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Transformation of Cellulose and its Derived Carbohydrates into Formic and Lactic Acids Catalyzed by Vanadyl Cations

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The transformation of cellulose or cellulose-derived carbohydrates into platform chemicals is the key to establish biomass-based sustainable chemical processes. The systems able to catalyze the conversion of cellulose into key chemicals in water without the consumption of hydrogen are limited. We report that simple vanadyl (VO^{2+}) cations catalyze the conversions of cellulose and its monomer, glucose, into lactic acid and formic acid in water. We have discovered an interesting shift of the major product from formic acid to lactic acid on switching the reaction atmosphere from oxygen to nitrogen. Our studies suggest that VO^{2+} catalyzes the isomerization of glucose to fructose, the retro-aldol fragmentation of fructose to two trioses, and the isomerization of trioses, which leads to the formation of lactic acid under anaerobic conditions. The oxidative cleavage of C–C bonds in the intermediates caused by the redox conversion of VO_2^+/VO^{2+} under aerobic conditions results in formic acid and CO_2. We demonstrate that the addition of an alcohol suppresses the formation of CO_2 and enhances the formic acid yield significantly to 70–75 %.

Introduction

Cellulose, which is the main constituent of the abundant and inedible lignocellulosic biomass and is a polymer of glucose linked by β-1,4-glycosidic bonds, is a promising candidate for renewable carbon resources to partially replace petroleum for the production of chemicals and fuels.[1] The development of chemocatalytic processes for the efficient transformation of cellulose under mild conditions into platform chemicals, from which various chemicals and fuels can be derived easily, has attracted much attention in recent years.[2,3] Many studies have been devoted to the acid-catalyzed conversion of cellulose to its monomer, glucose, or to 5-hydroxymethylfurfural (HMF), a platform compound.[4,5] The direct production of high-value-added chemicals such as polyols, particularly ethylene or propylene glycol of commercial interest, from cellulose can also be realized through the design of bi- or multifunctional catalytic systems.[6,7] However, these processes require expensive H_2. Studies on the transformation of cellulose into valuable chemicals without the consumption of H_2 are scarce.

As a key building-block chemical, lactic acid is widely used in the chemical, food, pharmaceutical, and cosmetic industries.[8,9] Polylactic acid, the polymer of lactic acid, has attracted much attention as a biodegradable plastic.[8,9] Currently, lactic acid is produced mainly by the fermentation of carbohydrates such as glucose and sucrose, but this biological process is expensive and cannot be applied directly to cellulose.[8,9] The development of new chemical processes for the production of lactic acid from cellulose is highly desirable. In addition, formic acid is a promising source and storage platform for H_2.[10] Many recent studies have demonstrated that H_2 can be produced easily from formic acid under mild conditions.[11] The transformation of cellulose directly into formic acid under mild temperatures would provide an energy-efficient alternative for the sustainable production of H_2.

A few studies have been devoted to the oxidative conversion of cellulose or cellulose-derived carbohydrates to formic acid.[12–14] Wasserscheid and co-workers reported that a Keggin-type V-substituted heteropolyacid $H_5PV_2Mo_{10}O_{40}$ could catalyze the conversion of glucose and some oligosaccharides under an O_2 atmosphere to formic acid.[12] A formic acid yield of ~50 % was obtained after 26 h of reaction at 353 K and an oxygen pressure of ~3 MPa. With the assistance of *p*-toluenesulfonic acid, cellulose could also be transformed to formic acid with a yield of 22 % after 66 h reaction at 363 K and an oxygen pressure of ~3 MPa.[13] Fu and co-workers further demonstrated that $H_5PV_2Mo_{10}O_{40}$ could catalyze the conversion of cellulose to formic acid at high reaction temperatures in the absence of organic sulfonic acid; a formic acid yield of 35 % was obtained after 9 h of reaction at 443 K.[14]

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However, only scarce studies have succeeded in the chemocatalytic production of lactic acid from carbohydrates under mild conditions (<473 K). Holm et al. found that a beta zeolite with Sn^{IV} in the framework as Lewis acid sites was efficient for the conversion of glucose, fructose, or sucrose in methanol into methyl lactate at 433 K.[15] Sn^{IV} grafted onto MCM-41 modified with carbon also catalyzed the transformation of carbohydrates to methyl lactate in methanol under similar conditions.[16] However, these Sn^{IV}-based catalysts are limited to the transformation of mono- or disaccharides. Solid Lewis acids such as tungstated zirconia and alumina as well as lanthanide triflates were reported to catalyze the conversion of cellulose in water to lactic acid.[17,18] Recently, we found that a simple Pb^{II} ion was highly efficient for the conversion of cellulose into lactic acid in water.[19] Lactic acid yields of 68 and 62 % were attained for the conversion of ball-milled and microcrystalline cellulose at 463 K for 4 and 15 h, respectively. The toxicity of Pb may hamper the practical application of this system.

It is highly desirable to develop more efficient and environmentally friendly catalytic systems for the production of lactic or formic acid from cellulose or cellulose-derived carbohydrates. Moreover, the formations of lactic and formic acid both involve the selective cleavage of C–C bonds in carbohydrates. We still lack insight into how the C–C bond is cleaved and how to control the C–C bond cleavage.

Very recently, we found that a cheaper and less toxic vanadium salt, $VOSO_4$, could catalyze the transformations of glucose and cellulose into either formic acid or lactic acid by simply tuning the reaction atmosphere from O_2 to N_2. This paper reports a new “two birds, one stone” catalytic system. The reaction pathways and mechanisms for the formation of lactic and formic acid are investigated and discussed to gain an insight into the chemistry that controls the cleavage of C–C bonds in carbohydrates and the derived intermediates.

Results and Discussion

Catalytic behavior under aerobic and anaerobic conditions

As mentioned above, $H_5PV_2Mo_{10}O_{40}$ has been studied extensively as a homogeneous catalyst for the oxidative conversion of glucose to formic acid.[12–14] To explore the possibility of other catalysts for this transformation, we have investigated the catalytic performances of various metal cations for the conversion of glucose in water under O_2. Without a metal catalyst (blank reaction), no formic acid was formed. Among the metal salts examined, vanadyl sulfate showed the highest yield of formic acid, followed by Fe, Cu, and Cr salts (Figure 1). The yield of formic acid reached 53 %, which is better than the best yield obtained for the conversion of glucose with the $H_5PV_2Mo_{10}O_{40}$ catalyst.[12] Thus, simple $VOSO_4$ is a highly efficient catalyst for the oxidative conversion of glucose into formic acid in water under an O_2 atmosphere.

