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# Fabrication of trifunctional polyoxometalate - decorating chitosan nanofibers in highly selective production of DFF from 5-HMF, fructose and glucose

#### Yiming Li, Peili Li, Ping Cao, Ying Li, Xiaohong Wang \* and Shengtian Wang

Abstract: Trifunctional polyoxometalate (POM) decorating chitosan nanofibers ( $H_5PMo_{10}V_2O_{40}$ /chitosan nanofibers, abbreviated as HPMoV/CS-f) had been synthesized using electrospinning method, which realized highly efficient oxidation of 5-hydroxymethylfurfural (5-HMF) to 2,5-diformylfuran (DFF). Decorating chitosan nanofibers by POMs generated enhanced catalytic activity by emerging their unique individual properties of redox ability, Brønsted acidity, basic property, and nanofiber structure with higher surface area. As results, HPMoV/CS-f (25) (25, represented the POM amount) was found to be most active in aerobic oxidation of 5-HMF to give 94.1 % yield of DFF at 96.2 % conversion in dimethyl sulfoxide (DMSO) at 120 °C for 6 h, while 56.2 % yield of DFF at 95.0 % conversion was obtained in water system at 140 °C for 8 h. Most importance was that DFF could be produced in one-pot one-step to give 61.9 % and 31.4 % yields directly from fructose and glucose under the reaction conditions as 140 °C, 6 h in DMSO, which was due to the suitable balancing of Brønsted acidity and basicity of the trifunctional HPMoV/CS-f (25). Moreover, HPMoV/CS-f showed good stability and duration for being reused at least ten times without leaching of POMs from chitosan nanofibers.

#### Introduction

Chitosan is a kind of natural polymers with potentials for biologicals, industrial treatment of waste water, and catalyst supports due to its high adsorbing or chelating ability. <sup>[1]</sup> For various applications, chitosan has been decorated with some functional groups or noble metals. <sup>[2]</sup> Polyoxometalates (POMs) functionalizing chitosan had been synthesized by doping POM molecules into chitosan through anion-cation interaction between protonated amino groups in chitosan and polyanions. <sup>[3]</sup> Such POM-chitosan hybrids exhibited larger size more than 0.1  $\mu$ m and surface area lower than 0.4 cm<sup>3</sup>/g. Electrospinning has been recognized as an efficient technique for fabrication chitosan nanofibers ranging from 5 to 500 nm with amazing characteristics of very large surface area-to-volume ratio. <sup>[4]</sup> Therefore, fabrication of POM-functionalizing-chitosan hybrids with good physical-chemical characteristics is desirable, especially for catalysis.

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5-hydroxymethylfurfural (HMF) has drawn increasing attention as a member of bio-platform chemicals, <sup>[5]</sup> which could be synthesized by acid-catalyzed dehydration of carbohydrates including mono- or polysaccharides. [6] HMF could be converted into a series of bulk intermediates through and chemicals various chemical [7] transformations including maleic anhydride (MA), 2.5furandicarboxylic acid (FDCA) [8] and 2,5-diformylfuran (DFF), [9] 2,5bishydroxymethyl furan (BHMF), [10] 2,5-di-hydroxy-methyltetrahydrofuran (THFDM), [11] 2,5-dimethylfuran (DMF), [12] and 3hydroxymethylcyclopentanone (HCPN) 3and hydroxymethylcyclopentanol (HCPL) (Scheme S1). [13] Among these, selective oxidation of HMF was one of the most essential transformations in biorefinery to produce DFF, FDCA or MA. DFF is a versatile compound that can be used as a precursor in the synthesis of functional polymers, <sup>[14]</sup> pharmaceuticals, <sup>[15]</sup> antifungal agents, <sup>[16]</sup> furan-urea resins, <sup>[17]</sup> heterocyclic ligands, <sup>[18]</sup> and other value added products. However, several kinds of furan compounds like FDCA, 5-(FFCA), formyl-2-furancarboxylic acid 5-hydroxymethyl-2furancarboxylic acid (HMFCA), companied with DFF can possibly be formed during the HMF oxidation. Highly selective oxidation of HMF is important for DFF production. By now, both homogeneous and heterogeneous metal catalysts have been explored for the oxidation of HMF to DFF using various oxidants. [19-21] From the "Green Chemistry" concept, aerobic oxidation of HMF to produce DFF is a challenge with a promising application. Various solid catalysts had been designed to achieve HMF convert to DFF under aerobic oxidative conditions (Table S1). Among all, materials containing vanadium had been paid more attentions, which showed the conversion ranging from 84 to 100 % and DFF yields of 82 ~ 99.9 % at 120 °C to 140 °C for about 3 ~ 11 h in DMSO.  $^{\left[22\text{-}25\right]}$ Polyoxometalates (POMs) containing vanadium also showed potentials for oxidation of HMF to give a series of products including DFF<sup>[9]</sup> and MA<sup>[7]</sup>: Cs<sub>3</sub>HPMo<sub>11</sub>VO<sub>40</sub> gave 99 % conversion and 99 % yield of DFF at 110 °C for 6 h in DMSO under N2 and O2 in one-pot two-step process;  $H_5PMo_{10}V_2O_{40}$  presented 100 % conversion and 64 % yield of MA at 90 °C for 8 h in acetonitrile under 10 atm of O2. It can be concluded that the existence of Lewis base could favor for activating the hydroxyl group hence promoting the formation of DFF. <sup>[26]</sup> Therefore, the combination of Lewis base and POMs to fabricate multifunctional hybrids might open a new way for production of DFF from 5-HMF or even from monosaccharides.

