Supporting information

Acid-base bifunctional HPA nanocatalysts promoting heterogeneous transesterification and esterification reactions

[a] Key Lab of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, P. R. China. Fax: 0086-431-85099759; Tel.: 0086-431-88930042; E-mail address: wangxh665@nenu.edu.cn

[b] Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. Tel.: 0086-431- 85262452; E-mail address: jzj2002@sohu.com

Experimental

The Hammett acid strength was measured by exposing samples of ly_2HPW (0.1g) to benzene solutions of a known amount of selected Hammett indicators (methyl violet, pKa = +0.8; anthraquinone, pKa = -8.2; 2,4,6-trinitroaniline, pKa = -10.1; p-nitrotoluene, pKa = -11.35; p-nitrochlorobenzene, pKa = -12.7; 2,4- dinitrotoluene, pKa = -13.75; 2,4-dinitrofluorobenzene, pKa = -14.52). UV-Vis spectra of the air dried samples were recorded to quantify the amount of indicator adsorbed on the surface of the catalyst. And the Hammett base strength was also determined in the same method, which was measured by exposing samples of catalysts (0.1g) to benzene solutions of a known amount of selected Hammett indicators (bromothymol blue, pKa = 7.2; phenolphthalein, pKa = 9.3; 2,4,6-Trinitrobenzene amine, pKa = 12.2; 2,4-dinitraniline, pKa = 15.0; 4-chloride-2–nitroaniline, pKa = 17.2).

The acid capacity of $(C_6H_{15}O_2N_2)_2HPW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ was measured by titration. A sample of catalyst (0.1g) was stirred with 2M NaCl (20 mL). After 24 h, Filter to remove the solid, the filtrate was measured by titration with NaOH (0.05 M). The indicator was phenolphthalein.[1-2]

