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Syntheses of 5-hydroxymethylfurfural and levoglucosan by selective dehydration of glucose using solid acid and base catalysts

Mika Ohara, Atsushi Takagaki, Shun Nishimura, Kohki Ebitani*

School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

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1. Introduction

Currently, the world faces serious environmental and economic issues related to our overwhelming dependence on fossil fuels for energy and chemical production and the resulting global warming that arises from their conversion to carbon dioxide. Biomass offers a promising alternative to fossil fuels as a renewable resource as it can be produced in a carbon neutral way [1,2]. To avoid competition for land resources dedicated to food and animal-feed production, it is strongly desirable to utilize an inedible biomass. Wood-based biomass offers an abundant resource comprising cellulose (35–50%), hemicellulose (25–30%) and lignin (25–30%). Cellulose and hemicellulose can be depolymerized into monosaccharides including glucose, fructose and xylose. Among them, glucose is the most abundant monosaccharide, and therefore transformation of glucose has attracted much attention for the production of alternative chemicals as an efficient biorefinery [3–5].

Dehydration of glucose is an important and attractive chemical reaction because it produces two valuable derivatives, anhydroglucose and 5-hydroxymethylfurfural (Fig. 1) [6]. These anhydroglucoses, 1,6-anhydro- β -D-glucopyranose and 1,6-anhydro- β -D-glucofuranose, are highly valuable chemicals. 1,6-Anhydro- β -D-glucopyranose, also known as levoglucosan, can be used as an intermediate for biodegradable surfactants, stereoregular polysaccharides, hyperbranched polymers and phar-

ABSTRACT

Selective dehydration of glucose, the most abundant monosaccharide, was examined using a solid acid catalyst individually or a combination of solid acid and base catalysts to form anhydroglucose (levoglucosan) or 5-hydroxymethylfurfural (HMF), respectively. Glucose was dehydrated to anhydroglucose by acid catalysis in polar aprotic solvents including *N*,*N*-dimethylformamide. Amberlyst-15, a strongly acidic ion-exchange resin, functioned as an efficient solid acid catalyst for anhydroglucose production with high selectivity. In the presence of solid base, aldose–ketose isomerization of glucose to fructose preferentially occurred by base catalysis, even in coexistence with the solid acid, resulting in successive dehydration of fructose to 5-hydroxymethylfurfural by acid catalysis with high yield in a one-pot reaction. A combination of Amberlyst-15 and hydrotalcite, an anionic layered clay, afforded high HMF selectivity under a moderate reaction temperature, owing to prevention of anhydroglucose formation.

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maceuticals [7–10]. These anhydroglucoses are obtained by dehydration of one water molecule from 1,6- β -D-glucopyranose and 1,6- β -D-glucofuranose, respectively, where the pyranose and furanose forms are under tautomeric equilibrium. The efficient production of anhydroglucose has recently been examined in detail using 2-chloro-1,3-dimethylimidazolinium chloride as a strong dehydrating agent [11] and hydrophobic ionic liquids including *N*,*N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium bis(trifluoromethanesulfonyl)amide [12].

5-Hydroxymethylfurfural (HMF) as a furan derivative can be formed by elimination of three water molecules from hexoses (glucose or fructose), and is a desirable intermediate for plastics, polymers and fuels [3,4,13]. For instance, HMF can be oxidized to form 2,5-diformylfuran [14-17] and 2,5-furandicarboxylic acid [18-21]. These derivatives are expected to be highly useful intermediates for a variety of polymers and plastics. Levulinic acid, which is obtained by rehydration of HMF, is also an important intermediate for polymers [3,4]. Further, Dumesic et al. proposed that a dimethylfuran derived from HMF is a promising biofuel with a higher energy density and boiling point than ethanol [22]. Because of the great potential of HMF as a versatile platform, a large number of researchers have investigated the more efficient production of HMF by several different methods [23-51]. For example, efficient production of HMF has been reported using an organic-water biphasic system, in which hydrochloric acid in the water phase dehydrates fructose or glucose to form HMF, which is subsequently extracted into the organic phase, resulting in high HMF selectivity [25–28]. The use of ionic liquids containing metal ions such as chromium has also been a notable method for

^{*} Corresponding author. Tel.: +81 761 51 1610; fax: +81 761 51 1625. *E-mail address*: ebitani@jaist.ac.jp (K. Ebitani).

