Catalysis Today 255 (2015) 97–101

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Gold nanoparticles immobilized onto supported ionic liquid-like phases for microwave phenylethanol oxidation in water

Julian Restrepo [a], Pedro Lozano [b], M. Isabel Burguete [a], Eduardo García-Verdugo [a,*], Santiago V. Luis [a,*]

[a] Department of Inorganic and Organic Chemistry, University Jaume I, Avda. Sos Baynat s/n, E-12071 Castelló de la Plana, Castellón, Spain
[b] Departamento de Bioquímica y Biología Molecular B e Inmunología, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain

ARTICLE INFO

Article history:
Received 1 November 2014
Received in revised form 5 December 2014
Accepted 6 December 2014
Available online 4 February 2015

Keywords:
Ionic liquid
Supported ionic liquid
SILLPs
Polymeric ionic liquid
Supported polymeric catalysis
Gold
NPs oxidation
Microwave

ABSTRACT

Advanced crosslinked polymeric materials based on poly(ionic liquid)s, also named supported ionic liquid-like phases (SILLPs) combine some unique characteristics of ionic liquids with the general property profile of macromolecular architectures, and present huge potential in energy-/environment-/catalysis-oriented applications, in the development of "smart" dispersants and stabilizers, *etc*. One of these relevant applications is highlighted by the present results that involve their use for the preparation and stabilization of different type of catalytic units, in particular metal nanoparticles (MeNPs) in order to develop greener catalytic processes. Different kinds of stable AuNPs can be prepared from SILLPs-related polymeric materials and have been used for the efficient oxidation of phenyl ethanol, under aerobic conditions, using H_2O_2 as the oxidant and under microwave irradiation.

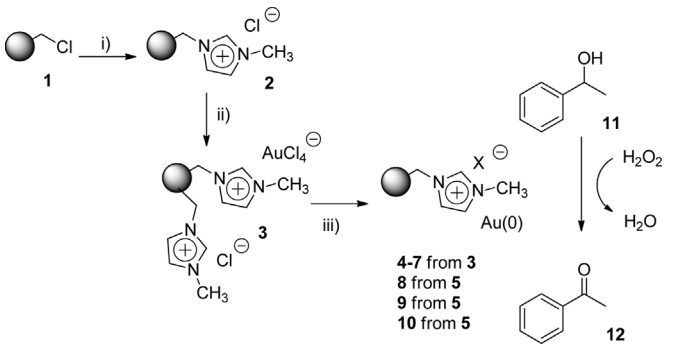
1. Introduction

Ionic liquids are organic salts whose tunable physico-chemical properties make them very interesting for a wide range of applications [1]. Indeed, ILs have emerged as very attractive homogeneous media for the immobilization and stabilization of different types of catalytic species including nanoparticles (NPs), organometallic complexes, organocatalytic species or enzymes within others [2]. Nevertheless, their high cost, low biodegradability and ecotoxicity concerns limit their applicability. A solution to overcome these problems consists of supporting them on an insoluble material of organic or inorganic nature [3]. The immobilization of ILs onto a solid support provides a simple way for reducing the amount of IL required for a given application, reducing accordingly the associated cost; facilitates their handling and manipulation, decreasing the need of using traditional solvents in the corresponding processes; and, finally, greatly reduces the potential leaching to the environment of the ILs. Two main strategies have been assessed to support the IL-phase: (i) non-covalent support of IL phases on the surface of inorganic or organic supports (SILPs) or (ii) covalent attachment of IL-like phases on the surface of inorganic or organic supports (SILLPs) [3,4]. It is clear that in the second case, when the IL-like fragment is covalently attached to the support, the problem of leaching is totally eliminated. However, the transfer of the proper essential properties of the ILs to the solid phase need to be guaranteed, and this is not a simple matter. We and others have demonstrated that, through a proper design, it is feasible to transfer the IL properties to the surface of the solid and, thus, the resulting materials present the advantages associated to ILs but can overcome some of the drawbacks of bulk ionic liquids, facilitating their technological application [5,6]. This open new avenues for the development of new advanced materials derived of ILs. In particular, we have focused our work on some of the most promising systems of this class: those obtained by direct polymerization of monomeric units bearing ionic liquid-like moieties and those prepared by post-modification with IL-related fragments of preformed polymeric materials (Scheme 1).

Here we examine and discuss some essential properties of polymer-supported ionic liquid-like phases (SILLPs), using crosslinked insoluble polymeric matrices as supports, and their ability to immobilize and stabilize metal nanoparticles (MNPs), specially gold nanoparticles (AuNPs). Different experimental

* Corresponding authors. Tel.: +34964728751.
E-mail addresses: cepeda@uji.es (E. García-Verdugo), luiss@uji.es (S.V. Luis).

http://dx.doi.org/10.1016/j.cattod.2014.12.023
0920-5861/



Scheme 1. Preparation of AuNPs–SILLPs composites as catalysts for the oxidation of 1-phenyl-ethanol to acetophenone. (i) Merrifield resin (4.3 mmol Cl g^{-1}, 2% DVB) and methylimidazole, 80 °C; (ii) r.t., $AuCl_4^-$ aqueous solution, 2 h; (iii) reducing agent.

variables were investigated for the synthesis of the supported AuNPs onto the polymeric ionic liquid like phases and how these variables affect their performance as catalysts for the oxidation of 1-phenyl-ethanol.

