# Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

# Selective oxidation of 5-hydroxymethylfurfural with $H_2O_2$ catalyzed by a molybdenum complex

Shuang Li[1], Kunmei Su *[1], Zhenhuan Li[12], Bowen Cheng[1]

[1]State Key Laboratory of Separation Membranes and Membrane Processes, School of environment Science and Chemisty Engineering of Tianjin Polytechnic University,Tianjin, China.

[2]School of Materials Science and Engineering, Tianjin Polytechnic University, 300160 Tianjin, China.

---

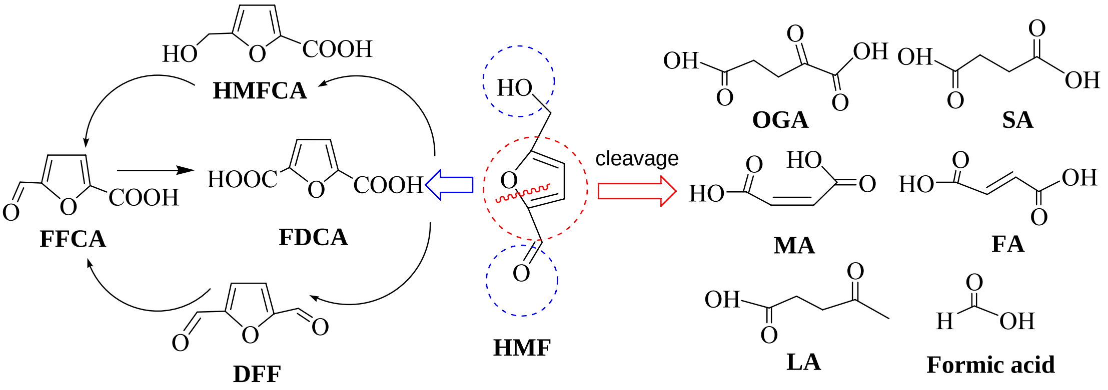
Corresponding author: School of Materials and Chemical Engineering, Tianjin Polytechnic University, Tianjin, 300160, China
Tel: +86 022 83955358; Fax: +86 022 83955055
E-mail address: Zhenhuanli1975@aliyun.com; Sukunmei@tjpu.edu.cn.

**Abstract:** Organic solvent-freely 5-hydroxymethylfurfural (HMF) oxidation into 2,5-furandicarboxylic acid (FDCA) with hydrogen peroxide using quaternary ammonium octamolybdate and quaternary ammonium dectungstate was studied. Tetra-1-ethyl-3-methylimidazolium octamolybdate ($[EMIM]_4Mo_8O_{26}$), tetra-hexadecyltrimethyl ammonium octamolybdate ($[CTAB]_4Mo_8O_{26}$) and tetra-ethylpyridinium octamolybdate ($[EPy]_4Mo_8O_{26}$) displayed the high activity for selective oxidation of HMF to FDCA, and the selectivity of FDCA could reach 100% with 99.5% conversion of HMF in presence of $[EMIM]_4Mo_8O_{26}$. The byproduct formed in competition with FDCA was identified as intermediate 5-hydroxymethyl-2-furan carboxylic acid (HMFCA) and 5-formyl-2-furan carboxylic acid (FFCA), and neither 2,5-diformyl furan (DFF) nor other byproducts from the oxidative cleavage of HMF furan ring were detected during oxidation process, which indicated the aldehyde group of HMF oxidizes first followed by the oxidation of hydroxymethyl group in this reaction system. Although the quaternary ammonium salts, such as [EMIM]Br, EPyBr and CTAB, prevented FDCA formation from HMFCA advanced oxidation, they could eliminate the oxidative cleavage of furan ring and improve the affinity of HMF and catalysts to make the catalytic active centers readily accessible to HMF molecules. However, tetra-1-ethyl-3-methylimidazolium dectungstate ($[EMIM]_4W_{10}O_{32}$), tetra-hexadecyltrimethyl ammonium dectungstate ($[CTAB]_4W_{10}O_{32}$) and tetra-ethylpyridinium dectungstate ($[EPy]_4W_{10}O_{32}$) were unfavorable of FDCA formation. The great difference performance of quaternary ammonium octamolybdate and quaternary ammonium dectungstate in HMF oxidation with $H_2O_2$ was attributed their different structure.

**Keywords**: 2,5-Furandicarboxylic acid; 5-hydroxymethylfurfural; hydrogen peroxide; quaternary ammonium octamolybdate; quaternary ammonium dectungstate

# Introduction

Due to the rapid development of the world economy and the limitation of fossil resource, biomass has been regarded as ideal resource to provide carbon sources for chemical and petroleum industry.[1-3] 2,5-furandicarboxylic acid (FDCA), obtained from the oxidation of 5-hydroxymethylfurfural (HMF) ,[4,5] has been identified as one of twelve potential building blocks to produce important chemicals.[6] For example, FDCA can be as the alternative monomer of terephthalic acid to produce polyamides, polyesters and polyurethanes.[7, 8]



**Scheme 1 Reaction pathway for aqueous HMF oxidation**

The preferred route of FDCA production involves the efficient catalytic transformation of biomass or biomass-derived carbohydrates to HMF followed by catalytic oxidation of HMF. [9, 10] HMF can be oxidized with aldehyde and methyl alcohol to give 2,5-diformyl furan (DFF) [11], 5-hydroxymethyl-2-furan carboxylic acid (HMFCA), 5-formyl-2-furan carboxylic acid (FFCA) and FDCA [12-15]. [16] At the same time, the oxidative cleavage of furan ring of HMF could take place. In this case, succinic acid (SA) and 2-oxoglutaric acid (OGA) were obtained as a major product, and maleic acid (MA) and fumaric acid (FA) existed with low yields. [17] In addition, levulinic acid (LA) and formic acid also produced through a hydration of HMF in the presence of acid catalyst [18](see scheme 1).

