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Short communication

# Toward glucuronic acid through oxidation of methyl-glucoside using PdAu catalysts



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# ABSTRACT

The production of glucuronic acid via enzyme catalysis from biomass is slow. Here we studied the oxidation of methoxy-protected glucose (MG) using Pd-on-Au nanoparticle model catalysts to generate methoxy-protected glucuronic acid (MGA), a precursor to glucuronic acid. Pd-on-Au showed volcano-shape activity dependence on calculated Pd surface coverage (sc). The 80 sc% Pd-on-Au catalyst composition showed maximum initial turn-over frequency (413 mol-MG mol-surface-atom<sup>-1</sup> h<sup>-1</sup>) that was 5× higher than that of Au/C, while Pd/C was inactive. This Pd-on-Au composition gave the highest MGA yield (46%), supporting a bimetallic approach to glucuronic acid production.

#### 1. Introduction

Biomass-derived carbohydrates are a promising feedstock due to their natural abundance. [1,2] Value-added chemicals can potentially be produced from carbohydrates by applying dehydration, hydrogenation, and oxidation treatments [1]. Carboxylic compounds from the oxidation of carbohydrates is of particular interest [3,4]. One example is glucuronic acid, a precursor for pharmaceutical chemicals (e.g. heparin and hyaluronic acid) and drink additives (e.g. glucuronolactone) [5]. Current commercial processes to produce glucuronic acid include the aerobic enzymatic oxidation of glucose by *Ustulina deusta* bacteria and *Bacterium industrium* var. *Hoshigaki* [6]. However, these suffer from low productivity. Efforts have been made to improve the productivity by using homogeneous catalysts [7], but their separation from the product is problematic. Heterogeneous catalysts are widely investigated due to their fast biomass conversion, and are, by definition, readily separable from reaction mixtures [8].

In the liquid-phase catalytic oxidation of glucose over heterogeneous platinum catalysts, selectivity to glucuronic acid (i.e. glucose oxidized at the  $C_6$  primary alcohol group) is low, forming mostly gluconic acid (i.e. glucose oxidized at the  $C_1$  carbonyl group) instead [9]. This highlights a problem with glucose as a biomass feedstock for glucuronic acid [10,11]: its selective conversion to the desired product is challenging, due to the competing functional groups. Protecting groups on the glucose ring can be used to control selectivity, as reported recently, for example, by Chen et al. [12]. The protection of the oxidatively more active  $C_1$  carbonyl groups was reported to increase the selectivity toward the glucuronate structure by the oxidation of  $C_6$  primary alcohol groups. [13–16] Acid hydrolysis can be subsequently used to remove the protecting group to generate the glucuronic acid [15].

However, the reported examples of heterogeneously catalyzed oxidation of protected glucose were not straightforward to carry out; there is ample room to improve catalyst activities and glucuronic acid selectivities [13-16]. van Dam et al. studied glucose 1-phosphate oxidation at 30 °C and pH 9 using activated carbon supported monometallic platinum (Pt/C) [13]. The authors reported ~70% conversion of 0.1 M glucose 1-phosphate to glucuronic acid 1-phosphate at ~60% selectivity using 40 g/L 5wt%Pt/C after 23 h. Schuurman et al. studied MG oxidation using a similar catalyst at the reaction conditions of 20-40 °C and pH 7-10 [14]. They reported ~80% conversion of 0.5 M MG and ~70% selectivity to MGA after 28 h at 35 °C and pH 7. Catalyst deactivation was observed in both cases though, due to platinum overoxidation. Yuan et al. studied the MG oxidation using supported palladium at 70 °C and pH 9 [15,16]. The authors found that the commercial carbon supported palladium (Pd/C) catalyst was inactive in MG oxidation, but a complex metal oxide (e.g., La<sub>0.5</sub>Pb<sub>0.5</sub>Mn<sub>0.9</sub>Sn<sub>0.1</sub>O<sub>3</sub>) supported palladium led to  $\sim$ 76% yield of glucuronic acid.

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**Scheme 1.** Direct synthesis of glucuronic acid via biocatalyzed glucose oxidation (red path), and indirect synthesis of glucuronic acid via metal-catalyzed MG oxidation (blue path).

