Catalysis Today 164 (2011) 461–466

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Direct transformation of cellulose into methyl and ethyl glucosides in methanol and ethanol media catalyzed by heteropolyacids

Weiping Deng, Mi Liu, Qinghong Zhang, Ye Wang*

State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history:
Available online 13 November 2010

Keywords:
Alcoholysis
Cellulose
Ethyl glucoside
Methyl glucoside
Heteropolyacid

ABSTRACT

The alcoholysis of cellulose in methanol and ethanol media has been studied in the presence of various kinds of acid catalysts. Keggin-type tungstosilicious and tungstophosphoric acids ($H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$) were found to be highly efficient for the alcoholysis of cellulose. Methyl and ethyl glucosides (both containing α and β isomers) could be obtained in methanol and ethanol with yields as high as 57% and 63%, respectively. The ratio of α and β isomers was ~1.4–1.6 in both methyl or ethyl glucosides, suggesting the intermolecular transformations between α and β isomers. Our comparative studies show that the alcoholysis of cellulose in methanol or ethanol proceeds more efficiently than the hydrolysis of cellulose in water medium. Glucose yields of only about 5–10% were obtained in water in the presence of an acid catalyst under similar reaction conditions.

1. Introduction

The utilization of biomass as chemical feedstock can decrease our dependence on fossil resources and has attracted much attention in recent years. The biomass-based chemical production may also have the possibility to reduce the emission of CO_2, because the CO_2 released from chemical processes will be consumed in the growth of biomass through photosynthesis [1–3]. Lignocellulose is one of the most abundant biomass resources, and may act as a promising alternative for the sustainable production of chemicals [4–6]. Cellulose, a polysaccharide of glucose connected by β-1,4-glucoside bonds, is the main component of lignocellulose. The selective conversion of cellulose to chemicals under mild conditions is a difficult challenge because of the robust crystalline structure of cellulose formed by the extensive network of hydrogen bonding. Thus far, processes have been developed for the pyrolysis or gasification of cellulose at high temperatures to bio-oils or syngas, but these processes suffer from the problems of high energy input and low selectivity [1].

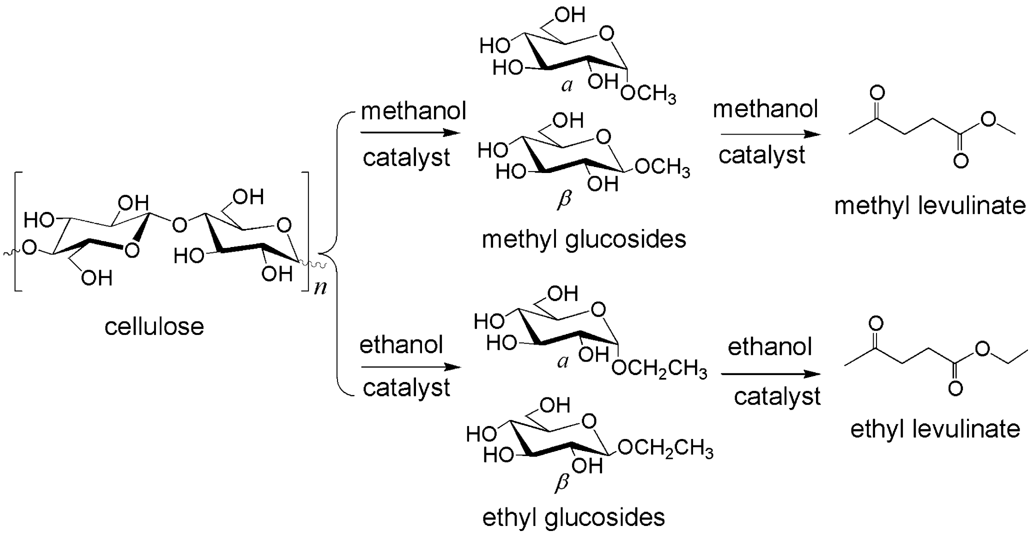
From the viewpoint of sustainable chemistry, the conversion of cellulose selectively to a platform molecule, which can be used for the production of various chemicals in the subsequent step, under mild conditions is highly desirable [7–10]. Many studies have been contributed to the production of glucose, the monosaccharide of cellulose, through hydrolysis in water medium, and glucose may be transformed into chemicals such as alkyl-glucosides [11,12], 5-hydroxymethyl furfural (HMF) [13], sorbitol [14] and gluconic acid [15]. Mineral liquid acids, especially H_2SO_4, and a few solid acids have been investigated as catalysts for the conversion of cellulose into glucose in water medium [16–22]. However, the use of H_2SO_4 requires corrosion-resistant apparatus and has the problem of separating products from acids. Moreover, higher glucose yields (30–70%) could only be obtained in concentrated H_2SO_4, and the use of dilute H_2SO_4 (<1 wt%) only afforded lower glucose yields. Solid acids such as amorphous carbon materials bearing SO_3H groups [18], layered transition metal oxides ($HNbMoO_6$) [19], and sulfated resin [21] have been tested for the hydrolysis of cellulose, but glucose yields are still quite low.

