TiO$_2$-supported gold nanoparticles as efficient catalysts for oxidation of cellobiose into organic acids in aqueous medium

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TiO$_2$-supported Au nanoparticles were prepared by deposition-precipitation method, followed by reduction in hydrogen flow. The catalytic activity of these as-prepared catalysts has been explored in the oxidation of cellobiose into gluconic acid using molecular oxygen, while the properties of these catalysts were examined by XRD, TEM, NH$_3$-TPD, EDX, UV-vis and XPS. The catalyst sample reduced at high temperature showed remarkable catalytic activity in the oxidation of cellobiose. Characterization results showed the strong metal-support interaction between the Au nanoparticles and the TiO$_2$ support. Hydrogen reduction at higher temperatures (usually above 600 °C) plays a crucial role in affording a unique interface between gold nanoparticles and TiO$_2$ support surfaces, consequently enhancing the catalytic activity of Au/TiO$_2$ by fine tuning both the electronic and structural properties of the Au nanoparticle and TiO$_2$ support.

Introduction

It has been extensively discussed that biomass conversion will substantially contribute to the sustainable development of our society. The production of fuels and chemicals from renewable biomass has significant impact on decreasing CO$_2$ emission from fossil fuel combustion since the released CO$_2$ can be consumed during the subsequent re-growth of biomass. Among various biomass sources, cellulose is a promising candidate as it is abundant in nature, forms 40-50 % of biomass composition and also does not compete with food. Nonetheless, there are several technical issues that hamper the utilization of cellulose to produce energy fuels and platform chemicals [1].

Catalytic hydrotreating of cellulose has been investigated to produce a wide range of sugars and polyols such as glucose, ethylene glycol, propylene glycol and sorbitol, which are key raw materials or intermediates in petrochemical, pharmaceutical, food and cosmetic industries and also considered as a new generation of green energy platform [2, 3]. In addition to the cellulose hydrotreating process, selective oxidation of cellulose also attracted growing attention because it yields important bio-derived chemicals such as gluconic acid and its derivatives, which are widely used in pharmaceutical applications and in the food industry as water-soluble cleanser and additives [4]. Furthermore, air can be employed as the oxidant, which significantly reduces the processing cost as compared to hydrotreating processes.

For the direct conversion of cellulose into organic acids under oxidative atmosphere, bifunctional or multifunctional catalysts are often required [5]. These bifunctional catalysts not only perform cascade or multi-step reactions in one pot, but also may increase overall efficiency and product selectivity. A number of bifunctional catalysts have been tested for the oxidative conversion of glucose into organic acids. Recent studies showed that Au catalysts, especially supported Au nanoparticles, are able to catalyze the oxidation of glucose to gluconic acid [6].

Wang and co-workers examined the conversion of cellobiose (a representative compound of cellulose) over Au nanoparticles supported on various supports [7]. They found that CNT was the best support for the formation of gluconic acid in aqueous medium with cellobiose conversion of 91 % and gluconic acid selectivity of 60 % at a reaction time of 3 h. This group further investigated the conversion of cellobiose over CNT supported Pd, Pt, Rh, Cu and Ag catalysts. The best results were obtained with Pt/CNT catalyst (cellobiose conversion of 53 % and gluconic acid selectivity of 23 %) [7]. An et al. converted cellobiose into gluconic acid over Au nanoparticles loaded on Al$_2$O$_3$, HZSM-5, C$_{51}$H$_{13}$PW$_{12}$O$_{40}$ and C$_{51}$H$_{13}$PW$_{12}$O$_{40}$. A cellobiose conversion of 92 % and gluconic acid selectivity of 71 % over Au catalyst loaded on C$_{51}$H$_{13}$PW$_{12}$O$_{40}$ was achieved, being the most efficient catalysts for cellobiose conversion [8].

These results clearly showed that the nature of the support

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played an important role in cellobiose conversion. In addition, other parameters, such as reaction temperature, reaction time, pressure and solvent may also influence the conversion of cellobiose to organic acids, although the effects of these parameters have not been studied systematically. In this study, we report the work using Au nanoparticles supported on TiO₂ for the oxidation of cellobiose. In particular, the effect of reduction temperature of catalyst pretreatment was investigated. High temperature reduction under hydrogen atmosphere was generally considered to agglomerate the Au nanoparticles; surprisingly, the catalyst pre-reduced at high temperature in this study afforded excellent catalytic activity and selectivity toward desired organic acid. Furthermore, kinetics study was carried out and the reaction parameters such as temperature, pressure and solvent were optimized.

