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: jzh2002@sohu.com

Experimental

The Hammett acid strength was measured by exposing samples of ly2HPW (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 (C₆H₁₅O₂N₂)₃HPW₁₂O₄₀ and H₃PW₁₂O₄₀ 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

**Fig S1** The IR spectra of $\text{ly}_2\text{HPW}_{12}\text{O}_{40}$ and lysine
Fig. S2 The TEM image of (C₆H₁₅O₂N₂)₂HPW₁₂O₄₀
**Fig. S3** The Energy dispersive X-ray spectroscopic data of (C₆H₁₅O₂N₂)₂HPW₁₂O₄₀
Fig. S4 The CMC of ly2HPW in room temperature.
Fig. S5 Low-angle XRD pattern of $\text{ly}_2\text{HPW}$
Fig. S6 Binding energy of ly3HPW and lysine
**Fig. S7a** The XPS of lysine and $\text{ly}_2\text{HPW}_{12}\text{O}_{40}$ for N1s

**Fig. S7b** The XPS of lysine and $\text{ly}_2\text{HPW}_{12}\text{O}_{40}$ for C1s
Fig. S8 The thermal analysis (TGA/DTA) curves of ly2HPW
Fig. S9 The MAS NMR of \( \text{H}_2\text{HPW} \) (a) \(^{31}\text{P}\) MAS NMR; (b) \(^{13}\text{C}\) MAS NMR
### Table S1 The surface composition of ly2HPW in XPS

<table>
<thead>
<tr>
<th>Element</th>
<th>At. %</th>
<th>Atom ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>10.92</td>
<td>12.13</td>
</tr>
<tr>
<td>P</td>
<td>0.9</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>3.85</td>
<td>4.27</td>
</tr>
<tr>
<td>W</td>
<td>11.2</td>
<td>12.44</td>
</tr>
<tr>
<td>O</td>
<td>41.3</td>
<td>45.88</td>
</tr>
</tbody>
</table>