If the reaction was performed under N_2 instead of O_2, we found that lactic acid was formed as a major product instead of formic acid in the presence of some metal salt catalysts (Figure 1). Interestingly, $VOSO_4$ also exhibited the highest yield to lactic acid. The yield of lactic acid with $VOSO_4$ under the conditions of the experiments shown in Figure 1 (56 %) was better than that with the Pb^{II} catalyst (<30 %), which was reported to be an efficient catalyst in our previous paper.[19]

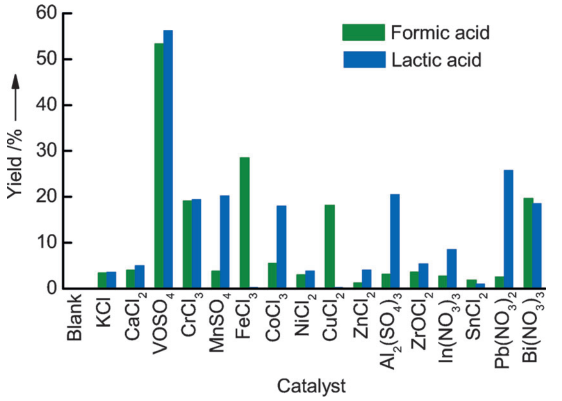


Figure 1. Catalytic performances of metal salts for the conversions of glucose under aerobic conditions to formic acid and under anaerobic conditions to lactic acid. Aerobic reaction conditions: glucose, 1.0 mmol; water, 20 cm^3; catalyst, 0.20 mmol; temperature, 413 K; reaction time, 1 h; O_2 pressure, 2 MPa. Anaerobic reaction conditions: glucose, 1.0 mmol; water, 20 cm^3; catalyst, 0.050 mmol; temperature, 433 K, time, 1.5 h; N_2 pressure, 2 MPa.

It becomes clear that $VOSO_4$ is a unique catalyst for the formation of both formic and lactic acid from glucose with yields >50 %. We have also investigated the catalytic performances of several V compounds (which include $VOSO_4$, $VOHPO_4$, VOC_2O_4, NH_4VO_3, and V_2O_5) for the conversion of glucose under aerobic and anaerobic conditions. Under an O_2 atmosphere, the catalytic performance did not depend on the source of the V catalyst significantly, and all the catalysts provided formic acid in yields of 45–55 % (Figure S1 in the Supporting Information). If N_2 was used instead of O_2, lactic acid was formed for all the V compounds examined. Thus, it is the V cation and not the counteranion that is responsible for the formation of both formic and lactic acid. The yield of lactic acid is somewhat dependent on the source of the V compounds, and $VOSO_4$ exhibits the highest lactic acid yield.

We have further investigated the effect of the concentration of $VOSO_4$ on its catalytic behavior. In the absence of a catalyst, we found that the conversion of glucose was low under either O_2 or N_2 and the major products were fructose and HMF, which were expected to be formed by the isomerization of glucose and the dehydration of fructose (Scheme S1). The presence of $VOSO_4$ increased the conversion of glucose significantly under both aerobic and anaerobic conditions (Figure S2). The formic acid and lactic acid yields increased with the $VOSO_4$ concentration to reach 64 and 56 % at $VOSO_4$ concentrations of 25 and 2.5 mm, respectively. The highest turnover frequencies (TOFs) for the formation of formic and lactic acid, that is, the moles of formic and lactic acid produced per mole of catalyst per unit time, were 63 and 21 h^{-1} at 413 and 433 K, respectively (Figure S2).

$VOSO_4$ was also efficient for the transformation of cellulose into formic or lactic acid. For the conversions of ball-milled and microcrystalline cellulose at 433 and 453 K under O_2,

Table 1. Catalytic performance of $VOSO_4$ for the conversion of cellulose and other biomass under aerobic and anaerobic conditions.[a]

Entry	Substrate	Yield[b] [%]				
		Glu.	Fru.	FA	LA	HMF
1[c]	cellulose (ball-milled)	1.1	0	39	0	0
2[d]	cellulose (ball-milled)	2.1	1.4	3.8	54	11
3[e]	cellulose (microcrystalline)	0	0	39	0	0
4[f]	cellulose (microcrystalline)	1.7	0.7	4.9	24	2.6
5[g]	inulin	0	0	39	0	0
6[h]	inulin	1.9	1.9	2.2	54	9.5
7[g]	starch	0.4	0	46	0	0
8[h]	starch	4.6	5.0	3.0	46	11

[a] Reaction conditions: glucose or fructose units in biomass, 1.0 mmol; water, 20 cm^3. [b] Glu., Fru., FA, and LA denote glucose, fructose, formic acid, and lactic acid, respectively. [c] O_2, 2 MPa; $VOSO_4$, 0.10 mmol; temperature, 433 K; time, 2 h. [d] N_2, 2 MPa; $VOSO_4$, 0.050 mmol; temperature, 453 K; time, 2 h. [e] O_2, 2 MPa; $VOSO_4$, 0.20 mmol; temperature, 453 K; time, 2 h. [f] N_2, 2 MPa; $VOSO_4$, 0.050 mmol; temperature, 453 K; time, 4 h. [g] O_2, 2 MPa; $VOSO_4$, 0.10 mmol; temperature, 413 K; time, 1.5 h. [h] N_2, 2 MPa; $VOSO_4$, 0.050 mmol; temperature, 433 K; time, 1.5 h.

a formic acid yield of 39% was obtained (Table 1, entries 1 and 3). Under a N_2 atmosphere at 453 K, lactic acid in yields of 54 and 24% was obtained for the conversions of ball-milled and microcrystalline celluloses, respectively (Table 1, entries 2 and 4). Our catalytic system was also applicable to the conversion of other biomass such as starch and inulin into formic or lactic acid. For example, inulin, which is also an inedible polysaccharide composed of fructose units with terminal glucose units and exits in many plants such as jerusalem artichoke,[20] can be transformed into formic and lactic acid with yields of 39 and 54% after reaction for 1.5 h under O_2 at 413 K and under N_2 at 433 K, respectively (Table 1, entries 5 and 6).

Acidity is typically required for the hydrolysis of cellulose and other biomass to monosaccharides (glucose or fructose), which are expected to undergo further conversions into formic and lactic acid. The pH value of the aqueous solution that contains 0.10 mmol $VOSO_4$ in 20 cm^3 H_2O was approximately 3.7–3.8 at ambient temperature. In addition, it is known that H_3O^+ can be generated reversibly in hot water because of the increased ionization constant of water at high temperatures.[6b,21] We speculate that both may contribute to the hydrolysis of cellulose or other biomass to monosaccharides. Furthermore, the product, that is, formic or lactic acid, may autocatalyze the hydrolysis of the biomass.[19]

Reaction pathways under aerobic and anaerobic conditions

To further clarify the role of the reaction atmosphere to determine the reaction route, we investigated the effect of the fraction of O_2 in the atmosphere on the product distribution in glucose conversion catalyzed by $VOSO_4$ at 423 K. A decrease in the fraction of O_2 leads to the gradual decrease of the yield of formic acid and increases that of lactic acid (Figure 2). The major product gradually shifts from formic acid to lactic acid with a decrease in O_2 fraction. CO_2 is a major byproduct at a higher fraction of O_2 (Figure 2). The yield of CO_2 decreased upon decreasing the fraction of O_2. In the absence of O_2, the major byproducts became fructose and HMF, and no CO_2 was formed. The other byproducts in the absence of O_2 were glyceraldehyde, 1,3-dihydroxyacetone, and pyruvaldehyde (denoted Others I). If O_2 was added to the reaction system, the yield to Others I decreased, and the byproducts that included glyceric acid, glycolic acid, oxalic acid, and acetic acid (denoted Others II) were detected.

