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Catalytic transformation of carbohydrates into 5-hydroxymethyl furfural over tin phosphate in a water-containing system

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ABSTRACT

The dehydration of carbohydrates to produce 5-hydroxymethylfurfural (HMF) in the presence of tin salt and hydrogen phosphate is examined. The precipitate freshly formed from $SnCl_4$and $(NH_4)_2HPO_4$ shows a good performance in a water-dimethylsulfoxide (DMSO) mixed solvent. The highest HMF yield achieves 71% at 135 °C for 1 h. The tin valence number, the type of phosphate and the molar ratio of Sn/PO_4 affect the yield of HMF. In addition, the reaction time, temperature and water to DMSO ratio also influence the yield. Glucose and sucrose as the reactant are compared, and the reaction pathways are discussed.

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1. Introduction

At the present time, the liquid fuels and industrial chemicals are mostly derived from the refining of fossil fuels, such as petroleum, coal, and natural gas; however, the rapid consumption of the fossil fuels and the increasingly serious environmental pollutions lead to a great demand for the development of sustainable substitutes of the fossil resources [1,2]. Biomass, which is self-produced by the biosphere in great amount and CO_2-neutral, provides potential substitutes for the fuels and chemicals. Therefore efficient technologies for the transformation of biomass to fuels and chemicals are becoming a hot topic in the chemical research [3–9]. Nowadays, one of the focuses in the field is the dehydration of carbohydrates into 5-hydroxymethylfurfural (HMF), which is an important platform molecule and can be converted to many value-added derivatives [10–15].

Recently, intensive work on the synthesis of HMF from the dehydration of fructose has been reported. Therein, mineral acids, inorganic salts and solid acids have been frequently used as catalysts in water, organic solvents or ionic liquids (ILs) [16]. For example, Tuercke et al. [17] utilized HCl as the catalyst to dehydrate fructose to HMF in a continuous flow microreactor at 185 °C and within 1 min residence time, and achieved a HMF selectivity of 75% at 71% conversion. Tong et al. [18] reported that a 86% HMF yield was achieved from fructose using $FeCl_3$ as the catalyst in *N*-methyl-2-pyrrolidone (NMP) solvent. Ngee et al. [19] found that the conversion of fructose to HMF can be successfully performed with sulfated mesoporous niobium oxide (MNO-S) as the catalyst in a water-DMSO, with an HMF yield of up to 88%. Furthermore, in the dehydration of fructose to HMF, ILs can function both as catalyst and solvent [20–22]. Moreau et al. [23] investigated the production of HMF from sucrose under Amberlyst-15 in a binary solvent composed of dimethyl sulfoxide (DMSO) and ILs, and achieved a HMF yield of 80% in 24 h. Although high yields of HMF have been produced in these systems, the exploration of new, efficient and clean systems is still meaningful. Low cost and environmentally friendly solvent and catalyst are critical for the success of a process in industry [24].

In the synthesis of HMF, water-containing solvent has been considered the ideal and promising reaction medium for the large-scale process. Various metal phosphates showed promising catalytic performances in dehydration reactions [25,26]. Recently NbPO, AlPO, TiPO and ZrPO were tested in glucose dehydration to HMF in water solvent, in which the activity depends on the amount of strong acid sites over the catalysts [27].

In this work, a novel approach for the dehydration of fructose is investigated with the *in situ* generated tin phosphate as the catalyst in a water-dimethylsulfoxide (DMSO) mixed solvent, and a 71% yield of HMF is obtained at 135 °C for 1 h. The *in situ* generated tin phosphate is more efficient than the prepared solid tin phosphate

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Table 1
Dehydration of fructose into HMF with different catalysts and solvent.[a]

Entry	Catalysts	Mole ratio	Solvent	Yield, %
1	$SnCl_4$-$(NH_4)_2HPO_4$	1:2	DMSO:water (65:35, w/w)	71
2	$SnCl_4$-$(NH_4)_2HPO_4$	1:2	DMSO:water (0:100, w/w)	36
3	$SnCl_4$-$(NH_4)_2HPO_4$	1:2	DMSO:water (100:0, w/w)	14
4	SnPO[b]	–	DMSO:water (65:35, w/w)	20
5	$SnCl_4$-Na_2HPO_4	1:2	DMSO:water (65:35, w/w)	70
6	$SnCl_4$-K_2HPO_4	1:2	DMSO:water (65:35, w/w)	70
7	$SnCl_4$-$(NH_4)_3PO_4$	1:1	DMSO:water (65:35, w/w)	64
8	$SnCl_2$-$(NH_4)_2HPO_4$	1:0.5	DMSO:water (65:35, w/w)	25
9	$SnCl_4$	–	DMSO water (65:35, w/w)	38
10	$(NH_4)_2HPO_4$[c]	–	DMSO:water (65:35, w/w)	2

