Supporting information

Lewis - acid- promoted catalytic cascade conversion of glycerol to lactic acid by polyoxometalates

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Experimental Methods

General Information

All solvents and chemicals were used as obtained from commercial supplies. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES. IR spectra (4000 - 500 cm-1) was recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. X-ray diffraction (XRD) patterns of the sample were collected on a Japan Rigaku Dmax 2000 X-ray diffractometer with Cu Kα radiation (λ= 0.154178 nm). The measurements were obtained in the step of 0.04° with account time of 0.5 s and in the 2θ rang of 5-90 °. Raman spectroscopy was obtained on a Renishaw-UV-vis Raman System 1000 equipped with a CCD detector at room temperature. The air-cooled frequency doubled Nd-Yag laser operating at 532 nm was employed as the exciting source with a power of 30 MW. SEM micrographs were recorded on a scan electron microscope (XL30 ESEM FEG 25kV). EDX spectra were obtained using 20 kV primary electron voltages to determine the composition of the samples. The redox potential were tested on a CS Corrtest electrochemical workstation equipped with glassy carbon as both working and counter electrodes and saturated calomel as reference electrode. Electrochemical measurements were performed with 0.1 M sulfuric acid solution as the supporting electrolyte. Surface areas were calculated using the BET equation on a Micromeritics ASAP2010 micropore analyzer.

Preparation of MPMo

The MPMo catalysts were synthesized by an ion-exchanged method. 9.125 g (0.005 M) of $H_3PMo_{12}O_{40}$ was dissolved in 20 mL of deionized water at room temperature under vigorous stirring. Then, the appropriate amount of metal salts aqueous solution (5 mmol) (nitrates for Cr and sulfate for Al) was added dropwise to the former solution with continuous stirring. Then the mixture was dried in nitrogen to produce the desired HPA catalyst. The remaining powder was dried at 80 °C overnight and then calcined at 250 °C in static air for 4 h. The formation of MPMo reaction undergoes based on the following equations:

$$M^{3+} + H_3PMo_{12}O_{40} \rightarrow 3H^+ + MPMo_{12}O_{40} \quad (M=Al, Cr)$$
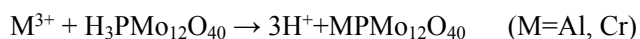
MPMo catalysts were calcined at different temperatures ranging from 150 to 250 °C. These catalysts are denoted as MPMo -150 to 250. The number indicates the calcination temperature. The resulting $AlPMo_{12}O_{40}$ was obtained with yield 78.6 %. IR (1% KBr pellet, 4000 - 400 cm^{-1}): 1050 (sh, vas P-O_a, internal oxygen connecting P and Mo), 956 (s, vas Mo-O_d, terminal oxygen bonding to Mo atom), 882 (m, vas Mo-O_b, edge-sharing oxygen connecting Mo), 763 cm^{-1} (s, vas Mo-O_c, corner-sharing oxygen connecting Mo_3O_{13} units). Anal. Calcd for $AlPMo_{12}O_{40}$: Mo, 62.72; Al, 1.69; P, 1.70

%. Found: Mo, 62.26; Al, 1.46; P, 1.68 %. The EDX analysis of the catalyst: Al, 0.02; Mo, 0.23 ; P, 0.02 (At%). The EDX measurement results showed that the approximate ratio of atomic percentage of Al, Mo and P was 1: 11.5: 1. The resulting $CrPMo_{12}O_{40}$ was obtained with yield 78.6 %. IR (1% KBr pellet, 4000 - 400 cm^{-1}): 1054 (sh, vas P-O_a, internal oxygen connecting P and Mo), 944 (s, vas Mo-O_d, terminal oxygen bonding to Mo atom), 861 (m, vas Mo-O_b, edge-sharing oxygen connecting Mo), 747 cm^{-1} (s, vas Mo-O_c, corner- sharing oxygen connecting Mo_3O_{13} units). Anal. Calcd for $CrPMo_{12}O_{40}$: Mo, 62.11; Cr, 2.14; P, 1.61 %. Found: Mo, 61.43; Cr, 2.77; P, 1.65 %. The EDX analysis of the catalyst: Cr, 0.02; Mo, 0.25; P, 0.02 (At%). The EDX measurement results showed that the approximate ratio of atomic percentage of Cr, Mo and P was 1: 12.5: 1.

