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Catalytic aerobic oxidation of renewable furfural to maleic anhydride and furanone derivatives with their mechanistic studies†

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Catalytic transformation of biomass-based furfural to value-added chemicals is an alternative route to the on-going fossil feedstock-based processes. This work describes catalytic aerobic oxidation of furfural to maleic anhydride, an important polymer starting material having a large market with $H_5PV_2Mo_{10}O_{40}$ and $Cu(CF_3SO_3)_2$ catalysts. Under the optimized conditions, 54.0% yield of maleic anhydride can be achieved with about 7.5% yield of 5-acetoxyl-2(5*H*)-furanone formation. Notably, 5-acetoxyl-2(5*H*)-furanone is a highly value-added, biologically important intermediate that has been applied in pharmaceutical synthesis. The catalytic mechanism for furfural oxidation to maleic anhydride and 5-acetoxyl-2(5*H*)-furanone has been investigated in detail with identification of several key intermediates.

Introduction

Biomass, dominantly comprised of carbon, hydrogen, oxygen and nitrogen, is the largest renewable carbon resource on Earth. With diminishing fossil resources, biomass has been regarded as a promising feedstock for the chemical industry in future.[1] To explore new chemicals from polysaccharides, C6-based biomass and its sub-products have been fully recognized,[2] while the explorations of C5-based resources are still very limited. Compared with C6-based HMF, its analog, *i.e.* C5-based furfural, comes from rich agricultural materials like corncobs, oat, wheat bran, and sawdust, and they are not competitive with food of human beings. Particularly, unlike HMF, which is currently synthesized on a lab scale, furfural production is an on-going industrial process; therefore, exploring the sub-products using furfural as the platform to replace the fossil resources is greatly attractive.[3]

Maleic anhydride is a starting material for the manufacture of unsaturated polyester resins and many other important chemicals.[4] Currently, maleic anhydride is commercially produced by catalytic oxidation of petroleum-derived chemicals such as *n*-butane and benzene in millions of tons annually.[5] Due to the depletion of petroleum feedstock and environmental concerns associated with the petroleum industry there has been a gradual technological transition from petroleum to biomass, a greener and more renewable feedstock.[6] As early as in 1926, Sessions had demonstrated the vapor phase oxidation of furfural to maleic anhydride in the presence of V_2O_5 catalyst at 200–300 °C,[7] and in 1947, Nielsen introduced an iron molybdate catalyst that can provide more than 70% selectivity of maleic anhydride based on converted furfural by vapor phase oxidation. However, continuing studies on transformations of furfural to maleic anhydride were very limited, possibly due to its poor competition with the petroleum based on-going processes. Recently, Ojeda applied VO_x/Al_2O_3 as a solid catalyst for vapor phase oxidation of furfural, which provides a considerably high yield (73%) of maleic anhydride under 593 K.[8] Combining earlier mechanistic studies using solid catalysts like $Sn(VO_3)_4$ and promoted V–Mo–P like P_2O_5, $Fe_2(MoO_4)_3$, MoO_3, V_2O_5,[9–12] Ojeda proposed that decarbonylation is the first step in furfural vapor phase oxidation, which generates furan as the intermediate, followed by further oxidation of furan to maleic anhydride.

In 2011, we reported the aerobic oxidation of furfural to maleic acid in aqueous solution using heteropolyacid catalysts,[13] in which phosphomolybdic acid, $H_3PMo_{12}O_{40}$ and copper(II) nitrate as catalyst demonstrated considerably high catalytic activity by providing a 50% yield of maleic acid. To further improve the selectivity of maleic acid and potential recycling of catalyst and unconverted furfural, we further built up an aqueous/organic biphase system in which phosphomolybdic acid alone as catalyst could provide 68% selectivity of maleic acid.[14] The relatively high selectivity was achieved

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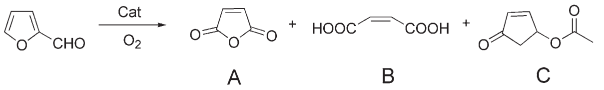
because, with the oxidation proceeding, hydrophobic furfural was slowly released through phase equilibrium from organic phase into aqueous phase in which the oxidation reaction happens. However, due to the oxidation being carried out in aqueous phase, there was no maleic anhydride product observed. Compared with maleic acid, maleic anhydride has a much larger market due to its wide applications in the polymer industry. Here, we report a furfural-based maleic anhydride synthesis in liquid phase, and its catalytic transformation mechanism has been elucidated, which is apparently different from those in vapor phase oxidation. Notably, a highly value-added, biologically important product, 5-acetoxyl-2(5*H*)-furanone, was unexpectedly co-produced under catalytic conditions.

