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## Design of a highly ordered mesoporous H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>–Si(Ph)Si hybrid catalyst for methyl levulinate synthesis†

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A highly ordered mesoporous ZrO<sub>2</sub>-based material functionalized by benzene-bridged organosilica groups and the Keggin type heteropolyacid, prepared in a single co-condensation–hydrothermal treatment step, exhibited much higher catalytic activity towards methyl levulinate synthesis compared to alkyl-free H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>.

#### 1. Introduction

Levulinate esters including methyl, ethyl, and n-butyl levulinate are the esterification products of levulinic acid (LA), and they are versatile chemical feedstocks with numerous potential applications in the flavoring and fragrance industry or as a blending component in biodiesel.<sup>1</sup> The synthesis of levulinate esters from LA has been attracting special attention because LA is one of the top biomass-derived platform molecules that can be made by the treatment of 6-carbon sugar carbohydrates from renewable biomass such as starch or lignocellulosics with an acid.<sup>2</sup> Traditional catalysts for the synthesis of levulinate esters are strong Brönsted mineral acids. More recently, a "green" approach to levulinate ester synthesis has stimulated the application of recyclable strong solid acids as replacements for such liquid acid catalysts so that the use of harmful substances and generation of toxic wastes are avoided. For this purpose, environmentally benign solid acid catalysts including sulfated metal oxides (i.e., SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>), ionexchange resins (i.e., Amberlyst 70), SBA-15 silica-supported sulfonic acid (SO<sub>3</sub>H-SBA-15), and silica-supported or acidtreated clay montmorillonite-supported heteropolyacids (i.e., HPA/SiO<sub>2</sub> and HPA/K10) were used in this process.<sup>3-6</sup>

Nevertheless, design of robust and stable solid acid catalysts that can improve the efficiency of levulinate ester production dramatically is still an important challenge, and a number of factors such as acid strength, textural properties,

surface hydrophobicity, and stability of the catalysts need to be considered. Bearing this in mind, herein, ZrO<sub>2</sub> materials functionalized by both Keggin type HPA and benzene-bridged organosilica moieties with ordered mesostructure in hexagonal p6mm symmetry (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph)Si) were successfully developed by careful design of a one-step co-condensationhydrothermal route. HPAs are an interesting class of welldefined super strong Brönsted acids, exhibiting excellent catalytic behaviors in a wide variety of acid-catalyzed reactions. The disadvantages of HPAs including small specific surface area and high solubility in polar media can be overcome by dispersing them within porous supports. Recently, H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>/SiO<sub>2</sub> and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/K10 have been reported to exhibit catalytic activity towards ethyl and n-butyl levulinate production. However, their catalytic activity is unsatisfactory since only H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> or H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is the active site. For example, over a period of 10 h the ethyl levulinate yield reached 78% under the conditions of the H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>/SiO<sub>2</sub> amount of 1.6 wt%, 78 °C and a LA to ethanol molar ratio of 1:3.<sup>5</sup> For the synthesis of *n*-butyl levulinate catalyzed by H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/K10 (H<sub>3</sub>PW<sub>12</sub>O<sub>4</sub> loading of 20 wt%), 97% LA conversion and 100% selectivity towards n-butyl levulinate were achieved under the conditions of the catalyst amount of 10 wt%, 120 °C, a LA to *n*-buthanol molar ratio of 1:6 and 4 h.<sup>6</sup> Compared with the above supported HPA catalysts, the as-designed multifunctionalized H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph)Si hybrid catalyst possessed the following advantages: (i) ZrO<sub>2</sub> itself displays Brönsted acid sites capable of protonating pyridine,<sup>7</sup> after introduction of HPA in the ZrO2 framework, the Brönsted acidity is enhanced compared with their individual components due to the interaction between the Keggin unit and the ZrO<sub>2</sub> support, which can promote the release of protons more easily.<sup>8,9</sup> Moreover, this strong interaction is expected to inhibit the leaching of the Keggin unit in polar solvents, which often occurred in the supported HPA systems prepared by the post-synthesis route; (ii) incorporation of benzene-bridged organosilica groups can ameliorate the textural properties and enhance the surface hydrophobicity of the as-prepared hybrid catalyst simultaneously. In comparison with disordered

