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# Microwave-assisted oxidation of a secondary alcohol using a Gold catalyst immobilized onto gel-supported Ionic Liquid like phases (g-SILLPs)

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## Abstract

Here we present the results obtained in the development of Au nanoparticles (AuNPs) immobilized on a gel-supported Ionic Liquid (gel-Supported Ionic Liquid like phase, g-SILLP) and their study as catalysts for the oxidation of alcohols. The benchmark reaction selected for this purpose was the 1-phenylethanol oxidation. Besides, the reactions were performed under benign conditions using: Water (as the solvent and reaction medium), hydrogen peroxide (as the benign oxidant agent), microwave irradiation (as the heating source) and supported catalyst (providing a more efficient catalytic process).

## Introduction

A leading direction of chemical research is, nowadays, the design and development of "benign and greener" products and processes, inside the framework of Sustainable Development. The concept of "Green Chemistry" intends to give answers to this challenge through a more rational use of our resources and knowledge. In this context we can consider the use of "enabling techniques" [1] as old or traditional methodologies improved with the new vision of improving simultaneously not only the reaction yields, but also the isolation and purification of the obtained products. On the other hand, in the field of the metallic catalysis one of most important and relatively recent developments has been the discovering that gold, for a long time considered as a noble inert metal, is an active heterogeneous catalyst highly selective.

The discovery of the high reactivity of gold as catalyst has led in the last years to a growing of the interest for the catalysis with this metal [2], in particular for the design of selective catalytic oxidations based on gold nanoparticles [3].

## Results and Discussion

*Synthesis and characterization of the catalyst.*

The *g*-SILLP employed as the support was 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). The resin was allowed to react with methylimidazole, used as solvent and reagent, at 80°C, to give the corresponding supported methyl imidazolium salt in quantitative yield. The reaction progress was followed by Raman spectroscopy and the polymer was characterized by the NBP test [4,5] The combined use of both techniques allowed us to observe that the reaction time required to achieve a fully conversion of the $CH_2$–Cl groups is much shorter than previously reported for related systems (30 min *vs* 12–78 h) [6]. 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 [7]. This indicates that the supported phases can be expected to show similar properties than the related bulk ILs.
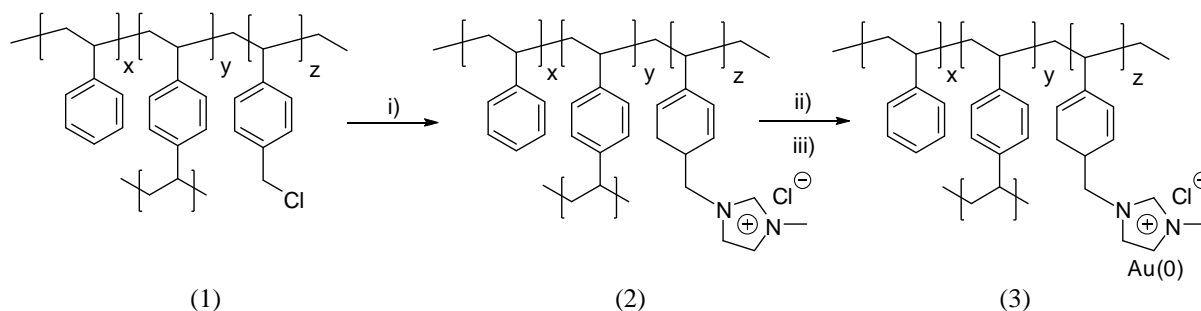


**Scheme 1:** Synthesis of the supported Au(0) catalyst. i) 1-methylimidazole, 80°C, 1h.
ii) $HAuCl_4$, followed by iii) the reduction employing Hydrazine as reducing agent;
all processes in water at room temperature (see figure 1).



**Figure 1:** g-SILLPs supported gold species before and after reduction:
left, Au(III) supported; right, Au(0) supported.

First the $HAuCl_4$ was absorbed into the g-SILLP (see scheme 1, product 2). Then the reduction reaction of Au(III) to Au(0) to obtain gold nanoparticles was carried out using hydrazine as the reducing agent (scheme 1, product 3). The presence of UV-vis band characteristic of Au(0) nanoparticles confirm the presence of reduced gold species together with X-ray diffraction (XRD) analysis.