Results and Discussion

Catalytic activity of Au nanoparticles loaded on different supports

Catalytic oxidation of cellobiose over Au/TiO₂, Au/CNT and Au/HY (zeolite-HY) catalysts was carried out under the same reaction conditions and the results were shown in Figure 1. Although both CNT and zeolite (HY) supported Au nanoparticles were able to convert cellobiose into gluconic acid with a reasonably good selectivity, the catalytic results clearly indicated that TiO₂ outperformed other supports and the Au nanoparticles on TiO₂ showed the highest conversion and selectivity towards gluconic acid.

![Figure 1. Au catalyst loaded on various supports (HY, CNT, and TiO₂). Reaction conditions; cellobiose, 0.300 mmol; H₂O, 20 mL; Catalyst, 0.050 g; time, 3 h; O₂ pressure, 0.5 MPa (other reaction products includes: fructose, glycolic acid, sorbitol and ethylene glycol).](image)

The acid-base properties of different supports may not play a key role with respect to the selectivity towards gluconic acid because hydrolysis of cellobiose was not the limiting step [11]. Hence, oxidation was considered as the key step for high selectivity towards gluconic acid in one-pot oxidative conversion of cellobiose into gluconic acid. In view of this, finely tuning the properties of Au nanoparticles, e.g., particle size, electronic structure, and the specific interaction between gold and support will be able to control the catalyst selectivity towards gluconic acid. If the gold catalyst possessed a high activity for glucose oxidation, then the glucose produced via cellobiose hydrolysis which is considered as step 1, in the overall reaction mechanism should be readily converted into gluconic acid which is also considered as step 2, resulting in a high selectivity. Otherwise, glucose being multifunctional in nature will be substantially decomposed to complex degradation products, or the formed gluconic acid may suffer further hydrogenolysis to yield polyols during the reaction, resulting in a poor selectivity.

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Characterization of Au/TiO₂ catalysts reduced at different temperatures

NH₃-TPD characterization was conducted to survey the acid strength of the catalyst sample. Figure 3 represents the strength of acid sites on the supported TiO₂ catalyst. It is well documented...
that, catalytic activities are correlated with acid strength of a catalyst. And it is worth stating that, the strong Lewis acid center in the TiO₂ as indicated in figure 3 is responsible for the hydrolysis of cellobiose into glucose and that the cellobiose conversion greatly depends on the acid strength of the catalyst support. The peaks in the high and low temperature can be attributed to desorption of NH₃ from the strong and weak acid sites, respectively. The high temperature desorption ammonia was ascribed to desorption of coordinated NH₃ bound Lewis acid sites [8]. The peak at 261 °C was ascribed to the adsorption of ammonia on weak Bronsted acid sites of TiO₂ lattice while the strong and conspicuous peak appearing at 375 °C was attributed to the desorption of NH₃ on the strong Lewis acid sites of TiO₂. The latter acidity was the main acidity responsible for the cellobiose hydrolysis. The total acidity estimated from the analysis of NH₃-TPD was 354.54 µmol/g which were comparable to the acid strength of TiO₂ estimated by Yang et al. (362 µmol/g, with a BET surface area of 79 m²/g) [12].

Figure 3. 3 NH₃-TPD of Au/TiO₂ sample

The as-prepared TiO₂-supported Au nanoparticles were reduced under hydrogen flow at different temperatures and then characterized by various characterization techniques. Energy-dispersive X-ray spectroscopy (EDX) analysis revealed the existence of Au and Ti, indicating that Au nanoparticles were successfully deposited on the TiO₂ surfaces. The metal loading of Au determined by X-ray florescence (XRF) (1.1 wt. %) was consistent with the pre-decided value of Au loading during the catalyst synthesis. After the cellobiose oxidation, the catalyst was collected and dried. XRF analysis was carried out on the recycled catalyst and the metal loading of 1.0 wt. % was obtained, indicating that no significant leaching occurred and the Au/TiO₂ catalyst can be recycled. For brevity, the EDX image was not shown.

