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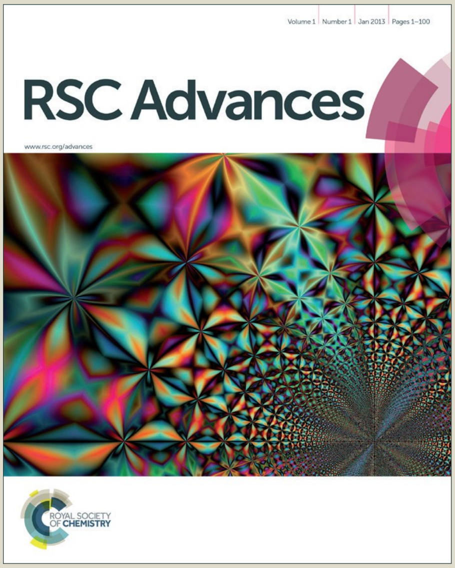

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Fabrication of micellar heteropolyacid with Lewis-Brønsted acid sites and application for the production of 5-hydroxymethylfurfural from saccharides in water

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ABSTRACT

Supramolecular complexes $(C_nH_{2n+1}N(CH_3)_3)H_4PW_{11}TiO_{40}$ (n = 4, 8, 12, 14, 16, and 18) consisting heteropolyacids (HPAs) and amphiphilic quaternary ammonium were fabricated through self-assembly. $(C_{16}H_{33}N(CH_3)_3)H_4PW_{11}TiO_{40}$ was found to exhibit both Lewis acidity and Brønsted acidity. Meanwhile its amphiphilic property resulted in self-assembly in water, which could concentrate sugar molecules around the catalytic sites. Its unique structures contributed to their high performance in the production of 5-hydroxymethylfurfural (HMF) from saccharides with HMF yields of 53.7, 50.8 % for fructose and glucose in water, 66.4, 55.9, and 40.6% for sucrose, cellobiose and cellulose in biphasic solvent, respectively. Moreover, the catalyst can be recycled and reused for about six times with negligible loss in activity.

Keywords: Heteropolyacids; micellar assembly; dehydration; saccharide; HMF

1. Introduction

Unique catalytic activities of materials in nanoscale or microscale have been reported in recent years. [1] It is known that surfactants are building blocks to assemble the nanoreactor in water. [2] Heteropolyacids (HPAs) could self-assemble with amphiphilic quaternary ammonium to form nano- or micro-materials.[3] Cetyltrimethyl ammonium bromide (CTAB) and HPAs [4, 5] were combined together to fabricate nanoreacter in various organic synthesis reactions. [6,7] By now, only a few reports of our group focused on the formation of CTAB and HPAs as well as the application for acid catalysis in biomass conversions. [8, 9] The HPA precursors $PW_{12}O_{40}$ and $PW_{11}CrO_{39}$, selected as HPA precursors, had exhibited catalytic activity for the production of 5-

hydroxymethylfurural from glucose. 5-HMF, one of the top ten bio-based platform chemicals, has received significant attention due to the wide use in chemicals and liquid transportation fuels. [10] It can be produced using homogenous mineral acid, Brønsted acidic ionic liquids (IL), Lewis acidic metal halides and heterogeneous solid catalysts in pure organic or aqueous solvents[11] (Table S1). Among solid catalysts, several heteropolyacids had been used to produce HMF in organic solvent or in bi-phasic systems. For instance, Shimizu studied the dehydration of fructose to HMF catalyzed by $FePW_{12}O_{40}$ at 120 ºC for 2 h in dimethylsulfoxide (DMSO) under a continuous water removal model and a yield > 95 % was obtained. [12] Our group reported that $Ag_3PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as solid catalysts could give 77.7 % yield at 100 % conversion and 74 % yield at 78 % conversion from fructose in water-MIBK biphase, respectively. [13] MOF-supported $H_3PW_{12}O_{40}$ had been reported to catalyze fructose to dehydrate in IL with a yield up to 63 % at 84 % conversion. [14] 1-(3 sulfonic acid) propyl-3-methyl imidazolium phosphotungstate had been used in the production of HMF from fructose with the maximum yield of 99.1 % at 99.7 % conversion in the condition of 120 ºC for 2 h in sec-butanol, using a large amount of catalyst up to 50 wt%. [15] Hwang reported that silver exchanged silicotungstic acid $Ag_4SiW_{12}O_{40}$ catalyzed fructose (10 wt%) to HMF with 85.7 % yield at 98 % conversion at 120 ºC for 2 h. [16] From the above reports, it can be concluded that most studies about HPAs focused on the production of HMF from fructose rather than glucose or other polysaccharides. Our group has further developed HPAs $CTAPW_{11}CrO_{40}$ and $Cr[(DS)H_2PW_{12}O_{40}]_3$ with both Lewis and Brønsted acid sites, [17, 18] which could catalyze fructose, glucose and cellulose to produce HMF in water with yields of 40.6 %, 35.2 %, and 53 %, respectively. The good performance was attributed to double acidic centers and surfactant centers concentrating substrates. But these catalysts containing Cr atom as Lewis center were not environmental benign.

