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Catalytic Transformations of Biomass-derived Materials into Value-added Chemicals

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Abstract: This manuscript reviews recent literatures on synthesis of furfurals (5-hydroxymethylfurfural, furfural, 5-methyl-2-furaldehyde) from various sugars (glucose, fructose, D-galactose, D-arabinose, xylose, L-rhamnose, lactose, cellobiose, sucrose) and furfural conversions into other carbonyl compounds (2,5-diformylfuran, 2,5-furandicarboxylic acid, levulinic acid, succinic acid) using catalytic methodology. Our recent achievements on one-pot synthesis of furfurals using solid acid and base catalysts and selective oxidations of furfurals using heterogeneous catalysts are also included.

1. Introduction

Use of carbon dioxide (CO₂), H₂O, and sunlight is one of the most important challenging tasks for present scientists and engineers to avoid energy crisis in near future generations. Plant is a product from CO₂, H₂O, and sunlight via photosynthesis, and considered as a renewable and an alternative source (biomass) instead of fossil fuel. Transformation of plant into energy source and valuable chemicals, therefore, will serve our turn [1-9]. Especially, non-edible biomass should be used to evade the food problem.

Sugars are obtained from cellulose and hemicellulose, main components of wood, and could be converted into valuable furfurals which are transformed into various carbonyl compounds. Recent progresses of catalytic transformations of biomass-derived materials have been reviewed, and biomass-based catalytic routes into liquid fuels have been proposed [1-9]. In this review, we focused on reviewing recent literatures for synthesis of furfurals from various sugars, synthesis of levulinic acid and succinic acid from furfurals, and selective oxidations of 5-hydroxymethylfurfural (HMF) into the corresponding dialdehyde and dicarboxylic acid, as shown in Scheme 1.

(Scheme 1 near here)

2. Syntheses of Furfurals from Sugars

2.1. Furfurals as Renewable Chemical Platforms

Carbohydrates have large amount of oxygen atoms, led to the difficulty of use for fuels and

chemicals. Dehydration of sugars is one of the desired approaches for removal of oxygen atoms, affording furfurals which are considered as renewable chemical platforms [1-9]. Hexoses including glucose and fructose and pentoses such as xylose are transformed into 5-hydroxymethylfurfural (HMF) and furfural, respectively through dehydration of three water molecules. These furfurals are very useful intermediates. For instance, HMF is allowed to be functionalized by selective oxidation, which gives corresponding dialdehyde (2,5-diformylfuran) and dicarboxylic acid (2,5-furandicarboxylic acid), which are useful intermediates for bio-based polymer. Moreover, 2,5-dimethylfuran can be obtained by reduction of hydroxyl groups of HMF, which is suggested to be an alternative fuel [10]. In addition, rehydration of HMF affords levulinic acid, which is also important chemical platform. Recently, Heeres et al. demonstrated the production of caprolactone from HMF via 1,6-hexanediol formation by hydrogenation/dehydration, indicating that Nylon 6, a widely used synthetic polymer could be provided from lignocellulosic biomass [11].

2.2. Synthesis of 5-Hydroxymethylfurfural by using Homogeneous Catalysts

Fructose which is a most common ketohexose was widely studied as a substrate for HMF synthesis [12-16]. HMF is easily formed from fructose in the presence of liquid acid such as H_2SO_4 and HCl in aprotic polar solvents including dimethyl sulfoxide (DMSO). However, this method has drawbacks of difficulty of separation and purification of HMF from high-boiling solvents. In water, poor HMF selectivity was observed because of successive sugar decomposition, condensations and rehydration of HMF.

A notably efficient production of HMF was reported by using a homogeneous acid catalyst in biphasic system [17]. HMF is formed by dehydration of fructose in HCl-containing aqueous phase. HMF obtained is then extracted in methyl isobutyl ketone (MIBK)-2-butanol organic phase. This method affords high fructose conversion (90%) with high HMF selectivity (80%). HMF and furfural were produced from a variety of sugars including glucose, xylose, sucrose, cellobiose, inulin, starch and xylan [18-20]. Under the optimum condition for glucose dehydration, glucose conversion and HMF selectivity were 43% and 53%, respectively, much lower than the case of fructose.

One of the most important reactions is HMF synthesis from glucose. Glucose is the unit of cellulose which is major component of lignocellulosic biomass, and the most abundant monosaccharide. In 2007, an innovative report for HMF production from glucose has been provided by Zhang et al [21]. They used chromium chloride (CrCl_2) in an ionic liquid, 1-ethyl-3-methylimidazolium chloride [EMIM]Cl for HMF production from glucose, resulting in 68-70% HMF yield at 373 K. This method is applicable for HMF production from cellobiose and cellulose. Cellulose is easily dissolved in [EMIM]Cl ionic liquid, and 58% HMF yield was obtained in the presence of a mixture of CuCl_2 and CrCl_2 at 393K [22].

The metal halide catalysis for HMF production from sugars is extensively studied by many researchers. Raines et al. demonstrated high HMF yield from cellulose and lignocellulosic biomass

in $\text{CrCl}_2/\text{HCl}/N,N$ -dimethylacetamide (DMA) - $\text{LiCl}/[\text{EMIM}]\text{Cl}$ [23, 24]. Instead of chromium chloride, the uses of tin chloride (SnCl_4) [25] and germanium chloride (GeCl_4) [26] in ionic liquid are also reported for HMF production. The metal halide catalysis involves two important reactions. First step is mutarotation from α -glucopyranose to β -glucopyranose. Second is isomerization from glucopyranose to fructofuranose which further dehydrates to form HMF. The isomerization of glucose to fructose requires a hydride shift between C2 and C1 of the open form of the sugar, which is considered as rate-determining step. This isomerization of glucose toward fructose is catalyzed by Lewis acid character of chromium ions. Hensen et al. proposed that the former mutarotation is catalyzed by single Cr center and the latter isomerization by transient binuclear Cr centers from the results of XAFS and DFT calculation [27, 28].

2.3. Synthesis of 5-Hydroxymethylfurfural from Fructose and Glucose by using Heterogeneous Catalysts

The use of heterogeneous catalysts has many advantages such as easy separation, nontoxicity and recyclability. A variety of solid acids such as ion-exchange resins, zeolites, metal oxides and heteropoly acid salts have been examined for HMF production from fructose [29, 30]. Early study was carried out by using a strongly acidic ion-exchange resin, DIAION PK216 in DMSO [31]. Moreau et al. reported that a remarkable HMF selectivity (~99%) was obtained by using H-mordenite at 433 K in water—MIBK biphasic system [32, 33]. Niobic acid, niobium phosphate, vanadium phosphate, sulfated zirconia, Amberlyst-15 and acid-functionalized mesoporous silica were also found to exhibit high activity for the fructose dehydration [34-40]. Moreover, the use of solid acids in ionic liquid was examined [41-48].

On the contrary to fructose, efficient HMF synthesis from glucose by using heterogeneous catalysts has not been reported until 2009. To achieve successful production of HMF from glucose, isomerization of glucose toward fructose by heterogeneous catalysts is a key reaction as well as homogeneous catalyst. There are two mechanisms for glucose isomerization *via* proton transfer and intramolecular hydride shift. These are generally catalyzed by base and Lewis acid, respectively.

The former base-catalyzed aldose-ketose isomerization is named as Lobry-de Bruyn-van Ekenstein transformation [49]. Deprotonation of α -carbonyl carbon of aldose (glucose) takes place by base, resulting in the form of a series of enolate intermediates. Moreau et al. reported that solid bases such as cation-exchanged zeolites and Mg-Al hydrotalcite catalyze isomerization of glucose in water [50-52]. The present authors adopted this base-catalyzed isomerization for efficient one-pot reaction (see below). Some literatures proposed that solid basicity is effective for HMF formation from glucose. For instance, Hu et al. used $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3$ catalysts where the optimum HMF yield was obtained over $\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3$ with Zr-Al mole ratio of 1:1 [53]. They concluded that stronger acidity and moderate basicity are favorable.

The latter isomerization via intramolecular hydride shift is catalyzed by Lewis acid. Recently, Davis et al. revealed that tin-containing zeolite, Sn-Beta exhibits a remarkable activity for

glucose-fructose isomerization in water, which is catalyzed by Lewis acid [54]. They used glucose deuterated at the C-2 position for ^{13}C and ^1H NMR spectroscopy in order to elucidate the glucose isomerization mechanism. A clear difference was observed between Sn-Beta and NaOH.

Much attention has been paid to solid Lewis acidity of metal oxides [55]. Hara et al. found that amorphous niobium oxide hydrate ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$), so called niobic acid, has Lewis acid sites along with Brønsted acid sites [56]. Owing to its water-tolerant Lewis acidity, niobic acid showed high performance on HMF production from glucose in water and allylation of benzaldehyde with tetraallyl tin in water. Interestingly, phosphoric acid-treated niobic acid ($\text{H}_3\text{PO}_4/\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) exhibited much higher HMF selectivity (52%) than non-treated niobic acid (12%). They described that most of phosphate ions were fixed on neutral OH groups and 70% of Brønsted acid sites. The Brønsted acid sites do not play an important role for the reaction. This conclusion is contrary to the previous report by Du et al [57]. They also used H_3PO_4 -treated niobic acid for HMF formation from glucose and fructose in a water-2-butanol biphasic system. H_3PO_4 -treated niobic acid possessed larger number of acid sites with moderate and strong acid strength than that of niobic acid. Du et al. also demonstrated that H_3PO_4 -treated tantalum oxide hydrate ($\text{H}_3\text{PO}_4/\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) analogous to niobic acid exhibited much higher activity than niobic acid in a water-2-butanol biphasic system at 433 K [58]. In addition to V group elements (Nb and Ta), Saha et al. used mesoporous titanium nanoparticulates with Lewis acid sites for HMF formation from glucose [59, 60].

The combination of Lewis acid and Brønsted acid is beneficial to HMF formation from glucose. Davis et al. used heterogeneous Lewis acid Sn-Beta with homogeneous Brønsted acid HCl in a water-tetrahydrofuran (THF) system [61]. Isomerization of glucose into fructose is catalyzed by Lewis acid Sn-Beta and successive dehydration of fructose into HMF is catalyzed by homogeneous Brønsted acid HCl. Over 70% HMF selectivity was obtained at 453 K. The Sn-W mixed oxide which possesses both Brønsted acid sites and Lewis acid sites was examined for HMF and furfural production from sugars [62]. The Sn-W mixed oxide catalyzed both glucose isomerization and fructose dehydration. High HMF and furfural yields were obtained from a variety of sugars including glucose, fructose, mannose, galactose, cellobiose, sucrose, starch, xylose and arabinose in a water-THF system at 393 K.

