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# Stabilization of Pd, Pt and Ru nanoparticles by optically active CO/styrene copolymers

Isabelle Favier<sup>a</sup>, David Picurelli<sup>b</sup>, Christian Pradel<sup>a</sup>, Jérôme Durand<sup>c</sup>, Barbara Milani<sup>c</sup>, Montserrat Gómez<sup>a,\*</sup>

<sup>a</sup> Laboratoire Hétérochimie Fondamentale et Appliquée, UMR CNRS 5069, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 9, France

<sup>b</sup> Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11, 08028 Barcelona, Spain

<sup>c</sup> Dipartimento di Scienze Chimiche, Università di Trieste, Via Licio Giorgieri 1, 34127 Trieste, Italy

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## ABSTRACT

Fully isotactic, chiral CO/styrene copolymers were used as stabilizers for palladium, platinum and ruthenium nanoparticles synthesis. The tuning of copolymer/metal ratio and metal concentration were found to be key parameters in order to adjust the size and the agglomeration tendency of the metallic nanoclusters. These new materials were fully characterized by elemental analysis, infrared, solid state <sup>13</sup>C MAS NMR spectroscopies, and transmission electronic microscopy. Platinum and ruthenium nanoparticles were tested as catalysts in the ethyl pyruvate hydrogenation, giving high activities; in this preliminary work, no enantioselectivity induction was observed.

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The use of macromolecules (such as dendrimers [1–4], polymers [5–10] or cyclodextrins [11]) in the preparation of metallic nanoparticles for catalytic purposes represents a useful means to prevent the agglomeration of these nanometric-scale catalysts towards the bulk metal [12,13]. In order to apply these nanomaterials in asymmetric processes without additional chiral modifier, the use of optically pure polymers could be an attractive way to induce enantioselectivity. One approach based on the stabilization of metallic nanoparticles by polymer, introducing chiral groups in the polymeric chains was tested. We have recently described Pd, Pt and Rh nanoparticles stabilized by chiral ester or amide Gantrez® (registered trademark of GAF corporation for poly(methyl vinyl ether-co-maleic anhydride) derivatives [14]. These catalytic systems were active in Suzuki C–C coupling and hydrogenation reactions. However, the chirality present on the lateral chains of the polymer was inefficient to induce any asymmetry.

Another approach is based on the use of polymers featured by main-chain chirality. With this aim, we planned to use isotactic, optically active polymers as stabilizers of metallic nanoparticles. For several years, some of us have extensively investigated the catalytic synthesis of CO/vinyl arene copolymers [15–17], which belong to the family of CO/alkene polyketones. Thanks to their physical, chemical and mechanical properties CO/ethylene/propylene terpolymers were exploited at industrial level under the trademark of Carilon® [18]. To the best of our knowledge no application of these copolymers as stabilizers for metal nanoparticles has been reported so far. Here we describe the first example of CO/styrene polyketones used as

stabilizers for Pd, Pt and Ru nanoparticles. In particular, fully isotactic, optically active copolymers were employed to obtain active metal nanoparticles as catalytic precursors in asymmetric hydrogenations with the ambitious aim to transfer the chiral information from the polymer to the prochiral substrate.

Platinum, palladium and ruthenium nanoparticles (MNP) were prepared from the corresponding organometallic precursor,  $[M_2(dba)_3]$ (for M = Pt, Pd; dba = dibenzylidenacetone) and [Ru(cod)(cot)](cod =1,5-cyclooctadiene;  $\cot = cyclooctatriene$ ), in the presence of isotactic, optically active, CO/styrene copolymers under hydrogen atmosphere in THF solution (Scheme 1), following the methodology previously described [14,19,20]. Two CO/styrene copolymers, which were previously synthesized by us [21], were chosen differing for the number of repetitive units in the chain (n = 22 and 31, average values calculated from the molecular weights <Mw> determined by gel-permeation chromatography versus polystyrene standards) and for the sign of the optical activity (specific optical rotations measured in CHCl<sub>3</sub> at 0.1 g of polymer in 100 mL: +285 for 1 and -267 for 2); the stereochemistry of these copolymers was determined by <sup>13</sup>C NMR: only the signal related to the *ll* triad was observed, indicating the formation of a fully isotactic material [21].

