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2-Dimensional Nanoleaf-like Porous Copper Nitrate Hydroxide as an Effective Heterogeneous Catalyst for Selective Oxidation of Hydroxymethylfurfural to Diformylfuran

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Abstract

Background:

2,2,6,6-tetramethylpiperidin-oxyl (TEMPO) accompanied with Cu has been validated as a promising oxidative catalytic process for oxidizing 5-hydroxymethylfurfural (HMF) to value-added products. Since Cu-O cluster plays an important role in TEMPO-based HMF oxidation, and N-O moiety would facilitate the catalytic cycle of TEMPO regeneration, an interesting solid-phase material, copper nitrate hydroxide (CNH) ($\text{Cu}_2(\text{OH})_3\text{NO}_3$) is proposed for the first time for co-catalyzing TEMPO to oxidize HMF into a valuable product, 2,5-diformylfuran (DFF).

Methods:

In particular, a CNH with a 2D elliptical and porous surface is fabricated to become the leaf-like porous CNH (LPCNH) to maximize surface contact via a relatively simple procedure, and LPCNH would be an advantageous catalyst with TEMPO for converting HMF into DFF.

Significant Findings:

While TEMPO or LPCNH was unable to oxidize HMF into DFF, the combination of LPCNH/TEMPO rapidly, and efficiently converted HMF to DFF with high selectivities. At 140 °C, a significantly high $Y_{\text{DFF}} = 99.3\%$ with $S_{\text{DFF}} = 100\%$ can be obtained, and surpass almost all reported values, indicating that LPCNH+TEMPO is advantageous and selective to convert HMF into DFF. LPCNH could be also reusable for co-catalyzing with TEMPO for converting HMF to DFF. These findings validate that LPCNH is certainly a useful heterogeneous catalyst for valorizing HMF.

Keywords: Hydroxymethylfurfural, Diformylfuran, copper nitrate hydroxide, TEMPO, oxidation

1. Introduction

Valorization of lignocellulosic biomass-derivatives into value-added products represents a crucial step for sustainable utilization of lignocellulosic resources. While several techniques are already reported to valorize these bio-derivatives, such as pyrolysis and chemical techniques, oxidative chemical conversion of biomass-derivatives gains increasing attention as it can be implemented under relatively mild conditions [1]. To date, several biomass-derivatives have been also successfully valorized through oxidative chemical conversion, including vanillyl alcohol, trans-ferulic acid, and hydroxymethylfurfural (HMF) (as displayed in Fig. S1).

Among these biomass-derivatives, 5-hydroxymethylfurfural (HMF) is an interesting derivative because HMF would be generated from miscellaneous cellulosic biomass [2]. More importantly, HMF would be oxidized to produce a variety of value-added molecules, such as 2,5-diformylfuran (DFF) (as displayed in Fig. S1), which is an important and valuable precursor for synthesizing cross-linking reagents, organic conductors, polymers, and pharmaceuticals [3-5].

As transformation of HMF into DFF would necessitate oxidation of alcohol moiety of HMF into an aldehyde moiety, it is extremely decisive to establish useful processes to oxidize the alcohol group of HMF into the aldehyde group. Traditionally, chemical oxidation of biomass-derivatives can be achieved by addition of oxidants accompanied with catalysts [6-8]. To date, a few oxidants, such as NaOCl, BaMnO₄, pyridinium chlorochromate [9], and H₂O₂ [6, 10-14], are also usually adopted for oxidizing HMF [6, 10-12, 15-17]. Even though these oxidants are feasible to oxidize HMF, these oxidants typically cannot selectively oxidize HMF into DFF, resulting in low selectivities and yields [6, 10-12, 15-17], making these approaches less favorable.

However, several critical issues of using these oxidants still impede their progress of large-scale implementation, such as intensive consumption of these stoichiometric oxidants, and poor selectivity of yield of conversion into target products [6, 12]. Therefore, more feasible and efficient oxidation processes should be developed.

Lately, increasing studies of oxidation of alcohol-containing compounds explored utilization of oxygen molecules (O_2) as an oxidant [18, 19] to develop more sustainable oxidation processes. Thus, it would be certainly advantageous to employ oxygen molecules for oxidation of HMF into DFF. To this end, an interesting oxidation process by utilizing 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) accompanied with copper (Cu) has been revealed recently as TEMPO would act as an organic oxidation catalyst which would catalytically utilize O_2 for oxidation of organic compounds [18-20]. Such a combination of TEMPO and Cu has also successfully and selectively converted alcohols into aldehydes under mild conditions [4, 18-24].

Nevertheless, there are still very limited studies of employing TEMPO/Cu for converting HMF to DFF, and most studies available in literature of employing TEMPO/Cu involved usage of homogeneous Cu ions [25], making recovery of Cu catalysts very challenging. Therefore, it would be imperative to create heterogeneous-phase Cu catalysts to co-catalyze with TEMPO for oxidizing HMF. Specifically, since Cu-O cluster has been validated to play an important role in TEMPO-based oxidation of organics [4, 18-20, 24, 26], Cu-based oxides and hydroxides would be suitable catalysts. Moreover, many studies of employing TEMPO for oxidation of organics have also found that the presence of NO-containing molecules would enhance the oxidation via facilitation of the catalytic cycle of TEMPO [27-31]. Thus, it should be promising to combine Cu-O and N-O moieties into a heterogeneous catalyst for HMF oxidation.

