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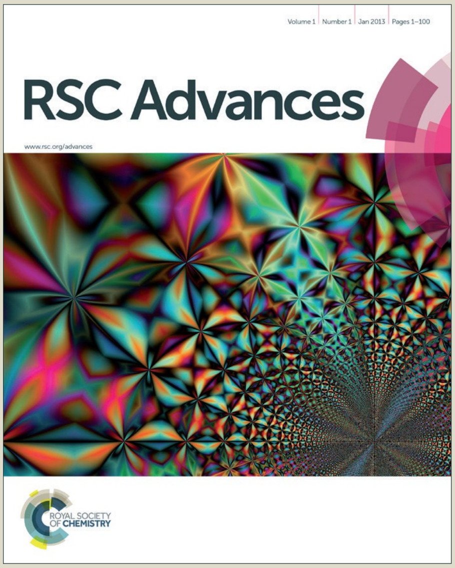

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High efficient conversion of carbohydrates into 5-hydroxymethylfurfural using the bi-functional $CrPO_4$ catalyst

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Abstract

High efficient synthesis of 5-hydroxymethyfurfural (HMF) from carbohydrates was achieved using inexpensive and bi-functional $CrPO_4$ catalyst in biphasic system. The effect of various reaction conditions including reaction temperature, time, solvent, etc. on HMF yields were explored. A HMF yield up to 83% was obtained using fructose as the reactant at 140 ℃ for 15 min. A maximum HMF yield of 63% was also achieved from glucose when the reaction was carried out at 140 □ for 30 min. Among the reported catalysts, $CrPO_4$ showed one of the most effective in the conversion of glucose into HMF, which is comparable to ionic liquid reaction system. Moreover, the $CrPO_4$ catalyst exhibited high activity to convert micro-crystalline and lignocellulosic feedstock to HMF without the addition of homogeneous mineral acids. The possible conversion mechanism of carbohydrates into HMF catalyzed by the bi-functional $CrPO_4$ catalyst was discussed.

Keywords: 5-hydroxymethylfurfural; isomerization; dehydration; $CrPO_4$.

1. Introduction

With the depletion of fossil resources and increasing concerns for global warming, the search for renewable alternative resources is extremely urgent. The abundant renewable biomass is considered as a promising alternative for non-renewable resources and possesses a great potential to become raw materials for the production of valuable chemicals [1-3]. Among those products, 5-hydroxymethylfurfural (HMF), which can be produced by the dehydration of hexose [1-3], has attracted much attention. HMF can be further transformed into useful chemicals such as 2, 5-furandicarboxylic acid, 2,5-dihydroxymethylfuran, and dimethylfuran through oxidation, hydrogenation and hydrogenolysis [3-13]. So far, a great deal of scientific effort has been put into the HMF production derived from lignocellulosic biomass and carbohydrate compounds.

The production of HMF was usually performed by mineral acid-catalyzed hydration of biomass such as glucose, fructose, inulin, and cellulose [11, 14-22]. The use of mineral acid has some drawbacks, including some environmental pollutions and corrosion. Therefore, a new type of catalytic system has been developed recently. Since ionic liquids (ILs) have shown to be excellent reaction media for many chemical reactions in terms of their transcendent advantages [9, 23-25]. Some ILs can dissolve various carbohydrates such as monosaccharides, polysaccharides, even lignocellulosic materials. Zhao et al. reported that a 5-HMF yield of 91% was obtained with fructose as a feedstock at 100 ℃ by using $CrCl_2$ in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) [26]. In addition, acidic ionic liquid $[HSO_3BMIM]HSO_4$ and $[BMIM]HSO_4$ in [BMIM]Cl also efficiently catalyzed the hydrolysis of corn stalk [27]. However, the ILs system is high cost and not easy to separate and recovery, making it difficult to be industrialized [2]. Therefore, some novel, inexpensive, and cost-efficient routes which are suitable for large-scale production of HMF must be developed.