The new materials were characterized by IR spectroscopy, elemental analysis and transmission electronic microscopy (see Figs. S1 and S2 in Supplementary material). For all the metallic nanoparticles stabilized by copolymers **1** and **2**, their IR spectra (KBr pellets) showed the characteristic absorption bands corresponding to the polymers, without any shifting relative to the signals of the pure polymer which proves that no strong covalent interactions between polymer and metallic surface were established. A new band at ca. 1000–1100 cm<sup>-1</sup> was observed, especially strong for Pt and Ru nanoparticles, absorption due to C–O

<sup>\*</sup> Corresponding author. Tel.: +33 561557738; fax: +33 561558204. *E-mail address*: gomez@chimie.ups-tlse.fr (M. Gómez).

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Scheme 1. Synthesis of Pd (Pd1), Pt (Pt1, Pt2) and Ru (Ru1, Ru2) nanoparticles.

single bond stretching. The presence of this kind of bond was also suggested by the solid state <sup>13</sup>C MAS NMR spectra of Ru nanoparticles (Fig. S3a and S3b). Actually, **Ru1** and **Ru2** showed large bands at ca. 80 and 45 ppm, in addition to those corresponding to the polymer, assigned to C–O single bond and methylene groups respectively (Fig. S3b and S3c vs S3a). In order to evidence the origin of these bands, Ru nanoparticles stabilized by **1** were prepared in pentane instead of tetrahydrofuran (Fig. S3d). The related <sup>13</sup>C MAS NMR spectrum did not exhibit the bands corresponding to C–O and additional CH<sub>2</sub> moieties proving that the signals at ca. 80 and 45 ppm are due to tetrahydrofuran and not to the partial reduction of the carbonyl group of the polymer in the presence of a metal source. The IR spectrum of **Ru1** prepared in pentane also confirmed the absence of the C–O function.

Monomer/metal ratio and metal concentration effects were studied in order to obtain small and well-dispersed nanoparticles suitable for further catalytic applications in wet medium (Table 1) [22]. An increase of the polymer proportion (monomer/metal ratio = 4.4) led to the formation of smaller nanoparticles depending on the metal concentration employed.

In particular, for platinum materials, spherical associations of nanoparticles of mean size of 22 nm were obtained at the most diluted conditions used (entry 3, Table 1), while for ten times more concentrated conditions, these associations show a mean diameter ca. 40 nm (entries 1 and 4, Table 1); only agglomerates were observed at  $10^{-2}$  M metal concentration (entry 5, Table 1). The same trend was observed for the analogous Pd nanoparticles (entries 2, 6 and 7, Table 1), but in this case, even for the most diluted conditions (entry 6, Table 1), only large particle associations were formed. In order to compare the stabilizing polymer effect, platinum nanoparticles were also prepared with the copolymer 2, obtaining big nanoparticles analogously to those containing 1 (entry 8 vs 1, Table 1). For ruthenium, under the most appropriated conditions ( $[Ru] = 2.5 \cdot 10^{-2} M$  and monomer/metal = 2) very small and well-dispersed nanoparticles were obtained for both 1 and 2 stabilizers (entries 9 and 10, Table 1). This dissimilar behaviour between ruthenium in relation to palladium

able 1
Mean size for Pd1, Pt1 and Ru1 nanoparticles in relation to the metal concentration and
nonomer/metal ratio

