

Article

Effects of Support and Synthetic Procedure for Sol-Immobilized Au Nanoparticles

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Abstract: New gold catalysts supported on CeO₂, ZrO₂ and TiO₂ were synthesized by two different techniques: deposition-precipitation and colloidal method. The role of the surfactant (PVA, PVP, THPC) was also investigated. The catalysts were tested in the oxidation of glucose to gluconic acid, in aqueous environment and under mild conditions (60 °C and atmospheric pressure). TEM and SEM analyses have shown that the small size of gold nanoparticles is a necessary condition, but not sufficient for a good conversion. In fact, for an active sample, we have verified that the excess of surfactant must be removed because it would coat the surface of the catalyst. The surfactant, however, should not be completely eliminated, since it has the fundamental role of stabilizing the sample preventing nanoparticles from aggregation. It was evidenced that both the synthetic approach and the kind of support affect the catalysts' activity. In fact, by focusing on the three different supports, with all the preparation methods, the ceria has proved to be the best support. This is due to its ability to obtain small gold nanoparticles and to its ability to accumulate oxygen. The most appropriate synthesis methodology proved to be the colloidal method with PVA. Recyclability issue was investigated too.

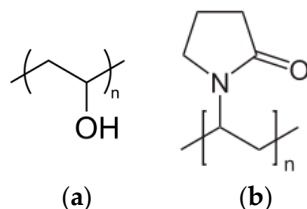
Keywords: gold catalyst; CeO₂; ZrO₂; TiO₂; glucose; oxidation; Au sol-immobilization; PVA; PVP; THPC

1. Introduction

The catalytic activity of a gold-based heterogeneous catalyst depends on the nature of the support and in particular on the size of the gold nanoparticles deposited on it, which in turn depends on the synthetic methodology. The size of the nanoparticles is of significant importance, since in many studies it was evidenced a correlation of inverse proportionality between the activity of the catalyst and the size of the gold nanoparticles [1]. The techniques for the preparation of gold nanoparticles are various. Almost all use chloroauric acid (HAuCl₄·3H₂O) as the metal precursor. The most used techniques in order to obtain an efficient heterogeneous catalyst are: impregnation (IMP), deposition-precipitation (DP) and colloidal methods. As regard as gold samples, dry impregnation is the first method historically used. The procedure involves filling the pores of the support by adding an aqueous HAuCl₄ solution to form a wet paste, which is then dried and calcined. However, this technique does not allow obtaining high gold dispersion. In fact, it leads to nanoparticles of size above 30 nm, due to sintering during the heat treatment, promoted by the Cl[−] ions still present on the sample [2]. Therefore, the gold-based catalysts prepared by this technique have a low catalytic activity [3]. An alternative synthetic approach for Au loading has been recently reported [4,5], namely a liquid phase reductive deposition (LPRD).

The method consists of mixing a solution of HAuCl_4 with a solution of NaOH . The resulting solution was aged for 24 h, in the dark, to complete the hydroxylation of Au^{3+} ions. Then the appropriate amount of support was added to the solution. In LPRD, unlike IMP, a washing procedure is carried out, in order to eliminate residual chloride. DP is a widely used procedure for the preparation of gold-based catalysts supported on metal oxides. In fact, this method works very well with support whose isoelectric point is greater than 5, such as magnesia, alumina, titania, zirconia and ceria. In a typical procedure, after the addition of the support to an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, the pH of the suspension is brought to a fixed value by the addition of NaOH . The whole is heated under stirring, before washing to remove the Na^+ and Cl^- ions, drying and calcining in air. This basic approach has many variables such as for example the synthesis temperature and the pH. In general the pH is set between 7 and 9, since previous studies have shown that this value corresponds to the proper compromise between the loading of high gold amount on the support and the achievement of particles with the proper size (1–10 nm) [6].

The colloidal methods involve the use of a surfactant, which has the fundamental role of limiting the growth and aggregation of the particles, forming a monolayer on the surface of the metal particles; in this way also the long-term stability of the catalyst increases. Such a stage of formation of micelles by the protective agent is followed by a reduction stage from Au^{3+} to Au^0 . Historically, the first colloidal method involves the reduction of gold ions by citrate [7]. Methods that are much more efficient use the NaOH /tetrakis (hydroxymethyl) phosphonium chloride (THPC) system or organic polymers using NaBH_4 as a reducing agent. In the first case the NaOH /THPC system protects the gold particles, to prevent aggregation, and it also works as *in situ* generator of the reducing agent [8]. In the second case, polymers such as polyvinyl alcohol (PVA) or polyvinylpyrrolidone (PVP) may be used as stabilizing agents. They are commercially available, relatively inexpensive, soluble in water, non-toxic and both have a long chain of carbon atoms functionalized, respectively, with OH groups and pyrrolidone groups, as reported in Scheme 1.



Scheme 1. (a) polyvinyl alcohol (PVA) and (b) polyvinylpyrrolidone (PVP).

As the choice of the support plays a vital role in determining the activity and selectivity of a catalyst, in order to assess the effect of the support we have investigated three different metal oxides. In particular, we have chosen TiO_2 , as it is inexpensive and has high chemical stability; ZrO_2 , for its thermal and chemical stability; CeO_2 , because it has a high ability to store and deliver oxygen (this is a very important point for oxidation reactions), due to its ability to change the oxidation state from +3 to +4 [9]. Moreover, essential characteristics for a support are its stability in the reaction media, a low cost, adequate porous structure, acid-base properties [10] and high surface area. In fact, a good support must be able to allow a high dispersion of the active phase with a high degree of thermal stability of the catalyst.

The aim of the work is the synthesis of new gold catalysts active in oxidation reactions. As catalytic test we have investigated the oxidation of glucose, which is a product derivable from biomass and exploited for the future bio-refinery. The biomass conversion processes must be competitive from an economic point of view but must be also environmentally sustainable. Therefore, we need the development of specific technologies. Particular attention is paid to the fraction of lignocellulosic biomass (LCF) that is the indigestible part of plants; in fact, it is not only the most abundant fraction in nature, but it is completely made up of carbohydrates, in particular glucose, which are a rich source of

carbon. In fact, they can be then converted into a set of “bio-platform” molecules (BPM) which can be used as starting materials for the production of high commercial value products. In the literature there are few studies on the oxidation of glucose to glucaric acid [11], while great interest is placed at the oxidation to gluconic acid, because of its wide field of industrial applications (the annual world production of gluconic acid is of 100,000 tonnes [12]). Currently, at industrial level, the gluconic acid is produced by enzymatic oxidation of glucose, using biotechnological processes involving bacteria such as *Aspergillus niger* and *Gluconobacter suboxydans* [13]. However, this process presents considerable disadvantages, both from the practical point of view and from the economic point of view, as the removal of waste water; the low rate of reaction, the death of the bacteria and the accumulation of the substances secreted by these [14]. The existence of such problems using enzymatic oxidation for the production of gluconic acid, has led the scientific community to look for an alternative view by green chemistry. A sustainable method is the oxidation with oxygen in mild reaction conditions of an aqueous glucose solution using a heterogeneous catalyst.

