



## Stabilizer effects on the synthesis of gold-containing microparticles. Application to the liquid phase oxidation of glycerol



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### ABSTRACT

Gold-containing poly(urea-formaldehyde) microparticles were prepared by the in situ polymerization method using a series of stabilization agents with different chemical nature. The effects of cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and tetrakis(hydroxymethyl)phosphonium chloride (THPC) on the morphology, the particle size of encapsulated gold, the gold particle size distribution and the encapsulation efficiency were investigated by using scanning electron microscopy, X-ray diffraction and atomic absorption analyses. The chemical nature of stabilizer had a marked influence on both the encapsulated gold particle size and the encapsulation efficiency. Both gold particle size and gold encapsulation efficiency increased when decreasing the stabilizer polarity number. All the microparticles here prepared were tested in the liquid phase selective oxidation of glycerol. The glycerol conversion increased and the glyceric acid selectivity decreased when decreasing gold particle sizes. Results showed that use of stabilizers with hydrophobic surfaces enhanced the selectivity to C<sub>3</sub> products in the resulting catalysts. On the other hand, the use of stabilizers with hydrophilic surfaces increased the C–C bond cleavage products in the resulting catalysts.

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### 1. Introduction

The increasing demand of new products with high quality is in opposite with the need to reduce all types of pollution during the different manufacturing processes. One of the ways to satisfy the environmental requirements, such as decrease in wastes, use of materials with low toxicity, reduction of assistant materials or energy consumption, is the use of nanoreactors or microreactors [1]. Environment friendly chemistry plays an important role in the design of novel catalysts [2]. In this sense, microencapsulation method has been recently recognized as a useful technique to immobilize metal catalysts onto polymers. In addition, it is an alternative strategy to enable safe handling, easy recovery, reuse and disposal at an acceptable economic cost [1,3]. The microencapsulation refers to the incorporation of an active substance in a shell or a matrix of a carrier component. Resulted catalysts could be separated from a reaction mixture by simple filtration and recycled, which makes them suitable for green chemistry processes.

Glycerol is a co-product of the triglyceride transesterification in the production of fatty acid esters employed as biodiesel. The increasing production of biodiesel worldwide has led to an over-supply of glycerol in the market. Consequently, the revalorization of glycerol is nowadays of great interest, especially as a raw material in the manufacture of added-value products through oxidation [4]. Selective oxidation of glycerol leads to various valuable oxygenates such as glyceric acid, tartronic, and glycolic acid [5]. Heterogeneous catalytic oxidation processes are low cost and environmentally friendly and these are, therefore, considered attractive alternatives to the traditional homogeneous ones used in the fine chemicals industry.

Despite the gold is often considered as chemically inert due to bulk gold cannot be oxidized in air and it cannot react with most chemical reagent. In the last decades, gold based catalysts have demonstrated to show a great potential for selective oxidation reactions [6,7].

Microencapsulation of gold particles could improve the catalytic activity, selectivity and stability [8] in those reactions in which Au is used as the catalytic phase. The resulting microstructures lead to gold particles that are active in the liquid phase

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selective oxidation of glycerol [9,10]. Moreover, during the process of microencapsulation, it is possible to tune the size and morphology of the metal particles. This is quite important since glycerol oxidation was found to be structure-sensitive. It has been reported that the size of the gold particles influences both the catalytic activity and selectivity [11–13]. For instance, in the preparation of microcapsules, the dispersion of the organic phase in the continuous phase is the determining step in establishing the particle size distribution of the final microcapsules, which is in turn influenced by the geometrical factors of the reactor (type of stirrer, stirrer diameter, internal fittings), operating parameters (stirrer velocity, stirring and polymerization time) and substance parameters (type and concentration of stabilizers, viscosities of continuous and dispersed phases and interfacial tensions of phases) [14–16].

In previous works, the synthesis procedure of gold-containing poly(urea-formaldehyde) microparticles for the selective oxidation of glycerol was studied [9]. Some parameters such as the amount of organic solvent (dimethyl sulfide) and the gold precursor to polymer mass ratio were afterward optimized [10]. This work is focused on the study of effect of different kinds of stabilizers or stabilization agents on the synthesis of gold particles, whose influence was observed to be remarkable [17]. The addition of stabilizers during the microencapsulation process plays an important role in the stabilization of liquid–liquid dispersions. In many microencapsulation techniques, stabilization agents are used to form a film or skin around the particle surface in order to prevent coalescence and agglomeration by a mechanism analogous to steric stabilization [18].