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Fig. 1. Selective dehydration of glucose to anhydroglucose and 5-hydroxymethylfurfural.

HMF production, providing high selectivity with high conversion [29–39].

HMF can be much more easily synthesized from fructose than glucose by dehydration because of the difference in their chemical structures. Fructose, as a ketohexose, readily dehydrates to form HMF under mild acid conditions. In contrast, glucose, as an aldohexose, gives poor HMF selectivity in direct dehydration due to side reactions, including cross-condensation, resulting in the formation of humins and oligomers.

We have adopted an alternative approach for HMF synthesis from glucose through a two-step reaction in one-pot [52]. It is known that glucose can be transformed into fructose by aldose-ketose isomerization catalyzed by a base [53]. The obtained fructose could easily be converted into HMF in the presence of acid. This simple methodology can be performed using a solid acid catalyst along with a solid base catalyst in one-pot. The combination of solid acid and base catalysts offers the opportunity to utilize acid or base activity separately even in one reactor, whereas for a liquid acid-base pair, neutralization and subsequent deactivation would naturally occur. One-pot reactions using heterogeneous catalysts afford environmentally friendly benefits, including avoidance of isolation and purification of intermediate compounds, which saves time, energy and solvent [54–58].

In this study, selective dehydration of glucose was examined using either a solid acid individually or a combination of solid acid and base catalysts for the production of anhydroglucoses or 5hydroxymethylfurfural, respectively. Fig. 2 illustrates the proposed reaction pathway for selective dehydration of glucose using the solid acid and base catalysts. A strong acidic ion-exchange resin, Amberlyst-15 was used as the solid acid catalyst, and a layered clay compound, hydrotalcite, was used as the solid base catalyst [59–68]. The former is a macroreticular sulfonated polystyrene-based ion-exchange resin with 20% divinylbenzene. The latter is a layered anionic clay denoted as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are di- and trivalent metal ions, and A^{n-} represents the interlayer anions. Anionic species such as carbonate and hydroxide are located to compensate the positively charged brucite layer. Mg–Al hydrotalcite, i.e. Mg₆Al₂(OH)₁₆CO₃·nH₂O, is generally used as the active solid base catalyst for several reactions including aldol condensation, Knoevenagel reaction, epoxidation and transesterification [59–68].

2. Experimental

2.1. Materials

D-glucose and D-fructose were purchased from Wako Pure Chemical Industries, Ltd. Amberlyst-15 was purchased from Sigma–Aldrich Corporation. Hydrotalcite (Mg/Al = 3) was supplied from Tomita Pharmaceutical Co. Ltd. *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO) and acetonitrile (MeCN) were purchased from Kanto Chemical Co. Inc. Solvents were used after purification by distillation.

2.2. Glucose and fructose dehydration

Glucose and fructose dehydrations were performed using 0.1 g of glucose or fructose, 3-10 mL of DMF, 0.025–0.1 g of Amberlyst-15 and/or 0.05–0.2 g of hydrotalcite in an oil bath at 353-413 K. The experiments were carried out in a Schlenk tube attached to a reflux condenser under an N₂ atmosphere.

2.3. Analytical procedures

The conversions and yields were estimated using highperformance liquid chromatography (HPLC) (Waters) with an Aminex HPX-87H column from Bio-Rad Laboratories, Inc. Samples were diluted with water before HPLC measurement. The products were analyzed using a refractive index (RI) detector. The analysis conditions were set as follows: eluent, 10 mM H₂SO₄; flow rate, 0.5 mL/min; column temperature, 323 K. The retention times for detected compounds were 11.6, 12.5, 14.8, 13.6, 38, 20.2 and



Fig. 2. A reaction pathway for anhydroglucose and 5-hydroxymethylfurfural formation from glucose in the presence of solid acid and base catalysts.



