Diffusion and molecular exchange in hollow core-shell silica nanocapsules

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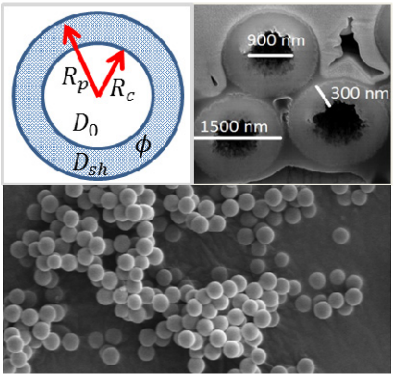

Hollow core-shell silica nanoparticles (HCSN) have recently attracted increasing attention due to their potential applications in many important areas, such as catalysis, drug/gene delivery and medical imaging [1, 2]. Among different properties, diffusive transport of molecular species encapsulated in HCSNs plays often a key role for many processes. In particular, translational dynamics of molecules within the nanoparticles, which is evidently determined by their internal pore structure, controls the rates of chemical reactions occurring within the particles and of drug release rates to the surrounding medium. Due to its appropriate length scale and due to its non-invasive nature, pulsed field gradient nuclear magnetic resonance (PFG NMR) turns out to be a promising experimental technique to probe translational dynamics in HCSNs [3]. The main goal of this work was to explore the potentials of PFG NMR to deliver the transport-structure relationship for small, micrometer-sized HCSNs with well-defined structural properties.

In this work, we present a comprehensive study of the diffusion behavior of perfluoro-crown-ether (PFCE) confined in 1.5 micrometer-sized hollow mesoporous silica spheres (HMSS, see figure) using PFG NMR. By purposefully selecting the liquid saturating the hollow core and the porous shell and the solvent between the nanoparticles, two different situations corresponding to the excluded and admitted molecular exchange between the intra- and inter-particle liquids at the external boundary of the nanoparticles were covered.

In the former case, corresponding to the reflective boundary condition for the molecules approaching the nanocapsules boundary, restricted diffusion in the complex pore space formed by the hollow core and the porous shell was observed. A very high uniformity of the structural details over the whole ensemble of HMSSs allowed to establish the accurate relationship between the physical quantities measured by PFG NMR and the structural properties of HMSSs. In this way, the analysis of the time-dependent diffusivities measured using PFG NMR yielded the structural information, namely on the nanoparticle sizes and the shell thicknesses, which were found to be in a good agreement with the data obtained using electron microscopy. In the second case considered, i.e. in the presence of the molecular exchange at the external particle boundaries, we have probed the long-time release rates of the PFCE molecules from the nanoparticles. In addition we discuss how the diffusion behavior of the molecules remaining in the nanoparticles is coupled to their pore structure and how these transport-structure correlations can be assessed using PFG NMR.

References

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