Catalytic oxidative conversion of cellulosic biomass to formic acid and acetic acid with exceptionally high yields

Jizhe Zhang [a], Miao Sun [b], Xin Liu [c], Yu Han [a],*

[a] Advanced Membranes and Porous Materials Center, Physical Science and Engineering division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia
[b] Cooperate Research and Development Center in King Abdullah University of Science and Technology, Saudi Aramco, Thuwal 23955-6900, Saudi Arabia
[c] School of Chemistry, Dalian University of Technology, Dalian 116024, PR China

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ABSTRACT

Direct conversion of raw biomass materials to fine chemicals is of great significance from both economic and ecological perspectives. In this paper, we report that a Keggin-type vanadium-substituted phosphomolybdic acid catalyst, namely $H_4PVMo_{11}O_{40}$, is capable of converting various biomass-derived substrates to formic acid and acetic acid with high selectivity in a water medium and oxygen atmosphere. Under optimized reaction conditions, $H_4PVMo_{11}O_{40}$ gave an exceptionally high yield of formic acid (67.8%) from cellulose, far exceeding the values achieved in previous catalytic systems. Our study demonstrates that heteropoly acids are generally effective catalysts for biomass conversion due to their strong acidities, whereas the composition of metal addenda atoms in the catalysts has crucial influence on the reaction pathway and the product selectivity.

1. Introduction

The use of biomass to produce biofuels, such as bio-diesel, ethanol, and hydrogen (H_2), which are sustainable alternatives to fossil fuels with reduced carbon dioxide (CO_2) emission, has been extensively explored. Of equal importance is the conversion of biomass to various fine chemicals, because currently their production is also based on the depleting fossil raw materials. However, biomass conversion is usually a very complex process with many parallel reactions involved, resulting in low yields to the designated products. Consequently, very few processes for directly converting biomass raw materials into value-added chemicals have been practically successful.

Formic acid (FA) and acetic acid (AA) are both important commodity chemicals in high demand in the chemical, pharmaceutical and agricultural industries. Particularly, as new processes were developed to store/generate H_2 using FA as a carrier [1–13], FA has attracted substantial research interest in recent years in the context of the future hydrogen economy. The current production of FA and AA is mainly based on fossil materials through carbonylation of methanol [14,15]. Developing alternative routes to directly produce them from biomass is desirable from both economic and ecological perspectives. To avoid conflict with food supply as well as to be cost-effective, widely available crude cellulosic biomass materials, such as bagasse and hay, are preferred substrates for the conversion. Non-catalytic conversions of biomass into FA and AA by hydrothermal treatment in subcritical water with H_2O_2 as an oxidant have been reported, but high yields could only be achieved when water soluble substrates, e.g. glucose, was used [16–18]. More efficient processes that allow the conversion of crude biomass to FA and AA under milder conditions remain to be developed. FA is often detected as a byproduct with a low yield in various catalytic biomass conversion systems, which aim to produce other compounds, such as levulinic acid [19–21], sorbital [22,23], ethylene glycol [24], 5-hydroxymethylfurfuran (5-HMF) [25], lactic acid [26], glycolic acid [27], and gluconic acid [28]. For example, the rehydration of 5-HMF, which is a dehydrated intermediate from hexoses, generates levulinic acid along with FA. Recently, selective conversion of cellulose and biomass-derived carbohydrates to FA by catalytic oxidation has been investigated by different research groups. Wasserscheid et al. reported that a Keggin-type heteropoly acid $H_5PV_2Mo_{10}O_{40}$ catalyst can effectively convert water soluble mono- and disaccharides to FA with yields of ~50% [29]. They later optimized the reactions by use of additives, reaching 53% and 22% yields of FA from water-insoluble xylan and cellulose respectively [10]. Fu et al. independently reported the use of $H_5PV_2Mo_{10}O_{40}$ as

* Corresponding author. +966544700032.
  E-mail address: yu.han@kaust.edu.sa (Y. Han).

a selective oxidation catalyst for biomass conversion. In their system, the highest yield of FA was 35% when cellulose was used as the substrate [13]. By comparison, catalytic conversion of biomass to AA has rarely been reported because of the low selectivity. Although the production of AA from biomass can in principle be realized through selective oxidation of bio-ethanol, a one-step direct conversion process with a fair yield would be more attractive.

