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FULL PAPER

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

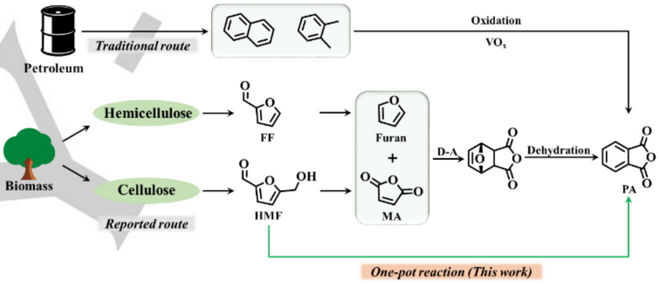
Wenlong Jia,[a] Yong Sun,*[a], [b], [c] Miao Zuo,[a] Yunchao Feng,[a] Xing Tang,[a] Xianhai Zeng,[a] Lu Lin [a]

Abstract: Herein, we reports a renewable synthetic pathway of phthalic anhydride (PA) from 5-hydroxymethfurfural (HMF) in one pot for the first time. The commonly available catalysts $MoO_3/Cu(NO_3)_2$ played a crucial role in integrating the multistep reactions, 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 a mild reaction conditions, a 63.2 % yield of PA was obtained from HMF. Compared to the currently reported route to renewable PA based on the Diels-Alder cycloaddition of biomass-derived MA and furan, this convenient one-pot synthesis pathway presents great advantage in efficiency.

Introduction

Phthalic anhydride (PA) is a versatile intermediate for the chemical industry with a global production of over 3 million tons per year,[1] serving a vast range of industries including phthalate esters plasticizers,[2] polyester resins,[3] dyestuffs,[4] pharmaceuticals,[5] and so on. Currently, PA is primarily produced via catalytic oxidation of naphtha or ortho-xylene, which is refined from petroleum or coal.[6, 7] In consideration of current concern on fossil fuel depletion and environmental footprint, limited progress has been made to seek 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 et al.[10] envisaged a renewable route to PA using biomass-derived maleic anhydride (MA) and furan based on Diels-Alder (D-A) and following dehydration reaction, establishing an approach for transforming abundant renewable biomass resources into PA (**Scheme 1**).

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



Scheme 1. The synthesis pathway of PA

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

From the studies described above, we note that the current renewable route to produce PA from HMF or FF needs to undergo four steps: decarbonylation of FF to furan, oxidation of HMF or FF to MA, D-A cycloaddition of furan and MA, and following dehydration reaction of D-A adduct.[21] It is considered as a promising sustainable strategy for the production of PA. Whereas it is worth noting that multistep reactions result in low efficiency for the production of PA from HMF or FF. To make renewable PA cost-competitive compared to the traditional synthetic route, a simpler process is expected.[21]

To the best of our knowledge, one-pot and straightforward procedure capable of directly producing PA from HMF has not been reported. This challenging goal would be of clear significance and interest, the key to success is to develop a highly advanced and versatile catalyst system that can integrate four independent reactions mentioned-above in one pot. Herein, we report such a combined catalyst of $MoO_3/Cu(NO_3)_2$, which unexpectedly exhibited the excellent catalytic activities in

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decarbonylation, oxidation, D-A cycloaddition and dehydration, enabling the one pot process. It spured us to reveal the intrinsic reaction pathway in this one pot process of HMF to PA in detail.

