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Highly Efficient Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid with Heteropoly Acids

Ruru Chen,^[a,b] Jiayu Xin, *^[a,c] Dongxia Yan,^[a] Huixian Dong,^[a] Xingmei Lu,^[a,c] Suojiang Zhang*^[a,c]

Abstract: 5-furandicarboxylic acid (FDCA) is regarded as an important bio-derived substitution of petrochemically terephthalic acid (PTA) applied in polymer industry. This work delineates the base-free oxidation of 5-hydroxymethylfurfural (HMF) to FDCA in a novel ionic liquids-heteropoly acids (ILs-HPAs) catalytic system. HPAs displayed high activity for the selective oxidation, the active center (Mo /V) was activated by O₂, and transformed from single and double oxygen bonds to epoxy groups, and the yield of FDCA reached 89% using HPMV₆ in presence of [Bmim]Cl under optimized reaction conditions. High solubility of imidazole ionic liquids to FDCA improved the affinity of HMF and the active centers of catalysts, and prevented the furan ring from oxidative cleavage. Furthermore, multiple hydrogen bonds simultaneously formed between electronegative anions and hydroxyl protons of HMF, 2-H of imidazole rings and hydroxyl groups, promoting the transformation to aldehyde groups. Various starting materials were studied, a moderate FDCA yield of was obtained from glucose. This work provided a novel ILs-HPAs catalytic system for the base-free synthesis of FDCA directly from more accessible monosaccharides and illustrated a great potential of FDCA production from renewable carbohydrates.

Introduction

Considering the contradiction between increasing demand of bulk chemicals and the depletion of nonrenewable petroleum resources, conversion of biomass to chemicals is more attractive.^[1] Among plenty of biomass-derived chemicals, selective oxidation of 5-hydroxymethylfurfural (HMF) could lead to 2,5-furandicarboxylic acid (FDCA), listed as one of the twelve top value-added chemicals obtained from biomass by the U.S. Department of Energy.^[2] FDCA is regarded as a promising alternative to petroleum-derived terephthalic acid (TPA).^[3] TPA is a monomer in the production of polyethylene terephthalate (PET), which are widely applied in numerous fields including bottle

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packaging, fibers and clothing.^[1a, 4] Compared with petroleum derived-PET, polyethylene-2,5-furandicarboxylate (PEF) from polymerization of FDCA is degradable,^[5] and possesses a better gas barrier and mechanical strength.^[2c, 6]

As illustrated in Figure 1, the oxidation of HMF to FDCA is performed via procedures of either 5-hydroxymethyl-furan-2-carboxylic acid (HMFA) or furan-2,5-dicarbaldehyde (DFF), and further oxidative 5-formyl-2-furancarboxylic acid (FFCA) as intermediates.^[7]



Figure 1. Possible oxidative routes for the synthesis of FDCA from HMF.

Currently, synthesis of FDCA is extensively achieved by applying supported noble metal catalysts in basic solvents with O₂ as oxidant.^[2b, 8] In the earliest, Pt/C was found to catalyze the selective oxidation of HMF with a FDCA yield of 69%.^[9] Zhang and co-workers developed a series of magnetic materialsupported noble metal catalysts, which provided high FDCA vields with addition of base and could be easily separated by a magnet and efficiently reused.^[10] Recently, supported Au-Pd alloy catalysts displayed excellent catalytic activity.[8a, 11] Further employing hydrophilic mesoporous poly(ionic liquid) (MPIL) as the support, it was feasible to control the surface wettability of Au-Pd/MPIL by varying the cross-linkers with different hydrophilic or hydrophobic properties.^[11] Dinesh et al. reported MnCo₂O₄ spinel supported Ru catalyst and provided a high FDCA yield in 10 h.[12] Noble metal catalysts showed great performance for FDCA production, while the major drawback is high costs of metal, therefore the larger-scale production is limited.^[13] A series of nonoble metal catalysts were employed to the HMF oxidation.[5a, 14] Zhang et al. first prepared a photocatalyst CoPz/g-C₃N₄, and used Na₂B₄O₇ solution, and led to excellent yield of FDCA.^[15] Mn-Co bimetallic oxides with different Mn/Co molar ratio were prepared, and nanoscale center-hollow hexagon MnCo₂O₄ spinel presented higher activity, with a FDCA yield of 70.9%. [5a] Eri Hayashi and coworkers successfully synthesized MnO₂ with different crystal structure, and demonstrated that high-surface-area β -MnO₂ presented suitable catalytic activity for the selective oxidation of HMF to FDCA.^[16] The FDCA production with no-noble metal catalysts is more cost-effective compared with noble metal catalysts.

Using either noble or no-noble metal catalysts, excessive base or high pH is generally used to produce FDCA salts, preventing FDCA agglomeration and deactivation of catalysts.^[17] However, FDCA salt neutralization to pure FDCA requires subsequent