Results and discussion

Catalyst scanning for furfural oxidation

The catalytic reactivity of heteropolyacids has attracted much attention in redox chemistry, and they were also employed in our recent furfural oxidations and one of these authors' earlier studies on oxidative carbonylation of phenol to diphenyl carbonate.[13–15] To avoid the hydrolysis of maleic anhydride, here, catalytic oxidations of furfural were performed in organic solvent, and a list of heteropolyacids were tested as catalyst. The reaction was performed under pressurized oxygen (20 atm) in acetonitrile–acetic acid (2 : 1.3, v/v) at 383 K. Through GC-MS analysis of the reaction mixtures after oxidation, three products, including maleic anhydride (**A**), maleic acid (**B**) and 5-acetoxyl-2(5*H*)-furanone (**C**), were identified as illustrated in eqn (1). Among the heteropolyacids tested in Table 1, vanadium(V)-substituted heteropolyacid, $H_5PV_2Mo_{10}O_{40}$, demonstrates the highest catalytic activity for furfural oxidation. After 14 h reaction, 93.8% conversion of furfural could be achieved with $H_5PV_2Mo_{10}O_{40}$ catalyst, the total yields of three products are 43.5%, including 29.5% yield of maleic anhydride, 9.8% yield of maleic acid and 4.2% of 5-acetoxyl-2(5*H*)-furanone (entry 7). When furfural is exposed to air, it generally leads to polymerization, and the color turns black gradually. Here, although the reaction solution remains clean after catalytic oxidation, it does not exclude the formation of certain oligomers under the pressurized oxygen with elevated temperature, which leads to a relatively low yield of the three major products. Particularly, formation of 5-acetoxyl-2(5*H*)-furanone was absolutely unexpected, which cost these authors a lot of time to isolate and characterize it, and finally it was identified by GC-MS and NMR analysis. The unique carbon skeleton of 2(5*H*)-furanone is biologically important and widely present in a variety of natural products, and the pharmaceutical synthesis based on 2(5*H*)-furanones has attracted much attention recently.[16] Under the optimized conditions, *i.e.*, adding minor acetic anhydride to an acetonitrile–acetic acid (2/1.3, v/v) solvent mixture, the yield of 5-acetoxyl-2(5*H*)-furanone can be improved up to 11.4% (see Table S1 in ESI†). Even though the yield of 5-acetoxyl-2(5*H*)-furanone is not as high as that of maleic anhydride in this catalytic system, direct transformation of renewable furfural to the highly value-added, biologically important pharmaceutical intermediate, 2(5*H*)-furanone, is of great interest for its potential commercial production.



(1)

Remarkably, adding 1 equiv. of $Cu(CF_3SO_3)_2$ to the catalytic solution further improved the yield of maleic anhydride up to 54.0% but without maleic acid observed in analysis, while the yield of 5-acetoxyl-2(5*H*)-furanone also slightly improved (7.5%) (entry 8). This improvement was also observed when $H_4PVMo_{11}O_{40}$ and $H_4PV_3Mo_{10}O_{40}$ were used as catalysts. For the $H_4PVMo_{11}O_{40}$ catalyst, the total yields of three products can be sharply improved from 6.2% to 20.1% by adding $Cu(CF_3SO_3)_2$, while for $H_6PV_3Mo_9O_{40}$, the total yields can be improved from 43.6% to 49.2%. For other heteropolyacids, their catalytic activities are quite poor, and adding copper(II)

Table 1 Catalyst scanning for furfural oxidation[a]

Entry	HPA	Cu(II) (mmol)	Conv. (%)	Yield A (%)	Yield B (%)	Yield C (%)	Yield[b] (%)
1	$H_3PMo_{12}O_{40}\cdot xH_2O$	—	51	0.3	<0.1	<0.1	0.4
2	$H_3PMo_{12}O_{40}\cdot xH_2O$	0.02	34.9	1.2	1.9	0.3	3.4
3	$H_3PW_{12}O_{40}\cdot xH_2O$	—	15.4	0.1	0.1	<0.1	0.2
4	$H_3PW_{12}O_{40}\cdot xH_2O$	0.02	39.4	0.3	<0.1	0.3	0.6
5	$H_4[SiO_4(W_3O_9)_4]\cdot xH_2O$	—	44.2	0.4	<0.1	0.1	0.5
6	$H_4[SiO_4(W_3O_9)_4]\cdot xH_2O$	0.02	50.1	0.4	0.1	0.5	1.0
7	$H_5PV_2Mo_{10}O_{40}\cdot xH_2O$	—	93.8	29.5	9.8	4.2	43.5
8	$H_5PV_2Mo_{10}O_{40}\cdot xH_2O$	0.02	98.7	54.0	—	7.5	61.5
9	$H_4PVMo_{11}O_{40}\cdot xH_2O$	—	53.7	0.3	4.4	1.5	6.2
10	$H_4PVMo_{11}O_{40}\cdot xH_2O$	0.02	72.7	13.9	2.0	4.2	20.1
11	$H_6PV_3Mo_9O_{40}\cdot xH_2O$	—	97.3	25.9	10.3	7.4	43.6
12	$H_6PV_3Mo_9O_{40}\cdot xH_2O$	0.02	99.1	30.3	12.1	6.8	49.2

[a] Conditions: 0.02 mmol heteropolyacid, 0.02 mmol $Cu(CF_3SO_3)_2$, 2.4 mmol furfural, 2 mL CH_3CN, 1.3 mL HOAc, 20 atm O_2, 383 K, 14 h. [b] Total yields of maleic acid, maleic anhydride and 5-acetoxyl-2(5*H*)-furanone.

Table 2 Lewis acids scanning for the furfural oxidation[a]

Entry	Lewis acid	Conversion (%)	Yield A (%)	Yield B (%)	Yield C (%)	Yield[b] (%)
1	—	93.8	29.5	9.8	4.2	43.5
2	$AgCF_3SO_3$	99.5	32.6	13.7	5.9	52.2
3	$NaCF_3SO_3$	98.5	34	9.7	5.4	49.1
4	$Mg(CF_3SO_3)_2$	97.1	29.7	14.3	5.6	49.6
5	$Zn(CF_3SO_3)_2$	100	29.3	11.6	5.9	46.8
6	$Cu(CF_3SO_3)_2$	98.7	54	—	7.5	61.5
7	$Pd(OAc)_2$	94.2	28.6	14.5	5.6	48.7
8	$FeCl_2$	99.4	33.6	10.9	5.7	50.2
9	$Y(CF_3SO_3)_3$	98.5	27.4	19.2	2.3	48.9
10	$Yb(CF_3SO_3)_3$	97.8	28.2	17	2.3	47.5
11	$Sc(CF_3SO_3)_3$	98.2	27.3	15.5	4.8	47.6
12	$Al(CF_3SO_3)_3$	98.8	30.5	10.6	3.3	44.4

[a] Conditions: 0.02 mmol $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$, 0.02 mmol Lewis acid, 2.4 mmol furfural, 2 mL CH_3CN, 1.3 mL HOAc, 20 atm O_2, 383 K, 14 h. [b] Total yields of maleic acid, maleic anhydride and 5-acetoxyl-2(5*H*)-furanone.