HMF is a dehydrated product from fructose and also could be obtained from glucose through isomerization to fructose then dehydration in presence of basic or Lewis acidic catalysts (Scheme 1). <sup>[27]</sup>Compared to HMF as feedstocks, direct production of DFF from saccharides is more economics with well-tolerance to feedstocks and energy-release. By now, direct synthesis of DFF from fructose had already been achieved using POMs as catalysts. Liu's group reported that 58 % yield of DFF was obtained directly from fructose through  $H_3PMo_{12}O_{40}$  with 100 % conversion under reaction conditions as

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160 °C, 6 h in DMSO. [28] The catalytic activity was attributed to the co-existence of Brønsted acid and redox centers. Then Cs<sub>3</sub>HPMo<sub>11</sub>VO<sub>40</sub> was adopted in one step dehydration-oxidation of fructose to DFF with 60 % yield at > 99 % conversion under reaction conditions as 120 °C, 8 h in DMSO. [9] And Ghezali et al conducted the production of DFF directly from fructose and inulin over  $H_{(3+n)}PMo_{(12-n)}V_nO_{40}$  (n = 0 ~ 2) in choline chloride/DMSO solvent, which H<sub>4</sub>PMo<sub>11</sub>V<sub>1</sub>O<sub>40</sub> was found to be most active to give 84 % yield of DFF at 120 °C for 360 min. [29] Recently, Lee's group achieved H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> encapsulated on MIL-101 (PMA-MIL-101) to catalyze fructose convert into DFF in DMSO with 75.1 % yield of DFF at 81 % fructose conversion at 110 °C for 1 h. [30] Such PMA-MIL-101 overcame the drawbacks that one-pot conversion of fructose to DFF might suffer from low yield of DFF due to the co-existence of oxidative catalysts favoring for humin or the side-products formation. [31, 32] Also PMA-MIL-101 showed good reusability without separation procedures. Nevertheless, more efficient and recyclable catalysts containing multifunctionalized active sites are more desirable in one-pot one-step production of DFF from fructose even glucose.



Herein, we designed to synthesize chitosan nanofibers being decorated by  $H_5PMo_{10}V_2O_{40}$  (HPMoV) to check the physical-chemical properties on production DFF from HMF, and even from fructose or glucose. Firstly, chitosan nanofibers acted as a support to load POMs forming heterogeneous catalyst with large surface area-to-volume ratio. Secondly, such HPMoV/chitosan nanofiber hybrids could adjust Lewis basicity, Brønsted acidity and redox potentials through simply changing its components, which resulted in controllable triple sites favoring for HMF to DFF, even for fructose or glucose. This might provide some information for targeting high conversion of HMF and selectivity to DFF in the absence of bases in the reaction system, but also give some advice on designation of triple-functionalized POMs catalysts in other organic synthesis. Thirdly, DFF could be produced from glucose via base-catalyzed isomerization, acid-catalyzed dehydration, and successive selective oxidation by one-pot one-step reaction through HPMoV/chitosan nanofiber and O2.

