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Importance of the synergistic effects between cobalt^{oo225A} sulfate and tetrahydrofuran for selective production of 5-hydroxymethylfurfural from carbohydrates

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Abstract

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In this study, an effective catalytic system (CoSO₄·7H₂O/THF) for selective conversion of fructose to 5-hydroxymethylfurfural (HMF, yield: 88%), was developed. The synergistic effects among Co²⁺, SO₄²⁻, the crystal water and THF were crucial for achieving selective dehydration of fructose to HMF. Co²⁺ worked as Lewis acid for catalyzing mainly dehydration of fructose to HMF but not the further decomposition of HMF to levulinic acid. THF could help to retain HMF while CoSO₄ could coordinate with HMF, enhancing the thermal stability of HMF in THF. The crystal water in cobalt sulfate could help to coordinated with fructose, which facilitated the conversion of fructose the dehydration reactions. CoSO₄·7H₂O/THF catalytic system could also catalyze the conversion of inulin and cellulose into HMF. The main advantages for CoSO₄·7H₂O/THF catalytic system are the low cost, the easy recycle of CoSO₄·7H₂O/

Keywords:fructose/glucose/inulin/cellulose,5-hydroxymethylfurfural,CoSO4·7H2O/THF, synergistic effects, acid-catalysed conversion

5-Hydroxymethylfurfural (HMF) is an important platform chemical for manufacturing the value-added products such as 2,5-diformylfuran [1], 2,5-furandicarboxylic acid (FDCA) [2, 3] or be potentially used in the prevention and treatment of cardiovascular disease [4]. How to efficiently and selectively produce HMF from monosaccharides [5-7], cellulose [8, 9], or biomass [10-12] has been a research foci in biorefinery. Catalyst and reaction medium are essential parameters affecting selectivity for HMF production from biomass or biomass derived sugars [13, 14].

In existing literatures, the acid catalysts employed for the conversion of the sugars to HMF include mineral acids [15], solid acidic resin catalysts [16, 17], organic acids [18] and some salts with Lewis acid sites [19-21]. Mineral acids and solid acidic resin catalysts like Amberlyst 70 are Brønsted acids and they could not only catalyze the dehydration of fructose to HMF, but also the further conversion of HMF to levulinic acid (LA), due to their strong acidity [22]. The organic acids have lower acidity and the effectiveness for suppression of the secondary decomposition of HMF strongly depends on the pH of the reaction medium [23]. Furthermore, how to separate the liquid organic acid and HMF is a remaining issue to be considered. As for the use of salts as the Lewis acid catalysts for the conversion of sugars to HMF, Zhao and the co-workers [24] found that CrCl₂ could effectively transform glucose into HMF in ionic liquid-water. CrCl₂ dissolved in ionic liquid-water and interacted with ionic liquid to form CrCl₃⁻, which played an important role in the isomerization of glucose into fructose through improving the hydride transfer. Nevertheless, how to separate HMF from ionic liquid, which is not volatile, is also an issue to be resolved.

Distillation is a simple method for the separation of products from reactants, which, however, would be energy-intensive if the boiling point of the reaction medium (solvent) is

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too high. Unfortunately, the separation of HMF from ionic liquid via distillation 350 decorrection cost-effective. Furthermore, the ionic liquid used in the work is not an abundantly available feedstock with cheap price. It is necessary to find a simple, low cost while robust catalytic system for the effective conversion of sugars to HMF. The catalytic system should include both the catalyst that could achieve the selective conversion of the sugars to HMF and the reaction medium that could achieve the cost-effective separation of HMF from the reaction medium. Although dimethyl sulfoxide (DMSO) could effectively inhibit the secondary decomposition reactions to achieve high yield of HMF [25, 26], DMSO has a high boiling point and was difficult to be separated from HMF.

With this in mind, we made an effort to develop the effective catalytic system for the conversion of sugars to HMF by selecting the organics with the low boiling point as the reaction medium and the salts with the properties of Lewis acid as the catalyst. The use of the Lewis acid catalyst, instead of Brønsted acids, was to minimize the secondary decomposition of HMF. Initially, we screen the catalytic activity of some sulfates for the conversion of fructose/glucose in tetrahydrofuran (THF) and found that CoSO₄·7H₂O/THF was an effective catalytic system for the selective conversion of fructose to HMF, with the yield of HMF up to 88%. The coordination between CoSO₄·7H₂O and THF played an essential role for the selective conversion of fructose into HMF. In addition, we found that the CoSO₄·7H₂O/THF could also effectively catalyse the conversion of inulin and cellulose into HMF with no organic acid by-products like LA formed. More importantly, CoSO₄·7H₂O has a negligible solubility in THF and can be separated from the liquid mixture via simple filtration, while THF and HMF can also be separated via distillation at low cost, due to the high volatility of THF.