The gold nanoparticles observed by TEM are characterized with semispherical shape practically without well detectable crystallographic planes. The gold nanoparticles were homogenously dispersed on the TiO₂ support. The distributions of gold particle size for samples reduced at 400, 600 and 700 °C and the spent Au/TiO₂ (reduced at 700 °C) were presented in Figure 4. The particle size depended on the nature of the catalyst pretreatment, smaller gold particles were detected for samples reduced at 400 and 600 °C (particles sizes centered at 4-5 nm and 6-8 nm, respectively) than samples reduced at 700 °C (particles sizes centered at 10-12 nm). This was in agreement with the results reported by Tsubota et al. [13]. Hydrogen atmosphere and high temperature induced migration of metal clusters, which was evidently shown in the TEM image of the sample reduced at 700 °C as having larger particle size than the sample reduced at 600 °C. The TEM observation of spent sample (reduced at 700 °C) showed Au nanoparticles centered at 11-12 nm, indicating no significant particle size changes during the oxidation reaction.

Figure 4. TEM micrographs and particle size distribution of (a) 1 wt. % Au/TiO₂ – reduced at 400 °C, (b) 1 wt. % Au/TiO₂ – reduced at 600 °C, (c) 1 wt. % Au/TiO₂ – reduced at 700 °C and (d) Au/TiO₂ (after reaction)

Phase identification of fresh and spent Au/TiO₂ catalyst was performed by XRD, as given in Figure 5. The patterns exhibited strong diffraction peaks at 25°, 27.54°, 54.29°, 70° and 75°, suggesting the mixture of rutile and anatase phases of TiO₂ supports. The diffraction peaks at 2θ of 36.29°, 41.09° and 64.19° are attributed to the (111), (200), and (220) facets of its face-centered cubic (FCC) Au metal structure, respectively. Au particle sizes calculated from XRD using the Scherrer method was found to be in conformity with the particle sizes observed with TEM analysis. The XRD pattern of spent Au/TiO₂ catalyst (reduced at 700 °C) was similar compared to the XRD pattern of fresh Au/TiO₂ catalyst prior to catalytic reaction, suggesting that the gold nanoparticle on TiO₂ after reduction at 700 °C were stable during the oxidative conversion of cellobiose.
The UV-vis spectra of Au nanoparticles loaded on TiO\textsubscript{2} were shown in Figure 6. The absorbance in the visible region was significantly pronounced for Au/TiO\textsubscript{2} catalyst. The broad absorption peak appearing at 600 nm can be ascribed to the surface plasmon resonance of Au nanoparticles \cite{14}. Though Au had a low refractive index in the visible region, the high refractive index of TiO\textsubscript{2} caused the surface plasmon resonance to shift to a longer wavelength (red shift) from its nominal value of 520 nm in water \cite{15}. The red shift may also have been caused by the interaction between gold nanoparticles and TiO\textsubscript{2} support. The bands displayed between 300 and 400 nm are ascribed to TiO\textsubscript{2} in both spectra, which was in agreement with the UV-vis spectra of Au nanoparticles loaded on TiO\textsubscript{2} support reported by Kumaresan et al. \cite{16}.

To obtain information on the chemical states of the gold species, XPS was employed and Figure 7 compared the XPS spectra of Au 4\textit{f} core level performed on the Au/TiO\textsubscript{2} reduced under hydrogen flow at different temperatures. Each sample showed two peaks due to Au 4f\textsubscript{5/2} and to the Au 4f\textsubscript{7/2} transitions. The XPS spectra of Au 4f\textit{f} level for all samples were deconvoluted into three pairs of peaks with Au 4f\textsubscript{5/2} binding energy 83.7, 84.8 and 86.4 eV for Au\textsuperscript{0}, Au\textsuperscript{+} and Au\textsuperscript{3+} species, respectively for samples reduced at 400 °C; Au 4f\textsubscript{7/2} binding energy 83.0, and 84.2 eV for Au\textsuperscript{0} and Au\textsuperscript{3+} species, respectively for samples reduced at 600 °C and finally 83.0 and 85.9 eV for Au\textsuperscript{0} and Au\textsuperscript{3+} species, respectively for samples reduced at 700 °C \cite{23}. Samples reduced at low temperature (400 °C) showed the presence of both reduced gold nanoparticles (Au\textsuperscript{0}) and cationic nanoparticles (Au\textsuperscript{+} and Au\textsuperscript{3+}), suggesting that reduction at 400 °C cannot completely reduce all the gold species into the metallic state. For samples reduced at 600 and 700 °C, only the presence of Au\textsuperscript{0} and Au\textsuperscript{3+} oxidation states were observed.

