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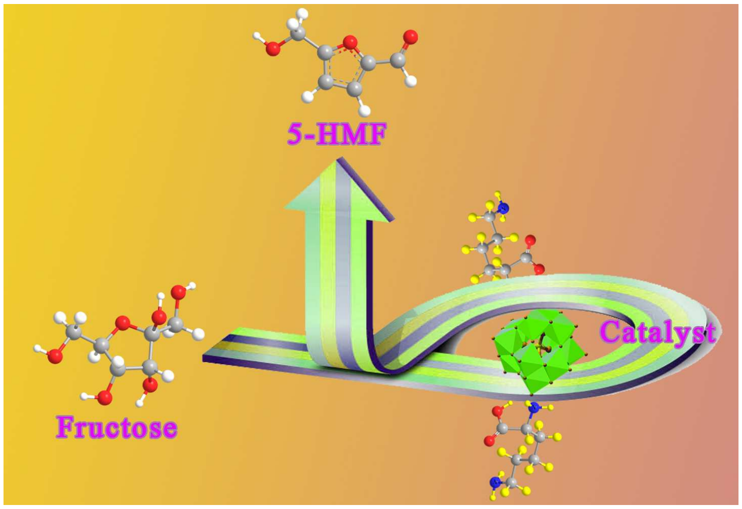
A acid-base bifunctional heteropolyacid had been used in conversion of fructose into

5-hydroxymethylfurfural



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# Conversion of highly concentrated fructose into 5-hydroxymethylfurfural by acid-base bifunctional HPA nanocatalysts induced by choline chloride

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A series of acid-base bifunctional heteropolyacids (HPAs) $(C_6H_{15}O_2N_2)_{3-x}H_xPW_{12}O_{40}$ (abbreviated as $Ly_{3-x}H_xPW$) had been designed using different ratios of HPAs with amino acid lysine in order to control their acid/base properties. Meanwhile, the amino acid group facilitated the HPAs forming micellar assembly in choline chloride/fructose deep eutectic solvents. In the dehydration of fructose to 5-hydroxymethylfurfural (HMF), $Ly_{3-x}H_xPW$ exhibited different catalytic activity because of their different acid/base properties. Among all HPA catalysts, $Ly_2HPW$ gave the best results with 93.3 % conversion and 92.3 % HMF yield within very short time, i.e. 1 min under conventional temperature of 110 ºC using choline chloride (ChCl) as solvent, and this was almost the best result by far. The highest activity and selectivity of $Ly_2HPW$ came from the synergistic effect between certain acidic and basic capacity, which provides readily accessible to the nucleophilic ($-NH_2$) and electrophilic (H) sites. Moreover, this catalyst was tolerant to high concentrated feedstock (~ 66.7 wt %) with the additive of ChCl. $Ly_2HPW$ performed as a heterogeneous catalyst in the ChCl system and could be recycled by simple washing treatment.

## 1. Introduction

Carbohydrates derived from biomass are one of the most abundant renewable resources and possess a great potential of acting as raw materials for the production of many high-value

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products.[1] In this context, much attention has been paid to the synthesis of 5-hydroxymethylfurfural (5-HMF) which was a chemical platform for the production of various non-petroleum valuable chemicals and fuels.[2] HMF was mainly produced by acid-catalytic dehydration of fructose,[3] and many acid catalysts, such as mineral or organic acids, zeolites, metal ions,[4-5] acidic ionic liquids, [6-9] acidic resins,[10] and heteropolyacids ,have been investigated for this important transformation.[11] It is well known that mineral acids possess the advantages of high reactivity, low cost and suitability for applications in industrial processes.[12-13] However, mineral acids generally give low yield and selectivity of HMF because of various byproducts like formic acids, levulinic acids and polymers. At the same time, the harsh reaction conditions are needed.[14-15] In addition, there may be many side reactions when high concentrated fructose is used as substrates.[16] It is generally recognized that it is very difficult to inhibit side reactions at high temperature within long reaction time. On the other hand, the using of homogeneous acids often accompanys with inherent drawbacks in the separation of products and the corrosion of equipment. Heterogeneous ones are the best candidates for the dehydration of fructose into 5-HMF.[17] But some solid acids exhibit low catalytic performance, and it often costs us a very long time to finish a reaction .[18] Therefore, the development of a green and efficient acid catalyst is still a challenge.