The strong stoichiometric oxidation reagents, such as chromate ($CrO_4^{2-}$), dichromate ($Cr_2O_7^{2-}$) and permanganate ($MnO_4^-$), were often employed to oxide HMF. [19] However, these oxidants are highly toxic, and some of them leave a lot of undesirable metal waste after usage. The aerobic oxidation of HMF to FDCA had been examined with the homogeneous Co/Mn/Br catalyst, where DFF was the major oxidation product. [20, 21] The aerobic effective oxidation of HMF to FDCA could be carry out over Pt, Ru and Au-based catalysts. [22-24] For example $\gamma$-$Fe_2O_3$@HAP-Pd(0) magnetic catalyst showed high activity in HMF oxidation with 97.0% HMF conversion and 92.9% FDCA yield under optimal reaction conditions. [25] Using supported gold-copper nanoparticles as catalyst 99% yield of FDCA was obtained. [26] However, these catalytic systems are absence of stability and cost highly, and molecular oxygen or air is difficult to control. [27, 28]

Hydrogen peroxide ($H_2O_2$) is another environmental friendly and green oxidation reagent. Choudhary applied $H_2O_2$ to the oxidative cleavage of furan ring of HMF with 99% conversion. [29] Recently, the increasing concerns have been arisen from the use of heteropoly acids,[30] which are widely used for their well-defined structure, strong Brönsted acidity, fast multi-electron transfer, high proton motility, resistance to hydrolytic and oxidative degradations in solutions. [31] When heteropoly acid was used as catalysts, $H_2O_2$ is regarded as ideal oxidant with high tunability. For example, when coupled $H_2O_2$ with W-based phase-transfer catalyst as catalytic system, alcohols, olefins and sulfide can be well oxidized. [32] Most of heteropoly acid catalysts are insoluble in the water, but they can dissolve in a mixture system of $H_2O_2$.[33-35] The insoluble catalyst forms soluble active species by the action of $H_2O_2$, and when $H_2O_2$ is used up, the catalyst precipitates for easy recycling.

In this work, we used quaternary ammonium octamolybdate and quaternary ammonium dectungstate to directly convert HMF to FDCA by $H_2O_2$. These W- and Mo-based catalysts, when coupled with $H_2O_2$, are regarded as phase-transfer catalysts. It demonstrated that $[EMIM]_4Mo_8O_{26}$ exhibited highly efficient performance for the selectivity of FDCA and the conversion of HMF. Under the optimized conditions, the selectivity of FDCA reached almost 100%, and the HMF conversion of 99.5% was achieved. At same time the great different performance of quaternary ammonium octamolybdate and quaternary ammonium dectungstate in HMF oxidation by $H_2O_2$ was well studied.

## Experiment

## Materials

All of used reagents with analysis reagents degree were purchased from Leon Reagent Company and Alfa Aesar Reagent Company, for eample HMF, FDCA, HMFA, FFCA, DFF, $Na_2MoO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$, ethyl bromide, hexadecyl trimethyl ammonium bromide (CTAB) and glacial acetic acid et al.

## Catalyst preparation and characterization

According to the method introduced by Ming-lin Guo and his coworkers, [34, 35] the catalysts were prepared. $[EMIM]_4W_{10}O_{32}$, $[CTAB]_4W_{10}O_{32}$ and $[EPy]_4W_{10}O_{32}$ were prepared by mixing boiling solutions of 16 g of $Na_2WO_4{\cdot}2H_2O$ in 100 ml of distilled water and 33.5 ml of 3 M HCl. After boiling for a few minutes, the clear yellow solution was precipitated by addition of an aqueous solution of [EMIM]Br, CTAB and [EPy]Br. The white precipitate was filtered, and washed with boiling water, and dried at 60 °C to give a colorless powder. $[EMIM]_4Mo_8O_{26}$, $[CTAB]_4Mo_8O_{26}$ and $[EPy]_4Mo_8O_{26}$ preparation was listed as following: a mixture of 40 ml aqueous solution of $Na_2MoO_4{\cdot}2H_2O$ (12.0 g, 0.05 mol) and 12% dilute hydrogen chloride (19.0 ml, 0.076 mol) was added dropwise into a solution of [EMIM]Br, CTAB and [EPy]Br (0.093 mol) in 100 ml of distillated water under stirring at 70 °C. A white precipitate was immediately formed. After continuously stirring for 20 min, the resulting product was filtered, washed with water and dried at 60 °C. The prepared catalysts were characterized by single X-ray diffraction (SXRD) and Ultraviolet spectrum (UV). The octamolybdate anion lies about an inversion centre and is structurally a β-isomer.

## Oxidation reactions

50 ml three-necked flask was used as reactor which was equipped with a reflux condenser. The reactor was loaded with 9 mmol HMF, 18 mmol NaOH and 20 ml distilled water. The mass ratio of HMF to catalyst was 10:1, and the reactor was heated by oil bath. When the mixture was heated to required temperature, 25 ml 6%

$H_2O_2$ was added into reactor by drop during 2 h. After 2 h, the reaction was finished and the mixture was characterized.