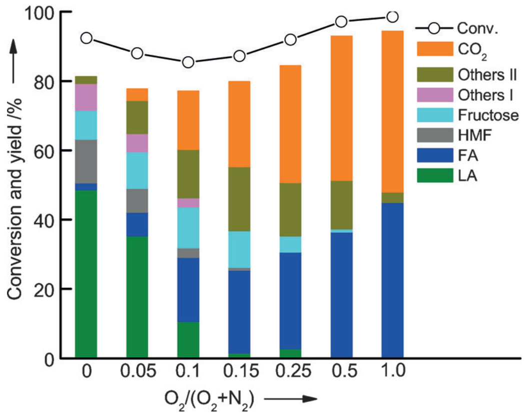
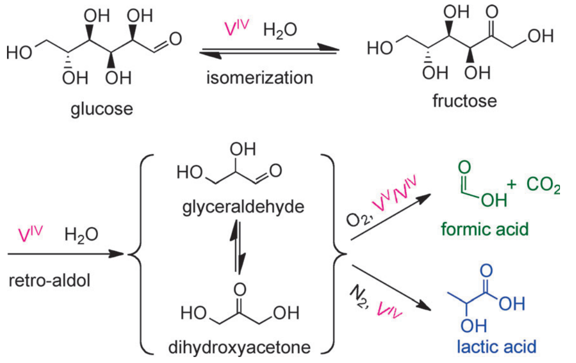


Figure 2. Effect of the fraction of O_2 in the reaction atmosphere on the product distribution in the conversion of glucose catalyzed by $VOSO_4$. Reaction conditions: glucose, 1.0 mmol; catalyst, 0.10 mmol; temperature, 423 K; reaction time, 1 h; total pressure, 2 MPa.

The analysis of the time course for the conversion of glucose catalyzed by $VOSO_4$ can provide insights into the reaction pathways that lead to the formation of different products under aerobic and anaerobic conditions. Our results showed that the conversion of glucose increased almost linearly in the initial 40 min under both aerobic and anaerobic conditions (Figures S3 a and S4 a). It is of interest that, in both cases, fructose is formed as a major product at the initial stage (Figures S3 b and S4 b). If the reaction time was prolonged, the selectivity to fructose decreased and that to formic acid under O_2 or to lactic acid under N_2 increased. These observations suggest that the isomerization of glucose to fructose occurs in the first step, and formic acid or lactic acid is formed by the consecutive conversion of fructose. The selectivity to HMF increased with reaction time under N_2 (Figure S4b), which confirms that HMF was a secondary product via fructose (Scheme S1). Glyceraldehyde and 1,3-dihydroxyacetone were also formed under N_2, the selectivities of which first increased and then decreased with increasing reaction time (Figure S4 b), which implies that these trioses were reaction intermediates during the formation of lactic acid. Similarly, our result suggests that glyceric and glycolic acid are intermediates during the formation of formic acid under O_2 (Figure S3 b).

Based on these results, we propose a scheme for the conversion of glucose into formic and lactic acid catalyzed by $VOSO_4$ (Scheme 1). Fructose, formed by the isomerization of glucose in the first step, undergoes retro-aldol fragmentation in the second step to form two C_3 intermediates, that is, glyceraldehyde and 1,3-dihydroxyacetone. Lactic acid is formed by the isomerization of the trioses under anaerobic conditions. However, the oxidative conversions of the trioses provide formic



Scheme 1. Reaction scheme for the conversion of glucose in water into formic and lactic acid under O_2 and N_2 atmospheres catalyzed by $VOSO_4$.

acid and CO_2 as the major products via glyceric and glycolic acid under aerobic conditions. As we have not observed the formation of any C_4 or C_5 intermediates (Figure S5), we speculate that the selective cleavage of the C_3–C_4 bond in fructose occurs as a major pathway in our system.

Conversions of possible intermediates under aerobic and anaerobic conditions

To understand the catalytic functions of $VOSO_4$ in the formation of lactic acid under anaerobic conditions in depth, we performed the conversions of several possible intermediates under a N_2 atmosphere. In the absence of $VOSO_4$, neither lactic acid nor C_3 intermediates were formed from glucose under N_2 (Table 2). The conversion of fructose without $VOSO_4$ was higher than that of glucose to produce HMF as a major product along with minor amounts of C_3 products. This indicates that the dehydration of fructose proceeds preferentially. The presence of $VOSO_4$ enhanced the conversions of both fructose and glucose significantly to 96% with high yields of lactic acid (56 and 58%, respectively) at 433 K. The product distribution for the conversion of fructose was almost the same as that for the conversion of glucose, which further confirms that fructose was a key intermediate. If glyceraldehyde and 1,3-dihydroxyacetone, two intermediates formed by the retro-aldol fragmentation of fructose, were used as the reactants, lactic acid yields were quite low in the absence of $VOSO_4$, although the conversions were high. Unknown polymeric products and humins were formed. The presence of the $VOSO_4$ catalyst increased the lactic acid yield to >90% for both glyceraldehyde and 1,3-dihydroxyacetone. In short, $VOSO_4$ plays a significant catalytic role in the isomerization of glucose, the retro-aldol fragmentation of fructose, and the conversion of the formed trioses into lactic acid under anaerobic conditions.

Table 2. Conversion of possible intermediates catalyzed by $VOSO_4$ under anaerobic conditions.[a]

Substrate[b]	Catalyst[c]	Conversion [%]	Yield[d] [%] LA	GA	1,3-DHA	HMF
glucose	–	26	0	0	0	11
fructose	–	56	6.9	3.1	1.6	25
glucose	VO^{2+}	96	56	3.3	2.5	13
fructose	VO^{2+}	96	58	2.9	3.1	13
glyceraldehyde	–	99	11	–	9.1	0
1,3-DHA	–	88	5.2	8.3	–	0
glyceraldehyde	VO^{2+}	>99	91	–	1.3	0
1,3-DHA	VO^{2+}	>99	92	0	–	0

[a] Reaction conditions: substrate, 6.0 mmol based on carbon; H_2O, 20 cm^3; N_2, 2 MPa; temperature, 433 K; reaction time, 1.5 h. [b] 1,3-DHA denotes 1,3-dihydroxyacetone. [c] None: without $VOSO_4$; VO^{2+}: $VOSO_4$, 0.05 mmol. [d] LA and GA denote lactic acid and glyceraldehyde, respectively.

Under an O_2 atmosphere, the conversion of glucose in the absence of $VOSO_4$ was low (2.3%) at 413 K (Table 3). Although the noncatalytic conversion of fructose was relatively high (55%), the reaction was unselective and a number of products, which included glyceraldehyde, 1,3-dihydroxyacetone, glyceric acid, pyruvaldehyde, pyruvic acid, acetic acid, formaldehyde, formic acid, and CO_2, were obtained. In the presence of $VOSO_4$, the conversions of glucose and fructose were both accelerated to >99%, and formic acid and CO_2 were produced as the major products (Table 3). The minor products were glyceric and glycolic acid. The presence of $VOSO_4$ also enhanced the oxidative conversion of the C_3 intermediates, that is, glyceraldehyde and 1,3-dihydroxyacetone, and increased the selectivities to formic acid and CO_2. These observations allow us to speculate that the formations of formic acid and CO_2 also proceed via glyceraldehyde and 1,3-dihydroxyacetone.

Table 3. Conversion of possible intermediates catalyzed by $VOSO_4$ under aerobic conditions.[a]

Substrate[b]	Catalyst[c]	Conversion [%]	Yield[d] [%] FA	GA1	GA2	CO_2
glucose	–	2.3	0.1	0	0.3	0.9
fructose	–	55	5.2	0	0	14
glucose	VO^{2+}	>99	45	0.5	1.3	43
fructose	VO^{2+}	>99	44	0.7	3.1	53
glyceraldehyde	–	88	11	0	0	14
1,3-DHA	–	88	14	0	0	24
glyceraldehyde	VO^{2+}	>99	48	1.3	8.4	27
1,3-DHA	VO^{2+}	>99	35	0	5.5	37

[a] Reaction conditions: substrate, 6.0 mmol based on carbon; H_2O, 20 cm^3; O_2, 2 MPa; temperature, 413 K; reaction time, 1.0 h. [b] 1,3-DHA denotes 1,3-dihydroxyacetone. [c] None: without $VOSO_4$; VO^{2+}: $VOSO_4$, 0.10 mmol. [d] FA, GA1 and GA2 denote formic acid, glyceric acid, and glycolic acid, respectively.