The surface acidity of MPMo

Titration was used to evaluate the total acid content of the solids. 0.05 g MPMo suspended in 45 mL acetonitrile and then the mixture was stirred for 3 h. The density of acid sites in the catalysts was measured by titration with a solution of n-butylamine in acetonitrile (0.05 M) using the indicator anthraquinone (pKa = -8.2). The IR spectra of adsorbed pyridine (Py-IR) helped to measure the acid content and distinguish the properties of acid sites (Lewis or Brønsted). The samples were exposed to the pyridine vapor for 12 h under vacuum (10-3 Pa) at 60 ºC. The quantification of acidity was calculated by Lambert–Beer equation:

$$A= \frac{\varepsilon \cdot W \cdot c}{S}$$

where A is the absorbance (area in cm^{-1}), ε is the extinction coefficient (m^2/mol), W the sample weight (kg), c the concentration of acid (mol/kg or mmol/g) and S is the sample disk area (m^2). The amount of Brønsted and Lewis acid sites was estimated from the integrated area of the adsorption bands at ca. 1540 and 1450 cm^{-1}, respectively, using the extinction coefficient values based on the previous report (Fig. S8).

The morphology, BET surface area, and solubility of MPMo

A representative selection of SEM images of CrPMo and AlPMo samples were presented in Fig. S9. It can be found that these as-synthesized materials displayed well-shaped crystalline particles. Furthermore, EDX was examined to determine the elemental compositions of these samples, which determined the analytic results.

And from BET (Fig. S10) it can be seen that MPMo formed mesopore structure and the pore sizes were 4.32 and 4.36 nm corresponding to CrPMo and AlPMo, respectively. In addition, the

surface areas were 9.16, and 12 m^2/g corresponding to CrPMo and AlPMo, respectively. The difference of surface area and pore sizes for these two compounds was not high enough to influence the conversion of glycerol. The absorption of glycerol by these two different catalysts showed no difference.

MPMo catalysts were calcined at different temperatures in the range of 150-250 °C. The solubility of MPMo was given in Table S2. It can be seen that with the increase in calcination temperature from 150 to 250 °C, the solubility of the MPMo decreased. This determined that calcinations of MPMo could give insoluble samples in water. Meanwhile, the total acidity of MPMo catalysts being calcinated or not also gave us useful information that is the acid content increased to some extent being treated by calcinations(Table S1).

Typical procedure for glycerol oxidation

Glycerol oxidation was performed in a high-pressure batch autoclave of stainless steel with a polytetrafluoroethylene inlet (10 mL). The autoclave was equipped with gas supply system and a magnetic stirrer. A catalyst was suspended in 5 mL aqueous glycerol, and the mixture was heated up to 60 °C. During the reaction, oxygen pressure was maintained at 10 bar. After the experiment, the reaction mixture was diluted 10 times with distilled water and analyzed by high performance liquid chromatography (HPLC) using a Shimadzu LC10A-VP chromatograph equipped with a SPB-10A Variable UV (210 nm) and a RID-10A R.I. detector. Prevail TM C18 column (4.6 mm ×250 mm) was used with a solution of H$_2$SO$_4$ (0.1% w/w) in H$_2$O/acetonitrile (1/2 v/v)(1.0 mL min-1) as the eluent at 50 ℃. External standard method was used to test the yields of intermediates including DHA, GCA, GlyA and AcA, a serious of different concentrations of standard solutions were prepared and analyzed by HPLC, then the corresponding yield of different intermediates was obtained clearly.