#### **Results and Discussion**

#### Characterization of HPMoV/CS-f

peaks in the range of 1100-700 cm<sup>-1</sup>, which are attributed to the Keggin unit of  $u_{as}(P-O_a)$ ,  $u_{as}(Mo-O_d)$ ,  $u_{as}(Mo-O_b-Mo)$ , and  $u_{as}(Mo-O_c-Mo)$ , respectively. Meanwhile,  $u_{as}(P-O_a)$ ,  $u_{as}(Mo-O_d)$ ,  $u_{as}(Mo-O_b-Mo)$ , and  $u_{as}(Mo-O_c-Mo)$  were observed with some blue shifts after formation of HPMoV/CS materials. Such shifts were due to the strong interaction between POM anion and  $-NH_3^+$  in chitosan nanofiber. <sup>[33]</sup> The typical vibrational peak of  $-NH_2$  in chitosan nanofiber was observed to shift from 1578 cm<sup>-1</sup> to 1520 cm<sup>-1</sup> belonging to  $-NH_3^+$ . <sup>[34]</sup> further determined the interaction between PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub><sup>5</sup> and  $-NH_3^+$ .

The XRD of HPMoV/CS-f (n) was used to study the dispersion of the Keggin POM unit throughout the nanofiber hybrids (Fig. S2). A broad peak centered at 20 of 19.7° was observed for all nanofibers, which was assigned to the chitosan. Meanwhile, there were no diffraction peaks corresponding to the parent  $H_5PMo_{10}V_2O_{40}$  in all HPMoV/CS-f except HPMoV/CS-f (35). This indicated that the POM molecules were homogeneously dispersed in the mattric of chitosan as the loading amount lower than 30 %. Increasing the loading amount to 35 %, the diffraction peaks at 20 of 21.2°, 26.7° and 29.5° were observed belonging to  $H_5PMo_{10}V_2O_{40}$ , which showed that POM molecules unevenly dispersed or aggregated across the nanofibers in higher loadings. The DR-UV-vis (Fig. S3) gave the characteristic peak at 210 nm corresponding to Keggin structure. Meanwhile, the absorption intensity of the peak increased gradually as increasing the loading amount of HPMoV on chitosan nanofiber.

The <sup>31</sup>P MAS NMR for HPMoV/CS-f (25) gave two peaks at -4.54 and -2.19 ppm (Fig. S4a), which one was attributed to the existence of PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub><sup>5-</sup> anion (-4.55 ppm) and one was assigned to the interaction between PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub><sup>5-</sup> anion and -NH<sub>3</sub><sup>+</sup> group in chitosan nanofibers. <sup>[36]</sup> These results indicated the structural integrity of POM anion in hybrids, and also permitted their less leaching from chitosan support. The SEM images and EDX of HPMoV/CS-f (n) were given in Fig. 1, showing that all HPMoV/CS-f (n) were consisted of uniform fibers with diameters of 180-200 nm in good dispersity. And the EDX results for HPMoV/CS-f were similar to those of elementary analysis with HPMoV loading amounts as 5, 12, 25, 30 and 35 wt%, respectively.

The XPS analysis mainly reflects the composition and chemical elementary state of the surface and the inferior surface of sample. <sup>[36]</sup> The binding energy of HPMoV/CS-f (25) was given in Fig. 2a. It can be found the peaks of the O1s, N1s, C1s, V2p, P2p and Mo3d at 532.4 eV, 399.1 eV, 284.6 eV, 516.3 eV, 133.4 eV and 232.4 eV, respectively. This can prove that element O exists as O<sup>2-</sup>, N as N<sup>3-</sup>, C as C<sup>4+</sup>, P as P<sup>5+</sup>, V as V<sup>5+</sup>, and Mo as Mo<sup>6-</sup>. The XPS for N1s (Fig. 2b) presented the peak of -NH<sub>2</sub> at 399.0 eV and protonated -NH<sub>3</sub><sup>+</sup> at 401.5 eV in HPMoV/CS-f (25). This could be explained as that the proton from H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>. reacted with some of -NH<sub>2</sub> in chitosan through PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>...H...NH<sub>2</sub> to form protonated -NH<sub>3</sub><sup>+</sup>. Furthermore, some of amino groups did not react with heteropolyacids to retain some of basicity.

Furthermore, the stability of HPMoV/CS-f (n) was studied by thermogravimetric analysis (TGA), which gave the decomposition temperatures at 100 and 200 ~ 250 °C with the mass losses as around 8 % and 27 %, respectively (Fig. S5). The first mass loss was contributed to the loss of crystal water, while the second one was assigned to the dehydration of hydroxyl group in chitosan<sup>[37]</sup> similar to chitosan. It was indicated that the hybrids were stable within 500 °C.

