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Transformation of 5-Hydroxymethylfurfural (HMF) to Maleic Anhydride by Aerobic Oxidation with Heteropolyacid Catalysts

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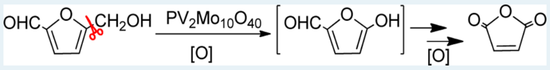
Ⓢ *Supporting Information*



ABSTRACT: Developing novel technologies to utilize renewable biomass as the source of energy and carbon to partially replace the fossil resources has been well recognized by the global governments and both industrial and academic communities. This work explored a catalytic transformation of biomass-based 5-hydroxymethylfurfural to maleic anhydride and maleic acid through aerobic oxidation with vanadium-substituted heteropolyacid. Under the optimized conditions, total yields of 64% for maleic anhydride and maleic acid could be achieved. Mechanistic studies with control experiments excluded 2, 5-furandicarboxylic acid, 2, 5-diformylfuran, 5-formyl-2-furancarboxylic acid, and 5-hydroxymethyl-2-furancarboxylic acid as the intermediates in the pathway of 5-hydroxymethylfurfural oxidation to maleic anhydride. Alternatively, a new mechanism initialized by the C−C bond cleavage between the hydroxymethyl group and furan sketch of HMF by heteropolyacid has been proposed for MA formation, in which several intermediates have been identified through GC-MS analysis.

KEYWORDS: *biomass utilization, 5-hydroxymethylfurfural, heteropolyacid, catalytic oxidation, maleic anhydride*

■ INTRODUCTION

Due to the limitation of fossil resources as well as the environmental concerns induced by petroleum industry, renewable biomass has been attracting much attention as an alternative resource to provide carbon sources for chemical industry.[1−28] Currently, maleic anhydride (MA) and its derivatives are manufactured with a large capacity, which are widely employed to synthesize unsaturated polyester resins, agricultural chemicals, food additives, lubricating oil additives, pharmaceuticals, and so forth.[29−32] In industry, MA is mainly produced via oxidation of petroleum-derived chemicals such as *n*-butane and benzene.[31,32] Regarding the diminishing of the fossil resources, developing new chemical process to transform biomass, a greener and more renewable feedstock into MA than fossil feedstock is greatly attractive in both academic and industrial communities. In 2011, using heteropolyacids like phosphomolybdic acid ($H_3PMo_{12}O_{40}$) and copper(II) nitrate as catalyst, we explored a new catalytic route to synthesize maleic acid, one of the MA derivatives, in aqueous solution through aerobic oxidation of furfural, where furfural originates from C5-based raw agricultural materials which are noncompetitive with human beings.[33] To control the selective transformation of furfural to maleic acid, an aqueous/organic biphase system using $H_3PMo_{12}O_{40}$ alone as catalyst was next developed in which the oxidation event happens in aqueous phase, while the organic phase serves as a reservoir to supply furfural through phase equilibrium. With this process, 68% selectivity of maleic acid can be achieved.[34]

However, because the oxidation reaction was carried out in aqueous phase, no MA can be produced as a result of its hydrolysis. To obtain MA through oxidation of furfural, which has a much larger market capacity than maleic acid, we recently explored aerobic oxidation of furfural in pure organic solvent with $H_5PV_2Mo_{10}O_{40}$ as catalyst, which successfully achieved 54.0% yield of maleic anhydride.[35] In particular, remarkable yield of 5-acetoxyl-2(5H)-furanone, a biologically important intermediate, was obtained as well. Detailed mechanistic studies have also been conducted to unveil the MA and 5-acetoxyl-2(5H)-furanone formations.