Table 3 The stability of maleic acid & anhydride under dehydration process[a]

Entry	Lewis acid	Starting maleic acid (g)	Starting maleic anhydride (g)	After reflux[b] (g)	Loss (%)
1	—	—	0.1022	0.1025	0
2	—	0.1051	—	0.0879/(0.0888)[c]	1
3	$Cu(CF_3SO_3)_2$	—	0.1022	0.0855	16.6
4	$Cu(CF_3SO_3)_2$	0.1051	—	0.0692/(0.0888)[c]	21.3
5	$AgCF_3SO_3$	—	0.1149	0.1154	0
6	$AgCF_3SO_3$	0.116	—	0.0983/(0.0980)[c]	0
7	$Sc(CF_3SO_3)_3$	—	0.1149	0.1127	1.9
8	$Sc(CF_3SO_3)_3$	0.116	—	0.098/(0.0980)[c]	0

[a] Conditions: 0.02 mmol $H_5PV_2Mo_{10}O_{40}$, 0.02 mmol Lewis acid, 2 mL CH_3CN, 1.3 mL HOAc, 5 mL Ac_2O, 373 K, 2 h. [b] The mass of maleic anhydride. [c] The theoretical mass of maleic anhydride generated.

also does not improve their efficiencies too much under current conditions.

Influence of the additives on furfural oxidation

Recently, redox inactive metal ions serving as Lewis acids in redox transition metal ions mediated oxidations has attracted considerable attentions in academic communities.[17] After investigating the reactivity relationship of the active intermediates in oxidation, we have also explored Al(III) promoted Pd(II) catalyzed benzene hydroxylation and manganese(II) complex catalyzed sulfide oxidations.[18] To further pursue the synergistic effect between the $H_5PV_2Mo_{10}O_{40}$ and Lewis acids, a wide range of metal ions were tested as additives in furfural oxidation, and the results are summarized in Table 2.

Apparently, the catalytic activity of $H_5PV_2Mo_{10}O_{40}$ can be improved by adding Lewis acids in each case. For example, the total yields of three listed products can be improved up to 52.2% for $AgCF_3SO_3$, 50.2% for $FeCl_2$ and 48.9% for $Y(CF_3SO_3)_3$, respectively, while $H_5PV_2Mo_{10}O_{40}$ alone gives a 43.5% of total yield. Particularly, adding $Cu(CF_3SO_3)_2$ leads to the highest total yield (61.5%). However, adding Cu(II) also leads to the disappearance of maleic acid as product, whereas other metal ions may improve the maleic acid formation in most cases. For example, Y(III) as an additive provides a 19.2% yield of maleic acid, while the yield is 9.8% for $H_5PV_2Mo_{10}O_{40}$ as catalyst alone.

Since the quantitative analysis of maleic acid was conducted after dehydration of the reaction mixtures by adding acetic anhydride to generate maleic anhydride under reflux conditions (independent analysis of maleic anhydride and 5-acetoxyl-2(5*H*)-furanone products was performed prior to this procedure, see Experimental section for details), the presence of copper(II) may cause the decomposition of maleic anhydride and maleic acid during the dehydration process. In complimentary experiments, we investigated the stability of maleic acid and maleic anhydride during the dehydration process, and the results are listed in Table 3. One may see that, with the tested Lewis acids, copper(II) can decompose maleic acid, leading to a 21.3% loss of the initial maleic acid substrate, while the other two tested Lewis acids, Ag(I) and Sc(III), do not. Similar decomposition of maleic anhydride was also observed in the dehydration procedure when using maleic anhydride in place of maleic acid; therefore, the amount of maleic anhydride after dehydration treatment is less than its original amount. This decomposition explained that no formation of maleic acid was observed when using copper(II) as an additive in furfural oxidation (Table 2). Other Lewis acids as additives demonstrate the formation of maleic acid because they do not decompose maleic acid and maleic anhydride.

Table 4 Catalytic efficiency on furfural oxidation by $Cu(CF_3SO_3)_2$ and $H_5PV_2Mo_{10}O_{40}{\cdot}xH_2O$ acid[a]

Entry	$H_5PV_2Mo_{10}O_{40}$ (mmol)	Cu(II) (mmol)	Con (%)	Yield A (%)	Yield B (%)	Yield C (%)	Yield[b] (%)
1	0.01	0.01	98.8	42.1	—	4.8	46.9
2	0.01	—	97.3	33.4	7.9	4.2	45.5
3	0.02	—	93.8	29.5	9.8	4.2	43.5
4	0.03	—	99.2	29.9	10	3.2	43.1
5	—	0.02	22	0.2	<0.1	0.4	0.6
6	0.02	0.02	98.7	54	—	7.5	61.5
7	0.02	0.04	99.4	33.3	—	9.9	43.2
8	0.02	0.08	100	35.1	—	8.9	44
9	0.02	0.32	100	16.7	—	7.8	24.5
10	0.03	0.03	99.5	40.2	—	2	42.2
11	0.04	0.04	99	33	—	1.8	34.8
12	0.08	0.16	100	13.3	—	6.8	20.1