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mesoporous catalysts that possess broad pore size distributions and small surface areas, the catalysts with ordered mesostructure exhibit obvious advantages including well-distributed pore sizes, large surface areas and high pore volumes, which in turn can provide more active sites and speed up the mass-transport of reactants and products inside the pores.<sup>10,11</sup> Therefore, the development of catalysts with ordered mesostructure has generated increasing interest in heterogeneous catalysis; and (iii) a one-step preparation route can ensure homogeneous dispersion of the Keggin units throughout the catalysts. By the combination of the above advantages the catalytic activity and stability of the  $H_3PW_{12}O_{40}/ZrO_2-Si(Ph)Si$  hybrid catalyst towards the esterification of LA with methanol to produce methyl levulinate is expected to be further improved.

#### 2. Experimental

The ordered 2D hexagonal H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph)Si hybrid material was prepared as follows. Pluronic P123 (0.275 g) was dissolved in a mixture of water (8.5 mL) and HCl (12 mol  $L^{-1}$ , 0.6 mL) under vigorous stirring at room temperature. Subsequently, 1,4-bis-(triethoxysilyl)benzene (abbreviated BTESB, 96%, 0.32 mL),  $Zr(OC_4H_9)_4$  (0.75 mL) and aqueous  $H_3PW_{12}O_{40}$ (0.1010 g in 1.5 mL water) were added dropwise to the above solution at hourly intervals, successively. The resulting mixture was stirred at 40 °C for 24 h, and then it was subjected to hydrothermal treatment at 120 °C for another 24 h at a heating rate of 2 °C min<sup>-1</sup>. The resulting white solid powder was airdried at 100 °C overnight, and then P123 in the product was removed by washing in boiling ethanol. The final product is denoted as H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph)Si, and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> loading (7.6 wt%) in the product was determined by a Leeman Prodigy Spec ICP-AES. The above procedure has been illustrated in Scheme 1. For comparison,  $H_3PW_{12}O_{40}/ZrO_2$  ( $H_3PW_{12}O_{40}$ loading of 7.0 wt%) was also prepared via the above route in the absence of BTESB. Similarly, ZrO<sub>2</sub> was prepared by following the above procedure in the absence of both BTESB and H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

XRD patterns were obtained on a D/max-2200 VPC diffractometer using Cu K $\alpha$  radiation. TEM observations were performed on a JEM-2100F high resolution transmission electron microscope at an accelerating voltage of 200 kV. A nitrogen porosimetry measurement was performed on a Micromeritics ASAP 2020M surface area and porosity analyzer after the



 $\mbox{Scheme 1}$  Route for the preparation of the  $\mbox{H}_3\mbox{PW}_{12}\mbox{O}_{40}/\mbox{ZrO}_2\mbox{-Si}(\mbox{Ph})\mbox{Si}$  hybrid catalyst.

samples were outgassed under vacuum at 363 K for 1 h and 373 K for 4 h. The surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation, while pore size distribution curves were calculated using the Barrett–Joyner–Halenda (BJH) desorption branch of the isotherms, and the pore volume was accumulated up to  $P/P_0 = 0.99$ . <sup>31</sup>P MAS NMR and <sup>13</sup>C CP-MAS NMR spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probehead. The dried and finely powdered samples were packed in the ZrO<sub>2</sub> rotor closed with a Ke–F cap, and were spun at a 12 kHz rate. Chemical shifts for all <sup>31</sup>P MAS NMR and <sup>13</sup>C CP-MAS NMR spectra were referenced to the signal of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> standard ( $\delta = 0.00$ ) and C<sub>10</sub>H<sub>16</sub> standard ( $\delta$ CH<sub>2</sub> = 38.5), respectively.

