Palladium containing aromatic colloidal nanoparticles for heterogeneous catalysis

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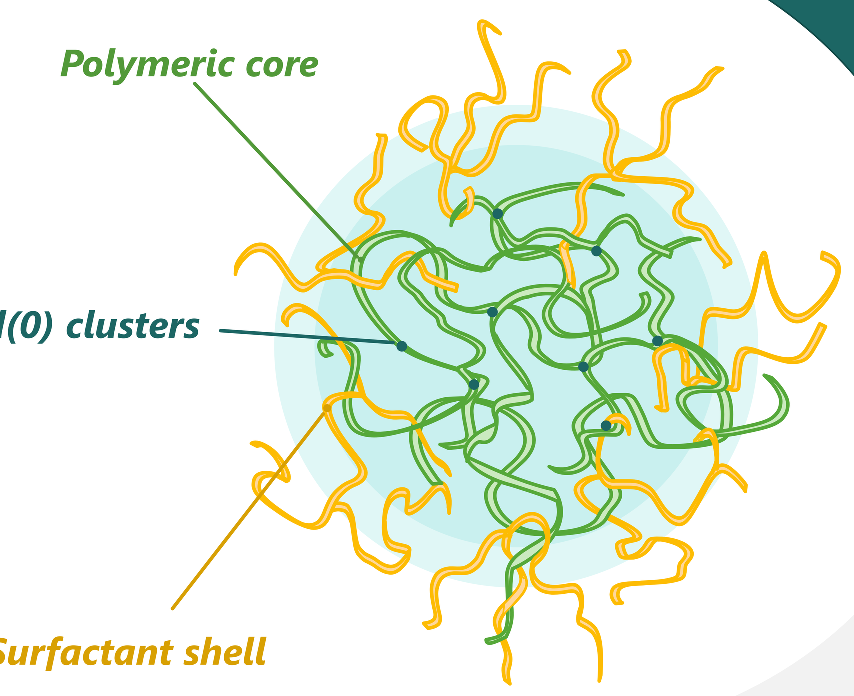
THE SUSTAINABILITY ISSUE

A sustainable synthetic procedure must rely on simple, highly efficient and less resource-intensive protocols and generate the lowest amount of waste. In this respect micellar methods[1] and heterogeneous catalysis are two powerful tools that helps in:

a. Creating enhanced reagent local concentrations
b. Getting rid of toxic ligands
c. Reducing the use of organic solvents



