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

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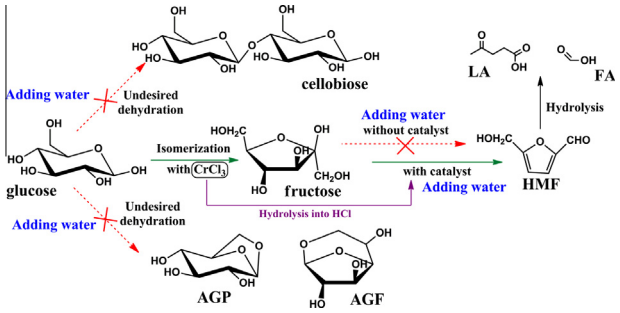
HIGHLIGHTS

- 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_2O with $\chi_w \leqslant 0.3$ is capable of stabilizing HMF.

GRAPHICAL ABSTRACT



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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_2O mixtures (χ_w = 0–1) with chromium trichloride hexahydrate ($CrCl_3{\cdot}6H_2O$) 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 (χ_w = 0.17–0.50) was found to significantly suppress the undesired dehydration side reactions while preserving high HMF yield over the $CrCl_3{\cdot}6H_2O$ catalyst, therefore remarkably improving the total selectivity of HMF and fructose from glucose conversion. While $CrCl_3{\cdot}6H_2O$ was essential in isomerizing glucose into fructose, hydrochloric acid (HCl) from $CrCl_3{\cdot}6H_2O$ hydrolysis in DMSO/H_2O 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 [2,3]. 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_2O) binary mix. Tsilomelekis et al. studied the origin of HMF stability in DMSO/deuterium oxide (D_2O), 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 $\chi_{D2O} < 0.4$ [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 $CrCl_3{\cdot}6H_2O$ 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 (χ_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 $\chi_w \geqslant 0.7$ [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

D-Glucose (99%), D-fructose (99%), 1,6-anhydro-β-D-glucose (AGP, 99%) and D-cellobiose (98%) were purchased from Alfa Aesar. Chromium trichloride hexahydrate ($CrCl_3{\cdot}6H_2O$, 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_2O) 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), $CrCl_3{\cdot}6H_2O$ (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_2O, and the 1 mL was defined as the sum volume of DMSO and H_2O. Eight DMSO/H_2O solutions with volume ratios (μL/μL) 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_2O are 1.1 g/mL and 1.0 g/mL, and the molecular weights of DMSO and H_2O are 78.13 g/mol and 18.02 g/mol, respectively, the molar fraction of H_2O (χ_w) in the above DMSO/H_2O 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 909 mg/mL and 540 mg/mL,