Catalytic conversion of glucose in dimethylsulfoxide/water binary mix with chromium trichloride: Role of water on the product distribution

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**Highlights**

- Tuning water content in DMSO leads to desirable product distribution from glucose.
- Pure DMSO solvent causes undesired dehydration of glucose and low HMF yield.
- The available water in DMSO effectively suppressed undesired dehydration of glucose.
- DMSO/H\textsubscript{2}O with $\chi_\text{w} \leq 0.3$ is capable of stabilizing HMF.

**Graphical Abstract**

The production of 5-Hydroxymethylfurfural (HMF) from hexoses is a stoichiometric dehydration process. Water content in a solvent is expected to play an important role in HMF formation by affecting the equilibrium and the reaction kinetics. In this work, the impact of water content on the catalytic conversion of glucose was investigated in detail in different dimethylsulfoxide (DMSO)/H\textsubscript{2}O mixtures ($\chi_\text{w} = 0–1$) with chromium trichloride hexahydrate ($\text{CrCl}_3\cdot 6\text{H}_2\text{O}$) as the catalyst at 110–130 °C. Water content in the binary mix was found to dominantly affect the product distribution. Anhydrous DMSO system is favored for HMF formation from glucose but caused a number of side reactions, especially the undesired dehydration of glucose into cellobiose. Adding an appropriate amount of water in DMSO ($\chi_\text{w} = 0.17–0.50$) was found to significantly suppress the undesired dehydration side reactions while preserving high HMF yield over the $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ catalyst, therefore remarkably improving the total selectivity of HMF and fructose from glucose conversion. While $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ was essential in isomerizing glucose into fructose, hydrochloric acid (HCl) from $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ hydrolysis in DMSO/H\textsubscript{2}O mixed system catalyzed the dehydration of in situ formed fructose to HMF. Although effective water removal was pronounced toward improving HMF yield from hexose dehydration in previous work, the results of this work indicate that a controlled amount of water in the non-aqueous system is favorable to drive the thermodynamic equilibrium for high HMF yield and desired product selectivity, providing reference information on designing a one-pot process for HMF synthesis from cellulosic materials.

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1. Introduction

Biomass, the most abundant and available renewable carbon source on the earth, has attracted a great deal of attention in view of the diminishing fossil fuels [1]. Biomass consists primarily of lignocellulose, which includes polysaccharides (cellulose and hemicellulose) and lignin [2]. Compared with the complex and recalcitrant lignin, the polysaccharides have relatively regular structures with monosaccharide units and can be hydrolyzed into various sugars [23]. Thus, the development of biomass biorefinery is critically dependent on catalytic carbohydrate conversions with high selectivity.

5-Hydroxymethylfurfural (HMF) has recently been regarded as one important precursor for the production of biofuels and bio-based compounds [4]. Dehydration of hexoses into HMF has emerged as a promising path toward sustainable development [4]. For the above purpose, fructose is a good starting material, which can be smoothly converted into HMF in varieties of reaction media, such as water/organic solvent biphasic system [5], dimethylsulfoxide (DMSO) [6], dimethylacetamide (DMA)-lithium chloride (LiCl) [7], and ionic liquid [8], with many different catalysts, including mineral acid [9], organic acid [10], metal salt [11], solid acid [12], and functionalized ionic liquid [13]. However, fructose is of limited abundance in nature and typically at a higher cost than glucose [14].

Glucose is the most abundant monosaccharide in nature and, as the main monomer, can be produced from the hydrolysis of starch and cellulose [14]. However, the obstacle of effectively converting glucose into HMF has slowed the development of HMF based biorefinery. Zhang and co-workers first reported that chromium chloride (CrCl$_2$ or CrCl$_3$) catalyzed the efficient production of HMF from glucose in ionic liquids by enabling the isomerization of glucose into fructose [15]. Since then, ionic liquids have been mostly employed as the reaction media for the HMF production from glucose based feedstocks with chromium chloride [16-20]. Except ionic liquids, other solvents, such as DMA and DMSO, have been employed for glucose conversion as well, and it was found that chromium chloride was also effective in those systems for the isomerization of glucose into fructose [7,21,22]. The versatility of chromium chloride catalyst in different solvents offers more options toward the development of alternative reaction systems for saccharide conversions.