Esterification of LA was carried out in a three-necked round bottomed glass flask fitted with a water cooled condenser. For each reaction, 88 mg (2 wt%) of air-exposed catalyst was added, and the reaction was performed at 65 °C with different LA to methanol molar ratios (1:1 to 1:9) and constant volume (5 mL). The produced methyl levulinate was determined by a Shimadzu 2014C gas chromatograph equipped with an HP-INNOWAX capillary column (film thickness 0.5  $\mu$ m; i.d. 0.32 mm; length 30 m) and a flame ionization detector. The catalytic activity of the catalysts was evaluated quantitatively by the yield of methyl levulinate.

#### 3. Results and discussion

It is a challenge to obtain ordered mesoporous HPA-based catalysts by a one-step route, originating from the complicated preparation process and special structure characteristics of HPA clusters. In the present work, the above problems were solved by carefully designing and controlling the co-condensation–hydrothermal treatment procedure, and an ordered mesoporous  $H_3PW_{12}O_{40}/ZrO_2$ –Si(Ph)Si hybrid catalyst was prepared by using nonionic surfactant P123 as a structure directing agent.

Successful introduction of both inorganic and organic functionalities into the ZrO<sub>2</sub> framework is confirmed by <sup>31</sup>P MAS NMR and <sup>13</sup>C CP-MAS NMR measurements. Fig. 1a shows a <sup>31</sup>P MAS NMR spectrum of the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph)Si material, and two signals at -16.2 ppm (intense) and -11.6 ppm (very weak) were found. The intense peak is assigned to the resonance of the PO4 unit within the bulk H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> environment, indicating that the primary Keggin structure remains intact after immobilization. As for the very weak peak, it originates from the new species formed at the interface between the Keggin unit and the ZrO<sub>2</sub> support.<sup>12</sup> This new species slightly perturbs the chemical environment of P atoms in the PO<sub>4</sub> units. During the hybrid catalyst preparation procedure, the surface  $\equiv$  ZrOH groups of the ZrO<sub>2</sub> framework were protonated in the presence of Keggin units, giving  $(\equiv ZrOH_2^+)_n [H_{3-n}PW_{12}O_{40}]^{n-}$  species by an acid-base reaction.8 Additionally, considering the well-matched electronegativity and ionic radius of the  $Zr^{4+}$  ion (1.33, 0.072 nm) and



**Fig. 1** (a) The <sup>31</sup>P MAS NMR spectrum, (b) <sup>13</sup>C CP-MAS NMR spectrum, (c) TEM image, and (d) nitrogen gas adsorption–desorption isotherms and pore size distribution profile of the  $H_3PW_{12}O_{40}/ZrO_2$ –Si(Ph)Si hybrid catalyst.

the W<sup>6+</sup> ion (1.70, 0.060 nm), it can be reasonably inferred that the terminal W=O groups within the Keggin units coordinate to the surface =ZrOH groups within ZrO<sub>2</sub> *via* Zr-O-W bonds in this species.<sup>13</sup> Both of the interactions ensure strong combination of the two components. Fig. 1b displays the <sup>13</sup>C CP-MAS NMR spectrum of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph)Si material, and two resonance signals at 133.4 ppm (intense) and 15.9 ppm (weak) were detected. The intense peak is due to the carbon atoms from benzene-bridged organosilica groups, confirming successful introduction of the organic functional groups into the ZrO<sub>2</sub> framework through -Zr-O-Si-C<sub>6</sub>H<sub>4</sub>-Si-Olinkages (Scheme 2). The weak peak is assigned to ethoxy groups that were formed during the procedure of P123 removal.<sup>14</sup>

Wide-angle XRD patterns of the starting  $H_3PW_{12}O_{40}$  and  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si hybrid catalysts are shown in Fig. S1a.<sup>†</sup> The absence of diffraction peaks corresponding to the starting  $H_3PW_{12}O_{40}$  for the hybrid catalyst suggests the



**Scheme 2** Wall components of  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si and esterification of levulinic acid with methanol to produce methyl levulinate catalyzed over the  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si hybrid catalyst.

homogeneous dispersion of Keggin units throughout the material.

