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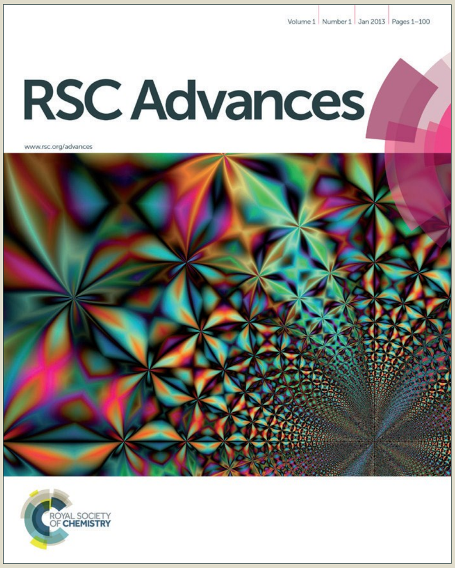

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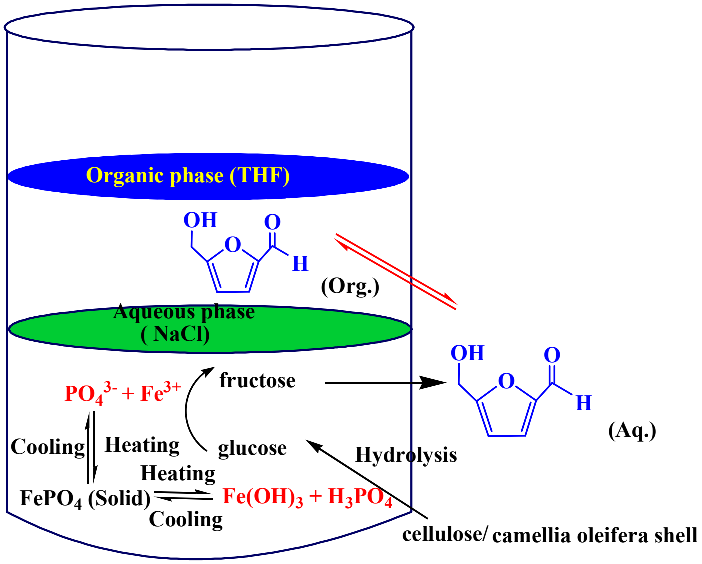

A “double character” $FePO_4$ catalyst, which acts as a homogeneous catalyst at high temperature, was used to produce 5-HMF starting from cellulose and woody biomass without the addition of homogeneous acids.

One-pot synthesis of 5-hydroxymethylfurfural from carbohydrates using an inexpensive $FePO_4$ catalyst

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Abstract

Catalytic conversion of carbohydrates to 5-hydroxymethylfurfural (5-HMF) provides a way toward obtaining renewable biomass-based fuels and chemicals. Herein, we use an inexpensive $FePO_4$ catalyst, which is insoluble at low temperature but can be partially dissolved and act as a homogeneous catalyst at high temperature, in a one-vessel biphasic reactor to generate 5-HMF from carbohydrates such as fructose, glucose, sucrose, cellulose, and camellia oleifera shell (a lignocellulosic feedstock) without the addition of homogeneous acids. The effects of various reaction conditions including reaction temperature, reaction time, feedstock types and the amount of catalyst on fructose conversion and 5-HMF yield were investigated. The highest 5-HMF yield (71.5 mol%) starting from fructose feedstock was achieved using this "one-pot" biphasic water/tetrahydrofuran (THF) reactor system at 140 ^{o}C for 15 min. More interestingly, at high temperature, the $FePO_4$ catalyst was also highly active in the conversion of cellulose and camellia oleifera shell, which are very difficult to be converted to 5-HMF without the addition of mineral acids. A high 5-HMF yield of 48 mol% starting from microcrystalline cellulose was also obtained using the biphasic reaction system. Moreover, the $FePO_4$ catalyst could be easily separated and recycled from the aqueous solution via precipitation after cooling to room temperature since it is insoluble at low temperature. Possible dehydration reaction mechanisms of these carbohydrates catalyzed by $FePO_4$ were also proposed.

Keywords: 5-hydroxymethylfurfural (5-HMF); dehydration; $FePO_4$; rehydration, isomerization

Introduction

In recent years, much effort has been focused on finding viable alternatives to the fossil fuel-based industry of today, and as such, the development of a new, long term, environmentally friendly and sustainable chemical source has received wide attention.[1] 5-hydroxymethylfurfural (5-HMF), a versatile and key renewable platform molecule produced from biomass feedstock,[1-11] can be transformed into fuels and various valuable chemicals through catalytic conversion, including the gasoline additives 2,5-dimethylfuran (DMF),[12] an alternative polymer precursor of 2,5-furandicarboxylic acid (FDCA),[13-16] and levulinic acid.[17-19]

The production of 5-HMF was usually performed by mineral acid-catalyzed hydration of biomass such as glucose, fructose, inulin, and cellulose.[1,20,21] The drawbacks of using mineral acids include severe environmental pollution and corrosion, and therefore, some novel and green reaction systems have been developed recently. Ionic liquid systems represent a hot research field due to their excellent catalytic effectiveness for producing 5-HMF with high yield through catalytic hydrolysis of carbohydrates.[2,8-10,22-25] Zhao et al. have suggested that by using $CrCl_2$ in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl), a 5-HMF yield of 91% was obtained with fructose as a feedstock at 100 ^oC.[9] In addition, a biphasic reactor system has also attracted increasing attention since it could be suitable for large scale industrial applications due to the use of low-boiling solvents.[26] Ma et al. have reported that a high 5-HMF yield of 53 mol% was obtained by direct degradation of cellulose in a biphasic system with concentrated $NaHSO_4$ and $ZnSO_4$ as co-catalysts.[27]