Scheme 1. Anhydroglucose formation from D-glucose over Amberlyst-15.

17.5 for glucose, fructose, 1,6-anhydro-β-D-glucopyranose (AGP), 1,6-anhydro-β-D-glucofuranose (AGF), 5-hydroxymethylfurfural (HMF), levulinic acid and formic acid, respectively.

3. Results and discussion

3.1. Anhydroglucose formation from glucose by dehydration over Amberlyst-15

Anhydroglucose was found to be selectively synthesized from glucose in the presence of Amberlyst-15 in N,Ndimethylformamide (DMF), whereas no anhydroglucose was formed in the absence of acid (Scheme 1) [69]. Table 1 summarizes the formation of anhydroglucose from D-glucose in different volumes of DMF over Amberlyst-15 at 393 K for 3 h. The yields of the anhydroglucoses (sum of 1,6-anhydro- β -D-glucopyranose (AGP) and 1,6-anhydo- β -D-glucofuranose (AGF)) were not affected much by the solvent amount. In contrast, glucose conversion decreased markedly with an increase in solvent amount, resulting in an increase in anhydroglucose selectivity (from 43% to 78%). Thus, since a high glucose concentration leads to undesired by-products such as oligomers, a low concentration of the substrate is therefore much preferred to ensure high selectivity of anhydroglucose. The use of 0.1 g of catalyst improved both the conversion and yield while maintaining the anhydroglucose selectivity (entry 4).

The anhydroglucose yield was found to increase with increasing reaction temperature. Fig. 3 shows the dependence of glucose conversion, anhydroglucose yield and selectivity on reaction temperature. Both the glucose conversion and the anhydroglucose yield increased with increasing reaction temperature. The anhydroglucose selectivity remained high at \sim 80%. Glucose conversion of 93% and a selectivity of 77% were obtained at 413 K for 3 h. A similarly high conversion and selectivity were also observed at 393 K by increasing the reaction time (76% selectivity and 87% conversion at 393 K for 5 h). It should be noted that formation of anhydroglucose by dehydration was suppressed below 373 K, which is a beneficial feature for one-pot synthesis of HMF from glucose (vide infra).



Fig. 3. Dependence of glucose conversion (filled circle), anhydroglucose yield (open square) and selectivity (filled triangle) on reaction temperature for dehydration of glucose in DMF solution using Amberlyst-15. Reaction conditions: glucose (0.09 g), Amberlyst-15 (0.1 g), DMF (10 mL), 3 h.



Scheme 2. Isomerization of glucose over hydrotalcite.

3.2. Isomerization of glucose to fructose over hydrotalcite

In the presence of a base, glucose can be transformed into fructose by aldose-ketose isomerization. Hydrotalcite is known to efficiently catalyze this base reaction (Scheme 2) [67,68]. Table 2 summarizes the isomerization of glucose to fructose over hydrotalcite (0.1 g) at 353–393 K for 3 h with DMF as solvent. Glucose conversion increased with increasing reaction temperature from 47% at 353 K to 81% at 393 K. Correspondingly, however, the fruc-

Table 1

Anhydroglucose formation from D-glucose in N,N-dimethylformamide over Amberlyst-15.^a.

| Entry | Solvent amount (mL) | Conv. (%) | Yield (%) | | Selec. (%) | |
|----------------|---------------------|-----------|------------------|------------------|------------|----|
| | | | AGP ^b | AGF ^c | AGP + AGF | |
| 1 | 2.5 | 67 | 16 | 13 | 29 | 43 |
| 2 | 5 | 53 | 16 | 11 | 27 | 51 |
| 3 | 10 | 30 | 14 | 9 | 23 | 77 |
| 4 ^d | 10 | 44 | 19 | 16 | 35 | 80 |

^a Reaction conditions: glucose (0.09 g), Amberlyst-15 (0.05 g), DMF, 393 K, 3 h.