In previous works, it was reported that DMSO could improve the HMF yield from fructose by suppressing side reactions [5,23]. Shimizu et al. reported that the in situ formed water from fructose dehydration lowered the HMF yield in DMSO system over Amberlyst-15 [24], so that effective water removal was pronounced toward the enhanced production of HMF [24]. Nevertheless, as water formation is inevitable in a dehydration reaction, information on whether and how water content in non-aqueous media affects HMF production from hexoses, especially glucose, is an important subject of research and the existing literature remains lacking in such information. Recently, a few studies focused on the effect of water content in HMF chemistry by employing DMSO/water (H$_2$O) binary mix. Tsilemoleks et al. studied the origin of HMF stability in DMSO/deuterium oxide (D$_2$O), and proposed that HMF solvation by DMSO reduced its susceptibility to nucleophilic attack, therefore minimizing undesirable hydrolysis of HMF and humin formation [25]. HMF solvation by DMSO remained preferential at $\chi_{D_{2}O} < 0.4$ [25], indicating that an appropriate amount of water in such a system does not lower the stability of HMF. Kimura et al. studied the non-catalytic conversion of cellobiose in DMSO/water at high temperature (170 °C), in which higher HMF yield (≈70%) was obtained after 23-26 h in the DMSO/water mixtures with $\chi_{w} = 0.2-0.3$ than that in pure DMSO (HMF yield of ≈45%) or water (HMF yield of ≈40%) [26]. In our previous study, it was shown that isomerization of glucose into fructose catalyzed by CrCl$_2$·6H$_2$O followed a general curve in water independent of reaction variables, while adding a controlled amount of DMSO as co-solvent significantly changed the reaction behavior [27]. For example, when a DMSO/water mixture (v/v, 8/2) was used as the solvent, the obtained HMF yield (11.0%) was comparable to that (12.4%) in pure DMSO at 110 °C after 4 h [27]. The above studies demonstrate that an appropriate amount of water may be tolerated and even more beneficial for HMF synthesis in DMSO.

It is noted that the DMSO/water mixture solvent has been well studied. For instance, several characteristic parameters of the mixture, such as melting point, density and viscosity, deviate from the ideal solution as a function of the molar fraction of water ($\chi_{w}$) [28,29]. As reported, water appears tetrahedrally hydrogen bonded, linking each water molecule to four water molecule neighbors in tetrahedral geometry [30]. In DMSO/water binary mixtures with higher water content ($\chi_{w} > 0.5$), the local tetrahedral structure of water is still preserved [31,32], especially at $\chi_{w} > 0.7$ [33], implying that the mixtures have water-like properties. However, in the DMSO-rich aqueous system ($\chi_{w} < 0.5$), DMSO molecules retain the same molecular arrangement as in the pure state [34]. Therefore, the DMSO/water binary mix may offer unique properties for biomass conversion research.

In this work, we investigated the catalytic conversion of glucose with chromium trichloride catalyst in varied DMSO/water/binary solvents. The objective was to explore how water content of the mixed solvents may affect the catalytic conversion of glucose. Achieving such an understanding may also help reconcile the large difference between very high glucose conversion and relatively low HMF yield in some previous literatures [21,22].

2. Experimental

2.1. Materials

$\alpha$-Glucose (99%), $\alpha$-fructose (99%), 1,6-anhydro-$\beta$-$\alpha$-glucose (AGP, 99%) and $\alpha$-cellobiose (98%) were purchased from Alfa Aesar. Chromium trichloride hexahydrate (CrCl$_3$·6H$_2$O, 96%) was purchased from Sigma-Aldrich. 5-Hydroxymethylfurfural (HMF, 98%) and levulinic acid (LA, 99%) were purchased from Aladdin. Glycerol (99%) and dimethylsulfoxide (DMSO, 99%) were purchased from Sinopharm (China). Hydrochloric acid (HCl, 36–38 wt%) was provided by a local supplier. All the chemicals were used as received. Deionized water (DI H$_2$O) with a resistivity of 18.2 MΩ-cm was produced by a Milli-Q Integral 5 system.