By now, the efficient production of HMF from fructose was often conducted in ionic liquids systems, which is more expensive and thus hinders the applications in industries.[19] König and co-workers firstly reported the successful conversion using choline chloride (ChCl)-based deep eutectic solvent (DES) with fructose.[20] A series of acid catalysts such as Amberlyst-15, $FeCl_3$, $ZnCl_2$, $CrCl_2$, $CrCl_3$, *p*TsOH, Sc(OTf), and Montmorillonite had been used in the above evaluation ,with the HMF yields as 40, 59, 8, 40, 60, 67, 55, and 49 %, respectively, at 100 ºC and 0.5 h. The using of DES not only decreased the reaction temperature, but also shortened the reaction time when treating with substrates of high concentrations. This may be of interest for the development of efficient continuous processes for the conversion of carbohydrates into HMF. Nevertheless, more catalysts need to be evaluated about their catalytic activity in the ChCl systems for the purpose of developing efficient (low temperature and short reaction time) and selective (high yield of HMF) systems. Here, we develop a new synthesis protocol for reaching the goal of getting HMF with high yield and selectivity within very short time even at low temperature. To achieve this, we introduce a base site into the Brønsted acidic heterpolyacids

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using amino acids as building blocks (Scheme S1), and investigate the dehydration of fructose using the base-assisted Brønsted acid as catalysts. The acid-base HPA catalyst which gave the formula as $(C_6H_{15}O_2N_2)_2HPW_{12}O_{40}$ contains double $NH_2$ groups from amino acids as base functional groups and a $H_3PW_{12}O_{40}$ fragment as the acid one. This kind of catalyst was firstly reported[21] by us applying in the process of the heterogeneous transesterification and esterification reactions, and it shows an assistance effect of base on reactions catalyzed by Brønsted acids. As a continuation of our work, we synthesized a series of acid-base HPAs catalysts, $(C_6H_{15}O_2N_2)_{3-x}H_xPW_{12}O_{40}$ (abbreviated as $Ly_{3-x}H_xPW$), using the same strategy and evaluated their catalytic activity in the production of HMF from fructose in the solvent of choline chloride. Up to 92% yield of HMF can be obtained in the ChCl/ $Ly_2HPW$ system within 1 min. The main advantages lie in (1) the bifunctional catalytic system with readily accessible to the nucleophilic sites and electrophilic sites for the selective and efficient conversion from fructose to HMF, (2) less side-reactions within short reaction time (1 min) accompanying with high efficiency, (3) the formation of assembly micelle in fructose/ChCl, (4) the tolerance to high loading of fructose (~ 66.7 wt % ), and (5) the little leaching of the heterogeneous catalysts.

## 2. Experimental

### 2.1. Materials

All solvents and chemicals used were obtained from commercial suppliers. $H_3PW_{12}O_{40}$ was prepared according to the literature procedure [22].

IR spectra (4000 - 500 $cm^{-1}$) were recorded on a Nicolet Magna 560 IR spectrometer (KBr discs). XRD patterns of the samples were collected on a Japan Rigaku $D_{max}$ 2000 X-ray diffractometer with Cu $K_\alpha$ radiation ($\lambda$= 0.154178 nm). TEM micrographs were recorded on a Hitachi H-600 transmission electron microscope. $^{31}P$ MAS (magic-angle spinning) and $^{13}C$ MAS NMR spectra of the samples were measured with a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CPMAS probe with the X channel turning to 162 and 100.62 MHz, respectively. Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a PE 2400 CHN elemental analyzer. The consumption of saccharides was measured by measuring its concentration in the aqueous phase by High-performance liquid chromatography (HPLC) equipped with a refractive index detector (Shimadzu LC-10A, HPX-87H column). And

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the concentration of the HMF in the aqueous phase was determined by HPLC with ION-300H column using a 2: 8 v/v methanol: water (pH = 2) gradient at the flow rate of 0.7ml/min and the column temperature of 303K, using a UV detector.

The conductivity experiment was used for confirming the formation of the micelle in aqueous solutions. The catalysts with different concentrations ranging from 0.1 to 2.0 mM were prepared, and then the electrical conductivity was measured by a conductivity meter.

The surface acidity was investigated using the titration method. The base strength of the catalysts was determined by using conductivity titration method.[23]

### 2.2. Preparation of catalysts

Lysine (Ly, 4mmol) and $H_3PW_{12}O_{40}$ (HPW) (2mmol) was dissolved in dilute hydrochloric acid solution (1M, 10mL), respectively. Then the lysine hydrochloric acid solution was added dropwise into the HPW dilute hydrochloric acid solution with vigorous stirring at the room temperature. The precipitates were obtained by continuously stirring for 2 h followed by filtering. The white precipitates were then dried at 303 K for 4 h. The resulting $(C_6H_{15}O_2N_2)_2HPW_{12}O_{40}$ was obtained with a yield of 52 %. Anal. Calcd. for $(C_6H_{15}O_2N_2)_2HPW_{12}O_{40}$ : W, 69.54; P, 0.98; C, 4.54; N, 1.76; H, 0.97 %. Found: W, 69.77; P, 0.82; C, 4.61; N, 1.65; H, 1.01 %.

