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PII: S1381-1169(16)30042-5
DOI: http://dx.doi.org/doi:10.1016/j.molcata.2016.02.008
Reference: MOLCAA 9773

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 29-10-2015
Revised date: 4-2-2016
Accepted date: 4-2-2016

Please cite this article as: Robert Wojcieszak, Iolanda M.Cuccovia, Márcia A.Silva, Liane M.Rossi, Selective oxidation of glucose to glucuronic acid by cesium-promoted gold nanoparticle catalyst, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2016.02.008

Selective oxidation of glucose to glucuronic acid by cesium-promoted gold nanoparticle catalyst

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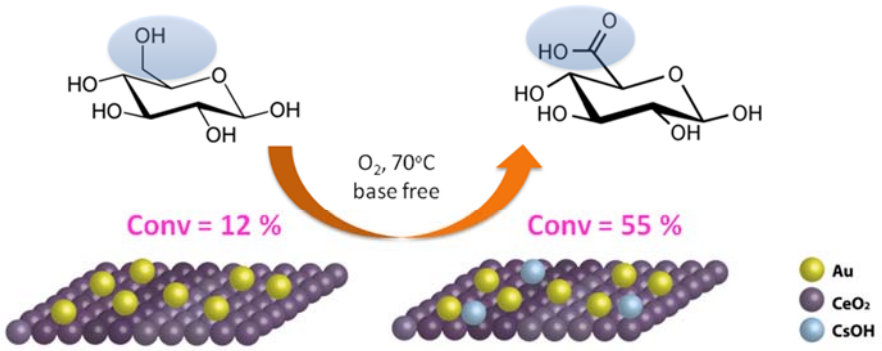
Graphical abstract



Highlights

- First gold catalyzed oxidation of sugars into glucuronic acid;
- Selective oxidation of glucose, fructose and maltose into glucuronic acid;
- Cesium hydroxide as an excellet dopant for Au/CeO_2 catalyst;
- Oxidation in the presence of added base is not selective.

Abstract: Gold catalysts outperform palladium and platinum catalysts for the oxidation of sugars with high activity and selectivity towards aldonic acids. The oxidation into other sugar acids, such as uronic and aldaric acids, has been scarcely investigated. Au nanoparticles supported on CeO_2 using a soft chemical reduction method with hydrazine, were active for the selective oxidation of low weight carbohydrates (glucose, fructose, maltose) into glucuronic acid. The oxidation occurred in aqueous solution at low temperature using O_2 as final

oxidant and without adding any base. The activity was improved by modifying the supported Au catalyst with cesium, while selectivity was maintained. Under these conditions, high selectivity to glucuronic acid was achieved; however, in the presence of base many by-products were obtained. The preparation of glucuronic acid in high yield using gold catalysts was never reported, which makes the catalyst developed here very interesting for liquid phase oxidation processes.

Keywords: gold nanoparticles, carbohydrates, glucuronic acid, heterogeneous catalysis, basic catalysts

1. Introduction:

The oxidation of low molecular weight carbohydrates is a highly attractive process in the area of catalytic conversion of renewable compounds. Sugar acids produced in these processes have many applications in the detergent industries as well in food industries, pharmaceutics and cosmetics. Until now, sugar acids are produced by biochemical processes, which very often display disadvantages regarding the separation of the products and the control of by-products. The oxidation of the C1 position of D-glucose is easier than that of the primary or secondary alcohol functions, when performed in the presence of supported metal catalysts, such as Au, Pd and Pt [1-3]. The oxidation of sugars is generally carried out in batch reactors containing an aqueous solution of sugar and the catalyst with a bubbling air or oxygen through the slurry at temperatures range of 20- 80 °C. The reactions are performed in a basic medium (pH 7-9) so that the carboxylate anions are readily desorbed from the catalyst surface, whereas in an acid medium the carboxylic acid remains strongly adsorbed on the surface giving undesirable by-products or degradation of formed acids [4]. However, gold was less sensitive to low pH and was active even at pH 2 [5-6].

Gold catalysts have shown to outperform the activity and selectivity of catalysts based on palladium or platinum hitherto used for the oxidation of carbohydrates [7-15]. A very interesting property of gold is the ability to convert different type of aldoses (e.g., glucose, lactose, maltose, xylose, arabinose) to their corresponding aldonic acids (e.g., gluconic acid). It is also possible to directly oxidize oligosaccharides. Tan *et al*. [16] used an Au/CNT catalyst for converting cellobiose without addition of base and observed a 70% yield at 145°C under a pressure of 1.0 MPa O_2. On the other hand, An *et al.* [17] developed Au/$Cs_{1.2}H_{1.8}PW_{12}O_{40}$ catalyst that is able to convert cellobiose to gluconic acid with a yield of 97% at 145°C under 0.5 MPa of O_2. The direct synthesis of gluconic acid from cellulose has also been studied with the same catalyst, providing a yield of 60% after 11 h at 145°C. This reaction consists of two steps: (i) hydrolysis of cellulose to glucose and oligosaccharides promoted by $Cs_{1.2}H_{1.8}PW_{12}O_{40}$ and (ii) oxidation of glucose by the Au nanoparticles. However, the reaction time is very large and a decrease in catalytic performance was observed with the number of cycles [17]. Biella *et al.* [18] reported that Au nanoparticles are active for glucose oxidation with high selectivity towards gluconic acid. However, even though these systems are very active and selective, they showed relatively low stability [19]. The stability of Au nanoparticles was improved after

immobilization on carbon support. Similarly prepared Au nanoparticles supported on carbon were studied by Önal *et al.* [20]. They observed superior performance in terms of activity but lower selectivity when compared with non-supported Au nanoparticles. The gold–support interaction was declared to be essential for the formation of a stable catalyst system [21-22]. Different catalytic activity was observed using different type of carbon supports with the same Au particle size, indicating a specific metal–support interaction [20]. On the contrary, Ishida et al. observed that gold particle size influences the catalytic effect more significantly than the nature of the support comparing carbon and different metal oxide supports such as Al_2O_3, ZrO_2, TiO_2, CeO_2 [12, 23].

