted in the weight ratio of PW_{12} to ZIF-8 being 2.9%, 5.5%, 14.2%, 22.1% and 33.3% in the final PW_{12}@ZIF-8 thin films. The corresponding thin films are named as PW_{12}@ZIF-8-0.05, PW_{12}@ZIF-8-0.1, PW_{12}@ZIF-8-0.25, PW_{12}@ZIF-8-0.5, and PW_{12}@ZIF-8-1, respectively.

PMo_{12}@ZIF-8 catalytic thin film was prepared in similar method, except using sodium phosphomolybdate (PMo_{12}) to replace PW_{12}. 0.25 mL PMo_{12} was added in 100 mL ZHNs with fast stirring for 5 min. After filtrating and immersing, PMo_{12}@ZIF-8 thin film was obtained.

Synthesis of PW_{12}@HKUST-1

PW_{12}@HKUST-1: Analogous to ZHNs, the copper hydroxide nanostrands were prepared by mixing the same volume of 4 mM copper nitrate $Cu(NO_3)_2$ aqueous solution and 1.4 mM AE aqueous solution by 5 minutes stirring and aging for 24 h at room temperature. 0.20 mL 5.25 mg • L^{-1} PMo_{12} aqueous solution was added in 100 mL CHNs with fast stirring for 5 min. After filtering the mixture solution on a porous PVDF membrane, the obtained PW_{12}@CHNs film was immersed in 2-Hmim solution for 2 h. After that, the PW_{12}@HKUST-1 thin film was successfully obtained.

Characterization

X-ray diffraction (XRD, PANalytical instrument) was performed with a Cu-Kα X-ray radiation source at 0.02°step at room temperature to verified the phase of synthesized thin film and identify the crystal structure of all prepared POMs@MOF catalysts. The morphologies were characterized by scanning electron microscopy (SEM, SU-4800 and SU-70, Hitachi), assisted with accessories of X-ray energy dispersive analysis (EDS). The samples treated with ultrasonic treatment for 20 minutes and dropped on ultrathin carbon film before observed by transmission electron microscopy (TEM, HT-7700, Hitachi; JEM 2100F, JEOL) equipped with X-ray energy dispersive analysis (EDS, X-MAXn65 T, Oxford) to demonstrate the elemental analyses. The Fourier-transform infrared spectroscopy (FTIR) spectra were recorded from KBr pellets as background in the range 4000-400cm^{-1} on a TENSOR 27 spectrometer (Bruker). X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, Krato) was used to indicate valence state of POMs, further comfirming interaction between POMs and MOFs. ^{31}P Nuclear Magnetic Resonance (NMR, Agilent DD2 600) spectra were obtained to confirm the Keggin structure intetegrity of polyoxometalates with H_3PO_4 (85%) as external reference. Gas Chromatography (GC) analyses were performed on a equipment Agilent 7890B instrument with FID detector equipped with Agilent 7697A headspace sample injector with DB-624 capillary column. The heating rate was 20 ^{o}C/min from 60 ^{o}C to 200 ^{o}C, and kept this temperature for 3 min. The hydrolysis of ethyl acetate generated two products, making three peaks at different time on GC spectra, the first peak represented ethyl acetate, the next was ethanol, and the last one was acetic acid. The conversion of ethyl acetate and catalytic activity of hydrolysis was indicated in GC instrument with external standard method. First, we prepared a series of solution at known concentrations, by fitting the peak area with concentration, a standard line can be obtained. After that, the content of reaction product were determined by compared samples peak area with standard line.

They were determined using the following equation:

$$M_{\text{product}} = \left(A_{\text{sample}} \times V\right)/K$$

Where *M* defined as the mass of products, and we chose acetic acid as testing product. *A* was peak area of sample, *V* is solution volume and *K* was the slope of standard line.

1 mg thin film samples were added in nitric acid and ultrasonic for 10 min in order to completely dissolve, then diluted solution into appropriate concentration with deionized water. The results of inductively coupled plasma optical emission spectrometry (ICP-OES, 730-ES, Varian) can be obtained by contrast with corresponding standard solution, which was performed to quantify the weight contents of W and Mo in MOF.