A biphasic reactor system has attracted increasing attention due to the use of low boiling solvents, so it could be suitable for large-scale industrial applications [28-31]. Ma et al. reported that a high 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 [28]. The HMF yield of 57% was achieved from glucose using Sn-beta zeolite and HCl in a biphasic (H_2O/THF) system [30]. The HMF yield from fructose conversion was up to 90% and the HMF yield of 58% was obtained by using glucose as feedstock, when the tantalum hydroxide treated by H_3PO_4 was used as a catalyst in the water–2-butanol biphasic system [32]. Using Titanium hydrogenphosphate (TiHP) as catalyst, the 55% and 35% HMF yield was obtained starting from fructose and glucose, respectively [33]. Nijhuis and co-workers showed that aluminum, titanium, zirconium, and niobium-based phosphates afforded 5-HMF selectivity in the range of 30–60% using glucose as a feedstock [34]. Maximum yields of HMF of 77 and 50 mol% were achieved from fructose and glucose, respectively, using large-pore mesoporous tin phosphate in a water/methyl isobutyl ketone biphasic solvent [35]. Use phosphated TiO_2 as catalyst, the HMF yield of 81% from glucose was obtained at 175 □ [36].

In our previous study, the $FePO_4$ catalyst exhibited high catalytic activity toward the conversion of lignocellulosic materials [37]. In addition, $CrCl_3$ was also reported to have higher catalytic activity [38]. Therefore, in this work, the inexpensive $CrPO_4$ catalyst was applied to produce HMF with high yield from carbohydrate conversion. To the best of our knowledge, the use of $CrPO_4$ in the conversion of carbohydrate has not been reported yet. The aim of this study is to improve the HMF yield and disclose the reaction mechanism. To this end, the effects of various reaction conditions on HMF yields were explored. Possible dehydration reaction mechanisms of these carbohydrates catalyzed by $CrPO_4$ were also proposed.

2. Experimental (Materials and Method)

2.1 Materials

Microcrystalline cellulose and D-Fructose were purchased from the Sigma-Aldrich company in China. Microcrystalline cellulose (50 mm) was directly used for the dehydration reaction without any other pretreatment. $CrPO_4$ were used as the reaction catalyst. All other chemicals were purchased from Jianghua Chemical Reagent (Nanjing, China). Wheat straw was obtained from local resources in Hebei province, China and was crushed and sieved to around 75 mm. Structural carbohydrates and acid insoluble lignin mass fraction for the wheat straw were determined using the standard NREL laboratory analytical procedures [37]. The glucan content of wheat straw is about 35.5%.

2.2 Methods

Bath catalytic experiments 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.

Alter 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 literature report [39]. The conversion of mono- and di- saccharides was calculated as follows: conversion (%) = (moles of substrate reacting)/(moles of substrate staring) × 100, while the conversion of cellulose and wheat straw was calculated by the weight change of substrate before and after the reaction. The yields of 5-HMF using fructose and glucose as starting materials were calculated using the following equation: yield (%) = (moles of 5-HMF in the products)/(moles of feedstocks put into the reactor) × 100. For cellulose and wheat straw, the yields of 5-HMF were defined as follows: yield (%) = (moles of 5-HMF in the products)/(moles of glucose unit put into the reactor) × 100.

Results and discussion

2.3 Effect of catalyst dosage on the yield of HMF produced from fructose

The influence of catalyst dosage on the fructose conversion into HMF in biphasic H_2O/THF system was investigated and the results are shown in Table 1. On the basis of our previous work [37], we firstly used the temperature of 140 ℃ and the ratio of H_2O/THF equal to 3 to perform the dehydration reaction. In H_2O/THF biphasic system, the conversion of fructose into HMF was obviously dependent on the catalyst used. Without any catalyst addition, the low yield of HMF of 48 % was obtained. It can be seen from Table 1 that the addition of $CrPO_4$ remarkably promoted the production of HMF, indicating that $CrPO_4$ can efficiently catalyze the conversion of fructose into HMF. The yield of HMF initially increased with increasing the $CrPO_4$ dosage. However, when 0.25 g catalyst was used, the yield of HMF was decreased. The reason might be that excessive catalyst accelerated the formation of HMF from fructose while it also favored the rehydration of HMF into levulinic acid, which offsets increase in HMF yield [40]. Thus, the optimum amount of catalyst was 0.125 g for the maximum HMF yield.