Many catalysts, especially gold, with high activity, for the oxidation of glucose and selectivity towards gluconic acid have been reported. However, the conversion of glucose into other high valuable chemicals (Scheme 1), such as glucuronic or glucaric acids, has been scarcely investigated although these both acids have a very important industrial potential. Indeed, D-glucaric and D-glucuronic acids are identified as top value-added chemicals from biomass due to their potential use as a building block for a number of polymers, including new nylons and hyperbranched polyesters resulting in a presumably biodegradable fiber.

Pamuk *et al.* [24] obtained a 63% yield of D-glucaric acid directly from the sugar beet molasses using sodium nitrite, nitric and sulphuric acid. Matthey [25] oxidized D-glucose with a yield of 80% using $Hg(OH)_2$ at 40±60°C Other sugar acids were already obtained on platinum catalysts; however, metal leaching and not very high yields are important issues. Mehltretter [26] attained a selectivity of 54% for D-glucaric acid by the oxidation of D-glucose with Pt/C as catalyst. The rates of oxidation of primary hydroxyl groups on Pt catalysts are usually low, because strongly adsorbed products or by-products easily poison the catalysts. Owing to the low activity, besides the oxidation of primary alcohol groups, secondary alcohol are also oxidized along with the formation of more oxidized products such as tartarate and oxalate, leading to very poor selectivity to the desired aldaric acid. Oxidation of D-gluconic acid on Pt/C catalysts yielded, under optimized conditions, about 40% of D-glucarate as reported by [27]. Slightly higher yields (55% at 97.2% conversion) were reported by Besson *et al.* [28] working with more concentrated solutions of D-gluconate and lower amounts of catalyst.

The literature on gold catalysts for the oxidation of glucose shows exclusively the production of gluconic acid, mostly promoted by the addition of base, e.g. NaOH, K_2CO_3 and KOH. To the best of our knowledge, gold catalyzed oxidation of glucose into other sugar acids, such as glucaric or glucuronic acid with high selectivity and yields, was never claimed. Only few works stated on the production of glucuronic acid on Au catalysts [29-30], however the yields reported are very low. Herein we present the direct synthesis of glucuronic acid from glucose, fructose, and maltose using supported gold nanoparticles promoted by cesium. Au/CeO_2 and $Au\text{-}Cs/CeO_2$ catalysts were prepared by microemulsion method and studied in the base free oxidation of carbohydrates using O_2 as oxidant.

2. Experimental:

2.1. Catalyst synthesis

2.1.1. Microemulsion method

The catalyst was prepared using a microemulsion method adapted from previous reports [31-32]. It consists on the reduction of an aqueous phase containing the metallic precursor (0.066 mL of $HAuCl_4$ solution (30 wt% in dilute HCl, Sigma-Aldrich) diluted in 1 mL of distilled water), which is forming a microemulsion with an oil phase by means of an amphiphilic surfactant. Herein, cyclohexane (50 mL, commercial grade, Sigma-Aldrich) was the oil phase, AOT (6.30 g, sodium bis(2-ethylhexyl)sulfosuccinate, 96%, Sigma-Aldrich) was the surfactant, and hydrazine (80 wt.% in water, Fluka) was the reducing agent. A nominal Au metal content of 2.5 wt.% was fixed during the preparation. An appropriate amount of CeO_2 (1 g, commercial grade, Sigma-Aldrich) employed as support without further treatment was added to the reactant flask containing the microemulsion at 50°C and under magnetic stirring. After 30 min, 3 mL of hydrazine were injected under stirring to the reactant flask while keeping the temperature constant. Upon reduction completion (30 min), the solid was recovered from the suspension by filtering and washing with acetone and hot distilled water. The catalysts thus synthesized were afterwards dried at 100°C for 30 min and used as such for the catalytic tests. Further details on the microemulsion method are presented elsewhere [31, 32].

2.1.2. Sol-immobilization method

The catalyst Au_{PVA}/CeO_2 was prepared using the sol immobilization method adapted from the literature [33]. It consists in the preparation with polyvinyl alcohol (PVA) stabilized Au NPs and its subsequent immobilization on an appropriate amount of support. CeO_2 (commercial grade, Sigma-Aldrich) was employed as support without further treatment. First, 0.6 mL of a 2wt% aqueous solution of PVA (Sigma-Aldrich, MW 13000-23000 g/mol, 98% hydrolyzed) was added to an aqueous solution containing 17.25 mg of $HAuCl_4$ (0.035 mL of $HAuCl_4$ solution 30wt% in dilute HCl, Sigma-Aldrich) diluted in 40 mL of distilled water under vigorous stirring. A freshly prepared solution of $NaBH_4$ (2.55 mL, 0.1 $mol.L^{-1}$) was then added to form a light-red sol. Within 30 minutes of sol generation, the colloid (acidified at pH 1 by sulphuric acid) was immobilized on 0.5 g of CeO_2 under vigorous stirring conditions. The amount of support was calculated to give a total final metal loading of 2 wt%. After 2 h the slurry was separated by centrifugation (20 min, 7000 rpm), the solid washed with hot water (2 x 25 mL) and ethanol (2 x 25 mL) and dried at 100 °C for 10 h.

2.2. Catalyst doping with cesium

Catalyst doped with cesium ions was prepared using the same conditions as described above. Appropriate quantity of CsCl solution (0.1 wt%) was added to the microemulsion at the same time as Au precursor. The microemulsion containing Au and Cs precursors and CeO_2 was then treated with hydrazine.

2.3. Catalysts characterization

2.3.1. ICP AES

The chemical composition of the catalysts was determined by inductively coupled plasma atomic emission spectrometry, using Thermo Jarrel Ash Iris Advantage equipment. The samples were first brought into solution by subsequent dissolution with diluted *aqua regia* (HNO_3/HCl 1:3).