The low-angle XRD pattern shown in Fig. S1b<sup>+</sup> indicates that the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph)Si exhibits an intense diffraction peak at 0.86° and two weak diffraction peaks at 1.64° and 1.92°, which are indexed as the 100, 110, and 200 Bragg reflections of 2D hexagonal p6mm structure. As for the benzene-free  $H_3PW_{12}O_{40}/ZrO_2$ , the above reflections were not found. The result suggests that the incorporation of benzene-bridged organosilica moieties plays a key role in creating ZrO<sub>2</sub>-based hybrid material with ordered mesostructure. This structural ordering is further confirmed by TEM observation, revealing the 2D hexagonal arrangement of pore channels (Fig. 1c). The result is consistent with that of the nitrogen porosimetry analysis (Fig. 1d). H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>-Si(Ph)Si exhibits a type IV isotherm with an H1 hysteresis loop, characteristic of the material with regular and even mesopores without interconnecting channels. The narrow BJH pore-size distribution curve also indicates uniform pore sizes (mainly centering at 5.5 nm) of the hybrid catalyst. As for the benzene-free H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ ZrO<sub>2</sub>, it has a type III isotherm with an H3 hysteresis loop, together with a broad pore-size distribution curve (Fig. S2 of ESI<sup>†</sup>), implying poor porosity of the material. Through analyzing the textural parameters summarized in Table 1 it was found that the BET surface area and pore volume of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub> were improved significantly after the introduction of benzene-bridged organic silica groups.

As-prepared  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si was successfully tested in the esterification of LA with methanol to produce methyl levulinate under atmosphere refluxing (65 °C) (Scheme 2).

At first, the influence of the molar ratio of LA to methanol was studied because it is one of the most important experimental parameters of the esterification reaction. From the result shown in Fig. 2 it is found that the yield of methyl levulinate continuously increases with the molar ratio of LA to methanol from 1:1 to 1:7, and with further increasing the molar ratio to 1:9, the yield begins to decrease. For example, over the period of 3 h, methyl levulinate yield reaches 45.6%, 99.9% and 75.0%, respectively, at the LA to methanol molar ratios of 1:1, 1:7 and 1:9. This is due to the fact that esterification is a reversible reaction, and excessive methanol is favorable to ester formation. However, much more methanol may dilute the reactant, thereby resulting in lower methyl levulinate yield. Additionally, excessive methanol may also lead to side reactions such as ether formation or methanol dehydration in

 Table 1
 Textural parameters and acid property of ZrO2-based materials

Catalyst	$S_{\text{BET}}$ $(\text{m}^2 \text{g}^{-1})$	D <sub>p</sub> (nm)	$V_{\rm p} \ ({\rm cm}^3 {\rm g}^{-1})$	$\begin{array}{c}A_{\rm titration}^{}^{}a\\\left(\mu {\rm eq~g}^{-1}\right)\end{array}$
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /ZrO <sub>2</sub>	18	n.d.	0.05	1331
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /ZrO <sub>2</sub> -Si(Ph)Si	250	5.5	0.38	933
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /ZrO <sub>2</sub> -Si(Ph)Si <sup>3rd</sup>	235	5.3	0.36	915

 $^a$  Acid capacity (A<sub>titration</sub>) of the tested catalysts was measured by titration with NaOH (0.002 mol  $L^{-1}).^{15}$ 



Fig. 2 Influence of the molar ratio of LA to methanol on the yield of methyl levulinate.  $H_3PW_{12}O_{40}/ZrO_2-Si(Ph)Si$  (2 wt%); 65 °C; atmosphere refluxing.

the presence of an acid catalyst. However, in the current catalytic system, 100% selectivity towards methyl levulinate is achieved, and neither dehydration products nor ether is detected.