2.4. Synthesis of Furfural from Xylose by using Heterogeneous Catalysts

Furfural is formed by dehydration of pentose. Xylose is a major aldopentose and is involved as a form of xylan in hemicelluloses. Moreau et al. showed H-mordenite and H-Y faujasite were found to exhibit dehydration at 433K in water-MIBK or water-toluene solution [63]. Valente et al. have investigated the dehydration using a variety of solid acid catalysts including sulfonic acid appended porous silicas [64], porous niobium silicates [65], metal oxide nanosheets [66], heteropolyacids [67, 68], sulfated zirconia [69], delaminated zeolite [70], H-MCM-22 zeolite [71] in water-toluene biphasic systems. Furfural formation from xylose is also examined by using $\text{SO}_4^{2-}/\text{ZrO}_2\text{-Al}_2\text{O}_3/\text{SBA-15}$ [72]. Contrary to glucose, furfural can be formed from xylose by using

sole Brønsted acid at high temperature. An ion-exchange resin Nafion 117 [73], propylsulfonic acid-functionalized mesoporous silica SBA-15 [74] and sulfonic acid-modified mesoporous shell silica [75] showed good furfural yield. Tatsumi et al. reported that sulfated tin oxide ($\text{SO}_4^{2-}/\text{SnO}_2$) was an effective catalyst for furfural formation due to the combination of Lewis acid and Brønsted acid properties [76]. Similar to transformation of glucose into HMF, Sn-Beta affords aldose-ketose isomerization of pentose [77]. In the presence of Sn-Beta, xylose was isomerized into xylulose in water, and combining Sn-Beta with a liquid Brønsted acid catalyst can produce furfural.

2.5. One-pot Synthesis of 5-Hydroxymethylfurfural from Glucose by using Solid Acid and Base Catalysts

One-pot reactions using heterogeneous catalysts afford remarkably unique and environmentally-friendly benefits, including avoidance of isolation and purification of intermediate compounds, which saves time, energy and solvent [78-85]. The concept of site isolation can be realized by the coexistence of acid and base without neutralization, which has been demonstrated using acid–base pairs of polymers, sol–gel matrices, porous silicas and layered clays.

The present authors have adopted this approach for HMF synthesis from glucose through a two-step reaction in one-pot [86, 87]. Simple use of conventional solid acids and bases has afforded the efficient production of HMF. Our strategy involves separating HMF synthesis from glucose into two reactions, (1) isomerization of glucose into fructose catalyzed by solid base and (2) dehydration of fructose into HMF by solid Brønsted acid. Such an approach has never been adopted for liquid acid–base pair due to their neutralization.

To select efficient heterogeneous catalysts for the one-pot reaction, two individual reactions were first tested, the isomerization of glucose and dehydration of fructose.

Among solid bases tested, Mg–Al hydrotalcite (HT), consisting of layered clays with HCO_3^- groups on the surface, was found to display the highest activity for isomerization (Table 1). Table 1 also lists the temperature dependence of catalytic activity of hydrotalcite on isomerization of glucose to fructose. Glucose conversion increased with increasing reaction temperature from 47% at 353K to 81% at 393 K. Correspondingly, however, the fructose yield gradually decreased from 40% at 353K 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, 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.

(Table 1 near here)

For acid-catalyzed dehydration of fructose into HMF, ion-exchange resins, such as Amberlyst-15 and Nafion NR50, as well as sulfated zirconia exhibited high activity, whereas niobic acid and H-type zeolites were inactive under the conditions listed in Table 2. The transformation of glucose over solid acids (not shown) indicates that ion-exchange resins did not produce HMF directly from glucose but caused intramolecular dehydration into anhydroglucoses (1,6-anhydro- β -D-glucopyranose and 1,6-anhydro- β -D-glucofuranose)[88]. This is one of the major drawbacks in using only an acid catalyst for the direct formation of HMF from glucose. From these results, HT and Amberlyst-15 were chosen as the solid base and acid, respectively.

(Table 2 near here)

Direct formation of HMF from glucose using solid acid and base in the one-pot reaction is shown in Table 3. Remarkably, HMF synthesis from glucose was successfully achieved in the presence of both HT and Amberlyst-15 catalysts (entry 1). 64% of glucose conversion and 38% of HMF selectivity were obtained at 373 K for 3 h. Anhydroglucoses (AHG; 1,6-anhydro- β -D-glucopyranose and 1,6-anhydro- β -D-glucofuranose) and a small amount of fructose were detected as by-products (AHG selectivity: 28%, fructose selectivity 3%). Glucose conversion and HMF yield continually increased with increasing reaction time. HMF selectivity was almost the same after 3 h reaction. After 9 h, glucose was fully converted (>98%), resulting in HMF selectivity of 34%. The pair of HT and Nafion NR50 also produces HMF from glucose (glucose conversion: 60%; HMF selectivity: 27%) (entry 2). As mentioned above, glucose was converted, not into HMF, but fructose, over only solid base (HT) (entry 3) and anhydroglucoses over only solid acid (Amberlyst-15) (entry 4). On the other hand, HMF was not formed using a liquid acid–base pair (entry 6).

(Table 3 near here)

The effects of reaction temperature on the product distribution of glucose transformation using Amberlyst-15 and hydrotalcite are shown in Figure 1. The reaction was performed using 0.1 g of glucose, 0.1 g of Amberlyst-15, 0.1 g of hydrotalcite in 3mL of DMF at 353–393K for 3 h. With increasing reaction temperature glucose conversion increased from 43% at 353K to 99% at 393 K. HMF yield remained unchanged from 353K 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, 373K and 393 K, respectively.

(Figure 1 near here)

The product distribution was also influenced by the amounts of solid acid and base catalyst. Table 4 summarizes the dependence on the amount of Amberlyst-15 and hydrotalcite catalysts used in a one-pot synthesis of HMF from glucose at 373K for 3 h in DMF. 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 1). In this case, fructose was slightly formed at 2% yield. The yield of anhydroglucoses (sum of 1,6- β -D-anhydroglucopyranose and 1,6- β -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 2 and 3). 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 4). In contrast, increasing the amount of hydrotalcite to 0.2 g improved the HMF yield to 41% with 57% selectivity (entry 5). Anhydroglucose formation was 10%, which was lower than that obtained using 0.1 g of hydrotalcite (entry 1). The formation of anhydroglucose could be suppressed by reducing the amount of solid acid, Amberlyst-15 (entries 7 and 8). 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 8). 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 373K for 3 h (entry 5). A similar result was observed at 353K for 9 h (entry 6).

(Table 4 near here)

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. 2. 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.

(Figure 2 near here)

2.6. One-pot Synthesis of Furfural from Xylose and Arabinose by using Solid Acid and Base Catalysts

As well as glucose dehydration, a combination of Amberlyst-15 and hydrotalcite affords furfural from xylose under mild reaction conditions. Table 5 shows furfural formation from xylose using solid acid and/or base catalysts at 373K for 3 h. The individual use of Amberlyst-15 gave 51% xylose conversion, but negligible yield and poor selectivity of furfural as a desired product (below 1%) (entry 1). In the presence of hydrotalcite, no production of furfural was observed (entry 2). An efficient production of furfural was obtained in the presence of Amberlyst-15 and hydrotalcite (entry 3). 42% furfural selectivity at high xylose conversion (57%) has been achieved using 0.1 g of

Amberlyst-15 and 0.1 g of hydrotalcite in *N,N*-dimethylformamide at 373 K for 3 h. Both furfural selectivity and xylose conversion increased with increasing hydrotalcite amount, affording 51% selectivity at 72% xylose conversion using 0.2 g of hydrotalcite in the presence of Amberlyst-15 (entry 3), much higher than those of *para*-toluenesulfonic acid (entry 6) and sulfuric acid (entry 7). It should be noted that the one-pot synthesis of furfural could be applied using other combinations of solid acid and base. The pairs of ion-exchange resins of Amberlyst-15 acid resin and commercial anion-exchange base resins including Amberlyst A26 OH (OH form) and Amberlyst A21 (tertiary amine form) also gave furfural (entries 4 and 5).

(Table 5 near here)

Arabinose is a pentose derived from hemicellulose as well as xylose. One-pot synthesis of furfural from arabinose was also tested over the solid acids and base catalysts. The results are listed in Table 6. Nafion SAC13, nanosized Nafion resin stabilized onto high porous silica catalyst, showed low conversion and selectivity (entry 7). Amberlyst-15, Nafion NR50 and hydrotalcite indicated a high conversion but low selectivity, individually (entries 4-6). In the pair catalysts with hydrotalcite, Nafion SAC13 exhibited low selectivity whereas Nafion NR50 was a little active pair acid (entries 2 and 3). As well as xylose conversion, the pairs of hydrotalcite and Amberlyst-15 seemed to be the best catalysts for arabinose conversion (entry 1).

(Table 6 near here)

2.7. One-pot Synthesis of 5-Methylfurfural from Rhamnose by using Solid Acid and Base Catalysts

5-Methylfurfural (MF) is an important chemical intermediate which can be used in production of biofuel, flavors, perfumes, agrochemicals and medicines. Synthesis of MF *via* HMF hydrogenation was widely examined. Bell and coworkers reported that 47% conv. of HMF and 36% selectivity of MF in a mixed-solution of an ionic liquid (1-ethyl-3-methylimidazolium chloride) and acetonitrile were obtained by using Pd/C catalyst under the high pressure H₂ (62 bar) [89]. Interestingly, the *in-situ* hydrogenation of extracted HMF obtained from glucose dehydration was also achieved with same activity. Direct synthesis of MF from biomass-derived carbohydrates such as glucose, fructose, sucrose, cellulose and inulin in aqueous HI solution was investigated by RuCl₃ or Pd/C catalysts under mild H₂ pressure (6.9-20.7 bar) [90]. 5-Chloromethylfurfural hydrogenation also can be applied for the synthesis of MF [91, 92]. Sheldon et al. reported the Pd(P(C₆H₄-*m*-SO₃Na)₃) complex catalyzed a reduction of HMF by using CO, and they achieved 77% conversion of HMF with 52% selectivity of MF in the presence of HBr [93]. 2-Methylfuran formylation with dimethylformamide and phosphorous oxychloride (POCl₃) became 76% yield of MF [94]. Production of MF was also detected during acidic pyrolysis of corncobs [95], thermal

degradation of HMF [96], maturation of red, white, and model wines [97], glucose-glycine Maillard reaction [98]. Halogen-free synthetic route of MF under milder reaction conditions has been envisaged for effective utilizations of MF. Very recently, we reported the environmentally benign one-pot synthesis of MF via one-pot conversion of rhamnose, a naturally-occurring deoxy hexose, and which is a base component of glycoside in many plants [99]

Isomerization of rhamnose to rhamnulose, and successive dehydration of rhamnulose to MF is examined over the pair catalysts using three common solid acid catalysts with solid base hydrotalcite (Table 7). It was observed that the combination of Amberlyst-15 and hydrotalcite catalysts showed the highest activity (75% conv., 52% sel.) for the one-pot synthesis of MF from rhamnose among these three acid catalysts. The combination of Amberlyst-15 and hydrotalcite catalysts also showed good activities for one-pot conversions of glucose and xylose (*vide supra*). This reaction presents an excellent procedure for the synthesis of MF under mild conditions.