From an economic point of view, the production of HMF in aqueous solution from glucose or other saccharides is more promising than from fructose. It had been reported that the yield of HMF was 51.4 % under the condition of 5 wt% of fructose and 50 mol% of $AlCl_3$ at 120 ºC for microwave 5 min in water, while 13.0 % yield was obtained under oil-batch heating for 60 min. [19] Watanabe et al. studied TiO_2 catalyst in aqueous system at 200 °C by microwave heating, but the yield was below 30 %. [20] Another report [21] of mesoporous TiO_2 with Lewis acidity showed that it could catalyze dehydration of fructose in water under microwave with the 31.5 % yields of HMF.

Nb_2O_5, a water-tolerant heterogeneous Lewis acid, had been reported to result in 100% glucose conversion with a 12.1 % yield of HMF. [22] However, a yield of HMF would be promoted to be 52.1 % by adding some Brønsted acid such as H_3PO_4 (1 wt% of glucose in water at 393 K for 3 h), showing synergistic effect between Lewis acid and Brønsted acid. Recently, R. C. Sun's group selected $InCl_3$ as a Lewis acid catalyst to yield 59.8 % HMF at 81.9 % conversion of glucose (5 wt%) at 180 ºC for 10 min in water. [23] Nevertheless, the yield would be at a low level due to the poor selectivity or conversion rate. The best yield (60 %) was achieved with FeVOP as a catalyst at 80 ºC for 1 h. [24] Therefore, it is still a challenge to seek water-tolerant heterogeneous catalysts in order to catalyze saccharides into HMF with high conversion and good selectivity, especially in water system.

In this concept, amphiphilic HPAs could act as water-tolerant catalysts with hydrophobic surroundings to fulfill the conversion of saccharides into HMF in water. In addition, from the previous reports, the Lewis acidic centers was essential for the isomerization of glucose to fructose then Bronsted ones was required for further dehydration to HMF [25]. Therefore, we fabricated a series of Brønsted–Lewis–surfactant-combined heteropolyacids $(C_nH_{2n+1}N(CH_3)_3)H_4PW_{11}TiO_{40}$ (n = 4, 8, 12, 14, 16, and 18, abbreviated as $C_nH_4PW_{11}Ti$), and studied its catalytic activity in dehydration of saccharides to HMF in detail. There are many advantages, such as (1) owning Brønsted and Lewis acidity available for isomerization/dehydration from glucose into HMF; (3) protecting HMF from further dehydration by its hydrophobic surroundings, and resulting in a high HMF yield in water system; (3) concentrating substrates around the catalytic sites by the formation of micelle; (4) stability in water or solvent for reuse; (5) environmental benign instead of Cr center and more Lewis acidic strength than Cr center.

2. Experimental

2.1 Materials

All solvents and chemicals were obtained from commercial suppliers. They were of AR grade and used without further purification. $K_5PW_{11}TiO_{40}$ was prepared following the reference [27, 28] and characterized by IR spectroscopy.

2.2 Physical measurements

Elemental analysis was carried out with a Leeman Plasma Spec (I) ICP-ES. IR spectra (4000 -

500 cm^{-1}) were recorded on a Nicolet Magna 560 IR spectrometer. DR-UV-vis spectra (200-800nm) experiments were conducted on a Cary 500 UV-vis-NIR spectrophotometer. The ^{31}P MAS NMR spectrum was recorded on a Bruker AVANCE III 400 WB spectrometer. The X-ray diffraction analysis was carried out on Japan Rigaku D_{max} 2000 X-ray diffractometer with Cu K_α radiation (λ= 0.154178 nm) to analyze the structure of the catalyst. The consumption of saccharide was measured via the change of its concentration in the aqueous phase by High-performance liquid chromatography (HPLC, Shimadzu LC-10A) equipped with a refractive index detector. The concentration of HMF in water was determined by HPLC with ION-300H column with a 2: 8 v/v methanol: water (pH = 2) gradient at a flow rate of 0.7 ml/min and a column temperature of 303 K using a UV detector.

The acidic characteristics of the catalysts were evaluated by titration. [26] 0.05 g catalyst suspended in 45 ml acetonitrile was stirred for 3 h. Then, the density of acid sites in catalysts were measured by titration with a solution of n-butylamine in acetonitrile (0.05 M) with anthraquinone as the indicator (pKa = -8.2).

2.3 Preparation of catalyst

$H_5PW_{11}TiO_{40}$ was obtained from K^+ exchanging with H^+ by cation exchange resin. $(C_{16}TA)H_4PW_{11}TiO_{40}$ was prepared as followed: 10 mL, 40 mM of hexadecyltrimethylammonium bromide (CTAB) in aqueous solution was added into 10 mL, 40 mM of $H_5PW_{11}TiO_{40}$ with stirring under 200 rpt at room temperature. The precipitate formed immediately, further stirred for 10 min, collected by filtration, and dried at 50 °C for about 3 h. Other $(C_nH_{2n+1}N(CH_3)_3)H_4PW_{11}TiO_{40}$(n = 4, 8, 12, 14, 16, and 18) had been prepared in the same way with different ammonium bromides.

