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Effect of metal precursors on polyol synthesis of palladium nanoparticles towards C-N bond formation

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ABSTRACT

In the present work, palladium nanoparticles were synthesized in glycerol following the bottom-up methodology, using Pd(II) and Pd(0) precursors. The as-prepared materials were characterized by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD), evidencing the formation of zero-valent palladium spheres in the nanosize ranges. The effects of metal precursors on the size of nanoparticles and their dispersion in medium reaction were illuminated, accompanying with the different catalytic activities towards C-N bond formation between acrylonitrile and morpholine. In particular, the recycling of catalytic phase was also desired thanks to immobilization of PdNPs in glycerol.

Introduction

Palladium-based catalysts seem to be the most versatile and effective systems in organic syntheses such as cross-couplings, carbonylations, oxidations and hydrogenations [1,2]. In general, these catalysts can be salts or organometallic complexes of palladium (homogeneous catalysis), surface-modified palladium catalysts or palladium nanoparticles immobilized on solid and liquid supports (heterogeneous catalysis). The diverse structures of palladium-based systems resulted in the different catalytic activity, raising their applications in organic synthesis field [3]. Recently, metal nanoparticles and their catalytic applications, in particular palladium nanoparticles (PdNPs), have been underway [4,5]. In fact, the controls of size, composition and morphology of nanomaterials can tune their catalytic activity and selectivity [4,5]. From a mechanistic point of view, the metal catalyst precursors at the nanosizes can act as a "reservoir" of small metal atoms, permitting to approach the homogeneous catalysis and thus improve catalytic activity. The synthesis of metal nanoparticles can be controlled by reaction conditions, metal precursors, stabilizers and solvents [4,5]. PdNPs were firstly prepared in organic solvents by the reduction of palladium salts (by Bönnemann *et al.*) [6] and electrochemical method (by Reetz *et al.*) [7] for catalytic applications in C-C coupling reactions.

In comparison with conventional organic solvents (expensive and toxic), imidazolium-based ionic liquids or polyols (hydrogen bonding, π-π interaction) permit to disperse and immobilize metal nanoparticles in their supermolecular networks, avoiding the agglomeration of nanoparticles [8-10]. In general, metal nanoparticles were synthesized in ionic liquids by reduction of metal salts or pyrolysis of metal organometallic complexes under hydrogen pressure [8,9]. In particular, ionic liquids can act as solvents and stabilizers (electrostatic

and steric effects). Despite of their advantages, ionic liquids are expensive, highly viscous and toxic; in some cases, ionic liquids can be involved in the reaction, modifying catalytic activity [11]. Therefore, reactions carried out in environmentally friendly solvents such as water, supercritical fluids and polyols, even solvent-free reactions have been recently paid a great attention [9,10].

Firstly developed in 1989 by Fiévet *et al.*, metal nanoparticles were prepared in alcohols that have many adjacent hydroxyl groups, called polyol synthesis [12]. The preeminent properties of polyols involve (i) high solubility of metal precursors, (ii) high boiling point (up to 320 °C), (iii) reducing properties assisting in the metal nanoparticles synthesis, (iv) surface modification and stability of metal nanoparticles in colloidal solutions, (v) large compatibility, variable physical and chemical properties depending on molecular weight (from ethylene glycol to polyethylene glycol) [10,12]. After three decades, polyol synthesis of metal nanoparticles has been considered as a simple and effective chemical method, thanks to (i) low cost, (ii) easy to operate, (iii) availability in large-scale [10,12]. However, the high activity of their hydroxyl groups can cause some side effects, especially in strong acidic or basic environments. Furthermore, the high viscosity of the polyols also requires that the reactions must be carried out at high temperatures.

Taking into account our experiences in polyol synthesis of metal nanoparticles [13]; in the present work, PdNPs coming from various metal precursors were synthesized in neat glycerol (inexpensive, non-toxic and biodegradable) under hydrogen pressure, using polyvinylpyrrolidone (PVP) as a stabilizing agent. The nature of metal precursors affected the size of obtained PdNPs, provoking their different catalytic behaviors in C-N bond formation.