We recently reported the direct conversion of cellulose to glycolic acid with remarkably high yields ($\sim$50%) using molecular oxygen in a water medium, in which a phosphomolybdic acid ($H_3PMo_{12}O_{40}$) acts as a bi-functional catalyst to catalyze both the hydrolysis of cellulose and the subsequent oxidation reactions [27]. We have demonstrated that many heteropoly acids (HPAs) can effectively convert cellulose under oxidative conditions due to their strong Brönsted acidity, while the reaction pathway is largely determined by the type of addenda atom in the HPA catalyst. Here, we report the selective oxidation of cellulose to FA and AA catalyzed by vanadium-substituted phosphomolybdic acids ($H_{3+n}PV_nMo_{12-n}O_{40}$) under mild reaction conditions in water using molecular oxygen (O_2) as an oxidant. Our work is different from the above-mentioned studies [10,13] of biomass conversion by $H_5PV_2Mo_{10}O_{40}$ in three respects: (i) we found that the concentration of vanadium (V) has an important influence on the selectivity, i.e., $H_4PVMo_{11}O_{40}$ could yield much more FA than $H_5PV_2Mo_{10}O_{40}$; (ii) under optimized reaction conditions, a FA yield of 67.8% was obtained from cellulose, which is almost double the results achieved in previous studies; (iii) in addition to FA, a remarkable quantity of AA was produced simultaneously, giving a total yield as high as 81.2% (FA: 66.0% and AA: 15.2%). These results demonstrate that the incorporation of vanadium in a phosphomolybdic acid catalyst can significantly change the reaction pathway by its special ability to cleave C–C bonds of vicinal diols to carboxylic acids [30,31]. More importantly, $H_4PVMo_{11}O_{40}$ is also capable of converting crude cellulosic materials, such as bagasse and hay, to FA and AA with remarkable yields.

2. Experimental

The oxidative conversions of cellulose by various HPA catalysts were carried out in a 75 mL Teflon-lined stainless autoclave at 453 K for 3 h under 0.4–2 MPa O_2 with a stirring rate of 600 rpm. Typically, the reaction mixture comprised 20 mL of H_2O, 0.2 g of α-cellulose powder (containing 1.23 mmol glucose units), and 0.1 mmol of HPA catalyst. In the reactions with other substrates, a fixed amount of reactant (200 mg) and the typical reaction conditions were used unless otherwise specified. In the reactions where the solid substrates were not completely converted, the residual substrates were separated from the solution after the reactions and the supernatants were used for analysis. After each reaction, the liquid phase was analysed by HPLC (Agilent, 1260 Infinity Quaternary System) equipped with refractive index (RI) and ultraviolet (UV) detectors, and a Waters Shodex SUGAR SH-1011 column (8 × 300 mm) with 0.05 M H_2SO_4 aqueous solution as the mobile phase at 313 K. The gas phase was analysed by a GC with a FID detector. Quantification of products was carried out for HPLC and GC analysis using an external standard method. Calibration was done by using a series of standards covering the concentration range of interest. The peak for each component was integrated and the peak area was plotted against concentration to give a calibration curve. The concentrations of the major products were determined from the calibration curves. Yields of the products were calculated based on the contents of carbon in the substrates, which were determined via C elemental analysis.
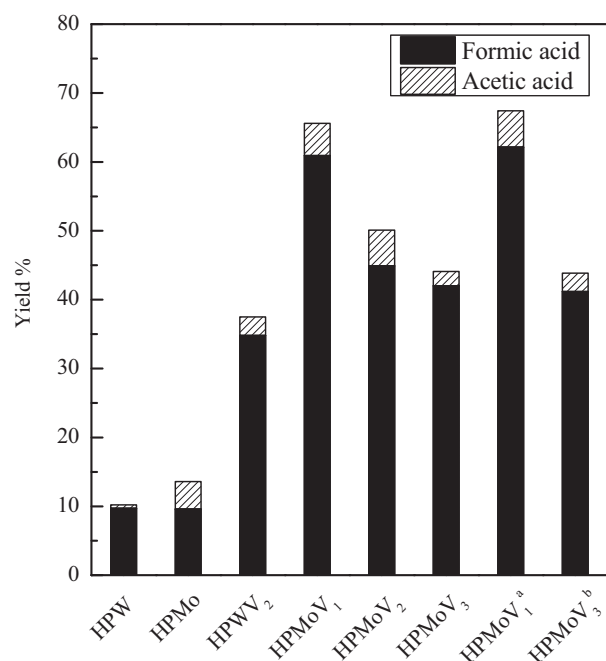

