



## New palladium catalysts on polyketone prepared through different smart methodologies and their use in the hydrogenation of cinnamaldehyde

Anna Maria Raspolli Galletti<sup>a,\*</sup>, Luigi Toniolo<sup>b</sup>, Claudia Antonetti<sup>a</sup>, Claudio Evangelisti<sup>c</sup>, Claudia Forte<sup>d</sup>

<sup>a</sup> Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 36, 56126 Pisa, Italy

<sup>b</sup> Department of Molecular Sciences and Nanosystems, University Ca' Foscari of Venice, Dorsoduro 2137, 30123 Venice, Italy

<sup>c</sup> ICCOM CNR, Via G. Moruzzi 1, 56124 Pisa, Italy

<sup>d</sup> CNR ISTM, Via Fantoli 16, 20138 Milano, Italy

### ARTICLE INFO

#### Article history:

Received 10 June 2012

Received in revised form 31 August 2012

Accepted 1 September 2012

Available online 13 September 2012

#### Keywords:

Pd nanoparticles

Polyketone

Cinnamaldehyde

Hydrocinnamaldehyde

### ABSTRACT

For the first time, polyketone (poly-3-oxotrimethylene, PK) has been employed as support for Pd nanoparticles. Three different approaches have been adopted: (i) reduction of Pd(OAc)<sub>2</sub> in EtOH under microwave irradiation, (ii) hydrothermal reduction of the same precursor in EtOH or *n*-BuOH employing traditional heating and (iii) vaporization of Pd metal through metal vapour synthesis. These supported systems have been characterized by solid state NMR, TEM, ICP, XPS, BET and tested in the selective hydrogenation of cinnamaldehyde (CAL) to hydrocinnamaldehyde (HCAL) as probe reaction. Their catalytic performances have been compared in relation to their preparation procedure and morphology. It is remarkable that these catalysts do not show significant leaching even after several catalytic recycles, thus indicating their high stability and recyclability, ascribed to a stabilizing capacity of this particular polymeric support.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

The synthesis of metal nanoparticles for catalytic applications, characterized by high catalytic activity and selectivity, is an attractive research area of great current interest, not only restricted to the catalysis field, but also for applications in electronics, biotechnology, medical science and magnetism [1,2]. A broad range of approaches is suitable for their preparation, from top-down to bottom-up ones and combinations thereof [3–9]. It is important to highlight that during their preparation the use of stabilizing agents represents a useful and widely applied approach in order to prevent their agglomeration toward the bulk metal [10–14]. In this context, the use of polymeric stabilizers, such as poly-(1-vinylpyrrolidone), polypyrrole, polyvinylpyridine, poly(ethyleneglycol), polystyrene, nafen and also natural polymers has been deeply investigated [15–21]. These “quasi” homogeneous metal nanoparticles offer the advantage of high catalytic activity as the homogeneous ones but, on the other side, they are not easily separated and recycled as the heterogeneous ones. In order to improve this last drawback, they are generally supported on a solid inorganic carrier. On the contrary, the applications of polymers as support for metal nanoparticles are less investigated [22–25]. In particular, Pd catalysts were supported and thus “heterogenized” by anchoring the

[PdCl<sub>2</sub>(PhCN)<sub>2</sub>] complex on copolymers of styrene/divinylbenzene with *N*-vinylpyrrolidone or 1-vinylimidazole monomers via ligand exchange reaction. The obtained systems were reduced during hydrogenation tests or by reaction with sodium borohydride and employed in the hydrogenation of cinnamaldehyde to cinnamyl alcohol [22]. In the work of Zhan, hydrophilic interpenetrating polymer networks and Pd nanoparticles were obtained by simultaneous crosslinking of polyvinyl alcohol and polyacrylamide, leading to very promising samples for Heck coupling reactions [23]. The synthesis of supported Pd complexes by the easy and quantitative coordination of Pd(OAc)<sub>2</sub> to a cross-linked styrene/divinylbenzene resin functionalized with bis(diphenylphosphino)methane ligands has been reported and these systems were tested in the hydrogenation of nitrocompounds and  $\alpha,\beta$ -unsaturated aldehydes under mild reaction conditions resulting active, versatile and recyclable heterogenized catalysts [24].

The use of polyketones as supports for metal nanoparticles (MNPs) has been almost neglected. A recent investigation on polyketones is reported by Gomez and co-workers. The use of isotactic and chiral CO/styrene copolymers as stabilizers for Pd, Pt and Ru nanoparticles was studied with the aim of applying those systems in asymmetric catalytic processes. Platinum and ruthenium nanoparticles stabilized in this way were tested in the hydrogenation of ethyl pyruvate giving high activities without enantioselectivity induction. In this study the authors highlight the main role of stabilizing agent played by this polymer [25].

\* Corresponding author. Tel.: +39 050 2219290; fax: +39 050 2219260.

E-mail address: [roxy@dccl.unipi.it](mailto:roxy@dccl.unipi.it) (A.M. Raspolli Galletti).