^b 1,6-Anhydro- β -D-glucopyranose.

^c 1,6-Anhydro- β -D-glucofuranose.

^d Using 0.1 g of Amberlyst-15.

Table 2

Fructose formation by isomerization of glucose over hydrotalcite.^a.

| Reaction temperature (K) | Glucose conversion (%) | Fructose yield (%) | Fructose selectivity (%) |
|--------------------------|------------------------|--------------------|--------------------------|
| 353 | 47 | 40 | 85 |
| 373 | 62 | 38 | 62 |
| 393 | 81 | 32 | 40 |

^a Reaction conditions: glucose (0.1 g), hydrotalcite (0.1 g), DMF (3 mL), 3 h.



Fig. 4. Time course of HMF formation from fructose over Amberlyst-15. Reaction conditions: fructose (0.1 g), Amberlyst-15 (0.1 g), DMF (3 mL), 353 K and 373 K. Fructose conversion (353 K (\bigcirc) and 373 K (\bullet)). HMF yield (353 K (\square) and 373 K (\blacksquare)).

tose yield gradually decreased from 40% at 353 K to 32% at 393 K, leading to a decrease in fructose selectivity at high temperatures. The appearance of humins was observed on the surface of hydrotalcite after the isomerization, especially at high temperature reaction, presumably attributable to base-catalyzed condensation. Low temperatures are preferred to maintain a high fructose selectivity even though glucose conversion is relatively low (85% fructose selectivity and 47% glucose conversion at 353 K) in these conditions. The aldose–ketose isomerization is an equilibrium reaction. When fructose was first added to DMF containing 0.1 g of hydrotalcite at 373 K, 20% of the fructose was converted after 3 h, resulting in a 13% yield of glucose with 64% selectivity, which is equivalent to glucose isomerization.

3.3. HMF formation from fructose by dehydration over Amberlyst-15

In contrast to glucose, fructose readily dehydrates to form HMF using Amberlyst-15 under mild conditions. Fig. 4 shows the time course of HMF formation from fructose over Amberlyst-15 at 353 K and 373 K. At 373 K, 66% of the fructose was converted into HMF after 15 min. After 1 h, the fructose was fully converted, providing HMF with considerable selectivity (91%). HMF was successfully obtained even at 353 K, with a 46% yield for 1 h and a 77% yield with



Fig. 5. Effect of reaction temperature on product distribution of glucose transformation using Amberlyst-15 and hydrotalcite. Reaction conditions: glucose (0.1 g), Amberlyst-15 (0.1 g), hydrotalcite (0.1 g), DMF (3 mL), 353–393 K, 3 h.

88% selectivity for 2 h. High selectivity of \sim 90% at high yield could be obtained at both 353 K and 373 K. It should be noted that fructose dehydration for HMF could proceed at much lower temperatures (below 373 K) than glucose dehydration for anhydroglucose (above 383 K) using the same catalytic system. This indicates a significant difference between glucose dehydration and fructose dehydration over Amberlyst-15 in DMF.

3.4. HMF formation from glucose in the presence of solid acid and base catalysts in one-pot

One-pot synthesis of HMF from glucose was examined using Amberlyst-15 and hydrotalcite (Scheme 3). This methodology has the potential to improve HMF selectivity *via* the formation of fructose as an intermediate under a moderate temperature. The effects of reaction temperature on the product distribution of glucose transformation using Amberlyst-15 and hydrotalcite are shown in Fig. 5. The reaction was performed using 0.1 g of glucose, 0.1 g of Amberlyst-15, 0.1 g of hydrotalcite in 3 mL of DMF at 353–393 K for 3 h. With increasing reaction temperature glucose conversion increased from 43% at 353 K to 99% at 393 K. HMF yield remained unchanged from 353 K to 393 K, resulting in a decrease in selectivity from 52% to 18% with increasing temperature. In contrast, anhydroglucose formation increased with increasing temperature, giving yields of 7%, 18% and 22% at 353 K, 373 K and 393 K, respectively.

