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Promoted role of Cu(NO₃)₂ on aerobic oxidation of 5-hydroxymethylfurfural to

2,5-diformylfuran over VOSO₄

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Highlights

➢ The essential role of Cu(NO₃)₂ how to activate VOSO₄ is investigated.

➢ The role of Cu²⁺ cation on high 2,5-diformyfuran selectivity is discussed.

➢ Solvent polarity depended 2,5-diformyfuran selectivity is observed.

➢ Kinetic studies have been done to evaluate the possible reaction mechanism.

Abstract

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The promoted effect of $Cu(NO_3)_2$ on aerobic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-diformylfuran (DFF) catalyzed by $VOSO_4$ in acetonitrile was intensively investigated. It was revealed that $Cu(NO_3)_2$ facilitated the activation of $VOSO_4$ to generate active V^{5+} species via the generation of NO_x gas. The high DFF selectivity is ascribed to Cu^{2+} cation which can effectively prohibit oxidative C-C bond cleavage reaction of HMF and prevent radical reaction of DFF to humins. In addition, the polarity of solvent plays a great role on high selectivity of DFF.

Keywords: Catalysis; Copper nitrate; 2,5-Diformylfuran; Oxidation; Sustainable chemistry

1. Introduction

Catalytic conversion of renewable biomass resources to value-added chemicals is significant for sustainable chemistry [1]. 5-Hydroxylmethylfurfural (HMF), a versatile biomass-derived platform chemical, can be obtained by dehydration of carbohydrates in the presence of acid catalysts [2]. A growing interest has been devoted to catalytic transformation of HMF to valuable chemicals in the past few years [3]. 2,5-Diformylfuran (DFF), via selective oxidation of HMF, indeed finds applications as intermediate for pharmaceuticals, macrocyclic ligands and others [4]. Moreover, DFF gained interests as a monomer for synthesis of functional materials [5]. For example, a fluorescent material, furan-based imine-linked porous organic frameworks and a 2,5-diformylfuran-urea resin have been synthesized using DFF as the key monomer.

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However, owing to the presence of both a furan ring and an aldehyde group in the molecule, the oxidation of HMF to DFF often involves many side reactions, for example, overoxidation to 5-hydroxymethyl-2-furancarboxalic acid or 2-formyl-5-furancarboxylic acid or 2,5-furandicarboxalic acid, oxidative C-C bond cleavage, decarbonylation, and cross-polymerization. Therefore, it is challenging to convert HMF into DFF with high selectivity via catalytic oxidation with molecular oxygen as oxidant. Recently, great effort has been made in selective aerobic oxidation of HMF to DFF and a number of catalytic systems have been developed. The catalytic systems include Co/Mn/Zr/Br [6], Ru-based catalysts [7], TEMPO/Cu(I) and $Fe_3O_4@SiO_2$–TEMPO catalysts [8], and Mn-based catalysts [9]. It was reported that vanadium-based catalysts were active in the oxidation of alcohols [10] and have been explored for the oxidation of HMF to DFF [11]. For example, vanadyl phosphates have been investigated by Carlini et al. and an HMF yield of 84% with DFF selectivity of 97% was achieved in dimethyl sulfoxide (DMSO) at 150 ^{o}C [11h]. Immobilized vanadyl-pyridine complexes reported by Corma and co-workers gave >99% selectivity of DFF at HMF conversion of 82% in triflurotoluene at 130 ^{o}C [11g]. A reaction selectivity towards DFF of >99% at 84% HMF conversion was obtained with V_2O_5/H-beta catalyst in DMSO at 125 ^{o}C [11a].

Recently, our group reported a highly efficient catalyst system consisting of $Cu(NO_3)_2$/$VOSO_4$, and 99% DFF selectivity at 99% HMF conversion was obtained in acetonitrile at 80 ^{o}C [5a].We found that $VOSO_4$ alone was nearly inactive in the oxidation of HMF to DFF. Interestingly, with the addition of $Cu(NO_3)_2$, conversion of

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HMF and selectivity for DFF were both remarkably enhanced with nearly quantitative conversion of HMF to DFF under mild conditions. The promoting effect of $Cu(NO_3)_2$ is still unclear. Herein, the essential role of the $Cu(NO_3)_2$ for high activity and selectivity in the oxidation of HMF to DFF catalyzed by $VOSO_4$ in acetonitrile was investigated in detail. Moreover, the polarity of solvent plays a great role on selectivity of DFF. Kinetic studies are also carried out to establish a detailed reaction mechanism.