To further investigate the differences among acid catalysts, physical properties of them are together listed in Table 7. It seemed that the larger pore size of acid catalysts induced the higher conversion. The dispersibility of substrate into pore might play one of key factors for the reaction. On the other hand, the surface area scarcely affected on the catalytic activities; the Nafion SAC13 exhibited a high surface area ($227 \text{ cm}^2 \cdot \text{g}^{-1}$) but low selectivity of MF (3%). From the view point of acid strength (H_0), the Amberlyst-15 is a mild acid ($H_0 = -2.2$) whereas Nafion SAC13 and NR50 are strong acids ($H_0 \leq -12$). In the case of strong acids, the color changes of the catalysts from white to brown were observed after the reaction, indicating undesirable by-product formation such as humins and polymers *via* side reaction. Furthermore, it was known that Amberlyst-15 possessed the largest concentration of acid sites (*ca.* $4.8 \text{ mmol} \cdot \text{g}^{-1}$) in these three catalysts; Nafion NR50 (*ca.* $0.9 \text{ mmol} \cdot \text{g}^{-1}$) and Nafion SAC13 (*ca.* $0.17 \text{ mmol} \cdot \text{g}^{-1}$). According to these results, it was proposed that Amberlyst-15 was the most effective solid acid catalyst in one-pot synthesis of furfurals with hydrotalcite catalyst since its mild acidity, large number of acid sites and large pore size which contributed to inhibition of side reaction, enhancement of reaction rate, and promotion of accessibility of substrate onto acidic sites, respectively.

(Table 7 near here)

2.8. One-pot Synthesis of Furfurals from Disaccharides and Mixed-sugars by using Solid Acid and Base Catalysts

For the actual synthesis of furfurals from natural saccharides, one-pot synthesis of furfurals over combination of solid acid Amberlyst-15 and solid base hydrotalcite catalysts were performed from disaccharides such as sucrose, cellobiose and lactose or a variety of mixed-sugars including glucose, fructose, xylose, arabinose, rhamnose and/or lactose were demonstrated. Table 8 shows the results of one-pot synthesis of HMF from three disaccharides. Sucrose consists of glucose and fructose,

cellobiose is a glucose dimer linked with a β glycosidic bond, and lactose composed of glucose and galactose (a C-4 epimer of glucose) linked with a β glycosidic bond, respectively. To achieve one-pot synthesis of HMF from disaccharides, three cascade reactions including hydrolysis of disaccharides by acid, isomerization of aldose (glucose or galactose) to ketose (fructose) by base, and dehydration of ketose by acid are necessary.

Sucrose and cellobiose indicated similar activities with different selectivity (entries 1 and 2). A very high selectivity of 93% was obtained from sucrose whereas a moderate selectivity of 67% from cellobiose. For sucrose, a half of composed monosaccharide is already fructose. Fructose is an intermediate in the one-pot synthesis of HMF from glucose, therefore the opportunity of side-reactions in glucose conversion might diminish in the one-pot synthesis from sucrose. On the other hand, lactose showed a high conversion (100%) but a low selectivity (25%) (entry 3). In this case, a large amount of monosaccharides of galactose and tagatose (a ketose obtained by isomerization from galactose) still remained. This is due to the hardness of dehydration of tagatose to HMF than that of fructose, which comes from their optical differences (epimer). In fact, 10% yield of galactose and 8% yield of tagatose were obtained after 3 h reaction.

Table 9 lists the results of one-pot synthesis of furfurals in the presence of Amberlyst-15 and hydrotalcite using mixed-sugars as a substrate. HMF, furfural and/or MF could be formed together from mixtures of hexose and pentose in this one-pot system. The pair afforded HMF and furfural from glucose and xylose (entry 1) or fructose and xylose (entry 2), and the pair gave furfural and MF from arabinose and rhamnose (entry 3). Even in three sugars use, the one-pot synthesis of corresponding furfurals was also performed (entry 4). These results strongly indicated that the one-pot synthesis of furfurals with solid acid and solid base catalysts is one of promising procedures for biomass utilizations.

This strategy has been applied for the different combination such as solid Lewis acid with liquid Brønsted acid [61, 77], and solid Brønsted acid with solid Lewis acid catalysts [100]. For instance, a combination of Sn-Beta and Amberlyst-15 in ethanol affords 5-(ethoxymethyl)furfural in one pot reaction.

(Table 8 near here)

(Table 9 near here)

3. Furfurals Conversions into Other Carbonyl Compounds

3.1. Carbonyl Compounds as Renewable Chemical Platforms

Carbonyl compounds obtained from HMF and furfural such as levulinic acid, succinic acid, 2,5-diformylfuran, and 2,5-furandicarboxylic acid (Scheme 1) *via* hydration or oxidation are important chemical platforms for polymers. Formation of levulinic acid and succinic acid needs carbon-carbon bond cleavage of furfural skeleton. Selective dehydrogenation of aldehyde moiety is

an essential reaction for the production of 2,5-diformylfuran or 2,5-furandicarboxylic acid. Furthermore, use of clean oxidants such as H_2O_2 and O_2 is preferable from the viewpoint of green and sustainable chemistry.

3.2. Synthesis of Levulinic Acid

Levulinic acid (LA) is a value-added chemical derived from biomass, it can be applied for chiral reagents, inks, coatings, batteries and so on [101]. LA is also focused on as the starting material for the synthesis of chemicals and intermediates. The levulinate esters formed from esterification reaction with C_1 - C_2 alcohols can be used as blending component in biodiesel [102-104]. The reaction of LA with two molecules of phenol serves the diphenolic acid which can be replaced with bisphenol A in the area of industrial epoxy resins and polycarbonates formation processes [105, 106]. δ -Aminolevulinic acid and pyrrolidone produced *via* amination are attractive derivatives of LA as important intermediates in the synthesis of agricultural and pharmaceutical compounds [107, 108]. Notably, the formation of γ -valerolactone (GVL) has been widely investigated in this decade because it can provide the valeric acid which serves a new biofuels called as valeric biofuels [109], butene by decarboxylation [110], and 1,4-pentanediol and methyl tetrahydrofuran (MTHF) as a fuel extender by reduction [111, 112].

A major process for LA production is carbohydrate decomposition through acid-catalyzed hydrolysis of HMF to LA along with an equivalent formation of formic acid. Mineral acid catalysts such as HCl, H_2SO_4 and H_3PO_4 were strenuously investigated for the synthesis of LA [113-116] because they were capable of adapting to various cellulosic feedstocks; whole kernel grain sorghum [117], water hyacinth [118], bagasse [119], and paper [120, 121]. Very recently, production of LA in biphasic solvents with high yield and selectivity (60-70%) was accomplished from HMF and furfuryl alcohol by HCl and H_2SO_4 , respectively [122]. Alonso and co-workers proposed the utilization of biphasic alkylphenol/water solvent in the LA synthesis from cellulose by H_2SO_4 to take advantages of high efficiencies for LA extraction and successive hydrogenation of LA to GVL over RuSn/C catalyst [123].

One of the most attractive biorefinery processes is GVL production through LA formation. Some economic processes of GVL production from mixture of LA and formic acid in aqueous solution have been provided, which will avoid the energy-consuming separation of LA [107, 124, 125]. The process for the direct synthesis of levulinate esters and GVL from cellulose in a cascade of flow reactors was described by Gurbuz et al [126]. The economic and environmentally-friendly processes for utilization of mineral acid catalyst have been discussed.

In order to easily separate the catalyst from solvent after the reaction, development of solid catalyst for the synthesis of LA is tried by many research groups. Conversion of cellulose to LA in water was examined by using metal chlorides as catalyst. Peng et al. achieved 67% yield of LA with CrCl_3 catalyst from cellulose *via* hydrolysis and successive dehydration of formed glucose in hydrothermal condition at 473 K [127]. LaCl_3 catalyst was demonstrated in water at 523 K for 150 s,

and it served 2.3wt% LA from cellulose [128]. It mentioned that these catalysts exhibited easy handling and recovery.

Several kinds of sulfonated polymers are one of promising solid acid catalysts for LA production. Vyver et al. reported that sulfonated hyperbranched poly(arylene oxindole)s indicated 30% yield of LA in the conversion of cellulose at 443 K in water [129]. The acid polymers showed significant activities for the synthesis of LA (63-76% yield) in the conversion of fructose, HMF and inulin. Notably, α -cellulose and ball-milled cellulose served 8% and 27% yield of LA at 438 K in water, respectively. 33% yield of LA from glucose dehydration over Amberlyst-70 was performed in the hydrothermal condition at 433 K by Weingarten and co-workers [130]. They attempted a dehydration/rehydration step of cellulose by Amberlyst-70, and got 21% yield of LA at 433 K from the water-soluble organics obtained from the hydrothermal decomposition of cellulose at 493 K. Hegner and coworkers investigated the Nafion SAC13 catalyst for cellulose conversion to LA [131]. Interestingly, the addition of 25% NaCl in the reaction mixture of Nafion SAC13, cellulose and water showed 5 times higher LA yield [132]. The authors explained that the NaCl effectively interrupted the hydrogen bonding network under the high temperature and pressure. Nafion NR50, Amberlyst-15 and other highly acidic ion-exchange resins also could feed the LA from saccharides [133, 134]. The advantage of a polymer catalyst in use is little amount of humin formation and lower operation temperature.

Chen et al. studied a solid superacid catalyst denoted as $S_2O_8^{2-}/ZrO_2-SiO_2-Sm_2O_3$ for the conversion of rice straw to LA [135]. They showed 23wt% LA yield from steam-treated rice straw. Sulfated TiO_2 [136], MFI-type zeolite [137], LYZ-zeolite [138], for cellulose, glucose or fructose decompositions have been reported. Notably, Lai et al. proposed a magnetic $Fe_3O_4-SBA-SO_3H$ catalyst with a LA yield of 54% derived from cellulose in order to remove the catalyst from the reaction residues such as insoluble humins and lignin [139]. The use of solid catalyst for the synthesis of LA from carbohydrates leads to easy separation of products from reaction mixture. The use of the solid catalyst is, however, currently limited under harsh reaction conditions (high temperature and pressure), *e.g.* subcritical water, which should be improved from the viewpoint of environmentally friendly process.

Kinetic studies for the synthesis of LA were also investigated in the decomposition of cellulose [114, 140], glucose [141], fructose [115], HMF [116], rehydration of HMF formed by glucose dehydration [142] by using HCl or H_2SO_4 catalyst. Although high temperature operation enhances the conversion of carbohydrates to LA, undesired side reactions such as humin formation were also accelerated. Therefore, high temperature with short reaction time in the presence of strong acid catalyst is essential to achieve the maximum yield of LA. The short reaction time inhibits the humins formation derived from glucose and/or HMF and allows the high selectivity for LA formation. Wheat straw collected from a local farm provided 20 wt% LA in the optimum condition predicted by experimental design with acid catalyst [143].

