DOI: 10.1002/cssc.201000273

Efficient Aerobic Oxidation of 5-Hydroxymethylfurfural to 2,5-Diformylfuran, and Synthesis of a Fluorescent Material

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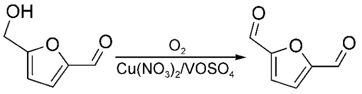
The present organic-chemical and polymer industries mainly depend on resources derived from fossil fuels.[1] Hence, the transformation of abundant biomass resources into chemicals is attractive from the viewpoint of sustainable chemistry.[2] Many efforts have recently been made to produce 5-hydroxymethylfurfural (HMF), which is viewed as a key platform chemical,[3] from carbohydrates. 2,5-Diformylfuran (DFF), one of the most important derivatives of HMF, is a furan dialdehyde, and various applications of DFF have been described, including its use as starting material for synthesis of the pharmaceuticals, macrocyclic ligands, and others.[4] Furthermore, it can be used as a monomer for preparation of many functional materials.[5] For example, Gandini and co-workers described a polymer of DFF and *ortho*-phenylenediamine,[5a] while Amarasekara et al. reported the synthesis and characterization of a 2,5-diformylfuran–urea resin.[5c] Thus, the direct conversion of HMF to DFF via selective oxidation is attractive and important.

Compared to methods that use a stoichiometric quantity of oxidant,[6] the catalytic oxidation of HMF to DFF by using molecular oxygen as terminal oxidant is an intriguing prospect, for both economical and environmental reasons. However, owing to the presence of both a furan ring and an aldehyde group in the molecule, the oxidation of HMF often involves many side reactions, for example, overoxidation, decarbonylation, and cross-polymerization. The efficient conversion of HMF into DFF via catalytic oxidation with molecular oxygen is a great challenge. Recently, much progress has been made in the development of catalytic systems, such as Co/Mn/Zr/Br,[7] Pt-Bi/C,[8] and vanadium-based catalysts.[9] Carlini et al. reported an HMF conversion of 84% and a DFF selectivity of 97% with vanadyl phosphate as catalyst, at 150 °C.[9b] Corma and co-workers designed immobilized vanadyl–pyridine complexes; 82% HMF conversion was achieved, with DFF 99% selectivity, at 130 °C.[9c] These works have provided us with important information concerning the selective oxidation of HMF to DFF. In particular, a good selectivity for DFF can be achieved by using vanadium-catalyzed systems.[9] However, more efficient and economical catalytic systems, especially for use in mild conditions, remain to be developed. In essence the conversion of HMF to DFF can be viewed as the oxidation of a heteroaromatic alcohol. We have recently disclosed several vanadium-based catalytic systems for the oxidation of benzyl alcohols with molecular oxygen.[10] Based on these results, we report herein a homogenous catalytic system, $Cu(NO_3)_2/VOSO_4$, that oxidizes HMF to DFF in a facile manner, with good yields under mild conditions (Scheme 1).



Scheme 1. Oxidation of HMF to DFF.

Vanadium compounds are widely used for the catalytic oxidation of organic compounds: the V^{IV}/V^{V} redox cycle is often proposed during the catalytic oxidation of alcohols with molecular oxygen.[11, 12] Because $Cu(NO_3)_2$ is a strong oxidant, its use to assist the formation of V^{V} species during oxidation with molecular oxygen is interesting. We chose $VOSO_4$ as vanadium source because of its unique performance during catalytic oxidation of benzyl alcohols.[10]

Neither $Cu(NO_3)_2$ nor $VOSO_4$ alone exhibited a high efficiency towards the catalytic oxidation of HMF, as shown in Table 1, entries 1 and 2. Under the same conditions, HMF conversion was enhanced remarkably when $Cu(NO_3)_2$ and $VOSO_4$ were used in combination (entries 3–5). An HMF conversion of up to 99%, with 99% DFF selectivity, could be obtained within 1.5 h by using only 2 mol% $Cu(NO_3)_2/VOSO_4$ (1:1 molar ratio) as the catalyst (entry 3). When the oxidation was carried out with less catalyst (catalyst/HMF = 0.005), a high conversion of HMF into

Table 1. Aerobic catalytic oxidation of HMF.[a]

