

Hierarchically porous monolithic microstructures as catalysts for intensified syngas-to-liquid processes



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The assembly of macroporous microstructures by directional freeze-casting (DFC) methods attracts interest in areas from life science to energy storage.^[1] The aim of this project is to explore the application of such hierarchical structures as solid catalysts. Their ordered macroporosity can offer advantages in catalytic processes such as the Fischer-Tropsch synthesis (FTS), for which pore mass-transport phenomena are determinant for activity and product selectivity. Ultralight, macro-mesoporous micromonoliths have been prepared with hybrid ZrO₂-Al₂O₃/carbon-nanotube (CNT) backbones by directional freeze-casting and annealing. The use of Zr(acetate) as ice growth modulation agent led to tubular macroporosity while mesoporosity and high surface area were realized with γ -Al₂O₃ after annealing. The conductive CNT component improves mechanical stability and thermal conductivity, of relevance for reactions with high thermal signatures such as the FTS. After incorporation of cobalt FTS-active species by impregnation, EDX spectroscopy verified the metal deposition within the ZrO₂-Al₂O₃ mesoporous monolith walls. X-ray microtomography, coupled to quantitative image analysis, correlated structural features (e.g. wall thickness and diameter of pore) to directional cooling rates, revealing complex vertical propagation of the macropores with notable deviations from the monolith axial direction. The results shed new light into freeze casting methods and show their potential in the field of heterogeneous catalysis.

