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One-Pot Synthesis of Renewable Phthalic Anhydride from 5-Hydroxymethfurfural by using $MoO_3/Cu(NO_3)_2$ as Catalyst

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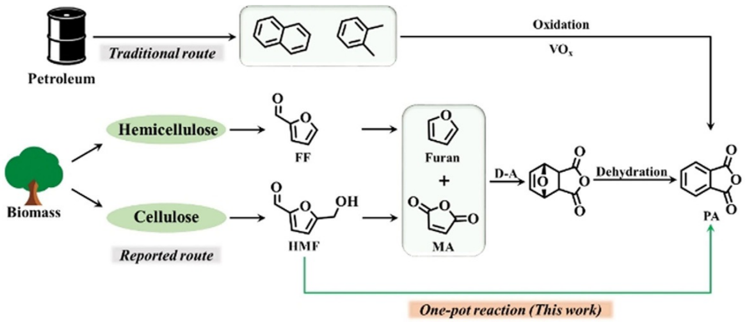
Herein, a synthetic pathway to renewable phthalic anhydride (PA) from 5-hydroxymethfurfural (HMF) in one pot is reported. The commonly available catalysts MoO_3 and $Cu(NO_3)_2$ play a crucial role in integrating the multiple steps of the reaction, namely decarbonylation of HMF to active furyl intermediate (AFI), oxidation of HMF to maleic anhydride (MA), Diels–Alder cycloaddition of AFI and MA, and subsequent dehydration, in one pot. Under mild reaction conditions, a 63.2% yield of PA is obtained from HMF. Compared with the currently reported route to renewable PA based on the Diels–Alder cycloaddition of biomass-derived MA and furan, this convenient one-pot synthesis represents a great improvement in efficiency.

Introduction

Phthalic anhydride (PA) is a versatile intermediate for the chemical industry with global production of more than three million tons per annum,[1] serving a wide range of industries including phthalate ester plasticizers,[2] polyester resins,[3] dyestuffs,[4] and pharmaceuticals.[5] Currently, PA is primarily produced by catalytic oxidation of naphthalene or *ortho*-xylene, which is refined from petroleum or coal.[6,7] Given current concerns about fossil fuel depletion and environmental footprint, some progress has been made in seeking sustainable solutions for the production of chemicals from renewable biomass.[8] Alternative routes to PA from renewable starting materials have been explored.[9] In 2014, Lobo and co-workers[10] reported a renewable route to PA using biomass-derived maleic anhydride (MA) and furan based on Diels–Alder (D–A) and subsequent dehydration reactions as an approach for transforming abundant renewable biomass resources into PA (Scheme 1).



Scheme 1. The synthetic pathway of PA.

Industrially, MA is manufactured by the oxidation of petroleum-derived benzene, butane, or butadiene.[11] It can also be produced by the aerobic oxidation of 5-hydroxymethylfurfural (HMF) or furfural, which is a biomass-derived platform compound.[12,18] In 1949, Nielsen reported an early investigation of the oxidation of furfural to MA.[12] In 2012, Ojeda and co-workers[13] achieved an MA yield of up to 73% through selective gas-phase oxidation of furfural at 593 K in a tubular fixed-bed reactor. Several studies describe liquid-phase catalytic oxidation of furfural to maleic anhydride with heterogeneous catalysts.[14,15] Although the reaction conditions are mild, the oxidation efficiency is lower. For the oxidation of HMF to MA, Li and Zhang developed a heterogeneous catalyst system using vanadium-based solid catalysts for the oxidation HMF to MA, achieving a yield of 52% under conditions of 1 MPa O_2, 100 °C, and 4 h.[16] There are some reports on the preparation of MA from HMF, but the yield of MA was hardly more than 52%.[17,18]

Furan is commercially produced by the decarbonylation of furfural (FF) in the vapor or liquid phase over supported Pd catalysts.[19,20] Vapor-phase decarbonylation usually requires higher reaction temperature (>300 °C) than liquid-phase decarbonylation, whereas the latter usually causes deactivation of catalysts and polymerization of feedstock and product.[17,20]

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From the studies described above, we note that the current renewable route to produce PA from HMF or FF requires four steps: decarbonylation of FF to furan, oxidation of HMF or FF to MA, D–A cycloaddition of furan and MA, and dehydration of the D–A adduct.[21] Although it is considered to be a promising sustainable strategy for the production of PA, the multistep reactions result in low efficiency for the production of PA from HMF or FF. To make renewable PA cost-competitive compared with the traditional synthetic route, a simpler process is required.[21]

To the best of our knowledge, a one-pot and straightforward procedure capable of directly producing PA from HMF has not been reported. Meeting this challenging goal would be of significance and interest, and the key to success is to develop a highly advanced and versatile catalyst system that can integrate the above-mentioned four independent reactions in one pot. Herein, we report such a catalyst, namely $MoO_3/Cu(NO_3)_2$, which unexpectedly exhibited excellent catalytic activities in decarbonylation, oxidation, D–A cycloaddition, and dehydration to enable the one-pot process. This spurred us to elucidate the intrinsic reaction pathway in this one-pot HMF-to-PA process in detail.

