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Direct Conversion of Cellulose to Glycolic Acid with a Phosphomolybdic Acid Catalyst in a Water Medium

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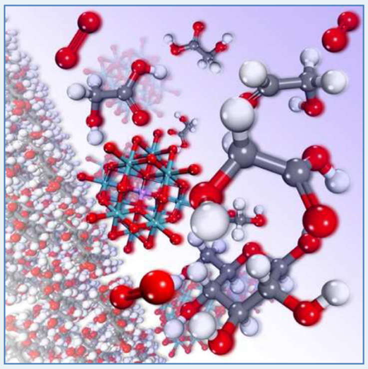
Supporting Information

ABSTRACT: Direct conversion of cellulose to fine chemicals has rarely been achieved. We describe here an eco-benign route for directly converting various cellulose-based biomasses to glycolic acid in a water medium and oxygen atmosphere in which heteromolybdic acids act as multifunctional catalysts to catalyze the hydrolysis of cellulose, the fragmentation of monosaccharides, and the selective oxidation of fragmentation products. With commercial α-cellulose powder as the substrate, the yield of glycolic acid reaches 49.3%. This catalytic system is also effective with raw cellulosic biomass, such as bagasse or hay, as the starting materials, giving rise to remarkable glycolic acid yields of ~30%. Our heteropoly acid-based catalyst can be recovered in solid form after reaction by distilling out the products and solvent for reuse, and it exhibits consistently high performance in multiple reaction runs.



KEYWORDS: *biomass conversion, heteropoly acid, selective oxidation*

Cellulosic biomass is a natural resource that is both abundant and sustainable. Its efficient utilization has long been the focus of research and development efforts, with the aim to compete with and replace petroleum-based products. In addition to the production of biofuels (e.g., ethanol) from cellulosic biomass, which has been to some degree successful,[1−5] its conversion to high-value-added chemicals is equally important.[5−9] In comparison with conventional fermentation processes, the use of catalysis would provide a greener and more cost-efficient route for producing chemicals of commercial interest from biomass.[4] There have been numerous studies on catalytic conversions of various carbohydrates to useful compounds or important chemical intermediates. For example, sorbitol and gluconic acid were produced from glucose or cellobiose by catalytic hydrogenation and oxidation, respectively;[10−13] 5-hydroxymethylfurfural (5-HMF) and levulinic acid were prepared by catalytic dehydration of different carbohydrates;[14−17] and high yields of methyl lactate were derived from sucrose, glucose, and fructose using a Sn-doped Lewis acidic zeolite catalyst.[18] Catalytic isomerization between fructose and glucose has also been studied.[19,20] Despite the great success achieved with small-molecule biomass derivatives (e.g., mono- and disaccharides) in these studies, the direct catalytic conversion of cellulose remains a challenge, mainly because cellulose is highly stable and insoluble to most solvents. To overcome this problem, ionic liquids are usually used as the solvent for their special abilities to dissolve cellulose,[21−23] or alternatively, reactions are run under extreme conditions.[5,24−26]

We recently reported the development of a novel composite catalyst, cesium hydrogen phosphotungstate-supported Au (Au/$Cs_2HPW_{12}O_{40}$). It was found to be highly selective and able to convert cellobiose, a disaccharide, to gluconic acid with 95% yield. The phosphotungstate and Au nanoparticles, respectively, provided solid acid sites for hydrolysis and redox sites for selective oxidation.[11] Advancing a step, we here report the direct conversion of primitive biomass, cellulose, via successive hydrolysis and selective oxidation in a noble metal-free system. Instead of using expensive ionic liquid to dissolve the reactant, we use water as the reaction medium and heteropoly acids (HPA) as the catalyst. Unlike conventional solid acid catalysts, HPAs are soluble in water and therefore more efficient for catalyzing the reactions of cellulose; on the other hand, they can be recovered in solid form after reaction by distilling out the products and solvent, which is a significant advantage over common volatile liquid acids. Indeed, HPAs have been widely used as catalysts or catalyst supports for biomass conversion.[17,27−43] Most of these previous studies utilized the strong acidity of HPAs for hydrolysis[27−31] or involved the use of noble metals to convert biomass through hydrogenation[32−34] and oxidation.[35−43] Herein, we demonstrate that in addition to the strong acidity that facilitates the hydrolysis and fragmentation of cellulose, certain HPAs have moderate oxygen activation abilities that allow them to oxidize

