



Lysine functional heteropolyacid nanospheres as bifunctional acid–base catalysts for cascade conversion of glucose to levulinic acid



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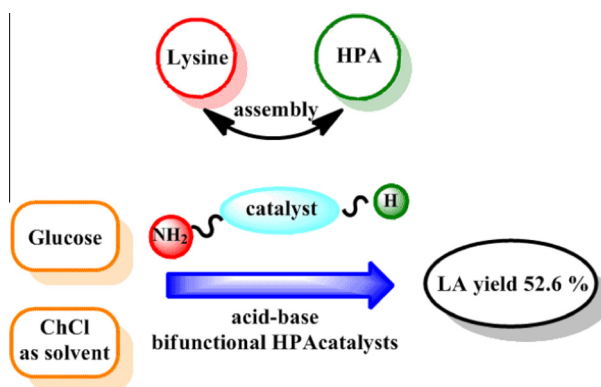
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HIGHLIGHTS

- Application of acid/base bifunctional HPA catalysts in glucose conversion.
- The catalyst gave high yield of LA (52.6%) within 30 min at 130 °C using ChCl as solvent.
- The catalyst performed as a heterogeneous catalyst in ChCl system.
- Easily recycled by simple washing treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Acid–base bifunctional heteropolyacid (HPA) nanospheres ($C_6H_{15}O_2N_2)_3-xH_xPW_{12}O_{40}$ (abbreviated as $Ly_{3-x}H_xPW$) have been evaluated in cascade isomerization/dehydration of glucose to 5-hydroxymethylfurfural (HMF) or levulinic acid (LA) in choline chloride (ChCl) based on deep eutectic solvent system. Compared to other heterogeneous catalysts, the dehydration of glucose catalyzed by $Ly_{0.5}H_{2.5}PW$ gave almost the best efficiency (75.1% conversion and 52.6% LA yield) within very short time (30 min) at 130 °C using ChCl as solvent. The main reason was its unique property of double Brønsted acidity and base property, while the base sites were main candidate for isomerization of glucose to fructose; in addition, the Brønsted acidity might promote the conversion of glucose to product LA rather than HMF. Moreover, this catalyst was suitable for high concentrated glucose (up to 66.7 wt.%) conversion which was obtained after the additive of ChCl. $Ly_{0.5}H_{2.5}PW$ was easily recovered and recycled by simple washing treatment.

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1. Introduction

Multifunctional heterogeneous catalysts, with two or more isolated sites integrated on one solid platform, have attracted a great deal of attention, while they can efficiently catalyze several reactions to occur in one-pot cascade reaction without isolation of intermediates and self-quenching of catalysts [1–4]. Therefore, multifunctional heterogeneous catalysts are required in the field

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of fine chemical synthesis due to the low-cost, step-saving and environmentally friendly properties. However, it is not an easy task to design and fabricate such catalysts with excellent performance including activity and selectivity, precise control over the spatial distribution, and the relative concentrations of different active sites, especially for mutually hostile acid and base groups [5–10]. In recent years, a few catalysts with isolated acidic and basic sites embedded in silica, carbon materials, MOF, zeolite, and polymer resins have been shown to be active in cascade synthetic transformations [1,11–13]. The common strategy is to functionalize the supports by acidic group $-\text{SO}_3\text{H}$ and basic group NH_2^+ . Such methods faced a series of problems such as troublesome and complicated preparation procedures, relatively low activity and selectivity. Because of the increasing interest for developing cascade reactions in catalysis, other new possible strategies to create higher numbers of catalytic centers are desirable and would open unforeseen avenues in catalysis.

Heteropolyacids (HPAs, also called polyoxometalates) are common used Brønsted acid catalysts in fine chemical preparations [14]. Faced the problem of cascade conversion of glucose to HMF or LA, multifunctional HPAs are required to be fabricated. The first acid/base bifunctional HPAs were designed with mesoporous silica modified with site-isolated amine and phosphotungstic acid groups by Shiju and co-workers, which had tunable antagonistic functions for one-pot tandem reactions [15]. Then our group firstly designed a series of HPAs with acid/base double sites using lysine and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as building blocks [16,17]. Lysine functionalized HPAs ($\text{C}_6\text{H}_{15}\text{O}_2\text{N}_2$) $_{3-x}\text{H}_x\text{PW}_{12}\text{O}_{40}$ (abbreviated as $\text{Ly}_{3-x}\text{H}_x\text{PW}$) were active in transesterification and dehydration of fructose to 5-hydroxymethylfurfural (5-HMF) due to the changeable acid/base property and micellar structure. $\text{Ly}_{3-x}\text{H}_x\text{PW}$ exhibited significant activity in dehydration of fructose to HMF with 92.3% yield at 93.3% conversion within very short time. More recently, Shunmugavel reported that acid/base HPA hybrid nanospheres were efficient in alcoholysis of carbohydrates to 5-ethoxymethylfurfural [18], which used the same method as our report selecting different amino acids as functional groups.