2.3 Dehydration Reaction

A typical reaction protocol was as follows: a fructose aqueous solution (30 wt% fructose), an acid catalyst (0.01 mM) and solvent were mixed in a Parr reactor (size, 25 mL). The experiments were carried out at 130 °C for 90 min with electrically-heated oil bath. The reaction was stopped by rapidly cooling the reactor down in an ice bath at 0 °C for 30 min. The catalyst was centrifuged and washed with water three times to separate unreacted sugar. Then it was calcinated at 50 °C for 3 h to remove water.

3. Results and discussion

3.1 Characterization of catalyst

The results of the elemental analysis of $C_{16}H_4PW_{11}Ti$ are: W, 66.69; Ti, 1.6; P, 0.98; C, 7.35; H, 1.53; N, 0.48 %, which is satisfactory with the calculated values W, 66.75; Ti, 1.58; P, 1.02; C, 7.5; H, 1.5; N, 0.46 %,. The results of EDAX measurement proved the existence of C: P: W: Ti whose molar ratio was 19:1:11:1.

The FT-IR spectrum of $C_{16}H_4PW_{11}Ti$ was investigated (Fig. 1a). The peaks in the range of 600-1100 cm^{-1} corresponding to Keggin structural vibrations could be easily distinguished at 1075，970，891 and $808 cm^{-1}$, which were attributed to the asymmetry vibrations of $P-O_a$ (internal oxygen connecting P and W), $W-O_d$ (terminal oxygen bonding to W atom), $W-O_b$ (edge-sharing oxygen connecting W) and $W-O_c$ (corner- sharing oxygen connecting W_3O_{13} units), respectively. This indicated that $C_{16}H_4PW_{11}Ti$ maintained the Keggin structure.

Fig. 1

To identify the structure of $C_{16}H_4PW_{11}Ti$, XRD spectroscopy was performed and the result was given in Fig. S1. It can be seen that $C_{16}H_4PW_{11}Ti$ (Fig. S1b) had the same patterns as $H_5PW_{11}TiO_{40}$ phase (Fig. S1a), indicating that it kept Keggin structure in solid state. The three characteristic absorbance bands at 260, 340-350 and 450nm (Fig. S2) of the DR-UV-vis spectrum corresponded to the transfer of $O_{b/c}$ –W belonging to the Keggin structure, charge transition of O-Ti, and the band $^4Ti_1$ (F) – $^4A_2$ (P) of PO_4, respectively. This indicated the formation of titanium-substituted HPAs. The ^{31}P MAS NMR of $C_{16}H_4PW_{11}Ti$ and $(C_{16})_5PW_{11}Ti$ has a signal at δ = -14.9 ~ -16.0 ppm, whereas its parent $H_5PW_{11}TiO_{40}$ has a peak at δ = -13.7 ppm (Fig. 2). The shift was attributed to the introduction of organic cation into $[PW_{11}O_{40}Ti]^{5-}$ anion, which confirmed the formation of $C_{16}H_4PW_{11}Ti$ rather than the physical mixture of $[PW_{11}O_{40}Ti]^{5-}$ and CTAB cation.

Fig. 2

The morphology of $C_{16}H_4PW_{11}Ti$ in water was observed by TEM (Fig. 3). 50 nm particles in average were shown in the TEM image, showing the formation of relatively uniform micellar droplets. In addition, the critical micelle concentration (CMC) of $C_{16}H_4PW_{11}Ti$ was determined to be 0.92 mM by conductivity versus concentration plot (Fig. S3), which further proved the formation of micelles in aqueous solutions.

Fig. 3

The surface acidic property of $C_{16}H_4PW_{11}Ti$ was determined by pyridine adsorption infrared spectroscopy (Fig. 1b). It can be seen that the IR spectrum exhibits strong bands at 1450 cm^{-1}, which were attributed to the Lewis acidity. Meanwhile, the peaks at 1538 cm^{-1} attributing to Brønsted acidity appeared. The result showed that $C_{16}H_4PW_{11}Ti$ owns both Lewis acidity and Brønsted acidity. [29]

