Unlocking the Potential of 5-Hydroxy-2(5H)-furanone as a Platform for Bio-Based Four Carbon Chemicals

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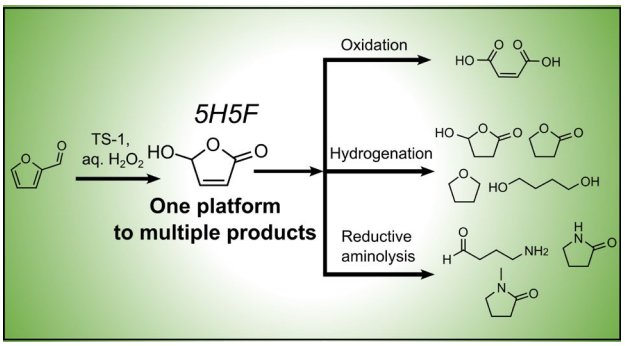

KEYWORDS Biomass • C4 chemicals • platform chemical • 1,4-butanediol • Maleic acid • pyrrolidone derivatives

Abstract: Industrial chemicals with a four-carbon structure, including maleic acid, 1,4-butanediol, γ-butyrolactone, and pyrrolidones, are derived from petroleum. Catalytic synthesis of these C4 chemicals from biomass is challenging because of scarcity of C4 sugars in biomass feedstock. We show that 5-hydroxy-2(5H)-furanone (5H5F), produced by catalytic oxidation of biomass derived furfural, is a versatile platform for several oxygen and nitrogen containing C4 chemicals. In our study, 5H5F was synthesized in 92 % yield by room temperature oxidation of furfural using TS-1 catalyst. As a platform chemical, 5H5F's mild reactivity, attributed to the electrophilic carbon attached to the hydroxyl group, enabled its oxidation, reduction, and reductive aminolysis using carbon supported noble metal catalysts. Industrial C4 chemicals like maleic acid (81 %), γ-butyrolactone (93 %) 1,4-butanediol (60 %), tetrahydrofuran (64 %) and 2-pyrrolidone (67 %) were obtained from 5H5F under mild conditions (100

– 150 °C). We envision that 5H5F will be adopted as a platform for C4 chemicals owing to its ease of synthesis and selective transformation to multiple chemicals using heterogeneous catalysts.

Introduction

Chemical synthesis from biomass is an attractive way to reduce the dependence of chemical industry on petroleum resources. Platform chemicals play a pivotal role towards this goal by serving as a bridge between the polymeric composite of biomass and the value-added chemical stream in industry. Owing to the abundance of hexose and pentose sugars in biomass, platform chemicals with six and five carbon atoms, like 5-hydroxymethylfurfural and furfural have been extensively studied.[1–9] C4 platform chemicals have received less attention despite a huge demand for oxygen and nitrogen containing C4 chemicals in industry. For example, more than 2 million tonnes of 1,4-butanediol (BDO) is produced each year for the manufacture of polymers.[10–12] Maleic anhydride is another C4 chemical widely used as a precursor for polymers and C4 derivatives such as γ-butyrolactone (GBL), and 2-pyrrolidone.[13,14] Apart from the microbial fermentation, synthesis of C4 chemical from sugars found in biomass is challenging due to the low selectivity of C-C bond cleavage step.[15–17] Consequently, a C4 platform chemical that can be catalytically produced from biomass in high yield and serve as a versatile precursor for value added chemicals is highly desirable.

A good platform chemical should be an intermediate in the value chain with the ability to transform into diverse value-added products. This would make the manufacturing process flexible and reinforce commercial applicability. The platform chemical should feature multiple functional groups that can be targeted for different reactions. In addition, the synthesis of the platform should be facile with high selectivity, and it should not be prone to degradation during downstream reactions.