Oxidative cleavage of C–C bonds in model compounds under aerobic conditions

Our present work has demonstrated that the simple $VOSO_4$ can catalyze the cleavage of the C–C bonds in carbohydrate molecules to produce formic acid and CO_2 selectively under aerobic conditions. It is of high significance to understand the factors that control the cleavage of C–C bonds in carbohydrate molecules as such information is very limited. Thus, we have studied the oxidative conversion behaviors of 12 model compounds comprehensively using the present catalytic system.

First, we checked the stability of formic acid under our reaction conditions in the presence of $VOSO_4$. No conversion of formic acid was observed after 1 h reaction at 413 K (Table 4). This clarifies that formic acid is stable and does not undergo consecutive oxidation to CO_2 under our reaction conditions. The oxidation of HCHO could take place, which produced formic acid and CO_2 with selectivities of 54 and 46 %, respectively. However, the conversion of HCHO under our reaction conditions was low (4.6 %), which suggests that the oxidation of HCHO is not the main pathway for the formation of formic acid and CO_2.

Table 4. Conversion of model compounds catalyzed by $VOSO_4$ under aerobic conditions.[a]

Entry	Substrate	Conversion [%]	Yield[b] [%]				
			FA	GA	AA	FAld	CO_2
1	formic acid	0	–	–	–	–	–
2	formaldehyde	4.6	2.5	0	0	0	2.1
3	oxalic acid	70	2.1	0	0	0	65
4	glycolic acid	91	24	0	0.4	17	45
5	acetic acid	2.0	0.2	0	0	0	1.1
6	glyoxal	>99	80	1.6	0	0.5	12
7	glycolal dimer	>99	53	1.1	0	34	3.6
8	acetaldehyde	83	0	0	74	0	5.6
9	ethylene glycol	10	4.9	0.9	0	1.0	1.6
10	lactic acid	98	7.5	0	46	7.4	24
11	pyruvaldehyde	>99	30	0	63	2.3	2.0
12	3-hydroxy-2-butanone	>99	3.0	0	70	3.9	2.1

[a] Reaction conditions: substrate, 6.0 mmol based on carbon; $VOSO_4$, 0.010 mmol; water, 20 cm^3; temperature, 413 K; O_2 pressure, 2 MPa; time, 1.0 h. [b] FA, GA, AA, and FAld denote formic acid, glycolic acid, acetic acid, and formaldehyde, respectively.

Then, we studied the oxidative conversions of some C_2 model compounds. The conversion of oxalic acid proceeded easily under our reaction conditions to produce CO_2 with a selectivity of 93 % (Table 4, entry 3). This suggests that the C–C bond, which links two carboxylic groups, can be broken to form CO_2 [Scheme 2, Eq. (3)]. The conversion of glycolic acid, in which the α-carbon atom of the carboxylic group is joined to an OH group, provided formic acid, HCHO, and CO_2 (Table 4, entry 4). The selectivity to CO_2 was close to the sum of the selectivities to formic acid and HCHO. This reveals that the C–C bond in glycolic acid can be cleaved, and the carboxylic group is transformed to CO_2 [Scheme 2, Eq. (4)]. The remaining moiety after decarboxylation is expected to be oxidized into HCHO. As formic acid and HCHO have actually been formed and the consecutive oxidation of HCHO to formic acid is a slow reaction (Table 4, entry 2), we speculate that some of the glycolic acid may be first oxidized into glyoxylic acid [Scheme 2, Eq. (4), structure in the square brackets], which further undergoes oxidative decarboxylation to CO_2 and formic acid. The conversion of acetic acid was very low (2.0 %). Thus, the decarboxylation of acetic acid almost did not proceed in our system. Actually, the oxidative decarboxylation of mandelic acid, 2-bromo-2-phenylacetic acid, or α-amino acid, in which the α-carbon atom of the carboxylic group is linked by a OH, Br, or amino group, respectively, can occur by C–C cleavage catalyzed by V.[22]

Besides these C_2 carboxylic acids, we further investigated the oxidative conversions of some other model compounds. The conversion of glyoxal provided formic acid as the major product with 80 % selectivity (Table 4, entry 6). Thus, the C–C bond that links two aldehydic groups can be cleaved easily in the presence of $VOSO_4$ under O_2, and the aldehydic groups are oxidized into carboxylic groups [Scheme 2, Eq. (6)]. CO_2 was also formed with a selectivity of ~12 %. It has already been demonstrated that formic acid cannot be oxidized to CO_2 in our system [Scheme 2, Eq. (1)]. We propose that a small part of glyoxal may be first converted to glyoxylic acid [Scheme 2, Eq. (6), structure in the square brackets], which then undergoes decarboxylation to CO_2 and formic acid. The oxidative conversion of glycolal dimer was performed as glycolal itself is too reactive to be stable (Table 4, entry 7). As expected, the main products were formic acid and HCHO, which suggests that the C–C bond that links an aldehyde group and a carbon atom joined to a OH group could also be cleaved [Scheme 2, Eq. (7)]. However, although acetaldehyde could be converted in our system, acetic acid was the major product, and the cleavage of the C–C bond in acetaldehyde did not proceed. Thus, only a C–C bond with an O-containing group joined to each end can be cleaved. Notably, the conversion of ethylene glycol under our reaction conditions was low (10 %) (Table 4, entry 9), which indicates that the direct cleavage of C–C bond only joined to hydroxyl groups in polyols was difficult. Further analysis of the oxidative conversions of lactic acid, pyruvaldehyde, and 3-hydroxy-2-butanone [Scheme 2, Eqs. (10)–(12)] suggests again that the C–C bond that links a carboxylic (or aldehyde or ketone) group and a carbon atom joined to an O-containing group can be cleaved easily, and the group at each side is oxidized.