## Analytical methods

The mixture of samples was analyzed by high-performance chromatography (HPLC, Waters1525 ) using a column (Scienhome Kromasil C18, 250 mm×4.6 mm) with UV detection ( 278 nm) and a 996 photodiode array detector. Acetonitrile and 0.1wt.% acetic acid aqueous solution, volume ratio 10:90, were used as the mobile phase, and flow rate was 1ml/min. The products were characterized by standard addition method, which is the special internal standard method. The characterization process was listed as followings: the reaction mixture was diluted to 100 ml with pure water, and 0.3 g HMF was dissolved into 100 ml pure water. Then 4 ml diluted reaction solution was diluted to 5 ml with pure water and diluted HMF in two colorimetric tubes. The mass concentrations of products were calculated from HPLC-peak integrations, and the selectivity of HMFCA and FFCA was calculated based on the carbon balance. Related formula is followed as:

$$m_1 = \frac{W}{A'/A - 1}$$

m1: mass of HMF after reaction, A′ : HPLC areas of HMF when 0.03g HMF added, A: HPLC areas of HMF after reaction, W: The mass of HMF added, 0.03g.

$$\text{HMF conversion (mas\%)} = (1 - \frac{m1}{m2}) \times 100\%$$

M2: mass of HMF before reaction, S: HPLC areas of reaction products.

$$\text{Selectivity of FDCA} = \frac{S_1}{S_1 + S_2 + \ldots}$$

## Results and discussion

### Effects of different catalysts on HMF oxidation by $H_2O_2$

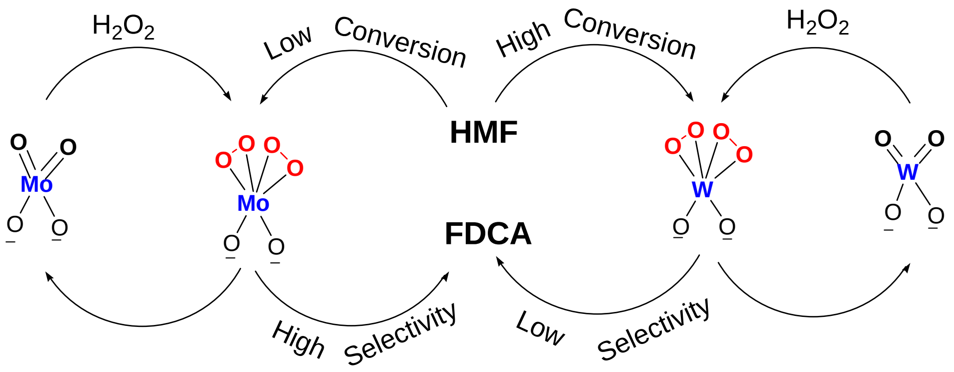
**Table 1** HMF oxidation by $H_2O_2$ using different catalysts

| Entry | Catalysts | Product Selectivity (mol%) | | | Conversion |
|---|---|---|---|---|---|
| | | FDCA | HMFCA | Cleavage | (HMF %) |
| 1 | $[EMIM]_4Mo_8O_{26}$ | 92.7 | 7.3 | ---- | 96.2 |
| 2 | $[CTAB]_4Mo_8O_{26}$ | 90.4 | 9.6 | ---- | 94.5 |
| 3 | $[EPy]_4Mo_8O_{26}$ | 77.0 | 23.0 | ---- | 85.1 |
| 4 | NO CATALYST and $H_2O_2$ | - | - | 100 | 12.6% |
| 5 | NO CATALYST | 49.7 | 46.3 | 4.0 | 98.0 |
| | NO CATALYST* | 60.0 | 34.2 | 5.8 | 99.0 |
| 6 | $Na_2MoO_4$ | 85.2 | 12.8 | 2.0 | **75.4** |
| 7 | [EMIM]Br | 23.2 | 76.8 | ---- | 90.6 |
| 8 | EPyBr | 34.1 | 65.9 | ---- | 85.1 |
| 9 | CTAB | 32.7 | 67.4 | ---- | 97.6 |
| 10 | $Na_2WO_4$ | 79.0 | 19.2 | 1.8 | **97.8** |
| 11 | $[EMIM]_4W_{10}O_{32}$ | 50.2 | 49.8 | ---- | 81.1 |
| 12 | $[CTAB]_4W_{10}O_{32}$ | 47.0 | 53.0 | ---- | 62.1 |
| 13 | $[EPy]_4W_{10}O_{32}$ | 68.6 | 31.4 | ---- | 84.2 |

Reaction conditions: 9 mmol HMF, 18mmol NaOH, the mass ratio of HMF to catalyst=1/10, 20 ml deionized water, 25 ml 6% $H_2O_2$, 70 °C and 2h. * indicated reaction time was 12h.

Previous studies have shown that the presence of some amounts of base in the reaction mixture can restrain the by-product formation from the side reactions of HMF.[11] In order to avoid some side reaction occurrence, HMF oxidation by $H_2O_2$ was carried out in presence of some NaOH, and the efficiencies of various acid catalysts for the oxidation of HMF to FDCA in the presence of $H_2O_2$ were listed in Table 1. $[EMIM]_4Mo_8O_{26}$, $[CTAB]_4Mo_8O_{26}$ and $[EPy]_4Mo_8O_{26}$ displayed the high activity for selective oxidation of HMF to FDCA (entry 1-3). The selectivity of FDCA reached 92.7% with 96.2% conversion of HMF in presence of $[EMIM]_4Mo_8O_{26}$, and the byproduct formed in competition with FDCA was identified as intermediate HMFCA by HPLC. In the absence of both catalyst and $H_2O_2$, FDCA was not detected and 12.6% HMF was consumed into some other byproducts which came from the oxidative cleavage of furan ring of HMF (entry 4). When HMF was oxidized by $H_2O_2$ without catalyst existence, the selectivity of FDCA and HMFCA was 49.7% and 46.3%, and the conversion of HMF reached 98.0%. Importantly, some other byproducts from the oxidative cleavage of furan ring were also detected, while the increase of FDCA selectivity was not obvious by prolonging the reaction time to 12 h (entry 5). $Na_2MoO_4$ significantly promoted the advanced oxidation from HMFCA to FDCA, which resulted in FDCA selectivity increase to 85.2% and furan ring cleavage byproduct selectivity decline to 2.0% (entry 6). Although the quaternary ammonium salts such as [EMIM]Br, EPyBr and CTAB prevented FDCA formation from HMFCA advanced oxidation, they could effectively eliminate the oxidative cleavage of furan ring and acted as the phase transfer catalyst to well promote the conversion of HMF into HMFCA (entry 7, 8 and 9). These results in Table 1 clearly demonstrated that the simultaneous presence of both quaternary ammonium and molybdate is essential for the selective conversion of HMF to FDCA. Herein, inorganic anions acted as active center, but organic cations improved the affinity of HMF and catalysts, making the catalytic active centers readily accessible to HMF molecules to promote HMF conversion into HMFCA and preventing furan ring from oxidative cleavage.