2.3.2. XRD

X-ray diffraction study was carried out on a Siemens D5000 diffractometer using the Kα radiation of Cu (λ□= 1.5418 Å). The 2Θ range was scanned between 2 and 70° at a rate of 0.01 deg°×s^{-1}. The identification of the crystalline planes was made using the ICDD-JCPDS database. The Scherrer equation was employed for estimating the crystallite size of the detected crystalline phases [34].

2.3.3. BET

The textural properties of the support and reduced materials were studied by means of N_2 adsorption/desorption at −196 °C with a Micromeritics ASAP2000 apparatus. Before the analysis the samples were degassed at 150°C for 12 hours. Low temperature nitrogen adsorption isotherms enable the BET calculation of the specific surface area and the BJH calculation of the pore volume and the pore diameter.

2.3.4. XPS

XPS analysis was performed on a Kratos Axis Ultra spectrometer (Kratos Analytical, U.K.). The spectrometer was equipped with a monochromatized aluminum X-ray source (powered at 10 mA and 15 kV). The pressure in the analysis chamber was about 10^{-6} Pa. The angle between the normal to the sample surface and the direction of photoelectrons collection was about 0°. Analyses were performed in the hybrid lens mode corresponding to a combination of magnetic and electrostatic lenses. The analyzed area was about 700 μm × 300 μm. The pass energy of the hemispherical analyzer was set at 160 eV for the wide scan and 40 eV for narrow scans. In the latter conditions, the full width at half- maximum (fwhm) of the Ag 3d5/2 peak of a standard silver sample was about 0.9 eV. Charge stabilization was achieved by using the Kratos Axis device. Peak decomposition was performed using curves with a 70% Gaussian type and a 30% Lorentzian type and a Shirley nonlinear sigmoid-type baseline. The following peaks were used for the quantitative analysis: O 1s, C 1s, Ce 3d, Cs 3d, and Au 4f. Moreover, the Cl 2p, S 2p and N 1s peaks were also monitored and C 1s again to check for charge stability as a function of time. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters after a Shirley background subtraction and corrected with experimental sensitivity factors and transmission factors provided by the manufacturer. Au foil was used as the reference material for study of prepared catalysts. Au foil was analyzed before and after

Ar^+ etching during 50 min with the Kratos Minibeam I ion gun (4 kV, 15 mA) to remove oxidized species from the foil surface. The surface atomic concentrations were calculated by correcting the intensities with theoretical sensitivity factors based on Scofield [35] cross sections and the mean free path varying according to 0.7 power of the photoelectron kinetic energy. The **C**-(C,H) component of the C 1s peak of adventitious carbon was fixed to 284.8 eV to set the binding energy scale, and the data treatment was performed using CasaXPS software (Casa Software Ltd., U.K.).

2.3.5. TEM

The morphology of the obtained nanoparticles was obtained on a JEOL JEM 2100F–LNNano microscope operating at an accelerating voltage of 200 kV. The samples for TEM were prepared by dispersion of the nanoparticles in aqueous solution at room temperature and then collected on a carbon-coated copper grid.

2.4. Catalytic tests

2.4.1. Oxidation reactions

The reactions were carried out in 75-mL stainless steel reactors (Series 5000 Multiple Reactor System, Parr Instrument Co., USA). The test reactor unit is a magnetically stirred high-pressure reactor equipped with a Parr 4843 controller for the setup and control of reaction temperature and stirring speed. Reactor pressure measurements were accomplished via a pressure transducer attached to the reactor. Temperature, pressure and stirring speed are recorded by a SpaceView® data acquisition system. The total volume of carbohydrate aqueous solution used was 10 mL and the charged weight of catalyst was about 20 mg. The catalytic reactions were carried out for the desired time or temperature without any base addition. The oxygen pressure was of 15 bar in all experiments.

2.4.2. HPLC analysis

The liquid products were analyzed by HPLC (Waters 2410 RJ) equipped with a RI and UV detectors and a Shodex SUGARSH-1011 column (8*300 mm). Diluted H_2SO_4 (5 mM, 1mL/min) was used as a mobile phase. Commercial standards (glucose, gluconic acid, glucaric acid, glucuronic acid, 2-keto-gluconic acid and 5-keto-gluconic acid) were used for calibration of the HPLC set up. Shimadzu UHPLC-LCMS NEXERA XZ LC 30AD equipment was used for determination of the exact molar mass of the products.

Mono and oligosaccharides can only be detected on a refractive index (RI) detector, whereas oxidized sugars exhibit UV absorption and can be detected using a UV- detector at 210 nm. The glucose data have been corrected by subtracting the glucuronic acid values obtained from the UV-detector. Conversion of glucose was calculated using the difference between the moles of glucose in starting mixture and that after catalytic test. Taking into account the stoichiometry of the reaction, the yield of glucuronic acid was calculated (for the tests with 100% selectivity to glucuronic acid). In case of the

tests in the presence of base, the yield of different products was calculated using the calibration curves obtained for commercial standards and/or area peaks ratio.

3. Results and discussion

The chemical reduction of noble metals such as gold, with hydrazine, occurs very fast and even at low temperature. In this study, gold nanoparticles were prepared by adding hydrazine to a microemulsion containing the Au^{3+} precursor. The hydrazine to Au molar ratio was fixed at 100. As a metal particle size is independent on hydrazine concentration [36], in our condition the particle size should be mainly governed by the nature of solvent and surfactant used in the microemulsion method [37]. The crucial step of the preparation is the formation of nanoparticles and their deposition on the external surface of the support immediately after formation. ICP OES analysis enables to determinate the chemical composition of the catalyst after preparation. The results, given in Table 1, showed that the metal loading on the Au-Cs/CeO_2 catalyst was very close to the nominal value (2.5 wt.%), but the amount of gold in Cs free sample was lower than expected. This could be explained by loss of gold during filtration. The gold nanoparticles, which are not deposited on the support, can, indeed, pass more easily through the filter during the separation and washing step. This is also valid for the support, because a loss of about 8 wt% was observed for all catalysts after filtration and drying. In addition, the pore volume and specific surface area did not change significantly after deposition of gold nanoparticles, as showed by the N_2 adsorption at low temperature results in Table 1. This confirmed that all gold is deposited almost exclusively on the external surface instead of pores.