Herein, copper nitrate hydroxide (CNH) ($\text{Cu}_2(\text{OH})_3\text{NO}_3$) is then proposed here as CNH has been also validated as it contains Cu-O and N-O moieties and has been a useful oxidation catalyst in many oxidative applications [32, 33]. Nevertheless, no relevant studies have been conducted for examining CNH incorporated with TEMPO to oxidize HMF. Therefore, the aim of this study is for the first time to investigate CNH with TEMPO for HMF oxidation to DFF. Especially, an alternative method is invented here for obtaining a special CNH which can exhibit nanoscale and 2-dimensional (2D) morphology with porous structures to maximize surface contact via a relatively simple procedure. In particular, a CNH with a 2D elliptical and porous surface is fabricated to become the leaf-like porous CNH (LPCNH), which would be an advantageous heterogeneous catalyst for co-catalyzing with TEMPO to convert HMF into DFF.

2. Experimental

2.1 Synthesis and characterization of LPCNH

In this study, all chemicals were purchased from commercial sources and used as received. The preparation of leaf-like porous CuNHO can be schematically depicted in Fig. 1(a). Firstly, 1 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 100 mL of DI water at ambient temperature, followed by the addition of 30 mL of NH_4OH (0.15 M) while stirring. Next, the mixture was adjusted to $\text{pH} = 9.5$ and the resulting precipitate was collected, rinsed and dried to afford LPCNH. The XRD pattern of LPCNH was identified by an X-ray diffractometer (Bruker, USA), whereas its surface chemistry was analyzed by X-ray photoelectron spectroscopy (XPS) (PHI 5000, ULVAC-PHI, Japan). Surface areas and porosities of LPCNH were measured using a volumetric gas adsorption analyzer (Anton Paar Autosorb IQ, USA).

2.2 Oxidation of HMF to DFF using LPCNH

HMF oxidation by LPCNH would be evaluated using batch-type experiments. In brief, HMF (25 mg) was first added to the reactor containing 50 mL of dimethyl sulfoxide (DMSO). Next, 25 mg of TEMPO, and 50 mg of LPCNH was then added to the HMF solution. The resulting mixture was placed on a stirring plate at a desired temperature with exposure to the ambient air as a source of O₂ instead of pressurized O₂ gas. In the end of the experiment, the reaction mixture was filtrated and the filtrate was determined by HPLC (KNAUER, Germany) equipped with a UV detector. The mobile phase consisted of aqueous sulfuric acid (1mM) and DI water at a flowrate of 0.8 mL/min, and the detector was set for 254 nm and a reverse-phase HPX-87H column. Chromatographs of reactants, and products can be seen in Fig. S2. Quantitative analyses for conversion of HMF to a product (e.g., DFF) was determined as follows [34]:

$$\text{Conversion of HMF } (C_{\text{HMF}}) = \frac{\text{Consumed HMF}}{\text{Total HMF}} \times 100\% \quad (1)$$

$$\text{Selectivity for a product } (S_{\text{product}}) = \frac{\text{Product (mol)}}{\text{Consumed HMF (mol)}} \times 100\% \quad (2)$$

$$\text{Yield of a product } (Y_{\text{product}}) = \frac{\text{Product (mol)}}{\text{Total HMF (mol)}} \times 100\% \quad (3)$$

3. Results and Discussion

3.1 Physical and chemical properties of LPCNH

Firstly, the resulting CNH is displayed in Fig. 1(b), and it showed a morphology of elliptical leaf with a length of *ca.* 600 nm and a width of 300 nm. A closer view (Fig. 1(c)) indicates that these nanoscale elliptical leaves showed very roughened surfaces with hierarchical structures. In addition, its corresponding transmission image (Fig.1d)) displayed that the

edges of these elliptical leaves were porous, validating that the resultant CHN possessed the leaf-like porous nanostructure.