[a] Reaction condition: 1.0 g D-fructose, 30 mol % metal chloride, in 20 g of solvent, reaction time: 1 h, temperature: 135 °C.
[b] 0.5 g SnPO catalyst.
[c] 60 mol % hydrogen phosphate.

catalyst in the reaction. Moreover, the existence of water plays a key role in the reaction.

2. Experimental

2.1. Reagents

Fructose, glucose, sucrose, $SnCl_4$, $SnCl_2$, Na_2HPO_4, K_2HPO_4, $(NH_4)_2HPO_4$, $(NH_4)_3PO_4$ and DMSO were all of analytical grade and bought in Tianjin Guangfu Fine Chemical Research Institute. A standard sample of HMF was purchased from Aladdin Industrial Corporation. Ultrapure water was supplied by an Ultrapure Water System (electrical resistivity = 10^{-16} MΩ cm).

2.2. The preparation of catalyst

White tin phosphate was generated *in situ* with adding $SnCl_4$ and $(NH_4)_2HPO_4$ into the water-containing mixture, and directly used as the catalyst without further treatment. A solid phosphate catalyst Sn–P–O was synthesized with the modification of a reported process in literature [28]. A 0.6 M aqueous solution of disodium hydrogen phosphate (Na_2HPO_4) was added dropwise to a 0.3 M stirred aqueous solution of $SnCl_4$ at room temperature. The obtained precipitate was filtrated and washed with distilled water to a pH 3–4 and then dried in vacuum at 100 °C. The material was then treated with 1 M HNO_3 for 24 h. After the treatment the material was washed with water to a pH 4–5 and dried at 110 °C overnight.

2.3. Dehydration reaction

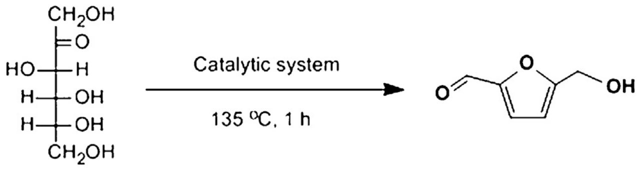
All the dehydration reactions were carried out in a 250 mL sealed stainless steal autoclave with magnetic stirring and automatic temperature controlling. A typical procedure was presented as follows: fructose (1 g), tin chloride (0.56 g, 30 mol% based on fructose), $(NH_4)_2HPO_4$ (0.42 g), water (7 g) and DMSO (13 g) were successively added into the reactor. The reactor was purged with N_2, then preheated to the preset temperature with stirring, and kept at the temperature for a period. After the reaction, the reactor was cooled down in an ice bath and then the slurry was filtrated and the solid was washed with ultrapure water. Therein, the volume of the filtrated liquid was measured with a volumetric flask and the HMF concentration was analyzed with an Agilent 1200 HPLC equipped with both UV and refractive index detectors. Moreover, the effect of reaction time, temperature and DMSO proportions on the fructose dehydration was further studied through changing one of those factors under similar conditions.

2.4. Characterization

The XRD patterns of the phosphate catalysts after treatment were recorded with a D8-Focus diffractometer (BrukerAXS), employing CuKα radiation at 40 kV and 200 mA with a scan speed of 5°/min. The samples were prepared as follows: after stirring in the mixed solvent for 10 min, the *in situ* generated catalyst samples were filtrated and then dried at room temperature in a vacuum for 24 h. The FTIR adsorption spectra of the phosphate catalyst diluted with KBr was recorded with a Nicolet Nexus-870 instrument with a 4 cm^{-1} optical resolution. The samples tested with FTIR were the same ones as those used in XRD. The particle size and distribution of the *in situ* generated tin phosphate in the mixed solvent were measured with a laser particle size analyzer at room temperature (90PALS, Brookhaven Instruments Corp., the United States). In the measurement, after adding chloride and hydrogen phosphate into the solvent, all the samples were stirred for 10 min, and then were quickly transferred into the cuvette for analysis.