Besides homogeneous systems, heterogeneous solid acidic catalysts such as metal oxides,[28] phosphate catalysts,[29-33] and acidic zeolites[34-37] have also been applied to carbohydate degradation reactions due to their ease of separation and reusability. Both high activity and selectivity towards the dehydration of carbohydrates to 5-HMF were achieved. For instance, Ebitani et al. used the combined catalysts of Mg-Al hydrotalcite and Amberlyst-15 to achieve HMF selectivity of 58% at glucose conversion of 73%.[38] Nijhuis and co-workers showed that aluminum, titanium, zirconium, and niobium-based phosphates afforded 5-HMF selectivities in the range of 30-60% using glucose as a feedstock.[31]

Additionally, high 5-HMF selectivities of over 70% from sugars were achieved using Sn-beta zeolite and HCl in a biphasic (H_2O/THF) system, which is comparable to activities obtained using metalloenzymes.[39] To date, a 5-HMF yield of up to 90% from fructose has been achieved using tantalum hydroxide as the catalyst in a water-2-butanol biphasic system.[40] Furthermore, the development of a cheap, reusable, more effective solid acid catalyst for the large-scale production of 5-HMF in a biphasic reaction system is of great relevance, with the exception of the use of low-boiling solvents. However, the main disadvantage of solid acid systems is the lack of sufficiently high enough catalytic activity to degrade raw biomass feedstocks such as cellulose and lignocellulosic materials with the exception of ionic liquid systems. One reason is that the contact and interaction between insoluble raw reactants and solid acid active sites is not sufficient enough despite most solid acids possessing impressive activity for the conversion of soluble monosaccharide.

Here, we develop an efficient “one-pot” synthesis of 5-HMF from carbohydrates using an inexpensive catalyst, i.e. $FePO_4$, without the addition of mineral acids. To the best of our knowledge, the use of $FePO_4$ in the conversion of carbohydrates to 5-HMF has not been reported until now. The $FePO_4$ is considered as a “soluble” acidic catalyst, which is insoluble at low temperature (solubility product, $K_{sp} = 1.3 \times 10^{-22}$ at RT) [41] but is partially dissolved and act as homogeneous catalyst during high temperature reaction. The reaction system successfully avoids the drawback of difficult separation and recycling of homogeneous catalysts because partially dissolved or hydrolyzed $FePO_4$ will be precipitated again after cooling to room temperature.

2. Experimental

Microcrystalline cellulose were purchased from the Sigma-Aldrich company in China. Microcrystalline cellulose (50 um) were directly used for the dehydration reaction without any other pretreatment. Camellia oleifera shell was obtained from local resources in Hunan province, China and was crushed and sieved to around 75 um. $FePO_4.2H_2O$ (Sigma-Aldrich) and H_3PO_4 were used as the reaction catalyst. Reactions were conducted in a 100 mL autoclave equipped with a thermostat and an electronically controlled magnetic stirrer. The reactor was pressurized at 5 bar of N_2 and heated to desired reaction temperature. Once the reaction temperature was reached, the monitoring of the reaction started.

After the reaction, the liquid products were analyzed by high-performance liquid chromatography (HPLC, Agilent 1200) using a column (Zorbax SB-C18) with a UV detector to analyze 5-HMF yield. The reducing sugar was detected by DNS method according to the reference.[42] The conversion of mono- and di-saccharides was calculated as follows: conversion (%) = (moles of substrate reacting)/(moles of substrate starting)*100, while the conversion of cellulose and camellia oleifera shell was calculated by the weight change of substrate before and after the reaction. The yield of 5-HMF was calculated as: yield (%) = (moles of 5-HMF in the products)/(moles of feedstocks put into the reactor)*100.

IR spectra of fresh $FePO_4.2H_2O$ and the used catalyst were recorded on a Thermo Nicolet Nexus 470 spectrometer. The Fe content of the water solution after the reaction was measured by atomic absorption spectroscopy (AAS).

3. Results and Discussion

3.1 Conversion of fructose into 5-HMF

H_3PO_4 and $FePO_4$ were tested for their activity toward conversion of fructose to 5-HMF using both a single phase and a biphasic reactor system. The single-phase system contained the catalyst, feedstock, and water, while the biphasic system was composed of a THF phase, an aqueous phase of fructose, and $FePO_4$ or H_3PO_4 catalyst. The data listed in Table 1, entries 2 and 3, clearly shows that the use of a biphasic system results in higher 5-HMF yield at the same temperature and reaction time. This is due to the presence of a water-immiscible THF phase that extracts 5-HMF from the aqueous phase, thereby preventing the quick degradation of 5-HMF into undesired by-products under high temperature.

To improve 5-HMF selectivity, we examined the effects of adding inorganic salts to the aqueous phase of the biphasic systems. It has been previously shown that addition of inorganic salts to biphasic systems remarkably improves the partitioning of 5-HMF into the organic phase by means of the salting-out effect, whereby electrolytes alter the intermolecular bonding interactions between liquid components, decreasing the mutual solubility of the aqueous and organic phases.[1] It has also been shown that NaCl was the most efficient extracting agent of 5-HMF from the aqueous to organic phase and gave the highest 5-HMF selectivity among a number of different salts such as $MgCl_2$, KBr, and NaCl.[39] The results listed in Table 1, entries 4-8, clearly indicate that the selectivity to 5-HMF is remarkably increased with the addition of NaCl to the aqueous phase and suggest that the activity of $FePO_4$ is not affected by the presence of NaCl. For example, compared to experiments performed without salts, a 20 mg/mL fructose solution saturated with NaCl using THF as the extraction solvent results in an improvement in 5-HMF yield from 39.3% to 63.4% (Table, entries 3 and 4). The NaCl mainly contributed to the extraction of 5-HMF from aqueous phase to the THF phase, thereby suppressed side reactions. Notably, the presence of NaCl has the additional benefit of allowing higher volumetric ratio of organic to aqueous phases ($V_{org.}/V_{aq.}$) to be used, thus resulting in higher 5-HMF selectivity, while maintaining biphasic reaction conditions. Specifically, when the ratio $V_{org.}/V_{aq.}$ is equal to 5, the water/THF biphasic system without NaCl becomes monophasic, whereas the system saturated with NaCl remains biphasic at the same $V_{org.}/V_{aq.}$ ratio, with an HMF yield of 71.5% (Table 1, entry 8). It should be noted that $FePO_4$ catalyst gave a similar 5-HMF yield to that of a homogeneous H_3PO_4 catalyst under identical reaction conditions, which demonstrates that solid acid catalyst has a competing catalytic activity compared to the corresponding homogeneous acid catalyst.