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catalytic hydrolysis with strong acids and generates a large amount of waste water, increasing the operating cost and time with additional by-product formation.^[18] Furthermore, strong oxidants were used to activate the catalysts in some reaction systems, such as or t-BuOOH with acetonitrile.^[19] Thus, from the view of green and sustainability, the conversion of HMF to FDCA using no-noble metal catalysts in base-free solvents is expected. Ionic liquids (ILs) with their multifunctionalities and acid-base properties are in continuous development. Notably, imidazoliumbased ILs show preferable solubility to furan compounds including HMF and FDCA compared with conventional aqueous solutions or organic solvents.^[20] The oxidation of HMF in imidazole ILs would eliminate the use of additional base, mineral acids, and complex downstream process, which is economic feasible and environmentally friendly. Recently, we demonstrated a base-free conversion of HMF to FDCA in ionic liquids using Fe-Zr-O catalysts, and a yield of 60% was obtained.^[4b, 20b] Particularly, ILs are also favored for the synthesis of HMF by acid-catalyzed dehydration of sugars or cellulose.^[21] The merger of the reaction chemistry of direct conversions of sugars to FDCA with the solvents having catalytic behavior will extend their utilization in one-pot synthesis. On the other hand, with strong Brønsted acidity.^[22] Keggin-type heteropoly acids (HPAs) are extensively investigated in biomass conversion, especially hydrolysis of cellulose.^[23] The combination of Brønsted acidity and redox ability makes HPAs promising for the selective synthesis of FDCA from HMF and accessible monosaccharides.

Herein, a novel base-free ionic liquids-heteropoly acids (ILS-HPAs) system was developed in oxidation of HMF to FDCA via the formation of DFF and FFCA intermediates. By screening catalysts and solvents, it was indicated that Keggin phosphormolybdic acid $H_3PMo_{12}O_{40}$ (HPM) was an outstanding catalyst, and [Bmim]Cl served as excellent solvent and co-catalyst. This novel catalytic system provided efficient FDCA production with a high FDCA yield under mild conditions, while no-noble metal catalysts normally required more than 12 h or even 24 h to achieve high FDCA yield. Considering the multifunctionality of HPAs, the utilization of cellulose, glucose, and fructose for the one-pot production of FDCA was investigated, and a moderate FDCA was obtained. To the best of our knowledge, this is the first report for the use of heteropoly acids-ionic liquids to the oxidation of HMF to FDCA.

Results and Discussion

Catalyst Preparation and Characterization

Four types of Keggin HPAs, including HPM, HPW, HSM, HSW were tested for the reaction. As summarized in Table 1, all tested HPAs catalysts provided nearly full conversion of HMF under the reaction conditions, among which HPM showed high selectivity towards FDCA with a yield of 83%. The two heteropoly tungstic acids (HPW and HSW), however, showed poor catalytic behaviors. FDCA and furanic intermediates were synthesized in total yields of less than 30%, although 99% conversion of HMF were achieved. Therefore, it was determined that Mo mainly favored the selective oxidation, which was then confirmed by

using MoO₃ as the catalyst for the reaction and approximately 69% of FDCA was obtained. Since MoO₃ readily forms molybdic acid in water,^[24] thereafter exhibiting same valence state (VI) and Mo-O bonds as HPM, it was agreed that MoO₃ showed similar oxidative ability to HPM to some degree. On the other hand, HPM is more tunable and multifunctional compared to MoO3 as a catalyst, such as adjusting Brønsted acidity, or selectivity to products by varying addenda atoms. By contrast, basic Na₂MoO₄ performed badly, with a low FDCA yield of 24%. The poor activity was presumably caused by the basic reaction conditions due to Na₂MoO₄, which ultimately led to base-induced polymerization of HMF thereby forming humins. It is revealed, consequently, that acid-base properties of catalysts greatly influence the transformation. In addition, Si-based heteropoly acids are thermally unstable compared with P-based heteropoly acids according to melting points and presented mostly in liquid state. Thus, HSM showed relatively poor catalytic performance. In summary. HPM was the most effective catalyst among heteropoly acids, and it was Mo that mainly catalyzed the oxidation. It was reported that, at high temperature, the conversion of HMF

was not stable and degraded into humins significantly.^[4b, 10b] Therefore, HMF was highly converted in [Bmim]Cl in the absence of catalysts, and some insoluble humins caused by HMF polymerization or cross-linked polymerization were observed after reaction. Generally, the difference between high conversion and relative low yield of furanic compounds was a result of the side reactions due to different catalysts. Ring-opening products glycolic acid, and inorganic CO₂ were identified by GC-MS, and furfural identified by ESI (Figure S4).

Table 1. Selective oxidation of HMF to FDCA using different catalysts.							
Entry	Catalysts	HMF Conv.	Yield [mol %]				
		[mol %]	FDCA	FFCA	DFF		
1	HPW	99.8±0.3	18.5±2.7	5.3±1.2	0.1±0.0		
2	HPM	98.1±1.0	83.3±3.1	1.5±0.3	1.2±0.1		
3	HSW ^[b]	99.7±0.2	8.6±1.5	21.5±1.7	0.2±0.0		
4	HSM	99.8±0.1	38.4±3.0	15.3±0.9	0.8±0.1		
5	MoO ₃	99.9±0.1	69.5±2.4	1.3±0.5	0.1±0.0		
6	Na ₂ MoO ₄	99.5±0.2	23.8±1.3	7.0±1.1	5.0±0.2		
7	Blank ^[a,b]	99.2±0.5	18.7±0.9	2.4±0.3	0.7±0.0		

Reaction conditions: 0.1 mmol HMF, 1 g [Bmim]Cl, 0.05 g catalysts, 140 °C, 1 MPa O₂, 6 h. [a] No catalysts were used. [b] HMFA was the intermediate rather than DFF, and the molar content of HMFA was 0.2%.