3.2 Effect of reaction temperature and time on HMF yield

The influence of reaction temperature on the yield of HMF was also investigated, and the results are shown in Fig. 1. When the dehydration of fructose was carried out at 120 ℃, the reaction was very slow. A HMF yield of 61% was obtained after 15 min. As the reaction was further carried out at 130 ℃ for 15 min, the yield of HMF increased to 71 %. When the reaction proceeded at 140 ℃ for 15 min, the highest HMF yield of 83% was obtained. When it was 150 ℃, the HMF yield was lower than that at 140 ℃, and only 74%. This is because that higher temperature gave rise to side reactions that formed undesired byproducts. Therefore, 140 ℃ was determined the optimal reaction temperature. Impact of the reaction time on the conversion of fructose and HMF yield was also evaluated at 140 ℃. The yield of HMF improved from 69 % to 74% upon increase of the reaction time from 5 min to 15 min (Table 1, entries 4 and 5). However, when the reaction time reached 30 min, HMF yield decreased to 64%. After a long period of reaction, HMF was rehydration and formation of humins. The results demonstrated that both reaction temperature and time had significant influences on the production of HMF. Thus, a reaction temperature of 140 ℃ and a reaction time of 15 min were selected as the optimum conditions for conversion of fructose into HMF.

3.3 The effects of solvents on yield of HMF from conversion of fructose

Catalytic conversion of fructose into HMF was then carried out in different polar solvent systems, and the result is listed in Table 2. A lower HMF yield of 33% was obtained when the protic solvent MIBK was used (Table 2, entry 1). The HMF yield of 63% and 81% were obtained using n-butanol and 2-butanol as organic solvent, respectively (Table 2, entries 2 and 3). When H_2O/THF biphasic system was used, the yields of HMF was also improved (Table 2, entry 4). Subsequently, the influence of different ratio of H_2O/THF on the degradation of fructose was investigated (Table 2, entries 4-7). It was found that the HMF yield was up to 83 % when the ratio of H_2O/THF was 1:3. In order to reveal that whether the reaction occurred through homogeneous or heterogeneous catalysis, the filtered aqueous solution containing dissolved $CrPO_4$ was used to carry out the fructose dehydration reaction without the addition of fresh $CrPO_4$ catalyst (Table 2, entry 8). The results suggested that the filtered aqueous solution exhibit an almost comparable HMF yield as compared to solid $CrPO_4$ catalyst (Table 2, entries 5 and 8). It is obvious that the reaction mainly proceeded through homogeneous catalysis by dissolved $CrPO_4$ catalyst.

3.4 The effect of different biomass materials on the HMF production

It is well reported that a variety of feedstocks have been used to produce HMF, including monosaccharides, disaccharides, or more complex, high-molecular-weight polysaccharides or raw lignocellulosic biomass [2, 3, 38, 39]. 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 [3, 40]. In order to test catalytic activity of $CrPO_4$ toward different biomass materials, glucose, cellulose, and wheat straw were also used for the HMF production, and the result is shown in Fig. 2. It can be seen from Fig. 2 that a high HMF yield (83%) was obtained using fructose as a starting material. And a HMF yield of 51.7% was obtained from glucose with a high conversion at 140 ℃ for 15 min. For cellulose, a good HMF yield of 37% at the conversion of 65% was also achieved. The results provide a promising alternative for the conversion of less-expensive and renewable carbohydrates into HMF.

Subsequently, the reaction conditions, including reaction time, reaction temperature, catalyst dosage, etc. on the conversion of glucose were investigated. The results are presented in the Table 3. It can be found that the reaction time, reaction temperature and catalyst amount significantly affected the yield of HMF. A yield of HMF up to 63% was achieved at 140 ℃ for 30 min (Table 3, entry 2). It was reported that a high HMF yield of 67% was achieved starting from glucose using $CrCl_3$ as the catalyst in ionic liquid reaction system [38]. So, $CrPO_4$ is one of the effective catalysts in the conversion of glucose to HMF, which is comparable to the ionic liquid reaction system [38].