Other catalysts were synthesized in the same method by using different molar ratios of lysine to $H_3PW_{12}O_{40}$. The yields of the $(C_6H_{15}O_2N_2)_{0.5}H_{2.5}PW_{12}O_{40}$, $(C_6H_{15}O_2N_2)H_2PW_{12}O_{40}$ and $(C_6H_{15}O_2N_2)_3PW_{12}O_{40}$ were 49, 55, and 51%, respectively. Anal. Calcd. for $(C_6H_{15}O_2N_2)_{0.5}H_{2.5}PW_{12}O_{40}$: W, 74.70; P, 1.05; C, 1.22; N, 0.47; H, 0.34 %. Found: W, 75.22; P, 1.15; C, 1.06; N, 0.39; H, 0.42 %. Anal. Calcd. for $(C_6H_{15}O_2N_2)H_2PW_{12}O_{40}$: W, 72.89; P, 1.02; C, 2.38; N, 0.93; H, 0.56 %. Found: W, 74.48; P, 1.19; C, 2.03; N, 0.81; H, 0.66 %. Anal. Calcd. for $(C_6H_{15}O_2N_2)_3PW_{12}O_{40}$: W, 66.48; P, 0.93; C, 6.51; N, 2.53; H, 1.36 %. Found: W, 66.79; P, 1.22; C, 6.29; N, 2.61; H, 1.24 %.

### 2.3. Dehydration reaction

In a typical experiment: 0.4 g of fructose and 0.6g of choline chloride was mixed together in a single neck flask at 110 °C. Then 0.016 mmol of catalyst was added and then the reaction was started . All reaction times provided in the manuscript were the net reaction times and the heating

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periods of the reactors were not taken into account. At the end of the reaction, the reactor was cooled to the room temperature. Then the resulting productions were diluted by water for detecting the conversion of fructose and the yield of the HMF. The mixture was centrifuged to separate the insoluble catalyst for reuse.

## 3. Results and discussion

### 3.1. Characterization of catalysts

The IR spectra of as-prepared catalysts (Fig. 1) gave four characteristic peaks at 1083, 978, 900, and 795cm$^{-1}$, which can be attributed to $\upsilon_{as}$(P–Oa), $\upsilon_{as}$(W–Od), $\upsilon_{as}$ (W–Ob–W), and $\upsilon_{as}$ (W–Oc–W), respectively, and these bands are coincident with those of its parent $PW_{12}O_{40}^{3-}$ (1080, 983, 890, 800 cm$^{-1}$). It indicated that the original Keggin structure of HPW was retained after the formation of nanoparticles. Peaks at 1615, 1733 and 1489 cm$^{-1}$ were due to the stretching bands of $NH_3^+$, –COOH and C-N of lysine molecules, indicating the existence of lysine in the assembly spheres. There were a little shifts of the bands of $\upsilon_{as}$(W–Od), $\upsilon_{as}$ (W–Ob–W), and $\upsilon_{as}$ (W–Oc–W), demonstrating that the existence of the strong interactions between the HPAs and lysine. The blue shifts of $NH_2$ from 1710 to 1733 cm$^{-1}$ proved that the $NH_2$ group of lysine is protonated as $NH_3^+$. Therefore, the lysine cation and HPW anion were combined through electrostatic effects.

**Fig. 1**

The TEM image of $Ly_2HPW$ (Fig. S1) in ChCl/fructose demonstrated that the diameters of the assembly colloid spheres range from 5 to 10 nm. The Energy Dispersive X-ray (EDAX) (Fig. S1) spectroscopy indicated that these hybrids were composed of $PW_{12}O_{40}$ and lysine, and the composition was evidenced by the presence of tungsten, phosphorus, and carbon elements in the assemblies ,with the molar ratio of C: P: W almost 12:1:12. This result was identified with the results getting from the elementary analysis.

The critical micelle concentrations (CMC) of $Ly_{0.5}H_{2.5}PW$, $LyH_2PW$, $Ly_2HPW$, and $Ly_3PW$ were 0.50, 0.65, 0.6 and 0.55 mM by break points of two nearly straight-line portions of the specific conductivity versus concentration plot 23 (Fig. S2), which confirmed the formation of micelle in the aqueous solution.

The low-angle XRD patterns (Fig. S3) gave one Bragg diffraction peak appeared at 1.56, 1.46, 1.22 and 1.04º, corresponding to $Ly_{0.5}H_{2.5}PW$, $LyH_2PW$, $Ly_2HPW$, and $Ly_3PW$, respectively. The low-angle XRD showed that $Ly_{3-x}H_xPW$ formed layered superstructures with the layer spacing of 5.66, 6.04, 7.27, and 8.48 nm, respectively.

To investigate the thermal stability of $Ly_{3-x}H_xPW$, TG-DTA analyses had been carried out (Fig. S4). The first decrease at up to 200°C corresponds to the loss of water molecules in the material. The second weight losses (ca. 2%, 4%, 9% and 13%) correspond to $Ly_{0.5}H_{2.5}PW$, $LyH_2PW$, $Ly_2HPW$, and $Ly_3PW$, respectively. The curve change at up to 320 °C is probably due to the decomposition of lysine group, which is in good coordination with the content of lysine in the catalyst. An exothermic peak with maxima at around 570°C is due to the structure decomposition of the Keggin anion, which indicating that the sample decomposed into simple oxides at a temperature higher than 570°C. The results showed the good thermo-stability of $Ly_{3-x}H_xPW$.