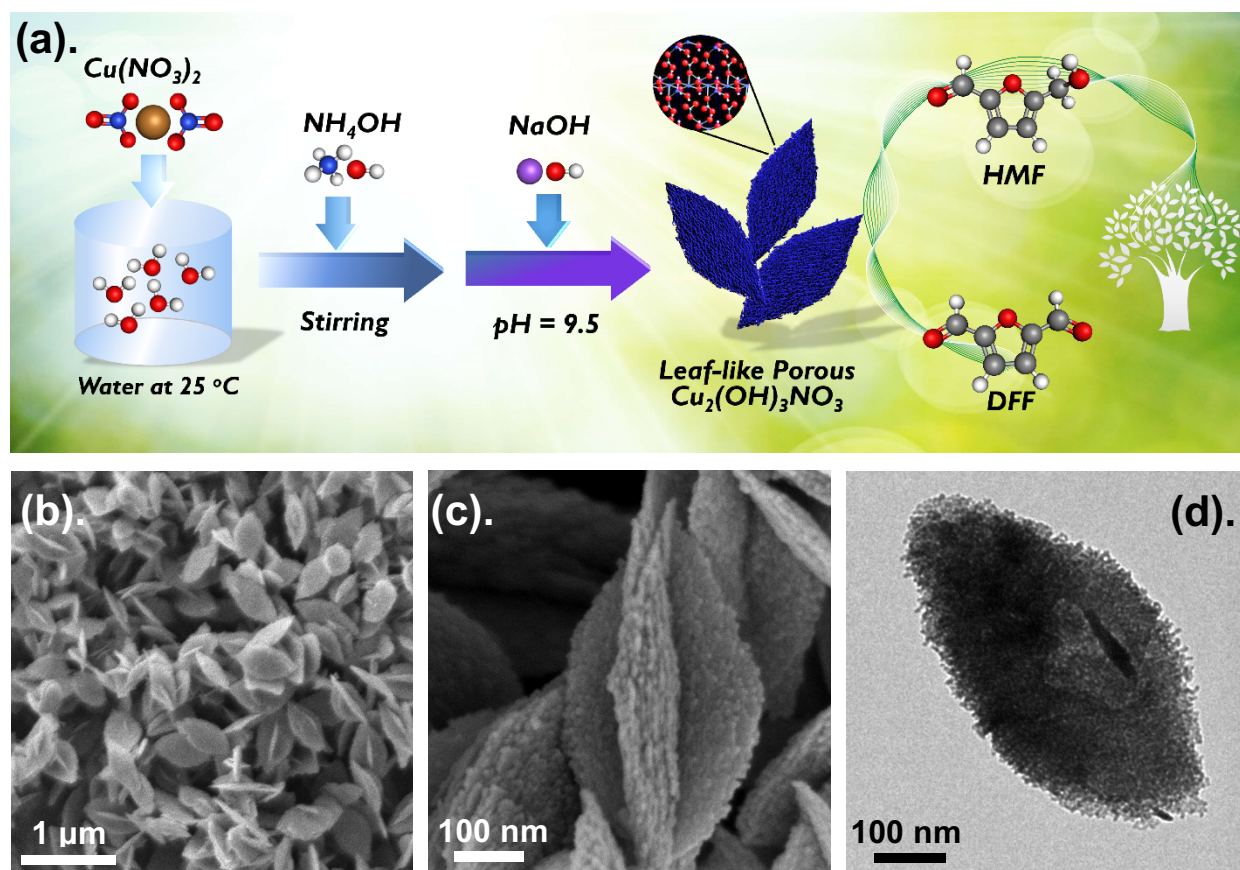


Fig. 1. Nanoscale leaf-like porous copper nitrate hydroxide (LPCNH): (a) preparation scheme, (b, c) SEM images, and (d) TEM image.

Fig. 2(a) further shows the XRD pattern of the leaf-like porous nanostructure which can be well-indexed to CHN ($\text{Cu}_2(\text{OH})_3\text{NO}_3$) based on JCPDS card# 14-0687, confirming that CHN was successfully prepared with the leaf-like porous nanostructure, forming LPCHN. Fig. 2(b) reveals the full-survey XPS spectrum of this LPCHN, in which significant signals of Cu, O, and N can be all detected.

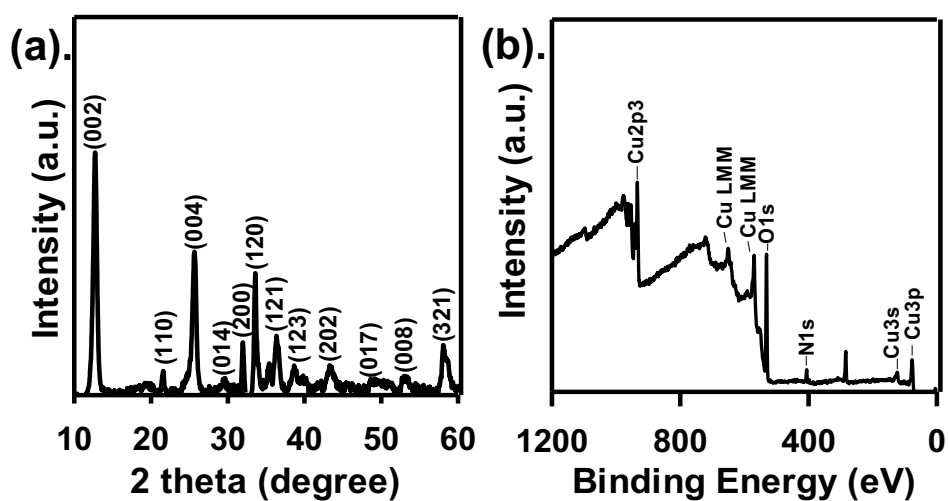


Fig. 2. Characterization of LPCNH: (a) XRD, and (b) full-survey XPS spectrum.

Furthermore, the Cu2p core-level spectrum is then displayed in Fig. 3(a), and the peaks at 933.3 and 952.3 eV could be attributed to Cu^{2+} [35], which was consistent to the valence state of Cu species in $\text{Cu}_2(\text{OH})_3\text{NO}_3$. On the other hand, the O1s core-level spectrum of LPCNH was deconvoluted into two underlying peaks (Fig. 3(b)), and the peak at 528.8 eV could be attributed to O^{2-} species, where the peak at 539.6 eV corresponded to OH^- [36]. Moreover, the N1s core-level spectrum consisted of a significant peak at 405.9 eV which could be then ascribed to NO_3^- as constituted in CHN [37]. As both XRD and XPS analyses indicated the successful formation of CNH here, the relatively simple and convenient method proposed here could be validated to afford CHN.