3. Results and discussion

The dehydration of fructose was first carried out as a model reaction, presented as Scheme 1, using different catalysts in the water-DMSO mixed solvent. The experimental results are listed in Table 1. The highest HMF yield of 71 % was achieved within 1 h at 135 °C with the $SnCl_4$ to $(NH_4)_2HPO_4$ ratio equaling 1:2 as the catalyst in the water-DMSO mixed solvent (entry1). However, when the reaction was carried out only in pure water or pure DMSO, only 36% and 14% yields of HMF were obtained, respectively (entries 2 and 3). Moreover, when the prepared solid tin phosphate catalyst was employed as the catalyst, the HMF yield is only 20% (entry 4). It is probably due to that the tin phosphate solid catalyst has less acid sites and lower specific surface area than the *in situ* generated tin phosphate in the dehydration process. In addition, the effect of the cations, like Na^+ and K^+, in the phosphate was also examined. As a result, the HMF yields are both 70% when $(NH_4)_2HPO_4$ was replaced by Na_2HPO_4 or K_2HPO_4 with the same ratio to $SnCl_4$ (entries 5 and 6). It exhibits that the cations NH_4^+, Na^+ and K^+ have little influence to the catalytic activity. The combination $SnCl_4$-$(NH_4)_3PO_4$ also gave excellent activity, and a yield of 64% HMF was obtained (entry 7). Here, the lowering of the yield may be attributed to that



Scheme 1. Catalytic dehydration of fructose into HMF.

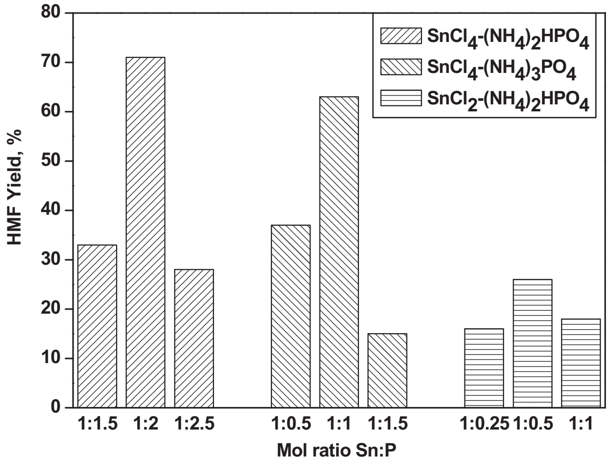


Fig. 1. Effect of the mol ratio of Sn to P on the dehydration of fructose to HMF. Reaction conditon: 1.0 g fructose, 30 mol% Sn, 20 g solvent, DMSO: water = (65:35, w/w), 1 h, 135 °C.

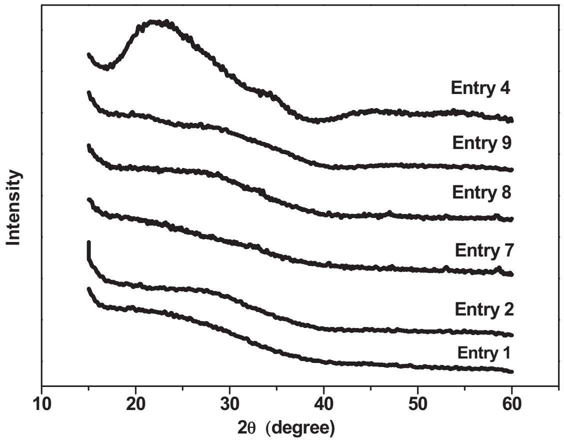


Fig. 2. XRD patterns of the tin phosphate catalysts used in different entries.