2.2. Typical reaction procedure

Glucose (50 mg) or fructose (50 mg), CrCl$_3$·6H$_2$O (3.7 mg, 5 mol% with respect to glucose or fructose) and total 1 mL of solvent were added into each reaction vial with a magnetic stir bar for reaction. The reaction vial was sealed and it was used as an autoclave. The reaction is conducted at autogenic pressure. It should be specified that some solvents may be composed of both DMSO and DI H$_2$O, and the 1 mL was defined as the sum volume of DMSO and H$_2$O. Eight DMSO/H$_2$O solutions with volume ratios ($\mu$L/$\mu$L) of 1000/0, 950/50, 900/100, 800/200, 600/400, 400/600, 200/800 and 0/1000 were employed. Based on that the relative densities of DMSO and H$_2$O are 1.1 g/mL and 1.0 g/mL, and the molecular weights of DMSO and H$_2$O are 78.13 g/mol and 18.02 g/mol, respectively, the molar fraction of H$_2$O ($\chi_{w}$) in the above DMSO/H$_2$O solutions was calculated to be 0, 0.17, 0.30, 0.50, 0.72, 0.86, 0.94 and 1, respectively. The feedstocks have good solubilities in either water or DMSO. For example, the solubility of glucose in water and DMSO is 908 mg/mL and 540 mg/mL.
respectively, around room temperature [35,36]. As reported, fructose has higher solubility than other sugars as well as other sugar alcohols in water [37], and it also has a good solubility in DMSO [38]. Moreover, HMF is also soluble in water and many polar organic solvents [39]. Therefore, it is believed that the used feedstocks and produced HMF completely dissolved in the above reaction systems. The reactions were operated on a heating and stirring module (TS-18821, Thermo Scientific) with the stirring rate at 500 rpm for a specified time at the reaction temperature. After the reaction was quenched in ice water bath, 1 mL of DI H2O and the internal standard were added into the reaction mixture. Then, a small amount of the sample mixture was taken out and further diluted by DI H2O for ~15 times and analyzed by high performance liquid chromatography (HPLC).

2.3. Analyses

HPLC analysis was performed on an Agilent 1260 series with a refractive index detector and a PL Hi-Plex H column (300 × 7.7 mm, 8 µm). The mobile phase was 0.005 M H2SO4 aqueous solution at a flow rate of 0.6 mL/min and the volume for each injection was 10 µL. The column and detector temperatures were 65 °C and 50 °C, respectively. Authentic chemical compounds were used to identify the retention times. Glycerol was added as the internal standard for the quantitative calculations. The pH values were measured by Core Module 3 (CM3) System (Freeslate).

3. Results and discussion

The production of HMF from hexoses is a stoichiometric dehydration process in a solvent. The effect of water content on the catalytic conversion of glucose was studied in DMSO/H2O mixtures with CrCl3·6H2O. The initial investigations were carried out in various DMSO/H2O ratios at 110 °C.

As illustrated in Fig. 1a, after the experiments were run for 2 h, the glucose conversion for all the systems reached a similar level of ~23%. However, the product distribution showed different patterns. In anhydrous DMSO, the HMF yield (9.6%) was the highest among all the systems with only a little fructose (3%) detected. As reported, CrCl3·6H2O is a good catalyst for isomerizing glucose into fructose [15,27,40,41]. Anhydrous DMSO is a strong dehydration medium, which facilitates HMF formation from the in situ formed fructose. As a general trend, with increasing χw from 0 to 1, HMF yield was decreased along with increased fructose yield, indicating that water addition suppressed the dehydration of fructose into HMF. It is noted that, however, in the system with χw = 0.17, the HMF yield (6.4%) remained close to that in anhydrous DMSO, while fructose yield was much increased (11.2%). The total yield of HMF and fructose was much higher than that in anhydrous DMSO. With χw > 0.50, HMF production was essentially quenched, and fructose was the primary product as a result of the isomerization of glucose over CrCl3·6H2O, which is consistent with previous work [27]. Cellobiose, 1,6-anhydro-D-glucopyranose/glucofuranose (AGP/AGF) and levulinic acid (LA) were also detected. Cellobiose, AGP and AGF are the products by undesired intermolecular or intramolecular dehydration of glucose. LA is a downstream product due to the hydrolytic cracking of HMF, with formic acid (FA) as a concomitant product [5,23]. However, the LA yields in the above systems were generally lower than 2% and no FA was detected by HPLC, so they were not discussed herein. The total yield of cellobiose, AGF and AGP is hereafter called by-product yield. Notably, quantities of by-products (9.1%) were produced in anhydrous DMSO, where cellobiose was the main component with a yield of 7.5%. With increasing χw, the yield of by-product dropped substantially to a very low level, which can be attributed to the increased water concentration that suppressed the dehydration of fructose into HMF as well as the undesired dehydration of glucose into by-products.