2. Experimental

2.1. Materials

HMF was purchased from Wutong Aroma Chemicals Co. Ltd. $Cu(NO_3)_2 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $NaNO_3$, $Fe(NO_3)_3 \cdot 9H_2O$, toluene, dichloromethane, *n*-butanol, *iso*-propyl alcohol (IPA), tetrahydrofuran (THF), ethanol, methanol, acetonitrile, DMSO and *N,N*-dimethyl formamide (DMF) were from Tianjin Kermel Chemical Reagent Development Center, China. Acrylonitrile was from Tianjin Guangfu Fine Chemical Research Institute. Benzonitrile (Chemical Purity), *tert*-butyl hydroperoxide and hydroquinone were from Sinopharm Chemical Reagent Co. Ltd. $VOSO_4 \cdot xH_2O$ was from Shanghai Lvyuan Fine Chemical Co. Ltd. 4-(2-pyridylazo)resorcinol (PAR), iodo-nitro-tetrazolium chloride (INT), 1,2,-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (CDTA), sodium acetate, 2,6-di-*tert*-butyl-*p*-cresol and azodiisobutyronitrile were obtained from Aladdin Chemistry Co. Ltd. Acetonitrile was HPLC grade. A trace amount of water in acetonitrile was removed by using 4A molecular sieve.

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$VOSO_4 \cdot xH_2O$ (USP28) was dried at 120 ^{o}C overnight. Other reagents were analytic grade unless otherwise specified and used as received.

2.2. Reaction system and analysis method

The aerobic oxidation of HMF was carried out in a 50-mL stainless steel autoclave equipped with a magnetic stirrer, a pressure gauge and automatic temperature control apparatus. Typically, $VOSO_4$ (0.2 mmol, 34.3 mg), $Cu(NO_3)_2 \cdot 3H_2O$ (0.2 mmol, 48.3 mg) and HMF (10 mmol, 1.26 g) were put into the autoclave with Teflon lining, followed by 5 mL acetonitrile. After the autoclave was closed, oxygen was added (0.1 MPa). The autoclave was then heated to 80 ^{o}C within ca. 20 min. The reaction temperature was maintained at 80 ^{o}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, which were conducted on Agilent GC 7890D equipped with 19095J-323 capillary column (30 m × 530 μm × 1.5 μm) and a flame ionization detector. The quantitative results were based on the internal standard method using mesitylene as internal standard. The results reported as conversion and selectivity are expressed in mol% based on the total HMF intake.

2.3. Detection of NO_x by MS

Mass spectra were performed on a mass analyzer (Thermal Star, GSD 320, Germany) with argon flow of 50 mL·min^{-1}.

Sample: To a 20 mL sealed sample vial equipped with a magnetic stirring, 1 mmol $VOSO_4$ and 1 mmol $Cu(NO_3)_2$ were added. The sealed sample vial was kept at

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ambient temperature with stirring. The reaction was stopped after 1.5 h, and the mass

spectra of the afforded NO_x were recorded.

2.4. Detection of V^{5+} species by UV-vis

The UV-vis spectrum was recorded on a SHIMADZU UV-2550 spectrometer

with quartz cells at 298 K. The reference cell was filled with the same concentration

of CDTA and pH 5.6 buffer solutions. Wavelength range: 190-900 nm.

Sample: for reaction mixture: 0.2 mmol $VOSO_4$, 5 mL acetonitrile charged with

NO_x generated from the mixture of $VOSO_4$ and $Cu(NO_3)_2$, 80 ^{o}C, 0.1 MPa O_2, 1.5 h.

Then cooled to room temperature and diluted to 25 mL with acetonitrile.

Coordination process: 1 mL diluted mixture, 2 mL 0.125 M aqueous solution of

CDTA, 2 mL pH 5.6 buffer of acetate, 1 mL 2×10^{-3} M aqueous solution of PAR, 0.5

mL 3×10^{-3} M acetonitrile solution of INT, then dilute to 25 mL with acetonitrile.

