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Carbon nanotube-supported gold nanoparticles as efficient catalysts for selective oxidation of cellobiose into gluconic acid in aqueous medium†

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Gold nanoparticles loaded on nitric acid-pretreated carbon nanotubes are efficient for the selective oxidation of cellobiose by molecular oxygen to gluconic acid in aqueous medium without pH control; a gluconic acid yield of 80% has been obtained at 145 °C.

The development of novel routes for the transformation of renewable biomass resources into useful chemicals is of great importance for establishing sustainable chemical processes.[1] As the most abundant source of biomass and because of its non-edible nature, cellulose may be a promising sustainable feedstock for production of chemicals.[2] However, the direct utilization of cellulose is still a difficult challenge although limited success has recently been achieved in catalytic hydrogenation of cellulose into polyols.[3] The degradation of cellulose in ionic liquids, which can dissolve cellulose, has attracted much attention.[4] The development of an efficient heterogeneous catalyst for the conversion of polysaccharides containing a β-1,4-glycosidic bond is of major significance. Cellobiose, a D-glucose dimer connected by a β-1,4-glycosidic bond, may be viewed as a simple model of cellulose although differences exist in the structures of cellobiose and cellulose.[5] The study of catalytic conversions of cellobiose may provide helpful clues for the development of efficient routes for cellulose transformations. Moreover, the insights obtained from cellobiose conversions should also be useful for transformations of the decrystallized or soluble oligosaccharides released in hydrothermal or acidic treatments of cellulose.[6] Only a few reports exist on heterogeneous catalytic conversions of cellobiose by hydrolysis or hydrogenation in acidic aqueous medium.[7,8] Herein, we report a novel oxidative conversion of cellobiose to gluconic acid in the presence of oxygen catalysed by gold nanoparticles loaded on nitric acid-pretreated carbon nanotubes (CNTs).

Gluconic acid, an important intermediate widely used in the pharmaceutical and food industries, is mainly produced by enzymatic oxidation of glucose. Many recent studies showed that Au catalysts, especially Au nanoparticles supported on activated carbon (AC), could catalyze the oxidation of glucose to gluconic acid.[9] Thus, in this work, we first examined the possibility of the application of supported Au catalysts for the conversion of cellobiose to gluconic acid in aqueous medium without pH adjustment. We tested Au catalysts loaded on different types of supports, which were prepared by an impregnation method followed by H_2 reduction (see the ESI† for experimental details). Table 1 demonstrates that the Au/CNT catalyst provides the highest yield of gluconic acid. The employment of Al_2O_3, MCM-41 and MgO as supports also provided higher cellobiose conversions, but gluconic acid selectivity was lower. We have clarified that, as compared to these supports, the CNT is relatively inert toward the conversion of gluconic acid (see Table S1, ESI†). This may result in the higher gluconic acid selectivity of the Au/CNT. We have investigated the catalytic performances of some other CNT-supported transition metal catalysts, and clarified that the supported Au catalyst is unique for the selective oxidation of cellobiose to gluconic acid (see Table S2, ESI†).

Table 1 Catalytic performances of Au catalysts loaded on some typical supports (Au loading, 0.5 wt%) for cellobiose oxidation[a]

Catalyst	Surface area/ $m^2\ g^{-1}$	Cellobiose conversion/ %	Selectivity[b]/%		Gluconic acid yield/%
			Glucose	Gluconic acid	
Au/SiO_2	1.0	17	76	12	2.0
Au/Al_2O_3	277	93	6.5	19	12
Au/MCM-41	612	97	17	20	19
Au/H-ZSM-5	285	77	39	41	32
Au/MgO	106	100	0	10	10
Au/AC	1200	38	82	14	5.3
Au/graphite	4.0	48	40	31	15
Au/XC-72	163	58	64	21	12
Au/CNT	122	91	0	60	55

[a] Reaction conditions: catalyst (reduced at 350 °C), 0.050 g; T = 145 °C; cellobiose, 0.30 mmol; water, 20 mL; $P(O_2)$ = 0.5 MPa; time, 3 h. [b] Other products include acetic acid, glycolic acid, oxalic acid and succinic acid.