Potential C4 platforms like succinic acid, BDO and GBL lack the reactive diversity of an ideal platform. Harsh conditions are needed for their reaction to produce other C4 chemicals owing to their stable structure.[18] In this study, we introduce 5-hydroxy-2(5H)-furanone (5H5F) produced from furfural, as a versatile C4 platform for oxygen and nitrogen containing C4 chemicals. Furfural is a commercially

available and affordable feedstock to establish a bio-based chemical supply chain.[19] At present 5H5F finds use as a niche precursor for biologically active compounds.[20–23] In our study, 5H5F was obtained by oxidation of furfural at room temperature using titanium silicalite-1 (TS-1) with 92 % yield and isolated using extraction. The downstream reactions of 5H5F to C4 chemicals occurred at mild conditions and a variety of value-added chemicals were produced in a single step using carbon supported noble metal catalysts (Figure 1). In addition to oxygenates, nitrogen containing heterocyclic compounds were also produced directly from 5H5F by reductive aminolysis over Ru/C catalyst. We envision that as a green platform, 5H5F will grant access to a diverse pool of C4 chemicals and enable adoption of biomass derived C4 chemicals in industry.

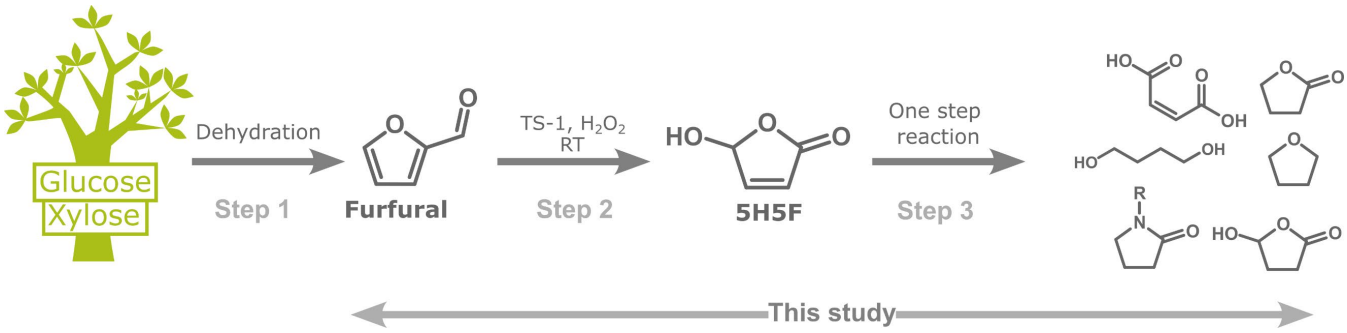

Figure 1. Overview of C4 chemical synthesis pathway through 5-hydroxy-2(5H)-furanone platform showing accessibility to a diverse C4 chemical pool from biomass in three steps.

Results and Discussion

Oxidation of furfural to 5H5F

5H5F was synthesized by oxidation of furfural at room temperature with Lewis acid zeolites in the presence of H_2O_2. See supporting information (SI) section 1.1, Figure S1-S3 for details of reaction procedure and analysis of reaction mixture. TS-1 catalyst was much more active at room temperature when compared with Ti-Beta, Nb-Beta and Zr-Beta zeolite catalysts prepared by post-synthetic incorporation of metal ions in the Beta zeolite (See SI section 1.2,Figure S4-S9 and Table S1 for synthesis and characterization of catalysts). 5H5F yield of 92 % was obtained in 8 h when TS-1 was used as catalyst along with 93 % yield of formic acid (Table 1). Ti-Beta and Nb-Beta zeolites produced 15 % and 8 %

