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One-Pot Synthesis of 2,5-Diformylfuran from Carbohydrate Derivatives by Sulfonated Resin and Hydrotalcite-Supported Ruthenium Catalysts

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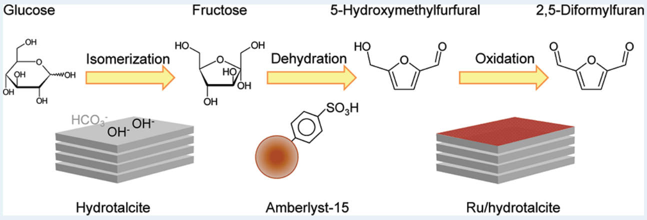
S *Supporting Information*

ABSTRACT: 2,5-Diformylfuran (DFF) was selectively synthesized from 5-hydroxymethylfurfural using a hydrotalcite-supported ruthenium catalyst (Ru/HT) by oxidation with molecular oxygen under mild reaction conditions. A combination of hydrotalcite, Amberlyst-15, and Ru/HT catalysts successfully afforded direct synthesis of DFF from hexoses such as fructose and glucose *via* isomerization, dehydration, and successive selective oxidation in one pot. Stepwise addition of catalyst improved DFF yield up to 49% from fructose and 25% from glucose, respectively.



KEYWORDS: 2,5-diformylfuran, biomass transformation, heterogeneous catalysts, one-pot reaction, selective oxidation, acid—base catalysis

Biorefinery, efficient production of fuels and chemicals from biomass has received much attention to reduce the impact on the environment.[1,2] 5-Hydroxymethylfurfural (HMF), which is obtained from dehydration of hexose,[3−6] is considered as one of the most important platforms of a variety of chemicals including plastics and polymers because it has two different functional groups, hydroxyl- and aldehyde groups, which allows us to make a variety of chemicals by functionalization *via* oxidation, reduction, hydrogenolysis, and condensation.[1,2]

Selective oxidation of the hydroxyl group of HMF into a corresponding dialdehyde, 2,5-diformylfuran (DFF), has been attracting much attention due to its versatility in use as a monomer of furan-based biopolymers and an intermediate of pharmaceuticals, antifungal agents, and ligands.[7−10] However, HMF oxidation produces a variety of derivatives including 5-formyl-2-furancarboxylic acid (FFCA), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), and 2,5-furandicarboxylic acid (FDCA) as shown in Scheme 1, resulting in the strong requirement of selective oxidation of the hydroxyl group of HMF for DFF production. DFF synthesis had been examined using classical oxidants,[11−13] including $BaMnO_4$, pyridinium chlorochromate (PCC), NaOCl, and 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) free radicals with co-oxidants, and also demonstrated by homogeneous metal/bromide (Co/Mn/Br) catalysts *via* autoxidation.[14] Previous study has been performed using vanadium-based catalysts including V_2O_5,[15] $VOPO_4 \cdot 2H_2O$,[16] and a V-containing polymeric catalyst.[17] Very recently, Pang et al. have achieved an efficient DFF synthesis from HMF by using a homogeneous $Cu(NO_3)_2/VOSO_4$ catalyst under mild conditions and demonstrated its application to a fluorescent material.[18]

The progress in green chemistry could realize selective oxidation by heterogeneous catalyst using molecular oxygen as a sole oxidant, affording a more environmentally benign chemical process. Kaneda et al. have disclosed that a hydrotalcite-supported metal catalyst exhibits remarkable activity for selective alcohol oxidation with molecular oxygen or oxidant-free alcohol dehydrogenation under moderate conditions.[19−23] Very recently, the present authors have reported that hydrotalcite-supported platinum and gold catalysts (Pt/HT and Au/HT) were applicable for selective oxidation of biomass derivatives.[24−26] Pt/HT and Au/HT afforded selective oxidation of glycerol toward glyceric acid and HMF toward FDCA in water, respectively.

Herein, we demonstrated that a hydrotalcite-supported ruthenium catalyst (Ru/HT) afforded remarkable activity and selectivity for DFF synthesis from HMF with molecular oxygen under mild conditions. In addition, 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.