Compared with C5-based biomass, C6-based polysaccharides have attracted much more attention,[36,37] because cellulose and hemicellulose represent two of the three largest categories in bioresources on earth. Among the top 12 platform molecules from biomass, 5-hydroxymethyl-2-furfural (HMF) is one of the most attractive under investigation,[38] which can be potentially produced from cellulose but is currently synthesized from glucose and/or fructose in lab scale.[39−48] Up to now, the development of versatile downstream products from HMF has been extensively investigated.[49] Through oxidation, HMF can be transformed to 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), 5-formyl-2-furancarboxylic acid (FFCA), and 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) (Scheme 1),[50−54] and these products have a large market in the polymer industry. In addition, oxidation of HMF can also provide MA as product. Xu with co-workers demonstrated an early example of aerobic oxidation of HMF using $VO(acac)_2$ catalyst, which achieves 52% yield of MA.[55] Those authors also provided mechanistic studies for MA formation partially based on theoretic calculations. Because oxidation of HMF can generate a list of products, as shown in Scheme 1, clearly

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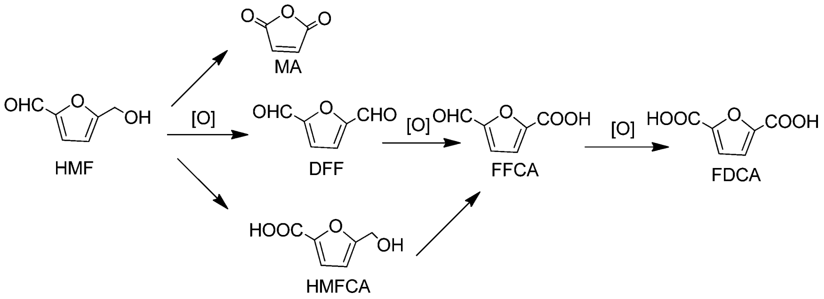
Scheme 1. Schematic Illustration of the Potential Oxidation Products during the Oxidation of HMF



elucidating the mechanism of HMF to MA may also benefit understanding oxidation of those furan-sketch-based biomass, thus benefiting the rational catalyst design to obtain the targeted product. Herein, we report transformation of HMF to MA by aerobic oxidation using heteropolyacids like $H_5PV_2Mo_{10}O_{40}$ as catalyst, and a related mechanism has been elucidated by conducting a series of control experiments with identifications of several oxidation intermediates.

EXPERIMENTAL SECTION

All of the reagents are analytic purity grade and were 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.[56] 5-Hydroxymethyl-2-furfural was purchased from Shanghai DEMO Medical Technical Co. 5-Formyl-2-furancarboxylic acid and 2,5-diformylfuran were purchased from Nanjing Chemlin Chemical Industry Co. 5-Hydroxymethyl-2-furancarboxylic acid was purchased from Shanghai Shuya Medical Technical Co. 2,5-Furandicarboxylic acid was purchased from Tianjin Heowns Biochem LLC. Acetonitrile and acetic acid were purchased from local Sinopharm Chemical Reagent. The HMF oxidation was performed in a stainless autoclave, equipped with a magnetic stirring, a pressure gauge and an automatic temperature control apparatus. The product identification by GC-MS was conducted on an Agilent 7890A/5975C, HPLC-MS was conducted on Agilent 1100 LC/MSD Trap, NMR analysis was conducted on Bruker AV400, and water content in reaction media was determined on Fuli 9790 with GDX-102 packed column.

General Procedure for the HMF Oxidation. In a typical experiment, $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) was dissolved in 2 mL of acetonitrile and 1.3 mL of acetic acid in a glass tube, and HMF (305 mg, 2.4 mmol) was added into the solution. The glass tube was put into a 50 mL stainless autoclave; then the autoclave was charged with 10 atm of oxygen. The reaction solution was magnetically stirred at 363 K in an oil bath for 8 h. After the reaction, the autoclave was cooled to room temperature and depressurized carefully to normal pressure. Product analysis was performed by GC using the internal standard method.

Analytic Procedure for Maleic Acid by Dehydration. After an 8 h catalytic reaction of HMF oxidation, the solution was cooled and depressurized to room temperature and normal pressure. Then the mixture was diluted with acetonitrile to a 5 mL volumetric flask. Subsequently, 2.5 mL of the 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 is next analyzed by the GC method as described above. Particularly, the validity of this procedure has been verified in furfural oxidation in previous studies.[35]

Control Experiment Using DFF as Substrate. $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) was dissolved in a glass tube with 2 mL of acetonitrile and 1.3 mL of acetic acid as solvent; afterward DFF (298 mg, 2.4 mmol) was added to the solution. The glass tube was put into a 50 mL stainless autoclave. Then the autoclave was charged with 10 atm of oxygen. The reaction solution was magnetically stirred at 363 K in an oil bath for 8 h. Next, similar analysis procedures were operated as well as those for HMF oxidation.