The studies on cellulose catalytic conversions in reaction media other than water are scarce. It has been demonstrated that the use of ionic liquids, which can dissolve cellulose, as reaction media, can enhance the efficiency of the hydrolysis of cellulose to glucose in the presence of an acid catalyst [23,24]. Cellulose could also be converted in an one-pot reaction to octyl-α,β-glucosides in ionic liquids [25]. Ionic liquids, however, are still expensive for cellulose utilization. A few early papers reported the alcoholysis of cellulose in alcohol medium in the presence of a liquid acid, but the products were not analyzed [26,27]. Non-catalytic degradations of cellulose to methyl glucosides were reported to proceed in supercritical methanol under severe conditions, and the highest yield of methyl glucosides of ~30% was attained at 623 K and 43 MPa [28]. Recently, we succeeded in converting cellulose into methyl glucosides (including methyl-α-glucoside and methyl-β-glucoside) with good yields (50–60%) under relatively milder conditions

---

* Corresponding author. Tel.: +86 592 2186156; fax: +86 592 2183047.
E-mail address: wangye@xmu.edu.cn (Y. Wang).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.10.055



Scheme 1. Catalytic conversions of cellulose in methanol and ethanol media.

($\leq$473 K and 3 MPa of N_2) in the presence of several kinds of acids [29]. Alkyl glucosides are widely used as biodegradable surfactants or chemical intermediates [11,30]. In this paper, we report the superior catalytic performances of Keggin-type heteropolyacids for the conversions of cellulose into methyl and ethyl glucosides in methanol and ethanol media (Scheme 1). The effect of reaction conditions and the catalyst recycling uses for the heteropolyacid-catalyzed cellulose conversions will be investigated in detail.

2. Experimental

2.1. Materials and catalyst preparation

$H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were prepared by an established method. Typically, H_2SO_4 with a concentration of 90% was added into an aqueous solution containing Na_2WO_4 and Na_2HPO_4, and then the mixture was stirred for 1 h at ambient temperature. The formed $H_3PW_{12}O_{40}$ crystallites were extracted by diethyl ether from water. $H_4SiW_{12}O_{40}$ was prepared using a similar procedure except for using Na_2SiO_3 to replace Na_2HPO_4 as a starting material.

H-ZSM-5 was purchased from Nankai University. Nafion and Amberlyst-15, two polymeric resin-based acids, were purchased from Alfa Aesar. Sulfated ZrO_2 was prepared by treating ZrO_2 (Alfa Aesar) in an aqueous solution of H_2SO_4 with a concentration of 0.5 mol L^{-1}, and then, the solid was collected by filtration and dried at 393 K overnight, followed by calcination in air at 923 K. Amorphous carbon materials bearing SO_3H groups were prepared by heating the commercial cellulose and lignin at 723 K in N_2 flow for 5 h, and the obtained carbon powders were boiled in concentrated sulfuric acid (98%) at 353 K for 15 h under N_2, followed by washing and drying, and the obtained samples were denoted as C(cell.)-SO_3H and C(lig.)-SO_3H, respectively.

2.2. Catalytic reactions and catalyst characterizations

Microcrystalline cellulose powders purchased from Alfa Aesar with a crystallinity of 85% were directly used for reactions. The reaction was carried out in a Teflon-lined stainless-steel autoclave with a volume of 75 mL. After the catalyst and the cellulose (typically 0.5 g, equivalent to 3 mmol $C_6H_{10}O_5$ units) were added into the autoclave, which was pre-charged with methanol or ethanol (20 mL), N_2 of 3 MPa was introduced. The reaction was started by heating the mixture to a reaction temperature. After the reaction, the products were analyzed by a HPLC (Shimazu LC-20A) equipped with a RI detector and a Shodex^{TM} SH1011 column (10 μm, 6.5 mm × 300 mm), and the aqueous solution of H_2SO_4 with a 0.05 mol L^{-1} was used as a mobile phase.