2. Materials and Methods

2.1 Materials

Fructose, glucose, the metal salts (Na₂SO₄, K₂SO₄, Fe₂(SO₄)₃, NiSO₄·6H₂O, CuSO₄, CoSO₄·7H₂O, CoCl₂·6H₂O, Co(NO₃)₂·6H₂O, Co(C₂H₃O₂)₂·6H₂O) and the organic solvents (THF, DMSO, methanol, ethanol, isopropanol, acetic acid, acetone and furfural) were analytical grade and were supplied from Sinopharm Chemical Reagent Co., Ltd. Inulin was purchased from Shandong west Asia chemical industry Co., Ltd. Cellulose (AR, partical size: 65 μm) and HMF (99%) were purchased from Shanghai Macklin Biochemical Co., Ltd.

2.2 Catalytic tests

The catalytic conversion of sugars/inulin/cellulose to HMF with the salts as catalyst and the different solvent as reaction medium was conducted in an autoclave reactor with a volume of 10 mL. After loading feedstock, catalyst, and solvent, the reactor was purged with pressurized N_2 (99.99%) for removing the residual air for 3 times, which was then heated to the targeting temperature in 10 min and maintained for 120 min. After finishing the experiments, the reactor was quenched, and the liquid products as well as the solid products were then collected and separated for further analysis.

2.3 Characterizations

The distribution of the liquid products was analysed by a Shimadzu GC-MS-2020 plus equipped with a Wax pillar column (30 m of length, 0.25 mm of internal diameter, 0.25 um of film thickness). The temperature of the column was initially maintained at 50°C for 3 min and then raised to 250°C with a ramping rate of 10°C/min and hold at 250°C for 3 min. The products were identified with a standard library (NIST MS Search 2014). The yields of LA

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(1)

and HMF were calculated via the following equations:

$$Y_{HMF-1} (\%) = \frac{Mole \text{ of HMF produced}}{Mole \text{ of glucose/fructose loaded}} \times 100\%$$

$$Y_{HMF-2} (\%) = \frac{Mass of HMF produced}{Mass of inulin/cellulose loaded} \times 100\%$$
(2)

$$Y_{LA-1} (\%) = \frac{\text{Mole of LA produced}}{\text{Mole of glucose/fructose loaded}} \times 100\%$$
(3)

$$Y_{LA-2} (\%) = \frac{\text{Mass of LA produced}}{\text{Mass of inulin/cellulose loaded}} \times 100\%$$
(4)

Y_{HMF-1}: the yield of HMF from glucose/fructose;

Y_{HMF-2}: theoretical yields of HMF from inulin/cellulose;

Y_{LA-1}: the yield of LA from glucose/fructose;

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Y_{LA-2}: theoretical yields of LA from inulin/cellulose;

The concentration of glucose or fructose after the catalytic tests was detected by a high-performance liquid chromatography (HPLC, Shimadzu) equipped with a size-exchange column (Shodex, SH1011 of type, 30 m of length, 8 mm of internal diameter). The procedures were detailed as follows. The liquid sample, without further dilution, was fed into the SH1011 column directly for the analysis with a mobile phase (0.01 mol/L of H_2SO_4). The temperature of column was set at 50°C and a flow speed of 0.6 mL/min for the mobile phase was employed. Conversion of glucose/fructose was calculated via the following equation:

The conversion of sugars (%) =
$$\frac{\text{Mole of sugar consumed}}{\text{Mole of glucose/fructose loaded}} \times 100\%$$
 (5)

A UV-fluorescence spectrometer (Shimadzu, RF-6000) was used to characterize the soluble polymer with the π -conjugated structure. The testing conditions were set as below: the range

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of excitation wavelength: 200–400 nm; the range of emission wavelength: 250-500 mgo225A scanning speed: 600 nm/min. Prior to the measurement, the residual liquid after the reaction was diluted to four hundred ppm with anhydrous ethanol as the solvent. The different colours represent the different fluorescence intensity.

The hydroxyl and other groups in the mixed of solvent and sugars were characterized by using a Nicolet iS50 FT-IR spectrometer at room temperature. 1 mg of the sugar and 199 mg of potassium bromide powder were mixed and grounded evenly, and then added a drop of solvent under an infrared light. The mixture was pressed into a thin disc at the pressure of 15 MPa. The thin disc was tested by using an infrared spectrometer.

UV-Vis spectra of various solvents dissolved $CoSO_4 \cdot 7H_2O$ was measured by a Metash UV-visible photometer (UV-8000S). The scanning wavelength was from 800 to 300 nm. The right solution was measured as soon as it was prepared.