1 D. E. Lopez, K. Suwannakarn, D. A. Bruce, J. G. Goodwin Jr. , J. Catal. 2007, 247, 43 –50.

2 A. A. Kiss, A. C. Dimian, G. Rothenberg, Adv. Synth. Catal. 2006, 348, 75–81.

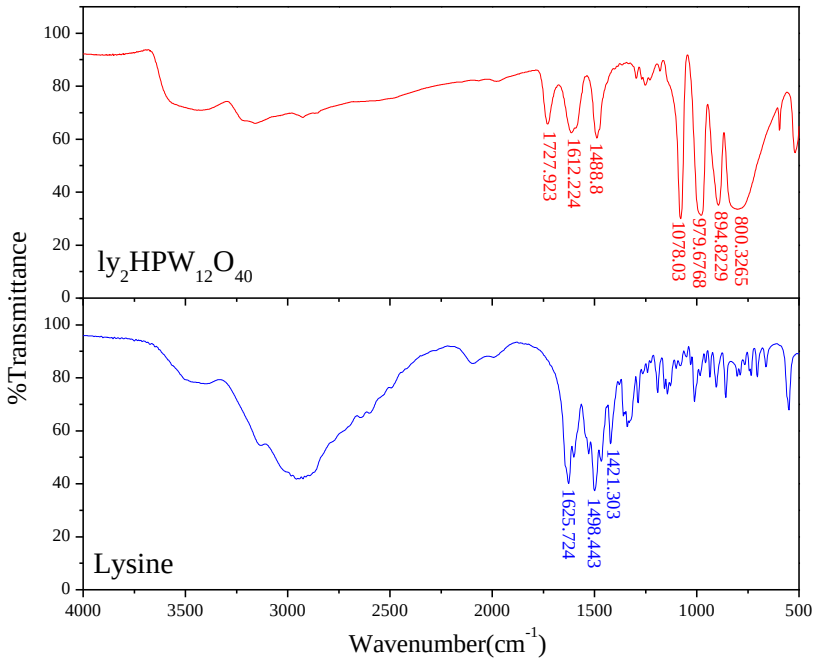


Fig S1 The IR spectra of $ly_2HPW_{12}O_{40}$ and lysine

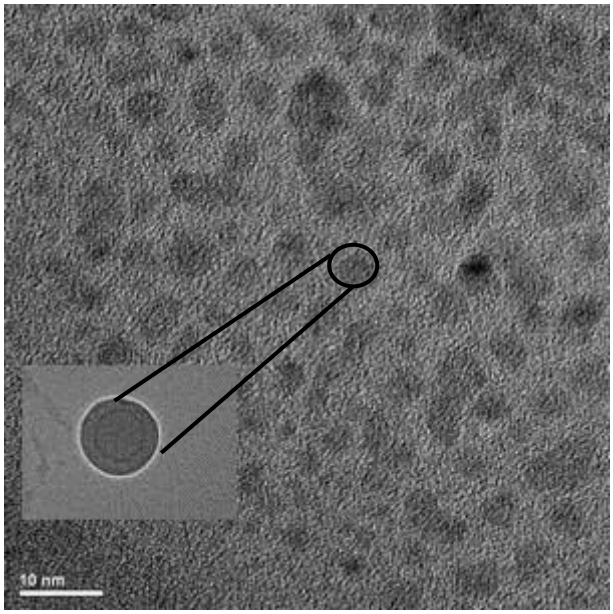


Fig. S2 The TEM image of $(C_6H_{15}O_2N_2)_2HPW_{12}O_{40}$

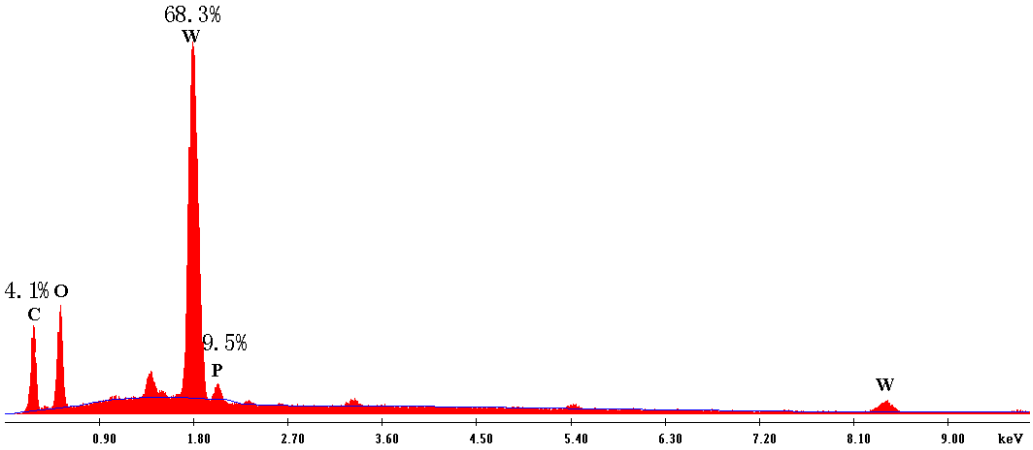


Fig. S3 The Energy dispersive X-ray spectroscopic data of $(C_6H_{15}O_2N_2)_2HPW_{12}O_{40}$

