



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



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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.

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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], sorbitol [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

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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 (~50%) using molecular oxygen in a water medium, in which a phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) 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 Brønsted 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 ($\text{H}_{3+n}\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}$) 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 $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ in three respects: (i) we found that the concentration of vanadium (V) has an important influence on the selectivity, i.e., $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ could yield much more FA than $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$; (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, $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ 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.

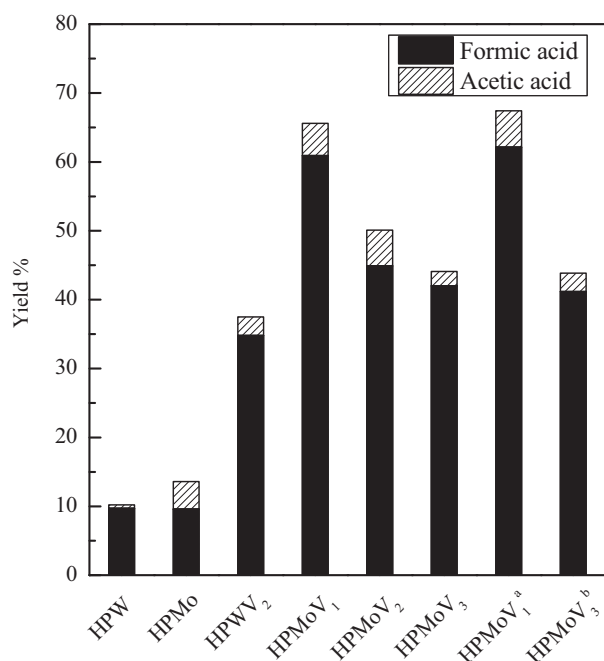


Fig. 1. Yields of FA and AA produced from cellulose using different HPA catalysts: $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPMo), $\text{H}_5\text{PV}_2\text{W}_{12}\text{O}_{40}$ (HPWV₂), $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ (HPMoV₁), $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (HPMoV₂), and $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ (HPMoV₃). 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 HPMoV₁ and HPMoV₃ (the last two columns): ^a 0.2 mmol of HPMoV₁; ^b 0.066 mmol of HPMoV₃.

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. $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$) has thus far been investigated. To provide more insight into this, we prepared three phosphovanadomolybdic acids with different contents of vanadium, namely $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ and $\text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40}$, 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 ($\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$) and one phosphovanadotungstic acid ($\text{H}_5\text{PV}_2\text{W}_{12}\text{O}_{40}$). Although relatively low temperatures (~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, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ can efficiently catalyze the hydrolysis of cellulose to glucose but is nearly inactive for the catalytic oxidation of monosaccharide [32,33], while $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ selectively converts cellulose to glycolic acid with FA as a secondary product [27]. These results were well reproduced in this study, i.e., $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ 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 (~5%), indicating the important role of V on the selectivity

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