In order to improve the catalyst performance, enhancing the selectivity of FDCA, the catalyst HPM was modified by varying addenda atoms. As reported in the conversion of cellulose to formic acid, introduction of vanadium into HPM could promote the selectivity, and then it would mainly be V that favored the oxidation.^[25] In addition, on the basis that HPMV_n with over 3 vanadium atoms are especially easy to re-oxidise,^[26] the oxidation

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rate was expected to be significantly improved. HPMV_n catalyzed the reaction by change of V(V) to V(IV) mostly. $HPMV_n$ was successfully synthesized and confirmed by FTIR, XRD, ICP, ESR and XPS analysis. Table S3 shows the list of prepared HPAs together with the results for the ICP of dried compounds, and it was indicated that all HPAs were obtained in good purity and desired metal component. The ESR spectra (Figure S3) of HPMV_n catalysts shows the characteristic signal for V⁵⁺ species with hyperfine structure, according to Lingaiah et al.[27] The intensity of spectra increased with V atoms increase in HPAs, confirming that more V(IV) exists in HPMV_n with a larger value of n, also proved by XPS.^[28] Afterwards, the catalyst ability was tested for the oxidation, and HMF conversion, furanic yields were determined. The FTIR spectra of HPMV_n are depicted in Figure 2. Four main vibration bands emerged around 1064, 961, 869, and 785 cm⁻¹ were assigned to the P-O, M=O_d (terminal oxygen), M-O_b-M (corner-sharing oxygen), and M-O_c-M (edge-sharing oxygen), respectively, which are the characteristic of HPAs with a Keggin structure (M represents Mo or V).^[26, 28-29] Typical V₂O₅ bands at 1021, 829 and 617 cm⁻¹, related to V=O, asymmetric and symmetric vibration of V-O-V.^[30] were not presented independently in the spectra but showed a combining influence on the four vibration bands of Keggin structure. With the increase of introduced vanadium atoms, the characteristic bands P-O and M=Od became broader and shifted to lower wavenumbers and M-Oc-M shifted to higher wavenumbers, further indicating the incorporation of V in the primary structure and the destruction of Keggin structure cetro-symmetry.^[31]



Figure 2. FT-IR spectra of HPMV_n, a: HPM, b: HPMV₁, c: HPMV₂, d: HPMV₃, e: HPMV₄, f: HPMV₅, g: HPMV₆.

The XRD patterns of synthesized HPAs are shown in Figure 3. A series of peaks at $8 \sim 11^{\circ}$, $18 \sim 20^{\circ}$, $25 \sim 30^{\circ}$, denoted the triclinic crystal phase of Keggin structural HPM.^[28] The XRD pattern containing V species exhibited some broader and weaker peaks compared with HPM. With the increase of the introduced vanadium atoms, the peaks at 10.4° , 20.1° was broaden. The

peak at 8.6° vanished, reflecting a shrinking unit cell due to the replacement of Mo atoms with smaller V atoms. It was indicated that V was present in the primary structure of Keggin, and the symmetry of anion structure decreased by the addition of V. During the catalyst preparation, insoluble V₂O₅ was removed by filtration. No characteristic peaks about crystal structure of V₂O₅ was shown in the XRD patterns, thus all vanadic species were presented in the form of heteropoly anions.



Figure 3. XRD spectra of HPMV_n, a: HPM, b: HPMV₁, c: HPMV₂, d: HPMV₃, e: HPMV₄, f: HPMV₅, g: HPMV₆.

The valence change of catalysts plays a key role in the oxidation pathway. Reduced Mo and V promote electron and oxygen transfer between reactants and catalysts. To gain more insight into the reaction mechanism, XPS analysis of catalysts was performed. The XPS spectra of synthesized samples were shown in Figure 4 below. As shown in Figure 4A, there was only binding energy of Mo⁶⁺ presented at 233.4 eV, and almost no Mo⁵⁺ was found in V-free HPM, revealing a stable Keggin structure. By contrast, in V-substituted HPMV_n, the binding energy of Mo 3d_{5/2} consisted of two peaks corresponding to Mo⁶⁺ and Mo⁵⁺ species at 233.4 and 232.1 eV, respectively, suggesting the presence of partially reduced catalysts during preparation with little content of Mo^{5+, [31-32]} In addition the relative content of reduced Mo⁵⁺ grew with increasing V atoms, attributing to the removal of the bridging oxygen in the orthorhombic distortion with defect Keggin unit.^[31] Spectrum of V 2p_{3/2} in HPMV was depicted in Figure 4B, two broad peaks of V were observed, 509.6 and 512.7 eV, which could be deconvoluted to V⁴⁺ and V⁵⁺, respectively. The existence of both V⁴⁺ and V⁵⁺ indicated the exchange of electrons between V and Keggin structure, and further suggested the formation of monomeric pervanadyl (VO2+) cation, which was favorable for the selectivity to FDCA. The Mo⁶⁺/Mo⁵⁺ molar ratio in HPMV₁ was obtained according to the relative peak area, as well as V⁵⁺/V⁴⁺. In HPM catalyst, there was almost no Mo⁵⁺, indicating that Mo⁶⁺ was stable in Keggin unit and hard to be reduced during the preparation. On the contrary, in HPMV₁, the content of Mo⁵⁺ was

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increased because the removal of bridging oxygen, suggesting the formation of partially reduced catalysts during synthesis.