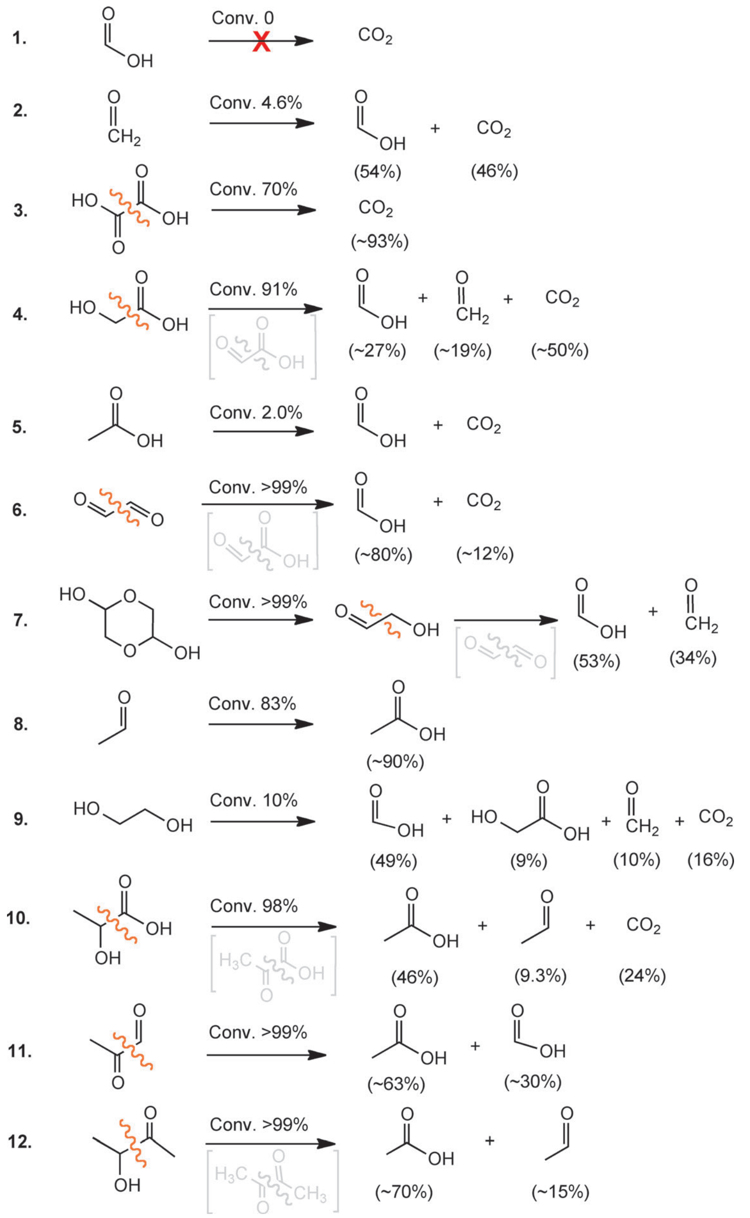
Based on these studies on model molecules, we have obtained the following insights into the oxidative cleavage of the C–C bond and the formation of products catalyzed by $VOSO_4$ under aerobic conditions.

(1) Formic acid is stable under our reaction conditions and does not undergo consecutive oxidation to CO_2. The oxidation of HCHO under our reaction conditions proceeds slowly.

(2) The decarboxylation of carboxylic acid intermediates causes the formation of CO_2. The presence of an O-containing group (–OH or =O) at the α-carbon atom of the carboxylic acid is required for the decarboxylation. The remaining moiety is oxidized accompanied by the formation of CO_2.

(3) The C–C bond that links an aldehyde (or ketone) group and a C atom joined to an O-containing group (–OH or =O) can be cleaved easily. The aldehydic (or ketonic) group is transformed into formic acid (or another carboxylic group), and the remaining moiety is oxidized.

(4) The direct cleavage of a C–C bond only joined to hydroxyl groups in polyols is difficult.



Scheme 2. Key reactions involved in the conversion of model C_2 and C_3 compounds catalyzed by $VOSO_4$ in the presence of O_2. The number in parenthesis represents product selectivity, and some of the reactant may be transformed into the structure in brackets before the C–C bond was cleaved. The numbering of the reaction corresponds with the entry number in Table 4.

Mechanism for the formation of formic acid and CO_2

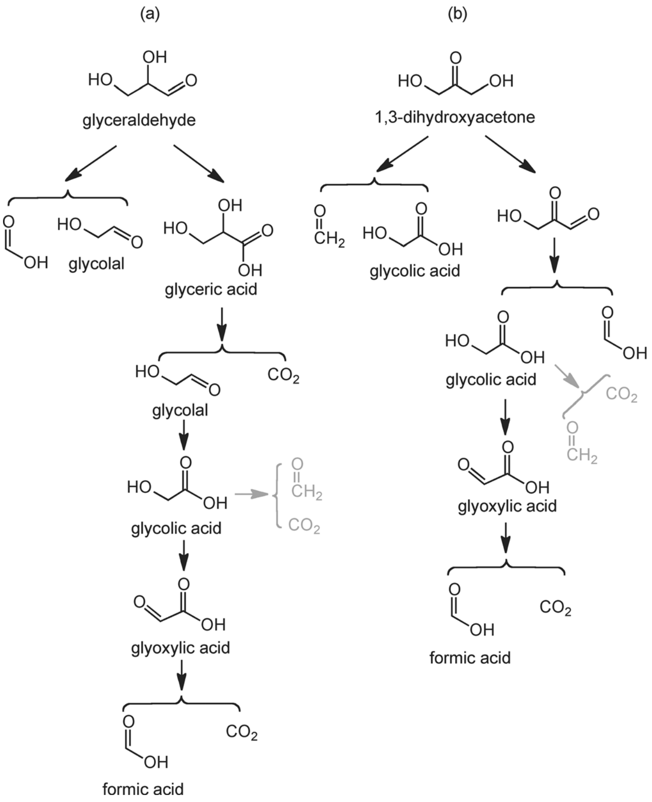
Based on the insights gained from the studies using model molecules, we propose a possible mechanism for the conversions of glyceraldehyde and 1,3-dihydroxyacetone, two major C_3 intermediates, into formic acid and CO_2 (Scheme 3). Glyceraldehyde may undergo oxidative C–C cleavage to formic acid and glycolal or may be oxidized to glyceric acid, which has been observed as an intermediate under an O_2 atmosphere (Scheme 3 a). The decarboxylation of glyceric acid produces CO_2 and glycolal. Glycolal is a highly reactive molecule, which probably undergoes fast oxidation to glycolic acid, a detected intermediate. Glycolic acid may be decarboxylated to CO_2 and HCHO or oxidized to glyoxylic acid, which is further converted to formic acid and CO_2. There are also two possible pathways for the conversion of 1,3-dihydroxyacetone (Scheme 3 b). One is the direct oxidative C–C cleavage to form HCHO and glycolic acid, and the other is the oxidation to hydroxypyruvaldehyde, which can further undergo oxidative C–C cleavage to form glycolic acid and formic acid. Finally, formic acid, CO_2, and HCHO are produced from glycolic acid as described above. During the conversion of glucose or fructose, formic acid and CO_2 were formed as the major products. This suggests that the pathway via glyoxylic acid is probably a major route.

Strategy to increase formic acid yield under aerobic conditions

The yield of formic acid is limited to ~50% because of the formation of CO_2 not only for $VOSO_4$ but also for the $H_5PV_2MoO_{10}O_{40}$ catalyst reported previously.[12–14] It would be highly attractive to find a strategy to suppress the formation of CO_2 and to increase the selectivity of formic acid. From the above mechanistic studies, we can expect that the suppression of the formation of carboxylic acid intermediates by protecting the aldehydic group may increase the selectivity to formic acid. It is known that the presence of an alcohol can transform reactive aldehydic groups into hemiacetal intermediates.[23] If we added methanol or ethanol into the reaction system, we succeeded in the suppression of the formation of CO_2 during the conversions of glucose and cellulose under aerobic conditions (Table 5). The yield of formic acid increased to 70–75%. HCHO was also formed with a yield of ~10%. We performed control reactions in the absence of glucose or cellulose. The conversion of methanol or ethanol catalyzed by $VOSO_4$ under an O_2 atmosphere was negligible under our reaction conditions. In other words, formic acid could not be formed from the direct oxidation of methanol or ethanol. To the best of our knowledge, this is the first report to describe the highly selective production of formic acid from cellulose or cellulose-derived carbohydrates without the significant formation of CO_2.