The conversion of cellulose was calculated by the weight difference of cellulose before and after the reaction. The yield of a product was calculated by the following equation:

$$\text{Yield}\ (\%) = \frac{\text{amount of the target product (mol)}}{\text{amount of } C_6H_{10}O_5 \text{ unit in cellulose (mol)}} \times 100\%$$

X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) spectroscopic measurements were carried out to characterize the catalyst. XRD was performed on a Panalytical X'pert Pro diffractometer with Cu K_α radiation. FT-IR spectra were recorded on a FT-IR Nicolet 380 spectrometer equipped with an MCT detector.

3. Results and discussion

3.1. Catalytic effects of various acids for conversions of cellulose in alcohols

Various acids were investigated for the catalytic conversions of cellulose to methyl and ethyl glucosides in methanol and ethanol media at 468 and 453 K, respectively. No conversion of cellulose was observed without an acid catalyst either in methanol or in ethanol. Fig. 1A shows that, among the dilute mineral liquid acids including HCl, HNO_3, H_2SO_4 and H_3PO_4 with an H^+ concentration of 6.7 mmol L^{-1}, H_2SO_4 is the most effective for the conversion of cellulose in methanol to methyl glucosides. For solid acid catalysis, H-ZSM-5 was less active possibly due to its microporous structure. Solid acidic materials bearing SO_3H groups, such as sulfated ZrO_2, Nafion, Amberlyst-15, C(cell.)-SO_3H, and C(lig.)-SO_3H were efficient for the conversion of cellulose in methanol, providing methyl glucosides with yields of 25–45%. However, unfortunately, these materials could not be used repeatedly because of the leaching of the SO_3H groups from solid to liquid during the reaction. For example, the recovered C(lig.)-SO_3H catalyst only provided methyl glucosides with a yield of 5.3% in the second run. The elemental analysis showed that the sulfur content decreased from 4.2 wt% to 1.8 wt% after the reaction, suggesting the loss of SO_3H groups. We

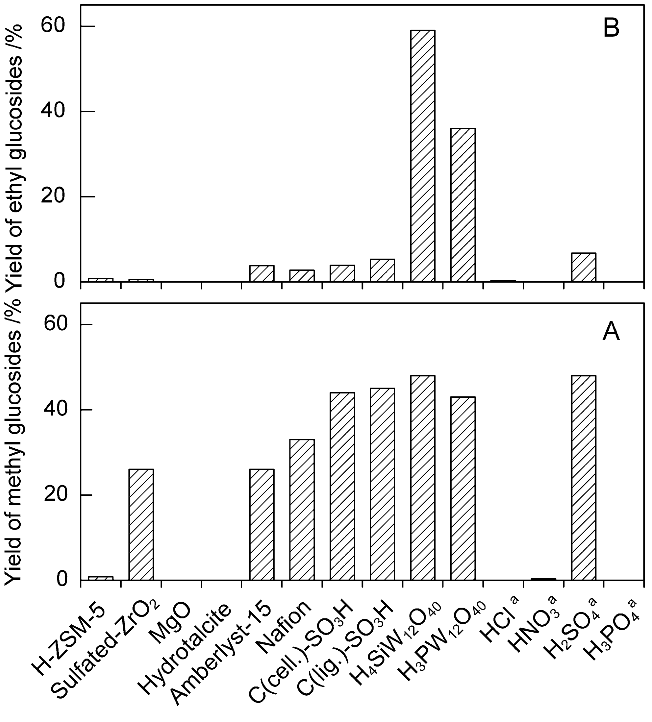


Fig. 1. Catalytic performances of various catalysts for the conversions of cellulose in methanol (A) and ethanol (B). Reaction conditions: (A) $T = 468$ K; W(catalyst) = 0.1 g; W(cellulose) = 0.2 g; V(methanol) = 20 mL; $t = 1$ h; $P(N_2) = 3$ MPa, $^a[H^+] = 6.7$ mmol L^{-1}, V(methanol) = 30 mL. (B) $T = 453$ K; W(catalyst) = 0.05 g; W(cellulose) = 0.5 g; V(ethanol) = 20 mL; $t = 0.5$ h, $^a[H^+] = 3.5$ mmol L^{-1}.