Given in Fig. 1b, when the reaction time was extended to 3 h, the glucose conversion in anhydrous DMSO was much improved by ~12%, while the other aqueous systems gave an average of ~5% increase, indicating that water addition did retard the glucose conversion. The product distribution was comparable to that obtained at 2 h. The formation of by-products was significantly enhanced in anhydrous DMSO, especially cellobiose, of which the yield increased from 7.5% to 12.4%. However, the by-product yields just slightly increased in other water containing systems (Fig. 1b), which further demonstrates that water addition could drive the thermodynamic equilibrium to circumvent undesired dehydration of glucose. The HMF production remained at a very low level with χw > 0.50, possibly because the DMSO/H2O mixed solvents displayed water-like properties [31–33], and the potential of DMSO for the dehydration of in situ formed fructose was much inhibited under these conditions. Remarkably, with χw = 0.17, the HMF yield (13.5%) was higher than that (11.3%) in anhydrous DMSO system, evidently demonstrating that an appropriate amount of water could be tolerated and beneficial for a non-aqueous system in producing HMF from glucose. With χw = 0.30 and 0.50, the HMF yields were 8.7% and 7.5%, respectively, both close to that in anhydrous DMSO. The above results imply that higher water content up to

Fig. 1. Catalytic conversion of glucose in different DMSO/H2O mixtures at 110 °C. (a) 2 h; (b) 3 h. Conditions: 50 mg of glucose with CrCl3·6H2O (5 mol% with respect to glucose) was added into 1 mL of DMSO/H2O solvent and heated at 110 °C for different times.
$\chi_w = -0.50$ is also not significantly inhibitive for HMF production, because DMSO molecules still retain similar feature as its pure state at $\chi_w < 0.5$ according to the well studied properties of the DMSO/H$_2$O binary mixture [34].

To explore whether DMSO with higher water content was also effective for HMF production from glucose, we next investigated the effect of reaction temperature. As illustrated in Fig. 2a, when the reactions were run at 120 °C for 1 h, the glucose conversion for all the systems were around ~26%. In anhydrous DMSO, the HMF yield was 12%. With increasing $\chi_w$, the HMF yield decreased from 9.7% ($\chi_w = 0.17$) to 1.2% ($\chi_w = 1$), while the fructose yield increased accordingly. It was again found that much higher yield (9%) of by-product was observed in anhydrous DMSO. Since isomerization of glucose as well as the rate limiting step in the dehydration of fructose are endothermic [42–44], it is not surprising that similar glucose conversions and HMF yields were obtained in varied DMSO/H$_2$O systems at 120 °C within short time (1 h) and at 110 °C for 2 h (Figs. 1a and 2a). Dehydration of glucose into HMF is considered to undergo a two-step tandem reaction, including isomerization of glucose into fructose and dehydration of fructose into HMF [15,17]. HMF and fructose are the desired products. As seen in Fig. 2a, due to the large formation of by-products, the selectivity of desired product (56.2%) was low in anhydrous DMSO, while the corresponding selectivities in other aqueous systems stood at the level of ~80%, mainly because water did suppress the undesired dehydration from glucose.

