

Efficient and Bio-inspired Conversion of Cellulose to Formic Acid Catalyzed by Metalloporphyrins in Alkaline Solution

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A bio-inspired approach for efficient conversion of cellulose to formic acid (FA) was developed in an aqueous alkaline medium. Metalloporphyrins mimicking cytochrome P450 exhibit efficiently and selectively catalytic performance in catalytic conversion of cellulose. High yield of FA about 63.7% was obtained by using sulfonated iron(III) porphyrin as the catalyst and O₂ as the oxidant. Iron(III)-peroxo species, TSPFe^{III}OO⁻, was involved to cleave the C—C bonds of gluconic acid to FA in this catalytic system. This approach used relatively high concentration of cellulose and ppm concentration of catalyst. This work may provide a bio-inspired route to efficient conversion of cellulose to FA.

Keywords metalloporphyrin, bio-inspired, catalyzed, cellulose, formic acid

Introduction

Formic acid (FA) is the simplest and important organic acid and has been widely used in chemical, agricultural, pharmaceutical, and rubber industries.^[1] The worldwide capacity for producing this acid was 800 kt/year.^[2] Recently, FA has attracted much attention due to its potential capacity of hydrogen storage.^[3] So far, formic acid was mainly produced from fossil raw materials, such as carbonylation of methanol.^[4] Obviously, the replacement of fossil resources with biomass, such as glucose and cellulose, would be a more promising and sustainable alternative to produce FA.

Currently, various biomass resources such as glycerine, glucose, cellulose and even waste biomasses have been employed for the production of FA through chemocatalytic processes.^[5,6] Although significant progress was made in this field, the yield of FA is far from satisfactory when using non-edible cellulose as the feed stock.^[7] For instance, Fu *et al.*^[7a] reported a relatively efficient catalytic system, moderate yield of FA (35%) was obtained at full conversion of cellulose by using a bifunctional catalyst, the polyoxometalate catalyst (H₅PV₂Mo₁₀O₄₀, 50 mmol), at the temperature of 170 °C and air pressure of 5 MPa within 9 h. Although high FA yield up to 67.8% and 61% was achieved by converting cellulose^[8] and beech wood^[9] respectively using heteropoly acids (HPAs) containing vanadium as catalysts, lower concentration of cellulose (about 0.01–0.03 g/mL H₂O) was required. When increasing the concentration of cellulose to 0.05 g/mL H₂O, the FA yield was reduced almost by half.^[8] Besides, leaching of

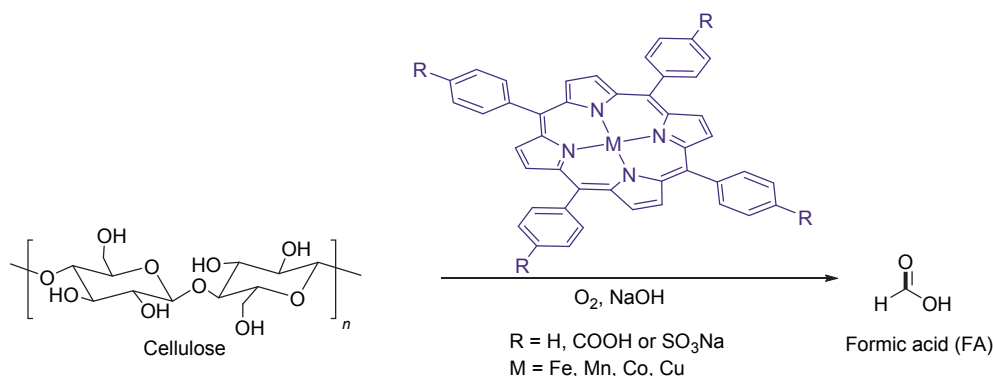
the HPA in hot water is inevitable, even at modest temperatures, which prevents them from being an industrially feasible catalyst.^[9] On the other hand, it should be noted that most of the studies on the conversion of cellulose to FA focus on using acidic catalysts, *i.e.* Lewis acid^[10] or heteropolyacid.^[6–9] Only few conversion processes proceed in basic media, even though FA is often detected as a byproduct with a low yield in alkaline conversion of cellulosic biomass.^[11] For example, Yan *et al.*^[12] reported recently that hydrothermal degradation of cellulose in its alkaline aqueous solution could provide 37.4% of FA at 280 °C. As a result, the development of efficient and mild approach for selective conversion of cellulose to FA is highly desired.