*Synthesis under Microwave irradiation*

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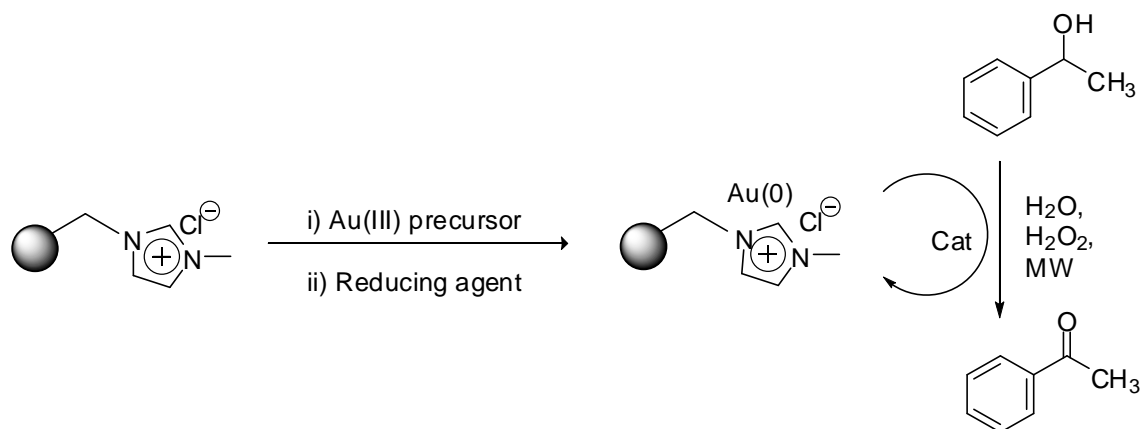


**Scheme 2:** Synthesis of the supported catalyst and catalytic process.

The influence of the temperature and reaction time was evaluated. Table 1 gathers the yields obtained at different reaction temperatures after 15 minutes of reaction under microwave irradiation.

**Table 1:** Variation of yields with temperature reaction.[a]

| Test | Reaction temperature (ºC) | Yield (%) |
|------|---------------------------|-----------|
| 1 | 50 | 0 |
| 2 | 75 | 2 |
| 3 | 100 | 5 |
| 4 | 125 | 15 |
| 5 | 150 | 57 |

[a] Determined by GC analysis. Reaction conditions: MW power = 40 psi; time reaction = 15 minutes; $H_2O_2$ = 0.5 mL; solvent = water; reaction volume = 2 mL.

All the reactions were carried out under microwave irradiation in a closed vial in CEM equipment allowing an internal control of the temperature. As expected, yields increased significantly with the temperature being necessary to work at temperatures above 100ºC in order to obtain good yields.

**Table 2:** Variation of yields with time reaction.[b]

| Test | Reaction time (min.) | Yield (%) |
|------|----------------------|-----------|
| 6 | 15 | 57 |
| 7 | 30 | 60 |
| 8 | 60 | 72 |
| 9 | 120 | 92 |

Microwave-assisted oxidation of a secondary alcohol using a supported Gold catalyst immobilized

The table 2 shows the results obtained at 150ºC as a function of the reaction time. After 2 hours, the reaction is essentially complete, although the longer reaction times are also accompanied by a slight decrease in selectivity.

**Conclusions**

The present preliminary results clearly show the possibility of using g-SILLPs to support gold nanoparticles (AuNPs) as catalysts for useful synthetic transformations. Besides, the use of those supported catalytic systems is compatible with the use of more environmentally benign conditions such as microwave irradiation of the use of water as the solvent. Our heterogeneised catalytic systems show activities that compare well with these reported in the literature for the AuNPs-based catalytic systems. On the other hand, the use of the catalysts here reported allows their easy recovery and reuse after the catalytic reaction, without any appreciable lost in performance.

**General and experimental procedure**

*General procedure for the synthesis of g-SILLPs*
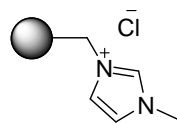


A Merrifield resin (5g, 2% cross-linked, 4.3 mmol Cl/g, 21.5 mmol) was introduced in a round-bottomed flask and suspended in 1-methylimidazole (40 mL, 4.87 mol). The suspension was heated at 80 ºC for 1 h. Then, the reaction was filtered and the polymer was washed with Methanol, MeOH:$CH_2Cl_2$ (1:1) and $CH_2Cl_2$ and dried in a vacuum oven.

FT-IR (cm$^{-1}$) KBr: 3855, 3422, 3056, 2921, 2580, 1612, 1571, 1512, 1492, 1451, 1358, 1331, 1224, 1112, 1019, 824, 762, 704, 621, 544. Raman (cm$^{-1}$): 1603, 1570, 1441, 1404, 1377, 1321, 1178, 1081, 1012, 992, 824, 753, 706, 657, 634, 611, 560, 403, 318. Elemental analysis found: %N 8.37; calculated for: $(C_{10}H_{10})_{0.0.2}$ $(C_8H_8)_{0.56}$ $(C_{13}H_{15}ClN_2)_{0.43}$ %N 8.50.