As shown in Fig. 2b and c, when the reaction time was extended to 2 h and 3 h, glucose conversions were significantly improved in anhydrous DMSO than in other water containing systems. HMF was more effectively produced in DMSO/H$_2$O systems with $\chi_w = 0.17$–0.50. For 2 h reaction at 120 °C, the HMF yield (19.4%) in $\chi_w = 0.17$ system was higher than that (15.3%) in anhydrous DMSO. The $\chi_w = 0.30$ and 0.50 systems gave HMF yields of 14% and 12.7%, respectively. Remarkably, for 3 h reaction, the HMF yields in $\chi_w = 0.17$, 0.30 and 0.50 systems were 21.5%, 20.1% and 17.6%, respectively, all of which were higher than that (16.6%) in anhydrous DMSO. However, the selectivity of desired product decreased with prolonging reaction time. After 3 h at 120 °C, the selectivity of desired product dropped to only 33.8% in anhydrous DMSO. Due to much increased formation of by-products, the selectivity of desired product decreased to 60.4% in $\chi_w = 0.17$ system, while the selectivity of desired product still remained at the level of ~70% with $\chi_w = 0.30$–1 under these conditions. The difference between glucose conversions and total product yields as shown in Fig. 2 represents unaccounted by-products. However, as illustrated in Figs. S1 and S2, no obvious other products could be detected by HPLC analysis except the known compounds. The difference could be ascribed to the formation of polymeric by-products or humins [45]. Mass balance is an important indicator for a reaction, and further study is essential for reducing mass loss by circumventing undesired side reactions and humin formation.

When the reaction temperature was elevated to 130 °C, HMF production was further improved. As illustrated in Fig. 2d, after 3 h, the HMF yields in DMSO/H$_2$O with $\chi_w = 0.17$, 0.30 and 0.50 reached up to 35%, 33.5% and 31.6%, respectively, which were much higher than that (24.5%) in anhydrous DMSO. Although a
little more by-products (22.5%) were produced in anhydrous DMSO after 3 h at 130 °C, the cellobiose yield (9.2%) was lower than that (13.4%) after 3 h at 120 °C, possibly because more cellobiose underwent deep polymerization into cellotriose, cellotetrose and even oligomers. The above results further demonstrate that an appropriate aqueous DMSO system is more beneficial for the HMF production under specified conditions.

The blank tests for glucose conversion were also studied in different DMSO/H2O systems. As seen in Table S1, when the reactions were run at 120 °C for 2 h, negligible glucose conversions were observed. However, the glucose conversion reached about 10.8% with cellobiose (9.1%) as the primary product in anhydrous DMSO at 130 °C for 2 h. The results indicate that pure DMSO system is capable of causing the undesired direct dehydration of glucose even in the absence of a catalyst. However, the available water in DMSO could effectively suppress the side reactions, which explains why lower yields of by-products were formed in aqueous systems.

As reported in the literature, fructose is generally considered as the intermediate for the conversion of glucose into HMF [15,17,21]. We also studied how water content affected the conversion of fructose into HMF in varied DMSO/H2O systems with CrCl3·6H2O. Fig. S3 presents the results for blank tests of fructose conversion in different DMSO/H2O mixtures. It was found that fructose underwent effective dehydration into HMF in anhydrous DMSO even without a catalyst, which is consistent with the existing literature [23,46]. At 120 °C for 1 h, fructose conversion was 86% with HMF yield of 56.4%, and at 130 °C for 1 h, fructose was almost completely converted with HMF yield of 67.2%. However, the dehydration of fructose into HMF stopped when only a little water (i.e. \( \chi_w = 0.17 \)) was added, indicating that the available water in the system was detrimental to the conversion of fructose in the absence of a catalyst.

When CrCl3·6H2O (5 mol%) with respect to fructose) was added, the dehydration of fructose was recovered at different levels in different DMSO/H2O systems. As illustrated in Fig. 3, moderate to high yield of HMF could be achieved in \( \chi_w = 0.17–0.50 \) systems. However, HMF production remained at a low level when \( \chi_w \) was higher than 0.50, which is consistent with the low HMF yields from glucose at \( \chi_w > 0.50 \) as shown in Fig. 2a. CrCl3·6H2O could be hydrolyzed into Cr species and HCl in an aqueous solution. In previous works, Cr species was proposed as the catalyst for the isomerization of glucose [27,40,41], while HCl worked for the conversion of fructose [40]. Therefore, the different levels of HMF yield in Fig. 3 could be attributed to the pH value in available water. We then checked the above hypothesis by employing two DMSO/H2O solutions with \( \chi_w = 0.30 \) and 0.50. The \( \chi_w = 0.30 \) system contained 3.7 mg of CrCl3·6H2O and 100 μL of water, while the \( \chi_w = 0.50 \) system contained 3.7 mg of CrCl3·6H2O and 200 μL of water. On the assumption that HCl was formed by CrCl3·6H2O hydrolysis in available water, the pH values of the two CrCl3·6H2O solutions with concentrations of 3.7 mg/100 μL and 3.7 mg/200 μL were ~2.08 and ~2.34, respectively, at room temperature. However, the conversion of fructose was conducted at 120 °C for 1 h, high temperature would accelerate the hydrolysis of CrCl3·6H2O, leading to a low pH value [27]. After the above CrCl3·6H2O solutions were heated at 120 °C for 1 h, the corresponding pH values dropped to ~1.09 and ~1.42, respectively. Then two solutions with pH of 1.09 and 1.42 were prepared by diluting concentrated HCl solution, and used for fructose conversion. As shown in Fig. 4, both fructose conversions and HMF yields in DMSO/H2O with \( \chi_w = 0.30 \) (900 μL DMSO/100 μL H2O, pH(H2O) = 1.09) and \( \chi_w = 0.50 \) (800 μL DMSO/200 μL H2O, pH(H2O) = 1.42) were comparable to those with CrCl3·6H2O as catalyst, indicating that the conversion of fructose in aqueous DMSO system is correlated with the pH value in available water.