As was reported previously, the $^{31}P$ NMR spectrum of $H_3PW_{12}O_{40}\cdot 6H_2O$ gave one peak at -15.6 ppm.[24] The $^{31}P$ NMR spectra of $Ly_{0.5}H_{2.5}PW$, $LyH_2PW$, $Ly_2HPW$, and $Ly_3PW$ (Fig. 2) had been tested to determine the Keggin structure. The $^{31}P$ NMR spectra of all gave one peak at -16.161, -16.168, -16.000, and -16.211 ppm, belonging to $Ly_{0.5}H_{2.5}PW$, $LyH_2PW$, $Ly_2HPW$, and $Ly_3PW$, respectively. The above results confirmed that the samples kept Keggin structure after assembling. The change of chemical shift was attributed to the interactions between HPAs and Ly molecules.

**Fig. 2**

The Brønsted acidic capacity of the samples was measured by titration with diluted NaOH, and was expressed by the number of equivalents of $H^+$ in the catalysts. The corresponding values of $Ly_{0.5}H_{2.5}PW$, $LyH_2PW$, $Ly_2HPW$, $Ly_3PW$ and $H_3PW_{12}O_{40}$ were 4.36 mmol/g, 4.15 mmol/g, 3.60 mmol/g, 0.31mmol/g and 4.75 mmol/g, respectively. Meanwhile, the acidic strength of acid-base HPAs was $H_0$ -13.6~ -12.7. Compared with $H_3PW_{12}O_{40}$ ($H_0$ = -13.6), the acidic strength of as-prepared HPAs decreased due to the partial exchange of proton with lysine cation. The basic strength of $Ly_{0.5}H_{2.5}PW$, $LyH_2PW$, $Ly_2HPW$ and $Ly_3PW$ was between 7.2 and 9.3, which was higher than that of lysine (pKa = 10.53). This result indicated that the basic strength of the HPA catalysts was weaker than that of lysine. The basic capacity of $Ly_{0.5}H_{2.5}PW$, $LyH_2PW$, $Ly_2HPW$ and $Ly_3PW$ was 0.09, 0.13, 0.20, and 0.24 mmol/g, respectively. From the above results, it can be concluded that $Ly_{3-x}H_xPW$ exhibited double acid and base property in one.

### 3.2. Catalytic activity

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### 3.2.1. Effect of different catalysts

It is known that dehydration of fructose could be catalyzed by Brønsted acid. In order to determine the base assistance effect on the conversion reaction, different acid-base HPAs had been used in the dehydration of fructose (Fig. 3) under the reaction conditions of weight ratio of fructose/ChCl is 2:3, 110 ºC, 1 min. The conversion followed the order as none (28.0 %) < Lys (34.1 %) < $LyH_2PW$ (79.9 %) ~ $Ly_3PW$ (81.0 %) < $Ly_{0.5}H_{2.5}PW$ (82.5 %) < $Ly_2HPW$ (93.3 %) ~ $H_3PW_{12}O_{40}$ (94.0 %). The yields of 5-HMF were different when using different catalysts ,ordering as none (19.0 %) < Lys (24.0 %) < $LyH_2PW$ (73.1 %) ~ $Ly_{0.5}H_{2.5}PW$ (73.4 %) < $H_3PW_{12}O_{40}$ (75.1 %) < $Ly_3PW$ (79.0 %) < $Ly_2HPW$ (92.3 %). The catalyst with certain base and acid property could promote the dehydration of fructose, and $Ly_2HPW$ gave the highest efficiency (92.3 % yield) with the selectivity of 98.9 %. It is reported that the rate-determining step of fructose dehydration is the enolisation of fructose.[25] $Ly_2HPW$ could provide the concerted activation of fructose at the C-OH bond of the anomeric cation by the proton (electrophile) and at the C-H of $C_1$ of the fructose via hydrogen bonding by N (nuclophile) (Scheme 1) as well. This demonstrated that the co-existence of hydrogen-bond donors (−$NH_2$) and protons in $Ly_2HPW$ gave synergic potentials for the selective and efficient conversion of fructose to HMF. Therefore, high efficiency (low temperature and short time) and high yield of HMF was obtained catalyzed by double acid-base HPA $Ly_2HPW$.

**Fig. 3**

**Scheme 1**

Compared to pure Brønsted acid catalyst $H_3PW_{12}O_{40}$, $Ly_2HPW$ gave higher efficiency and selectivity. The reason was that strong Brønsted acid could catalyze the further rehydration of HMF into levulinic acid and fomic acid, thus the yield of HMF catalyzing by $H_3PW_{12}O_{40}$ was lower. The pKa of lysine is 10.53, so lysine could act as a base in the reaction, so it could not play any role in the dehydration of fructose. It meant that without any acid center, pure base could not activate fructose at the C-OH bond of the anomeric cation. Therefore, the synergic effect of base and acid was the main reason for the high efficiency and high yield.