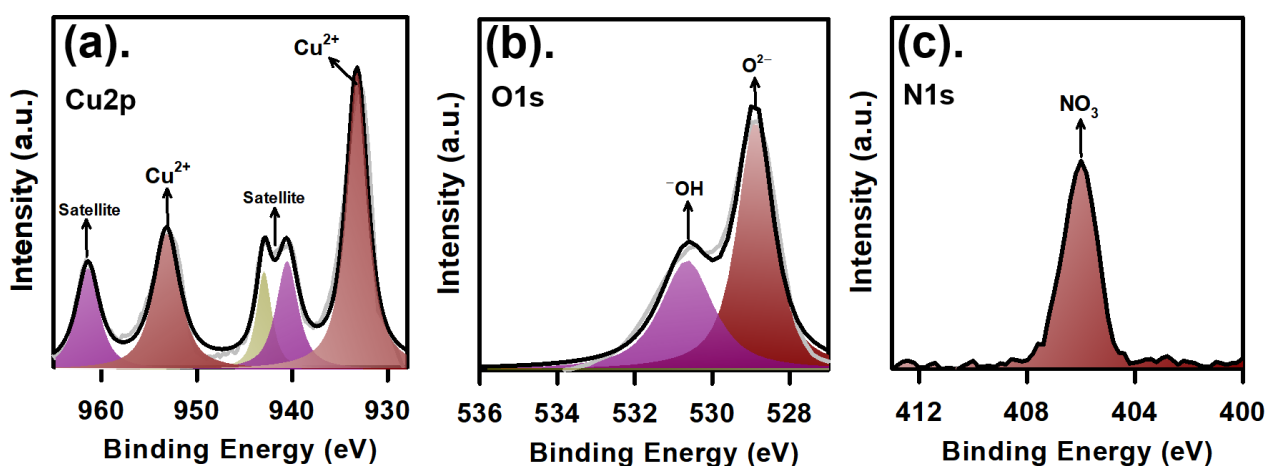


Fig. 3. (a) Cu2p, (b) O1s, and (c) N1s core-level XPS spectra of LPCNH.

In view of the special morphology of LPCNH, its textural properties were then analyzed. Fig. 4(a) shows its N_2 sorption isotherm of LPCNH, which can be classified as the IUPAC type III isotherm, indicating that LPCNH comprised of porous structures. The pore size distribution (Fig. 4(b)) further validated that LPCNH certainly contained pores ranging from a few nanometers to ~ 40 nm. The surface area of PLCNH was then determined as $32 \text{ m}^2/\text{g}$ with a total pore volume of 0.086 cc/g .

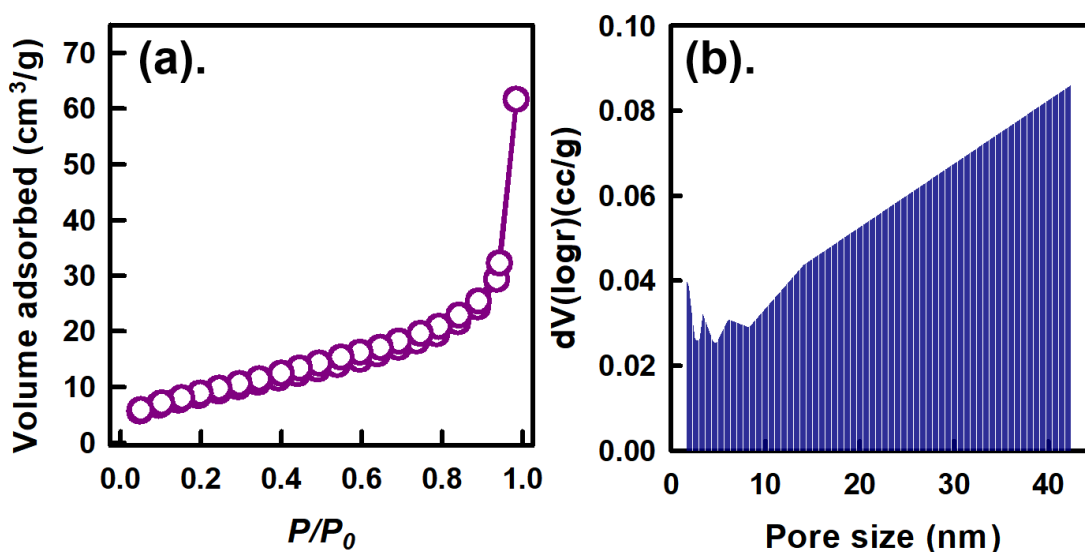


Fig. 4. (a) N_2 sorption isotherm and (b) pore size distribution of LPCNH.

3.2 HMF Oxidation by LPCNH/TEMPO

Prior to investigating oxidation of HMF using LPCNH co-catalyzed with TEMPO (LPCNH/TEMPO), it would be critical to determine whether HMF would be transformed and oxidized into DFF by LPCNH and TEMPO individually. Fig. 5(a) indicates that as TEMPO alone was adopted, HMF would be barely converted as its corresponding C_{HMF} was merely 2.8% even though the converted HMF was almost transformed into DFF. This validates that TEMPO itself could not effectively convert HMF to DFF. Nevertheless, when LPCNH alone was used, the corresponding C_{HMF} was also extremely low as 6.2%, also indicating that the pristine LPCNH could not efficiently oxidize HMF to DFF.