Further detailed studies were carried out using the Au/CNT catalysts to gain insights into the catalyst requirements for the selective oxidation of cellobiose to gluconic acid. Table 2 shows that the reduction temperature for the Au/CNT affects the catalytic performances. Only lower cellobiose conversion and gluconic acid selectivity were obtained at a reduction temperature of 200 °C. The increase in reduction temperature to 250 °C significantly increased both cellobiose conversion and gluconic acid selectivity. A gluconic acid yield of 68% could be obtained at a selectivity of 84%. XPS measurements revealed that the binding energy of Au $4f_{7/2}$ was 84.6 eV after H_2 reduction at 200 °C, and it shifted to 84.2 eV when the reduction temperature was raised to ≥ 250 °C (see Fig. S1, ESI†). This indicates that the Au species are reduced completely to

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† Electronic supplementary information (ESI) available: Experimental details, conversion of gluconic acid, oxidation of cellobiose over CNT-supported transition metal catalysts, Au 4f XPS spectra, TEM micrographs, effect of reaction temperature and time course for cellobiose conversions. See DOI: 10.1039/b917224f

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Table 2 Catalytic performances of the 0.5 wt% Au/CNT catalysts reduced at different temperatures for cellobiose oxidation[a]

Reduction temperature/°C	Cellobiose conversion/%	Selectivity[b]/% Glucose	Gluconic acid	Gluconic acid yield/%
200	54	61	26	14
250	81	3.7	84	68
350	91	0	60	55
500	94	0	60	56
250[c]	87	4	76	66
250[d]	75	3	81	61

[a] Reaction conditions: catalyst, 0.050 g; T = 145 °C; cellobiose, 0.30 mmol; water, 20 mL; $P(O_2)$ = 0.5 MPa; time, 3 h. [b] Other products include acetic acid, glycolic acid, oxalic acid and succinic acid. [c] After two repeated uses. [d] After three repeated uses.

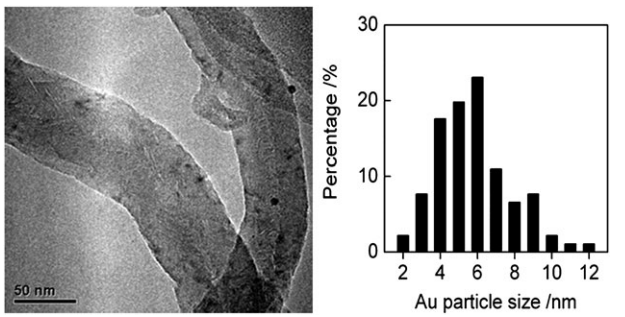

Fig. 1 TEM micrograph and Au particle size distribution for the 0.5 wt% Au/CNT catalyst reduced by H_2 at 250 °C.

Au^0 only at ≥ 250 °C.[10] TEM observations showed that the mean size of the Au particles was 5.8 nm for the catalyst reduced by H_2 at 250 °C (Fig. 1). The correlation of these characterization results with the significant increases in both cellobiose conversion and gluconic acid selectivity on increasing the reduction temperature from 200 to 250 °C (Table 2) suggests that Au^0 nanoparticles are responsible for the formation of gluconic acid. However, a further increase in the reduction temperature to 350 or 500 °C decreased gluconic acid selectivity to 60% although cellobiose conversion rose slightly. We found that the consecutive conversion of gluconic acid increased on increasing the reduction temperature from 250 to 350 and 500 °C (see Table S3, ESI†). We investigated the repeated uses of the Au/CNT catalyst reduced at 250 °C for cellobiose

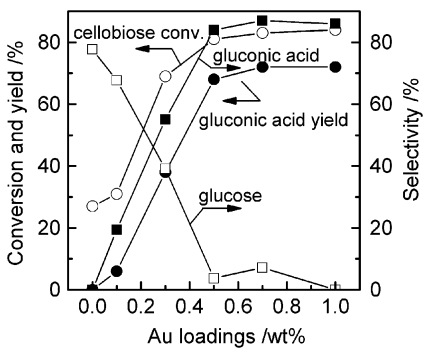

Fig. 2 Effect of Au loadings on catalytic performances of the Au/CNT catalysts for the selective oxidation of cellobiose. Reaction conditions: catalyst (reduced at 250 °C), 0.050 g; T = 145 °C; cellobiose, 0.30 mmol; water, 20 mL; O_2 pressure, 0.5 MPa; time, 3 h.