Metalloporphyrins as biomimetic catalysts mimicking cytochrome P450 exhibit efficiently and selectively catalytic performance in catalytic oxidation of hydrocarbon C—H bonds^[13] and oxidative cleavage of C—C bond of vicinal diols^[14] or aldehydes^[15] under mild condition. For instance, ppm concentration of cobalt porphyrin has been used as the bio-inspired catalyst for the first industrial-scale oxidation of hydrocarbon with air under mild condition.^[16] In addition, biomass, particularly starch^[17] and lignin^[18] has also been modified or delignified to carbonyl compounds via oxidative cleavage of C—C bonds of monosaccharide unit or phenylpropane unit by using metalloporphyrin and its analogues as the catalysts and H₂O₂ as the oxidant. However, to the best of our knowledge, no bio-inspired system is known for selective conversion of cellulose to FA with oxygen as the oxidant. Herein, we report an efficient and bio-inspired approach for aerobic conver-

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Scheme 1 Transformation of cellulose to FA catalyzed by metalloporphyrin

sion of cellulose to FA by using water soluble metalloporphyrin as the catalyst in NaOH solution (Scheme 1). The concentration of cellulose in this approach maintains relatively high level (0.1 g/mL H₂O).

Experimental

All reagents were obtained commercially and used without further purification. Sulfonated metalloporphyrins TSPPMCl (M=Fe, Mn, Co, Cu) were synthesized according to the literature.^[13e]

General reaction conditions for bio-inspired conversion of cellulose are shown as follows: in a 10 mL autoclave, 1 mg metalloporphyrin (0.9×10^{-4} mmol) was added to a reaction mixture containing 0.5 g cellulose and 5 mL NaOH (0.5 mol/L) aqueous solution. After the reaction mixture was stirred at 150 °C and 2.0 MPa O₂ for 6 h, the reaction mixture was added to 10 mL water and directly analyzed by a Shimadzu LC-20A liquid chromatography. Organic acid and H₂O₂ were analyzed with VP-ODS C18 column and PDA detector using phenols as the internal standard. Glucose was analyzed with HRC-NH₂ column and RID detector using xylose as the internal standard. Cyclohexene was detected by a Shimadzu GC-2010 gas chromatography with FID detector. As for conversion of intermediate products, a fixed amount of reactant (0.25 g) and the typical reaction conditions were used except shortening the reaction time by half.

ESR spectra were obtained at 77 K in 5.0-mm diameter ESR quartz tubes on a JEOL JES FA2000 spectrometer.

The conversion of cellulose and product selectivities were defined as follows:

conversion (%) = $\{1 - (\text{mass of unconverted cellulose}) / (\text{mass of initial cellulose})\}$

Yield (%) = $(\text{moles of carbon in product } i) / (\text{moles of carbon in initial cellulose})$