Fig. 1. Yields of FA and AA produced from cellulose using different HPA catalysts: $H_3PW_{12}O_{40}$ (HPW), $H_3PMo_{12}O_{40}$ (HPMo), $H_5PV_2W_{12}O_{40}$ (HPWV$_2$), $H_4PVMo_{11}O_{40}$ (HPMoV$_1$), $H_5PV_2Mo_{10}O_{40}$ (HPMoV$_2$), and $H_6PV_3Mo_9O_{40}$ (HPMoV$_3$). Reaction conditions: 0.2 g of α-Cellulose powder, 0.1 mmol of catalyst, at 453 K for 3 h, under 2 MPa O_2. The catalyst amount was varied for HPMoV$_1$ and HPMoV$_3$ (the last two columns): [a] 0.2 mmol of HPMoV$_1$; [b] 0.066 mmol of HPMoV$_3$.

3. Results and discussions

Previous studies have demonstrated that V atoms in the HPA catalyst account for the selective oxidative cleavage of C–C bonds in the conversion of carbohydrates to FA. However, it remains unknown how the V concentration in the catalyst influence the reaction selectivity, because only one catalyst (i.e. $H_5PV_2Mo_{10}O_{40}$) has thus far been investigated. To provide more insight into this, we prepared three phosphovanadomolybdic acids with different contents of vanadium, namely $H_4PVMo_{11}O_{40}$, $H_5PV_2Mo_{10}O_{40}$ and $H_6PMo_9V_3O_{40}$, and evaluated their catalytic performance for the conversion of cellulose. For comparison purpose, we also prepared another three kegging-type HPA catalysts including two V-free HPAs ($H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$) and one phosphovanadotungstic acid ($H_5PV_2W_{12}O_{40}$). Although relatively low temperatures ($\sim$373 K) were used to convert soluble carbohydrates [10,13], a higher reaction temperature (>423 K) is essential to an effective conversion of water-insoluble biomass (e.g. cellulose) with HPAs [13,27,32]. Initially, we tested the six HPA catalysts for the conversion of cellulose in water at 453 K under an oxygen atmosphere of 2 MPa. In each reaction, 0.2 g of α-cellulose powder containing 1.23 mmol glucose units was used as the substrate and the catalyst load was 0.1 mmol. The yields of FA and AA for each catalyst are shown in Fig. 1. As cellulose was fully converted by these selected HPA catalysts, the yields of FA and AA are equal to their selectivities. Our recent studies indicated that under similar aqueous phase aerobic oxidation conditions, $H_3PW_{12}O_{40}$ can efficiently catalyze the hydrolysis of cellulose to glucose but is nearly inactive for the catalytic oxidation of monosaccharide [32,33], while $H_3PMo_{12}O_{40}$ selectively converts cellulose to glycolic acid with FA as a secondary product [27]. These results were well reproduced in this study, i.e., $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ gave low yields (<10%) for FA and AA (Fig. 1). In contrast, the four V-substituted HPAs all showed remarkable yields of FA (>35%) along with small amounts of AA ($\sim$5%), indicating the important role of V on the selectivity

in oxidative conversion of cellulose [28,31]. We noted that in these reactions, FA and AA were the major products in the liquid phase and CO_2 was the sole product detected in the gas phase. Among the four V-substituted HPAs, $HPWV_2$ gave the lowest FA yield (35%) and the highest CO_2 yield (62%) (Fig. 1), possibly because its stronger acidity promoted the over-oxidation of the produced FA to CO_2. Further investigation was therefore focused on phosphovanado-molybdic catalysts.