After developing color 15 min, UV-vis spectrum was recorded.
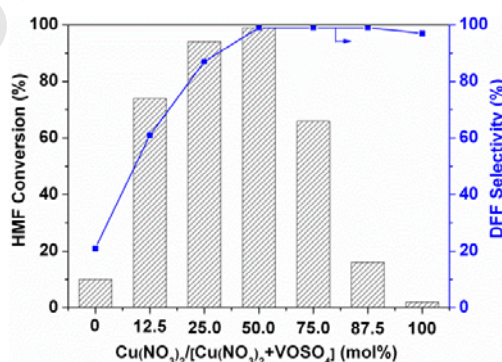
3. Results and Discussion

3.1. The role of $Cu(NO_3)_2$

Fig. 1. The effect of molar ratio of $Cu(NO_3)_2$ on the HMF conversion and DFF

selectivity. Reaction conditions: 10 mmol HMF, 0.4 mmol catalysts, 5 mL solvent, 80

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^{o}C, 0.1 MPa O_2, 1.5 h.

As shown in Fig. 1, the molar ratio of $Cu(NO_3)_2$ to $Cu(NO_3)_2$ and $VOSO_4$ apparently influenced the reactivity and selectivity. With increase of the molar ratio of $Cu(NO_3)_2$, the conversion of HMF firstly increased and then decreased after the molar ratio of $Cu(NO_3)_2$ was up to 50.0%. Whereas, the selectivity display another behaves. High selectivity could maintain when $Cu(NO_3)_2$ was the major composition. The selectivity gradually decreased with further increasing the amount of $VOSO_4$. These results revealed that $Cu(NO_3)_2$ could effectively prohibit the side reactions and thus obtaining high DFF selectivity. The optimization of molar ratio of $Cu(NO_3)_2$ to $VOSO_4$ is 1, and at this point the conversion of HMF and selectivity for DFF were up to more than 99%. Lower than 10% HMF conversion was observed when solely $VOSO_4$ or $Cu(NO_3)_2$ was used. This suggested that neither $VOSO_4$ nor $Cu(NO_3)_2$ was the active species.
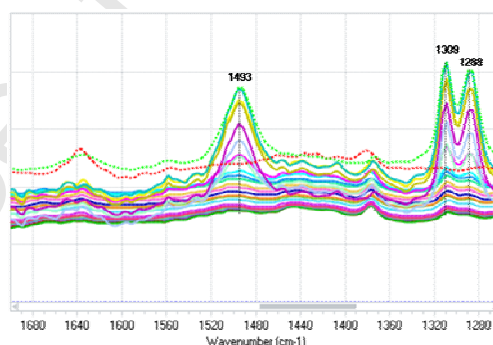

Fig. 2. Interaction between $Cu(NO_3)_2$ and $VOSO_4$ characterized by *in situ* FT-IR. Reaction conditions: 0.2 mmol $Cu(NO_3)_2$, 0.2 mmol $VOSO_4$, 5 mL CH_3CN, room temperature, 0.1 MPa O_2, 10 h. Red dotted line is standard $VOSO_4$, green dotted line is standard $Cu(NO_3)_2$.

In our previous paper, it was demonstrated that V^{5+} species were the active

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species which could directly oxidize HMF to DFF. However, in the catalytic system of $Cu(NO_3)_2/VOSO_4$, the initial vanadium species are V^{4+}. This indicates that the V^{5+} species were firstly formed mediated by $Cu(NO_3)_2$. In order to make sure how $Cu(NO_3)_2$ facilitates the V^{5+}/V^{4+} redox cycle, we investigated the interaction between $Cu(NO_3)_2$ and $VOSO_4$ using *in situ* Fourier transform infrared (FT-IR) (Fig. 2). When $Cu(NO_3)_2$ and $VOSO_4$ were mixed together in CH_3CN, the colour of the solution changed from blue to brown. Simultaneously, the decrease of the intensity of the characteristic peaks of $Cu(NO_3)_2$ at 1493, 1309 and 1288 cm^{-1} was clearly observed. This suggested that $Cu(NO_3)_2$ may gradually decompose and NO_x gas occur even at room temperature. In order to confirm this hypothesis, we then mixed $VOSO_4$ and $Cu(NO_3)_2$ under solid state. Again, we found that brown gas generated when equivalent molar of $VOSO_4$ was mixed with $Cu(NO_3)_2$ at room temperature under air atmosphere (Fig. S1a, supporting information). Whereas, $Cu(NO_3)_2$ is stable when it is stirred under the same conditions (Fig. S1b, supporting information).