Results and Discussion

One-pot synthesis of renewable phthalic anhydride from 5-hydroxymethylfurfural

On the basis of the previous preparation of 2,5-diformylfuran (DFF) from HMF with $Fe(NO_3)_3/Cu(NO_3)_2$ as catalyst, a 99% yield of DFF was obtained with the assistance of $K_2S_2O_8$ in acetonitrile.[22] On adding water to the reaction, PA was unexpectedly found in a yield of 8%, along with a substantial drop in the yield of DFF (Table 1, entry 1). Spurred by this result, we sought to identify a superior catalyst that could increase the conversion efficiency of HMF to PA by using $K_2S_2O_8$ as oxidant. The investigation was initiated by examining a series of multimetal catalysts, including transition metals such as iron, copper, vanadium, manganese, and molybdenum. The results showed that most catalysts led to a high HMF conversion in 7 h, and the iron-based catalysts appeared to be more favorable for the generation of DFF (Table 1, entries 2–7). Chloride salts such as $FeCl_3$ and $VOCl_3$ were inclined cause production of 5-chloromethylfurfural (CMF) as byproduct (Figure S1 in the Supporting Information), which contributes to low selectivity to the target product PA, as well as the intermediates DFF and MA (Table 1, entries 2 and 10). Generally, vanadium-based oxides are reported as effective catalysts for the oxidation of alcohols to ketones or oxidative decarboxylation.[23,24] In this case, the vanadium oxides showed moderate selectivity to PA with almost complete conversion of HMF (Table 1, entries 8–10). Then, several molybdenum oxides and manganese oxides combined with copper(II) nitrate were examined. Both $MnO_2/Cu(NO_3)_2$ and $MoO_3/Cu(NO_3)_2$ gave promising results in the one-pot conversion of HMF into PA, which was isolated in yields of 54.4 and 63.2% respectively (Table 1, entries 11 and 16). Iron oxides and cerium oxide decreased the generation of PA to some extent (Table 1, entries 12–15). Thus, $MoO_3/Cu(NO_3)_2$ is the preferred catalyst for the one-pot conversion of HMF into PA.

Table 1. Effect of catalysts on the oxidation of HMF.[a]

Entry	Catalyst	Conversion [%]	Selectivity [%] PA	MA	DFF
1	$Fe(NO_3)_3/Cu(NO_3)_2$	90	8.0	5.0	70.0
2	$FeCl_3/CuO$	93	20.0	<1	25.0
3	Fe_3O_4/CeO_2	58	22.0	<1	61.0
4	Fe_2O_3/CaO	25	12.0	<1	50.0
5	Fe_2O_3/Nb_2O_5	78	<1	<1	40.0
6	Fe_3O_4/CuO	97	<1	18.4	43.0
7	$Fe_3O_4/Cu(NO_3)_2$	95	28.0	56.0	3.0
8	$VOSO_4/Cu(NO_3)_2$	91	34.0	13.0	<1
9	V_2O_5/CuO	93	36.0	23.0	4.0
10	$VOCl_3/CaO$	95	36.0	5.0	7.0
11	$MnO_2/Cu(NO_3)_2$	97	54.4	<1	<1
12[b]	$MnO_2/Fe_2O_3/Cu(NO_3)_2$	100	20.0	9.0	49.0
13[b]	$MnO_2/Fe_3O_4/Cu(NO_3)_2$	99	55.0	<1	<1
14[b]	$MoO_3/CeO_2/Cu(NO_3)_2$	98	57.8	<1	<1
15[b]	$MoO_3/Fe_3O_4/Cu(NO_3)_2$	89	57.8	<1	<1
16	$MoO_3/Cu(NO_3)_2$	100	63.2	<1	<1
17[c]	–	–	–	–	–

[a] Reaction conditions: 0.63 g HMF (5 mmol), 10 wt% catalyst (mass ratio 1:1), 40 mL water/acetonitrile (33:7), 5 mmol $K_2S_2O_8$, 90 °C, 7 h. [b] 10 wt% catalyst (mass ratio 1:1:1). [c] Without catalyst.