We have chosen to use a low water to surfactant molar ratio (lower than 10) during the synthesis, which allowed obtaining very small size of gold nanoparticles [38]. The size of the Au nanoparticles was estimated from the XPS elemental intensity ratios using an adequate modelling of the signal. Different XPS models could be applied for estimation of average particle size [39]. The Kerkhof-Moulijn model [40], used in our study, predicts the average particle size from intensity ratio of monolayer and crystallite samples and it depends strongly on the physical properties of the support. The results are given in Table 1. Small Au nanoparticles (< 4 nm), as estimated from XPS were obtained. The presence of Au nanoparticles with an average particle size of about 4 nm was also confirmed by TEM images (Figures SI 1A and B). XRD studies (pattern shown in Figure SI 2) did not permit to estimate Au average particle size. The diffractions peaks from Au were not present in the XRD pattern, which contain only support diffraction peaks. This is due to the limitation of the XRD method owing to the low metal weight fraction or the size of crystallites. Further information about the chemical composition and oxidation degrees of components present on the catalyst surface was obtained by XPS study. The decomposition of the C 1s peak was performed taking into account three components: one C-[C,H] contribution plus other two contributions corresponding to oxygenated carbon species (C-Ox = -C-OH + [C-(C=O)-O- C]. The results are given in Table 2.

Carbon molar concentrations observed are higher than those usually reported for adventitious carbon contamination over other inorganic oxides analyzed by XPS. This suggests that the increase in the carbon concentration for studied catalysts is due to the use of cyclohexane during the preparation. No other contamination was evidenced by XPS. The XPS spectrum of Au-Cs/CeO_2 catalyst showed two well resolved peaks in the Cs 3d region (Figure 1 a). The first high-energy peak is located at 724.17 eV and the second, low energy peak, at about 738.10 eV. The $3d_{5/2}$ and $3d_{3/2}$ doublet difference is about 13.90 eV. These values correspond well to the hydroxide form of Cs as described in the literature [41]. Indeed, the reduction of the Cs salt with N_2H_4 is responsible for formation of hydroxide. As expected, the XPS spectra of Au region (Figure 1 b) showed well resolved peaks originated from metallic gold contribution for all samples. These results confirmed that the reduction of gold ions with hydrazine during the preparation was effective.

The catalytic activity of Au/CeO_2 was investigated in the oxidation of glucose, fructose and maltose. The oxidation reactions were performed in aqueous solution at low temperature using O_2 as oxidant and without adding any base. We evaluated different reaction parameters using Au/CeO_2 catalyst: time, temperature, O_2 pressure, glucose concentration and Cs dopant effect. The results are given in Table 3 and 4. Tests in the presence of base (NaOH, K_2CO_3, CH_3COONa, $Zn(CH_3COOH)_2$) were also conducted for comparison and will be discussed later.

Under base free conditions, glucuronic acid was the only product observed for glucose oxidation catalyzed by Au/CeO_2. The identity of this product was obtained by HPLC analysis and electrospray ionisation mass spectrometry (ESI-MS) (Figure 2 and Figure SI 3) and confirmed using commercially available standards. The retention time of the glucose oxidation product (4.96 min) was more than 2 minute shorter than most of the expected products and only comparable with the retention time of glucuronic acid (Figure 2). The *m/z* of the glucose oxidation product was 194, which can correspond to several products (Scheme 1). The mass analysis of the fragment MH^+ confirmed the identity of the reaction product. These results clearly indicate that gluconic acid (*m*/*z*=196 and retention time 7.02 min) is not being formed, which is quite intriguing since it is the commonly found product of glucose oxidation by gold. These results suggest that the primary alcohol group of glucose is being oxidized on the Au catalysts.

The conversion of glucose increases with time of the reaction, but reached only 12% after 4 h at 70°C (Table 3, entries 1-4). The conversion of glucose was highly dependent on the temperature (Table 3, entries 4-7) and 100% conversion was reached at 150°C; however, the yield of glucuronic acid decreased drastically. Indeed, the formation of different by-products was observed (several peaks in HPLC spectra). The highest yield of glucuronic acid was achieved at 70°C. Above this temperature, new products started to appear, which are due to the thermal decomposition and polymerization.

Interesting results were observed when the reaction was carried out in the presence of base using Au/CeO_2 catalyst (Table 3, entry 8) and in the presence of base without catalyst (Table 3, entry 9). The total conversion of glucose was achieved in both cases; however, the production of more than 8 different products was observed (as described below). It is worth to mention that bare CeO_2 oxide was inactive in the oxidation reaction at 70°C for 4 h (Table 3, entry 10). Higher conversion of glucose was achieved using a smaller glucose/Au molar ratio (Table 3, entry 11).