As shown in Fig. 3, glucose was also detected in the reaction. According to previous literature, the isomerization between glucose and fructose is reversible [42]. Most recent work also indicates that CrCl3·6H2O catalyzed the conversion of aldoses (i.e. glucose, xylulose) and established a reversible path between aldose and ketose (i.e. fructose, xylulose) [40,47]. Therefore, the formation of glucose from fructose is expected. As shown in Fig. S4, when the reaction time was extended or the temperature was elevated, the HMF yields in DMSO/H2O systems with \( \chi_w = 0.30 \) or 0.50 were further improved, either superior or very close to that in anhydrous DMSO, which is consistent with the results that HMF production from glucose was superior or close to that in anhydrous DMSO (Fig. 2b-d). The results indicate that the negative effect of water on the dehydration of fructose into HMF could be overcome by adding a catalyst under specified conditions.

We finally tested the stability of HMF in different DMSO/H2O mixtures. As seen in Table 1, HMF was essentially stable in DMSO/H2O with \( \chi_w \leq 0.50 \) at 120 °C in the absence of a catalyst, of which the recovery was higher than 95%. However, when the \( \chi_w \) was further increased, HMF recovery slightly decreased. Tsi-lomelekis et al. recently studied the origin of HMF stability in DMSO/D2O mixtures [25]. It was found that DMSO could bind to both the hydroxyl and carbonyl groups of HMF more strongly than water. When HMF was solvated by DMSO, the LUMO energy of HMF was higher, which indicates that solvation by DMSO reduces...
its susceptibility to nucleophilic attack, therefore minimizing undesirable hydrolysis of HMF and humin formation [25]. In HMF/DMSO/D$_2$O ternary mixtures, DMSO preferentially solvated the carbonyl group of HMF if $\chi_{D2O}$ was less than $\sim 0.4$ [25], which may explain why HMF was more stable at $\chi_w = 0.50$ without a catalyst in this work. Since HMF was produced from glucose or fructose under catalytic reaction conditions, the stability of HMF was also examined in the presence of CrCl$_3$6H$_2$O. HMF was still stable at $\chi_w \leq 0.30$, while its recovery showed remarkable decrease than those without catalyst at $\chi_w \geq 0.50$, possibly because the solvation of DMSO was disrupted to some extent, and the catalyst, especially the formed HCl, caused the degradation of HMF. In previous study, it is also reported that in DMSO/H$_2$O binary mixtures, the local tetrahedral structure of water is still preserved in the presence of DMSO molecules at higher water content ($\chi_w > 0.5$) [31–33]. However, in the DMSO-rich system ($\chi_w < 0.5$), DMSO molecules retain the same molecular arrangement as in the pure state [34], which offers a perspective basis for the stability of HMF. In brief, DMSO is a solvent capable of stabilizing HMF and the stabilization persists in the presence of an appropriate amount of water.