Figure 4. XPS spectra of A: $Mo3d_{5/2}$, B: $V2p_{3/2}$ of HPAs. (a: HPM, b: HPMV₁, c: HPMV₂, d: HPMV₃, e: HPMV₄, f: HPMV₅, g: HPMV₆)

The synthesized HPMV_n was employed to the selective oxidation of HMF to FDCA and the results are demonstrated in Table 2. As stated previously, full HMF conversion was easily achieved regardless of the number of V atoms. To state the synergetic effect of V in Keggin structure, the catalytic performance of V₂O₅ was conducted as well. V₂O₅ showed poor selectivity to FDCA, with only 0.5 yield, even lower than that in blank reaction. In reaction system, V₂O₅ catalyzed the conversion of HMF to other inorganic byproducts, but restrained the selective oxidation to FDCA. V promoted effective selectivity to FDCA in Keggin HPAs, and show synergetic effect with Mo. With the increase of V atoms in Keggin structure, the selectivity to different furanics varied significantly.

Table 2. The effect of V species in HPAs on the oxidation of HMF to FDCA.							
Entry	Catalysts	HMF Conv.	Yield [mol %]				
		[mol %]	FDCA	FFCA	DFF		
1	V_2O_5	96.7±0.2	0.5±0.1	0	0		
2	$HPMV_1$	99.4±0.4	70.6±2.7	1.3±0.5	0.9±0.2		
3	HPMV ₂	99.7±0.2	68.8±3.8	3.9±1.0	0.5±0.1		
4	HPMV ₃	99.8±0.1	45.0±2.1	4.1±0.8	0.3±0.0		
5	HPMV ₄	99.8±0.1	23.8±4.5	4.3±0.5	0		
6	HPMV₅	99.4±0.1	44.6±2.7	2.9±0.3	0.8±0.1		
7	$HPMV_6$	99.4±0.3	88.8±2.5	0.7±0.0	1.1±0.1		

Reaction conditions: 0.1 mmol HMF, 1 g [Bmim]Cl, 0.05 g catalysts, 140 °C, 1 MPa O₂, 6 h.

The yield of FDCA firstly declined with vanadium content increasing, from 83% (HPM) to 23.8% (HPMV₄), then with a

higher degree of V substitution, the yield of FDCA rose as well. The same tendency was observed for the total yield. With V increasing, the dissociation of the parent HPMV_n led to VO²⁺ cation and complex thereof. The leaching VO²⁺ has a higher redox activity,^[26] therefore favorable for the selective oxidation to FDCA. On the other hand, higher V-substituted HPAs possesses improved pH or reduced acidity, leading to lower selectivity to FDCA. Considering two aspects, for n<4 decreased acidity mainly influenced the activity of HPAs, whereas free pervanadyl (VO²⁺) increased oxidative selectivity for n>4. However, it was indicated that HPAs were less stable and irreversibly catalytic with even higher V content. Overall, HPMV₆ provided highest FDCA yield of 89% among series of V-substituted HPAs.

Oxidation of HMF to FDCA in Various Solvents

The application of ionic liquid [Bmim]Cl in the oxidation of HMF to FDCA was reported to increase the solubility of FDCA, furthermore create base-free system.^[20b] The influence of ILs on the reaction was discussed, by comparing with various solvents including H₂O, H₂O₂, DMSO, toluene, Choline chloride (ChCl), and 1-Butylpyridinum chloride (IBPyICI), shown in Table 3. The oxidation was substantially determined by the solubility of FDCA. and H₂O, H₂O₂, DMSO, toluene as well as ChCl revealed poor solubility compared with ILs. Consequently, though HMF was totally converted, little furanic compounds were synthesized due to insolubility of FDCA, and humins from polymerization of HMF were the main byproducts. Reversely, selectivity to FDCA was highly enhanced using ionic liquids solvents, attributing to the excellent solubility of FDCA. In this way, FDCA was less adsorbed on the surface of catalysts, thereby ensuring the activation of catalysts. In addition, base-free condition avoided base-induced polymerization of HMF,[7a] and eliminated further acidification of FDCA salts, making the reaction more environmentally friendly and cost-efficient.

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Table 3.	Table 3. The selective oxidation of HMF to FDCA in different solvents.								
Entry	Solvents	HMF Conv.	Yield [mol %]						
		[mol %] F		FFCA	DFF				
1	H ₂ O	99.9±0.1	0	0	0				
2	H_2O_2	97.3±0.9	0	0.6±0.1	0.4±0.0 ^[a]				
3	DMSO	100±0	0.1	8.4+0.7	0				
4	Toluene	99.6	0.2	0.3	0.6 ^[a]				
5	ChCl	100±0.0	3.7±0.4	0.6±0.0	0.2±0.0				
6	[BPy]Cl	100±0.0	0.7±0.1	9.6±0.5	27.5±1.3				
7	[Bmim]Cl	100±0.0	88.8±3.9	1.1±0.1	0				

Reaction conditions: 0.1 mmol HMF, 1 g solvents, 0.05 g catalysts, 140 $^{\circ}$ C, 1 MPa O₂, 6 h. [a] HMFA was the intermediate rather than DFF.

The oxidation of HMF in [Bmim]Cl afforded full HMF conversion and highest FDCA yield among ionic liquids. After reaction in [BPy]Cl under identical conditions, approximately 38% intermediates including DFF and FFCA were obtained, and DFF

was the main product, exhibiting slower transformation and lower selectivity compared with that in [Bmim]Cl. The lower activity of HPM in [BPy]Cl might be ascribed to the presence of the basic nitrogen atoms on the pyridinium ring.^[33] This ultimately made the protons related to nitrogen atoms difficult to dissociate, and then reduction in the acidity of the solvents affected the selective oxidation.