Hydrolysis of furfuryl alcohol which was formed by reduction of furfural was also proposed for

the synthesis process of LA. Maldonado and coworkers investigated the transformation of furfuryl alcohol to LA by Amberlyst-15 in water with mechanistic studies [144]. They proposed multistage reactions through formation of intermediates (a germinal diol species and a dimer-like species) in water. This reaction was catalyzed by acids such as HCl, H₂SO₄, Amberlyst-15, and ZSM-5 [122, 145]. Direct synthesis of alkyl levulinate from furfuryl alcohol was also demonstrated [146, 147].

3.3. Synthesis of Succinic Acid via Furfural Oxidation

Succinic acid (SA, butanedioic acid) is identified as an interest biomass-derived building-block chemical. It can be transformed into 1,4-butanediol, γ -butyrolactone (GBL), adipic acid, tetrahydrofuran (THF), pyrrolidones, and linear aliphatic esters [148-151]. And biodegradable polymers called as polybutyrate succinate (PBS), its copolymers, and polysuccinamides (PSA) are prospective for engineering plastic materials [152-155].

Currently, SA has been synthesized by bacterial fermentation using a large number of bacteria such as *Anaerobiospirillum succiniciproducens*, *Actinobacillus succinogenes*, and metabolically engineered *Escherichia coli* [156-159]. These processes are capable for various kinds of sugars as feedstocks; *e.g.* glucose, fructose, xylose, wheat, whey, and so on. The fermentative SA production system is very attractive because it supplies a large amount of SA productivity and fixed a greenhouse CO₂ gas into SA during reaction, which suits for large-scale industrial production of SA. To recover and purify the formed SA from the fermentation broth, nanofiltration using membrane, salt precipitation, electrodialysis, and solvent extraction have been investigated [160]. One of drawbacks is a high cost for bioreactor and strict control of reaction conditions (*ex.* pH and temperature).

For a wide utilization of SA, development of chemical synthesis of SA is an important issue. Traditionally, SA can be produced by hydration and/or hydrogenation of fossil-derived maleic anhydride or maleic acid (MA, *cis*-butenedioic acid) which was manufactured by oxidation of *n*-butene or butadiene [161, 162]. Reduction of MA to SA with electronic reaction over Ti/ceramic TiO₂ [163], Ti cathode [164] and a lead cathodes [165] were investigated in mild reaction temperature (below 373 K). Galvanostatic electrolysis for SA synthesis from MA using stainless steel, Cu or Pd cathodes in an ion conducting polymer electrolyte flow cell obtained >95% yield of SA with a coulombic efficiency of 80-90% [166]. In the homogeneous catalytic system, reduction of MA and fumaric acid (FA, *trans*-butenedioic acid) by solution of chromous sulfate in water achieved 86 and 91 % yield of SA, respectively [167]. Interestingly, it was claimed that Vitamin B_{12s} (Cob(I)alamin) smoothly reduced MA and FA to SA [168]. Hydrogenation of MA over Ru/Al₂O₃ catalyst [169], oxidation of 2-butene over precious metal catalysts with phosphoric acid in the vapor phase [170], and oxidation of petroleum wax and/or other paraffinic hydrocarbons [171] to yield SA were also announced. Additionally, the succinic anhydride and GBL formation by hydrogenation of maleic anhydride has been progressed over the Ni and Pd supported catalysts [172-174].

From the view point of green chemistry, it was envisaged to build the bio-based SA formation process. Oxidation of renewable furfural which can be formed from various saccharides (*vide supra*) is a hot topic for “green” SA formation process.

The two-step synthesis; *i.e.* furfural oxidation of MA or FA and successive reduction of MA or FA to SA; is considerable. Therefore, furfural oxidation to MA or FA by vanadium pentoxide (V_2O_5), sulfate iron ($FeSO_4$), selenium dioxide (SeO_2), and copper nitrate ($Cu(NO_3)_2$) catalysts in water were also examined by several research groups [175-178]. Guo and Yin proposed furfural oxidation to MA using phosphomolybdic acid ($H_3PMo_{12}O_{40} \cdot xH_2O$), which is water-soluble but insoluble in organic phase, in aqueous/organic biphasic system possessing the simple product separation and reactant recycle [179]. 38% yield of MA was obtained at 383 K under high pressure O_2 (20 atm). Two steps reaction involving furfural oxidation to FA over V_2O_5 and $NaClO_3$, and successive hydrogenation of the purified FA by recrystallization toward SA over Pd/C was reported by Tachibana and co-workers [152].

Very recently, we achieved that simple oxidation of furfural to produce SA with a combination of heterogeneous acid catalyst and hydrogen peroxide [180]. Table 10 shows the results of furfural oxidation with various acid catalysts in the presence of H_2O_2 . It was confirmed that Amberlyst-15 indicated the highest activity for the synthesis of SA among cation exchange resins (entries 1-3). Solids acid catalysts exhibited low activities (entries 4-6). *p*-Toluenesulfonic acid (*p*-TsOH) was more selective than H_2SO_4 (entries 7 and 8). Without catalyst, furoic acid (FuA, 2-furancarboxylic acid) formation was observed with moderate conversion of furfural without SA formation (1% yield) (entry 9). Comparing from the structure of Amberlyst-15 and *p*-TsOH, it was supposed that the presence of not only $-SO_3H$ functional group but also aromatic ring was attributed to the high catalytic activity for furfural oxidation to SA. It seems that there is a contribution of the π - π interactions between furfural and the aromatic ring of catalyst favor the good conformation in the catalysis for the SA formation.

(Table 10 near here)

Badovskaya and coworkers reported that Na_2MoO_4 catalyst which serves the Mo complex catalyst in the reaction media performed the classical Baeyer-Villiger oxidation of furfural by H_2O_2 and gave 2(5*H*)-furanone (33%) with 8% of SA [181]. Furthermore, it was mentioned that the pH value during the reaction affected the different reaction pathway in the oxidation of furfural. 2(5*H*)-Furanone and SA were mainly obtained under acid condition (pH < 2) whereas 2-furancarboxylic acid was produced under base condition (pH > 7) [182]. They also proposed the 2-hydroxyfuran formation through 2-formylfuran from furfural, then which soon converts into the 2(5*H*)-furanone and 2(3*H*)-furanone. Thereafter, the 2(3*H*)-furanone is transformed into SA through β -formylpropionic acid form. The Lewis acidity is suggested to promote ready oxidation of substrate and intermediates since it partly compensates the proton deficiency and high oxidation

potential. The transformation from 2(5*H*)-furanone *via* 2(3*H*)-furanone isomer to SA [183], and MA formation *via* 2-furanol formate and 2-hydroxyfuran in the presence of H₂O₂ [184, 185] were also suggested.

According to these proposals, we suggested the possible reaction mechanisms for furfural oxidation to SA in the presence of H₂O₂ described in Figure 3. The furfural was oxidized to 2-formyloxyfuran *via* Baeyer-Villiger oxidation by H₂O₂ in the acidic condition, and then 2-hydroxyfuran and formic acid were formed, smoothly. The 2-hydroxyfuran has isomers as 2(3*H*)-furanone and 2(5*H*)-furanone, the former provides SA whereas the latter served MA and FA. From the H¹ and C¹³ NMR spectra during the reaction to determine the intermediate species, the presences of MA, formic acid, 2(5*H*)-furanone and SA were detected [180]. However, further investigation to reveal the details of reaction mechanism of furfural oxidation to SA over acid catalyst in the presence of H₂O₂ is still necessary. The effect of water solvent for furfural oxidation by H₂O₂ is also discussed because water can promote the buildup of acids which may play a catalytic role during the reaction process [186].

(Figure 3 near here)

3.4. Synthesis of Dialdehyde via Selective Oxidations of Functional Groups of 5-Hydroxymethylfurfural

Selective oxidation of the hydroxyl group of HMF into a corresponding dialdehyde, 2,5-diformylfuran (DFF), has been attractive much attention due to its versatility in use as a monomer of furan-based biopolymers and an intermediate of pharmaceuticals, antifungal agents, and ligands [187-190]. Generally, the oxidation of HMF into DFF will be accompanied by a formation of by-products such as 5-formyl-2-furancarboxylic acid (FFCA), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), and 2,5-furandicarboxylic acid (FDCA) as shown in Scheme 2. Selective oxidation of the hydroxyl group of HMF, therefore, strongly required to form DFF. DFF synthesis had been examined using classical oxidants, including BaMnO₄, pyridinium chlorochromate, NaOCl, and 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO), and also demonstrated by homogeneous metal bromide (Co/Mn/Br) catalysts *via* autoxidation [191-194]. Furthermore, vanadium-based catalysts including V₂O₅ [195], VOPO₄·2H₂O [196], and a V-containing polymeric catalyst [197] have been used previously. Recently, Ma et al. have achieved an efficient DFF synthesis from HMF by using a homogeneous mixture of Cu(NO₃)₂ and VOSO₄ catalysts under mild reaction conditions [198].

(Scheme 2 near here)

We found that a hydrotalcite-supported ruthenium catalyst (Ru/HT) [199] afforded remarkable activity and selectivity for DFF synthesis from HMF with molecular oxygen under mild reaction

conditions [200]. Additionally, a combination of HT, Amberlyst-15, and Ru/HT was found to produce DFF from fructose and glucose via base-catalyzed isomerization, acid-catalyzed dehydration, and successive selective oxidation by a one-pot reaction.

Supports have a significant effect on catalytic activity. Table 11 highlights the superiority of hydrotalcite support for Ru species over other support materials such as Al_2O_3 , $\text{Mg}(\text{OH})_2$, and carbon to give the highest DFF yield with excellent selectivity (92% yield and 97 % selectivity). Ru/HT can be easily separated from the reaction mixture, and could be reused at least 2 times while keeping high catalytic activity and DFF selectivity. This oxidation of HMF by Ru/HT is truly heterogeneous because the reaction stopped immediately when Ru/HT was removed from the reaction mixture.

(Table 11 near here)

As mentioned above, Amberlyst-15 is able to catalyze the dehydration of fructose into HMF. Therefore, in the second stage of this research, we tried to use Ru/HT with Amberlyst-15 catalyst for one-pot synthesis of DFF from fructose [200]. In the previous work by Grushin et al. [195], DFF was obtained in 45% yield by dehydration of fructose using acidic ion-exchange resin into HMF, followed by oxidation using $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$. Their catalytic system needs separation of the first product (HMF) and the acidic ion-exchange resin before performing the oxidation reaction. On the other hands, our catalytic system enables to synthesize DFF from fructose without separation of the first acid catalyst (Amberlyst-15) from the reaction mixture before the subsequent oxidation by Ru/HT, as shown in Table 12 (entry 3), where individual use of them never produce DFF (entries 1 and 2). Use of 0.2 g of Ru/HT further increased the DFF yield up to 49% under moderate reaction conditions (373 K, 9 h).

Furthermore, we demonstrated one-pot synthesis of DFF from glucose based on our findings that a combination of solid acid (Amberlyst-15) and base (HT) catalyst afforded HMF from glucose as well as fructose via glucose-fructose isomerization by base and successive fructose dehydration by acid (*vide supra*) [86, 201]. Therefore, one-pot synthesis of DFF from glucose by using a combination of triple heterogeneous catalysts, HT, Amberlyst-15, and Ru/HT has been examined. The results were also included in Table 12. Addition of Ru/HT into the mixture of HT and Amberlyst-15 catalysts afforded DFF from glucose (entries 7 and 8). The coexistence of three catalysts from the initial stage of the reaction gave only 8% yield of DFF (entry 7). Two-step conversion in the one-pot reaction without catalyst separation improved DFF yield from 8% to 25% (entry 8) due to a decrease of the side reaction of glucose decomposition by Ru/HT (entry 6).