Catalytic properties measurements

Catalytic activity

The catalytic activity of solid acid catalysts POMs@MOF thin film was carried out by the hydrolysis of ethyl acetate. A standard hydrolysis procedure was performed in an oil bath reactor (a three-neck Pyrex flask ca. 50 cm^3) with a water cooler condenser, a thermometer and a needle to extract the solution. Ethyl acetate hydrolysis was implemented in a 0.5 wt% of the aqueous (30 cm^3, or 1.69 mM ethyl acetate was included). The PW_{12}@ZIF-8 thin film was dried in vacuum at 80 °C for 12 h before hydrolysis, and other catalysts PMo_{12}@ZIF-8, PW_{12}@HKUST-1 were treated in the same way. All the reactions were took place at 70°C in a sealed condenser condition in an oil bath under magnetic stirring. At certain time intervals, the reaction solution was taking out by needle and filtrated with aqueous needle filter (0.2 mm) to separate the solution and residual deciduous catalysts, and then analyzed by gas chromatography using a capillary column. Selecting 2 h reaction GC results to compare catalytic activity per POMs weight with different types of POMs@MOF catalysts. After reaction, a portion of solution was disposed to do ICP test to see whether catalysts dissolved in solution or fell off from substrate.

The catalytic activity is expressed as k ($\mu mol \cdot g_{POMs}^{-1} \cdot min^{-1}$) rate on the basis of POMs weight. They were determined using the following equation[1]:

$$\mathrm{k} = (CN)/(\mathrm{t}m_{POMs})$$

where C designates the conversion that was defined as (amount of acetic acid formed)/(amount of ester added); N is the molar amount of ester added; t is the reaction time; and m_{POMs} denotes the weight of the POMs among catalyst, which are obtained by ICP results.

Catalytic stability

Five times recycling tests were carried out at 70 °C in order to investigate the stability of PW_{12}@ZIF-8 thin film. After 2 h, the data were obtained by GC. After each cycle, the solid catalyst film was took out and washed by ethanol and ultrapure water consecutively, and then drying it in vacuum oven at 80 °C all night and reused for the next cycle.

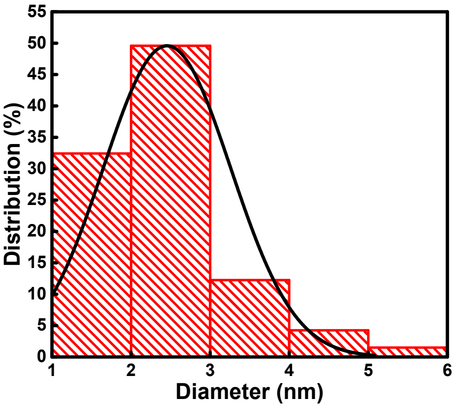


Figure S1. Statistics of PW_{12} particle size on ZHNs, the average diameter of encapsulated PW_{12} is 2.47 nm.

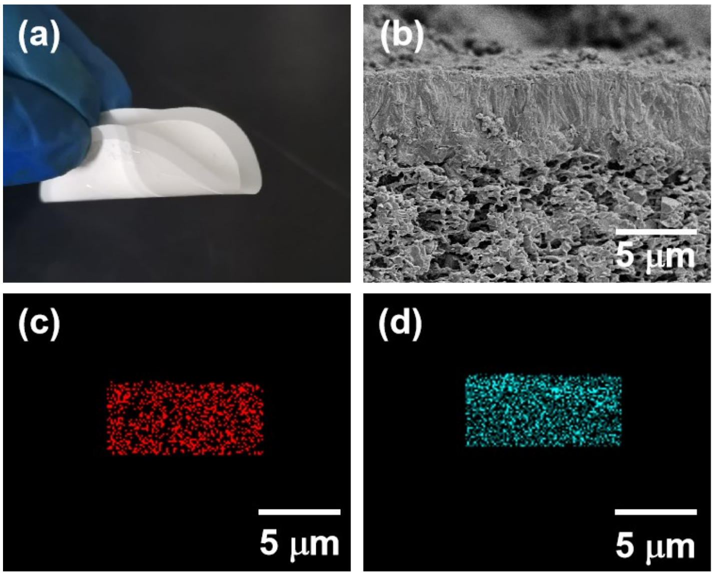
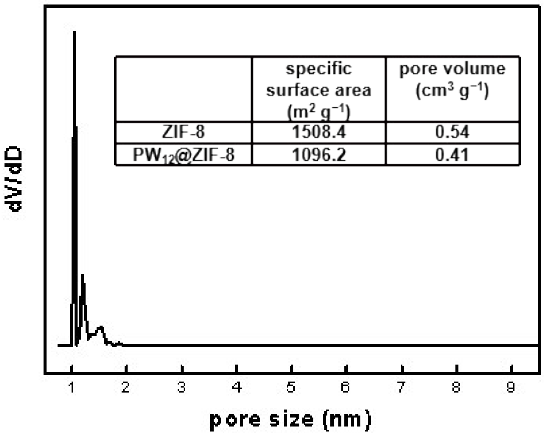