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Fig. 1 SEM images (a) and EDX patterns (b) of HPMoV/CS-f (n)





As chitosan is a kind of basic biomacromolecules containing a large number of -NH<sub>2</sub> groups. Here, the purpose that we selected chitosan as a support for loading of POMs was to fabricate trifunctional hybrids combined POMs with Brønsted acidity and redox property, and chitosan nanofibers with basicity. It can be seen that all samples presented a similar CO<sub>2</sub> desorption temperature centered around 280-330 °C, which were assigned to the contribution of chitosan (Fig. 3) since HPMoV/CS-f (n) and chitosan nanofiber were stable within 500 °C. Meanwhile, increasing of loading amount of H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub>, the desorption temperature showed a decreasing trend from 317.3 °C (pure chitosan) to 291.8 °C (HPMoV/CS-f (25). This indicated that basicity of the hybrids decreased depending on the increasing of POM loading amount, which also determined that H<sub>5</sub>PMO<sub>10</sub>V<sub>2</sub>O<sub>40</sub> molecule homogeneously dispersed in chitosan matrix through interaction with amino groups hence decreasing the amount of -NH<sub>2</sub>. The CO<sub>2</sub> desorption temperature of HPMoV/CS-f (35) at 291.5 °C was lower than that of HPMoV/CS-f (25) at 291.8 °C, showing that there were some aggregation of POM molecules as increasing of its loading amount. Nevertheless, POM/CS-f (n) hybrids presented strong basicity in order of chitosan nanofibers (0.62 mmol g<sup>-1</sup>) > HPMoV/CSf (5) (0.46 mmol g<sup>-1</sup>) > HPMoV/CS-f (12) (0.37 mmol g<sup>-1</sup>) > HPMoV/CS- f (25) (0.21 mmol g<sup>-1</sup>) > HPMoV/CS-f (30) (0.16 mmol g<sup>-1</sup>) > HPMoV/CS-f (35) (0.11 mmol g<sup>-1</sup>).



Fig. 3 CO<sub>2</sub>-TPD spectra of chitosan nanofiber, HPMoV/CS-f (5), HPMoV/CS-f (12), HPMoV/CS-f (25), HPMoV/CS-f (30) and HPMoV/CS-f (35)

#### The catalytic activity for HPMoV/CS-f (n) in HMF oxidation Scanning the activity in HMF oxidation

In order to evaluate oxidative activity of POMs/CS nanofibers, we tested in the conversion of HMF under reaction conditions as 100 mg of 5-HMF and 60 mg of catalyst at 120 °C, 0.8 MPa for 6 h in 4 mL DMSO. As shown in Table 1, various catalysts including chitosan, chitosan nanfiber, HPMoV/CS (25) without nanofiber morphology, HPMoV/CS-f (5), HPMoV/CS-f (12), HPMoV/CS-f (25), HPMoV/CS-f (35) and H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> had been evaluated in aerobic oxidation of HMF. It can be seen that without any catalysts, HMF was only oxidized with 22.0 % conversion and 48.0 % selectivity to DFF, showing that the oxidative ability of oxygen was not strong enough to confirm the oxidation of HMF under our reaction conditions. Adding chitosan, the conversion of HMF was only increased to 23.3 %, but DFF selectivity increased to 77.3 %. Chitosan is a kind of basic biopolymer with a lot of amino groups, which could interact with -OH group of HMF through