3.2 Catalytic Activity

Dehydration of fructose

It is known that the fructose can be catalyzed to generate HMF by acid catalysts, including homogeneous HCl, $AlCl_3$, metal phosphates, and solid Lewis acids, *et al.*, which had attracted much attention on its dehydration in water system. However, the yield of HMF was at a low level due to the low selectivity or conversion. FeVOP was the best catalyst to give as high as 60% yield at 80 ºC for 1 h using 6 wt% of fructose. In order to develop a new solid catalyst to fulfill the dehydration of fructose in water, a series of HPAs containing titanium had been employed in this reaction (Fig. 4), including $H_5PW_{11}TiO_{40}$ (acid content 0.97 mmol/g), $(C_{16})_{2.5}H_{2.5}PWTi$ (acid content 0.13 mmol/g), $(C_{16})_{1.25}H_{3.75}PW_{11}Ti$ (acid content 0.24 mmol/g), $(C_{16})H_4PW_{11}Ti$ (acid content 0.34 mmol/g), $(C_{16})_{0.8}H_{4.2}PW_{11}Ti$ (acid content 0.31 mmol/g), and $(C_{16})_{0.6}H_{4.4}PW_{11}Ti$ (acid content 0.4 mmol/g). It can be concluded that the variation of the amount of the proton would result in different acid contents. The acid contents of the above catalysts were in range of $H_5PW_{11}TiO_{40}$ > $(C_{16})_{0.6}H_{4.4}PW_{11}Ti$ > $(C_{16})_{0.8}H_{4.2}PW_{11}Ti$ ~ $(C_{16})H_4PW_{11}Ti$ > $(C_{16})_{1.25}H_{3.75}PW_{11}Ti$ > $(C_{16})_{2.5}H_{2.5}PW_{11}Ti$. The catalytic activity of these HPAs at 130 ºC for 30 min was: for conversion effect, $(C_{16})_{0.6}H_{4.4}PW_{11}Ti$ ~ $(C_{16})_{0.8}H_{4.2}PW_{11}Ti$ ~ $(C_{16})H_4PW_{11}Ti$ > $H_5PW_{11}TiO_{40}$ > $(C_{16})_{1.25}H_{3.75}PW_{11}Ti$ ~ $(C_{16})_{2.5}H_{2.5}PW_{11}Ti$; for HMF yield, $(C_{16})_{1.25}H_{3.75}PW_{11}Ti$ > $(C_{16})_{2.5}H_{2.5}PW_{11}Ti$ > $(C_{16})H_4PW_{11}Ti$ > $(C_{16})_{0.8}H_{4.2}PW_{11}Ti$ > $(C_{16})_{0.6}H_{4.4}PW_{11}Ti$ > $H_5PW_{11}TiO_{40}$. This result showed that the catalysts with high acidic content could convert more fructose in water. $H_5PW_{11}TiO_{40}$ is homogeneous and could not form micellar spheres, while HMF further decomposed leading to low HMF yield. The stability of HMF in $(C_{16})H_4PW_{11}Ti$ and $H_5PW_{11}TiO_{40}$ systems was studied: 50 mg HMF was added into 2 mL water containing 0.1 mmol catalyst in a steal autoclave and heated at 130 °C (Fig. 5). It can be seen that HMF was decomposed into levulinic acid (LA) and formic acid (FA) more slowly with $(C_{16})H_4PW_{11}Ti$ as the catalyst than with $H_5PW_{11}TiO_{40}$ as the catalyst, which was attributed to the protecting effect of hydrophobic environment provided by $(C_{16})H_4PW_{11}Ti$. It was confirmed by S. H. Chai [30] that hydrophobic ionic liquid could significantly inhibited the side reaction of HMF with H_2O and led to 91 % selectivity to HMF at 89 % conversion of fructose catalyzed by nanostructured vanadium phosphated and mesostructured cellular foam. Therefore, micellar titanium-HPAs $(C_{16})H_4PW_{11}Ti$ proved to be an active, and water-tolerant catalyst for HMF production in water system with a yield of 47.9 % and a conversion of 98.2 % using 30 wt% of fructose at 130 °C for 90 min.

Fig. 4

Fig. 5

In order to confirm the real nature of micellar HPA catalyst, the heterogeneous nature of the catalytic reaction had been confirmed. For this purpose, a test had been performed where the $(C_{16})H_4PW_{11}Ti$ reacted in water at 130 °C (without fructose) for 90 min and then the solid was separated from the aqueous phase by an ultrafiltration membrane; afterwards, the fructose was added into the liquid phase and the reaction at 130 °C was monitored during 90 min. The conversion and yield were 49.2 % and 8.8 %, respectively. Under the condition without the catalyst, fructose could convert into HMF with a conversion of 48.2 % and a yield of 8.6 %. It can be confirmed that $(C_{16})H_4PW_{11}Ti$ was a heterogeneous catalyst and its leaching was little.

It has been reported that the conversion of fructose with high concentration in water may increase the amount of by-products. The addition of a water-immiscible solvent may suppress the secondary transformation of HMF like DMSO and n-butanol, which had been proved to be effective solvents for the dehydration of fructose to generate HMF. [31] Fig. 6 showed that the yield and selectivity of HMF were low (47.9 % and 48.8 %, respectively) in pure water with 30 wt% fructose. The addition of excess 1-butanol (Butanol/H_2O = 1:3) to the aqueous solution led to a higher yield about 75.6 % for HMF. The organic solvent was used to extract HMF from water, and HMF rehydration was significantly inhibited. The addition of organic solvent did not lead to a significant change in fructose conversion because $(C_{16})H_4PW_{11}Ti$ was the active sites.

Fig. 6

It is known that the length of the lipophilic tail would influence the catalytic activity in micellar catalytic system. The different chain length of quaternary ammonium cations with different length of chain had been chosen for comparison (Fig. S4), including $(C_4)_4H_4PW_{11}Ti$, $(C_8)H_4PW_{11}Ti$,

$(C_{12})H_4PW_{11}Ti$, $(C_{14})H_4PW_{11}Ti$, $(C_{18})H_4PW_{11}Ti$. The hydrophobic chain of a surfactant must have a certain length (>C10) to enable successful micelle formation[32]. $(C_4)_4H_4PW_{11}Ti$ with a short carbon chain comprising less than C10, has difficulty forming a micelle and only acts as a heterogeneous catalyst, resulting in low fructose conversion. With the length of the carbon chain growing, the catalytic activity increased significantly from $(C_4)_4H_4PW_{11}Ti$ to $(C_{18})H_4PW_{11}Ti$. A conversion of 99.4 % and a yield of 59.0 % was obtained with $(C_{18})H_4PW_{11}Ti$ as the catalyst. Therefore, the length of the carbolic chain plays an important role both in the formation of the micellar system and catalytic activity.

