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Gold supported on carbon nanotubes for the selective oxidation of glycerol

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ABSTRACT

Gold nanoparticles were supported on multi-walled carbon nanotubes (MWCNTs) by different methods and tested in the selective oxidation of glycerol under basic conditions, with the main purpose of evaluating the effect of the preparation technique on the activity and selectivity. The catalytic performances largely depended on the gold crystallite size. The sol immobilization method was the most suitable technique to prepare gold supported on carbon nanotubes. The use of MWCNTs as support for Au nanoparticles resulted in the oxidation of the secondary hydroxyl group, and therefore, a remarkable high dihydroxyacetone selectivity of about 60% is obtained independently of the preparation method used. A possible explanation based on the peculiar characteristics of the support is proposed. It was also concluded that dihydroxyacetone in the final mixture can be stabilized by lowering the pH to about 3.

1. Introduction

Glycerol is a highly functionalized molecule widely available from bio-sustainable sources. Therefore, its conversion into high-value chemicals is of large industrial importance. Recently, the oxidation of glycerol for the production of valuable oxygenated derivates has received remarkable attention [1–6]. However, the extensive functionalization of this molecule, with three hydroxyl groups, renders its selective oxidation particularly difficult since, in general, a large number of products can be obtained [5,7,8] (Fig. 1). Among these, glyceric acid (GLYCEA) and dihydroxyacetone (DIHA) are potentially useful as chemical intermediates for the fine chemicals industry, particularly in pharmaceuticals [1,9]. Nowadays, these compounds are produced commercially either using costly and polluting stoichiometric oxidation processes (GLYCEA) or by incomplete microbial fermentation of glycerol by *Gluconobacter oxidans* (DIHA) [1,8,10].

In order to control the selectivity, a careful design of the catalyst is required. Gold catalysts are well known for their high activity in glycerol oxidation. Their better resistance to oxygen poisoning compared with catalysts based on metals of the platinum group allows the use of high oxygen partial pressures in the reactor [11]. However, when using gold-containing catalysts, a basic medium is necessary in order to obtain significant glycerol conversions [12,13]. Gold nanoparticles supported on different carbon materials or oxides are active for the oxidation of glycerol, but show very different performances, being carbon-supported catalysts more active than most oxide-supported catalysts [2,11,14]. Accordingly, in the majority of the reported studies, the supports used are activated carbon, carbon black or graphite [1,15]. On the other hand, except from a very recent publication from Prati et al. [16], multi-walled carbon nanotubes (MWCNTs) have not been investigated as supports for gold nanoparticles in the scope of the liquid phase oxidation of glycerol. Recently, this type of material has been drawing increasing attention for catalytic applications because of its unique features, such as high graphitization, high specific surface area, good physical and chemical stability and excellent electronic properties [17], which were recently reported as being important in the performance of gold catalysts [18]. Furthermore, an increasing amount of studies suggest that the textural and chemical properties of the support influence directly the selectivity of the glycerol oxidation reaction [4,12,16]. As a result, the use of MWCNT as support is appealing due to its strictly mesoporous nature, differing largely from the classical activated carbon support.

Nevertheless, both the performance of catalysts and the selectivities attained are also sensitive to gold nanoparticle sizes, which in turn depend on the preparation method and type of supporting material used [19,20]. In particular, the presence of chloride is very detrimental for the catalytic performance, since it is known to

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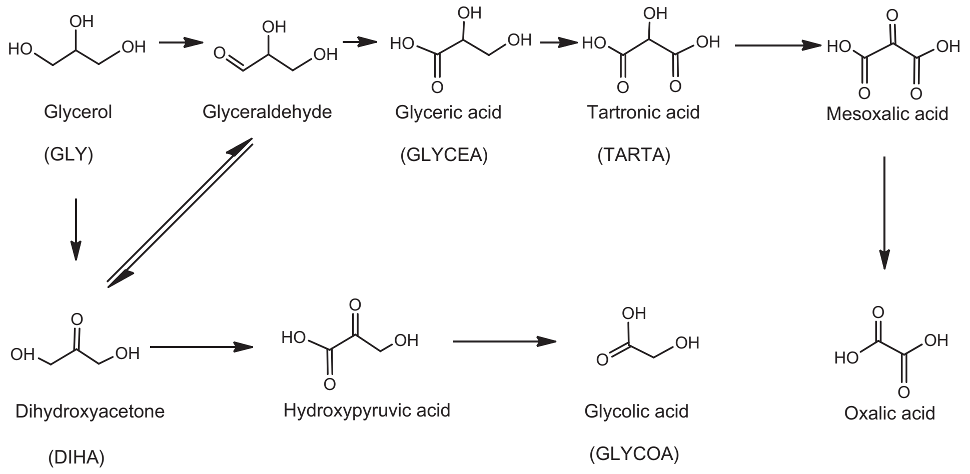

Fig. 1. General reaction pathways (adapted from [4]).

cause agglomeration of gold particles [21,22]. Apparently, the gold-sol immobilization method is the most appropriate technique in order to obtain well-dispersed nanoparticles on activated carbons [19,23]. However, there is no information about the most suitable method to support gold on MWCNTs for the oxidation of glycerol. Therefore, in the present work, gold nanoparticles were supported on MWCNTs by different methods and tested for the selective oxidation of glycerol. Besides the well-known incipient wetness impregnation (IW) and immobilization techniques, some less usual methods were also considered for the preparation of the samples, namely liquid phase reductive deposition (LPRD), double impregnation (DIM) and reduction with citric acid (citric). As far as we know, these methods had not been used for the preparation of Au/MWCNT catalysts.

The influence of the preparation method on the catalytic performance in glycerol oxidation and on the selectivity was analyzed. Moreover, the important difference observed in the distribution of products relatively to the activated carbon-supported gold catalysts previously reported [18] was also highlighted.