Be similar to $Na_2MoO_4$ performance, $Na_2WO_4$ also could catalyze the advanced oxidation of HMFCA to FDCA, and FDCA selectivity reached 79.0% with 98.0% HMF conversion (entry 10). However, the simultaneous presence of quaternary ammonium and dectungstate was unfavorable of FDCA formation due to the high steric hindrance, and the molar ratio decrease of metal to HMF and $H_2O_2$ was another minor factor to result in HMF conversion and FDCA selectivity decline (entry 11, 12 and 13). By comparisons of $Na_2MoO_4$ with $Na_2WO_4$, $Na_2MoO_4$ displayed the higher activity in HMFCA oxidation to FDCA and lower activity in HMF conversion, while $Na_2WO_4$ was benefited to HMF conversion into HMFCA and unfavorable of FDCA formation from HMFCA. In addition, inorganic anions are rapidly oxidized to new form during HMF oxidation by $H_2O_2$[36] (scheme 2).



**Scheme 2.** HMF oxidation by $H_2O_2$ in presence of molybdate anion and tungstate anion

### Difference performance of $Mo_8O_{26}$ anion and $W_{10}O_{32}$ anion in HMF oxidation

**with $H_2O_2$**

Herein UV spectrum was used to study the great difference performance of $Mo_8O_{26}$ anion and $W_{10}O_{32}$ anion in HMF oxidation with $H_2O_2$, namely the presence of quaternary ammonium and $Mo_8O_{26}$ anion is essential for the selective conversion of HMF to FDCA, however, the simultaneous presence of quaternary ammonium and $W_{10}O_{32}$ anion is unfavorable of FDCA formation. As shown in Figure 1, the intensive UV spectrum of Mo=O located at 208 λ/nm, but a weak UV spectrum of $[EMIM]_4W_{10}O_{32}$ and $[EPy]_4W_{10}O_{32}$ appeared around 259λ/nm despite no UV spectrum of W=O detection in near ultraviolet region (200-400λ/nm), which implied there existed the strong π-d interaction between the imidazole or pyridine and W center. The bonds of Mo (or W) and O in octamolybdate (or dectungstate) were built in the form of single and double without $H_2O_2$ existence. [34, 35, 37] When $H_2O_2$ added, only one new UV spectrum appeared around 291 λ/nm and 283λ/nm for quaternary ammonium octamolybdate and quaternary ammonium dectungstate, respectively, which showed the epoxy groups were formed and Mo=O (or W=O) species disappeared [36, 38] (see scheme 3). The epoxy groups in quaternary ammonium octamolybdate and quaternary ammonium dectungstate played a crucial role in HMFCA advanced oxidation to FDCA. The strong π-d interaction between the imidazole (or pyridine) and W center resulted in UV spectrum peak tailing of epoxy groups, which was responsible for the higher activities of $[EMIM]_4W_{10}O_{32}$ and $[EPy]_4W_{10}O_{32}$ than $[CTAB]_4W_{10}O_{32}$ in HMF conversion and HMFCA oxidation to FDCA. The great difference performance of quaternary ammonium octamolybdate and quaternary ammonium dectungstate in HMF oxidation with $H_2O_2$ was attributed to their different structure.