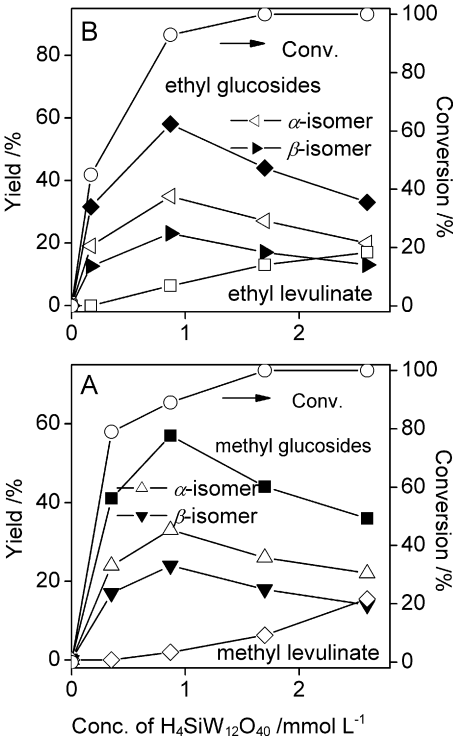


Fig. 2. Effect of $H_4SiW_{12}O_{40}$ concentration on the conversions of cellulose in methanol (A) and ethanol (B). Reaction conditions: W(cellulose) = 0.5 g, W(catalyst) = 0.05 g, V(methanol or ethanol) = 20 mL, $t = 0.5$ h, $P(N_2) = 3$ MPa. (A) $T = 468$ K; (B) $T = 453$ K.

found that the Keggin-type heteropolyacids, i.e., $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$, also exhibited superior catalytic performances for the formation of methyl glucosides, providing methyl glucosides with yields of 48% and 43%, respectively. On the other hand, solid bases, i.e., MgO and hydrotalcite, were inactive for cellulose transformations in alcohols. The dehydration of methanol to dimethyl ether was also observed in the presence of an acid catalyst, and the conversion of methanol to dimethyl ether was 28% in the presence of $H_4SiW_{12}O_{40}$ under the reaction conditions of Fig. 1.

For the conversion of cellulose in ethanol (Fig. 1B), heteropolyacids became outstanding for the formation of ethyl glucosides. The performances of other acid catalysts even H_2SO_4 became significantly poorer than the heteropolyacids. In the presence of $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ catalysts, the yields of ethyl glucosides reached 59% and 40%, respectively at 453 K. The dehydration of ethanol to diethyl ether also occurred at the same time, and the conversion of ethanol to diethyl ether was 16% in the presence of $H_4SiW_{12}O_{40}$. The difference in catalytic performances between $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ may arise from the difference in the concentration of H^+. When the amount of $H_3PW_{12}O_{40}$ was raised from 0.05 to 0.067 g ($[H^+] = 3.5$ mmol L^{-1}, which was the same with those for 0.05 g $H_4SiW_{12}O_{40}$ and H_2SO_4 used in Fig. 1B), a 57% yield of ethyl glucosides was obtained. Thus, $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ possess similar catalytic performances in essence, and their performances for the conversion of cellulose in ethanol are significantly better than that of H_2SO_4.

It is known that heteropolyacids may show Brønsted acidity even stronger than H_2SO_4 [31]. Moreover, the handling of heteropolyacids would be more facile than that of H_2SO_4, and the corrosion problem in the case of heteropolyacids is less serious than that in the case of H_2SO_4. Thus, the heteropolyacids may play important roles in the transformation of cellulose. However, to date, reports using heteropolyacids as catalysts for cellulose conversions are very scarce [32,33]. Our present study has demonstrated that $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ are very unique for the conversion of cellulose in alcohols (especially ethanol) to alkyl glucosides.

3.2. *Effect of acid concentration on conversions of cellulose in alcohols*

The concentration of H^+ of heteropolyacids is expected to influence the conversions of cellulose in alcohols to alkyl glucosides. We have performed a detailed study on the effect of the concentration of $H_4SiW_{12}O_{40}$ on its catalytic behavior. As shown in Fig. 2, the increase in $H_4SiW_{12}O_{40}$ concentration enhanced the cellulose conversion remarkably both in methanol and in ethanol media, and the yields of alkyl glucosides also increased in both cases. However, too high an $H_4SiW_{12}O_{40}$ concentration led to lower yields of methyl or ethyl glucosides. A maximum yield of methyl glucosides of 57% was attained in the presence of $H_4SiW_{12}O_{40}$ (0.87 mmol L^{-1}) with an $[H^+]$ concentration of 3.5 mmol L^{-1}. A similar trend in the change of ethyl glucoside yield with $H_4SiW_{12}O_{40}$ concentration was observed for the reaction in ethanol, and the maximum yield of ethyl glucosides (59%) was obtained also at an $H_4SiW_{12}O_{40}$ concentration of 0.87 mmol L^{-1}.