Control Experiment Using FFCA as Substrate. $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) was dissolved in a glass tube with 2 mL of acetonitrile and 1.3 mL of acetic acid as solvent; afterward 5-formyl-2-furancarboxylic acid (336 mg, 2.4 mmol) was added to the solution. The glass tube was put into a 50 mL stainless autoclave. Then the autoclave was charged with 10 atm of oxygen. The reaction solution was magnetically stirred at 363 K in oil bath for 8 h. Next, the yield of MA was analyzed by GC as well as those for HMF oxidation, and meanwhile, the conversion of FFCA was analyzed by HPLC.

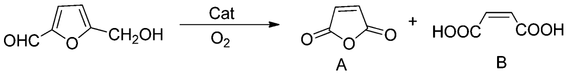
Control Experiment Using FDCA as Substrate. $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) was dissolved in a glass tube with 2 mL of acetonitrile and 1.3 mL of acetic acid as solvent; afterward FDCA (374 mg, 2.4 mmol) was added to the solution. The glass tube was put into a 50 mL stainless autoclave. Then the autoclave was charged with 10 atm of oxygen. The reaction solution was magnetically stirred at 363 K in oil bath for 8 h. Next, the yield of MA was analyzed by GC as well as those for HMF oxidation, and meanwhile, the conversion of FDCA was analyzed by HPLC.

Control Experiment Using HMFCA as Substrate. $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ (34.8 mg, 0.02 mmol) was dissolved in a glass tube with 2 mL of acetonitrile and 1.3 mL of acetic acid as solvent; afterward HMFCA (341 mg, 2.4 mmol) was added to the solution. The glass tube was put into a 50 mL stainless autoclave. Then the autoclave was charged with 10 atm of oxygen. The reaction solution was magnetically stirred at 363 K in oil bath for 8 h. Next, the yield of MA was analyzed by GC as well as those for HMF oxidation, and meanwhile, the conversion of HMFCA was analyzed by HPLC.

RESULTS AND DISCUSSION

Oxidation of HMF with Different Heteropolyacids. The HMF oxidation was first conducted using heteropolyacid catalysts under pressured oxygen (10 atm) in acetonitrile/acetic acid solvent (2:1.3, v/v) at 363 K. Detailed optimizations of reaction temperature and pressure are presented in Supporting

Information (see Figure S2 and S3). Because the formation of water naturally happens with the oxidation proceeding, the hydrolysis of maleic anhydride cannot be avoided under the reaction conditions, thereof, and both maleic anhydride (A) and maleic acid (B) will be produced as products (eq 1).



Eq. 1

As shown in Table 1, a list of heteropolyacids have been scanned as catalysts, and all of them lead to complete conversion of HMF in 8 h. Among these heteropolyacids, vanadium-substituted heteropolyacid, $H_5PV_2Mo_{10}O_{40}$, demonstrates the highest catalytic activity for MA formation. After an 8 h reaction in acetonitrile/acetic acid (2/1.3, v/v), it provides 31.7% yield of MA and 32.3% yield of maleic acid, representing 64.0% of the total yields on MA and maleic acid formation (entry 5). Using pure acetonitrile as solvent, $H_5PV_2Mo_{10}O_{40}$ catalyst gives a total yield of 50.9% (entry 6), which is lower than that conducted in mixed solvents comprising acetonitrile and acetic acid. However, a higher yield of MA (41.8%) can be achieved in acetonitrile when compared with mixed solvents with acetic acid, possibly because no extra water was introduced into the reaction medium by commercial acetic acid (vide infra). In addition to the expected products as shown in eq 1, certain oligomers having the number-average molecular weight (W_n) of 1125 with the polydispersity indices (PDI) of 4.038 were indicated by GPC analysis in reaction mixture. $H_4PVMo_{11}O_{40}$ and $H_6PV_3Mo_9O_{40}$ demonstrate less activity for MA and maleic acid formation with total yields of 44.5% and 55.4%, respectively, whereas other heteropolyacids are much less active. However, in each case, the conversion of HMF is above 99%. In gas phase analysis, it also indicated the formation of CO and CO_2, and the active vanadium-substituted heteropolyacids produced more CO and CO_2 (up to 5.77% of volume contents in gas phase for $H_5PV_2Mo_{10}O_{40}$, see Table 1) than the less active catalysts, which is consistent with that formation of MA or maleic acid from HMF needs to release one carbon atom from HMF. In particular, when the catalyst is inactive for MA and maleic acid formation, there is almost no CO and CO_2 generated, supporting that most of CO and CO_2 do not come from the burning (overoxidation) of substrate or intermediate.