3.1.1 Effect of temperature and reaction time on 5-HMF yield

The influence of the reaction temperature on fructose conversion into 5-HMF catalyzed by $FePO_4$ in the biphasic reaction system was investigated (Table 2). When the reaction was carried out at 120 ^{o}C, high fructose conversion was observed after only 15 min though 5-HMF yield was only 35%. When the reaction temperature was heated to 140 and 160 ^{o}C, 5-HMF yields of 60.0% and 62.6% were obtained, respectively, for 15 min reaction time. Higher reaction temperatures not only favored the dehydration of fructose into 5-HMF, but also accelerated the formation of humins or resulted in the rehydration of 5-HMF into levulinic acid and formic acid. The effect of reaction time on fructose conversion and 5-HMF conversion was examined as well, and the results are shown in Table 2. No significant increase in the 5-HMF yield was observed at 140 ^{o}C with increasing reaction time, indicating that the catalyst has very high activity and that fructose was almost completely converted after the reaction time of 5 min.

3.1.2 Influence of catalyst amount on 5-HMF yield

Fig. 1 shows the effects of different amounts of catalyst on the fructose conversion and 5-HMF selectivity. In the presence of 0.02 g $FePO_4$, a 5-HMF yield of 44.5% was obtained after 15 min. After adding more catalyst (0.10 and 0.20 g), the 5-HMF yield increased to 64.8 and 68.8%, respectively, under the same reaction conditions. On further increasing the amount of catalyst (0.25 g), the 5-HMF yield increased slowly to 70.6%.

3.1.3 Effect of fructose concentration on 5-HMF yield

The effectiveness of a catalytic reaction system to high feedstock concentration is an important factor used to evaluate its efficiency and its potential for use in practical applications. In the acid-catalyzed dehydration reaction of fructose, 5-HMF molecules produced tend to react with fructose molecules and cross-polymerize to form humins.[1,39] Therefore, the fructose concentration has a significant influence on the 5-HMF yield and selectivity, especially in aqueous solvents.[1] The effect of initial fructose concentration on 5-HMF yield for the reaction in the biphasic system was investigated (Fig. 2). As can be seen, the yield of 5-HMF produced from fructose decreases with increasing fructose concentration. For example, when fructose concentrations of 20, 50, and 100 mg/mL were used, the 5-HMF yields were 69.7, 63.7, and 48.2%, respectively. Similarly, the 5-HMF selectivity also decreases on increasing the fructose concentration. This result is in good agreement with literature reports that increasing the fructose concentration results in a decrease in the 5-HMF yield and selectivity.[1]

3.2 Effect of different feedstocks on 5-HMF yield

Because the $FePO_4$ catalyst exhibited good activity in the conversion of fructose, we also used other carbohydrates such as glucose and sucrose as renewable raw materials. Glucose is the most abundant monosaccharide and the cheapest hexose, making it a promising candidate as renewable raw material for the production of 5-HMF.[6,7] Synthesis of 5-HMF from sucrose involves a hydrolysis into glucose and fructose in the presence of an enzyme or acidic catalyst, followed by isomerization of glucose to fructose and subsequent dehydration of fructose to 5-HMF.[43,44] The data listed in Table 3, entries 2-3, shows the results of conversion of glucose and sucrose to 5-HMF catalyzed by $FePO_4$. 5-HMF yields of ～23.9% and 39.3% at the complete conversion of 100 mg/mL glucose and 100 mg/mL sucrose, respectively, were achieved in a biphasic H_2O/THF system. It is assumed that the conversion of glucose to 5-HMF can occur via an isomerization of glucose to fructose in the presence base catalysts or Lewis acid catalysts such as Sn-beta,[35,39] followed by the dehydration of fructose to 5-HMF using acid catalysts. Here we propose a similar mechanism for $FePO_4$ catalyzed glucose conversion to 5-HMF.

The promising activity of the $FePO_4$ catalyst in synthesize 5-HMF from glucose and sucrose opens up the possibility of using more complex carbohydrates such as cellulose and lignocellulosic feedstocks, i.e., camellia oleifera shell, as renewable raw materials. Synthesis of 5-HMF from cellulose and camellia oleifera shell involves their hydrolysis into their glucose monomers in the presence of an acidic catalyst, followed by an isomerization of glucose to fructose and subsequent dehydration of fructose to 5-HMF.[39,45] In addition, catalytic dehydration of camellia oleifera shell may produce furfural besides 5-HMF since it contains semi-cellulose. Table 3, entries 4-5 display the results obtained using $FePO_4$ catalyst for the conversion of cellulose and camellia oleifera shell to 5-HMF. 5-HMF yields of 31.8% and 7.8%, respectively, were achieved using the biphasic reactor system at 180 ^{o}C for 15 min. A 5-HMF yield of 48% was achieved at 160 ^{o}C for 60 min. It should be noted that we did not examine the most optimal reaction conditions for the dehydration of cellulose and camellia oleifera shell, since we only investigate whether $FePO_4$ catalyst can catalyze dehydration of cellulose and the lignocellulosic feedstock to generate 5-HMF or not. Further attempts to explore the optimum reaction conditions of cellulose and camellia oleifera shell are in progress. Moreover, we found that a higher 5-HMF yield was obtained using cellulose as the feedstock than glucose (Table 3, entries 2 and 6). It is well known that dehydration of cellulose to 5-HMF is more difficult than that of glucose because conversion of cellulose to 5-HMF needs an extra step of hydrolysis of cellulose to glucose monomers catalyzed by an acid catalyst.[9] The higher yield of 5-HMF from cellulose here can be explained by the fact that at high temperature trace amounts of partially dissolved $FePO_4$ could be hydrolyzed to $Fe(OH)_3$ and H_3PO_4, with the latter acting as a highly effective homogeneous acid to hydrolyze β-1,4-glucosidic bonds of cellulose and camellia oleifera shell to monosaccharide, which is then eventually converted to 5-HMF.