Results and Discussion

One pot Synthesis of Renewable Phthalic Anhydride form 5-Hydroxymethfurfural. Building upon the previous work of preparing 2, 5-diformylfuran (DFF) from HMF using $Fe(NO_3)_3/Cu(NO_3)_2$ as catalyst, a 99 % yield of DFF was obtained with the assistant of $K_2S_2O_8$ in acetonitrile.[22] When adding water into the reaction, PA was unexpectedly found with 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 promote the conversion efficiency of HMF to PA by using $K_2S_2O_8$ as oxidant. the investigation was initiated by examining a series of multi-metallic catalysts, including transition elements of iron, copper, vanadium, manganese or molybdenum. The results showed that most catalysts led to a high HMF conversion in 7 h, moreover the iron-based catalysts appeared to be more favorable to the generation of DFF (**Table 1,** entries 2-7). It should be noted that chloride salts, such as $FeCl_3$ or $VOCl_3$ used in this reaction, were inclined to produce by-product 5-chloromethyl furfural (CMF) (**Figure S1**), contributing to the low selectivity to the target product PA, as well as the intermediates DFF and MA (**Table 1,** entries 2, 10). Generally, vanadium-based oxides are reported as effective catalysts for the oxidation of hydroxyl to ketones or oxidative decarboxylation.[23, 24] In this case, the vanadium oxides demonstrated a moderate selectivity to PA with almost complete conversion of HMF (**Table1**, entries 8-10). Then, several molybdenum oxides and manganese oxides catalysts combined with cupric nitrate were examined respectively. In wonder, both $MnO_2/Cu(NO_3)_2$ and $MoO_3/Cu(NO_3)_2$ gave promising results for the one-pot conversion HMF to PA, with isolated yields of 54.4 % and 63.2 % respectively (**Table1**, entries 11, 16). It is further noteworthy that iron oxides and cerium oxide caused negative effect on the generation of PA to some extent (**Table1**, entries 12-15). In sum, $MoO_3/Cu(NO_3)_2$ are preferred catalysts for the one-pot conversion of HMF to PA.

Table 1. Effect of Catalysts on the Catalytic Oxidation of HMF.[a]

Entry	Catalyst	Conv.(%)	Sele.(%)		
			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 (the mass ratio of each metallic catalyst was controlled as 1:1), 40 ml mixed solvents of water and acetonitrile (33:7), 5 mmol $K_2S_2O_8$, 90 °C, 7 h; [b] 10 wt% catalyst (the mass ratio of each metallic catalyst was controlled as 1:1:1); [c] without catalyst.

In study, the significant effect of water on product distribution was also observed. The works performed by Otto et al. [25] and Thomas et al. [26] showed aqueous solvent tended to enhance the reaction rate and selectivity of D-A reaction. The effect of water on D-A reaction is attributed in part to the benefit of decreasing hydrophobic surface area, as well as the hydrogen-bond donating capacity.[27-29] Obviously, compared with sole water, the common polar aprotic solvents, including MeCN, DMSO, dioxane, MIBK, toluene, carbon tetrachloride chloride and dichloromethane, achieved 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 if at the condition of high MA concentration in these polar aprotic solvents (**Table 2**, entries 2, 4-6), the yield of PA was lower than that obtained in sole water. Once Water/MeCN was used as solvent, the yield of PA was substantially increased (**Table 2**, entries 9-10). These results suggest that water facilitated the oxidation of HMF, D-A cycloaddition and following dehydration of adduct. Therefore, the lower PA yields obtained by these aprotic organic solvents employed in this study is reasonably ascribed to the less contribution in their hydrogen-bond donating capacity.

Despite obvious benefits, water as solvent alone only obtained 37.6 % yield of PA. It ignited the speculation that water insoluble intermediates were generated in the reaction, eventually effecting the yield of PA. In view of this assumption, the mixed solvents of water with MeCN or dioxane, were examined in the investigated reaction based on the results that MeCN and dioxane preformed relatively better than other organic solvents. As we expected, water/organic solvents performed better than sole water, moreover the high-water-content mixed solvent of water/MeCN (5:1) obtained 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 and MA was conducted in water based on the low water-solubility of furan. As expected, no PA and MA were obtained in water (**Figure**

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S2), whereas by contrast, 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 reactant or intermediate in reaction solvent, which facilitates product yield. Therefore, it is in reason that the mixed solvent performed well in the oxidation of HMF to produce PA.