Methyl and ethyl levulinates were formed as the main by-products in the conversions of cellulose in methanol and ethanol, respectively, in the presence of $H_4SiW_{12}O_{40}$. The yield of methyl or ethyl levulinate increased monotonically with the concentration of $H_4SiW_{12}O_{40}$ at the expense of methyl or ethyl glucosides (Fig. 2). This suggests that the alkyl glucosides may undergo consecutive reactions to levulinate, which is also catalyzed by an acid (Scheme 1). It was once reported that glucose could readily be dehydrated to form HMF in the presence of acids, and the further hydration of HMF could produce levulinic acid [1]. We speculate that alkyl levulinates may be produced in a similar route.

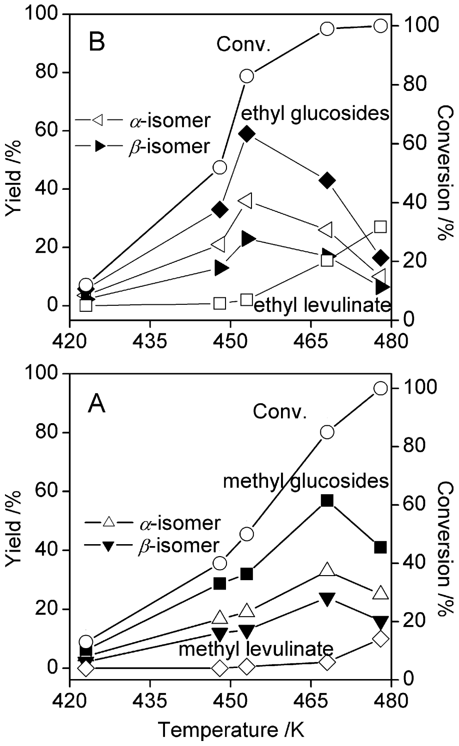


Fig. 3. Dependence of catalytic performances on reaction temperature for the conversions of cellulose catalyzed by $H_4SiW_{12}O_{40}$ in methanol (A) and ethanol (B). Reaction conditions: W(cellulose) = 0.5 g, W(catalyst) = 0.05 g, t = 0.5 h, $P(N_2)$ = 3 MPa, V(methanol or ethanol) = 20 mL.

3.3. Kinetic studies on cellulose conversions in alcohols in the presence of heteropolyacids

To gain further insights into the transformation of cellulose in alcohols in the presence of heteropolyacids, we examined the effects of reaction temperature and reaction time on catalytic performances. As shown in Fig. 3A, the conversion of cellulose was less than 10% at a relatively low temperature (423 K) in methanol, and it increased steeply with temperature. The yield of methyl glucosides also increased significantly with temperature and reached a maximum (57%) at 468 K. A further increase in temperature to 478 K decreased the yield of methyl glucosides but increased that of methyl levulinate, indicating the transformation of methyl glucosides to methyl levulinate at higher temperatures. In ethanol medium (Fig. 3B), the conversion of cellulose and the yield of ethyl glucosides changed in similar trends with those observed in methanol medium. It should be noted that the maximum yield of ethyl glucosides (59%) was obtained at 453 K, which was 15 K lower than the temperature, over which the maximum yield of methyl glucosides was achieved. Because the temperature for obtaining the maximum yield of ethyl glucosides is lower than that for obtaining the maximum yield of methyl glucosides, it is reasonable to speculate that the activation of glycosidic bonds of cellulose in ethanol is easier than that in methanol. Moreover, when the reaction temperature was increased to >453 K, the yield of ethyl glucosides decreased rapidly, while that of ethyl levulinate increased significantly (Fig. 3B), suggesting that the consecutive conversion of ethyl glucosides proceeds quickly at higher temperatures. A yield of 27% was attained for ethyl levulinate in the conversion of cellulose in ethanol at 478 K.