2. Experimental

2.1. Catalyst preparation

A commercial Nanocyl 3100 MWCNT sample was used as support for this study. According to the supplier, these nanotubes have an average diameter of 9.5 nm, an average length of 1.5 μm and carbon purity higher than 95%. In a recent work, it was shown that this material presents average inner and outer diameters of 4 and 10 nm, respectively [24].

In this work, gold catalysts with a nominal metal loading of 1% were prepared on the original MWCNT using $HAuCl_4{\cdot}3H_2O$ as precursor and different techniques: incipient wetness impregnation (IW), double impregnation (DIM), liquid phase reductive deposition (LPRD), reduction with citric acid (citric) and sol immobilization (c).

2.1.1. Incipient wetness impregnation

An appropriate volume of an aqueous solution of the gold precursor was added dropwise via a peristaltic pump to the support until incipient wetness ($6\ cm^3\ g^{-1}$). During the impregnation, the sample was placed in an ultrasonic bath. After 1.5 h, the resultant wet sample material was dried at 110 °C overnight. Finally, the catalyst was heat treated under nitrogen flow for 3 h at 350 °C and subsequently activated by reduction under hydrogen flow for 3 h at 350 °C.

2.1.2. Double impregnation

This method consists in impregnating the support with an aqueous solution of the gold precursor and then with a solution of Na_2CO_3, in order to precipitate gold hydroxide within the pores [25]. Firstly, $HAuCl_4{\cdot}3H_2O$ was dissolved in a small amount of water and impregnated on the support using a peristaltic pump, as described above. During impregnation, the sample was placed in an ultrasonic bath. It should be noticed that the amount used is insufficient to wet the support. Then, an additional aqueous solution of Na_2CO_3 1 M was added to the support. The amount of this solution was just sufficient to reach the incipient wetness point. A constant ultrasonic stirring of the sample was maintained during 1.5 h. The mixture was washed five times with 14 mL of the sodium carbonate solution in 100 mL of water, followed by five washings with 100 mL of water for chloride removal from the sample. The resultant material was dried at 110 °C overnight.

2.1.3. Liquid phase reductive deposition

In this method, gold (III) ions from the precursor are hydroxylated by reaction with NaOH, and a washing procedure is carried out in order to eliminate residual chloride [26]. Therefore, an aqueous solution of $HAuCl_4{\cdot}3H_2O$ was mixed with a solution of NaOH (ratio of 1:4 in weight) while stirring at room temperature. The resulting yellow solution was aged for 24 h in the dark at room temperature to complete the hydroxylation of Au^{3+} ions. At this point, the solution was colorless. Then, the appropriate amount of support was added to the solution and, after ultrasonic dispersion for 30 min, the suspension was aged in the oven at 110 °C overnight. The resulting solid was washed repeatedly with distilled water in order to remove impurities such as chlorides and finally dried at 110 °C overnight.

2.1.4. Reduction with citric acid

In this procedure, the gold nanoparticles were prepared by the reaction of $HAuCl_4.3H_2O$ with citric acid (used as reducing agent) [27]. The colloidal gold forms because the citrate ions can act as reducing and capping agent. Typically, after ultrasonic dispersion of the sample in 2-propanol for 15 min, the same weights of $HAuCl_4$ and citric acid, both dissolved separately in 2-propanol, were simultaneously added dropwise to the suspension. The ultrasonication was then interrupted, and the resulting dispersion was vigorously stirred at room temperature for 2 h. The mixture was subsequently washed several times with 2-propanol in order to remove impurities and dried at 110 °C overnight.

2.1.5. Sol immobilization

A catalyst sample was synthesized via the sol immobilization technique using polyvinyl alcohol (PVA) as protective agent and $NaBH_4$ as reducing agent [28]. Briefly, $HAuCl_4.3H_2O$ (35.1 mg) was dissolved in 690 mL of H_2O, and PVA was added (1.6 mL, 0.2 wt.%) under stirring. PVA is necessary to stabilize the nanostructured colloidal gold and to prevent agglomeration. $NaBH_4$ (4 mL, 0.1 M) was added to the yellow solution under vigorous magnetic stirring. The resulting sol was ruby-red in color. Within a few minutes of sol generation, the colloid was immobilized by adding the support under fast stirring. After 3–4 days, the solution becomes colorless, and the suspension was filtered. The catalyst was washed thoroughly with distilled water until the filtrate was free of chloride (checked by the $AgNO_3$ test) and dried at 110 °C for 24 h. The organic scaffold was removed from the support by a heat treatment under nitrogen flow for 3 h at 350 °C, and then, the catalyst was activated by reduction under hydrogen flow for 3 h also at 350 °C. A TG-DSC experiment was carried out under N_2 atmosphere in a Netzsch STA 409 PC Luxx® System. About 15 mg of PVA was loaded into a ceramic crucible, and the temperature was raised to 350 °C at 10 °C/min. It was verified that PVA decomposition occurs in the range 240–320 °C.

2.2. Catalyst characterization

Catalysts and supports were characterized by N_2 adsorption at −196 °C in a NOVA Quantachrome Instruments apparatus. Pore size distributions were obtained by using the non-local density functional theory (NLDFT), applying the kernel file provided by Quantachrome's data reduction software, where a cylindrical-pore model is assumed.

The determination of oxygenated surface functional groups was performed by temperature programmed desorption–mass spectrometry (TPD–MS) [29,30]. CO and CO_2 TPD spectra were obtained with a fully automated AMI-200 equipment (Altamira Instruments). Briefly, the sample (150 mg) was placed in a U-shaped quartz tube inside an electrical furnace and subjected to a 5 °C min^{-1} linear temperature increase up to 1100 °C under helium flow (25 cm^3 min^{-1}). A quadrupole mass spectrometer (Dymaxion 200, Ametek) was used to monitor CO and CO_2 signals. For quantification of the CO and CO_2 released, calibration of these gases was carried out at the end of the analysis.