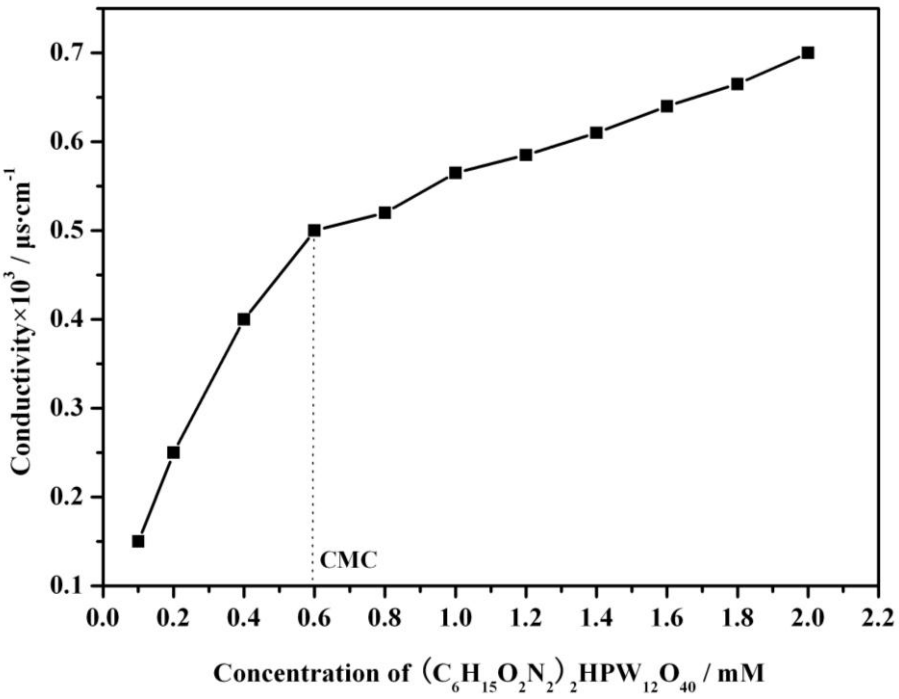


Fig. S4 The CMC of ly_2HPW in room temperature

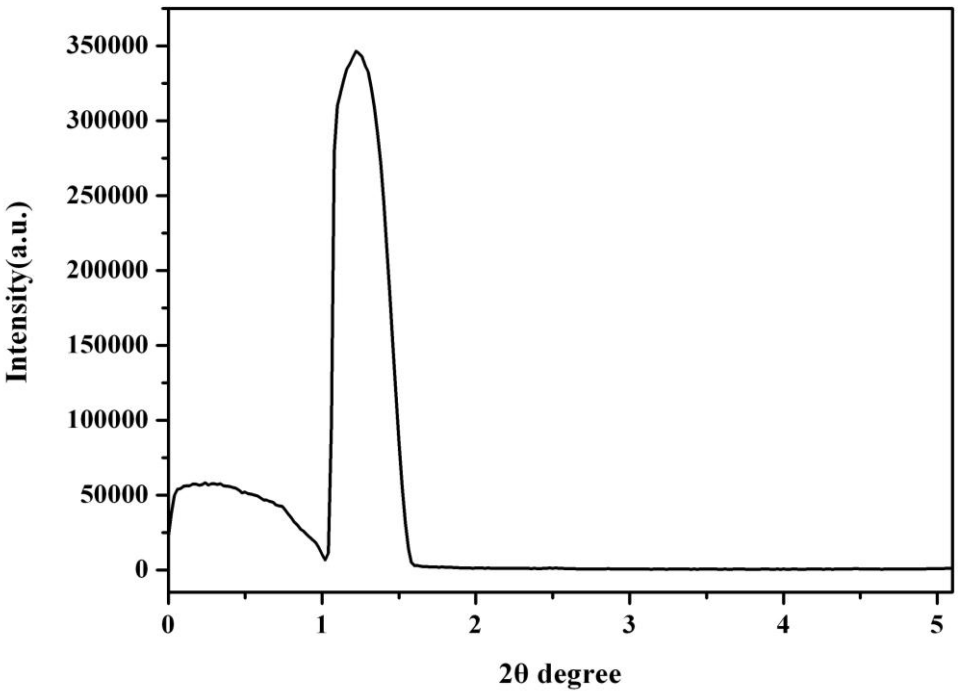


Fig. S5 Low-angle XRD pattern of ly_2HPW

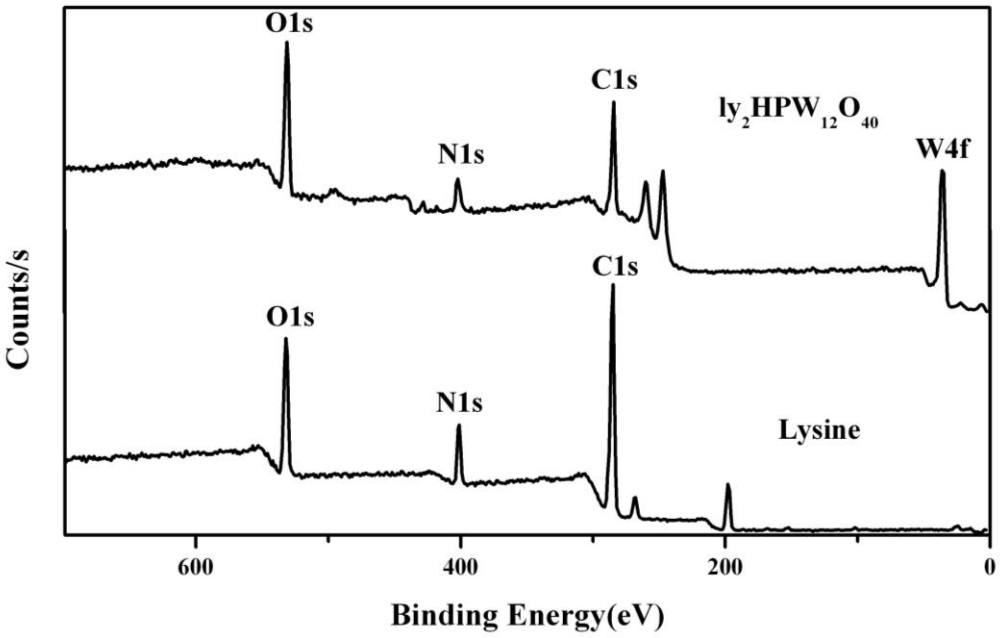