Influence of Solvent Composition on HMF Oxidation. Because the presence of acetic acid can improve the total yields of MA and maleic acid to a certain extent, the influence of solvent composition was next investigated in detail, and the results are summarized in Table 2. Although acetonitrile or acetic acid alone as solvent provides total yields of 50.9% or 48.6%, respectively, the presence of 40% volume of acetic acid offers the highest total yields (64.0%). Notably, the yield of maleic acid in products increases as the content of acetic acid increases, which has been attributed to the hydrolysis of MA as stated above. Clearly, the presence of acetic acid as cosolvent can improve the total yields of MA and maleic acid; however, its overloading also harms the catalytic activity to MA and maleic acid. From Table 2, one may also see that the water content before and after reactions increases as the content of acetic acid increases in the solvent mixture, which leads to the increase of maleic acid formation in products. In the complementary experiment using freshly dehydrated solvent (acetonitrile/acetic acid, 2/1.3, v/v), it provides 51.9% of MA with only 9.4% of maleic acid, representing a total yields of 61.4%. Clearly, the presence of minor water will cause the hydrolysis of MA product, but it does not affect the activity of catalyst significantly.

Catalytic Kinetics of HMF Oxidation. Catalytic kinetics of HMF oxidation was performed using acetonitrile and acetonitrile/acetic acid (2:1.3, v/v) as solvent, respectively. As shown in Figure 1, the oxidation performed in pure acetonitrile solvent demonstrates a relatively faster rate than that performed in acetonitrile/acetic acid solvent mixture. However, the mixed solvent demonstrated a more efficient influence on MA and maleic acid formations. That is, a maximum total yield of 50.9% was obtained in 4 h with acetonitrile as solvent, whereas a total yield of 64.0% could be achieved in 8 h from acetonitrile/acetic acid solvent mixture. Apparently, the presence of acetic acid improved the selectivity of MA and maleic acid but slightly reduced the generation rate of MA and maleic acid.

Product identifications by GC-MS analysis revealed that, after 4 h reaction at 363 K, in addition to MA and maleic acid formations, other minor products including formic acid, DFF, two esters including 5-acetoxymethyl-2-furaldehyde, and 5-(formyloxymethyl)furfural have also been identified (see Figure S5-6, 7). Although both FDCA and HMFCA cannot be detected through GC analysis, after being compared with their authentic samples, they were also not observed by HPLC and LC-MS analysis. However, another minor product, FFCA, has been identified by LC-MS. Formation of two esters can be rationalized by esterification of HMF with acetic acid solvent or formic acid, which is an oxidation product. On the basis of the above information, 5-acetoxymethyl-2-furaldehyde was successfully isolated from the reaction mixture after a 1 h oxidation of HMF, and it was further confirmed by 1H NMR analysis (Figure S1). In the kinetics of HMF oxidation monitored by GC analysis (Figure S4), formation of 5-acetoxymethyl-2-furaldehyde generally remains at a relatively low level and gradually disappears with the oxidation proceeding, even