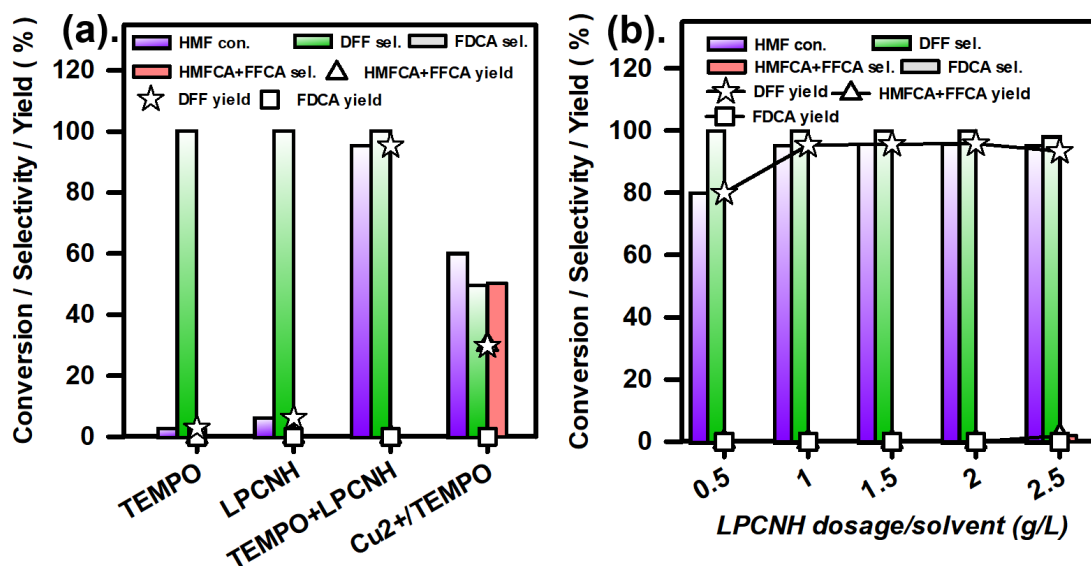


Fig. 5. (a) Conversion of HMF to DFF using LPCNH, TEMPO, LPCNH/TEMPO, and Cu²⁺/TEMPO (catalyst = 1 g/L); (b) Effect of LPCNH dosage on oxidative conversion of HMF by LPCNH/TEMPO (HMF = 0.5 g/L, TEMPO = 0.5 g/L, T = 100 °C, t = 60 min)

However, when LPCNH and TEMPO were both added in the HMF solution, a significantly high fraction of HMF was transformed with a $C_{\text{HMF}} = 95.3\%$, and, interestingly, the selectivity for DFF (S_{DFF}) was almost 100%, affording the yield of DFF ($Y_{\text{DFF}} = 95.3\%$). Since TEMPO and LPCNH were incompetent for converting HMF into DFF respectively,

this indicates that LPCNH combined with TEMPO would oxidize HMF successfully and transform it to DFF.

More importantly, the result also reveals that no other by-products were produced in addition to DFF, demonstrating that LPCNH/TEMPO was exceptionally selective to oxidize HMF to DFF. Since LPCNH consisted of Cu^{2+} , Cu^{2+} was combined with TEMPO to test the homogeneous phase of Cu^{2+} for oxidation of HMF. Fig. 5(a) shows that Cu^{2+} /TEMPO would also convert HMF; however, the corresponding C_{HMF} was relatively low as $\sim 60\%$, and S_{DFF} was also relatively low as many by-products were generated. This validates that the homogeneous phase Cu^{2+} /TEMPO might be unfavorable because the over-oxidation of HMF to FDCA (or others) might occur, and the overall conversion efficiency was low as nitrogen-containing ligands are necessitated to coordinate with Cu^{2+} for improving its conversion [38]. Such a comparison further reveals the advantage of LPCNH as a heterogeneous catalyst and, more importantly, noticeably more superior conversion and selectivity could be obtained.

As LPCNH was comprised of copper hydroxide, Cu-OH bonds would exist, and Cu-OH cluster has been considered as an active site for conversion of HMF. According to literatures [39, 40], this Cu-OH would firstly react with the alcohol group of HMF to form an intermediate as depicted in Fig. 6. After introduction of TEMPO to the system, the TEMPO radical would then react with an intermediate of HMF to withdraw a proton while TEMPO became TEMPOH, and, simultaneously, HMF was transformed to DFF [39, 40]. This resulting TEMPOH would then converted back to a TEMPO radical through contact with oxygen atoms [30, 40]. Through these catalytic processes of LPCNH, TEMPO and O_2 molecules, HMF molecules would be selectively, and constantly oxidized to become DFF.

