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Gold catalyst recycling study in base-free glucose oxidation reaction

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ABSTRACT

This work is devoted to the study of viability of immobilized gold colloids on carbon as catalysts for the base-free glucose oxidation reaction with a special emphasis made on catalysts' recycling, operational life and possible routes for deactivation/reactivation under batch conditions. The observed catalytic behavior is related to all possible manners of deactivation, like gold metal state changes (particle size agglomeration or leaching), support modifications or active sites blocking by intermediates. In an attempt to recover the initial catalytic activity, the samples are subjected to different treatments such as H₂O and NaOH washings and calcination. The failure of the regeneration procedures to recover the initial activity and after detailed catalyst' characterization allows us to find out the main cause of deactivation.

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1. Introduction

In the last decades, an increasing necessity of readdressing the interest from fossil raw materials to renewable feedstocks arises due to the continuous depletion of the formers. A reorientation of the scientific interest towards carbohydrates as feedstock for fine chemistry is currently of actuality [1]. The "green catalysis" approach including orientation toward aqueous media low temperature catalytic transformations and carbohydrates highly functionalized type molecules increases by far its potential as fine chemical feedstock [2,3]. It is then of crucial importance to explore this potential toward efficient, environmentally friendly and economically viable technologies for large-scale conversion of carbohydrates into industrially viable bulk or intermediate compounds for chemical, pharmaceutical or polymeric use [4]. Among the existing reactions for carbohydrates conversion, the selective oxidation of plant-biomass monomers (hexoses or pentoses) to corresponding carboxylic acids presents a possibility to easy integration in already existing technologies and therefore an important economic interest. The heterogeneously catalyzed transformation of glucose to gluconic acid received important attention [5–8]. Nevertheless, the proposed processes must show an important activity/selectivity balance and especially long term stability in order to be competitive to the existing biotechnological process for gluconic acid production. The slow to severe catalyst deactivation

and side reactions products are considered as the main challenges to undertake for future industrialization of heterogeneous process [9].

Among the metal catalysts discussed for selective oxidation of glucose to gluconic acid, the noble metal based ones are the most frequently reported. Important productivity was reported for Pt and Pd based catalysts [10–12]. Especially improved activities and product selectivity of the Pt based catalysts were obtained after doping with Bi [12,13]. However, during the reaction, bismuth leaching was observed which converts this catalytic system inadequate for pure chemicals production and may cause deactivation. In addition, alkaline conditions are required to increase the reaction rate and to avoid deactivation by reaction intermediates. Although beneficial for the reaction rate, the use of base conditions affects negatively the economics of the process as gluconate salt instead of pure gluconic acid is obtained at the end of reaction. Often, a decrease of selectivity due to the favored glucose to fructose isomerization reaction at high pH is observed [6,14]. Considering that the catalysts operate continuously under oxygen rich atmospheres Pt and Pd based catalyst could suffer also deactivation by "over-oxidation" responsible for active sites lost by oxidation. The majority of these inconvenients could be resolved by using gold based catalysts instead of platinum and palladium based ones. High selectivity and activity were reported for supported gold catalysts and convert them in the most promising candidates for future industrial implantation [8,15–19]. Gold catalysts successfully operate under oxygen. The inert nature of the metal avoids loss of activity by oxidation and present an important activity for aldehyde group oxidation and inertness towards secondary alco-

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Table 1
Synthesis parameters of the prepared samples.

Sample	NaBH ₄ :Aumolar ratio
AuC.I	3
AuC.II	5
AuC.III	10

holic group oxidation [6]. Probably the most important findings concerning gold based systems is that they could operate under a wide range of pH with the same activity, which allows avoiding the glucose to fructose isomerization under base conditions.

Recently, the great potential of gold catalysts for direct glucose oxidation in base free conditions was demonstrated [20–23]. It was confirmed that catalyst productivity is barely influenced by the pH of the reaction and that the proper choice of support is very important for catalyst performance. Mineral oxides, as pure ceria or mixed cerium oxides, are not suitable as supports, since the catalysts suffer slow deactivation by metal leaching [21,23]. On the other hand, basic supports are reported to be most suitable in acidic conditions [20], although their stability towards hydroxylation has to be improved. Pointing industrial application, the catalysts should withstand continuous operation and repeated recycling for a long time, which implies low deactivation rate and/or easy activity recovery. Carbon based catalysts present excellent stability in acidic media and low active metal leaching which converts them in potential candidates to study their operation under base free glucose oxidation reaction.

In this context, the aim of this work is to study the catalytic performance of a series of Au/C catalysts prepared by gold colloids immobilization and their recyclability under repeated operation. All possible deactivation causes as gold leaching, sintering and chemical poisoning (active sites blocking by reaction intermediates) are contemplated and related to the variation of the initial gold particle size. The viability of some catalyst treatments between the operation cycles aiming to recover the initial deactivation was also investigated.