The catalytic activity was strongly dependent on the method of preparation of the catalysts, as shown in Table 4. The Au/CeO_2 catalyst prepared by a microemulsion method and reduced with hydrazine (Table 4, entry 1) was more active than a catalyst containing PVA-stabilized gold nanoparticles (2.8±1.0 nm) but prepared by sol-immobilization method [33] without any hydrazine (Table 4, entry 2). Generally, the hydrazine treatment permits to increase the basicity of the catalyst [40], and it can explain the better performance of hydrazine treated catalyst. There is still no consensus on the main parameter that governs the activity of the gold nanoparticles in oxidation reactions. The hypotheses proposed so far can be classified in: (*i*) specific size of the Au nanoparticles, (*ii*) junction perimeter between gold and the supports and (*iii*) the acid base properties of catalyst. In order to study if a change in the acidity of the support implies changes in the catalytic properties, we incorporated a small amount of Cs ions (0.1 wt.%) into the microemulsion method used to prepare the Au/CeO_2 catalyst. The Cs doped sample significantly increased the activity, reaching 55% conversion for glucose and 67% conversion for fructose, which is more than 5 times higher than the conversion reached by the Au/CeO_2 catalyst under similar conditions (Table 4, entry 3). The selectivity to glucuronic acid was maintained as any other products were observed by HPLC analysis. It is worth to note that the addition of Cs salt (CsCl) in the reactant solution did not change the activity of the catalyst (Table 4, entry 4). Increase in the catalytic activity was only observed when cesium was added to the microemulsion, before hydrazine reduction, during the preparation of the gold catalyst. Surface analysis by XPS shown in Figure 2a revealed the presence of cesium hydroxide on the catalyst surface, which suggests that only hydroxide form of Cs is playing its promoting role for gold in the reaction. It is worth to note that ICP OES analysis was performed on the solutions after catalytic test and neither Au nor Cs ions were detected in the solution, which confirmed that no leaching occurred. These results suggest that the CsOH increased the superficial basicity of the catalyst owing to increased activity in the oxidation reaction. The beneficial effect of Cs ions on the catalytic activity in sugar oxidation was already described in the literature [42]. Indeed, An et al. studied Cs modified Au/HPA catalysts in the direct oxidation of cellobiose to gluconic acid and further oxidation of gluconic acid to glucuronic acid and other products [17]. Moreover, they stated that the selectivity to gluconic acid was depended on the quantity of Cs in the materials. They found that higher acidity of the catalyst at lower Cs content hindered the adsorption of gluconic acid, thereby resulting in the lower conversion.

A lower conversion was achieved in the conversion of maltose into glucuronic acid, most probably because of the lack of acidic sites responsible for the hydrolysis of maltose with the expected formation of glucose as an intermediate. The hydrolysis should be improved in acidic media, after some molecules of glucuronic acid are formed, decreasing the pH and allowing increasing the overall hydrolysis rate. This was also observed by An *et al*. [17], who has stated that the gluconic acid formed in the presence of Au nanoparticles played the role of a liquid acid and accelerated the hydrolysis of cellobiose. They found that the addition of gluconic acid into the reaction medium caused an enhancement in the hydrolysis of cellobiose in the case of a blank reaction, with Cs/HPA and Cs-Au/HPA samples. The Au nanoparticles accounted for the oxidation of glucose into glucuronic acid as in the case of glucose or fructose oxidation.

According to the most accepted alcohol oxidation mechanism over heterogeneous catalysts recently reviewed by Davis *et al* [43], a metal-catalyzed oxidation of an alcohol to an aldehyde is likely to occur in three steps: (1) alcohol adsorption on the metal surface, producing an adsorbed metal alkoxide and a metal hydride (or a water molecule, if metal hydroxide species are involved); (2) β-hydride elimination to produce a carbonyl species and a metal hydride; and (3) metal hydride oxidation by dioxygen to regenerate the metal surface (or metal hydroxide species). This last step may leads to the production of water (metals that dissociatively adsorbed oxygen) or hydrogen peroxide (metals that do not dissociatively adsorb oxygen; e.g. Au) that will desorbs to regenerate the metal surface. The aldehyde formed can be subsequently oxidized to a carboxylic acid through a geminal diol intermediate. It is well known that aldehydes undergo reversible hydration to geminal diols, which can also adsorb to a metal surface and undergo a β-hydride elimination to form a carboxylic acid. The presence of surface adsorbed hydroxides, similar to an alkaline solution, facilitates both the formation of an adsorbed alkoxide (or geminal diol), as well as β-hydride elimination steps towards the production of aldehydes and carboxylic acids. A similar mechanism, which corresponds to a modified oxidative dehydrogenation mechanism, was also suggested as the most probable for glucose oxidation into gluconic acid on gold catalysts [44-45]. A deprotonated geminal diol of glucose formed in alkaline solution is likely to adsorb at the catalyst surface and undergo a β-hydride elimination to form gluconic acid. After gluconic acid desorption, both a metal hydride and the non-dissociatively adsorb oxygen species will react to form an adsorbed peroxide species, which subsequently desorbs. Similarly, sugar molecules adsorption on a metal surface is facilitated by surface hydroxyl species, via hydrogen bonds with the aldehyde (or geminal diol intermediate), with a concomitant pairing of the enediol conformation of glucose with Au-OH sites. Many conformations are involved in the process, but the importance of the enediol intermediate for more extensive oxidations of glucose to occur beyond formation of gluconic acid was reported [46]. In our study, only traces of gluconic acid were detected during the oxidation reactions and glucuronic acid was the main product. We could expect that the oxidation of glucose may proceed through the formation of gluconic acid (oxidation of the aldehyde at carbon atom C1) and then the oxidation of the primary hydroxyl at carbon atom C6. The

oxidation of glucose into glucaric acid (along with aldonic and aldaric acids) was demonstrated to occur at Pt/C catalyst with O_2 in alkaline solution [47] and is also possible at the surface of an Au rotated disc electrode by voltammetry [46]. The oxidation of free gluconic acid into glucaric acid was also demonstrated on Pt/C catalysts [46, 48]. The first step of this reaction is the formation of glucuronic acid, an intermediate, which then undergoes oxidation to glucaric acid. We have performed also an oxidation test with gluconic acid on Au-Cs/CeO_2 catalyst and the only product formed was again glucuronic acid with conversions comparable to that obtained for glucose oxidation (Table 4, entry 3). This result suggests that the first step of the glucose oxidation on Au-Cs/CeO_2 catalyst should be the fast formation of gluconic acid and its further oxidation into glucuronic acid. It has been reported that the rate of the reaction between chemisorbed oxygen and adsorbed gluconic acid is much lower than the reaction rate between chemisorbed oxygen and adsorbed glucose [48]. However, it was also demonstrated that gluconic acid, which is formed during the oxidation of glucose, is oxidized much faster than when used as starting molecule under the same reaction conditions. It could be explained by the low pH of started solution in the case of gluconic acid oxidation and its adsorption on the catalysts surface that could deactivate the active sites.