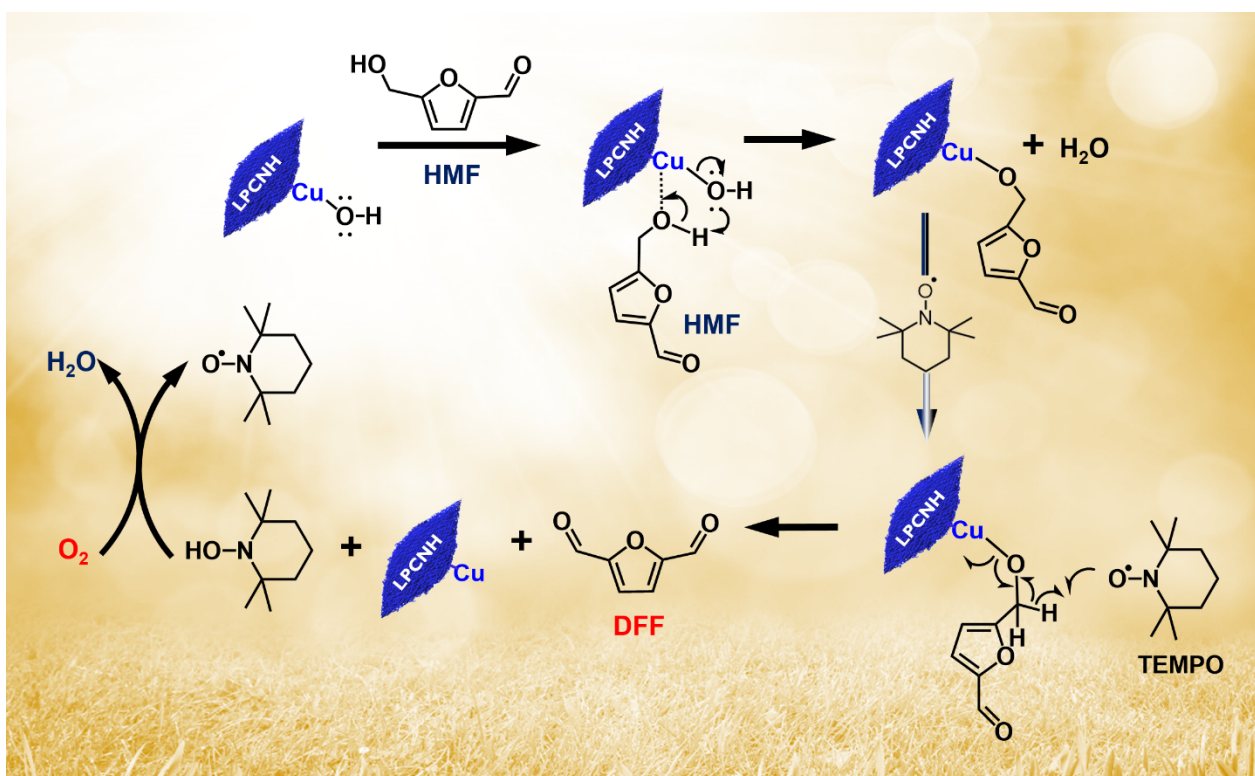


Fig. 6. A proposed mechanism for HMF conversion to DFF by LPCNH/TEMPO.

3.3 Effect of LPCNH dosage on HMF oxidation

While LPCNH /TEMPO could successfully convert HMF into DFF, it would be also important to investigate the effect of LPCNH dosage as LPCNH was employed as a heterogeneous catalyst. Fig. 5(b) reveals HMF conversion efficiency as a function of LPCNH dosage. When the dosage of LPCNH was relatively low as 0.5 g/L, HMF was still oxidized with $C_{\text{HMF}} = 80\%$, and S_{DFF} was remained as 100%, showing that even though a low dosage of LPCNH was adopted, HMF was still selectively oxidized to DFF. Once the dosage of LPCNH increased from 0.5 g/L to 1 g/L, the corresponding C_{HMF} was then improved to 95.3% with $S_{\text{DFF}} = 100\%$, suggesting that LPCNH at a higher dosage would improve HMF oxidation. When the LPCNH dosage was raised up to 1.5 and 2.0 g/L, the corresponding C_{HMF} did not noticeably increase while S_{DFF} also remained as 100%, affording the consistent yield of DFF. Nevertheless, if the dosage of LPCNH became 2.5 g/L, although C_{HMF} was retained comparably, S_{DFF} was decreased marginally and by-products of 5-Hydroxymethyl-

2-furancarboxylic acid (HMFCFA) and 2,5-formylfurancarboxylic acid (FFCA) occurred, indicating that redundant LPCNH might cause slight over-oxidation of HMF and DFF. As depicted in the potential mechanism (Fig. 6), HMF conversion involved with both the solid catalyst, and oxidant. HMF was considered to react with the active sites of solid catalysts to form more reactive intermediates, which would be more easily attacked by the oxidant [39, 40]. Therefore, a higher dosage of catalyst was considered to provide more reactive sites, and the chance of reaction between derivatives of HMF and catalysts might also increase, resulting in further oxidation of derivatives of HMF to become FDCA.

Thus, the optimal dosage of LPCNH would be 1.0 g/L as it would achieve a higher C_{HMF} with a relatively low LPCNH dosage in the absence of by-products. Thus, the dosage of 1.0 g/L was then employed throughout the rest of this study.

3.4 Effects of time and temperature on HMF oxidation

As LPCNH/TEMPO was capable of oxidizing HMF and generating DFF, it would be essential to examine the effect of reaction time for further realizing behaviors of HMF conversion (e.g., kinetics). Fig. 7(a) displays HMF conversion efficiencies after different durations. After a duration of 5 min, HMF could be also oxidized into DFF, achieving $C_{\text{HMF}} = 24\%$, $S_{\text{DFF}} = 95\%$ and $Y_{\text{DFF}} = 23\%$. This reveals that while the duration of reaction was just 5 min, LPCNH/TEMPO could still oxidize HMF into DFF.

