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Influence of gold particle size in Au/C catalysts for base-free oxidation of glucose

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ABSTRACT

A series of gold colloids were prepared and immobilized on commercial activated carbon. The influence of the colloid preparation and stability were studied and related to the gold particle size in the final catalyst. The catalysts show an important activity in the glucose to gluconic acid oxidation reaction, leading to gluconic acid yield close to 90% in base free mild conditions (0.1 MPa O_2 and 40 °C). The size-activity correlation and probable mechanism were also discussed. Finally, the viability of the catalyst was tested by recycling it up to four times.

1. Introduction

Biorefinery, defined as the efficient transformation of renewable materials to fuels and intermediate chemicals, and associated to environmental and economic benefits, has driven the research in this area to notable increase in the last decades [1–4]. Within the renewable materials the vegetal biomass, mostly constituted by carbohydrates, represents around 75% of the total renewable biomass [5]. Among the carbohydrates represented in this biomass the cellulose remains the most attractive fuel precursor, mainly due to its low price, chemical purity and because it is formed only by one monomer – glucose [6]. After cellulose depolimerazion the subsequent transformation of glucose to valuable compounds involves a variety of processes such as hydrogenation [7], isomerization [8], dehydration [9] and oxidation [10]. Every single mentioned process or a combination of them lead to the formation of different 'platform chemicals'. As an example, the D-Gluconic acid, derived from the oxidation of glucose at anomeric position, results to be an useful food additive and raw material for drugs and biodegradable polymers manufacturing [11,12]. Industrially D-Gluconic acid is produced by enzymatic fermentation process [13,14] for which the principal inconvenient for sustainable large-scale production is the necessity of a neutralization step in order to avoid enzymes deactivation by the produced acid [15]. This problem could be solved either by using a base or by the substitution of the enzymes with a heterogeneous catalyst able to oxidize glucose under mild base-free conditions by using either O_2 or H_2O_2 as oxidants [16–19].

Although the use of base (NaOH and a relatively high pH of around 9-9.5) results in increase of heterogeneous catalyst's activity due to particle size stabilization and metal leaching suppression [20–22], a decrease in the selectivity to gluconic acid is often observed caused by the glucose to fructose isomerization process [23]. In addition, the formation of gluconate salt instead of pure gluconic acid occurs and entails the need of cost effective post-reaction treatment to obtain the target acid. Therefore, a simple base-free heterogeneously catalyzed process able to produce selectively gluconic acid and avoiding the problems of particle size sintering and metal leaching is highly desirable.

Within the catalyst's candidates for such a process, the most promising alternative is nanometric gold. Glucose oxidation has been carried out over both unsupported [24,25] and supported [20,26] gold catalysts with good results in activity and selectivity; however, some issues must be addressed in order to improve the catalytic system. Various studies reported the base-free aero-

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bic oxidation of glucose over gold supported catalysts with good results in activity and selectivity [22,27–29]. Most authors found a clear dependence of glucose oxidation activity on average gold particle size, suggesting that the oxidation proceeds directly on gold metal surface rather than on the contact perimeter between gold and support [26,28,30]. On the other side, it is still under debate the optimal gold particle size and if the nanoparticle shape plays any significant role in oxidation process. A serious inconvenient for the use of supported nanogold catalysts in the base-free glucose oxidation is related to the possible metal leaching and/or the gold sintering during the reuse cycles, driving to loss of activity [29]. The latter suggests the importance of adequate choice of support, able to stabilize the gold particles thus avoiding the leaching/sintering phenomena.

Most of the studied supports are simple or mixed metal oxides such as TiO_2 [27], MgO [31] Al_2O_3, CeO_2, CeO_2(25 wt%)/ZrO_2, CeO_2(50 wt%)/ZrO_2 and CeO_2(20 wt%)/Al_2O_3 [29]. The use of carbon supports has been also widely reported [32–36]. No matter the type of carbon supports i.e., activated carbon, carbon nanotubes or carbon nanofibers, Au/C systems showed high activity and selectivity in the oxidation of glucose [22,37,38].