yield of 5H5F at room temperature, respectively. Figure S10 shows diffuse reflectance infrared Fourier transformation spectroscopy (DRIFTS) of furfural adsorbed on the catalysts (Section 1.6, experimental details). All the catalysts showed similar redshift in both C=O stretching frequencies and C=C stretching frequencies, suggesting similar furfural adsorption behavior. Hence, the 5H5F yield was correlated with the activation of H_2O_2 over the metal sites as observed in the diffused reflectance UV-Vis spectrum of the H_2O_2 treated catalyst (Figure 2a). Bands were observed in Ti-Beta, Nb-Beta and TS-1 catalyst, associated with charge transfer transition of metal peroxo or hydroperoxo species (Figure S11 shows models of different chemisorption modes of H_2O_2)[24,25], which are known to catalyze the epoxidation reaction. Unlike the band for H_2O_2 treated Ti-Beta and Nb-Beta, the band for H_2O_2 treated TS-1 catalyst was centered around 395 nm, suggesting a different structure of chemisorbed H_2O_2 in case of TS-1. Formation of bridging peroxo species in the presence of dinuclear Ti^{4+} site has been reported in literature, which is predicted to have a lower energy pathway for epoxidation reactions.[26] According to the UV-Vis peak analysis of H_2O_2 adsorbed catalysts and the catalytic activity it is likely that TS-1 possesses such bridged peroxy species, which are responsible for high activity for furfural oxidation to 5H5F.

Table 1. Yield of products after furfural oxidation with aq. H_2O_2 in the presence of different catalysts. Reaction conditions: Furfural 1 mmol, aq. H_2O_2 1-16 mmol, catalyst 100 mg, water 5 mL, 8 h, room temperature.

Entry	Catalyst	H_2O_2 (mmol) [c]	Conversion (%)[a]	Product Yield (%)				
				5H5F[a]	Maleic acid[a]	2(3H)-Furanone[a]	Succinic acid[a]	Formic acid[b]
1	TS-1	16(3.1.)	>99	92	5	0	0	93
2	Ti-Beta	16 (4.2)	>99	15	2	0	0	96
3	Nb-Beta	16 (0.95)	27	8	<1	13	5	25
4	Ti/SBA15	16 (7.6)	14	0	0	3	1	9
5	Zr-Beta	16 (0.34)	11	<1	0	<1	1	8
6	Zr/SBA15	16 (1.7)	5	<1	<1	<1	<1	5
7	TS-1	1	>99	29	<1	0	0	37

8	TS-1	2	>99	55	<1	0	0	73
9	TS-1	2[d]	>99	80	<1	0	0	95
10	TS-1	3 (2.8)	>99	69	<1	0	0	97
11	TS-1	4 (3.5)	>99	75	1	0	0	96

[a]Determined by HPLC, [b]Determined by NMR (See Figure S2), [c]The number in the parenthesis shows the amount of H_2O_2 used during the reaction, determined by NMR (See Figure S3), remaining H_2O_2 could be determined accurately for entries 7-9. [d]reaction time was 24 h