A significant effect of water on the product distribution was also observed. Otto et al.[25] and Thomas et al.[26] showed that aqueous solvent tended to enhance the rate and selectivity of D–A reactions. The effect of water on D–A reactions is attributed in part to the benefit of decreasing the hydrophobic surface area, as well as the hydrogen-bond donating capacity.[27,28] Clearly, compared with water alone, common polar aprotic solvents, including MeCN, DMSO, dioxane, methyl isobutyl ketone (MIBK), toluene, carbon tetrachloride, and dichloromethane, resulted in lower conversion of HMF and yield of PA. The low conversion of HMF indicated low catalytic activity of catalysts for the oxidation of HMF to PA in these polar aprotic solvents. In these reactions, the dominant product, either DFF or MA, was obtained. Even under conditions of high MA concentration in these polar aprotic solvents (Table 2, entries 2 and 4–6), the yield of PA was lower than that obtained in water alone. When water/MeCN was used as solvent, the yield of PA substantially increased (Table 2, entries 9 and 10). These results suggest that water facilitated the oxidation of HMF, D–A cycloaddition, and dehydration of the D–A adduct. Therefore, the lower PA yields obtained in the aprotic organic solvents employed in this study are reasonably ascribed to their lower hydrogen-bond donating capacity.

Despite obvious benefits, water as solvent alone only gave 37.6% yield of PA. We speculated that water-insoluble intermediates are generated in the reaction and that this eventually affects the yield of PA. In view of this assumption, the mixtures of water with MeCN or dioxane were examined in the investigated reaction, because MeCN and dioxane performed better than other organic solvents. As we expected, water/organic solvents performed better than water alone, and the high-

Table 2. Effect of solvents on the catalytic oxidation of HMF.[a]

Entry	Solvent[b]	Conversion [%]	Selectivity [%] PA	MA	DFF
1	water	100	37.6	5.0	4.0
2	MeCN	78	23.2	44.3	31.5
3	DMSO	56	12.0	8.0	78.0
4	dioxane	43	17.0	21.0	9.0
5	MIBK	61	14.4	23.0	12.0
6	toluene	59	12.6	35.0	8.0
7	CCl_4	100	–	–	14.0
8	dichloromethane	100	–	–	15.0
9	water/MeCN (1:1)	100	45.0	11.0	8.0
10	water/MeCN (5:1)	100	63.2	5.0	<1
11	water/dioxane (1:1)	100	38.0	28.0	<1
12	water/dioxane (5:1)	100	44.6	32.0	<1
13[c]	water/MeCN (2:1)	100	8.0	85.0	–
14[c]	water/MeCN (1:5)	100	4.0	73.0	–
15[c]	water	100	–	–	–

[a] Reaction conditions: 0.63 g HMF (5 mmol), 10 wt% catalyst (MoO_3/$Cu(NO_3)_2$ mass ratio 1:1), 5 mmol $K_2S_2O_8$, 90 °C, 7 h. [b] 40 mL solvent; [c] With furan as substrate.

water mixed solvent water/MeCN (5:1) gave a relatively high PA yield of 63.2% (Table 2, entry 10). This result appeared to demonstrate the scenario mentioned above. To further confirm this result, the D–A reaction of furan, which has low water solubility, and MA was conducted in water. As expected, no PA and MA were obtained in water (Figure S2), whereas a little PA and a large quantity of MA were obtained in the mixed solvents (Table 2, entries 13–15). These results underscore the critical importance of the dispersity of the reactant or intermediate in the reaction solvent, which facilitates product yield. Therefore, it is reasonable that the mixed solvent performed well in the oxidation of HMF to produce PA.

To establish optimal reaction conditions, the effects of reaction parameters, including dosage of oxidant, amount of catalyst, reaction time, and temperature, were investigated, as shown in Figure 1. An excess of oxidant and high temperature decreased the PA yield (Figure 1 a and d). The experiments using mono- or bimetallic catalysts to oxidize HMF to PA demonstrated strong synergy between MoO_3 and $Cu(NO_3)_2$ in this catalytic reaction (Figure 1 b). No MA was observed within 1 h during the oxidation of HMF, whereas on prolonging the reaction time to 2 h, MA was gradually detected accompanied by a drop in the yield of DFF. The product distribution for the prolonged reaction time implies that the conversion of HMF into PA appears to involve an intermediate oxidation step of HMF to DFF and subsequently to MA (Figure 1 c), which amply substantiates that target PA is generated through a stepwise reac-