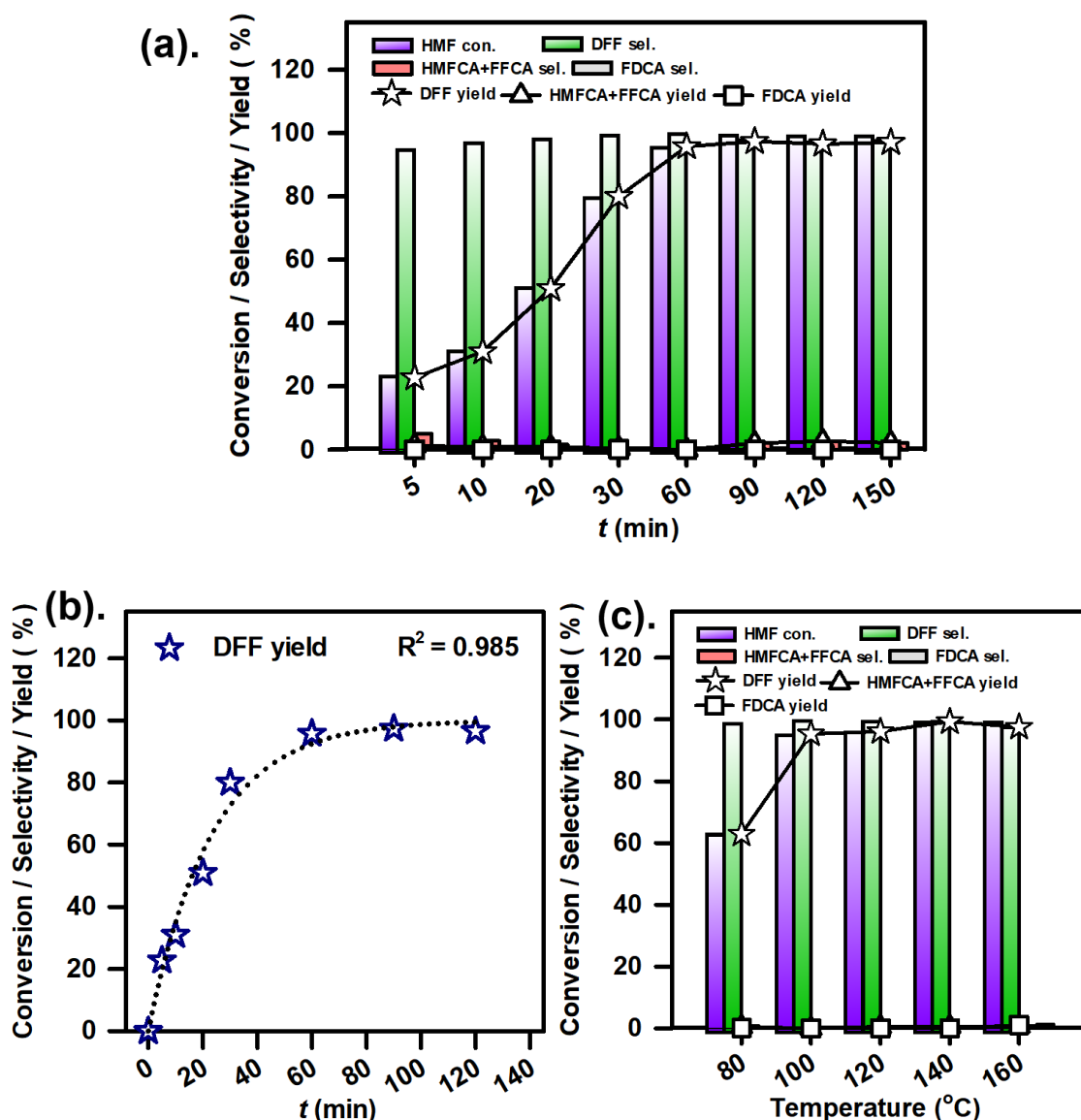


Fig. 7. (a) Effect of reaction time on oxidative conversion of HMF (HMF = 0.5 g/L, TEMPO = 0.5 g/L, $T = 100\text{ }^{\circ}\text{C}$) and (b) kinetics of DFF yield; (c) effect of temperature on HMF conversion by LPCNH/TEMPO (HMF = 0.5 g/L, TEMPO = 0.5 g/L, $t = 60\text{ min}$)

When the reaction duration extended incrementally, C_{HMF} was correspondingly increased, and reached 96% after 60 min with $S_{\text{DFF}} = 100\%$, leading to a significantly high yield of DFF of 96%. Later, when the reaction duration increased to 90 min, C_{HMF} was further improved to 99.4% whereas S_{DFF} was slightly decreased from 100% to 98%, affording $Y_{\text{DFF}} = 97.4\%$. This result suggests that the elongated reaction duration certainly benefited HMF

conversion, the slight over-oxidation might occur. Such a phenomenon became more pronounced when the reaction duration further exceeded 90 min as noticeable amounts of by-products were detected. This result also demonstrated that the optimal reaction duration would be 60 min to obtain the highest selectivity towards DFF while achieving a significantly high conversion. On the other hand, as the yield of DFF grew rapidly along with increasing reaction duration, it was insightful to characterize the kinetics of DFF yield. Thus, Fig. 7(b) further shows Y_{DFF} as a function of time and Y_{DFF} increased quickly from $t = 0$ to $t = 60$ min, and then almost reached the equilibrium of $Y_{\text{DFF}} \sim 97\%$. To further interpret the kinetics, a pseudo first order equation $Y_{\text{DFF}(t)} = Y_{\text{DFF}(\text{equilibrium})} \cdot e^{-kt}$ was then employed. The data points in Fig. 7(b) were well fit by the pseudo first order rate law with $R^2 = 0.985$, suggesting that the yield of DFF might be described by the pseudo first order rate law.

In addition to the effect of reaction time, the effect of temperature also plays an important role and then investigated here. Fig. 7(c) reveals HMF conversion efficiency as a function of temperature ranging from 80 to 160 °C. At 80 °C, LPCNH/TEMPO was still capable of oxidizing HMF with $C_{\text{HMF}} = 64\%$, and, more importantly, S_{DFF} was remained as 100%, suggesting that a relatively low temperature was also useful for converting HMF to DFF by LPCNH/TEMPO. When temperature further increased to 100 °C, C_{HMF} considerably increased from 64 to 96%, and maintaining S_{DFF} as 100%. When temperature was raised up to 120 °C and 140 °C, C_{HMF} noticeably increased to 96.5 and 99.3% correspondingly, while S_{DFF} remained almost the same as 100%. While the temperature exceeded 150 °C and a slight decrease in S_{DFF} was noticed as the over-oxidation might occur, higher temperatures were certainly beneficial to HMF conversion as it HMF oxidation was a thermo-chemical reaction. More importantly, HMF conversion at 140 °C by LPCNH/TEMPO could lead to a $Y_{\text{DFF}} = 99.3\%$, which was much higher than many reported values, including results obtained by noble metal catalysts, in literature as listed in Table 1, showing that LPCNH is certainly

a promising and advantageous heterogeneous catalyst to co-catalyze with TEMPO for oxidizing HMF.

Table 1. Comparison of conversion of HMF to DFF by various catalytic system.