The effect of Choline Chloride in the reaction mixtures had been determined by the comparison with other deep eutectic mixtures of fructose using imidazole, malonic acid, urea, or guanidine acetic acid (Table S1). It can be seen that Choline Chloride was the best one among all.

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### 3.2.2. Effect of different time and different temperature

We studied the dehydration of fructose at 70 ºC -120 ºC (Fig. 4) in order to determine the effect of the reaction time and temperature on the formation of HMF. It can be seen that the reaction time and temperature had a large effect on the dehydration of fructose into HMF. At low temperature such as 70 ºC, the conversion of fructose and the yield of HMF only reached 78.9 % and 70.2 % in 30 min, respectively. Raising the temperature to 110 ºC, the conversion of 93.3 % and the yield of 92.3 % were obtained only in 1 min. To the best of our knowledge, this might be the best result because of the short time under the conventional heating conditions (Table S2). As for the yield of HMF under different temperatures, it can be seen that below 100 ºC, the yield increased with the time increasing. Over 100 ºC, the yield of HMF decreased because of the formation of polymers. That is to say high temperature leads to side reactions such as condensation or polymerization.

**Fig. 4**

### 3.2.3. Effect of catalyst dosage

The performance of catalyst was examined through using the degradation of fructose (Fig. 5) and different amount of catalysts under the reaction conditions as fructose/ChCl weight ratio 2:3, 110 ºC in 1 min. The dehydration of fructose could be enhanced by increasing the dosage of $Ly_2HPW$. The conversion of fructose and the yield of HMF could reach 64.0 % and 47.1 %, respectively, using 0.003 mmol catalyst. Increasing the usage of catalyst to 0.016 mmol, the best results of conversion and selectivity were obtained. Further increasement of the amount of the catalyst did not enhance the conversion and decreased the selectivity due to the accelerating decomposition of HMF using high dosage of catalyst.

**Fig. 5**

### 3.2.4. Effect of feedstock's concentration

Under the reaction conditions of 0.4 g of fructose, 0.016 mmol of $Ly_2HPW$ , 110 ºC , 1 min, the influence of the fructose/ChCl weight ratio such as 2:6, 3:6, 4:6, and 5:6 had been evaluated (Fig. 6). It can be seen that the conversion and the HMF selectivity were affected by different initial concentrations of fructose. The conversion of fructose and the HMF yield first increased and then decreased with the increase of fructose weight. In this reaction, the usage of fructose was kept constant while changing the usage of ChCl. From the experiment (Fig. S5), it can be seen that large amount of ChCl (2:6 or 3:6) did not help fructose dissolving totally and lead to low

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conversion. For the ratio of 4:6, fructose dissolved totally leading to increasing conversion. For the weight ratio of 5:6, fructose dissolved well but catalytic sites decreased, which resulting in lower conversion. The highest yield of HMF was obtained as 92.3 % at the fructose/ChCl ratio of 4:6. The loss of selectivity to fructose/ChCl ratio of 3:6 or less was attributed to the more catalytic sites compared to that of 4:6, resulting in more by-products like levulinic acid. Compared to 4:6 of fructose/ChCl ratio, the 7 % reduction of selectivity for that of 5:6 might be attributed to the higher fructose concentration leading to higher rates of condensation reactions. This result was in agreement with literature reports 26.

**Fig. 6**

### 3.2.5. Recycling experiments

As mentioned above, the catalyst can be easily separated from the production mixtures. At the end of the reaction, the catalyst was centrifuged and rinsed with water three times. Then it was calcinated to dry for 4 h at 60 °C. In Fig. S6, the IR spectrum of reused $Ly_2HPW$ exhibited the four characteristics W–$O_d$, W–$O_b$–W, W–$O_c$–W and P–$O_a$ asymmetric stretching vibrational peaks of heteropolyanions, indicating the stability of catalyst during the reaction and regeneration procedures. The experiments were repeated six times under the same dehydration procedure and the conversion and yield to HMF were given in Fig. 7. It showed that there was no considerable change in the catalytic activity of the catalyst even after six reaction cycles. So it is believable that our solid acid catalyst is stable and can be reused up to a minimum of six reaction cycles.

**Fig. 7**

To test for leaching of the $Ly_2HPW$ catalyst, the catalyst was filtered after mixturing of $Ly_2HPW$, fructose and ChCl for 20 min and the mixture was allowed to react for 1 min at the same temperature of 110 ºC. It can be seen that the conversion of fructose was only 30.6 % similar to the result without any catalysts (Fig. 3), which demonstrated a little leaching of $Ly_2HPW$ into the mixture and $Ly_2HPW$ performed as heterogeneous catalysts in ChCl system. The total amount of $Ly_2HPW$ leaching through six runs of the reaction reached 5.0 % of its starting amount .