It is worth noting that [Bmim]Cl could also provide 18.7% FDCA without catalysts (Table 1, Entry 7), revealing that ionic liquid [Bmim]Cl possesses moderate catalytic ability to the oxidation of HMF. However, the reaction pathway differs from HPAs, via intermediate HMFA. As a catalyst, [Bmim]Cl is competing with HPAs, however less effective and affording a lower yield. In the presence of HPAs, HMFA from catalytic [Bmim]Cl was negligible, and [Bmim]Cl rather acted as a co-catalyst by strong hydrogen bonds with furanics, and electron transfer between heteropoly anions and reactants. Hence, it was concluded that [Bmim]Cl acted not only as a solvent but a co-catalyst in the oxidation of HMF to FDCA

Optimization of the Oxidation of HMF

Since imidazole ionic liquids displayed high dissolving capacity to FDCA,^[20b] and concerted promoting effect on the oxidation, various imidazole ILs with different cations and anions were employed as the solvents for the reaction. The results are summarized in Table 4. On the basis of the same cation [Bmim]+. it is observed that different anions substantially influenced the oxidation. Among tested anions, Cl⁻ led to highest FDCA yield, while BF4⁻, PF6⁻, NTf2⁻ displayed poorer catalytic ability and scarcely any product was obtained. Br- mainly produced intermediates DFF and FFCA under the same conditions, with a total furanic yield of 24% and 90%, respectively. The influence of anions is discussed from two aspects. Firstly, electronegativity of anions determines the strength of hydrogen bond between anions and HMF molecule. Higher electronegative anions help the deprotonation and promote the oxidation of -OH. Unlike CI⁻ or Br-, BF₄, PF₆, NTf₂ anions cannot form hydrogen bonds with HMF, because hydroxyl group is in shielding cone of the aromatic imidazolium ring in ILs with BF4⁻, PF6⁻, NTf2⁻ anions (see Figure S5). Anions of ionic liquids dramatically influenced the reaction, and ionic liquids with halide ions provided preferable yields.

By varying the alkyl substituent on cation of ILs, it was revealed that ILs with long alkyl substituent on the cation led to lower selectivity. [Bmim]⁺, [Amim]⁺, [Emim]⁺, and [Hmim]⁺ showed better performance on the catalytic reaction, whereas lower results were obtained in [Omim]⁺ and [C₁₄mim]⁺, showing 48% and 7.6% yield of FDCA, respectively. Presumably due to the unfavorable steric effect of long alkyl chain, the catalytic activity of HPA was restrained. In addition, as electron-donating group, longer alkyl chain diminished the activity of acidic proton on the imidazolium cation. On the other hand, aggregation of ILs is easier with longer alkyl chains, and the well-defined aggregates hinder the reaction as well.

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Table 4.	The	effect	of ILs	with different	anions	and cations.

Entry	Solvents	HMF Conv.	Yield [mol %]		
		[mol %]	FDCA	FFCA	DFF
1	[Bmim]BF ₄	100±0.0	0	2.3±0.5	0.3±0.0
2	[Bmim]PF ₆	99.8±0.1	0	0.2±0.0	3.1±1.1
3	[Bmim]Br	100±0	14.7±5.1	5.0±1.3	70.7±2.2
4	[Bmim]Cl	99.5±0.3	88.8±3.9	1.1±0.1	0
5	[Emim]Cl	98.9±0.7	86.3±2.8	2.2±1.0	1.7±0.2
6	[Amim]Cl	98.8±0.5	79.1±5.9	1.8±0.3	6.1±0.7
7	[Hmim]Cl	95.1±2.7	70.9±3.0	0	2.1±0.8
8	[Omim]Cl	96.7±3.1	48.0±3.5	15.1±1.9	1.4±0.3
9	[C ₁₄ mim]Cl	100±0	7.6±2.1	4.8±1.6	0.1±0.0

Reaction conditions: 0.1 mmol HMF, 1 g solvents, 0.05 g catalysts, 140 °C, 1 MPa $O_{2},\,6$ h

Figure 5a shows the dependence of HMF conversion and yields of FDCA and intermediates on the reaction time. It is clear that HMF converted rapidly in the beginning and the conversion reached 100% within 1 h, revealing that the transformation of HMF was readily complete in a short time. On the other hand, products were greatly influenced by the reaction time. The FDCA yield increased with reaction time, where the increasing rate in the first two hours was comparatively faster than that at later stages, showing a yield of 88.8% after 6 h. Meanwhile, as intermediates, the yield of FFCA and DFF was the highest in the beginning and decreased with time. Furthermore, the decrease of DFF was faster than that of FFCA, and the main reason was that (1) FFCA was the downstream product of continuous DFF oxidation, and it was accumulated and consumed simultaneously; (2) the oxidation rate of DFF was faster than that of FFCA. As presented, the highest FDCA yield was achieved when FFCA totally transformed. Since the yield of DFF was already reduced to 0 within 2 h, the increase of FDCA yield was mainly determined by the transformation of FFCA, indicating that the oxidation of FFCA to FDCA was the rate-determining step. Prolonging the reaction time to 7 h, a slight decrease of the FDCA yield was observed, and only 69% FDCA was obtained after reaction for 24 h. The reduction of FDCA yield presumably was due to the deep oxidation and degradation to inorganic compounds such as CO₂. The reaction temperature was another important factor influencing the conversion of HMF and product selectivity. Experiments were conducted at different temperatures between 80 and 160 °C under otherwise similar reaction conditions. As shown in Figure 5b, the conversion of HMF increased from 90% to 100% as the temperature changed from 80 to 100 °C and kept stable with a further temperature increase. Thus, HMF was easy to be converted at low temperature, and 100 °C was sufficient for complete conversion of HMF. On the other hand, selectivity of FDCA and intermediates varied with the temperature. At temperatures lower than 100 °C, the main products were intermediates DFF and FFCA, whereas little FDCA was obtained. As the temperature increased, the yield of DFF was reduced

