Acid-catalysed direct transformation of cellulose into methyl glucosides in methanol at moderate temperatures

Weiping Deng, Mi Liu, Qinghong Zhang*, Xuesong Tan and 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

Electronic Supplementary Information

1. Experimental Details

(1) Catalytic materials and catalyst preparation methods

(1) HCl, HNO_3, H_2SO_4, H_3PO_4 and CF_3COOH: These chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China.
(2) H-ZSM-5: This acidic zeolite was purchased from Nankai University.
(3) Nafion and Amberlyst-15: These two polymeric resin-based materials were purchased from Alfa Aesar.
(4) Sulfated ZrO_2:[1] ZrO_2 (5 g, Alfa Aesar) was sulfated using 200 mL aqueous solution of H_2SO_4 (0.5 mol L^{-1}). The slurry containing powdery ZrO_2 and an appropriate quantity of H_2SO_4 was stirred for 2 h. Then, the solid was collected and dried at 393 K overnight, followed by calcination in air at 923 K.
(5) Carbon (cell.)-SO_3H-98% and carbon (lig.)-SO_3H-98%:[2] The starting materials (cellulose and lignin purchased from Alfa Aesar and Tokyo Chemical Industry Co., Ltd., respectively) were heated at 723 K in N_2 flow for 5 h to produce black solids, which were then ground to powders. Subsequently, the carbon powders were boiled in 100 mL of concentrated sulfuric acid (98%) at 353 K for 15 h under N_2. After cooling to room temperature, the suspension was filtered to yield a black precipitate, which was washed repeatedly until sulfate ions could not be detected in the filtrate.
(6) Lig.-SO_3H-64% and lig.-SO_3H-17%: Typically, lignin (5 g) was heated in sulfuric acid (64% or 17%, 100 mL) at 483 K for 20 h under a flow of N_2. The resulting carbon materials were washed repeatedly with water at room temperature until sulfate ions could not be detected in the filtrate.
(7) $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$:[3] Na_2WO_4 (200 g) and Na_2HPO_4 (8 g) were dissolved in 200 mL water to make a clear solution. H_2SO_4 (90%) was then added into the solution and then stirred for 1 h at room temperature. Finally, $H_3PW_{12}O_{40}$ was extracted by diethyl ether (100 mL) from water. $H_4SiW_{12}O_{40}$ was prepared using a similar procedure except for using Na_2SiO_3 instead of Na_2HPO_4 as a starting material.

(2) Catalytic reactions

Microcrystalline cellulose purchased from Alfa Aesar with a crystallinity of 85% was used in this work. The conversion of cellulose was performed in a Teflon-lined stainless-steel autoclave. After the catalyst and cellulose (typically 0.5 g, equivalent to 3 mmol $C_6H_{10}O_5$ unit) were added into the autoclave pre-charged with methanol (typically 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 HPLC (Shimazu LC-20A) equipped with a RI detector and a Shodex^{TM} SH1011 column (10 μm, 6.5 × 300 mm). The conversion of cellulose was also estimated by the change of the weight of cellulose after the reaction.

2. Properties of Liquid Acids

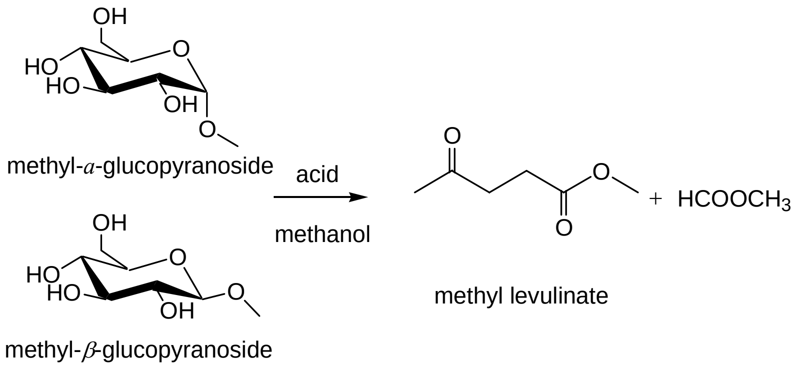
Table S1 shows some properties of the liquid acids used in Table 1 in the main text. Table 1 in the main text demonstrates that only dilute H_2SO_4 can provide a significant yield of methyl glucosides. H_2SO_4 is a relatively stronger acid with a pK_a of -3.00, while the pK_a values for HCl, HNO_3, H_3PO_4 and CF_3COOH are -4.00, -1.00, 2.15 and 0.52, respectively. Moreover, the boiling point of H_2SO_4 (610 K) is significantly higher than those of the other acids. Because we have used a reaction temperature of 473 K in our reaction, we speculate that the higher boiling point of H_2SO_4 may be beneficial for the catalytic conversion of cellulose at such a temperature.

Table S1 Some properties of liquid acids[a]

Acid	Boiling point /K	pK_a
HCl	334	-4.00
CF_3COOH	346	0.52
H_3PO_4	431	2.15
HNO_3	356	-1.00
H_2SO_4	610	-3.00

[a] CRC Handbook of Chemistry and Physics, 87th edition, 2006-2007.