It was interesting to observe that the selectivity of FA increased with decreasing vanadium contents in the phospho-vanadomolybdic catalysts. The FA yields given by the three catalysts follow the order: $H_4PVMo_{11}O_{40}$ (60.9%) > $H_5PV_2Mo_{10}O_{40}$ (44.9%) > $H_6PV_3Mo_9O_{40}$ (42.0%). One may wonder whether these results are associated with the different intrinsic activities of the three catalysts or simply due to the different absolute amounts of V in the three reaction systems. To address this question, we adjusted the catalyst loadings to ensure that the absolute amounts of V were identical in the three reaction systems. Specifically, we carried out two more reactions using 0.2 mmol of $H_4PVMo_{11}O_{40}$ and 0.066 mmol of $H_6PV_3Mo_9O_{40}$, respectively, with other conditions unchanged, to compare with the case using 0.1 mmol of $H_5PV_2Mo_{10}O_{40}$ (Fig. 1). The results showed that with the absolute V amounts normalized (0.2 mmol), $H_4PVMo_{11}O_{40}$ was still superior to the other two catalysts in terms of FA selectivity. This confirms that mono-V-substituted phosphomolybdic acid intrinsically has a higher selectivity towards FA and a lower tendency to produce CO_2 than do its multi-substituted counterparts. We propose that in comparison with the single V atom in $H_4PVMo_{11}O_{40}$, the V atoms in $H_{3+n}PV_nMo_{12-n}O_{40}$ ($n = 2, 3$) molecules may have a synergetic effect to cause over-oxidation, as implied by their higher yields of CO_2. Notably, the FA yield from cellulose that we achieved with $H_5PV_2Mo_{10}O_{40}$ is comparable with those reported in the literature using the same catalyst and similar reaction conditions [13], whereas our new finding is that $H_4PVMo_{11}O_{40}$ performs even better for this reaction than does $H_5PV_2Mo_{10}O_{40}$. Besides, we detected the presence of AA as a minor product in our experiments, which was not observed in previous similar reaction systems.

To optimize the reaction conditions for the $H_4PVMo_{11}O_{40}$ catalyst, we first investigated the effect of reaction temperature on the conversion of cellulose, and the yields of FA and AA. Experiments were carried out at 373 K, 393 K, 413 K, 433 K, 453 K and 473 K, under 2 MPa O_2 for 3 h. As shown in Fig. 2, cellulose could be completely converted only when the reaction temperature was higher than 433 K. This is consistent with earlier studies [27,32], which demonstrated that complete conversion of highly stable and water insoluble cellulose required a high reaction temperature combined with a strong acid to facilitate its hydrolysis and fragmentation.
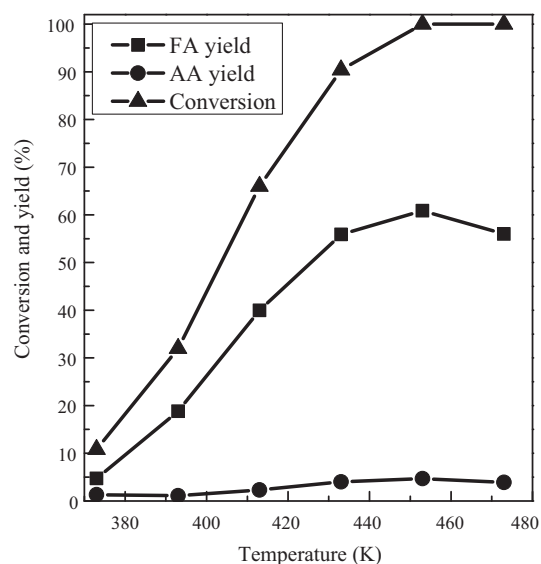

Fig. 2. The effect of reaction temperature on the cellulose conversion and the yields of FA and AA. The reaction were carried out with 0.2 g of α-Cellulose powder as the substrate and 0.1 mmol of $H_4PVMo_{11}O_{40}$ catalyst under 2 MPa O_2 for 3 h.