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sharply and it was totally converted at 120 °C, meanwhile, moderate FDCA and FFCA yields of 50% was achieved. The optimal temperature for the oxidation of HMF to FDCA was presented as 140 °C, and barely no intermediates and substrate remained. It was demonstrated that relatively low temperature was advantageous to the oxidation of hydroxyl to aldehyde, while the transformation of aldehyde to carboxyl required higher temperature and more energy. Further rising temperature resulted in a decrease of FDCA yield, presumably because of (1) the decomposition of ionic liquids, which was confirmed by HPLC, (2) degradation of HMF, and (3) polymerization and resinification of HMF to humins.



Figure 5. Dependence of HMF conversion, yields of FDCA and intermediates on reaction conditions. (a) reaction time; (b) reaction temperature; (c) oxygen pressure; (d) catalyst amount (g/g ILs). Default reaction conditions: 0.1 mmol HMF, 1 g [Bmim]Cl, 0.05 g catalysts, 140 $^{\circ}$ C, 1 MPa O₂, 6 h.

The pressure in the reaction system determines the oxygen availability in solvents and oxygen mass transfer from the gas phase to the liquid phase, and further influences the re-oxidation of catalysts. The effect of oxygen pressure on the oxidation reaction was investigated and shown in Figure 5c. Contrary to the results from changing temperature and time, pressure variation did not exert obvious influence on the reaction. Intermediates FFCA and DFF could be effectively obtained under low pressure (0.5 MPa). The yield of FDCA achieved maximum value (88.8%) under 1 MPa, afterwards slightly reduction with the pressure increasing. Moderate pressure favored the dissolving of oxygen into solvents and further promoted the oxidation on the active sites of the catalyst. However, excessive pressure resulted in deep oxidation and thereby decomposition of products.

The aerobic oxidation of HMF to FDCA was conducted with different catalyst amount (g/g ILs). As shown in Figure 5d, the conversion of HMF was 99% with 0.01 g HPMV₆ addition and kept stable with the variation of catalyst amount. On the other hand, the yield of FDCA was relatively affected by the catalyst amount.

The FDCA yield firstly increased with the catalyst amount from 69%, and best result was obtained with 0.05 g catalysts, which was attributed to the increase in the availability and number of catalyst active sites. Further increase in catalyst/HMF ratio led to a decrease of the FDCA yield. Thus, 0.05 g catalysts under the reaction condition provided sufficient active sites for the oxidation, and the decrease may be a result of deep oxidation and decomposition of products on excess active sites.

Catalyst was successively reused three times under optimal conditions for the oxidation of HMF to FDCA. The FDCA yields were significantly reduced from 88.8% in the first run to 75.1% in the third run. It was mainly because the instability of catalyst during the recovery, Mo^{6+} is leaching from catalyst. Specific results of recycling are shown in Table S6.

Reaction Mechanism

To gain insight into the reaction and improve the selectivity of FDCA, an integrated reaction mechanism is proposed, as illustrated in Figure 6. As for HPM, Mo(VI) acted as the active sites where the reaction takes place, and then the oxygen transfer is completed by oxygen atmosphere via a redox cycle. For HPMV_n (n=1~6), it was rather V(V) that principally promoted the oxidation. For the sake of clarity, it is assumed that at least one of the three protons in HPA remains associated with the anion.



Figure 6. Proposed reaction mechanism of the oxidation of HMF to FDCA. (M=Mo, V)

Firstly, hydroxyl group of HMF interacted with ILs and multiple hydrogen bonds were formed with the [Bmim]⁺ cations and Cl⁻ anions, leading to HMF-ILs complex a (proton in [Bmim]+ with O, and Cl⁻ with H). In the presence of O₂, β -hydride elimination subsequently occurred, affording the corresponding aldehyde b (DFF) accompanied with water. Secondly, with HPAs as catalysts, electron transfer occurred and formed a protonated aldehyde c, then the aldehyde group underwent reversible hydration to a hydrate intermediate d (geminal diol) and subsequent dehydrogenation to produce the corresponding carboxylic acid e with eliminating H⁺. Consequently, intermediate FFCA was

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generated by the epoxy groups and Mo=O was reduced, which would be further re-oxidized by O₂. As shown in Figure 7, the intensive UV spectrum peak of Mo=O in HPM is located at λ = 210 nm, and the bonds of Mo and O were single and double bonds.^[34] When HPM was exposed to high O₂ pressure, one new UV spectrum peak appeared around λ = 312 nm, indicating the epoxy groups were formed. The epoxy groups played a crucial role in further oxidation of -CHO to -COOH and DFF advanced oxidation to FFCA. The strong π -d interaction between the imidazole and Mo center resulted in a UV spectrum peak tailing of epoxy groups,[34] which was responsible for the higher activities of heteropoly acids in imidazole ionic liquids. Finally, the other aldehyde group was continuously catalyzed via the same oxidation route and finally provided FDCA. Here, the molybdic species exhibited both Brønsted acidity and redox activity during the oxidation.