hydrogen bond as chitosan-NH<sub>2</sub>...<sup>H</sup> V <sup>0</sup>. Hence the activation of the hydroxyl was favored, [38] and the generation of DFF was improved. When chitosan was electrospinned to form nanofibers, the activity of chitosan nanofiber was improved to 27.5 % of conversion but 85.5 % of selectivity. Although the surface area of chitosan nanofiber was larger than that without nanofiber structure, the catalytic activity in aerobic oxidation of HMF was /not increased significantly. This indicated that chitosan was not active in oxidative reaction. The selectivity to DFF was increased from 73.3 to 85.5 %, which was due to the increase of surface basicity in chitosan nanofibers. HPMoV presented strong redox capacity and strong Brønsted acidity, [39] which gave 58.9 % selectivity at 98.2 % conversion. The relationship between their activity of HPMoV/CS-f (n) and the HPMoV loading amount on chitosan nanofiber was also studied: (1) All HPMoV/CS-f hybrids showed higher activity than HPMoV and chitosan nanofibers. For same loading amount of HPMoV, HPMoV/CS nanofibers showed higher activity than HPMoV/CS nonnanofibers; (2) The conversion of HMF followed the order of HPMoV/CS-f (5) < HPMoV/CS-f (12) < HPMoV/CS-f (25) < HPMoV/CS-f (30) < HPMoV/CS-f (35), which was similar to the increasing of HPMoV loading amount. The HMF conversion was 62.7 % for HPMoV/CS-f (5), while increased to ~100 % for HPMoV/CS-f (35). The influence of loading amount of HPMoV on HMF conversion was also observed in Fig. 4a of conversion verse

reaction time, while the maximum conversion upon HPMoV/CS-f was achieved at different time depending on the HPMoV loading amount. It was attributed to the increasing of redox sites and also the increasing in Brønsted acidity, which was similar to Chen's report as stronger Brønsted acidity of H5PMo10V2O40 influencing the equilibrium shift for HMF oxidation; [9] (3) The selectivity to DFF increased as enhancement of HPMoV loading amount from 5 % to 25 %, then decreased as further increasing HPMoV amount to 35 %. And the maximum value was obtained as 91.8 % as using HPMoV/CS-f (25) with TOF as 14.73 h<sup>-1</sup> (TOF = converted HMF (mmol)/actual usage of HPMoV in chitosan (mmol) x h). Based on the previous reports, the coexistence of basic center and redox center might affect the oxidation of HMF and the distribution of the products [38]: there are two main competitive reactions in HMF oxidation as alcohol oxidation to DFF in the presence of slightly basic or neutral medium, and the aldehyde oxidation to HMFCA in strong basic media. Then DFF and HMFCA are further oxidized to FFCA under a strong basic condition. <sup>[38]</sup> Therefore, the properties for POM/chitosan nanofibers as distribution of Brønsted acidity or Lewis basic sites and redox potentials might influence HMF conversion and also product selectivity as well. In presence of HPMoV/CS-f, DFF yields increased firstly then decreased as reaction time changing from 0 to 6 h then to 8 h (Fig. 4b). For HPMoV/CS-f (n), the highest yields of DFF varied according to the difference of POM loading amounts as HPMoV/CS-f (5) (Brønsted acidity/Lewis basicity = 1.5: 100) < HPMoV/CS-f (12) (B/L = 2.7: 100) < HPMoV/CS-f (35) (B/L = 21.8: 100) < HPMoV/CSf (30) (B/L = 16.8: 100) < HPMoV/CS-f (25) (B/L = 8.9: 100). It can be seen that the oxidation of formyl group of HMF to HMFCA was observed around all reaction procedure with the vield lower than 10 % to 5 %, which indicated that the existence of Brønsted acid and Lewis basicity of hybrid materials did not favor for oxidation of formyl group of HMF (Fig. 4c). Meanwhile, the by-product of FDCA was observed at the end of the reaction, showing not stronger enough oxidative ability of O2 to oxidize DFF and HMFCA to FDCA through HPMoV/CSf (n) catalysts (Fig. 4d). As results, HPMoV/CS-f (25) with B/L = 8.9: 100 gave the highest yield as 94.1 % of DFF with 1.3 % HMFCA and 0.4 % FDCA among all chitosan-POM nanofibers. For HPMoV/CS-f (25), the total yield of DFF, FDCA and HMFCA after 6 h was close to the conversion of HMF being tested by TOC (total organic carbon). The TOC still kept balancing at 6 h with only decreasing of 2.6 %. This indicated that no other by-products being produced under our reaction conditions.