Table 2. Effect of Solvents on the Catalytic Oxidation of HMF.[a]

Entry	Solvent[b]	Conv.(%)	Sele.(%)		
			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	Carbon tetrachloride	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 (the mass ratio of $MoO_3/Cu(NO_3)_2$ was controlled as 1:1), 5 mmol $K_2S_2O_8$, 90 °C, 7 h; [b] 40 ml solvent; [c] Using furan as substrate.

To establish optimal reaction conditions, effects of reaction parameters, including dosage of oxidant, amount of catalyst, reaction time and temperature, were investigated, as showed in the **Figure 1.** The results revealed that excess oxidant and high temperature caused decline in the PA yield (**Figure 1a and d**). The experiments using nonometallic or bimetallic catalysts to oxidized HMF to PA demonstrated strong synergy between MoO_3 and $Cu(NO_3)_2$ in this catalytic reaction (**Figure 1b**). No MA was observed within 1 h during the oxidation of HMF, whereas prolonging the reaction time to 2 h, MA was gradually detected accompanied by a drop in the yield of 2, 5-diformylfuran (DFF). The product distribution with the prolonged reaction time infers that the conversion of HMF to PA appears to undergo an intermediate oxidation step of HMF to DFF, subsequently to MA (**Figure 1c**), amply substantiating that target PA is generated through a stepwise reaction. Nevertheless, another essential intermediate furan, together with MA, for the D-A reaction to generate PA is not detected, motivating our curiosity to investigate the reaction pathway.

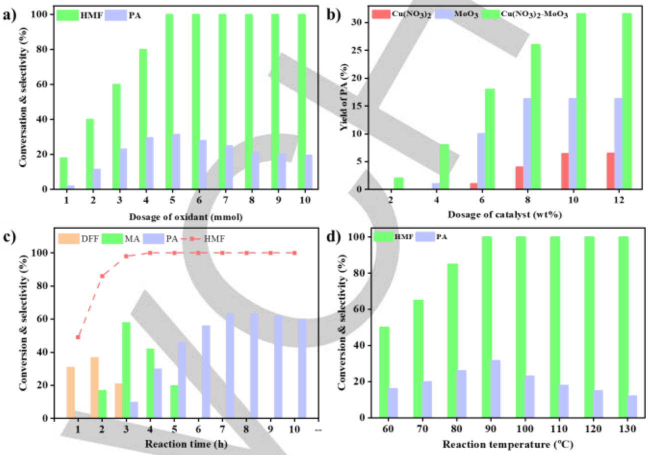


Figure 1. Effect of reaction parameters on the conversion of HMF to PA. a) Effect of the dosage of $K_2S_2O_8$; b) Effect of the dosage of catalyst; c) Effect of reaction time; d) Effect of reaction temperature. Reaction conditions: 5 mmol HMF, 40 ml mixed solvent of water and acetonitrile (33:7). a)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

Reaction Pathway Study on the one-pot conversion of HMF to PA. Generally, aldehyde tends to form corresponding acid under an oxidation atmosphere, especially in the presence of transition metal catalyst. At the outset of our work, several 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), 2, 5-furandicarboxylic acid (FDCA) as starting materials, to figure out the reaction pathway of the one-pot conversion of HMF to PA. Only DFF achieved a better PA yield than HMF, whereas FFCA, HFCA and FDCA were hardly converted (**Table 3**, entries 1-4), indicating that DFF was an essential intermediate for the conversion of HMF to PA. The kinetic study in the above section also identified DFF as a dominant intermediate. These results confirm that the conversion of HMF to PA certainly underwent the intermediate DFF as the dominant route.