3.Results and discussion

3.1 Conversion of glucose/fructose with various metal sulfates in THF

In the initial trials, a series of metal sulfates were selected as the catalysts to estimate their capabilities for the conversion of glucose/fructose into HMF in THF, an aprotic solvent resembling DMSO but with a much lower boiling point (189°C versus 66°C). As shown in Table 1, the full-conversions of glucose/fructose were obtained for all the runs, while the different metal sulfates displayed distinct catalytic behaviors. For the blank experiments in the absence of salts, the yield for HMF from fructose (13.8%) was higher than that from glucose (4.9%) (Entry 1 and 2, Table 1). This was expected as the dehydration of the furanose form of fructose directly produced HMF, while glucose has to isomerize into fructose form firstly before being further transformed into HMF [27].

The typical alkali metal sulfates (Na_2SO_4, K_2SO_4) could neither enhance the isomerization of glucose to fructose nor improve the formation of HMF from either glucose or fructose. Conversely, Na_2SO_4 or K_2SO_4 coordinated with the sugars, interfering with their

conversion to HMF and leading to their polymerization to form the insoluble polymers of the Online yield of coke: glucose-Na₂SO₄: 41.5%, frucose-Na₂SO₄: 77.8%, glucose-K₂SO₄: 50.9%, fructose-K₂SO₄: 63.3%).

Fe₂(SO₄)₃ can hydrolyze partially in water and create an acidic reaction medium, which, however, was not the case in THF. Instead of hydrolysis, it was believed Fe₂(SO₄)₃ coordinated with the sugars, promoting the retrograde aldol condensation of the sugar to form acetic acid and the polymers (the yield of coke: glucose-Fe₂(SO₄)₃: 26.5%, glucose-Fe₂(SO₄)₃: 50.8%,). CuSO₄, in comparison to Fe₂(SO₄)₃, could not only improve the dehydration of fructose into HMF in THF (Entry 9 and 10, Table 1), but also the further decomposition of HMF to LA. CuSO₄ clearly could catalyse the hydrolysis reactions, as also evidenced by the conversion of glucose to LA (Entry 9, Table 1). Encouraged by this interesting result, other divalent transition-metal salts were also used in the conversion of glucose/fructose into both HMF and LA, especially for the formation of HMF from fructose (Entry 11 and 12, Table 1). However, NiSO₄·6H₂O could also catalyse the retrograde aldol condensation of the sugars to form acetic acid.

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 $CoSO_4 \cdot 7H_2O$ also catalysed the formation of acetic acid and selectively promoted the dehydration of fructose to HMF with the yield reaching 79.3% (Entry 13 and 14, Table 1). The cobalt ions were probably active for the dehydration of fructose to HMF. However, if $CoCl_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Co(C_2H_3O_2)_2 \cdot 6H_2O$ were used as the catalysts, the yield of HMF decreased significantly or the dehydration of fructose could not take place at all (Entry 15-20, Table 1). The results indicated the synergistic effects between cobalt ion and the sulfate in $CoSO_4$ must exist. Either the cation or the anion or both could coordinate with fructose to facilitate the dehydration of fructose. Nevertheless, whether the synergistic effects between cleared

from the above results. Our previous studies showed reaction medium played significant of the solution of the solid acid resin catalysts [28, 29]. For the salt catalysts, they have different solubilities in different solvents and coordination status. How the solvent with the distinct properties affect the catalytic activity of the $CoSO_4$ was further investigated.

3.2 Conversion of glucose/fructose in various solvents

Some typical aprotic solvents (acetone, DMSO THF, furan and furfural) and protic solvents (methanol, ethanol, isopropanol, water and acetic acid) were employed in the conversion of glucose/fructose. The results displayed in Table 2 indicated that solvents significantly impacted the activity of CoSO₄·7H₂O catalyst. DMSO is a well-known solvent for achieving high yields of HMF from fructose dehydration, as DMSO could coordinate with HMF and prevent the further decomposition of HMF to LA and formic acid [25]. Nevertheless, in DMSO, the yields of HMF were negligible with CoSO₄·7H₂O as the catalyst. This result clearly suggested, from an indirect angle, that the synergistic effects between CoSO₄ and THF existed and was crucial for achieving of the high yields of HMF.

The UV-fluorescence results for characterizing the soluble polymers showed (Figure 1c) the significant polymerization of fructose in DMSO, while the polymerization reactions in THF were negligible (Figure 1c and d).