The gold loading of the prepared catalysts was determined in duplicate by inductively coupled plasma-optical emission spectroscopy (ICP/OES) in an external laboratory, using a PerkinElmer Optima 4300 DV spectrometer.

Electron micrographs of samples were obtained using a JEOL2010F instrument (equipped with an energy dispersive X-ray spectroscopy detector), with 0.19-nm spatial resolution at Scherzer defocus conditions. High Angel Annular Dark Field–Scanning Transmission Electron Microscopy (HAADF–STEM) images were acquired with the same equipment. Particle size distributions were obtained by the measurement of at least 200 particles, and the average diameter was calculated by $d_M = \sum d_i n_i / \sum n_i$, where n_i is the number of particles of diameter d_i.

In order to determine Au oxidation states, X-ray photoelectron spectroscopy (XPS) analyses were carried out with a VG Scientific ESCALAB 200A spectrometer using Al Kα radiation (1486.6 eV). The accuracy of the resulting data was checked by performing at least five repetitions for each sample.

Further details of the experimental setup and analytical techniques used can be found elsewhere [31].

2.3. Catalytic experiments

Typically, a NaOH solution and the gold catalyst (700 mg) were added to a 0.3 M aqueous solution of glycerol (total volume 195 mL; NaOH/glycerol molar ratio = 2) under stirring at 1000 rpm. The reactor was pressurized with nitrogen at 3 bar. After heating under this atmosphere to 60 °C, the reaction was initiated by switching from inert gas to oxygen (3 bar). Additionally, a limited number of runs were carried out at different NaOH/glycerol molar ratios.

The reaction was monitored by taking samples (0.5 mL) for analysis at regular time intervals. The quantitative analysis of these samples was carried out by high-performance liquid chromatography (HPLC). The chromatograph (Elite LaChrom HITACHI) was equipped with an ultraviolet (210 nm) and a refractive index detector in series. Products were identified by comparison with standard samples.

In order to investigate the reproducibility of the catalytic tests and the errors associated to the glycerol conversion, four experiments with the same batch of the Auc/MWCNT catalyst were carried out. The maximum relative error observed was ±7%.

The selectivities (S_i) into the different products i at time t were calculated as:

$$S_i = \frac{C_i}{v_i \cdot C_0 \cdot X} \qquad (1)$$

where C_i is the concentration of product i (mol L^{-1}), C_0 is the initial concentration of glycerol (mol L^{-1}), X is the glycerol conversion, and v_i corresponds to the moles of i produced per mol of glycerol consumed, according to the stoichiometry.

3. Results and discussion

3.1. Characterization of supports and catalysts

3.1.1. Textural properties

The carbon nanotubes sample shows a N_2 adsorption isotherm typical of non-porous materials. The BET surface areas (S_{BET}) of the support and catalysts are presented in Table 1. It can be observed that the surface areas of catalyst samples are quite similar to the respective unloaded support. The pore size distribution result confirms the previous observation. Most of the porosity observed in the MWCNT support corresponds to large mesopores (widths as large as 40 nm are present), which result from the free space between carbon nanotubes in the respective bundles [17]. In fact, carbon nanotubes are not used individually but as aggregates, leading to the formation of pores. So, the NLDFT method shows the MWCNT mesoporous nature. Therefore, it can be concluded that pores in MWCNT are widely distributed and are formed by interaction of isolated nanotubes.

3.1.2. Surface chemistry characterization

TPD is a thermal analysis method that is becoming popular for the characterization of the oxygen-containing groups on the surface of carbon materials. In this technique, the total amount of

Table 1
Surface areas of support and gold catalysts.

Sample	S_{BET} (m^2/g)
MWCNT	285
Au IW/MWCNT	296
Au DIM/MWCNT	298
Au LPRD/MWCNT	266
Au citric/MWCNT	283
Auc/MWCNT	288

the various oxygenated surface groups (carboxylic acids, carboxylic anhydrides, lactones, phenols, and carbonyls or quinones) on carbon materials can be determined, since these groups are decomposed upon heating by releasing CO and/or CO_2 at different temperature ranges. Accordingly, it is possible to identify and estimate the amount of the oxygenated groups on a given carbon material by TPD experiments. The nature of the groups can be assessed by the decomposition temperature and the type of gas released, and their respective amounts determined by the areas of the component peaks, obtained by deconvolution techniques [29,30]. Actually, the oxygen content obtained from the CO and CO_2 TPD spectra of the support tested in this work is very low. In fact, the MWCNT sample only has a limited content of oxygenated functional groups on its surface corresponding to an oxygen content of 532 μmol g^{-1}. For comparison, results obtained with moderately and highly oxidized carbon materials can be found elsewhere [18,29,30,32,33]. Therefore, it can be concluded that the support used in this work has a very small amount of oxygenated groups on their surface, which is important since this may influence the performance of catalysts. In fact, in a recent work, we demonstrated that the presence of surface oxygenated acid groups lowers significantly the activity of gold supported on activated carbon [18].

3.1.3. ICP analyses

It is important to mention that the oxidation of the support has been carried out by some authors before anchoring the metal -containing species, in order to improve the interaction between support and the catalyst precursor [17,27]. However, despite the chemical inertness and very regular structure of carbon nanotubes, gold was successfully anchored without any pretreatment of the surface, as it can be seen in Table 2, which summarizes the metal loadings achieved with the different techniques. The gold content obtained by ICP analysis is lower than the nominal. Most of the preparation methods do not influence substantially the gold content of catalysts, and the corresponding prepared samples present a similar value of approximately 0.7%. The unique exception is the Au LPRD/MWCNT catalyst, which has a significantly lower loading (0.40%). This latter result indicates that a large fraction of gold present in the aqueous solution was not deposited on the support.