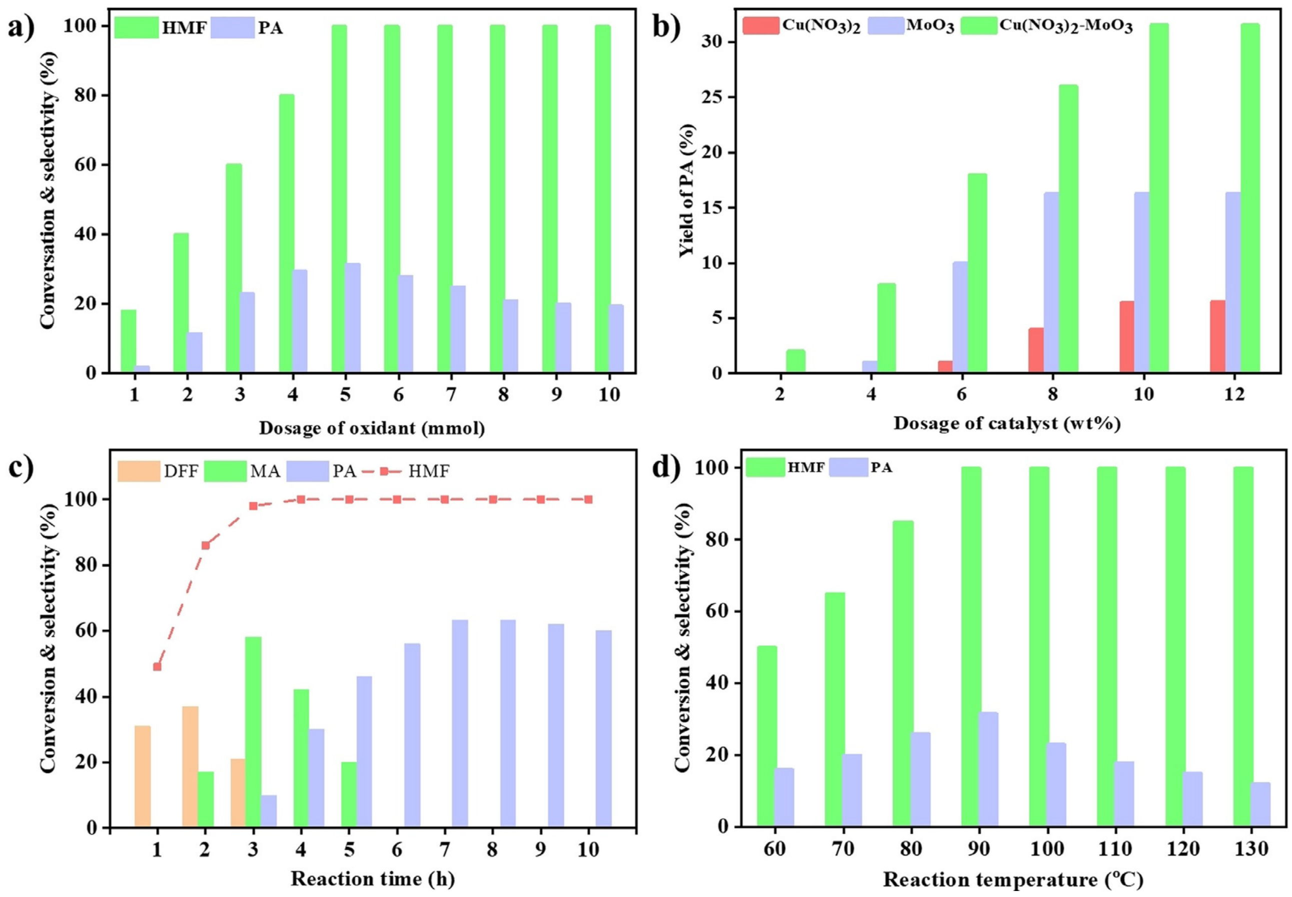


Figure 1. Effect of reaction parameters on the conversion of HMF into PA. a) Effect of the dosage of $K_2S_2O_8$. b) Effect of the dosage of catalyst. c) Effect of reaction time. d) Effect of reaction temperature. Reaction conditions: 5 mmol HMF, 40 mL water/acetonitrile (33:7). a) 10 wt% catalyst (MoO_3/$Cu(NO_3)_2$ mass ratio 1:1), 90 °C, 7 h. b) MoO_3/$Cu(NO_3)_2$ mass ratio 1:1, 5 mmol $K_2S_2O_8$, 90 °C, 7 h. c) 10 wt% catalyst (MoO_3/$Cu(NO_3)_2$ mass ratio 1:1), 5 mmol $K_2S_2O_8$, 90 °C; d) 10 wt% catalyst (MoO_3/$Cu(NO_3)_2$ mass ratio 1:1), 5 mmol $K_2S_2O_8$, 7 h.

tion. Nevertheless, another essential intermediate, namely furan, together with MA, for the D–A reaction to generate PA was not detected, and this motivated our curiosity to investigate the reaction pathway.

