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Short communication

Microwave-assisted base-free oxidation of glucose on gold nanoparticle catalysts

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ABSTRACT

Base-free oxidation of glucose to gluconic acid with supported gold catalysts was studied using microwave heating. High conversion and selectivity were obtained in a remarkably shortened reaction time; in 10 min gluconic acid was obtained with up to 76% yields with 0.09 mol% Au/Al_2O_3 and hydrogen peroxide as oxidant. Very high turn-over frequencies over 10,000 h^{-1} were measured for the microwave assisted oxidation. Moreover, the catalyst activity remained constant in four consecutive runs, even though minor particle growth was observed.

1. Introduction

Catalytic transformations of carbohydrates are essential for the sustainable production of chemicals [1–3]. Gluconic acid, a product of selective oxidation of glucose, is widely used e.g. as a food additive, in pharmaceuticals and as a chelating agent in detergents [4]. Currently, gluconic acid is manufactured by enzymatic glucose oxidation with annual production estimated at 60,000 tons [5]. In this process, low pH causes deactivation of the enzymes and therefore sacrificial Brönsted base is required to neutralize the formed carboxylic acid [6]. In search for more efficient methods, the aerobic oxidation of glucose catalyzed by Pd group metals has been extensively studied [7]. In recent years, gold nanoparticle (Au NP) catalysts have gained increasing attention due to their exceptional selectivity, activity and stability compared to catalysts based on palladium or platinum [6,8,9]. With metal oxide supported Au NPs turn-over frequencies (TOF) of up to 160,000 $mol_{Glc}\ mol_{surface\ Au}^{-1}\ h^{-1}$ have been reported in oxidation of glucose to gluconic acid [10].

Noble metal catalysts require alkaline conditions (pH 9–10) to maintain high activity and consequently, the corresponding gluconate salt is produced [11]. However, oxidation without pH control eliminates both the need for an added base during the oxidation and the use of a strong acid to isolate gluconic acid from the generated salt. As such, base-free oxidations would enable direct, one-pot production of gluconic acid from cellulose through acid hydrolysis followed by the catalytic oxidation [12]. Consequently, there is great interest in developing catalysts that are highly active in acidic conditions [13].

Early studies showed that Au NPs can oxidize glucose also without the additional base [14]. However, the catalytic activity was significantly lower at acidic conditions than at alkaline pH and leaching of Au from the carbon support led to catalyst deactivation. Therefore, the research on Au catalyzed carbohydrate oxidation has mainly focused on alkaline conditions [6], and base-free glucose oxidation has gained more attention only recently [15–17]. In comparison to alkaline oxidation, which is carried out e.g. with air or oxygen bubbling at temperatures below 60 °C, the reported base-free oxidations require pressurized oxygen and/or significantly longer reaction times to reach reasonable conversions (Table 1). Also, acidic conditions are clearly demanding for the catalysts; deactivation due to Au leaching, sintering, adsorption of organic species or support instability were reported. Apparently, significant development is required for base-free oxidation to be a viable alternative to alkaline oxidation.

We initiated studies on base-free glucose oxidation using Au NPs supported on different metal oxides under pressurized oxygen. Similarly to the earlier reports, we observed low conversions and catalyst deactivation leading to decreased activity upon recycling. To promote the oxidation, we introduced microwave assisted heating. Employing such systems have led to dramatically improved yields and decreased reaction times in organic synthesis [18] as well as in heterogeneous catalysis [19]. To our knowledge however, the use of microwave irradiation in Au NP catalysis has been studied only in oxidation of benzylic

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Table 1
Previous reports on base-free glucose oxidation with supported Au NPs.

Entry	Catalyst	Glc:Au	T[a] (°C)	Time (h)	Oxidant	Conv. (%)	Select. (%)	Ref.
1	1% Au/C	1000	100	6	3 bar O_2	100	100	[14]
2	0.5% Au/CeO_2	140	65	2	2.3 bar O_2	76	96	[15]
3	0.5% Au/MgO	1600	60	24	air[b]	57	100	[16]
4	1% Au/CMK-3[c]	1000	110	2	3 bar O_2	92	88	[17]

[a] Conventional heating.
[b] Atmospheric air.
[c] Au supported on mesoporous carbon.

and aliphatic alcohols by gold on mesoporous silica [20]. Herein, we report very high catalytic activity for Au NP catalyzed base-free oxidation of glucose under microwave irradiation (Scheme 1).

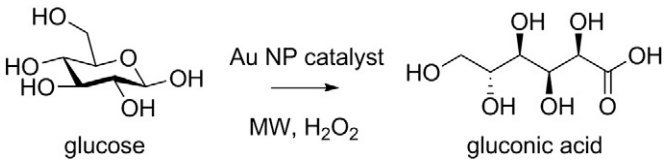
2. Experimental

2.1. Catalyst preparation and characterization

Au/MgO was prepared by deposition-precipitation with urea according to reference [21]. Au/Al_2O_3 was prepared by direct ion-exchange method; preparation and characterization were reported in ref. [22]. The $MgAl_2O_4$ spinel support was prepared by coprecipitation and Au was deposited on the support by deposition precipitation as described previously [23]. Au loading was determined by AAS (Atomic Absorption Spectrophotometer, PerkinElmer 3030) after dissolving the catalyst into aqua regia. Au particle size distribution was determined by transmission electron microscopy (TEM) based on 100 particles, and gold dispersion calculated from the particle size distribution according to ref. [24]. See Supplementary data for detailed experimental procedures and catalyst characterization.