Figure S2. (a) Slightly Folded PW_{12}@ZIF-8-0.25 thin film, which displayed the flexibility of thin film. Cross-section SEM images of (b)PW_{12}@ZIF-8. (c) Zn element and (d) W element EDS mapping of (b).



	specific surface area (m^2 g^{-1})	pore volume (cm^3 g^{-1})
ZIF-8	1508.4	0.54
PW_{12}@ZIF-8	1096.2	0.41

Figure S3. Pore size distribution of PW_{12}@ZIF-8 thin film.

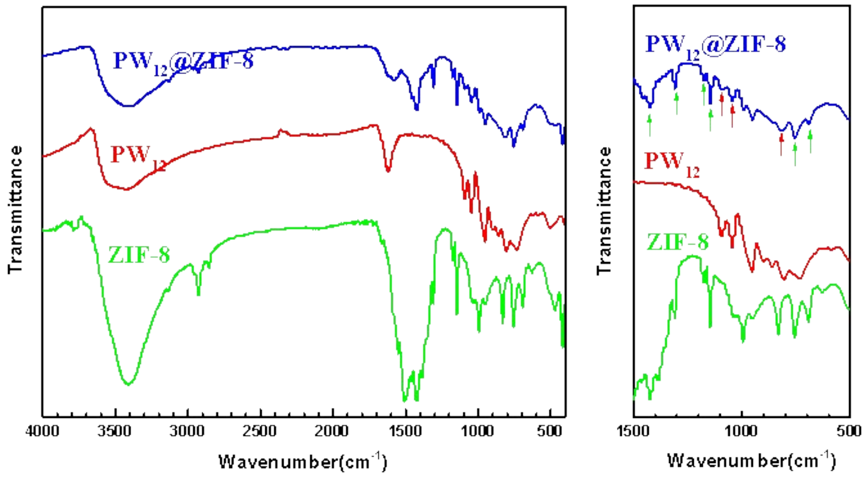


Figure S4. FTIR spectra of PW_{12}@ZIF-8-0.25,PW_{12} and ZIF-8, the right chart manifested local magnification of FTIR spectra from 500~1500cm^{-1}.

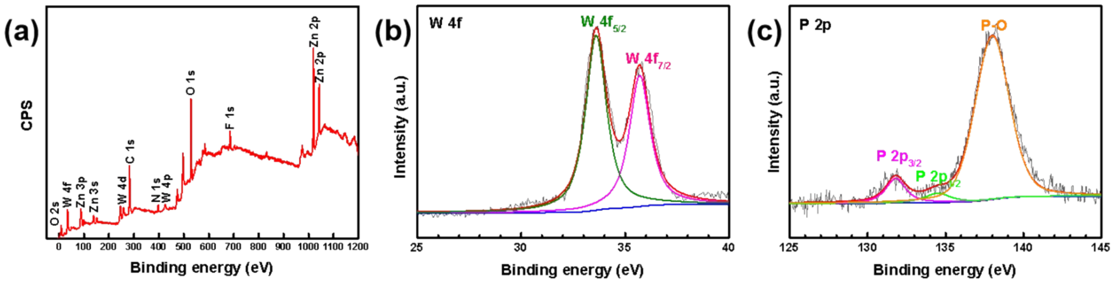


Figure S5. (a) XPS wide spectrum; (b)W 4f spectrum; (c) P 2p spectrum of PW_{12}@ZIF-8-0.25.

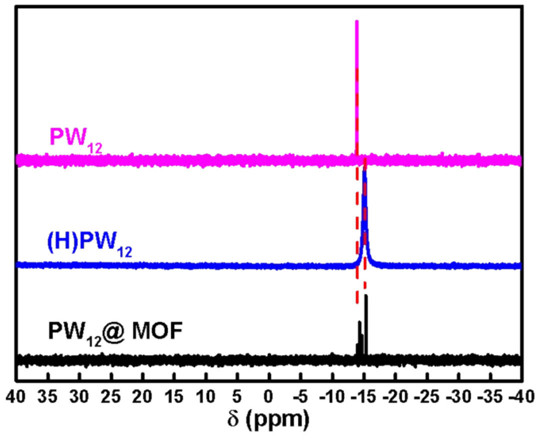


Figure S6. ^{31}P NMR spectra of PW_{12}, (H)PW_{12} and PW_{12}@ZIF-8.