The higher efficiency of HPMoV/CS-f (n) was also contributed to the interaction between -OH from HMF and -NH<sub>2</sub> from chitosan, which could concentrate 5-HMF around the active sites of HPMoV. The adsorption capacity of the catalysts on HMF also depended on the composition and structure of hybrids as: HPMoV/CS-f (5) (11 mmol/g) > HPMoV/CS-f (12) (6.4 mmol/g) > HPMoV/CS-f (25) (3.5 mmol/g) > HPMoV/CS-f (30) (2.7 mmol/g) > HPMoV/CS-f (35) (2.1 mmol/g) > HPMoV/CS (25) (1.7 mmol/g). It can be seen that increasing POM amount gave rise to decreasing of adsorption of HMF, indicating that chitosan mattric played a main role on adsorption effect. Meanwhile, HPMoV/CS-f (25) with nanofiber structure presented almost two times higher than that of HPMoV/CS-f (25) without nanofiber structure. This was attributed to the enhancing surface area and increasing surface basic sites of chitosan nanofibers. The essential adsorption of HMF by HPMoV/CS-f (n) was further determined by IR spectrum of HPMoV/CS-f (25) after absorbing HMF (Fig. S6). Compared with fresh HPMoV/CS-f (25), the IR spectrum of adsorbing HMF displayed

significant differences at 1666 cm<sup>-1</sup> (Fig. S6a) assigned to amide vibrations representing the C=O groups along HMF involved in the intrasheet hydrogen bonds with the NH<sub>2</sub> group along the chitosan. <sup>[40]</sup>

Table 1 Comparison of catalysts used in HMF oxidation and product distribution.

Catalyst	Basic content (mmol⋅g⁻¹)	HMF conver -sion (%)	Yield (%)		
			DFF	HMFCA	FDCA
None	-	22.4	10.6		-
Chitosan	0.69	23.3	18.0	0.4	0.2
Chitosan nanofiber	0.62	27.5	23.5	0.1	0.5
(25) without nanofiber	0.23	76.6	62.9	1.3	1.3
HPMoV/CS-f (5)	0.46	62.7	47.8	2.0	0.3
HPMoV/CS-f (12)	0.37	88.4	73.5	1.7	0.5
HPMoV/CS-f (25)	0.21	96.2	94.1	1.3	0.4
HPMoV/CS-f (30)	0.16	98.2	84.4	6.7	1.4
HPMoV/CS-f (35)	0.11	100.0	81.4	2.6	1.7
H <sub>5</sub> PM0 <sub>10</sub> V <sub>2</sub> O <sub>40</sub>	-	98.2	58.9	4.3	4.2

Reaction conditions: HMF (100 mmg), catalyst usage (60 mg), DMSO (4 mL), 120 °C, 6 h, O2 (0.8 MPa)



Fig. 4 Catalytic performance for various catalysts in oxidation of 5-HMF by O2. Reaction conditions: 100 mg of 5-HMF, 60 mg of catalyst, and 4 mL solvent at

The influence of catalyst dosage, temperature and usage of HMF oxidation catalyzed by HPMoV/CS-f (25) was optimized (Fig. S7). Varying amounts of HPMoV/CS-f (25) from 40 to 80 mg were used for the DFF production at 120 °C for 6 h. As shown in Fig. S7a, the conversion increased from 83.1 % to 100 % as increasing the amount of HPMoV/CS-f (25) from 40 mg to 80 mg, respectively. It is clear that the catalyst dosage had a significant effect on the oxidation of HMF. The yield of DFF increased when the catalyst usage was increased from 40 mg to 60 mg, and then sharply reduced as further increasing the usage of catalyst to 80 mg. This was contributed to the subsequent oxidation of DFF to FDCA. These results showed that the usage of

120 °C for 6 h.

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catalyst as 60 mg was sufficient in the oxidation reaction. Fig. S7b showed the influence of temperature on oxidation of HMF in presence of HPMoV/CS-f (25). The conversion increased with the increase of the temperature from 90 to 130 °C. It can be seen that increasing to 120 °C, the yield of DFF reached the maximum. Further enhancement of temperature led to decreasing DFF yield due to subsequent oxidation occurred. The effect of HMF usage of was studied at 80, 90, 100, 110 and 120 mg under similar conditions. Conversion of HMF was found to be decreased with increasing HMF usage (Fig. S7c). It can be seen that increasing to 100 mg, the yield of DFF reached the maximum. All further experiments were carried out by keeping 100 mg of HMF.