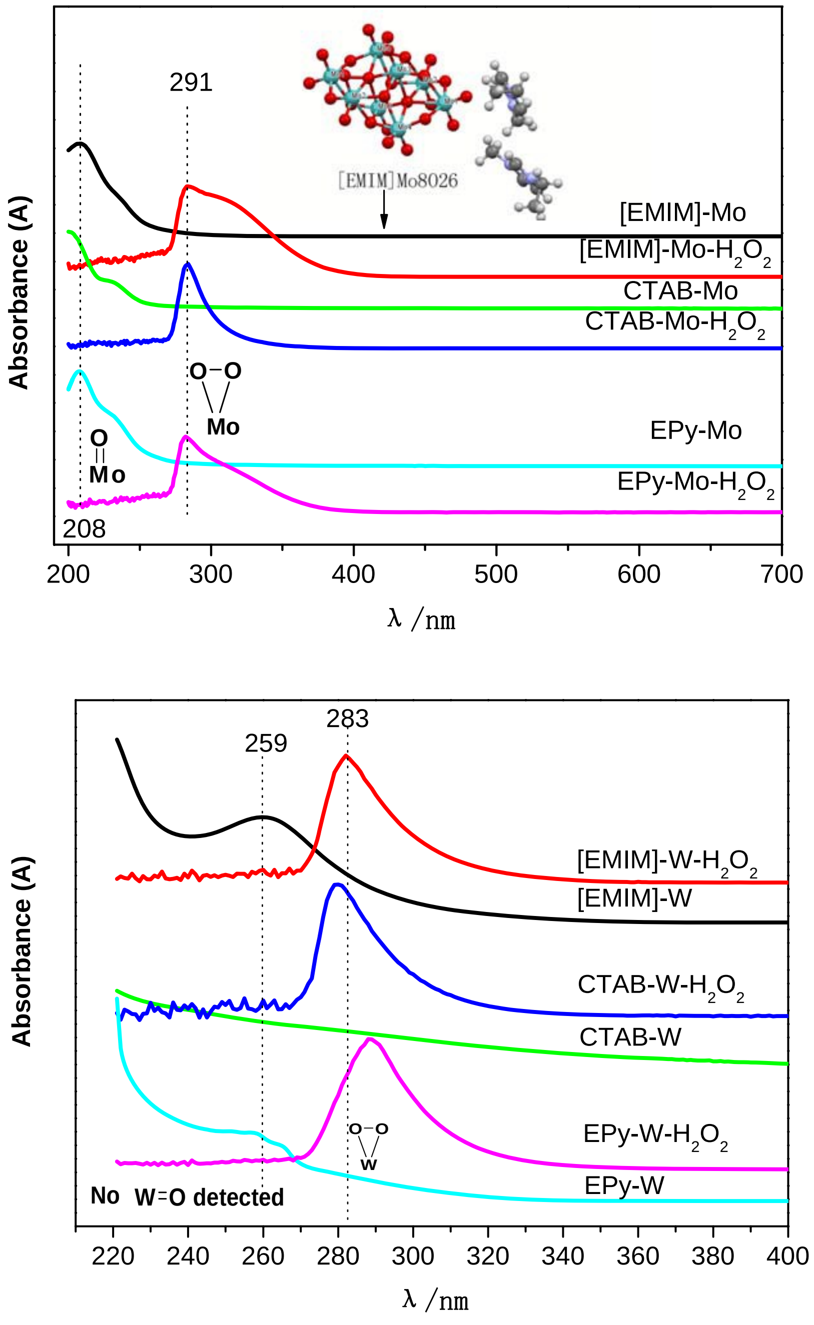
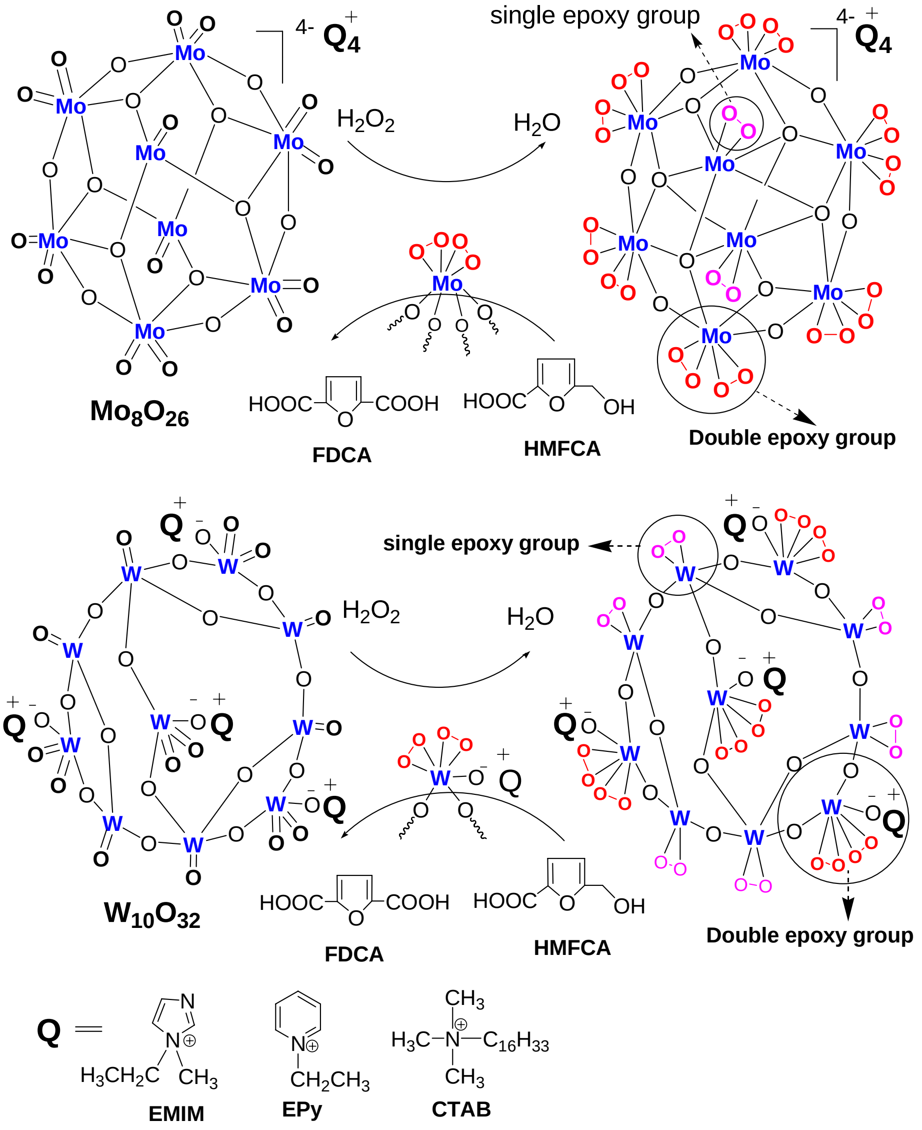


**Figure 1.** UV spectra of quaternary ammonium octamolybdate and quaternary ammonium dectungstate within and without $H_2O_2$

Quaternary ammonium dectungstate had an equal number of single epoxy groups and double epoxy groups in presence of $H_2O_2$, but the double epoxy groups was simultaneously attached by a quaternary ammonium (see scheme 3). Most importantly, the double epoxy groups acted as the main active sites for HMFCA oxidation to FDCA, but this process was inhibited by the high steric hindrance of quaternary ammonium which prevented HMFCA from approaching to the active double epoxy group sites. However, quaternary ammonium octamolybdate contained a quarter of single epoxy groups and three quarters of double epoxy group in presence of $H_2O_2$, and no quaternary ammonium was bundled to a certain double epoxy group sites, which made Mo based catalyst display the higher activity in HMF oxidation.



