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COMMUNICATION

Oxidation of 5-hydroxymethylfurfural to maleic anhydride with molecular oxygen†

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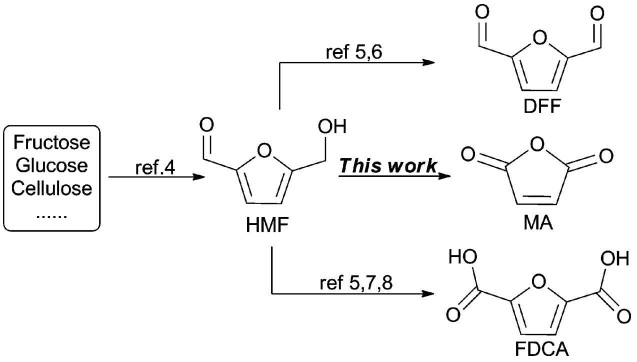
5-Hydroxymethylfurfural (HMF) was converted to maleic anhydride in 52% yield *via* selective oxidation with molecular oxygen using $VO(acac)_2$ as catalyst in liquid phase.

Maleic anhydride (MA) is a versatile chemical intermediate used to produce a variety of products such as unsaturated polyester resins, 1,4-butanediol, fumaric acid, and tetrahydrofuran.[1,2] The global production capacity is more than one million tons per year.[1] In industry, MA is mainly produced *via* selective oxidation of benzene, *o*-xylene or *n*-butane under relatively high temperature; *e.g.* catalytic oxidation of *n*-butane to MA is usually performed at 400–450 °C, and the selectivities of MA are 67–75 mol% at 70–85% conversions of *n*-butane.[2] All these routes above depend on petroleum-based feedstocks. Herein we provide a potential biomass-based route for the preparation of MA.

Biomass is viewed as a promising feedstock for the chemical industry in the future.[3] Conversions of biomass into chemicals have become a hot topic recently; many "roadmaps" with far-sightedness were plotted.[3] For example, carbohydrates, including fructose, glucose and cellulose, could be converted into 5-hydroxymethylfurfural (HMF),[4] which is a versatile platform chemical. Many researchers concentrated on the oxidation of HMF to 2,5-diformylfuran (DFF) or 2,5-furandicarboxylic acid (FDCA) (Scheme 1),[5–8] as these furan products could be used as polymer monomers.[9] The molecules of both MA and HMF contain furyl rings in the basic structure, thus it would be interesting to convert HMF into MA from the viewpoint of sustainable chemistry. This transformation could be achieved *via* oxidative C–C bond cleavage of HMF. In this communication, we report $VO(acac)_2$ catalyzed oxidation of HMF to MA with molecular oxygen in liquid phase.

HMF, which can be taken as a heteroaromatic alcohol, was usually oxidized to DFF using vanadium-based catalysts (Scheme 1).[6] Recently we developed several vanadium-based systems for catalytic oxidation of benzyl alcohols with molecular oxygen.[10] When the oxidation of HMF was performed using $VO(acac)_2$ as catalyst under 0.1 MPa oxygen in acetonitrile,‡ the main product was DFF. Unexpectedly, MA appeared rather than FDCA under higher oxygen pressure. Both the conversions of HMF and the yields of MA were significantly enhanced when the pressure of oxygen was increased from 0.1 MPa to 1.0 MPa (Fig. 1) The yield of MA remained roughly constant when the oxygen pressure was further raised to 1.5 MPa. These results suggested that high pressure of oxygen facilitated the conversion of HMF into MA.



Scheme 1 Several routes for the selective oxidation of HMF.