The first reaction of carbohydrate oxidation mediated by catalysts was conducted in 1861 by von Gorup-Besanez [15], using a Pt-based catalyst. In the last two decades studies have been conducted on the use of catalysts based on Pt and Pd for the oxidation reaction of D-glucose to gluconic acid, which, however, have the disadvantages of not being selective against oxidation of the group aldehyde [16] and undergo deactivation in basic and acid environments. This last point is crucial: the rate of the oxidation reaction of a carbohydrate mainly depends on the metal and on the pH, while the selectivity depends primarily on pH and temperature [17]. The dependence of the reaction by the pH rate is determined by the fact that in basic conditions, the carbohydrate is present in the open linear form, in which it is present an aldehyde group, which is much more reactive towards oxidation than hydroxyl. The selectivity problems can be overcome by promoting catalysis, by the Pt or Pd [18], with metals such as Bi or Pb, but these catalysts are not stable since they suffer from leaching.

After the discovery of the ability of gold nanoparticles to catalyze oxidation reactions, the interest in gold as a catalyst in selective oxidation of carbohydrates increased. In fact, gold is more resistant to deactivation than Pt and Pd. Moreover, due to this characteristic, the use of gold-based catalysts takes the advantage of being able to work in a wide range of pH, which is not possible with the biotechnological process. In 2002, Biella *et al.* [19] published studies on glucose oxidation reaction using Au/C catalyst and obtaining a selectivity of 100% with respect to gluconic acid.

An effect of the support for the reaction was found by Ishida *et al.* [20] comparing catalysts supported on metal oxides (TiO₂, CeO₂, ZrO₂ and Al₂O₃) and one supported on C. The stability of the catalyst was proven by Baatz *et al.* [21] who recycled 20 times at 40 °C an Au/Al₂O₃ catalyst and from Mirescu *et al.* [22] who recycled 17 times at 40 °C an Au/TiO₂ catalyst. In the present paper it was investigated the oxidation of glucose. The aim of the work is the synthesis of new gold catalysts active in oxidation reactions. The catalysts must have very small gold particles and must be well dispersed on the support. For this reason, we have compared the two synthetic approaches of deposition precipitation (DP) and colloidal methods. It was also rated as the different surfactants used in the colloidal method affect the behavior of the catalyst.

2. Results and Discussion

2.1. Preliminary Characterizations

N₂ physisorption analyses were carried out in order to determine surface areas and pore size distributions of the supports. The supports exhibited isotherms with hysteresis loops typical of mesoporous materials (Figure 1) and had unimodal pore size distribution. The adsorption for zirconia support is shifted towards higher values, indicating the presence of larger pores (21 nm) than ceria and titania (5 nm and 4 nm). Zirconia exhibited the lowest surface area (≈ 40 m²/g), while ceria and titania exhibited surface area values of 105 m²/g and 166 m²/g respectively.

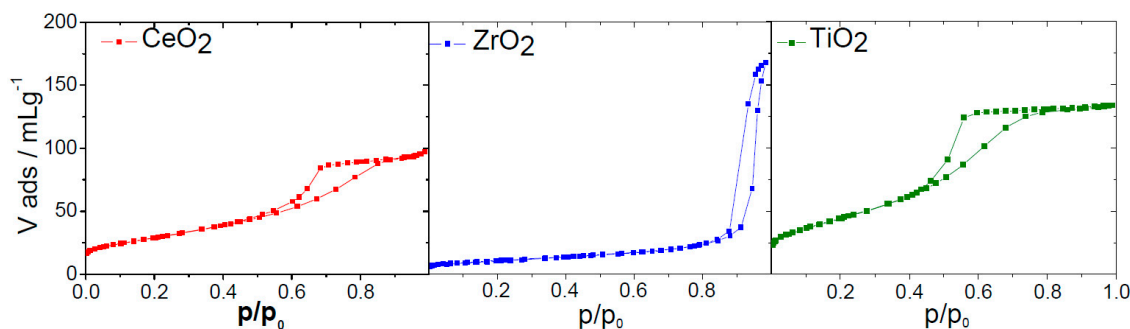


Figure 1. Adsorption—desorption isotherms for the three supports.

All the catalysts were prepared with a nominal value of 2 wt. % Au. The analyses by atomic absorption (Table 1) show that for the samples prepared by colloidal method with a neutral surfactant, such as PVA and PVP, it is possible to load all the theoretical metal; only ATiPVP is an exception. On the contrary, the use of THPC as surfactant, allows obtaining catalysts with only the 1 wt. % of the metal. As regard as DP technique, it allows synthesizing catalysts with a gold content between 1.5–1.8 wt. %.

Table 1 reports also the amounts of SO_4^{2-} ions, determined by ion chromatography, that are present in the final catalysts. In fact during some synthetic procedures, the support was acidified at $\text{pH} = 1$ with H_2SO_4 . In particular, it is possible to observe that for the samples supported on TiO_2 the quantity of sulphate ions is remarkable. This is reasonable, since for this support in order to load an adequate gold amount it is necessary to acidify the support before metal introduction [23].

Table 1. Metal and sulphates content by AAS and IC.

Sample	Au Content (wt. %)	SO_4^{2-} Content (wt. %)
ACeDP300	1.7	
AZrDP300	1.5	
ATiDP300	1.8	
ACePVA	1.8	0
AZrPVA	1.9	0
ATiPVA	1.8	0.59
ACePVP	1.8	0
AZrPVP	1.9	0
ATiPVP	1.4	
ACeTHPC	1.0	0
AZrTHPC	0.9	0.8
ATiTHPC	1.0	1.0

As previously reported, in the sol immobilization method the surfactant has the fundamental role of maintaining gold nanoparticles separated, in order to avoid their sintering and deactivation. With the aim of check for surfactant presence in the final samples, we have performed FT-IR analyses (Figure 2). In the range between $2950\text{--}2850\text{ cm}^{-1}$, it's possible to observe as for PVA and THPC series some bands that are associated to the stretching of C–H aldehydic groups. This is a clear indication of the presence of surfactant in the final catalysts.