In general, the substantial importance of active carbon as metal support in industrial catalysis is well recognized. Its stability in both acidic and basic media, its tunable pore structure and stability at high temperatures, the easiness of metal phase recovery by carbon burn away and its lower costs in comparison with conventional supports such as alumina and silica [39,40] convert it in a versatile material for heterogeneous catalysis. The real relevance of carbon in aqueous-phase oxidation reactions derived from its hydrophobicity, which usually difficults active metal phase leaching, thus improving catalyst's inherent activity. In fact, higher activity of hydrophobic catalysts in glucose oxidation compared to hydrophilic catalysts application has been reported [41,42]. This difference in activity was assigned to stronger adhesion between hydrophobic catalyst grains and oxygen bubbles leading to an increase of the catalyst grains number at the gas-liquid interface and, therefore, to an increase in the rate of the gas transfer towards the catalysts [38]. The only disadvantage of using hydrophobic support is that the conventional methods for gold nanoparticles preparation, such as deposition-precipitation or direct anionic exchange are less useful resulting in important gold loss and low reproducibility. Within the existing gold nanoparticles preparation methods, the gold colloidal route seems the most appropriated to obtain a homogeneous and reproducible gold nanoparticles size distribution which allows a more direct gold size/activity correlation. Nevertheless, the use of the colloidal route for preparing Au/C samples includes the utilization of particles stabilizing agents as citrates, polyvinyl alcohol (PVA) etc. which if not removed from the gold surface could influence the measured activity due to some shielding effects [30]. It is important therefore to remove any rests of stabilizing agents in order to observe the "real" size/activity effect on the reaction of glucose oxidation.

From all above, the aim of this work is to gain insights into the role of gold particle size and shape in the base free oxidation of glucose to gluconic acid. For that, a series of Au/C catalysts with different gold particle size were prepared and their catalytic performances evaluated in the oxidation reaction. The catalysts resulted from immobilization of gold colloids with different gold sizes on a commercial activated carbon, and were subjected to a calcination treatment at 300 °C in order to remove any precursor leftovers and to stabilize the gold nanoparticles onto the carbon surface in order to assure as much as possible the permanence of the gold size during the reaction course. The evaluation of the catalyst's reusability was also undertaken.

2. Experimental

2.1. Synthesis

Activated charcoal powder DARCO® (Sigma Aldrich, 100 mesh particle size) and $HAuCl_4$ (Johnson Matthey) gold precursor were used as received.

The deposition of gold (2 wt.% nominal value) on the carbon support was carried out according to the colloidal method assisted by polyvinyl alcohol (PVA) where $NaBH_4$ (Sigma Aldrich) was used as reducing agent [43]. The necessary amount of gold precursor was dissolved in water to a final concentration of 5.10^{-4} M and the corresponding quantity of PVA (1% wt. aqueous solution) was added and stirred during 20 min. After that, the appropriate amount of 0.1 M freshly prepared $NaBH_4$ solution was quickly added to reduce the gold precursor. After 20 min stirring, sample of 5 mL was taken to characterize the colloid and the rest of solution was put in contact to the adequate amount of the commercial activated carbon in order to have a nominal gold loading of 2%wt. 45 min later, the final mixture was centrifuged at 15000 rpm for 20 min in order to ensure the anchorage of the totality of gold nanoparticles on carbon. The resulted samples were filtered and dried at 100 °C for 2 h and finally calcined at 300 °C for 2 h in static air. Following this procedure, 11 samples, were prepared as a function of PVA:Au weight ratio (Series 1) and $NaBH_4$:Au molar ratio (Series 2). The Table 1 summarizes the synthesis parameters of both series of gold samples. Gold colloids and their corresponding catalysts were named as 'Col X' and 'AuC X' respectively, being X a distinctively roman number of order.

2.2. Characterization techniques

UV–vis measurements were carried out on UV–vis Avantes AvaLight-DH-S-BAL spectrometer equipped with optic fiber liquid sensor for wavelengths ranged from 100 to 1000 nm.

XRD measurements were performed at room temperature on Panalitycal X'Pert Pro diffractometer, equipped with Cu anode with 0.05° step size and acquisition time of 300 s in 10–90° 2θ range. The average gold crystallite size of the Au/C catalysts was calculated from the broadening of the (111) Au plane at 38.28° 2θ applying Scherrer's equation.

Transmission electron microscopy (TEM) micrographs were acquired on PHILIPS CM-200. The mean gold particle diameter was considered on the basis of its homogeneity, degree of dispersion and number of particles. The average gold particle size was estimated considering the surface distribution calculation, expressed in Eq. (1).

$$D[3,2] = \frac{\sum_{1}^{n} D_i^3 \nu_i}{\sum_{1}^{n} D_i^2 \nu_i} \qquad (1)$$

where D_i is the geometric diameter of the i^{th} particle, and ν_i the number of particles with this diameter. For every distribution the total number of measured particles overcomes 200 particles per sample (colloid or catalyst).

The gold loadings were estimated through ICP analysis by using Horiba Jobin Yvon spectrometer after fluorhydric acid digestion of the samples.

2.3. Catalytic tests

Aerobic oxidation of glucose (D-(+)-Glucose anhydrous, 99%, from Alfa Aesar) was carried out in a glass batch reactor (50 mL) equipped with Young valve, magnetic stirrer and saturated with

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