

# Catalytic conversion of biomass-derived carbohydrates to formic acid using molecular oxygen†

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Here we report a catalytic process for the efficient production of formic acid (FA) from common carbohydrates via  $\text{VO}_2^+$  formed by dissolving sodium metavanadate in acidic water. The polysaccharides undergo a hydrolysis reaction and an immediate oxidation reaction successively to produce FA in the same reaction system. The hydrolysis reaction decomposes the polymerized structures to produce mono-saccharides, which are readily oxidized to FA under catalysis of  $\text{VO}_2^+$ . Typically, formic acid mole yields are 64.9% from cellulose and 63.5% from xylan (hemicellulose). The separation of FA from the catalytic system and recycling of the catalyst are demonstrated.

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Various strategies for producing chemicals and fuels from biomass are being researched in the interest of developing alternatives to fossil fuels. Carbohydrates, representing the largest fraction of biomass, are attracting the major attention.<sup>1–3</sup> At present, compounds of commercial interest that can be obtained directly from carbohydrates by non-fermenting approaches are very few and limited mainly to simple carbohydrates such as glucose and fructose. These include the production of gluconic acid and sorbitol from glucose by oxidation and hydrogenation, respectively, and 5-hydroxymethyl-furfural (HMF) from glucose and fructose using acidic catalysts.<sup>4–6</sup> The ultimate goal of producing chemicals by direct reaction with cellulose or hemicellulose is still far away because they are not soluble in conventional solvents and are very resistant to chemical and biological transformations.<sup>7–9</sup>

Formic acid (FA) is a basic chemical feedstock widely used in chemical, textile, leather, pharmaceutical, rubber and other industries. Recent research has demonstrated that FA has the potential to power fuel cells for electricity generation and automobiles.<sup>10,11</sup> Additionally, with respect to a possible hydrogen economy, FA has been proposed as a suitable hydrogen storage compound, having a mass fraction of

0.044 hydrogen.<sup>12–14</sup> It can be easily and selectively decomposed to  $\text{H}_2$  and  $\text{CO}_2$  through catalysis under mild conditions.<sup>15,16</sup> Thus FA from biomass offers a mild and sustainable way to produce  $\text{H}_2$ .

Many researchers have studied the production of FA from carbohydrates using thermal cracking,<sup>17</sup>  $\text{SCW}/\text{H}_2\text{O}_2$ ,<sup>18</sup>  $\text{Fe}_2(\text{SO}_4)_3/\text{O}_2$  or  $\text{CuSO}_4/\text{O}_2$ ,<sup>19,20</sup>  $\text{OH}^-/\text{H}_2\text{O}_2$ ,<sup>21</sup> Keggin-type  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}/\text{O}_2$ ,<sup>22,23</sup> and the recent  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40} + p$ -toluenesulfonic/ $\text{O}_2$  systems.<sup>24</sup> Due to its unique properties, high temperature water (HTW) is suitable as a solvent for the oxidation of carbohydrates to FA. However, the attainment of a high FA yield with a satisfactory reaction rate is still a great challenge, especially from polysaccharides such as cellulose and hemicellulose, because the oxidative pathway is intricate and difficult to control.

Because of the stability of polysaccharides, the catalytic oxidation of cellulose to FA in HTW must undergo two reactions: (1) acid hydrolysis of cellulose to give glucose or other small molecular intermediates and (2) selective oxidation of glucose or other small molecular intermediates to produce FA.<sup>23,24</sup> The conversion conditions should satisfy simultaneously the two reactions, hydrolysis and oxidation, because they occur in one solution.

For hydrolysis of polysaccharides in acidic HTW, the by-product humin is always produced from glucose or other small molecular intermediates, resulting in low selectivity towards the target product. Hence, the oxidation should be faster than hydrolysis in order to avoid producing humin.

Initially, Wasserscheid *et al.*<sup>24</sup> performed the selective catalytic conversion of biobased carbohydrates to formic acid using molecular oxygen, and reported that cellulose could be

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oxidized in HTW using  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  as a catalyst at 80 °C for 26 h with a low FA yield of 1%. And then they added *p*-toluenesulfonic acid as an additive to improve the FA yield to 22% at 90 °C for 66 h. The time was very long, such as 26 h or 66 h, and the FA yield was still very low. Fu *et al.*<sup>23</sup> also used  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  as a catalyst and added  $\text{H}_2\text{SO}_4$  as an additive to oxidize cellulose with a FA yield of 28% at 170 °C and the cellulose was completely converted in 9 h. The increase in temperature and acidity (by adding  $\text{H}_2\text{SO}_4$ ) increased the FA yield, and the time was shortened to 9 h, but it was still too long for practical application, which suggests that the conversion rate is low. It is reported that higher temperatures and higher acidities are necessary for hydrolysis of cellulose in a short time (less than 0.5 h<sup>25</sup>) which hints that the temperature or acid amount or both of them used previously are too low to reach completion in a short time.