The product distribution was also influenced by the amounts of solid acid and base catalyst. Table 3 summarizes the depen-



Scheme 3. One-pot synthesis of 5-hydroxymethylfurfural from glucose using Amberlyst-15 and hydrotalcite.

| Tabl | e 3 |
|------|-----|
|------|-----|

One-pot synthesis of 5-hydroxymethylfurfural from glucose using a variety of Amberlyst-15 and hydrotalcite combinations.^a.

| Entry | Catalyst amount (g) | | Glucose conv. (%) | Product yield (%) | | |
|----------------|---------------------|--------------|-------------------|---------------------------|----------|------------------|
| | Amberlyst-15 | Hydrotalcite | | HMF ^b (selec.) | Fructose | AHG ^c |
| 1 | 0.1 | 0 | 69 | 0(0) | 0 | 32 |
| 2 | 0 | 0.1 | 62 | 0(0) | 38 | 0 |
| 3 | 0.1 | 0.1 | 64 | 24 (38) | 2 | 18 |
| 4 ^d | 0.1 | 0.1 | 63 | 23 (37) | Trace | 16 |
| 5 ^e | 0.1 | 0.1 | 63 | 24 (38) | 1 | 16 |
| 6 | 0.1 | 0.05 | 71 | 12 (17) | 0 | 30 |
| 7 | 0.1 | 0.2 | 72 | 41 (57) | 4 | 10 |
| 8 ^f | 0.1 | 0.2 | 73 | 42 (58) | 0 | 13 |
| 9 | 0.05 | 0.2 | 76 | 41 (54) | 4 | 8 |
| 10 | 0.025 | 0.2 | 81 | 36 (45) | 5 | 7 |

^a Reaction conditions: glucose (0.1 g), Amberlyst-15, hydrotalcite, DMF (3 mL), 373 K, 3 h.

^b 5-Hydroxymethylfurfural.

^c Anhydroglucose. Sum of 1,6-anhydro-β-D-glucopyranose and 1,6-anhydro-β-D-glucofuranose.

^d 2nd use.

e 3rd use.

^f 353 K, 9 h.

dence on the amount of Amberlyst-15 and hydrotalcite catalysts used in a one-pot synthesis of HMF from glucose at 373 K for 3 h in DMF. In the presence of either the solid acid or the solid base. HMF was not obtained (entries 1 and 2). The former reaction selectively gave anhydroglucose (entry 1) and the latter gave fructose (entry 2). A combination using the same amount of solid acid and solid base (0.1 g) gave a 24% yield of HMF with 38% selectivity (entry 3). In this case, fructose was slightly formed at 2% yield. The vield of anhydroglucoses (sum of 1,6-β-D-anhydroglucopyranose and $1,6-\beta$ -D-anhydroglucofuranose) was 18%. The combination of Amberlyst-15 and hydrotalcite could be reused for this HMF synthesis at least three times without loss of activity (entries 4 and 5). The acid and base catalysts were simply recovered by decantation, washing with solvent (DMF, 6 mL) and drying in vacuo overnight, and recycled for further reaction. Decreasing the hydrotalcite from 0.1 g to 0.05 g resulted in a poorer yield of HMF (12%) with 17% selectivity, attributable to a decrease in fructose formation by base-catalyzed isomerization (entry 6). In contrast, increasing the amount of hydrotalcite to 0.2 g improved the HMF yield to 41% with 57% selectivity (entry 7). Anhydroglucose formation was 10%, which was lower than that obtained using 0.1 g of hydrotalcite (entry 3). The formation of anhydroglucose could be suppressed by reducing the amount of solid acid, Amberlyst-15 (entries 9 and 10). Using 0.025 g of Amberlyst-15 and 0.2 g of hydrotalcite, 81% glucose conversion and 36% HMF yield (corresponding to 0.2 mmol) were obtained (entry 10). The amounts of acid and base catalysts used were 4.8 mmol g^{-1} for Amberlyst-15 and 0.7 mmol g^{-1} for hydrotalcite, respectively. Turnover numbers were estimated to be 1.7 and 1.4 for Amberlyst-15 and hydrotalcite, respectively. These results showed that the highest HMF selectivity (57%) was obtained using 0.1 g of Amberlyst-15 and 0.2 g of hydrotalcite at 373 K for 3 h (entry 7). A similar result was observed at 353 K for 9 h (entry 8).