(Table 12 near here)

Sequential reactions have been confirmed by successive addition of Amberlyst-15 and Ru/HT into

a solution containing fructose, which had previously formed from glucose in the presence of base HT catalyst (three-step reaction), as shown in Figure 4. The addition of Amberlyst-15 resulted in the disappearance of fructose and simultaneous formation of HMF. Further addition of Ru/HT under an oxygen atmosphere afforded DFF from the selective oxidation of HMF [200].

(Figure 4 near here)

3.5. Synthesis of Dicarboxylic Acid via Selective Oxidations of Functional Groups of 5-Hydroxymethylfurfural

It has been well known that 2,5-furandicarboxylic acid (FDCA) is also promising platform of biomass derivatives [202] because it has a large potential as a replacement for terephthalic acid, a widely used component in diverse polyesters, and intermediates for other polymers, fine chemicals, pharmaceuticals and agrochemicals [2, 3, 5]. FDCA synthesis is, therefore, considered to be a representative biorefinery process as alternatives for chemical production from petroleum.

Oxidation of HMF into FDCA has been examined using stoichiometric oxidant like KMnO_4 [203] and homogeneous metal salts (Co/Mn/Br) by autooxidation under high pressure air (70 bar) [204], which is currently employed for terephthalic acid production. Heterogeneous catalysts also afforded FDCA *via* HMF oxidation with molecular oxygen. Supported platinum catalysts were first demonstrated with the aid of homogeneous base, resulting in near quantitative FDCA yield [205]. Recently, two noticeable researches have been reported using supported gold catalysts for an aqueous oxidation of HMF [206, 207]. Riisager et al. demonstrated that Au/TiO₂ was able to oxidize HMF into FDCA in 71% yield at near room temperature [206]. Corma et al. showed Au/CeO₂ was more active and selective [207]. These catalysts, however, require addition of 1-20 equiv. base (NaOH) and high oxygen pressures (10-20 bar).

We found base-free selective oxidation of HMF into FDCA using HT-supported Au nanoparticle catalyst (Au/HT) in water solvent under an ambient oxygen pressure [208]. Au/HT catalyst was prepared by deposition-precipitation methods [209] using NH₃ aqueous solution followed by calcination at 473 K. The X-ray diffraction measurement confirmed that the crystal structure of Au/HT is identical to that of parent HT. The amount of loaded gold was determined to be 1.92 wt% analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP). Au L_{III}-edge X-ray absorption near-edge structure (XANES) study revealed that Au/HT catalyst has completely reduced Au metal on HT. Figure 5 shows a TEM image and particle size distribution of Au/HT catalyst, indicating that Au nanoparticles of 3.2 nm in average size ($\sigma = 1.2$) are highly dispersed on HT surface.

(Figure 5 near here)

Table 13 lists the result of HMF oxidation in water solvent using supported gold catalysts without

addition of homogeneous base. It was shown that Au/HT catalyst afforded FDCA with >99% selectivity at total conversion of HMF (entry 1). Au/HT could catalyze the oxidation reaction at high HMF/metal ratio, 150 and 200 (entries 3 and 4), reaching high turnover numbers of at least 138 (entry 4), which is simply calculated by moles of used Au. It should be noted that high selectivity of FDCA (81 %) was also achieved under air atmosphere with total HMF conversion at 368 K (entry 2). In contrast, unreduced Au/HT obtained without calcination showed negligible FDCA yield (1 %) (entry 5). The activity of Au/HT was much higher than those of Au/Al₂O₃, Au/C and Au/SiO₂ (entries 7-9). HT itself could not convert HMF (entry 10). Au/HT also exhibited higher activity than Au/MgO (entries 1 and 6) although MgO is more basic as determined by color indicator method [210]. This indicates that not only solid basicity of support material but also formation of metal active sites played important roles for the HMF oxidation reaction. A TEM measurement of Au/MgO showed that Au particles with larger size (> 10 nm) were aggregated on MgO surface, which was responsible for low catalytic activity of Au/MgO.

(Table 13 near here)

Figure 6 shows the time course of product formation for HMF oxidation over Au/HT catalyst. We observed the formation of 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) and 5-formyl-2-furancarboxylic acid (FFCA) intermediates at the initial stage of the reaction. Both intermediates gradually converted into the final product FDCA. This tendency is in good agreement with the previous studies using Au/TiO₂ and Au/CeO₂ catalysts under different reaction conditions [206, 207].

(Figure 6 near here)

For elucidation of reaction mechanism, a radical scavenger (2,6-di-*tert*-butyl-*p*-cresol) was added to the reaction medium, which hardly influenced the HMF oxidation (FDCA yield 78 %). This result suggests that the HMF oxidation did not proceed by the free radical mechanism. Temperature dependence of product distribution showed oxidation of HMF to HMFCFA occurs even at room temperature (HMFCFA yield 87%; HMF conversion >99 %). For the synthesis of dicarboxylic acid (FDCA), the rate-determining step is considered to be oxidation of hydroxyl group, that is transformation of HMFCFA to FFCA, as suggested in the literatures [206, 207]. Once FFCA is formed, FFCA is rapidly oxidized into FDCA *via* hemiacetal intermediate [208].

The Au/HT catalyst could be reused at least three times without significant loss of activity. The catalyst was simply reused again after washing thoroughly with water at room temperature followed by drying *in vacuo*. HMF was completely converted for all cases and FDCA yields were > 99 %, 92 % and 90 % for 1st, 2nd and 3rd uses, respectively. No change of gold oxidation state, morphology and particle size distribution of Au/HT catalyst was observed by XANES and TEM

measurements. The possibility of leaching of the gold catalyst was also verified as follows. The reaction was stopped after 3 h of reaction and catalyst was filtered. The filtrated reaction mixture was again reacted up to 10 h under the same conditions. As a result, after the catalyst removal no change of each product yield was observed. Furthermore, ICP analysis with 0.2 ppm detection limit gave no gold species in the filtrate solution. The above results indicate that gold species were not leached from HT surface.

4. Conclusions

This review was intended to show the importance of catalytic process in utilization of biomass-based materials such as sugars and furfurals as renewable and alternative sources instead of fossil fuels. The catalytic process for biomass utilization involves well-known deoxygenation (*via* dehydration), skeletal arrangement (isomerization), carbon-carbon bond cleavage, and dehydrogenation as elemental reactions. Multifunctionalization of solid surface through catalytic science, chemistry, and technology, therefore, will open up a possibility for sustainable and fruitful society based on biomass-derived materials.

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Figure Captions

Figure 1. Effect of reaction temperature on product distribution of glucose transformation using Amberlyst-15 and HT.

Figure 2. Time course of glucose transformation into fructose and 5-hydroxymethylfurfural. Amberlyst-15 was added after 2.5 h.

Figure 3. One of possible reaction mechanisms for furfural oxidation to SA over acid catalyst in the presence of H₂O₂.

Figure 4. Plot of yields of fructose (■), 5-hydroxymethylfurfural (▲), 2,5-diformylfuran (●) for the transformation of glucose as a function of reaction time. Amberlyst-15 was added after 3 h. Ru/HT was added after 6h under oxygen flow (20 ml/min). *Reaction conditions:* Glucose (0.1 g), HT (0.2 g), DMF (3 mL), 373 K.

Figure 5. TEM image and Au particle size distribution of 1.92 wt% Au/HT.

Figure 6. Time course of products in HMF oxidation by Au/HT catalyst in water using atmospheric pressure of oxygen. *Reaction conditions:* HMF (1 mmol), HMF/Au = 40 (mol/mol), H₂O (6 mL), O₂ flow (50 mL/min), 368 K.

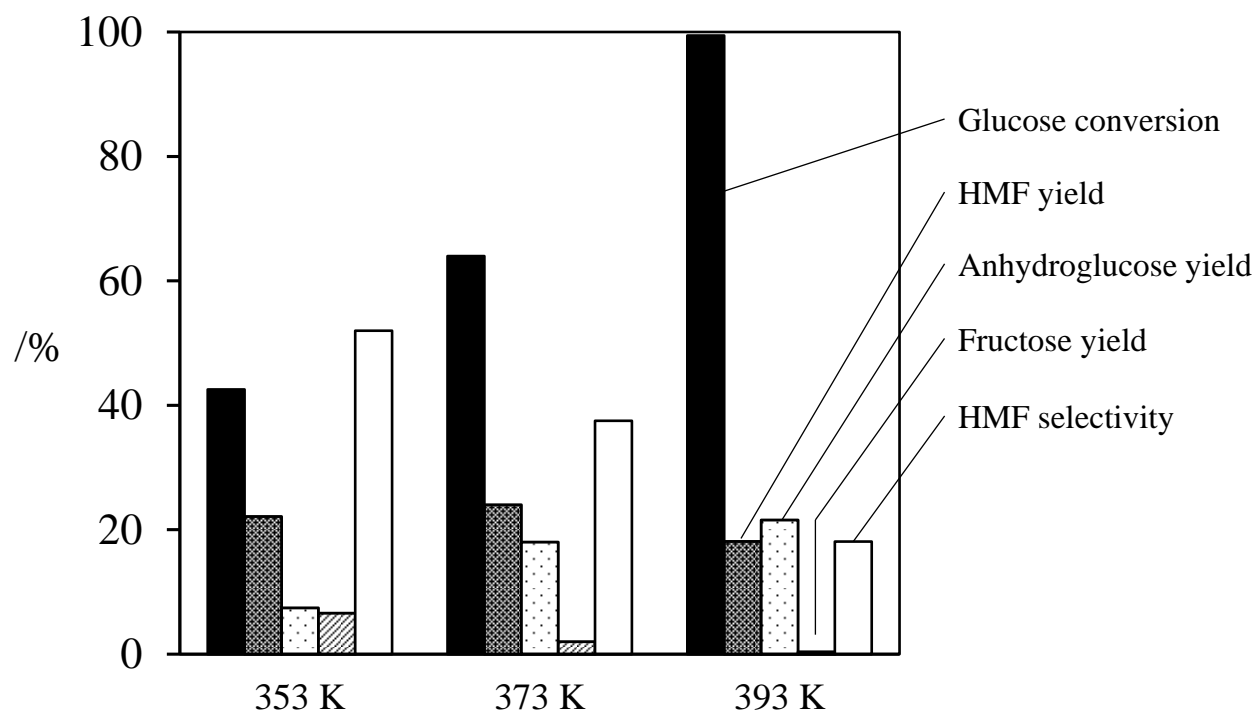


Figure 1. Effect of reaction temperature on product distribution of glucose transformation using Amberlyst-15 and HT.