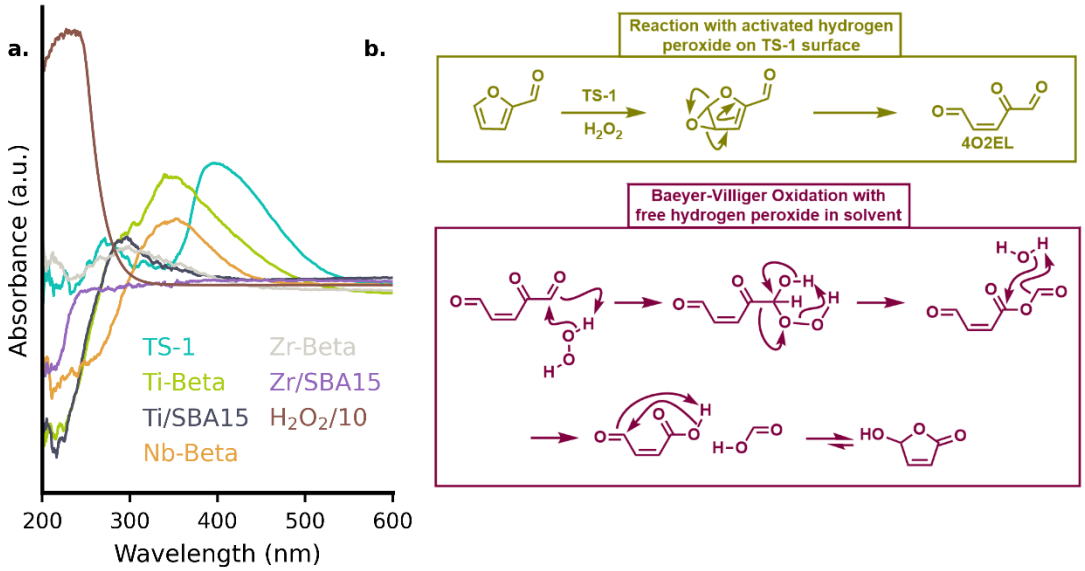

Figure 2. a. DRUV-Vis spectrum of catalysts treated with H_2O_2, showing activation of H_2O_2. The spectrum of H_2O_2 was recorded in transmission mode in liquid phase for comparison and the absorbance was divided by 10 to make the intensities comparable to the solid samples. b. Proposed reaction mechanism for catalyst furfural oxidation to 4O2EL followed by oxidation of 4O2EL to 5H5F.

5H5F is formed as an intermediate in maleic acid synthesis from furfural with H_2O_2 [27,28] and we have previously shown that the rate of formation of 5H5F was 37 times faster than its conversion to maleic acid at 80 °C in presence of TS-1.[29] Therefore, in this study 5H5F was selectively produced at room temperature with H_2O_2 because its further oxidation to maleic acid would require higher activation energy.

Although excess amount of H_2O_2 (16 eq.) was used during the reaction with TS-1, the actual amount of H_2O_2 consumed was 3.1 eq. (calculated by determining the remaining amount of H_2O_2 in the reaction mixture by NMR analysis as shown in Figure S3). In the presence of stoichiometric H_2O_2 amount (2 eq.),

the reaction was slower and 80 % yield of 5H5F was obtained after 24 h (Table 1 entry 9). Formation and accumulation of (Z)-4-oxopent-2-enedial (4O2EL), a C5 intermediate, was observed at lower H_2O_2 concentrations (see LC-MS of 4O2EL in Figure S12). Epoxidation of the double bond away from carbonyl group in furfural would yield 4O2EL as shown in Figure 2 b. When furfural-α-^{2}H was used as reactant only deuterated formic acid was obtained after reaction, originating from the cleavage of aldehyde group (Figure S13). Hence, we propose that the conversion of 4O2EL occurs through non-catalytic Baeyer-Villiger oxidation to produce 5H5F because the terminal aldehyde group is highly electrophilic due to the presence of acyl substituent and susceptible to reaction with H_2O_2 (Figure 2b). At low H_2O_2 concentration, accumulation of 4O2EL would slow the reaction, as it would be in equilibrium with its hydrated structures in water as evidenced by NMR analysis of mixture after reaction with sub-stoichiometric amount of H_2O_2 (Figure S14). Furthermore, it is likely that the formation of polymeric products by condensation reaction of hydrated aldehyde groups in 4O2EL would reduce the 5H5F selectivity as shown in Figure S15. Therefore, increasing the H_2O_2/furfural ratio accelerated the oxidation of 4O2EL and 5H5F yield increased (Figure S16, S17).

After oxidation 5H5F was extracted from the reaction mixture with ethyl acetate as a yellowish compound with more than 99 % purity (See SI Section 1.7 for detailed procedure). Formic acid and by-products like dicarboxylic acids were easily separated because they were retained in the aqueous phase during extraction. NMR analysis and mass fragmentation pattern of the purified product confirmed the 5H5F structure (Figure S18 and S19). Melting point of the purified 5H5F was determined to be 50 – 55 °C (Figure S20), which was in good agreement with literature.[30,31] Elemental analysis of 5H5F revealed the composition to be 47.2 % C, 48.9 % O and 3.9 % H by weight, which gives the molecular formula of $C_4H_4O_3$.

5H5F was stable under ambient conditions without degradation for at least four months as determined by NMR. Thermal and hydrothermal stability of 5H5F was tested by heating 5H5F in acetonitrile and water, respectively. In the absence of any reactive environment 91 % of original 5H5F was recovered

after 1 h in acetonitrile at 200 °C (Table S2). In water 5H5F was stable at 100 °C and 95 % was recovered after 1 h. At higher temperature, β-formyl acrylic acid (BFA) was formed by hydrolysis of 5H5F along with some undetected products.

