

# Nano-catalizadores en glicerol: Diseño y aplicaciones en síntesis

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Metal-based nanoparticles (MNPs) have been largely studied in the last decades due to their distinctive properties, which found applications in several fields (microelectronics, medicine, catalysis) [1]. “Nanocatalysis” emerged as a new concept that combines both colloidal catalysis and catalysis based on engineered nano-objects, showing defined structures and composition. Like most MNPs, aggregation during the catalytic reaction can lead to structure modifications, precluding their unique properties and then the lack of the expected reactivity. A way to avoid these drawbacks is to use solid supports in order to immobilize the nanocatalysts, favoring their recycling, but adding plausible effects due to the metal-support interactions. With the aim of preserving the surface state, the immobilization of MNPs in a liquid phase has been considered. Besides environmentally friendly properties, glycerol is characterized by a complex supramolecular network, permitting to trap the catalyst and easily extract the organic products; the catalytic phase can be then recycled, obtaining metal-free target molecules [2].

Our team has proved the glycerol ability for the synthesis of both mono- (Pd, Cu and Cu<sub>2</sub>O, Ni) and bi-metallic nanoparticles (Pd/Cu), leading to stable colloidal catalytic solutions in the presence of polymers (such as PVP) [3], phosphines [4] and biomass-based stabilizers such as cinchona derivatives [5]. In particular, bimetallic nanoparticles have opened new horizons in energy conversions and organic transformations, thanks to cooperative effects between the two counterparts, due to structure-reactivity relationships (alloy, core-shell, hetero-dimer...) [6].

In this lecture, an account of our work in this field will be presented, from the synthesis and full characterization of metal-based nanoparticles in glycerol to the catalytic applications, with the final goal of obtaining target molecules of interest for the fine chemistry sector.

## References

1. Murphy, C. J.; Gole, A.M.; Hunyadi, S. E.; Stone, J. W.; Sisco, P. N.; Alkilany, A.; Kinard, B. E.; Hankins, P. *Chem Commun.* **2008**, 544.
2. For selected reviews, see: a) Gu, Y.; Jérôme, F. *Green Chem.* **2010**, *12*, 1127; b) Chahdoura, F.; Favier, I.; Gómez, M. *Chem. Eur. J.* **2014**, *20*, 10884.
3. a) Dang-Bao, T.; Pradel, C.; Favier, I.; Gómez, M. *Adv. Synth. Catal.* **2017**, *359*, 2832; b) Chahdoura, F.; Pradel, C.; Gómez, M. *ChemCatChem*, **2014**, *6*, 2929.
4. a) Chahdoura, F.; Pradel, C.; Gómez, M. *Adv. Synth. Catal.* **2013**, *355*, 3648; b) Chahdoura, F.; Favier, I.; Pradel, C.; Mallet-Ladeira, S.; Gómez, M. *Catal. Commun.* **2015**, *63*, 47; c) Chahdoura, F.; Mallet-Ladeira, S.; Gómez, M. *Org. Chem. Front.* **2015**, *2*, 312.
5. a) Reina, A.; Pradel, C.; Martin, E.; Teuma, E.; Gómez, M. *RSC Adv.* **2016**, *6*, 93205; b) Reina, A.; Serrano-Maldonado, A.; Teuma, E.; Martin, E.; Gómez, M. *Catal. Commun.* **2018**, *104*, 22; Reina, A.; Favier, I.; Gómez, M. *Adv. Synth. Catal.* **2018**, *360*, 3544.
6. Dang-Bao, T.; Pla, D.; Favier, I.; Gómez, M. *Catalysts* **2017**, *7*, 207.

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## SHORT Curriculum Vitae of Montserrat GOMEZ

### ACADEMIC DEGREES

**1986:** Licentiate in Chemistry by the Universitat de Barcelona.

**1988:** Licentiate thesis in Chemistry by the Universitat de Barcelona.

**1991:** Doctor in Chemistry by the Universitat de Barcelona.

### POSITIONS

**1993-2004:** Permanent position in the Departament de Química Inorgànica of Universitat de Barcelona as Assistant Professor in Homogeneous Catalysis group (Prof. G. Muller).

**Since 2005:** Full Professor in Laboratoire Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier, Toulouse. Head of SYMAC (*Systèmes Métalliques Appliqués en Catalyse*) research group.

## STAYS

**1992:** One-year post-doctoral stay in Laboratoire de Chimie de Coordination, CNRS, Toulouse, Dr Denis Neibecker research group. Subject: Synthesis of chiral phospholes. Applications in asymmetric hydrogenation.