The LPRD technique is based on the adsorption of metal-containing ions on the surface followed by reduction, being that initial adsorption of metal the key point of the method [26]. In the citric acid method, contrarily to the LPRD method, MWCNT and the gold precursor were immersed in a large amount of 2-propanol, which improve the support dispersibility, leading to a better contact between support and metal when compared to water, once carbon nanotubes are hydrophobic. Regarding the sol immobilization method, the electrostatic interactions between the stabilized Au particles and the support play an important role during the preparation [34]. The pH of the gold sol is about 6, and its zeta potential is negative [34], while the surface charge of MWCNT is slightly positive, considering that their pH_{pzc} is 7.0 [33]. Thus, there is an attractive interaction between the support surface and the gold sol, although the attraction forces between them seem to be relatively low since the solution only becomes colorless after 3–4 days, as mentioned in Section 2.1.5. Accordingly, apart from the LPRD method, the other techniques used in this work were able to originate catalysts with gold contents reasonably close to the expected loading.

3.1.4. Microscopy analyses

The gold average size (d_M) of the different catalysts is presented in Table 2. Fig. 2 shows representative HAADF-STEM micrographs of the gold catalysts prepared by the different methods and their respective particle size distributions. It can be seen that small spherical metal particles are found for all the methods used. LPRD, citric and immobilization methods produced smaller particle sizes (from 0.5 to 11 nm) than DIM (1.5–50 nm, although in this case, most of the particles have sizes between 1.5 and 17 nm), and especially than IW (0.5–65 nm). This latter technique does not remove chloride, which is known to cause poisoning and excessive sintering of the Au particles during thermal treatments. This is due to the ease with which gold and chloride ions combine to form bridges, favoring the growth of particles upon heating [22]. However, heating steps are necessary to decompose the gold precursor and reduce the metal, and consequently activating the catalyst (in the case of the IW method). In the sol immobilization technique, they are also required in order to achieve a strong metal/support interaction [18]. Therefore, chloride removal is a very important step in the preparation of well-dispersed gold catalysts.

In the DIM method, gold is deposited on the surface of MWCNT as $Au(OH)_3$, i.e. without involving chloride as in the IW method. As a result, Cl is not associated with Au and is removed from the catalyst by washing. This explains the more homogeneous distribution when compared to the Au IW catalyst. However, as it can be seen in Fig. 2, this catalyst still has a limited percentage of large gold crystallites. On the contrary, catalysts prepared by LPRD, citric or immobilization methods exhibit a relatively narrow distribution of gold nanoparticles, which have small average sizes (5.5 nm, 3.2 nm and 5.0 nm, respectively). In all these techniques, Cl largely remains in solution and is eliminated by extensive washing.

3.1.5. XPS analyses

XPS analysis of the Au 4f region was carried out, and the gold oxidation states obtained with the different preparation methods can be seen in Table 2, where the values of binding energies (BE) are referred to the Au $4f_{7/2}$ peak, and the half-widths of the XPS peak are given inside round brackets. XPS data confirmed the presence of Au in the metallic state in the case of Au IW/MWCNT, Au DIM/MWCNT, Au citric/MWCNT and Auc/MWCNT catalysts. Whereas Au IW/MWCNT, Au citric/MWCNT and Auc/MWCNT catalysts were directly reduced, respectively with hydrogen, citric acid and both $NaBH_4$ and hydrogen, in the DIM method the Na_2CO_3 added can dissociate and its reaction with water leads to the generation of hydroxyl ions, which can hydroxylate the Au^{3+} species of the gold precursor. Subsequently, Au^{3+} can be reduced to metallic gold by electron transfer from coordinated OH^- ions on the surface of the

Table 2
Characterization of the gold catalysts prepared by different methods on MWCNT and activities (TOFs) after 2 h of reaction.

Catalyst	Metal loading (%) [ICP]	d_M (nm) [TEM]	Au $4f_{7/2}$ BE (eV)[a] [XPS]	Surface Au species [XPS]	TOF $\times 10^{-3}$ (h^{-1})[b]
Au IW/MWCNT	0.75 ± 0.05	23	83.9 (1.50)	Au^0	0
Au DIM/MWCNT	0.74 ± 0.03	6.5	84.0 (1.41)	Au^0	1.1 ± 0.6
Au LPRD/MWCNT	0.40 ± 0.01	5.5	–	–	5.9 ± 2.1
Au citric/MWCNT	0.76 ± 0.01	3.2	84.1 (1.69)	Au^0	n.d.
Auc/MWCNT	0.66 ± 0.02	5.0	84.2 (1.70)	Au^0	4.2 ± 1.3

[a] Half-width of XPS peaks inside round brackets.

[b] Errors of TOF calculated on the basis of errors related to the measurements of gold loadings and standard deviations of particle size distributions.

