Ablation energy, water volume and ablation time: Gold nanoparticles obtained through by pulsed laser ablation in liquid

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Abstract. It was studied the production of gold nanoparticles from a gold target by pulsed laser ablation in liquid medium. This technique allows replacing conventional methods of preparing nanoparticles without the need for precursors, where gold is used in its metallic state. Experimental tests were performed to determine the appropriate synthesis conditions to achieve small particle sizes. The variables studied were water volume, ablation time and ablation energy. Gold nanoparticles with spherical geometry, in metallic, and nanocrystalline state were obtained without the need to use precursors and stabilizers. Ablation energy is the most influential variable on the particle size, because it was observed that when is increased the ablation energy is generate greater particle sizes.

1. Introduction

The catalytic combustion reaction has been widely used in petrochemical industry to treat gaseous effluents from oil refining processes. This type of reactions requires high temperatures (~ 1800 °C) [1], which leads to the production of volatile organic compounds and emission of a large amount of greenhouse gases. The industry seeks to lower the reaction temperature; for this a catalyst with high catalytic activity capable of reducing the activation energy of the reaction is needed. These catalysts are usually noble metals (i.e., gold), synthesized from costly and polluting precursor sales. Several precious metals have been investigated as catalysts for methane combustion; and particular emphasis has been placed on palladium [2]. However, gold, being a much more abundant and lower cost metal, has aroused great interest [3]. Previous results have shown that gold improves the catalytic activity towards the oxidation of volatile organic compounds, this effect being dependent on the catalyst preparation method [4]. An important aspect to keep in mind is that gold must be brought to a nano-scale, which is key to be able to demonstrate its catalytic activity and favoring reactions in terms of selectivity and conversion [5].

Colombia exports approximately 4 tons of gold per year hence having an enormous potential for the production of gold-based catalysts. Metal oxide supported gold nanoparticles are highly active catalysts for oxidation reactions [6]. The most common method to obtain gold nanoparticles is impregnation of gold salts [7]. This is rather an expensive method in a country where gold is exported since gold itself
is the raw material for their production. Therefore, it is important to develop alternative methods for producing gold nanoparticles directly from metallic gold as pulsed laser ablation in liquid medium (PLAL) technique. However, PLAL is rather a complicated process where several variables might alter the properties of the produced nanoparticles. As a first step in the development of a PLAL process to produce catalytic nanoparticles it has been decided to study the effects of ablation energy, liquid volume an ablation time on key physicochemical properties of gold nanoparticles aimed to be applied on methane combustion. In this paper, we were studied the effects of ablation energy, liquid volume and time of ablation.

2. Experimental setup
Pulsed laser ablation in liquid was performed using a Q-Smart equipment (Quantel) with a laser of a wavelength of 532 nm. A gold target (99.99% purity, ø = 50 mm, δ = 0.1 mm) immersed in Milli-Q type water was exposed to the laser. Experiments were carried out varying energy, pulse, time of ablation and volume of water. Some constant parameters were maintained such as the height or distance between the mirror and the target, and the size of the incident spot on the target. According to the bibliographic review carried out, preliminary tests were carried out varying the laser energy between 100 mJ and 180 mJ, solvent volume between 10 mL and 15 mL, and the ablation time between 5 min and 10 min. Every experiment showed were made at constant laser pulse of 8 ns and a frequency of 10 Hz. Particle size was measured through Zetasizer Nano ZS90 equipment. Particle size distributions were obtained by dynamic light scattering (Z-Sizer, Malvern) and image obtained in a scanning electron microscope (SEM), field emission gun (FEG) QUANTA 650 FEG. Crystallinity was determined via X-ray diffraction (XRD, Bruker) and the surface chemical state by X-ray photoelectron spectroscopy (XPS/ISS/UPS-A Centeno platform, SPECS). In addition, gold nanoparticles production yields were estimated by weight mass difference. The gold nanoparticles obtained were marked according to the preparation conditions following the nomenclature: Au (E-V-t). Where, E = Ablation energy; V = volume of water used during ablation; and, t = ablation time. Thus, an nanoparticle (NP) prepared with 120 mJ, 10 mL and 5 min, would be called: Au (120-10-5). A graph with the experimental set-up is shown below (Figure 1).