3. Formation of Methyl Levulinate



Scheme S1. Formation of methyl levulinate from methyl glucosides.

4. Effect of Reaction Time on Catalytic Performances of Three Typical Catalysts for the Conversion of Cellulose in Methanol

Table S2 shows the effect of reaction time on catalytic performances of three typical acid catalysts, i.e., H_2SO_4, $H_3PW_{12}O_{40}$ and lig.-SO_3H-17% for the conversion of cellulose in methanol.

Table S2 Effect of reaction time on catalytic performances of three typical catalysts for the conversion of cellulose in methanol[a]

Catalyst	H^+ conc. /mmol L^{-1}	Time /min	Conv. /%	Yield[b] /% M-α-G	M-β-G	ML	TON[c]
H_2SO_4[d]	6.7	20	66	20	14	3.0	5.2
		30	76	28	20	2.8	7.4
		40	85	25	18	9.3	6.6
		60	90	20	14	16	5.2
$H_3PW_{12}O_{40}$	2.6	6	50	20	14	0.3	20
		20	71	28	20	1.0	29
		30	86	31	22	3.0	31
		40	88	27	20	4.0	28
		60	95	25	18	5.3	26
Lig.-SO_3H-17%	5.0	20	16	14	10	0	7.4
		30	59	22	16	0	12
		45	65	24	18	0	13
		60	72	28	20	0.50	15
		90	78	29	21	1.0	15
		120	82	35	26	3.0	19
		150	90	30	22	4.0	16

[a] Reaction conditions: cellulose, 0.50 g; methanol, 20 mL; temperature, 468 K. [b] M-α-G, M-β-G and ML denote methyl-α-glucopyranoside, methyl-β-glucopyranoside and methyl levulinate, respectively. [c] TON was calculated by the moles of methyl glucosides formed per mole of H^+. [d] Temperature, 473 K; methanol, 30 mL.

5. Activity and Structure of the Recovered $H_3PW_{12}O_{40}$ Catalyst after Reaction

The recovered $H_3PW_{12}O_{40}$ catalyst was re-used in the conversion of cellulose in methanol under the following conditions: cellulose, 0.50 g; N_2, 3 MPa; methanol, 20 mL; temperature, 468 K; time, 0.5 h. We obtained products of methyl-α-glucopyranoside, methyl-β-glucopyranoside and methyl levulinate with yields of 31%, 20% and 2.0%, respectively. These yields were quite close to those obtained in the first-time reaction (yields of methyl-α-glucopyranoside, methyl-β-glucopyranoside and methyl levulinate were 31%, 22% and 3.0%, respectively). Therefore, we conclude that there are no significant changes in activity for the recovered catalyst.

The recovered $H_3PW_{12}O_{40}$ catalyst has also been characterized by X-ray diffraction measurements. Fig. S1 shows that the XRD pattern for the recovered catalyst is almost the same with that for the fresh catalyst. Thus, it can be concluded that the structure of the $H_3PW_{12}O_{40}$ catalyst did not undergo significant changes after the reaction.

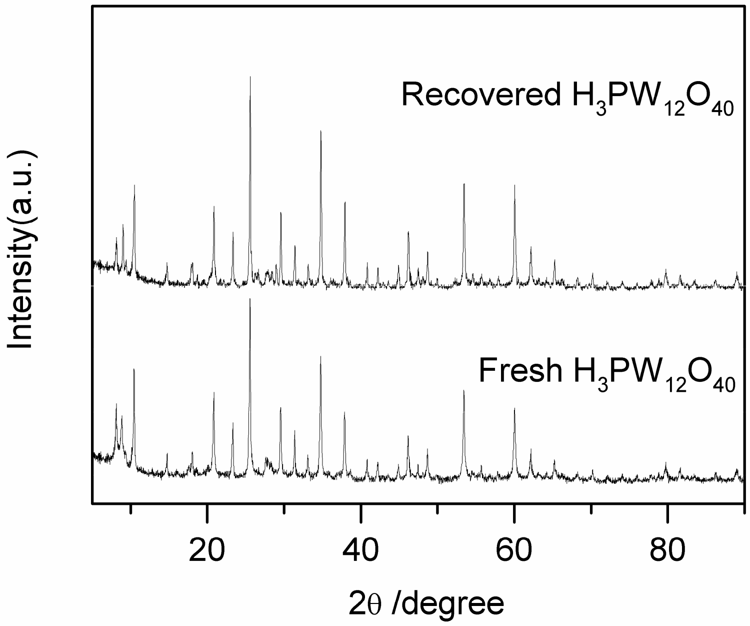


Fig. S1 XRD patterns of the fresh and the recovered $H_3PW_{12}O_{40}$ catalysts.

References

1 R. Srinivasan, T. Watkins, C. Hubbard and B. H. Davis, *Chem. Mater.*, 1995, **7**, 725.

2 S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi and M. Hara, *J. Am. Chem. Soc.*, 2008, **130**, 12787.

3 M. T. Pope, Heteropoly and Isopoly Oxometalates, Springer Verlag, Berlin, 1983.