The solvent also played an important role for the oxidation of HMF to MA (Table 1). 52% yield of MA was obtained in acetonitrile at 90 °C in 4 h (entry 2), meanwhile 14% yield of DFF was detected too. Besides acetonitrile, acetic acid was preferred for the formation of MA (entry 4). The yields of MA were about 7% in DMF and TFT respectively (entries 5 and 6), which were much less than that in acetonitrile or acetic acid. These results further confirmed the great influence of oxygen pressure on vanadium-catalyzed oxidation of HMF, as good yields of DFF were achieved under lower oxygen pressure in these solvents according to the previous reports.[6] About 19% of HMF was converted and little MA was detected in DMSO (entry 7). When dichloromethane was used as the solvent, much oxygen was consumed, however, only 16% of MA was received and black insoluble was observed (entry 8 and ESI† Fig. S16). The effects of solvents on vanadium-catalyzed oxidation were also described in many literatures previously.[10–12]

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Table 1 Catalytic oxidation of HMF in different solvents[a]

Entry	Solvent	Conversion of HMF (mol%)	Yield of main furan products (mol%)[b] MA	DFF
1[c]	CH_3CN	<1	—	—
2	CH_3CN	99	52	14
3[d]	CH_3CN	97	50	15
4	CH_3COOH	>99	50	<1
5	DMF	96	7	11
6	TFT	96	7	6
7	DMSO	19	<1	9
8	CH_2Cl_2	>99	16	<1

[a] Reaction conditions: 2.5 mmol HMF, 0.125 mmol $VO(acac)_2$, 5 ml solvent, 1.0 MPa O_2, 90 °C, 4 h. Acetonitrile contained 1% acetic acid. TFT: α,α,α-trifluorotoluene; DMF: *N*,*N*-dimethyl-formamide. [b] The yields were calculated as the molar ratio of their amounts to the initial amount of HMF. The yield of MA included maleic acid. [c] Without catalyst. [d] 5 mol% 2,6-di-*tert*-butyl-*p*-cresol was added.

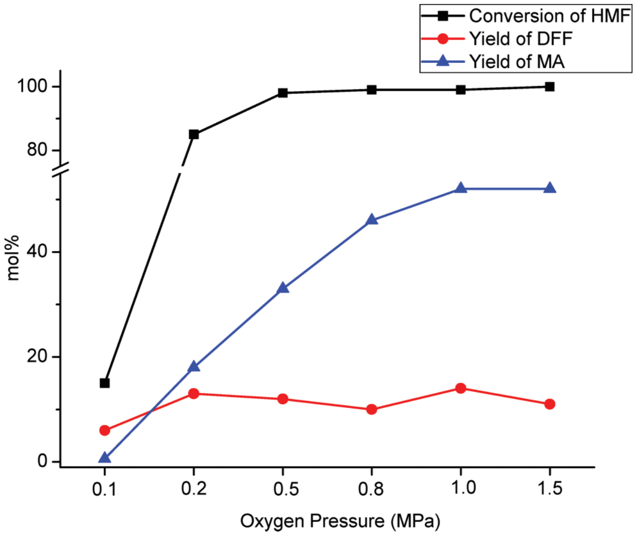


Fig. 1 Effect of oxygen pressure. Reaction conditions: 2.5 mmol HMF, 0.125 mmol $VO(acac)_2$, 5 ml acetonitrile, 90 °C, 4 h.

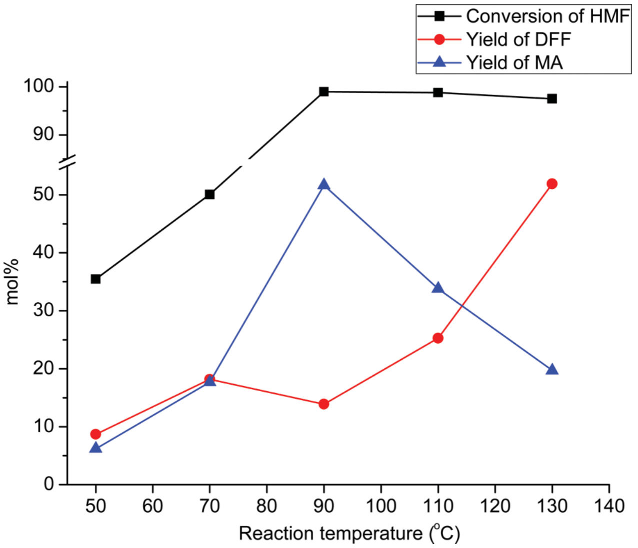


Fig. 2 Effect of reaction temperature. Reaction conditions: 2.5 mmol HMF, 0.125 mmol $VO(acac)_2$, 5 ml acetonitrile, 1.0 MPa O_2, 4 h.