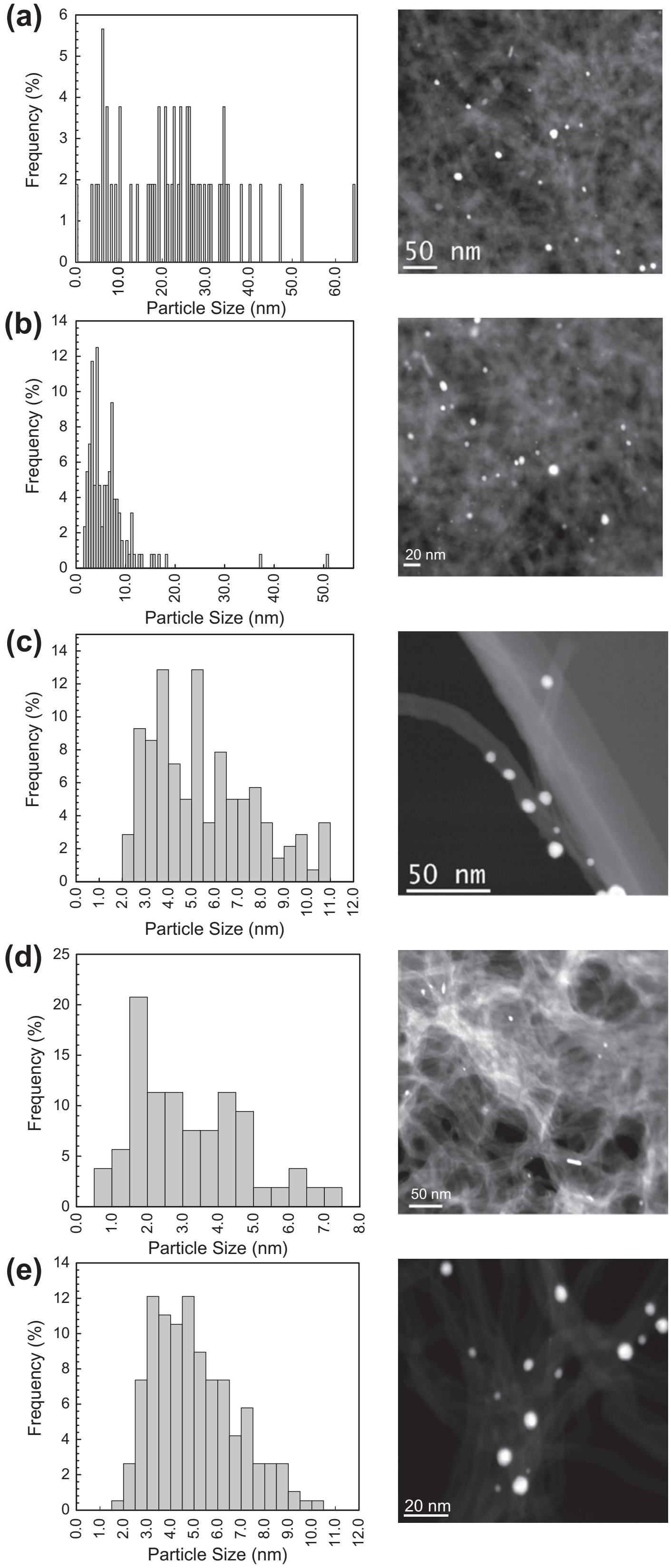

Fig. 2. Particle size distributions and HAADF-STEM images of the Au catalysts prepared on MWCNT by the following methods: (a) IW, (b) DIM, (c) LPRD, (d) reduction with citric acid and (e) sol immobilization.

support [26]. This can explain the presence of only Au^0 in the Au DIM/MWCNT catalyst. In the case of the Au LPRD/MWCNT catalyst, gold was not detected by this technique, most likely due to the low loading and the small particle sizes. However, it cannot be excluded that gold could be located in the pores of the aggregates formed by interaction of isolated MWCNT and not in their surface.

3.2. Catalytic studies

3.2.1. Influence of the preparation method

In this part of the work, the effect of the preparation method on the activity and selectivity of gold catalysts was evaluated. For this purpose, gold was supported on MWCNT by several techniques as described before.

3.2.1.1. On the catalytic activity

Firstly, a glycerol oxidation blank experiment was carried out with the MWCNT support, and no glycerol conversion was detected.

Fig. 3 shows the evolution of glycerol conversion in the presence of the gold catalysts prepared by different methods. Since the support is the same for all catalysts (MWCNT), the differences observed must be related to the metal phase. In fact, it is well known that the preparation method is crucial to obtain catalysts with small particle sizes. However, for gold, a high dispersion of the active phase on the support is not so easily achieved as with other metals [35,36]. Therefore, the inactivity observed with Au IW/MWCNT is due to the low metal dispersion. As it was observed with activated carbons [31], this method is not suitable to obtain active catalysts. Indeed, as already mentioned in Section 3.1, this classical method leads to a broad particle size distribution (Fig. 2) mainly caused by the presence of chloride. The average gold particle size obtained with this catalyst (23 nm) appears to be too high for being active in glycerol oxidation, contrarily to what was observed for gold nanoparticles supported on carbon black. In this latter support, although small gold particle sizes (<5 nm) have a higher activity, catalysts with gold crystallites as large as 42 nm have already shown a relevant activity in glycerol oxidation [37].

DIM is a less usual method for gold impregnation, although the procedure is very similar to the incipient wetness technique. The main reason for the enhanced performance observed in the corresponding catalyst is related to the lower gold particle sizes obtained, when compared to the Au IW/MWCNT catalyst, once most of the gold crystallites are smaller than 17 nm (Fig. 2). Thus, the mere fact of depositing gold as gold hydroxide instead of gold chloride is sufficient to obtain an active catalyst.

Considering that the average crystallite size is an important parameter in reactions catalyzed by gold, other preparation methods were tested. It can be observed that Auc/MWCNT, Au LPRD/MWCNT and Au citric/MWCNT catalysts stand out relatively to the other two, due to the high performance achieved. In fact, all these samples have small average particle sizes and exhibit fairly homogeneous distributions of gold particles when compared with Au IW/MWCNT and Au DIM/MWCNT (Table 2 and Fig. 2). As a result, it could be concluded that the catalytic performance can be dramatically increased by appropriate choice of the preparation method of carbon nanotubes supported gold catalysts.