the basicity of $(NH_4)_3PO_4$ is stronger than that of $(NH_4)_2HPO_4$. Otherwise, $SnCl_2$ is found less active than $SnCl_4$, and a yield of only 25% HMF was attained with the $SnCl_2$ and $(NH_4)_2HPO_4$ combination as the catalyst (entry 8). Visually, a milk white gel was formed during the reaction when the combination $SnCl_4$-$(NH_4)_2HPO_4$ was used, while white precipitation was generated when the combination of $SnCl_2$-$(NH_4)_2HPO_4$ was used as the catalyst. As comparison, when only $SnCl_4$ or $(NH_4)_2HPO_4$ was employed as the catalyst in the water-DMSO solvent, the yield of HMF was 38% or 2%, respectively (entries 9–10). This shows that the synergy of $SnCl_4$ and $(NH_4)_2HPO_4$ is important for the reaction. The molar ratio of Sn and P is a critical parameter for all the catalyst samples. As shown in Fig. 1, the optimal molar ratios of catalyst $SnCl_4$-$(NH_4)_2HPO_4$, $SnCl_4$-$(NH_4)_3PO_4$ and $SnCl_2$-$(NH_4)_2HPO_4$ are 1:2, 1:1 and 1:0.5.

The *in situ* generated catalytic materials were purified and characterized using different methods. The XRD patterns of these catalysts in Fig. 2 indicate that all the catalysts typically exhibit an amorphous structure. A broad band in the range of about 20°-30° is observed for all the samples. The FT-IR spectra of these solid catalysts were shown in Fig. 3. The broad band in the range of 1100–1200 cm^{-1} is attributed to the O=P=O asymmetric stretching of phosphate. The particle size and the distribution of the *in situ* generated tin phosphate are shown in Fig. 4 and Table 2. It can be seen that the *in situ* generated materials, whose particle sizes–are distributed from 268 nm to 447 nm in the mixed solvent, have higher activity than that with the size 1861 nm formed in pure water and the size 2621 nm formed with only $SnCl_4$ (entries 2 and 9 in Table 2). Fig. 3a and b also shows that entries 1 and 7 produce almost the same particle size distribution, while entries 2 and 9 give very large but similar sized particles. Entry 8 produces a wide particle size distribution within the range of 200–1000 nm.

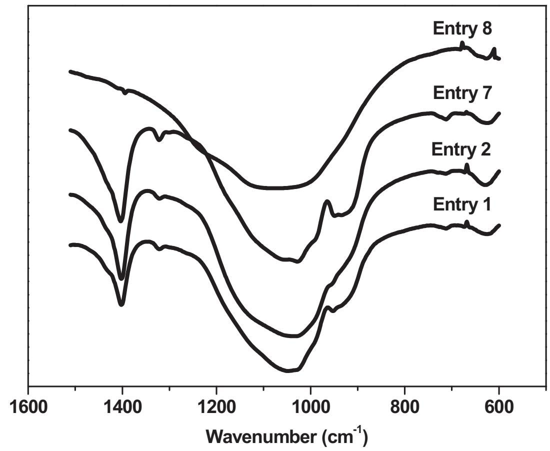


Fig. 3. FTIR spectra in the region of structrual vibration of the phosphates.

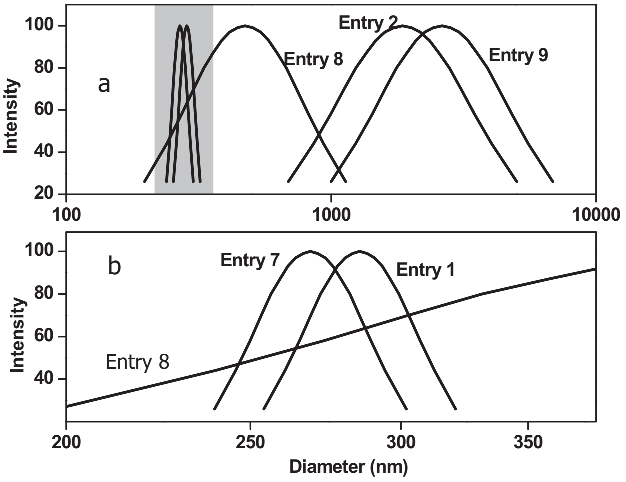


Fig. 4. The particle size distribution of the *in situ* generated tin phosphate catalysts in different entries.

The effect of the reaction temperature on the yield of HMF was examined, and the results are illustrated in Fig. 5, which clearly shows that the optimum temperature is 135 °C in either pure water or the mixed solvent. Moreover, when the temperature increases from 115 °C to 135 °C, the yield of HMF increased rapidly. However, with the further increase of the temperature from 135 °C to 145 °C the HMF yield drops slightly. It is also observed that when the temperature increased from 115 °C to 145 °C, more and more dark humans were generated and the color of the reaction liquid became darker.

