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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/Al_2O_3, Au/CeO_2, $Au/CeO_2(20\,wt\%)/Al_2O_3$, $Au/CeO_2(25\,wt\%)/ZrO_2$ and $Au/CeO_2(50\,wt\%)/ZrO_2$ 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/Al_2O_3 for which the influence of the reaction time, temperature and stirring rate are further evaluated and discussed.

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 γ-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. $HAuCl_4$ (Johnson Matthey) was used as gold precursor. All supports are commercially available solids and were used in this study without any previous treatment: γ-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 Kogio Co., Ltd.).

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

Gold loadings were determined by X Ray Fluorescence (XRF) using Panalitycal 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 μLof sample was taken from the final mixture, diluted in 500 μL of MilliQ water and immediately analyzed by HPLC. The conversion, selectivity, yield and C balance calculations were based on 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%.

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

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

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

$$Yield\,(\%) = \frac{Conversion\,(\%)}{100} \times Selectivity\,(\%) \qquad (3)$$

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° 2θ, 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 2θ 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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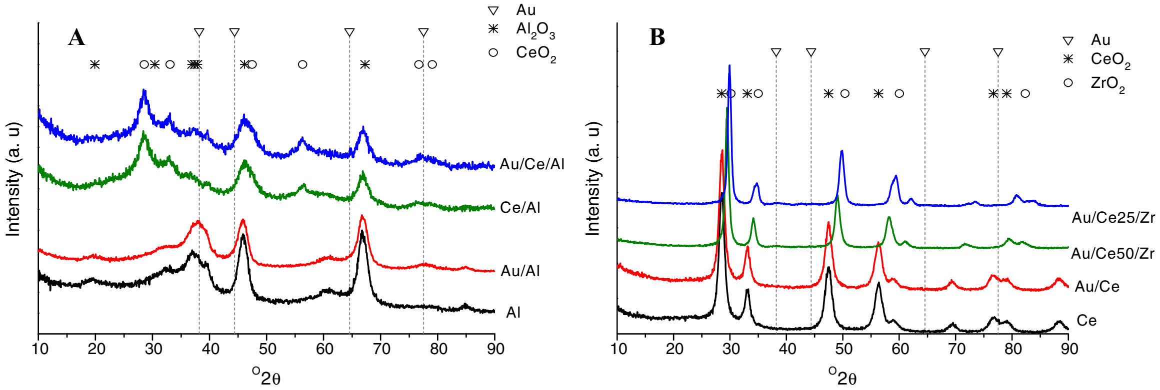

Fig. 1. XRD of the supported systems: A) Al_2O_3 containing supports, B) CeO_2 containing supports.