2. Experimental

2.1. Catalyst preparation

Gold was deposited from pre-formed colloids prepared by reducing of the PVA stabilized gold precursor with NaBH₄. 5.10⁻⁴ M aqueous solution of HAuCl₄ (2 wt% nominal value) was mixed with the corresponding quantity of PVA (1 wt.% aqueous solution) and stirred for 20 min. After, appropriate amount of 0.1 M freshly prepared NaBH₄ solution was quickly added for other 20 min and the solution was put in contact with commercially available activated carbon powder DARCO® (Sigma Aldrich, 100 mesh particle size). After aging, the final mixture was centrifuged at 15000 rpm for 20 min and resulted solids separated by filtration. Samples were finally calcined in static air at 300 °C for 2 h.

Following this procedure, four samples were prepared keeping constant PVA: Au weight ratio of 0.85 and varying the NaBH₄: Au molar ratio from 3 to 10. The later was chosen in order to get different final gold particle size, as reported in previous studies [24]. Table 1 summarizes the synthesis parameters and labelling of the catalysts.

2.2. Characterization

The gold contents were estimated through ICP analysis by using Horiba Jobin Yvon spectrometer.

Transmission electron microscopy (TEM) study on particle size and dispersion of the catalysts was performed on PHILIPS CM-200.

The average gold particle size was estimated based on surface distribution calculations as shown in Eq. (1)

$$D[3, 2] = \frac{\sum_1^n D_i^3 v_i}{\sum_1^n D_i^2 v_i} \quad \text{Eq. (1)}$$

where D_i is the geometric diameter of the i^{th} particle, and v_i the number of particles with this diameter. For particle size distribution, the total number of measured particles overcomes 200 for every sample.

The DRIFTS spectra were recorded at room temperature without sample dilution using a Thermo Nicolet Nexus FT-IR spectrometer equipped with a liquid nitrogen cooled MCT detector at 4 cm⁻¹ resolution and average of 128 scans. The whole optical path was purged with CO₂- and H₂O-free nitrogen. About 50 mg of fresh or used catalyst finely grounded was loaded in the Praying Mantis™ cell for each measurement.

XPS measurements were carried out on Leybold-Heraus LHS-1020 instrument coupled with EA200 detector and using non chromatic Mg Kα (220W, 11 kV, 1253,6 eV). Prior to use the sample were pressed into a thin disk. The XPS spectra of all sample were recorded at room temperature and the binding energy was calibrated on C1 s at 284,6 eV with an uncertainty ±0.2 eV. The spectra were recorded with constant pass energy of 44 eV and 0.1 eV resolution for the studied zones.

2.3. Base free aerobic oxidation of glucose

The oxidation of glucose was performed in a glass batch reactor (50 mL) at constant temperature and stirring rate at saturated oxygen atmosphere (approximate P_{O₂} of 0.1 MPa). In a typical experiment, the reactor was charged with 0.2 M glucose aqueous solution, catalyst in Glucose/Au molar ratio of 100 and oxygen saturated by bubbling 20 mL/min of pure oxygen flow for few minutes. The reactor was then closed and reaction mixture stirred at 600 rpm, at 40 °C during 18 h in base-free conditions.

The recycling study was carried out in a similar manner separating the catalyst from the products by filtration between the runs and re-using it maintaining Glucose/Au molar ratio of 100 at every run. In some cases reactivation treatments were performed. The samples after filtration were treated either with distilled water, 0.1 M NaOH solution or thermally treated at 300 °C for 2 h before every run.

The reaction products were identified and quantified by HPLC equipped with refractive index detector (Varian 360-LC) and Hi-Plex H column (300 × 7,7 mm) set to 40 °C using MilliQ water as mobile phase.

Glucose conversion and product selectivity to gluconic acid (GA) were calculated as described by Eqs. (2) and (3).

$$\text{Conversion (\%)} = \frac{[\text{Glucose}]_{\text{in}} - [\text{Glucose}]_{\text{out}}}{[\text{Glucose}]_{\text{in}}} \times 100 \quad \text{Eq. (2)}$$

$$\text{Selectivity GA (\%)} = \frac{\text{moleGA}}{\text{totalmolesofproducts}} \times 100 \quad \text{Eq. (3)}$$

3. Results and discussion

The real gold loading measured by ICP and the mean particle size deduced from TEM is presented in Table 2.

All fresh samples present similar gold loadings close to the targeted value. The average gold particle size varies within the series attributed to the modification of the synthesis parameters, chosen in a way to have a real disparity of the initial particle size. Higher the NaBH₄: Au ratio at a constant PVA: Au ratio, lower the average gold particles size. The synthesis parameters influence strongly the average particle size but not the actual metal loadings. The

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