So far, many reports had been focused on the dehydration of fructose with low concentrations. It is difficult to convert the fructose with high concentration. As-prepared $(C_{16})H_4PW_{11}Ti$ showed high efficiency in dehydration of fructose with high concentration (30 wt%), but also active for the one with low concentration (Fig. S5). It can be seen that the conversion of 100 % with 77.2 % yield was obtained as using 1 wt % of fructose at 130 ºC for 30 min. It might be a good result for such high concentration fructose catalyzed by solid acid catalyst in water. The increasing of fructose usage fructose resulted in a decreasing conversion as well as the yield. As for 50 wt % fructose, the conversion and yield were 26.8 % and 67.3 %, respectively.

The activity of $(C_{16})H_4PW_{11}Ti$ towards fructose dehydration was studied at different temperatures (110, 120, 130 and 140 °C) and times (Fig. 7). It can be seen that an increase in temperature could promote the dehydration of fructose. At 140 °C, fructose conversion and HMF yield increased rapidly in the early stage, and the maximum HMF yield of 57.7 % was received with 89.4 % fructose conversion at 60 min catalyzed by $(C_{16})H_4PW_{11}Ti$. At 110 °C, the maximal HMF yield of 50.6 % and 67.9 % conversion were detected after 120 min.

Fig. 7

Conversion of glucose to HMF

Producing HMF from glucose is more difficult compared to that from fructose, especially in water system. Until a water-tolerant heterogeneous Lewis acid Nb_2O_5 had been reported to yield 12.1 % HMF at 100 % conversion of glucose. However, the catalytic activity of Nb_2O_5 would be further promoted by adding some Brønsted acid like H_3PO_4, which yielded 52.1 % HMF by catalyzing 1 wt% of glucose in water at 393 K for 3 h. In this concept, HPAs with both Brønsted acidity and Lewis acidity would be more helpful for the conversion of glucose. Meanwhile, the water-tolerant HPA catalyst would be significant for the reaction occurring in water. For the purpose of conversing glucose to HMF with a high efficiency, $(C_{16})H_4PW_{11}Ti$ had been selected as a catalyst, whose performace had been compared with other solid catalysts (Table 1).

Table 1

It found no or trace of HMF in the conversion of saccharides catalyzed by pure Brønsted acids HCl or $H_3PW_{12}O_{40}$ in water system. Such result was attributed to the rapid hydration of HMF to levulinic acid and formic acid (FA) catalyzed by Brønsted acid. [20, 33] Solid catalysts with Lewis acidity favored for the isomerization of glucose to fructose then Brønsted acidity led to further dehydration to HMF. The yield of HMF was 50.8 % catalyzed by $(C_{16})H_4PW_{11}Ti$ as 88.1 % glucose conversion, which could be comparable to solid $Nb_2O_5 \cdot nH_2O/H_3PO_4$ and reached almost the best result up to now. Compared to the homogeneous $H_5PW_{11}TiO_{40}$, $(C_{16})H_4PW_{11}Ti$ exhibited a higher activity due to the formation of micellar assembly and its hydrophobic properties in water. Therefore, micellar HPA $(C_{16})H_4PW_{11}Ti$ functioned as a heterogeneous catalyst with double acid sites and water-tolerant property for the conversion of glucose to HMF in water. In order to obtain the high yield of HMF from glucose, some solvents like n-butanol and DMSO were used. It can be seen that the use of DMSO and n-butanol suppressed the formation of the unknown products. The yield of HMF was improved to 77.4 and 83.6 % after adding DMSO and n-butanol, respectively.

Conversion of polysaccharide to HMF

The scope of this study was further extended to examine the conversion of cellobiose, sucrose, and cellulose, which contain poly of glucose unites (Table 2) catalyzed by $(C_{16})H_4PW_{11}Ti$. As for polysaccharides, the reaction steps are involved (1) the hydrolysis of substrates into monosaccharides including fructose (sucrose) and glucose (cellobiose and cellulose) catalyzed by Brønsted acid, (2) the isomerization of glucose into fructose catalyzed by Lewis acid, and (3) the dehydration of fructose to HMF catalyzed by Bronsted acid. A reaction between 0.1 g cellobiose and 0.01 mmol $(C_{16})H_4PW_{11}Ti$ in water/butanol biphasic solvent produced 55.9 % HMF with 99.6 % conversion at 140 °C for 7 h. Up to now, the best yields of HMF were achieved by the utilization of homogeneous catalysts $FeCl_3$ and $CrCl_3$ in pure of mixed 1-butyl-3-methylimidazolium chloride as 41 and 50 % [34, 35], respectively. Compared to these results, the present catalyst is promising green process in aqueous medium with 55.9 % yield of HMF. The high yield of HMF from sucrose was 66.4 % at 80 °C for 7 h. In the case of cellulose, 40.6 % yield of HMF was obtained at 160 °C for 8 h with 91.1 % conversion in water/butanol biphasic solvent. The relative low yield was attributed to the lower solubility and strong H-bonded network in its structure. In pure water, the conversion and yield were lower than that in biphasic solvent.