Entry	Catalyst	Molar ratio catalyst/HMF	T [°C]	t [h]	Conversion [mol%]	Selectivity[b] [mol%]
1	$Cu(NO_3)_2$	0.02	80	1.5	trace	–
2	$VOSO_4$	0.02	80	1.5	10	31
3	$Cu(NO_3)_2/VOSO_4$	0.02	80	1.5	99 (96)	99
4	$Cu(NO_3)_2/VOSO_4$	0.005	80	5	99	99
5	$Cu(NO_3)_2/VOSO_4$	0.02	RT[c]	48	99	99

[a] Reaction conditions: 10 mmol HMF, molar ratio Cu/V = 1, 0.1 MPa O_2, 5 mL acetonitrile. The value in parenthesis is the isolated yield of DFF. [b] Selectivity towards DFF. [c] Room temperature.

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Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201000273.

DFF could still be achieved after 5 h (entry 4). The oxidation even proceeded at room temperature, and good results were obtained after a reaction time of 48 h (entry 5). In addition to the use of mild reaction conditions and the high efficiencies achieved, the inorganic catalyst could also be easily removed after oxidation, rendering this process rather attractive.

Further studies showed that DFF remained stable under the oxidative conditions employed. After complete conversion of the HMF after 1.5 h, the selectivity of the reaction towards DFF was still nearly 99 % even after prolonging the reaction time to 5 h (Figure 1). 2,5-Furandicarboxylic acid was not detected by NMR analysis. However, HMF conversions of only 21–78 % were achieved when $Ni(NO_3)_2$, $Co(NO_3)_2$, $Ce(NO_3)_3$, $NaNO_3$, or $Fe(NO_3)_3$ was employed instead of $Cu(NO_3)_2$, even after 5 h under 0.5 MPa O_2. Thus, the combination of $VOSO_4$ with $Cu(NO_3)_2$ was the most effective one among the tested metal nitrates (see Supporting information, Figure S1). The type of vanadium compound had a strong effect on the HMF oxidation reaction, also. The combination of $VOSO_4$ and $Cu(NO_3)_2$ appears to exhibit a unique chemistry: $VOSO_4$ showed a much higher efficiency than $NaVO_3$, $VOPO_4$, $VO(OEt)_3$, $VO(acac)_2$, and $VO(pic)_2$ [bis(pyridine-2-carboxylato)oxo-vanadium(IV)]. The HMF conversions were lower than 33 % when the vanadium compounds mentioned above were used (Table S1). Similar observations were described in previous reports on the catalytic oxidation of alcohols.[10] Notably, $Cu(NO_3)_2/VOCl_3$ was also effective towards the catalytic oxidation of DFF (Table S1, entries 3 and 4). Moreover, 85 % HMF conversion and 97 % DFF selectivity were achieved when the reaction time was prolonged to 3 h. This result indicates that the initial valence of vanadium (IV or V) is not a crucial factor.

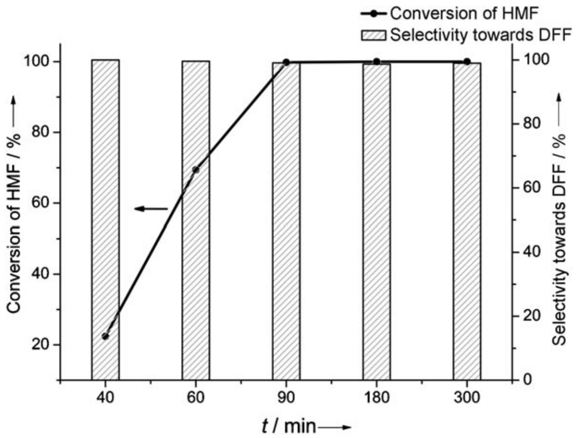


Figure 1. Time course of the reactions. Conditions: 10 mmol HMF, 0.2 mmol $VOSO_4$, 0.2 mmol $Cu(NO_3)_2$, 0.1 MPa O_2, 5 mL acetonitrile, 80 °C.