Experimental

Chemicals were used as received without further purification, including palladium(II) acetate Pd(OAc)$_2$, dichloro(1,5-cyclooctadiene)palladium(II) [PdCl$_2$(cod)], tris(dibenzylideneacetone)dipalladium(0) [Pd$_2$(dba)$_3$], polyvinylpyrrolidone (PVP, FW = 10,000), glycerol and toluene.

The mixture of palladium precursors and PVP (molar equivalent of palladium/monomer and [Pd] = 10^{-2} M) was firstly dissolved in 5 mL of neat glycerol at room temperature to obtain the homogeneous solution. This system was then pressurized under hydrogen and stirred at 80 °C for 1 hour, resulting in a black colloidal

suspension as a consequence of the formation of PdNPs. The solid materials were then centrifuged at 10,000 rpm for 15 minutes. The crystalline structure of PdNPs in the solid was characterized by powder X-ray diffraction (XRD), collecting on a D8 BRUCKER ADVANCE powder diffractometer with a Cu-K radiation source (= 1.5406 Å), at a voltage of 40 kV and a 40 mA power, from 30 to 90 degrees (2). The crystal size was calculated using the Debye-Scherrer equation (1). The size and shape of PdNPs were observed on a JEOL JEM-1400 transmission electron microscope at 120 kV.

$$d = \frac{k\lambda}{\beta\cos\theta} \ (1)$$

where: k is the Scherrer constant, taken to be 0.94;   is the wavelength of the X-ray;   is the line width at half maximum height of the peak in radians; and   is the position of the peak in radians.

Pd-catalyzed C-N bond formation: acrylonitrile and morpholine (1.2 molar equivalent to acrylonitrile) were added to 1 mL of preformed PdNPs in glycerol. The resulting mixture was heated up to 80 °C, stirred for 2 hours and then cooled down to room temperature. Organic products were extracted from glycerol using dichloromethane. Conversions were determined by GC-MS analysis using *n*-decane as internal standard.

Results and discussion

Palladium(0) nanoparticles (PdNPs) were prepared following a bottom-up approach, by reduction of Pd(OAc)$_2$ in neat glycerol under hydrogen pressure, using PVP as a stabilizing agent (Figure 1). The formation of PdNPs was observed as the black colloidal solution; on the other hand, only black precipitates were obtained in the absence of PVP.
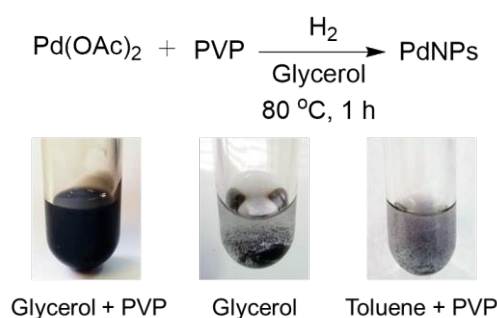

Figure 1: Synthesis of PdNPs from Pd(OAc)$_2$ under hydrogen pressure, using PVP as stabilizer at 80 °C for 1 h

The addition of an auxiliary stabilizer, PVP in this case, was necessary to preserve the nano-sized structure

thanks to the steric stabilization based on its bulky structure and weak binding to the metal surface [14]. According to the similar methodology, the synthesis of PdNPs was carried out in toluene and in the presence of PVP, exhibiting the quick precipitation in reaction medium. These results evidenced the important role of glycerol in the dispersion of metal nanoparticles, avoiding their agglomeration due to its supramolecular structure [15]. In short, polyol synthesis of PdNPs in glycerol permitted to obtain the colloidal systems, being stable up to some months.