In the end, we use Fig. 5 to summarize the conversion of glucose in DMSO/H$_2$O mixed solvents. Anhydrous DMSO with CrCl$_3$6H$_2$O significantly accelerated glucose conversion, leading to effective production of HMF. In the meantime, however, glucose is apt to undergo undesired dehydration to produce cellobiose, AGP and AGF as well as high temperature, reducing the selectivity of desired product. In the literature, glucose was converted in DMSO at 120 or 140 °C with about 100% conversion and $\sim 50$% yield of HMF [21,22], but the large difference between glucose conversion and HMF yield was not explained. The results in this work imply that by-product such as cellobiose, AGP and AGF may account for bulk of the missing products. However, a number of other products remained unknown, possibly humins. Compared with anhydrous DMSO system, the key role of added water in DMSO was to suppress the undesired dehydration of glucose. Water addition also limited the dehydration of in situ formed fructose into HMF in DMSO without a catalyst. CrCl$_3$6H$_2$O catalyzed the isomerization of glucose. HCl from the hydrolysis of CrCl$_3$6H$_2$O was sufficient for the dehydration of fructose into HMF. In aqueous solution, HMF also is known to undergo hydrolysis to form LA and FA under acid catalyzed conditions [5,23]. However, only a very low amount of LA was detected in this work, which may be explained by the following reasons: (1) LA was effectively synthesized from carbohydrates at temperature up to 160–200 °C in strongly acidic media [48–50], while the employed conditions in this work were much milder; (2) at $\chi_w < 0.5$, the DMSO/H$_2$O systems preserved the DMSO-like properties, which may suppress the side reactions as mentioned above [5,25,51]; (3) although the reaction media had water-like properties at $\chi_w > 0.5$, HMF formation was much inhibited, and the low HMF concentration in the media would not effectively drive the equilibrium into LA.

4. Conclusions

Water content in DMSO/H$_2$O binary mixture effectively affected the product distribution in the catalytic conversion of glucose. Anhydrous DMSO system was favored for the effective production of HMF from glucose but also gave rise to many side reactions, such as the undesired intermolecular and intramolecular dehydrations of glucose. The key role of added water in DMSO was to suppress undesired formation of cellobiose, AGP and APF so that to improve the selectivity of desired product. Employing a catalyst in an appropriate DMSO/H$_2$O mixed solvent may overcome the limitation of water addition on the dehydration of fructose into HMF. With $\chi_w = 0.17–0.50$, HMF yield reached up to $\sim 35$% after 3 h at 130 °C, which was much higher than that obtained in anhydrous DMSO. Therefore, tuning the water content in DMSO is an effective approach to achieve high HMF yield. CrCl$_3$6H$_2$O catalyzed the isomerization of glucose into fructose. The conversion of fructose into HMF was achieved by HCl from the hydrolysis of CrCl$_3$6H$_2$O, and by a comparable acid concentration with the same pH value in available water of the DMSO/H$_2$O mixture. HMF was stable in DMSO/H$_2$O with $\chi_w \leq 0.30$ with or without CrCl$_3$6H$_2$O in this work, implying that a certain amount of water was tolerated in DMSO in terms of HMF stability. In short, although effective water removal is pronounced toward the enhanced production of HMF from hexose dehydration in previous work, a system with an appropriate amount of water is superior to an anhydrous system in producing HMF by effectively circumventing side reactions.

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**Table 1**

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<th>$\chi_w$</th>
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<td>96.9</td>
<td>96.8</td>
<td>92.9</td>
<td>92.2</td>
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<td>HMF recovery (%) with catalyst</td>
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<td>96.0</td>
<td>95.3</td>
<td>89.2</td>
<td>89.1</td>
<td>86.6</td>
</tr>
</tbody>
</table>

Reaction conditions: $\sim 17$ mg of HMF and 1 mL of solvent were added into each reaction vial and heated at 120 °C for 2 h.

$^a$ 3.7 mg of CrCl$_3$6H$_2$O (10 mol% with respect to HMF) was added.

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**Fig. 5.** Schematic diagram on the conversion of glucose in DMSO/H$_2$O binary mix system.
The results reported herein may provide reference information for the one-pot synthesis of HMF from cellulose materials, because water is necessary for the hydrolysis of the polymer feedstocks.

Acknowledgements

This work was supported by the China Postdoctoral Science Foundation (2013MS50952, 2013MS40236), National Natural Science Foundation of China (21306186), and the Chinese Government “Thousand Talent” program funding.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jcej.2014.05.121.

References