Although the yield of HMF reached 40.9% in acetone, acetone was not an ideal solvent for dehydration of fructose. Acetone contains α -hydrogen and carbonyl functionalities, which could trigger aldol condensation and polymerization with the fragment of sugars [30, 31], leading to the decrease of HMF production. Alcohols could protect the sugars or furans from polymerization [32-34]. Nevertheless, alcohols could react with HMF via acetalization and/or etherification reactions [35]. As shown in Table 2 (Entry 7-12), CoSO₄ could effectively The substances with π -conjugated structures could be detected by UV-fluorescence spectrophotometer [36,37]. The UV-fluorescence spectra (Figure 1a) showed fructose in water mainly polymerized to form the soluble polymers with π -conjugated structures. The aprotic solvent like furan or furfural could facilitate the dehydration of fructose to HMF. Nevertheless, these furans are very reactive to polymerization reactions [38] and could cross-polymerize with the sugars or HMF [39], diminishing the production of HMF. The liquid products from the conversion of the sugars in methanol, ethanol, THF and DMSO were characterized with FT-IR. The results (Figure 2a and 2b) were generally in line with those in Table 2. The carbonyl group at 1670 cm⁻¹ belonged to HMF while that at 1713 cm⁻¹ was assigned to LA. In THF, the carbonyl group belonging to HMF was the dominate one. Interestingly, in DMSO the absorption peak ca. 1100 cm⁻¹ was weakened.

DMSO possibly coordinate with the sugars, interfering with the coordination of the sugars with $CoSO_4$ and then negatively affecting the dehydration of the sugars. The above results showed that THF as the reaction medium could facilitate the selective conversion of fructose to HMF, while water could not. The dehydration of fructose produces water, while the $CoSO_4 \cdot 7H_2O$ catalysts used contains water. The water from fructose or the catalysts thus might negatively impact the production of HMF, which was further investigated.

3.3 Roles of water on the conversion of glucose/fructose

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The amount of fructose loaded determined the amount of water produced from the dehydration of fructose. Hence, the effects of fructose loading on the formation of HMF were

its catalytic activity.

investigated and the results were displayed in Table S1. If the amount of fructose loaded way at the Online lower than 0.1 g, LA, derived from the ring-opening and decomposition of HMF, could not be Catalysis Science & Technology Accepted Manuscript formed. HMF was the main product and its yield was higher with the loading of 0.04 g than with 0.02 g (88% versus 56.9%). The further increase of loading of fructose led to a remarkable decrease of HMF production, while enhanced the production of LA. THF is not a good solvent to dissolve $CoSO_4$ while water is (3.6 g THF only dissolved 0.54 mg $CoSO_4$). The presence of a small amount of water seemed to aid the catalytic activity, while too much water produced from the dehydration of fructose facilitated the formation of LA. The solvation or hydration of CoSO₄ with water would change its coordination status and impact To further understand the effects of water on catalytic activity and the decomposition of

HMF to LA, the conversion of glucose/fructose in the mixture of THF/water with varied ratio of water was further investigated. The results in Table S2 showed, after removing the crystal water in the cobalt sulfate, the CoSO₄ catalyst showed little activity for the conversion of glucose to HMF, while the yields of HMF from fructose were also much lower $CoSO_4$ than that over CoSO₄·7H₂O (3.1% versus 25.7%). The crystal water in CoSO₄·7H₂O was clearly crucial for maintaining activity of the catalysts. Nevertheless, with external water added, glucose and fructose behaved differently towards the formation of HMF. For glucose, the addition of more water promoted its conversion to HMF, and only with the proportion of water reaching 70%, the HMF started to decompose to LA. With fructose as a feedstock, the addition of water led to a substantial decrease of the yields of HMF, while no LA were detected. For glucose, it needs to isomerize to fructose for further conversion into HMF [40]. With the addition of external water, CoSO₄ would be dissolved and the generated cation and/or anions might promote the isomerization of glucose. For fructose, the only step required for its conversion to HMF is the dehydration reactions, and the externally added water,

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obviously, did not favor the dehydration of fructose. Further to this b_{OI} under other sub-supercritical conditions, water acted as both acid and base [41], which probably promoted the polymerization of fructose/HMF. The above results indicated that the crystal water in cobalt sulfate was essential for the conversion of fructose into HMF. The synergistic effects among cobalt ion, the sulfate functionality and the crystal water were crucial for maintaining the high activity for the dehydration of fructose to HMF. In addition, the loading of CoSO₄ also significantly impacted the conversion of glucose/fructose to HMF, as shown in Table 3.

With either glucose or fructose as the feedstock, the increase of the loading of the cobalt sulfate initially enhanced the yields of HMF while diminished the formation of HMF if the loading of cobalt sulfate was too high. The higher loading of the cobalt sulfate would introduce too much crystal water, which might negatively impact the formation of HMF. The results herein and in the Section 3.2 clearly indicated that THF was a favourable reaction medium for the production of HMF from fructose, the detailed reason for this was further explored.