Subsequently, the influence of the  $H_3PW_{12}O_{40}/ZrO_2-Si(Ph)Si$ amount on the yield of methyl levulinate was studied at a molar ratio of LA to methanol of 1:7. From the result shown in Fig. S3<sup>†</sup> it can be seen that the catalytic activity of  $H_3PW_{12}O_{40}/ZrO_2-Si(Ph)Si$  is significantly enhanced after increasing the catalyst amount from 1 to 2 wt%, however, the yield of methyl levulinate remains unchanged when the catalyst amount was further increased to 3 or 5 wt%.

Finally, at a LA to methanol molar ratio of 1:7 and a catalyst amount of 2 wt%, the catalytic activity of  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si was further compared with as-prepared  $ZrO_2$ -based catalysts (*i.e.*,  $H_3PW_{12}O_{40}/ZrO_2$  and  $ZrO_2$ ) and the reference catalysts (*i.e.*,  $H_3PW_{12}O_{40}$  and  $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ ) under identical conditions. As can be seen in Fig. 3a, the catalytic activity of  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si outperforms  $H_3PW_{12}O_{40}/ZrO_2$  and  $ZrO_2$  as well as  $H_3PW_{12}O_{40}$  and  $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ . For example, over a period of 3 h, methyl levulinate yield reaches 99.9% ( $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si), 69% ( $H_3PW_{12}O_{40}/ZrO_2$ ), 61.8% ( $ZrO_2$ ), 49.9% ( $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ ) and 69%  $H_3PW_{12}O_{40}$ , respectively.

The excellent heterogeneous acid catalytic performance of the  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si hybrid catalyst is explained in terms of its strong Brönsted acid property, well-defined mesostructure and surface hydrophobicity. Among these factors, the strong Brönsted acid property of the hybrid catalyst plays a dominant role in its catalytic activity. From the results summarized in Table 1 it can be seen that  $H_3PW_{12}O_{40}/ZrO_2$  possesses a strong Brönsted acid property with an acid capacity of 1331 µeq g<sup>-1</sup>, mainly due to the contribution from both  $H_3PW_{12}O_{40}$  and  $ZrO_2$ . Additionally, new ( $\equiv$ ZrOH<sub>2</sub><sup>+</sup>)<sub>n</sub>-[ $H_{3-n}PW_{12}O_{40}$ ]<sup>n-</sup> species formed at the interface between  $H_3PW_{12}O_{40}$  and ZrO<sub>2</sub> can enhance the interaction between the polyanions ( $PW_{12}O_{40}^{3-}$ ) and hence the formation of larger



**Fig. 3** (a) Comparison of the catalytic activity of the  $H_3PW_{12}O_{40}/ZrO_2-Si(Ph)Si$  hybrid catalyst with other  $ZrO_2$ -based materials, homogeneous  $H_3PW_{12}O_{40}$  and  $H_{0.5}Cs_{2.5}PW_{12}O_{40}$  towards the esterification of LA. LA: MeOH = 1:7; catalyst amount 2 wt%; 3 h; 65 °C; atmosphere refluxing, and (b) recyclability of  $H_3PW_{12}O_{40}/ZrO_2-Si(Ph)Si$  for the synthesis of methyl levulinate. LA: MeOH = 1:7; catalyst amount 2 wt%; 3 h; 65 °C; atmosphere refluxing.

polyanions. Larger polyanions can effectively delocalize the negative charge required for the formation of Brönsted acid centers, ultimately resulting in strong Brönsted acidity of the  $H_3PW_{12}O_{40}/ZrO_2$ .<sup>9,13,16</sup> The decreased acid capacity of  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si (933 µeq g<sup>-1</sup>) compared with  $H_3PW_{12}O_{40}/ZrO_2$  is due to the introduction of non-acidic benzene-bridged organic silica groups into the hybrid catalyst.