Table S1 Acid strength distribution of of MPMo

Catalyst	[a]Brønsted acidity (mmol/g)	[a]Lewis acidity (mmol/g)	[a]Total acidity (mmol/g)	[b]Total acidity (mmol/g)	[c]Total acidity (mmol/g)
$H_3PMo_{12}O_{40}$	1.01	0.03	1.04	1.12	0.95
$CrPMo_{12}O_{40}$	0.14	0.40	0.54	0.59	0.50
$AlPMo_{12}O_{40}$	0.19	0.60	0.79	0.82	0.69

[a]The B, L acidity and total acidity were valued by the IR spectra of adsorbed pyridine and calculated by Lambert-Beer equation.

[b]The total acidity was measured by titration and the catalysts were calcined at 250 °C.

[c]The total acidity was measured by titration and the catalysts were not calcined.

Table S2 The solubility and catalytic performance of MPMo catalysts calcined at different temperatures.

Entry	Catalysts	Solubility (g/L)	catalytic activity	
			Conversion (%)	Sel. to LA (%)
1	CrPMo-150	0.512	78.2	76.0
2	CrPMo-200	0.309	84.8	81.6
3	CrPMo-250	0.106	88.0	85.3
4	AlPMo-150	0.329	86.6	79.0
5	AlPMo-200	0.206	90.2	86.8
6	AlPMo-250	0.084	93.7	90.5

Reaction conditions: 5 mL, 1.1 M of glycerol, 2.3×10^{-5} mol of MPMo, 10 bar O_2, 800 rpm, 5 h.
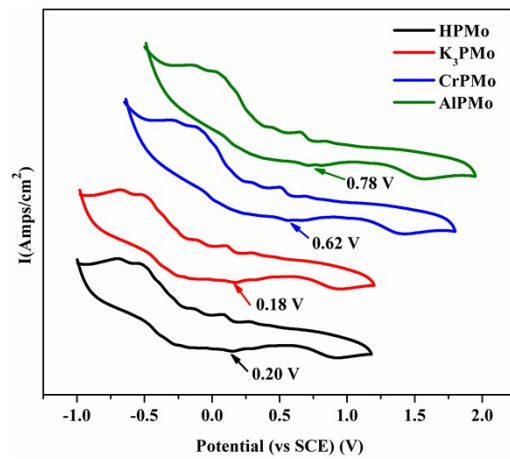
Fig. S1. CV-potential curves of MPMo catalysts.
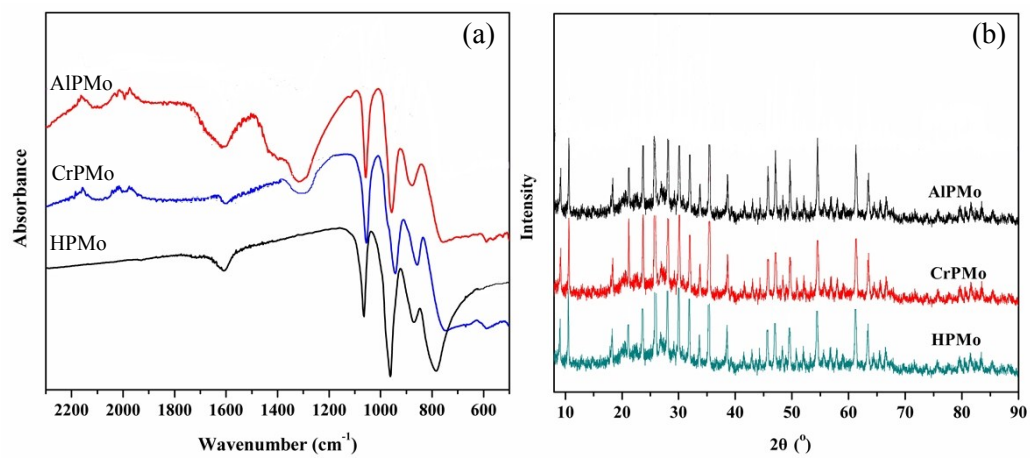
Fig. S2. FTIR spectra (a) and XRD patterns (b) of MPMo catalysts.
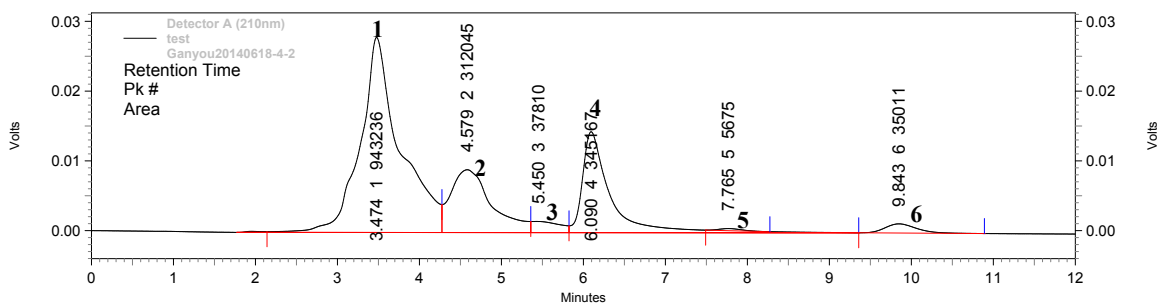
Fig. S3. HPLC spectra of the products after reaction for 1 h catalyzed by CrPMo:

1) Dihydroxyacetone (DHA); 2) Glyceraldehydes (GCA);

3) Pyruvaldehyde (PLA); 4) Lactic acid (LA); 5) Glyceric acid (GLA); 6) Acitic acid (AcA).
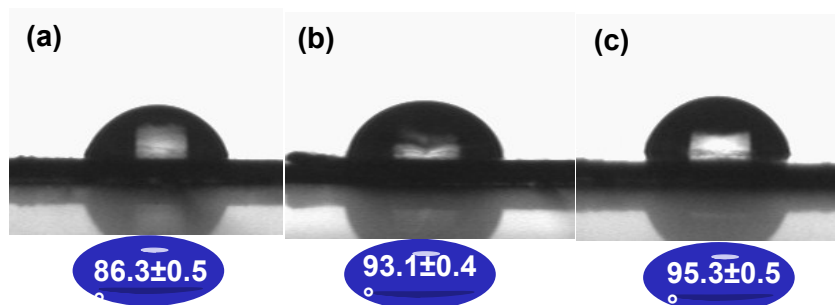
(a) 86.3±0.5°

(b) 93.1±0.4°

(c) 95.3±0.5°

Fig. S4. The CA of the two surfaces of the KPMo (a), CrPMo (b) and AlPMo.
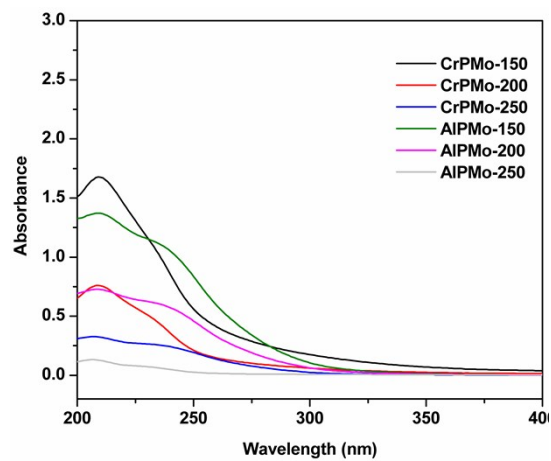
Fig. S5. Uv-Vis spectrum of MPMo after being calcined over different temperature.