3.3 Recycling of $FePO_4$ catalyst

To investigate the activity and stability of the $FePO_4$ catalyst in the biphasic reaction system, recycling of the $FePO_4$ catalyst was studied over five successive cycles (Fig. 2). Experiments were performed at 140 °C for 15 min. After the reaction, the mixture was cooled to room temperature and filtered to obtain solid $FePO_4$ catalyst. Then the catalyst was washed using diethyl ether and water. It can be seen from Fig. 2 that 5-HMF yield of 50.5% was obtained for the first use of the $FePO_4$ catalyst and the activity was almost the same after five successive recycles. This indicates that the $FePO_4$ catalyst retained good activity for the conversion of fructose to 5-HMF after repeated use. IR spectra obtained showed that the structure of the used $FePO_4$ catalyst did not change after the reaction since the band at 1052 cm^{-1} assigned to P-O bond did not change, as shown in Figs. 4a and 4b. Interestingly, it was found that some light-yellow solid was precipitated from the aqueous phase after cooling to room temperature, as shown in Fig. 5. The IR spectra further show that the solid is the $FePO_4$ catalyst (Fig. 4c). This provides direct evidences that part of the $FePO_4$ catalyst was dissolved at high temperature. This could be explained by the fact that the $FePO_4$ catalyst is almost insoluble at room temperature ($K_{sp} = 1.3 \times 10^{-22}$),[41] but less amount of the $FePO_4$ catalyst can be dissolved when the temperature is greater than 140 °C (Table 1S, Supporting information). AAS result shows that the Fe ion concentration of the aqueous solution is ca. 0.022 mg/ml after the reaction (i.e. the precipitation reaction had been finished) when using 0.5 g $FePO_4$ catalyst at the reaction temperature of 180 °C. This suggests that the $FePO_4$ loss is smaller than 0.5% after it was precipitated upon cooling to room temperature. To investigate whether the reaction proceeds through homogeneous or heterogeneous catalysis, we used the filtered aqueous solution containing dissolved $FePO_4$ to carry out the fructose dehydration reaction without the addition of fresh $FePO_4$ catalyst (Table 1, entry 9). It should be noted that the filtered aqueous solution contained high concentration Fe^{3+} ions since the solution was immediately filtered after the reaction and the precipitation phenomenon did not occur (Table 1S, Supporting information). Under the same reaction conditions, we found that the filtered aqueous solution exhibit an almost comparable 5-HMF yield as compared to solid $FePO_4$ catalyst (Table 1, entries 6 and 9). Therefore we propose that the reaction mainly proceeds through homogeneous catalysis by dissolved $FePO_4$ catalyst for the dehydration of fructose. Although the dehydration reaction take place by homogeneous catalysis, the $FePO_4$ catalyst can be readily recycled and separated via cooling to the room temperature since the $FePO_4$ catalyst is almost insoluble at room temperature ($K_{sp} = 1.3 \times 10^{-22}$). Therefore, this novel catalytic system can be reused without loss of catalytic activity, being beneficial to the potential application for large scale 5-HMF synthesis and from the industrial point of view.

3.4 Possible production pathways of 5-HMF

In general, the production of 5-HMF from cellulosic or lignocellulosic feedstocks must be via acid-catalyzed depolymerization of cellulose to produce glucose in the first step.[9] However, the $FePO_4$ catalyst is not a proton acid but has the activity of cracking β-1,4-glucosidic bonds of cellulose, so we propose that partially dissolved $FePO_4$ could be hydrolyzed to produce $Fe(OH)_3$ and H_3PO_4 at high temperature. A mixture of $Fe(OH)_3$ and H_3PO_4 was employed to carry out the catalytic conversion of cellulose at 160 ^{o}C, the result as shown in Table 3, entry 9. It can be seen that the mixture of $Fe(OH)_3$ and H_3PO_4 gave 36.6% yield of 5-HMF. It should be noted that it is very difficult to identify the hydrolyzed product of $FePO_4$ in a sealed and high-pressure autoclave during the high temperature reaction. It is well-known that H_3PO_4 is an effective acid catalyst that can hydrolyze cellulose to produce glucose[46] and therefore, it is reasonable that cellulose would be hydrolyzed to glucose by H_3PO_4 produced from the hydrolysis of $FePO_4$. After the formation of glucose, the glucose molecule isomerizes into fructose which was then converted into 5-