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carbohydrates. The best result is achieved by $H_3PMo_{12}O_{40}$, which enables the production of glycolic acid, an important compound widely used in organic synthesis, biodegradable polymer synthesis, skin-care products, industrial rust removal, and food processing,[44,45] from commercial α-cellulose powder with a yield of 49.3%. Interestingly, $H_3PMo_{12}O_{40}$ is even capable of converting raw cellulosic materials, such as bagasse and hay, to glycolic acid with remarkable yields of ~30%.

Four types of Keggin-type HPAs, including $H_3PW_{12}O_{40}$ (HPW), $H_3PMo_{12}O_{40}$ (HPM), $H_4SiW_{12}O_{40}$ (HSW), and $H_4SiMo_{12}O_{40}$ (HSM), were tested as catalysts for the conversion of α-cellulose powder at 180 °C in water under 0.6 MPa oxygen using an autoclave setup. Typically, the reaction mixture comprised 20 mL of H_2O, 200 mg of α-cellulose powder (containing 1.23 mmol glucose units), and 0.3 mmol of HPA catalyst. The reaction was rather complex, with over 20 products generated. The major products were identified by high-performance liquid chromatography (HPLC). As summarized in Table 1, all tested HPA catalysts converted over 90% cellulose under the reaction conditions, among which HPM and HSM showed specific selectivity toward glycolic acid, giving high yields of 49.3% and 46.5%, respectively (see the Supporting Information for methods). The purity of the product was confirmed with NMR spectroscopy (Supporting Information, Figure S1).

Table 1. Yields (%) of the Main Products Derived from Cellulose Using Different Catalysts[a]

	catalysts					
products	HPW	HPM	HSW	HSM	MO[b]	NaMO[b]
glycolic acid	6.2	49.3	5.3	46.5	24.5	1.8
formic acid	9.7	9.6	10.9	12.6	10.8	2.2
acetic acid	0.5	4.0	7.8	4.7	4.6	1.6
glucose	18.5	1.6	16.6	0.9	1.2	0.5
fructose	4.2	5.2	3.2	4.8	4.3	0.9
levulinic acid	17.7	5.5	25.4	6.8	6.9	0.2
5-HMF	4.6	0.1	2.6	0.5	1.2	1.0
others[c]	4.4	7.9	5.1	6.3	5.4	1.1
total yield	65.7	83.3	76.8	83.2	58.7	9.2
conv. (%)[d]	88.3	90.5	89.6	96.2	75.7	21.0

[a] α-Cellulose powder (200 mg) containing 1.23 mmol glucose units, 0.3 mmol of HPA catalyst, and 20 mL of H_2O was stirred (1000 rpm) in a Teflon-lined stainless autoclave (75 mL) at 180 °C for 1 h under 0.6 M Pa O_2. Yields are calculated on a carbon basis and given as mean values. [b] Equivalent molar amount of Mo as for the Mo-containing HPA catalysts. [c] Other identifiable products include propionic acid, glyceric acid, glycolaldehyde dimer, glycolaldehyde, formaldehyde. [d] Conversion of cellulose.

The two heteropoly tungstic acids (HPW and HSW), however, showed very different catalytic behaviors. They produced only a small amount of glycolic acid in yields of less than 6%, as well as the major products of glucose, levulinic acid, and 5-HMF (Table 1), which were formed through the hydrolysis of cellulose and subsequent isomerization and dehydration processes.[14,15,29] These results suggested that the reaction pathway is mainly determined by the type of addenda atom in the HPA catalyst and that Mo favors a selective oxidation reaction. This suggestion was confirmed by the fact that MoO_3 (MO), which forms molybdic acid in water, also led to a remarkable cellulose conversion of 75.7% and a glycolic acid yield of 24.5% (Table 1). Basic molybdate Na_2MoO_4 (NaMO), however, performed badly, with a low cellulose conversion of 21%. We thus demonstrated that the molybdate species accounted for the high glycolic acid selectivity and the strong acidity was needed to initiate the reaction by hydrolyzing cellulose.