Results and Discussion

We started our investigation with an initial catalyst

testing for screening the best catalyst in the conversion of cellulose. Microcrystalline cellulose (hereafter referred to as cellulose) was used as the reactant without pretreatment, and the results are shown in Figure 1. The products in the bio-inspired conversion of cellulose mainly contain FA, together with a small amount of glycolic acid, lactic acid, levulinic acid, acetic acid and gluconic acid (see Figure S1). Traces of oxalic acid, *cis*-fumaric acid and *trans*-fumaric acid were also detected. It is important to note that the real acidic product mentioned above is sodium salt, rather than carboxylic acid. For simplicity, we used the same terminology. In the absence of catalyst, 42.5% of cellulose converted, but gave only 8.9% yield of FA. Upon addition of ferric salt, the cellulose conversion increased to 53.6%, while the products lacked selectivity, yielding 8.4% of FA. In the presence of metalloporphyrin catalysts, however, the cellulose conversion increased and the yield of FA enhanced dramatically. Of the metalloporphyrins tested, sulfonated iron porphyrin (TSPPF_{Fe}Cl) exhibited the highest catalytic activity, affording 49.4% yield of FA at complete conversion of cellulose. These results indicated that bio-inspired conversion of cellulose might proceed via a different mechanism from ferric salt and alkaline degradation of carbohydrates.^[19] The catalytic behavior of sulfonated metalloporphyrin with different metal ions is consistent with that observed in the metallophthalocyanine-catalyzed starch oxidation with H₂O₂.^[20] We attributed the best catalytic performance of iron porphyrin to its extreme catalytic activity with H₂O₂ generated in situ.^[21] This possible explanation will be further discussed later in the mechanistic parts. The substituent of porphyrin rings could also influence the catalytic activities for conversion of cellulose. Water soluble sulfonated iron porphyrin (TSPPF_{Fe}Cl) and carboxyl-substituted iron porphyrin (TCPPF_{Fe}Cl) were more effective for conversion of cellulose than tetraphenylporphyrin iron(III) chloride (FeTPP_{Fe}Cl). Considered together, we used TSPPF_{Fe}Cl as the bio-inspired catalyst for the cellulose conversion and the exploration of optimal reaction condition.

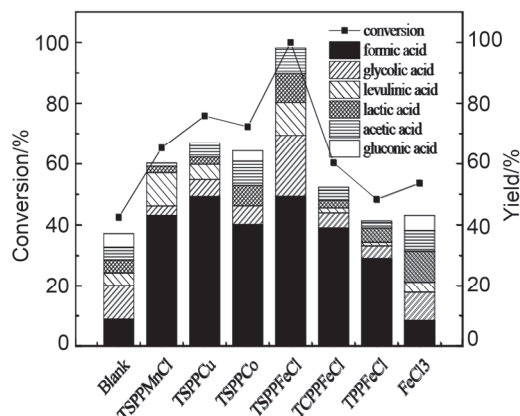


Figure 1 Effect of different catalysts on catalytic performance. Reaction conditions: cellulose 0.5 g, catalyst 1 mg, $0.5 \text{ mol}\cdot\text{L}^{-1}$ NaOH 5 mL, $p(\text{O}_2)=2.0 \text{ MPa}$, $T=150 \text{ }^\circ\text{C}$, $t=6 \text{ h}$.

To optimize the reaction condition, various reaction parameters such as reaction time, temperature, oxygen pressure and NaOH concentration were considered in the process of conversion of cellulose to FA. The reaction time was first examined. As can be seen in Figure 2, the conversion of cellulose and the yield of FA initially increased remarkably and then declined slightly after 6 h. Thus, we chose 6 h as the best reaction time. For other organic acids, however, the yields increased indistinctively and decreased before 6 h. Especially for gluconic acid, the yield of gluconic acid decreased considerably after 3 h, while the FA yield enhanced markedly. This result suggested that gluconic acid might be an intermediate for the formation of FA.