Oxidation of 5H5F

Oxidation of 5H5F with H_2O_2 in the presence of TS-1 catalyst at 80 °C produced maleic anhydride and maleic acid (quantified together and referred as maleic acid) with a total yield of 93 % (Figure 3a-b). Other Lewis acid zeolites like Nb-Beta, Ti-Beta and Zr-Beta also oxidized 5H5F with reasonable yield of maleic acid. In this reaction, the hydroxyl group of 5H5F was oxidized by peroxo species formed on metal sites. Net maleic acid yield of 86 % was obtained from furfural after the two-step reaction via 5H5F, in comparison to 56 % in a single step reaction using H_2O_2 and 73 % in gas phase oxidation using O_2.[28,29,32]

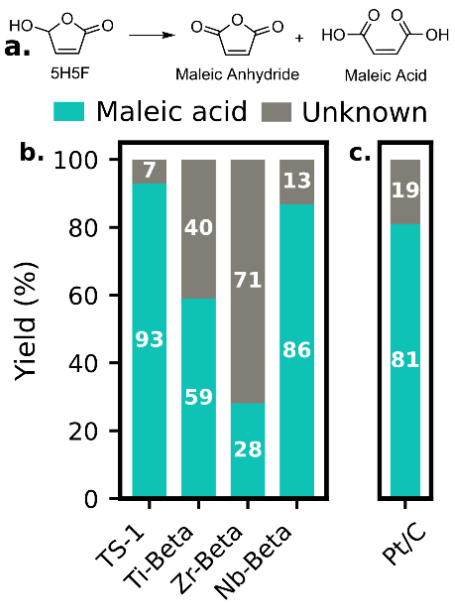

Figure 3. a. Reaction scheme of 5H5F oxidation to maleic acid and maleic anhydride (quantified together as maleic acid), b. Product yield after 5H5F oxidation over zeolite catalysts in presence of H_2O_2. Reaction conditions: 5H5F 1 mmol, catalyst 50 mg, water 5 mL, 30 % aq. H_2O_2 2 mL, 80 °C, 2 h., c. Product yield after 5H5F oxidation over Pt/C catalyst in presence of O_2. Reaction conditions: 5H5F 1 mmol, catalyst 50 mg, water 5 mL, O_2 0.9 Mpa, 100 °C, 12 h. Unknown represent the difference between 5H5F conversion and yield of maleic acid.

Unlike the epoxidation reaction, the oxidation of 5H5F was not specific to the structure of metal peroxo species. Therefore, 5H5F oxidation also proceeded under typical oxidation conditions using molecular oxygen. In the presence of Pt supported on carbon black (Pt/C) catalyst at 100 °C and 0.9 MPa O_2, 81 % yield of maleic acid was obtained after 12 h (Figure 3c). Therefore, oxidation of 5H5F was facile with high yield of maleic acid under mild conditions.

Hydrogenation of 5H5F

Hydrogenation of 5H5F was carried out in the presence of different metal catalysts supported on carbon black (catalyst characterization Figure S21-25, Table S3). Pt/C catalyst selectively hydrogenated the double bond in 5H5F to yield 5-hydroxy-γ-butyrolactone (HGBL) as shown in Figure 4a-b (HPLC profile and NMR of reaction mixture is given in Figure S26-27), contrary to the results reported by Chen et al.,[33] which could be due to difference in reaction conditions. At 100 °C the yield of HGBL was 89 % in the presence of Pt/C catalyst. Rh/C produced 72 % yield of HGBL along with small amount of GBL, BDO, succinic acid (SA) and propionic acid (PA). GBL yield increased to 12 % over Pd/C catalyst with 75 % of HGBL. Ru/C catalyst on the other hand produced GBL in 93 % yield, and there was no HGBL present after reaction. Hydrogenation of HGBL as reactant with Ru/C produced GBL with >95 % selectivity (Table S4), which shows the ability of Ru to open the ring. When 5H5F was treated in the absence of H_2 under same condition, β-formyl acrylic acid (BFA) was produced in 5 %, and 0 % yield over Ru, and Pt catalyst respectively (Table S4), which further confirms that Ru could catalyze the ring opening of both 5H5F and HGBL. 5H5F hydrogenation can proceed via one of the two pathways shown in Figure S28. In the first pathway, the double bond is hydrogenated to form HGBL followed by ring opening, hydrogenation and dehydration to GBL. In the second pathway, 5H5F is converted to its open chain isomer BFA via hydrolysis and dehydration. BFA is then further hydrogenated to form GBL. Based on our results we propose that double bond hydrogenation of 5H5F to HGBL followed by ring opening is the major pathway.