In order to further improve the HMF yield, we tried to use other catalyst to perform the dehydration reaction of glucose, and the results are shown in Table 4. Interestingly, when using $CrCl_3$ as the catalyst, a low HMF yield of 15% was obtained in the H_2O/THF system (Table 4, entry 4). This finding is completely different from the result that $CrCl_3$ gave a high HMF yield of 67% starting from glucose in ionic liquor reaction system, suggesting that solvents play an important role in the reaction [38]. In addition, we used NaH_2PO_4 to modify the pH value of aqueous phase in order to improve the HMF yield. However, the results showed that the yield of HMF decreased with the addition of NaH_2PO_4 compared to a single $CrPO_4$ or NaH_2PO_4 as a catalyst. The possible explanation is that the presence of $H_2PO_4^{2-}$ changes the pH value and hydrolysed species thus suppressing the glucose isomerization to fructose. The catalytic activity of H_3PO_4 under identical reaction conditions was also tested as a control experiment, and the yield of HMF was 22%.

3.5 The reaction mechanism of carbohydrates into HMF

In general, the production of 5-HMF from cellulosic or lignocellulosic feedstocks must include acid catalyzed depolymerization of cellulose to produce glucose in the first step [41, 42]. A glucose isomerization to fructose followed by its subsequent dehydration to HMF. Vlachos et al have already reported that the hydrolyzed Cr(Ⅲ) complex $[Cr(H_2O)_5OH]^{2+}$ was the most active Cr species in glucose isomerization and probably acts as a Lewis acid- Brønsted base bifunctional site [20]. However, the $CrPO_4$ catalyst was not a proton acid but has the activity of cracking β-1, 4-glucosidic bonds of cellulose. It is well know that H^+ can hydrolyze cellulose to produce glucose [15, 43-45]. Hence, we tested the pH of the aqueous phase which was obtained by filtering and separating the reaction system (Table 1, entry 5), the result of pH measurement was 2.48. In contrast, pH of aqueous phase containing dissolved $FePO_4$ is 3.75 at room temperature. Therefore, we propose that partially dissolved $CrPO_4$ could be hydrolyzed to produce $[Cr(H_2O)_5OH]^{2+}$ and H^+, both of which were responsible for the catalytic conversion of cellulosic or lignocellulosic feedstocks. It is reasonable that cellulose can be hydrolyzed to glucose by H^+ produced from the hydrolysis of $CrPO_4$. After the formation of glucose, the glucose molecule isomerizes into fructose which was then converted into 5-HMF via the acid-catalyzed dehydration. So, we prospect a possible reaction route about conversion of carbohydrates to 5-HMF proceeded through a cascade reaction sequence which involves the homogeneous acid catalyzed depolymerization of carbohydrates to glucose, a Lewis acid site $[Cr(H_2O)_5OH]^{2+}$-catalyzed isomerization of glucose to fructose, and a homogeneous acid (H^+)-catalyzed dehydration of fructose to 5-HMF, as shown in Scheme 1.

Conclusions

$CrPO_4$ shows to be an efficient, inexpensive bi-functional catalyst for renewable HMF production, and even the conversion of cellulose and lignocellulose without the addition of mineral acid. A HMF yield up to 83% was obtained using fructose as the reactant at 140℃ for 15 min. A maximum HMF yield of 63% was also achieved from glucose when the reaction was carried out at 140□ for 30 min. The high activity of the catalyst is attributed to the hydrolysis of the Cr (Ⅲ) ion releases H^+ and Cr hydroxylated species. This Lewis acid-derived (intrinsic) Brønsted acidity was primarily responsible for the fructose dehydration to HMF when no external Brønsted acids were added. Besides, the catalyst was shown to act as a highly effective homogeneous acid to hydrolyze β-1, 4-glucosidic bonds of cellulose and wheat straw to monsaccharides, which were eventually converted to HMF via an isomerization reaction of glucose to fructose and then fructose dehydration reaction. The $CrPO_4$ catalyst has a great potential to facilitate the cost-efficient conversion of carbohydrates into HMF in future.

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Notes and References

[1] J. Carlos Serrano-Ruiz, R. Luque, and A. Sepulveda-Escribano, Chem. Soc. Rev. 2011, **40**, 5266-5281.

[2] M.E. Zakrzewska, E. Bogel-Lukasik, and R. Bogel-Lukasik, Chem. Rev. 2011, **111**, 397-417.

[3] R.-J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, and J.G. de Vries, Chem. Rev. 2013, **113**, 1499-1597.