Both the yields of FA and AA increased with the reaction temperature and the maximum values (60.9% for FA and 4.7% for AA) were obtained at 453 K. The FA yield starts to decrease at temperatures above 453 K, which is therefore considered as the optimal temperature for the conversion of cellulose to FA and AA.

When glucose was used as substrate to produce FA with molecular oxygen at low temperatures (<373 K), higher oxygen pressures (>2 MPa) were beneficial to the reaction that significantly enhanced the glucose conversion rate [13]. However, such high oxygen pressures are not necessary in our system because of the high reaction temperature. As revealed in Table 1, cellulose could be completely converted in 3 h at 453 K under moderate oxygen pressures (>0.5 MPa). More significantly, we found that with decreasing the oxygen pressure, the FA yield gradually increased from 60.9% at 2 MPa to 67.8% at 0.6 MPa. The yield of AA followed the same trend and the maximum (15.2%) was obtained at oxygen pressure of 0.5 MPa, leading to a total yield of FA and AA as high as 81.2% (Table 1). To the best of our knowledge, direct conversion of cellulose with such high efficiency and selectivity has rarely been reported before. Further decreasing oxygen pressure resulted in incomplete conversion of cellulose and consequently decreased the yields of FA and AA. The optimal oxygen pressure is therefore
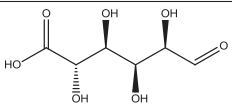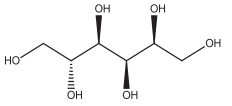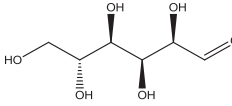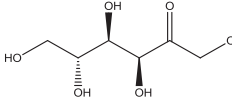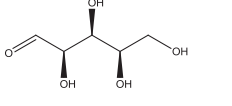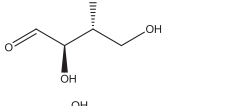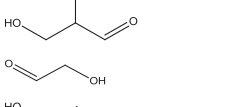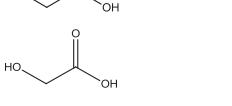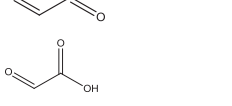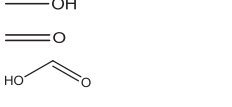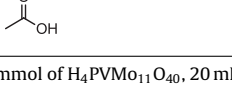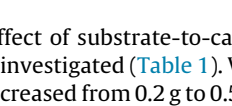
Table 1
Oxidative conversions of various cellulosic biomass substrates using the $H_4PVMo_{11}O_{40}$ catalyst under different O_2 pressures[a]

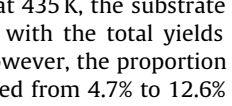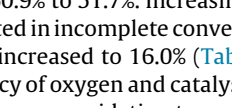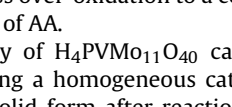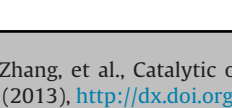| Substrate	O_2 pressure (MPa)	Conversion (%)	Total yield (%)	FA yield (%)	AA yield (%)
Cellulose	2.0	100	65.6	60.9	4.7
Cellulose	1.5	100	69.6	64.8	4.8
Cellulose	1.0	100	73.2	65.4	7.8
Cellulose	0.6	100	80.1	67.8	12.3
Cellulose	0.5	100	81.2	66.0	15.2
Cellulose	0.4	Incomplete	75.9	61.1	14.8
Cellulose (0.5 g)	2.0	100	64.3	51.7	12.6
Cellulose (1.0 g)	2.0	Incomplete	50.8	34.8	16.0
Bagasse	2	100	74.3	57.0	17.3
Bagasse	0.6	100	81.3	61.0	20.3
Bagasse	0.5	Incomplete	77.5	56.7	20.8
Hay	2	100	68.8	54.5	14.3
Hay	0.6	Incomplete	69.0	52.3	16.7
Hay	0.5	Incomplete	64.1	50.4	13.7

[a] Reaction conditions: 0.2 g of substrate (except the two reactions with specific substrate amounts indicated), 0.1 mmol of $H_4PVMo_{11}O_{40}$, 20 mL of H_2O, 180 °C, 3 h. Yields are calculated based on the contents of carbon in the substrates, which were determined via C elemental analysis. For the reactions with incomplete conversions, the exact conversion values were not measured.