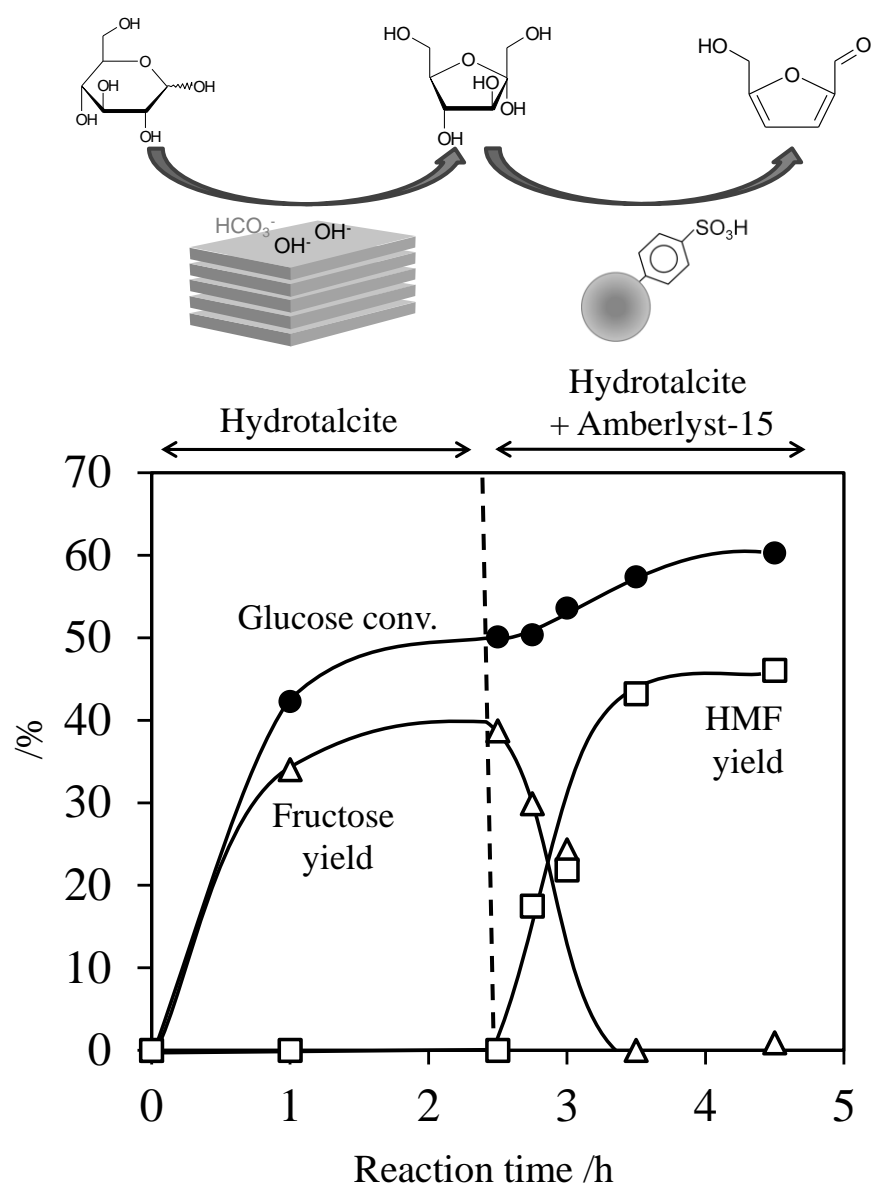


Figure 2. Time course of glucose transformation into fructose and 5-hydroxymethylfurfural. Amberlyst-15 was added after 2.5 h. *Reaction conditions:* glucose (0.1 g), Amberlyst-15 (0.1 g), hydrotalcite (0.2 g), DMF (3mL), 373 K.

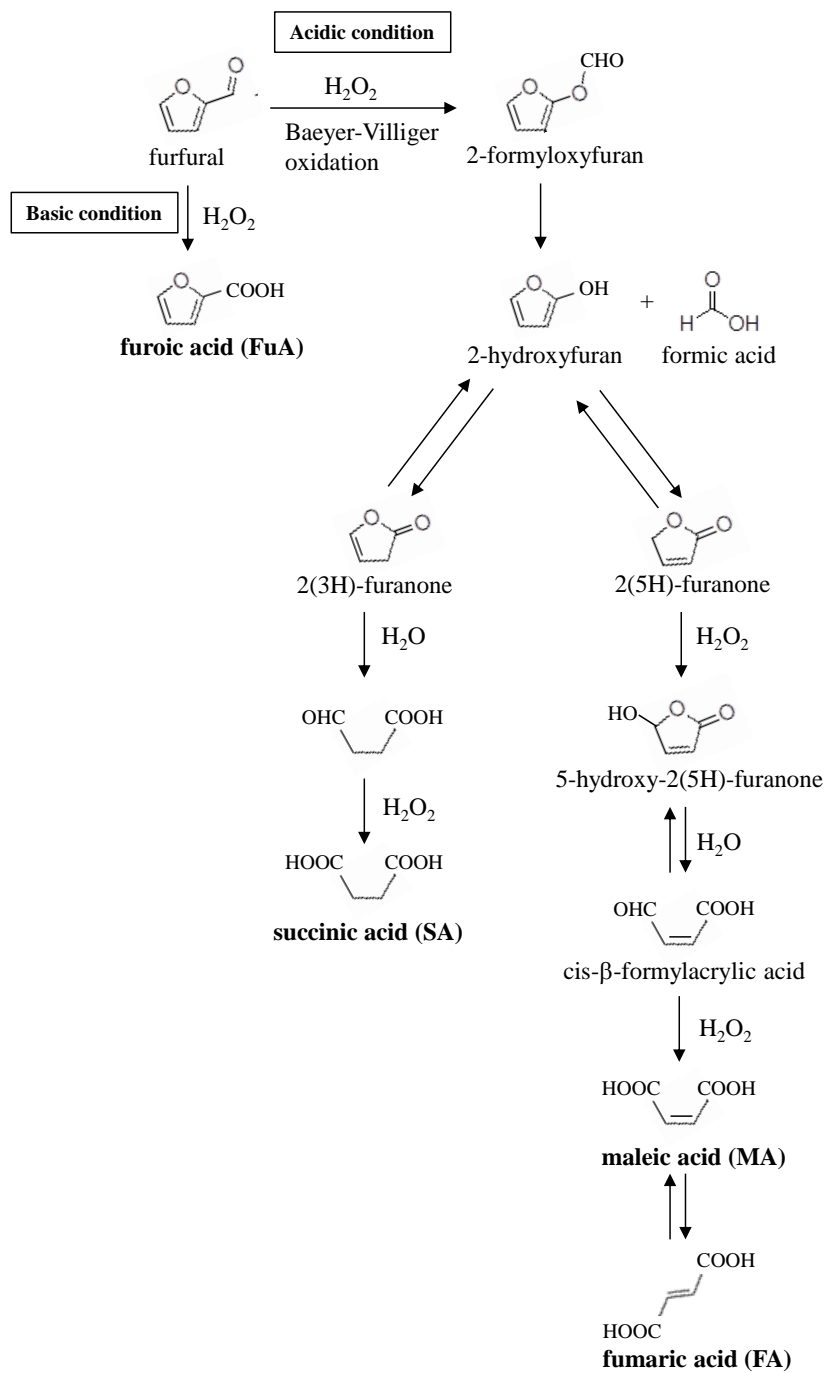


Figure 3 One of possible reaction mechanisms for furfural oxidation to SA over acid catalyst in the presence of H₂O₂.

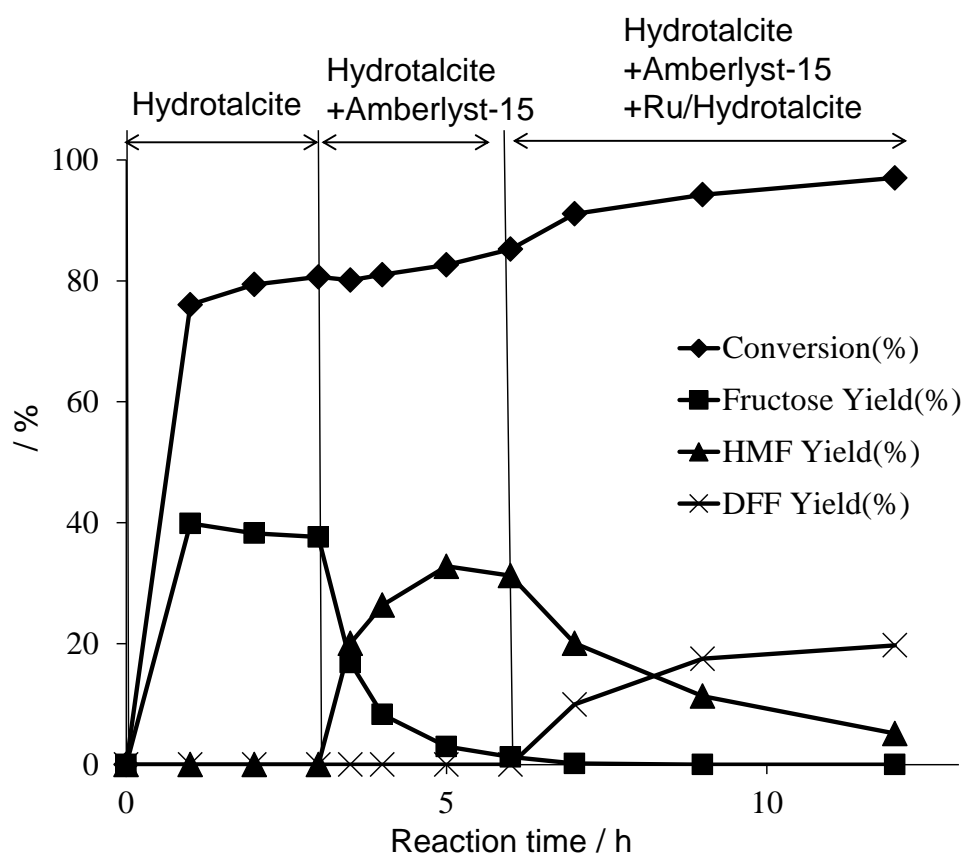


Figure 4. Plot of yields of fructose (■), 5-hydroxymethylfurfural (▲), 2,5-diformylfuran (●) for the transformation of glucose as a function of reaction time. Amberlyst-15 was added after 3 h. Ru/HT was added after 6h under oxygen flow (20 ml/min). *Reaction conditions:* Glucose (0.1 g), HT (0.2 g), DMF (3 mL), 373 K.

