Cryoextraction and supercritical drying: a novel hybrid process for processing of porous materials

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Low-temperature supercritical drying (SCD) with CO_2 remains the golden standard for processing of wet gels into corresponding aerogels [1]. In a typical protocol, a gel is first prepared from nano-scaled building blocks in an organic medium or water followed by a solvent exchange with a light organic solvent, usually ethanol. At the final step the solvent is extracted in a dynamic process with the process conditions above the critical point for the binary CO_2/solvent mixture, typically at 100 – 150 bar and 40 – 60 °C.
The described pathway preserves a considerable amount of the space between the building blocks created at the gelation step and results in highly porous materials (aerogels). Such a pathway is however fundamentally limited as the starting material must have ability to form a gel [2]. The aim of this work to pave the way for the processing of any kind of starting materials into aerogels.

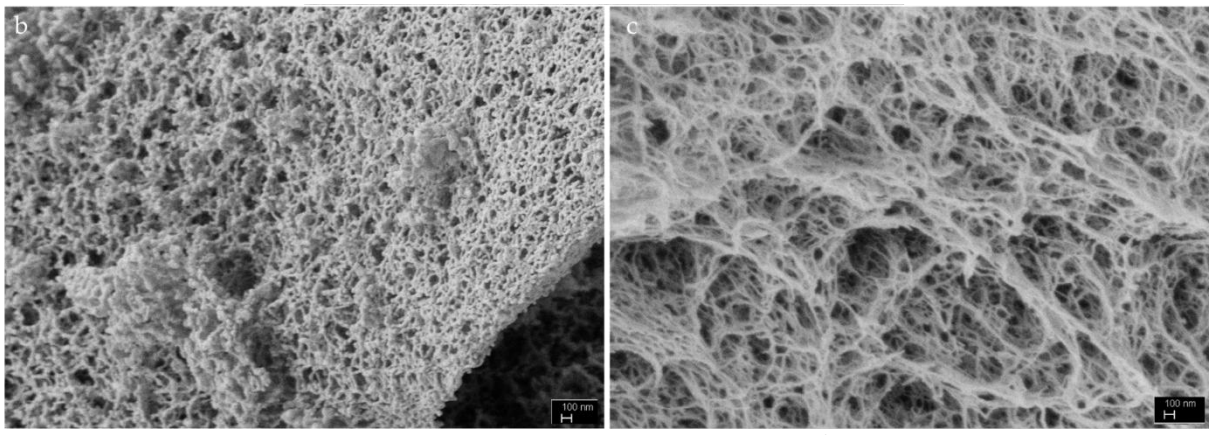

Figure 1: Porous structure of porous materials from the hybrid cryoextraction/sc-drying process (scale bar: 100 nm)

The core idea of the novel approach is to dissolve or disperse the starting material in a pure or mixed solvent with a moderate melting point (0 – 25 °C). The mixture is then frozen and subjected to cryoextraction with an organic solvent as extracting agent (e.g., acetone) or directly with liquid/sc-CO_2. The cryoextraction temperature is determined from corresponding solid-liquid equilibrium data. Finally, the extracting agent recovered in the SCD process leaving behind a highly porous matrix (Figure 1).
We exemplify the suggested approach by processing industrial polymers and some low-molecular weight compounds into novel nanoporous materials. In many cases such materials can be processed in a fully water-free manner what remain a challenge in conventional approaches. We discuss how the pore size and morphology can be controlled by the solvent composition and how the process parameters can be deduced from phase equilibria data.

[1] Smirnova, I., Gurikov, P.; *Annual Review of Chemical and Biomolecular Engineering* **2017,** *8*, 307 – 334.
[2] Gurikov, P., Smirnova, I.; *Gels* **2018,** *4*, 14.