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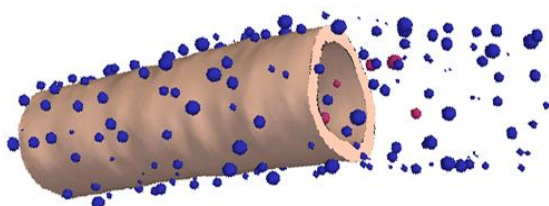
Parameters controlling the location of metal nanoparticles inside or outside hollow carbon nanofibers

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Carbon nanotubes and nanofibers show many interesting properties, which make them attractive supports for heterogeneous catalysis: they are chemically stable in most reaction media and they offer a high surface area as well as a good accessibility to the active phase. Very often, the catalysts are synthesized by simply performing an incipient wetness impregnation with an aqueous solution containing the metal precursor, followed by steps of drying, calcination and reduction. This procedure typically leads to nanoparticles with a narrow size distribution and homogeneously distributed on the surface of the support. However, it is possible to better control the particle size as well as their location inside or outside the nanotube by controlling the solution-carbon support interface energy or the surface chemistry of the support. Both routes have been investigated in the present work.

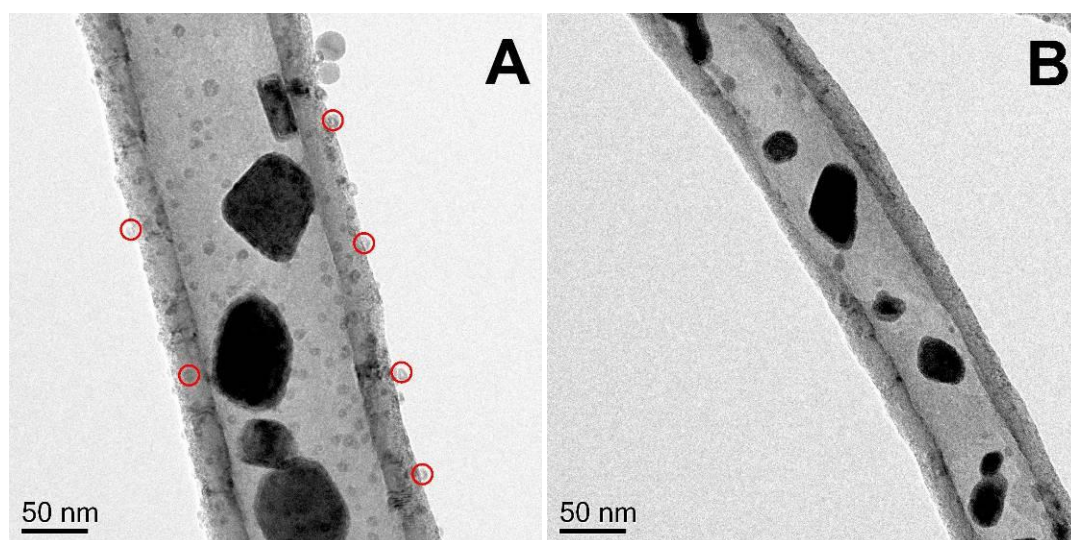
Control of the interface energy. Carbon nanotubes and hollow vapour-grown carbon nanofibers (VGCNF) exhibit a better affinity for organic solvents than for water, even after functionalization of their surface with heteroelements (O or N for example). The resulting difference in the interface energies of organic and aqueous solutions with the VGCNF surface can be employed to disperse nanoparticles either on the inner or on the outer surface, without any chemical modification of the VGCNF surface. Here, the volume of the two phases, aqueous and organic, was accurately controlled in order to fill the nanotube with the organic phase only, while the aqueous solution remains outside.



Model calculated from TEM image series obtained by tomography. 5 nm Ni particles were deposited on the outer surface with a selectivity of 85%.

By simply dissolving the metal precursor in the corresponding phase, it was possible to form Ni particles either inside or outside VGCNFs with a selectivity of 75 to 85%.

Control of the nature of the surface functional groups. VGCFs graphitized at 700, 1500 and 3000°C were functionalized with concentrated nitric acid at 100°C for 16 h. The nature of the O-containing groups was found to depend on the graphitic character of the pristine VGCFs. TG-MS performed in Ar, as well as acid-base titrations and XPS show that the acid groups are not created in the case of the most graphitic supports. The carboxylic acid groups play an important role during the catalyst preparation. They get deprotonated during the step of incipient wetness impregnation, and consequently metal cations present in the solution (here Fe^{3+}) interact strongly with both the outer and the inner surfaces. As a result, metal nanoparticles are deposited on the outer surface, only for the VGCF with the lowest graphitic character. For more graphitic supports, or when these groups are removed by defunctionalization in Ar at high temperature (see below), all the metal is found inside the VGCFs.



Fe nanoparticles deposited on (a) functionalized and (b) defunctionalized VGCFs.

References:

1. J.-P. Tessonnier, O. Ersen, G. Weinberg, C. Pham-Huu, D.S. Su, R. Schlögl, *ACS Nano* 3 (2009) 2081-2089.
2. J.-P. Tessonnier, D. Rosenthal, F. Girgsdies, J. Amadou, D. Bégin, C. Pham-Huu, D.S. Su, R. Schlögl, *Chem. Commun.* (2009), DOI: 10.1039/b916150c.