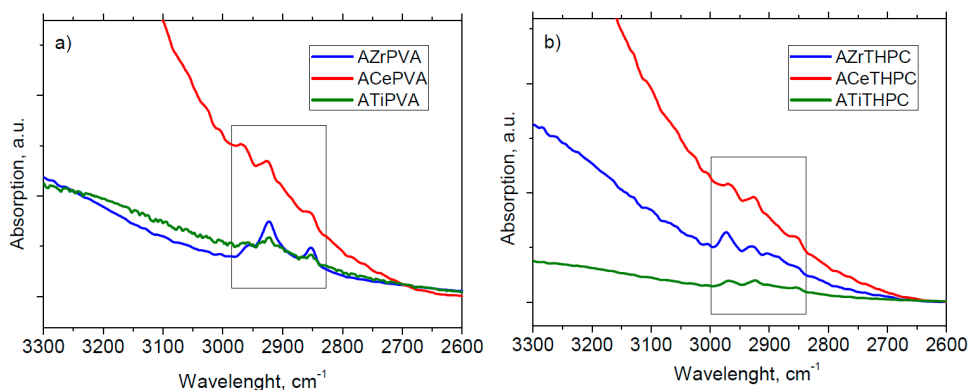


Figure 2. FT-IR spectra for catalysts synthesized by sol immobilization method with PVA (section a) and THPC (section b).

2.2. Effect of Support and of Synthetic Method

Figure 3 shows catalysts' activity for D-glucose oxidation, which was used as reaction test. In order to highlight the support's effect, all the catalysts were assembled by synthesis method. To monitor the conversion of D-glucose to gluconic acid, the latter was titrated with NaOH, while keeping the pH constant at 9.5 during the reaction. All the results obtained with the titration were compared with those obtained by means of ion chromatography. In all cases IC results were comparable with those of titration. The moles of initial glucose are exactly the same moles of final product when conversion is complete. At the same time, no other byproduct have been detected. Regardless of the synthetic methodology, the catalysts supported on ceria are those that show the highest activity. On the contrary, those supported on titania present the lowest conversion. Moreover, the effect of the support seems to have little influence on the catalysts prepared by PVP as surfactant: in this case, all as prepared samples show limited activity.

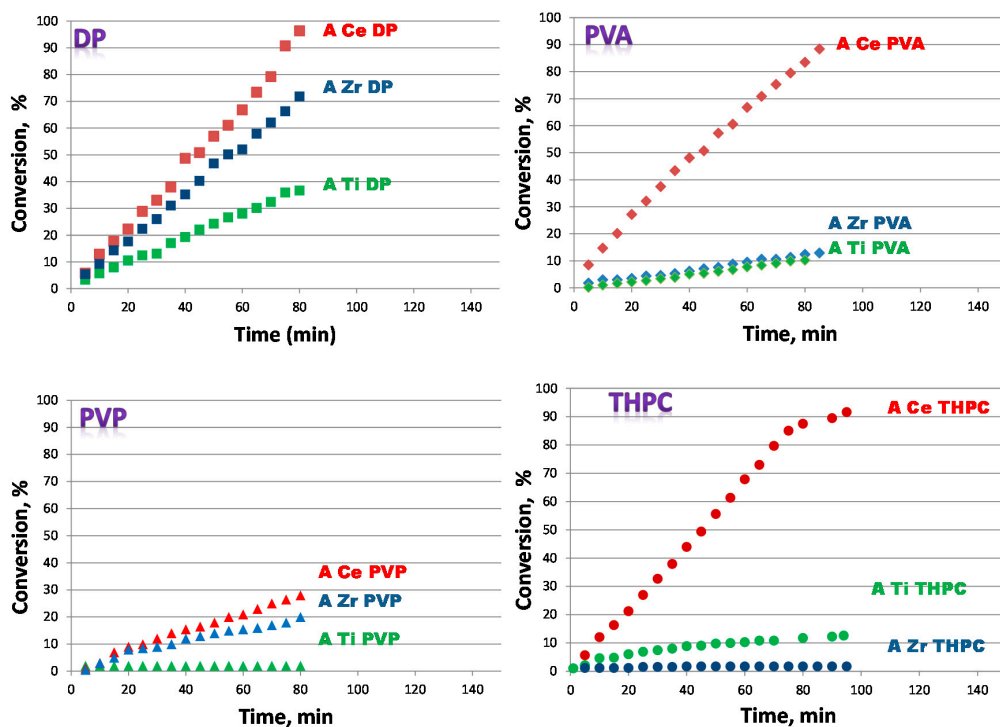


Figure 3. Conversions *vs.* time of reaction for D-glucose oxidation at 60 °C and 100 cc/min of O₂ for samples synthesized by DP, PVA, PVP and THPC.

As regard as catalysts prepared using PVA as surfactant, the CeO_2 supported sample is very active unlike those supported on ZrO_2 and TiO_2 ; the latter present very similar profiles and there seems to be no effect of the support. To test whether the low activity depends on the size of the gold particles, the samples were analyzed by SEM and TEM.

Figure 4 reports EDX-SEM analyses, in particular the elemental mapping for ACePVA (section a), AZrPVA (section b) and ATiPVA (section c) samples. Both ACePVA and AZrPVA present almost all gold particles smaller than 10 nm. On the contrary, sample supported on titania present some big agglomerates and very big gold particles.

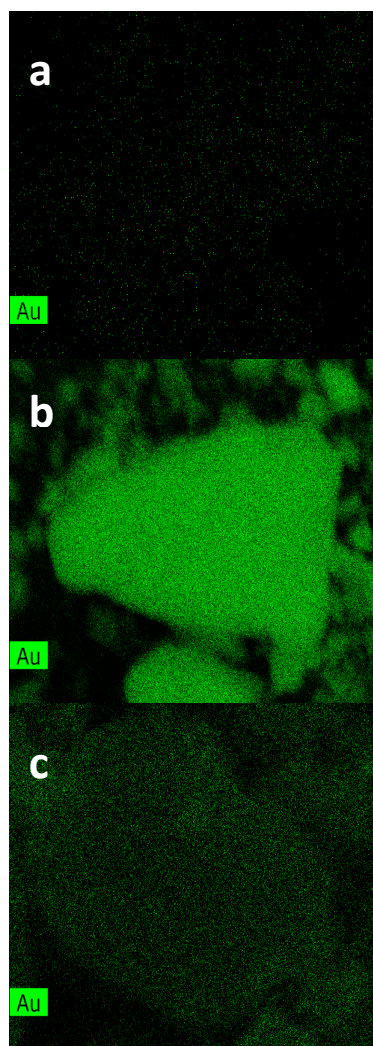


Figure 4. EDX elemental mapping of samples ACePVA (section a), AuZrPVA (section b) and ATiPVA (section c).

In Figure 5 there are shown, respectively for the CeO_2 (section a), ZrO_2 (section b) and TiO_2 (section c) samples, TEM images. TEM data agree with SEM results. The average particle diameter of ACePVA is 3.5 nm, while that of AZrPVA is 4.8 nm. The sample supported on CeO_2 shows a particle size distribution narrower than that based on ZrO_2 . Therefore, both samples have particles small enough to be able to catalyze the glucose oxidation. As regard as ATiPVA, the TEM images, shows the presence of some particles with small size (5–7 nm) but also of many particles whose diameter is much larger than those of the two other catalysts prepared in the same way.