Catalyst	Oxidant	Solvent	T (°C)	time (h)	O ₂	Conversion (%)	Selectivity (%)	Yield (%)	Ref.
Cu₂(OH)₃NO₃/TEMPO	Air	DMSO	140	1	0.02MPa	99.3	100	99.3	This study
Cu(NO ₃) ₂	O ₂	CH ₃ CN	80	24	0.5MPa	68.3	97	66.5	[38]
4-Acetamido-TEMPO	O ₂	EtOAC	40	2	10 ml/min	100	89	89	[41]
CuCl/TEMPO	O ₂	ACN	RT	24	0.1MPa	44	97	42	[42]
CuI/TEMPO	O ₂	DMSO	130	10	0.3MPa	95.1	97		[43]
Ru/C	Air	MTBE	80	1	2.0 MPa	54.5	-	43.7	
Pd/C	Air	MTBE	80	1	2.0 MPa	19.4	-	8.8	[44]
Pt/C	Air	MTBE	80	1	2.0 MPa	28.5	-	1.3	
Cs/MnOx	O ₂	DMF	100	10	1.0MPa	76.8	98.1		[9]
MnO ₂	O ₂	DMF	100	10	1.0MPa	2.4	89.8		
Ru/AC	H ₂ O ₂	H ₂ O	75	1	-	94	-	14	[45]
Co _{3.3} Ce _{3.3} Ru _{3.3}	H ₂ O ₂	MIBK	120	12	-	98.7	80.2	79.2	[6]

3.5 Reusability of LPCNH for HMF oxidation

Since LPCNH was a heterogeneous catalyst to oxidize HMF to DFF, its reusability was then examined. Fig. 8(a) displays HMF conversion efficiencies at 140 °C for 60 min over 5 cycles by using LPCNH without regeneration of LPCNH, and HMF was constantly oxidized to afford DFF with consistent HMF conversions, DFF selectivities and DFF yields. This validates that LPCNH can be reusable and exhibit stable and effective catalytic activities towards HMF oxidation and selectively converted HMF to DFF. Fig. 8(b) and its inset further

displays the XRD pattern and SEM image of the spent LPCNH, which were all comparable to those of the pristine LPCNH, confirming that LPCNH was a robust catalyst.

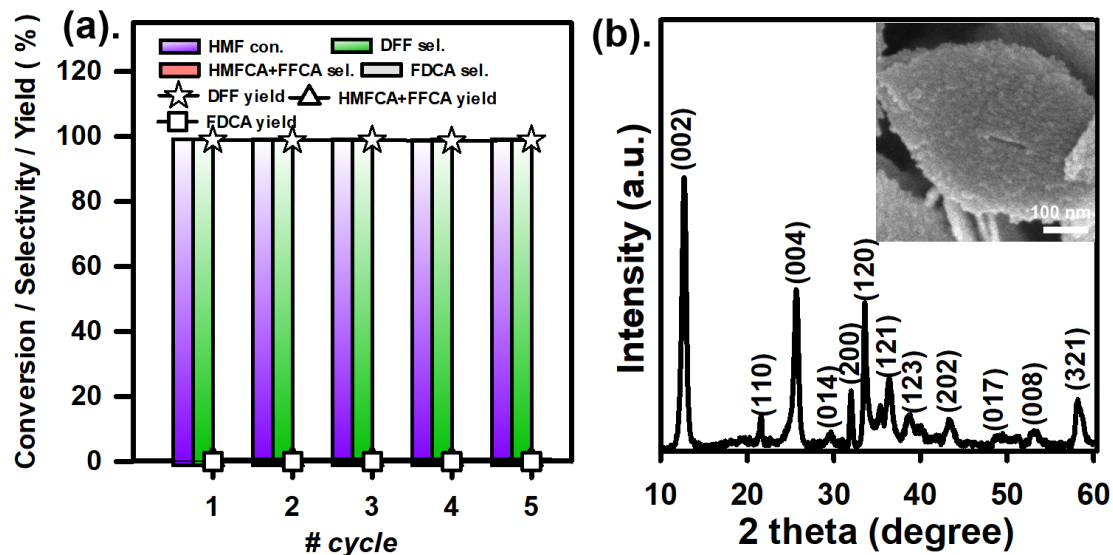


Fig. 8. Recyclability of LPCNH for HMF oxidation to DFF (HMF = 0.5 g/L, TEMPO = 0.5 g/L, LPCNH = g g/L, T = 140 °C, t = 60 min); the XRD pattern of used LPCNH (the inset: SEM image of used LPCNH).

4. Conclusions

Herein, a specially-shaped LPCNH was developed as an easy-to-prepare and highly-effective heterogeneous catalyst for oxidizing HMF into DFF by co-catalysis of TEMPO. While TEMPO or LPCNH was barely capable of oxidizing HMF into DFF individually, the combination of LPCNH/TEMPO rapidly as well as efficiently converted HMF to DFF with very high selectivities. The reaction time could be just 60 min at 100 °C to achieve $C_{\text{HMF}} = 96\%$ and $S_{\text{DFF}} = 100\%$. At 140 °C, a significantly high $Y_{\text{DFF}} = 99.3\%$ with $S_{\text{DFF}} = 100\%$ can be also obtained, and surpassed almost all reported values in literature, indicating that LPCNH+TEMPO was advantageous and selective to convert HMF into DFF. LPCNH could be also reusable for co-catalyzing with TEMPO for converting HMF to DFF. These findings

validate that LPCNH is certainly a useful heterogeneous catalyst for valorizing HMF. The information obtained here would be also utilized for developing a TEMPO-involved oxidation process for valorizing bio-derivatives through aerobic oxidation.

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