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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.

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

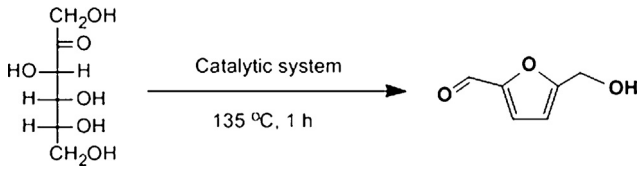
All the dehydration reactions were carried out in a 250 mL sealed stainless steal autoclave with magnetic stirring and automatic temperature controlling. A typical procedure was presented as follows: fructose (1 g), tin chloride (0.56 g, 30 mol% based on fructose), $(NH_4)_2HPO_4$ (0.42 g), water (7 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.