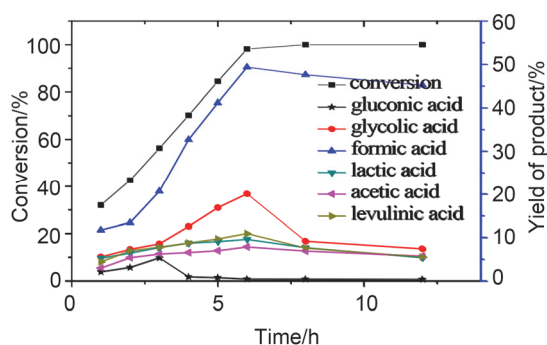


Figure 2 Effect of reaction temperature on catalytic activities. Reaction conditions: cellulose 0.5 g, TSPPFeCl 1 mg, $0.5 \text{ mol}\cdot\text{L}^{-1}$ NaOH 5 mL, $p(\text{O}_2)=2.0 \text{ MPa}$, $T=150 \text{ }^\circ\text{C}$.

As can be seen in Figure S2, the reaction temperature played a crucial role in the process of cellulose conversion. When the temperature was below $100 \text{ }^\circ\text{C}$, only trace of organic acid (e.g. FA) was obtained. However, when the reaction temperature was increased from 110 to $170 \text{ }^\circ\text{C}$, the conversion of cellulose increased significantly and kept full conversion after heating above $150 \text{ }^\circ\text{C}$. This result is consistent with previous reports,^[7,8] which indicated that complete con-

version of highly stable and water insoluble cellulose required a high reaction temperature. Whereas, for the yield of FA, it was initially increased then decreased. This trend was identical to that obtained in the conversion of cellulose in alkaline solution by CuO-based catalytic process.^[11e] It implied that decomposition of formed FA occurred.

In general, increasing the oxygen pressure can enhance the solubility of molecular oxygen in the liquid phase and then can increase the oxidative conversion of biomass. When the oxygen reached a saturated concentration, further increase of oxygen pressure has no effect on the oxidation reaction. Indeed, the yield of FA increased dramatically with increasing the oxygen pressure from 0.5 to 2 MPa in TSPPFeCl-catalyzed cellulose conversion (see Figure S3), whereas the further increase of the oxygen pressure led to slight decrease of FA yield. The optimal oxygen pressure was 2 MPa.

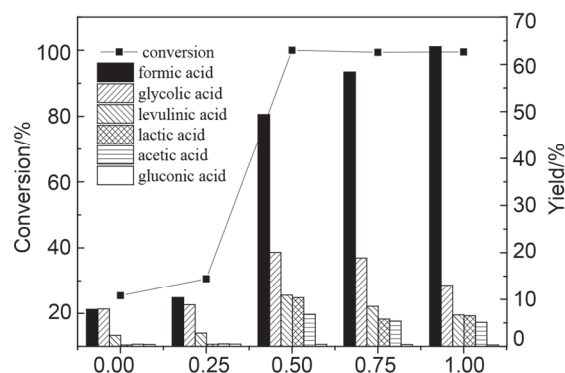


Figure 3 Effect of the concentration of NaOH on catalytic performance. Reaction conditions: cellulose 0.5 g, catalyst 1 mg, NaOH solution 5 mL, $p(\text{O}_2)=2.0 \text{ MPa}$, $T=150 \text{ }^\circ\text{C}$, $t=6 \text{ h}$.

Since it has been known that addition of alkali could prevent the oxidative decomposition of FA during the hydrothermal conversion of glucose,^[22] in this study the effect of the concentration of NaOH on the bio-inspired conversion of cellulose was examined, and the results are summarized in Figure 3. As can be seen from Figure 3, cellulose conversion increased remarkably from 25.4% to 100% and remained unchanged when the NaOH concentration increased from 0 to $1 \text{ mol}\cdot\text{L}^{-1}$. Similar tendency was observed for the yield of FA. The highest yield of FA reached up to 63.7% as the NaOH concentration increased to $1 \text{ mol}\cdot\text{L}^{-1}$. This result indicated that the addition of alkali may be an effective way for production of FA starting from cellulose. In addition, the total yields of other organic acids (i.e. glycolic acid, lactic acid, levulinic acid, acetic acid and gluconic acid) first increased and then decreased with the increase of the concentration of NaOH. This result suggests that glycolic acid, lactic acid, levulinic acid, acetic acid and gluconic acid may be the intermediates for FA formation.