Table 1. Oxidation of HMF with Different Heteropolyacids[a]

entry	heteropolyacid	yield A (%)	yield B (%)	total yields[b] (%)	CO[c] (%)	CO_2[c] (%)
1	$H_3PMo_{12}O_{40}\cdot xH_2O$[d]	0.2	12.3	12.5	0.04	0.18
2	$H_3PW_{12}O_{40}\cdot xH_2O$[d]	0	5.5	5.5	0	0.04
3	$H_4[SiO_4(W_3O_9)_4]\cdot xH_2O$[d]	0.1	5.4	5.5	0	0.03
4	$H_4PVMo_{11}O_{40}\cdot xH_2O$[d]	24.3	20.2	44.5	0.79	3.78
5	$H_5PV_2Mo_{10}O_{40}\cdot xH_2O$[d]	31.7	32.3	64.0	0.92	4.85
6	$H_5PV_2Mo_{10}O_{40}\cdot xH_2O$[e]	41.8	9.1	50.9	0.86	4.18
7	$H_6PV_3Mo_9O_{40}\cdot xH_2O$[d]	28.2	27.2	55.4	0.91	4.42

[a] Conditions: heteropolyacid 0.02 mmol, HMF 2.4 mmol, O_2 10 atm, temperature 363 K, reaction time 8 h. [b] The total yields of maleic acid and maleic anhydride. [c] The volume percentage in gas phase. [d] 2 mL of CH_3CN plus 1.3 mL of HOAc as solvent. [e] 3.3 mL of CH_3CN as solvent.

Table 2. Influence of Solvent Composition on HMF Oxidation[a]

entry	percentage of HOAc (%)	H_2O^b (g)	H_2O^c (g)	yield A (%)	yield B (%)	total yields[d] (%)	CO^e (%)	$CO_2{}^e$ (%)
1	0	0.0166	0.0322	41.8	9.1	50.9	0.91	4.18
2	15	0.0217	0.0363	31.1	21.1	52.8	0.87	4.71
3	30	0.0259	0.0392	31.9	28.1	60.0	0.89	4.59
4	40	0.0287	0.0433	31.7	32.3	64.0	0.92	4.85
5	45	0.0302	0.0409	27.5	33.7	61.2	0.83	4.59
6	60	0.0356	0.0481	25.0	34.5	59.5	0.79	4.68
7	75	0.0407	0.0489	21.5	32.3	53.8	0.78	4.12
8	100	0.0485	0.0547	14.3	34.3	48.6	0.71	3.98

[a] Conditions: $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ 0.02 mmol, HMF 2.4 mmol, O_2 10 atm, temperature 363 K, reaction time 8 h, solvent, total 3.3 mL of CH_3CN and HOAc. [b] The mass of water before reaction. [c] The mass of water after reaction. [d] The yield of maleic acid and maleic anhydride. [e] The volume percentage in gas phase.

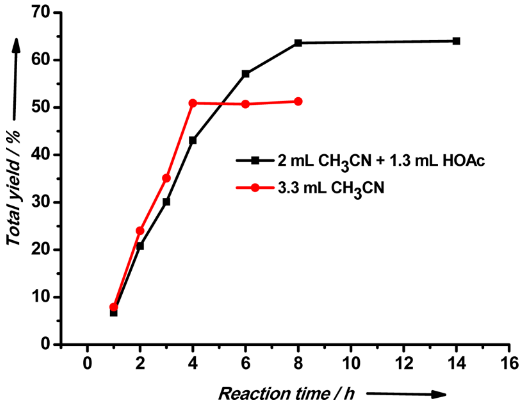


Figure 1. Catalytic kinetics of HMF oxidation in different solvents. Conditions: $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ 0.02 mmol; HMF 2.4 mmol; O_2 10 atm; temperature 363 K. Red line: CH_3CN 2 mL plus HOAc 1.3 mL; black line: CH_3CN 3.3 mL.

though sufficient acetic acid exists as cosolvent. Furthermore, after an 8 h reaction, only a trace of 5-acetoxymethyl-2-furaldehyde was detected.