Besides the above conditions, solvents also played a principal role in the conversion of HMF and selectivity of DFF. Here, six kinds of solvents were used including organic solvents of DMF (N, Ndimethylformamide), C2H5OH, Toulene, MIBK (methyl isobutyl ketone), DMSO and H<sub>2</sub>O (Fig. S8). It also can be seen that the selectivity of DFF depended on the polarity of solvents using HPMoV/CS-f (25) catalyst, which strong polarity and high boiling point for solvent were beneficial for HMF conversion. In these organic solvents, where DMSO emerged as the best solvent, which a good HMF conversion of 96.2 % and 94.1 % vield of DFF were obtained after 6 h. And the HMF conversion (51.4 %) and 20.1 % yield of DFF were obtained in water at 120 °C for 6 h. 95.0 % conversion of HMF and 56.2 % vield of DFF were obtained in water as temperature was increased to 140 °C and time was prolonged to 8 h. By now, the best efficiency of 98 % selectivity to DFF at 97.8 % HMF conversion was obtained upon MgO·CeO2 in water system under 100 °C for 15 h. [38] By now, aerobic oxidation of 5-HMF to produce DFF in water has not been concerned using POMs as catalysts before. And the study on this field would be done further. Fig. S8 also presented the influence of the O<sub>2</sub> pressure on the conversion and selectivity in the oxidation of HMF. By increasing the O2 pressure from 0.4 to 1.2 MPa, the conversion increased from 88.7 to 98.2 %, indicating higher oxygen pressure increased the HMF conversion. However, the yields of DFF at 0.4 MPa, 0.8 MPa and 1.2 MPa changed as 82.3 %, 94.1 % and 72.8 %, respectively. Higher oxygen amount could increase the HMF conversion but decrease the DFF yield due to the occurrence of overoxidation. Therefore, the best considerable oxygen pressure was 0.8 MPa for oxidation of HMF to DFF.

# The catalytic activity of HPMoV/CS-f in oxidation of monosaccharides

Compared to production of DFF from HMF, the direct one-pot conversion of monosaccharides (fructose and glucose) into DFF with high yield is desirable and still a great challenge, <sup>[22, 41, 42]</sup> which involves the selective dehydration of carbohydrates into HMF over acid sites and the consequent oxidation of HMF to DFF over redox sites. <sup>[22]</sup> However, production of DFF was often obtained in one-pot and two-step containing acidification and oxidation reaction facing one major drawbacks as the formation of humins and other undesired byproducts due to the co-existence of acid and redox sites. <sup>[40, 43]</sup> Moreover, the existence of acid sites might cause the degradation of formed HMF to levulinic acid or lactic, *et al.* Therefore, designation of new multifunctional catalysts with suitable distribution of acid sites and redox sites is still desirable. On this concept, HPMoV/CS-f (n) might be a good candidate for production of DFF through monosaccharides. Initially, their activity was evaluated in conversion of fructose under the reaction conditions as catalyst (60 mg), fructose (100 mg), DMSO (4 mL), 140 °C and 6 h with 0.8 MPa of O<sub>2</sub> (Fig. 5a). It can be seen that hybrids with higher amount of Brønsted acidity gave the highest conversion of fructose, while HPMoV/CS-f (35) showed highest conversion efficiency. The yields of DFF depended on the acid-base distribution of the catalysts. Chitosan nanofiber was a kind of solid Lewis base, which could not catalyze fructose dehydration, hence no DFF or HMF generated. H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> is a kind of Brønsted acidredox POMs, which gave 40.3 and 9.2 % yields of DFF and HMF at 71.8 % conversion of fructose. As expected, the DFF yield increased significantly as increasing loading amount of HPMoV on chitosan nanofibers. For all HPMoV/CS-f (n), the yields of 5-HMF were lower than 16.4 %, showing that the oxidation of 5-HMF was faster than dehydration of fructose due to the stronger redox ability of HPMoV. The influence of loading amounts of HPMoV on DFF yield and fructose conversion was similar to those in oxidation of 5-HMF, while the HPMoV loading amount of 25 % was suitable for transformation. Upon HPMoV/CS-f (25), the maximum DFF vield of 61.9 % was achieved with 14.1 % yield of HMF at 83.1 % conversion of fructose.

Due to the existence of basicity of HPMoV/CS-f (n), it might be more available for production of DFF directly from glucose. As expected, yield of DFF was achieved as 31.4 % upon HPMoV/CS-f (25) at almost 82.3 % conversion of glucose (Fig. 5b) under reaction conditions similar to fructose. By now, direct production of DFF from glucose had been achieved by using a base-acid-redox combination of HT (Mg-AI hydrotalcite), Amberlyst-15 and Ru/HT as a heterogeneous catalyst giving 98 % conversion and 25 % yield. <sup>[43]</sup> It can be seen that there were three main products being generated as fructose, 5-HMF and DFF in presence of HPMoV/CS-f (n), indicating that the co-existence of Brønsted acidity, Lewis basicity and redox potential synergistically influenced the glucose oxidation (Fig. 5b).