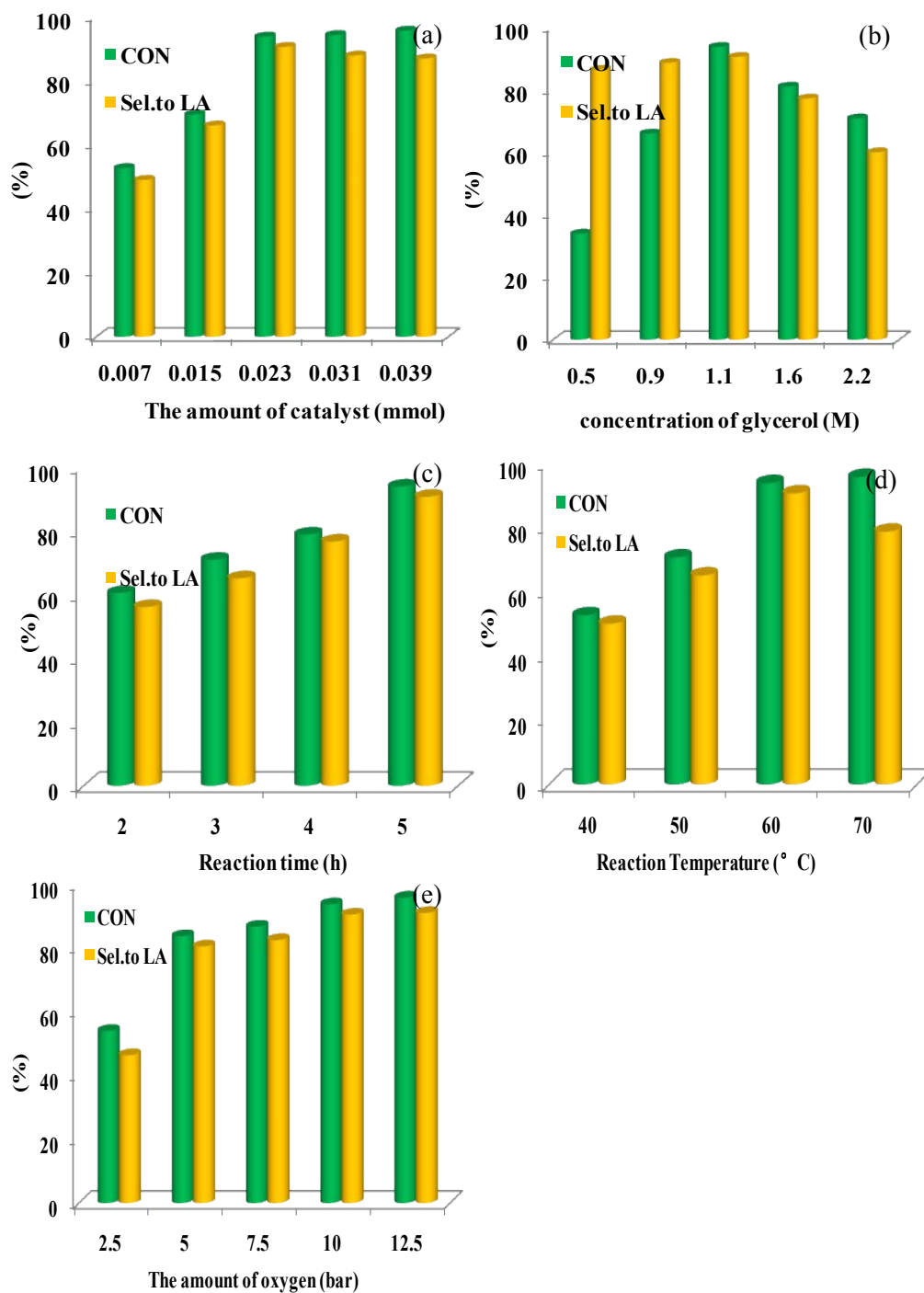
Fig. S6. The conversion and selectivity of oxidation of glycerol with various process parameters:
(a) Amount of catalyst (AlPMo, 1.1 M of glycerol, 60 ºC, 5 h, 10 bar);
(b) Concentration of glycerol (2.3×10^{-5} mol of AlPMo, 60 ºC, 5 h, 10 bar);
(c) Reaction time (2.3×10^{-5} mol g of AlPMo, 1.1 M of glycerol, 60 ºC, 10 bar);