On the other hand, pentavalent V in the catalyst  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  plays a key role in the oxidation of glucose or intermediates to FA.<sup>22–24</sup> The question arises whether  $\text{NaVO}_3$ , which is readily available and inexpensive, has an efficient catalytic performance for the same oxidation.

It is well known that V–O species in an aqueous solution of  $\text{NaVO}_3$  exists in various forms depending on the acidity of the solution (pH).<sup>26,27</sup> Among them  $\text{VO}_2^+$  showed a high oxidative potential for selective oxidations, such as benzene oxidation to phenol<sup>28</sup> and alkane oxidation.<sup>29</sup>  $\text{VO}_2^+$  mainly appears under strong acidic conditions (pH < 1). Therefore, it is possible that FA selectivity is high even under drastic hydrolysis conditions (pH < 1) because  $\text{VO}_2^+$  is capable of oxidizing glucose or intermediates readily.

According to previous work, the simple catalyst sodium metavanadate ( $\text{NaVO}_3$ ) with sulphuric acid as an additive in HTW was employed to convert carbohydrates into FA. We found that the catalyst system could satisfy the two reactions of hydrolysis and oxidation, and monosaccharides, disaccharides and polysaccharides could be converted readily into FA with high selectivity under an oxygen pressure of about 3 MPa. The typical results are the FA yield of 64.9% based on carbon (77.9% based on hydrogen) with cellulose as the substrate, and 63.5% (79.4% based on hydrogen) FA yield with xylan (hemicellulose) as the substrate. The produced FA could be easily separated by solvent extraction after the reaction. The catalytic system could be reused directly after simple purification. This route has great potential for industrial application.

Table 1 shows the conversion of carbohydrates and the yield of FA for different catalytic systems. Cellulose conversion and FA yield are very low in the absence of sulfuric acid (Table 1, entries 1, 2). When only sulfuric acid is used, the yield of FA reaches 13.1% with a cellulose conversion of 72.1% (Table 1, entry 3). When  $\text{NaVO}_3$  and sulfuric acid are used simultaneously, the yield of FA increases significantly with an elevated cellulose conversion (Table 1, entries 4–12). Interestingly, the yield of FA increases with an increase of sulfuric acid concentration until a selectivity plateau of 64.9% is reached at a sulfuric acid mass fraction equal to or greater than 0.007. Several other carbohydrates including glucose, fructose,

**Table 1** Conversion of carbohydrates in an aqueous sodium metavanadate solution with and without sulfuric acid under an initial oxygen pressure of 3 MPa at time. Substrate (100 mg), sodium metavanadate (22 mg), and water (6 g) were stirred in an autoclave at 160 °C. FA yields are calculated on a carbon basis and given as mean values. The key experiments were repeated five times (see Table S3). Conversion is calculated based on the amount of unconverted carbohydrates. The content of sulfuric acid is calculated based on the mass fraction of sulfuric acid in water

Entry	Substrate	$\text{H}_2\text{SO}_4$ /wt%	Time/min	Conversion/%	FA yield/%
1 <sup>a</sup>	Cellulose	0	120	1	<0.5
2	Cellulose	0	120	3	<1
3 <sup>a</sup>	Cellulose	0.1	120	72.1	13.1
4	Cellulose	0.1	120	74.3	31.8
5	Cellulose	0.2	120	83.5	41.2
6	Cellulose	0.4	120	92.1	49.9
7	Cellulose	0.5	120	94.6	56.8
8	Cellulose	0.7	120	100	64.9
9 <sup>a</sup>	Cellulose	0.7	120	95.2	20.6
10	Cellulose	0.9	120	100	63.7
11	Cellulose	1.5	120	100	62.8
12	Cellulose	2.0	120	100	61.2
13	Glucose	0	1	96.8	42.8
14	Glucose	0.7	1	100	68.2
15	Fructose	0.7	1	100	61.5
16	Cellose	0.7	10	100	65.3
17	Sucrose	0.7	5	100	64.6
18	Xylose	0.7	1	100	66.2
19	Xylan	0	30	6	2.3
20	Xylan	0.7	30	100	63.5

<sup>a</sup> The reaction was carried out without  $\text{NaVO}_3$ .

cellose, xylose, sucrose and xylan were also examined in the same reaction system, and excellent performance was attained under non-optimized conditions (Table 1, entries 13–20). For xylan (hemicellulose) and cellulose, the most abundant biomass in nature, the FA yield can reach 63.5% and 64.9% based on carbon, or 79.4% and 77.9% based on hydrogen, respectively. It is worth noting that 30% yield of FA from cellulose has been the highest recorded in the literature to date, which was obtained in the  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  + *p*-toluenesulfonic/ $\text{O}_2$  system.<sup>24</sup> Moreover, the reaction time was shortened drastically in the suggested system.