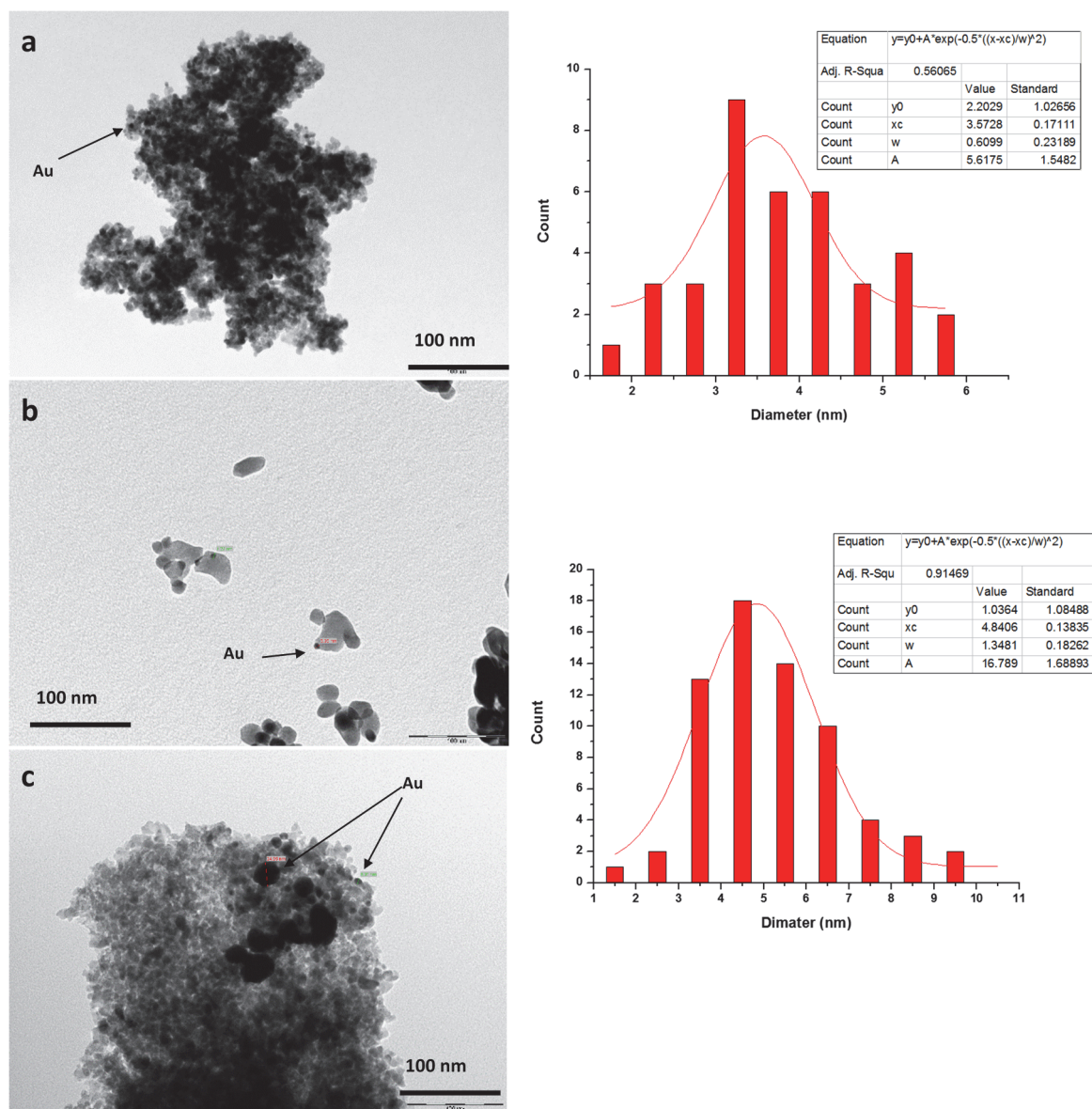


Figure 5. TEM images for ACPePVA (section a); AZrPVA (section b) and ATiPVA (section c).

Also as regard as samples prepared by THPC, the catalyst supported on ceria is the most active. To determine whether the poor activity of the other samples depends on the size of the particles the catalysts were analyzed by SEM and TEM microscopy. From these analyses (Figure 6) it's evident that the particle size does not depend only on the synthesis methodology but also on the kind of support. In fact for the sample supported on ceria it is possible to obtain gold nanoparticles of about 4 nm, and the sample is active in the oxidation reaction of glucose. As for the catalyst based on zirconia it shows a particle size only slightly larger than that supported on ceria. For this reason, by TEM analysis it's impossible to understand why it is inactive. Conversely, the catalyst supported on titania is inactive due to some metallic agglomerates (Figure 6 section c).