Table 2
Oxidative conversions of various substrates catalyzed by $H_4PVMo_{11}O_{40}$ [a].

Substrate	Chemical formula	Conversion (%)	Formic acid yield (%)
Glucuronic acid [b]		100	34.6
Sorbitol		100	43.7
Glucose		100	54.5
Fructose		100	54.6
Xylose		100	33.1
Erythrose		100	38.0
Glyceraldehyde [b]		100	52.0
Glycolaldehyde [b]		100	70.8
Ethylene glycol		88.1	63.3
Glycolic acid [b]		100	73.9
Glyoxal [b]		100	84.3
Glyoxylic acid [b]		100	39.1
Methanol		5.8	0.3
Formaldehyde		43.9	36.8
Formic acid		15.8	-
Acetic acid		5.7	-

[a] Reaction conditions: 0.2 g of substrate, 0.1 mmol of $H_4PVMo_{11}O_{40}$, 20 mL of H_2O, 2 MPa O_2, 180 °C, 3 h.
[b] The reactions were carried out at 150 °C.

determined to be 0.5–0.6 MPa. The effect of substrate-to-catalyst ratio on the FA and AA yields was also investigated (Table 1). When the mass of α-cellulose powder was increased from 0.2 g to 0.5 g for the conversion under 2 MPa oxygen at 435 K, the substrate could still be completely converted in 3 h with the total yields of FA and AA nearly unchanged (∼65%). However, the proportion of AA in the product was markedly increased from 4.7% to 12.6% along with a decrease of the FA yield from 60.9% to 51.7%. Increasing the mass of cellulose substrate to 1 g resulted in incomplete conversion, whereas the yield of AA was further increased to 16.0% (Table 1). These results suggest that the deficiency of oxygen and catalyst relative to the substrate helps to suppress over-oxidation to a certain extent, and thus favor the production of AA.

We also evaluated the reusability of $H_4PVMo_{11}O_{40}$ catalyst for cellulose conversion. Despite being a homogeneous catalyst, $H_4PVMo_{11}O_{40}$ can be recovered in solid form after reactions by

distilling the products and solvent out, which is a noteworthy advantage over common volatile liquid acids. After each reaction cycle, the water and products were removed by rotary evaporation at 363 K. The remaining solid material was re-dissolved in water. The resulting solution contains only $H_4PVMo_{11}O_{40}$ without residual FA or AA, as determined by HPLC, which was then added with new cellulose substrate for the next reaction run. As indicated in Fig. 3, the $H_4PVMo_{11}O_{40}$ catalyst exhibited constant catalytic performance during four successive reaction runs with steady yields of ∼65% for FA and ∼15% for AA.

The exact mechanism of selective oxidation of cellulose to FA and AA over vanadium-substituted phosphomolybdic acids remains unclear. We propose that cellulose was firstly hydrolyzed in the strongly acidic solution to produce glucose that was subsequently converted to FA and AA by selective oxidation. An electron transfer and oxygen transfer (ET-OT) reaction mechanism was
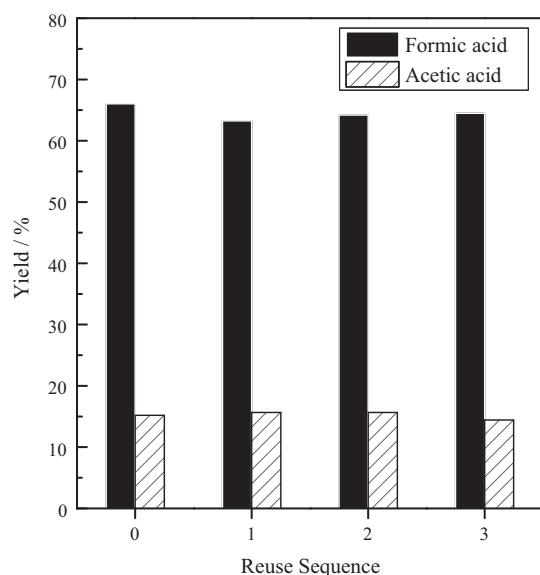
Fig. 3. Yields of FA and AA in sequential cellulose conversion reactions using the $H_4PVMo_{11}O_{40}$ catalyst. Reaction conditions: 0.2 g of α-Cellulose powder, 0.1 mmol of catalyst, at 453 K for 3 h, under 0.5 MPa O_2. After each reaction cycle, the water and products were removed by rotary evaporation at 363 K. The remaining solid material was re-dissolved in water, and then added with new cellulose substrate for the next reaction run.