**1997:** Sabbatical stay in University of Amsterdam in Piet W.N.M. van Leeuwen group (8 months). Subject: Pd complexes containing oxazoliny- phosphine chiral ligands. Co-polymerisation reactions. Monitoring processes by NMR under high pressure.



**2001:** Sabbatical stay in Laboratoire de Chimie de Coordination, CNRS, Toulouse, in Bruno Chaudret team (4 months). Subject: Stabilization of Pt nanoparticles using chiral oxazoline ligands.

## RESEARCH FIELDS

Organometallic chemistry. Design of ligands. Heteropolymetallic complexes. Synthesis of mono- and bi-metallic nanoparticles stabilized by ionic liquids, ligands and/or polymers.

(Stereo)selective catalysis: Cooperative effects.

Immobilization of nanocatalysts in non-conventional solvents (ionic liquids, glycerol, deep eutectic solvents), and on functionalized nano-materials (multi-walled carbon nanotubes, halloysites)

Hydrogenations and hydrogen transfer reactions (Ru, Rh, Pt, Pd, Ni); Allylic substitutions (Pd); C-C couplings (Pd, Ni); Olefin epoxidations (Mo); Direct couplings and cycloadditions (Rh, Pd, Ni, Cu, Cu<sub>2</sub>O); Activation of small molecules; Tandem / sequential processes

## 5 SELECTED PUBLICATIONS (2014-2017)

- F. Chahdoura, C. Pradel, M. Gómez, *Copper(I) oxide nanoparticles in glycerol: a convenient catalyst for cross-coupling and azide-alkyne cycloaddition processes*, *ChemCatChem*, **6** (2014) 2929-2936
- Y. Gu, I. Favier, C. Pradel, D. L. Gin, J.-F. Lahitte, R. D. Noble, M. Gómez, J.-C. Remigy, *High catalytic efficiency of palladium nanoparticles immobilized in a polymer membrane containing poly(ionic liquid) in Suzuki-Miyaura cross-coupling reaction*, *J. Membrane Sci.*, **492** (2015) 331-339
- D. Pla, M. Gómez, *Metal and metal oxides, a lever for C-H functionalization*, *ACS Catal.*, **6** (2016) 3537-3552.
- M. Rodríguez-Rodríguez, P. Llanes, C. Pradel, M. A. Pericàs, M. Gómez, *Key non-metal ingredients for Cu-catalyzed "Click" reactions in glycerol: nanoparticles as efficient forwarders*, *Chem. Eur. J.*, **22** (2016) 18247-18253.
- T. Dang-Bao, C. Pradel, I. Favier, M. Gómez, *Making Copper(0) Nanoparticles in Glycerol: a Straightforward Synthesis for a Multipurpose Catalyst*, *Adv. Synth. Catal.*, **359** (2017) 2832-2846.

## OTHERS

- **Distinction** as Young Researcher by the Generalitat de Catalunya in 2002.
- **Publications:** 126 papers. 7 reviews. 4 book chapters. 1 patent (with international extension).
- **Lectures:** 40 as invited speaker in several Universities (France, Spain, Italy, Holland, Germany, Portugal, Venezuela, Mexico); 20 in national (5) and international (15) Conferences.
- Supervisor of: 13 PhD theses - 12 Master in Chemistry - 8 Post-doctoral stays
- Participation to 28 research **funded projects**; 18, as main researcher.
- **Guest (co)editor** for special issues "Catalysis in Innovative Solvents" for *Catalysts* journal (2017); "Palladium nanoparticles: applications in sustainable synthesis" for *Tetrahedron* journal (2017); "Metal Nanocatalysts in Solution: Characterization and Reactivity" for *Topics in Catalysis* journal (2013)
- **Collaborations** with several research groups (B. Chaudret and K. Philippot in Toulouse, C. Claver and A. Masdeu in Tarragona (Spain), Guillermo Muller in Barcelona (Spain), A. Trzeciak in Poland, E. Martin in Mexico, B. Royo in Lisbon (Portugal))
- **Coordinator** of the French-Spanish network "Heteroelements and Coordination Chemistry: from concepts to applications" (<http://gdri-hc3a.cnrs.fr>)
- Coordinator of the group Catalysis in Toulouse (<http://cat.ups-tlse.fr/>)
- Member of **Scientific Advisory Board** of *Catalysis Letters* and *Topics in Catalysis*.

- **Reviewer** of several international publications: Advanced Synthesis and Catalysis, ACS Catalysis, Catalysis Science and Technology, Catalysis Communications, Journal of Catalysis, European Journal of Inorganic Chemistry, Dalton Trans, Chemical Communications, Inorganic Chemistry, Catalysis Letters, New Journal of Chemistry etc.
- **Reviewer** of European, French and Spanish evaluation commissions.