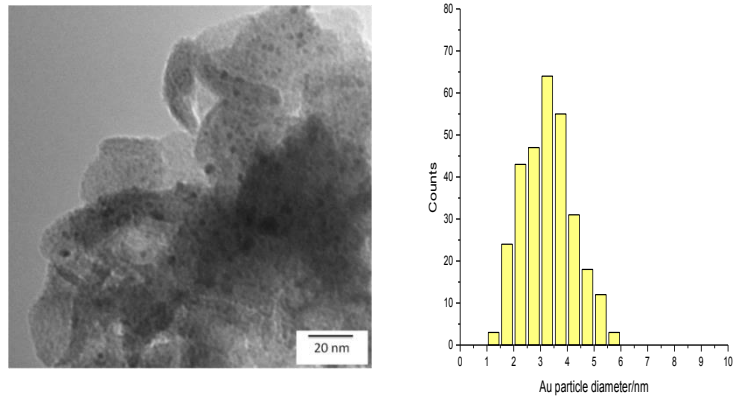


Figure 5. TEM image and Au particle size distribution of 1.92 wt% Au/HT.

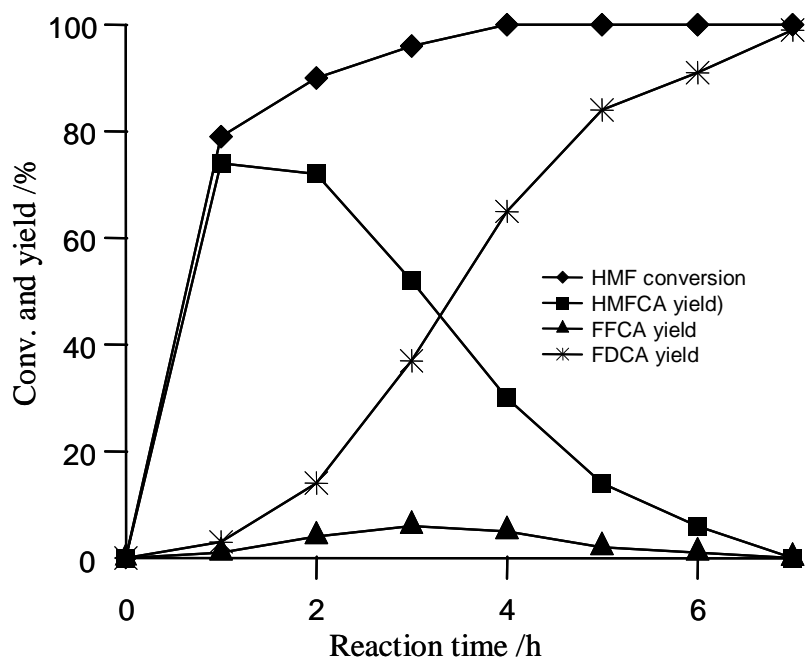
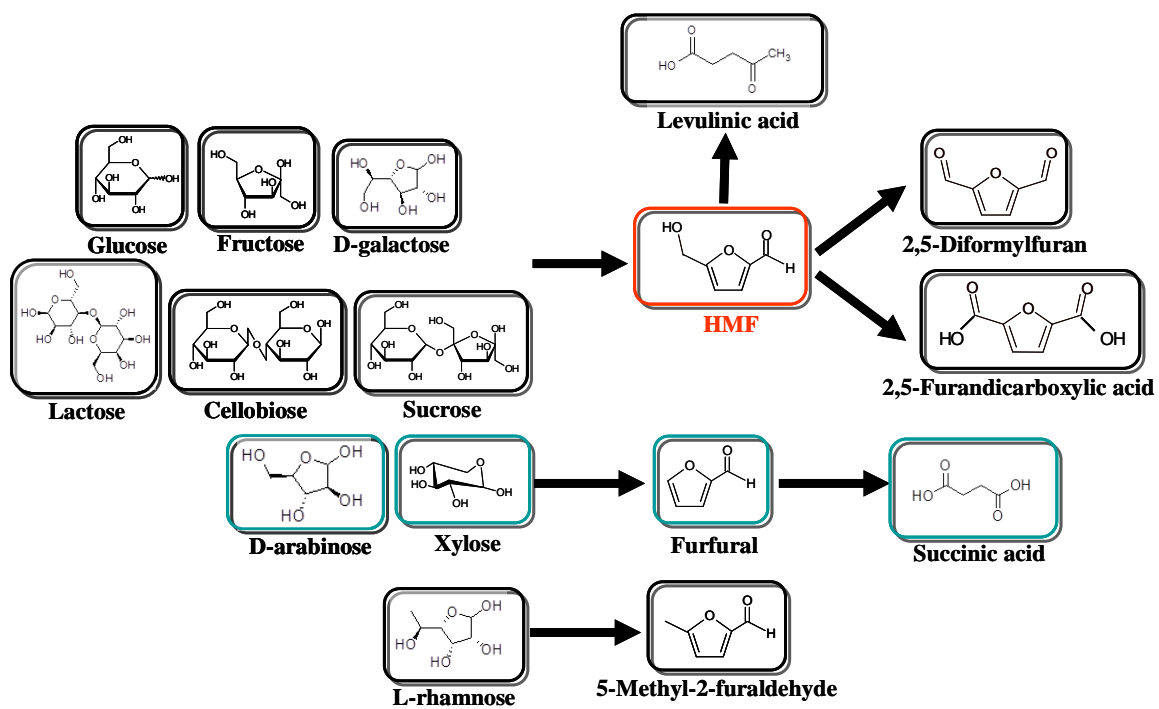
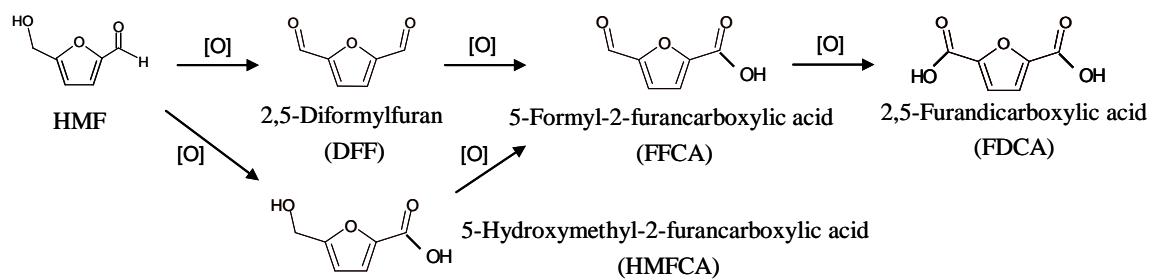


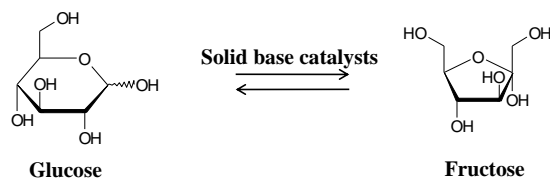
Figure 6. Time course of products in HMF oxidation by Au/HT catalyst in water using atmospheric pressure of oxygen. *Reaction conditions:* HMF (1 mmol), HMF/Au = 40 (mol/mol), H₂O (6 mL), O₂ flow (50 mL/min), 368 K.



Scheme 1. Transformations of sugars into carbonyl compounds *via* furfurals

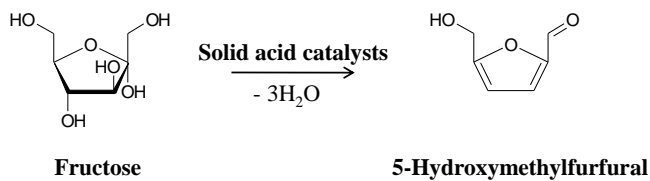


Scheme 2. Oxidation of HMF into various carbonyl compounds

Table 1. Isomerization of glucose to fructose over solid base catalysts^a

Entry	Catalyst	Glucose conversion /%	Yield /%		Fructose selectivity /%
			Fructose	HMF	
1 ^b	Hydrotalcite	47	40	0	85
2		62	38	0	62
3 ^c		81	32	0	40
4	MgO	22	8	0	36
5	CaO	89	8	0	9
6	Mg(OH) ₂	16	0	0	0
7	Piperidine ^d	83	5	0	6
8	Blank	0	0	0	-

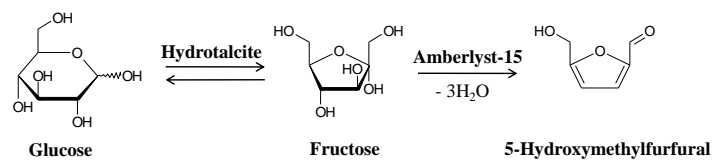
^aReaction conditions: Glucose (0.1 g), Catalyst (0.1 g), *N,N*-dimethylformamide (3 mL), 373 K, 3 h. ^b 353 K. ^c 393 K. ^d70 μmol

Table 2. Dehydration of fructose to HMF over solid acid catalysts^a

Entry	Catalyst	Fructose conversion /%	HMF yield /%	HMF selectivity /%
1	Amberlyst-15	>99	73	73
2	Nafion NR50	>99	45	45
3	SO ₄ /ZrO ₂	57	21	37
4	Nb ₂ O ₅ •nH ₂ O	8	0	0
5	H-ZSM5	Trace	0	-
6	H-Beta	Trace	0	-
7	Blank	0	0	-

^aReaction conditions: Fructose (0.1 g), Catalyst (0.1 g), *N,N*-dimethylformamide (3 mL), 373 K, 3 h

Table 3. One-pot synthesis of 5-hydroxymethylfurfural from glucose using acids and bases^a



Entry	Base catalyst	Acid catalyst	Glucose conversion /%	HMF Selectivity /%
1	Hydrotalcite	Amberlyst-15	64	38
2	Hydrotalcite	Nafion NR50	60	27
3	Hydrotalcite	—	62	0
4	—	Amberlyst-15	69	0
5	—	HCl (pH 1)	>99	0
6 ^b	Piperidine	<i>p</i> -TsOH•H ₂ O	0	0

^aReaction conditions: Glucose (0.1 g), Hydrotalcite (0.1 g), Amberlyst-15 (0.1 g), *N,N*-dimethylformamide (3 mL), 373 K, 3 h.

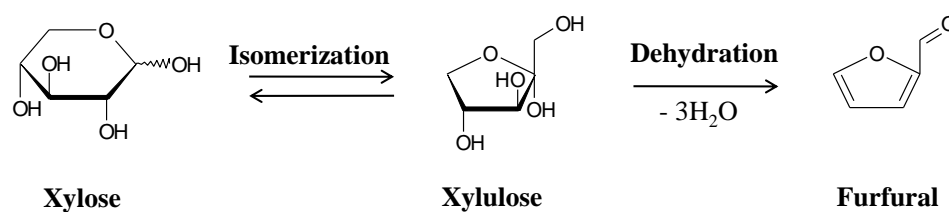
^b Piperidine (0.2 mmol), *p*-toluenesulfonic acid (0.07 mmol)

Table 4. One-pot synthesis of 5-hydroxymethylfurfural from glucose using a variety of Amberlyst-15 and HT combinations^a

Entry	Catalyst amount /g		Conv. /%	Product selectivity /%		
	Amberlyst-15	Hydrotalcite		HMF ^b	Fructose	AHG
1	0.1	0.1	64	38	3	28
2 ^d	0.1	0.1	63	37	<1	25
3 ^e	0.1	0.1	63	38	<1	25
4	0.1	0.05	71	17	0	42
5	0.1	0.2	72	57	6	14
6 ^f	0.1	0.2	73	58	0	18
7	0.05	0.2	76	54	5	11
8	0.025	0.2	81	45	6	9

^a Reaction conditions: Glucose (0.1 g), Amberlyst-15, hydrotalcite, DMF (3mL), 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.