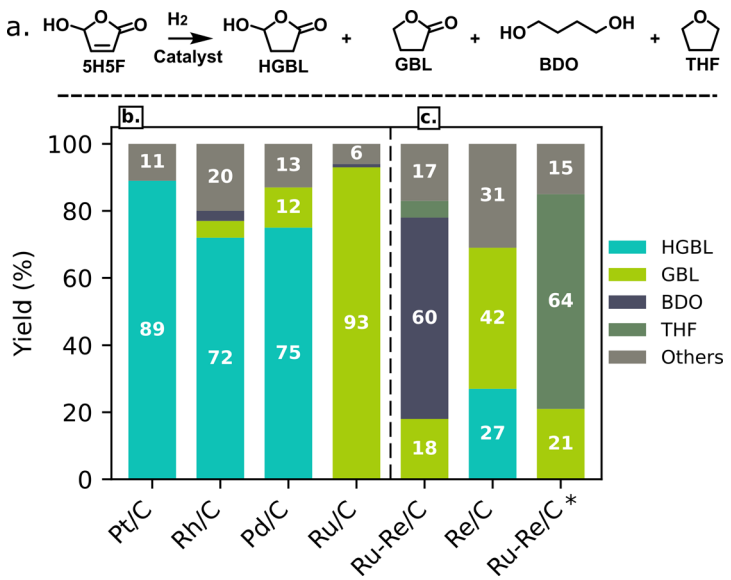

Figure 4. a. Reaction scheme showing possible products from hydrogenation of 5H5F. b. 5H5F hydrogenation to HGBL and GBL, reaction conditions – 5H5F 1 mmol, catalyst 50 mg, water 5 mL, H_2 2 MPa, 100 °C 1 h. c. 5H5F hydrogenation to BDO and THF. Reaction conditions – 5H5F 1 mmol, catalyst 50 mg, water 5 mL, H_2 4 MPa, 150 °C, 12 h. Others represent butanol, succinic acid, propionic acid and undetected products. *The reaction was carried out with ethanol as solvent

Direct conversion of 5H5F to BDO and THF was achieved over bimetallic Ru-Re/C catalyst as shown in Figure 4c (See HPLC profile and GC-MS, Figure S29-31). At 150° C, 60 % of BDO was obtained from 5H5F in 24 h. BDO was formed by hydrogenation of GBL, and it underwent dehydration to THF. Monometallic Re catalyst produced HGBL (42 %) and GBL (27 %) and BDO was formed only in the presence of bimetallic catalyst. H_2 TPR of Ru-Re/C suggested that Ru helps in reduction of rhenium oxide (Figure S32). Reduced Re species are known to promote hydrogenation of GBL and succinic acid to BDO due to its acidity, oxophilicity and ability to dissociate hydrogen heterolytically.[34–36] THF was formed by dehydration of BDO and performing the reaction in the presence of ethanol as solvent instead of water produced THF in 64 % yield. Small quantities of diethyl and monoethyl ether of BDO were also obtained (Figure S30).