HMF via the acid-catalyzed dehydration. To further investigate the conversion mechanism of cellulose, two control experiments were carried out by using $FeCl_3$ or Na_3PO_4 as the catalyst, the results of which are shown in Table 3, entries 7-8. It can be seen that the two catalysts gave very low yields of 5-HMF. This shows that it is very important for the co-exist of iron and phosphate ions to obtain high 5-HMF yield. It is widely accepted that the catalysts containing Lewis acid centers, such as Sn-Beta and Ti-Beta, can isomerize glucose into fructose at relative low temperatures.[39] In this work, a Lewis acid catalyst, i.e. $FeCl_3$, was also proved to be active for the isomerization of glucose into fructose during the transformation of cellulose, which is agreement with the results that $FeCl_3$ was reported to be active for the dehydration of fructose, glucose and sucrose to 5-HMF,[11,47] Similarly, we propose that the "one-pot" conversion of sucrose to 5-HMF proceeds through a cascade reaction sequence involving the homogeneous acid catalyzed depolymerization of sucrose to fructose and glucose, a Lewis acid site (Fe^{3+}) - catalyzed isomerization of glucose to fructose, and a homogeneous acid (H_3PO_4) - catalyzed dehydration of fructose to 5-HMF (Scheme 1). Camellia oleifera shell was converted to furfural besides 5-HMF because it contains cellulose and semi-cellulose. The production pathways of furfural and 5-HMF proceed through the route in which camellia oleifera shell may be firstly hydrolyzed into monosaccharide including C_5 sugars such as xylose, and glucose, which subsequently undergo an isomerization reaction (glucose) to fructose followed by the catalytic dehydration to generate 5-HMF or a dehydration reaction (xylose) to produce furfural via xylose intermediate.[48]

As mentioned above, the higher temperature will result in an increase of $FePO_4$ solubility (Table 1S, Supporting information), moreover, the soluble $FePO_4$ will be precipitated into the light-yellow solid after 48 h storage at room temperature (Fig. 4). Moreover, we infer that $FePO_4$ could be hydrolyzed to H_3PO_4 and $Fe(OH)_3$ at high temperature based on the results that the reaction system can hydrolyze cellulose and camellia oleifera shell at higher temperatures and the catalytic result of the mixture of H_3PO_4 and $Fe(OH)_3$ (Table 3, entry 9). After the reaction, H_3PO_4 might react with $Fe(OH)_3$ to form insoluble $FePO_4$ again upon cooling to room temperature (Fig. 4 and Table 1S). This temperature-controlled separation process overcomes the concerns of recycling cost and pollution of adding mineral acids, which were usually used in the conversion of cellulose or lignocellulosic feedstocks to 5-HMF in ionic liquid solvents or a biphasic reactor system.[9,24,49] Therefore, the $FePO_4$ catalyst not only has the comparable catalytic performances of homogeneous acids (e.g. hydrolysis of cellulose), but it avoids the drawback of difficulties to be separated and recycled. Although the $FePO_4$ catalyst is not perfect since about 0.5% $FePO_4$ was final loss into the reaction solution, the strategy of “double character” catalyst in the dehydration of lignocellulosic materials will provide some new ideas for the industrial application of 5-HMF production.

4. **Conclusion**

In conclusion, a novel, readily recycled $FePO_4$ catalyst was developed for the direct conversion of carbohydrates including fructose, glucose, sucrose, cellulose, and camellia oleifera shell to 5-HMF catalyzed by the inexpensive $FePO_4$ without the addition of homogeneous acids. Using the $FePO_4$ catalyst, a 5-HMF yield of 71.5% from fructose could be achieved in the biphasic reaction system. Furthermore, the catalyst was shown to act as highly effective homogeneous acid to hydrolyze β-1,4-glucosidic bonds of cellulose and camellia oleifera shell to monosaccharides, which were eventually converted to 5-HMF via an isomerization reaction of glucose to fructose and then fructose dehydration reaction. The “double character” catalyst has the combined character of both homogeneous and heterogeneous catalysts, which could act as a dissolved homogenous acid at higher temperature and as an insoluble solid acid that is easily separated and recycled after cooling to room temperature. The catalyst was stable over five reaction cycles and the biphasic reaction system could be applied to the conversion of lignocellulosic feedstocks without the addition of homogeneous acids under mild conditions.

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Table 1 Results for the conversion of fructose to 5-HMF[a]

Entry	**System**	**Catalyst**	**Catalyst amount/g**	**Reaction time/min**	**Conversion /%**	**5-HMF yield/mol%**
1	single phase(H_2O)	H_3PO_4	0.25	30	97.4	44.5
2	single phase(H_2O)	$FePO_4$	0.10	30	95.4	17.0
3	biphasic(H_2O/THF)	$FePO_4$	0.10	15	99.5	39.3
4	biphasic(H_2O/THF/NaCl)	H_3PO_4	0.10	15	99.9	63.4
5	biphasic(H_2O/THF/NaCl)	$FePO_4$	0.10	15	99.7	65.0
6	biphasic(H_2O/THF/NaCl)	$FePO_4$	0.20	15	99.9	68.8
7	biphasic(H_2O/THF/NaCl)	$FePO_4$	0.05	15	99.5	62.8
8	biphasic(H_2O/THF/NaCl)	$FePO_4$	0.20	15	99.9	71.5
9[b]	biphasic(H_2O/THF/NaCl)	$FePO_4$(soluble)	/	15	99.9	71.7

[a] Reaction conditions: Fructose (20 mg/mL H_2O), the reaction temperature (140 °C). Entries 3-6: aqueous to organic phase volume ratio of 3. Entries 7-8: aqueous to organic phase volume ratio of 5. Entries 4-8: NaCl (0.35 g dissolved in 1 g H_2O) was added.

[b] The aqueous phase solution was used as the catalyst, which was obtained by filtering and separating the reaction system (entry 6) in order to remove both the solid and the organic phase.

Table 2 Effect of reaction temperature and time on fructose conversion and 5-HMF yield using $FePO_4$ as the catalyst [a]

Entry	**Temperature /°C**	**Reaction time /min**	**Conversion /%**	**5-HMF yield /mol%**
1	120	15	98.8	34.6
2	140	15	99.9	62.6
3	160	15	99.7	60.2
4	180	15	99.9	54.2
5	140	5	99.7	59.5
6	140	30	99.9	62.8

[a] Reaction conditions: Fructose (0.2 g), $FePO_4$ (0.05 g), H_2O (10 mL), THF (30 mL), NaCl (3.5 g).