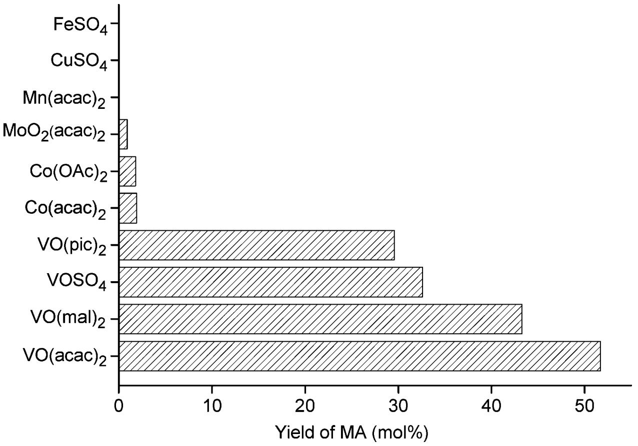


Fig. 3 Oxidation of HMF to MA catalyzed by different transition metals. Reaction conditions: 2.5 mmol HMF, 0.125 mmol [M], 5 ml acetonitrile, 90 °C, 1.0 MPa O_2, 4 h.

Furthermore, the reaction temperature could affect the oxidation efficiency as well as products distribution (Fig. 2). When the reaction was performed under 70 °C, the conversions of HMF were not more than 50% in 4 h. Interestingly, when the temperature was raised from 90 °C to 130 °C, the yields of MA gradually decreased from 52% to 20% meanwhile the yields of DFF increased from 14% to 52%. Higher reaction temperature favoured the formation of DFF rather than MA. This observation was consistent with the previous reports on vanadium-catalyzed oxidation of HMF to DFF. In those papers, oxidations of HMF to DFF were usually performed at around 130–150 °C.[6]

Besides $VO(acac)_2$, some other vanadium compounds also exhibited activities for catalytic oxidation of HMF to MA. About 30–43% yields of MA were obtained using $VO(pic)_2$ [bis(pyridine-2-carboxylato)oxovanadium(IV)], $VO(mal)_2$ [bis(maltolato)oxovanadium(IV)] and $VOSO_4$ respectively under the same conditions (Fig. 3). In contrast to vanadium compounds, transition metals such as $FeSO_4$, $CuSO_4$, $Mn(acac)_2$, $MoO_2(acac)_2$, $Co(acac)_2$ and $Co(OAc)_2$ were much less effective for catalytic oxidation of HMF into MA, and the yields of MA were less than 2%. These results indicated that vanadium species were unique for catalytic C–C bond cleavage of HMF. To the best of our knowledge, this is the first report on vanadium-catalyzed oxidation of HMF to MA with molecular oxygen.

Then an important issue arose: the formation route of MA from HMF. Generally, aldehydes such as benzaldehyde tend to form corresponding acids with molecular oxygen *via* autoxidation, especially in the presence of transition metal ions.[13] The aldehyde group of HMF seemed to be the breakthrough point to form MA *via* an autoxidation/decarboxylation reaction pathway. If this hypothesis was right, DFF should be easily converted to MA in good yield under the same conditions. Unexpectedly, most of DFF remained stable and only 2% of MA was obtained when DFF was oxidized (ESI† Fig. S14 and S15). No MA was detected when FDCA was employed as substrate. Furthermore when a typical free radical inhibitor (5 mol% 2,6-di-*tert*-butyl-*p*-cresol) was added, both the oxidation process of

HMF and the products distribution were almost not affected (Table 1, entry 3), suggesting that the main reaction course might not be a free-radical one. From the oxidation products of HMF (or DFF), no FDCA was detected by both NMR and esterification method (ESI† pp. 10–14). These experiments showed that the aldehyde group of HMF was relatively stable under oxygen atmosphere, which was quite different from that of benzaldehyde. All these results above indicated that MA was probably not formed *via* decarboxylation reaction, *i.e.* the oxidation of HMF to MA did not involve DFF or FDCA as the key intermediate. The $VO(acac)_2$ catalyzed oxidation of HMF was quite different from those using Co/Mn/Br/Zr, Pt-based or Au-based catalytic systems.[5,7,8] In those examples, FDCA or its derivatives were often generated *via* further oxidation of the aldehyde group as proposed by the authors.