Table 3 Catalytic performances of the 0.5 wt% Au/CNT catalysts with CNT pretreated with different concentrations of HNO_3 or with HCl for cellobiose oxidation[a]

CNT pretreatment	Cellobiose conversion/%	Selectivity[b]/% Glucose	Gluconic acid	Gluconic acid yield/%
37 wt% HCl	68	0	44	30
5 wt% HNO_3	80	1.3	64	51
22 wt% HNO_3	84	1.3	73	61
37 wt% HNO_3	80	3.3	83	66
68 wt% HNO_3	81	3.7	84	68

[a] Reaction conditions: catalyst (reduced at 250 °C), 0.050 g; T = 145 °C; cellobiose, 0.30 mmol; water, 20 mL; $P(O_2)$ = 0.5 MPa; time, 3 h. [b] Other products include acetic acid, glycolic acid, oxalic acid and succinic acid.

conversion. The catalyst after each run was washed with water and then reused in the next run after drying. Cellobiose conversion and gluconic acid selectivity decreased only slightly after three repeated uses (Table 2).

To gain further information about the function of Au, we have investigated the effect of Au loadings on catalytic performances. As shown in Fig. 2, CNTs alone afforded a lower cellobiose conversion (27%), and the main product was glucose (selectivity ~80%) without any formation of gluconic acid. Because the blank reaction only gave a cellobiose conversion of 9% (glucose selectivity ~100%) under the same reaction

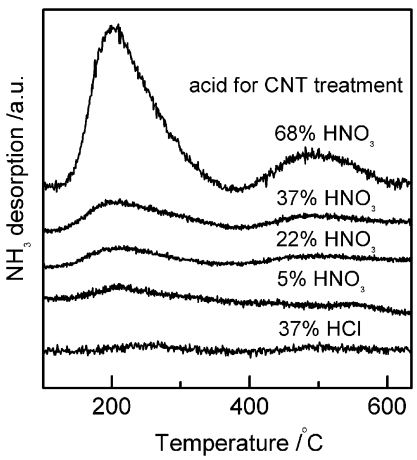

Fig. 3 NH_3-TPD profiles of the 0.5 wt% Au/CNT catalysts (reduced at 250 °C) with CNT pretreated with different concentrations of HNO_3 or with HCl.

Table 4 Effect of oxygen pressure on catalytic performances of the 0.5 wt% Au/CNT catalyst for oxidation of cellobiose[a]

O_2 (or N_2 or air) pressure/MPa	Cellobiose conversion/%	Selectivity[b]/% Glucose	Gluconic acid	Gluconic acid yield/%
0.3	68	16	75	51
0.5	81	4.0	84	68
0.5[c]	38	84	3.0	1.0
1.0	84	0	83	70
1.0[d]	73	18	73	53

[a] Reaction conditions: catalyst (reduced at 250 °C), 0.050 g; T = 145 °C; cellobiose, 0.30 mmol; water, 20 mL; time, 3 h. [b] Other products include acetic acid, glycolic acid, oxalic acid and succinic acid. [c] N_2. [d] Air.

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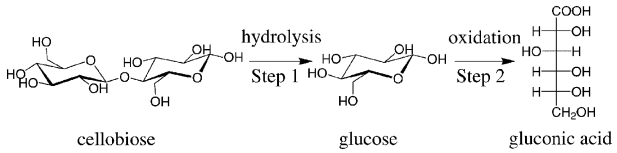

Scheme 1 Reaction pathways for the conversion of cellobiose to gluconic acid.

conditions, CNTs participated in the conversion of cellobiose to glucose. The loading of Au onto CNTs up to 0.5 wt% gradually decreased the selectivity to glucose (from ~80% to <5%) and increased that to gluconic acid (from 0 to ~85%). Cellobiose conversion was also remarkably enhanced by increasing the Au loading up to 0.5 wt%. Thus, Au nanoparticles not only account for the oxidation of glucose (a possible reaction intermediate) but also accelerate the conversion of cellobiose significantly.