Fig. 6 shows the time course of HMF formation from glucose in the presence of Amberlyst-15 and hydrotalcite at 353 K. In the initial stage of reaction (1 h), fructose formation was clearly observed, indicating that glucose was firstly transformed into fructose by isomerization over the solid base hydrotalcite. The yield of fructose decreased over the reaction time, falling to zero after 9 h. Correspondingly, the HMF yield increased over this time, indicating that fructose was successively dehydrated into HMF by acid catalysis by Amberlyst-15. After 9 h, the glucose conversion and HMF yield were 73% and 42%, respectively. HMF selectivity improved with increasing reaction time, from 31% for 1 h to 58% for 9 h. Anhydroglucose formation as a side reaction via acid catalysis by Amberlyst-15 also gradually proceeded during the reaction, giving a yield of 13% for 9 h. Levulinic acid and formic acid as rehydrated products of HMF were not formed. The mechanism of sequential reactions was confirmed by the addition of Amberlyst-15 into a solution containing fructose formed from glucose in the presence of hydrotalcite, as shown in Fig. 7. Upon the addition of Amberlyst-15, fructose was quickly consumed and HMF correspondingly formed, resulting in a 46% yield of HMF with high selectivity (76%) after 4.5 h.







Fig. 7. Time course of glucose transformation into fructose and 5hydroxymethylfurfural (HMF). Amberlyst-15 was added after 2.5 h. Reaction conditions: glucose (0.1 g), Amberlyst-15 (0.1 g), hydrotalcite (0.2 g), DMF (3 mL), 373 K.

| | | 54 | 1 |
|--|--|----|---|
| | | | |

One-pot synthesis of 5-hydroxymethylfurfural from glucose using Amberlyst-15 and hydrotalcite in various solvents.^a.

| Entry | Solvent ^b | Glucose conv. (%) | Product yield (%) | Product yield (%) | |
|----------------|----------------------|-------------------|---------------------------|-------------------|------------------|
| | | | HMF ^c (selec.) | Fructose | AHG ^d |
| 1 | DMF | 72 | 41 (57) | 4 | 10 |
| 2 | DMA ^e | 97 | 14 (14) | Trace | Trace |
| 3 | DMSO ^f | 94 | 12 (13) | 0 | Trace |
| 4 ^g | DMSO ^f | 41 | 25 (61) | 0 | 0 |
| 5 | MeCN ^h | 88 | 10(12) | 1 | 12 |
| 6 | H ₂ O | 40 | 0(0) | 23 | 0 |
| 7 | $DMF + H_2O(3)$ | 45 | 29 (64) | 0 | 0 |
| 8 | $DMF + H_2O(10)$ | 31 | 0(0) | 6 | 0 |
| 9 | $MeCN + H_2O(3)$ | 91 | 28 (31) | 2 | 12 |
| 10 | $MeCN + H_2O(6)$ | 92 | 25 (27) | 2 | 0 |
| 11 | $MeCN + H_2O(16)$ | 91 | 0(0) | 2 | 0 |

^a Reaction conditions: glucose (0.1 g), Amberlyst-15 (0.1 g), hydrotalcite (0.2 g), 373 K, 3 h.