In the case of using isolated 5-acetoxymethyl-2-furaldehyde in place of HMF as substrate for oxidation, it was found that 5-acetoxymethyl-2-furaldehyde can be oxidized to MA and maleic acid but by a slower rate (Figure 2). After an 8 h reaction, there is still 24.0% of 5-acetoxymethyl-2-furaldehyde substrate left in the reaction mixture. In the case of using freshly dehydrated solvent as reaction media, it left more 5-acetoxymethyl-2-furaldehyde substrate (39.5%) in the reaction mixture after an 8 h reaction, and the total yields of MA and maleic acid are also less (45.5%). In HMF oxidation, the concentration of in situ generated 5-acetoxymethyl-2-furaldehyde is much lower, as stated above (Figure S4). Taken together, it supports that 5-acetoxymethyl-2-furaldehyde cannot be the intermediate for MA and maleic acid formations in HMF oxidation. As evidence, both MA and maleic acid can be produced in pure acetonitrile solvent with total yields of 50.9%. If 5-acetoxymethyl-2-furaldehyde were the intermediate for their formations, the absence of acetic acid as solvent would seriously affect the progression of oxidation, because it will block the 5-acetoxymethyl-2-furaldehyde formation. Apparently, esterification of HMF with acetic acid to form 5-acetoxymethyl-2-furaldehyde would decrease the concentration of HMF in the reaction mixture and thus reduces its polymerization under the oxidative conditions. As evidence, it was found that under the reaction conditions but without pressured oxygen, 36% of HMF can be rapidly converted to 5-acetoxymethyl-2-furaldehyde through esterification in 0.5 h. With the reaction proceeding, hydrolysis of 5-acetoxymethyl-2-furaldehyde supplies HMF through hydrolysis−esterification equilibrium, but HMF is kept at a relatively low concentration and thus benefits its selective oxidation to MA and maleic acid, as demonstrated in Table 2.

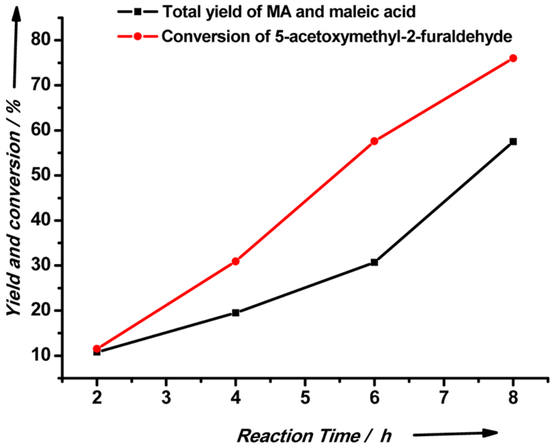
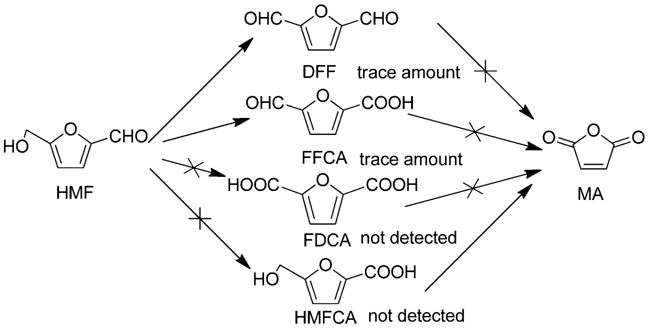


Figure 2. Catalytic kinetics of 5-acetoxymethyl-2-furaldehyde oxidation with $H_5PV_2Mo_{10}O_{40}$ catalyst. Conditions: $H_5PV_2Mo_{10}O_{40}\cdot xH_2O$ 0.02 mmol, 5-acetoxymethyl-2-furaldehyde 2.4 mmol, CH_3CN, 2 mL, HOAc, 1.3 mL, O_2 10 atm, temperature 363 K.