Table 2

Reusability of the catalyst

The catalyst was easily separated from the mixture and could be reused after being washed with water. The recycled reaction procedure retained high activity throughout the conversion of fructose into HMF. The results were showed in Fig. 8. It can be seen that the catalytic activity of the catalyst for the dehydration of fructose to HMF had a constant activity after being reused six times at 130 °C for a 90 min reaction time in each case. The fructose conversion and the yield of HMF remained at about 95.5 % and 43.2 %, respectively after six times. The total amount of $(C_{16})H_4PW_{11}Ti$ loss is 4.12 % compared to the initial usage. Therefore, it demonstrated that $(C_{16})H_4PW_{11}Ti$ produces HMF with no decrease in activity after several reuse. The stability of micellar assembly had been checked by TEM (Fig. 8 insert), which showed no change of the morphology after the reaction.

Fig. 8

4. Conclusion

Heteropolyacid salts $(C_nH_{2n+1}N(CH_3)_3)H_4PW_{11}TiO_{40}$ were fabricated through self-assembly between HPA anions and surfactant cations. The $(C_{16})H_4PW_{11}Ti$ showed excellent catalytic activity for the conversion of fructose, glucose, sucrose, cellobiose and cellulose into HMF in biphasic solvent (47.9 % in water) with maximum yields of 75.6 %, 77.2 (50.8) %, 66.4 %, 55.9 %, and 40.6 %, respectively. The high efficiency was attributed to double Brønsted and Lewis acid sites, and the micellar structure with hydrophobic groups that concentrated substrates around the active sites. The HMF produced was protected by its hydrophobic groups to obtain a higher yield. Moreover, the catalyst is tolerant to feedstock with high concentrations and water, which can also be recycled.

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Figure caption

Fig. 1. IR spectra of (a) $(C_{16})H_4PW_{11}Ti$ and (b) adsorbed pyridine of $(C_{16})H_4PW_{11}Ti$

Fig. 2. ^{31}P MAS NMR spectra of (a) $(C_{16})H_4PW_{11}Ti$, (b) $(C_{16})_5PW_{11}Ti$, and (c) $H_5PW_{11}Ti$

Fig. 3. The cryo-TEM image of $(C_{16})H_4PW_{11}Ti$

Fig. 4. The different performance of different HPA catalysts. Reaction conditions: 0.6 g of fructose, 0.01 mmol of catalyst, 2 mL of water, 130°C for 90 min.

Fig. 5. The stability of HMF in $(C_{16})H_4PW_{11}Ti$ and $H_5PW_{11}TiO_{40}$ water systems.

Fig. 6. Effect of solvent on the dehydration of fructose. Reaction conditions: 0.6 g of fructose, 0.01 mmol of catalyst, 2 ml of solvent, and 130°C for 90 min.

Fig. 7. The influence of reaction time and temperature on fructose dehydration. Reaction conditions: 0.6 g of fructose, 0.01 mmol of catalyst, 2 ml of water.

Fig. 8. The catalyst activity in six reaction cycles. Reaction conditions: 0.6g of fructose, 0.01 mmol of catalyst, 2 ml of water, 130°C for 90 min. Insert: the TEM of reused $(C_{16})H_4PW_{11}Ti$.

Table 1 The activity and selectivity of different catalysts for glucose dehydration in water

Table 2 The activity of catalyst for polysaccharide dehydration in water

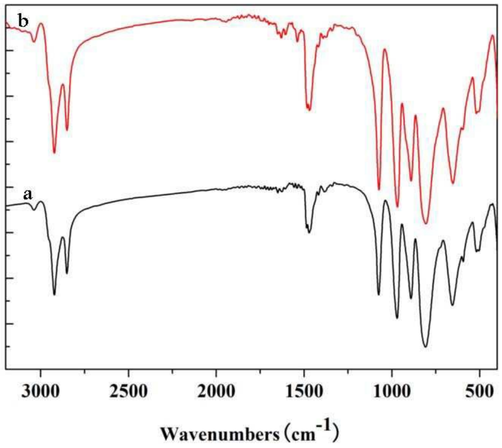


Fig. 1. IR spectra of (a) $(C_{16})H_4PW_{11}Ti$ and (b) adsorbed pyridine of $(C_{16})H_4PW_{11}Ti$

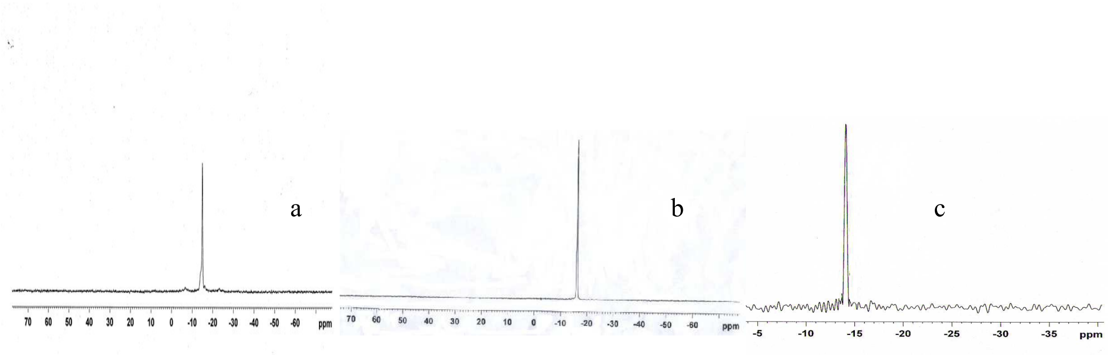


Fig. 2. ^{31}P MAS NMR spectra of (a) $(C_{16})H_4PW_{11}Ti$, (b) $(C_{16})_5PW_{11}Ti$, (c) $H_5PW_{11}Ti$.