In the case of the Ti 2p photoemission spectra, the XPS peaks of Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} binding energies were located at 459.3 and 464.8 eV, respectively, indicative of stoichiometric or defect free TiO\textsubscript{2} structure for samples reduced at 400 °C. In the case of Au/TiO\textsubscript{2} samples reduced at 600 °C, the Ti 2p\textsubscript{3/2} peak located at 458.8 eV, indicative of Ti\textsuperscript{3+}, while the peaks located at 460.1 and 464.9 eV were both indicative of Ti\textsuperscript{4+}. Catalyst sample reduced at 700 °C showed Ti 2p\textsubscript{3/2} peaks at 457.9 and 458.8 eV and Ti 2p\textsubscript{1/2} peaks at 459.7 and 464.5 eV, indicating that the valence state of Ti in TiO\textsubscript{2} reduced at 700 °C comprised a mixture of Ti (IV) and Ti (III). The Ti 2p peaks located at lower binding energy (457- 458.8 eV) were possibly due to the charge transfer by the overlayer Au nanoparticles under the reducing pretreatment conditions and adsorbed OH (or H\textsubscript{2}O) \cite{17}.

**Figure 5.** XRD patterns of (a) Au/TiO\textsubscript{2}-600 °C, (b) Au/TiO\textsubscript{2}-700 °C and (c) spent Au/ TiO\textsubscript{2} catalyst reduced at 700 °C.

**Figure 6.** UV-vis spectra of Au-TiO\textsubscript{2} reduced at different temperatures.

**Figure 7.** X-ray photoemission spectroscopy of Au/TiO\textsubscript{2} samples reduced at different temperatures.

**Correlation between catalyst structure and catalytic performance**

TEM characterization revealed the particle size of 6-8 nm and 10-12 nm for catalyst samples reduced at 600 and 700 °C, respectively, while catalyst samples reduced at 400 °C had particle size of 4-5 nm. It is obvious that, particle size increased...
with increased reduction temperature due to Ostwald ripening effect or particle size agglomeration [18]. However, the catalytic activity for cellubiose conversion into gluconic acid increased with increasing particle size, contrary to the reports in literature which emphasized on effective catalytic activity of Au nanoparticles having size below 5 nm [2, 3, 8, 7, 8]. This interesting observation prompted that, for catalytic oxidation, the activity of supported Au metal nanoparticles as a whole did not solely depend on the size range of the metal nanoparticles, but several other factors may also play critical roles in determining the activity.

As characterized by XPS, the electronic structure of Au significantly changed for samples reduced at 600 and 700 °C, which was characterized by the binding energy shift to a lower value. This shift in binding energy is as a result of the formation of a Schottky junction formed at the metal-oxide support interface. This unique interface allowed electron transfer to occur from the conduction band of the TiO2 support to the gold metal particles and this charge may be concentrated on atoms at the interface and periphery. The particles are then described as being ‘electron-rich’, thus creating oxygen vacancies at the oxide surfaces. These oxygen vacancies created at the oxide surfaces hence interacted strongly with the Au nanostructure which resulted in a significant rearrangement in the electronic structure of Au and also resulted in covalent bonding between the Au and the defect oxide support. The electrons that are stored in these chemical bonds led to the formation of active Au atoms in the vicinity of the Au-oxide perimeter interface and contributed to the catalytic process by providing an additional adsorption site for the reactant due to the effective nucleophilic attack of O=O substrate bonds by activated oxygen (O*) at the Au-oxide perimeter interface [18-28].

Furthermore, critical Au-O-Ti interactions which coupled the Au particles to the support were anticipated to be formed in the metal-support interaction. The Au-O bond being polarized to give the gold a partial positive charge and this interaction led to unique dual catalytic active sites for adsorbing and activating O2 [29]. In an equivalent view for the detailed mechanism of O2 adsorption and activation, Green et al. also reported a back-donation of electron density phenomena which creates unique Au-Ti site at the Au/TiO2 interface which is crucial in activating O2 because this unique Au-Ti site at the perimeter interface of the metal-support interaction allowed for electron transfer from Au to Ti and subsequent electron transfer into 2π* antibonding states of O2, aiding in O-O bond activation. Also adsorption of O2 thus occurred via δ-δ bonding to Au and Ti to form an Au-O-O-Ti state. The basic O/Au and O/Ti species residing at the perimeter interface of Au/Ti extracted electron density from the substrate and as such readily attacked bond C=O and C=C containing species and activate C-H and O-H bonds, thus catalyzing a range of partial and full oxidative reactions [30].