(d) Reaction temperature (2.3×10^{-5} mol of AlPMo, 1.1 M of glycerol, 5 h, 10 bar).
(e) Amount of oxygen (2.3×10^{-5} mol of AlPMo, 1.1 M of glycerol, 5 h, 60 ºC).
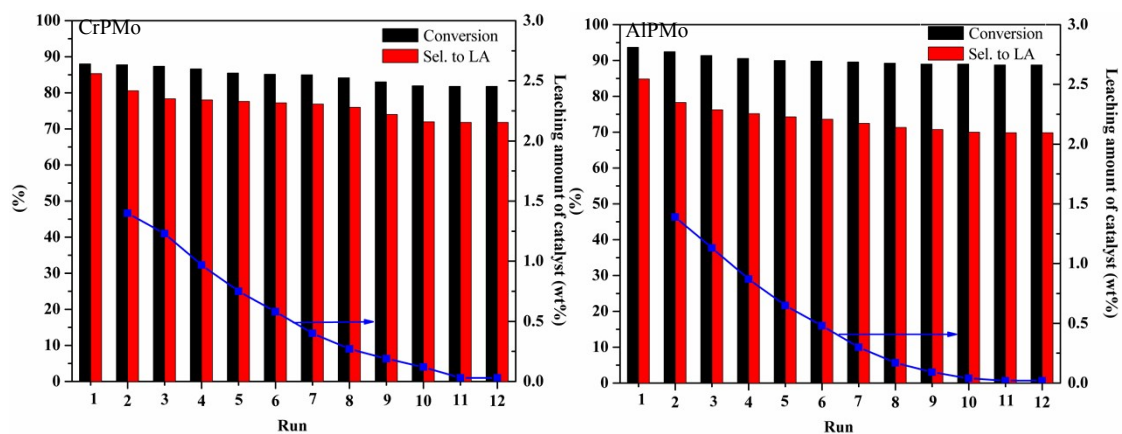
Fig. S7. Reusability test catalyzed by MPMo in oxidation of glycerol.
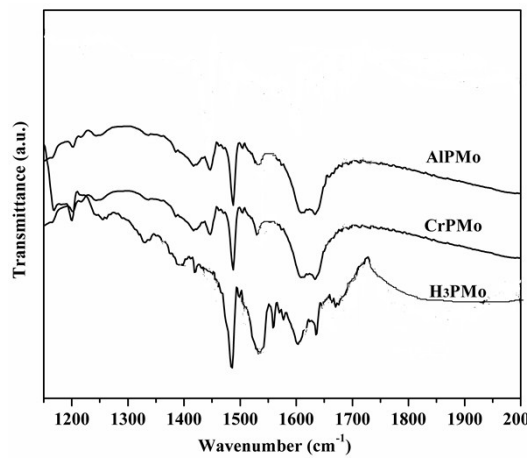Reaction conditions: 2.3×10^{-5} mol of catalyst, 1.1 M of glycerol (5 mL), 60 ºC, 5 h, 10 bar.