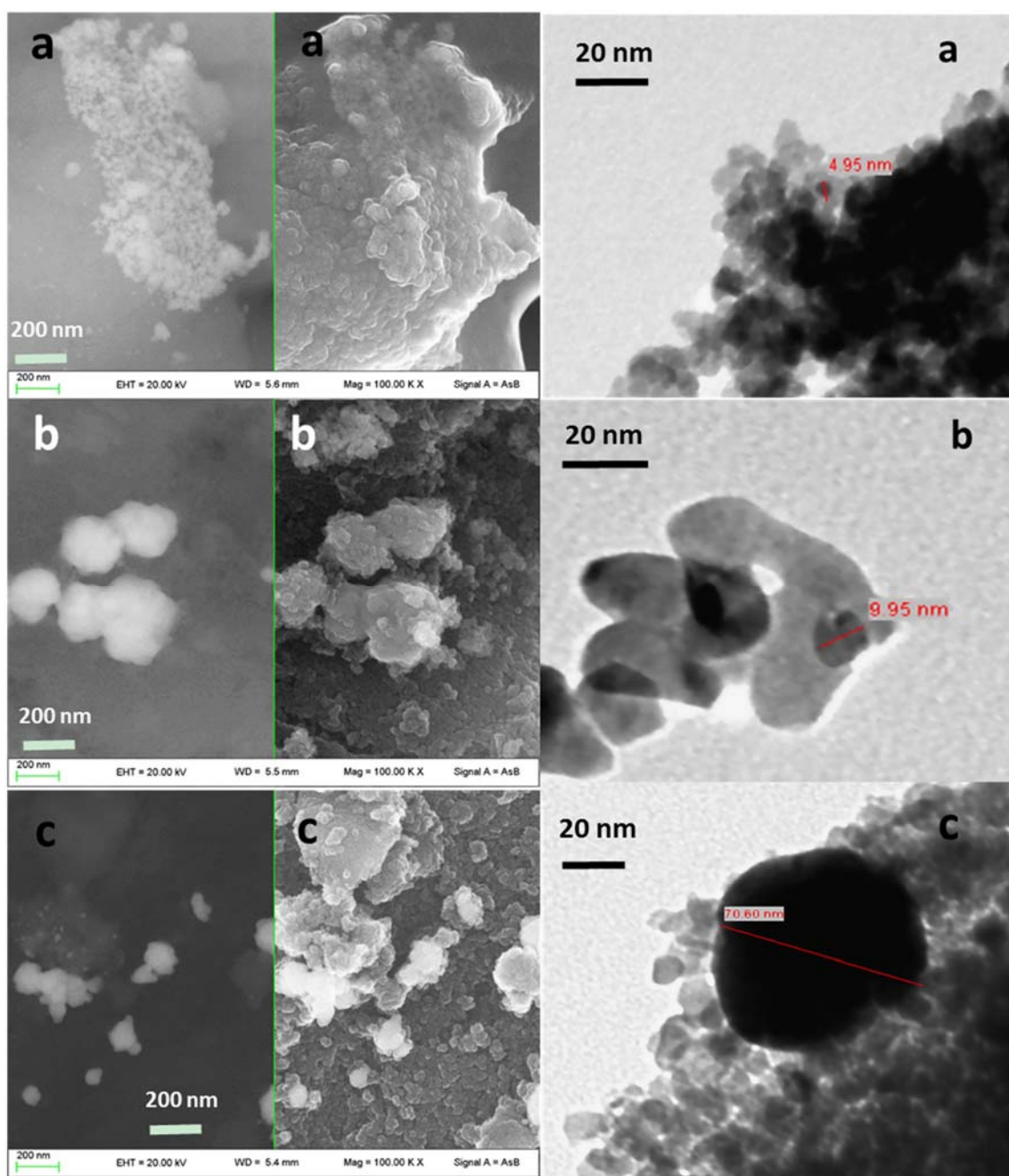


Figure 6. Double SEM images obtained by two detector (AsB and Inlens) and TEM: ACeTHPC (section **a**); AZrTHPC (section **b**) and ATiTHPC (section **c**).

In order to explain the reason for the inactivity of some samples with a proper gold size, we have assumed that an excess of surfactant could cover the surface of the catalyst, and affect its activity. So, the samples were subjected to temperature programmed oxidation (TPO) in order to assess the temperature of oxidation for the organic component. Figure 7 reports the trend for $m/e = 44$, corresponding to the CO_2 mass, which is formed from PVA (section a), THPC (section b) or PVP (section c) oxidation. For all the three systems, the TPO of ceria supported samples present peak at the lowest temperature. For the AZrPVA sample two wide peaks between 200 and 530 °C were observed. The TPO analysis of ATiPVA sample shows three very intense peaks, indicating that the organic part of the surfactant is oxidized between 300 and 600 °C. As regard as samples prepared by THPC, the TPO analysis of the sample supported on ceria shows a single peak between 200 and 400 °C. Both AZrTHPC and

ATiTHPC present two peaks between 250 and 600 °C, at higher temperature than ACeTHPC sample. Samples prepared using PVP as surfactant show low activity, regardless of the used support (Figure 3, section c). Their TPO profiles are reported in Figure 7 (section c). As regard as ceria, the TPO shows a single peak between 200 and 300 °C. The TPO analysis for AZrPVP shows three peaks between 300 and 600 °C, while that for ATiPVP shows three peaks in the temperature range 400–550 °C.

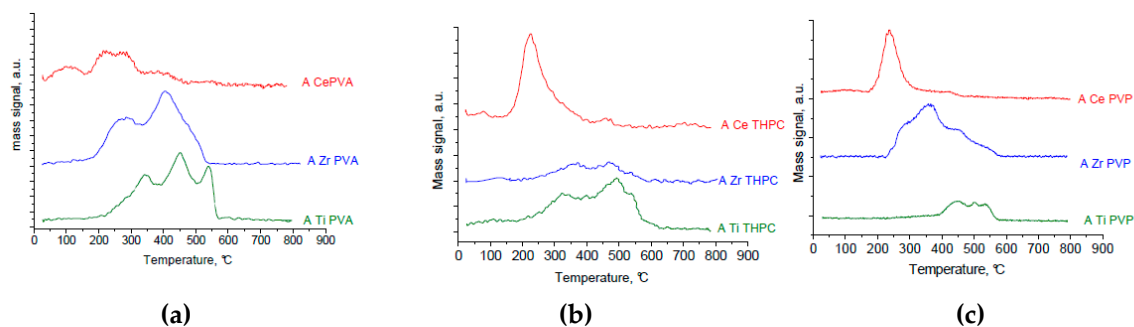


Figure 7. TPO analysis ($m/e = 44$) for samples synthesized by PVA (section a), THPC (section b), PVP (section c).

Therefore, the inactive samples were calcined at proper temperatures in order to remove part or almost all the surfactant. Calcined catalysts were then tested in the glucose oxidation (Figure 8). As regard as PVA series, both the samples calcined at 300 °C, where only part of PVA was removed, are much more active than the corresponding non-calcined samples. On the contrary, a drop in activity was observed after calcination at 500 °C of the AZrPVA and therefore after removal of almost all PVA. As regard as ATiPVA sample calcination at 500 °C does not lead to a total collapse of the activity. In fact, at that temperature the surfactant is still partially present, as evidenced by TPO analysis. The surfactant has the fundamental role of keeping separate the gold particles and preventing the sintering. When PVA is totally eliminated the particles coagulate and are no more able of activate oxygen.

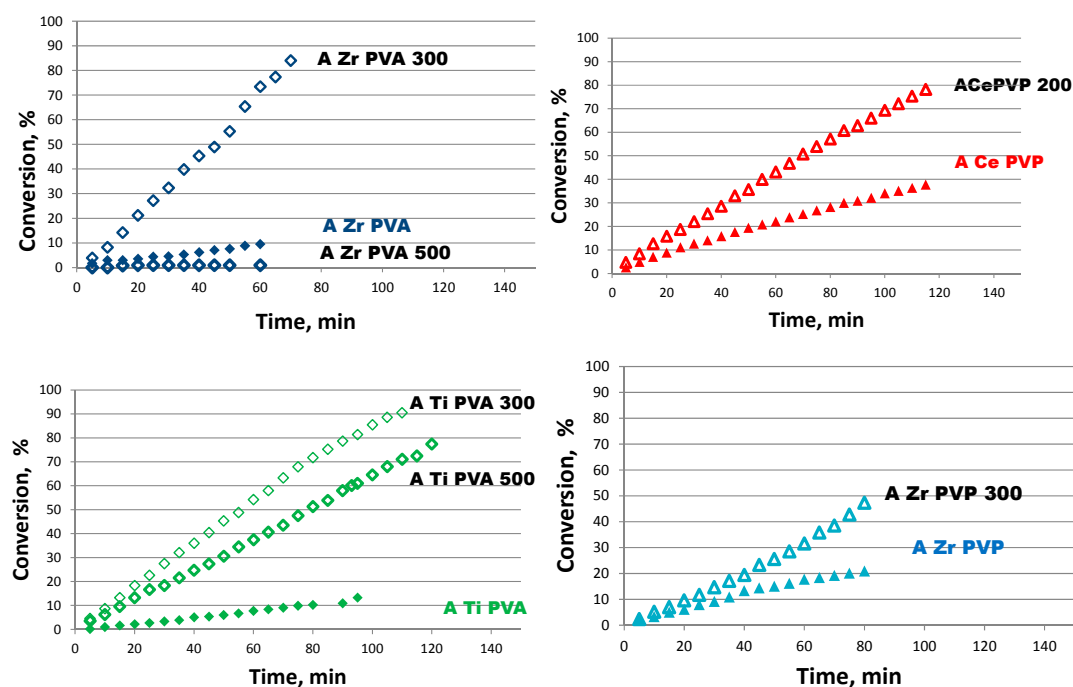


Figure 8. Conversions *vs.* time of reaction for D-glucose oxidation at 60 °C and 100 cc/min of O₂ for calcined samples.