Mechanism for HMF Oxidation Catalyzed by $H_5PV_2Mo_{10}O_{40}$. As stated above, DFF has been detected as a minor product through GC-MS analysis in HMF oxidation, and FFCA was also detected by HPLC by comparing with the authentic sample. In literature, these compounds, including FDCA, DFF, FFCA, and HMFCA, have been reported in HMF oxidation as the intermediates or final products (Scheme 2).[50,51] Accordingly, any of them could potentially occur as the intermediate to MA and maleic acid formations in the HMF oxidation performed in present study. To address whether these compounds occur in the pathway of MA and maleic acid formations, control experiments using them as substrate one by one were conducted under the identical conditions of HMF oxidation. It was found that using DFF or FFCA as the substrate provides less than 1% yield of MA. Therefore, even though the hydroxymethyl group of HMF can be oxidized to aldehyde or acid, formation of MA from HMF does not proceed by DFF or FFCA as the intermediate followed by their further decarboxylation.

Although HMFCA and FDCA were not detected as products in HMF oxidation in the present study, they can be generated

Scheme 2. Plausible Intermediates for Maleic Acid Formation in the Oxidation of HMF to MA

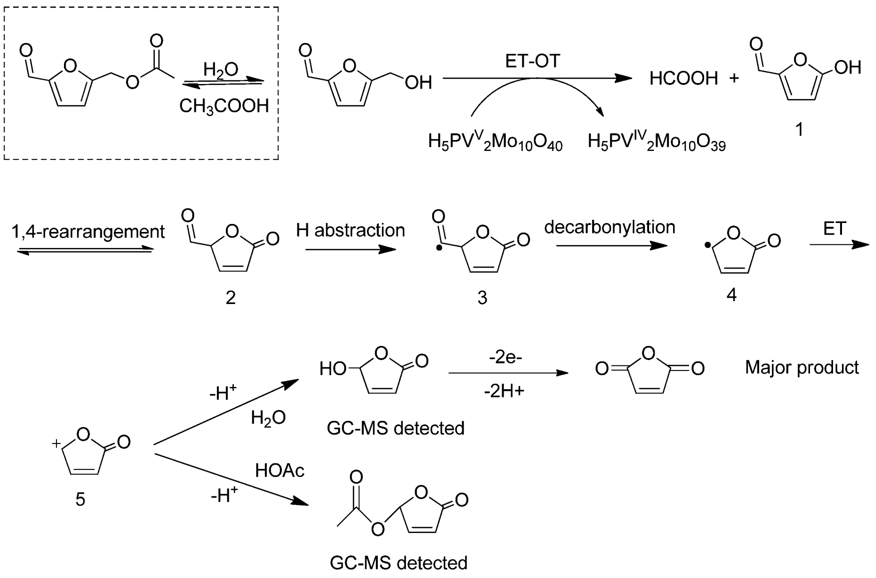


under certain conditions.[52−54] Notably, using HMFCA as the substrate in the control experiment achieves 86.1% conversion with 52.8% total yields of MA and maleic acid in 8 h, indicating that HMFCA may have a chance to serve as the intermediate in MA formation. However, it was found that oxidation of HMFCA to MA is relatively slow, as was also the case with 5-acetoxymethyl-2-furaldehyde. If formation of MA proceeded by HMFCA as an intermediate, accumulation of HMFCA should happen in HMF oxidation due to its relatively sluggish oxidation to MA. However, even in a short reaction period (4 h), HPLC-MS analysis still confirmed that there was no any HMFCA detected as well in an 8 h reaction. Therefore, HMFCA was excluded as the intermediate of MA formation. For the compound FDCA, using it as substrate does not generate MA as product, supporting that it also does not occur in the pathway of MA formation. Taken together, these control experiments clearly reveal that no DFF, FFCA, FDCA, and HMFCA were involved as the intermediate in the oxidation of HMF to MA, supporting that the transformation of HMF to MA is not initialized by oxidation of aldehyde or the hydroxymethyl group of HMF.