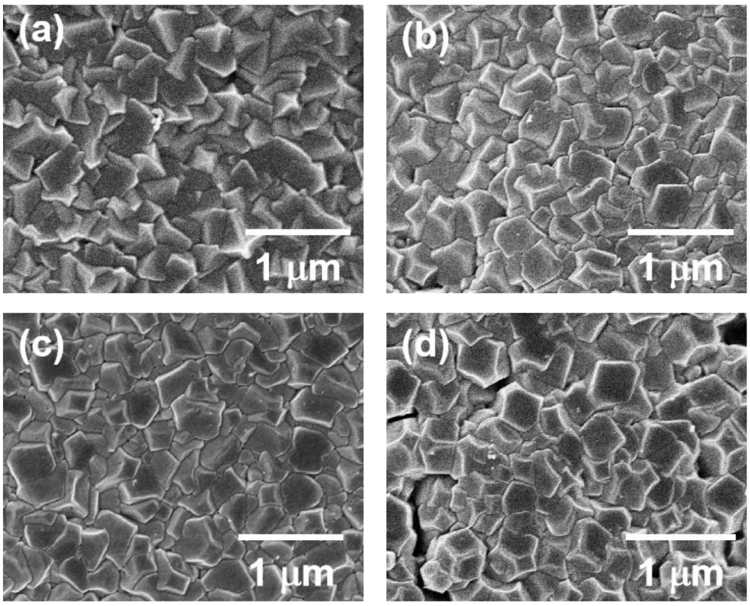


Figure S7. Surface SEM images of (a) PW_{12}@ZIF-8-0.05; (b) PW_{12}@ZIF-8-0.1; (c) PW_{12}@ZIF-8-0.5; (d) PW_{12}@ZIF-8-1.

Table S1 ICP-AES analysis of PW_{12}@ZIF-8 with different content of PW_{12}

sample	Precursor solution POMs:MOF (wt%)	Zn (mg/L)	W (mg/L)	Final thin film POMs:MOF (wt%)
PW_{12}@ZIF-8-0.05	2.9	90.03	7.090	2.9
PW_{12}@ZIF-8-0.1	5.8	23.15	3.398	5.5
PW_{12}@ZIF-8-0.25	14.4	16.94	6.418	14.2
PW_{12}@ZIF-8-0.5	28.8	1.810	1.067	22.1
PW_{12}@ZIF-8-1	57.7	4.144	3.677	33.3

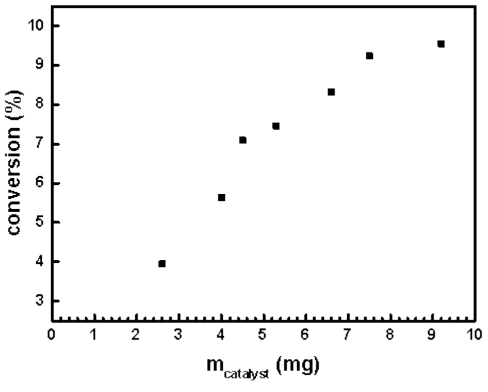


Fig S8. Conversion of hydrolysis of ethyl acetate with different weight of catalysts.

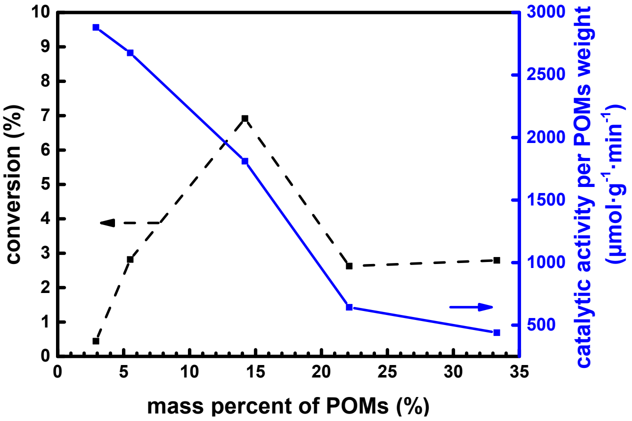


Figure S9. Catalytic activity and conversion of PW_{12}@ZIF-8 with different content of PW_{12}, the black dash line is conversion of PW_{12}@ZIF-8 hydrolysis ethyl acetate for 2 h, the blue line represents catalytic activity of catalysts, the valid catalyst depend on the weight of POMs. The mass percent of POMs is determined by ICP results.

