Aqueous Oxidation of Sugars into Sugar Acids Using Hydrotalcite-supported Gold Nanoparticle Catalyst under Atmospheric Molecular Oxygen

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Hydrotalcite-supported gold nanoparticles show good activity as a heterogeneous catalyst for the oxidation of monosaccharides (xylose, ribose, galactose and mannose) and disaccharides (lactose and cellobiose) into the corresponding sugar acids under external base-free conditions in water solvent using atmospheric pressure of molecular oxygen. The produced sugar acids were thoroughly identified by ^{1}H-, ^{13}C-, and HMQC-NMR and ESI-FT-ICR MS spectroscopic techniques.

Sugar acids have many significant applications in various industrial fields.[1–3] For example, metal complexes with sugar acids have versatile industrial applications such as water purification and asymmetric organic syntheses. 1,2,4-Butanetriol, a precursor of butanetriol trinitrate, has been synthesized from xylonic acid.[4] Lactobionic acid can be applied in the therapeutic, pharmaceutical, and food grad fields.[5]

Sugar acids can be obtained from the oxidation of sugars derived from biomass (cellulose and hemicellulose biomass), which is considered a cheap, easily available, and renewable resource in the near future. The present industrial processes that convert sugars into specialty chemicals are mainly based on fermentation or enzymatic steps, which require strict reaction condition control.[6] Generally, the chemical oxidation of sugars has been performed with supported metal catalysts in the presence of base (pH between 8–9) at 323–343 K using air or oxygen as an eco-friendly oxidizing agent.[7–9] Lactose has been oxidized into lactobionic acid using supported metal catalysts with bases such as NaOH.[8] Xylonic acid, galactonic acid, mannonic acid, ribonic acid, and cellobionic acid have also been produced using supported metal catalysts in alkaline medium.[9] In the presence of base, the salts of sugar acids are formed, which require additional neutralization or acidification.[10]

Gold nanoparticles and clusters show noticeable catalytic activity.[11] In the case of sugar oxidation, supported Au catalyst has better activity than Pt.[8d] Furthermore, Au-based catalysts are cheaper than Pt-based ones.[8b,10] Hydrotalcite (HT) is known to have a double layered structure with brucite-like layers, which shows a basic nature due to the OH^- and HCO_3^- species even in water. Therefore, HT has been used as heterogeneous base catalyst for epoxidation, aldol condensation, condensation of carbonyl group, reduction of unsaturated carbonyl compounds, and biodiesel synthesis[12] and as a metal support.[11i] Kaneda et al. reported that Au/HT acted as an efficient catalyst for the oxidation of various monoalcohols and diols into the corresponding carbonyl compounds and lactones using molecular oxygen[13] as well as the deoxygenation of epoxides into olefins.[14]

Recently, we found that an HT-supported Au catalyst could oxidize 5-hydroxymethylfurfural (HMF) into the corresponding carboxylic acid,[15] and glucosamine–HCl and its derivatives into α-amino acids, under base-free conditions in water.[16] In this study, we have extended the base-free oxidation system using an HT-supported Au catalyst to various sugars in water using atmospheric pressure of molecular oxygen (Scheme 1).

Au/HT was prepared by a deposition–precipitation method using $HAuCl_4 \cdot 4H_2O$ and HT (Mg/Al = 5.4), supplied by WAKO and Tomita Pharmaceutical Co., Ltd., respectively (see Supporting Information (SI)). The oxidation of sugars was performed in a 30 mL Schlenk flask in 7 mL of water solvent at 313 K with stirring (500 rpm) under atmospheric O_2 flow (10 mL min⁻¹). The products were analyzed by using a HPLC equipped with a Shodex Asahipak NH2P-50 4E column at 308 K with pure water as the eluent (1.0 mL min⁻¹). Maleic acid was used as an internal standard. An isolated product (as white powder) by evaporation was subjected to ^{1}H-, ^{13}C-, and HMQC-NMR and ESI-FT-ICR MS spectroscopic techniques.

Table 1 lists the results of xylose oxidation to xylonic acid in water solvent using different supported Au catalysts under 1 atm O_2 with the actual amount of Au loading. The turnover number (TON) is defined as the ratio of moles of product to moles of the supported metal. Au/SiO$_2$ was completely inactive under the present conditions (Entry 5). In the previous study, Au/Al$_2$O$_3$ was found to be a good catalyst for the oxidation of
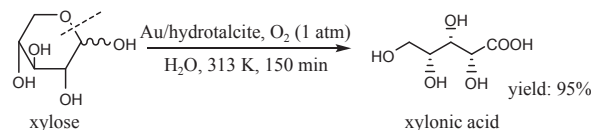

Scheme 1. Aqueous oxidation of xylose into xylonic acid using Au/HT catalyst under 1 atm of molecular oxygen.