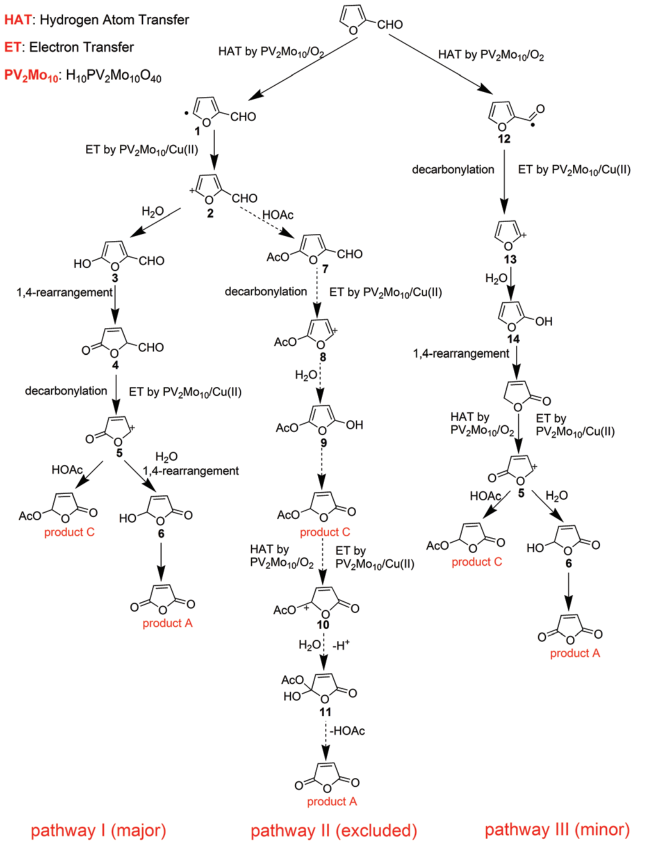
[a] Reaction conditions: 2.4 mmol furfural, 2 mL CH_3CN, 1.3 mL HOAc, 20 atm O_2, 383 K, 14 h. [b] Total yield of maleic acid, maleic anhydride and 5-acetoxyl-2(5*H*)furanone.

Optimization of furfural oxidation

The influence of the ratio between $H_5PV_2Mo_{10}O_{40}$ and Cu(II) on catalytic activity was next investigated and listed in Table 4. When $H_5PV_2Mo_{10}O_{40}$ was employed as catalyst alone, different catalyst concentrations provided similar activity; *i.e.*, the total yields were 45.5%, 43.5% and 43.1% under the $H_5PV_2Mo_{10}O_{40}$ loading of 0.01, 0.02 and 0.03 mmol (entries 2–4), respectively; moreover, the selectivities of products were similar. For example, the yields of maleic anhydride, maleic acid and 5-acetoxyl-2(5*H*)-furanone are 33.4%, 7.9% and 4.2% by 0.01 mmol of $H_5PV_2Mo_{10}O_{40}$, and 29.5%, 9.8% and 4.2% by 0.02 mmol of $H_5PV_2Mo_{10}O_{40}$, respectively. On the other hand, very limited products were detected after 14 h reaction when $Cu(CF_3SO_3)_2$ alone was employed as the catalyst (entry 5), indicating that $Cu(CF_3SO_3)_2$ alone is not catalytically active in furfural oxidation. However, when 0.02 mmol of $H_5PV_2Mo_{10}O_{40}$ and 0.02 mmol of $Cu(CF_3SO_3)_2$ were introduced as catalysts in this reaction, a total yield of 61.5% was achieved, including 54% of maleic anhydride and 7.5% of 5-acetoxyl-2(5*H*)-furanone (entry 6). When the concentration of $Cu(CF_3SO_3)_2$ was increased from 0.02 mmol to 0.32 mmol (entries 6–9) with a fixed loading (0.02 mmol) of $H_5PV_2Mo_{10}O_{40}$, the total yields of products decreased obviously from 61.5% to 24.5%. This can be explained by the fact that, in addition to improving the catalytic efficiency, Cu(II) may also decompose both maleic acid and anhydride as disclosed above.

Mechanistic studies of furfural oxidation

It is well known that furfural is not very stable because of its polymerization when exposed to oxygen. The initial step of polymerization is that the hydrogen atom at the 5-position of furfural is first abstracted by oxygen to generate a furfural radical that attacks the C═O bond of another furfural, which initializes the polymerization.[19] Similarly, the maleic anhydride formation could be initialized from the same furfural radical intermediate (**1**), as well as in polymerization, and a plausible mechanism has been proposed in Scheme 1. The first hydrogen atom is abstracted by either oxygen or $H_5PV_2Mo_{10}O_{40}$ to generate the furfural radical, which may initialize polymerization to form resins or proceed with electron transfer to generate the furfural cation intermediate **2**. This cation intermediate **2** may next react with either H_2O or HOAc. If it is attacked by H_2O, the intermediate **3** is generated *via* pathway **I**, followed by 1,4-rearrangement to generate the intermediate **4**. The intermediate **4** further goes through decarbonylation and electron transfer to form the intermediate **5**. The decarbonylation is indicated by the detection of CO with the online gas analyzer, which revealed a volume fraction of



Scheme 1 Proposed mechanism for furfural oxidation catalyzed by $H_5PV_2Mo_{10}O_{40}$ and $Cu(CF_3SO_3)_2$.

0.80% for CO and 3.44% for CO_2 in the gas mixture after reaction. The intermediate **5** is next attacked by H_2O to form the intermediate **6**, which is finally oxidized to maleic anhydride, the major product of this reaction. The formation of the key intermediate **6** has been identified by GC-MS. Possibly due to poor stability under the catalytic conditions, other intermediates in pathway **I** were not detected. Alternatively, the intermediate **5** can also be attacked by HOAc to form 5-acetoxyl-2(5*H*)-furanone, which represents 7.5% of products in analysis. Formation of maleic acid can be explained by hydration of maleic anhydride, because water is naturally generated in oxidation.

Alternatively, the intermediate **2** can also be attacked by HOAc to generate the intermediate **7** (see pathway **II**). Through similar decarbonylation and electron transfer, the intermediate **7** gives the intermediate **8**. In view of the structure of the identified products, the intermediate **8** is more likely to react with H_2O rather than HOAc to produce the intermediate **9**, which goes through 1,4-rearrangement to yield 5-acetoxyl-2(5*H*)-furanone, one identified product in this reaction. After hydrogen abstraction and electron transfer, 5-acetoxyl-2(5*H*)-furanone gives the intermediate **10**, which reacts with water, followed by releasing of H^+ to form the intermediate **11**. The intermediate **11** can release HOAc to form maleic anhydride as the major product.