The effect of temperature on the conversion of substrate and the yield of FA was studied (shown in Fig. S7†). When the temperature is increased from 140 °C to 160 °C, the conversion of cellulose increases from 28.0% to 100%, and the yield of FA increases from 13.4% to a maximum value of 64.9%, which means that the rate of cellulose oxidation increases with increasing temperature. But when the temperature is further increased to 190 °C, the yield of FA decreases gradually to 49.7%, resulting from the over-oxidation of FA at high temperatures. The effect of the amount of initial substrate on the reaction was also investigated (as shown in Fig. S8†). At low amounts of cellulose, not more than 0.1 g, the conversion of cellulose is 100% and the yield of FA increases with the amount of cellulose and reaches a maximum value of 64.9% at 0.1 g of cellulose. Then both the conversion and the yield of FA decrease with increasing cellulose. The low yield of FA at

<0.1 g of cellulose results from the over-oxidation of FA, and the low yield of FA at >0.1 g of cellulose is due to the low conversion of cellulose.

The byproducts were determined by HPLC analysis; however, no other products were detected with a mass fraction of sulfuric acid of 0.007 (Fig. S9†). Besides, CO<sub>2</sub> is the sole product in the gas phase as detected by GC, and the carbon balance shows that FA and CO<sub>2</sub> are exclusive in the products (Table S2†).

The role of vanadium–oxygen catalyst in redox reactions is well known, such as V<sub>2</sub>O<sub>5</sub> for SO<sub>2</sub> to SO<sub>3</sub>,<sup>30</sup> V–Mo oxides for naphthalene to phthalic anhydride<sup>26</sup> and H<sub>7</sub>PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub> for benzene to phenol,<sup>28</sup> *etc.* During these oxidation reactions, the vanadium–oxygen (V–O) species are reduced and then oxidized by an oxidant such as oxygen or hydrogen peroxide to complete a catalytic cycle, or the vanadium–oxygen species activates the oxidant to form an intermediate that oxidizes the reactants. The selectivity of the products is highly dependent on the V–O species present in these reactions. In the aqueous sodium metavanadate solution, the V–O species varies with the acidity of the solution (pH)<sup>26,27</sup> and consequently determines the selectivity for FA. The experimental results in Table S1† show that the pH of the solution is lower than 1 when the mass fraction of sulfuric acid reaches 0.007 (this should be the case under the reaction conditions due to evaporation of water at higher temperature). Generally, V<sub>4</sub>O<sub>12</sub><sup>4–</sup> is predominant with a small amount of V<sub>5</sub>O<sub>15</sub><sup>5–</sup> at pH around 7; V<sub>10</sub>O<sub>28</sub><sup>6–</sup> appears at pH < 6 and becomes dominant in a pH range of 4.1–3.0; VO<sub>2</sub><sup>+</sup> appears at pH < 2 and becomes dominant at pH < 1. This suggests that the high FA selectivity at a sulfuric acid mass fraction greater than 0.007 may be attributed to catalysis *via* VO<sub>2</sub><sup>+</sup>, which is different from the V–O species at sulfuric acid mass fractions lower than 0.007. The high FA selectivity at sulfuric acid mass fractions greater than or equal to 0.007 in comparison with the many byproducts produced at sulfuric acid mass fractions lower than 0.007 (Fig. S3 and S4†) indicates an exclusive reaction pathway to FA under catalysis by VO<sub>2</sub><sup>+</sup>. <sup>51</sup>V-NMR and XPS analyses have established that VO<sub>2</sub><sup>+</sup> is the only V–O species in the solution at a sulfuric acid mass fraction of 0.007 and VO<sub>2</sub><sup>+</sup> can be reduced to a tetravalent form by carbohydrates in the absence of oxygen (Fig. S10 and S11†). Thus, it is considered that VO<sub>2</sub><sup>+</sup> oxidizes carbohydrates by giving an oxygen atom first, and then is regenerated through oxidation by molecular oxygen.

