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Gold catalysts screening in base-free aerobic oxidation of glucose to gluconic acid

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ABSTRACT

Base-free aerobic oxidation of glucose in presence of Au/Al₂O₃, Au/CeO₂, Au/CeO₂(20 wt%)/Al₂O₃, Au/CeO₂(25 wt%)/ZrO₂ and Au/CeO₂(50 wt%)/ZrO₂ catalysts using molecular oxygen at atmospheric pressure is studied. Within the whole series high conversion and selectivity to gluconic acid are observed after 18 h of reaction at 120 °C. The activity and especially the selectivity changes are related to the support nature in a way that the higher the Lewis acidity of the support the lower the selectivity to gluconic acid and the higher the production of lactic acid. The highest yield to gluconic acid is obtained over Au/Al₂O₃ for which the influence of the reaction time, temperature and stirring rate are further evaluated and discussed.

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1. Introduction

Biomass is the most abundant and sustainable carbon source nowadays. Carbohydrates constitute 75% of the annual renewable biomass with glucose as monomer of cellulose the most abundant monosaccharide [1]. Efficient conversion of cellulose and glucose to valuable compounds, so called platform chemicals, is of great importance and it is current topic of interest in Chemistry [2,3]. Within the glucose platform chemicals, D-Gluconic acid obtained by aerobic oxidation of glucose is an important compound. It is widely used as environmentally friendly chelating agent and water soluble cleansing agent in food and pharmaceutical industries with an annual market of about 100,000 tons per year [2,4,5]. It is usually produced by fermentation of glucose with microbial species such as *Aspergillus niger*, *Penicillium* sp., *Zymomonas mobilis*, *G. oxydans* and *Gluconobacter* sp. [6–8]. However in the fermentation medium, the accumulation of gluconic acid inhibits the microbes function leading to lower yields and slow overall reaction rate [5,6]. In recent years, due to the complexity of fermentation process, increased research efforts are devoted to find environmentally friendly alternative, such as technology based on heterogeneous catalysis [9]. Several studies have been reported on gluconic acid production over platinum group metals (PGM) catalysts [10–12]. being main

drawback of these systems their deactivation due to oxygen poisoning of the metal surface [13]. In order to improve PGM catalysts activities, bimetallic Bi-Pt and trimetallic Bi-Pd-Pt catalysts were reported with higher activity and selectivity [11,14]. However, Bi is prone to leaching which converts these catalysts in inadequate candidates for the production of chemicals for food and pharmaceutical industries.

As an alternative, gold has been successfully used in aerobic oxidation of carbohydrates [15,16]. Specifically, aerobic oxidation of glucose carried out over different unsupported and supported gold catalysts, showed important activity and very good resistance to oxygen poisoning. However, an important drawback of these processes is the strong dependence of gold activity on the reaction pH value which entails the use of base, usually sodium hydroxide [17,18]. Biella et al. [19] have demonstrated that the use of alkaline conditions improves the activity and increases the catalyst stability during recycling tests. Additionally, basic conditions (pH at 9.5) seems to avoid gold nanoparticles leaching and sintering, and therefore, prevents catalyst deactivation. Besides gold leaching, another cause of deactivation is the strong interaction between gold nanoparticles and carboxylic compounds, also suppressed in presence of base due to salt formation. Despite all the advantages of using base in glucose oxidation reaction, base-free process is highly desired in order to simplify the treatment of the post-reaction mixture and to obtain pure acid instead of gluconate salt. In addition, glucose isomerization to fructose occurs catalyzed by the presence of base and lowers the selectivity to gluconic acid.

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Some recent studies report the base-free oxidation of glucose over gold supported catalysts under mild conditions. Qi et al. [20] studied glucose oxidation over gold supported on structured carbon and ZrO_2 at 110 °C and 0.3 MPa $P(O_2)$ and reported high initial glucose conversion over Au/C (92.4%) in comparison to zirconia based catalyst (12.7%), with conversion decrease of approx. 20% after 4 runs. Wang et al. [21] investigated base-free oxidation of glucose over different CeO_2 and ZrO_2 supported gold catalysts at 65 °C and 0.23 MPa $P(O_2)$ and reported activity dependence on gold loading, being the catalysts with lower gold content the most active. Approximately 30% to 60% decrease of glucose conversion over Au/ CeO_2 catalysts after 5 runs were observed. To palliate this effect the authors proposed a catalyst treatment, calcination and/or base washing before the reuse cycles, in order to improve the activity and to avoid fast deactivation. Those treatments suggest that any change of the support state, such as particle size or acid-base properties could influence in a great manner the activity towards gluconic acid formation.

In this context, we report herein the base-free aerobic glucose oxidation study under mild conditions over different gold supported catalyst as a function of the support nature. Various gold supported systems are screened, using $\gamma-Al_2O_3$, CeO_2 as simple oxides and $CeO_2(20\%wt)/Al_2O_3$, $CeO_2(25\%wt)/ZrO_2$, and $CeO_2(50\%wt)/ZrO_2$ as mixed oxides combinations. The effect of support nature, reaction time, temperature and stirring rate on the catalytic activity and product distribution are evaluated and the catalyst reusability discussed.