Reaction pathway study on the one-pot conversion of HMF into PA

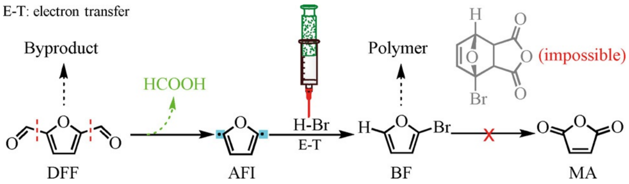
Generally, an aldehyde tends to form the corresponding acid under an oxidizing atmosphere, especially in the presence of transition metal catalysts. At the outset of our work, experiments were devised with several downstream oxidation derivatives of HFM, such as 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HFCA), 5-formyl-2-furancarboxylic acid (FFCA), and 2,5-furandicarboxylic acid (FDCA), as starting materials, to elucidate the reaction pathway of the one-pot conversion of HMF into PA. Only DFF gave a better PA yield than HMF, whereas FFCA, HFCA, and FDCA were hardly converted (Table 3, entries 1–4). This indicates that DFF is an essential intermediate in the conversion of HMF into PA. The above study also identified DFF as a dominant intermediate. These results confirm that the dominant route for the conversion of HMF into PA certainly involved the intermediate DFF.

Table 3. Effect of starting materials on the production of PA.[a]

Entry	Reactant 1	Reactant 2	*t* [h]	Yield [%] PA	MA	M acid
1	DFF	–	5	77.2	4.2	14.4
2	FDCA	–	5	0.0	0.0	0.0
3	FFCA	–	5	0.0	0.0	0.0
4	HFCA	–	5	0.0	0.0	0.0
5	Furan	MA	2	4.3	187.0	0.0
6	furan	M acid	2	4.8	169.0	<1
7	furan	–	3	0.0	86.0	<1
8	M acid	–	2	0.0	98.3	<1
9	MA	–	2	0.0	100.0	0.0
10	FF	–	7	0.0	0.0	0.0
11	FFA	–	8	4.0	23.0	>70[b]
12[c]	furan	MA	7	18.6	147.8	0.0

[a] Reaction conditions: 5 mmol reactant 1, 5 mmol reactant 2, 10 wt% catalyst ($MoO_3/Cu(NO_3)_2$ mass ratio 1:1), 40 mL water/acetonitrile (33:7), 5 mmol $K_2S_2O_8$, 7 h, 90 °C, 100% conversion for all reactions, except that FDCA, FFCA, HFCA, MA, and FF were hardly converted. [b] Yield of FF. [c] With addition of 0.5 mmol formic acid 2.5 mmol $K_2S_2O_8$ (the amount of $K_2S_2O_8$ was halved).

Commonly, a diene and a dienophile are essential for the D–A cycloaddition reaction,[30] which is a critical step for the formation of PA. MA, a key dienophile, was detected as intermediate in the course of the reaction, whereas a diene was never found so far. Initially, furan was considered as the diene involved in the D–A reaction. However, less than 4.3% PA yield was obtained from the reaction of furan and MA or maleic acid (M acid), along with the dominant MA product (Table 3, entries 5 and 6). Moreover, M acid also was converted to MA, which indicates that this reaction system facilitated dehydration to form anhydride (Table 3, entry 8). Since furan was not detected in the reaction, we inferred that the diene should be an active intermediate associated with furan. To capture this active furyl intermediate, the electrophilic reagent HBr was added dropwise to the reaction solution. As a result, 2-bromofuran (BF) from the trapping of the active furyl intermediate (AFI) by HBr was detected by GC-MS (Scheme 2 and Figure S3), which led us to believe that cleavage of the C–C bond between the carbonyl group and the furan ring of DFF by MoO_3 yielded the AFI. In addition, free-radical inhibitor 4-*tert*-butylphenol was added to the reaction solution to induce the reaction. As expected, no MA or PA was detected, even with DFF as substrate. These results suggest that the free-radical reaction should be involved in this catalytic conversion of HMF into PA, followed by an electron-transfer process.



Scheme 2. Trapping of AFI by HBr.