[4] S. Nishimura, N. Ikeda, and K. Ebitani, Catal. Today 2014, **232**, 89-98.

[5] S. Wang, Z. Zhang, and B. Liu, ACS Sus. Chem. Eng. 2015, **3**, 406-412.

[6] Z. Zhang, J. Zhen, B. Liu, K. Lv, and K. Deng, Green Chem. 2015, **17**, 1308-1317.

[7] A.J. Kumalaputri, G. Bottari, P.M. Erne, H.J. Heeres, and K. Barta, ChemSusChem 2014, **7**, 2266-2275.

[8] E.A. Pidko, V. Degirmenci, and E.J.M. Hensen, ChemCatChem 2012, **4**, 1263-1271.

[9] V. Degirmenci, E.A. Pidko, P.C.M.M. Magusin, and E.J.M. Hensen, ChemCatChem 2011, **3**, 969-972.

[10] Y. Roman-Leshkov, C.J. Barrett, Z.Y. Liu, and J.A. Dumesic, Nature 2007, **447**, 982-U985.

[11] A. Takagaki, S. Nishimura, and K. Ebitani, Catal.Sur. Asia 2012, **16**, 164-182.

[12] H. Zheng, Z. Sun, X. Yi, S. Wang, J. Li, X. Wang, and Z. Jiang, RSC Adv. 2013, **3**, 23051-23056.

[13] A.J. Crisci, M.H. Tucker, J.A. Dumesic, and S.L. Scott, Top. Catal. 2010, **53**, 1185-1192.

[14] H. Xie, Z.K. Zhao, and Q. Wang, ChemSusChem 2012, **5**, 901-905.

[15] S. Xiao, B. Liu, Y. Wang, Z. Fang, and Z. Zhang, Bioresour. Technol. 2014, **151**, 361-366.

[16] Z.-D. Ding, J.-C. Shi, J.-J. Xiao, W.-X. Gu, C.-G. Zheng, and H.-J. Wang, Carbohydr. Polym. 2012, **90**, 792-798.

[17] F. Tao, H. Song, and L. Chou, J. Mol. Catal. A-Chem. 2012, **357**, 11-18.

[18] X. Qi, H. Guo, L. Li, and R.L. Smith, Jr., ChemSusChem 2012, **5**, 2215-2220.

[19] H. Huang, C.A. Denard, R. Alamillo, A.J. Crisci, Y. Miao, J.A. Dumesic, S.L. Scott, and H. Zhao,

ACS Catal. 2014, **4**, 2165-2168.

[20] V. Choudhary, S.H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N.S. Marinkovic, A.I. Frenkel, S.I. Sandler, and D.G. Vlachos, J. Am. Chem. Soc. 2013, **135**, 3997-4006.

[21] Y. Qu, C. Huang, Y. Song, J. Zhang, and B. Chen, Bioresour. Technol. 2012, **121**, 462-466.

[22] X. Tong, M. Li, N. Yan, Y. Ma, P.J. Dyson, and Y. Li, Catal. Today 2011, **175**, 524-527.

[23] A. Chinnappan, A.H. Jadhav, H. Kim, and W.-J. Chung, Chem. Eng. J. 2014, **237**, 95-100.

[24] Y. Zhang, E.A. Pidko, and E.J.M. Hensen, Chem. Eur. J. 2011, **17**, 5281-5288.

[25] Z. Zhang, and Z. Zhao, Bioresour. Technol. 2011, **102**, 3970-3972.

[26] H. Zhao, J.E. Holladay, H. Brown, and Z.C. Zhang, Science 2007, **316**, 1597-1600.

[27] F. Jiang, Q. Zhu, D. Ma, X. Liu, and X. Han, J. Mol. Catal. A-Chem. 2013, **334**, 8-12.

[28] N. Shi, Q. Liu, Q. Zhang, T. Wang, and L. Ma, Green Chem. 2013, **15**, 1967-1974.

[29] V.V. Ordomsky, J. van der Schaaf, J.C. Schouten, and T.A. Nijhuis, ChemSusChem 2012, **5**, 1812-1819.

[30] E. Nikolla, Y. Roman-Leshkov, M. Moliner, and M.E. Davis, ACS Catal. 2011, **1**, 408-410.