2. Materials and methods

2.1. Materials

All required reagents were obtained from Sigma-Aldrich and used without further purification. The Merrifield resin used for the preparation of SILLPs was a gel-type (*g*) polystyrene-divinylbenzene resin with 4.3 mmol Cl g^{-1}, and 2% crosslinking. Gas chromatography (GC) analyses were carried out in a Varian 3900 instrument using a CyclodexB column (length 30 m, I.D. 0.25 mm, film 0.25 μm). The Microwave irradiation experiments were performed with a Discover System Model 908010 from CEM Corporation using custom-made high purity quartz vials (capacity 10 mL). The initial SILLPs prepared were analyzed through IR and Raman spectroscopy (for further information, see [7–9].

2.2. General procedure for the synthesis of AuNPs–SILLPs

The gold AuNPs–SILLPs were synthesized as already reported by us (see [10]). In brief, the corresponding SILLP was suspended in deionized water and an aqueous solution of $HAuCl_4$ was added. The suspension was stirred for 2 h at r.t. The polymer was then filtered and washed. Finally, the polymer was vacuum dried at 60 °C. The dry SILLP resin with $AuCl_4^-$ adsorbed was suspended in water and a solution of the corresponding reducing agent added. The suspension was stirred during to 2 h at r.t. for completing the reduction. Afterwards, the polymer was filtered and washed with deionized water and MeOH (3×). Finally, the polymer was dried under vacuum. The AuNPs–SILLPs obtained had a red–brown color indicating the formation of gold nanoparticles. The different samples were analyzed and characterized by DR-UV–vis, TEM, and XRD.

2.3. Synthesis of the AuNPs in solution and adsorption onto SILLPs

These AuNPs–SILLPs were also synthesized as already reported by us (see [10]). In brief, the solution of stabilized NPs was first obtained in solution (method (i) and (ii)) and then they were absorbed onto the corresponding supported ionic liquid-like phase (**2**).

2.3.1. Synthesis of the AuNPs in solution

Method (i) an aqueous solution of the precursor ($HAuCl_4$) was heated till boiling and then a solution of sodium citrate was added. After 5 min, the Au(III) to Au(0) reduction could be observed, associated with the color change of the solution from yellow to light reddish up to turn into an intense red–violet solution. At this point, the solution was kept at reflux for 30 min and, after this time, the solution was maintained in the dark to avoid aggregation of the AuNPs formed, due to the UV light effect, and cooled. Then it was stored in the refrigerator. Method (ii) A sodium citrate solution was added under vigorous stirring to an aqueous solution of the precursor ($HAuCl_4$). After 5 min, 1 mL of an aqueous solution of $NaBH_4$ (0.081 wt% solution of $NaBH_4$ dissolved in a 44.75 mM solution of sodium citrate) was slowly added at room temperature for 10 min. An immediate change in the color was observed from the initial yellow solution to red–violet solutions.

2.3.2. Adsorption of preformed AuNPs onto SILLPs

The corresponding polymer containing imidazolium subunits (100 mg, **2**) was suspended in a round bottomed flask containing 2 mL of deionized water; an aqueous solution containing the AuNPs solutions prepared either by method (i) or (ii) was added and the resulting suspension was stirred for 2 h at r.t. The polymer was then filtered and washed with water (3 × 1 mL) and methanol (1 × 0.75 mL). Finally, the red–brown polymer was vacuum dried at 60 °C until constant weight.

2.4. General procedure for the oxidation reaction

The corresponding supported AuNPs–SILLPs catalyst (20 mg, 0.0507 mmol Au g^{-1}), 1-phenyl-ethanol (50 μL, 0.41 mmol), hydrogen peroxide (0.5 mL, 5.71 mmol) and deionized water as the reaction solvent (1.5 mL) were introduced in a reinforced glass tube of 10 mL of capacity. The resultant mixture was heated in a microwave oven (CEM Discover, CEM Microwave Technology Ltd, USA) at 150 °C with slow stirring. The system was run at the constant temperature operation mode by using the air cooling feature of the apparatus and hold at this temperature for 15 min. Then, the tube was cooled down to room temperature. The reaction mixture was extracted with HPLC grade dichloromethane (3 × 7.5 mL). From the extracted organic phase, 10 mL were taken and 1 mL of acetonitrile containing 10 μL of butyl-butyrate was added as internal standard. The resulting mixture was analyzed by GC. All the experiments were carried out in duplicate.

3. Results and discussions

SILLPs can be used for the simple preparation and stabilization of metal nanoparticles (MNPs) from different metal precursors [10]. In an analogous manner than that the observed for bulk ILs, the SILLPs are suitable "solid solvents" for the synthesis of NPs, based on the fact that the polymeric SILLPs prepared by any of the methodologies considered present, at the molecular level, the same fundamental properties of the bulk ILs [11]. The preparation of different NPs–SILLPs composites is a very simple procedure. The ability of supported ionic liquids to absorb inorganic or organic anions from a solution, as described for other systems, can be used advantageously for the preparation of NPs–SILLPs [12]. Thus, a two-step methodology, involving the initial absorption of the corresponding soluble metallic anionic precursor species onto the polymer, followed by the controlled reduction to the corresponding NPs by the treatment of these materials with an adequate reducing agent, have been reported in several instances [7].

When using this approach, the same SILLP (**2**), synthesized by grafting the corresponding methylimidazole onto a commercial Merrifield-type resin (**1**), was used. The metal precursor was immobilized onto the SILLP by putting in contact the resin **2** with an aqueous solution of $AuCl_4^-$ leading to a polymer with 0.05 mmol Au g^{-1} of support. The nature of the reducing agent can play an important role to define the size and shape of the resulting