Subsequently, the brown gas was characterized by mass spectrometry (MS). The peaks with m/z of 30, 44 and 46 were detected by MS (Fig. S2, supporting information). The peak intensity ratio of 30 to 46 is much higher than that of pure NO_2 (Fig. S3, supporting information). Also, the intensity of 44 of the brown gas is much higher than that of air (Fig. S4, supporting information). It is probably that NO and N_2O could not be excluded from the components of the in situ formed NO_x gas. However, it was believed that NO can quickly convert to NO_2 under air atmosphere even at room temperature. It seems that it is enigmatical that NO existed in the brown

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gas generated from $Cu(NO_3)_2$ and $VOSO_4$ under air atmosphere. Hence, the brown gas was further characterized by FT-IR (Fig. S5, supporting information). Four Typical bands of NO_2 centred at 2918, 2812, 1628 and 1601 cm^{-1} were detected.[12] Another absorption band at 1806 cm^{-1} associated with nitroso stretch is approximate to that of N_2O_3 which could decompose into NO and NO_2.[13] N_2O_3 with m/z of 76 was not detected by mass spectroscopy could arise from that N_2O_3 is unstable under MS detection conditions and may degrade to NO and NO_2 during the analysis process.
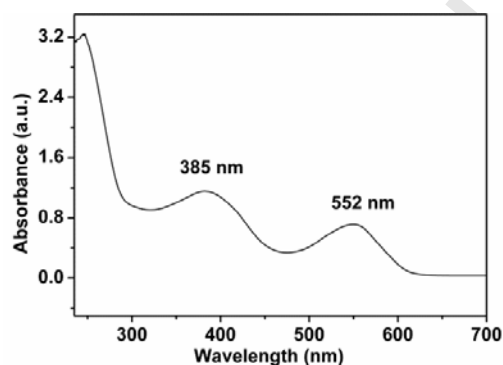

Fig. 3. Detection of V^{5+} species using UV-vis spectroscopy.

It is well-known that NO_x is oxidative gas [14]. The V^{5+} species may be formed from the oxidation of $VOSO_4$ by NO_x. In previous work, we have shown that the UV-vis spectroscopy could detect the V^{5+} species after chelation [5a]. In order to further confirm whether this brown gas derived from the interaction of $Cu(NO_3)_2$ and $VOSO_4$ could oxidize $VOSO_4$ to V^{5+} species, we directed the brown gas into the acetonitrile solution of $VOSO_4$ and treated the mixture under the reaction conditions, followed by pretreating with chelating agents of PAR and INT in the presence of masking agent CDTA to detect by UV-vis spectroscopy (Fig. 3). The peak at ca. 385 nm is assigned to a π-π* electronic transition of PAR. A new absorption band

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appeared at ca. 552 nm which is characteristic of complex of V^{5+} with PAR and INT

[15]. The above results suggest that the brown gas derived from the interaction of

$Cu(NO_3)_2$ and $VOSO_4$ can oxidize $VOSO_4$ to V^{5+} species, thus realizing the V^{5+}/V^{4+}

redox cycle. To verify the obtained V^{5+} species can oxidize HMF to DFF, control

experiment was performed under the same reaction conditions. A 97% conversion of

HMF with 92% selectivity for DFF was obtained in the presence of $CuSO_4$, which is

comparable to that of $Cu(NO_3)_2/VOSO_4$ catalytic system.