[31] Y. Roman-Leshkov, J.N. Chheda, and J.A. Dumesic, Science 2006, **312**, 1933-1937.

[32] F. Yang, Q. Liu, M. Yue, X. Bai, and Y. Du, Chem. Commun. 2011, **47**, 4469-4471.

[33] M.I. Alam, S. De, B. Singh, B. Saha, and M.M. Abu-Omar, Appl. Catal. A: Gen. 2014, **486**, 42-48.

[34] V.V. Ordomsky, V.L. Sushkevich, J.C. Schouten, J. van der Schaaf, and T.A. Nijhuis, J. Catal. 2013, **300**, 37-46.

[35] A. Dutta, D. Gupta, A.K. Patra, B. Saha, and A. Bhaumik, ChemSusChem 2015, **7**, 925-933.

[36] L. Atanda, A. Shrotri, S. Mukundan, Q. Ma, M. Konarova, and J. Beltramini, ChemSusChem.

2015, **8**, 2907-2916.

[37] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, , Determination of structural carbohydrates and lignin in biomass, National Renewable Energy Laboratory, 2011, 18.

[38] A. Corma, S. Iborra, and A. Velty, Chem. Rev. 2007, **107**, 2411-2502.

[39] R.J.H. Grisel, J.C. van der Waal, E. de Jong, and W.J.J. Huijgen, Catal. Today 2014, **223**, 3-10.

[40] V.V. Ordomsky, J. van der Schaaf, J.C. Schouten, and T.A. Nijhuis, ChemSusChem 2013, **6**, 1697-1707.

[41] N. Meine, R. Rinaldi, and F. Schueth, ChemSusChem 2012, **5**, 1449-1454.

[42] R. Weingarten, A. Rodriguez-Beuerman, F. Cao, J.S. Luterbacher, D.M. Alonso, J.A. Dumesic, and G.W. Huber, ChemCatChem 2014, **6**, 2229-2234.

[43] L. Yang, X. Yan, Q. Wang, Q. Wang, and H. Xia, Carbohydr. Res. 2015, **404**, 87-92.

[44] A. Wang, and T. Zhang, Acc. Chem. Res. 2013, **46**, 1377-1386.

[45] Z. Tai, J. Zhang, A. Wang, J. Pang, M. Zheng, and T. Zhang, ChemSusChem 2013, **6**, 652-658.

Figure captions

Figure 1 Effect of reaction temperature on fructose conversion and HMF yield.

Reaction condition: fructose (1.0 g), NaCl (3.5 g), $CrPO_4$ (0.125 g), H_2O (10 mL), THF (30 mL), 15 min.

Figure 2 Result for the conversion on different feedstocks to HMF.

Reaction condition: feedstock (1.0 g), NaCl (3.5 g), $CrPO_4$ (0.125 g), H_2O (10 mL), THF (30 mL), 140 ℃, 15 min.

Scheme 1 The proposed reaction pathways of $CrPO_4$ catalyzed conversion of cellulose to 5-HMF.

Table 1 The effects of catalyst dosage and reaction time on conversion of fructose to 5-HMF [a]

Entry	**Amount of catalyst/g**	**Reaction Time/min**	**Conversion%**	**HMF Yield/mol%**
1	0	15	97	48
2	0.065	15	100	81
3	0.125	15	100	83
4	0.250	5	98	69
5	0.250	15	99	74
6	0.250	30	100	64

[a] Reaction conditions: Fructose (1.0 g), NaCl (3.5 g), H_2O (10 mL) and THF (30 mL), 140 ℃.

Table 2 Dehydration of fructose into HMF in different solvent systems [a]

Entry	System (mL/mL)	Conversion/%	HMF Yield/mol%
1	H_2O/MIBK (10/30)	98	33
2	H_2O/n-Butanol (10/30)	99	63
3	H_2O/ 2-Butanol (10/30)	100	81
4	H_2O/THF (10/20)	100	56
5	H_2O/THF (10/30)	99	83
6	H_2O/THF (10/40)	100	78
7	H_2O/THF (10/60)	98	70
8[b]	H_2O/THF (—)	100	79

[a] Reaction conditions: Fructose (1.0 g), $CrPO_4$ (0.125 g), NaCl (3.5 g), H_2O (10 mL), 140 ℃, 15 min.