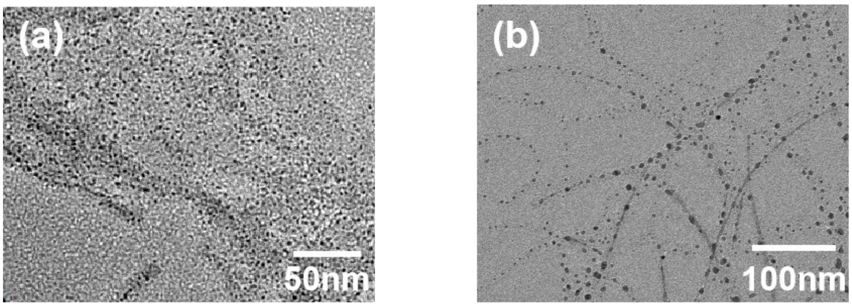


Figure S10. (a) TEM image of PMo_{12}@ZHNs. (b)PW_{12}@CHNs.

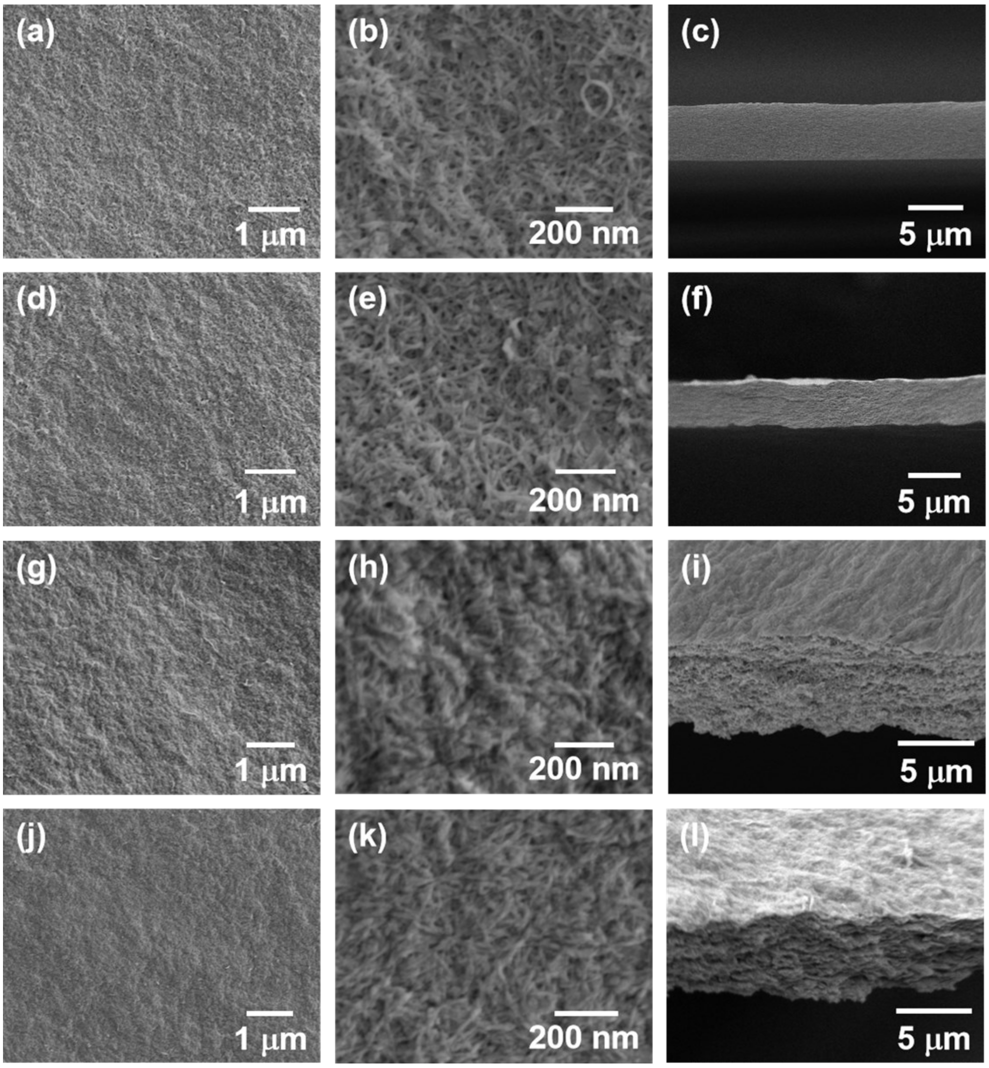


Figure S11. Surface and cross-section SEM images of (a)-(c) CHNs; (d)-(f) PW_{12}@CHNs (g)-(i) ZHNs;(j)-(l) PW_{12}@ZHNs.