Fig. S8. FTIR spectra of pyridine adsorption of bulk MPMo catalysts.
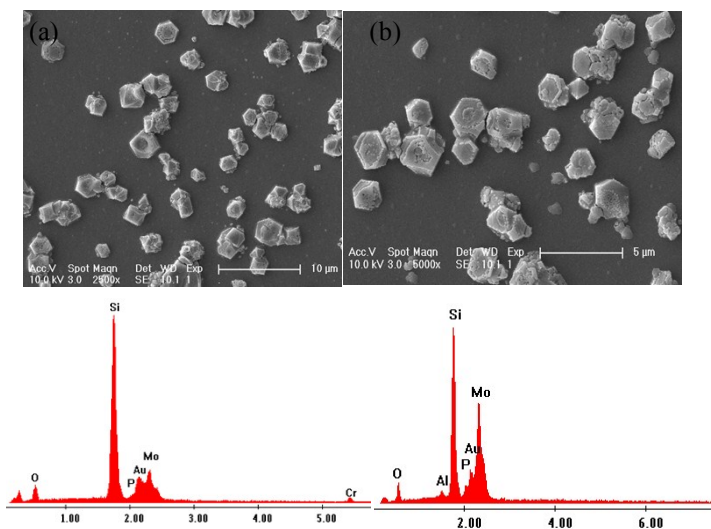
Fig. S9. SEM micrographs and EDX of (a) CrPMo, and (b) AlPMo.
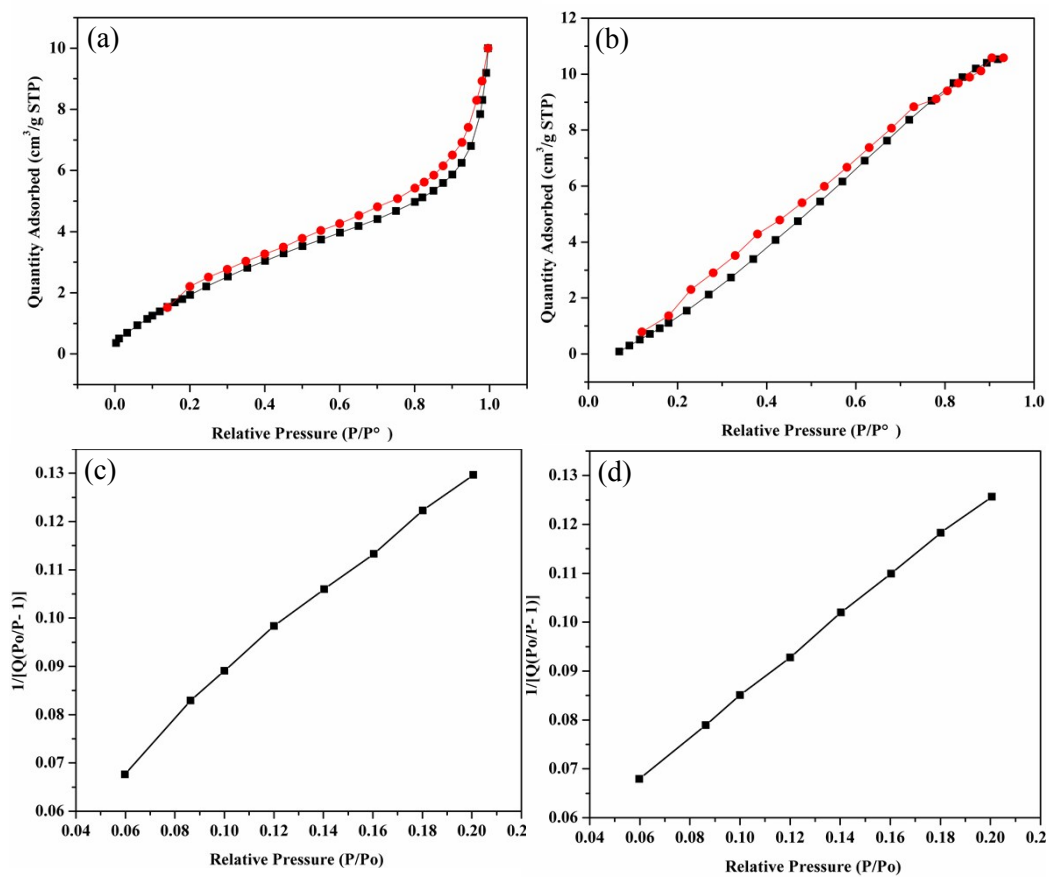
Fig. S10. N$_2$ sorption isotherms of CrPMo (a) and AlPMo (b) and BET of CrPMo (c) and AlPMo (d)