The CNT was typically pretreated in concentrated HNO_3 under reflux conditions to remove the remaining Ni catalyst used for CNT preparation.[11] We found that the concentration of HNO_3 used for CNT pretreatment exerted an effect on catalytic performances of the Au/CNT catalyst. A lower concentration of HNO_3 caused lower gluconic acid selectivity (Table 3). Moreover, the use of HCl (37 wt%) to replace HNO_3 led to both lower cellobiose conversion and lower gluconic acid selectivity. We clarified that the Au/CNT catalyst with CNT pretreated with a lower concentration of HNO_3 or with HCl was more active toward the consecutive conversion of gluconic acid (see Table S4, ESI†). We have recently demonstrated that the concentration of HNO_3 used for CNT pretreatment affects the property of acidic functional groups formed on CNT surfaces.[12] NH_3-TPD studies for the present catalysts reveal that almost no NH_3 desorption occurs from the Au/CNT with CNT pretreated with HCl, whereas the desorption of NH_3 can be clearly observed over the catalysts with CNT pretreated with a higher concentration of HNO_3 (Fig. 3). We propose that the weak acid sites with a NH_3 desorption peak at ~210 °C may correspond to the carbonyl or hydroxyl groups, while the stronger ones with a NH_3 desorption peak at ~500 °C may be related to the carboxylic groups on CNT surfaces.[13] TEM measurements show that there are no significant differences among the mean sizes of Au nanoparticles in these catalysts (see Fig. S2, ESI†). Thus, the differences in catalytic performances among the catalysts in Table 3 may indicate that the acidic groups on catalyst surfaces contribute both to the conversion of cellobiose and to the inhibition of consecutive oxidation of gluconic acid.

Kinetic studies have been performed using the 0.5 wt% Au/CNT catalyst (reduced at 250 °C) to gain information on the reaction mechanism. On increasing the reaction temperature from 105 to 190 °C, cellobiose conversion increased from 12% and reached 100% at 175 °C (see Fig. S3, ESI†). Simultaneously, the selectivity to glucose decreased, while that to gluconic acid increased and reached a maximum at 145 °C. Further increase in temperature decreased the selectivity to gluconic acid and increased those to degradation products. The time course at 145 °C further demonstrated the change of glucose to gluconic acid in the initial 3 h (see Fig. S4, ESI†). A gluconic acid yield of 80% was achieved after 6 h of reaction, but a further prolonging of reaction time led to significant consecutive oxidation of gluconic acid to degradation products such as acetic acid, glycolic acid, oxalic acid and succinic acid. Oxygen pressure was also found to play a key role in gluconic acid formation. The use of N_2 instead of O_2 resulted in lower cellobiose conversion and almost no formation of gluconic acid (Table 4). The increase in O_2 pressure up to 0.5 MPa increased both cellobiose conversion and gluconic acid selectivity. Air can also be employed as an oxidant, but a higher pressure must be applied to reach similar cellobiose conversion and gluconic acid selectivity. These results confirm that glucose is formed as an intermediate *via* the hydrolysis of cellobiose and the oxidation of glucose by O_2 provides gluconic acid (Scheme 1). Furthermore, the latter step can accelerate the former step.

In summary, we have demonstrated that CNT-supported Au nanoparticles can efficiently catalyse the selective oxidation of cellobiose to gluconic acid by oxygen. The acidic groups on CNT surfaces play a role in the hydrolysis of cellobiose to glucose, the reaction intermediate, and the Au^0 nanoparticles account for the selective oxidation of glucose to gluconic acid by oxygen. The Au^0 nanoparticles also accelerate cellobiose conversion. The catalyst acidity also enhances gluconic acid selectivity by suppressing its consecutive conversion.

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