In contrast to DFF, MA was obtained in 24% yield when 5-(hydroxymethyl)furfuryl alcohol (HMFA) was oxidized. Furthermore, some products derived from C–C bond cleavage were also observed when the oxidation of furfuryl alcohol or 5-methylfurfuryl alcohol was performed respectively under the same reaction conditions. Thus the presence of aldehyde group was not necessary for C–C bond cleavage. If a mixture of HMFA and DFF (10 mol% HMFA and 90 mol% DFF) was subject to oxidation, only 4% yield of MA was detected, which showed that the presence of HMFA could not significantly promote the oxidation of DFF to MA either. Therefore, the formation of MA was related to the hydroxymethyl group of HMF itself rather than the aldehyde group.

In a HMF molecule, the aldehyde group and furyl ring forms a π-conjugated system, leaving the hydroxymethyl group out (Fig. 4). Calculation results indicate that the C–C bond [C(4)–C(7)] connecting the hydroxymethyl group is longer than [C(1)–C(6)] near the aldehyde group; thus it is more easily broken from C(4)–C(7). From a different standpoint, the carbon-oxygen bond [C(1)–O(5) or C(4)–O(5)] of HMF contains a σ bond and π bond and the corresponding bond length is between that of typical C–O and C═O bonds. Thus, the right part of HMF [O(5)–C(4)–C(7)–O(9)] can be viewed as a quasi α-hydroxy ketone. Catalytic oxidative C–C bond cleavage of typical α-hydroxy ketones by vanadium compounds has been demonstrated by J. M. Brégeault and T. Momose *et al.* before.[11] Therefore the inherent structure of HMF might account for the C–C bond cleavage from the C–C bond [C(4)–C(7)] connecting hydroxymethyl group.

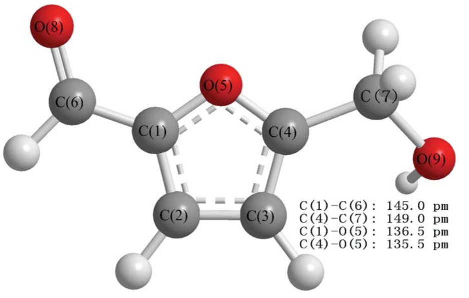
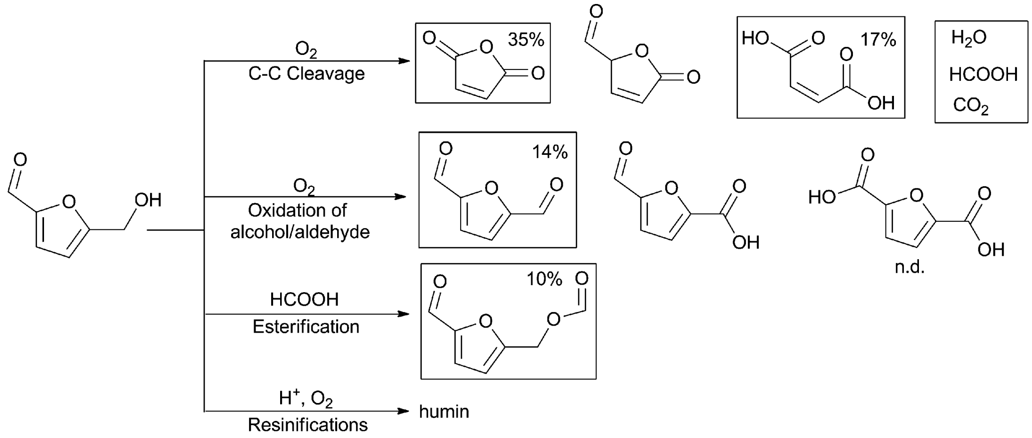