[b] The aqueous phase solution (soluble $CrPO_4$) was used as the catalyst, which was obtained by filtering and separating the reaction system (entry 5) in order to remove both the solid and the organic phase. Reaction conditions: Fructose (1.0 g), NaCl (3.5 g), THF (30 mL), 140 ℃, 15 min.

Table 3 The effects of reaction conditions on the conversion of glucose to 5-HMF [a].

Entry	Catalyst amount/g	Reaction Temperature/℃	Reaction Time/min	Conversion/%	HMF Yield/mol%
1	0.125	130	30	98	46
2	0.125	140	30	99	63
3	0.125	150	30	98	50
4	0.125	140	5	98	50
5	0.125	140	15	100	52
6	0.125	140	45	98	49
7	0.065	140	30	99	33
8	0.250	140	30	100	36

[a] Reaction conditions: Glucose (1.0 g), NaCl (3.5 g), H_2O (10 mL) and THF (30 mL).

Table 4 The effects of different catalysts on the conversion of glucose to 5-HMF [a]

Entry	**Catalyst**	**Conversion/%**	**HMF Yield/mol%**
1	$CrPO_4$	99	63
2[b]	$CrPO_4 + NaH_2PO_4$	97	20
3	NaH_2PO_4	96	26
4	$CrCl_3$	95	15
5	H_3PO_4	98	22

[a] Glucose (1.0 g), Catalyst (0.125 g), NaCl (3.5 g), H_2O (10 mL) and THF (30 mL), 140 ℃, 30 min.

[b] Glucose (1.0 g), $CrPO_4$ (0.125 g), NaH_2PO_4 (0.05 g), NaCl (3.5 g), H_2O (10 mL) and THF (30 mL), 140 ℃, 30 min.

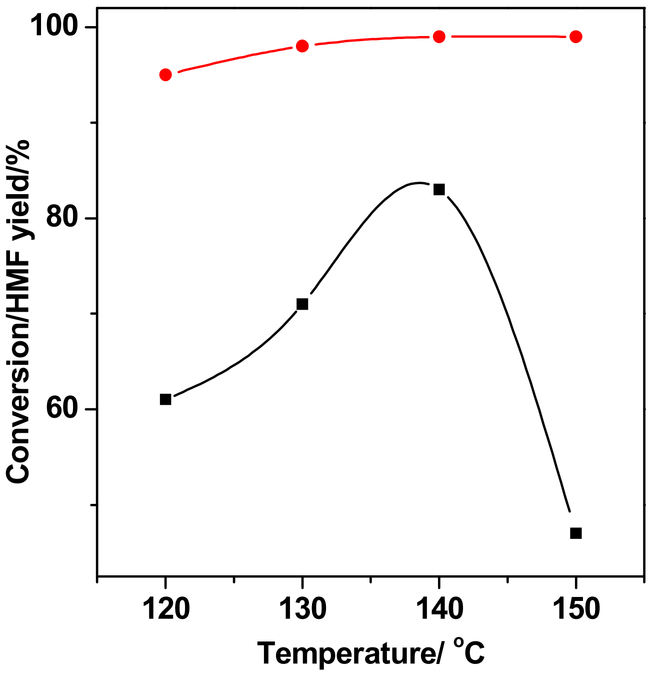


Figure 1 Effects of reaction temperature on (●) fructose conversion and (■) HMF yield. Reaction condition: fructose (1.0 g), NaCl (3.5 g), $CrPO_4$ (0.125g), H_2O (10 mL), THF (30 mL), 15 min.