![Experimental set up diagram.](image)

3. Results and discussion
Figure 2(a) shows the dispersion of particle diameter (PD) obtained by varying the laser energy with 5 and 10 min of ablation, leaving constant water volume of 10 mL. It can be observed that for 5 min (white rectangles) a gaussian curve represents the behavior of particle size, being 100 mJ and 180 mJ the greater energies to obtain small nanoparticles. However, with energies less than 100 mJ it was not possible to ablate the target, and above 180 mJ it became complex to obtain reproducibility in the experiments. For the experiments made at 10 min of ablation (red circles) the particle size increases with increasing laser energy; for all experiments with this time, the particle size is bigger than those made with 5 min of ablation. At this point it could be concluded that to obtain particle sizes between 10 nm and 20 nm it was necessary to study energies between 120 mJ and 140 mJ with 5 min of ablation time. However, it was also necessary to study the variation in water volume; therefore, energies between 120 mJ and 140 mJ were studied with an increase in volume of water to 15 mL.
Figure 2. Particle size and distributions. (a) size particle vs energy, and (b) comparison between three particle diameter distributions at different energies.

From these tests it is possible to recover that the particle sizes decreased considerably when increasing water volume. Table 1 shows the particle diameters obtained at 5 min and 10 min of ablation with a volume of water of 15 mL.

| Time = 5 min | Time = 10 min |
|--------------|---------------|
| Energy (mJ)  | Energy (mJ)   |
| PD (nm)      | PD (nm)       |
| 120          | 120           |
| 130          | 130           |
| 140          | 140           |
| 21           | 9             |
| 19           | 19            |
| 14           | 24            |

Considering that the smallest particle diameters converge between energies greater than 100 mJ and less than 150 mJ, at short ablation times and lower water volumes, the following ranges were chosen to study according to the main variables: (A) laser ablation energy; specifically, 120 mJ, 130 mJ and 140 mJ, and, (B) liquid water volume; namely, 10 mL and 15 mL. The effect of these variables on the particle size distributions, crystallinity, and surface chemical state of the produced gold nanoparticles was investigated. The effect of laser ablation energy and liquid water volume over the average particle size of gold nanoparticles was analyzed for the samples made with 5 minutes time of ablation, as it was seen that the time of ablation studied did not have any effect on the average particle size. These results showed that a higher laser energy ablation leads to bigger gold nanoparticles and a greater particle diameter distribution, as shown in Figure 3, where are represented three different particles diameter distributions obtained at three different energy. The PLAL method produced metallic gold nanoparticles, because that weight difference measurements (w) showed that the mean for the amount of gold contained in the samples presented a confidence interval (C.I) of $0.34 \leq m_{W_{\text{AuNps}}} \leq 0.66 \times 10^{-4} g$ (D.F. = 31); with this it was seen that the method produces very few quantities of the material required to the conditions studied.

The spherical geometry of the particles was observed through images of the SEM (Figure 3(a)). About the concentration of gold in the samples, a comparison was made between the atomic percentages of gold on the surface measured by XPS and the loss of mass obtained by ablation; it was observed that the samples with the highest concentration of gold on the surface correspond to the highest mass loss obtained by ablation. This comparison can be seen in Table 2 and Table 3. Table 2 shows the loss of mass per ablation obtained for each sample of AuNps. Now, XPS analysis showed the presence of gold in the nanoparticle samples, whose gold mass percentage values are presented in Table 3, for every 6 samples analyzed (those obtained at 5 min of ablation). Comparing both results, it is possible observe than the sample with to greater ablation energy, is the sample with the greater amount of gold was
obtained in the colloidal dispersion. The highest mass losses coincide with the samples in which the highest mass percentage of gold was found.

Figure 3 presents an Au4f spectrum for a gold nanoparticle sample made at 120 mJ, 10 mL and 5 min which was similar for all gold nanoparticle samples analyzed [8]. The XRD analysis (see Figure 3(c)) showed diffraction peaks typical of the Au plane (1 1 1), $\theta = 38^\circ$, attributed to gold crystallites with a cubic structure centered on the faces [9,10], also the planes (2 0 0) and (2 2 0) were observed.