We carried out the oxidation reaction with a stoichiometric amount of $VOSO_4$ or $VOCl_3$ under a nitrogen atmosphere (Scheme S1). $VOSO_4$ by itself was not an active oxidant for the direct oxidation of HMF to DFF: no oxidation of HMF was observed. In contrast, HMF was nearly completely converted and a DFF yield of 46 % was achieved when 1 equiv $VOCl_3$ was stirred with HMF for 5 h, even at RT (about 44 % of byproducts was formed, owing to chlorination). These results suggest that HMF is oxidized to DFF directly by a V^V species, rather than $VOSO_4$.[13]

V^V species were formed under the employed reaction conditions, although initially V^{IV} in the form of $VOSO_4$ was used. We applied UV/Vis spectroscopy to detect the V^V species after chelation.[14] V^{IV}, Cu^{II}, and NO_3^- species do not interfere with this detection method. Firstly, $VOSO_4$ and $Cu(NO_3)_2$ were stirred in acetonitrile under an O_2 atmosphere in the absence of HMF. The $Cu(NO_3)_2/VOSO_4$ reaction mixture was then pretreated with 4-(2-pyridylazo)resorcinol (PAR), iodo-nitro-tetrazolium chloride (INT), and 1,2,-diaminocyclohexane-*N*,*N*,*N′*,*N′*-tetra-acetic acid (CDTA), and examined by UV/Vis spectroscopy (see Supporting information). In acetonitrile, the absorption band of PAR appears at ca. 385 nm, and is assigned to a π-π^* electronic transition. After adding the $Cu(NO_3)_2/VOSO_4$ reaction mixture a new absorption band appeared at ca. 552 nm (Figure 2), characteristic of complex of V^V with PAR and INT.[14]

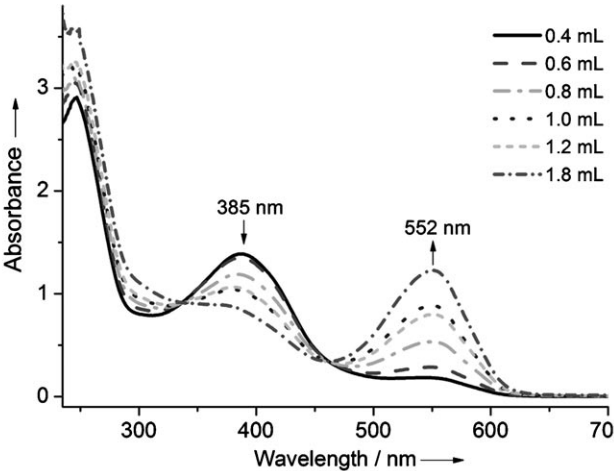
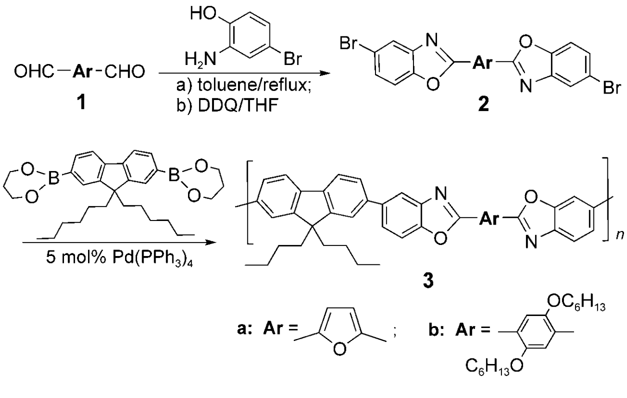


Figure 2. UV/Vis spectra after treating the $Cu(NO_3)_2/VOSO_4$ reaction mixture with different volumes of $Cu(NO_3)_2/VOSO_4$ reaction mixture.

All spectra intersected at ca. 460 nm, forming a clear isosbestic point and suggesting that only one new species is formed. No absorption band was observed around 552 nm when $VOSO_4$ or $Cu(NO_3)_2$ was treated with the same procedure (Figure S7 and S8). ^{51}V NMR provided additional evidence for the existence of V^V species. Because V^{IV} is paramagnetic, mononuclear V^{IV} species cannot be detected by ^{51}V NMR.[15] No ^{51}V NMR signal was apparent from the $VOSO_4$ sample (Figure S9). In contrast, the $Cu(NO_3)_2/VOSO_4$ reaction mixture exhibited strong ^{51}V NMR signals (Figure S10). All of these results indicate that a V^{IV}/V^V redox cycle is probably involved, consistent with previous reports on vanadium-catalyzed oxidation of alcohols with molecular oxygen.[12] The $Cu(NO_3)_2$ facilitates the generation of V^V species from $VOSO_4$. This may explain the enhanced performance of $Cu(NO_3)_2/VOSO_4$ even under mild conditions.