Ru/HT was prepared according to the literature by Kaneda et al.[21−23] Briefly, a solid Mg—Al hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3$, was added into a $RuCl_3 \cdot nH_2O$-containing aqueous solution at room temperature. After stirring for 1 h, the gray-colored solid

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Scheme 1. Selective Oxidation of 5-Hydroxymethylfurfural towards 2,5-Diformylfuran

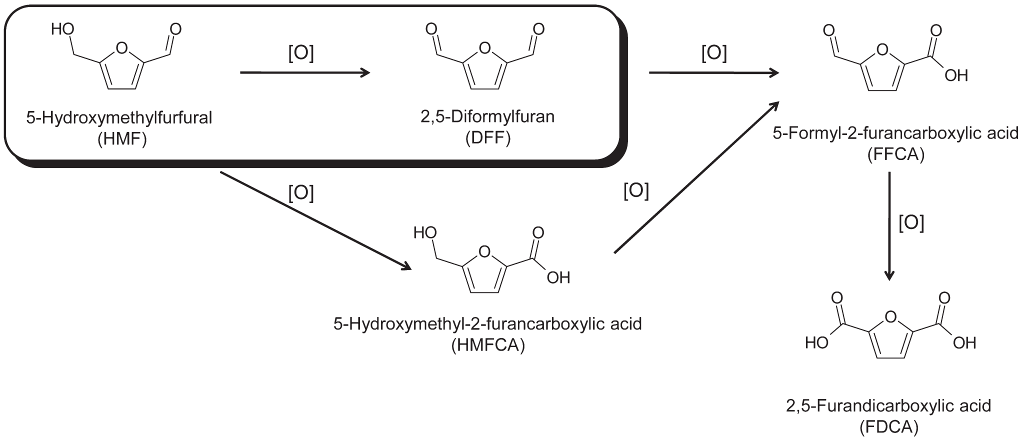


Table 1. 2,5-Diformylfuran Formation from 5-Hydroxymethylfurfural in the Presence of Various Heterogeneous Ruthenium Catalysts with Molecular Oxygen[a]

Entry	Catalyst	DFF yield/%[b]	FFCA yield/%[b]
1[c]	Ru/HT	92 (97)	3 (3)
2[d]	Ru/Al_2O_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/C	76 (77)	8 (8)
6[d]	Pd/C	21 (40)	2 (4)
7[d]	Pt/C	16 (39)	4 (10)
8	HT	0 (0)	0

[a] *Reaction conditions*: 5-Hydroxymethylfurfural (1 mmol), metal catalyst (0.1 g), *N*,*N*-dimethylformamide (3 mL), 393 K, 6 h, O_2 flow (20 mL/min). [b] Values in the parentheses are selectivity. [c] 4.4 wt % Ru/HT (0.1 g). [d] Purchased from Wako Pure Chemicals. 5 wt % metal catalysts (0.1 g). [e] 4.2 wt % Ru determined by ICP. [f] 0.05 mmol Ru was used.

was filtered off and washed with water. The obtained solid was dried *in vacuo* at room temperature overnight. The Ru/HT retained the original Mg−Al hydrotalcite structure determined by X-ray diffraction (XRD) measurement (see Supporting Information, Figure S1). X-ray absorption fine structure (XAFS) measurement confirmed that the prepared Ru/HT showed the same profile to that of previous study[21−23] indicating that monomeric Ru(IV) species were grafted onto the two-dimensional Mg−Al hydrotalcite structure (Figure S2). Inductively coupled plasma (ICP) analysis indicated the prepared catalyst contains Ru of 4.41 wt %.

Table 1 lists the results of DFF formation by oxidation of HMF using a variety of supported metal catalysts at 393 K for 6 h in the presence of oxygen (see Supporting Information, experimental procedure). Oxygen was simply introduced by passing over the solution at a speed of 20 mL/min under atmospheric pressure. Three conventional carbon-supported metal catalysts (Ru/C, Pd/C, and Pt/C) were tested as comparisons. First, it was found that the ruthenium catalyst gave high conversion and selectivity among the carbon-supported metal catalysts used (Table 1, entries 5−7). The catalytic activity increased in the order of Pt/C < Pd/C < Ru/C. The Ru/C catalyst afforded a high DFF yield of 76% with high selectivity (77%).

Supports also have a significant effect on catalytic activity. Among the supported ruthenium catalysts tested including HT, Al_2O_3, and $Mg(OH)_2$ (Table 1, entries 1−3), the hydrotalcite-supported ruthenium catalyst (Ru/HT) afforded the highest DFF yield with excellent selectivity (92% yield and 97% selectivity) (Table 1, entry 1). Even in the presence of air, 72% of DFF yield with 88% selectivity was obtained. In contrast, other Ru catalysts such as Ru/Al_2O_3, Ru/$Mg(OH)_2$, and RuO_2 gave low yields. These results clearly indicate that the Ru/HT catalyst is a highly active and selective catalyst for DFF formation from HMF under mild conditions. Ru/$Mg(OH)_2$ and Ru/C afforded the further oxidized product, 5-formyl-2-furancarboxylic acid (FFCA). Less than 1% yield of 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) was observed for Ru/C and Pt/C. For all samples tested, 2,5-furandicarboxylic acid (FDCA) was not formed in DMF. Most of the Ru catalysts afforded enough carbon balance (>90%) besides Ru/Al_2O_3 and Ru/C. In addition, values of carbon balance of other carbon-supported metal catalysts, Pd/C and Pt/C, were low. This is probably due to undesired decomposition of HMF.