As regard as THPC samples, to estimate changes in the activity of the catalysts by removing part or all the surfactant, the samples were calcined at 300 and 500 °C and then tested in the D-glucose oxidation. Even after calcination the AZrTHPC sample is inactive, indicating that the gold particles are in a size range too high to catalyze the reaction. In fact, as can be seen from the analysis TEM and SEM, they have a diameter twice than that of particles in the AZrPVA sample.

Taking into account the TPO analyses the samples ACePVP, ATiPVP and AZrPVP were calcined, respectively, at 200, 300 and 400 °C. As evidenced by the concentration profiles *vs.* time (Figure 8), in the case of the samples supported on ceria and zirconia calcination leads to an improvement in the activity. On the contrary, as regard the sample ATiPVP calcination does not lead to any change in its activity. Therefore, it is assumed that in this case the poor performance does not depend on an excessive amount of surfactant, but on the too large size of gold particles.

The AZrPVA300 and AZrPVA500 catalysts were analyzed by FT-IR spectroscopy (Bruker Tensor 27, Bruker Optik GmbH, Ettlingen, Germany) to confirm the disappearance of the PVA during calcination (Figure 9, section a). In the spectra of AZrPVA there are evidences of the peaks associated with the stretching vibration of the CH bond. Their intensity decreases with the calcination temperature, evidencing the gradual surfactant elimination.

TEM and SEM analysis were also performed in order to observe how the nanoparticles size changes by varying the calcination temperature (Figure 9, section b). In the sample calcined at 300 °C the mean particle size is almost the same of the uncalcined sample. On the contrary, the sample calcined at 500 °C shows agglomerates (Figure 9, section c). This is an indication of the collapse of the gold nanoparticles, due to the almost complete removal of the surfactant.

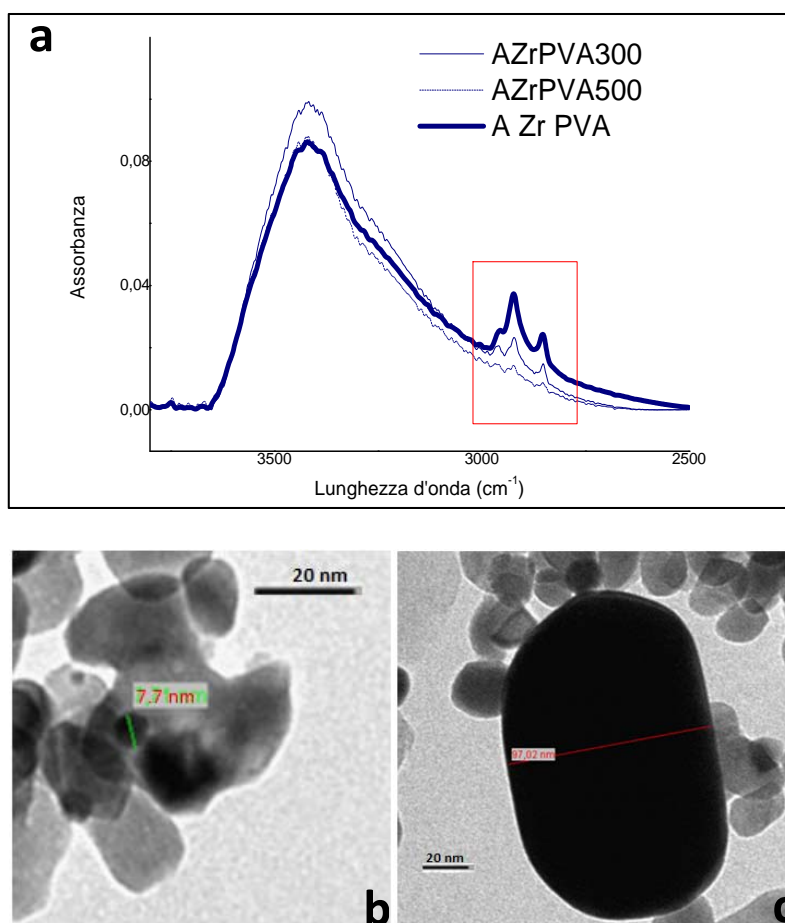


Figure 9. FT-IR spectra of AZrPVA (thick), AZrPVA300 (thin); AZrPVA500 (dashed) (section a). TEM images of the AZrPVA300 (section b) and AZrPVA500 samples (section c).

From this investigation it is evident that ceria is the best support, both for its ability to allow the synthesis of gold nanoparticles small enough to be active, both for its ability to function as oxygen pump. The latter is fundamental when using oxygen as reagent. Table 2 reports conversions of all catalysts in order to determine the effect of synthetic methodology on the catalytic activity.

By comparing the various synthetic techniques, it is clear that, regardless of the support, the method using the colloidal PVA, followed by calcination at 300 °C, is the one that allows obtaining samples with the best performance. This is a confirmation that a surfactant with a steric effect such as PVA acts as a better protective agent with respect nanoparticles, compared to THPC, which acts by electrostatic effect.

Table 2. Comparison of conversions after 60 min of reaction for D-glucose oxidation at 60 °C and 100 cc/min of O₂.

Sample	Conv. (%)
ACeDP300	67
AZrDP300	52
ATiDP300	28
ACePVA300	79
AZrPVA300	73
ATiPVA300	54
ACeTHPC	68
AZrTHPC	2
ATiTHPC	10
ACePVP200	43
AZrPVP300	32
ATiPVP400	4

2.3. Investigation on Catalysts' Recycle

To complete the work, we studied the recycling of the best performing catalyst, *i.e.*, ACePVA. At the end of the reaction, the catalyst was filtered, washed with distilled water, dried and subsequently reused. In Figure 10 there are shown the conversion profiles *vs.* time of the fresh and reused samples. The catalyst proves recyclable, without undergoing any treatment unless filtration, washing and drying. In fact, it shows no loss of activity after each reuse, indicating that it is not subject to phenomena of leaching, sintering or coating of the surface.