This hypothesis was supported by recent DFT studies by many researchers reported in literature [28, 31-34] which postulated that O2 dissociation was sensitive to the arrangement of the gold surface atoms and the most active sites for O2 dissociation are found at the metal-support interface and not the gold particle. It was thus reasonable to state that oxygen adsorbed on the edges, at the metal-support interface, and then migrates or diffuses to the surfaces of Au particles and as such oxidation reactions is thus said to also occur at the surfaces of Au nanoparticles because of the presence diffused O* which can initiate nucleophilic attacks on biomass substrates at the Au particle surfaces with subsequent reaction leading to the corresponding gluconic acid. Since theoretical studies reported in literature have shown that the active site for oxygen activation is the perimeter interface between gold nanoparticles and TiO2 support, a strong interaction should therefore be indispensable to afford high catalytic activity for cellubiose oxidation reaction [35].

The enhanced metal-support interaction that consequently constituted active sites for O2 adsorption and activation readily reacts with bound hydrocarbon intermediates via for the oxidation of C=O bonds contained in most biomass derived compounds and several carbonyl and aldehyde containing compounds [28]. Glucose, the main reaction intermediate which was oxidized to yield gluconic acid contains an aldehyde group (CHO), a primary alcohol group (CH2OH) and a secondary alcohol group (CH2–OH). The oxidation of the aldehyde group (-CHO) of glucose was what resulted in the formation of gluconic acid while the oxidation of both the primary and secondary alcohol to yield ketones is suppressed when the catalytic system used in the reaction is highly selective and active.

Indeed, the support properties can tune the interaction with the metallic particles deposited on or in it, thus modifying both the catalyst electronic and structural properties and also provide different anchoring sites for the reactants, acting as an active and sometimes reactive surfaces when strong metal-support interaction (SMSI) effects are induced. Our results and most reports by various researchers show that besides acid strength and density, and glucan sorption affinity, textural features of the support and electronic state of the nanoparticles as a result of electron transfer from the support to the Au nanoparticles during catalyst reductions under flowing hydrogen at high temperatures, critically determines catalyst success.

**Reaction parameter optimization for cellubiose Oxidation**

Further kinetic study was carried out over the Au/TiO2 catalyst to gain more insights into the reaction conditions to efficiently convert cellubiose into gluconic acid. Figure 8a shows the effect of the reaction time on cellubiose conversion and the distributions of oxidative reaction products. The pressure in the reactor is set at 0.5 MPa. Cellubiose conversion increases as the reaction time. The conversion sharply increases at the initial stage, reaching 93 % in 2 h, followed by a gradual increase slowly, and reaching 100 % after 12 h. The selectivity of gluconic acid did not follow the same trend. Gluconic acid selectivity is the highest at 2 h and decreases remarkably as the reaction time increases from 2 to 12 h, detailed analysis shows that gluconic acid further converted into other undesirable products such as lower carbon polyols at longer reaction time [34]. The best gluconic acid selectivity of 73.7% was obtained at 2 h of reaction and an oxygen pressure of 0.5 MPa, which is higher than those previously reported by An et al. (57 %) and Wang et al. (63 %). The difference can be attributed to different catalyst preparation method (impregnation) and lower reduction temperature (300 °C) they employed [8, 35].

The influence of oxygen pressure on cellubiose oxidation was studied by varying pressure from 0.5 to 2.5 MPa at 145°C (Fig. 8b). The conversion of cellubiose was almost constant with increased pressure from 0.5 to 2.5 MPa, which is higher than those previously reported by An et al. (57 %) and Wang et al. (63 %). The difference can be attributed to different catalyst preparation method (impregnation) and lower reduction temperature (300 °C) they employed [8, 35].