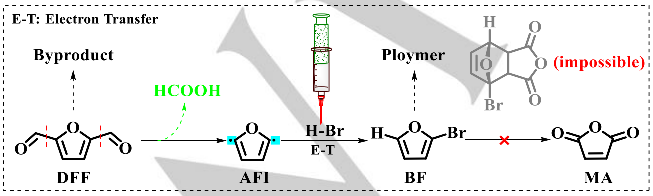
Table 3. Effect of starting materials on the production of PA.[a]

Entry	Reactant 1	Reactant 2	Time (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 (mass ratio of $MoO_3/Cu(NO_3)_2$ was controlled as 1:1), 40 ml mixed solvent of water and 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] The yield of FF; [c] Adding 0.5 mmol formic acid 2.5 mmol $K_2S_2O_8$ (the amount of $K_2S_2O_8$ was reduced by half.) ;

Commonly, diene and dienophile are essential for the D-A reaction characterized by cycloaddition [30], being a critical step for the formation of PA. MA, a key dienophile, was detected as intermediate in the course of the reaction, whereas diene was never found so far. Initially, furan was considered as the diene involved in the D-A reaction. Whereas in fact, less than 4.3 % PA yields were obtained from the reaction of furan and MA or maleic acid (M acid), along with the dominant product of MA (**Table 3**, entries 5-6). Moreover, M acid also was converted to MA, indicating 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 dropwise added into the reaction solution. As a result, 2-bromofuran (BF) came from the trapping of the active furyl intermediate by HBr was successfully detected by GC-MS (**Scheme 2 & Figure S3**), making us believe that the cleavage of the C−C bond between the carbonyl group and furan sketch of DFF by MoO_3 yielded the active furyl intermediate (AFI). In addition, free radical inhibitor 4-tertbutylphenol was added into the reaction solution to induce the reaction. As expected, no MA or PA was detected, even if DFF as substrate. These results suggest that the free radical reaction should be involved in this catalytic conversion of HMF to PA, followed by an electron transfer process.



Scheme 2. Trapping of active furyl intermediate by HBr

Notably, MA together with M acid were detected with a total yield of over 18.6 %, suggesting that DFF could be facilely converted to MA (**Table 3**, entry 1). Moreover, no PA was detected when furan used as substrate (**Table 3**, entries 7), only a little PA was obtain when using furan and MA as substrates (**Table 3**, entries 5), MA was dominant instead in these reactions. However, when formic acid was added into the reaction, a obvious increase in the PA yield was observed, suggesting that formic acid probably involved to the formation of dehydrant, which improved the dehydration of the D-A adduct to PA (**Table 3**, entry 12). The low PA yield obtained by furan and MA as substrates was probably caused by a lack of dehydrant, leading to the retro-D-A reaction. Eventually, most furan was oxidized to MA. In the kinetic study above, MA yield reached to a relatively high level in initial 3 h, while PA yield was low than 10 %. It was gradually raised after 4 h. These results show that HMF firstly is oxidized to MA. However, the reaction rate to MA become slow with the increase of MA, resulting in the oxidation of DFF tends to form AFI. Menawhile the increasing dehydrant with the course of reaction improves the dehydration of adduct to PA, facilitating the D-A cycloaddition of AFI and MA to form the adduct. Base on analysis above, it is inferred that HMF is simultaneously oxidized to MA and AFI via DFF. Meanwhile, AFI can also be oxidized to MA based on the result of the easy oxidation of furan to MA.

In the study of the oxidation of biomass-based furfural to MA by $H_5PV_2Mo_{10}O_{40}$, Yin et al.[18] deemed that the catalytic transformation should be initiated from the furfural radical intermediate generated from 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). It was probably attributed to lack enough catalytic activities to not only abstract the hydrogen atom at the 5-position, but also decarbonylate at the 2-position due to the π-conjugation of aldehyde group and furyl ring. Moreover, employing furfuralcohol (FFA) as the starting material, more than 70 % yield of FF was obtained, along with 23 % MA and 4 % PA generated (**Table 3**, entry 11), indicating that the C−C bond of hydroxymethyl group adjacent to furyl group can be directly cleaved in this reaction system. Whereas, the low yield of MA shows that it is only the minor reaction route. Several studies on the oxidation of HMF to MA also show that the C–C bond adjacent to the hydroxymethyl group in HMF molecule is easily broken under an oxidation condition.[17, 31] Therefore, it is inferred that the direct oxidation of HMF to MA also takes place as the minor reaction pathway.