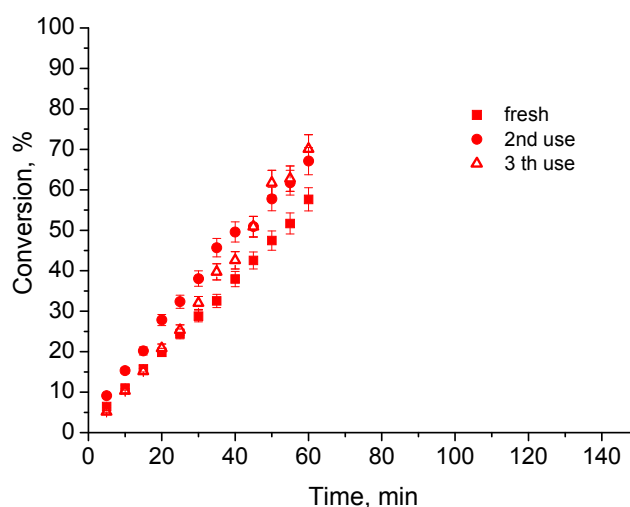


Figure 10. Comparison of conversions for fresh and used ACePVA catalysts.

3. Materials and Methods

3.1. Materials

$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ($\geq 98.5\%$, Sigma-Aldrich, St Louis, MO, USA); $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ($\geq 99.5\%$, Sigma-Aldrich, Sigma Aldrich Chemie, GMBH, Riedstr, Germany); $\text{TiOSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Aldrich Chemistry, Sigma-Aldrich, St Louis, MO, USA); PVA (98% P.M. 13.000–23.000 d, Sigma-Aldrich); PVP (P.M. 40.000 d, Sigma-Aldrich); THPC (80% in water, Aldrich Chemistry).

3.2. Synthesis of Supports

Ceria support was synthesized by precipitation from $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ by urea at 100°C in aqueous solution [24,25]. The solution was mixed and boiled for 6 h at 100°C , the precipitate was washed twice in boiling deionized water and dried at 110°C overnight. The material was then calcined in flowing air (50 mL/min) at 500°C for 3 h.

$\text{Zr}(\text{OH})_4$ was prepared by precipitation from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ at constant pH = 8.6 and then aged for 20 h at 90°C [26,27]. Then zirconium hydroxide was calcined in air (30 mL/min STP) at 650°C for 3 h.

Titanium hydroxide was precipitated at pH = 8.6 from 0.5 M titanyl sulphate aqueous solution [28,29]. In particular, 40 g of $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot y\text{H}_2\text{O}$ (Aldrich) were dissolved in 300 mL of distilled water at room temperature under vigorous stirring. The $\text{Ti}(\text{OH})_4$ precipitation was obtained by the drop wise addition of 9 M ammonia solution under vigorous stirring. The suspension was magnetically stirred at 60°C for 20 h. Then the precipitate was filtered, washed with distilled water in order to remove SO_4^{2-} ions and dried at 110°C for 18 h. The absence of sulphates in the material was verified by IEC analysis. Finally the hydroxide was calcined in air flow at 300°C for 3 h.

3.3. Synthesis of Catalysts

In all cases the amount of support was calculated as having a final gold loading of 2 wt. %.

3.3.1. Synthesis by Deposition Precipitation (DP)

Gold was added by DP method at pH = 8.6. The oxide supports were suspended in an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ for 3 h and the pH was controlled by the addition of NaOH (0.5 M). After filtration the samples were dried at 35°C overnight and finally calcined in air for 1 h at 300°C . Samples were denoted as ACeDP300, AZrDP300 and ATiDP300.

3.3.2. Synthesis by PVA Sol-Immobilization

A 1 wt. % polyvinyl alcohol (PVA) solution was added to an aqueous HAuCl_4 solution under vigorous stirring at 0°C (Au/PVA (w/w) = 2) [30]. Then a 0.1 M of freshly prepared solution of NaBH_4 (NaBH_4/Au (mol/mol) = 4) was added, to form a ruby-red metallic sol. Within a few minutes of sol generation, the sol was immobilized by adding the support (CeO_2 , ZrO_2 or TiO_2 . As regard as TiO_2 , this has been previously acidified with H_2SO_4 at pH = 1 [20]) under vigorous stirring and aged for 12 h. After filtration, the samples were washed for several times with distilled water. The samples were dried at 110°C overnight. Samples were denoted as ACePVA, AZrPVA and ATiPVA. Part of the final catalysts was finally calcined in air (30 mL/min) for 1 h at different temperatures.

3.3.3. Synthesis by PVP Sol-Immobilization

A 2 wt. % polyvinylpyrrolidone (PVP) solution was added to an aqueous HAuCl_4 solution under vigorous stirring at 0°C (Au/PVP (w/w) = 0.25) [31]. Then a 0.1 M of freshly prepared solution of NaBH_4 (NaBH_4/Au (mol/mol) = 4) was added, to form a ruby-red metallic sol. Within a few minutes of sol generation, the sol was immobilized by adding the support (CeO_2 , ZrO_2 or TiO_2 . As regard as TiO_2 , this has been previously acidified with H_2SO_4 at pH = 1) under vigorous stirring and aged for

20 h. After filtration, the samples were washed for several times with distilled water. The samples were dried at 110 °C overnight. Samples were denoted as ACePVP, AZrPVP and ATiPVP. Part of the final catalysts was finally calcined in air (30 mL/min) for 1 h at different temperatures.

3.3.4. Synthesis by THPC Sol-Immobilization

A 0.05 M solution of tetrakis (hydroxymethyl)phosphonium chloride (THPC) was added to a 10^{-3} M solution of NaOH (NaOH/THPC (mol/mol) = 0.042). Then, an aqueous HAuCl₄ solution was added dropwise under vigorous stirring at room temperature (Au/THPC (*w/w*) = 1) [27]. The sol was immobilized by adding the support (CeO₂, ZrO₂ or TiO₂ previously acidified with H₂SO₄ at pH = 1) under vigorous stirring and aged for 5 h. After filtration, the samples were washed for several times with distilled water. The samples were dried at 110 °C overnight. Samples were denoted as ACeTHPC, AZrTHPC and ATiTHPC. Part of the final catalysts was finally calcined in air (30 mL/min) for 1 h at different temperatures.

3.4. Methods

Surface areas and pore size distributions were obtained from N₂ adsorption/desorption isotherms at −196 °C (using a Micromeritics ASAP 2000 analyser, Micromeritics, Milan, Italy). Surface area was calculated from the N₂ adsorption isotherm by the BET equation, and pore size distribution was determined by the BJH method [32]. Total pore volume was taken at $p/p_0 = 0.99$.

The sulphate content was determined by ion chromatography (IC). Sulphate concentration was calculated as the average of two independent analyses, each including two chromatographic determinations.