The conversion of cellubiose was almost constant regardless to the oxygen pressure. The increase in oxygen pressure influences the distribution of reaction products to a large extent. At an oxygen pressure of 0.5 MPa, a gluconic acid selectivity of 73.7 % with an appreciable amount of glycolic acid (25 %) was observed. The formation of ethylene glycol and glycolic acid with subsequent decrease in the selectivity of gluconic acid when the oxygen pressure was increased from 1.5 to 2.5 MPa indicates that the increase in the amount of dissolved oxygen directly affects the distribution of reaction products. This phenomenon was consistent with the results reported by An et al.
and the binding and activation of O₂ could be significantly enhanced in the presence of water, when O₂ and water are co-adsorbed on supported gold nanoclusters. Moreover, high temperature induces a degradation of sugars with fragmentation of the molecules, resulting in short chain carboxylic acids, aldehydes, etc. Although maximum cellobiose conversion is obtained at a temperature. Higher temperatures, 150 to 175 °C, favors the formation of C₂ polyols (ethylene glycol and glycolic acid), implying that high temperature may cause cellobiose to carbonize and the produced gluconic acid further convert to other undesirable oxidative by-products. Moreover, high temperature increases the selectivity of desired product, the optimum reaction temperature was set as 145 °C in this study.

In order to study the influence of solvent (water) on cellobiose conversion and product distributions, some experiments were carried out at varying solvent amounts (Figure 8d). The presence of water favors to a large extent the conversion of cellobiose. Water is essential to promote the hydrolysis reaction of cellobiose to the intermediate glucose. When different amount of water is added to the reaction system, a substantial increase in conversion of cellobiose is observed. As the water amount in the reaction system increases from 15 to 20 mL, the conversion of cellobiose increases further from 96.22 % to 97.86 %, but drops slightly 97.52 % as the amount of water increases further to 25 mL. The selectivity towards gluconic acid increases sharply from 56.86 % to 73.72 % when the solvent amount in the reaction system was increased from 15 to 20 mL, but drops dramatically to 61.18 % when the solvent amount was further increased to 25 mL. The distribution of the reaction by-products observed (glycolic acid and ethylene glycol) showed that, at 20 mL solvent amount, the selectivity towards glycolic acid decreases remarkably from 43 % (at solvent amount of 15 mL) to 25 %, with no traces of ethylene glycol. As the water amount was further increased to 25 mL, appreciable amount of ethylene glycol and glycolic acid were observed with a selectivity of 26 % and 12 %, respectively. This implies that the highest catalytic activity of Au/TiO₂ could be reached at a proper solvent amount.

Efforts have been made to understand the nature behind the promotion effect of water on the catalytic activity of Au/TiO₂ in the selective oxidation of cellobiose into gluconic acid. Theoretical studies have shown that, the OH groups originating from the dissociation of water could facilitate the O₂ adsorption on TiO₂, and the binding and activation of O₂ could be significantly enhanced in the presence of water, when O₂ and water are co-adsorbed on supported gold nanoclusters. Additionally, other studies have revealed that surface water can increase the number of oxygen vacant sites.

From the reaction pathway of our experimental results and some relevant literature information, one can visualize that the hydrogen species released from the dissociation of H₂O may readily react with the oxygen adsorbed on the catalyst, yielding very reactive OOH species which further decompose to form O* species and OH groups. The OH groups would combine first and then dissociate to release O* and H₂O species. The released O* species are highly mobile and would readily react with glucose, which is formed as a result of cellobiose hydrolysis, to form gluconic acid. This has evidenced that it is the O* species formed on the Au/TiO₂ in the presence of water that help to improve the catalytic activity of Au/TiO₂ in the conversion of cellobiose into gluconic acid and also shown that, the presence of an optimum amount of water in the reaction system helps to facilitate the O₂ adsorption and activation on the catalyst surface sites. A plausible activation mechanism of oxygen in the presence of water, as shown in scheme 1, is proposed for the oxidative conversion of cellobiose into gluconic acid over Au/TiO₂.

**Figure 8.** (a) Time course for cellobiose conversion over 1 wt. % Au/TiO₂ catalyst (reduced at 700 °C) for selective oxidation of cellobiose. Reaction conditions: catalyst, 0.050 g; Temperature, 145 °C; Cellobiose, 0.300 mmol; H₂O, 20 mL; O₂ pressure, 0.5 MPa. (Other products include: Fructose and sorbitol) (b) Effect of oxygen pressure on catalytic performance of 1 wt. % Au/TiO₂ catalyst (reduced at 700 °C) for selective oxidation of cellobiose. Reaction conditions; cellobiose, 0.30 mmol; H₂O, 20 mL; Catalyst, 0.050 g; time, 3 h. (Other products includes: sorbitol and fructose) (c) Effect of reaction temperature on catalytic performance of 1 wt. % Au/TiO₂ catalyst (reduced at 700 °C) for selective oxidation of cellobiose. Reaction conditions; cellobiose, 0.300 mmol; H₂O, 20 mL; Catalyst, 0.050 g; time, 3h; O₂ pressure, 0.5 MPa. (Other products includes: sorbitol and fructose) (d) Effect of solvent amount on catalytic performance of 1 wt. % Au/TiO₂ catalyst (reduced at 700 °C) for selective oxidation of cellobiose. Reaction conditions; cellobiose, 0.300 mmol; H₂O, 20 mL; Catalyst, 0.050 g; time, 3h; O₂ pressure, 0.5 MPa. (Other products includes: sorbitol and formic acid)