The correct choice of the solvent to disperse carbon nanotubes is also very important. In the citric method, the use of 2-propanol is intended to enhance carbon nanotubes dispersibility and, according to Zanella et al. [27], avoid considerable agglomeration of gold over the nanotube bundles, which may occur when this method is carried out in the presence of water. Multi-walled carbon nanotubes nicely decorated with well-dispersed gold nanoparticles were successfully obtained (Fig. 2d). In fact, the smaller average gold particle size was obtained with this specific method (3.2 nm). However, although this method seems to be the most advantageous in terms of both gold particle size and gold loading (see Table 2), the Au citric/MWCNT catalyst does not exhibit the highest performance (Fig. 3). In fact, a closer inspection of the multi-walled carbon nanotubes reveals that gold entered and filled some of them, as it can be in Fig. 4. The presence of gold inside the nanotubes was confirmed by energy dispersive X-ray spectroscopy (EDS) and was observed with a high frequency. It should be noticed that these agglomerates of gold are not active and therefore correspond to a percentage of metal that does not contribute to the catalytic reaction, which means that the loading of active, available gold nanoparticles is actually lower than 0.76%. This phenomenon can explain the lower performance of this catalyst despite the presence of very well-dispersed gold nanoparticles. Ultrasonic cavitation has already been reported as an efficient way of breaking the regularity of the structure of carbon nanotubes [38]. In this particular case, an intense sonication may have led to the opening of some nanotubes. The possible importance of 2-propanol in this context should not be ignored too. It is important to note that this phenomenon was only observed with the Au citric/MWCNT catalyst.

The Au LPRD/MWCNT catalyst shows a good performance; however, this method does not seem appropriate to prepare gold

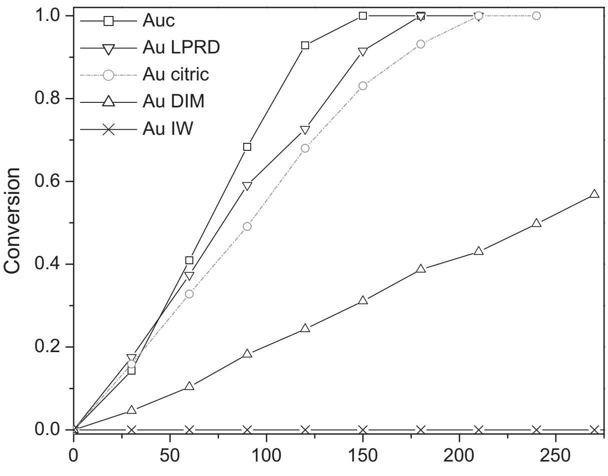

Fig. 3. Influence of the preparation method on the performance of gold catalysts supported on MWCNT. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg, NaOH/glycerol = 2 mol/mol.

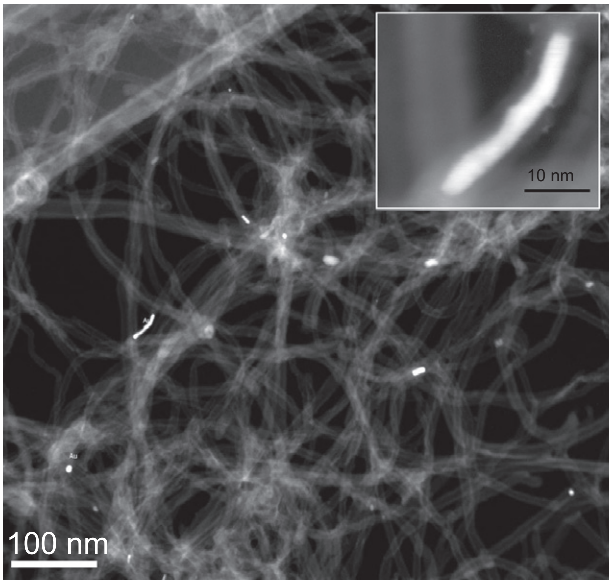

Fig. 4. Image of the Au citric/MWCNT catalyst showing some gold inside carbon nanotubes.

supported on MWCNT, since it leads to a significant loss of metal as described in Section 3.1. Nevertheless, considering the value of the relative error on the conversions measured (see Section 2.3), it may be concluded that performances of Au LPRD/MWCNT and Au citric/MWCNT are not too different.

The highest performance was obtained with the Auc catalyst (Fig. 3). In the sol immobilization technique, gold particles are formed in the solution and then transferred to the support. The protective agent (PVA) prevents efficiently the agglomeration in solution and during the supporting step by steric and polar stabilization of gold particles, leading to a narrow distribution of particle dimensions and to a low average size (5.0 nm). This catalyst presents a high turnover frequency (TOF) of $4.2 \times 10^3\ h^{-1}$ after 2 h of reaction, as shown in Table 2. This method was also described as being the most appropriate technique in order to obtain well-dispersed nanoparticles on activated carbon [19,23]. Gil et al. also confirmed recently that this preparation method is very efficient to prepare gold catalysts supported on carbon nanofibers [39].

It is important to note that the TOF value was not calculated for the Au citric/MWCNT catalyst, since this sample has a significant percentage of inactive gold and thus an overestimated content of active metal, as mentioned before.

3.2.1.2. *On the selectivity*

The effect of the preparation method on the distribution of products was also evaluated. The selectivities obtained in the presence of the different catalysts are compared at constant reaction time (2 h) and at the same glycerol conversion ($X = 50\%$) in Table 3. The selectivities are practically independent of time or glycerol conversion, varying only slightly during the reaction for all catalysts tested in this work. In some cases, the sum of the calculated selectivities is lower than 1 (see Table 3), since some oxalic acid was also detected but always with low concentrations. Contrary to it was observed for the catalytic performances, the differences in gold crystallite sizes do not influence significantly the selectivities, i.e. a similar distribution of products was obtained for all the catalysts tested. Contrary to literature data reported for gold on other carbon supports under similar typical basic reaction conditions [18,19,37,40,41], Au/MWCNT catalysts favor the formation of DIHA instead of GLYCEA. Consequently, a remarkably high and constant dihydroxyacetone selectivity of about 60% is obtained with all the catalysts. This result is particularly important. In fact, according to the literature, the oxidation of the secondary hydroxyl group seems to be preferred only under acid conditions [1,42]. However, when using gold-containing catalysts, a highly basic medium is necessary in order to observe significant glycerol conversions [12,13,37]. In this work, the combination of both high performance and selectivity to DIHA was successfully achieved. Nevertheless, it should be noticed that the amount of DIHA formed is not so easily comparable with the intrinsic selectivity of the gold catalysts toward the oxidation of the secondary OH group, since DIHA and glyceraldehyde can interconvert (Fig. 1). Therefore, the oxidation of secondary alcohol can result from a consecutive reaction. Besides the desired DIHA and GLYCEA, it can also be observed in Table 3 that limited amounts of glycolic acid (GLYCOA) and tartronic acid (TARTA) were also measured.