**Scheme 3.** HMF oxidation with $H_2O_2$ in presence of ammonium octamolybdate and ammonium dectungstate

## Effects of different temperature on HMF oxidation

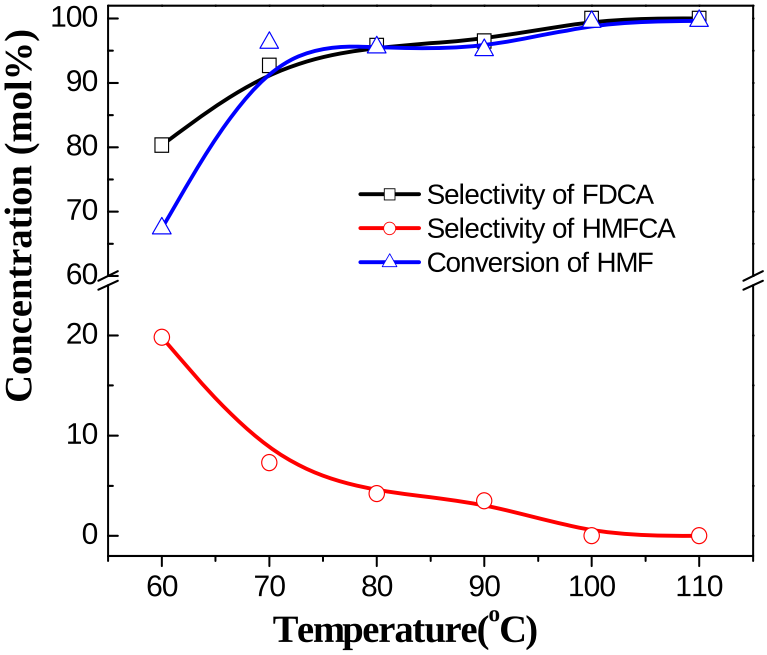


**Figure 2.** HMF Oxidation under different temperature (Reaction conditions: 9 mmol HMF, 18 mmol NaOH, the mass of $[EMIM]_4Mo_8O_{26}$ is 0.113g, the molar ratio of HMF to $[EMIM]_4Mo_8O_{26}$ is 1/129, 20 ml deionized water as reaction solvent, 0.16 mol $H_2O_2$ as oxidant and reaction time 2h.)

Effects of reaction temperature on HMF oxidation were studied under similar reaction condition. Figure 2 showed the effect of temperature on FDCA selectivity and HMF conversion in presence of $[EMIM]_4Mo_8O_{26}$. Experiments were conducted at 6 different temperatures between 60 and 110 $^{o}$C to study the effects of temperature on HMF conversion and FDCA formation. An increase in both HMF conversion and FDCA selectivity was observed when reaction temperature was raised from 60 to 110 $^{o}$C. For example, HMF conversion and FDCA selectivity were 67.4% and 80.3% after 2 h at 60 °C, respectively, whereas at 100 °C the figures were 99.5% and 100%.

However, there was practically no difference in FDCA selectivity and HMF conversion at reaction temperatures between 100 and 110 °C.

## Effects of reaction time on HMF oxidation

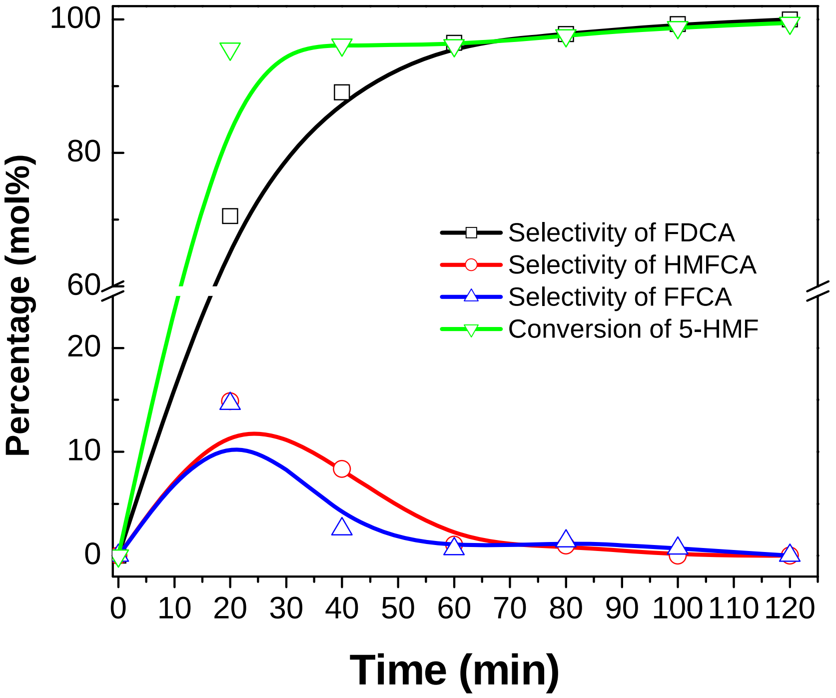
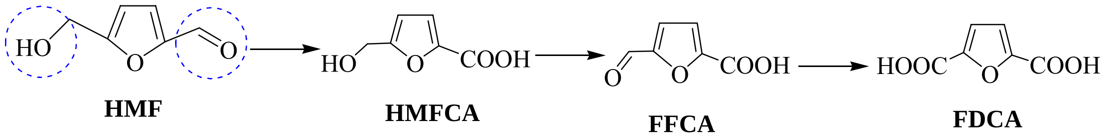


**Figure 3.** Effects of reaction time on HMF oxidation (Reaction conditions: 9 mmol HMF, 18 mmol NaOH, the mass of $[EMIM]_4Mo_8O_{26}$ is 0.113g, the molar ratio of HMF to $[EMIM]_4Mo_8O_{26}$ is 1/129, 20 ml deionized water as reaction solvent, 0.16 mol $H_2O_2$ as oxidant, 100 °C.)