Table 1. Xylose oxidation into xylonic acid in water using different supported Au catalysts under 1 atm molecular oxygen and TON[a]

Entry	Catalyst	wt %[b]	Conv./%[c]	Yield/%[c]	TON
1	Au/HT	1.7	100	94.8	110
2	Au/CeO$_2$	1.9	41.3	9.9	12
3	Au/TiO$_2$	1.8	37.0	8.1	9
4	Au/Al$_2$O$_3$	1.8	49.7	7.2	8
5	Au/SiO$_2$	1.7	27.1	0	0
6	—	0	0	0	0

[a]Reaction conditions: catalyst 50 mg, xylose 0.5 mmol, H$_2$O 7 mL, 313 K, 150 min, O$_2$ flow (10 mL min⁻¹), 500 rpm. Determined by [b]ICP and [c]HPLC.
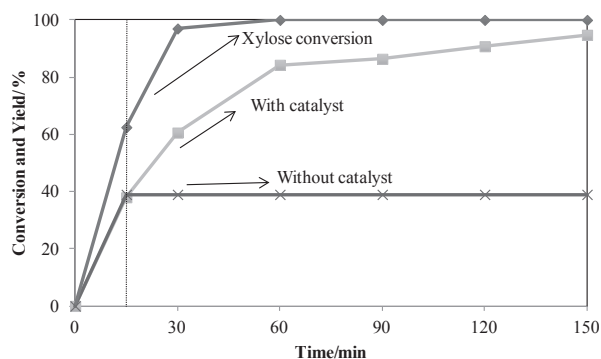
Figure 1. Time courses for xylose oxidation with Au/HT catalyst (■) and after removal of catalyst at 15 min (×). Reaction conditions: Au/HT 50 mg, xylose 0.5 mmol, H_2O 7 mL, 313 K, O_2 flow (10 mL min^{-1}), 500 rpm.
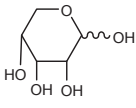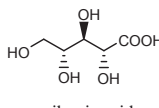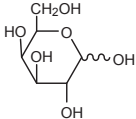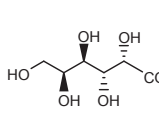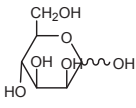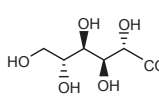
sugars in the presence of a homogeneous base;[17] however, in the absence of a homogeneous base, Au/Al_2O_3 gave xylonic acid with very low yield (Entry 4). Au/TiO_2 and Au/CeO_2 also showed low activities for xylose oxidation (Entries 2 and 3). It is noted that the TEM images suggested that although Au/CeO_2 and Au/SiO_2 possessed nanosized Au particles on the s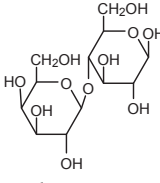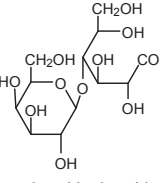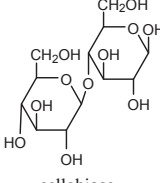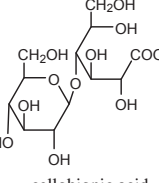upport, these were inactive under the base-free reaction condition (see SI). It was found that only the Au/HT catalyst exhibited high activity under such mild reaction conditions, with a high TON of over 100 (Entry 1). It is proposed that the Au^0 nanoparticles (3.2 nm in average size)[15] and base sites of the HT surface work cooperatively for the oxidation of xylose.[18] This result indicated that, as reported alcoholic oxidation reaction over Au/HT catalyst,[13,15,16] the surface basicity on HT could effectively proceed proton abstraction to form the Au-alcoholate intermediate smoothly, and then enhance the aerobic oxidation of sugars toward sugar acids in water.

Figure 1 represents the time course for xylose oxidation over the Au/HT catalyst. Xylose was completely converted within 60 min and the yield of xylonic acid gradually increased to over 90%. A simple increase of xylonic acid during the reaction suggests that the present oxidation occurs without any intermediates. In order to check the heterogeneity of this oxidation reaction, the Au/HT catalyst was removed at 15 min by hot-filtration and the yield was monitored continuously. As shown in Figure 1, a cease of the reaction after catalyst removal was clearly observed, indicating that the present reaction occurs in a heterogeneous manner.

Encouraged by the above results, we further applied this catalytic system to the aerobic oxidation of other sugars such as ribose, galactose, mannose, lactose, and cellobiose into the corresponding sugar acids. The results are summarized in Table 2. Various mono- and disaccharides could be efficiently oxidized into the corresponding sugar acids with high yields under mild reaction conditions within three hours.[19] The produced sugar acids were thoroughly characterized by ^1H-, ^{13}C-, and HQMC-NMR and ESI-FT-ICR-mass spectroscopic techniques (see SI).

In conclusion, various sugars could be efficiently converted into the corresponding sugar acids using Au/HT heterogeneous catalyst and 1 atm of O_2 in water solvent. This work opens-up a catalytic way for the synthesis of biomass-based fine chemicals.

Table 2. Aqueous oxidation of aldose sugars into the corresponding aldonic acids using Au/HT catalyst under 1 atm of O_2[a]

Entry	Substrate	Product	Time/min	Yield/%
1	ribose	ribonic acid	150	90.5
2	galactose	galactonic acid	120	87.1
3	mannose	mannonic acid	120	80.1[b]
4	lactose	lactobionic acid	180	96.1
5	cellobiose	cellobionic acid	180	92.3

[a]Reaction conditions: 1.7 wt % Au/HT 50 mg, substrate 0.5 mmol, H_2O 7 mL, O_2 flow (10 mL min^{-1}), 313 K, 500 rpm. [b]Determined by NMR (see Supporting Information).

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