Most of the oxidations of glucose reported in the literature are performed in alkaline conditions obtained by adding base during the course of the reaction (NaOH, KOH, K_2CO_3, etc.) [4], and gluconic acid is reported as the main (only) product. In order to compare our results with the literature, we performed catalytic glucose oxidation tests in the presence of added base using both microemulsion Au/CeO_2 and sol-immobilization Au_{PVA}/CeO_2 catalysts. The HPLC chromatograms shown in Figure 3a and 3b display multiple peaks corresponding to different oxidation products (glucuronic acids, gluconic acid and others not possible to identify), while the HPLC chromatogram of the base-free reaction display only one peak corresponding to glucuronic acid (Figure 1). The quantity of the base seems to play a significant role in the oxidation mechanism and also changed the product distribution. Moreover, a clear difference was observed also between the catalysts prepared by sol-immobilization and microemulsion (Figure 3b). The catalyst prepared without hydrazine produced less glucuronic acid than the catalysts prepared by soft reduction with hydrazine (microemulsion).

We have chosen different bases such as NaOH, K_2CO_3, CH_3COONa and $Zn(CH_3COO)_2$ since several of them are described in the literature for catalytic oxidation of glucose. The HPLC chromatograms showed in Figure 4a display multiple peaks corresponding to different oxidation products (glucuronic acids, gluconic acid and others not possible to identify). Full conversion of glucose was observed in all cases; however, the selectivity was very low, i.e., we did not achieve the high selectivity claimed in the literature for gold catalysts under alkaline conditions. The presence of multiple products was also observed in the presence of base and without catalyst (Figure 4b). Indeed, degradation of glucose was observed at 70°C after 4 h reaction in the presence of K_2CO_3. These results

have been already described in the literature [49]. Novotny *et al.* [50] observed formation of 3 low molecular carboxylic acids (formic, acetic and propionic), 24 hydrocarboxylic acids and 12 corresponding lactones. However, additional studies are needed to confirm and explain our results.

4. Conclusions

We have prepared highly selective gold nanoparticle catalyst for base-free oxidation of sugars. The catalyst was synthesized via a microemulsion method using CeO_2 as the support, $AuCl_4^-$, and hydrazine as the reducing agent. The catalyst was active for the oxidation of glucose, fructose and maltose, without the addition of base, to only one product: glucuronic acid. The activity of the gold catalyst was improved when doped with cesium. This could be attributed to the generation of CsOH surface species and an increase of the surface local basicity. Under these conditions, almost 100% of selectivity to glucuronic acid was also achieved; however, in the presence of added base many by-products, including gluconic acid, were obtained. The preparation of glucuronic acid in high yield using gold catalysis was never reported, which makes our catalysts very interesting for liquid phase oxidation processes. Additional studies are necessary to understand the exact mechanism of this reaction. Acid-base properties of the catalysts will be studied in more detail.

5. Acknowledgments

The authors are grateful for the financial support offered by Sao Paulo Research Foundation − FAPESP (grant 2012/08691-0 and 2012/21566-0) and CNPq (INCT-Catalise). The REALCAT platform benefits from a Governmental subvention administered by the French National Research Agency (ANR) within the frame of the 'Future Investments' program (PIA), with the contractual reference 'ANR-11-EQPX-0037'. The Nord-Pas-de-Calais Region and the FEDER are thanked for their financial contribution to the acquisition of the equipment of the platform. The authors also would like to thank the Electron Microscopy Laboratory (LME) of the Brazilian Nanotechnology National Laboratory (LNNano) for the use of their TEM facility, Dr. Erico Teixeira-Neto for TEM analysis and Marco Aurélio Suller Garcia for the Au_{PVA}/CeO_2 catalyst preparation.

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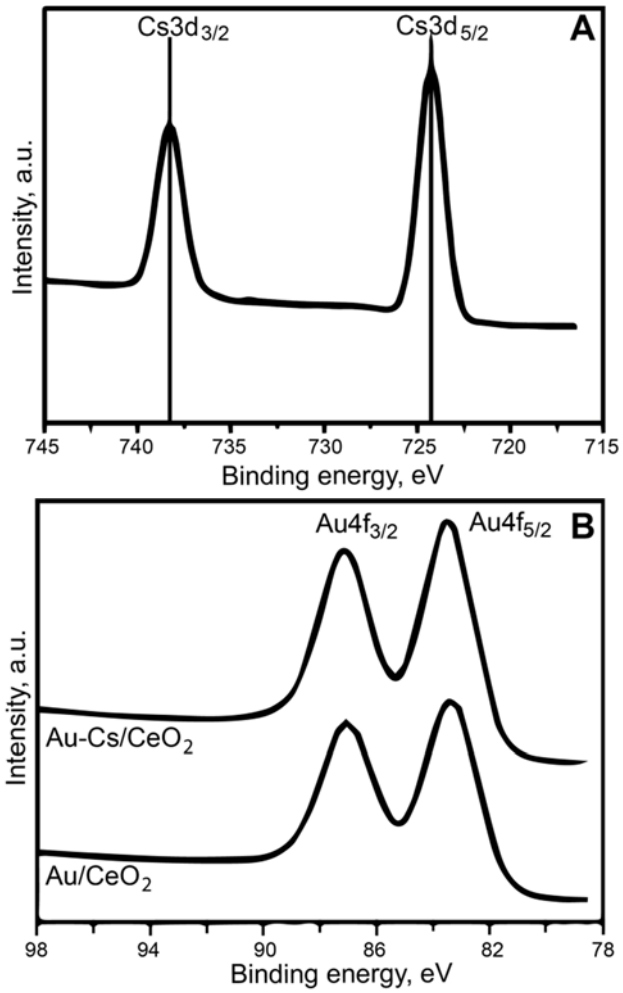


Figure 1. XPS spectra of Cs 3d (A) and Au 4f (B) regions.