In the previous report, Lobo et al.[10] regarded that the D-A cycloaddition of furan and MA to PA underwent the adduct exo-4, 10-dioxa-tricyclo[5.2.1.0]dec-8-ene-3,5-dione (oxanorbornene dicarboxylic anhydride, ODA) and subsequent dehydration. Whereas hitherto, ODA was not detected in our study. We speculated that the D-A adduct in this study was possibly an active intermediate (named AODA) associated with ODA. Then, an attempt was made to identify it by the analogy with the dehydration mechanism of ODA put forward by Lobo et al.[10]. In reported literature, mixed sulfonic-acetic anhydride was regarded as an effective dehydrant for the conversion of ODA to PA. Generally, $K_2S_2O_8$ can be readily decomposed to potassium sulfate, sulfur trioxide and oxygen at a temperature of 30-200 °C.[32] Considering $K_2S_2O_8$ was used as oxidant, sulfonic group

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was regarded to come from sulfur trioxide, while carboxylic (formate) should generate from the decarbonylation or oxidation of HMF to AFI or MA. Sulfur trioxide and formic acid formed mixed sulfonic-formic anhydride (**Scheme 3**).[33] Much to our delight, formic acid was detected in the reaction solution (**Figure S4**). The pH of the reaction solution after the reaction decreased from 7.3 to 0.1 indicated the formation of acids, such as H_2SO_4 generated from the reacion of SO_3 with water and formic acid came from the oxidation of aldehyde group in DFF (**Table S1**).

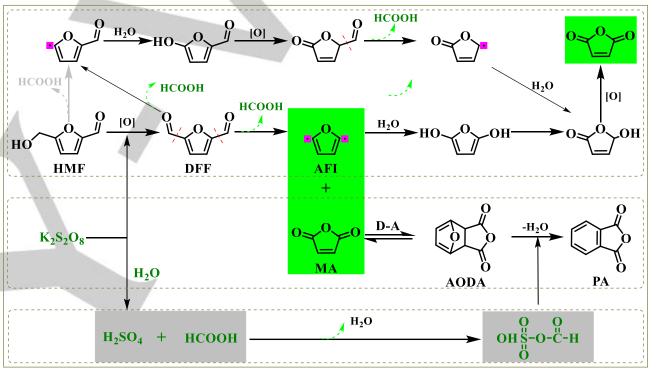
To confirm this inference, the effect of dehydrants on the dehydration of ODA to PA was investigated (**Table 4**). When using separate sulfuric acid, formic acid or maleic acid, no PA was detected in the dehydration of ODA, whereas MA was found as dominant product because of the retro-D-A reaction (**Table 4**, entries 1-3). The similar results was also obtained by the mixed acids of sulfuric acid and maleic acid (**Table 4**, entries 5 and 7), suggesting that maleic acid was not suitable to use as dehydrant for the dehydration of ODA. Using the mixed acids of sulfuric acid and formic acid, only 2 % PA was obtained (**Table 4**, entry 4). By comparison, after the mixed acids were reacted for 3 h, the resulting acid solution was used for the dehydration of ODA, as a result, 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, promoting the dehydration of ODA to PA. More importantly, when additional $K_2S_2O_8$ was added to the reaction using separate formic acid or the mixed acids of sulfuric and formic acid as dehydrant, a significant increase in the PA yield was obtained (**Table 4**, entries 8-9). These results amply demonstrates $K_2S_2O_8$ actually played an essential role in the conversion of HMF to 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 to PA.