Entry	Precursor	$[M](mol \cdot L^{-1})$	Monomer/metal	$\Phi_{\rm m}({\rm nm})$
1	$[Pt_2(dba)_3]$	$2.2 \cdot 10^{-3}$	0.5	38 <sup>a</sup>
2	[Pd <sub>2</sub> (dba) <sub>3</sub> ]	$2.2 \cdot 10^{-3}$	0.5	Aggl. <sup>b</sup>
3	[Pt <sub>2</sub> (dba) <sub>3</sub> ]	$2.2 \cdot 10^{-4}$	4.4	22 <sup>a</sup>
4	[Pt <sub>2</sub> (dba) <sub>3</sub> ]	$2.2 \cdot 10^{-3}$	4.4	39 <sup>a</sup>
5	[Pt <sub>2</sub> (dba) <sub>3</sub> ]	$2.2 \cdot 10^{-2}$	4.4	Aggl. <sup>b</sup>
6	[Pd <sub>2</sub> (dba) <sub>3</sub> ]	$2.2 \cdot 10^{-4}$	4.4	37 <sup>a</sup>
7	[Pd <sub>2</sub> (dba) <sub>3</sub> ]	$2.2 \cdot 10^{-3}$	4.4	Aggl. <sup>b</sup>
8 <sup>c</sup>	[Pt <sub>2</sub> (dba) <sub>3</sub> ]	$2.2 \cdot 10^{-3}$	0.5	35 <sup>a</sup>
9	[Ru(cod)(cot)]	$2.5 \cdot 10^{-2}$	2	1.13 <sup>d</sup> (Ru <sub>55</sub> )
10 <sup>c</sup>	[Ru(cod)(cot)]	$2.5 \cdot 10^{-2}$	2	1.22 <sup>d</sup> (Ru <sub>70</sub> )

<sup>a</sup> Spherical associations of nanoparticles.

<sup>b</sup> Aggl. = agglomerates.

<sup>c</sup> Nanoparticles stabilized by copolymer **2**.

<sup>d</sup> In brackets, the estimated metallic composition considering a compact packing arrangement of spherical nanoparticles.



Scheme 2. Ethyl pyruvate hydrogenation catalyzed by Ru2 and Pt2 systems.

and platinum could be explained on the basis of the different rate of the nanoparticles nucleation and growth [23–26].

As indicated above, polymer **2** was also used as nanoparticles stabilizer. In particular, the effect of the monomer/metal ratio for ruthenium was explored. Therefore, monomer/Ru ratios = 0.5, 2 and 10, at a metal concentration of  $2.5 \cdot 10^{-2}$  M, were considered (TEM images in Supplementary material). For the monomer/Ru = 0.5, small particles (mean diameter = 1.22 nm) were obtained (Fig. S2a), analogously to those prepared using the copolymer **1** as stabilizer (Fig. S1f). For higher copolymer/metal ratios (monomer/Ru = 2 and 10), the particles show a trend to be associated giving agglomerated materials (Fig. S2b and S2c), in contrast to the effect observed when PVP is used as stabilizer [27].

Pt and Ru nanoparticles stabilized by copolymer **2** were used as catalyst in the ethyl pyruvate hydrogenation (Scheme 2) (see Supplementary material for experimental details).

Under the same catalytic conditions, Ru2 system was found to be more active than that using Pt2 as catalyst (entry 1 vs 2, Table 2). For higher metal load, the conversion of substrate increases up to 60% (entry 3 vs 1, Table 2). However, no enantioselectivity induced by the optically pure copolymer 2 was observed. The ethyl pyruvate hydrogenation was also performed in the presence of cinchonidine (entries 4 and 5, Table 2), a chiral inducer used in metal-catalyzed pyruvate derivatives hydrogenation [28-31]. The addition of cinchonidine into the catalytic mixture resulted in an increase in the activity of the system (for Ru, entry 3 vs 5; for Pt, entry 2 vs 5) [32,33], probably due to the interaction between the substrate and the chiral modifier favouring the contact of the substrate with the metallic surface [34-36]. In addition, the basic nature of cinchonidine can also favour the heterolytic cleavage of H<sub>2</sub> induced by the metal. However, the product was again obtained as a racemic mixture. Polyketone, close to the metallic surface, probably avoids the approach of cinchonidine to the metallic surface, losing the chiral induction.