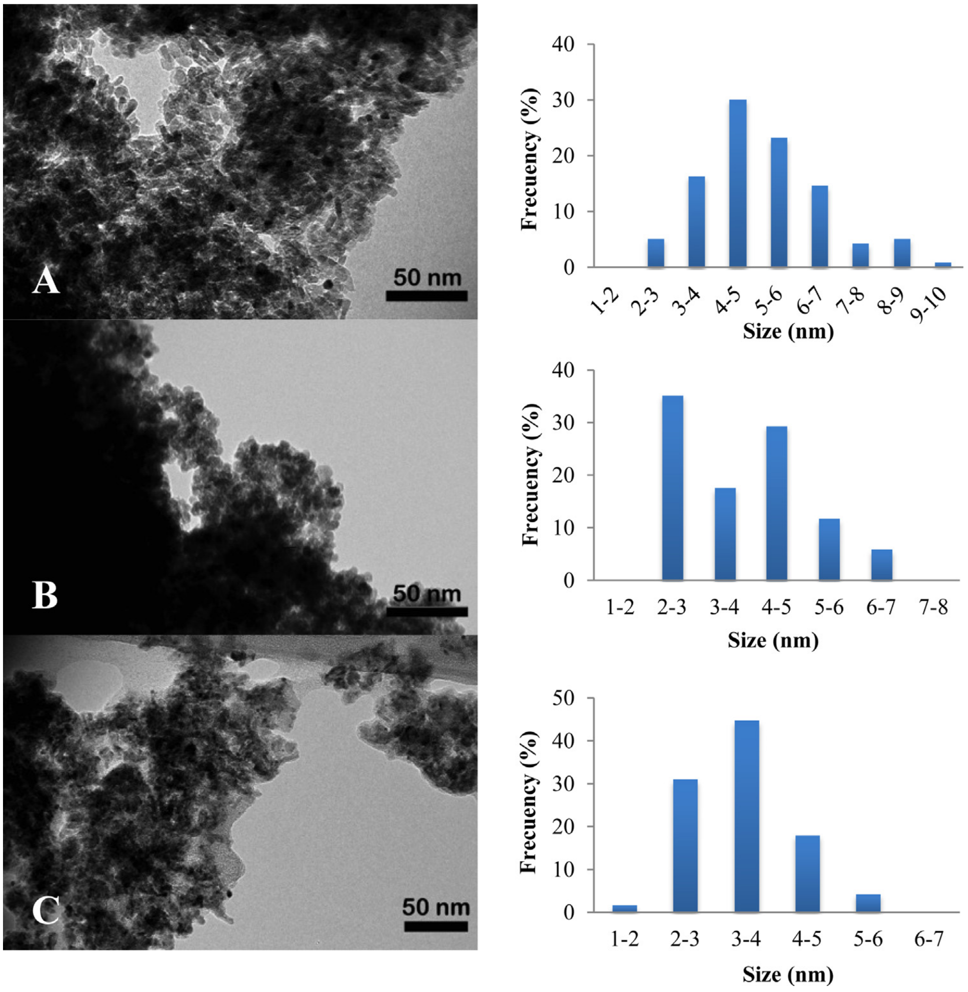

Fig. 2. TEM images and particle size distribution of fresh catalysts: A) Au/Al, B) Au/Ce, C) Au/Ce/Al.

samples. The former is chosen as the only one for which a diffraction peak attributed to gold is detected and the other two samples as representative for the rest of the samples. The corresponding micrographs and particle size distribution are presented in Fig. 2. As detected by XRD, the Au/Al catalyst present an average particle size slightly superior to 4 nm unlike the rest of the samples (Table 2). The particle size distribution follows a typical Gaussian curve except for Au/Ce sample, a possible cause being the low TEM contrast between gold and cerium, which complicates the detection of gold.

Table 2
Estimated particle size, dispersion and TOF for the samples.

Sample	Average particle size, nm	Dispersion, %	TOF, s^{-1}*10^{3}
Au/Al	5.1 ± 1.5 (5.6 ± 1.9)[a]	26	5.44
Au/Ce/Al	3.4 ± 0.8 (3.5 ± 0.8)[a]	38	2.64
Au/Ce	3.9 ± 1.5 (4.3 ± 1.2)[a]	33	1.66
Au/Ce25/Zr	3.4 ± 0.8[b]	38[a]	2.52
Au/Ce50/Zr	3.4 ± 0.8[b]	38[a]	1.58

[b] Assuming the same particle size and dispersion as Au/Ce/Al.
[a] Particle size of the spent catalyst in parenthesis.

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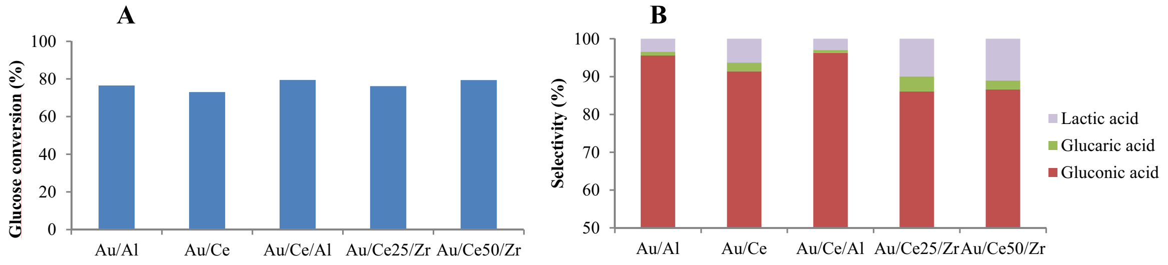

Fig. 3. A) Glucose conversion (%) over different gold supported catalysts (18 h, 120 °C, 600 rpm), B) Selectivity (%).