In relation to the nature of metal precursors, PdNPs coming from $Pd(OAc)_2$, $[PdCl_2(cod)]$ and $[Pd_2(dba)_3]$ were synthesized in glycerol, leading to the formation of the black colloidal systems. Taking the advantage of negligible vapor pressure of glycerol, the as-prepared PdNPs could be directly characterized by TEM analyses, recorded from the colloidal solutions (Figure 2). The well-dispersion of spherical nanoparticles in glycerol was observed on Pd(II) precursors (mean diameter of 4.1 nm for $Pd(OAc)_2$ and 11.5 nm for $[PdCl_2(cod)]$), in contrast to the agglomeration of nanoparticles recorded on Pd(0) precursor ($[Pd_2(dba)_3]$). Under hydrogen pressure, the reduction rate of the C=C bonds of dibenzylideneacetone to afford bare Pd(0) atoms is much greater than those of Pd(II) precursors, even exceeds the rate of the particle growth; the concentration of generated metal atoms is higher than the critical supersaturation level achieved at longer times, permitting to extend the nucleation step.
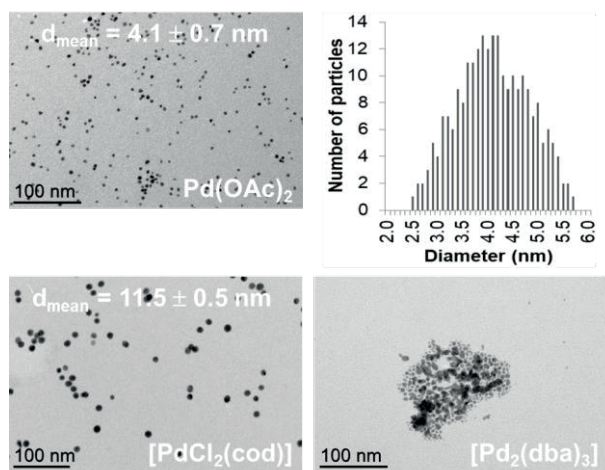

Figure 2: TEM micrographs of PdNPs from different metal precursors

Therefore, the growth period of nuclei occurs simultaneously than the nucleation, resulting in a broad size distribution of particles (polydisperse particles) [16]. In contrast, the narrow-size distribution (Gaussian distribution) of PdNPs coming from $Pd(OAc)_2$ indicated the smallest nanoparticles following the mono-dispersion model, among the as-prepared PdNPs [13,16]. The differences of particle size and their dispersion in reaction medium resulted in different catalytic activity as discussed below.

The crystalline structure of PdNPs synthesized from $Pd(OAc)_2$ was determined by powder XRD technique (Figure 3). As expected, the Bravais lattices of a face-centered cubic (fcc) structure of the bulk Pd(0) were exclusively exploited, corresponding to the (111), (200), (220), (311) and (222) plans characterized at 2 of 40.4°, 46.9°, 68.3°, 82.2° and 86.8°, respectively. The diffraction with broaden peaks proved the presence of small nanoparticles with uniform crystal size. According to the Debye-Scherrer equation, the crystal size was calculated to be 12.5 nm correlating the diffraction peak (111), being nearly triple than that determined by TEM analysis. This result can be explained by the lack of PVP and glycerol on the surface of PdNPs in the solid (separated from glycerol by centrifugation), as proven by FT-IR analysis. Therefore, both PVP and glycerol play important roles in preserving the nanostructures and preventing their agglomeration.
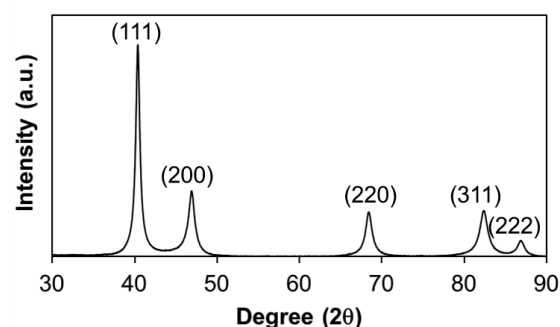

Figure 3: XRD diffractogram of PdNPs synthesized from $Pd(OAc)_2$

With the aim of studying the effect of metal precursors on polyol synthesis of PdNPs and thus their catalytic activities, the three as-prepared PdNPs from $Pd(OAc)_2$, $[PdCl_2(cod)]$ and $[Pd_2(dba)_3]$ were examined in C-N bond formation between acrylonitrile and morpholine (Figure 4). Note that the PdNPs solutions were directly used without any further treatments after synthesis and glycerol also acted as solvent in the catalytic reactions. As clearly, PdNPs from $Pd(OAc)_2$ constituted of the smallest nanoparticles gave the best catalytic reactivity, achieving 95% conversion and >99% selectivity after 2 hours (determined by GC-MS analysis). In contrast, the lowest catalytic performance was observed on those from $[Pd_2(dba)_3]$, caused by the agglomeration of nanoparticles. The optimization of reaction conditions