The effect of the reaction time under the optimized $SnCl_4$:$(NH_4)_2HPO_4$ ratio and reaction temperature was also

Table 2
The effective particle size of *in situ* generated tin phosphate from Table 1 in the solvent.

Catalyst	Entry 1	Entry 2	Entry 7	Entry 8	Entry 9
Particle Size/nm	285	1861	268	474	2621

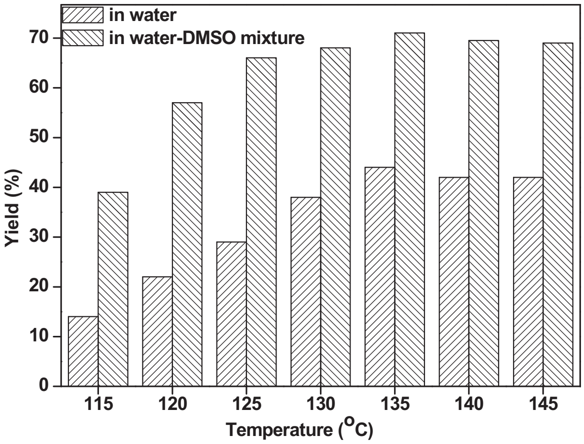


Fig. 5. Effect of reaction temperature on the dehydration of fructose to HMF. Reaction conditon: 1.0 g fructose, 30 mol% $SnCl_4$-$(NH_4)_2HPO_4$ (1:2), 20 g solvent, DMSO: water = (65:35, w/w), 1 h in mixed solvent and 2 h in water.

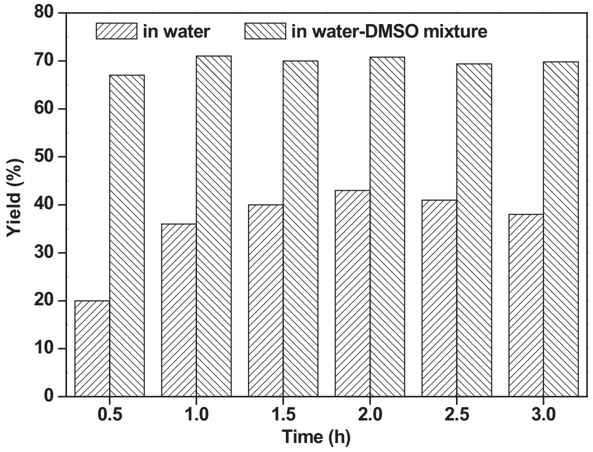


Fig. 6. Effect of reaction time on the dehydration of fructose to HMF. Reaction conditon: 1.0 g fructose, 30 mol% $SnCl_4$-$(NH_4)_2HPO_4$ (1:2), 20 g solvent, DMSO: water (65:35 w/w), 135 °C.

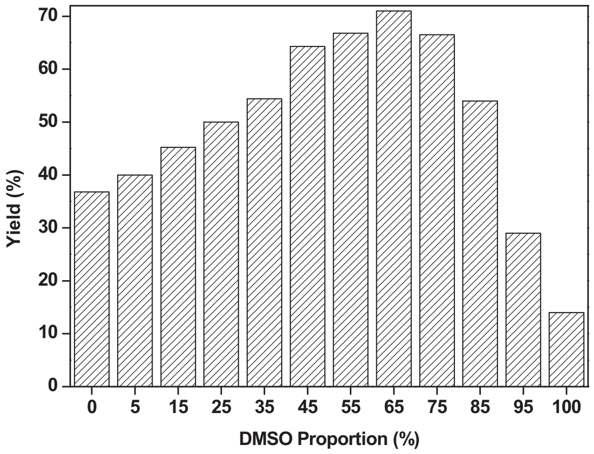


Fig. 7. Effect of DMSO proportions on the dehydration of fructose into HMF. Reaction conditon: 1.0 g fructose, 30 mol % $SnCl_4$-$(NH_4)_2HPO_4$ (1:2), 135 °C and time = 1 h.

Table 3
Dehydration of sugars into HMF with different tin phosphate as catalysts.