**Scheme 1.** Plausible activation of O₂ on the active sites of Au catalyst in the presence of water.
Insights into the reaction pathway

As mentioned earlier, reactions are first performed under the same reaction conditions by using TiO₂ support without gold nanoparticles and the main reaction product was glucose with a selectivity of 91%. Glucose oxidation under the same reaction conditions was also carried out and Table 1 shows the oxidative conversion of glucose by O₂ in H₂O over Au/TiO₂ catalysts reduced at different temperatures. Product analysis revealed the presence of gluconic acid, glycolic acid, sorbitol, ethylene glycol and erythritol (a mixture of C₂, C₆ and C₈ carboxylic acids). The formation of sorbitol may be as a result of in situ hydrogen produced. Similar reactions were performed using gluconic acid as the reactant, glycolic acid and ethylene glycol were the major products formed, indicating that gluconic acid which is a C₆ organic acid is further converted to smaller carbon containing organic compounds (C₂-organic acids) in the catalytic oxidation of cellobiose into gluconic acids.

The oxidation of glucose and gluconic acid gives a clearer insight into the reaction pathway, showing that sorbitol and erythritol (C₆ and C₄ organic compounds respectively) are formed from glucose while glycolic acid and ethylene glycol (both C₂ organic compounds) are formed from the deeper oxidation of gluconic acid. It also confirmed that a high reduction temperature resulted in better gluconic acid selectivity and less degradation products formed. The proposed mechanism of cellobiose oxidation is shown in Scheme 2.

The hydrolysis takes place via step 1 primarily catalyzed over TiO₂ surfaces, and the major product is glucose. This step is supported by the observation of a small amount of fructose, which is a typical product from glucose through isomerization. Step 2 represents the oxidation step with Au nanoparticles as the active sites, where glucose is further converted to gluconic acid in presence of oxygen. This step also yields other oxidation products such as ethylene glycol and glycolic acid through further hydrogenolysis of gluconic acid.

Conclusions

The catalytic activity of gold nanoparticles loaded on different supports was investigated, particularly focusing on the performance to selectively convert cellobiose into gluconic acid. Gold nanoparticles loaded on TiO₂ as a bifunctional catalyst showed superior catalytic activity for the oxidation of cellobiose into gluconic acid in water. The effects of key factors, such as the solvent (water) amount, reaction time, reaction temperature and oxygen pressure on the oxidation of cellobiose were also examined. Experimental results showed that cellobiose can be converted to gluconic acid with selectivity higher than 70% when the reaction was catalyzed by Au/TiO₂ at 145 °C, oxygen pressure of 0.5 MPa within a reaction time of 2 h. The conversion of cellobiose to gluconic acid catalyzed by Au/TiO₂ was observed to be a two-step reaction where cellobiose was first hydrolyzed to reducing sugar (glucose) and then subsequently oxidized in the presence of molecular oxygen to gluconic acid. In this process, the catalyst support, (TiO₂) promoted the cellobiose conversion into glucose by hydrolysis reaction while Au nanoparticles catalyzed the oxidation of glucose to gluconic acid.

Experimental Section

Catalysts preparation

Gold nanoparticles loaded on TiO₂ were prepared by the classic deposition-precipitation method. TiO₂ (10 g) was dispersed in 400 mL of DI water. An appropriate amount of HAuCl₄ solution (0.01 M) was added drop wise to this TiO₂ suspension while maintaining the pH at 6.5 by adding 0.1 M NaOH solution. The dispersion was thermostated at 70 °C and stirred vigorously for 2 h. After cooling down to room temperature, 0.5 g of magnesium nitrate dissolved in 100 mL of DI water was added and then stirred at room temperature for 1 h. The catalyst was then filtered, washed with DI water and dried in oven at 80 °C. The ground powder was reduced in flowing hydrogen at different temperatures for 4 h.