Fig. S6 Binding energy of ly_2HPW and lysine

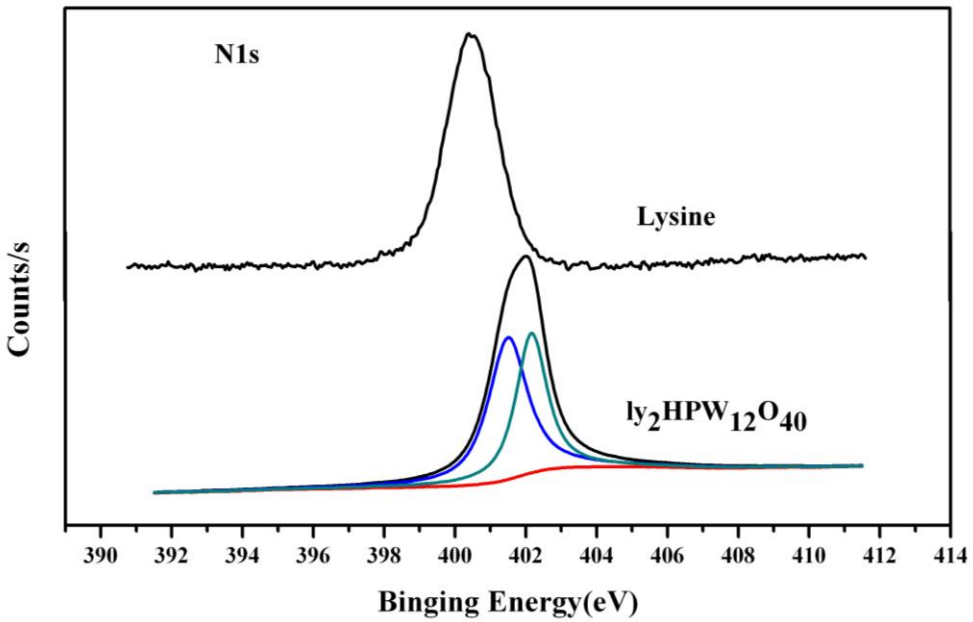


Fig. S7a The XPS of lysine and $ly_2HPW_{12}O_{40}$ for N1s

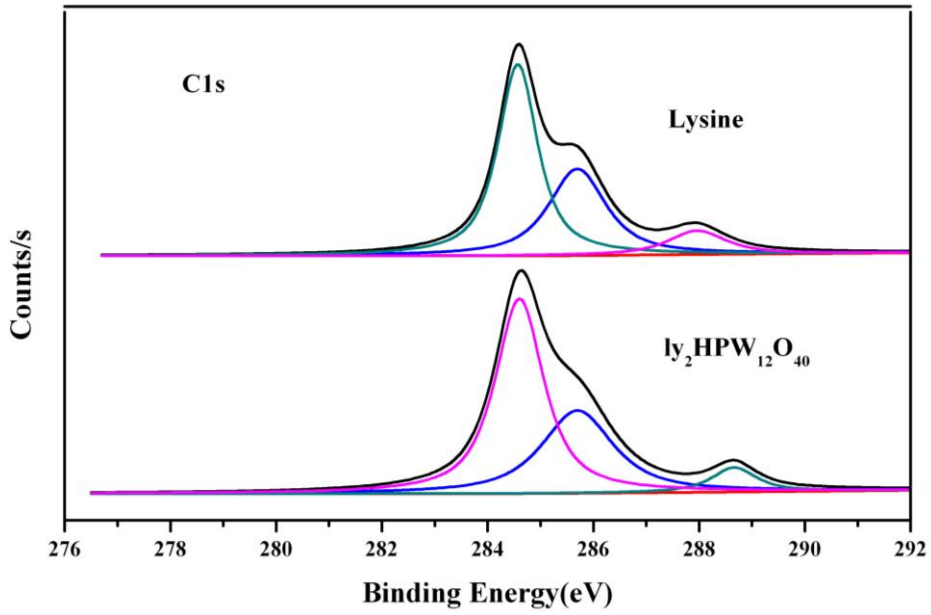