3.4 The role of THF in the high-yield catalytic system

HMF is an intermediate product from the conversion of fructose into LA [42], and how to suppress the conversion of HMF to LA is crucial to achieve a high selectivity of HMF. In DMSO, a higher yield of HMF could be achieved as DMSO could effectively prevent its further decomposition to LA [43]. THF might also have such effect, the thermal treatments of HMF in THF and other solvents in both the absence and presence of cobalt sulfates, with the purpose of comparison, were conducted. The results were shown in Table 4 and Figure 3.

More interestingly, with the presence of $CoSO_4$, the recovery rate of HMF is even higher (95.8%) (Entry 6, Table 4), indicating that $CoSO_4$ could not catalyse the further decomposition of HMF and even could coordinate with HMF, enhancing its stability in THF.

This is very different from the Brønsted acid catalysts, which could catalyse₁₀ both the ^{Coline} dehydration of fructose to HMF and the further decomposition of HMF to LA [44]. In water, in the presence of CoSO₄, the recovery rate of HMF was also higher than that in absence of CoSO₄. The significant degradation of HMF in water is mainly due to the acid/base roles of water played under the sub-supercritical conditions [45]. Acetic acid is a carboxylic acid, which catalyzed the degradation of HMF via probably the polymerization reactions, as evidenced by the deep color of the resultant solution with acetic acid or water as the reaction medium (Figure 3).

The recovery rates of HMF in ethanol, isopropanol and DMSO were also high but only in the absence of CoSO₄ (Entry 1-3, Table 4). In ethanol and isopropanol, the presence of CoSO₄ resulted in the conversion of HMF via etherification to form 5-ethoxy-methyl-furfural or 5-isopropoxy-methyl-furfural, respectively (Figure S1). The colour of the resulting solution became deeper, indicating the occurrence of the polymerization reactions (Figure 3). In the presence of Brønsted acid, DMSO could protect HMF and prevent its further conversion, while, in the presence of CoSO₄, the degradation of HMF proceeded remarkably (Figure 3). THF could coordinate with HMF, while the presence of CoSO₄ further strengthen the coordination effects, enhancing the stability of HMF in the catalytic system. This is a pre-requisite for achieving high yields of HMF. The coordination between cobalt sulfate and the reaction medium could be further confirmed with the UV-Vis absorption characterization.

3.5 The coordination between cobalt sulfate and THF

UV-Vis absorption spectra for the mixture of $CoSO_4 \cdot 7H_2O$ with ethanol, DMSO, H_2O or THF and the test conditions were shown in Figure S2. H_2O - $CoSO_4 \cdot 7H_2O$ had a characteristic peak at 502 nm, which originated from the d-d transition from cobalt itself. DMSO- $CoSO_4 \cdot 7H_2O$ showed the absorption at 555 nm in the visible light region, while the

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absorption of the THF-CoSO₄·7H₂O showed a distinct absorption at ca. 510_{10} mm²/D⁶CO⁶O_{2225A} ethanol-CoSO₄·7H₂O, no clear absorption peaks were visible. The different peaking wavelength indicated the distinct patterns for the coordination between cobalt sulfate and the solvent. The different coordination also led to the changed colours of the mixture of CoSO₄/solvent, as shown in Figure S3. CoSO₄ fully dissolved in water or DMSO, partially dissolved in ethanol while slightly dissolved in THF [46]. Nevertheless, the small amount of CoSO₄ in THF substantially changed the coordination status with THF, which was further investigated with FT-IR study.

The FT-IR spectra of $CoSO_4$ in THF showed three types of hydroxyl group in the region of 3600-3200 cm⁻¹ (Figure 4b). The first peak at 3222 cm⁻¹ belonged to O–H of the hydrogen bonds in water, as compared with the spectra of the pure water. The second peak at 3350 cm⁻¹ belonged to the hydroxyl group coordinated with cobalt ions but having blue shift from 3222 to 3350 cm⁻¹, as also compared with the absorption spectra for $CoSO_4$ -H₂O. The third peak at 3509 cm⁻¹ was attributed to the hydroxyl group which was affected by the hydrogen bond between water and THF. If $CoSO_4$ could coordinate with the hydroxyl group in water, it could also coordinate with the hydroxyl group in fructose and in HMF, impacting the dehydration of fructose and the further degradation of HMF.

In addition to this, the coordination between the solvents and sulfate ions were clearly displayed in Figure 4a. The S=O group of $CoSO_4$ had a stretching vibration at 1094 cm⁻¹. The addition of water forms the hydrogen band between water and shift the absorption of the S=O to a lower wavenumber (from 1094 to 1082 cm⁻¹). The same scenario happened for $CoSO_4$ -ethanol. The dissolution of cobalt sulfates, as discussed earlier, was improved owing to the coordination between sulfate ions and ethanol or water.