## 4. Conclusion

A series of acid-base catalysts based on HPA $H_3PW_{12}O_{40}$ and amino acid lysine had been developed. They can possess different acid/base properties through controlling of the ratio of HPA to lysine . The dehydration of fructose catalyzed by $Ly_2HPW$ catalyst gave almost the best efficiency in the previous reports (93.3 % conversion and 92.3 % HMF yield) within very short time, i.e. 1 min at 110 ºC using ChCl as a solvent. The highest activity and selectivity of $Ly_2HPW$ with certain acidic and base capacity came from the bifunctional catalytic system with readily accessible to nucleophilic ($-NH_2$) and electrophilic (H) sites. Moreover, this catalyst was tolerant to high concentrated feedstock (up to 66.7 wt %) with the additive of ChCl. $Ly_2HPW$ performed as a heterogeneous catalyst in the ChCl system and could be recycled by simple washing treatment.

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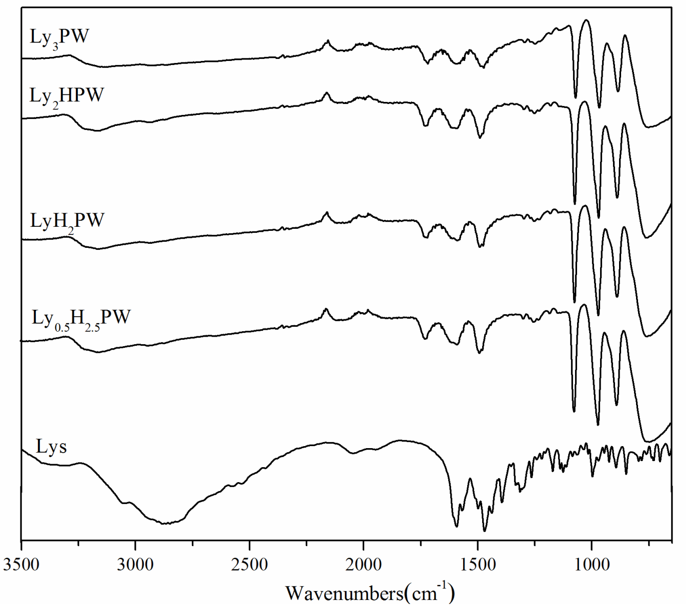

**Fig. 1** The IR spectra of $Ly_{3-x}H_xPW$ and lysine.

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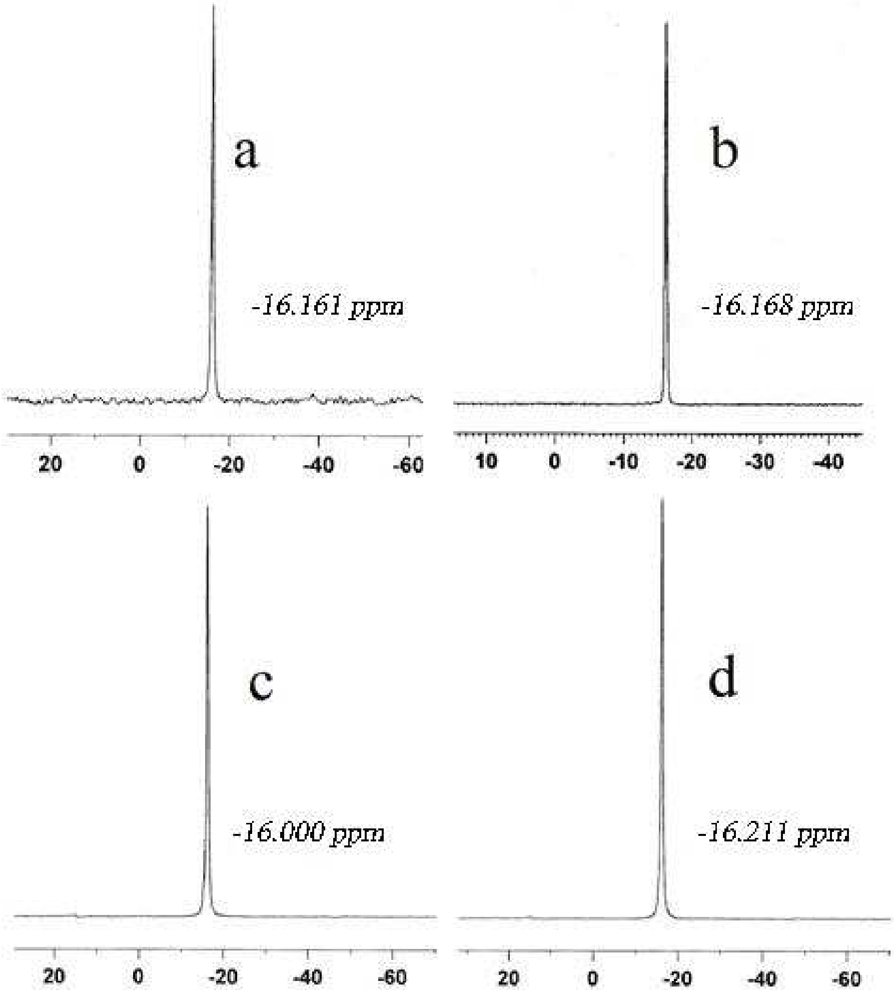

**Fig. 2** Solid-state $^{31}$P NMR spectra of $Ly_{3-x}H_xPW$. (a) $x = 2.5$, (b) $x = 2$, (c) $x = 1$, and (d) $x = 0$.