Fig. S7b The XPS of lysine and ly_2HPW for C1s

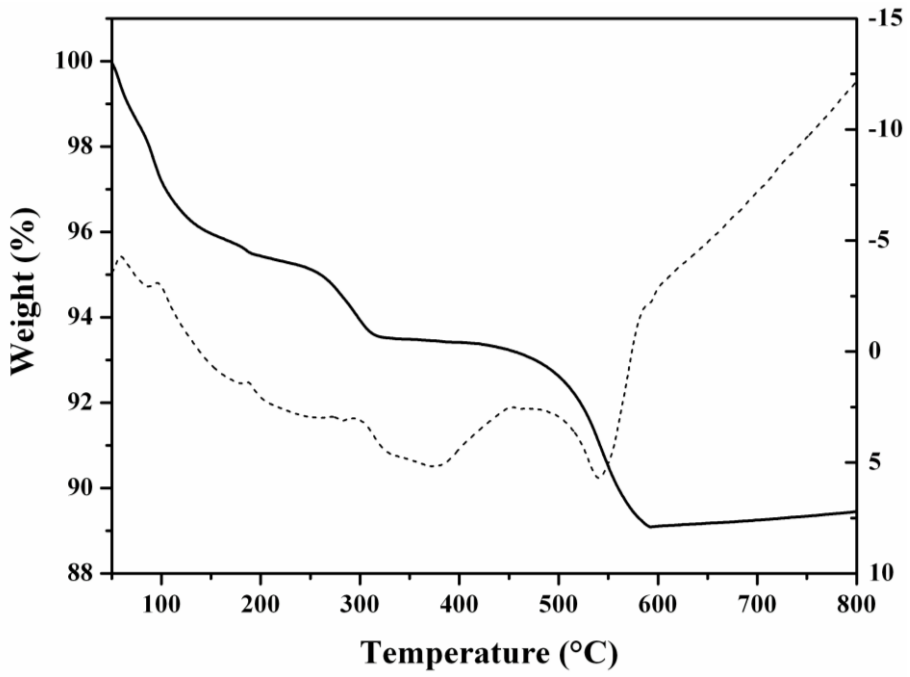
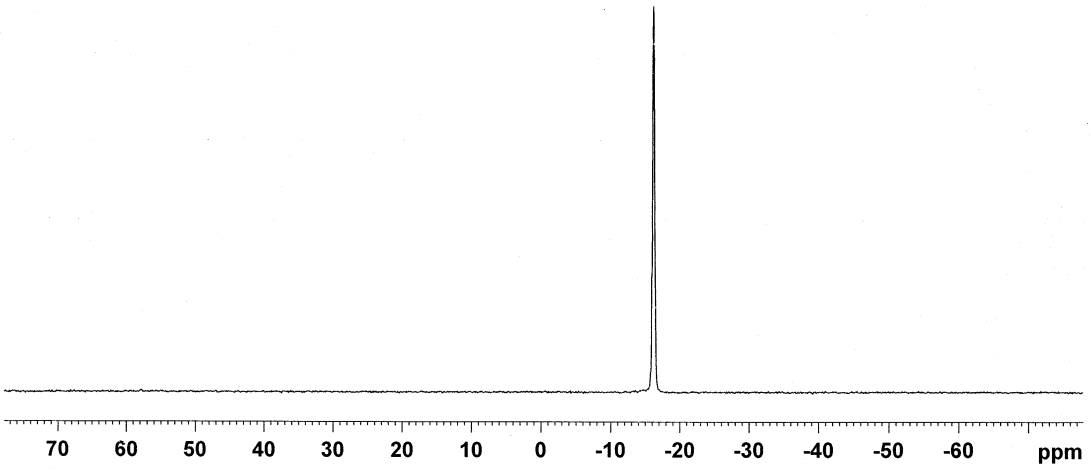
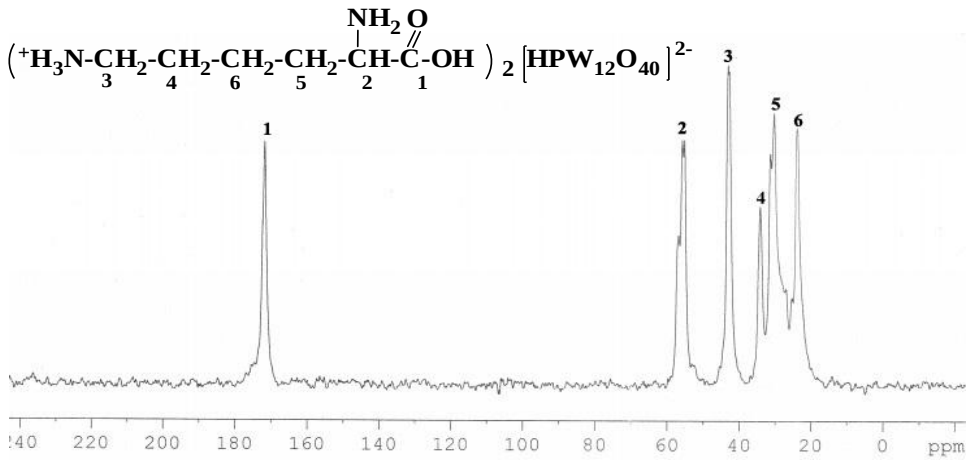


Fig. S8 The thermal analysis (TGA/DTA) curves of ly_2HPW



(a)



(b)

Fig. S9 The MAS NMR of ly_2HPW (a) ^{31}P MAS NMR; (b) ^{13}C MAS NMR

Table S1 The surface composition of ly2HPW in XPS

Element	At. %	Atom ratio
C	10.92	12.13
P	0.9	1
N	3.85	4.27
W	11.2	12.44
O	41.3	45.88