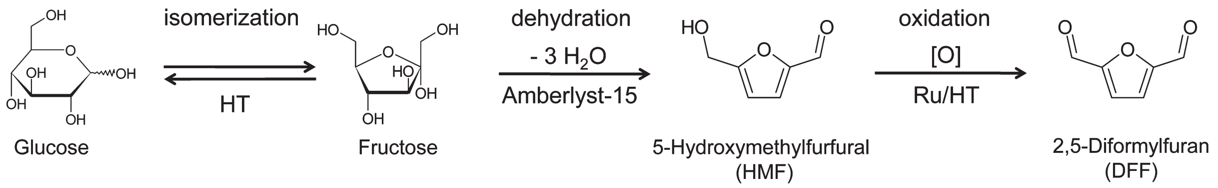
The Ru/HT catalyst was recovered by centrifugation, washed with water, dried *in vacuo* overnight, and recycled for further reaction. The formation rate of DFF was plotted against the reaction time, indicating that the initial activity of Ru/HT decreased after reuse (Figure S3). Although a slight decrease of DFF yield was first observed for fresh catalyst, the DFF yield for 6 h of activity remained unchanged after further reuse (Table S1). Then, the possibility of leaching of the ruthenium catalyst was also verified by carrying out the oxidation reaction. The reaction was stopped after 1 h of reaction, and the catalyst was filtered. The reaction mixture was again reacted up to 7 h under the same reaction conditions (Figure S4). As a result, after the catalyst removal no change of HMF conversion and DFF yield was observed. The Ru content in the reaction media after the reaction was determined by using ICP analysis. No Ru was observed in the reaction solution (below the detection limit of 30 ppb). In addition, a good result was obtained in the scale-up condition for the heterogeneous catalytic system; the DFF yield was 60% with 84% selectivity from 10 mmol (1.26 g) of HMF using 0.5 g of Ru/HT (Ru: 22 mg) at 373 K for 12 h under oxygen (Figure S5).

Table 2. One-Pot Synthesis of 2,5-Diformylfuran from Hexoses using Amberlyst-15 and Hydrotalcite-Supported Ruthenium Catalyst with 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	0
2^b		–	–	Ru/HT	25	0	0
3^b		–	Amberlyst-15	Ru/HT	>99	44	13
4^c		–	Amberlyst-15	Ru/HT	>99, > 99^d	34, 9^d	34, 49^d
5	Glucose	HT	Amberlyst-15	–	85	43	0
6^b		–	–	Ru/HT	48	0	0
7^b		HT	Amberlyst-15	Ru/HT	96	8	8
8^{c,d}		HT	Amberlyst-15	Ru/HT	98	9	25

[a] *Reaction 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, N_2 flow (20 mL/min). [b] O_2 flow (20 mL), 9 h. [c] Two-step reaction without catalyst separation. After 3 h under N_2 flow (20 mL/min), Ru/HT (0.1 g) was added under O_2 flow (20 mL/min) for 6 h. [d] 0.2 g of Ru/HT was used. FFCA (4% yield) was detected.

Scheme 2. One-Pot Synthesis of 2,5-Diformylfuran from Glucose through Isomerization, Dehydration, and Selective Oxidation



Direct synthesis of DFF from hexoses such as fructose and glucose is more desirable than the synthesis from HMF because it would avoid separation and purification of intermediates and save energy, time, and solvent. A notable example has been reported for DFF synthesis from fructose. Grushin et al. demonstrated DFF synthesis from fructose in dimethyl sulfoxide (DMSO).[15] After obtaining HMF from fructose by dehydration in the presence of an acidic ion-exchange resin at 353 K for 25.5 h, the resin was filtered off and a subsequent oxidation was carried out by using a vanadium catalyst. A 45% DFF yield was obtained in the presence of the $VOHPO_4 \cdot 0.5H_2O$ catalyst at 453 K for 13 h.

We have examined the one-pot synthesis of DFF from fructose by using Amberlyst-15 and Ru/HT (Table 2, entries 1–4). Fructose could be dehydrated in the presence of acid catalyst by removal of 3 mol of water (Scheme 2). Individual use of Amberlyst-15 produced HMF from fructose with 71% yield (Table 2, entry 1). A combination of Amberlyst-15 and Ru/HT afforded DFF from fructose (Table 2, entries 3 and 4). The coexistence of Amberlyst-15 and Ru/HT from the initial stage of reaction produced DFF with 13% yield (Table 2, entry 3). A lower yield of DFF for the one-pot reaction than that from HMF oxidation could be attributable to an undesired side reaction of fructose decomposition by Ru/HT in the presence of oxygen (Table 2, entry 2). Even in the presence of oxygen, a slight amount of fructose was isomerized to glucose (3% yield) by Ru/HT. Other products from fructose by Ru/HT were not detected in the experimental conditions, probably due to formation of a humin polymer by base-catalyzed reaction and/or oxidation. Then, two-step synthesis in a one-pot reaction where Ru/HT was added into the reaction solution containing Amberlyst-15 without catalyst separation after 3 h resulted in improvement of the DFF yield to 34% (Table 2, entry 4). Use of 0.2 g of Ru/HT further increased the DFF yield up to 49%. Half of the fructose was transformed into DFF by using Amberlyst-15 and Ru/HT under moderate conditions (373 K, 9 h).