Table 1 Oxidation of HMF catalyzed by $VOSO_4$.[a]

Entry	Metal nitrate	Conversion (%)	Selectivity [b] (%)
1	-	24	12
2	$Cu(NO_3)_2$	99	99
3	$Ce(NO_3)_3$	11	27
4	$Ni(NO_3)_2$	13	33
5	$Mn(NO_3)_2$	20	58
6	$Co(NO_3)_2$	22	75
7	$NaNO_3$	30	11
8	$Fe(NO_3)_3$	34	51

[a] Reaction conditions: 0.2 mmol $VOSO_4$, 0.2 mmol metal nitrate, 10 mmol HMF,

5 mL CH_3CN, 80 $^{\circ}C$, 0.1 MPa O_2, 1.5 h. Conversion and selectivity were determined

by GC using mesitylene as internal standard. For $Mn(NO_3)_2$, 50% aqueous solution

was used. [b] Selectivity for DFF.

As have been demonstrated above, $Cu(NO_3)_2$ played a vital role in catalytic

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performance. The addition of $Cu(NO_3)_2$ not only increased the activity but also the DFF selectivity (Table 1, entry 2). When other metal nitrate such as $Ce(NO_3)_3$, $Ni(NO_3)_2$, $Mn(NO_3)_2$, $Co(NO_3)_2$, $NaNO_3$, or $Fe(NO_3)_3$ was employed instead of $Cu(NO_3)_2$, they show lower activity and selectivity under the same reaction conditions. HMF conversions were only 11-34% with 11-75% selectivity for DFF (Table 1, entries 3-8). It has been demonstrated that $VOSO_4$ can promote $Cu(NO_3)_2$ degradation to NO_x which oxidized V^{4+} species to V^{5+} active species. The UV-vis results implied that other tested metal nitrate could not degrade to NO_x in the presence of $VOSO_4$ under the same conditions (Fig. S6, supporting information). These should account for lower activity for other tested metal nitrate than that of $Cu(NO_3)_2$.
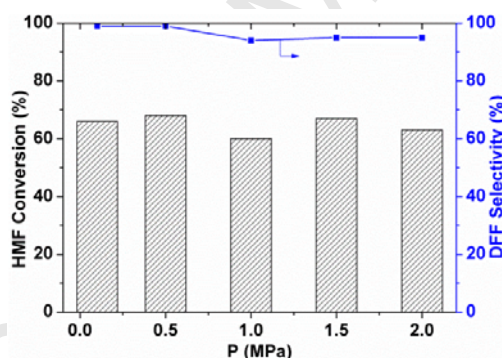

Fig. 4. The dependence of HMF conversion and DFF selectivity on O_2 partial pressure. Reaction conditions: 10 mmol HMF, 0.2 mmol $VOSO_4$, 0.2 mmol $Cu(NO_3)_2$, 5 mL CH_3CN, 80 ^{o}C, 50 min.

The effect of O_2 pressure on the HMF conversion and DFF selectivity was further examined (Fig. 4). When the O_2 pressure increased from 0.1 to 2.0 MPa, the HMF conversions were about 60% after 50 min, indicating that the reaction was not controlled by an oxygen mass-transfer process. Furthermore, O_2 pressure showed little effect on the DFF selectivity. Over 94% selectivity of DFF were obtained in the range

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of O_2 pressure tested. The phenomena are very different from our previous study that vanadium catalyzed oxidative cleavage of HMF to maleic anhydride (MA) is very sensitive to partial oxygen pressure. The yield of MA increased with increasing partial oxygen pressure [16]. In the absence of $Cu(NO_3)_2$, only 7% DFF selectivity at 94% HMF conversion was obtained under 1.0 MPa O_2 pressure. In order to easily examine the by-products via gas chromatography-mass spectrometry (GC-MS), the obtained reaction mixture was followed treatment with methanol catalyzed by $BF_3 \cdot (Et)_2O$. The main by-products are dimethyl fumarate, monomethyl maleate, dimethyl maleate and maleic anhydride. Other by-products, such as methyl glycolate, dimethyl oxalate, dimethyl malonate, methyl levulinate and dimethyl succinate were also examined (Fig. S7, supporting information). These results indicated that Cu^{2+} cation can effectively prohibit oxidative C-C bond cleavage of HMF.