Table 1 Comparison of yields of carboxylic acid products in bio-inspired process^a and in Kraft process^b

Entry	Conversion/%	Glucose/(g·L ⁻¹)
1 ^a	100	0.45
2 ^b	67.6	0.33
3 ^c	0	—
4 ^d	0	—
5 ^e	25.42	5.48

^a Bio-inspired process: cellulose 0.5 g, TSPPF₂Cl 1 mg, 0.5 mol·L⁻¹ NaOH 5 mL, *p*(O₂)=2.0 MPa, *T*=150 °C, *t*=6 h.

^b Kraft process: cellulose 0.5 g, 15% NaOH, 30% Na₂S, 4 : 1 liquor/cellulose ratio, 165 °C cooking temperature, 60 min to cooking temperature, and 60 min at cooking temperature. ^c Cellulose was replaced with α-cellulose in Kraft process. ^d 1 mg TSPPF₂Cl was added and cellulose was replaced with α-cellulose in Kraft process. ^e NaOH was replaced with water in bio-inspired process.

Besides the prevention of FA decomposition, alkali also could promote the hydrolysis of cellulose^[23] in water. For the sake of determining whether NaOH was involved in this conversion process, we compared the cellulose conversion and concentration of hydrolysis product *i.e.* glucose in bio-inspired process and in Kraft process (see Table 1). Cellulose in the latter process has been considered to be not hydrolyzed in aqueous solution of NaOH and Na₂S.^[24] Indeed, using high degree of polymerization (DP) of α-cellulose which is the major component of Kraft pulps,^[25] no conversion of cellulose occurred (Entry 3), even with TSPPF₂Cl as catalyst (Entry 4). However, 67.6% of conversion of cellulose was obtained with low DP of microcrystalline cellulose as substrate (Entry 2), which could be prepared from Kraft pulps via acidic hydrolysis.^[26] It indicated that microcrystalline cellulose was easily degraded in alkaline solution. In comparison with Kraft process, degradation of cellulose was enhanced in bio-inspired process (compare Entry 1 with Entry 2). One of degradation pathway in these processes may occur via hydrolysis with hot water, since 5.48 g/L hydrolysis product *i.e.* glucose was detected without addition of NaOH (Entry 5). Considering that glucose concentration significantly decreased with addition of NaOH in bio-inspired process (compare Entry 1 with Entry 5), NaOH more likely participated in further conversion of glucose. Further experiments revealed that glucose was converted into gluconic acid in the presence of NaOH (see Table S1). Since H₂O₂ was also found in alkaline oxidation of glucose to gluconic acid over a gold catalyst,^[27] we mixed glucose with NaOH aqueous solution in an oxygen atmosphere. Apart from gluconic acid, H₂O₂ was also detected (Table 2, Entry 1). Then we explored whether H₂O₂ was produced in bio-inspired conversion of cellulose. Comparing Entry 2 with Entries 3, 4, it indicated that NaOH also promoted the formation of H₂O₂ in the presence of cellulose and oxygen.

Table 2 H₂O₂ formation in different reaction condition^a

Entry	TSPPF ₂ Cl/mg	NaOH/ (mol·L ⁻¹)	<i>t</i> /h	Conversion/%	H ₂ O ₂ / (mmol·L ⁻¹)
1 ^b	0	0.5	2	58.5	9.3
2	0	0.5	6	42.5	9.0
3	1	0	6	25.4	0
4 ^c	1	0.5	6	23.9	0
5	1	0.5	6	100	5.4
6	2	0.5	6	59.3	3.5
7	3	0.5	6	43.5	1.3

^a Cellulose 0.5 g, *T*=150 °C, *p*(O₂)=2.0 MPa, NaOH 5 mL, *t*=6 h; ^b Cellulose was replaced with 0.5 g glucose. ^c N₂ atmosphere.