Based on the calculated average particle size for the fresh catalysts and using the hemispherical ball model, the Au dispersion can be evaluated [23] (Table 2). The calculated dispersion for all samples varies within the 25–40% range with all alumina-containing samples positioned in the lower limit.

Several effects on catalytic activity are studied. Firstly, the influence of support nature is evaluated and on the base of the obtained results, few samples chosen for subsequent reaction parameters study.

3.1. Effect of the support

The conversion of glucose after 18 h of reaction does not seem to be influenced by the nature of support being over 75% in all cases (Fig. 3A). As all the catalysts present different gold loadings, a normalization of the activity to the surface available gold atoms is needed to properly compare the samples. The TOF is calculated on the basis of Au dispersion and presented in Table 2. Due to low mass contrast, gold particles are difficult to measure with adequate accuracy for CeZr supported samples. That is why, their particle size and dispersion are considered equal to those of Au/Ce/Al sample because of sample's similar gold loading, and absence of visible XRDiffractions.

The Au/Al sample doubles the activity of almost all ceria-containing samples, which within its series obey the following order:

$$\mathrm{Au/Ce/Al} > \mathrm{Au/Ce25/Zr} > \mathrm{Au/Ce50/Zr} \sim \mathrm{Au/Ce}$$

It looks like the activity is inversely proportional to the ceria loading, the higher the ceria loading the lower the TOF. Nevertheless, above 50% of ceria, the activity maintains the same order, suggesting that the activity is related to the support nature and more particularly to its Lewis acidity. Using the Pearson concept for hard and soft Lewis acids and bases, the relative Lewis acids hardness can be calculated by considering all ions in its real proportions. The acidity hardness decreases almost in the same order as the activity Au/Al > Au/Ce/Al > Au/Ce25/Zr > Au/Ce50/Zr > Au/Ce indicating that the change of the support nature plays some role during the reaction [24,25].

The products distribution (Fig. 3B) is also influenced by the support nature. The alumina supported sample presents the highest selectivity to gluconic acid (95%) followed by the Au/Ce/Al sample and Au/Ce. The zirconia containing samples show the lowest selectivity to gluconic acid, favoring some lactic acid formation (10%) in comparison to Au/Al (3%) and Au/Ce (6%) based catalysts. The formation of glucaric acid seems to follow the same trend. In general, the formation of lactic acid involves several reactions such as isomerization [26] retro-aldol reaction [27], and secondary isomerization reaction, which normally occurs in the presence of Lewis acid sites. However, it looks like the lactic acid formation is not guided by acid strength of sites as the opposite tendency is observed. The presence of some specific acid sites and more probably their density on the support changes the product distribution and leads to lactic acid formation. For the zirconia-containing solids, the glucose conversion and the product distribution follows the same trend, the lowest selectivity and activity in terms of TOF are registered. It is obvious that the support plays an important role in the process and further research about support acidity, type and strength are required.

Based on the results only three samples are selected for further study of the reaction time effect, Au/Al, Au/Ce and Au/Ce/Al.

3.2. Effect of the reaction time

As expected, the conversion increases with the reaction time (Fig. 4), and insignificant differences between the catalysts are observed. No matter the reaction time the selectivity is clearly governed by the support.

Gluconic acid yield (Fig. 4B) for the Au/Al catalyst increases linearly with the reaction time unlike for Au/Ce and Au/Ce/Al (Fig. 4C, D) catalysts where the yield attains a constant value in the first 4 h of reaction. The presence of ceria in both samples suggests that the oxidation of the glucose might involve labile surface oxygen of this oxide. Therefore the oxidation process is improved, especially at short reaction times probably by the participation of its lattice oxygen and oxygen vacancies [28].