I. Directional freeze-casting: concept and experimental setup

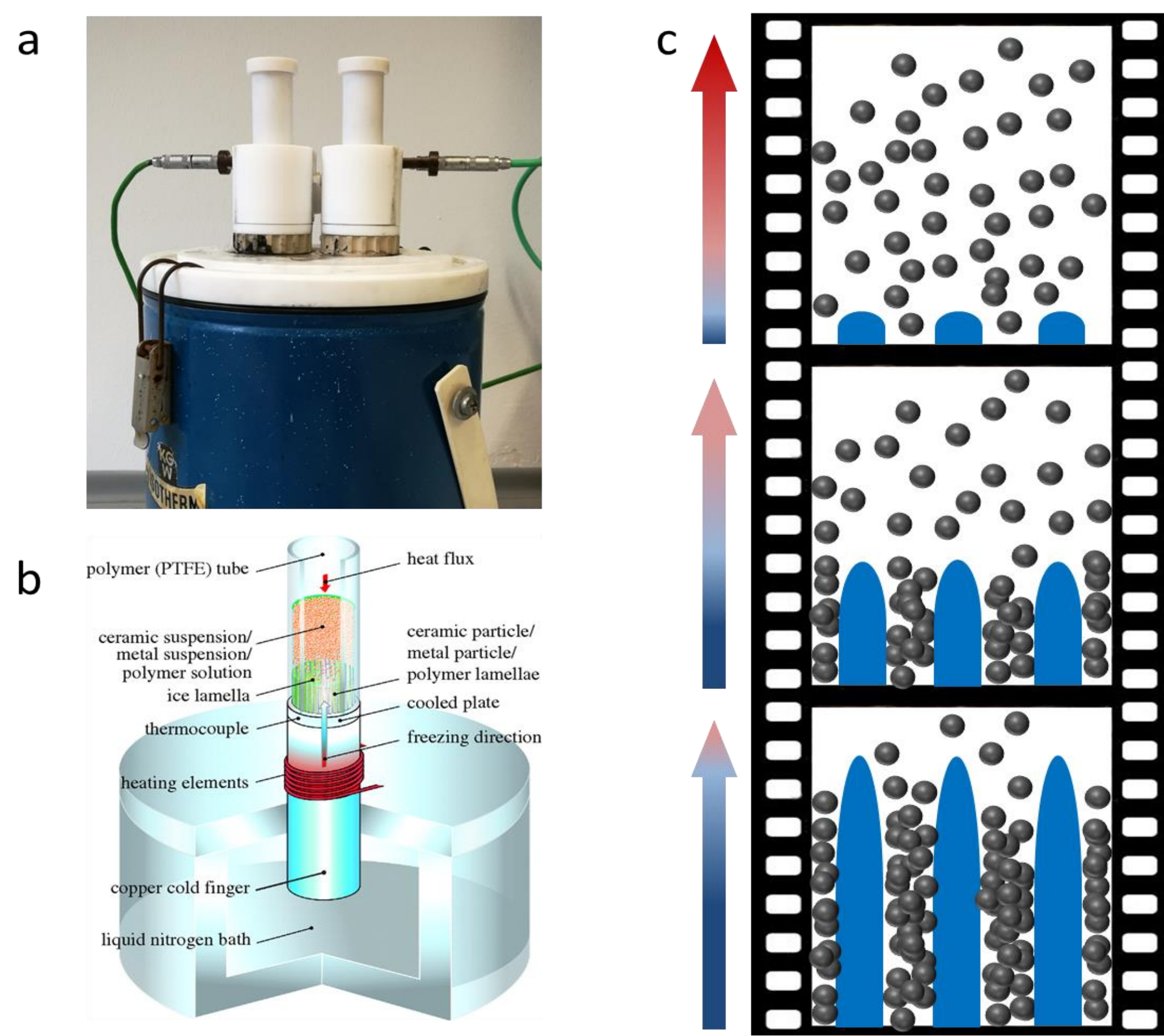


Figure 1 : (a) Picture and (b) schematic diagram of the setup employed for the directional freeze-casting assembly of microstructured catalysts. The precursors suspension is poured in to a PTFE tube and placed on flat copper rods connected to a cold finger. The cooling rate is controlled by the interplay of liquid nitrogen and heating elements around the Cu cold finger.^[2] (c) Top-down: microscale scheme of ice development during a directional freeze-casting experiment.

II. Hierarchically porous γ -Al₂O₃-ZrO₂/CNT monoliths by directional freeze-casting



Figure 2 : Pictures illustrating the lightweight and mechanical compliance of micromonolith catalysts.

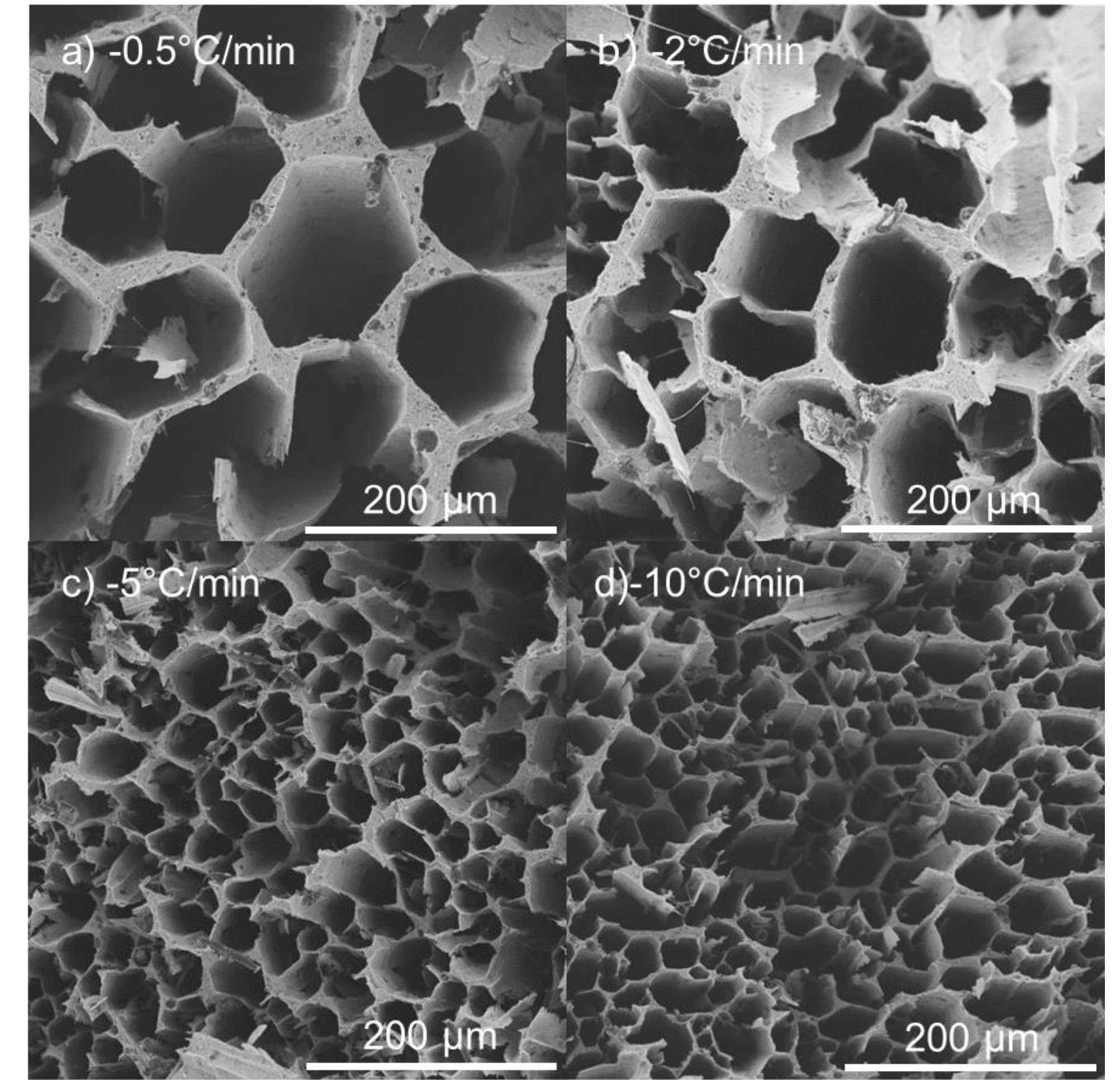


Figure 3 : Scanning Electron Microscopy (SEM) micrographs along the basal direction of monoliths synthesized at different cooling rates: (a) -0.5 (b) -2 (c) -5 (d) -10 K/min