Table 2 Influences of catalyst systems and additives on DFF stability. [a]

Entry	Catalyst	Copper salts	Additive	Recovery (%)
1	-	-	-	99
2	$VOSO_4$	-	-	74
3[b]	$VOSO_4$	-	-	35
4	-	$Cu(NO_3)_2$	-	99
5	$VOSO_4$	$Cu(NO_3)_2$	-	98
6	$VOSO_4$	$CuSO_4$	-	97
7	$VOSO_4$	-	ADBN[c]	69

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8	VOSO$_4$	-	TBHP[d]	67
9	VOSO$_4$	-	BQ[e]	98
10	VOSO$_4$	-	DTBP[f]	99

[a] Reaction conditions: 0.1 mmol VOSO$_4$, 0.1 mmol copper salt, 0.25 mmol additive, 5 mmol DFF, 5 mL CH$_3$CN, 80 $^{\circ}$C, 0.1 MPa O$_2$, 3 h. Conversion and selectivity was determined by GC using mesitylene as the internal standard. [b] 1.0 MPa O$_2$ was used. [c] ADBN: Azodiisobutyronitrile. [d] TBHP: Tert-butyl hydroperoxide. [e] BQ: Benzoquinone. [f] DTBP: 2,6-Di-tert-butyl-p-cresol.

It was reported that Cu^{2+} cation is an excellent carbon radical trapper frequently used in oxidation reactions [17]. We then investigated the stabilization of DFF by Cu^{2+} cation. DFF can keep stable in the absence of catalysts. 99% DFF recovery was obtained (Table 2, entry 1). Only 74% DFF recovery was achieved in the presence of VOSO$_4$ (Table 2, entry 2). Under more severe conditions, DFF is more likely to convert to by-products (Table 2, entry 3). In contrast, nearly quantitative recovery of DFF were obtained in the presence of cupric salts whether with or without VOSO$_4$ (Table 2, entries 4-6).
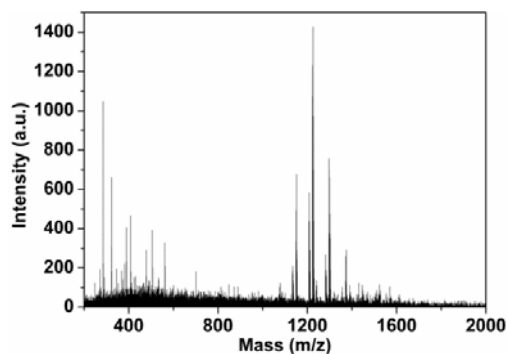

Fig. 5. MALDI TOF mass spectrum of humins derived from DFF (Table 2, entry 3).

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It is well known that furan derivatives, such as furfuryl alcohol and furfural are likely to cross-link by radical reaction to form soluble or insoluble humins in the presence of metal salts even under the ambient conditions. The HMF oxidation product of DFF, bearing reactive furan ring and aldehyde group, may be unstable in the presence of catalysts owing to the radical reactions. The recovery of DFF further decreased when free radical initiator such as azodiisobutyronitrile or tert-butyl hydroperoxide was added (Table 2, entries 7 and 8). While, nearly quantitative recovery of DFF was obtained in the presence of radical inhibitor such as benzoquinone or 2,6-di-tert-butyl-p-cresol (Table 2, entries 9 and 10). MALDI TOF mass spectrum of the products derived from DFF demonstrates that humins was formed via radical reaction (Fig. 5). Further comparison was examined between DFF and the humins derived from DFF by FT-IR spectroscopy (Fig. S8, supporting information), it shows an 8 cm^{-1} red shift of the C=O stretching vibrational absorption in the humins, and the absorption of furan rings was unconspicuous, implying that polymerization between furan rings occurred. These results confirmed that free radical reaction was the main side reaction and Cu^{2+} cation can inhibit the free radical reaction, thus achieving high DFF selectivity. These phenomena were also observed by Yin et al. in the aerobic oxidation of furfural to maleic acid [18].

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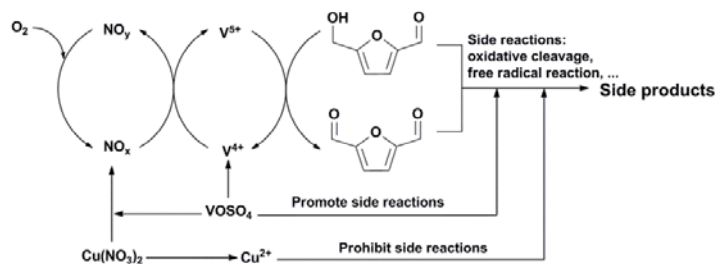
Scheme 1 Promoted role of $Cu(NO_3)_2$ on aerobic oxidation of HMF to DFF catalyzed by $VOSO_4$.