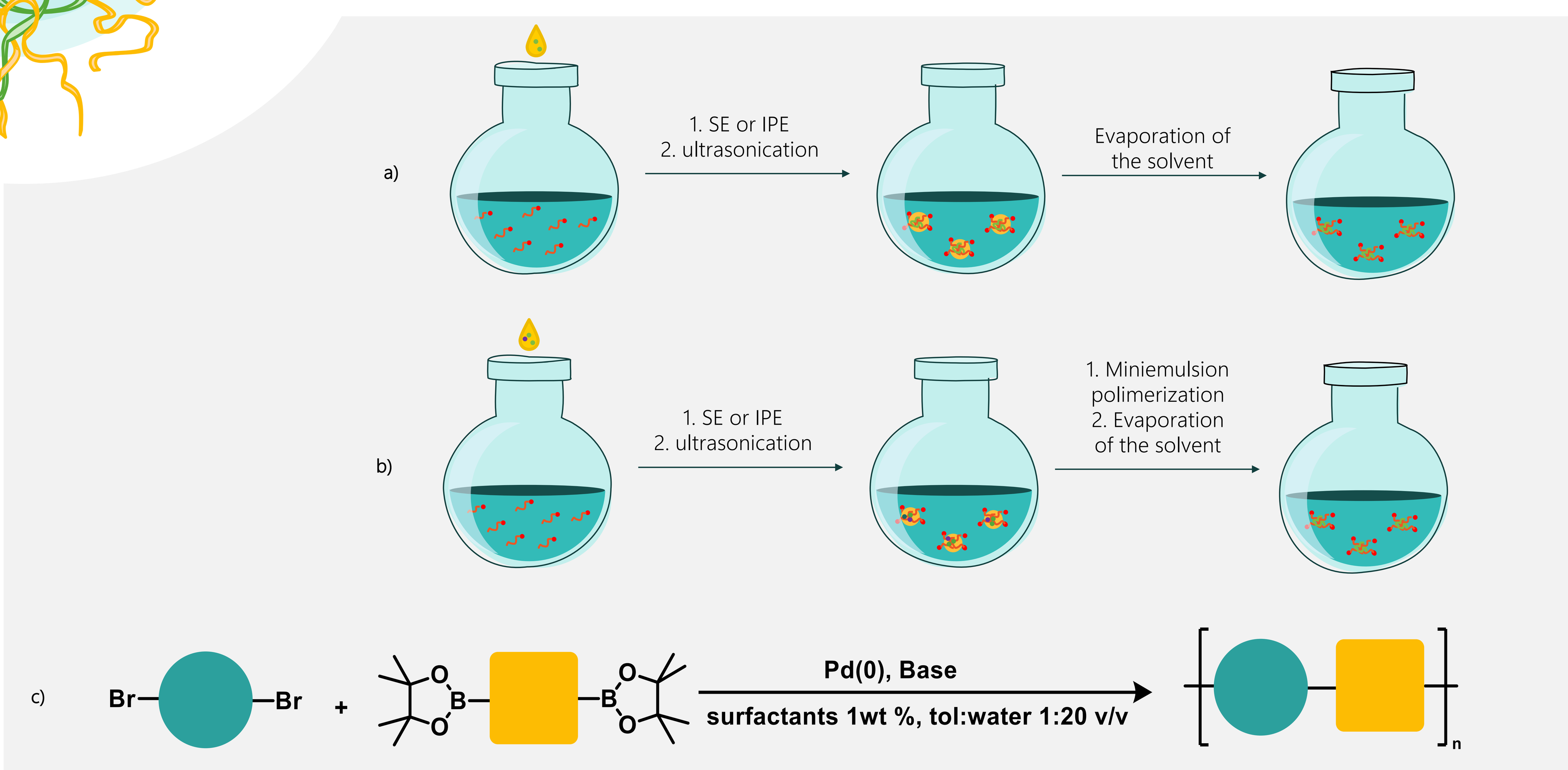
OUR APPROACH

Heterogeneous catalysts lower activity, selectivity, as far as metal leaching phenomena must be stemmed.[2] For this purpose, we exploited micellar polymerization to develop a new **heterogenized catalyst** composed by:

a. the π-conjugated organic polymer acting as nanostructured support
b. the surfactant shell allowing the dispersion of the polymeric nanoparticles in aqueous medium
c. Pd (0) clusters embedded into the polymeric core coming from polymer synthesis and acting as active sites

FROM POWDER TO DISPERSION

1. **First generation catalyst**: in-situ reduction of Pd nanoparticles (Pd-NPs) on reprecipitated polymeric nanospheres (**a**).
2. **Second generation heterogenized catalyst**: synthesis of conjugated polymer nanoparticles (CPNPs) by miniemulsion polymerization[3] (**b**, **c**). Surfactants constitute a template in which the polymeric nano-object can grow, and make it suitable for its final application.



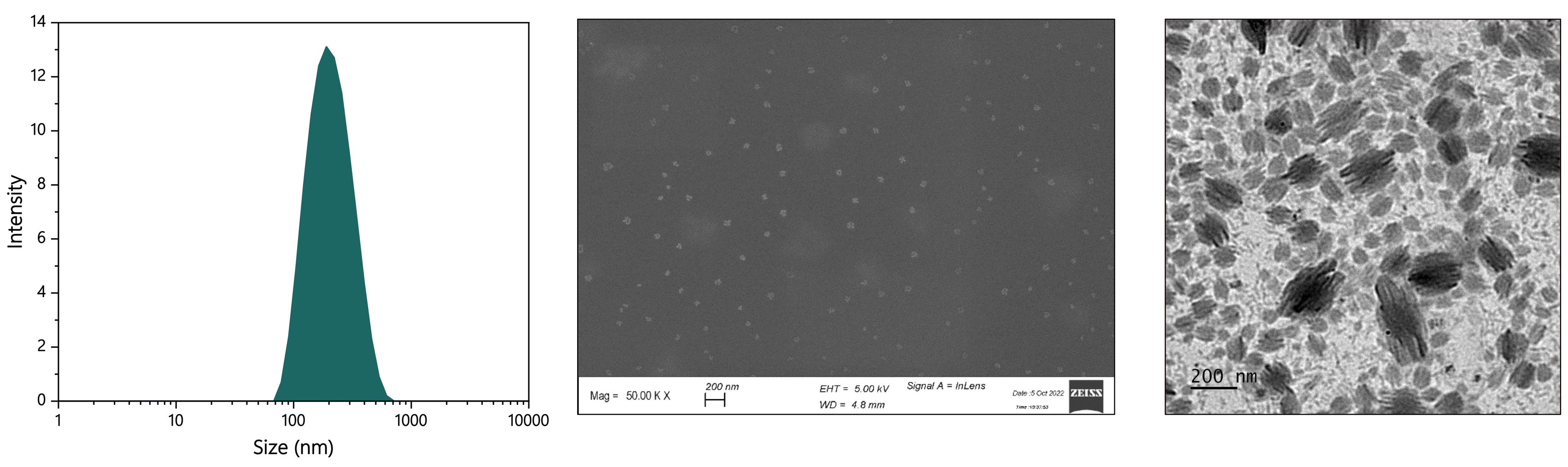
Schematic representation of the miniemulsion Suzuki polymerization protocol. Different bromides and boronic partners have been tested

Both catalysts have been tested in Suzuki cross-coupling reactions and their efficiency has been compared to that of the benchmark heterogeneous palladium catalyst Pd/C.[a] A simple recovery procedure allowing for catalyst recovery has also been developed.