Table 5. One-pot synthesis of furfural from xylose using acids and bases^a



Entry	Base catalyst	Acid catalyst	Xylose conversion /%	Furfural Selectivity /%
1	—	Amberlyst-15	51	<1
2	Hydrotalcite	—	60	0
3	Hydrotalcite	Amberlyst-15	57, 72 ^b	42, 51 ^b
4 ^b	Amberlyst A26 OH	Amberlyst-15	61	29
5 ^b	Amberlyst A21	Amberlyst-15	23	52
6	—	<i>p</i> -TsOH•H ₂ O ^c	62	25
7	—	H ₂ SO ₄ ^c	81	18

^aReaction conditions: Xylose (0.1 g), Hydrotalcite (0.1 g), Amberlyst-15 (0.1 g), *N,N*-dimethylformamide (3 mL), 373 K, 3 h.

^b Amberlyst-15 (0.1 g), solid base (0.2 g), ^c 0.5 mmol

Table 6. One-pot synthesis of furfural from arabinose using acids and bases^a

Entry	Base catalyst	Acid catalyst	Conversion / %	Furfural Selectivity / %
1	Hydrotalcite	Amberlyst-15	88	24
2	Hydrotalcite	Nafion NR50	66	13
3	Hydrotalcite	Nafion SAC13	63	8
4	Hydrotalcite	—	78	5
5	—	Amberlyst-15	73	5
6	—	Nafion NR50	70	6
7	—	Nafion SAC13	33	11

^aReaction conditions: Arabinose (0.1 g), Hydrotalcite (0.2 g), acid catalyst (0.1 g), *N,N*-dimethylformamide (3 mL), 373 K, 3 h.

Table 7. One-pot synthesis of 5-methylfurfural from rhamnose using several solid acids and hydrotalcites^a

Entry	Acid catalyst	Conversion /%	Furfural selectivity /%	Average pore size / nm ^b	Surface area / cm ² g ^{-1b}
1	Amberlyst-15	75	52	25.6	42
2	Nafion SAC13	63	3	9.23	227
3	Nafion NR50	50	1	—	< 1

^aReaction conditions: Rhamnose (0.1 g), Hydrotalcite (0.2 g), Acid catalyst (0.1 g), *N,N*-dimethylformamide (3 mL), 383 K, 6 h. ^b Determined by N₂ adsorption-desorption.

Table 8. HMF formation from disaccharides using Amberlyst-15 and hydrotalcite^a

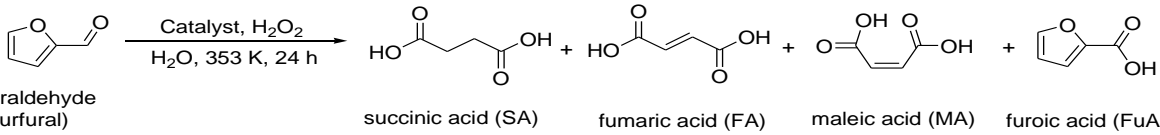
Entry	Substrate	Conversion / %	Selectivity of HMF / %
1	Sucrose	58	93
2	Cellobiose	52	67
3 ^b	Lactose	100	25

^aReaction conditions: Substrate (0.1 g), Hydrotalcite (0.1 g, ^b0.2 g), Amberlyst-15 (0.1 g), *N,N*-dimethylformamide (3 mL), 393 K, 3 h.

Table 9. Furfurals formation from mixed sugars using Amberlyst-15 and hydrotalcite^a

Entry	Substrate components	Yield / %		
		HMF	Furfural	MF
1 ^b	Glucose ^d , Xylose ^d	48	41	—
2 ^b	Fructose ^d , Xylose ^d	67	31	—
3 ^c	Arabinose ^d , Rhamnose ^d	—	33	33
4 ^c	Arabinose ^e , Rhamnose ^f , Lactose ^f	32	31	29

^aReaction conditions: Hydrotalcite (0.2 g), Amberlyst-15 (0.1 g), *N,N*-dimethylformamide (3 mL). ^b373 K, 3 h. ^c383 K, 6 h. ^d0.05 g. ^e0.04 g. ^f0.03 g.

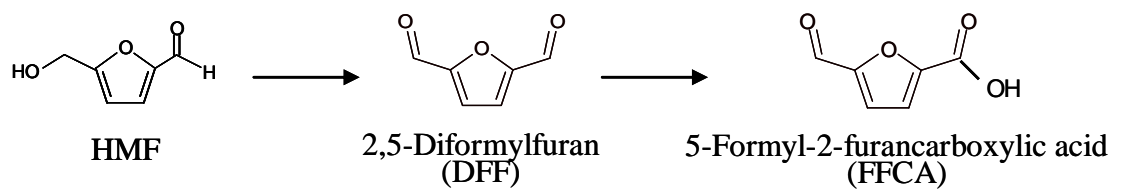
Table 10. Furfural oxidation with various acid catalysts in the presence of H₂O₂^a


2-furaldehyde (furfural) $\xrightarrow[\text{H}_2\text{O, 353 K, 24 h}]{\text{Catalyst, H}_2\text{O}_2}$ succinic acid (SA) + fumaric acid (FA) + maleic acid (MA) + furoic acid (FuA)

Entry	Catalyst	Furfural conv. / %	Yield / %			
			SA	FA	MA	FuA
1	Amberlyst-15	>99	74	0	11	2
2	Nafion NR50	>99	41	1	11	2
3	Nafion SAC13	>99	29	1	10	2
4	Nb ₂ O ₅	>99	24	5	5	0
5	ZSM-5 ^b	>99	17	2	2	0
6	ZrO ₂	>99	17	2	5	0
7	<i>p</i> -TsOH ^c	>99	72	0	11	1
8	H ₂ SO ₄ ^c	>99	45	0	6	0
9	Blank	69	1	1	5	18

^aReaction conditions: Furfural (1 mmol), H₂O₂ (4 mmol), H₂O (3 mL), catalyst (50 mg), 353 K, 24 h.

^bJRC-Z-5-90H(1). ^c1 mmol.

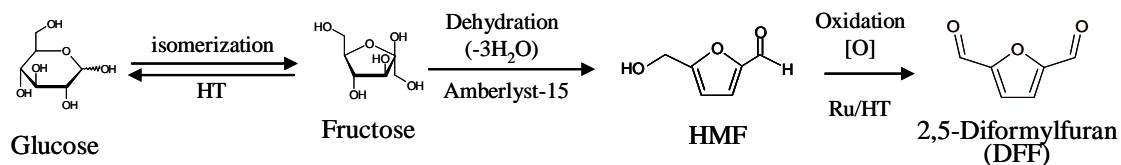
Table 11. 2,5-Diformylfuran formation from 5-hydroxymethylfurfural (HMF) in the presence of various heterogeneous ruthenium catalysts in the presence of molecular oxygen^a


Entry	Catalyst	DFF yield / % ^b	FFCA yield / % ^b
1 ^c	Ru/HT	92 (97)	3 (3)
2 ^d	Ru/Al ₂ O ₃	32 (61)	4 (8)
3 ^e	Ru/Mg(OH) ₂	72 (79)	12 (13)
4 ^f	RuO ₂	8 (43)	Trace
5 ^d	Ru/carbon	76 (77)	8 (8)
6 ^d	Pd/carbon	21 (40)	2 (4)
7 ^d	Pt/carbon	16 (39)	4 (10)
8	HT	0	0

^aReaction conditions: HMF (1 mmol), metal catalyst (0.1 g), *N,N*-dimethylformamide (3 mL), 393 K,

O₂ flow (20 mL/min), ^bValues in the parentheses are selectivity. ^c4.4 wt% Ru/HT(0.1 g), ^dPurchased from Wako Chemicals. 5 wt% metal catalysts (0.1 g), ^e4.2 wt% Ru determined by ICP. ^f0.05 mmol Ru was used.

Table 12. One-pot synthesis of 2,5-diformylfuran from hexoses using Amberlyst-15 and hydrotalcite-supported ruthenium catalysts in the presence of molecular oxygen under atmospheric pressure^a



Entry	Substrate	Base catalyst	Acid catalyst	Oxidation catalyst	Hexose conversion /%	HMF yield /%	DFF yield /%
1	Fructose	-	Amberlyst-15	-	>99	71	2
2 ^b		-	-	Ru/HT	2.5	0	2
3 ^b		-	Amberlyst-15	Ru/HT	>99	44	2
4 ^c		-	Amberlyst-15	Ru/HT	>99, >99 ^d	34, 9 ^d	0
5	Glucose	HT	Amberlyst-15	-	85	43	0
6 ^b		-	-	Ru/HT	48	0	0
7 ^b		HT	Amberlyst-15	Ru/HT	96	8	1
8 ^{c,d}		HT	Amberlyst-15	Ru/HT	98	9	18

^aReaction conditions: Fructose (0.2 g, 1.11 mmol), or glucose (0.1 g, 0.55 mmol), HT (0.2 g), Amberlyst-15 (0.1 g), Ru/HT (0.1 g), *N,N*-dimethylformamide (3 mL), 373 K, 3 h, N₂ flow (20 mL/min). ^bO₂ flow (20 mL/min), ^cTwo-step reaction without catalyst separation. After 3 h under N₂ flow (20 mL/min), Ru/HT was added under O₂ flow (20 mL/min) for 6 h ^d0.2 g of Ru/HT was used. FFCA was detected (4 % yield).

Table 13. HMF oxidation in water using supported gold catalysts in the presence of molecular oxygen without addition of homogeneous base^a

Entry	Catalyst	HMF/metal mole ratio	HMF conversion /%	FDCA select. /%	HMFCa yield /%	FFCA yield /%	FDCA yield /%
1	Au/HT	40	> 99	> 99	0	71	> 99
2 ^c	Au/HT	40	> 99	81	11	1	81
3	Au/HT ^d	150(13)	> 99	83	12	3	83
4	Au/HT ^d	200(13)	> 99	72	22	4	72
5	Au/HT ^e	40	73	1	64	7	1
6	Au/MgO	40	> 99	21	65	13	21
7	Au/Al ₂ O ₃	40	35	9	22	5	3
8	Au/Carbon ^f	40	28	4	6	1	1
9	Au/SiO ₂	40	0	0	0	0	0
10 ^g	HT	0	0	0	0	0	0
11	Blank	0	0	0	0	0	0

^aReaction conditions: HMF (1 mmol), HMF/metal = 40 (mol/mol), H₂O (6 mL), 368 K, 7 h, O₂ flow (50 mL/min). 1.92 wt% Au/HT, 2 wt% Au was used for different supports. ^bValues in parentheses are reaction time (h). ^cAir atmosphere. ^d1.03 wt% Au. ^eCatalyst was not reduced. ^fActivated carbon. ^g0.25 g of HT was used.

TOC

