Direct transformation of cellulose into ethanol catalysed by tungstic acid and zirconia supported Pt nanoparticles in water

Weiping Deng, Shi Li, Haiyan Song, Pan Wang, Qinghong Zhang, Ye Wang*

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

**Corresponding author: +86-592-2183047, wangye@xmu.edu.cn*

Abstract: The catalytic transformation of cellulose into ethanol provides a promising alternative route for sustainable production of biofuels from renewable biomass. Zirconia supported Pt nanoparticles (Pt/ZrO_2) in combination with tungstic acid is found to work bifunctionally and afford an ethanol yield of 31% from cellulose at 523 K in water. It has been clarified that tungstic acid acts as an active site for activation and breaking down C-C bonds within cellulose to C_2 intermediates, whereas Pt/ZrO_2 catalyses the selective cleavage of C-O bonds in C_2 intermediates to form ethanol.

Keywords: Cellulose, Ethanol, Bifunctional catalysis.

1. Introduction

Ethanol, as an attractive and alternative fuel, has received considerable attention because of its sustainable and environmental benign advantage over petroleum-based fuel.[1] Currently, the production of ethanol extensively relies on the fermentation of sugars that derived from agricultural feedstocks such as corn and sugarcane. Although the conversion of non-edible lignocellulose by enzymatic systems has recently emerged as a candidate route for ethanol synthesis, these systems suffered from the problems of easy deactivation of enzyme, mass transfer limitation, high cost etc.[2] Moreover, the emission of CO_2 is inevitable during the formation of ethanol in the fermentation processes,[3] which significantly reduced the efficiency of carbon atom utilization. In contrast, a chemocatalytic approach may offer new opportunities for conversion of cellulose to ethanol with high efficiency by using rationally designed, stable and cost-effective catalysts. Recently, an indirect two-step catalytic process has been proposed for the production of ethanol through the tungsten-promoted the oxidative conversion of cellulose to methyl glycolate in methanol, followed by a copper-catalyzed hydrogenation of methyl glycolate in tetrahydrofurfural.[4] However, to the best of our knowledge, there is still no direct chemocatalytic system presented for the transformation of cellulose to ethanol. Here, we report that zirconia-supported Pt nanoparticles combined with tungstic acid could efficiently catalyze the direct conversion of cellulose into ethanol in water in hydrogen. The reaction mechanism and functions of catalysts have also been analysed.

2. Experimental

Tungstic acid, and tungsten oxides purchased from Alfa Aesar were used as obtained. Pt nanoparticles loaded on zirconia and other supports were prepared by wet impregnation method. Microcrystalline cellulose purchased from Alfa Aesar with a crystallinity of 85% was used as a reactant. The conversion of cellulose was performed in a Teflon-lined stainless-steel autoclave. After the catalyst and cellulose (typically 0.2 g, equivalent to 1.2 mmol $C_6H_{10}O_5$ unit) were added into the autoclave pre-charged with water (typically 20 mL), H_2 of 4 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).

3. Results and discussion

Noble metal catalysts, in particular Pt, are active for the activation of C-O bonds via hydrogenation. By combining a Pt catalyst with tungstic acid, which has been employed to cleave the C-C bonds within cellulose, we expect to achieve the direct conversion of cellulose to ethanol in water. Figure 1 shows the catalytic performances of Pt catalysts loaded on several oxides such as Al_2O_3, MgO, ZrO_2, SiO_2 and CeO_2 for the conversion of cellulose in the presence of tungstic acid in water under H_2 at 523 K. Among these catalysts, Pt/ZrO_2 afforded the highest yield of ethanol (31%). Ethylene glycol, propylene glycol, and propanol are also formed with a total yield of 40%. Other catalysts, e.g. Pt/Al_2O_3, Pt/CeO_2, Pt/SiO_2, produce ethanol in yield of 10-19%, mainly giving ethylene glycol. This suggests that the supports have an influence on the product distribution. Compared to other oxides, ZrO_2 is reported to contain many oxophilic sites (e.g. Zr^{4+}, Zr^{3+}), which may facilitate the adsorption of hydroxyl group, thus favoring the activation of C-O bonds.[5] We have subsequently compared the performances of different noble metals including Pt, Pd, Rh, and Ru loaded on ZrO_2 for cellulose conversion. Pt/ZrO_2 remains the most active catalyst for production of ethanol (31%), which is two times higher than other metal catalysts. XPS analysis reveals that Pt nanoparticles are positively charged on ZrO_2. Upon reduction of Pt to metallic, the Pt/ZrO_2 results in a relatively low yield of ethanol (17%), and a high ethylene glycol yield (45%). This clearly indicates that positively charged Pt benefits the activation of C-O bond and promotes the formation of ethanol.

