Nanoporous materials comprise an extremely important class of functional solids suitable for a wide range of key technological applications including gas storage/separation and other sorption processes. The CarbonCROFs project aimed at the rational design and development of novel open-framework solids including metal organic-, zeolitic imidazolate- and covalent organic-frameworks as well as their smart combination with carbon nanostructures (mainly carbon nanotubes and graphene) towards advanced, multifunctional hybrid nanoporous materials. The combination of the unique and diverse physical and chemical properties of the selected carbon nanostructures (such as high surface area, and increased chemical and mechanical stability) in conjunction with the remarkable properties of the various types of Crystalline, Open-Framework solids (CROFs) yielded tailor made, composite materials exhibiting very promising potential especially for gas storage and separation. The overall project’s strategy involved the suitable chemical functionalization of the carbon nanostructured materials using “click chemistry” methods and the subsequent use of the synthesized chemical derivatives in solvothermal and/or sono-chemical reactions in the presence of the corresponding molecular precursors (for MOFs and ZIFs these were metal salts and bridging organic linkers while for COFs boronic acids and catechol-like molecules) for the development of the final Carbon-CROFs composites. In all evaluated cases, the suitably functionalized carbon nanostructures, acted as either one-dimensional (carbon nanotubes) or two-dimensional (graphene) templates for the nucleation and subsequent growth of the composite CROFs crystals. A critical prerequisite for the development of all composite CROFs, required the high yield chemical functionalization of the chosen carbon-based substrates using well established and widely accepted chemical protocols. Those protocols involved the use of common synthetic methods known under the term of “click chemistry”.

Various potential synthetic routes for the development of Carbon-CROFs composites were explored involving mainly *in-situ* synthetic approaches. Those synthetic routes involved the use of the previously functionalized carbon nanostructures as 1D or 2D templates for the nucleation of the structural building units of the chosen CROF resulting to the formation of the final composites. Within this context, the chemically functionalized carbon nanostructures were added into the corresponding reaction mixtures used for the development of bulk CROFs. Important synthetic parameters, including the concentration of the functionalized carbon nanostructures in the initial mixture, the solvent, temperature and reaction time, were systematically examined in order to define their optimum values. The structure of the resulting CROFs composites were studied and confirmed with a combination of analytical and advanced characterization techniques.

In addition to the structural/morphological characterisation described above the textural/porous properties of all CROFs composites were also studied by systematic N2 and Ar adsorption/desorption measurements at 77 K and 87 K respectively. Those measurements allowed the determination of critical characteristics of nanoporous materials such as BET specific surface area, (micro-, meso-, total) pore volumes and pore size distribution. Moreover detailed sorption measurements for selected technological important gases (N2, CO2) were also carried out. Both low and high (up to 200 bar) pressure adsorption/desorption isotherms were recorded at different temperatures from which were calculated the total capacities, the isosteric heat of adsorption and selectivity for the respective gases at the different evaluated conditions.

In terms of socio-economic impact, modern societies show increased attention to health aspects, quality of life and environment protection and in combing economic growth with environmental benefits. In this perspective, driven both by human, political and environmental concern, the fellowship combined and integrated specific knowledge, knowhow and expertise to make real advances in the development of novel nano-porous materials for environmental applications, and especially for gas storage/separation. Significant advances were achieved in this technologically important field in terms of developing novel, hybrid nanoporous materials comprised from carbon nanostructures and crystalline open framework solids (COFs, ZIFs and MOFs). Although the developed novel nanoporous adsorbents fall in relatively low technology readiness level (TRL=4, validated in lab) in the near future is strongly expected to reach higher TRLs due to their very promising performance and thus make significant impact in the environmental sector both in EU and worldwide.