Furthermore, we demonstrated one-pot synthesis of DFF from glucose. Very recently, Hu et al. reported the direct synthesis of DFF from glucose by the combination of $CrCl_3$ and $NaVO_3$ for HMF formation and HMF oxidation, respectively.[27] Chromium chloride is a well-known catalyst for HMF formation, which was reported by many researchers.[4,5] In contrast, we have recently disclosed that a combination of solid acid (Amberlyst-15) and base (HT) afforded HMF from glucose as well as fructose *via* glucose–fructose isomerization by base and successive fructose dehydration by acid.[28,29] Actually, a 43% yield of HMF was obtained from glucose in the presence of HT and Amberlyst-15 (Table 2, entry 5). Thus, we have examined one-pot synthesis of DFF from glucose by using a combination of heterogeneous catalysts, HT, Amberlyst-15, and Ru/HT catalysts. The results were also included in Table 2. Addition of Ru/HT as an oxidation catalyst afforded DFF from glucose in the presence of solid acid (Amberlyst-15) and base (HT) (Table 2, entries 7 and 8). The coexistence of three catalysts from the initial stage of the reaction gave an 8% yield of DFF (Table 2, entry 7). Two-step synthesis in the one-pot reaction without catalyst separation improved DFF yield from 8% to 25% (Table 2, entry 8) due to a decrease of the side reaction of glucose decomposition by Ru/HT (Table 2, entry 6). Similar to fructose decomposition, even in the presence of oxygen, fructose *via* isomerization by Ru/HT was detected (2%). Other products from glucose by Ru/HT were not detected in the experimental conditions, probably due to formation of a humin polymer. In the absence of oxygen (under nitrogen atmosphere), 65% of glucose was converted and 26% of fructose was formed by Ru/HT, indicating that Ru/HT could catalyze glucose–fructose isomerization as well as HT although the selectivity for isomerization was low. These sequential reactions have been confirmed by successive addition

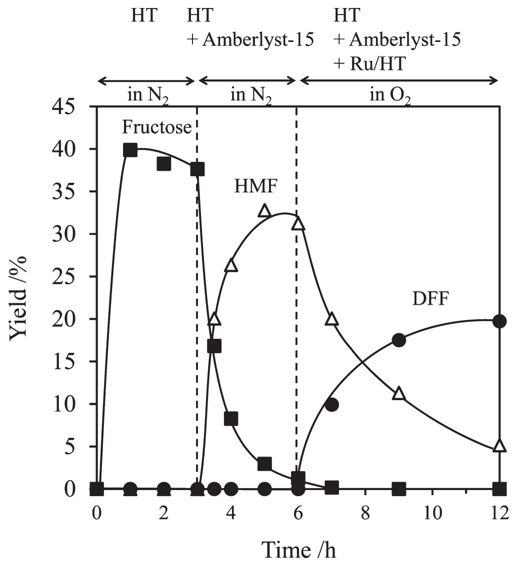


Figure 1. Plot of fructose yield (■), 5-hydroxymethylfurfural yield (△), 2,5-diformylfuran yield (●) for the transformation of glucose as a function of reaction time. Amberlyst-15 was added after 3 h. Hydrotalcite-supported ruthenium catalyst was added after 6 h under oxygen flow (20 mL/min). *Reaction conditions*: Glucose 0.1 g, HT 0.2 g, Amberlyst-15 0.1 g, Ru/HT 0.2 g, DMF 3 mL, 373 K.

of Amberlyst-15 and Ru/HT into a solution containing fructose, which had formed from glucose in the presence of a base catalyst (HT) (three-step reaction) (Figure 1). The addition of Amberlyst-15 resulted in the disappearance of fructose and simultaneous formation of HMF. Further addition of Ru/HT under oxygen flow afforded DFF from HMF by the selective oxidation.

In conclusion, 2,5-diformylfuran (DFF) was selectively obtained from 5-hydroxymethylfurfural (HMF) using a hydrotalcite-supported ruthenium catalyst (Ru/HT) with molecular oxygen under mild reaction conditions. In addition, direct formation of DFF from fructose and glucose was demonstrated using a combination of HT, Amberlyst-15, and Ru/HT by base-catalyzed isomerization, acid-catalyzed dehydration, and successive oxidation.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details, Table S1, and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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