[b] Fructose concentration is defined as fructose mass divided by the aqueous volume.

Table 3 Results for the conversion of different feedstocks to 5-HMF[a]

Entry	**Catalyst**	**Feedstock**	**Temperature/°C**	**Conversion /%**	**5-HMF yield /mol%**
1	$FePO_4$	Fructose	140	97.4	50.5
2	$FePO_4$	Glucose	140	97.8	23.1
3	$FePO_4$	Sucrose	140	96.1	39.3
4	$FePO_4$	Cellulose	180	/	31.8
5	$FePO_4$	Camellia Oleifera Shell	180	/	7.8[b]
6	$FePO_4$	Cellulose	160	87.4	48.0
7	Na_3PO_4	Cellulose	160	96.6	6.8
8	$FeCl_3$	Cellulose	160	82.3	8.6
9[c]	$Fe(OH)_3$ + H_3PO_4	Cellulose	160	/	36.6

[a] Entries 1-5: 1.0 g feedstock, 0.5 g catalyst ($FePO_4$), 10 mL H_2O, 30 mL THF, 3.5 g NaCl, the reaction time of 15 min; entries 6: 0.5 g catalyst, 1 g cellulose, 10 mL water, 30 mL THF, 3.5 g NaCl, 60 min; Entries 7-8: 0.1 g catalyst, 1 g cellulose, 10 mL water, 30 mL THF, 3.5 g NaCl, 60 min.

[b] The yield is defined as the 5-HMF mass divided by the feedstock mass;

[c] The reaction time of 60 min, 0.0015 mol H_3PO_4, 0.001 mol $Fe(OH)_3$, 30 Ml THF, 10 mL H_2O, 3.5 g NaCl.

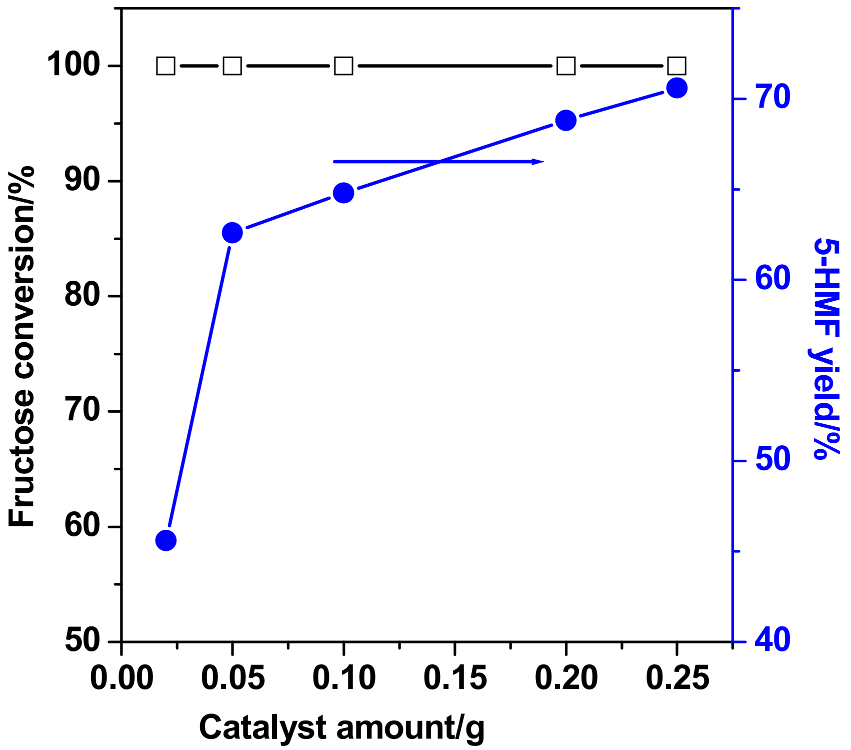


Fig. 1 Effect of $FePO_4$ amount on fructose conversion and 5-HMF yield. Reaction conditions: Feedstock (0.2 g), H_2O (10 mL), THF (30 mL), NaCl (3.5 g), 15 min, 140 °C.

