

## AuNPs immobilized onto gel-supported Ionic Liquid like phases (g-SILLPs) as catalysts under Microwave-Assisted Synthesis

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### Abstract

This work presents the results obtained in the characterization and development of gold nanoparticles (AuNPs) immobilized onto two kinds of gel-supported Ionic Liquids (gel-Supported Ionic Liquid like phases, g-SILLPs) and their study as catalysts for the oxidation of organic compounds. The benchmark reaction selected for this purpose was the oxidation of 1-phenylethanol. Besides, the reactions were performed under the concept of the exploitation of enabling techniques using: Microwave heating (as the energy source), water (as the solvent), hydrogen peroxide (as a benign oxidant agent), and supported catalysts (providing a more efficient catalytic processes and easy recovery of the catalyst).

### Introduction

The investigation and application of green chemistry principles has led to the development of cleaner and more benign chemical processes, with many new technologies being developed each year [1]. In today's world, synthetic chemists in both academia and industry are constantly challenged to consider more environmentally benign methods for generation of the desired target molecules. Among the 12 principles of green chemistry, the need for utilizing "safer solvents" and to "design for energy efficiency" can be considered two key principles of relevance to synthetic chemists [2].

So over the past decade the use of microwaves has grown exponentially in chemical synthesis. Microwave conditions are applied in many types of chemical transformations and the area of organic synthesis has benefited significantly from this technique [3]. Microwave conditions have been applied to most types of chemical transformations promoted by heat, largely due to the frequently observed acceleration in reaction rates, reduced reaction times and higher yields. Whilst the actual nature of the effect of microwaves remains a subject of intense debate, the heating under microwave conditions is explained by the wave-material interaction (dielectric and conduction losses) [4].

Considerable efforts have been devoted to develop and use nontraditional solvents for chemical synthesis [5]. Such unconventional media include, among others, solvent-free conditions, supercritical carbon dioxide, ionic liquids, perfluorated solvents, and last but not least water.

As new solvents, Ionic liquids (ILs) have attracted attention as alternative reaction media in biphasic media [6]. Because of their highly polar nature they are immiscible with many organic solvents. This forms the basis for biphasic reactions where the catalyst or the reagent is present in the ionic liquid while the substrate stays in the organic phase. Reagents or catalysts that are not polar enough in order to be only miscible in ionic liquids can be tagged with polar or ionic liquid type functional groups, for example, which may become task specific onium salts (TSOSs) that in conjunction with ionic liquids afford the so called task specific ionic liquids (TSILs) [7].

There is a widespread current debate over the relative “greenness” of these individual reaction media, but water can undoubtedly be considered the cleanest solvent available, and the use and release of clean water clearly will have the least impact to the environment. The combined use of Microwave-Assisted Organic synthesis (MAOS) in water as the solvent media [2] is an excellent combination of enabling techniques” [8] in the searching to obtain greener processes.

## **Results and Discussion**

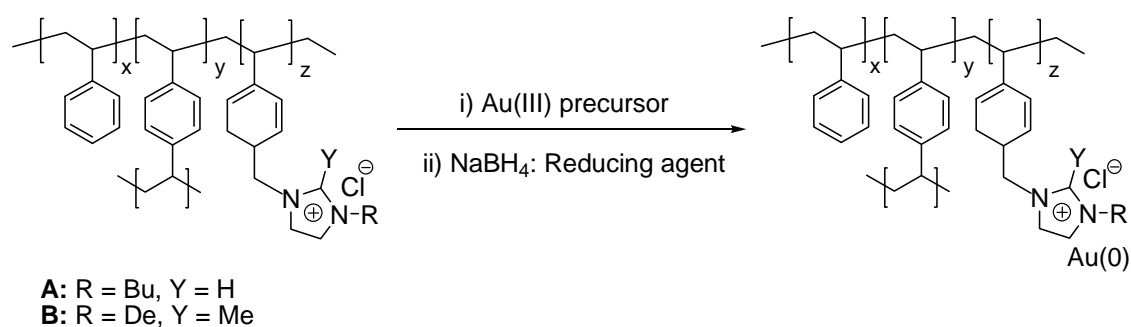
### *Synthesis and characterization of the catalysts.*

Two types of catalysts were synthesised: the g-SILLPs employed as the supports were synthesized through the modification of a commercially available Merrifield gel-type resin (4.3 meq. of Cl/g. of chlorine loading) by the covalent attachment of IL-like units (Scheme 1). For this purpose, the resin was allowed to react with the corresponding imidazole: **A**, 1-Butylimidazole; **B**, 1-Decyl-2-methylimidazole. Each imidazole was used as solvent and reagent, at 80°C, to give the corresponding supported imidazolium salts in quantitative yield. The reaction progress was followed by Raman spectroscopy and the polymer was characterized by the NBP test [9,10]. The polymer obtained was also analysed by XPS showing the characteristic peaks corresponding to the ionic liquid structure. The binding energies obtained were similar to those of its homogeneous counterpart [11]. This indicates that the supported phases can be expected to show similar properties than the related bulk ILs.