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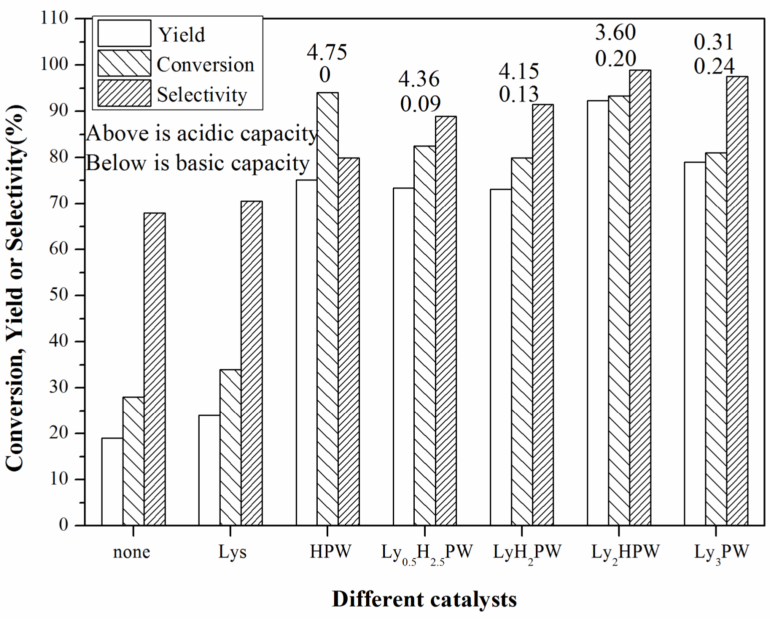

**Fig. 3** Catalytic conversion of fructose to HMF in different catalysts. Reaction conditions: 0.4g of fructose, 0.6g of ChCl, 0.016mmol of catalyst, 110 ºC and reaction time 1 min.

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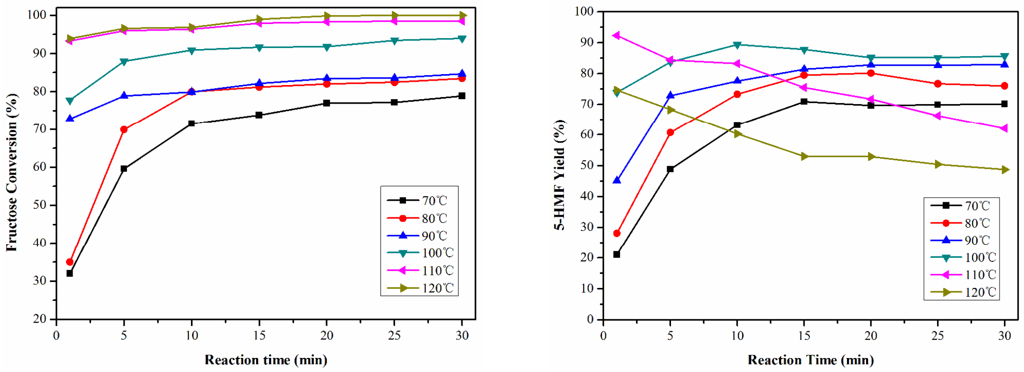

**Fig. 4** The activity of $Ly_2HPW$ on dehydration of fructose under the reaction conditions as 0.4g of fructose, 0.6g of ChCl, 0.016mmol of catalyst.

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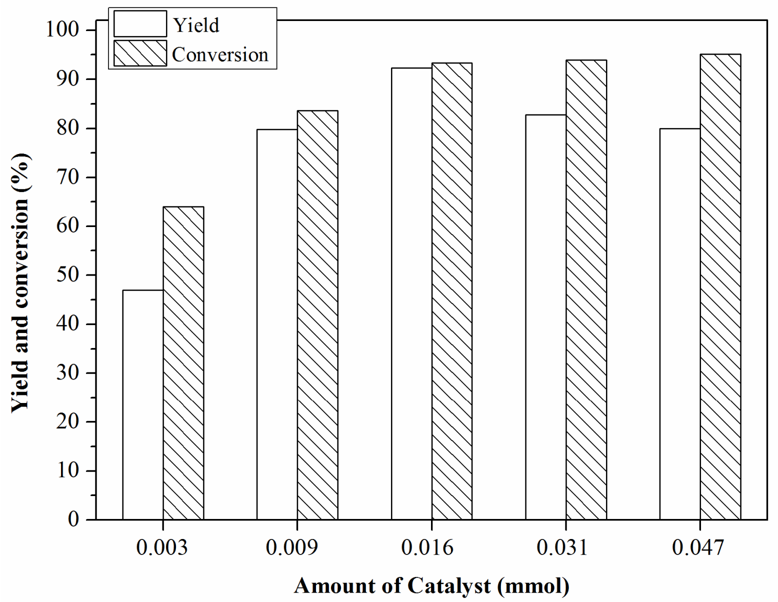

**Fig. 5** The yield and conversion of fructose in different amount of catalyst. Reaction conditions: fructose/ChCl = 4:6, 110 ºC and reaction time 1 min.