3.3. Effect of reaction temperature

All the other experiments are carried out over Au/Al catalyst. The temperature effect is studied in the 0–120 °C range with 2 h of reaction at every temperature and the results are shown in Fig. 5A.

The glucose conversion rises with the temperature till a constant value at around 55% at 60 °C. This result is expected as the oxygen solubility in water decreases with the temperature [29]. The solubility of oxygen reaches the lowest point at 60 °C and does not change significantly when the temperature increases [29]. To achieve then a higher activity the oxygen pressure has to be risen. It is interesting to underline that relatively high glucose conversion is achieved at 0 °C (35%) which indicates that Au/Al could work successfully at atmospheric pressure, low temperatures and in absence of base. The product distribution also changes with temperature (Fig. 5B), favoring lactic acid formation at low temperatures. Thus low temperatures imply low reaction rates for the glucose oxidation and higher selectivity to lactic acid formation.

3.4. Stirring rate dependence

It is well known for the liquid-phase reactions, that the diffusional processes of either reactants arrival to the active sites or products desorption from the catalyst' surface depend on mixing degree. For this reason, some experiments are carried out over Au/Al sample at 120 °C (2 h reaction time) by varying the stirring rate from 300 to 900 rpm. As expected, the higher the stirring rate, the higher the conversion of glucose (Fig. 6) and the higher the gluconic acid yield (47% vs. 59%).

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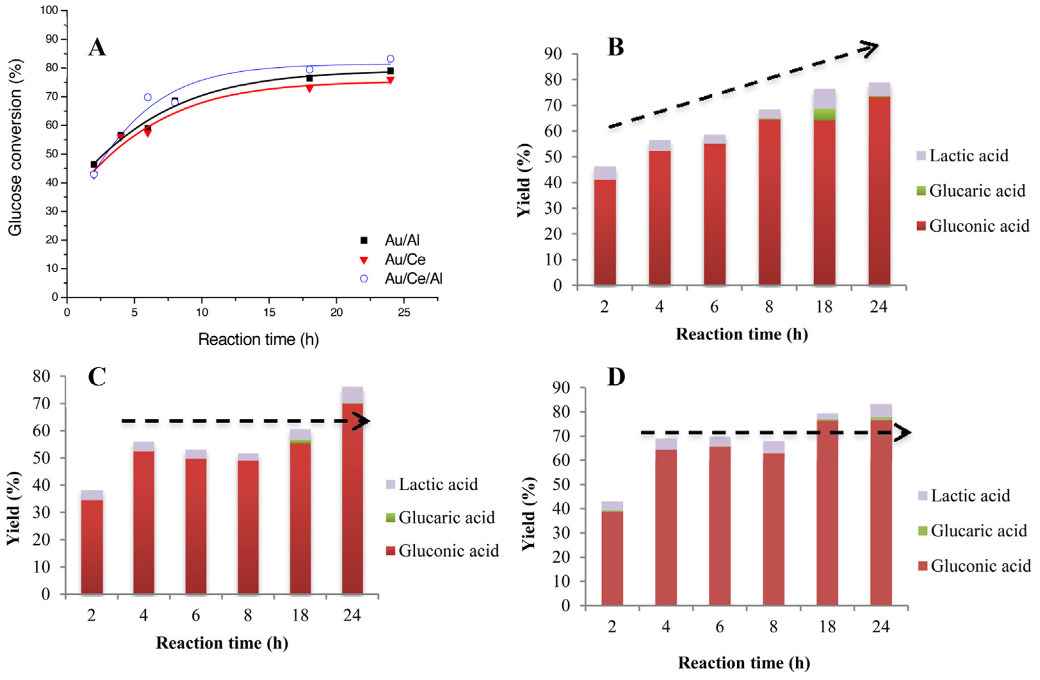

Fig. 4. A) Glucose conversion (%) vs. reaction time (120 °C, 600 rpm), B) Yield over Au/Al, C) Yield over Au/Ce, D) Yield over Au/Ce/Al.