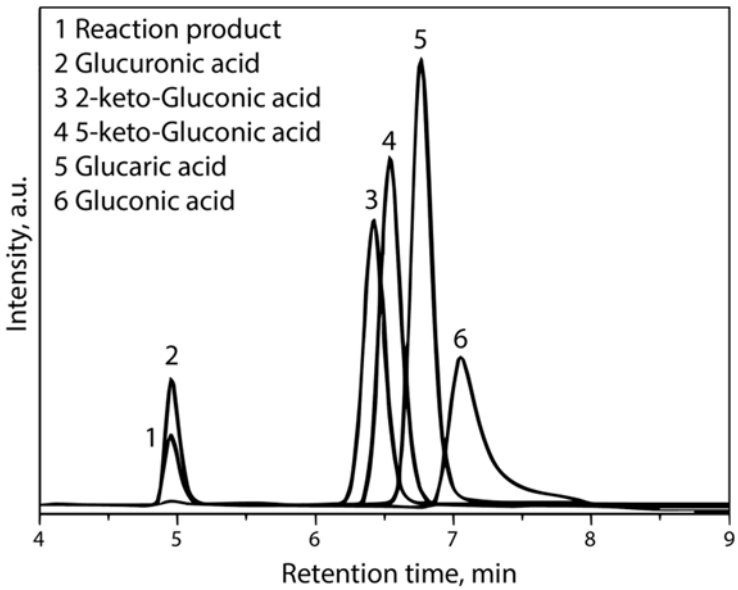


Figure 2. HPLC chromatogram (UV detection, t=retention time) for the glucose oxidation product (peak 1, t=4.96 min) and commercials standards: glucuronic acid (peak 2, t=4.96 min)), 2-keto-D-gluconic acid (peak 3, t=6.43 min), 5-keto-D-gluconic acid (peak 4, t=6.56 min) glucaric acid (peak 5, t=6.93 min) and gluconic acid (peak 6, t=7.09 min). Glucose does not give signal in UV.

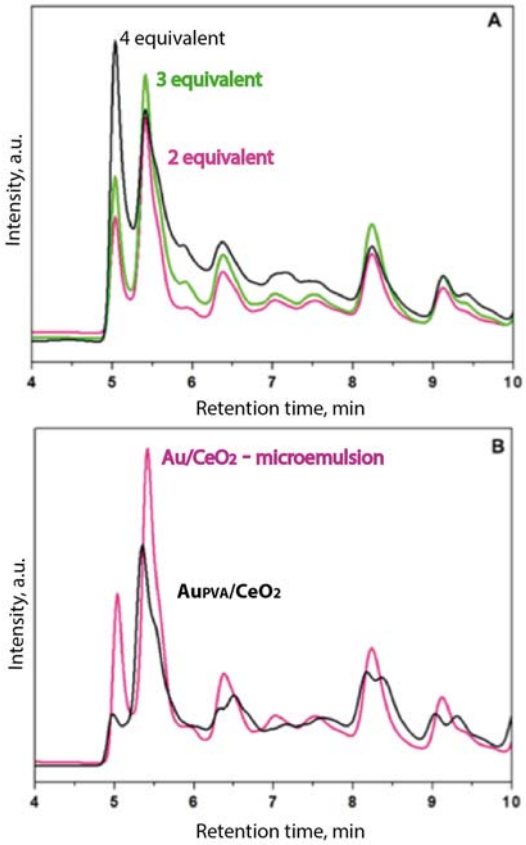


Figure 3. HPLC chromatograms (UV detection) for the reaction products obtained by catalytic oxidation of glucose in the presence of K_2CO_3. (A) The effect of base concentration (20 mg Au/CeO_2, 10 mL of H_2O, 0.55 mol/mL glucose, 70°C, 4h, K_2CO_3) and (B) comparison of sol-immobilization Au_{PVA}/CeO_2 and microemulsion Au/CeO_2 catalysts (20 mg catalyst, 10 mL of H_2O, 0.55 mol/mL glucose, 70°C, 4h, 2 equiv. K_2CO_3).