2.2. Microwave oxidation and product analysis

The oxidation of glucose (Glc) was conducted in sealed glass vials using a Biotage Initiator microwave reactor with a 2.45 GHz magnetron. The instrument measures temperature of the reaction mixture using IR and adjusts the heating power accordingly (Fig. S4). A 20 ml glass vial was charged with catalyst (6 mg), D-glucose (110 mg, 0.61 mmol), water (5 ml) and H_2O_2 (1 equiv.). The reaction mixture was heated with microwave irradiation for 5 min at the chosen reaction temperature after which the second H_2O_2 portion (1 equiv.) was added with a syringe through the septum. The mixture was heated at the same temperature for another 5 min, giving a total reaction time of 10 min. The reaction mixture was stirred with magnetic stirring at 600 rpm. The products were identified using ^{1}H-NMR and GC/MS, and yields were determined by HPLC. Reproducibility of the results was confirmed in repeated experiments; 1–2% deviation in conversion and max. 5% deviation in selectivity was detected in at least two repeated experiments. After a typical experiment, the pH value of the reaction solution was between 2.4 and 3. In these conditions, gluconic acid forms intramolecular esters, gluconolactones. While these lactones have often been reported as intermediates or byproducts, their formation from gluconic acid depends on the pH of the solution according to the chemical equilibrium [25]. These can easily be hydrolyzed to gluconic acid and therefore we included the lactones in the yield.



Scheme 1. Base-free oxidation of glucose with Au NP catalysts.

3. Results & discussion

Microwave-assisted oxidation of glucose was carried out using hydrogen peroxide as oxidant, since the use of pressurized oxygen in closed microwave vials was unfeasible with the current system (Biotage Initiator). The low solubility of oxygen in water can be a limiting factor on the oxidation rate, whereas these mass transfer limitations are avoided with H_2O_2 [26,27]. Hydrogen peroxide decomposes on gold catalysts producing dioxygen via intermediate peroxo and superoxo species [28]. Using H_2O_2 and Au/Al_2O_3, Saliger et al. reported very high selectivity and activity in alkaline oxidation of glucose [29]. Instead of hydrogen peroxide however, the effective oxidizing agent in the reaction was a species formed by decomposition of H_2O_2, presumably dioxygen.

The catalyst support affects the H_2O_2 decomposition rate [13] and therefore, we introduced Au NP catalysts with three different support materials including MgO, $MgAl_2O_4$ and Al_2O_3. Immediate O_2 formation occurred with all catalysts upon addition of H_2O_2 to the reaction mixture. The oxidant-to-substrate ratio was optimized to 2.2 equiv. of H_2O_2 and applied to all catalytic studies (Table S1).

Magnesia has been previously used as support in base-free oxidation of glucose and glycerol [16,30], which inspired to test Au/MgO in our studies. To our surprise however, microwave-assisted oxidation of glucose with Au/MgO resulted in complete dissolution of the support. The previous studies reported only minor instability of the magnesia support; ppm-levels of Mg^{2+} leached into the acidic solutions [16,30]. In search of a more stable catalyst support, Au NPs were supported on $MgAl_2O_4$ spinel, which is known for high hydrothermal stability [23,31]. Particle size analysis of the 2.3 wt.% Au/$MgAl_2O_4$ catalyst revealed a bimodal distribution; TEM analysis showed small Au particles with mean diameter of 3.8 nm, whereas very large particles with sizes over 100 nm were detected with FESEM (see SI). Presumably, the small NPs are responsible for the activity of the catalyst, and therefore dispersion and TOF values were calculated according to the particle size detected by TEM (Table 2, entry 1). Moderate conversion (23%) and high selectivity (94%) to gluconic acid were obtained with the Au/$MgAl_2O_4$ catalyst at 100 °C. Increasing temperature to 120 °C improved the conversion to 54% while selectivity remained the same.

Alumina supported gold catalysts are among the most active Au catalysts for glucose oxidation in alkaline conditions [10] and furthermore, their long-term stability has been demonstrated [32]. Recently, we showed that a 1.8 wt.% Au/Al_2O_3 catalyst oxidizes both aldoses and uronic acids at alkaline conditions with high activity [22]. Herein, the same catalyst was very active in base-free glucose oxidation; 83% conversion and 87% selectivity were obtained at 120 °C giving an extremely high TOF value of 12,900 $mol_{Glc}\ mol^{-1}_{surface\ Au}\ h^{-1}$ (Table 2, entry 2). Control experiment without any catalyst using 2.2 equiv. H_2O_2 at 120 °C gave 12% conversion and 51% selectivity. Respectively, 19% conversion and 41% selectivity were obtained using the Al_2O_3 support alone.

The effect of temperature on the oxidation was studied further with Au/Al_2O_3. Conversion doubled when temperature increased from 80 °C to 140 °C, and simultaneously, the selectivity decreased from 97% to 85% due to secondary reactions and product degradation (Fig. 1). High gluconic acid yields were obtained both at 100 °C and 120 °C; 62% and 72%, respectively. At 140 °C, only a small increase in yield (76%) was