Besides, DMSO itself had an S=O group, which had two peaks at 1019 and 996 cm⁻¹ (Figure 4a) and shifted to 1042 and 1020 cm⁻¹ when $CoSO_4$ coordinated with DMSO.

Meanwhile, the S=O group belonging to CoSO₄ shifted from 1124 to 1094 cm⁻¹. This section of the control of the coordination between DMSO and cobalt ions was stronger than hydrogen band so that the special peak of S=O group shift to a higher wavenumber. THF could not interact with cobalt or sulfate ions directly and only form the hydrogen band with crystal water of CoSO₄ so that there was a slight blue shift for the special peak of S=O from 1094 to 1096 cm⁻¹. That is to say, the coordination between CoSO₄ and THF depended on the hydrogen bond formed from crystal water and CoSO₄ or THF. The organic phase with higher volume ratio to aqueous phase was responsible for the excellent catalytic capability [47]. Here also, the catalytic system without water did not have the coordination between CoSO₄ and THF and thus did not aid catalytic performance (Entry 1 and 8, Table S2). Nevertheless, too much water could destroy the balance between CoSO₄, crystal water and THF and negatively affected the conversion of fructose to HMF.

The above discussions showed that the interaction between the cobalt sulfate and the crystal water could improve the dehydration of fructose. The synergies among cobalt sulfate, crystal water and THF in $CoSO_4$ /THF catalytic system promoted the formation of HMF from fructose.

3.6 The conversion of inulin and cellulose in CoSO₄/THF catalytic system

To further investigate the catalytic behaviors of $CoSO_4/THF$ catalytic system, the conversions of inulin and cellulose were conducted and the results were compared with that in sulfuric acid/THF system. The yields of HMF from the conversion of fructose, inulin and cellulose with 0.1 M of H₂SO₄ as the catalyst in THF were zero (Entry 1-3, Table 5).

The resulting products showed a black color, indicating the dominance of the polymerization reactions. The concentration of sulfuric acid applied was too high, leading to the quick polymerization of the reactants. With the decreasing concentration of sulfuric acid,

the yields of HMF was increased significantly, but was much lower than that in CoSO4/THECO225A catalytic system (Entry 2, Table S3). Furthermore, the coordination between HMF and THF prevented the further decomposition of HMF to LA with sulfuric acid as the catalysts. In CoSO₄/THF catalytic system, both the reaction temperature and the amount of CoSO₄ loaded affected the yields of HMF produced from inulin. Under the experimental conditions investigated, the maximum yield of HMF reached 40.1% from the hydrolysis of inulin, which was much higher than that in sulfuric acid/THF at the same temperature (Entry 9-14, Table S4).

As for cellulose, under the conditions employed the maximum yield of HMF was 35.3% (Entry 16, Table S4), which was also much higher than that in sulfuric acid-THF system and was even comparable to that from glucose. Inulin is mainly composed by fructose unit while cellulose is composed by glucose unit. Nevertheless, although the yields of HMF from fructose and glucose were significantly different (Table 3), the yields of HMF from the two macro sugar polymers were not significantly different. It seemed the depolymerization of inulin and cellulose determine the yields of HMF. How to enhance the catalytic efficiency of CoSO₄/THF catalytic system deserves further attention.

4. Conclusions

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In summary, this study investigated catalytic conversion of fructose and glucose for the production of HMF using cobalt sulfate as the catalyst in various reaction medium. The results showed that in THF the sulfates like Na_2SO_4 , K_2SO_4 and $Fe_2(SO_4)_3$ strongly coordinated with the sugars, interfering with their dehydration to HMF and promoting their polymerization. In comparison, the coordination of $CoSO_4.7H_2O$ with especially fructose in THF mainly catalyzed the dehydration reactions for the selective production of HMF with a maximum yield of 88%. There existed synergistic effects between cobalt ion and the sulfate in