Reductive aminolysis of 5H5F

In addition to opening the ring of 5H5F by nucleophilic addition of water, it is possible to use other nucleophiles to directly produce nitrogen containing heterocyclic C4 compounds. In the presence of H_2

and NH_3, 5H5F produced γ-aminobutanoic acid (GABA) and 2-pyrrolidone via reductive aminolysis over Ru/C catalyst (Figure 5a). After 1 h at 110 °C, GABA was obtained in 71 % yield (Figure 5b). Continuing the reaction while increasing the temperature to 130 °C produced 2-pyrrolidone with 67 % yield after 18 h as the GABA yield decreased (LC-MS profile and NMR of reaction mixture Figure S33 and Figure S34). Cyclization of GABA to 2-pyrrolidone was confirmed by using GABA as the reactant under the same reaction condition, which produced 71 % yield of 2-pyrrolidone at 83 % conversion after 14 h (Figure S35).

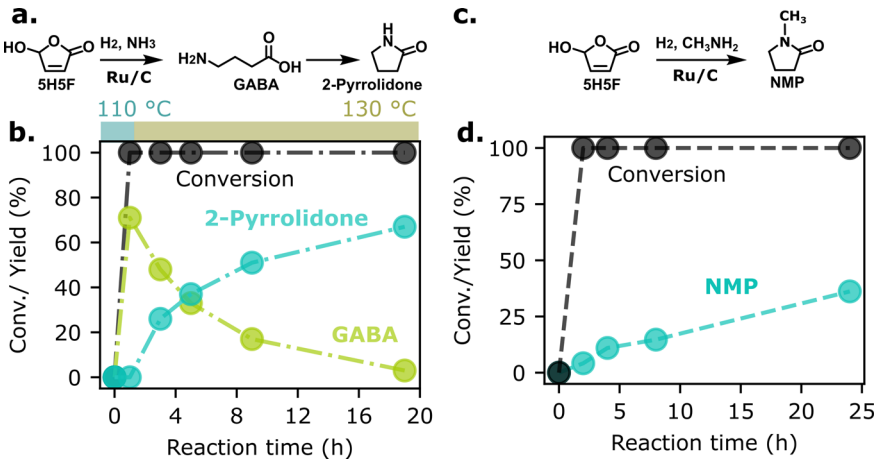

Figure 5. a. Reaction scheme showing formation of 2-pyrrolidone from reductive aminolysis of 5H5F via GABA. b. Time course of 5H5F to 2-pyrrolidonereaction in the presence of Ru/C catalyst. Reaction conditions – 5H5F 5.56 mmol, Ru/C catalyst 200 mg, water 30 mL, aq. NH_3 (27 %) 7.5 mL, H_2 2 MPa, 110 °C for 1 h and 130 °C for 18 h. c. Reaction scheme showing formation of NMP from reductive aminolysis of 5H5F. d. Time course of 5H5F reductive aminolysis reaction with methylamine as amine source. Reaction conditions – 5H5F 1 mmol, Ru/C catalyst 50 mg, CH_3NH_2 4 mmol, water 2 mL, H_2 2 MPa, 130 °C

We propose that 5H5F undergoes aminolysis to form a hemiaminal structure as shown in Figure S36. The hemiaminal would undergo dehydration to form an imine, which will then undergo hydrogenation to produce GABA followed by its cyclization to 2-pyrrolidone.

Ring opening of 5H5F by reductive aminolysis was not limited to 2-pyrrolidone formation. N-methyl pyrrolidone (NMP) was also directly produced from 5H5F as shown in Figure 5 (LC-MS of product,

Figure S37). Replacing NH_3 with methyl amine the reaction proceeded in a similar manner. All the 5H5F was consumed in the initial 30 minutes, with only 4 % NMP. N-methyl pyrrolidone yield increased to 36 % after 24 h reaction. However, an intermediate was not identified even after rigorous analysis of reaction mixture. It is likely that oligomeric imines are formed by aminolysis and dehydration of 5H5F with methyl amine, which would slowly convert to NMP under the reaction condition.

