Aerosol Casted Metal Organic Frameworks. A Complete Study from Meso to Microscale.

***Alfonso Garcia Marquez*[a,b]*, Patricia Horcajada*[a]*, David Grosso,*[b,c] *Gérard Férey,*[a] *Christian Serre,*[a]*Cédric Boissiere*[b,c] *and Clément Sanchez.*[b,c]

[a]Institut Lavoisier de Versailles, UMR CNRS 8180, Université de Versailles Saint-Quentin, 45 avenue des États-Unis 78045. Versailles, France. Fax: +331 3925 43 02; Tel:+331 3925 4407.
[b]UMR CNRS 7574 Chimie de la Matière Condensée de Paris. Collège de France, Université Paris 06-CNRS. 11 place Marcelin Berthelot, 75231 Paris Cedex 05, France Fax: +331 4827; Tel: +331 4827.

alfonso-ramon.garcia-marquez@uvsq.fr

Abstract

Metal Organic Frameworks (MOFs) and Porous coordination polymers (PCP) are type 2 hybrid materials presenting a large porosity (S_{BET} up to ~ 6000 m^2g^{-1}; V_p ~ 3.0 cm^3 g^{-1}) as well as easy tuneable topology and composition. Such family represents a plethora of useful compounds for catalysis, separation science or biomedicine.
Usual synthetic methods employed for such compounds are solvo/hydrothermal synthesis, microwave-assisted solvothermal [1], microfluidics [2], ionic liquids, sono-[3], mechano-[4] and electro-chemistry [5], as well as spray drying [6]. The latter, a typical sol-gel synthesis and processing method, allows a lower cost and environmentally friendly continuous-production alternative to the currently employed batch-synthesis. As a main advantage, the versatility of the industrial device allows obtaining a MOF or PCP from either 1 or 2 different precursor solutions. This fact allows control of the reaction time and stoichiometry avoiding rapid completion particularly when the precursors are very reactive.
In this work, three benchmarked MOFs: HKUST-1, ZIF-8 and MIL-100(Fe) polymorph $Fe_3(BTC)_2$ were synthesized via this spray casting method from two separated solutions injected at the same rate into a hot air flow. The aspect of the three product was micrometric diameter hollow spheres, some of them (HKUST-1 and ZIF-8) were constituted of nanocrystals. Some of the activated products presented competitive space time yields with respect to the commercial values reported for the corresponding Basolite analogues. In a second time, $Fe_3(BTC)_2$ like PCP were also synthesized via a template approach using two surfactants: non-ionic Pluronics F-127 and anionic cetyltrimethylammonium bromide (CTAB). The resulting template-assisted PCPs presented hollow sphere shapes and specific surfaces of 600 and 1010 m^2g^{-1}.for F-127-templated PCP and CTAB-templated PCP, respectively, (Figure 1).
Finally, the two template assisted $Fe_3(BTC)_2$ compounds were synthesized at nanoscale using a homemade spray drying device. The obtained particles showed diameters ranging within the nano-submicronic range. Moreover, CTAB-templated $Fe_3(BTC)_2$ presented hierarchically formed spherical pores (Figure 2) attributed to a phase separation between the surfactant and the $Fe_3(BTC)_2$.
A final comparison about the shape differences between the micrometer sized and the submicrometric sized spheres related to the drying process of both devices is also discussed.
In conclusion, this work represents a complete study of aerosol synthesized MOFs and PCPs from the nanometric to the micrometric scale. The space time yields of some of them place this method as a fair alternative to the current batch production of these porous solids.