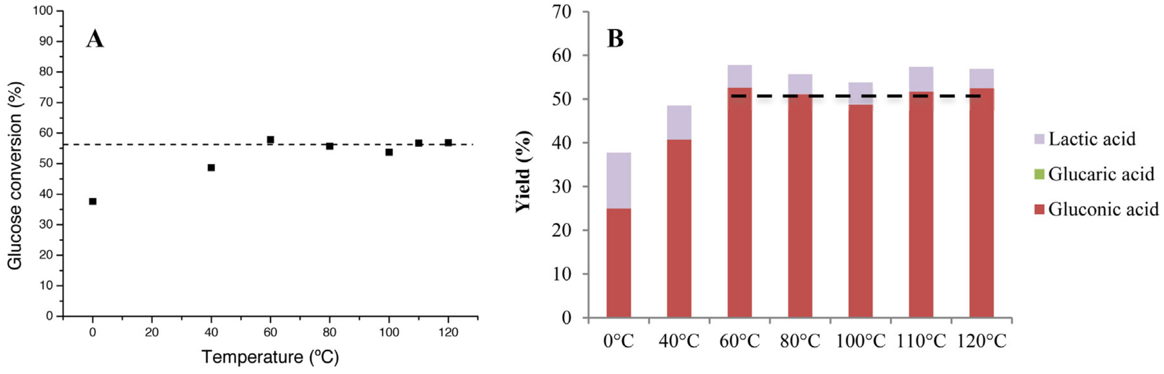

Fig. 5. A) Glucose conversion (%) as a function of the temperature over Au/Al (600 rpm, 2 h) B) Yield (%).

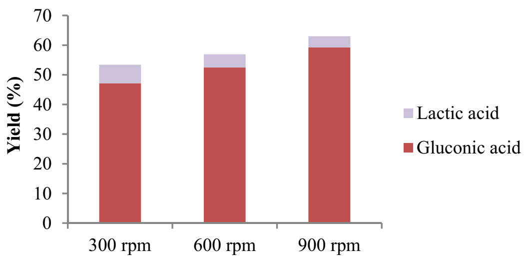

Fig. 6. Yield (%) as a function of the stirring rate over Au/Al (120 °C, 2 h).

Besides glucose conversion, the lactic acid yield is also related to the mixing degree, being higher at low stirring rates (6% of yield at 300 rpm vs. 3% at 900 rpm). This result could be tentatively explained by the higher residence time of the reactants on the surface of the catalyst at lower mixing and/or by lower oxygen concentration in solution, both allowing the secondary reaction to lactic acid formation. As observed above in reaction temperature effect, the lower the reaction rate of oxidation reaction the higher the selectivity towards lactic acid. The formation of lactic acid at low conversions and low mixing rate suggests that great glucose coverage on the catalyst surface is one of the key factors for a proper product distribution.

On the other hand, the limited conversions above 60 °C and the fact that higher conversions can be reached by increasing the stirring rate might also suggest some limitation due to the mass-transfer process. However, as reported by Delidovich et al. [30] the diffusional processes limiting the glucose oxidation reaction rate on Au/Al_2O_3 strongly depend on the Glucose:Au molar ratio. It was reported in this study that for low Glucose:Au molar ratios (below 750:1) the apparent reaction rate is only limited by the rate of oxygen dissolution. Therefore, we can consider that in our study (Glucose:Au 100:1) the limitations due to the mass-transfer process although existing are not so important as those caused by oxygen dissolution process.

3.5. Catalyst reusability

The reuse experiments are carried out over Au/Al catalyst in 4 successive runs. A clear drop of the glucose conversion is observed (Fig. 7).