As can be seen from Table 2, with the increase of catalyst loading, H₂O₂ concentration decreased dramatically (Entry 5–7). These experiments clearly indicated that iron porphyrin was involved in the activation of H₂O₂. More recently, Sorokin *et al.*^[20] found that water-soluble tetrasulfonatophthalocyanine iron complex (FePcS) could interact with H₂O₂ to produce PcS-Fe^{III}O₂⁻, which then cleaved the C(2)–C(3) bond of an anhydroglucose unit of carbohydrate to form the carboxyl group. This active species has long been known as an oxidant intermediates commonly associated with the catalytic cycle of cytochrome P450 and its mimics.^[28] To identify whether this active species produced in the interreaction between TSPPF₂Cl and H₂O₂ generated *in situ*, an additional experiment was carried out in which cyclohexanecarboxaldehyde, H₂O₂ generated from cellulose conversion, and TSPPF₂Cl were processed in water at 333 K for 3 h (see Table S2). Cyclohexanecarboxaldehyde has been considered as the best molecular probe for determination of PFeO₂⁻.^[28] It was found that oxidative deformylation of cyclohexanecarboxaldehyde to yield cyclohexene occurred. In comparison with the results of FeCl₃·6H₂O catalyst and blank test, high yield (2.69 mg/g) of cyclohexene was obtained using TSPPF₂Cl as catalyst. This experiment clearly proved that PFeO₂⁻ may be present in the bio-inspired conversion of cellulose. Since PFeO₂⁻ has two structures, *i.e.* side-on peroxo and end-on peroxo,^[29] ESR experiments were conducted to elucidate the structure of PFeO₂⁻ (Figure 4). Treatment of TSPPF₂Cl with or without H₂O₂ in 0.5 mol·L⁻¹ NaOH solution was carried out in an ESR tube and the resultant solution was immediately frozen at 77 K for spectroscopic analysis. The ESR spectrum of the mixture of TSPPF₂Cl and H₂O₂ has a typical rhombic signal at *g*≈4.23, which is similar to that of side-on peroxide species [(tmpIm)Fe^{III}(O₂)⁻].^[30] Furthermore, replacing oxygen with commercially available H₂O₂ as the oxidant was carried out in bio-inspired process, we obtained 45.6% yield of FA (see Table S3). This result also showed that PFeO₂⁻ indeed facilitates the further cleavage path way.

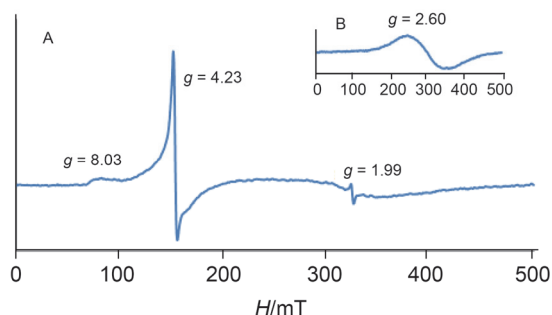


Figure 4 Experimental ESR spectra of TSPPFcCl treated with H_2O_2 (A) or without H_2O_2 (B) in NaOH solution. Reaction conditions: TSPPFcCl 0.1 mg, 0.02 mL H_2O_2 , 0.38 mL $0.5 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution, 77 K.