Table S2 ICP-AES analysis of different catalysts

Sample	Cu (mg/L)	Zn (mg/L)	W (mg/L)	Mo (mg/L)	POMs:MOF (wt%)
PW_{12}@ZIF-8-0.25	/	16.944	6.418	/	14.2
PMo_{12}@ZIF-8-0.25	/	23.438	/	5.818	11.3
PW_{12}@HKUST-1-0.2	13.707	/	3.687	/	14.1

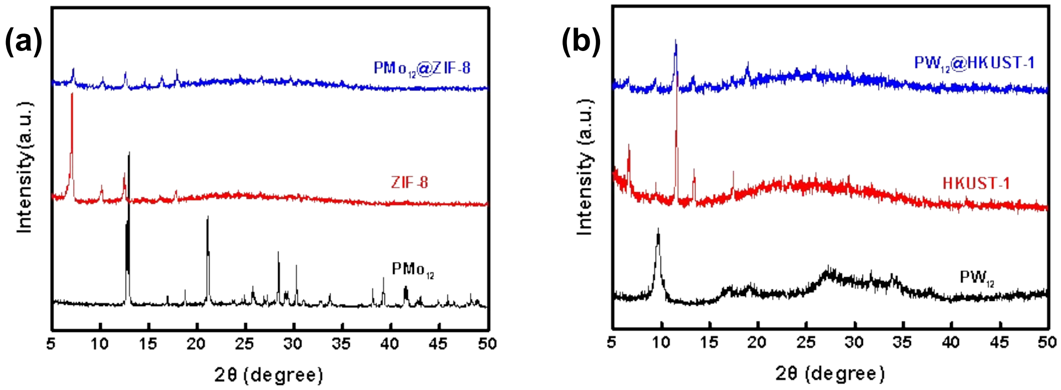


Figure S12. XRD patterns of (a) PMo_{12}@ZIF-8-0.25, PMo_{12} and ZIF-8.
(b) PW_{12}@HKUST-1, PW_{12} and HKUST-1-0.2.