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 $CoSO_4 \cdot 7H_2O_2$, as other cobalt salts such as $CoCl_2$, $Co(NO_3)_2$ and $Co(C_2H_3O_2)_2$, show $CoCl_2O_2$ insignificant activity for catalyzing the dehydration of fructose. Nevertheless, CoSO₄·7H₂O was only effective for the dehydration of fructose in THF, but not in other solvents such as DMSO, water, acetone, acetic acid, furan, furfural, methanol, ethanol and iso-propanol. This is because THF could help to retain HMF in the reaction medium while CoSO₄ did not catalyze the further decomposition of HMF and even could coordinate with HMF, enhancing its stability in THF. Furthermore, the characterizations showed that the crystal water in cobalt sulfate could help to coordinated with fructose, which facilitated the conversion of fructose the dehydration reactions. The synergistic effects among cobalt ion, the sulfate functionality, the crystal water and THF were crucial for achieving the high selectivity for the dehydration of fructose to HMF. The CoSO₄·7H₂O/THF catalytic system also worked for the conversion of inulin and cellulose into HMF, but the yields of HMF from these macro sugar polymers have much room to be further improved. The biggest advantage for the CoSO₄·7H₂O/THF catalytic system is the low cost, the easy recycle of CoSO₄·7H₂O catalyst and the easy separation of HMF from the volatile THF. The potential of such catalytic system for the conversion of other catalytic systems could also be further explored.

Conflicts of interest

There are no conflicts of interest to declare.

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Table 1 The conversion of glucose or fructose in THF^a

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Entry Catalyst		Sugar	Con.	Yield (%)			
					Acetic		
			(%)	Furfural	acid	LA	нмг
1	No catalyst	glucose	100	0.3	0	0	4.9
2	No catalyst	fructose	100	0.9	0	0	13.8
3	Na_2SO_4	glucose	100	0	0	0	0.1
4	Na_2SO_4	fructose	100	1.8	0	0	0.1
5	K_2SO_4	glucose	100	0	0	0	0.1
6	K_2SO_4	fructose	100	1.3	0	0	0.1
7	$Fe_2(SO_4)_3$	glucose	100	0	4.7	0	0
8	$Fe_2(SO_4)_3$	fructose	100	0.4	7.2	0.1	0
9	CuSO ₄	glucose	100	0.3	0	8.4	0
10	CuSO ₄	fructose	100	2.1	0	8.6	14.1
11	NiSO ₄ ·6H ₂ O	glucose	100	1.0	5.2	6.4	12.2
12	NiSO ₄ ·6H ₂ O	fructose	100	0.9	11.8	2.4	32.7
13	CoSO ₄ ·7H ₂ O	glucose	100	1.7	6.8	14.5	14.7
14	CoSO ₄ ·7H ₂ O	fructose	100	1.9	7.1	3.9	79.3
15	CoCl ₂ ·6H ₂ O	glucose	100	0.1	2.3	0	16.1
16	CoCl ₂ ·6H ₂ O	fructose	100	0.2	3.1	0	20.7
17	Co(NO ₃) ₂ ·6H ₂ O	glucose	100	0.5	0.6	0	0
18	Co(NO ₃) ₂ ·6H ₂ O	fructose	100	0.2	2.1	0	0
19	$Co(C_2H_3O_2)_2 \cdot 6H_2O$	glucose	100	0.1	1.1	0	0
20	$Co(C_2H_3O_2)_2 \cdot 6H_2O$	fructose	100	0.3	1.3	0	0

^aReaction condition: glucose or fructose: 0.4 g, THF: 3.6 g, sulfates: metal ions had the same mole number with glucose/fructose, $T = 170^{\circ}$ C, reaction time: 2 h, N₂: 3 MPa. ^bCon.: conversion.

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Entry Solvent		Sugar	Yield (%)				
Linu y	Solvent	Sugai	Furfural	LM/LE/LIP ^b	LA	Ethers/esters ^c	HMF
1	THF	glucose	1.7	-	14.5	-	14.7
2	THF	fructose	1.9	-	3.9	-	79.3
3	DMSO	glucose	0	-	0	-	3.6
4	DMSO	fructose	0	-	0	-	4.0
5	Acetone	glucose	0	-	0	-	-
6	Acetone	fructose	0.4	-	0.9	-	40.9
7	Methanol	glucose	0.7	2.0	0	3.4	0
8	Methanol	fructose	1.2	18.7	2.3	56.3	0
9	Ethanol	glucose	0	3.0	0	13.5	0
10	Ethanol	fructose	1.4	0.1	1.8	45.8	0
11	Isopropanol	glucose	0.6	6.4	0	13.7	12.8
12	Isopropanol	fructose	0.3	10.8	0	21.8	24.5
13	Acetic acid	glucose	0	-	0.7	5.6	1.1
14	Acetic acid	fructose	0	-	0.8	12.1	2.5
15	Water ^d	glucose	0.02	-	0.4	-	0
16	Water	fructose	0.04	-	1.1	-	0.2
17	Furan ^e	glucose	0.1	-	0	-	7.0
18	Furan	fructose	0.1	-	0	-	37.2
19	Furfural	glucose	0	-	0	0	20.4
20	Furfural	fructose	0	-	0	0	21.9

Table 2 The conversion of glucose or fructose with $CoSO_4 \cdot 7H_2O$ in different solvents a View Article Online View Article

^aReaction conditions: glucose or fructose: 0.4 g, solvent: 3.6 g, $CoSO_4$: cobalt ions had the same mole number with the sugar, T = 170°C, reaction time: 2 h, N₂: 3 MPa. All the conversions were 100%.