Summarizing, it can be concluded that among the various methods tested in this work, the sol immobilization method is the most suitable technique to prepare gold supported on carbon nanotubes since it allows a better use of gold, leading to a high activity and to the highest selectivity to the products of commercial interest (DIHA + GLYCEA = 86%).

The selectivities obtained under alkaline conditions could be due to the combination of the nature of the catalysts, such as particle dimensions and support, and to experimental conditions, specially the base concentration. However, the active catalysts prepared have variable average particle sizes (from 3.2 nm for Au citric/MWCNT to 6.5 nm for Au DIM/MWCNT catalyst), and this does not seem to lead to significant differences in the selectivity to DIHA (see Table 3). Therefore, the support may be responsible for the observed selectivities. In fact, in a study of Demirel et al. [2], it was reported that the selectivity to DIHA can be increased from 15%, when using gold supported on an activated carbon, to 27% using a carbon black; therefore, it seems that the textural properties of the support can influence the product distribution. Villa et al. [4] also concluded that during glycerol oxidation in the presence of gold on $MgAl_2O_4$, the selectivitiy of the reaction was only partially ruled out by the gold particle size, and indeed, the textural and chemical properties of the support seem to be fundamental. Moreover, in a recent study [18], we found that gold supported on activated carbon (essentially of microporous nature) by the sol immobilization method with an average particle size of 6.8 nm leads to the preferential formation of glyceric acid with a selectivity of 62% after 2 h of reaction and only 18% to dihydroxyacetone. This latter catalyst has a similar average gold particle size than that used in the current work with the Au DIM/MWCNT catalyst (6.5 nm), but the distribution of products is quite different. This makes us to believe that the support plays an important role in the selectivities achieved. So, the high DIHA selectivity observed may be explained by the peculiar porous characteristic of MWCNTs, including the presence of large mesopores, which may favor the binding of glycerol over the gold surface in an adequate configuration for the formation of DIHA by the direct oxidation of the secondary hydroxyl group. Alternatively, the displacement of the equilibrium from the intermediate glyceraldehyde to dihydroxyacetone (see Fig. 1) may also be promoted. Very recently, Prati et al. [16] tested gold supported on carbon nanofibers (CNF) and modified CNF in glycerol oxidation under base-free conditions. These catalysts lead to the formation of hydroxypyruvic acid (selectivities between 7% and 26% depending on the support used), showing that the secondary alcohol group can be significantly oxidized. Similarly, they hypothesized that the oxidation of the secondary alcohol probably depends on a different adsorption mode. Additionally, besides stereo chemical effects, a possible influence of MWCNTs particular electronic characteristics on the reaction mechanism cannot be excluded.

3.2.2. *Influence of base concentration*

As already mentioned and accordingly to the literature [12,13,37], the oxidation of the glycerol secondary OH group in the presence of platinum-group metal catalysts seems to be favored under acidic conditions. Therefore, in an attempt to enhance the DIHA selectivity, the base concentration was decreased.

Table 3
Influence of the preparation method of Au catalysts supported on multi-walled carbon nanotubes on conversion and selectivities to dihydroxyacetone (DIHA), glyceric acid (GLYCEA), glycolic acid (GLYCOA) and tartronic acid (TARTA).

Catalyst	t = 120 min					X_{GLY} = 50%			
	X_{GLY}	S_{DIHA}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}	S_{DIHA}	S_{GLYCEA}	S_{GLYCOA}	S_{TARTA}
Au DIM/MWCNT	0.24	0.54	0.24	0.20	0.02	0.56	0.19	0.20	0.03
Au citric/MWCNT	0.68	0.58	0.15	0.16	0.06	0.59	0.16	0.16	0.06
Au LPRD/MWCNT	0.73	0.58	0.20	0.15	0.04	0.56	0.20	0.17	0.04
Auc/MWCNT	0.93	0.60	0.26	0.13	0.01	0.60	0.26	0.13	0.01

For this purpose, the evolution of the glycerol conversion was examined using different NaOH/glycerol ratios (0, 0.5, 1 and 2) in the presence of the Auc/MWCNT catalyst. The results are shown in Fig. 5. It can be easily observed that the base concentration has a large influence on the reaction rate. In fact, as expected, no activity is observed when using gold catalysts without added base. In addition, the decrease of the base concentration leads to lower oxidation rates. In fact, Zope et al. [12] showed that glycerol oxidation is favored by high-pH conditions, since the hydroxide species adsorbed on gold are necessary to activate both C–H and O–H bonds of glycerol (also adsorbed on the surface). Moreover, it has been demonstrated that oxygen atoms incorporated into the reaction products were originated from hydroxide ions and not from molecular oxygen [12]. From our results (Fig. 5), a first-order reaction relatively to the hydroxide concentration was determined in the range studied, which effectively suggests its direct participation in the reaction mechanism.

On the other hand, the decrease of the NaOH/glycerol ratio only influences (negatively) the reaction rate, and no effect was observed in the distribution of products. The selectivity to DIHA remained the same independently of the base concentration (≈60%). Nevertheless, it should be noticed that even when working with a NaOH/glycerol ratio of 0.5 the pH of the medium remains high, far away from acid conditions. This is necessary to detect glycerol conversion.