Bimetallic catalysts (e.g. PdPt, PdAu, and PtAu) have enhanced activity, selectivity and/or stability compared with monometallic catalysts for aqueous alcohol oxidation, which is commonly attributed to a combination of geometric and electronic effects [17,18]. PdAu is one of the most widely studied bimetallic catalysts for primary alcohol oxidation. Silva et al. reported > 5 times improvement in activity using Au@Pd core-shell NP catalysts compared to monometallic Au and Pd for the oxidation of benzyl alcohol, for example [19]. Hutchings's group prepared carbon-supported PdAu alloy NPs catalysts and found they gave  $\sim 80\%$  selectivity to glyceric acid from glycerol oxidation and were 50% more active than supported monometallic Pd and Au NPs [20]. Our group has investigated structure-property relationships of Pd-on-Au NPs for the oxidation of glycerol; the catalytic NPs exhibited volcano-shaped activity dependence on Pd surface coverage, and had ~10 times higher activity than monometallic Pd or Au catalysts [21,22]. Also, these Pd-on-Au NPs showed improved resistance to deactivation from Pd over-oxidation [21,23].

In this work, we explored the oxidation of MG using Pd-on-Au NP model catalysts to generate MGA as a precursor to glucuronic acid (Scheme 1). We studied if these materials also exhibited volcano-shape oxidation activity dependence on Pd surface coverage. We quantified MGA selectivity and yield in relation to Pd surface coverage.

# 2. Experimental

## 2.1. Catalyst preparation and characterization

The carbon-supported NP catalysts were synthesized as reported previously [21,24]. The detailed material usage, preparation procedures and catalyst characterization were provided in Supplementary information.

#### 2.2. Catalytic testing

MG oxidation was conducted using a screw-cap bottle (100 mL, Alltech) as a semi-batch reactor. The bottle was capped by a teflon-silicone septum with one stainless steel needle inserted into the liquid as oxygen inlet, and a shorter one above the liquid as gas outlet. MG was added to 50 mL DI water at a concentration of 0.1 M. The solution pH was adjusted to 13 by adding 80 mg NaOH to the solution. The reactor was placed in an oil bath on a heating plate to control the temperature at 50 °C and magnetically stirred. After the temperature of liquid stabilized (~30 min), O<sub>2</sub> flow (100 mL min<sup>-1</sup>) was started, the stirring rate was increased to 1200 rpm, and 10 mg catalyst was added to start the reaction.

Aliquots of the reaction fluid (1 mL) were periodically withdrawn by a 5 mL plastic syringe via a stainless steel needle, filtered by a  $0.2 \,\mu$ m syringe filter (25 mm, VWR), stored in the 1 mL clear shell vials  $(8 \times 40 \text{ mm}, \text{VWR})$ , and analyzed by ion-exclusion high-performance liquid chromatography (HPLC).

A Shimadzu Prominence SIL 20 system (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA) equipped with an HPX-87H organic acid column (Bio-Rad, Hercules, CA, USA), a refractive index detector (RID), and a UV detector (210 nm) was used to separate and detect the reaction products. The operation conditions for the Shimadzu HPLC were at 42 °C with 30 mM  $\rm H_2SO_4$  as mobile phase flowing at 0.3 cm<sup>3</sup> min<sup>-1</sup>.

Pure reactant MG and reaction products (MGA, glyceric acid, oxalic acid, glycolic acid, formic acid, acetic acid, and lactic acid) standards were used to determine retention times, and concentration-peak area calibration curves were prepared in the range of 0 to 0.2 M. A slight loss in liquid volume due to water evaporation was observed during the reaction (~0.65 mL volume loss after 1 h at 50 °C), for which the measured concentrations were corrected during calculation. pH was checked before and after reaction, and no significant pH change was observed (< 0.4).

The conversion of MG  $(X_{MG})$  was defined as

$$X_{MG} = \frac{C_{MG,0} - C_{MG}}{C_{MG,0}}$$
(1)

where  $C_{MG,0}$  is the initial MG concentration and  $C_{MG}$  is the MG concentration at each sampling time. The MG oxidation reaction over the whole reaction time (8 h) cannot be modeled as pseudo first-order reaction since the generated products can also react on the catalyst surface competing with the MG oxidation. Due to the low amount of reaction products at beginning of reaction, MG oxidation was the dominant reaction. Thus, initial first-order reaction rate constants were calculated using data collected in the first 2 h:

$$-\frac{dC_{MG}}{dt} = k_{meas} \times C_{MG}$$
<sup>(2)</sup>

The initial apparent first-order reaction rate constant  $k_{meas}$  (with units of  $h^{-1}$ ) was obtained from the following equation:

$$-\ln\left(\frac{C_{MG}}{C_{MG,0}}\right) = k_{meas} \times t \tag{3}$$

Initial turnover frequency, normalized to the estimated moles of exposed catalytic surface atoms, (*TOF*, with units of mol-MG mol-surface-atom<sup>-1</sup> h<sup>-1</sup>) was given by:

$$TOF = \frac{k_{meas} \times C_{MG}}{C_{metal}} \tag{4}$$

where  $C_{metal}$  is the surface metal content of the catalysts. The amount of surface metal was estimated using the magic cluster model [25–28], where the 4 nm carbon-supported monometallic Au and Pd NPs were modeled as clusters with 7 shells of atoms, and the surface atoms were estimated to be the atoms in the 7th shell of the cluster. For carbon-supported Pd-on-Au NPs with Pd surface coverages < 100 sc%, all Pd atoms were assumed to be surface atoms in the 8th layer and uncovered Au atoms in the 7th layer were also counted as surface atoms. For Pd surface coverages > 100 sc%, the surface atoms were the Pd atoms in the 9th layer and the exposed Pd atoms in 8th layer. The charge amounts of catalysts with different surface coverage to reactor are shown in Table S4.

To quantify the percentage of reactant MG converted to the desired product MGA for different surface coverage catalysts, yield ( $Y_{MGA}$ ) of MGA using each catalyst was defined as:

$$Y_{MGA} = \frac{C_{MGA}}{C_{MG}} \tag{5}$$

where  $C_{MGA}$  and  $C_{MGA}$  is the MGA and MG concentration, respectively. MGA selectivity ( $S_{MGA}$ ) was defined as:

$$S_{MGA} = \frac{C_{MGA}}{C_{MG,0} - C_{MG}}$$
(6)

#### 3. Results and discussion

#### 3.1. Catalyst structure

Fig. S1a shows a TEM image of carbon-supported 80 sc%. Pd-on-Au NPs. The dark black spheres were the NPs while the gray regions was the carbon support. The NPs had a narrow size distribution, with a mean diameter of  $4.2 \pm 0.6$  nm (Fig. S1b). Elemental analysis via ICP-OES of Pd-on-Au NPs with calculated 0, 30, 80, and 150 sc% (Table S5) confirmed that actual metal content was close (within 2%) to calculated values. From our previous studies on nanostructure analysis [29,30], the Pd-on-Au NPs have a Pd-rich shell and a Au-rich core. At low surface coverage (< 30 sc%), Pd atoms are distributed as scattered atoms, and at medium surface coverage (30–80 sc%), Pd are found predominantly as two-dimensional (2D) ensembles on the Au surface. At higher surface coverages (> 80 sc%), Pd additionally form three-dimensional (3D) ensembles. The tested 80 sc% Pd-on-Au/C catalysts were stable with no detectable Au or Pd (< 50 ppb) in the filtered solution after MG oxidation.

#### 3.2. Effect of Pd surface coverage on catalyst activity of MG oxidation

Pd-on-Au NPs with surface coverages from 30 to 300% as well as monometallic Au/C , Pd/C catalysts and activated carbon were tested for MG oxidation. The concentration-time profiles of MG oxidation reaction showed that increasing Pd surface coverage from 0% to 80% led to higher MG conversion (Fig. 1a). The highest MG conversion of 92% after 8 h was achieved using the 80 sc% Pd-on-Au catalyst. The conversions for 0 sc% (monometallic Au), 30 sc% and 50 sc% Pd-on-Au catalysts after 8 h were 32%, 38% and 75%, respectively.

Materials with Pd surface coverages > 80 sc% showed decreasing MG conversion in the same reaction time period (Fig. 1b). The conversions for 100 sc%, 150 sc% and 300 sc% Pd-on-Au catalysts after 8 h were 71%, 66% and 40%, respectively. Both synthesized and purchased monometallic Pd/C catalysts tested showed no activity for MG oxidation after 8 h of reaction, which may due to the fast oxidation of Pd surface in oxygen-rich condition [31]. This finding was consistent with the results reported in literature [16]. Carrying out the same reactions using activated carbon did not show the conversion of MG.

The initial reaction rate constants of Pd-on-Au NPs with varying surface coverages were calculated (Fig. S2). The initial TOF of the reaction using Pd-on-Au NPs was then calculated by normalizing the initial reaction rate constant by the concentration of surface atoms (Table



Fig. 2. Plot of initial TOF with Pd surface coverage. Reaction conditions: 50 °C, 50 mL, 0.1 M MG, 0.4 M NaOH, pH = 13, and 100 mL min<sup>-1</sup> O<sub>2</sub>.