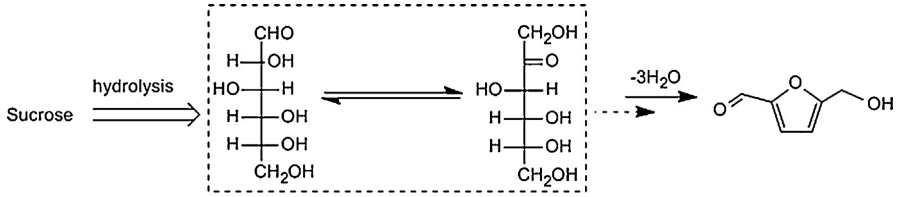
Entry	Reactant	Catalysts	Yield, %
1	GLUCOSE	$SnCl_4$-$(NH_4)_2HPO_4$	11
2	GLUCOSE	$SnCl_4$-$(NH_4)_3PO_4$	33
3	SUCROSE	$SnCl_4$-$(NH_4)_2HPO_4$	45
4	SUCROSE	$SnCl_4$-$(NH_4)_3PO_4$	44

Reaction condition: 1.0 g glucose or sucrose, water/DMSO (w/w) = 35: 65, in 20 g of solvent, reaction temperature: 135 °C, time: 1 h.

evaluated in two solvents, water and water/DMSO mixture, and the results are presented in Fig. 6. The trend of changing of the HMF yields in water and in the mixed solvent is different. In water-DMSO mixed solvent the HMF yield was gradually increased during the beginning 0.5-1.0 h period and reached the maximum value of 71 % after1 h, and then HMF yield remained unchanged in the following period up to 3 h, indicating a protecting effect of DMSO on the product HMF. While in water the yield of HMF reaches the maximum of 43% at 2 h, after that the HMF yield decreases to 33% in the next 1 h.

The effect of the water and DMSO ratio was tested in the dehydration reaction and the results are depicted in Fig. 7. The HMF yield was 32% in aqueous media, and was increased gradually along with the increase of the DMSO percentage in the mixed solvent to the maximum yield of the HMF 71% with a 65% ratio of DMSO, and then the HMF yield was decreased with the further increase of the ratio of DMSO and only a 14% HMF yield was obtained in pure DMSO. Most importantly, DMSO is an aprotic basic solvent which hinders the deep dehydration of fructose to formic acid and levulinic acid and the polymerization into humins. Nevertheless, it is difficult to form tin phosphate catalyst in the pure DMSO solvent, so that the yield of HMF becomes low when the ratio of DMSO is too high.

The dehydration of glucose and sucrose to HMF using the $SnCl_4$-$(NH_4)_2HPO_4$ and the $SnCl_4$-$(NH_4)_3PO_4$ combinationsin the water-DMSO solvent was also examined. The results are listed in Table 3. The HMF yield in the reaction of glucose with $SnCl_4$-$(NH_4)_2HPO_4$ as catalyst is only 11%, which is much lower than the HMF yield of 33% obtained with the $SnCl_4$-$(NH_4)_3PO_4$ catalyst (entries 1–2). However, for the reaction of sucrose, the catalytic activities of $SnCl_4$-$(NH_4)_2HPO_4$ and $SnCl_4$-$(NH_4)_3PO_4$ catalyst systems are similar, with the HMF yields being 45% and 44%, respectively (entries 3–4). Scheme 2 illustrates the process for the conversion of sucrose to HMF. Herein, fructose, glucose and sucrose are converted to each other with isomerization reactions and can be in equilibrium [29].



Scheme 2. General conversion route of sucrose to HMF.

4. Conclusion

The efficient dehydration of different sugars to produce HMF has been achieved in the presence of tin salt and hydrogen phosphate in water-DMSO mixed solvent. The *in situ* generated tin phosphate catalysts presented high catalytic activity. With fructose as the reactant, a 71% yield of HMF was obtained within 1 h at 135 °C. The catalyst formed from $SnCl_4$-$(NH_4)_2HPO_4$ has higher yield of HMF than that from $SnCl_4$-$(NH_4)_3PO_4$ and $SnCl_2$-$(NH_4)_2HPO_4$. The *in situ* generated phosphate catalysts in the mixed solvent exist in a amorphous form, and have a small particle size resulting in high specific surface area. Moreover, when the dehydration reaction occurs within 1 h at 135 °C with a 65% DMSO ratio in the solvent, the HMF yield is the highest.

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