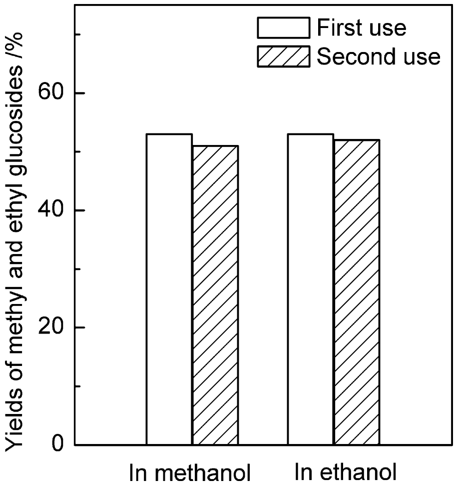


Fig. 4. Repeated uses of $H_3PW_{12}O_{40}$ for cellulose conversions in methanol and ethanol. Reaction conditions: in methanol: W(cellulose) = 0.5 g; $W(H_3PW_{12}O_{40})$ = 0.05 g; V = 20 mL; $P(N_2)$ = 3 MPa; t = 0.5 h; T = 468 K. In ethanol: W(cellulose) = 0.5 g; $W(H_3PW_{12}O_{40})$ = 0.06 g; V = 20 mL; $P(N_2)$ = 3 MPa; t = 0.2 h; T = 453 K.

Table 1 shows the effect of reaction time on catalytic performances in both methanol and ethanol. In the initial 10 or 5 min, more than 50% of cellulose could be converted in methanol or ethanol in the presence of $H_4SiW_{12}O_{40}$. With prolonging reaction time, the yield of methyl or ethyl glucosides increased firstly, and then reached maximum (57% or 63%) in each case. A too long reaction time decreased the yield of methyl or ethyl glucosides, and increased that of methyl or ethyl levulinate. This observation confirms the consecutive conversion of methyl or ethyl glucosides into methyl or ethyl levulinate. Turnover numbers (TONs) for the formation of methyl or ethyl glucosides have been calculated from the moles of methyl or ethyl glucosides formed per mole of H^+, and the results are also listed in Table 1. TONs of 25 and 28 were attained with yields of 57% and 63% for the formation of methyl and ethyl glucosides in methanol and ethanol, respectively.

It is of interest that the α/β ratios of isomers in products were all around 1.4–1.6, suggesting the intermolecular transformations between α and β isomers. Similar results were also reported in another system [1].

3.4. Comparison of cellulose conversions in alcohol medium and in water medium

The conversions of cellulose in methanol and in ethanol were compared with that in water under the same reaction conditions in the presence of $H_4SiW_{12}O_{40}$ catalyst. Table 2 shows that glucose, fructose, and HMF were produced from the conversion of cellulose in water medium. The yield of glucose attained in water medium was significantly lower than that of methyl glucosides obtained in methanol medium. The TONs obtained for the formation of methyl glucosides in methanol were 5–10 times higher than those for glucose in water under the same reaction conditions. By decreasing the reaction temperature from 468 K to 453 K, the conversion of cellulose in water medium decreased from 14–20% to 8–13% (Table 3). On the other hand, at 453 K, the conversion of cellulose in ethanol occurred very rapidly, and conversions of 90% and 83% were attained when the amounts of cellulose were 0.2 and 0.5 g, respectively. The TONs for the formation of ethyl glucosides were also 5–10 times higher in ethanol than the formation of glucose in water. It is likely that the interaction between cellulose and the organic alcohol molecules under reaction conditions is stronger than that between cellulose and water molecules. Such a difference may lead to the difference in cellulose conversions in water and in alcohol media.

Table 1
Effect of reaction time on catalytic behaviors of $H_4SiW_{12}O_{40}$ for cellulose conversions in methanol and ethanol.

	Time/min	Conv./%	Yield[a]/%			TON[c]
			M-α-G	M-β-G	ML	
In methanol	10	56	26	18	0.9	20
	30	85	33	24	2.0	25
	45	90	30	22	4.0	23
	60	100	24	16.4	12	18
	Time/min	Conv./%	Yield[b]/%			TON[c]
			E-α-G	E-β-G	EL	
In ethanol	5	56	23	15	0.9	17
	15	73	38	25	1.0	28
	30	83	36	23	2.0	26
	60	99	24	16	19	18

Reaction conditions: *W*(cellulose) = 0.5 g, *W*($H_4SiW_{12}O_{40}$) = 0.05 g, *V*(methanol or ethanol) = 20 mL, *P*(N_2) = 3 MPa, *T* = 468 K (in methanol) or *T* = 453 K (in ethanol).

[a] M-α-G, M-β-G and ML denote methyl-α-glucoside, methyl-β-glucoside, and methyl levulinate, respectively.

[b] E-α-G, E-β-G and EL denote ethyl-α-glucoside, ethyl-β-glucoside and ethyl levulinate, respectively.

[c] TON was calculated by the mole of methyl glucosides or ethyl glucosides formed per mole of H^+.

Table 2
Comparisons of cellulose conversions in methanol and in water in the presence of $H_4SiW_{12}O_{40}$.