^b Values in parentheses are the water concentrations (v/v, %).

^c 5-Hydroxymethylfurfural.

^d Anhydroglucose. Sum of 1,6-anhydro- β -D-glucopyranose and 1,6-anhydro- β -D-glucofuranose.

^e NN-dimethylacetamide

f Dimethyl sulfoxide.

g 353 K

h Acetonitrile.

Table 4 shows the effect of solvent on HMF formation in the presence of 0.1 g of Amberlyst-15 and 0.2 g of hydrotalcite at 373 K for 3 h. In addition to water, we used polar aprotic solvents (N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO) and acetonitrile (MeCN)). Glucose could be fully dissolved at 373 K for all solvents except in the case of MeCN. HMF was successfully formed in all the polar aprotic solvents tested (entries 1-5), whereas it was not produced at all in water (entry 6). The highest yield and selectivity for HMF formation were observed in DMF (entry 1). Among the other polar aprotic solvents, the HMF yields were 14%, 12% and 10% for DMA, DMSO and MeCN, respectively. In DMSO, at 353 K, the HMF yield was higher at 353 K (25% with 61% selectivity) than at 373 K (entries 3 and 4). In water, HMF was not obtained due to the loss of activity of Amberlyst-15 in dehydrating fructose into HMF, meaning the hydrotalcite acts alone as a base catalyst for isomerization, resulting in fructose formation at 23% yield (entry 6). The dehydration activity of Amberlyst-15 in forming HMF from fructose and anhydroglucose from glucose was considerably affected by the presence of water. Addition of a small amount of water (3 vol%) to DMF diminished anhydroglucose formation, resulting in a high HMF selectivity (67%) (entry 7). However, addition of a larger amount of water (10 vol%) gave 0% HMF yield (entry 8). These results indicate that anhydroglucose formation from glucose by acid catalysis is much more sensitive to water than HMF formation from fructose, and in this latter case a small amount of water could be beneficial. For example, the addition of a small amount of water (3-6 vol%) to acetonitrile improved the HMF yield from 10% to 25-28% (entries 9 and 10), which were higher than those obtained in DMA and DMSO. Because sugars, including glucose, are not fully dissolved in pure acetonitrile, addition of water to acetonitrile improves the solubility, resulting in enhancement of the HMF yield. An excess of water (16 vol%), however, leads to negative effects (0% HMF yield) (entry 11).

4. Conclusions

We have demonstrated selective formation of anhydroglucose and 5-hydroxymethylfurfural from glucose using heterogeneous acid-base catalysts. Anhydroglucose was selectively formed by dehydration of glucose in the presence of Amberlyst-15 as a solid acid catalyst. The anhydroglucose selectivity and yield were affected by the glucose concentration and reaction temperature, respectively. A low glucose concentration and a high reaction tem-

perature (above 383 K) were preferred, achieving 77% selectivity at 93% conversion in N,N-dimethylformamide at 413 K.

In contrast, using a combination of solid acid and base catalysts afforded selective formation of 5-hydroxymethylfurfural. Hydrotalcite was used as the base catalyst for isomerization of glucose to fructose, and Amberlyst-15 was used as the acid catalyst for dehydration of fructose to 5-hydroxymethylfurfural. This system gave a high HMF yield and selectivity under mild conditions (below 373 K). For example, using 0.1 g of Amberlyst-15 and 0.2 g of hydrotalcite at 353 K for 9 h, 58% HMF selectivity and 73% glucose conversion were obtained. A low reaction temperature is advantageous in formation of fructose from glucose by base catalysis and limits the amount of anhydroglucose formation by acid catalysis. The preferential formation of fructose results in high selectivity for HMF. Aprotic polar solvents, including N,N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide and acetonitrile can be used in this system, with the addition of a small amount of water improving HMF selectivity. The catalysts are recyclable and the method provides efficient conversion of glucose into important intermediates by an environmentally friendly catalytic reaction.

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