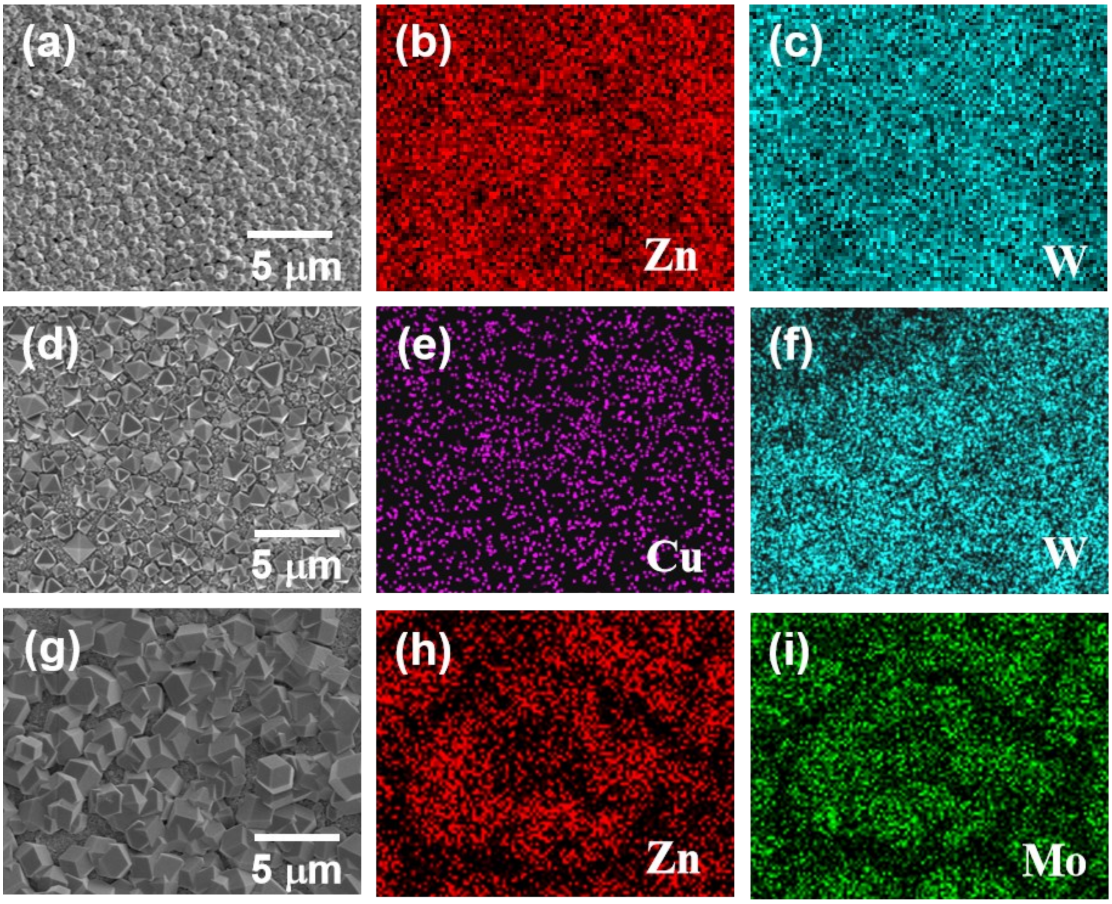


Figure S13. Surface SEM images of (a) PW_{12}@ZIF-8-0.25. (b) Zn element and (c) W element EDS mapping of (a). (d) PW_{12}@HKUST-1-0.2. (e) Cu element and (f) W element EDS mapping of (d). (g) PMo_{12}@ZIF-8-0.25. (h) Zn element and (i) Mo element EDS mapping of (g).

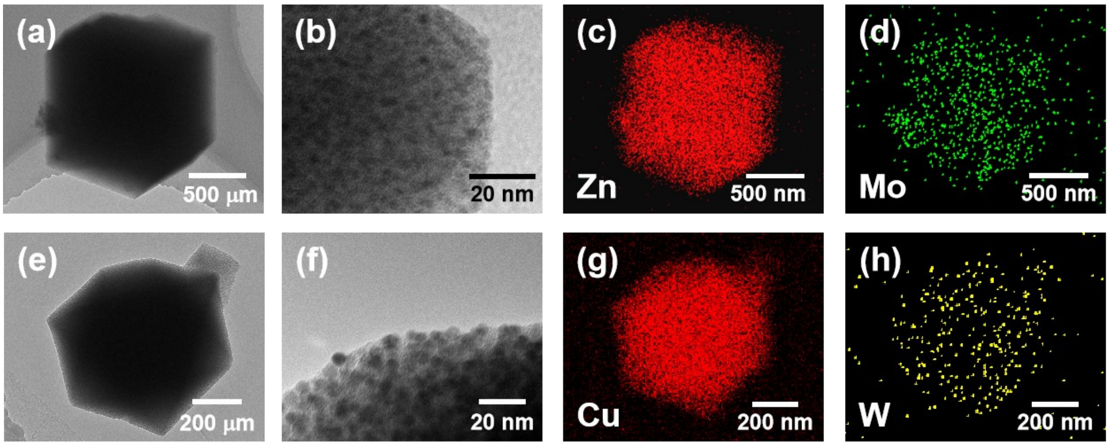


Figure S14. (a) TEM images of PMo_{12}@ZIF-8-0.25. (b) HRTEM images of PMo_{12}@ZIF-8-0.25. (c) Zn element and (d) Mo element EDS mapping of (a). (e) TEM images of PW_{12}@HKUST-1-0.2. (f) HRTEM images of PW_{12}@HKUST-1-0.2. (g) Cu element and (h) W element EDS mapping of (e).

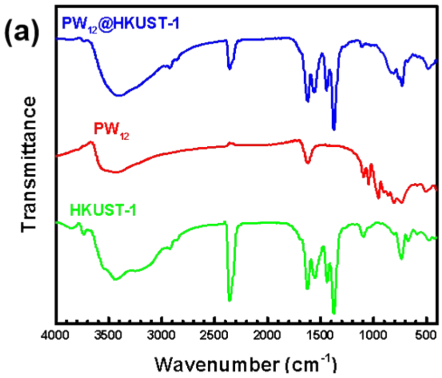


Figure S15. FTIR spectra of (a) PW_{12}@HKUST-1,PW_{12} and HKUST-1. (b)PMo_{12}@ZIF-8, PMo_{12} and ZIF-8.

