Gold Nanoparticles on Polyoxometalate as Efficient Catalysts for Selective Oxidation of Cellobiose and Cellulose to Gluconic Acid

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Introduction

Transformation of abundant renewable lignocellulose into chemicals has attracted much attention. Because of the robust crystalline structure, the selective transformation of cellulose under mild conditions remains a challenge. Many recent studies have been contributed to the hydrolysis or hydrogenation of cellulose to glucose or polyols over heterogeneous catalysts [1,2]. However, there are few papers on the selective oxidation of cellulose. Recently, we succeeded in oxidizing cellobiose, which is a D-glucose dimer connected by β-1,4-glycosidic bond and represents the simplest model molecule of cellulose, into gluconic acid over a Au/CNT catalyst [3]. It is expected that the design of a bifunctional catalyst containing acid support for cellobiose hydrolysis to glucose and Au nanoparticles for oxidation of glucose can enhance the direct oxidation of cellobiose or cellulose into gluconic acid. Polyoxometalates may play key roles in cellulose conversions because of their unique acidity. Here, we report a highly efficient polyoxometalate-supported gold catalyst for the selective oxidation of cellobiose and cellulose into gluconic acid. The effects of acidity and Au particle size on activity and selectivity will be discussed in detail.

Experimental

Keggin-type polyoxometalates, $Cs_xH_{3-x}PW_{12}O_{40}$ (x = 1.0-3.0), were synthesized with a procedure reported previously [4]. Supported Au catalysts were prepared by impregnation or by deposition-precipitation method [5], followed by drying at 353 K and H_2 reduction at 573 K. The catalysts were characterized by TEM, NH_3-TPD, XRD, IR and XPS techniques. The reaction was performed with a batch-type reactor, and the products were analyzed by HPLC.

Results/Discussion

Table 1 shows the catalytic performances of Au catalysts loaded on different supports for the selective oxidation of cellobiose in H_2O medium with O_2. Among the catalysts investigated, $Au/Cs_{2.2}H_{0.8}PW_{12}O_{40}$ exhibits the highest gluconic acid yield (86% at 418 K for 3 h reaction).

Particularly, the $Au/Cs_{2.2}H_{0.8}PW_{12}O_{40}$ catalyst provided significantly higher selectivity (99%) than other supported Au catalysts (including Au/CNT). We also studied the performances of $Cs_{2.2}H_{0.8}PW_{12}O_{40}$-supported various transition metal catalysts, and found that the supported Au catalyst demonstrated the best gluconic acid selectivity and yield.

Table 1. Selective oxidation of cellobiose by Au catalysts loading on various supports

Catalyst	Conv. /%	Selectivity /%			Gluconic acid yield /%
		Gluconic acid	Glucose	Others	
Al_2O_3	92	48	0	50	44
TiO_2	73	57	26	17	42
HZSM-5	20	70	20	10	14
CNT	83	84	0	14	70
$Cs_{3.0}PW_{12}O_{40}$	70	89	0	11	62
$Cs_{2.6}H_{0.4}PW_{12}O_{40}$	85	97	0	3	82
$Cs_{2.2}H_{0.8}PW_{12}O_{40}$	87	99	0	1	86
$Cs_{1.7}H_{1.3}PW_{12}O_{40}$	92	71	0	29	65
$Cs_{1.2}H_{1.8}PW_{12}O_{40}$	86	72	6	22	61

Reaction conditions: Au loading, 1 wt%; cellobiose, 0.3 mmol; H_2O, 25 ml; 418 K, 3 h. Others include glycolic acid, acetylpropionic acid, glucuronic acid, glyceric acid and acetic acid.

Our characterizations using NH_3-TPD and TEM revealed that the concentration of Brønsted acid sites in the $Au/Cs_xH_{3-x}PW_{12}O_{40}$ decreased with increasing Cs content from 1.2 to 3.0, and meanwhile, the size of Au nanoparticles decreased slightly from 4.2 to 2.5 nm. The catalytic performances of the $Au/Cs_xH_{3-x}PW_{12}O_{40}$ with different Cs contents (Table 1) are the interplay of acidity and Au particle size. The decrease in Cs content promoted cellobiose conversions by accelerating the hydrolysis, but too bigger Au particles over the $Au/Cs_{1.2}H_{1.8}PW_{12}O_{40}$ decreased the activity. It is of interest that gluconic acid selectivity also arrives at a maximum at a medium Cs content. A proper concentration of acid sites is proposed to enhance gluconic acid desorption, but too high an acid-site concentration might lead the formation of by-product. Our studies using catalysts with similar acidity but variable Au particle sizes, which were prepared by deposition-precipitation using urea under different conditions, clarified that the smaller Au nanoparticles favour the gluconic acid formation. Thus, a better catalyst should contain medium acidity and smaller Au particles. We further demonstrated that the $Cs_xH_{3-x}PW_{12}O_{40}$-supported Au nanoparticles were efficient for the hydrolysis/oxidation of cellulose into gluconic acid, and a gluconic acid yield of 54% was attained at 418 K for 11 h.

References

1. P. L. Dhepe, A. Fukuoka, *ChemSusChem*, **1**, 969, (2008).
2. S. Van de Vyver, J. Geboers, P.A. Jacobs, B. F. Sels, *ChemCatChem*, **3**, 82 (2011).
3. X. Tan, W. Deng, M. Liu, Q. Zhang, Y. Wang, *Chem. Commun.*, 7179, (2009).
4. M. Sun, J. Zhang, Q. Zhang, Y. Wang, H. Wan, *Chem. Commun.*, 5174, (2009).
5. W. Fan, J. Chen, Q. Zhang, W. Deng, Y. Wang, *Chem. Eur. J.*, **17**, 1247 (2011).