Additionally, to a great extent, the excellent acid catalytic activity of  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si is also determined by its unique textural properties and homogeneous dispersion of the active sites throughout the hybrid catalyst. Herein, the textural properties of  $H_3PW_{12}O_{40}/ZrO_2$  are obviously improved owing to the introduction of benzene-bridged organosilica moieties. The highly ordered pore channel, larger pore diameter (5.5 nm), and homogeneous dispersion of the active sites may reduce the mass transfer limitations of the reactants and

products to and from the active acid centers and increase the accessibility to their acid sites. In order to support this point of view, the influence of the stirring rate on the yield of levulinic acid was studied. From the result displayed in Fig. S4<sup>†</sup> it is found that the catalytic activity of the  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si is hardly affected by changing the stirring rate from 300, 600, 900 to 1200 rpm, implying that the  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si-catalyzed esterification reaction is free from the external mass transfer limitations. Besides, the larger surface area (250 m<sup>2</sup> g<sup>-1</sup>) and the higher pore volume (0.38 cm<sup>3</sup> g<sup>-1</sup>) of the hybrid catalyst may give rise to a higher population of available acid sites. All of these factors ensure that the  $H_3PW_{12}O_{40}/ZrO_2$ -Si(Ph)Si has significantly higher acid catalytic activity compared with  $H_3PW_{12}O_{40}/ZrO_2$ , although the latter has a higher Brönsted acid capacity.

Finally, the surface hydrophobicity of the hybrid catalyst is increased due to the incorporation of phenyl groups, which can tune the adsorption properties of the reactants and products, thereby enhancing the LA esterification rate. For benzene-free H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub>, its hydrophilic nature due to the presence of surface hydroxyl groups is not ideal for the LA esterification to produce methyl levulinate. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub> favors H<sub>2</sub>O adsorption and thereby inhibits the adsorption of LA molecules, which may slow down the formation rate of methyl levulinate. On the other hand, esterification is a reversible process, and the produced ester molecules can easily be hydrolyzed by water formed during the esterification process,<sup>17</sup> thereby the reaction is depressed to some extent. Enhancement of the surface hydrophobicity by the incorporation of phenyl groups can create a hydrophobic environment within mesopores, which serves to exclude the yielded water from the active sites, causing the catalyst to sustain a higher reaction rate.

Catalyst recycling is an important step as it can reduce the cost of the process. The reusability of as-prepared  $H_3PW_{12}O_{40}/ZrO_2-Si(Ph)Si$  was evaluated through three catalytic recycles. After the first catalytic run, the catalyst was recovered by centrifugation, and then it was washed with dichloromethane for three times and dried in an oven at 100 °C, weighted and returned to the reaction system again for the second and third catalytic runs, respectively, under the same conditions and regeneration method. As shown in Fig. 3b, the hybrid catalyst showed good catalytic stability maintaining a similar level of reactivity after three cycles. For the second and third catalytic runs, the loss of activity after 1 h reaction time may be due to the loss of catalyst powder during the recycling processes, but further increasing the reaction time can restore the activity.

Additionally, P and W were not detected in the catalyst-free reaction solutions; meanwhile, changes of the textural property and acidity of the reused hybrid catalyst were negligible (Table 1). The results revealed that the hybrid catalyst works effectively as a recyclable and water-tolerant solid catalyst in the esterification of LA to produce methyl levulinate. The high catalytic stability is due to the strong chemical rather than physical interaction that existed between the Keggin unit and the  $ZrO_2$  support. Moreover, deactivation of the catalyst due to the strong adsorption of  $H_3PW_{12}O_{40}/ZrO_2$  to water was inhibited owing to the surface hydrophobicity of the hybrid catalyst.

In conclusion, the one step co-condensation–hydrothermal treatment strategy was designed to create a 2D hexagonal mesostructured organic–inorganic hybrid catalyst,  $H_3PW_{12}O_{40}/ZrO_2$ –Si(Ph)Si. The catalyst exhibited excellent catalytic activity towards esterification of LA to produce methyl levulinate under mild conditions; meanwhile, the catalyst could be reused three times without significant loss of the activity. The unique catalytic performances of the as-prepared hybrid catalyst are due to the combination of strong Brönsted acidity, well-defined ordered mesostructure, homogeneous dispersion of the active sites and enhanced surface hydrophobicity, making it a promising environmentally friendly solid acid catalyst for methyl levulinate synthesis.

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