III. X-ray tomography: quantitative insight into the internal structure of micromonolithic catalysts

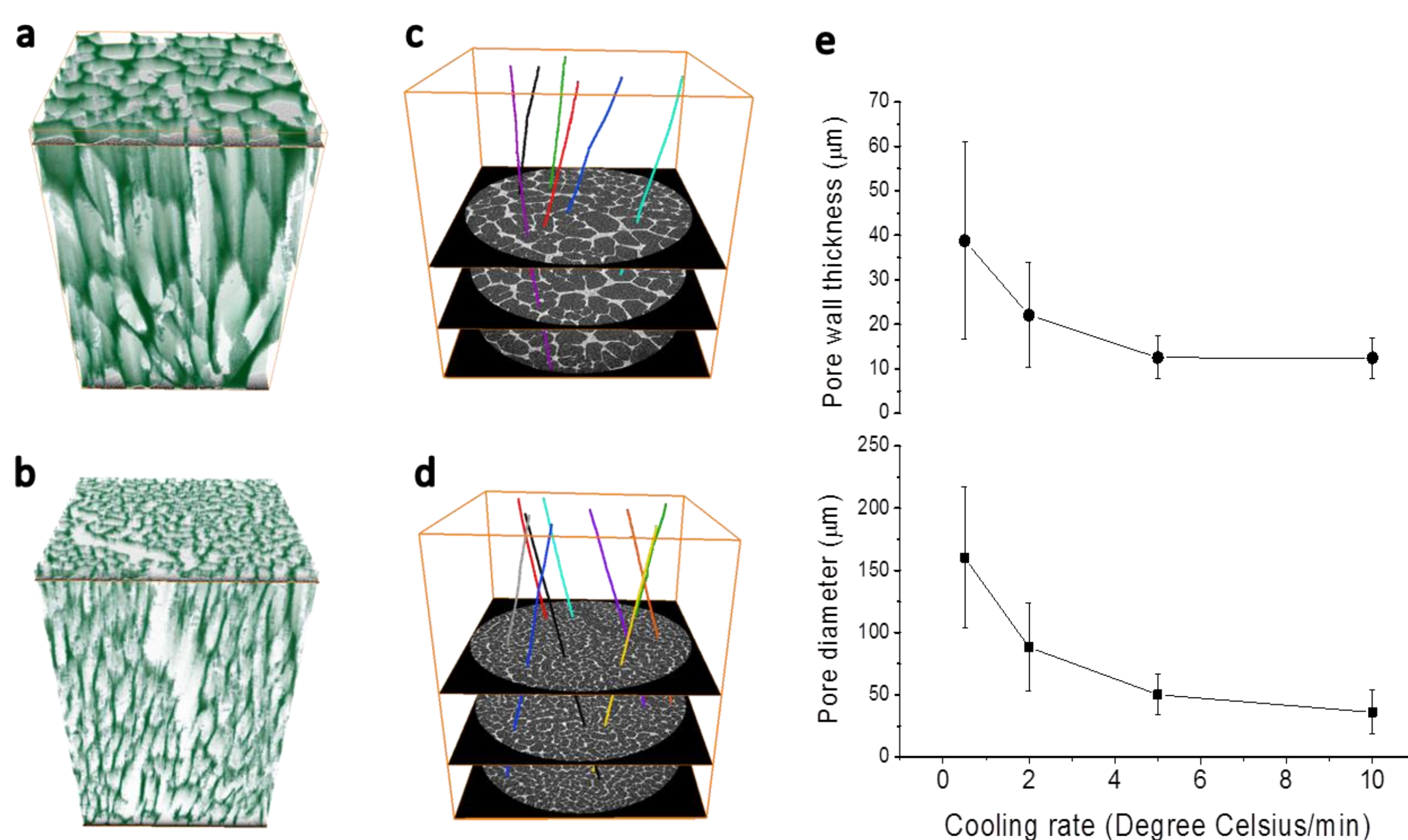


Figure 4: (a,b) 3D-rendered reconstructed X-ray tomograms for micromonolith catalysts obtained by directional freeze-casting using cooling rates of (a) 2 and (b) 10 K/min. (c,d) Reconstructed trajectories of the cross-sectional center of mass of selected macropores. (e) Evolution of the macropore diameter and pore wall thickness with the casting cooling rate as derived from quantitative image analysis. Error bars correspond to the standard deviation.