The effectiveness of $[EMIM]_4Mo_8O_{26}$ was evaluated by conducting the HMF oxidation reactions for a longer time under atmospheric pressure and analyzing the products by HPLC. We analyzed the specimens sampled from the reaction mixture at specified time intervals. The variation of product selectivity and HMF conversion with time reveals the evolution of products during HMF oxidation. As shown in

Figure 3, HMF conversed quickly, reaching a conversion of 95.6% at 20 min, and the selectivity of HMFCA and FFCA reached 14.9% and 14.6%, respectively. FDCA was detected as a major product with HMFCA and FFCA being the main intermediates while no DFF was detected. As the reaction progressed, the selectivity of FDCA increased to 97.8%, but that of HMFCA and FFCA decreased to 0.98% and 1.4% after 80 min. With prolonging the reaction time to 100 min, the intermediate HMFCA disappeared, and FFCA selectivity further declined to 0.7%. FDCA selectivity achieved 100% and HMF conversion came up to 99.5% at 120 min. No formation of DFF was attributed to the fact that the aldehyde group of HMF was oxidized first followed by the oxidation of hydroxymethyl group. Similar to the above our observation, when HMF was oxidized with basic hydrotalcite-supported gold catalyst in aqueous medium [39] and Au/$TiO_2$ and Au/$CeO_2$ catalysts in methanol in the presence of homogeneous base additive, the oxidation of the aldehyde group took place in the first step followed by the hydroxymethyl group (Scheme 4). [40, 41]



**Scheme 4.** The pathway of HMF oxidation to FDCA

## Conclusions

A simple and effective method to synthesize FDCA from HMF was developed, and the difference performance of $Mo_8O_{26}$ anion and $W_{10}O_{32}$ anion in HMF oxidation with $H_2O_2$ was studied. Quaternary ammonium dectungstate consisted of an equal number of single epoxy groups and double epoxy groups in presence of $H_2O_2$, and the double epoxy groups was attached by a quaternary ammonium. The double epoxy groups acted as the main active sites for HMFCA advanced oxidation to FDCA, but this process was inhibited by the high steric hindrance of quaternary ammonium. However, quaternary ammonium octamolybdate was constituted with a quarter of single epoxy groups and three quarters of double epoxy group in presence of $H_2O_2$, and no quaternary ammonium was bundled on a certain double epoxy group sites, which made Mo based catalyst display the high activity for HMF oxidation. Under the optimized conditions of 100 $^{o}$C and 2 h, almost 99.5% of the HMF conversion and 100% of the selectivity of FDCA can be achieved. Although the exact pathway of HMF oxidation to FDCA is a matter of debate, herein the aldehyde group of HMF oxidizes first followed by the oxidation of hydroxymethyl group by $H_2O_2$ in presence of quaternary ammonium octamolybdate or quaternary ammonium dectungstate, which was contrasted with some earlier observation that the hydroxymethyl group of HMF was oxidized first into DFF as an oxidation product, which was followed by the oxidation of aldehyde group.

## Acknowledgements

The authors are grateful for the financial support of the Tianjin and National Natural Science Foundation of China (nos. 12JCZDJC29800 and 21376177).

## References

1 S.E. Davis, L.R.Houk, E.C. Tamargo, A.K.Datye, R.J. Davis, Catal. Today, 2011, **160**, 55.

2 S. Siankevich, G. Savoglidis, Z. Fei, J. Catal., 2014, **315**, 67.

3 S.E. Davis, A.D. Benavidez, R.W. Gosselink, J. Mol. Catal.A, 2014, **388**, 123.

4 B. Liu, Z. Zhang, K. Lv, Appl. Catal.A, 2014, **472**, 64.

5 M. Toshinari, K. Hirokazu, K. Takenobu, M. Hirohide, Method for producing furan-2,5-dicarboxylic acid. US Patent, 20070232815, 2007-03-07.