References

[1] Seo, Y.-K.; Hundal, G.; Jang, I. T.; Hwang, Y. K.; Jun, C.–H; M Chang, J.–S*. Microp. Mesop. Mater.* **119** (2009) 331-337.
[2] a) Witters, D.; Vergauwe, N.; Ameloot, R.; Vermeir, S.; De Vos, D.;Puers, R.; Sels, B.; Lammertyn, J. *Adv. Mater.* **24** (2012) 1316-1320. b) Falcaro. P.; Buso, D.: Hill. A.J.; Doherty, C. M. *Adv.Mater.* **24** (2012) 3153-3168.
[3] Thompson, J. A.; Chapman, K. W.; Koros, W. J.; Jones, C. W.; Nair, S.; *Microp. Mesop. Mater.* **158** (2012) 292-299.
[4] Klimakow, M.; Klobes P.;Thunemann A. F.; Rademann, K.; Emmerling, F. *Chem, Mater.* **22** (2010) 5216-5221.; idem. *Microp.Mesop.Mater.* **154** (2012) 113-118; Yuan, W. B.; Garay, A. L.; Pichon, A.; Clowes, R.; Wood, C. D. *CrystEngComm.* **12** (2010) 4063-4065.
[5] Li, M. Y.; Dinca, M. *J. Am. Chem. Soc.* **133** (2011) 12926-12929.
[6] Carné-Sánchez, A.; Imaz, I; Cano-Sarabia, M.; Maspoch, D. *Nature Chem.* DOI: 10.1038/nchem.1569. Garcia Marquez, A ; Horcajada, P.; Grosso, D.; Férey, G.; Boissière, C.; Sanchez, C. *Chem. Commun*. (2013), Accepted.

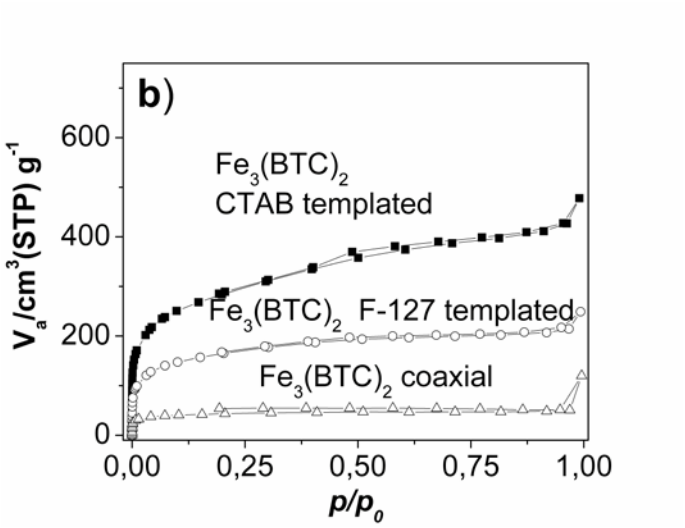

Figure 1. Nitrogen sorption isotherms of activated template synthesized PCPs.

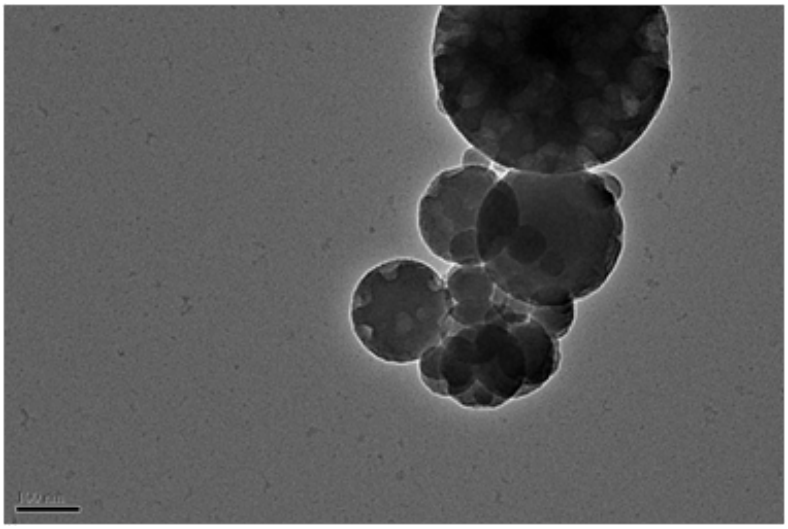

Figure 2. Transmission electron microscopy (SEM) image of CTAB-templated $Fe_3(BTC)_2$.