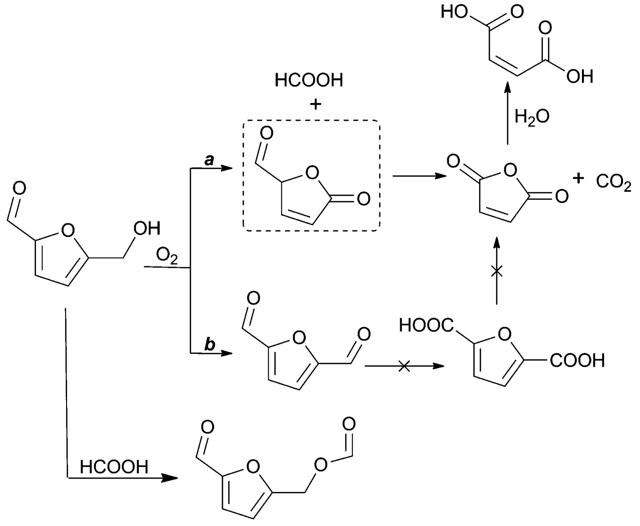
Fig. 4 Calculated bond lengths of HMF.

The other key issue is the distribution of products. In our recent report, HMF was converted to DFF in excellent yield under 0.1 MPa O_2.[14] The vanadium-catalyzed oxidation of HMF under high pressure of oxygen was quite different. The corresponding products *via* oxidation became complex due to the unique structure of HMF, which contains an aldehyde group, a hydroxymethyl group and a furyl ring. Some possible products were listed in Scheme 2. Besides MA and maleic acid, formic acid and carbon dioxide were detected as C1-products in this study, which further confirmed the C–C bond cleavage of HMF. About 14% of DFF was also obtained, which suggested that the oxidation of the hydroxymethyl group of HMF occurred at the same time as C–C bond cleavage. This agrees with the studies on vanadium-catalyzed oxidation of alcohols.[10,12] About 10% byproducts were mainly derived from the esterification of formic acid and HMF. Others (about 24%) were not detectable using GC. As mentioned above, though nearly 100% HMF was converted in CH_2Cl_2, most of HMF was transformed to a black resinous substance, which was almost insoluble in common solvents such as CH_2Cl_2, acetone or acetonitrile (ESI† Fig. S16). It was visible when CH_2Cl_2 was used, however we could not exclude the occurrence of similar products, which could not be detected by GC, in other solvents. Once formic acid was formed, diverse side reactions might be followed under the reaction conditions. This explanation was in accordance with the properties of furan compounds. Resinification of furfural or furfuryl alcohol in the presence of acid/oxygen is known.[9]



Scheme 2 Possible products from oxidation of HMF. (Those in boxes were determined to exist).

Based on the experiments mentioned above, we proposed a pathway for VO(acac)$_2$ catalyzed oxidation of HMF with molecular oxygen (Scheme 3). Both oxidation of hydroxymethyl group and C–C bond cleavage took place simultaneously. When the oxidation was performed under 0.1 MPa O_2, the oxidation of HMF to DFF prevailed (route b). In this work, the C–C bond adjacent to the hydroxymethyl group was easily broken under 1.0 MPa O_2 atmosphere; after the cleavage of C–C bond, a second α-hydroxy ketone might form on the other side *via* resonance (ESI† Fig. S9). Then further oxidation would lead to MA as the main product (route a). Oxidation of the hydroxymethyl group to an aldehyde group also occurred; however, DFF was relatively stable against further oxidation into FDCA or MA.



Scheme 3 Proposed reaction pathways for oxidation of HMF catalyzed by VO(acac)$_2$.

In summary, HMF was oxidized to maleic anhydride with molecular oxygen using VO(acac)$_2$ as catalyst in liquid phase. The C–C bond cleavage occurred due to the hydroxymethyl group of HMF itself rather than the aldehyde group. This work provides a possibility for the preparation of MA from biomass-based feedstocks *via* oxidation of HMF. Further study of this transformation is currently underway.

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Notes and references

‡ Acetonitrile contained 1% acetic acid.

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