Notably, MA together with M acid were detected with a total yield of greater than 18.6%, which suggested that DFF could be facilely converted to MA (Table 3, entry 1). Moreover, no PA was detected when furan was used as substrate (Table 3, entries 7), only a little PA was obtained when using furan and MA as substrates (Table 3, entries 5), and MA was instead dominant in these reactions. However, when formic acid was added to the reaction mixture, an obvious increase in PA yield was observed, suggesting that formic acid is probably involved in the formation of a dehydrating agent, which improves the dehydration of the D–A adduct to PA (Table 3, entry 12). The low PA yield obtained with furan and MA as substrates was probably caused by a lack of dehydrating agent leading to the retro-D–A reaction. Eventually, most furan was oxidized to MA. In the pathway study above, MA yield reached a relatively high level in the initial 3 h, and the PA yield was lower than 10%. It gradually increased after 4 h. These results show that HMF is first oxidized to MA. However, the reaction rate to MA becomes slow with increasing amount of MA, so that the oxidation of DFF tends to form AFI. Meanwhile the increasing amount of dehydrating agent with the course of reaction improves the dehydration of the adduct to PA, which facilitates the D–A cycloaddition of AFI and MA to form the adduct. On the basis of the above analysis, it is inferred that HMF is simultaneously oxidized to MA and AFI via DFF. Meanwhile, AFI can also be oxidized to MA owing to the easy oxidation of furan to MA.

In a study on the oxidation of biomass-based furfural to MA by $H_5PV_2Mo_{10}O_{40}$, Yin and co-workers[18] proposed that the catalytic transformation is initiated from the furfural radical intermediate generated by the abstraction of the hydrogen atom at the 5-position of furfural by $H_5PV_2Mo_{10}O_{40}$. However, in this study, when furfural (FF) was used as starting material, no conversion was observed (Table 3, entry 10). This is probably attributable to insufficient catalytic activity not only to abstract the hydrogen atom at the 5-position, but also to decarbonylate the 2-position owing to the π conjugation of aldehyde group and the furyl ring. Moreover, on employing furfuryl alcohol (FFA) as the starting material, more than 70% yield of FF was obtained, along with 23% MA and 4% PA (Table 3, entry 11). This indicates that the C–C bond of the hydroxymethyl group adjacent to the furyl group can be directly cleaved in this reaction system, whereas the low yield of MA shows that its formation is only a minor reaction route. Several studies on the oxidation of HMF to MA also showed that the C–C bond adjacent to the hydroxymethyl group in HMF is easily broken under oxidizing conditions.[17,30] Therefore, it is inferred that the direct oxidation of HMF to MA also takes place as the minor reaction pathway.

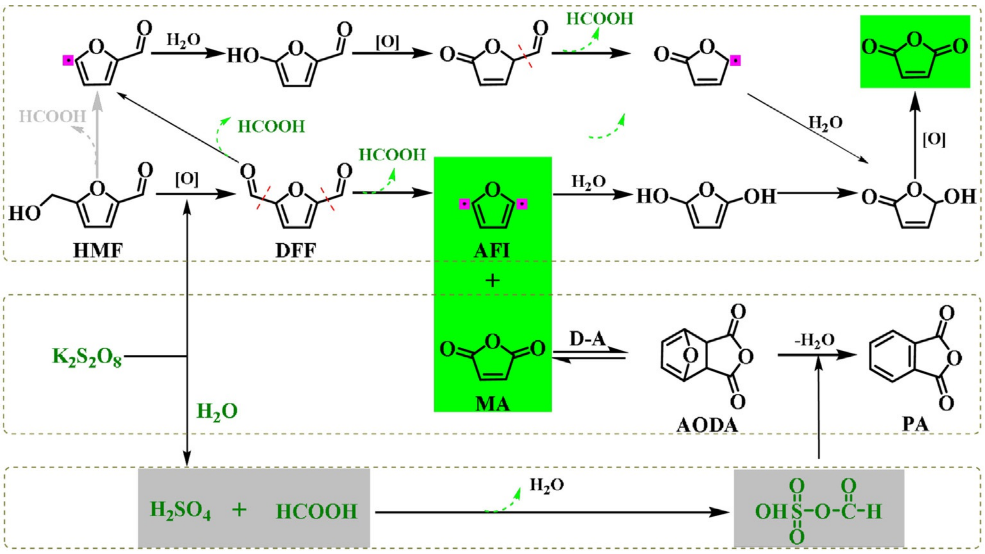
Lobo and co-workers considered that the D–A cycloaddition of furan and MA to PA involved the adduct *exo*-4,10-dioxatricyclo[5.2.1.0]dec-8-ene-3,5-dione (oxanorbornene dicarboxylic anhydride, ODA) and subsequent dehydration,[10] whereas, hitherto, ODA was not detected in our study. We speculated that the D–A adduct in this study was possibly an active intermediate (denoted AODA) associated with ODA. Then, an attempt was made to identify it by analogy with the dehydration mechanism of ODA put forward by Lobo and co-workers[10] In prior study, mixed sulfonic–acetic anhydride has been regarded as an effective dehydrating agent for the conversion of ODA into PA. $K_2S_2O_8$ can be readily decomposed to potassium sulfate, sulfur trioxide, and oxygen at a temperature of 30–200 °C.[31] Considering that $K_2S_2O_8$ was used as oxidant, the sulfo group was regarded to come from sulfur trioxide, and the carboxyl group (formate) should be generated by the decarbonylation or oxidation of HMF to AFI or MA. Sulfur trioxide and formic acid form mixed sulfonic–formic anhydride (Scheme 3).[32] Indeed, formic acid was detected in the reaction solution (Figure S4). The decrease in the pH of the reaction solution from 7.3 to 0.1 after the reaction indicated the formation of acids, such as H_2SO_4 generated from the reaction of SO_3 with water and formic acid from oxidation of the aldehyde group in DFF (Table S1).