Unlike pathway **I**, the product 5-acetoxyl-2(5*H*)-furanone is an intermediate for maleic anhydride formation in pathway **II**. To distinguish pathway **I** from pathway **II**, both of which include formation of the identified compound **6**, 5-acetoxyl-2(5*H*)-furanone was employed as the substrate in place of furfural under identical catalytic oxidation conditions. However, the yield of maleic anhydride from 5-acetoxyl-2(5*H*)-furanone is only 0.7%. If it was true that maleic anhydride formed through pathway **II**, using either furfural or 5-acetoxyl-2(5*H*)-furanone as the starting material would generate similar yields of maleic anhydride. In another experiment, formation kinetics of both maleic anhydride and 5-acetoxyl-2(5*H*)-furanone revealed that 5-acetoxyl-2(5*H*)-furanone is not the intermediate for maleic anhydride formation, and clearly, they are generated in parallel (Fig. 1). Thus, the trace formation of maleic anhydride from 5-acetoxyl-2(5*H*)-furanone as starting material has clearly excluded pathway **II** for maleic anhydride formation; *i.e.*, attacking of the intermediate **2** by water is preferred over HOAc, which leads to the pathway **I**.

In the oxidation of furfural to maleic anhydride, one carbon atom needs to be removed from the reactant. In literature reports, furan was frequently proposed as the intermediate in the vapor phase oxidation of furfural.[8–12] In this catalytic system, decarbonylation may also possibly take place prior to other steps. Thus, another plausible mechanism can happen as pathway **III** in Scheme 1. The hydrogen in the aldehyde functional group of furfural may be first abstracted by either oxygen or $H_5PV_2Mo_{10}O_{40}$ to generate the intermediate **12**. After decarbonylation and electron transfer of the intermediate **12**, the intermediate **13** can be generated. Attacking of the intermediate **13** by H_2O forms the intermediate **14**, which further goes through 1,4-rearrangement to yield 2(5*H*)-furanone. The formation of 2(5*H*)-furanone has been identified by GC-MS, but it does not exist as an intermediate in pathway **I** and **II**, thus supporting the existence of pathway **III** in furfural oxidation. After hydrogen abstraction from 2(5*H*)-furanone by either oxygen or $H_5PV_2Mo_{10}O_{40}$, a 2(5*H*)-furanone radical is generated, which further proceeds with electron transfer to form the intermediate **5**. Then, steps may occur similar to those in pathway **I**, which provides maleic anhydride and 5-acetoxyl-2(5*H*)-furanone as the final products. However, in the experiment using 2(5*H*)-furfuran in place of furfural, pathway **III** may exist but just serve as a minor pathway. It is worth noting that, in the complimentary experiments using furan in place of furfural as substrate, only a 0.2% yield of maleic anhydride was obtained with mostly conversion of furan to resins. Particularly, there is no furan product detected in furfural oxidation here. Therefore, this could confirm that furan is not the intermediate in maleic anhydride formation for furfural oxidation in liquid phase, which is different from the vapor phase oxidation of furfural.[7–12]

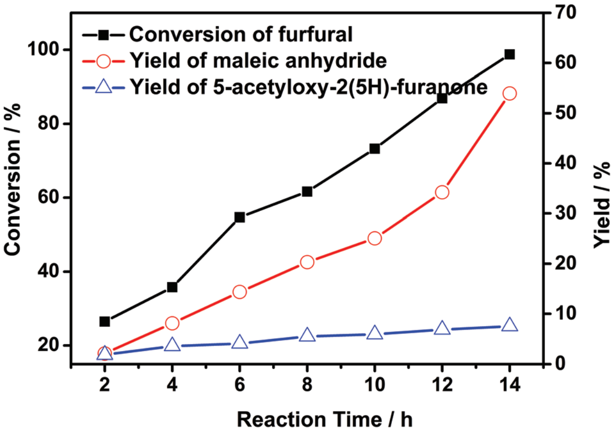


Fig. 1 Catalytic kinetics of furfural oxidation with $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ plus $Cu(CF_3SO_3)_2$ catalyst. Conditions: $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$, 0.02 mmol; $Cu(CF_3SO_3)_2$, 0.02 mmol; furfural, 2.4 mmol; CH_3CN, 2 mL; HOAc, 1.3 mL; O_2, 20 atm; temperature, 383 K.

Taken together, based on GC-MS identification of the reaction intermediates and the final products, the kinetic analysis of 5-acetoxyl-2(5*H*)-furanone and maleic anhydride formation, and the control experiments using furan, 5-acetoxyl-2(5*H*)-furanone and 2(5*H*)-furfuran as starting materials, the dominant pathway for maleic anhydride and 5-acetoxyl-2(5*H*)-furanone formation could be assigned to pathway **I** with the pathway **III** as a minor one for 2(5*H*)-furanone formation.

Another notable fact is that adding Lewis acids may improve the maleic anhydride formation as demonstrated in Table 2, and particularly, adding copper(II) provides the highest total yields of the three products. The promotion effects of Lewis acids in homogeneous oxidation have attracted more attention than ever, and it has been found that adding Lewis acids can greatly accelerate electron transfer reaction in both catalytic and stoichiometric oxidations.[17,18] The acceleration effects of Lewis acids in oxidations are generally attributed to their linkages to the redox metal ions, which leads to the increase of their redox potentials, thus accelerating the electron transfer rate. As demonstrated in Scheme 1, the electron transfer steps are crucial for furfural oxidation to maleic anhydride. In pathway **I**, electron transfer from furfural radical (**1**) to generate furfural cation (**2**) is crucial for competing with furfural polymerization, while electron transfer after decarbonylation of the intermediate **4** is also essential for the formation of the expected products. Since Lewis acids alone are inactive for maleic anhydride formation, the role of added Lewis acids may be to promote the electron transfer from these radical intermediates to the $H_5PV_2Mo_{10}O_{40}$ catalyst.