S6). The initial TOF in the range of 0 to 300 Pd sc% showed a volcanoshaped Pd surface coverage dependence (Fig. 2). All bimetallic Pd-on-Au/C catalysts showed improved catalyst activity compared with monometallic Au/C and Pd/C catalysts. The 80 sc% Pd-on-Au/C catalyst had the maximum activity for MG oxidation reaction. With a relatively small Pd loading (0.20 wt% Pd), this composition had an initial TOF value (413 h<sup>-1</sup>) that was > 5 times higher than that of Au/C (80 h<sup>-1</sup>).

The volcano behavior of Pd-on-Au NPs for this reaction was similar to their behavior for glycerol oxidation reaction [21]. Previous XAS results showed the Pd surface species at surface coverages below the volcano peak were in the form of 2D ensembles, which were relatively resistant to oxidation; and the Pd species above the peak were in the form of 3D ensembles, which were susceptible to oxidation, resulting in lowered catalyst activity [21,23].

#### 3.3. Effect of Pd surface coverage on MGA yield from MG oxidation

In the MG oxidation using the 80 sc% Pd-on-Au/C catalyst, the concentration of the desired product MGA increased from 0 to 45 mM over 8 h (Fig. 3). At the same time, the concentration of small organic acids (e.g. glyceric acid, oxalic acid, glycolic acid, formic acid, acetic acid, and lactic acid) were found to increase over time. These products were generated from the oxidative dehydrogenation of secondary hydroxyl groups in MG, which led to the cleavage of C–C bonds and the generation of the shorter chain compounds. The MGA selectivities did not vary with Pd-on-Au composition, which was roughly 55–57% at 20% MG conversion, higher than that for Au NPs (~50% at 20% MG conversion) (Fig. S3).



By dividing the sum of the carbon content of the HPLC-detected

**Fig. 1.** (a) Concentration-time profiles for 0, 30, 50 and 80 sc% Pd-on-Au/C catalysts and (b) concentration-time profiles for 80, 100, 150, 300 sc% Pd-on-Au/C and Pd/C (both synthesized and purchased) catalysts. Reaction conditions: 50 °C, 50 mL, 0.1 M MG, 0.4 M NaOH, pH = 13, and 100 mL min<sup>-1</sup>  $O_2$ .



Fig. 3. Reaction products and carbon balance of MG oxidation using 80 sc% Pd-on-Au/C catalyst. Reaction conditions: 50 °C, 50 mL, 0.1 M MG, 0.4 M NaOH, pH = 13, and 100 mL min<sup>-1</sup> O<sub>2</sub>.



**Fig. 4.** Plot of MGA yields (at the end of the 8-h reaction) with Pd surface coverage (black squares). Glucuronic acid yield from glucose oxidation using 80 sc% Pd-on-Au NPs (blue cross). Reaction conditions: 50 °C, 50 mL, 0.1 M MG (or glucose), 0.4 M NaOH, pH = 13, and 100 mL min<sup>-1</sup> O<sub>2</sub>. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

compounds over the initial carbon content of MG, the carbon balance for the 80 sc% Pd-on-Au/C catalyst was ~89% at the end of the 8 h reaction (Fig. 3). The decreasing carbon balance suggested the generation of CO and/or CO<sub>2</sub> undetected though HPLC, consistent with glycerol oxidation reported in literature. [21,32]

The concentration of MGA increased with reaction time for all catalysts, indicating no additional reaction of MGA with further MG conversion. The highest concentration of MGA (45 mM) was observed using 80 sc% Pd-on-Au catalyst (Fig. 4). The yield of MGA at reaction time of 8 h (calculated by dividing the concentration of generated MGA by initial concentration of MG) showed that the highest MGA yield (~46%) was achieved at the 80% Pd surface coverage, which was > 2 times greater than that for Au/C (20%).

For comparison, glucose oxidation at the same reaction conditions was conducted using the 80 sc% Pd-on-Au composition. The conversion of glucose was much faster than MG oxidation (Fig. S4). Glucose was completely oxidized in two hours and yielded 100% of the  $C_1$  oxidized product gluconic acid, consistent with literature [33]. The desired  $C_6$  oxidized product (i.e. glucuronic acid) was not detected during the reaction.

#### 4. Conclusion

Carbon supported Pd, Au and Pd-on-Au NPs were tested for MG

oxidation. Carbon supported bimetallic Pd-on-Au NPs exhibited a volcano-shape dependence of activity on Pd surface coverage, while monometallic Pd/C catalysts were inactive for the reaction. All Pd-on-Au NP catalysts were more active than monometallic Au/C, with maximum activity and yield to MGA observed over the 80 sc% Pd-on-Au/C. This study suggests carbon supported Pd-on-Au NPs are promising catalysts for the selective oxidation of primary alcohol group in MG for producing glucuronic acid.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.105895.

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