The overall reaction involved a series of successive or parallel steps: the hydrolysis of cellulose to glucose, the isomerization of glucose to fructose, the dehydration or fragmentation of hexoses, and the oxidation of the as-produced shorter carbohydrates. It has been shown that glucose and fructose undergo fragmentation in supercritical water to form C2−C4 carbohydrate products via a retro-aldol reaction.[18,46,47] This observation was also used to explain the formation of lactic acid derivatives from sugars.[18,46,47] Considering the similar reaction conditions, we assume that the Mo-containing HPA-catalyzed reaction in this study proceeds along the pathway depicted in Figure 1, where the hexoses are fragmented via retro-aldol reactions. Specifically, glucose obtained from the hydrolysis of cellulose undergoes successive retro-aldol reactions to form C2 α-hydroxylaldehyde (glycolaldehyde), which is then converted to glycolic acid through oxidation. In parallel, the isomerization of glucose gives rise to fructose, which can also be converted by retro-aldol reactions through dihydroxyacetone and glyceraldehyde to glycolaldehyde and formaldehyde and, finally, to glycolic acid and formic acid by oxidation. The absence of sugar acids with higher carbon numbers (e.g., gluconic acid and erythronic acid) in the products implies that the retro-aldol reaction is faster relative to the oxidation of sugars to sugar acids.

We conducted a series of control experiments to validate the proposed reaction pathway. Various monosaccharide alcohols, including mannitol, sorbitol, xylitol, erythytol, and glycerol, were first tested as reactants. None of them was converted under the reaction conditions used in this study (Supporting Information, Table S1), indicating that HPM is incapable of catalyzing the oxidation of hydroxyl groups in sugar derivatives. Hence, it is unlikely that the C1−C4 products from the cellulose reaction were formed from the direct decomposition through oxidation of hexoses. When gluconic acid, a monosaccharide acid, was used as the reactant, there was also just a negligible conversion observed. It is very interesting to note that under identical reaction conditions, glucuronic acid, which has the same molecular structure as gluconic acid except for the terminal group (carbonyl vs hydroxyl), was nearly completely converted, yielding glycolic acid and oxalic acid as the main products (Supporting Information Table S1). These results support the proposed reaction pathway in two respects: (i) only the sugar derivatives with carbonyl groups, which are eligible for the retro-aldol reaction, can be converted; and (ii) the fragmentation products of glucuronic acid via retro-aldol are glycolaldehyde and glyoxylic acid, which can be subsequently oxidized to form glycolic acid and oxalic acid, respectively, consistent with experimental observations.

From another point of view, the proposed reaction pathway implies that using glucose rather than fructose as the reactant should lead to higher selectivity of glycolic acid. Likewise, it should be expected that polysaccharides containing more glucose segments would produce more glycolic acid. To verify these expectations, we conducted reactions using glucose, fructose, cellobiose (a disaccharide of glucose), and sucrose (a disaccharide of fructose and glucose) as the reactants. The glycolic acid yields from these reactants were as follows: glucose (42.4%) ≈ cellobiose (40.0%) > sucrose (35.9%) > fructose