To confirm this hypothesis, the effect of dehydrating agents on the dehydration of ODA to PA was investigated (Table 4). With sulfuric acid, formic acid, or maleic acid alone, no PA was detected in the dehydration of ODA, whereas MA was found as dominant product because of the retro-D–A reaction (Table 4, entries 1–3). The similar results that were also obtained with a mixture of sulfuric acid and maleic acid (Table 4, entries 5 and 7) suggested that maleic acid is not a suitable dehydrating agent for the dehydration of ODA. With a sulfuric acid/formic acid mixture, only 2% PA was obtained (Table 4, entry 4). After the mixed acids were allowed to react for 3 h

Table 4. Effect of dehydrating agents on the conversion of ODA into PA.[a]

Entry	Dehydrating agent	Yield [%] PA	MA	M acid
1	5 mmol sulfuric acid	–	79.0	11.0
2	10 mmol formic acid	–	82.0	7.0
3	5 mmol maleic acid	–	99.0	99.0
4	5 mmol sulfuric acid and 10 mmol formic acid	2.0	63.0	11.0
5	5 mmol sulfuric acid and 5 mmol maleic acid	–	99.0	99.0
6[b]	5 mmol sulfuric acid and 10 mmol formic acid	17.0	20.0	34.0
7[b]	5 mmol sulfuric acid and 5 mmol maleic acid	–	89.0	96.0
8[c]	10 mmol formic acid	48.0	7.0	–
9[d]	5 mmol sulfuric acid and 10 mmol formic acid	9.0	35.0	30.0

[a] Reaction conditions: 5 mmol ODA, 40 mL water/acetonitrile (33:7), 10 wt% catalyst ($MoO_3/Cu(NO_3)_2$ mass ratio 1:1), 90 °C, 5 h. [b] After the mixed acids were allowed to react for 3 h, 5 mmol ODA was added to react for a further 2 h. [c] After 10 mmol formic acid and 5 mmol $K_2S_2O_8$ were mixed for for 3 h, 5 mmol ODA was added to react for a further 2 h. [d] After 5 mmol sulfuric acid, 10 mmol formic acid, and 1 mmol $K_2S_2O_8$ were mixed for 3 h, 5 mmol ODA was added to react for a further 2 h.



Scheme 3. Reaction pathway of the one-pot conversion of HMF into PA.

and the resulting acid solution was used for the dehydration of ODA, an obvious enhancement in the yield of PA was achieved (Table 4, entry 6). These results suggest that sulfuric acid and formic acid formed mixed sulfonic–formic anhydride, which promoted the dehydration of ODA to PA. More importantly, when additional $K_2S_2O_8$ was added to the reaction with formic acid alone or a mixture of sulfuric and formic acids as dehydrating agent, a significant increase in PA yield was obtained (Table 4, entries 8 and 9). These results amply demonstrate that $K_2S_2O_8$ actually played an essential role in the conversion of HMF into PA, similar to mixed sulfonic–acetic anhydride. The similar dehydration mechanism also indirectly verifies the existence of the active intermediate AODA in the conversion of HMF into PA.