Table 4. Effect of dehydrant on the conversion of ODA to PA.[a]

Entry	Dehydrant	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 mixed solvent of water and acetonitrile (33:7), 10 wt% catalyst (mass ratio of $MoO_3/Cu(NO_3)_2$ was controlled as 1:1), 90 ºC, 5 h; [b] After the mixed acids were reacted for 3 h, then 5 mmol ODA was added to react for another 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 another 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 another 2 h.

Previous studies[14, 18] on the oxidation of furfuran and HMF to MA showed that formation of furfural radical was 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 following 1, 4-rearrangement led to 5-hydroxyl-2(5H)-furanone. Actually, 5-hydroxyl-2(5H)-furanone was oxidized to MA. Therefore, based on the reported mechanism and results obtained in this study, the reaction pathway for the one-pot conversion of HMF to PA was proposed, as illustrated in **Scheme 3.** Initially, HMF is oxidized to DFF in the mixed solution of water/acetonitrile with $K_2S_2O_8$ as oxidant. Then, DFF undergo decarbonylation at the 2-position to form furfuran radical or at the 2 and 5-position of furan ring simultaneously to form AFI. Meanwhile, Furfuran radical and AFI is oxidized to MA. The increase of MA in the reaction slows the conversion rate of DFF to MA. More DFF tends to be oxidized to AFI. Eventually, AFI and MA involves in the essential D-A cycloadditio to generate PA though the dehydration of an active intermediate AODA by mixed sulfonic-formic anhydride.



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

Process Development for HMF to PA in one pot with O_2 as oxidan. According to the decomposition equation of $K_2S_2O_8$, only 1 mol oxygen atom was released by 1 mol $K_2S_2O_8$ to involve the oxidation of HMF to PA, which was considerably less than the required oxygen for the complete conversion of HMF to PA. Hence, it was reasonably doubted that the air remained in the reactor involved in the oxidation of HMF to PA. To gain more insight into the intrinsic function of $K_2S_2O_8$, the studies of substituting $K_2S_2O_8$ with O_2 and H_2SO_4 in the one pot conversion of HMF to PA were carried out. One amazedly found that O_2/H_2SO_4 also made it possible to oxidized HMF into PA in one-pot (**Table 5**), confirming the speculation that the oxygen in the reactor also took part in the oxidation of HMF to PA. It is worthwhile to point out here that excess oxygen resulted in high selectivity to MA, instead of PA (**Table 5**, entry 2). By contrary, insufficient oxygen also led to weak oxidizing power, accompanied by low selectivity of PA and MA (**Table 5**, entries 1 and 3). Once an amount of oxygen was controlled 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 to PA (**Table 5**, entries 5-7). Summarily, an efficient conversion of HMF to 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	Conv. (%)	Sele. (%)		
			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 (mass ratio of $MoO_3/Cu(NO_3)_2$ was controlled as 1:1), 40 ml mixed solvent of water and acetonitrile (33:7), 90 °C, 8 h, atmospheric pressure; [b] 0.1 Mpa O_2; [c] 4.5 mmol H_2SO_4 acid; [d] 4 mmol H_2SO_4 acid;

Conclusions

In summary, we demonstrated for the first time a highly efficient protocol for directly synthesizing renewable PA from HMF through an one-pot procedure mediated by $MoO_3/Cu(NO_3)_2$. With characteristics of green and sustainable feedstock, commonly available catalysts, mild reaction temperature and high yield of product, the pathway put forward in this study realized the integration of multistep (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 consisted 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 was formed by the crucial D-A cycloaddition of AFI and MA. Eventually, PA was generated by the following dehydration. The catalyst system played a vital role in making the efficient conversion of HMF to PA possible. Under a mild reaction condition, PA yield of 63.2 % was obtained. This convenient one-pot synthesis pathway exhibits great potential to produce renewable PA in a cost-competitive fashion compared to the current multistep synthesis approach.

Experimental Section

Synthesis procedures of PA form HMF, analysis of PA can be found in Supplemental Information.

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