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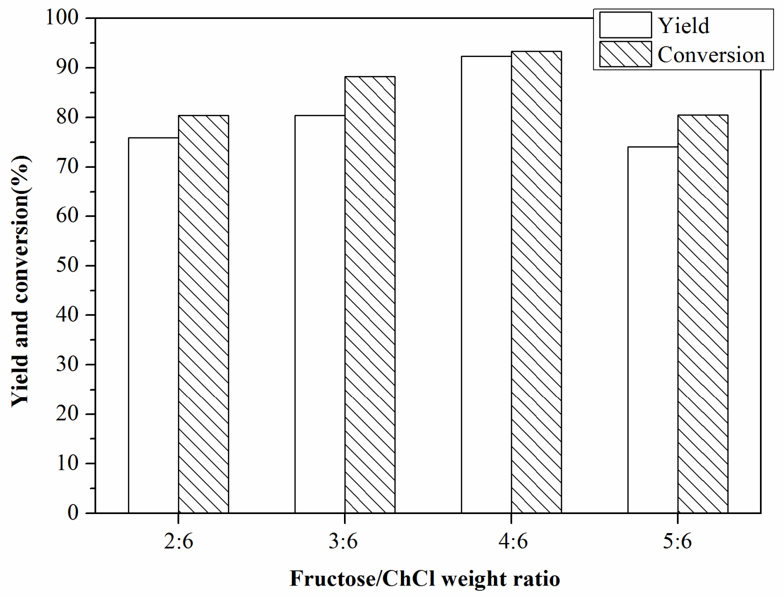

**Fig. 6** The influence of fructose/ChCl weight ratio. Reaction conditions: 0.4 g of fructose, 0.016 mmol of catalyst, 110 ºC and reaction time 1min.

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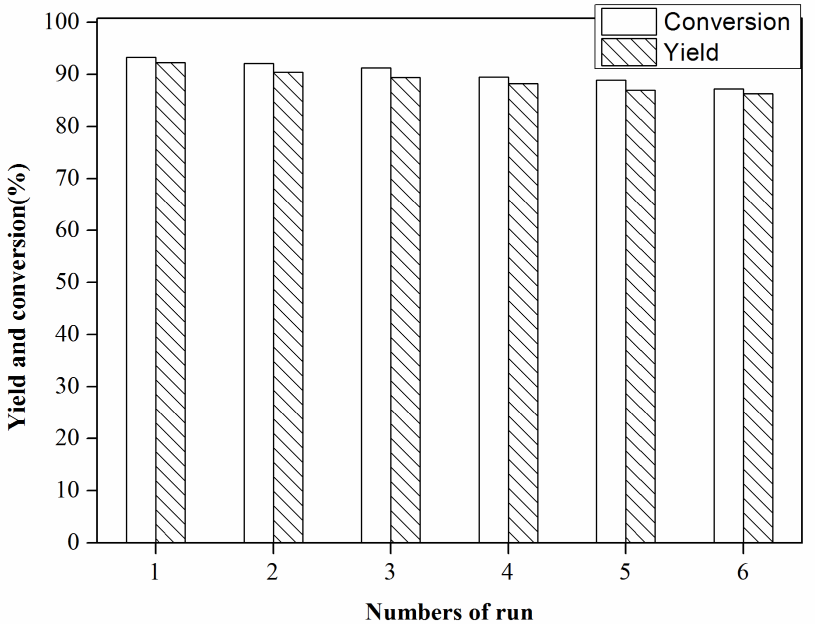

**Fig. 7** The catalyst activity in six reaction cycles. Reaction conditions: 0.4 g of fructose, 0.6 g of ChCl, 0.016 mmol of catalyst, 110 ºC and reaction time 1 min.

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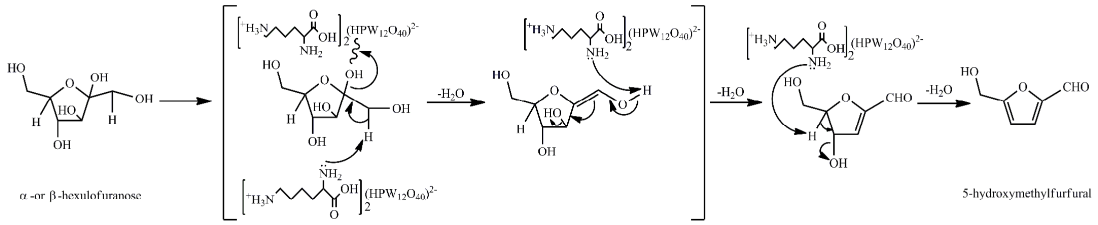

**Scheme 1** Mechanism for the dehydration of fructose to 5-hydroxymethylfurfural in ChCl catalyzed by acid/base HPA catalyst