Characterization of V species

The electron spin resonance (ESR) spectrum of $VOSO_4$ in an aqueous solution that contained glucose showed eight distinct peaks with a g value of 1.97 (Figure 3 A). This is consistent with the hyperfine coupling of the unpaired electron ($3d^1$) in VO^{2+} with the ^{51}V nucleus ($I=7/2$).[24] After reaction under a N_2 atmosphere at 433 K for 1.5 h, the spectrum of the mixture did not change significantly. In other words, VO^{2+} remained during the reaction, and no other V species were detectable. We speculate that VO^{2+} is the active species for the conversion of glucose into lactic acid. However, we cannot completely rule out



Scheme 3. Possible mechanism for the formation of formic acid and CO_2 from glyceraldehyde (a) and 1,3-dihydroxyacetone (b) catalyzed by $VOSO_4$ under aerobic conditions.

Table 5. Effect of the addition of methanol or ethanol on the catalytic performance of $VOSO_4$ for the conversion of glucose and cellulose under aerobic conditions.[a]

Additive	Reactant	Conversion [%]	Yield[b] [%] FA	GA	AA	FAld	CO_2
none	glucose	100	41	0.2	0.3	0.6	51
CH_3OH	glucose	95	75	2.8	0	11	2.5
CH_3OH	–	–	0	0	0	tr.[c]	0
C_2H_5OH	glucose	91	73	0.5	0.5	9.7	2.1
C_2H_5OH	cellulose[d]	92	70	0.2	0	9.5	2.9
C_2H_5OH	–	–	0	0	0	0	0

[a] Reaction conditions: glucose, 1.0 or 0 mmol; $VOSO_4$, 0.10 mmol; H_2O, 15 cm^3; alcohol, 5 cm^3; O_2, 2 MPa; temperature, 413 K; reaction time, 3.0 h. [b] FA, GA, AA, and FAld denote formic acid, glycolic acid, acetic acid, and HCHO, respectively. [c] A trace amount of HCHO was formed from CH_3OH. [d] Ball-milled cellulose based on glucose units, 1.0 mmol; catalyst, 0.1 mmol; H_2O, 15 cm^3; alcohol, 5 cm^3; O_2, 2 MPa; temperature, 433 K; reaction time, 5.0 h.

the possibility that another highly active species with a low concentration may work as the true catalyst. After the reaction under an O_2 atmosphere at 413 K for 1 h, VO^{2+} was again observed in the ESR spectrum of the mixture (Figure 3 A, spectrum c). However, if the reaction was performed under O_2 for a longer time (12 h) and no reductive reactant and intermediates remained, the ESR signal for the VO^{2+} species disappeared, which indicates the oxidation of V^{IV} to V^{V} under oxidative circumstance as V^{V} (d^0) is ESR silent.

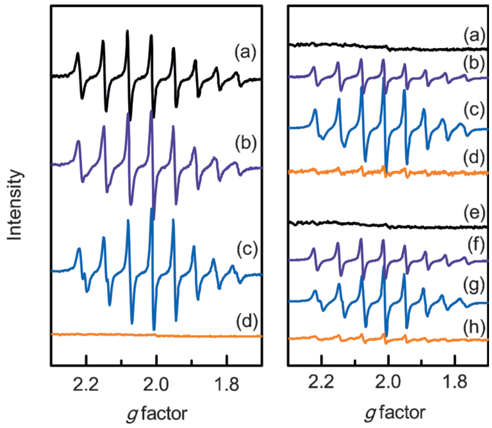


Figure 3. ESR spectra of V species in an aqueous solution that contains glucose (V/glucose = 1:10). $VOSO_4$ system (left): (a) before reaction, (b) after reaction under N_2 at 433 K for 1.5 h, (c) after reaction under O_2 at 413 K for 1 h, (d) after reaction under O_2 at 413 K for 12 h. V_2O_5 and NH_4VO_3 systems (right): (a) V_2O_5 before reaction, (b) V_2O_5 after reaction under N_2 at 433 K for 1.5 h, (c) V_2O_5 after reaction under O_2 at 413 K for 1 h, (d) V_2O_5 after reaction under O_2 at 413 K for 12 h, (e) NH_4VO_3 before reaction, (f) NH_4VO_3 after reaction under N_2 at 433 K for 1.5 h, (g) NH_4VO_3 after reaction under O_2 at 413 K for 1 h, (h) NH_4VO_3 after reaction under O_2 at 413 K for 12 h. See Figure 1 for other reaction conditions.

Although the yield of lactic acid was lower, V_2O_5 and NH_3VO_3 were also effective for the conversion of glucose into lactic acid under N_2 (Figure S1, Supporting Information). If these two compounds were used as the catalyst precursors, almost no ESR signals were observed before reaction (Figure 3 B, spectra a and e). This is in agreement with the fact that V^{V} in these compounds is ESR silent. After the reaction at 433 K for 1.5 h, the ESR signal attributed to VO^{2+} could be observed if either V_2O_5 or NH_4VO_3 was used as the catalyst precursor. This supports the idea that VO^{2+} is a key species for the conversion of glucose into lactic acid under a N_2 atmosphere. After the conversion of glucose in the presence of V_2O_5 or NH_4VO_3 under an O_2 atmosphere at 413 K for 1 h, we also observed the ESR signal ascribed to VO^{2+} species. The VO^{2+} signal became significantly weakened or disappeared after a longer reaction time under O_2. This change is similar to that observed for $VOSO_4$.

It is known that ^{51}V NMR spectroscopy can be used to study V^{V} ($3d^0$) species,[25] whereas V^{IV} ($3d^1$) species are NMR silent as a result of considerable line broadening caused by the presence of a paramagnetic center in the neighborhood of the nuclei.[26] Our ^{51}V NMR measurement for the $VOSO_4$ aqueous solution after oxidation under an O_2 atmosphere at 413 K for 0.5 h showed one distinct signal with a chemical shift at $\delta = -542.9$ ppm (Figure 4 A, spectrum a), which was attributable to VO_2^+ species in aqueous solution.[25] This indicates that the oxidation of VO^{2+} to VO_2^+ occurs under an O_2 atmosphere at 413 K. The addition of glucose into the VO_2^+ aqueous solution caused a decrease in the ^{51}V NMR signal even at 298 K for 24 h (Figure 4 A, spectrum b). The ^{51}V NMR signal of VO_2^+ cations disappeared after the addition of glucose followed by heating the mixture at 393 K for 10 min (Figure 4 A, spectrum c). Meanwhile, an ESR signal attributable to VO^{2+} appeared (Figure 4 B). These observations suggest that the VO_2^+ can be reduced

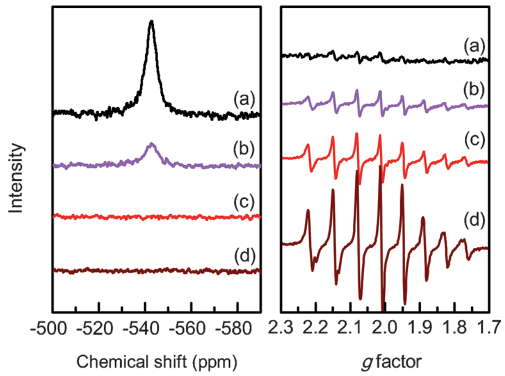


Figure 4. ^{51}V NMR (left) and ESR (right) spectra of V species in aqueous solution after (a) oxidation of $VOSO_4$ under O_2 at 413 K for 0.5 h,(b) addition of glucose to (a) (V/glucose = 1:10) and keeping the mixture at 298 K for 24 h, (c) addition of glucose to (a) (V/glucose = 1:10) and keeping the mixture under N_2 at 393 K for 10 min, and d) addition of glucose to (a) (V/glucose = 1:10) and keeping the mixture at 413 K for 1 h under O_2.

easily into VO^{2+} by glucose at our reaction temperatures. The redox conversion of VO_2^+/VO^{2+} has also been observed in other systems.[27–29] Therefore, we propose that the redox reaction between VO_2^+ and VO^{2+} is responsible for the formation of formic acid under an O_2 atmosphere.