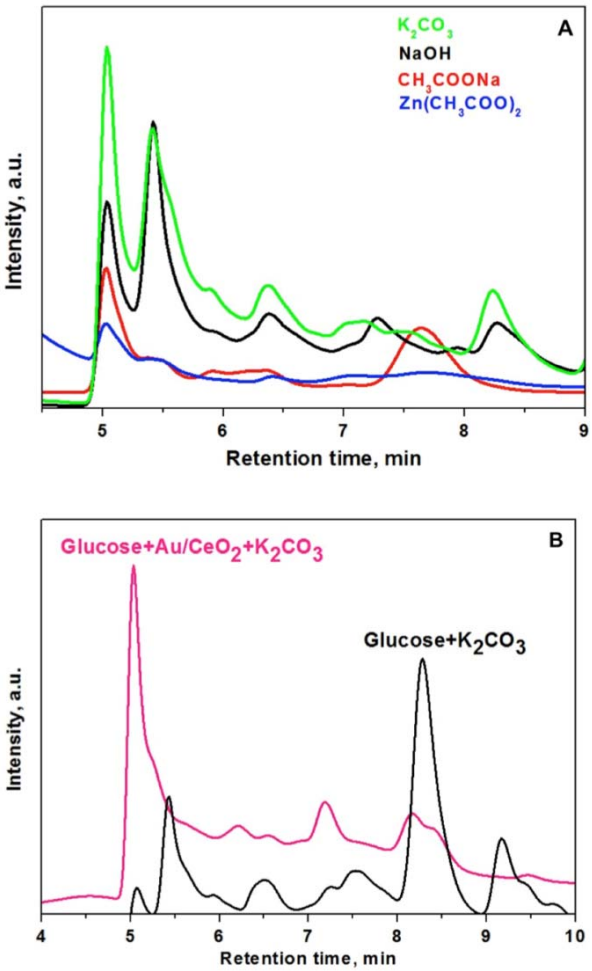
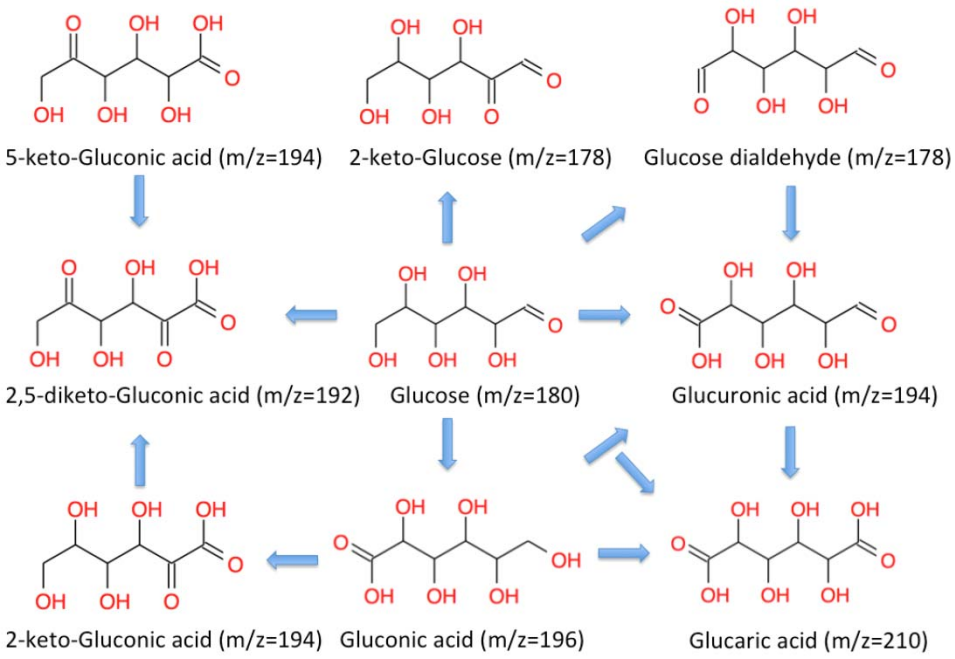


Figure 4. HPLC chromatograms (UV detection) for the reaction products obtained by catalytic oxidation of glucose in the presence of base. (A) different bases used (20 mg Au/CeO_2, 10 mL of H_2O, 0.55 mol/mL glucose, 70°C, 4h, 2 equivalence of base), and (B) oxidation of glucose in the presence of K_2CO_3 with and without catalyst (20 mg Au/CeO_2, 10 mL of H_2O, 0.55 mol/mL glucose, 70°C, 4h, 2 equivalence of K_2CO_3).



Scheme 1. Products of glucose oxidation.

Table 1. Support and catalysts characterization by ICP AES, XPS, BET and BJH.

Catalyst	Au (wt%)[a]	Cs (wt%)[a]	Au Particle size (nm)[b]	BET surface area (m^2/g)	Pore volume BJH (cm^3/g)
Au/CeO_2	1.72	-	3.6	21.2	0.064
$Au\text{-}Cs/CeO_2$	2.46	0.10	2.6	18.0	0.059
CeO_2	-	-	-	23.7	0.069

[a]from ICP AES, [b]estimated from XPS.

Table 2. XPS molar concentrations

Catalyst	XPS molar concentrations (%)				
	Au 4f	C 1s	O 1s	Ce 2p	Cs 3d
Au/CeO_2	1.82	12.76	56.08	28.16	-
$Au\text{-}Cs/CeO_2$	2.41	14.24	55.17	27.24	0.09
CeO_2	-	7.56	62.89	29.58	-

Table 3. Oxidation of glucose by Au/CeO_2 catalyst[a]

Entry	Glucose (mol L^{-1})	Temperature (^oC)	Time (min)	Conversion (%)[b]	Glucuronic acid Yield (%)[b]
1	0.55	70	30	6	6
2	0.55	70	60	8	9
3	0.55	70	90	10	10
4	0.55	70	240	12	12
5	0.55	110	240	65	53
6	0.55	130	240	89	48
7	0.55	150	240	100	23
8	0.55	70	240	100[c]	14
9	0.55	70	240	100[d]	2
10	0.55	70	240	0[e]	0
11	0.055	70	240	78	75

[a] All reactions were performed at 15 bar O_2 using 10 mL aqueous glucose solution, and 20 mg catalyst (0.002 mmol Au). [b]determined by HPLC, [c]reaction in the presence of base (K_2CO_3, 2 equivalents), [d]reaction in the presence of base without catalyst, [e]blank test with CeO_2.

Table 4: Oxidation of carbohydrates by Au catalysts supported on CeO_2.[a]

Entry	Catalyst	Conversion and Yield (%)[e]			
		Glucose	Fructose	Maltose	Gluconic acid
1	Au/CeO_2	12 (11)	12 (12)	7 (4)	-
2	Au_{PVA}/CeO_2[b]	1 (1)	2 (1)	-	-
3	$Au\text{-}Cs/CeO_2$[c]	55 (54)	67 (67)	23 (18)	44 (44)
4	Au/CeO_2+CsCl[d]	11 (11)	11 (11)	8 (7)	-
5	CeO_2	0	0	0	0

[a]All reactions were performed using 10 mL aqueous carbohydrate solution (0.55 mol L^{-1}), 20 mg catalyst (0.002 mmol Au), 15 bar O_2 pressure, 70°C and 4 h; [b]Catalyst prepared by sol-immobilization method; [c]0.1 wt.% of cesium; [d]Reaction carried out in the presence of CsCl; [e]Yield (%) of glucuronic acid as identified by HPLC is given in parentheses.