Table 2. Mass percentage of gold in the samples.

| Energy (mJ) | V=10 mL | V=15 mL |
|-------------|---------|---------|
| 120         | 4.80    | 2.88    |
| 130         | 16.75   | 14.22   |
| 140         | 5.66    | 22.50   |

Finally, by the PLAL method [11], AuNps were obtained with spherical geometry, in the metallic state, and crystalline with a gold content of the order of $10^{-4}$gr. Based on this it can be said that the increase in ablation energy broadens the particle diameter distribution. This can be explained taking into account that, the higher the laser energy that affects the surface of the gold target, the higher the amount of material extracted, therefore, the particles will be grouped in greater quantity giving rise to nanoparticles of bigger size. In line with the results of this work, Besner et al. reported a similar trend for the manufacture of gold nanoparticles in deionized water [12]. The produced gold nanoparticles of minor size will be deposited on silica for further use as catalysts for methane combustion reaction.
Table 3. Loss of mass by ablation.

| Energy (mJ) | $V_b=10\text{ mL}$ | $V_b=15\text{ mL}$ | $V=10\text{ mL}$ | $V=15\text{ mL}$ |
|-------------|---------------------|---------------------|------------------|------------------|
| 120         | 0.2                 | 0.4                 | 1.0              | 0.1              |
|             | N.D.                | 0.2                 | 0.1              | 0.7              |
|             | 0.3                 | 0.1                 | 0.8              | 0.9              |
| 130         | 1.0                 | N.D.                | 0.8              | N.D.             |
|             | N.D.                | 0.6                 | 0.4              | 1.2              |
|             | 0.2                 | 0.2                 | 0.8              | 1.2              |
| 140         | 0.5                 | 1.4                 | 1.2              | 1.2              |
|             | 0.2                 | 1.4                 | 0.2              | 1.1              |
|             | 1.0                 | 0.3                 | 1.1              | 1.2              |

*a*: ablation time.  
*b*: $V$: water volume.  
*c*: N.D.: Non detected.

4. Conclusion
In general, the technique of pulsed laser ablation in liquid medium was effective for the preparation of gold nanoparticles with spherical geometry, in metallic, and crystalline state, without the need to use precursors and stabilizers. However, controlling the variables that govern the process was complicated; in addition, the amount of gold obtained by ablation did not exceed the order of $10^{-4}$ gr. With regard to the variables studied during the synthesis of nanoparticles, it was found that energy is an influential variable on the particle size, and that at higher energy of ablation greater particle sizes were obtained; the volume of water and the time of ablation had no influence on this variable response in the ranges studied.

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References
[1] Yeste M P, Cauqui M A, Giménez-Mañogil J, Martinez-Múnera J C, Muñoz M A, García-García A 2020 Chemical Engineering Journal 380 122370
[2] Betta R D A 1997 Catalysis today 35(1–2) 129
[3] Corti C W, Holliday R J, and Thompson D T 2007 Topics in catalysis 44(1–2) 331
[4] Scire S, Minico S, Crisafulli C, Satriano C, and Pistone A 2003 Applied Catalysis B: Environmental 40(1) 43
[5] Della P C, Falletta E, Prati L, and Rossi M 2008 Chemical Society Reviews 37(9) 2077
[6] Haruta M, and Daté M 2001 Applied Catalysis A: General 222(1–2) 427
[7] Chen M, He Y, Liu X, Zhu J, and Liu R 2017 Powder Technology 311 25
[8] A Devia, V Benavides, H Castillo, J Quintero 2006 AIP Conf. Proc. 875 258
[9] J H Quintero, A Mariño, L Šiller, E Restrepo-Parra, F J Caro-Lopera 2017 Surface & Coatings Technology 309 249
[10] Nguyen Ngoc Long, *et al.* 2009 J. Phys. Conf. Ser. 187 012026
[11] A V Kabashin and M Meunier 2007 J. Phys. Conf. Ser. 59 354
[12] Besner S, Kabashin A V, Winnik F M, and Meunier M 2008 Appl Phys A 93 955