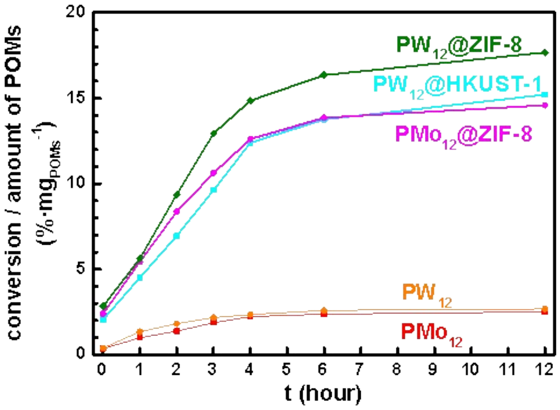


Figure S16. Conversion per POMs of hydrolysis of ethyl acetate with different catalysts depend on time. The red, orange, magenta, cyan and olive line represents PMo_{12}, PW_{12}, PMo_{12}@ZIF-8 (POMs mass percent: 11.3 wt%), PW_{12}@HKUST-1 (14.1 wt%) and PW_{12}@ZIF-8 (14.2 wt%), respectively. The samples are took from solution at beginning of hydrolysis and intervals of 1h, 2h, 3h, 4h, 6h and 12h, respectively.

Table S3 Catalytic activity comparison of different catalysts for ethyl acetate hydrolysis in water

Catalyst	Reaction time（h）	Reaction temperature (^oC)	Catalytic activity per weight（$\mu mol \cdot g_{POM}^{-1} \cdot min^{-1}$）	Reference
(H) PW_{12}@ZIF-8-0.25	**2**	**70**	**1027**	**This work**
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$-HMS	2	70	1350	[2]
H_2SO_4	2	70	911.9	[3]
(H) PW_{12}@MIL-101	2	60	458.67	[4]
(H) PW_{12}@HKUST-1（NENU-3a）	2	80	379.83	[1]
Sulfonated graphene	6	70	341.67	[5]
Amberlyst-15	2	60	193.6	[6]
PW/C_8-AP-SBA	2	60	190.1	[7]
$H_3PW_{12}O_{40}$	2	70	70.4	[3]
ZIF-8	2	70	0	This work
HKUST-1	2	70	0	[4]

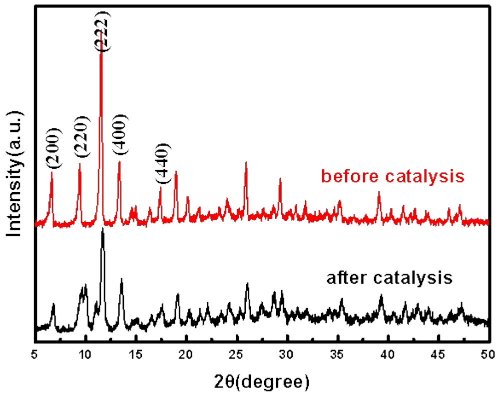


Figure S17. XRD pattern of PW_{12}@HKUST-1 before and after hydrolysis.

Table S4. ICP results of PW_{12}@ZIF-8-0.25 film catalyst before and after catalysis

	POMs:MOF (wt%)
Before catalysis	14.2
After 5th catalysis	12.95

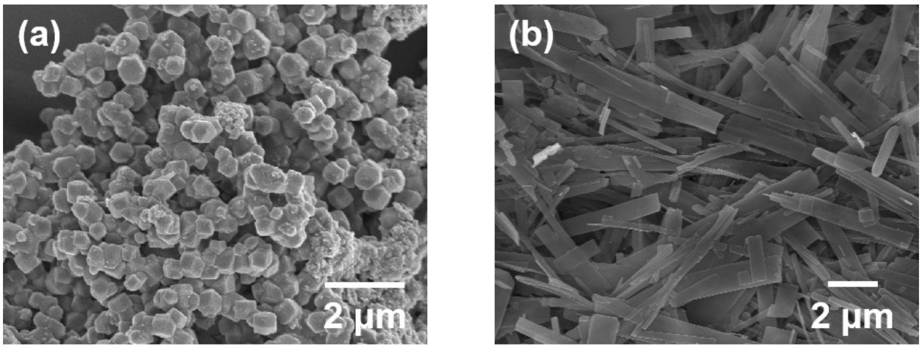


Figure S18. SEM images of (a) PW_{12}@ZIF-8-0.25 and (b)PW_{12}@HKUST-1-0.2 after hydrolysis.

References

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