The initial conversion of 53% achieved in the first run (120 °C, 2 h) drops to 44% in the second and 39% and 37% in the third and

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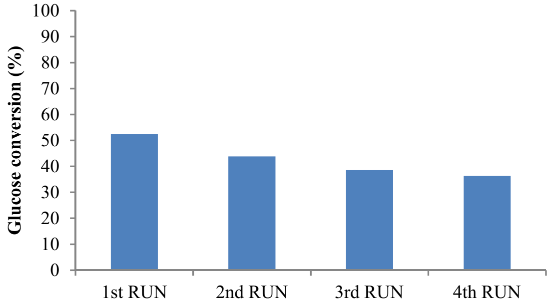

Fig. 7. Catalyst reuse, conversion of glucose (%) over Au/Al (120 °C, 2 h, 600 rpm).

fourth runs, respectively. The slope of activity loss becomes smaller with the number of runs, and appears to stabilize after the 3^{d} one. On the other hand, the change of the reaction solution color occurs, turning to mauve and pointing to gold leaching process. Indeed, the X ray fluorescence (XRF) analysis of the spent sample shows that after 18 h of reaction at 120 °C, the metal loading drops to 1.14% instead 1.64% for the initial catalyst. Generally, in the literature, the gold particle size growth during the reaction is reported as the main reason for gold catalysts deactivation. Comotti et al. [31] observed that the rate of glucose oxidation is inversely proportional to the gold particles diameter, being especially detrimental the size increase above 10 nm. In our case very slight increase of the gold particle size is detected. TEM images and particle size distribution of Au/Al, Au/Ce and Au/Ce/Al spent catalysts after 18 h reaction time are shown in Fig. 8.

Upon reaction the average gold particle size hardly changes, however, a broader particle size distribution is always obtained. The estimated particle size of the spent catalysts is presented in parenthesis in Table 2. Although, the increase of the average gold particle size observed, the difference in size is insignificant and might not be the cause of the observed activity loss, suggesting that leaching of gold should be the problem to solve in order to avoid catalyst deactivation.

In order to verify this assumption, Au/Al was tested again at the same reaction conditions (120 °C, 600 rpm) during 4 h and at this time, the catalyst was microfiltered, oxygen re-introduced the reaction continued to reach a total reaction time of 18 h but this time without solid catalyst. In this way the change of the activity in the last 14 h are caused by the leached gold particles. The obtained results (in red) compared with those of typical experience at 4 and 18 h (in blue) are shown in Fig. 9.

In a typical experiment after 4 h run, the obtained conversion is 57% which increases to 77% after 18 h, being the difference in the conversion directly attributed to the presence of supported catalyst and increase of the reaction time. On the other hand in the blank test, 59% of conversion is reached after 4 h with catalysts while 69% is measured after 18 h over the leached gold solution. Hence, this 10% can be ascribed to both leached gold and reaction time increase. As the change of the reaction time is the same, we can consider that the difference is due to the different gold present, in one case supported and leached in the other leached gold only. These results confirm that the leached gold is also participating in the reaction although lower conversion obtained. However, the color of the leached gold solution changes dramatically from purple