Based on the above results, the role of $Cu(NO_3)_2$ is more clear. Firstly, with the assistance of $VOSO_4$, $Cu(NO_3)_2$ was degraded to NO_x, which subsequently oxidized $VOSO_4$ to active V^{5+} species to further oxidize HMF to DFF. Secondly, Cu^{2+} cation can effectively prohibit oxidative C-C bond cleavage of HMF and prohibit radical reaction to keep high DFF selectivity under the reaction conditions. Promoted effect of $Cu(NO_3)_2$ on aerobic oxidation of HMF to DFF catalyzed by $VOSO_4$ was summarized in Scheme 1.
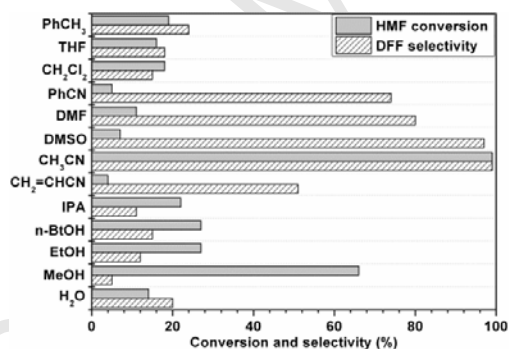
3.2. Solvent effect

Fig. 6. The dependence of HMF conversion and DFF selectivity on solvent. Reaction conditions: 10 mmol HMF, 0.2 mmol $VOSO_4$, 0.2 mmol $Cu(NO_3)_2$, 5 mL solvent, 80 ^{o}C, 0.1 MPa O_2, 1.5 h.

As shown in Fig. 6, the solvent has significant influence on the reactivity of HMF and the selectivity of DFF. Acetonitrile shows the best performance among the solvents tested with different polarity (described quantitatively by $E_T(30)$ [19] with unit of kcar mol^{-1}), including toluene (33.9), THF (37.4), dichloromethane (40.7), benzonitrile (41.5), DMF (43.2), DMSO (45.1), acetonitrile (45.6), acrylonitrile (46.7),

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IPA (48.4), n-butanol (49.7), ethanol (51.9), methanol (55.4) and water (63.1). Over

99% HMF conversion and DFF selectivity are achieved in acetonitrile.

The dependence of DFF selectivity on the solvent polarity is also studied (Fig. 7).

It seems that solvents with medium polarity ($E_T(30)$ is close to 46 kcar mol^{-1}) could

keep high selectivity of DFF. Poor selectivity is observed in solvent with too low or

strong polarity. This suggested that DFF selectivity was very closely related to the

solvent polarity. In order to further verify the hypothesis, mixed solvents of

acetonitrile/toluene (v/v = 4) and acetonitrile/acrylonitrile (v/v = 4) with polarity of

43.3 and 45.8 were tested, and moderate DFF selectivity of 86% and 88% were
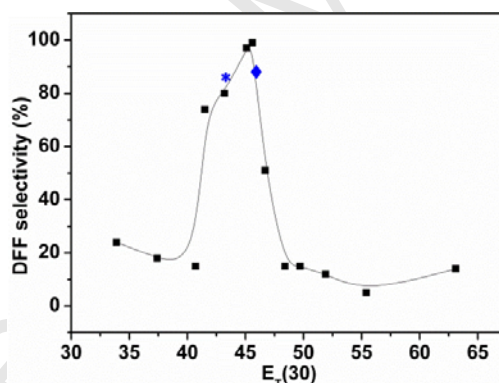
obtained, respectively.

Fig. 7. The dependence of DFF selectivity on the solvent polarity (the blue star and

diamond stand for mixed solvent of acetonitrile/toluene and acetonitrile/acrylonitrile

with volume ratio of 4, respectively).