Recently, the optimum catalyst composition in order to obtain preferentially DIHA was determined to be 3 wt% Pt–0.6 wt% Bi supported on activated carbon and working at 80 °C, 3 bar and at an initial pH of 2 [10]. This catalyst leads to a maximum DIHA selectivity of 60% (at 80% glycerol conversion), which is similar to that achieved in this work, but the glycerol oxidation rate is much lower (TOF = 372 h^{-1} vs. TOF = 4.2×10^3 h^{-1}). In fact, the platinum-based catalysts, contrarily to gold catalysts, are active under acid conditions, although high activities are only achieved with the addition of base [12].

3.2.3. Study of DIHA stability

It is known that DIHA is not stable under alkaline conditions [5]. Therefore, DIHA stabilization tests were carried out at different pH. For that purpose, the carbon nanotubes supported catalyst was removed by filtering off the solution after 3 h of reaction. Part of this solution was maintained at the high pH (>12) corresponding to the reaction conditions, whereas the pH values of other parts were adjusted to 9, 7, 5 and 3, using concentrated HCl in order to minimize the variation in DIHA concentration. The DIHA degradation of the different solutions was assessed by HPLC during several days. The obtained results can be seen in Fig. 6.

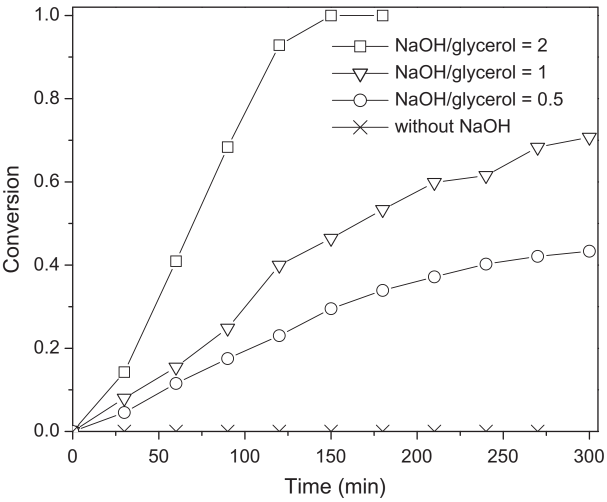

Fig. 5. Influence of the NaOH/glycerol molar ratio on the glycerol conversion over the Auc/MWCNT catalyst. Reaction conditions: 60 °C, $p_{O_2} = 3$ bar, 150 mL of glycerol 0.3 M, catalyst amount = 700 mg.

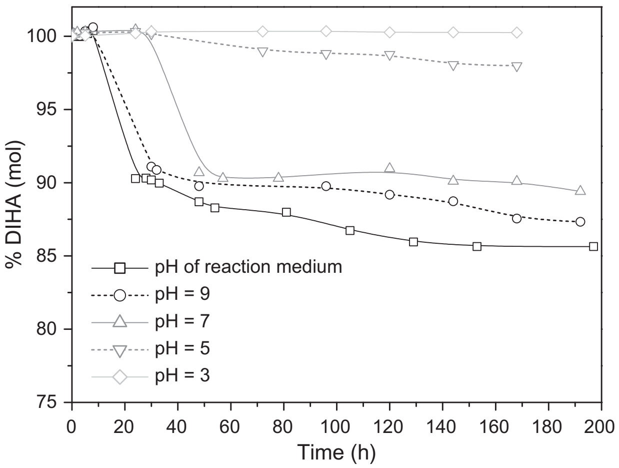

Fig. 6. Influence of pH on the stability of the DIHA produced in the reaction.

It can be observed that the DIHA maintained at the pH of the reaction medium is only stable during a short period (a few hours), and a concentration decrease of about 10% was measured after 24 h. A similar behavior was observed at pH 9. On the other hand, the same test with the same final solution, neutralized (pH = 7) immediately after separation from the catalyst, showed no degradation during the same period. However, it is only at pH 3 that the DIHA solution is perfectly stable during several days. This value is in agreement with the recommended pH to DIHA storage. In fact, DIHA is particularly stable between pH 3 and 4 [43].

Part of the dihydroxyacetone was decomposed into glyceric acid and over-oxidation products (e.g. oxalic acid), but some new compounds were also detected by HPLC. In fact, at high pH, DIHA can easily be decomposed into aldehydes, ketones, formaldehyde, organic acids and ultimately leads to the formation of oligomers [43]. Therefore, the conditions used during the reaction (mainly the very high pH) are not suitable to store DIHA-containing mixtures for long periods of time. Nevertheless, adjusting the solution pH to approximately 3 after reaction seems to be a reasonably adequate way to stabilize that target compound. In conclusion, for practical purposes, it would be necessary to lower significantly the pH of the liquid mixture obtained after reaction in order to prevent DIHA transformation reactions.

Finally, it is important to mention that a DIHA productivity of 5.4 g L^{-1} h^{-1} was obtained in the present work, which is much higher than that reached in the current commercial approach of DIHA production by microbial oxidation of glycerol (1.8 g L^{-1} h^{-1}) [44].

4. Conclusions

Gold was successfully supported on the surface of multi-walled carbon nanotubes by several methods. The performance of gold catalysts in glycerol oxidation greatly depends on the preparation technique used, which in some cases influences the particle size. Contrary to that was observed for the catalytic activities, the different preparation methods do not influence significantly the selectivities attained. Gold particles supported on MWCNTs resulted in the oxidation of the secondary hydroxyl group, and therefore, a remarkably high and constant DIHA selectivity of about 60% is obtained, independently of the preparation method used. The sol immobilization method was concluded to be the most suitable to prepare gold supported on carbon nanotubes, since it allows a better use of gold, leading to a high activity and to the highest selectivity to the products of commercial interest (DIHA + GLYCEA = 86%).

A DIHA productivity of 5.4 g L^{-1} h^{-1} was obtained in this work, which is much higher than that reached in the current commercial approach by microbial oxidation of glycerol (1.8 g L^{-1} h^{-1}). This important target product is not stable under the high-pH conditions of reaction, but the acidification of the medium to a pH around 3 allows the storage during a large period of time without any observed decomposition.

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