Figure 7. UV spectra of Phosphomolybdic acid (HPM) within and without O2.

The HMF-ILs complex is confirmed by NMR spectra. By comparing the ¹H NMR spectra of pure [Bmim]Cl, HMF and the mixture (Figure 8a), it is clear that many characteristic resonance signals of HMF and [Bmim]Cl changed after mixing, which verifies the special interaction between HMF and N-heterocyclic carbenes (NHCs) originated from [Bmim]Cl.[35] The resonance band of the hydroxyl group of HMF shifted towards the downfield region from 5.56 ppm to 5.88 ppm after [Bmim]Cl was mixed with HMF. due to the hydrogen bond formation between CI- anions and hydroxyl protons. Meanwhile, the band attributed to the active proton 2-H of imidazole ring (5) shifts from 9.54 ppm to 9.44 ppm, indicating the interaction and coordination between hydroxyl groups and the 2-H. It is worth noting that chemical shifts of -CHO assigned to HMF is negligible, therefore, hydroxyl group is transformed in advance and HMF is easily oxidized to DFF rather than HMFA. In contrast, the ¹³C NMR of [Bmim]Cl and HMF (Figure 8b) showed no obvious chemical shifts after mixing, suggesting the integration of imidazole ring and furan ring.

Substrate Exploration

Since the source of HMF is restrained and results in a higher cost, the synthesis of FDCA from accessible and inexpensive biomass or carbohydrates is further studied. It was expected to apply HPAs to the direct synthesis of FDCA from hexoses or cellulose, and the results are summarized in Table 5.



Figure 8. NMR spectra of [Bmim]Cl and HMF, a. ¹H NMR spectra of [Bmim]Cl, HMF and mixture of [Bmim]Cl and HMF; b. ¹³C NMR spectra of [Bmim]Cl, HMF and mixture of [Bmim]Cl and HMF.

Table 5	Table 5. The synthesis of FDCA from different substrates and systems.							
Entry	substrates	Base	Process	FDCA yield [mol %]	Time [h]	ref		
1	Fructose ^[a]	-	One pot	30.7	9	-		
2	Glucose ^[a]	-	One pot	48.6	9	-		
3	Fructose	Na ₂ CO ₃	Triphasic system	78	30	[36]		
4	Fructose	-	Biphasic system	25	70	[37]		

[a] Reaction conditions: 0.1 mmol substrates, 1 g [Bmim]Cl, 0.05 g HPMV_6, 140 °C, 1 MPa $O_2.$

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Table 6. Comparison of different catalytic system for the oxidation of HMF to FDCA.								
Entry	Catalyst	Oxidant	Additives	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)	Ref
1	Pt/C	40 bar air	2 equiv Na ₂ CO ₃	100	6	99	69	[9]
2	Pt/C-O-Mg	1 MPa O ₂	-	110	12	100	97	[8c]
3	CoPz/g-C ₃ N ₄	1 bar air	Na ₂ B ₄ O ₇	25	14	99	96	[15]
4	MoO _x -CeO ₂	2 MPa O ₂	2 equiv KHCO3	110	12	99	91	[13]
5	Fe ₃ O ₄ -CoO _x	TBHP	DMSO	80	12	97	68	[10a]
6	MnFe ₂ O ₄	TBHP	-	100	5	100	85	[38]
7	MnCo ₂ O ₄	1 MPa O ₂	3 equiv KHCO3	100	24	99.5	70.9	[5a]
8	Fe-Zr-O	2 MPa O ₂	[Bmim]Cl	160	24	99.9	60.6	[4b]
9	HPAs	1 MPa O ₂	[Bmim]Cl	140	6	100	89	-

FDCA was obtained with a yield of 6% from cellulose, 30.7% from fructose, and 48.6% from glucose. FDCA obtained from cellulose is a combined result of hydrolysis of cellulose to hexose, dehydration of hexose to HMF, and eventual oxidation of HMF. Catalysts employed are required to be multi-functional for all the procedures. Obviously, lower FDCA yield was accompanied with a longer reaction pathway, as more byproducts were presented on the active sites of catalysts, and side reactions occurred, thereby restraining the selective oxidation. During the glucose dehydration to HMF, it was proposed that 1,2-enediol was an intermediate stabilized by heteropoly anions, and no isomerized fructose was formed by HPAs in ionic liquid system. Brønsted acids induce the transformation of glucose to intermediate 1,2enediol and then oxidation of HMF to FDCA, no fructose presented as intermediate.^[33] Hence, the dehydration of glucose and fructose to HMF underwent different reaction paths, and there were wilder side reactions from fructose.

Compared with previous synthesis of FDCA from fructose (Table 5, Entry 3,4) using triphasic or biphasic reaction system as well as noble metal catalysts,^[36-37] the conversion of sugars to FDCA in ILs-HPAs system could be performed via one pot and one step, simplifying the reactor and reducing the cost. The reaction time was significantly reduced to less than 10 h, which greatly improved the production efficiency. Glucose is more accessible and earth-abundant than fructose, and it was first reported as substrate in ILs-HPAs, and provided a moderate FDCA yield, which is quite prior to other reported reaction system.

The results of FDCA synthesis from HMF in different reaction system were listed in Table 6 to illustrate the advantages of the novel catalyst system. Compared with other noble metal catalysts or no-noble metal catalysts, this novel catalyst system eliminated the use of expensive noble metal, additive base, inorganic acids for FDCA salt neutralization and complex industrial procedure. Moreover, high FDCA yield was achieved in relative shorter time, while 12 h to 24 h were required for other catalytic system. A rough capital of process was also listed in Table S8, and there are great capital differences mainly including catalysts, oxidants and base additives. It is regarded more economically and environmentally feasible to employ ILs-HPAs reaction system to the synthesis of FDCA.