Discussion

A major limiting factor in implementation of biomass as a chemical resource has been the energy consumption in synthesis and reaction of platform chemicals. Synthesis of 5H5F from furfural was feasible at room temperature owing to the ability of TS-1 to catalyze the epoxidation reaction at low temperature. Epoxidation of furan has also been reported to produce 5H5F in a similar way.[37] Considering that furan is obtained by decarbonylation of furfural, a single step reaction at room temperature is more efficient. Separation of 5H5F was also energy efficient because extraction was sufficient to obtain a product with 99 % purity.

5H5F was stable enough to avoid rapid degradation and at the same time it was reactive under oxidation, hydrogenation and aminolysis conditions at 100–150 °C. The fourth carbon of 5H5F was reactive towards nucleophilic addition leading to formation of oxygen and nitrogen containing value added C4 chemicals. Furfural is currently produced directly from biomass in a single step. Therefore, by using 5H5F as a platform chemical, it is feasible to synthesize industrially valuable C4 chemicals with high yield in three steps from raw biomass.

Currently, industrial processes and much of the literature in C4 chemistry are focused on synthesis of dicarboxylic acids and their conversion to products like GBL, BDO and pyrrolidone derivatives. Oxidation of biomass derived chemicals like 5-hydroxymethyl furfural, and levulinic acid can produce maleic acid but requires organic solvents or high temperature.[38–41] Direct oxidation of furfural both in liquid phase with H_2O_2 or O_2, and in gas phase with O_2 can produce maleic acid.[28,32,42] The gas phase oxidation of furfural to maleic anhydride is cost effective and holds some promise.[43] Subsequent hydrogenation of maleic acid and succinic acid to GBL and BDO also face issues owing to corrosion

caused by requirement of harsh reaction condition and acidity of dicarboxylic acid.[44] In industry, 2-pyrrolidone is produced industrially by reaction of GBL with ammonia in vapor phase.[14] The reaction is carried out at 250 – 300 °C. GBL itself is derived from petroleum by energy intensive reaction steps. Similarly, NMP is industrially made by reacting GBL with methyl amine at 250–400 °C and 6–12 MPa.[14] In contrast, the reaction conditions for direct aminolysis of 5H5F to 2-pyrrolidone and NMP were significantly milder. Consequently, owing to the simple synthesis and high reactivity of 5H5F it has the potential to be a wide application as a C4 platform chemical.

In this study we primarily used conventional carbon supported catalyst to test the viability of 5H5F as a platform. The commercial viability of 5H5F would depend on developing new catalysts to improve the selectivity of downstream hydrogenation and reductive aminolysis reactions, which will be the focus of our future research.

Conclusion

Synthesis of value-added chemicals from biomass relies on platform chemicals that serve as precursors for different classes of chemicals. While platform chemicals for C6 and C5 chemicals are well established a suitable platform for C4 chemical synthesis is lacking. In this study, we have shown that 5-hydroxy-2(5H)-furanone (5H5F) can function as a biomass derived platform for C4 chemical synthesis. 5H5F was produced by oxidation of furfural at room temperature with 92 % yield and it was isolated from the reaction mixture by extraction. Epoxidation of furfural by H_2O_2 activated on TS-1 catalyst produced an intermediate which underwent Baeyer-Villiger oxidation to form 5H5F. Oxidation of 5H5F to maleic acid proceeded with both H_2O_2 (TS-1) and molecular O_2 (Pt/C). Nucleophilic addition of water and amines under hydrogenation environment produced GBL, BDO, THF, 2-pyrrolidone and NMP over Ru/C or Ru-Re/C catalyst in a single step. In comparison to other biomass derived C4 platforms like succinic acid, 5H5F is easier to synthesize, isolate and it is susceptible to catalytic transformation under milder conditions. Owing to these traits we believe 5H5F is a good platform chemical for C4 synthesis and this work will open new avenues for research in C4 chemical synthesis from biomass.

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Supporting Information

The following files are available free of charge.

Materials and methods, Additional catalyst characterizations, Experiments for identification of key intermediates and products. Proposed mechanism for transformation of 5H5F.

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