W[a]/g	In water					In methanol				
	Conv./%	Yield[b]/%			TON[d]	Conv./%	Yield[c]/%			TON[d]
		Glu.	Fru.	HMF			M-α-G	M-β-G	ML	
0.2	18	10	4.3	1.2	1.8	90	35	24	0	11
0.5	20	7.1	4.2	0.6	3.2	85	33	24	2.0	25
1.0	14	6.1	0.5	0.2	5.3	82	34	24	4.5	52

Reaction conditions: *W*($H_4SiW_{12}O_{40}$) = 0.05 g; *V* = 20 mL; *P*(N_2) = 3 MPa; *T* = 468 K; *t* = 0.5 h.

[a] Weight of cellulose.

[b] Glu. and Fru. denote glucose and fructose, respectively.

[c] M-α-G, M-β-G, and ML denote methyl-α-glucoside, methyl-β-glucoside, and methyl levulinate, respectively.

[d] TON was calculated by the moles of glucose or methyl glucosides formed per mole of H^+.

Table 3
Comparison of cellulose conversion in ethanol and in water in the presence of $H_4SiW_{12}O_{40}$.

W[a]/g	In water					In ethanol				
	Conv./%	Yield[b]/%			TON[d]	Conv./%	Yield[c]/%			TON[d]
		Glu.	Fru.	HMF			E-α-G	E-β-G	EL	
0.2	13	6.4	0.9	0.4	1.1	90	34	22	0.3	9.9
0.5	9.0	4.3	0.6	0.3	1.9	83	36	23	2.0	26
1.0	8.0	5.6	0.8	0.42	4.9	44	18	12	1.0	26

Reaction conditions: *W*($H_4SiW_{12}O_{40}$) = 0.05 g; *V* = 20 mL; *P*(N_2) = 3 MPa; *T* = 453 K; *t* = 0.5 h.

[a] Weight of cellulose.

[b] Glu. and Fru. denote glucose and fructose, respectively.

[c] E-α-G, E-β-G, and EL denote ethyl-α-glucoside, ethyl-β-glucoside and ethyl levulinate, respectively.

[d] TON was calculated by the moles of glucose or ethyl glucosides formed per mole of H^+.

3.5. *Repeated uses of heteropolyacids for cellulose conversions*

The repeated uses of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ were carried out for cellulose conversions in alcohols. After reactions, methanol or ethanol was first evaporated under reduced pressure, followed by introducing a small amount of water. Subsequently, the catalyst (i.e., $H_4SiW_{12}O_{40}$ or $H_3PW_{12}O_{40}$) was recovered by extraction with diethyl ether. About 80% of $H_3PW_{12}O_{40}$ could be recovered after reactions in either methanol or ethanol by this simple method. The catalytic performances of $H_3PW_{12}O_{40}$ recovered did not undergo significant changes, and the yields of methyl and ethyl glucosides were maintained at ~53% and ~52%, respectively (Fig. 4). It should be noted that we accumulated the recovered $H_3PW_{12}O_{40}$ catalyst after the first run from two different batches, and the catalyst amount used in the second run in Fig. 4 was the same as that used in the first run. The Keggin structure of $H_3PW_{12}O_{40}$ was also sustained after the reaction as reflected by XRD and FT-IR characterizations.

However, the recovery of $H_4SiW_{12}O_{40}$ was more difficult after catalytic reactions than that of $H_3PW_{12}O_{40}$. At the moment, we achieved a degree of recovery of ~50% for the $H_4SiW_{12}O_{40}$. Nevertheless, the performance and the structure of the recovered $H_4SiW_{12}O_{40}$ were sustained.

4. Conclusions

Cellulose can be transformed into methyl-α,β-glucosides or ethyl-α,β-glucosides in the presence of $H_4SiW_{12}O_4$ or $H_3PW_{12}O_4$ in methanol or ethanol medium. The concentration of heteropolyacids, reaction temperature and reaction time were crucial factors in affecting the catalytic performances. Maximum yields of methyl glucosides (57%) and ethyl glucosides (63%) were obtained at a medium concentration of catalyst and proper reaction conditions. Although a higher concentration of catalyst (or H^+) could increase the conversion of cellulose, too higher a concentration of catalyst caused the consecutive conversion of methyl or ethyl glucosides to methyl or ethyl levulinate. Too high reaction temperatures or too long reaction times also led to the transformation of methyl or ethyl glucosides into methyl or ethyl levulinate. Our comparative studies revealed that the transformation of cellulose in alcohols was more facile than in water catalyzed by heteropolyacids. The present study has demonstrated that cheaper alcohols (i.e., methanol and ethanol) can be used as promising reaction media for the direct transformation of cellulose under relatively mild conditions.