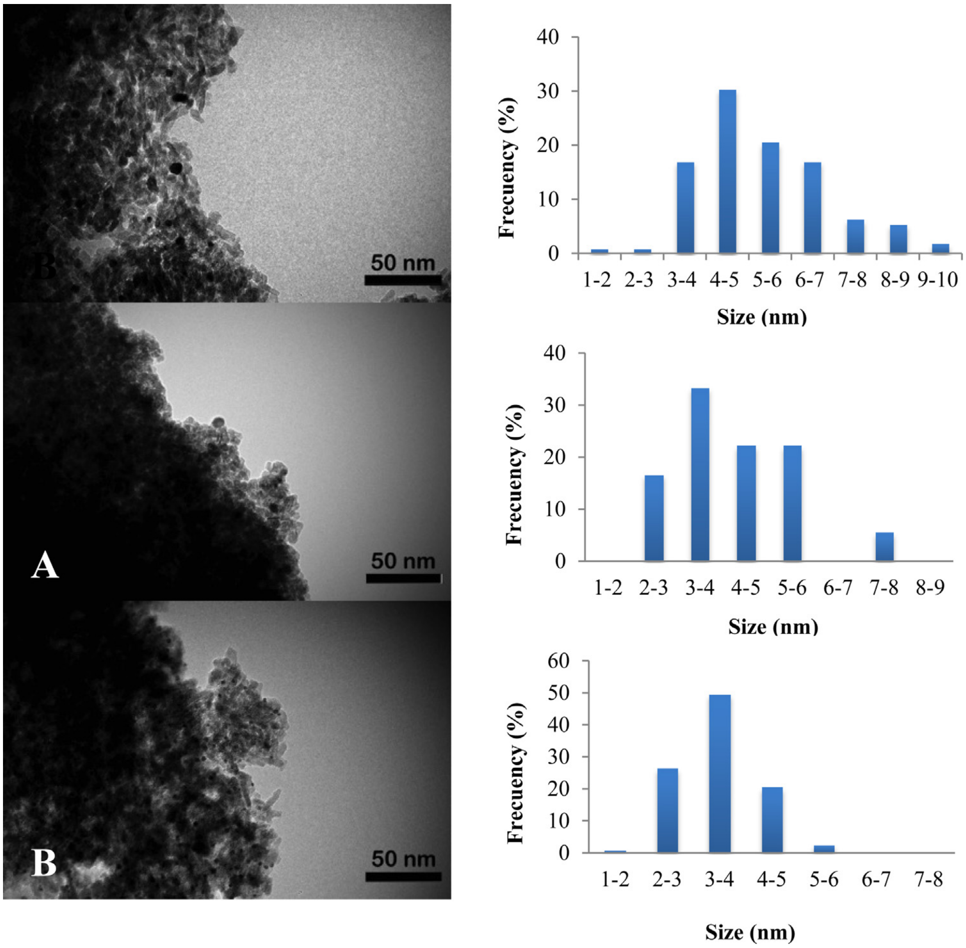

Fig. 8. TEM images and particle size distribution of spent catalysts: A) Au/Al, B) Au/Ce, C) Au/Ce/Al.

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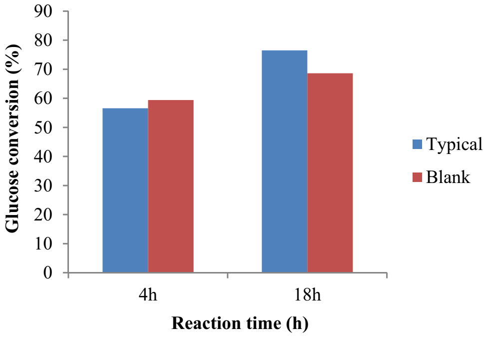

Fig. 9. Typical vs. Blank experiment over Au/Al at different reaction time. (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

to black after 18 h, indicating detrimental particles agglomeration in absence of support. Color change was not observed for any typical experiment including supported gold.

Even though leached gold can participate in the oxidation process, higher activity is observed for the supported catalysts. With the later experiments we can affirm that the loss of activity during reuses runs is due mainly to the gold metal leaching and active sites lost during the catalysts recuperation and also that the presence of support is necessary for particles stabilization against agglomeration.

4. Conclusions

A series of gold supported on different metal oxides are synthesized, obtaining uniform gold nanoparticles size in the 3.5–5.5 nm range. All screened catalysts show high glucose conversion and important selectivity to gluconic acid in base- free conditions. Both, selectivity and activity depend on the support nature, in a way, that the presence of ceria promotes the oxidation reaction at lower reaction times and the presence of zirconia promotes the secondary reactions to lactic acid formation. The higher the zirconia concentration, the lower the glucose conversion and the higher the selectivity to lactic acid. The secondary reaction is also promoted at low reaction temperatures and stirring rates.

When exposed to various catalytic cycles the Au/Al catalyst fails to maintain constant conversion, with the reason for this activity decrease being the gold metal leaching.

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