In the experiment using $H_5PV_2Mo_{10}O_{40}$ catalyst alone, it still provided quantitative conversion of furfural with a large amount of maleic anhydride formation, whereas the activity of copper(II) alone as catalyst was very poor, providing minor products (see Table 4). Thus, $H_5PV_2Mo_{10}O_{40}$ may independently function as a hydrogen abstraction agent to initialize the reaction and perform other hydrogen abstractions as shown in Scheme 1, while copper(II) ion does not. However, copper(II) has been well known as a trap for organic radicals to generate organic cation intermediates;[20] thus, copper(II) is able to independently trap the furfural radical and the radical intermediate after decarbonylation. Accordingly, adding copper(II) to the $H_5PV_2Mo_{10}O_{40}$ catalyst may further improve the total yield of the three products. Furthermore, in another experiment, we also found that, as a redox metal ion, copper(II) can re-oxidize the reduced $H_5PV_2Mo_{10}O_{40}$ catalyst; *i.e.*, on adding 2 equiv. of $H_5PV_2Mo_{10}O_{40}$ to the ascorbic acid solution at room temperature, the catalyst retains its brick red color. Upon heating the solution, the color turns to blue in several minutes, a typical color of reduced heteropolyacid. When adding 2 equiv. of $Cu(CF_3SO_3)_2$ to the resulting heteropoly blue solution, the color turns back to brick red immediately, supporting that copper(II) can efficiently re-oxidize the reduced $H_5PV_2Mo_{10}O_{40}$ catalyst back to the active form, thus speeding up the catalytic rate. Therefore, copper(II) may play two roles in furfural oxidation, *i.e.* trapping carbon radicals by electron transfer and re-oxidizing the reduced heteropolyacid; thus, adding copper(II) can provide the highest yields of expected products, while other Lewis acids may also improve the electron transfer ability of $H_5PV_2Mo_{10}O_{40}$, but generate less improvement than copper(II).

Experimental section

All of the reagents are analytic purity grade, and used without further purification. $H_4PVMo_{11}O_{40}$, $H_5PV_2Mo_{10}O_{40}$ and $H_6PV_3Mo_9O_{40}$ catalysts were synthesized according to the literature.[21] Furfural was purchased from Shanghai Lingfeng Chemical Reagent Co., copper(II) trifluoromethanesulfonate ($Cu(CF_3SO_3)_2$) was purchased from Alfa Aesar, sodium trifluoromethanesulfonate ($NaCF_3SO_3$), magnesium(II) trifluoromethanesulfonate ($Mg(CF_3SO_3)_2$), and scandium trifluoromethanesulfonate ($Sc(CF_3SO_3)_3$) were purchased from Aladdin, and other trifluoromethanesulfonates, including $Ca(CF_3SO_3)_2$, $Al(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$, and $Yb(CF_3SO_3)_3$, were purchased from Shanghai Dibai Chemical Co. Manganese(II) acetate, palladium(II) acetate, iron(II) chloride, acetonitrile and acetic acid were purchased locally from Sinopharm Chemical Reagent. The furfural oxidations were performed in stainless steel autoclaves, equipped with a magnetic stirrer, a pressure gauge and automatic temperature control apparatus. The product identifications by GC-MS were performed on Agilent 7890A/5975C, and NMR analysis was performed on Bruker AV400.

Analytical methods

All products were analyzed by HPLC and quantified using calibration curves generated with commercially available standards except 5-acetoxyl-2(5*H*)-furanone, which was isolated and purified from catalytic solution. After a typical catalytic oxidation reaction, the product mixture was diluted with a known mass of the mobile phase, and then filtered and analyzed by HPLC. The HPLC instrument was equipped with a UV detector and a CN column (250 mm × 4.6 mm), the mobile phase was iso-propanol with *n*-hexane (10% : 90%, v/v) containing acetic acid (0.1%) and the flowing rate was fixed at 1 mL min^{-1}. The temperature of the column was 303 K.

General procedure for the furfural oxidation

In a typical experiment, $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) and $Cu(CF_3SO_3)_2$ (7.4 mg, 0.02 mmol) were dissolved in 2 mL acetonitrile and 1.3 mL acetic acid in a glass tube, and furfural (231 mg, 2.4 mmol) was added into the solution. The glass tube was placed into a 50 mL stainless steel autoclaves, and then the autoclave was charged with 20 atm of oxygen. The reaction solution was magnetically stirred at 383 K in an oil bath for 14 h. After the reaction, the autoclave was cooled to room temperature and carefully depressurized to normal pressure. Yields of maleic anhydride and 5-acetoxyl-2(5*H*)-furanone, and conversion of furfural were quantitatively analyzed by HPLC. Because maleic acid cannot be detected under the analytic conditions of maleic anhydride and 5-acetoxyl-2(5*H*)-furanone, its yield was determined by comparing the total yields of maleic anhydride before and after the dehydration procedure with excess acetic anhydride as described below. This pretreatment has also been verified to be valid by using pure maleic acid in a control experiment. Isolation and characterization of 5-acetoxyl-2(5*H*)-furanone are also described as follows.

Analytic procedure for maleic acid by dehydration

After 14 h catalytic reaction, the solution was cooled and depressurized, and then the mixture was diluted with acetonitrile to a 5 mL volumetric flask. 2.5 mL of diluted solution was further transferred into to a 50 mL round-bottomed flask and 5 mL of acetic anhydride was added into the solution. The mixture was then heated to reflux for 2 h with stirring for dehydration. Through this procedure, the generated maleic acid can be completely converted to maleic anhydride which can be analyzed by the HPLC method described above. Particularly, the validity of this procedure has been verified by using pure maleic acid in a control experiment.