In the literature, vanadium-substituted heteropolyacids have been widely employed as catalyst in oxidations.[57−62] Particularly, Neumann and co-workers found that $H_5PV_2Mo_{10}O_{40}$ can catalyze oxidative C−C bond cleavage of primary alcohols and vicinal diols, and an electron transfer and oxygen transfer reaction mechanism (ET-OT) has been proposed for this cleavage.[63] Here, a similar C−C bond cleavage may happen between the hydroxymethyl group and furan sketch of HMF in $H_5PV_2Mo_{10}O_{40}$-mediated HMF oxidation. Thus, a similar ET-OT mechanism was proposed for the oxidation of HMF to MA at the initial step (Scheme 3).

At first, cleavage of the C−C bond between the hydroxymethyl group and furan sketch of HMF by $H_5PV_2Mo_{10}O_{40}$ through ET-OT process yields the intermediate **1** and formaldehyde with reduced $H_5PV^{IV}{}_2Mo_{10}O_{39}$, which is similar to those in Neumann's studies, and the formaldehyde can be feasibly oxidized to formic acid. Then, 1,4-rearrangement of **1** yields the compound **2**, which further goes through hydrogen atom abstraction on its aldehyde group by either dioxygen or $H_5PV_2Mo_{10}O_{40}$ to give the intermediate **3**. Decarbonylation of **3** yields the intermediate **4**, which provides the cation intermediate **5**. Attacking of acetic acid on **5** offers 5-acetoxyl-2(5H)-furanone, which has been identified by GC-MS analysis (Figure S5−5). Alternatively, its attacking by water generates 5-hydroxyl-2(5H)-furanone, which has also been identified by GC-MS analysis (Figure S5−2). Further oxidation of 5-hydroxyl-2(5H)-furanone can feasibly give MA as product. Certainly, hydrolysis of MA will yield maleic acid. In this mechanism, the C−C cleavage step was indirectly evidenced by the identifications of formic acid and 5-(formyloxymethyl)-furfural in the reaction mixture by GC-MS analysis. Also, decarbonylation was indicated by the detection of CO with the online gas analyzer, which reveals a volume fraction of 0.92% for CO and 4.85% for CO_2 in the gas mixture after reaction. One may argue that CO or CO_2 could be generated from further oxidation of formic acid under catalytic conditions. To further rule out this possibility, the control experiment using formic acid in place of HMF was conducted to catalytic oxidation; however, neither CO nor CO_2 was detected under identical conditions. The super activity of $H_5PV_2Mo_{10}O_{40}$ over other heteropolyacids is possibly related with two aspects: (1) Compared with other heteropolyacids, $H_5PV_2Mo_{10}O_{40}$ is well-known in dioxygen activation, which makes catalytic cycle more efficient than others. The classic example is that $H_5PV_2Mo_{10}O_{40}$

Scheme 3. Proposed Mechanism for HMF Oxidation Catalyzed by $H_5PV_2Mo_{10}O_{40}$



is employed as cocatalyst to regenerate active Pd(II) species from the reduced Pd(0) by dioxygen in versatile Pd(II)-catalyzed oxidations;[64] (2) As disclosed above, $H_5PV_2Mo_{10}O_{40}$ is very crucial in the cleavage of the C−C bond between the furan cycle and alcohol group in HMF to initialize the oxidation to maleic anhydride, whereas other heteropolyacids are possibly less active in this step.

CONCLUSIONS

The present work presented catalytic oxidation of biomass based HMF to MA and maleic acid with vanadium-substituted heteropolyacid catalyst. Under the optimized condition, 64% of the total yields on MA and maleic acid can be achieved in acetonitrile/acetic acid solvent. The mechanistic studies reveal that no DFF, FFCA, FDCA, and HMFCA appear in the pathway of MA formation, even though some of them have been identified in product analysis. On the basis of these findings, a new mechanism has been proposed for MA formation, in which the oxidation was initiated by the C−C bond cleavage between the hydroxymethyl group and furan sketch of HMF by $H_5PV_2Mo_{10}O_{40}$ catalyst. The mechanistic studies presented here may have provided new clues for the catalyst design in selective oxidation of furan-sketch-based biomass.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501776n.

NMR spectrum of 5-acetoxymethyl-2-furaldehyde, GC-MS graphs of product identification, reaction kinetics, and reaction condition optimizations (PDF)

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Notes

The authors declare no competing financial interest.

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