For the preparation of the gold NPs (AuNPs), first the HAuCl<sub>4</sub> was absorbed into the g-SILLP (figure 1 and scheme 1). Then the reduction reaction of Au(III) to Au(0) to obtain gold nanoparticles was carried out in aqueous medium using sodium borohydride as the reducing agent and reaction times were between 2 to 24 hours. The presence of UV-vis bands characteristic of Au(0) nanoparticles altogether with X-ray diffraction (XRD) analysis, confirms the presence of reduced gold species.

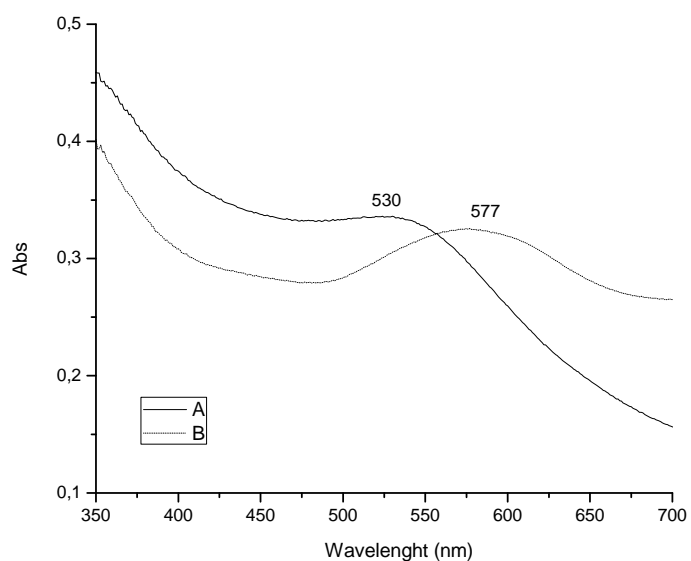


**Figure 1:** Gold precursor supported onto a g-SILLP before the reduction: left, SILLP; middle, Au(III) solution of HAuCl<sub>4</sub>; right, Au(III) supported.



**Scheme 1:** Synthetic procedure for the preparation of the AuNPs-supported catalysts evaluated.

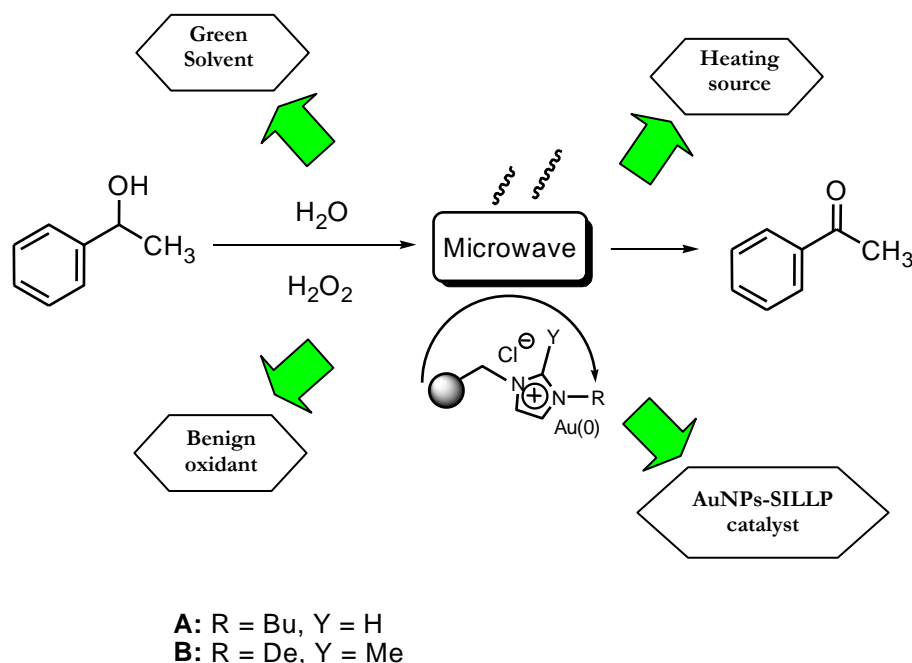
In the characterization processes of the catalysts, the UV-visible lectures confirm the presence of reduced gold species. The characteristic plasmon absorption maximum of AuNPs is observed (see figure 2).