Possible mechanism of the V catalyst

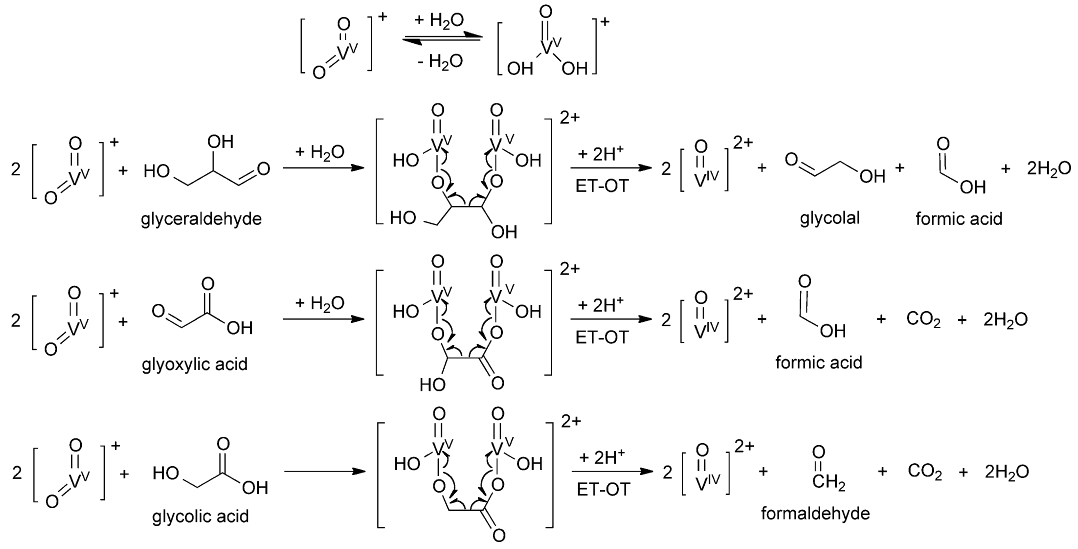
Our characterization results reveal that VO^{2+} is a key species during the conversion of glucose to lactic acid under a N_2 atmosphere. The comparative studies for the conversions of possible intermediates in the absence and presence of the $VOSO_4$ catalyst under a N_2 atmosphere suggest that the VO^{2+} species catalyzes a series of tandem steps, which include the isomerization of glucose to fructose, the retro-aldol fragmentation of fructose into trioses, and the conversion of trioses into lactic acid (Scheme 1). In particular, we found that in the absence of VO^{2+} HMF was formed as a major product instead of lactic acid during the conversion of either fructose or glucose (Table 2). This indicates that the dehydration of fructose to HMF is a major route without a catalyst. The presence of VO^{2+} not only increases the conversion of fructose or glucose but also shifts the major product to lactic acid. This suggests clearly that VO^{2+} plays a crucial role in the retro-aldol fragmentation of fructose.

The cleavage of the C–C bond (C_2–C_3) in glucose, which leads to the simultaneous formation of C_2 and C_4 compounds, did not proceed as a major pathway in our system, which might be because of several possibilities. The first reason may be the higher catalytic ability of our VO^{2+} catalyst in the isomerization reaction. In our system, VO^{2+} may function as a Lewis acid, which can catalyze the isomerization of glucose to fructose rapidly. Taarning et al. and Sels et al. found a similar cleavage of the C_3–C_4 bond in fructose during the conversion of glucose in the presence of Lewis acidic Sn^{IV}-based catalysts.[15,16] However, Zhang and co-workers proposed that a W-based catalyst mainly catalyzed the cleavage of the C_2–C_3 bond in glucose.[7] This is possibly because the W-based catalyst is efficient for C–C bond cleavage but not good at isomerization. Secondly, the higher reactivity of fructose than glucose in our catalytic system may also be responsible for the preferential occurrence of the cleavage of C–C bond in fructose but not in glucose (Tables 2 and 3). Furthermore, for the W-based catalytic system,[7] a significantly higher reaction temperature (518 K) was employed than that in our system (433 K). Possibly, the energy barrier for the C_2–C_3 bond cleavage in glucose is higher than that for the C_3–C_4 bond cleavage in fructose.

Our previous study uncovered that the C–C bond cleavage of fructose is triggered by proton transfer from C_4–OH to C=O.[19] The coordination of a Lewis acid such as Pb^{II} to the O atoms of fructose increases the positive charge on the H atom of C_4–OH.[19] This would enhance the acidity of the C_4–OH fragment and facilitate the proton transfer and the C–C bond cleavage of fructose to trioses. We speculate that VO^{2+} is also a better Lewis acid to be coordinated by the O atoms in fructose, which contributes to its outstanding ability in the retro-aldol fragmentation.

Our present work has further demonstrated that VO^{2+} can catalyze the formation of formic acid under an O_2 atmosphere. Without VO^{2+}, the conversion of glucose was quite low (2.3 %) under our aerobic reaction conditions (Table 3). Although the conversion of fructose reached 55 % under noncatalytic conditions (Table 3), the reaction did not result in the selective formation of specific products. The presence of VO^{2+} not only increased the conversion of either glucose or fructose to > 99 % but also led to the selective formation of formic acid together with CO_2. We have clarified that formic acid is very stable and does not undergo decomposition or consecutive oxidation under our reaction conditions (Table 4). The oxidative C–C cleavage of C_3 intermediates and subsequent C_2 intermediates results in the formation of formic acid along with CO_2. Our detailed studies using various model molecules have uncovered that the decarboxylation of carboxylic acid intermediates with an O-containing group at the α-carbon atom occurs easily in our catalytic system to produce CO_2 and an oxidized moiety (Scheme 2). The C–C bond that links an aldehyde group and a carbon atom joined to an O-containing group can also be cleaved easily to produce formic acid and an oxidized moiety.