^bLM: methyl levulinate, LE: ethyl levulinate, LIP: isopropyl levulinate.

^cThe product in methanol: 5-methoxy-methyl-furfural (MMF); the product in ethanol: 5-ethoxy-methyl-furfural (EMF); the product in isopropanol: 5-isopropoxy-methyl-furfural (IPMF); the product in acetic acid: FFA: methyl-furfuryl-acetate.

 $^{d}T = 200^{\circ}C$, the other conditions were the same with ^a.

^eReaction conditions: sugar: 0.04 g, solvents: 3.60 g, $T = 170^{\circ}$ C, reaction time: 2 h, N₂: 3 MPa. Catalyst: the mole number of CoSO₄·7H₂O was 1.5 times that of monosaccharide. All the conversions were 100%.

Entry	Sugar	$C_{0}SO_{1}7H_{2}O^{b}$	Yield (%)		
Liiti y		LA	HMF		
1	Glucose	0	0	0	
2	Glucose	0.1n	0	10.2	
3	Glucose	0.5n	0	13.0	
4	Glucose	n	0	23.4	
5	Glucose	1.5n	0	33.4	
6	Glucose	2n	0	35.7	
7	Glucose	5n	0	38.5	
8	Glucose	10n	0	28.9	
9	Glucose	12.5n	0	19.7	
10	Fructose	0	0	3.1	
11	Fructose	0.1n	0	44.7	
12	Fructose	0.5n	0	41.7	
13	Fructose	n	0	52.5	
14	Fructose	1.5n	0	70.3	
15	Fructose	2n	0	64.1	
16	Fructose	5n	0	63.0	
17	Fructose	10n	0	88.0	
18	Fructose	12.5n	0	39.2	

Table 3 Yields of HMF from	n sugars in THF with	different amounts of	CoSO _{4D} 7H	29039/D0CY00225/
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^aReaction conditions: sugar: 0.04 g, THF: 3.60 g, $T = 170^{\circ}$ C, reaction time: 2 h, N₂: 3 MPa. All the conversions were 100%.

^bn was the mole number of the sugar.

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Table 4 The thermal-treatment of HMF in different solvents ^a			View Article Onlin DOI: 10.1039/D0CY00225	
		Pagayary rata without	Recovery rate with	
Entry Solvent		CoSO ₄ ·7H ₂ O		
		$CoSO_4$ ·/ H_2O (%)	(%)	
1	Ethanol	93.2	0	
2	Isopropanol	95.6	47.8	
3	DMSO	89.7	73.3	
4	Acetic acid	2.0	4.8	
5	Water	58.7	66.7	
6	THF	92.2	95.8	

^aReaction conditions: HMF: 0.05 g, CoSO₄·7H₂O: 0.11 g, solvents: 3.60 g, T = 170°C, reaction time: 2 h, N₂:3 MPa.

Entry	Dopatant	Concentration of H ₂ SO ₄	Yield of LA	Yield of	
	Reactant	(mol/L)	(%)	HMF (%)	
1	Fructose	0.1	0	0	
2	Inulin	0.1	0	0	
3	Cellulose	0.1	0	0	
4	Fructose	0.01	0	34.1	
5	Inulin	0.01	0	8.2	
6	Cellulose	0.01	0	6.7	

Table 5 The conversion of raw materials with classic $H_2SO_4^a$

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^aReaction conditions: fructose/inulin/cellulose: 0.05 g, THF: 5 g, T = 200°C, reaction time = 6 h, $N_2 = 3$ MPa. All the conversions were 100%.

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Figure 1 UV-fluorescence spectra for the soluble polymers from the liquid products of fructose-conversion in various solvents (a), 3D fluorescence spectra of soluble polymers in acetone (b), DMSO (c) and in THF (d).



Figure 2 FT-IR spectra of liquid products from the conversion of fructose or glucose with different solvents.



Figure 3 The change in color of solution before and after the reaction. Reaction conditions: HMF: 0.05 g, $CoSO_4$ ·7H₂O: 0.11g, solvents: 3.60 g, T = 170°C, reaction time: 2 h, N₂: 3 MPa.



Figure 4 FT-IR spectra of $CoSO_4$ ·7H₂O in THF, ethanol, DMSO and H₂O, respectively. (a) Full range spectra of solvents and $CoSO_4$ -solvent; (b) Spectra of $CoSO_4$ -solvent in the range from 4000 to 2500 cm⁻¹.

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