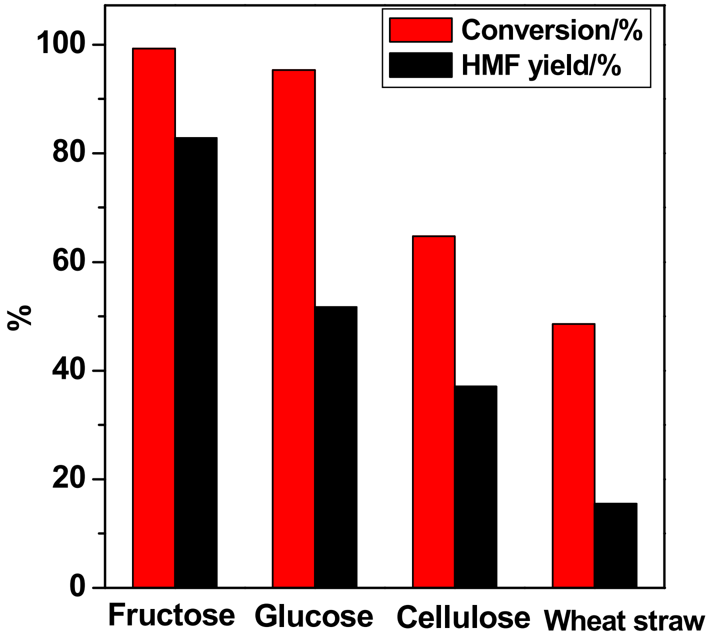
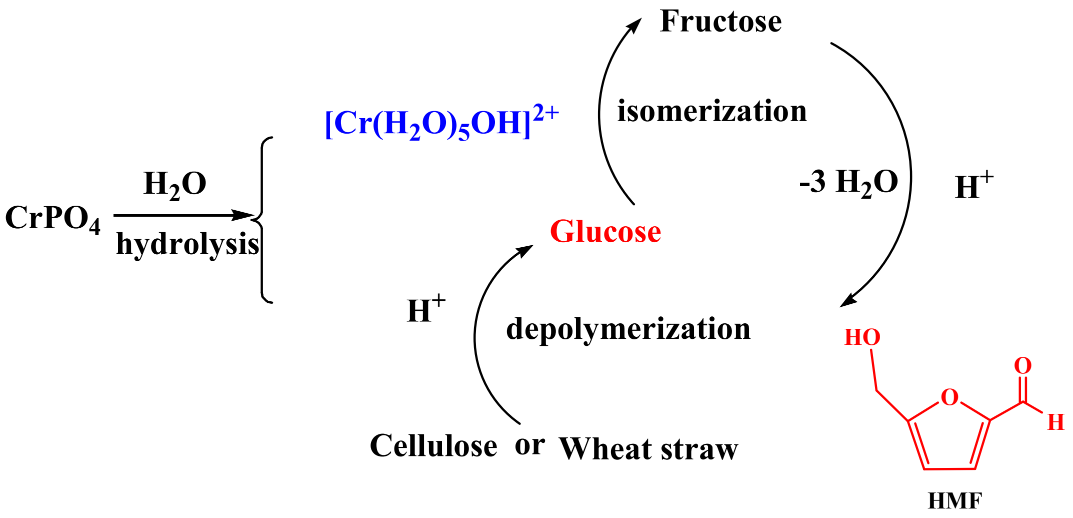
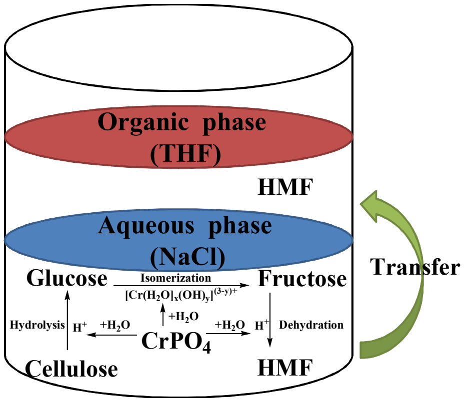


Figure 2 Result for the conversion of different feedstocks to HMF. Reaction condition: feedstock (1.0 g), NaCl (3.5 g), $CrPO_4$ (0.125g), H_2O (10 mL), and THF (30 mL), 140 ℃, 15min.



Scheme 1 A proposed reaction pathways of $CrPO_4$ catalyzed conversion of cellulose to HMF.


Organic phase
(THF)
HMF
Aqueous phase
(NaCl)
Transfer
Glucose
Isomerization
$[Cr(H_2O]_x(OH)_y]^{(3-y)+}$
Fructose
Hydrolysis
H^+
$+H_2O$
$+H_2O$
$+H_2O$
H^+
Dehydration
$CrPO_4$
Cellulose
HMF