An electron-transfer and oxygen-transfer (ET-OT) mechanism has been proposed for polyoxometalate $H_5PV_2Mo_{10}O_{40}$-catalyzed selective oxidations in the liquid phase.[30] In this mechanism, the two V^V centers in $H_5PV_2Mo_{10}O_{40}$ accept two electrons from the substrate to be reduced to V^{IV} and donate one O atom at the same time. For some heterogeneous V-catalyzed oxidation reactions, it is proposed that the redox conversion of V^V/V^{III} may participate in the catalytic cycle, in which one V^V center could accept two electrons from the substrate.[31] Our ESR and ^{51}V NMR spectra suggest that the redox conversion between VO_2^+ and VO^{2+} occurs during the reactions under aerobic conditions. This V^V/V^{IV} redox couple may participate in the oxidative cleavage of C–C bonds to form formic acid along with CO_2 as the major product. We speculate that such oxidative C–C cleavage may also follow the ET-OT mechanism suggested for the $H_5PV_2Mo_{10}O_{40}$ catalyst. If we consider that two electrons should be transferred at the same time, we propose



Scheme 4. Proposed ET-OT mechanism for the oxidative C–C cleavage for three possible reaction intermediates.

tentatively that two V^V species are required for the oxidative C–C cleavage in our case. Moreover, our reaction path studies suggest that the reaction proceeds via C_3 and C_2 intermediates such as glyceraldehyde, 1,3-dihydroxyacetone, glyceric acid, glyoxylic acid, and glycolic acid (Scheme 3). The possible reaction mechanism that we have in mind for the oxidative C–C cleavage of three typical intermediates is displayed in Scheme 4. If we take glyceraldehyde as an example, we speculate that one glyceraldehyde molecule may interact with two VO_2^+ species or its hydrolyzed form ($H_2VO_3^+$) in H_2O[27] to form an intermediate of binuclear V^V coordinated by glyceraldehyde. Each V^V center accepts one electron from the V–O bond connected to the C–O bond to be reduced to V^{IV}. This drives the formation of two C=O bonds and the simultaneous cleavage of the C–C bond to form glycolal and formic acid. The process involves the transfer of two electrons and one O atom. The reduced VO^{2+} can be reoxidized into VO_2^+ in the presence of O_2 at the temperature used in our reactions as indicated by ESR and ^{51}V NMR studies. Glyoxylic or glycolic acid would undergo similar oxidative C–C cleavage to form formic acid and CO_2 or HCHO and CO_2.

Conclusions

We have demonstrated that simple $VOSO_4$ is an efficient homogeneous catalyst for the transformations of cellulose and its monomer (glucose) into lactic or formic acid depending on the reaction atmosphere. We have discovered that the major product can be tuned by changing the atmosphere; a decrease in the fraction of O_2 in the atmosphere decreases the yield of formic acid and increases that of lactic acid. We have clarified that the reaction proceeds through the isomerization of glucose to fructose, which subsequently undergoes retro-aldol fragmentation to two trioses, that is, glyceraldehyde and 1,3-dihydroxyacetone. The isomerization of these trioses under N_2 leads to the formation of lactic acid. The VO^{2+} cation in water plays a key catalytic role in the formation of lactic acid by accelerating the isomerization of glucose, the retro-aldol fragmentation, and the further isomerization of the trioses. On the other hand, the oxidative C–C cleavage of the C_3 and subsequent C_2 intermediates under an O_2 atmosphere produces formic acid, a stable product under our reaction conditions, along with CO_2. The C–C bond that links an aldehyde group and a carbon atom joined to an O-containing group (–OH, =O) can be cleaved easily to form formic acid, whereas CO_2 is mainly produced by the decarboxylation of the carboxylic acid intermediates in which the α-carbon atom is joined to an O-containing group. We suppressed the formation of CO_2 and enhanced the yield of formic acid to 70–75 % by the addition of an alcohol such as methanol or ethanol. We propose that the redox conversion of VO_2^+/VO^{2+} plays a crucial role in the oxidative C–C cleavage reactions.

Experimental Section

Materials

The chemicals used primarily in this work were as follows: D-glucose (99.5 %, Alfa-Aesar), D-fructose (99.0 %, Alfa-Aesar), 1,3-dihydroxyacetone (98.0 %, J&K Chemical), glyceraldehyde (90.0 %, Sigma Aldrich), DL-lactic acid (85.0 %, TCI), formic acid (99.0 %, Sinopharm), and $VOSO_4 \cdot xH_2O$ (99 %, H_2O 24.4 wt %, Strem Chemicals). The other chemicals used as substrates (which include glyceric acid, pyruvaldehyde, pyruvic acid, glycolic acid, acetic acid, acetaldehyde, oxalic acid, glyoxal, glycolal dimer, glyoxylic acid, ethylene glycol, and glycerol) were purchased from Sinopharm, Alfa-Aesar, or TCI and their purity was higher than 98 %. The other metal salts used as catalyst candidates (which include VOC_2O_4, NH_4VO_3, V_2O_5, KCl, $CaCl_2$, $CrCl_3$, $MnSO_4$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $Al_2(SO_4)_3$, $ZrOCl_2$, $In(NO_3)_3$, $SnCl_2$, $Pb(NO_3)_2$, and $Bi(NO_3)_3$) were purchased from Sinopharm and their purity was higher than 99 %. $VOHPO_4 \cdot 0.5H_2O$ was prepared according to the reported procedure.[32] Microcrystalline cellulose was purchased from Alfa-Aesar. Ball-milled cellulose was obtained by ball-milling the microcrystalline cellulose at 60 rpm by using a SFM-1 Desk-top planetary ball miller (MTI Co.) for 48 h.

Catalytic reactions

The conversion of glucose, cellulose, possible reaction intermediates, model compounds, and other biomass was performed by using a batch-type Teflon-lined stainless-steel autoclave reactor. If we take the conversion of glucose as an example, the catalyst and glucose were added to the reactor, which was precharged with water (20 cm^3). After the purge with O_2 or N_2 and the introduction of O_2 or N_2 with a fixed pressure (typically, 2 MPa), the reactor was placed in an oil bath. When the system reached the reaction temperature, the reaction was started by stirring vigorously. The reaction was terminated quickly by cooling the reactor to RT in cold water after a fixed time. The liquid products were analyzed by HPLC (Shimazu LC-20A) with refractive index (RI) detection and a Shodex SUGARSH-1011 column (8 mm×300 mm) using a dilute H_2SO_4 aqueous solution as the mobile phase. The gas-phase products were analyzed by GC equipped with a thermal conductivity detector (TCD) and a Porapak Q column. We analyzed the amount of formaldehyde formed in both the liquid and gas phases by HPLC and GC, respectively. Formaldehyde was detected only in the liquid phase because of its high solubility in water. The total amount of organic carbon (TOC) in the reaction solution was determined by using a Multi N/C3100 TOC-TN analyzer (Analytik Jena, Germany). The conversion of the substrate and the selectivity to a specific product were defined as the molar percentage of the substrate converted and the molar percentage of the specific product in the substrate converted, respectively. Both the conversion and selectivity were calculated on a carbon basis. For example, the conversion of cellulose was calculated as the carbon molar percentage of the organic carbon products formed in the reaction solution detected as TOC and the carbon-containing products formed in the gas phase quantified by GC in the cellulose added to the system. The carbon balance was typically better than 90%, and the lost carbon appeared mainly as humins.

Characterization

ESR spectroscopic measurements were performed at RT by using a Bruker EMX-10/12 ESR spectrometer operated at X-band frequency. After the O_2 was removed, the sample solution was transferred into a capillary tube with an inner diameter of 0.8 mm. The height of the solution was typically 20 mm. The parameters for ESR measurements were as follows: microwave frequency, 9.8 GZ; microwave power, 20 mW; modulation frequency; 100 kHz; attenuator, 10 dB. ^{51}V NMR spectra were recorded by using a Bruker AVII 400 NMR spectrometer operated at 105.2 MHz at RT with 0.5 cm^3 sample solution in an NMR tube. The chemical shift of V was measured relative to an external reference, $VOCl_3$. The parameters for the NMR measurements were as follows: pulse width, 30°; spectral width, 100 kHz; acquisition time, 0.33 s; line broadening, 40 HZ; frequency domain size, 64 K data points.

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Keywords: biomass · carbohydrates · homogeneous catalysis · reaction mechanisms · vanadium

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