The low cellulose conversion in the absence of sulfuric acid, in comparison with that of glucose (see Table 1, entries 2, 13) which can be converted in 96.8% within 1 min, indicates the inertia of the polymeric structure of carbohydrates and the activeness of the monosaccharide structure with respect to oxidation. Thus the role of sulfuric acid in converting polysaccharides appears not only to transform the V–O species to VO<sub>2</sub><sup>+</sup>, but also to initiate and accelerate the hydrolysis reaction. The acid catalyzed hydrolysis of cellulose, an industrial process, produces glucose first and ultimately results in a mixture of glucose, HMF, levulinic acid, FA and humin of unknown structure.<sup>31,32</sup> The normal yield of glucose from cellulose under sulfuric acid-catalyzed reaction

conditions is only 40–50%.<sup>33,34</sup> The yields of FA from cellulose and glucose with sulfuric acid and NaVO<sub>3</sub> are comparable (64.9% *vs.* 68.2%). Thus, with the participation of NaVO<sub>3</sub> and oxygen, the glucose produced from hydrolysis of cellulose is readily oxidized to FA, thus resulting in a comparable FA yield and avoiding the production of byproducts. In other words, the generation of humin can be completely avoided because the glucose produced from hydrolysis cannot exist under the drastic oxidation conditions in the present system. The hydrolysis reaction is the rate-determining step with cellulose as a reactant because of the significant increase of oxidation reaction rate with an increase in the mass fraction of sulfuric acid (Fig. S5 and S6†).

To obtain the reaction pathway under catalysis by VO<sub>2</sub><sup>+</sup>, several two-carbon and three-carbon containing compounds that may be the intermediates were investigated under the same reaction conditions as those for glucose (see Table 1, entry 14), following the method suggested by Wasserscheid and coworkers.<sup>22</sup> Table 2 shows the reaction results for these compounds. FA is very stable under the reaction conditions, indicating that CO<sub>2</sub> is derived from reaction processes other than FA oxidation. According to the results of carbohydrate conversion, the intermediates should meet three criteria: they should be oxidized readily, have high selectivity to FA and exclusive selectivity to FA and CO<sub>2</sub>. Since glycolaldehyde, glyoxal and glyceraldehyde meet these criteria, they are most likely to be the oxidation intermediates of a monosaccharide such as glucose, and are formed *via* oxidative C–C scission. The oxidation of polysaccharides such as cellulose and xylan starts with hydrolysis first to yield a monosaccharide. These

**Table 2** The oxidation of possible intermediates in the carbohydrate oxidation process in the acidic aqueous sodium metavanadate solution by oxygen. Substrate (100 mg), sodium metavanadate (22 mg), sulfuric acid (42 mg, mass fraction of 0.007 in water), water (6 g) and oxygen (initial pressure 3 MPa) were stirred in an autoclave at 160 °C and the reaction time of 1 min. FA yields were calculated on a carbon basis and given as mean values. Conversion of substrates is calculated based on the amount of unconverted substrate. AC represents acetic acid

Entry	Substrate	Conversion/%	FA yield/%	Others
1	Formic acid	<1	—	—
2	Formaldehyde	2	0	CO <sub>2</sub>
3	Acetic acid	0	—	—
4	Glycol	67.5	16.7	CO <sub>2</sub>
5	Oxalic acid	85.2	0	CO <sub>2</sub>
6 <sup>a</sup>	Glycolaldehyde	100	62.6	CO <sub>2</sub>
7	Glycolic acid	90.2	30.1	CO <sub>2</sub>
8	Glyoxylic acid	100	30.2	CO <sub>2</sub>
9	Glyoxal	100	85.6	CO <sub>2</sub>
10	Glycerol	84	40.3	CO <sub>2</sub>
11	Glyceraldehyde	100	65.3	CO <sub>2</sub>
12	Lactic acid	100	15.1	AC 25.2%
13	Methylglyoxal	100	20.9	AC 50.4%
14 <sup>b</sup>	1,3-Dioxycetone	100	57.3	AC 21.1%
15	1,2-Propylene glycol	70.1	16.5	AC 17.8%
16	1,3-Propylene glycol	15.8	2.1	AC 3.0%

<sup>a</sup> The substrate was the glycolaldehyde dimer. <sup>b</sup> The substrate was the 1,3-dioxycetone dimer.