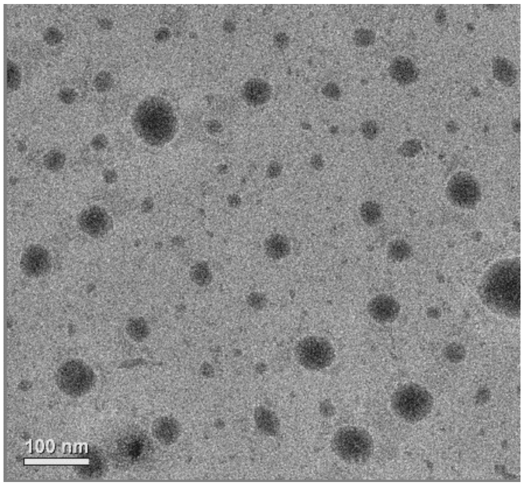
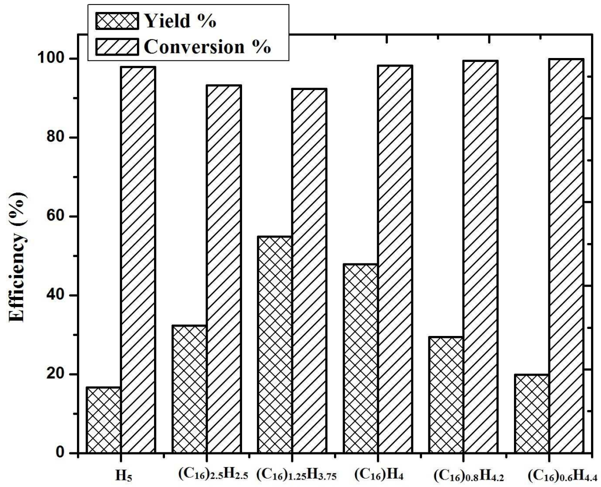


Fig. 3. The cryo-TEM image of $(C_{16})H_4PW_{11}Ti$



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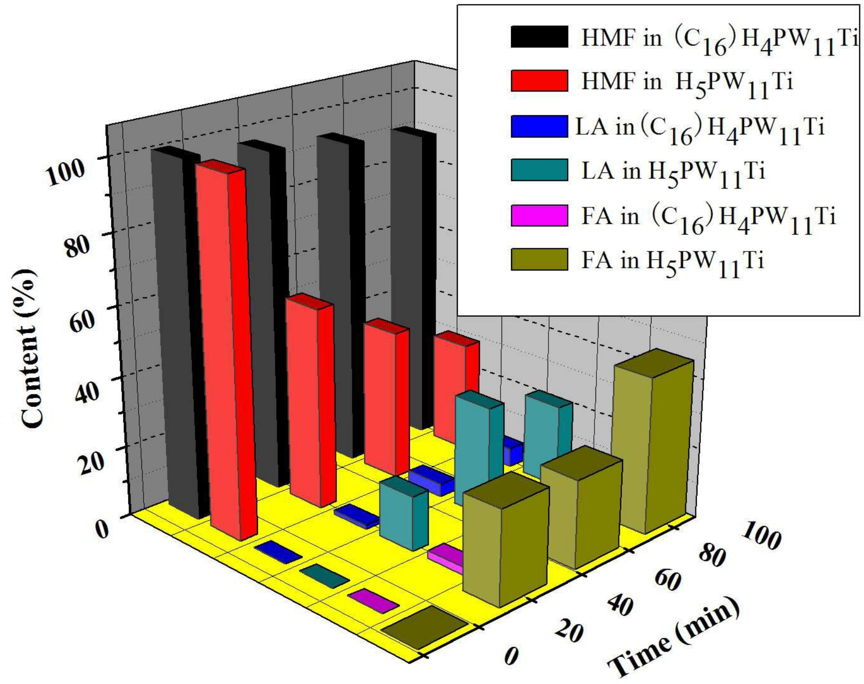

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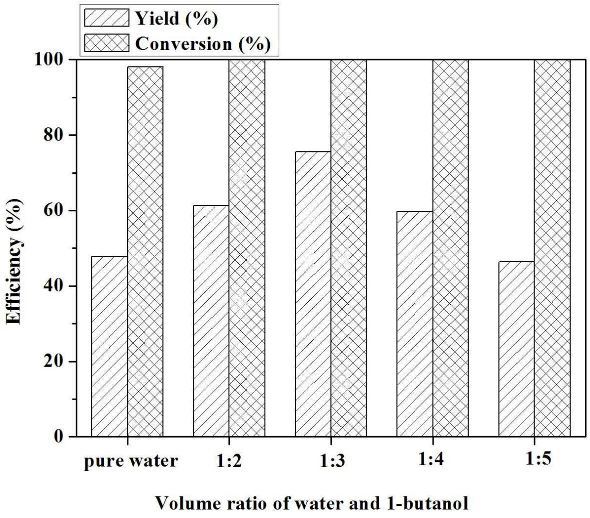