Finally, we distinguished the pathway of FA formation. Bio-inspired conversion of lactic acid, levulinic acid, acetic acid, gluconic acid, glucose as well as oxalic acid was performed to give evidences for FA formation (see Table 3). Oxalic acid was chosen as an intermediate, because oxalic acid was demonstrated as the key intermediate in alkaline hydrothermal conversion of glucose.^[22]

Table 3 The conversion of intermediate products and yield of FA in the presence of TSPPFcCl^a

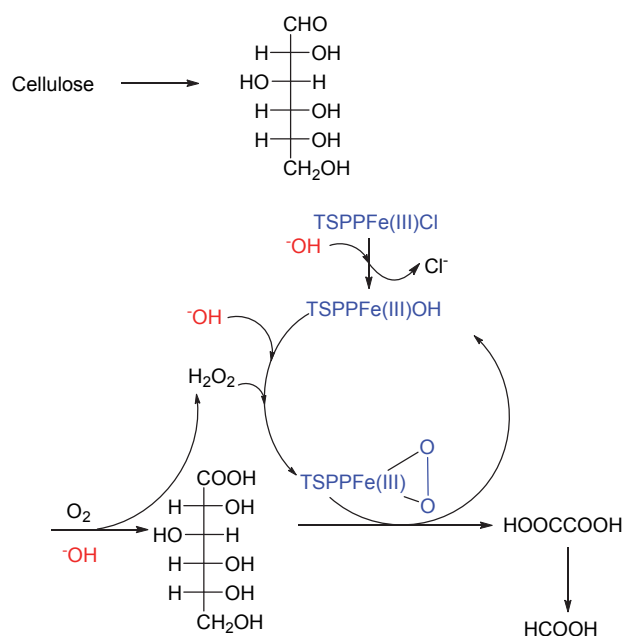
Intermediate	Conversion/%	Yield of FA/%
Glucose	100	25.2
Gluconic acid	82.0	55.2
Oxalic acid	94.8	94.7
Lactic acid	34.0	28.8
Acetic acid	20.2	18.3
Levulinic acid	47.3	19.6

^a Reactant 0.25 g, catalyst 1 mg, 0.5 mol/L NaOH 5 mL, $p(\text{O}_2) = 2.0 \text{ MPa}$, $T = 150 \text{ }^\circ\text{C}$, $t = 3 \text{ h}$.

As can be seen from the results of Table 3, when lactic acid, acetic acid, levulinic acid and glucose were used as the substrates, the yield of FA was low. However, when the substrates were oxalic acid and gluconic acid, the oxalic acid and gluconic acid conversions were 94.8% and 82% respectively, and the yield of FA approached to 94.7% and 55.2% separately. Obviously, oxalic acid and gluconic acid may be the key intermediates of FA formation in TSPPFcCl-catalyzed cellulose conversion reaction.

On the basis of these observations and literatures,^[11b,17b] a plausible pathway for cellulose conversion to FA can be proposed as shown in Scheme 2. Cellulose was initially hydrolyzed into glucose. Subsequently, glucose was further converted into gluconic acid and H_2O_2 in the presence of NaOH and oxygen. Under alkaline condition, iron porphyrin underwent oxidative addition to form side-on iron(III)-peroxo species by the reaction of H_2O_2 generated *in situ*. Iron(III)-peroxo species then catalyzed the oxidative cleavage of

Scheme 2 The mechanism for the bio-inspired conversion of cellulose



C—C bond of gluconic acid to form oxalic acid, which was finally converted to FA.

Conclusions

In conclusion, an efficient method to produce FA from cellulose was achieved when using TSPPFcCl as the bio-inspired catalyst with molecular oxygen as the oxidant in aqueous NaOH solution. The highest yield of FA (63.7%) was obtained at full cellulose conversion in the presence of TSPPFcCl (1 mg) and $1 \text{ mol}\cdot\text{L}^{-1}$ of aqueous NaOH solution at $150 \text{ }^\circ\text{C}$ and 2.0 MPa of O_2 . This bio-inspired approach used relatively high concentration of cellulose (0.1 g/mL H_2O), which could enhance the FA productivity. Notably, this bio-inspired catalyst does not need to be recycled because of its ppm concentration. Therefore, our work may provide an economic and eco-benign alternative route to efficient and selective conversion of cellulose to FA, a valuable chemical for future hydrogen storage.

Acknowledgement

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