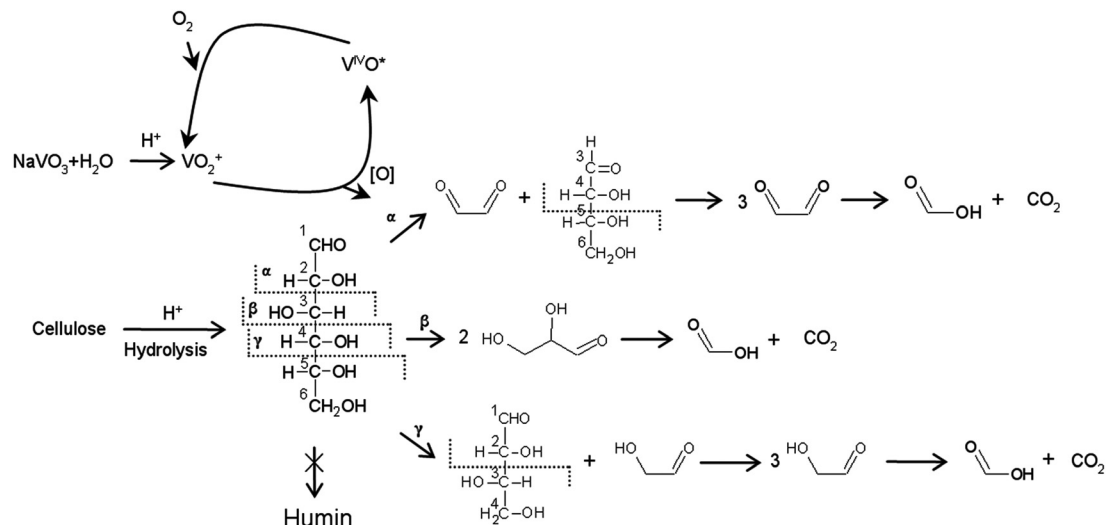


Fig. 1 Proposed reaction pathways for the conversion of cellulose into FA in an aqueous sodium metavanadate solution with sulfuric acid under oxygen pressure.

reaction pathways are shown in Fig. 1, including the catalytic cycle of the vanadium catalyst.

The separation of FA from water has been reported to be easy using the rectification method and energy-efficient extraction methods.<sup>24,35,36</sup> In this work the extraction method was investigated using butyl ether, dichloromethane, diethyl ether, ethyl acetate and *n*-octanol, and the results show that diethyl ether performs the best, offering a 99.9% extraction efficiency in five operation cycles (Table S4†). The diethyl ether and water mixture can be easily separated and recovered by distillation or gas sweeping (Fig. S12†). The recovered catalyst solution was reused five times with no substantial change in the cellulose conversion efficiency and FA selectivity as shown in Fig. 2.

In conclusion, we have proposed a mild and efficient method to convert biomass-based carbohydrates containing

various monosaccharides, disaccharides and polysaccharides to formic acid (FA) using an aqueous solution containing two common chemicals, sodium metavanadate and sulfuric acid, as catalysts. The carbohydrates undergo hydrolysis and an immediate oxidation to produce FA in the suggested system. High FA selectivity and production efficiency are obtained due to the excellent catalytic performance of VO<sub>2</sub><sup>+</sup>. FA can be easily separated by an extraction method. The catalyst solution can be reused multiple times without substantial change in the FA selectivity. This route can be an efficient and sustainable way to produce FA and hydrogen from biomass in the future.

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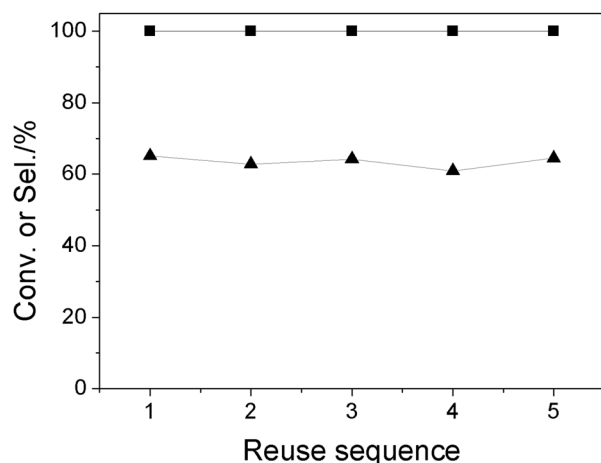


Fig. 2 Reuse of the catalyst system for cellulose conversion (■) and FA selectivity (▲). Reaction conditions: cellulose, 100 mg; NaVO<sub>3</sub>, 22 mg; sulfuric acid, 42 mg (mass fraction of 0.007 in water); water, 6 g; oxygen (initial pressure 3 MPa); temperature, 160 °C; reaction time, 120 min.

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