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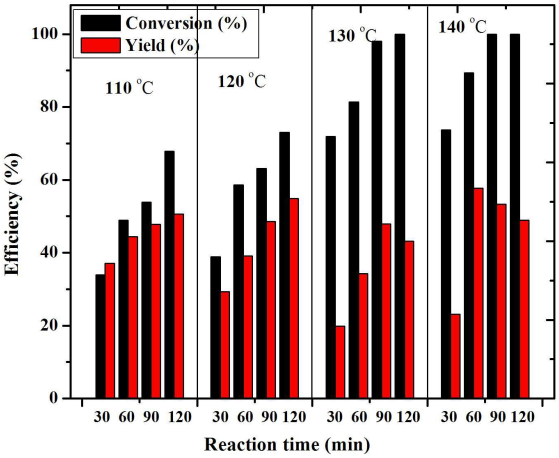

Fig. 7. The influence of reaction time and temperature on fructose dehydration. Reaction conditions: 0.6 g of fructose, 0.01 mmol of catalyst, 2 ml of water.

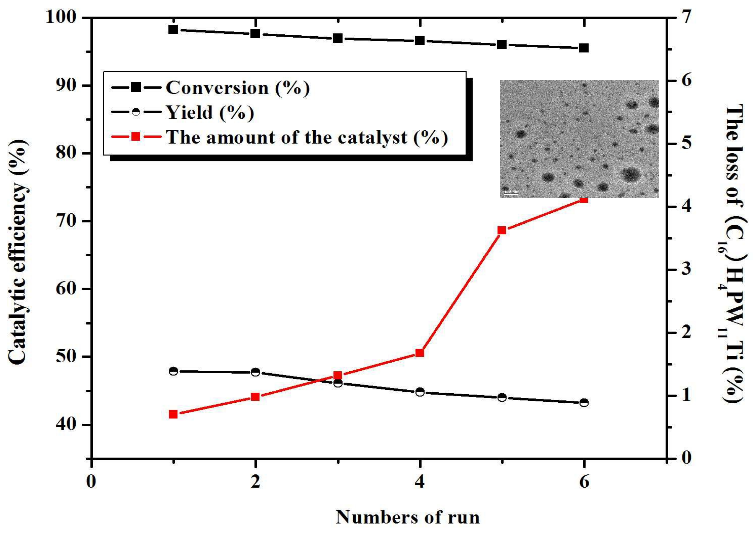

Fig. 8. The catalyst activity in six reaction cycles. Reaction conditions: 0.6 g of fructose, 0.01 mmol of catalyst, 2 ml of water, 130°C for 90 min. Insert: the TEM of reused $(C_{16})H_4PW_{11}Ti$.

Table 1 The activity and selectivity of different catalysts for glucose dehydration in water

Catalysts	Acid amount (mmol/g)		Conversion (%)	Selectivity to HMF (%)	Selectivity to LA (%)	Selectivity to FA (%)	Unknown (%)
	Brønsted	Lewis					
HCl	9.9[a]	-	93.3	2.1	17.2	3.9	76.8
Amberlyst-15	4.8[a]	-	67.6	1.4	33.9	5.2	59.5
$Nb_2O_5 \cdot nH_2O$	0.17[a]	0.15[a]	80.3	13.8	5.3	1.4	79.5
$Nb_2O_5 \cdot nH_2O/H_3PO_4$	0.04[a]	0.11[a]	78.6	44.6	5.0	1.1	49.3
$H_3PW_{12}O_{40}$[b]	0.89	-	81.5	1.5	36.7	45.7	16.1
$C_{16}H_4PW_{11}Ti$[b]	0.26	0.08	88.1	57.7	8.5	25.8	8.0
$H_5PW_{11}Ti$[b]	0.89	0.08	100	36.7	14.9	26.2	12.2

[b] Reaction condition: 0.3 g of glucose, 0.01 mmol of catalyst, 2 ml of water, 130 ºC, 120 min.

Table 2 The activity of catalyst for polysaccharide dehydration in water

Polysaccharide [a]	Solvent(volume ratio)		Temp. (°C)	Reaction time (h)	Conversion (%)	Yield of HMF (%)	Yield of LA (%)
	H_2O	n- butanol					
Fructose (0.6 g) [a]	1	3	130	1.5	100	75.6	-
Fructose (0.6 g) [a]	1	0	130	1.5	98.2	47.9	-
Glucose (0.3 g) [a]	1	3	130	2	92.3	77.2	3.7
Glucose (0.3 g) [a]	1	0	130	2	88.1	50.8	7.4
Sucrose (1 g) [a]	1	3	80	5	100	66.4	18.5
Cellobiose (0.1 g) [a]	1	3	140	7	99.6	55.9	10.2
Cellulose (0.1 g) [a]	1	3	160	8	91.1	40.6	20.3
Cellulose (0.1 g) [b]	1	0	160	8	58.2	18.4	-

[a] 0.01 mmol of catalyst, 2 ml of solvent. [b] 0.06 mmol of the catalyst, 2 ml of solvent.