Therefore, the aim of this work was to study the effect of different stabilizers in the preparation of gold-containing poly(urea-formaldehyde) microparticles. For that purpose, a series of stabilization agents with different chemical nature were used, including: cationic stabilizers as cetyltrimethylammonium bromide (CTAB) and tetrakis(hydroxymethyl)phosphonium chloride (THPC), anionic stabilizer as sodium dodecyl sulfate (SDS) and nonionic stabilizers as polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA). The synthesis was carried out under friendly environment conditions. The morphological and physical properties of the resulted microparticles containing gold were discussed as a function of the type of stabilization agent used. Finally, the microparticles containing gold were tested as catalysts in the liquid-phase oxidation of glycerol.

## 2. Materials and methods

### 2.1. Materials

Urea, ammonium chloride (Sigma Aldrich Chemical Company), formaldehyde (37% aqueous solution, Panreac Chemical Company) and resorcinol (Fluka Chemical Company) were used in the manufacture of the shell material. Emulsifier poly(ethylene-alt-maleic anhydride) (EMA) was purchased from Sigma Aldrich Chemical Company. Dimethyl sulfide (DMS) and gold acid chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) were also purchased from Sigma Aldrich Chemical Company and were used as the core material. Cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), tetrakis(hydroxymethyl) phosphonium chloride (THPC), polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA) from Sigma Aldrich Chemical Company were used as stabilization agents. Acetyl acetone (Sigma Aldrich Chemical Company) was used to remove free formaldehyde presents in the suspension medium.

### 2.2. Preparation of poly(urea-formaldehyde) microparticles containing gold

Gold-containing poly(urea-formaldehyde), PUF, microparticles particles and PUF particles were prepared by means of in situ poly-

merization. The procedure used is described in detail elsewhere [9,10]. For this purpose, 5 mL of stabilizer solution (1.2 wt.% in water) was added to the gold precursor just before the addition of the DMS, which acts as reducing agent and solvent. All steps in the preparation of the structured gold-containing PUF microparticles are schematized in Fig. 1.

### 2.3. Characterization of gold-containing poly(urea-formaldehyde) microparticles

The gold-containing microparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic absorption (AA) and  $\text{N}_2$  adsorption–desorption.

Powder XRD analyses were conducted with a Philips X'Pert MPD instrument using nickel-filtered  $\text{Cu K}\alpha$  radiation. The amount of sample was approximately 2 g. The sample was placed in the holder of aluminum and it was used an automatic divergence slit of 12.5 mm in the incident optical beam and an anti-scatter slit of 12.5 mm in the diffracted beam and a receiving slit of 0.1 mm. The samples were scanned at a rate of 0.02 per step over the range  $5^\circ \leq 2\theta \leq 90^\circ$  (scan time = 2 s per step) and the diffractograms were compared with the JCPDS-ICDD references.

Samples were observed by using a Quanta 250 SEM apparatus with a wolfram filament by means of a large field detector. The backscattered mode (BSE) of SEM showed the uniformly gold distribution supported on the poly(urea-formaldehyde) matrix. Mean Au particle size evaluated as the surface-area weighted diameter ( $\bar{d}_{Au}$ ) was computed according to the following equation:

$$\bar{d}_{Au} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (1)$$

where  $n_i$  represents the number of particles with diameter  $d_{Au}$  ( $\sum_i n_i = 400$ ). Moreover, the experimental error was evaluated using the standard deviation ( $\sigma$ ) from the equation:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (d_i - \bar{d})^2} \quad (2)$$

where  $\bar{d} = \frac{1}{N} \sum_{i=1}^N d_i$  and  $N$  is total number of particles counted.

The gold metal loading (Au encapsulated) was determined by atomic absorption (AA) spectrophotometry using a SPECTRA 220FS analyzer (relative error: 5.5 ppm). Samples (ca. 0.5 g) were treated in an aqueous solution of 2 mL HCl (37%), 3 mL HF (48%) and 2 mL  $\text{H}_2\text{O}_2$  (33%) followed by microwave digestion (523 K). The encapsulation efficiency of gold ( $\eta_{Au}$ ) in the PUF microparticles was calculated according to the following equation based on the gold values measured by the AA:

$$\eta_{Au} (\%) = \frac{Au_r}{Au_{th}} \times 100 \quad (3)$$

where  $Au_r$  is the gold metal loading measured by AA for the analyzed microparticles (ppm) and  $Au_{th}$  is the theoretical gold content (22,000 ppm).

### 2.4. Catalytic tests

Glycerol oxidation experiments were carried out in a batch reactor (0.5 L) at the following conditions: glycerol solution concentration = 0.3 M, glycerol/Au = 3500 mol mol<sup>-1</sup>,  $\text{P}_{\text{O}_2}$  = 5 bar, reaction temperature = 333 K, agitation speed = 1000 rpm and NaOH/glycerol = 2 mol mol<sup>-1</sup> [10,19]. A mass flow controller allowed to control the amount of oxygen introduced into the reactor. Pressure inside the reactor was measured by a sensor and controlled by a mass flow controller of oxygen. Temperature inside the reactor

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