

N°1151 / PC

TOPIC(s) : Homogenous, heterogenous and biocatalysis / Clean reactions

Eco-friendly synthesis of metallic nanoparticles and catalytic properties in aqueous media.

AUTHORS

Erwann GUÉNIN / LABORATOIRE TIMR, EA4297, SORBONNE UNIVERSITÉS - UNIVERSITÉ DE TECHNOLOGIE DE COMPIÈGNE, NIVERSITÉ DE TECHNOLOGIE DE COMPIÈGNE, CENTRE DE RECHERCHE DE ROYALLIEU, RUE DU DOCTEUR SCHWEITZER, COMPIEGNE

Caroline LEFEVRE / UNIVERSITÉ DE TECHNOLOGIE DE COMPIÈGNE, CENTRE DE RECHERCHE DE ROYALLIEU, COMPIEGNE

Elodie COLACO / UNIVERSITÉ DE TECHNOLOGIE DE COMPIÈGNE, CENTRE DE RECHERCHE DE ROYALLIEU, COMPIEGNE

Aissa Ould-Driss OULD-DRISS / UNIVERSITÉ DE TECHNOLOGIE DE COMPIÈGNE, CENTRE DE RECHERCHE DE ROYALLIEU, COMPIEGNE

Jessem LANDOULSI / SORBONNE UNIVERSITÉ, LABORATOIRE DE RÉACTIVITÉ DE SURFACE, 4 PLACE JUSSIEU, PARIS

Cristina BELDA MARIN / UNIVERSITÉ DE TECHNOLOGIE DE COMPIÈGNE, CENTRE DE RECHERCHE DE ROYALLIEU, COMPIEGNE

Anas IBEN-AYAD / UNIVERSITÉ DE TECHNOLOGIE DE COMPIÈGNE, CENTRE DE RECHERCHE DE ROYALLIEU, COMPIEGNE

PURPOSE OF THE ABSTRACT

Catalysis is among the 12 principles of green chemistry. However, this belonging may be balanced by the frequent use of high loads of toxic catalytic metals and the use of hazardous organic solvents. The toxicity of some of these metals is a real concern for the chemical industry due to the very low traces authorized for residue of heavy metals. Thus, when these metals cannot be substituted the drastic reduction of catalytic charge and the catalyst recycling become key-parameters. In addition, the replacement of harmful organic solvents by eco-friendly media (water) is another area of improvement to be addressed. The use of metallic nanoparticles (NPs) to develop innovative and greener catalytic system has attracted research endeavours around the world.¹ These NPs may be used as the catalyst or as the support and can facilitate the catalytic process in eco-friendly media.² NPs provide an increased surface area offering a unique solution at the interface between homogeneous and heterogeneous catalysis. Therefore, (i) to avoid the use of organic solvent and (ii) to achieve catalysis with low metals loading (<1000 ppm), one approach could be to stabilize and react the metallic nanocatalyst in aqueous media. However, two obstacles should be considered: - The development of a synthesis of well-controlled metallic NPs (composition, size, morphology) stabilized in water avoiding therefore the synthesis in organic medium and the tedious stabilizer exchange approach. - Second, to find a solution allowing mass transfer of organic substrates dispersed into the aqueous catalytic phase towards the surface of the nanocatalyst. It is worth noting that only few works have been reported to address these challenging problems. Among them, the Lipshutz group and Novartis used amphiphilic species to achieve micellar catalysis with Pd containing iron NPs. While the results appeared impressive, the NP catalysts are synthesized in an unsustainable manner³ (high temperatures, organic solvent, dry argon atmosphere) and from expensive metal derivatives. The remaining approaches are based on Pd NPs stabilizing agents (e.g. ionic liquids, water soluble NHC stabilizers, phosphine oxide polymer?),⁴ but not reaching comparable results to those of Lipshutz. Finally, no optimal solution has been reported so far. In line with these considerations, we have been developing new metallic NPs. The recently patented synthesis⁶ appears to be highly versatile allowing the production of several types of highly water stable

metallic NPs (Pd, Pt, Pd/Pt, Pd, Ni, Rh, Ru?) with a control of size and form. Contrary to literature precedents, these NPs are prepared under benign and green conditions (with eco-compatible reductant and designed biocompatible coating agents in 30 min, 80°C, in water under air). The rationale behind the design of the ligand is to have molecules able to stabilize the NPs in water media and to build a lipophilic environment around the NPs that will allow performing organic reaction in water. As preliminary experiments, we have demonstrated that these NPs are highly active for selected C-C coupling and reduction reactions in aqueous media under mild conditions with quantities of metal down to ppm levels (0.002 mol % Pd) and Turn Over Frequencies > 100 000 mol of Pd-1 h⁻¹ in best cases.

FIGURES

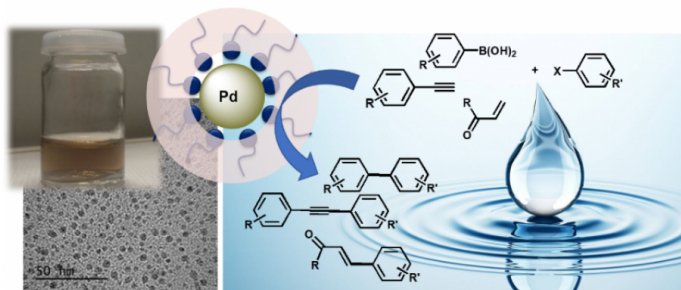


FIGURE 1

TEM and photograph of Pd-NPs nanocatalyst

FIGURE 2

KEYWORDS

nanocatalysis | green chemistry | C-C coupling | reduction

BIBLIOGRAPHY

- [1] a) Wu, Y. et al. *Chem. Soc. Rev.* 2014, 43, 2112. b) Chng, L. L. et al. *Acc. Chem. Res.* 2013, 46, 1825.
[2] Denicourt-Nowicki, A. et al. *Chem. Rec.* 2016, 16, 2127.
[3] Handa, S. et al. *Science* 2015, 349, 1087.
[4] a) Ge, J. et al. *Tet. Lett.* 2017, 58, 1142. b) Mejías, N. et al. *Eur. J. Org. Chem.* 2010, 5090. c) Luska, K. L. et al. *Adv. Synth. Catal.* 2011, 353, 3167. d) Gavia, D. J. et al. *ChemCatChem* 2015, 7, 892 e) Asensio, J. M. et al. *Chem. Eur. J.* 2017, 23, 13435. f) Taskin, et al. *M. RSC Adv.* 2017, 7, 41144.