Acknowledgements

This work was supported by the NSF of China (20625310, 20873110, 20923004 and 21033006), the National Basic Program of China (2010CB732303), and the Research Fund for the Doctoral Program of Higher Education (20090121110007).

References

[1] G.W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044–4098.
[2] J.N. Chheda, G.W. Huber, J.A. Dumesic, Angew. Chem. Int. Ed. 46 (2007) 7164–7183.
[3] P. Gallezot, ChemSusChem 1 (2008) 734–737.
[4] D. Klemm, B. Heublein, H.P. Fink, A. Bohn, Angew. Chem. Int. Ed. 44 (2005) 3358–3393.
[5] M. Stöcker, Angew. Chem. Int. Ed. 47 (2008) 9200–9211.
[6] P.L. Dhepe, A. Fukuoka, ChemSusChem 1 (2008) 969–975.
[7] B. Kamm, Angew. Chem. Int. Ed. 46 (2007) 5056–5058.
[8] A. Fukuoka, P.L. Dhepe, Angew. Chem. Int. Ed. 45 (2006) 5161–5163.
[9] C. Luo, S. Wang, H. Liu, Angew. Chem. Int. Ed. 46 (2007) 7636–7639.
[10] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J.G. Chen, Angew. Chem. Int. Ed. 47 (2008) 8510–8513.
[11] W. von Rybinski, K. Hill, Angew. Chem. Int. Ed. 37 (1998) 1328–1345.
[12] M.A. Camblor, A. Corma, S. Iborra, S. Miquel, J. Primo, S. Valencia, J. Catal. 172 (1997) 76–84.
[13] H.B. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Science 316 (2007) 1597–1600.
[14] K. van Gorp, E. Boerman, C.V. Cavenaghi, P.H. Berben, Catal. Today 52 (1999) 349–361.
[15] C. Baatz, U. Prube, J. Catal. 249 (2007) 34–40.
[16] H. Zhao, J.H. Kwak, Y. Wang, J.A. Franz, J.M. White, J.E. Holladay, Energy Fuel 20 (2006) 807–811.
[17] H. Zhao, J.E. Holladay, Y. Wang, J.M. White, Z.C. Zhang, J. Bio. Mater. Bioenergy 1 (2007) 210–214.
[18] S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, J. Am. Chem. Soc. 130 (2008) 12787–12793.
[19] A. Takagaki, C. Tagusagawa, K. Domen, Chem. Commun. (2008) 5363–5365.
[20] A. Onda, T. Ochi, K. Yanagisawa, Green Chem. 10 (2008) 1033–1037.
[21] R. Rinaldi, R. Palkovits, F. Schüth, Angew. Chem. Int. Ed. 47 (2008) 8047–8050.
[22] H. Kobayashi, T. Komanoya, K. Hara, A. Fukuoka, ChemSusChem 3 (2010) 440–443.
[23] C. Li, Z.K. Zhao, Adv. Synth. Catal. 349 (2007) 1847–1850.
[24] M. Mascal, E.B. Nikitin, Angew. Chem. Int. Ed. 47 (2008) 7924–7926.
[25] N. Villandier, A. Corma, Chem. Commun. 46 (2010) 4408–4410.
[26] R.E. Reeves, W.M. Schwartz, J.E. Giddens, J. Am. Chem. Soc. 68 (1946) 1383–1385.
[27] R.E. Reeves, L.W. Mazzeno Jr., C.L. Hoffpauir, J. Am. Chem. Soc. 72 (1950) 4773–4777.
[28] Y. Ishikawa, S. Saka, Cellulose 8 (2001) 189–195.
[29] W. Deng, M. Liu, Q. Zhang, X. Tan, Y. Wang, Chem. Commun. 46 (2010) 2668–2670.
[30] D. Wei, P. Zou, M. Tu, H. Zheng, J. Mol. Catal. B 18 (2002) 273–278.
[31] J. Macht, M.J. Janik, M. Neurock, E. Iglesia, Angew. Chem. Int. Ed. 46 (2007) 7864–7868.
[32] K. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya, A. Satsuma, Green Chem. 11 (2009) 1627–1632.
[33] J. Tian, J. Wang, S. Zhao, C. Jiang, X. Zhang, X. Wang, Cellulose 17 (2010) 578–594.