To sum up, we have been interested in the metallic nanoparticles stabilization by means of chiral copolymers with the aim of applying them in asymmetric catalytic processes. New Pd, Pt and Ru nanoparticles could be prepared using fully isotactic, optically active CO/ styrene copolymers. The influence of parameters such as polymer content and metal concentration has been considered in order to control size and dispersion in the nanomaterials synthesis. Palladium and platinum systems gave agglomerates or association of particles for different monomer/metal ratios even at diluted metal concentration  $(2.2 \cdot 10^{-4} \text{ M})$ . In contrast, ruthenium led to small spherical and well-dispersed nanoparticles (mean diameter ca. 1.2 nm) for monomer/Ru ratios up to 2 at relatively high metal concentration  $(2.2 \cdot 10^{-2} \text{ M})$ ; at

### Table 2

Ethyl pyruvate hydrogenation catalyzed by Ru and Pt systems.<sup>a</sup>

Entry	Catalyst <sup>b</sup>	Added cinchonidine (%) <sup>c</sup>	Conv. (%) <sup>d</sup>
1	Ru2 (2%)	-	25
2	Pt2 (2%)	-	13
3	Ru2 (10%)	-	60
4	Ru2 (10%)	10	100
5	Pt2 (2%)	10	35

<sup>a</sup> Reaction conditions: 0.5 mmol ethyl pyruvate, 10 mL ethanol, 40 bar hydrogen, 1 h, r.t.

<sup>b</sup> In brackets, percentage of metal (in mol) in relation to the substrate.

<sup>c</sup> Percentage of cinchonidine (in mol) with respect to the substrate.

<sup>d</sup> Determined by <sup>1</sup>H NMR.

higher copolymer contents aggregates were also formed. The solid state characterization of Ru materials, by means of IR and NMR spectroscopy, points to a weak interaction of the polymer with the metallic surface, without polymer modification under the employed synthesis conditions. Ru and Pt materials were tested as catalytic precursors in ethyl pyruvate hydrogenation. Their catalytic activity was considerably increased by addition of a chiral modifier (cinchonidine), mainly for ruthenium-catalyzed process, although no enantioselectivity induction was achieved. Attempts to obtain chiral polymers coming from copolymerization of cinchonidine with styrene, carbon monoxide and acrylate derivatives were unsuccessful (see Supplementary material).

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.03.042.

#### References

- [1] M. Wilson, M.R. Knecht, J.C. García-Martínez, R.M. Crooks, J. Am. Chem. Soc. 128 (2006) 4510–4511.
- [2] S.-K. Oh, Y. Niu, R.M. Crooks, Langmuir 21 (2005) 10209-10213.
- [3] C. Ornelas, L. Salmon, J. Aranzaes Ruiz, D. Astruc, Chem. Commun. (2007) 4946–4948.
- [4] T. Mizugaki, M. Murata, S. Fukubayashi, T. Mitsudome, K. Jitsukawa, K. Kaneda, Chem. Commun. (2008) 241–243.
- [5] D.E. Bergbreiter, J. Tian, C. Hongfa, Chem. Rev. 109 (2009) 530-582.
- [6] A. Corma, H. Garcia, Top. Catal. 48 (2008) 8-31.
- [7] J. Lu, P.H. Toy, Chem. Rev. 109 (2009) 815–838.
- [8] D.E. Bergbreiter, S.D. Sung, Adv. Synth. Catal. 348 (2006) 1352-1366.
- [9] R.B. Grubbs, J. Polym. Sci. Part A Polym. Chem. 43 (2005) 4323-4336.