6 B. Saha, D. Gupta, M.M. Abu-Omar, J. Catal. 2013, **299**, 316.

7 G. Yi, S.P. Teong, X. Li, ChemSusChem, 2014, **7(8)**, 2131.

8 C. Moreaua, M.N. Belgacemb, A. Gandini, Top. Catal., 2004, **27**, 11.

9 A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, Green Chem. 2011, **13**, 754.

10 S. Dutta, S. De, B. Saha, M.M. Abu Omar, J. Catal. 2012, **288**, 8.

11 F.H. Xu, Z.H. Zhang, ChemCatChem 2015, **7**, 1470.

12 N. Mei, B. Liu, J.D. Zheng, K.L. Lv, D.G. Tang, Z.H. Zhang, Catal. Sci. Technol. 2015, **5**, 3194.

13 S.G. Wang, Z.H. Zhang, B. Liu, ACS Sustainable Chem. Eng. 2015, **3**, 406.

14 B. Liu, Y.S. Ren, Z.H. Zhang, Green Chem. 2015, **17**, 1610.

15 Z.H. Zhang, B. Liu, K.L. Lv, J. Sun, K.J. Deng, Green Chemistry 2014, **16**, 2762.

16 B. Siyo, M. Schneider, J. Radnik, Appl. Catal. A, 2014, **478**, 107.

17 H. Choudhary, S. Nishimura, K. Ebitani, Appl. Catal. A, 2013, **458**, 55.

18 P.A. Son, S. Nishimura, K. Ebitani, React. Kinet. Mech. Catal., 2012, **106**,185.

19 T.S. Hansen, I. Sádaba, E. García-Suárez, J. Appl. Catal. A, 2013, **456**, 44.

20 B. Saha, S. Dutta, M.M. Abu-Omar, Catal. Sci. Technol. 2012, **2**, 79.

21 W. Partenheimer, V.V. Grushin, Adv. Synth. Catal., 2001, **343**, 102.

22 Y. Y. Gorbanev, S. Kegnæs, A. Riisager, Catal. Lett., 2011, **141(12)**, 1752.

23 N. KumaráGupta, Green Chem. 2011, **13(4)**, 824.

24 H.A. Rass, N. Essayem, M. Besson, Green Chem., 2013, **15(8)**, 2240.

25 Z.H. Zhang, J.D. Zhen, B. Liu, L.L. Lv, K.J. Deng, Green Chem. 2015, **17**, 1308.

26 T. Pasini, M. Piccinini, M. Blosi, R. Bonelli, S. Albonetti, N. Dimitratos, J.A. Lopez-Sanchez, M. Sankar, Q. He, C.J. Kiely, G.J. Hutchings, F. Cavani, Green Chem., 2011, **13(8)**, 2091.

27 R. Noyori, M. Aoki, K. Sato, Chem. Commun., 2003 (16), 1977.

28 J.Q. Lu, M.F. Luo, H. Lei, C. Li, Appl. Catal. A, 2002, **237(1)**, 11.

29 H. Choudhary, S. Nishimura, K. Ebitani, Appl. Catal. A 2013, ***458***, 55.

30 J. Lan, J. Lin, Z. Chen, ACS Catal., 2015, **5(4)**, 2035.

31 Y. Liu, L. Zhu, J. Tang, M. Liu, R. Cheng, C. Hu, *ChemSusChem*, 2014, ***7*****(12)**, 3541.

32 R. Noyori, M. Aoki, K. Sato, Chem. Commun., 2003 (16), 1977.

33 X, Zuwei, Z. Ning, S. Yu, Science, 2001, **292(5519)**, 1139.

34 M.L. Guo, Green Chem., 2004, **6**, 271.

35 M.L. Guo, H.Z. Li, Green Chem., 2007, **9**, 421.

36 R. Noyori, M. Aoki, K. Sato, Chem. Commun., 2003 (16): 1977.

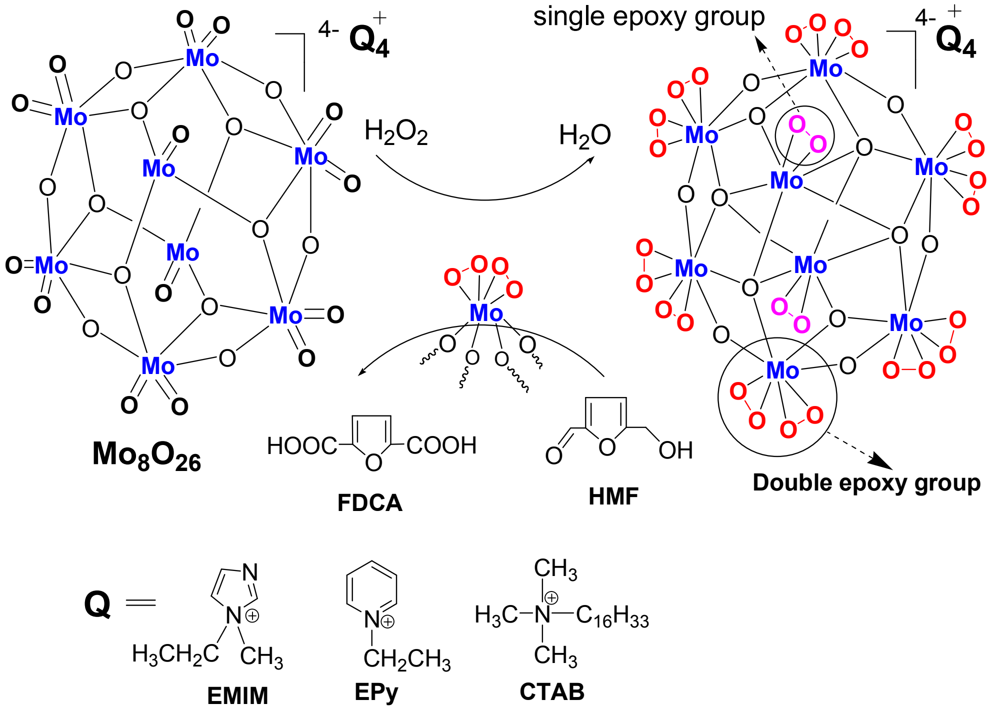
37 J. Fuchs, H. Hartl, W. Schiuer, U. Gerlach, Acta. Crytalorg., Sect B, 1976, **32**, 740.

38 A. Bayat, M. Shakourian-Fard, M.M. Hashemi, Catal. Commun., 2014, **52**, 16.

39 N.K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, Green Chem. 2011, **13**, 824.

40 Y.Y. Gorbanev, S.K. Klitgaard, J.M. Woodley, C.H. Christensen, A. Riisager, ChemSusChem 2009, **2**, 672.

41 O. Casanova, S. Iborra, A. Corma, ChemSusChem 2009, **2**, 1138.



A molybdenum complex exhibited the excellent performance in 5-hydroxymethylfurfural oxidation with $H_2O_2$.