

## Recycling of metallodendritic catalysts by their grafting onto superparamagnetic nanoparticles

*D. Rosario-Amorin,<sup>a</sup> S. Nlate,<sup>a</sup> M. Gaboyard,<sup>b</sup> R. Clérac,<sup>c</sup> K. Heuzé<sup>a\*</sup>*

<sup>a</sup> Institut des Sciences Moléculaire, Université Bordeaux I – UMR-CNRS N°5255, 351 cours de la libération, 33405 Talence Cedex, France.

<sup>b</sup> Ademtech, SA. Parc Scientifique Unitec 1, 4 allée du Doyen George Brus, 33600 Pessac, France.

<sup>c</sup> Centre de Recherche Paul Pascal – UPR-CNRS N°8641, 115 avenue du Dr A.Schweitzer, 33600 Pessac, France.

[rosarioamorin.daniel@caramail.com](mailto:rosarioamorin.daniel@caramail.com)

The homogeneous catalysis offers some major benefits for organic synthesis compared to heterogeneous catalysis. However, the difficulty in separating the catalyst from the reaction media is a limiting factor for their use in industrial processes especially when expensive and toxic complexes are employed.<sup>[1]</sup> Because of these economic, health and environmental factors, the development of methods for the recovery and recycling of homogeneous catalysts have been receiving a great attention during recent years, and supported catalysis has been used as an alternative way of recovery. One of the most common way consists in immobilizing the catalysts on organic or inorganic solid supports, and to separate the catalyst from reaction mixture *via* a simple filtration process.<sup>[2]</sup> However, a significant decrease in reactivity and selectivity of the catalysts is generally observed due to steric and diffusion effects. The use of small size matrices (< 100 nm) for the immobilization of catalysts may limit the negative impact of the support on the catalytic activity but the recovery processes becomes more difficult. Since few years, magnetic iron oxide nanoparticles (MNPs) have emerged as alternative supports and have opened wide a potential in the field of catalysis. Indeed, superparamagnetic nanoparticles-supported catalysts could be easily isolated and recycled from the reaction medium by simple magnetization with a low magnetic field magnet.<sup>[3]</sup> These functionalized superparamagnetic nanoparticles may be synthesized directly at the oxide surface, but the key of their recent success is the tremendous progresses of the surface chemistry on these nanomaterials in particular by their coating with silica or polymer shells. Indeed, these organic or inorganic layers protect the magnetic core from aggregation, and prevent changes in their chemical and physical properties. They also offer widespread and tunable functional surfaces for the immobilization of catalysts.<sup>[4]</sup>

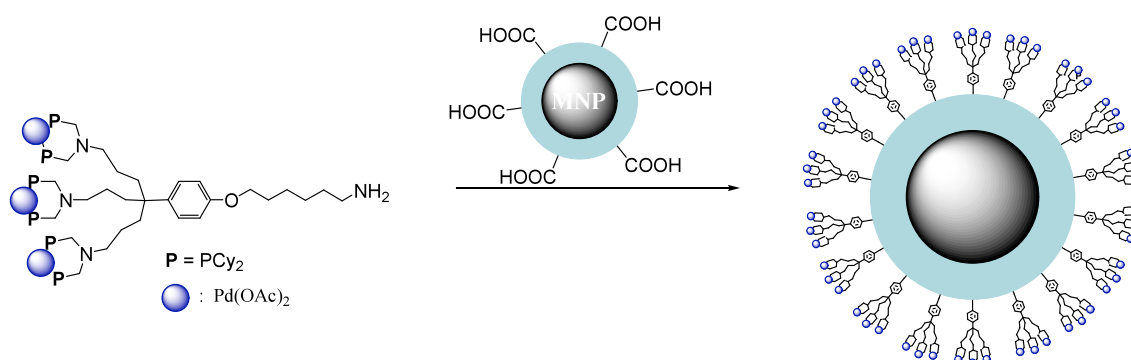
In this work, we report the synthesis of metallodendrons bearing pallado phosphine catalysts and their grafting on core-shell  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/polymer MNPs by a convergent approach. In contrast to the divergent grafting approach, that built on the MNPs surface, this method use well-defined dendrons, since the dendritic part are synthesized in homogeneous system and characterized before their grafting on MNPs.<sup>[5]</sup> The strategy used for the immobilization has been reported in previous work concerning the positive dendritic effect of dendrons grafting on the surface for the functionalization of these MNPs.<sup>[6]</sup> Here we describe the optimization of grafting conditions including various parameters such as solvent, coupling reagents or metallodendron loading. The grafting is based on the covalent coupling between the terminal primary amine of metallodendron and the free carboxyl acid groups at the MNPs polymer shell (see figure 1). Colloidal state and shape of the grafted MNPs remained unchanged especially when aqueous/organic medium with triton/MeOH was used as grafting solvent.

The catalytic activity of grafted MNPs has been investigated in C-C cross coupling reaction such as Suzuki coupling between halogenoarene derivatives and phenyl boronic acid derivatives. The reactivity of these grafted catalysts was studied in middle conditions and revealed a significant activity even towards chloroarenes. Recovery and re-use of grafted MNPs was achieved by magnetization of catalyst by a simple magnet (figure 2). These experiments indicated no decrease of catalytic activity even after 25 runs of recovery, indicating a good stability of the catalyst with this recovery technique.

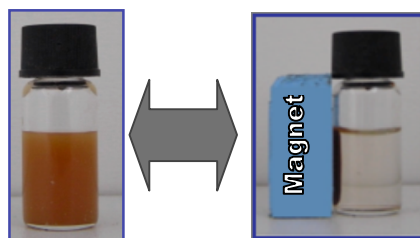
## References:

- [1] J. Hagen, *Industrial Catalysis : A Practical Approach*, Wiley-VCH, (1999) .  
 [2] (a) N.E. Leadbeater, M. Marco, *Chem. Rev*, **102** (2002) 3217; (b) C.E. Song, S.G. Lee, *Chem. Rev*, **102** (2002) 3495.  
 [3] T.J. Yoon, W. Lee, Y.S. Oh, J.K. Lee, *New. J. Chem*, **27** (2003) 227.  
 [4] A.K. Gupta, M. Gupta, *Biomaterials*, **26** (2005) 3995.  
 [5] N. Tsubokawa, H. Ichioka, T. Satoh, S. Hayashi, K. Fujiki, *Reac. & Funct. Polym.*, **37** (1998) 75.  
 [6] K. Heuzé, D. Rosario-Amorin, S. Nlate, M. Gaboyard, A. Bouter, R. Clérac. *New. J. Chem*, **32**(2008) 383.

## Figures:



**Figure 1** : Grafting of dendron catalyst onto core-shell  $\gamma\text{-Fe}_2\text{O}_3$ /polymer MNPs



**Figure 2** : Magnetization of a grafted MNPs catalyst in solution with an external magnet.