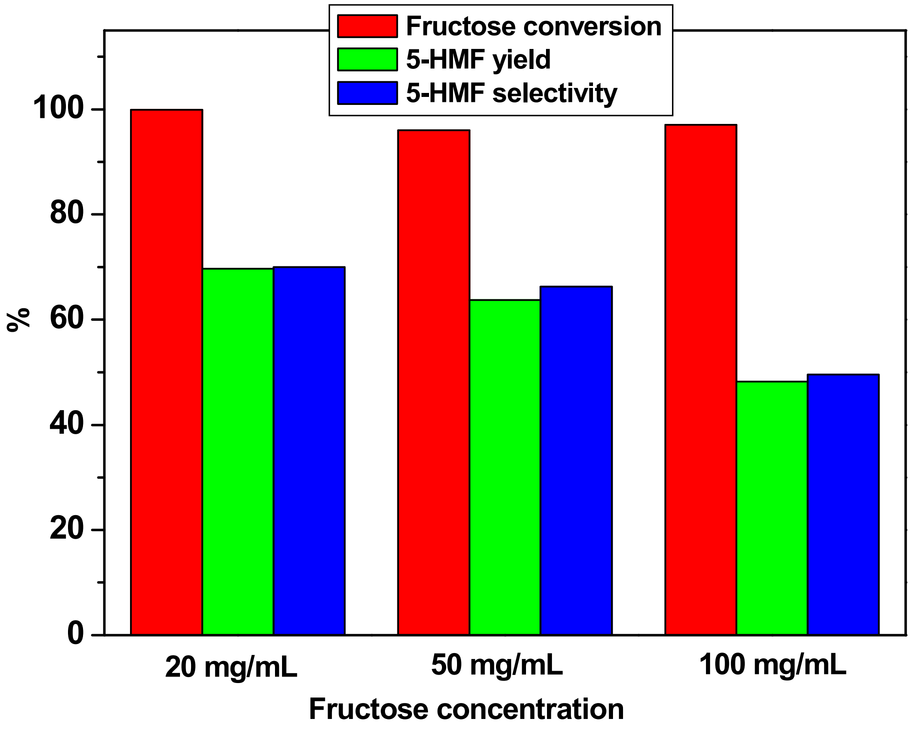


Fig. 2 Effect of fructose concentration on fructose conversion, 5-HMF yield and selectivity using $FePO_4$ catalyst in the H_2O/THF biphasic system. Reaction conditions: H_2O/THF 1:3 phase volume ratio (10 mL H_2O), NaCl (3.5 g), 140 °C, 15 min.

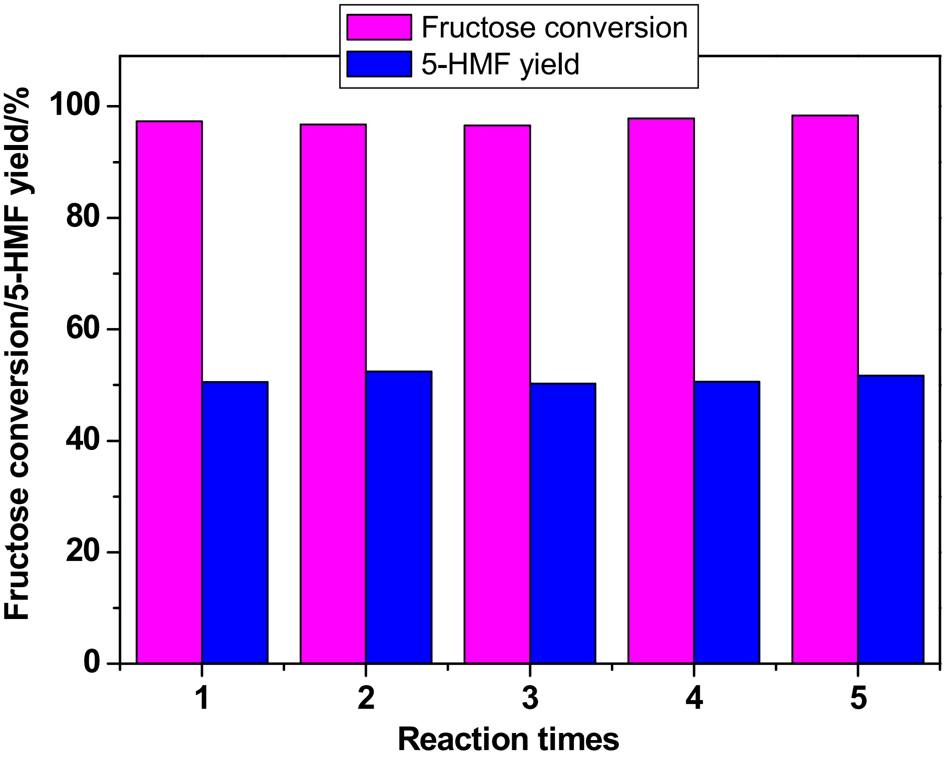


Figure 3 Catalyst recycling experiments. Reaction conditions: Feedstock (1.0 g), catalyst ($FePO_4$, 0.5 g) H_2O (10 mL), THF (30 mL), NaCl (3.5 g), 140 °C, 15 min. The filtered solid residue was washed and used to next recycle experiment.