Conclusions

In summary, a novel base-free IL-HPA catalytic system was developed for the selective oxidation of HMF to FDCA. Strong hydrogen bonds were formed between halide anions, 2-H of imidazole ring and HMF, promoting the catalytic oxidation. [Bmim]Cl served as excellent solvent and co-catalyst, and by introducing V atoms in HPAs, it was found that HPMV₆ was as an outstanding catalyst. The active M (Mo /V) center transformed from single or double oxygen bonds to epoxy groups in oxygen atmosphere, that promote electron and oxygen transfer between furanics and Keggin anions. Over 99% HMF conversion and 89% FDCA yield were achieved at 140 °C in 6 h. Meanwhile, ILs-HPAs exhibited moderate activity in the direct conversion of hexoses to FDCA, and provided 48% FDCA yield from glucose. Overall, this study provided convenient access to FDCA from biomass-derived feedstocks, and avoided the high cost of noble metal catalysts, the use of corrosive inorganic base and acid and the complex industrial procedure. Therefore, it can be regarded more economically and environmentally feasible to employ ILs-HPAs reaction system to the synthesis of FDCA.

Experimental Section

Catalysts preparation and characterization

Typical $H_4PMo_{11}V_1O_{40}$ (HPMV₁) was fabricated using a typical method as follows. 11 mmol MoO₃ and 1 mmol V₂O₅ was added into a 250 ml round flask with 100 ml water, subsequently mixed well at 80 °C with vigorous stirring. Afterwards, 1 mmol H₃PO₄

(85%) was added dropwise into the system, which was refluxed at 110 °C with vigorous stirring for 5 h. During the heating, a color change was observed from turbid to red and transparent. Eventually, the solution was evaporated at 80 °C, obtaining a bright orange solid. Other heteropoly acids HPMV_n (n=2~6) were synthesized via similar procedure, only with different quantity. The commercial $H_3PMo_{12}O_{40}$ (HPM), $H_3PW_{12}O_{40}$ (HPW), $H_4SiMo_{12}O_{40}$ (HSM), $H_4SiW_{12}O_{40}$ (HSW) were directly used as received.

 $HVOPMo_{12}O_{40}$ was prepared as follows. Required V₂O₅ was first dissolved in oxalic acid solution, and the new solution was obtained and turned to blue after stirring 2 h at 80 °C. H₃PMo₁₂O₄₀ was added afterwards, which was continuously stirred to solid. $HVOPMo_{12}O_{40}$ was finally obtained. $V_2O_5/H_3PMo_{12}O_{40}$ was prepared by following the procedure. Required amount of H₃PMo₁₂O₄₀ and V₂O₅ were added into 30 ml deionized water, followed by stirring for 2 h. The mixture was then heated with stirring at 80 °C, V₂O₅/H₃PMo₁₂O₄₀ was finally obtained.

Samples were analyzed via thermogravimetry/differential thermal analysis (TG/DTA, DTG-60H, Shimadzu, Japan), and heated from room temperature to 700 °C at a rate of 5 °C/min and oxygen as a gas carrier. Fourier transform infrared (FTIR), a Thermo Nicolet 380 Spectrometer, were used in the range of 400-4000 cm-1. X-ray diffraction (XRD) were performed on a Rigaku RINT 2500 diffractometer. All XRD patterns were collected in the 26 range of 5-90° at a scanning rate of 0.016 °/s. Inductively coupled plahsm optical emission (ICP-OES), was used for the detection of P/V/Mo ratio in prepared catalysts. 20 mg of catalysts were dissolved in 250 ml of double distilled water and analyzed. X-ray photoelectron spectroscopy (XPS) were recorded using a Thermos Fisher Scientific ESCALAB 250Xi spectrometer with a monochromatized AlKα radiation.

Catalytic Oxidation and Product Analysis

The oxidation of HMF was carried out in a 50 ml batch-type Teflon-lined stainless-steel autoclave equipped with an internal thermo-controller. In a typical procedure, 0.1 mmol HMF, 0.01 g catalysts, and 1 g ionic liquids were loaded into the reactor. The reactor was sealed and pressurized at 1MPa O₂ pressure after purged three times. Then reaction was started with vigorous stirring once reactor reached desired temperature. After reaction for a certain time, reactor was quickly cooled to room temperature and carefully depressurized. The major products were identified by high performance liquid chromatography (HPLC) of Shimazu LC-20A system using a method below. Compounds including FDCA, HMFCA, FFCA, HMF, and DFF, were separated using a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm) and 5 mM H₂SO₄ aqueous solution as a mobile phase flowing at 0.6 ml/min and 35 °C. The retention time of FDCA, HMFCA, FFCA, HMF, and DFF were 18.3, 23.6, 25.6, 35.7 and 44.7 min, respectively. The content of each chemical was determined using calibration curves.

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Conflict of interest

The authors declare no conflict of interest

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Base-free synthesis of FDCA from HMF and glucose in the novel ionic liquidsheteropoly acids (ILs-HPAs) reaction system. Ruru Chen, Jiayu Xin,* Dongxia Yan, Huixian Dong, Xingmei Lu, Suojiang Zhang*



Highly Efficient Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid with Heteropoly Acids