2. Experimental

2.1. Materials and methods

D-(+)-Glucose (anhydrous, 99%) was purchased from Alfa Aesar and used as received. $H AuCl_4$ (Johnson Matthey) was used as gold precursor. All supports are commercially available solids and were used in this study without any previous treatment: $\gamma-Al_2O_3$ (Sasol, hereinafter Al), $CeO_2(20\%wt)/Al_2O_3$ (Sasol, Ce/Al), CeO_2 (Ce), $CeO_2(25\%wt)/ZrO_2$ (Ce25/Zr) and $CeO_2(50\%wt)/ZrO_2$ (Ce50/Zr) (last three solids available from Daiichi Kigenso Kagaku Kogyo Co., Ltd.).

XRD measurements were carried out at room temperature on Panalytical X'Pert Pro diffractometer, equipped with Cu anode. All diffractograms were recorded in the 10–90° 2 θ range, with 0,05° step size and 240 s acquisition time.

Gold loadings were determined by X Ray Fluorescence (XRF) using Panalytical AXIOS spectrometer with Rh tube of radiation.

Transmission electron microscopy (TEM) observations were carried out on PHILIPS CM-200.

The products of glucose oxidation were identified and quantified by HPLC using a Hi-Plex H column (300 × 7.7 mm) and refractive index detector (Varian 360-LC) and MilliQ water as mobile phase.

2.2. Catalytic test conditions

The catalytic tests were performed in a glass batch reactor (50 mL) saturated with oxygen at atmospheric pressure (approximate $P(O_2)$ of 0.1 MPa) with 5 mL 0.2 M glucose solution and Glucose/Au molar ratio of 100. In a typical experiment, a 20 mL/min pure oxygen flux was introduced in the reactor in order to supply an oxygen rich atmosphere. Then, the reactor was closed and the mixture stirred at 600 rpm at various times and temperatures (0 °C–120 °C temperature range) without base addition. After reaction, 500 μ L of sample was taken from the final mixture, diluted in 500 μ L of MilliQ water and immediately analyzed by HPLC. The conversion, selectivity, yield and C balance calculations were based on

Table 1
Gold contents (%) for the fresh catalysts.

Au(%)	Au/Al	Au/Ce	Au/Ce/Al	Au/Ce25/Zr	Au/Ce50/Zr
	1.64	3.94	2.36	2.31	2.39

the HPLC measurements. The reported conversions were obtained after comparing the glucose concentration before and after the reaction, Eq. (1). Owing to the wide variety of products that could be obtained, selectivity was calculated on the base of the carbon moles, as described in Eq. (2). Finally, yields were calculated by Eq. (3). Carbon balance deviation from 100% was always less than 5%.

$$\text{Conversion}(\%) = \frac{[\text{Glucose}]_I - [\text{Glucose}]_F}{[\text{Glucose}]_I} \times 100 \quad (1)$$

$$\text{Selectivity}(\%) = \frac{\text{Carbon mol of specific product}}{\text{Carbon mol of total products}} \times 100 \quad (2)$$

$$\text{Yield}(\%) = \frac{\text{Conversion}(\%)}{100} \times \text{Selectivity}(\%) \quad (3)$$

For the reuse of catalyst, higher amount of glucose (0.2 M, 15 mL) and gold catalyst were used in order to maintain the same glucose-to-catalyst ratio during the recycle runs. Between runs the catalyst was recovered by filtration, and reused under the same reaction conditions without any further pretreatment.

3. Results and discussion

Gold was deposited (2 wt.% nominal value) by direct anionic exchange (DAE) method assisted by ammonia as proposed previously by Ivanova et al. [22]. Gold precursor solution (around 10⁻⁴ M) was heated to 70 °C, and then contacted with the support and 20 min later with NH_3 . The final solid was filtered, dried at 100 °C overnight and calcined at 300 °C during 4 h.

Table 1 presents the actual gold loading of the fresh catalysts.

For Au/ Al_2O_3 catalyst, a metal loss of around 18% from the nominal value was detected, due to incomplete gold deposition. On the other hand, all ceria-containing solids, present experimental values close or even higher to the expected ones. The later suggests that, although a complete metal deposition occurs some support loss is also possible. In the case of the bare ceria support, almost the double of gold loading is detected suggesting that the use of strongly basic media during gold deposition could provoke support dissolution. In addition, the support loss increases with the ceria content increase within support composition. In the preparation process the amount of gold precursor is always slightly higher than required to account for the metal losses; nevertheless, the greater values observed may be due to incident blends, or also to the fact that the commercial support could contain other components, which are removed after calcination.

The diffraction patterns of the prepared catalysts compared to their corresponding supports are presented in Fig. 1.

The diffraction peaks corresponding to the gold metal phase are, in general, not observed for the ceria containing catalysts, suggesting an average size of the gold crystallites under the detection limit of the technique (4 nm). Nevertheless, and despite the lower crystallinity of bare alumina support, weak diffraction, which could be attributed to gold at 77° 2 θ , is observed for Au/Al sample. The later suggests an average gold particles size slightly superior to 4 nm, which cannot be properly quantified by using Scherrer equation because of its low intensity.

It is worth to mention the $CeO_2 - ZrO_2$ solid solution formation (Fig. 1B), independently to the Ce/Zr molar ratio, confirmed by the diffraction shifts toward higher 2 θ with the increase of Zr content.

Transmission electron microscopy (TEM) was used to evaluate the average gold particle size for Au/Al, Au/Ce/Al and Au/Ce

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