Isolation and characterization of 5-acetoxyl-2(5*H*)-furanone

After 14 h reaction of the above described furfural oxidation, the autoclave was cooled to room temperature and depressurized to atmosphere pressure. The insoluble mass was filtered, and then acetonitrile was removed by rotary evaporator under vacuum. The resultant mixture was diluted with 2 mL water, and excess $NaHCO_3$ (2 g) was added to neutralize acetic acid and maleic anhydride. Next, the aqueous mixtures were extracted with dichloromethane (3 × 2 mL). The combined organic layers were concentrated under reduced pressure, and the oily residue was further purified by silica gel chromatography with hexane–ethyl acetate 1 : 1 as eluent to obtain yellow oil as the product (0.18 mmol, 7.5% yield). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) $\delta = 2.14$ (s, CH_3), 6.29 (dd, $J =$ 0.8 Hz, 1.6 Hz, CH), 6.96 (s, CH), 7.32 ppm (dd, $J = 1.2$ Hz, 5.6 Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 20.58$, 93.79, 125.13, 149.80, 168.88, 169.65 ppm.

Control experiment using 5-acetoxyl-2(5*H*)-furanone as substrate

$H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) and $Cu(CF_3SO_3)_2$ (7.4 mg, 0.02 mmol) were dissolved in 2 mL acetonitrile and 1.3 mL acetic acid in a glass tube, and then 5-acetoxyl-2(5*H*)-furanone (341 mg, 2.4 mmol) was added to the solution. The glass tube was placed into a 50 mL stainless steel autoclave. Then, the autoclave was charged with 20 atm of oxygen. The reaction solution was magnetically stirred at 383 K in an oil bath for 14 h. Next, analysis procedures were conducted, which were similar to those conducted for furfural oxidation.

Control experiment using 2(5*H*)-furanone as substrate

$H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) and $Cu(CF_3SO_3)_2$ (7.4 mg, 0.02 mmol) were dissolved in 2 mL acetonitrile and 1.3 mL acetic acid in a glass tube, and then 2(5*H*)-furanone (202 mg, 2.4 mmol) was added into the solution. The glass tube was placed into a 50 mL stainless steel autoclave. Then, the autoclave was charged with 20 atm of oxygen. The reaction solution was magnetically stirred at 383 K in an oil bath for 14 h. Next, analysis procedures were conducted similar to those for furfural oxidation.

Control experiment using furan as substrate

$H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) and $Cu(CF_3SO_3)_2$ (7.4 mg, 0.02 mmol) were dissolved in 2 mL acetonitrile and 1.3 mL acetic acid in a glass tube, and then furan (163 mg, 2.4 mmol) was added to the solution. The glass tube was placed into a 50 mL stainless steel autoclave. Then, the autoclave was charged with 20 atm of oxygen. The reaction solution was magnetically stirred at 383 K in an oil bath for 14 h. Next, analysis procedures were conducted, which were similar to those conducted for furfural oxidation.

Conclusions

A new oxidation method has been explored to catalytically convert renewable furfural to maleic anhydride using $H_5PV_2Mo_{10}O_{40}$ and $Cu(CF_3SO_3)_2$ as catalysts in liquid phase. Notably, a highly value-added synthetic intermediate with biological importance, 5-acetoxyl-2(5*H*)-furfuran, was also produced as a minor product. This method offers an alternative route to maleic anhydride synthesis, which is not competitive with food of human beings. Detailed mechanistic studies revealed that, in the dominant oxidation pathway, the reaction is initiated by hydrogen abstraction from the 5-position of furfural, and then maleic anhydride and 5-acetoxyl-2(5*H*)-furanone are formed in parallel. These results have provided novel insights to understand the oxidation mechanisms of furan sketch based biomass, which thus benefits the design of selective oxidation catalysts and control of their reactivity in biomass valorizations.

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Notes and references

1 (*a*) C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning and K. Egeblad, *ChemSusChem*, 2008, **1**, 283–289; (*b*) D. R. Dodds and R. A. Gross, *Science*, 2007, **318**, 1250–1251; (*c*) B. Kamm, *Angew. Chem., Int. Ed.*, 2007, **46**, 5056–5058; (*d*) N. Dimitratos, J. A. Lopez-Sanchez and G. J. Hutchings, *Top. Catal.*, 2009, **52**, 258–268; (*e*) J. N. Chheda, G. W. Huber and J. A. Dumesic, *Angew. Chem., Int. Ed.*, 2007, **46**, 7164–7183; (*f*) P. Gallezot, *Green Chem.*, 2007, **9**, 295–302; (*g*) J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, **12**, 539–554.

2 (*a*) L. Wang, H. Wang, F. Liu, A. Zheng, J. Zhang, Q. Sun, J. P. Lewis, L. Zhu, X. Meng and F.-S. Xiao, *ChemSusChem*, 2014, **7**, 402–406; (*b*) Y. Kwon, E. de Jong, S. Raoufmoghaddam and M. T. M. Koper, *ChemSusChem*, 2013, **6**, 1659–1667; (*c*) Z. Du, J. Ma, F. Wang, J. Liu and J. Xu, *Green Chem.*, 2011, **13**, 554–557; (*d*) N. Yan, C. Zhao, C. Luo, P. J. Dyson, H. Liu and Y. Kou, *J. Am. Chem. Soc.*, 2006, **128**, 8714–8715; (*e*) C. Luo, S. Wang and H. Liu, *Angew. Chem., Int. Ed.*, 2007, **119**, 7780–7783.