CHARACTERIZATION OF THE CATALYSTS

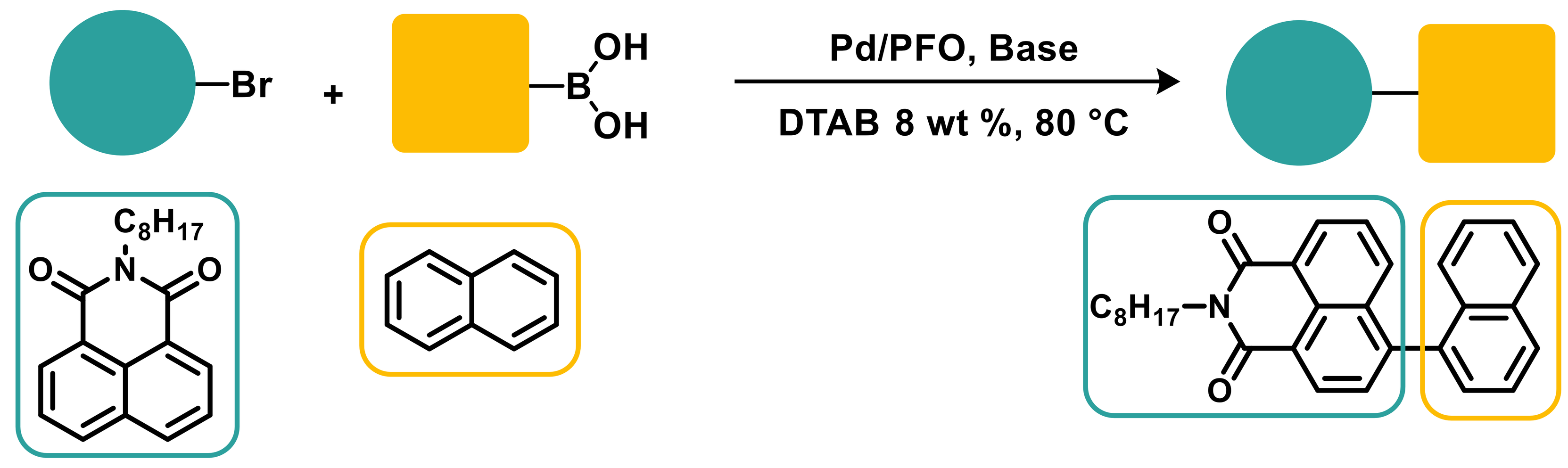
The dispersions have been characterized through DLS, SEM and TEM to check the morphology of the polymeric nanostructures

Poly(9,9-dioctyl)fluorene (PFO) (on the left) and Poly(9,9-dioctylfluorene-alt-benzothiadiazole) dispersion and their fluorescence.



DLS, SEM and TEM of the PFO dispersion after the purification step

EXPLORATION OF CATALYSTS PERFORMANCES



Catalyst	Conversion	By-products	Catalyst recovery
Pd/PFO powder	75 %	Homocoupling traces	1. Water removal through filtration 2. Catalyst recovery through a second filtration thanks to its insolubility in AcOEt
Pd/PFO dispersion	> 99 %	-	1. Water removal through filtration 2. Catalyst recovery through a centrifugation step thanks to its insolubility in AcOEt
Pd/C[a]	62 %	Homocoupling	-
Recycled Pd/PFO powder	40 %	Homocoupling traces	-

[a] Evonik Noblyst - Palladium, 5% on activated carbon (50-70% wetted powder)

CONCLUSION AND FUTURE PERSPECTIVES

Linear aromatic polymeric NPs entangled with branched surfactants forming a semi-interpenetrated network (sIPN) have been synthetised. They proved to act as heterogenized catalyst for Suzuki cross-coupling reactions as they host Pd(0) clusters coming from their synthesis and interacting with the aromatic structure.

The generality of the catalyst is currently under investigation, as far as the fine-tuning of the colloidal structure, the role of phosphines and the Pd leaching phenomena.

REFERENCES

[1] La Sorella, G.; Strukul G.; Scarso, A; Green Chemistry *17*, 2644-683 (**2015**).
[2] MacFarlane, L. R.; Shaikh, H.; Garcia-Hernandez, J. D.; Vespa, M.; Fukui, T.; Manners, I., Nature Research *1*, 7-26 (**2021**).
[3] Behrendt, J. M.; Esquivel Guzman, J. A.; Purdie, L.; Willcock, H.; Morrison, J. J.; Foster, A. B.; O'Reilly, R. K.; McCairn, M. C.; Turner, M. L., Reactive and Functional Polymers *107*, 69–77 (**2016**).