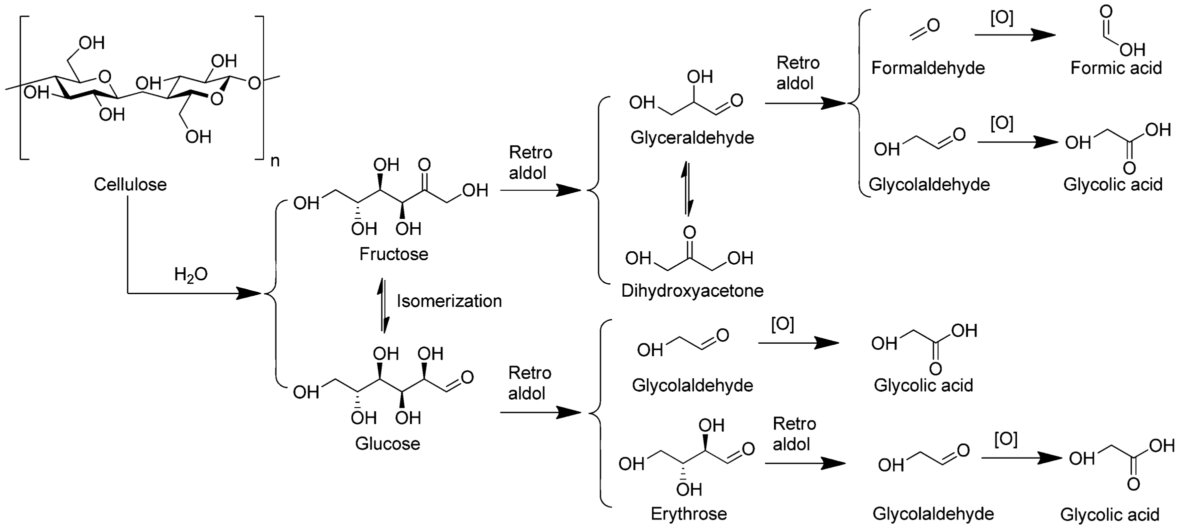

Figure 1. The proposed reaction pathway for the conversion of cellulose to glycolic acid.

Table 2. Yields of All the Identified Products from the Conversion of Different Sacchariferous Reactants Using HPM As the Catalyst[a]

products	reactants						
	glucose, %[b]	fructose, %[b]	cellobiose, %[b]	sucrose, %[b]	cellulose, %[c]	bagasse, %	hay, %
glycolic acid	42.4	24.6	40.0	35.9	24.2	32.2	27.9
formic acid	14.6	12.6	14.1	13.0	5.6	10.1	8.4
acetic acid	5.6	6.3	5.0	3.9	2.9	10.9	6.7
glucose	4.3	7.6	5.2	3.3	1.0	1.2	3.9
fructose	11.3	4.6	13.7	7.9	2.1	4.7	4.7
levulinic acid	7.4	8.8	7.6	3.3	1.5	5.8	4.9
5-HMF	1.0	2.0	1.4	0.5	0.9	0.8	0.6
propionic acid	2.4	1.1	0.0	13.7	4.0	1.4	5.1
glyceric acid	6.7	23.3	6.2	14.5	3.0	4.6	5.1
glycolaldehyde dimer	0.2	0.2	0.3	0.1	0.0	0.4	0.3
glycolaldehyde	<0.1	<0.1	<0.1	<0.1	0.5	<0.1	<0.1
formaldehyde	0.2	0.3	0.1	0.3	1.5	0.2	0.2
total yield	91.8	86.6	93.7	96.1	47.2	72.4	67.8
reactant conversion	95.7	95.4	100	100	51.2	91.7	80.1

[a] Reactant (200 mg), 0.3 mmol of HPM catalyst, and 20 mL of H_2O were stirred (1000 rpm) in a Teflon-lined stainless autoclave (75 mL) at 180 °C for 1 h under 0.6 M Pa O_2. Yields are calculated on a carbon basis and given as mean values. [b] The reactions were conducted at 150 °C. [c] A 0.025 mmol portion of the HPM catalyst was used.

(24.6%), in good agreement with our expectations (Table 2). Accordingly, these reactants also produced glyceric acid, which is an oxidative byproduct from the retro-aldol fragmentation of fructose (Figure 1), at yields in the opposite order (Table 2). These results provide strong support for the proposed reaction pathway and also demonstrate that the isomerization between glucose and fructose was slow under our reaction conditions.