3.3. Kinetic study

The dependence of the HMF concentration with reaction time at different reaction

temperature was studied (Fig. 8a). A linear relationship exists between $\ln(C_0/C_t)$ and

reaction time (s), indicating that the reaction is a pseudo-first-order reaction with

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respect to HMF. This is different from the heterogeneous Ru/C catalyzed oxidation of HMF to DFF reported by Liu's group [7a]. The apparent activation energy, Ea, is determined from the Arrhenius plot in the temperature range of 40-80 ^{o}C (Fig. 8b). The least-square fit analysis yields Ea value of 66 kJ mol^{-1}.
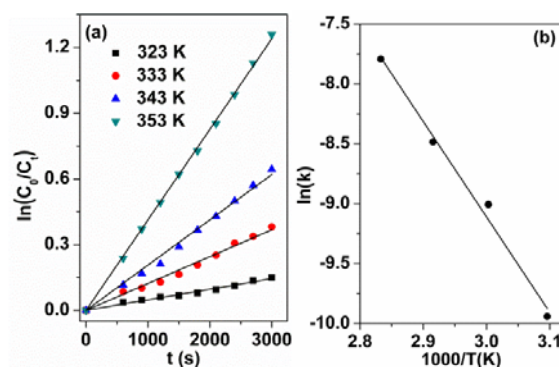

Fig. 8. (a) Relationship of In(C_0/C_t) and reaction time t of HMF oxidation to DFF. (b) Arrhenius plot for the oxidation of HMF. Reaction conditions: 20 mmol HMF, 0.4 mmol VOSO$_4$, 0.4 mmol Cu(NO$_3$)$_2$, 10 mL CH$_3$CN, 0.1 MPa O$_2$.

4. Conclusion

In summary, the promoted role of Cu(NO$_3$)$_2$ on aerobic oxidation of HMF to DFF catalyzed by VOSO$_4$ in acetonitrile was extensively investigated. How Cu(NO$_3$)$_2$ activate VOSO$_4$ to generate V^{5+} species can be clear. It was revealed that Cu(NO$_3$)$_2$ can facilitate the V^{5+}/V^{4+} redox cycle via the generation of NO$_x$ gas, thus achieving high activity. Moreover, the Cu^{2+} cation not only can effectively prohibit oxidative C-C cleavage reaction of HMF but also can prohibit radical reaction of DFF to humins, thus obtaining high selectivity. In addition, the polarity of solvent plays a great role on high selectivity of DFF. Kinetic study shows that it is a pseudo-first-order reaction with respect to HMF, and apparent activated energy of 66

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kJ mol^{-1}.

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[19] a) C. Reichardt, Chem. Rev. 94 (1994) 2319-2358; b) $E_T(30)$ values are based on the negatively solvatochromic pyridinium N-phenolate betaine dye as probe molecule, and they are simply defined as the molar electronic transition energies (E_T) of dissolved pyridinium N-phenolate betaine dye, measured in kilocalories per mole (kcal/mol) at room temperature (25 ^{o}C) and normal pressure (1 bar).

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Figure, Scheme and Table Captions:

Fig. 1. The effect of molar ratio of $Cu(NO_3)_2$ on the HMF conversion and DFF selectivity.

Fig. 2. Interaction between $Cu(NO_3)_2$ and $VOSO_4$ characterized by *in situ* FT-IR.

Fig. 3. Detection of V^{5+} species using UV-vis spectrum.

Fig. 4. The dependence of HMF conversion and DFF selectivity on O_2 partial pressure.

Fig. 5. MALDI TOF mass spectrum of humins derived from DFF.

Fig. 6. The dependence of HMF conversion and DFF selectivity on solvent.

Fig. 7. The dependence of DFF selectivity on the solvent polarity.

Fig. 8. (a) Relationship of $\ln(C_0/C_t)$ and reaction time *t* of HMF oxidation to DFF.

(b) Arrhenius plot for the oxidation of HMF.

Scheme 1 Promoted role of $Cu(NO_3)_2$ on aerobic oxidation of HMF to DFF catalyzed by $VOSO_4$.

Table 1 Oxidation of HMF catalyzed by $VOSO_4$.

Table 2 Influences of catalyst systems and additives on DFF stability.

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Graphical abstract

Promoted role of Cu(NO₃)₂ on aerobic oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over VOSO₄

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