The objective of this work is to achieve the production of HMF or levulinic acid (LA) directly through glucose rather than fructose with high yield and selectivity, simplifying the operation process and promoting its further utilization. Herein, the selective conversion of glucose to LA is achieved catalyzed by $\text{Ly}_{3-x}\text{H}_x\text{PW}$ under mild conditions for the first time. In order to develop an economic approach in glucose to HMF, we selected choline chloride (ChCl) as a solvent. Here, we firstly present the results of acid-base HPA nanosphere catalysts in cascade conversion of the highly concentrated glucose into HMF under ChCl system.

2. Experimental

2.1. Measurements

All solvents and chemicals used were obtained from commercial suppliers. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was prepared according to Ref. [19] ($\text{C}_6\text{H}_{15}\text{O}_2\text{N}_2$) $_{3-x}\text{H}_x\text{PW}_{12}\text{O}_{40}$ ($x = 0, 0.5, 1, 2, 3$) was prepared according to Ref. [20].

IR spectra ($4000\text{--}500\text{ cm}^{-1}$) was recorded in KBr disks on a Nicolet Magna 560 IR spectrometer. TEM micrographs were recorded on a Hitachi H-600 transmission electron microscope. The ^{31}P MAS (magic-angle spinning) was recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CPMAS probehead whose X channel was tuned 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 glucose was measured by measuring its

concentration in the aqueous phase by High-performance liquid chromatography (HPLC) was conducted on a system equipped with a refractive index detector (Shimadzu LC-10A, HPX-87H column). And the concentration of the HMF in the aqueous phase was determined by HPLC with an ION-300H column using a 2:8 v/v methanol:water (pH = 2) gradient at a flow rate of 0.7 mL min^{-1} and a column temperature of 303 K, using a UV detector.

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

2.2. Dehydration reaction

In a typical experiment of glucose/ChCl system: 0.4 g of glucose and 0.6 g of choline chloride were mixed together in a single neck flask at $130\text{ }^\circ\text{C}$. Then 0.016 mmol of catalyst was added. All reaction time provided in the manuscript was corresponded to the reaction time and did not consider the heating period of the reactor. At the end of the reaction, the reactor was cooled to room temperature by ice bath. HMF or LA was then extracted from MIBK. Then the left mixture was centrifuged to separate insoluble catalyst for reuse.

3. Results and discussion

3.1. Scanning of the activity for $\text{Ly}_{3-x}\text{H}_x\text{PW}$

HMF was mainly produced by acid-catalytic dehydration of fructose, and the direct use of glucose (directly available from lignocellulosic biomass) was much less widespread due to the difficulty in tackling the isomerization of glucose to fructose prior to the dehydration step to HMF. Traditional glucose isomerization was catalyzed by Lewis acid, bases on enzymes catalysts [21]. By now, there have been few reports on acid/base catalyzing glucose to HMF or LA (Table S1). The maximum conversion of glucose and yield of HMF was obtained by base NaAlO_2 and acid HCl in separated two steps with 82% yield [22]. In cascade production of HMF from glucose, bifunctional acid/base mesoporous silica only gave 13% yield at $120\text{ }^\circ\text{C}$ in 0.5 h in water [24]. In order to evaluate the effect of as-prepared $\text{Ly}_{3-x}\text{H}_x\text{PW}$, initial experiments of the catalytic conversion of glucose were conducted with various catalysts including lysine, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{Ly}_{0.5}\text{H}_{2.5}\text{PW}$, LyH_2PW , Ly_2HPW , and Ly_3PW (Table 1) in water/ChCl at $130\text{ }^\circ\text{C}$ for 3 min (Fig. 1). The conversion results followed the order of none (2.0%) < Lysine (37.5%) < $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (40.4%) < $\text{Ly}_{0.5}\text{H}_{2.5}\text{PW}$ (51.2%) < LyH_2PW (55.3%) < Ly_3PW (59.8%) < Ly_2HPW (64.9%). It could be seen that lysine and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ were only pure base and Brønsted acid, the conversion of glucose was not as high as other HPAs with double acid/base sites. For $\text{Ly}_{3-x}\text{H}_x\text{PW}$ due to their acid/base double sites, glucose conversion was higher than pure HPAs. The molar ratios between acid and base strength are 48.4, 31.9, 18, 1.3 corresponding to $\text{Ly}_{0.5}\text{H}_{2.5}\text{PW}$, LyH_2PW , Ly_2HPW and Ly_3PW , respectively. The

Table 1

Acid-catalyzed conversion of glucose in the presence of different catalysts in ChCl system under the reaction conditions: ChCl–glucose weight ratio is 6/4, $130\text{ }^\circ\text{C}$ in 3 min, 0.016 mmol catalyst.

Catalyst	Conv. (%)	HMF yield (%)	LA yield (%)	Acid density (mmol g^{-1})	Base density (mmol g^{-1})
$\text{Ly}_{0.5}\text{H}_{2.5}\text{PW}$	51.2	11.6	16.2	4.36	0.09
LyH_2PW	55.3	13.5	9.8	4.15	0.13
Ly_2HPW	64.9	19.7	9.0	3.60	0.20
Ly_3PW	59.8	19.9	8.7	0.31	0.24
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	40.4	10.8	11.2	4.75	–
Lysine	37.5	7.0	9.3	–	0.38
None	2.0	0	0	0	0

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