Au nanoparticles supported on CNT were prepared following the method reported by Murphy et al. [9]. Briefly, 0.5 mL of HAuCl₄·3H₂O aqueous solution (0.01 M) was mixed with 0.5 mL of trisodium citrate aqueous solution (0.01 M) and 18.4 mL of DI water. Ice-cold, freshly prepared 0.1 M NaBH₄ solution (0.6 mL) was then added to the above mixture under stirring. A measured amount of HNO₃ pretreated CNT (95%, Cnano) was added to the as-prepared gold nanoparticle suspension. Ethanol (6 mL) was introduced immediately under vigorous stirring and the mixture was ultrasonicated for 10 min. After stirring for an additional 10 h, the black solid was separated using a centrifuge, washed with DI water several times and then dried at 80 °C overnight.

Au supported on zeolite (HY) was prepared by a co-precipitation method. An appropriate amount of gold precursor (HAuCl₄) was dissolved in DI water. 0.5 g of HY was added to the aqueous solution, followed by adding sufficient amounts of urea.
pre-dissolved in 30 mL of DI water under vigorous stirring at 80 °C for 6 h. The solid was obtained by filtering and washing with DI water, followed by drying at 60 °C overnight. The ground powder was reduced for 4 h in flowing hydrogen of 20 mL/min.

Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 diffractometer under ambient conditions using CuKα radiation (λ = 0.15406 nm) from a Cu X-ray tube operated at 40 kV and 40 mA. The diffractograms were recorded in the 2θ range of 10-90°, in steps of 0.02° with a count time of 20 sec at each point. Prior to the test, samples were dried at 80 °C overnight. Transmission electron microscopic (TEM) images were obtained on JEOL JEM-2100F microscope, operating at an accelerating voltage of 200 keV. UV-vis spectra of the synthesized catalyst were recorded in the scan range of 210-900 nm, using a UV-visible spectrophotometer (Shimadzu model UV-2450; Shimadzu, Kyoto, Japan), equipped with an integrating sphere, with BaSO4 used as the reference.

Energy dispersive X-ray with an EDX-Gatan cyrotransfer system JSM-6700F and X-ray fluorescence analysis were also performed on the sample to confirm the Au loading present. Samples were also analyzed by X-ray photoemission spectroscopy (XPS). XPS spectra were collected with a Thermo Escalab 250 spectrometer. Spectra were recorded using Al anode (Al Kα = 1486.6 eV) with a 20 eV pass energy, a 0.1 eV energy step and 0.1 s dwelling time. Energy corrections were performed using C 1s (284.6 eV) with a 20 eV pass energy, a 0.1 eV energy step and 0.1 s dwelling time. Energy corrections were performed using C 1s (284.6 eV) as a reference. Temperature programmed desorption of NH3 (NH3-TPD) was performed on a Micromeritics AutoChem 2920 apparatus. The amount of 200 mg catalyst was placed into a quartz U tube, heated for 2 h at 600 °C in Ar, and then kept at 100 °C for NH3 adsorption. When saturated adsorption was achieved, the system was swept by He for 3 h. Then the temperature was programmed to increase to 600 °C under the heating rate of 10 °C/min. The desorbed NH3 was analyzed by a TCD detector.

Catalytic cellobiose oxidation

The oxidative conversion of cellobiose was performed in a 50 mL batch reactor with Teflon liner (PARR instrument). Cellobiose (typically, 0.300 mmol) and catalyst (0.050 g) were added into the reactor pre-charged with DI water. The system was charged with pure O2 at a controlled pressure, after removing air by pressurizing and de-pressurizing several times with pure O2. The reaction was performed at different reaction conditions under steady stirring (1200 rpm). After reaction, products were analyzed by liquid chromatography equipped with a RID – 6A refractive index detector and a Hi-Plex H (300 × 6.5 mm) column with 0.01 M H2SO4 acid solution as mobile phase (flow rate of 1 mL/min).

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Anchoring Gold nanoparticles on TiO₂ support for enhanced catalytic activity: Au/TiO₂ pretreated under hydrogen flow at high temperature exhibits a superior catalytic performance than samples reduced at lower temperatures and was particularly excellent in oxidative conversion of cellobiose into gluconic acid due to its extra enhanced catalytic sites that favors and promotes molecular oxygen adsorption and activation.