**Figure 2:** UV-vis spectra with the maximum of absorption of each catalyst (**A**: solid line, **B**: dotted line).

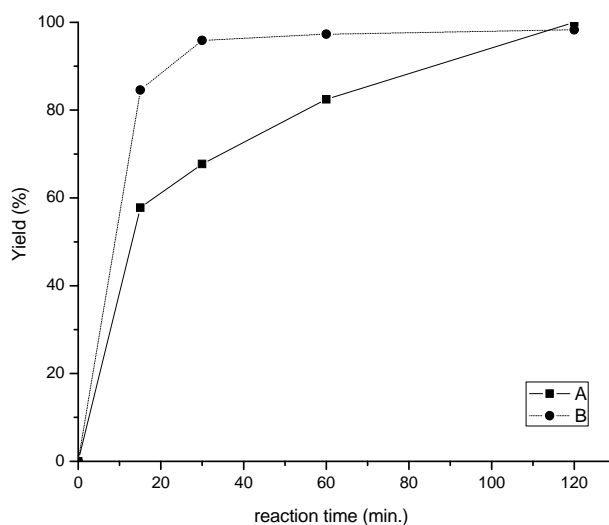
*Synthesis under Microwave irradiation*

The oxidation of 1-phenylethanol (1-PE) to obtain acetophenone was used as the benchmark reaction (see scheme 2) to study the catalytic behaviour of the AuNPs supported onto the two catalysts evaluated.



**Scheme 2:** Overview of the catalytic process and enabling techniques employed.

Using the two catalysts synthesised the influence the reaction time on the reaction yield was evaluated at four times between 15-120 minutes. Figure 3 shows the comparative yields obtained at different reaction times under microwave irradiation.



**Figure 3:** Yield variation with the time comparing the catalysts evaluated (A: squares; B: circles)

The analysis were determined by GC analysis using Butyl-butyrate as internal standard and the reaction conditions in the microwave were: MW power = 50 W; temperature reaction = 150°C; reaction time = 15, 30, 60, 120 minutes; 1-PE = 50  $\mu$ L; Butyl-butyrate = 50  $\mu$ L; H<sub>2</sub>O<sub>2</sub> = 0.5 mL (35% v/v, aqueous solution); solvent = 1.5 mL, deionised water; total reaction volume = 2.1 mL.

All the reactions were carried out under microwave irradiation in a closed vial in a CEM equipment allowing an internal control of the temperature. It is important to say that the yields increased significantly with the temperature reaction being necessary to work at temperatures above 100°C in order to obtain good yields, so the temperature was set at 150°C (the experiments were realized at constant temperature).

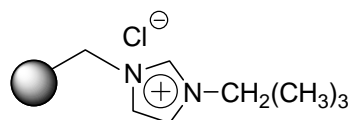
## Conclusions

The use of g-SILLPs to prepare and support AuNPs is a new approach to the obtention of efficient catalysts for the oxidation of secondary alcohols under benign reaction conditions.

If we bear in mind the successful combination of the catalyst synthesized with different “enabling technologies”, the present approach represents an efficient strategy towards the design of environmentally friendly processes, saving time, energy and reagents and reducing the waste generated.

## General and experimental procedure

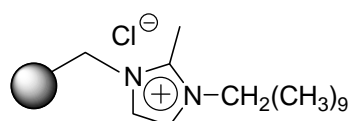
### *General procedure for the synthesis of g-SILLPs*



A Merrifield resin (5g, 4.3 mmol Cl/g, 21.5 mmol) was introduced in a round-bottomed flask and suspended in 1-butylimidazole (40 mL, 304.4 mmol). The suspension was heated at 80°C for 2 h. Then, the reaction was filtered and the polymer was washed with Methanol, MeOH:CH<sub>2</sub>Cl<sub>2</sub> (1:1) and CH<sub>2</sub>Cl<sub>2</sub> and dried in a vacuum oven.

FT-IR (cm<sup>-1</sup>)-ATR: 3747, 3385, 3136, 3058, 2926, 2863, 1629, 1559, 1513, 1450, 1359, 1155, 1021, 950, 822, 760, 702, 664, 640, 627, 614, 604.

FT-Raman (cm<sup>-1</sup>): 1600, 1497, 1436, 1296, 1175, 1111, 1068, 1020, 991, 824, 761, 709, 631, 610, 400, 264, 126.