The ease of DFF production from HMF prompted us to explore the furan counterpart of related, important polymers, such as fluorescent materials.[16] One potential application is to transform the aldehyde group into benzoxazole, a heterocyclic ring that is often seen in thermally stable rigid-rod polymers and optical materials.[17] Thus, the reaction of DFF with 2-amino-4-bromophenol afforded the benzoxazole dibromide **2**, which then underwent Suzuki coupling[18] with 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) to afford the polymer **3a** (Scheme 2; $M_w = 5077$, PDI = 1.3, Figure S11). A THF solution of the polymer exhibited an absorption maximum $\lambda_{max} = 366$ nm, and strong blue fluorescence (emission peak $\lambda_{em} = 462$ nm and quantum yield $\phi_{fl} = 0.57$; Figure 3). In comparison with its isoelectronic structure **3b** ($\lambda_{max} = 329$ and 381 nm; $\lambda_{em} = 425$ and 449 nm),[17b] the emission of the furan derivative **3a** is at longer wavelength and significantly broader, revealing the notable effect of the furan moiety on the electronic band structure and optical characteristic of π-conjugated materials.



Scheme 2. Synthesis of polymer **3a**.

In summary, we report a highly efficient catalytic system consisting of $Cu(NO_3)_2/VOSO_4$. HMF is oxidized to DFF in high yield with molecular oxygen under mild conditions. As an example, DFF was used as dialdehyde for the synthesis of a blue-emitting fluorescent material. The potential applications of DFF remain to be explored and the detailed catalytic mechanism also needs to be further studied.

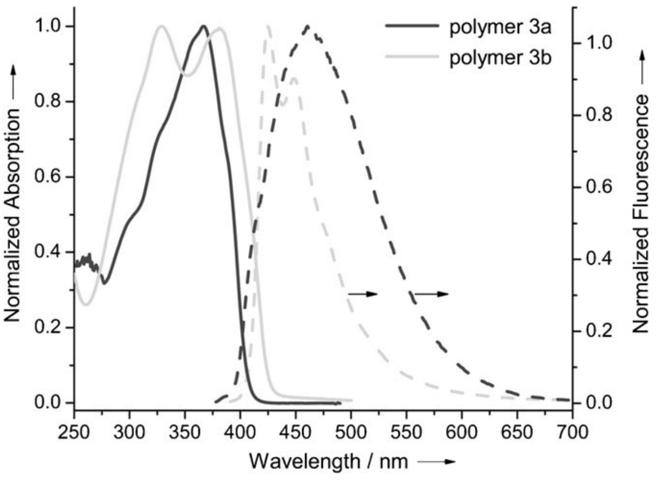


Figure 3. UV/Vis absorption (solid lines) and fluorescence (dashed lines) of **3** in THF.

Experimental Section

Typical procedure for HMF oxidation (Table 1, entry 3): Vanadyl sulfate (34.3 mg, 0.2 mmol), cupric nitrate trihydrate (48.3 mg, 0.2 mmol), and HMF (1.26 g, 10 mmol) were charged into a 50 mL autoclave, and acetonitrile (5 mL) was added. After the autoclave was closed, oxygen was added (0.1 MPa). The autoclave was then was heated to 80 °C within ca. 20 min. The reaction temperature was maintained at 80 °C for 1.5 h. Oxygen was recharged if consumed during the oxidation. The autoclave was cooled to room temperature and depressurized carefully. A sample of the reaction mixture was taken for GC analysis. Conversion and selectivity were determined based on area normalization without any purification. Crucial data were reconfirmed by NMR (Figure S3 and S4). Products were confirmed by GC-MS, NMR, and by comparison of their GC retention times with those of authentic samples. When GC showed that the conversion of HMF was more than 99 %, acetonitrile was removed by rotary evaporator after filtration. The crude product was purified by chromatography on silica gel using ethyl acetate and petroleum (3:5) as eluant. DFF was obtained as white solid (1.19 g, yield 96 %). ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K): $\delta = 9.82$ (2H), 7.68 ppm (2H); ^{13}C NMR: $\delta = 122.10$, 153.66, 180.73 ppm.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (projects 20736010 and 20803074).

Keywords: biomass · fluorescence · oxidation · polymers · vanadium

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Received: August 25, 2010
Revised: October 12, 2010