*Synthesis of the Au(0) supported catalyst*

The former g-SILLP (100 mg, 0.24 mmol) was introduced in a round bottomed flask containing 1 mL of water and then the Au(III)-precursor (3.51 uL, 0.017 mmol of $HAuCl_4$) along with 5 uL 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 (of light yellow), was dried under vacuum at 60ºC. 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 Hydrazine (9.06 uL, aqueous solution at 35%). The polymer was reacted for 2 hours, time after that was washed and filtered with 6 mL of deionised water and 1.7 mL

of methanol. Finally, the polymer was dried under vacuum. The catalyst obtained had a varying colour between pale rose, dark violet and dark brown.

*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/gr), 1-phenylethanol (50 uL, 0.41 mmol), hydrogen peroxide (0.5 mL, 5.71 mmol) and 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 150ºC (in the experiments realized at constant temperature) and the hold time at this temperature 15 minutes. Then, the tube was cooled down to room temperature. Due to the reactions were carried out in aqueous medium was necessary extract the reaction sample to realize the chromatographic analysis. So the reaction mixture was extracted with dichloromethane (3x7.5 mL), from which next was taken a sample of 10 mL of extracted organic phase and 1 ml of acetonitrile was added and 10 mL of butyl-butyrate (as reference compound) and analyzed by GC.

*Methodology to follow the oxidation reaction by GC*

All the measures were realized employing Varian 3900 GC equipment. The system has a column of VF-5ms: 30 m, 0.25 mm, 0.25 um. Conditions: Injection vol.; 10 uL, initial temp.: 60ºC; injection temp.: 230ºC; heating ramp: 60/130ºC; speed: 10ºC/min; pressure: 15 psi; detection temp.: 230ºC; helium flux: 25 mL/min; H2 flux: 30 mL/min; air flux: 300 ml/min; acquisition frequency: 20 Hz.

**References and notes**

[1] The concept of enabling techniques or technologies in organic synthesis was stabilized in the Gordon *Research Conference, Facilitating Organic Synthesis*, **2004**, 7. 3.-11. 3, Ventura Beach, CA, (USA).

[2] a) Xu, Y.-J.; Landon, P.; Enache, D.; Carley, A. F.; Roberts, M. W.; Hutchings, G. J. *Catal. Letters*. **2005**, 101, 3-4, 175; b) Hutchings, G. J. *Journal of Catal.*, **1985**, 96, 1, 292; c) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. *Chem. Letters*, **1987**, 16, 2, 405; d) Thomas, J. M. y otros. *Acc. Chem. Res.* **2001**, 34, 3, 191.

[3] a) Zhao, R.; Ji, D.; Lu, G.; Qian, G.; Yan, L.; Wang, X.; Suo, J. *Chem. Comm.*, **2004**, 904; b) Lü, G.; Zhao, R.; Qian, G.; Qi, Y.;Wang, X.; Suo, J. *Catal. letters*. **2004**, 97, 3-4, 115; c) Hashmi, A.S.K. *Chem. Rev.* **2007**, 107, 7, 3180.

[4] Galindo, F.; Altava, B.; Burguete, M. I.; Gavara, R.; Luis, S.V. *J. Comb. Chem.* **2004**, 6, 859.

[5] a) Altava, B.; Burguete, M.I.; García-Verdugo, E.; Luis, S.V.; Vicent, M.J. *Tetrahedron* **2001**, *57*, 8675. b) Altava, B.; Burguete, M.I.; García-Verdugo, E.; Luis, S.V.; Vicent, M.J. *Tetrahedron Lett.* **2001**, *42*, 8459.

[6] a) Byun, J.-W. ; Lee, Y.-S. *Tetrahedron Lett*. **2004**, *45*, 1837. b) Kim, D.-W.; Chi, D.-Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 483. c) Kim, D.-W.; Hong, D.-J.; Jang, K.-S.; Chi, D.-Y. *Adv. Synth. Catal.* **2006**, *348*, 1719.

[7] a) Smith, E. F.; Villar-Garcia, I. J.; Briggs, D.; Licence, P. *Chem. Commun.* **2005**, *45*, 5633. b) Smith, E. F.; Rutten, F. J. M.; Villar-Garcia, I. J.; Briggs, D.; Licence, P. *Langmuir* **2006**, *22*, 9386.