3 (*a*) W. Xu, Q. Xia, Y. Zhang, Y. Guo, Y. Wang and G. Lu, *ChemSusChem*, 2011, **4**, 1758–1761; (*b*) W. Xu, H. Wang, X. Liu, J. Ren, Y. Wang and G. Lu, *Chem. Commun.*, 2011, **47**, 3924–3926; (*c*) J. C. Serrano-Ruiz, R. Luque and A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 2011, **40**, 5266–5281; (*d*) S. Liu, Y. Amada, M. Tamura, Y. Nakagawa and

K. Tomishige, *Green Chem.*, 2014, **16**, 617–626; (*e*) F. Menegazzo, M. Signoretto, F. Pinna, M. Manzoli, V. Aina, G. Cerrato and F. Boccuzzi, *J. Catal.*, 2014, **309**, 241–247; (*f*) A. Takagaki, S. Nishimura and K. Ebitani, *Catal. Surv. Asia*, 2012, **16**, 164–182.

4 V. V. Guliants and M. A. Carreon, in *Catalysis: Volume 18*, ed. J. J. Spivey, The Royal Society of Chemistry, 2005, vol. 18, pp. 1–45.

5 G. Centi, F. Trifiro, J. R. Ebner and V. M. Franchetti, *Chem. Rev.*, 1988, **88**, 55–80.

6 (*a*) P. N. R. Vennestrøm, C. M. Osmundsen, C. H. Christensen and E. Taarning, *Angew. Chem., Int. Ed.*, 2011, **123**, 10686–10694; (*b*) P. N. R. Vennestrøm, C. M. Osmundsen, C. H. Christensen and E. Taarning, *Angew. Chem., Int. Ed.*, 2011, **50**, 10502–10509.

7 W. V. Sessions, *J. Am. Chem. Soc.*, 1928, **50**, 1696–1698.

8 N. Alonso-Fagúndez, M. L. Granados, R. Mariscal and M. Ojeda, *ChemSusChem*, 2012, **5**, 1984–1990.

9 M. S. Murthy and K. Rajamani, *Chem. Eng. Sci.*, 1974, **29**, 60–609.

10 K. Rajamani, P. Subramanian and M. S. Murthy, *Ind. Eng. Chem. Process Des. Dev.*, 1976, **15**, 232–234.

11 V. A. Slavinskaya, D. R. Kreile, E. Dzilyuma and D. Sile, *Chem. Heterocycl. Compd.*, 1977, **13**, 710–721.

12 D. R. Kreile, V. A. Slavinskaya, M. V. Shimanskaya and E. Y. Lukevits, *Chem. Heterocycl. Compd.*, 1972, **5**, 429–430.

13 S. Shi, H. Guo and G. Yin, *Chem. Commun.*, 2011, **12**, 731–733.

14 H. Guo and G. Yin, *J. Phys. Chem. C*, 2011, **115**, 17516–17522.

15 (*a*) I. Hatanaka, N. Mitsuyasu, G. Yin, Y. Fujiwara, T. Kitamura, K. Kusakabe and T. Yamaji, *J. Organomet. Chem.*, 2003, **674**, 96–100; (*b*) G. Yin, C. Jia, T. Kitamura, T. Yamaji and Y. Fujiwara, *Catal. Lett.*, 2000, **69**, 89–91; (*c*) G. Yin, C. Jia, T. Kitamura, T. Yamaji and Y. Fujiwara, *J. Organomet. Chem.*, 2001, **630**, 11–16.

16 (*a*) T. Hjelmgaard, T. Persson, T. B. Rasmussen, M. Givskov and J. Nielsen, *Bioorg. Med. Chem.*, 2003, **11**, 3261–3271; (*b*) P. Evans and M. Leffray, *Tetrahedron*, 2003, **59**, 7973–7981; (*c*) M. D. Guerrero, M. Aquino, I. Bruno, M. C. Terencio, M. Paya, R. Riccio and L. Gomez-Paloma, *J. Med. Chem.*, 2007, **50**, 2176–2184; (*d*) V. E. Juan Hikawczuk, J. R. Saad, O. S. Giordano, C. García, T. Martín, V. S. Martín, M. E. Sosa and C. E. Tonn, *J. Nat. Prod.*, 2008, **71**, 190–194.

17 (*a*) P. Leeladee, R. A. Baglia, K. A. Prokop, R. Latifi, S. P. de Visser and D. P. Goldberg, *J. Am. Chem. Soc.*, 2012, **134**, 10397–10400; (*b*) Y. Morimoto, H. Kotani, J. Park, Y. M. Lee, W. Nam and S. Fukuzumi, *J. Am. Chem. Soc.*, 2010, **133**, 403–405; (*c*) T. C. Lau and C. K. Mak, *J. Chem. Soc., Chem. Commun.*, 1993, **9**, 766–767.

18 (*a*) G. Yin, *Acc. Chem. Res.*, 2013, **46**, 483–492; (*b*) H. Guo, Z. Chen, F. Mei, D. Zhu, H. Xiong and G. Yin, *Chem. – Asian. J.*, 2013, **8**, 888–891; (*c*) L. Dong, Y. Wang, Y. Lv, Z. Chen, F. Mei, H. Xiong and G. Yin, *Inorg. Chem.*, 2013, **52**, 5418–5427.

19 K. J. Zeitsch, *The Chemistry and Technology of Furfural and Its Many By-products*, Elsevier Science, Amsterdam, 2000.

20 (*a*) G. Yin, D. Piao, T. Kitamura and Y. Fujiwara, *Appl. Organomet. Chem.*, 2000, **14**, 438–442; (*b*) J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, 1965, **87**, 4855–4866; (*c*) C. L. Jenkins and J. K. Kochi, *J. Am. Chem. Soc.*, 1972, **94**, 856–865; (*d*) I. A. Weinstock, *Chem. Rev.*, 1998, **98**, 113–170.

21 A. Shojaei, A. Rezvani and M. Heravi, *J. Serb. Chem. Soc.*, 2011, **76**, 1513–1522.