IV. Meso- and nano-spatial distribution of different components in hybrid γ -Al₂O₃-ZrO₂/CNT Fischer-Tropsch micromonolith catalysts

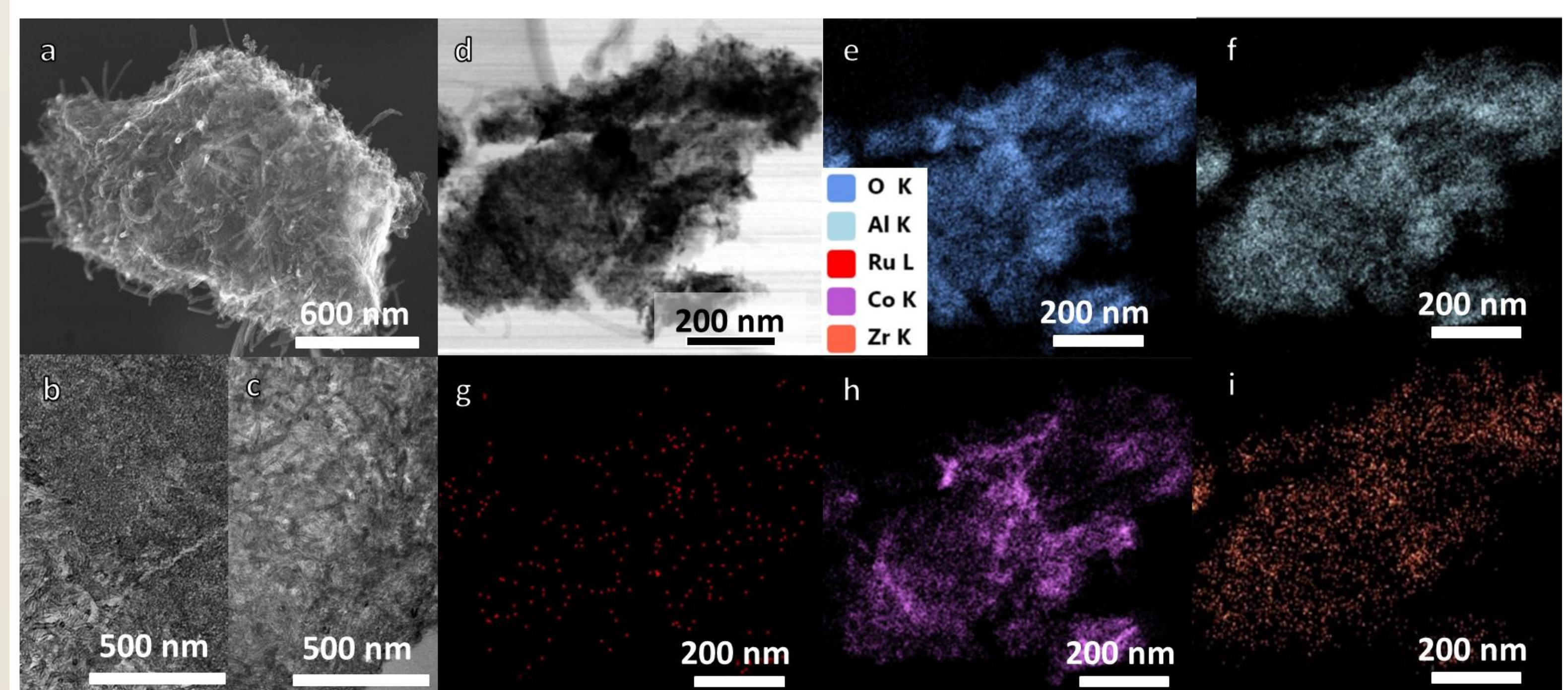


Figure 5: (a) High-resolution SEM micrograph of a piece of the γ -Al₂O₃-ZrO₂/CNT backbone of the monolith catalysts. Transmission Electron Microscopy (TEM) micrographs of microtomed slices of monoliths (b) with mesoscale-segregated γ -Al₂O₃ and CNT components and (c) with nanoscale intimate γ -Al₂O₃ and CNT components achieved by ultrasonic disruption and the addition of polyvinylpyrrolidone as a surfactant during the pristine dispersion. (d-i) Elemental EDX-spectroscopy mapping showing the nanospatial distribution of all components in a micromonolith Co-based FTS catalyst in the final activated catalyst.

References

- [1] M. Klotz, I. Amirouche, C. Guizard, C. Viazzi, S. Deville, *Adv. Eng. Mater.* **2012**, 14, 1123.
- [2] U. G. K. Wegst, M. Schecter, A.E. Donius, P. M. Hunger, *Phil Trans. R. Soc. A* (2010) **368**, 2099–2121