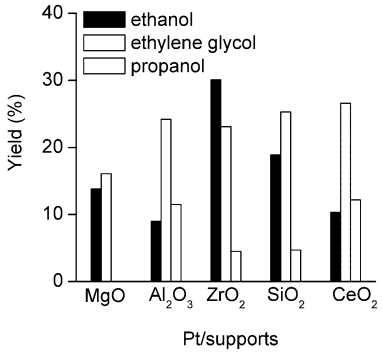
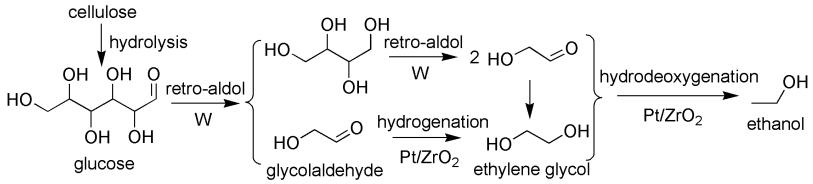


Figure 1. Catalytic conversion of cellulose to ethanol over Pt nanoparticles loaded on different supports. Reaction conditions: cellulose 0.2 g, Pt catalyst, 0.1 g, tungstic acid 0.1 g, H_2O 20 mL, H_2 4 MPa, 523 K, 5 h.

Tungstic acid also exerts effects on the formation of ethanol. In the absence of tungstic acid, Pt/ZrO_2 alone primarily facilitates conversion of cellulose to sorbitol; as tungstic acid is added, ethanol, ethylene glycol, and propanol are formed as major products. Similar results can be observed by using tungsten oxides as the co-catalyst, indicating the positive effect of tungsten in the C-C bond cleavage. Kinetic studies show that cellulose is firstly hydrolyzed to glucose and then undergoes retro-aldol fragmentation to form glycolaldehyde which is further converted to ethanol through hydrogenation and hydrodeoxygenation (Scheme 1). Combining these results together, we propose that tungstic acid catalyzes retro-aldol reactions that break the C-C bonds, whereas Pt/ZrO_2 is responsible for the hydrogenation and hydrodeoxygenation to cleave C-O bonds. Pt/ZrO_2 and tungstic acid can be recovered by filtration after reactions, and the catalytic performance is sustained.



Scheme 1. A proposed reaction path for the conversion of cellulose to ethanol.

4. Conclusions

Zirconia supported Pt nanoparticles (Pt/ZrO_2) and tungstic acid can provide an ethanol yield of 31% from the direct conversion of cellulose to ethanol at 523 K in water. Tungstic acid is active for the conversion of cellulose to C_2 intermediates via retro-aldol reaction, and Pt/ZrO_2 catalyses the subsequent hydrogenation and hydrodeoxygenation of C_2 intermediates to ethanol. The catalysts can be recycled without deactivation.

References

1. A. E. Farrell, R. J. Plevin, B. T. Turner, A. D. Jones, M. O'Hare, D. M. Kammen, Science 311 (2006) 506
2. X. Liu, W. Xu, L. Mao, C. Zhang, P. Yan, Z. Xu, Z. C. Zhang, Sci. Rep. 6 (2016) 20361
3. D. Kennes, H. N. Abubackar, M. Diaz, M. C Veiga, C. Kennes, J. Chem. Technol. Biotechnol. 91 (2016) 304.
4. G. Xu, A. Wang, J. Pang, X. Zhao, J. Xu, N. Lei, J. Wang, M. Zheng, J. Yin, T. Zhang, ChemSusChem 10 (2017) 1390.
5. P. M. de Souza, R. C. Rabelo-Neto, L. E. P. Borges, G. Jacobs, B. H. Davis,T. Sooknoi, D. E. Resasco, F. B. Noronha, ACS Catal. 5 (2015) 1318.