Previous studies[14,18] on the oxidation of furfuran and HMF to MA showed that formation of furfural radical is major route, followed by hydration and 1,4-rearrangement to form 5-oxo-2,5-dihydrofuran-2-carbaldehyde. Then, decarbonylation of 5-oxo-2, 5-dihydrofuran-2-carbaldehyde and subsequent 1,4-rearrangement leads to 5-hydroxyl-2(5*H*)-furanone, which is oxidized to MA. Therefore, on the basis of the reported mechanism and results obtained in this study, a reaction pathway for the one-pot conversion of HMF into PA was proposed (Scheme 3). Initially, HMF is oxidized to DFF in water/acetonitrile with $K_2S_2O_8$ as oxidant. Then, DFF undergoes decarbonylation at the 2-position to form a furanyl radical or at the 2- and 5-positions of the furan ring simultaneously to form AFI. Meanwhile, the furanyl radical and AFI are oxidized to MA. The increasing amount of MA in the reaction mixture slows the conversion of DFF into MA, and more DFF tends to be oxidized to AFI. Eventually, AFI and MA undergo the essential D–A cycloaddition to generate PA though the dehydration of active intermediate AODA by mixed sulfonic–formic anhydride.

Process development for HMF to PA in one pot with O_2 as oxidant

According to the decomposition equation of $K_2S_2O_8$, only 1 mol oxygen atoms is released by 1 mol $K_2S_2O_8$ involved in the oxidation of HMF to PA, which is considerably less than the oxygen required for complete conversion of HMF into PA. Hence, it was reasonably doubted that the air remaining in the reactor was involved in the oxidation of HMF to PA. To gain more insight into the intrinsic function of $K_2S_2O_8$, studies on substituting $K_2S_2O_8$ with O_2 and H_2SO_4 in the one-pot conversion of HMF into PA were carried out. Remarkably, O_2/H_2SO_4 also made it possible to oxidize HMF to PA in one pot (Table 5), and this confirmed the hypothesis that the oxygen in the reactor also took part in the oxidation of HMF to PA. It is noteworthy that an excess of oxygen resulted in high selectivity to MA instead of PA (Table 5, entry 2). By contrast, insufficient oxygen also led to weak oxidizing power, accompanied by low selectivity for PA and MA (Table 5, entries 1 and 3). Once the amount of oxygen was maintained at a reasonably level, an obvious enhancement in the PA yield was observed (Table 5, entries 4–7). Apart from the effect of oxygen, appropriate acidity was also a vital factor to facilitate the conversion of HMF into PA (Table 5, entries 5–7). In summary, efficient conversion of HMF into PA using $MoO_3/Cu(NO_3)_2$ as catalyst, oxygen as oxidant, and H_2SO_4 as accelerator was realized in one pot.

Table 5. Conversion of HMF to PA in one pot with oxygen as oxidant.[a]

Entry	Oxidant	Conversion [%]	Selectivity [%] DFF	MA	PA
1	air	100	28	43	6
2[b]	O_2	100	–	78	10
3	N_2	45	36	24	–
4	O_2	100	–	46	18
5[c]	O_2	100	–	15	56
6[d]	O_2	100	–	57	26
7[b,c]	O_2	100	11	42	24

[a] Reaction conditions: 5 mmol HMF, 5 mmol H_2SO_4 10 wt% catalyst ($MoO_3/Cu(NO_3)_2$ mass ratio 1:1), 40 mL water/acetonitrile (33:7), 90 °C, 8 h, atmospheric pressure. [b] 0.1 MPa O_2. [c] 4.5 mmol H_2SO_4. [d] 4 mmol H_2SO_4.

Conclusion

We have demonstrated for the first time a highly efficient protocol for directly synthesizing renewable PA from HMF through a one-pot procedure mediated by $MoO_3/Cu(NO_3)_2$. With the characteristics of a green and sustainable feedstock, commonly available catalysts, low reaction temperature, and high yield of product, the pathway put forward herein realizes the integration of multiple steps (decarbonylation of HMF to AFI, oxidation of HMF to MA, D–A cycloaddition of AFI and MA, and subsequent dehydration) into one pot with the assistance of O_2 and H_2SO_4. The process in detail consists of the initial oxidation of HMF to DFF, followed by the direct oxidation of DFF to MA and indirect oxidation of DFF to MA via intermediate AFI. Subsequently, the active intermediate related to ODA is formed by the crucial D–A cycloaddition of AFI and MA. Eventually, PA is generated by the subsequent dehydration. The catalyst system plays a vital role in making the efficient conversion of HMF into PA possible. Under mild reaction conditions, a PA yield of 63.2% was obtained. This convenient one-pot synthesis has great potential to produce renewable PA in a cost-competitive fashion compared to the current multistep synthetic approach.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cycloaddition · oxidation · one-pot reactions · phthalic anhydride · reaction mechanisms

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