To provide additional evidence that the retro-aldol reaction directs this reaction pathway, we intentionally decreased the reaction rate in another parallel experiment by using only 1/12 of the original amount of HPM catalyst to capture the proposed reaction intermediates. Although some of the expected intermediates, such as erythrose, dihydroxyacetone, and glyceraldehyde, were not detected, possibly because of their instability, formaldehyde and glycoaldehyde were clearly identified by HPLC in the products, which were formed via the retro-aldol reaction from fructose and glucose, respectively (Figure 1, Table 2). Taken together, our results suggest that the conversion of cellulose by HPA catalysts is strongly dependent on the type of addenda atom. Like other Brönsted acids in previous reports,[48] tungsten-based HPAs favor dehydration of the sugars and, thus, mainly produce levulinic acid and 5-HMF. Molybdenum-based HPAs, on the other hand, demonstrate a special ability to facilitate the fragmentation of monosaccharides and moderate the activity of subsequent oxidation reactions, leading to high selectivity of glycolic acid.

We also investigated the reusability of HPM catalyst in cellulose conversion. After each reaction cycle, the liquid phase, including the products and the catalyst, was first separated from the unreacted cellulose by filtration. The water was then removed by low-temperature rotary evaporation. Methanol was added to react with the glycolic acid and other acids to form methyl esters, which could be easily collected by vacuum distillation. The residual solid material was then hydrothermally treated with oxygen to decompose the remaining trace amounts of sugars (e.g., glucose and fructose) completely to obtain a clean HPM catalyst for the next reaction run. The last step is solely for getting accurate yield of the next reaction run, but unnecessary in practical applications. As indicated in Figure 2, our HPM catalyst exhibited constant catalytic performance during nine reaction runs with a stable yield of ~50% glycolic acid. X-ray photoelectron spectroscopy (XPS) showed that the oxidation state of Mo in HPM catalyst was unchanged after successive reactions (Supporting Information, Figure S2). The easy recovery and good reusability suggest that HPA catalysts are better candidates for practical applications compared with volatile and corrosive liquid acids.

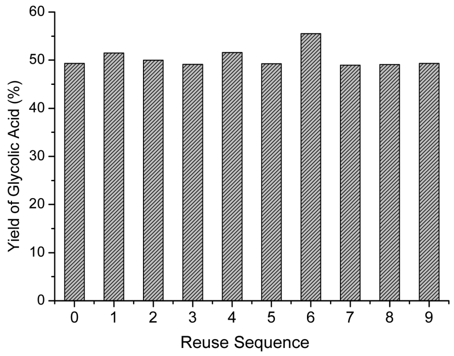

Figure 2. Glycolic acid yields in sequential cellulose conversion reactions using the HPM catalyst.

Previous studies have pointed out that the conversion efficiency of cellulose may be highly dependent on the form of the starting material and that special pretreatments (e.g., ball milling or ultrasonic processing) are usually necessary to achieve effective conversion.[49−52] In this sense, it is worth highlighting that in addition to commercially available α-cellulose powders, which are essentially purified "chemicals", HPM can also catalyze the conversion of "raw" cellulosic biomass. For example, we used dried but otherwise untreated bagasse and hay as the starting materials for the reaction (see the Supporting Information) and found that they were both converted to glycolic acid with high selectivity. Assuming that these two raw biomass materials consisted of 100% cellulose, the glycolic acid yields were 32.2% and 27.9% for bagasse and hay, respectively (Table 2). These results suggest the general applicability of HPM for directly converting various types of crude cellulosic biomass. Notably, few studies have reported such efficient catalytic production of value-added chemicals from raw biomass feedstock.[25,31,53,54]

In summary, Mo-containing HPAs are effective catalysts for the conversion of various cellulosic biomass materials. Their strong Brönsted acidity facilitates the hydrolysis of cellulose while the moderate oxidative activity allows selective oxidation of the aldehyde groups in the fragmentation products. Among a large number of parallel competing reactions, successive retro-aldol reactions dominate the fragmentation of monosaccharides generated from cellulose hydrolysis, resulting in high selectivity of glycolic acid. Given that the reactions are conducted in water with little restriction on the type of starting material, our findings provide a new cost-effective and eco-benign route for biomass conversion in which HPAs, which combine the merits of homogeneous and heterogeneous catalysts, play a crucial role.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, XPS spectra of fresh and used HPM catalysts, NMR spectra of the isolated glycolic acid, and the preparation method of hay and bagasse for catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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