The gold amount for both fresh and exhausted catalysts was determined by atomic absorption spectroscopy (AAS) after microwave disaggregation of the samples (100 mg) using a Perkin-Elmer Analyst 100 (Perkin Elmer, Waltham, MA, USA).

TEM images have been obtained using a Philips 208 Transmission Electron Microscope (FEI, Hillsboro, OR, USA). The samples were prepared by putting one drop of an ethanol dispersion of the catalysts on a copper grid pre-coated with a Formvar film and dried in air.

SEM images have been obtained using a Field Emission Gun Electron Scanning Microscopy LEO 1525 (Carl Zeiss Microscopy, Jena, Germany), after metallization with graphite. The images were acquired by AsB (angular selective BSE) detector (Carl Zeiss Microscopy, Jena, Germany) while elemental composition was determined using Bruker Quantax EDS (Bruker Nano GmbH, Berlin, Germany).

FTIR spectra were obtained on a Bruker spectrophotometer (Bruker Tensor 27, Bruker Optik GmbH, Ettlingen, Germany) (4 cm^{−1} resolution, MCT detector). Reduced samples were inspected in the form of self-supporting tablets (~25 mg·cm^{−2}). Quartz cells (equipped with KBr windows) connected to a gas vacuum line equipped with rotary and turbomolecular pumps were used.

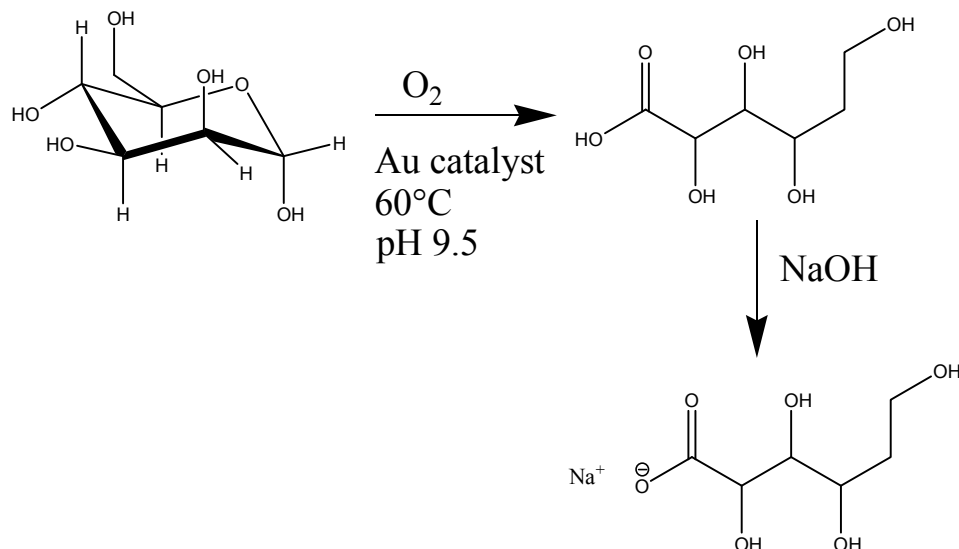
Thermal analyses (TG/DTA) were performed on a STA 409 PC/PG instrument (NETZSCH, Selb, Germany) in flowing air (20 mL/min) with temperature rate set at 5 °C/min in the 25–800 °C temperature range.

TPO measurements were carried out in a lab-made equipment: samples (100 mg) were heated with a temperature rate of 10 °C/min from 25 °C to 600 °C in a 5% O₂/He flow (40 mL/min). The effluent gases were analyzed by a TCD detector (GOW-MAC Instrument Co., Shannon, Ireland) and by a Genesys 422 quadrupole mass analyzer (QMS) (EES Genesys House Northwich, Cheshire, UK).

3.5. Catalytic Reactions

Commercial Dextrose (100% pure, PURE Dextro, distributed by Pro Nutrition) was used as substrate. Its oxidation to (Scheme 2) gluconic acid was carried out in a batch reactor, typically at atmospheric pressure and 60 °C. In particular, 1 g of D-glucose in 50 mL of distilled H₂O was brought to pH = 9.5 by adding a solution of NaOH 0.1 M. An O₂ flow (100 mL/min) was bubbled in the

solution through a porous septum. Separately, 130 mg of catalyst were suspended in 20 mL of distilled H₂O, brought to pH = 9.5 with a solution 0.1 M of NaOH and then charged into the reactor. To monitor the conversion of D-glucose to gluconic acid, the latter was titrated with NaOH 0.1 M, while keeping the pH constant at 9.5 during the reaction.



Scheme 2. Oxidation of D-glucose to gluconic acid. The latter is converted to sodium gluconate by addition of NaOH.

The results obtained with the titration were compared with those obtained by means of ion chromatography (IC). A precolumn Dionex AG11, a column Dionex AS11, a suppressor Dionex ASRS-300, a TCD Dionex ED40 (100 mA) were used. In all cases IC results were comparable with those of titration.

4. Conclusions

Heterogeneous catalysis plays a key role in the future biorefinery and there is great interest in the development of new catalysts. Focusing on the transformation of platform molecules through oxidation reactions, the use of nanostructured catalysts based on gold seems to be the most promising alternative. The work was focused on the synthesis of catalysts based on gold nanoparticles on three different supports (CeO₂, ZrO₂ and TiO₂) and two different techniques: deposition-precipitation and colloidal method. Moreover, in the latter case the role of the surfactant (PVA, PVP, THPC) was also investigated. The catalysts were tested in a model reaction: the oxidation of glucose to gluconic acid, which takes place in an aqueous environment and under mild conditions (60 °C and atmospheric pressure).

TEM and SEM analyses have shown as for catalysts prepared by colloidal method with PVA small gold nanoparticles are obtained. The latter is a necessary condition, but not sufficient for a good conversion. In fact, for an active sample, the excess of surfactant must be removed because it would coat the surface of the catalyst. The surfactant, however, should not be completely eliminated, since it has the fundamental role of stabilizing the sample preventing nanoparticles from aggregation.

As for the catalysts prepared by colloidal method with THPC, only the sample supported on ceria has sufficiently small nanoparticles. This is a clear indication that the size of the particles not only depends on the synthetic procedure but also on the kind of support.

As regard as catalysts prepared by DP, their activity is lower than samples prepared by PVA. Moreover it is observed a minor effect of the support: catalysts prepared with DP technique do not show a big difference in activity. Samples prepared by colloidal method with PVP gave the worst performance.

It was evidenced that both the synthetic approach and the kind of support affect the catalysts' activity. In fact, by focusing on the three different supports, with all the preparation methods, the ceria has proved to be the best support. This is due to its ability to obtain small gold nanoparticles and to its ability to accumulate oxygen.

The most appropriate synthesis methodology proved to be the colloidal method with PVA.

Combining the effect of the synthetic method and the effect of the support, ACePVA resulted the best performing catalyst. In fact, it is the most active and is completely recyclable after a simple washing with water.

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