- [10] V. Thomas, M. Namdeo, Y. Murali Mohan, S.K. Bajpai, M. Bajpai, J. Macromol. Sci. Pure Appl. Chem. 45 (2008) 107–119.
- [11] A. Denicourt-Nowicki, A. Ponchel, E. Montflier, A. Roucoux, Dalton Trans. (2007) 5714–5719.
- [12] A. Roucoux, J. Schulz, H. Patin, Chem. Rev. 102 (2002) 3757-3778.
- [13] R. Shenhar, T.B. Norsten, V.M. Rotello, Adv. Mater. 17 (2005) 657-669.
- [14] I. Favier, M. Gómez, G. Muller, D. Picurelli, A. Nowicki, A. Roucoux, J. Bou, J. Appl. Polym. Sci. 105 (2007) 2772–2782.
- [15] A. Scarel, M.R. Axet, F. Amoroso, F. Ragaini, C.J. Elsevier, A. Holuigue, C. Carfagna, L. Mosca, B. Milani, Organometallics 27 (2008) 1486–1494.
- [16] J. Durand, E. Zangrando, M. Stener, G. Fronzoni, C. Carfagna, B. Binotti, P.C.J. Kamer, C. Müller, M. Caporali, P.W.N.M. van Leeuwen, D. Vogt, B. Milani, Chem. Eur. J. 12 (2006) 7639–7651.
- [17] J. Durand, B. Milani, Coord. Chem. Rev. 250 (2006) 542-560.
- [18] N. Alperwicz, Chem. Week (1995) 127.
- [19] F. Dassenoy, M.-J. Casanove, P. Lecante, C. Pan, K. Philippot, C. Amiens, B. Chaudret, Phys. Rev. B 63 (2001) 235407.
- [20] Synthesis of metallic nanoparticles: The polymer was introduced in a Fischer-Porter bottle and purged by means of vacuum and argon cycles. The appropriate metallic precursor, [Pt<sub>2</sub>(dba)<sub>3</sub>], [Pd<sub>2</sub>(dba)<sub>3</sub>] or [Ru(cod)(cot)], was dissolved in a Schlenk vessel with previously degassed THF and then introduced under argon atmosphere in the Fischer-Porter bottle. The solvent volume was completed to 80 mL. The system was then pressurised with hydrogen (3 bars) and stirred at room temperature overnight. The hydrogen was next replaced by argon and the solvent was evaporated under *vacuum*. To eliminate the organic by-products, the black residue corresponding to the formed nanoparticles was washed with pentane and dried under vacuum.
- [21] A. Scarel, J. Durand, D. Franchi, E. Zangrando, G. Mestroni, C. Carfagna, L. Mosca, R. Seraglia, G. Consiglio, B. Milani, Chem. Eur. J. 11 (2005) 6014–6023.
- [22] J. Durand, E. Teuma, M. Gómez, Eur. J. Inorg. Chem. (2008) 3577-3586.
- [23] J. Turkevitch, Gold Bull. 18 (1985) 125–131.
- [24] M.A. Watzky, R.G. Finke, J. Am. Chem. Soc. 119 (1997) 10382-10400.
- [25] M.A. Watzky, R.G. Finke, Chem. Mater. 9 (1997) 3083-3095.
- [26] M.A. Watzky, E.E. Finney, R.G. Finke, J. Am. Chem. Soc. 130 (2008) 11959-11969.
- [27] H. Hirai, N. Yakura, Y. Seta, S. Hodoshima, React. Funct. Polym. 37 (1998) 121–131.
- [28] M. Studer, H.-U. Blaser, C. Exner, Adv. Synth. Catal. 345 (2003) 45-65.
- [29] H. Bönnemann, G.A. Braun, Chem. Eur. J. 3 (1997) 1200–1202.
- [30] X. Zuo, H. Liu, D. Guo, X. Yang, Tetrahedron 55 (1999) 7787–7804.
- [31] J.U. Köhler, J.S. Bradley, Langmuir 14 (1998) 2730–2735. [32] F. Toukoniity, D.Y. Murzin, J. Catal 241 (2006) 96–102
- 32] E. Toukoniity, D.Y. Murzin, J. Catal. 241 (2006) 96–102.
- M. Bartok, M. Sutyinszki, I. Bucsi, K. Felföldi, G. Szöllosi, F. Bartha, T. Bartok, J. Catal.
  231 (2005) 33–40.
  J.L. Margitfalvi, E. Tálas, E. Tfirst, C.V. Kumar, A. Gergely, Appl. Catal. A General 191
- [24] J.L. Wargittawi, E. Tatas, E. Tinst, C.V. Kunar, A. Gergery, Appl. Catal. A General 191 (2000) 177–191.
   [35] M. Schürch, T. Heinz, R. Aeschimann, T. Mallat, A. Pfaltz, A. Baiker, J. Catal. 173
- M. SCHUICH, I. HEILZ, K. AESCHIIHAHH, I. Wallat, A. Platz, A. Baiker, J. Catal. 175 (1998) 187–195.
   M. Missilan, C. Mattinda, J. Sakula, J. D. Balland, A. Baucanu, J. Catal. 225 (2004)
- [36] V. Mévellec, C. Mattioda, J. Schulz, J.-P. Rolland, A. Roucoux, J. Catal. 225 (2004) 1–6.