A Merrifield resin (5g, 4.3 mmol Cl/g, 21.5 mmol) was introduced in a round-bottomed flask and suspended in 1-decyl-2-methylimidazole (40 mL, 161.9 mmol). The suspension was heated at 80°C for 24 h. Then, the reaction was filtered and the polymer was washed with Methanol, MeOH:CH<sub>2</sub>Cl<sub>2</sub> (1:1) and CH<sub>2</sub>Cl<sub>2</sub> and dried in a vacuum oven.

FT-IR ( $\text{cm}^{-1}$ )-ATR: 3945, 3898, 3817, 3737, 3673, 3650, 3392, 3027, 2923, 2852, 1641, 1582, 1513, 1452, 1424, 1375, 1270, 1183, 1089, 1021, 822, 768, 701, 667, 637, 619.

FT-Raman ( $\text{cm}^{-1}$ ): 1602, 1570, 1497, 1438, 1358, 1296, 1176, 1144, 1111, 1069, 1021, 992, 955, 824, 762, 712, 633, 613, 402, 265, 127.

#### *Synthesis of the Au(0) supported catalyst*

The corresponding g-SILLP (100 mg, 0.24 mmol) was introduced in a round bottomed flask containing 1 mL of deionised water and then the Au(III)-precursor (3.51  $\mu\text{L}$ , 0.017 mmol of  $\text{HAuCl}_4$ ) along with 5  $\mu\text{L}$  of HCl. The system was stirred at room temperature for 2 hours. Then, after filtering, the resin was washed with water (3x1 mL) and methanol (1x0.75 mL). The resulting polymer (light yellow), was dried overnight under vacuum at 60°C. Once dried, the reduction from Au(III) to Au(0) was carried out using 0.6 mL of deionised water and 0.1 mmol of sodium borohydride. The polymer was reacted for 2 hours and then was filtered and washed with 6 mL of deionised water and 1.7 mL of methanol. Finally, the polymer was dried under vacuum. The catalysts obtained had a brown colour in both cases.

#### *X-ray photoelectron spectroscopy (XPS) analysis*

Samples were analysed using the Kratos AXIS ULTRA with a mono-chromated Al  $K\alpha$  X-ray source (1486.6eV) operated at 15mA emission current and 10kV anode potential. This was used in FAT (fixed analyser transmission) mode, with a pass energy of 80eV for wide scans and a pass energy of 20eV for high resolution scans. The g-SILLPs was characterized by means of XPS analysis. Wide scans of the high-loading g-SILLPs were performed. The results obtained only showed the presence of free chloride anion, confirming the complete conversion of the initial Merrifield resin.

#### *General procedure for the oxidation reaction*

The Au(0) supported catalyst (20 mg, 0.029 mmol Au/g.), 1-phenylethanol (50  $\mu\text{L}$ , 0.41 mmol), hydrogen peroxide (0.5 mL, 5.71 mmol) and deionised water as reaction solvent (1.5 mL) were introduced in a reinforced glass tube of 10 mL of capacity. The tube was closed with a septum and introduced in the microwave cavity. The temperature was set at 150°C (the experiments were realized at constant temperature) and the hold time at this temperature was adjusted to 15, 30, 60, 120 minutes according to the experiment. Then, the tube was cooled down to room temperature. As the reactions were carried out in aqueous medium, it was necessary to extract the product before the chromatographic analysis. So the reaction mixture was extracted with HPLC grade dichloromethane (3x7.5 mL), from which next was taken a sample of 10 mL 1 mL of acetonitrile added and 10 mL of butyl-butyrate (as the reference compound) and analyzed by GC.

### *Chromatographic analysis (GC)*

All the measures were realized with Varian 3900 GC equipment. The system has a VF-5ms column (30 m, 0.25 mm, 0.25  $\mu$ m. Conditions: Injection vol.: 10  $\mu$ L, initial temp.: 60°C; injection temp.: 230°C; heating ramp: 60/130°C; speed: 10°C/min; pressure: 15 psi; detection temp.: 230°C; helium flux: 25 mL/min; Hydrogen flux: 30 mL/min; air flux: 300 ml/min; acquisition frequency: 20 Hz.

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### **Acknowledgments**

Financial support by Ministerio de Ciencia e Innovación of Spain (CTQ2008-04415 and CTQ2008-04309) are acknowledged. E.G-V. thanks the financial support by (Ramón y Cajal Program) and J.A.R. thanks the AlBan Program by Banco Santander Foundation for a pre-doctoral fellowship (No. E07D402098CO).