widely accepted for explaining the oxidative C–C bond cleavage of primary alcohol and vicinal diols catalyzed by $H_5PV_2W_{12}O_{40}$. However, in previous studies that used $H_5PV_2W_{12}O_{40}$ to convert glucose to FA, it was suggested that the intermediates of this conversion be aldehyde group-containing compounds [13] and that there are more than one mechanisms involved in their oxidative degradation [29]. To investigate the application scope of $H_4PVMo_{11}O_{40}$ as well as to attempt to understand the conversion pathway, we tested different substrates including sugars, polyols, and possible reaction intermediates for the conversion under the above-described typical reaction conditions (see Table 2). From the data shown in Table 2, we can see the followings. First, when FA was used as the substrate, no obvious decomposition of FA was observed after 3 h and accordingly little CO_2 was detected in the gas phase. This result reveals that FA is stable in this catalytic reaction system, and thus that the CO_2 produced in cellulose oxidation is not from the degradation of FA. This conclusion is supported by the observation that varying the catalyst amount for cellulose conversion did not much change the selectivity of FA and CO_2 (Fig. 1). Second, when methanol and formaldehyde were used as the substrates, slower conversion with lower FA yields were observed, as compared with the cases of cellulose, glucose and many other substrates (Table 2). This result excludes methanol or formaldehyde to be the intermediates during the production of FA in this system. Third, all the tested substrates containing either aldehyde groups or a pinacol structure could be completely converted; the FA yields were substrated dependent, ranging from 33.1% for xylose to 84.3% for glyoxal. The only exception is ethylene glycol, which gave a slower conversion (88.1% in 3 h) but also a rather high FA yield of 63.3%. These observations are essentially consistent with the conclusions drawn in previous studies on the oxidative conversion of glucose to FA using $H_5PV_2W_{12}O_{40}$ at lower temperatures, whereas the FA yields achieved in our system are much higher.

$H_4PVMo_{11}O_{40}$ can also catalyze the conversion of crude cellulosic biomass materials. For example, we used dried but otherwise untreated bagasse and hay as the substrates for the reaction and found that they were both converted to FA and AA with high selectivity (see Table 1). Under optimized reaction conditions, remarkable FA yield 61.0% and AA yield of 20.3% were obtained from bagasse; for hay, the highest yields of FA and AA were 52.3% and 16.7%, respectively (Table 1). These results suggest the general applicability of $H_4PVMo_{11}O_{40}$ for directly converting various types of raw cellulosic biomass to FA and AA and the great potential of this oxidative conversion process for commercial applications.

4. Conclusions

Following our earlier work on the conversion of cellulosic biomass to chemicals by HPA catalysts, we further demonstrated in this study that the type of metal addenda atom in the HPA catalyst plays an essential role in determining the reaction pathway and thus the product selectivity. A series of vanadium-substituted phosphomolybdic acids were tested for converting cellulose with molecular oxygen in water media, and they all exhibited specific selectivity to FA and AA. Among all the tested catalysts, $H_4PVMo_{11}O_{40}$ has proved to be the most efficient for this reaction, giving the highest FA yield of 67.8% and total yield of 81.2% under optimized conditions. This catalyst is also capable of converting raw cellulosic materials, such as bagasse and hay, to FA and AA with remarkable yields of ∼60% and ∼20%, respectively. The high conversion efficiency along with the simple product compositions allows easy separation and recovery of the catalyst. Our findings thus provide a new cost-effective and eco-benign route to biomass conversion to important commodity chemicals.

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