was also governed, involving molar ratio of reactants (acrylonitrile/morpholine of 1/1.2), temperature (80 °C), time (2 hours), catalyst content (1 mol% Pd) using PdNPs from $Pd(OAc)_2$.
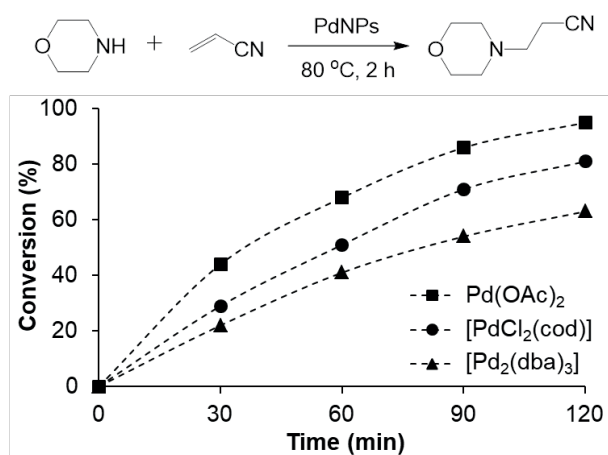

Figure 4: C-N bond formation between acrylonitrile and morpholine in glycerol catalyzed by PdNPs from different metal precursors

The most interesting aspects using glycerol as reaction medium include the easily extraction of organic products by a biphasic system and the recyclability of the catalytic solution, leading to Pd-free extracted products. The catalytic phase was recycled up to 4 times without loss of activity (Figure 5). No metal leaching was detected in the organic phase extracted from the catalytic solution by ICP-AES analyses (no traces of [Pd] detected in the extracted phase in comparison with 1.06 mg [Pd] added into the reaction medium at the beginning). These results proved the efficiency of glycerol in trapping metal species during reaction. The activity loss after the 5th run can be associated to the PdNPs size increase as evidenced by TEM analyses (Figure 6).
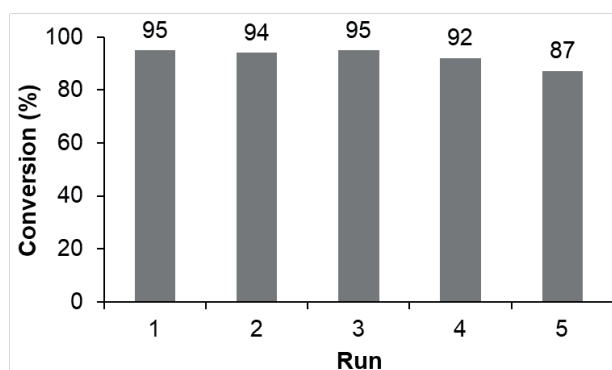

Figure 5: The recycling of the catalytic phase for C-N bond formation between acrylonitrile and morpholine at the optimal conditions

During the reaction, PdNPs can act as a "reservoir" of small metal atoms; after reaction completion, small dissolved crystals can be re-deposited on the surfaces of larger crystals, aggregating to form the larger partilces as described by Ostwald ripening process [17].
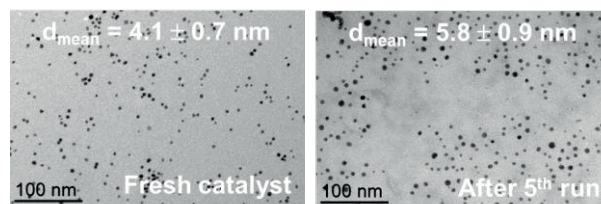

Figure 6: TEM micrographs of PdNPs before catalysis (left) and after the 5th run (right)

Conclusion

Polyol synthesis of PdNPs in glycerol permitted to obtain well-dispersed spherical nanoparticles. In particular, using $Pd(OAc)_2$ as metal precursor afforded the smallest nanoparticles (mean diameter of 4.1 nm), among those starting from $[PdCl_2(cod)]$ (mean diameter of 11.5 nm) and $[Pd_2(dba)_3]$ (mainly agglomerated). According to size/dispersion – reactivity relationship, the three as-prepared PdNPs exhibited the different catalytic activities towards C-N bond formation between acrylonitrile and morpholine. In general, the smaller the size is, the better the reactivity is. More interestingly, glycerol proved its efficient immobilization of PdNPs, permitting to recycle the catalytic phase several times with insignificant reactivity loss.

Acknowledgments

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