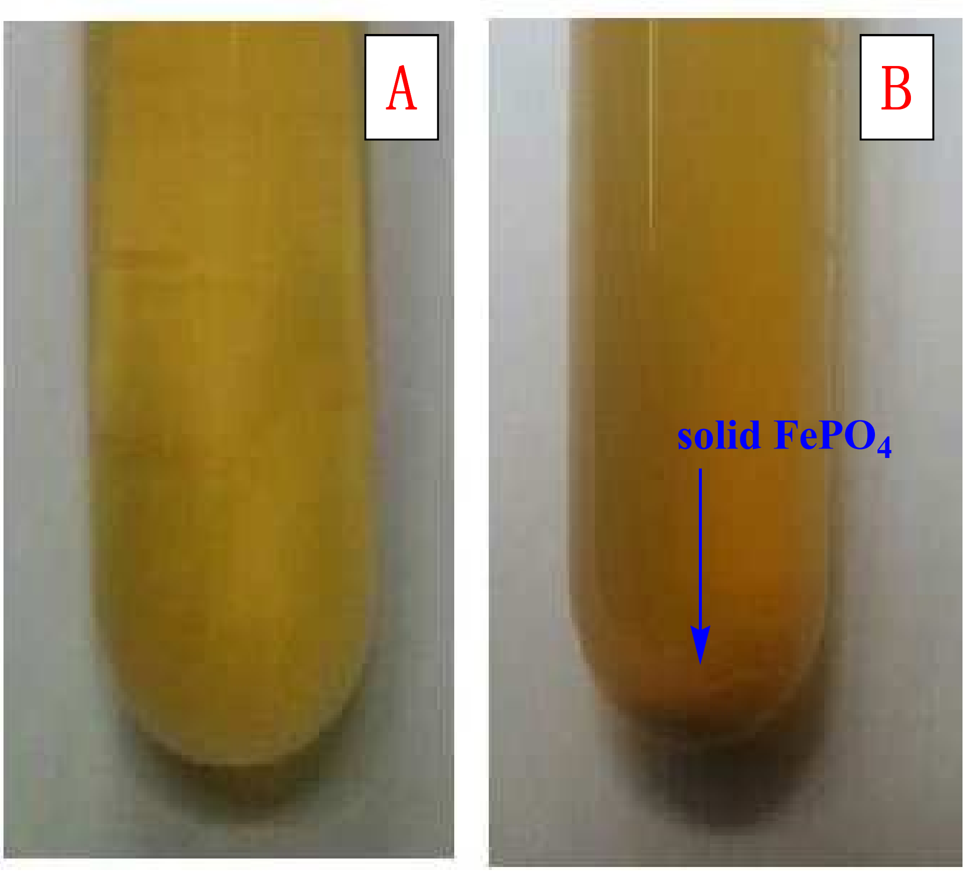


Figure 4 (A) The aqueous solution obtained via filtrating and separating the reaction mixture, and (B) after 2 days storage of solution A. Reaction conditions: Feedstock (1.0 g), catalyst ($FePO_4$, 0.5 g), H_2O (10 mL), THF (30 mL), NaCl (3.5 g), 140 °C, 15 min.

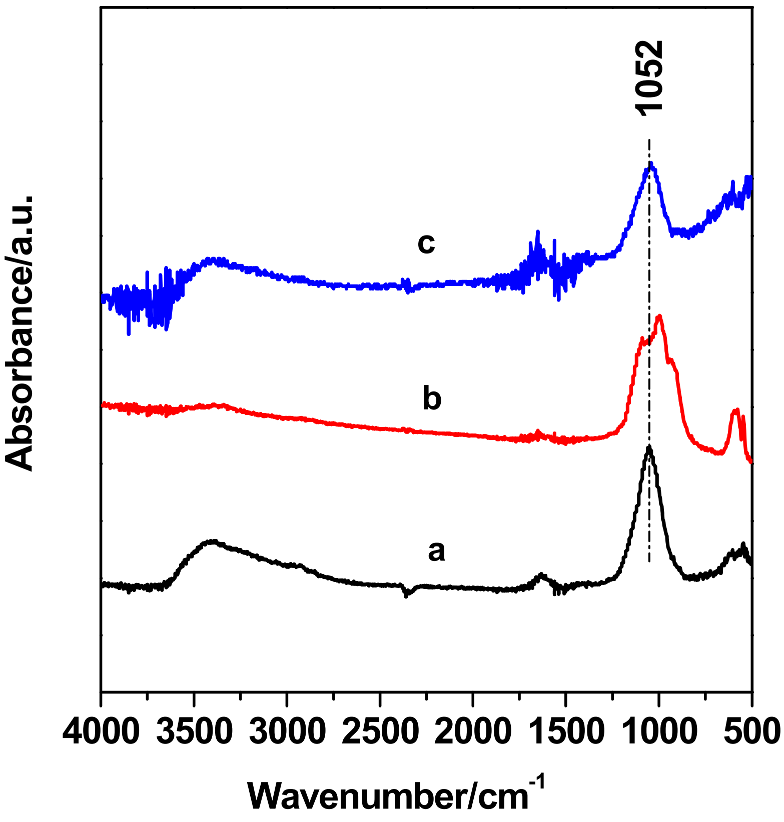
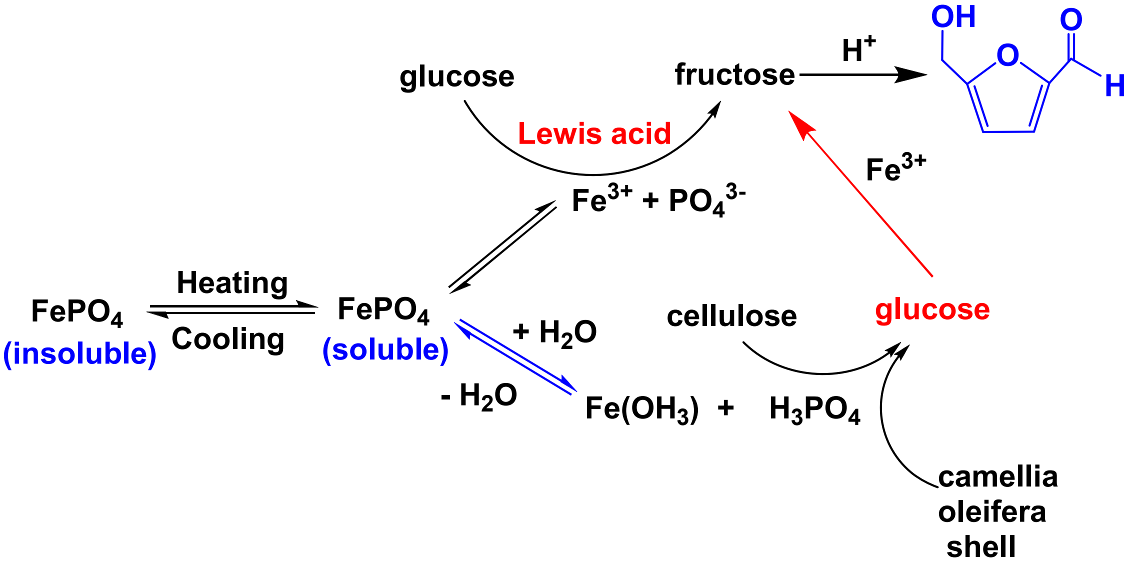


Fig. 5 IR spectra obtained for **(a)** fresh $FePO_4.2H_2O$, **(b)** the used $FePO_4$, and **(c)** the solid obtained from the precipitated mixture of the aqueous solution (i.e. Fig. 4B)



Scheme 1 The proposed reaction pathways of $FePO_4$ catalyzed dehydration of carbohydrates to produce 5-HMF.