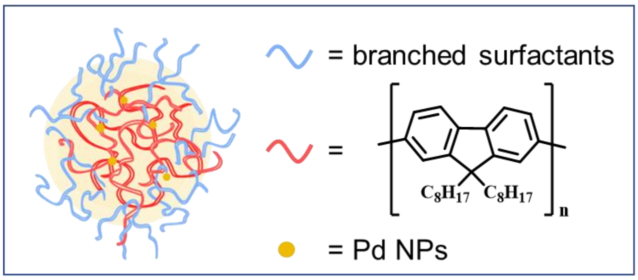
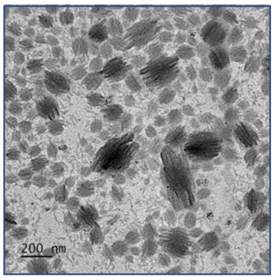
SYNTHESIS AND CHARACTERISATION OF PALLADIUM CONTAINING AROMATIC COLLOIDAL NANOPARTICLES FOR HETEROGENEOUS CATALYSIS

Annapia Fratepietro[1], Sara Mecca[1], Sara Mattiello[1], Miriam Ciallella[1] and Luca Beverina[1]

[1]*Department of Materials Science, University of Milano-Bicocca, 20126 Milan, Italy.*

Sustainability is becoming an increasingly important concern for organic semiconductor. Synthetic procedures should become simpler, more efficient and less resource-intensive. Furthermore, waste must be avoided as much as possible. Hence, the combination of heterogeneous catalysis and micellar methods can have a major impact on the field. Micellar catalysis helps in getting rid of organic solvents replacing them with water and in creating nanometric environments having enhanced reagent local concentrations to assure higher reaction rate and selectivity [1]. Easy reuse, recovery, and lack of toxic ligands make heterogeneous catalysts preferable with respect to homogeneous ones, although several challenges have yet to be faced: heterogeneous catalysts have lower activity, selectivity, and stability with respect to homogeneous ones and also suffer from metal leaching phenomena. The need for high surface area, reactant compatibility and homogeneous active sites distribution is the starting point for further development [2]. Having in mind all these challenges, we developed a new heterogenized catalyst whose supporting counterpart is formed by non-porous π-conjugated organic nanostructures obtained through micellar polymerization. They are designed to be intrinsically stable, water-dispersible and to embed the Pd catalyst involved into their own synthesis so that they could be directly reused as heterogenized catalyst in further micellar cross-coupling reactions. We prepared a first-generation catalyst through deposition of Pd metal nanoparticles (Pd-NPs) on reprecipitated Poly(9,9-dioctyl)fluorene (PFO) nanospheres, then and we tested its catalytic activity in *in-water* micellar Suzuki-Miyaura reactions. The efficiency of such catalyst was compared to that of the benchmark heterogeneous palladium catalyst Pd/C (Evonik hydrogenation catalyst). The initial findings shows higher conversion associated to the use of the polymer-supported Pd catalyst. Recycling of the catalyst is also possible thanks to the development of a straightforward workup procedure. The second-generation heterogenized catalyst requires the synthesis of conjugated polymer nanoparticles (CPNPs) by direct miniemulsion Suzuki polymerization. Literature examples of CPNPs synthesis always contemplate a purification step, to get rid of surfactants [3]. However, in this case, their entanglement within the colloidal structure is a crucial advantage: they constitute a template in which the polymeric nano-object can grow, and they make it suitable for its final application as catalyst. The synthesis produces dispersed spherical Pd-embedding polymer-surfactant semi-interpenetrated networks (sIPN). Such dispersion is then used as heterogenized catalyst showing the highest conversion rate. Encouraged by preliminary results both catalysts generalities are currently under investigation and a library of reactions is taking shape broaden their application field.





[1] G. La Sorella, G. Strukul and A. Scarso, *Green Chemistry* **17**, 2644-683 (2015).
[2] F. Poovan, V. Chandrashekha, K. Natte, and J. Rajenahally, *Catalysis Science & Technology* **12**, 6623-6649 (2022).
[3] J.M. Behrendt, J. A. E. Guzman, L. Purdie, H. Willcock, J. J. Morrison, A. B. Foster, M. L. Turner, *Reactive and Functional Polymers*, **107**, 69-77 (2016).