Fig. 5 One-pot, one-step synthesis of DFF from fructose (a) or glucose (b). Reaction conditions: catalyst (60 mg), fructose or glucose (100 mg), DMSO (4 mL), 0.8 MPa O<sub>2</sub>, 140 °C, 6 h.

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The time course for one-pot one-step conversion of glucose into DFF was also investigated in presence of HPMoV/CS-f (25) (Fig. S9). It was found that fructose and HMF were generated firstly then to DFF, while fructose and HMF were the main products at the initial stage of 4 h with the yields of 29.8 and 18.4 %, while the yield of DFF was obtained as 16.3 %. The yields of fructose and HMF then decreased as prolonging reaction time, while yield of DFF increased to 31.4 % at 6 h. The TOC still kept balancing at 6 h, determining no deep oxidation to CO<sub>2</sub> occurrence. The products verse reaction time determined that glucose underwent isomerization to fructose by base sites, dehydration to HMF upon Brønsted acidic sites, and final oxidation to DFF by redox sites. The optimization of the reaction conditions in production of DFF form fructose and glucose were undergoing.

#### Catalyst stability and reusability

Recovery and stability are important properties for practical heterogeneous catalysts. In each run, the catalyst was separated from the reaction mixture by centrifugation then washed with DMSO and ethanol. The obtained solid was dried at 40 °C overnight for reuse. The HPMoV/CS-f (25) catalyst could be reused for ten runs without significant loss of the activity under identical reaction conditions. DFF yield was maintained over 91 % and HMF conversion was kept > 94.2 % after ten runs, which indicated that the HPMoV/CS-f (25) catalyst was stable and little leaching of HPMoV from chitosan support. The above filtrate was checked by UV-vis spectroscopy to determine the leaching of HPMoV/CS-f (25) into reaction mixture (Fig. S10). Leaching experiments was carried out to check the loss of HPMoV from support during the reaction (Fig. S11). There was little increasing in HMF conversion and DFF yield for 5, 6, 7 and 8 h as the catalyst was filtered out at 4 h compared to the common experiment. It can be proved that HPMoV did not leaching from the support during the reaction showing higher stability. The stability of the catalyst was performed with the reaction time in the range of 0.5-6 h for ten cycles. The final leaching amount of HPMoV/CS-f (25) was about 1.7 % of the initial amount (Fig. 6) due to the personal operation. The used HPMoV/CS-f (25) catalyst was characterized by DR-UV-vis (Fig. S12), <sup>31</sup>P MAS NMR, FT-IR and XPS (Fig. S4b, Fig. S6 and Fig. S13), which showed no change compared to the fresh one. The SEM image (Fig. S14a) and EDAX (Fig. S14b) of reused HPMoV/CS-f (25) also showed no change in morphology and element compositions. The above results determined that HPMoV/CS-f (25) presented high stability and long duration.



Fig. 6 Reusability and leaching amount of HPMoV/CS-f (25) in oxidation of 5-HMF.

#### Conclusions

A series of trifunctional POM decorated chitosan nanofibers HPMoV/CS-f (n) had been prepared through electrosinning and characterized by IR, <sup>31</sup>P MAS NMR, XRD, XPS, SEM spectroscopy and CO2-TPD. Among all hybrids, HPMoV/CS-f (25) showed highest efficiency in aerobic oxidation of HMF with 96.2 % conversion and 94.1 % yield of DFF in DMSO, which was contributed to its unique properties of co-existence of Lewis basicity, Brønsted acidity, redox potentials, nanofiber morphology, suitable surface acid-base sites, and rational molar ratio for Brønsted acidity to Lewis basicity as 8.9: 100. Direct transformation of fructose and glucose was achieved in one-pot one-step process, which presented 61.9 % yield of DFF at 83.1 % fructose conversion and 31.4 % yield at 82.3 % glucose conversion. HPMoV/CS-f was easily separated through filtration and was reused for at least ten times without obvious loss of its catalytic activity. Furthermore, HPMoV/CS-f (25) showed potentials in converting 5-HMF to DFF in water system with 56.2 % yield at 95.0 % conversion.

#### **Experimental Section**

The synthesis and characterization of the hybrids were given in Supporting Information. And the oxidative experiment was also in Supporting Information.

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