Abstract

The Earth is threatened by climate change: global warming and ocean acidification are some of the dramatic effects linked to it. One of the main causes is the increasing atmospheric concentration of greenhouse gases such as CO_2. Carbon capture and sequestration have emerged as valuable mitigation solutions. Thus, the aim of this PhD thesis is to realize a hierarchical porous system for CO_2 capture, based on porous mullite ($3Al_2O_3 \bullet 2SiO_2$) substrates additively manufactured by Digital Light Processing and appropriately functionalized with Metal Organic Frameworks (MOFs).

Mullite scaffolds were successfully printed starting from the optimization of the slurry formulation. A ceramic load of 69 wt% dispersed into a photocurable commercial resin (with 5 wt% of dispersant and 1 wt% over the ceramic load of MgO as sintering additive) allowed a viscosity compatible with the shaping process (< 3 Pa s at 160 s^{-1}) and a shear thinning behavior. Powders calcination has proved to be an essential pre-treatment to improve the printed bodies' quality, in terms of uniform microstructure, higher densification (from ca. 50% to 60%) and reduced delamination defects. Then, different mullite geometries were accurately realized: from simple shapes (bars and pellets) to monoliths with complex and interconnected macroporous structures, such as traditional grid-like and innovative TPMS (Schwartz primitive and gyroid types).

The investigation of HKUST-1 two-step solvothermal synthesis led to the production of grown crystals with improved SSA (from 1,000 of the seeds crystals to 1,200 m^2/g) and CO_2 adsorption properties (from 3 to 4 mmol/g at 100 kPa).

The main originality of the work lies in the functionalization of mullite scaffolds with a continuous and well adherent HKUST-1 coating, which was investigated and promoted by different strategies. The role of mullite powder's chemical

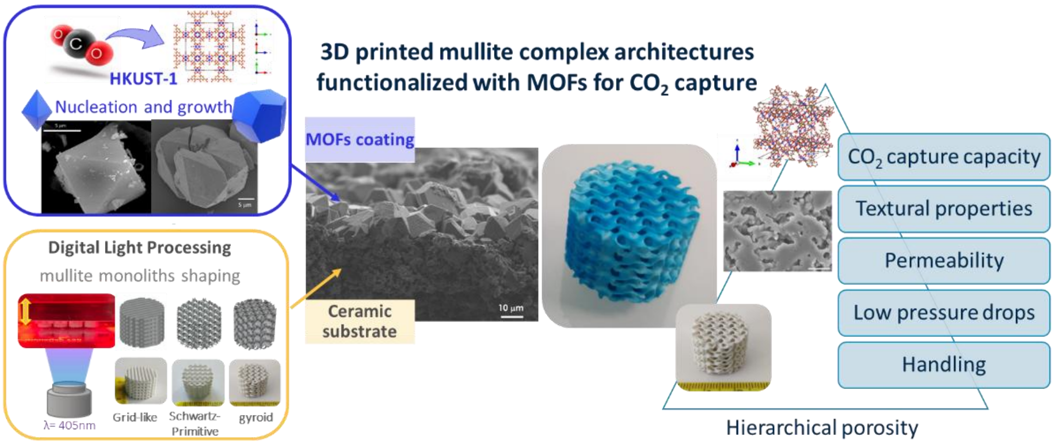
composition, in terms of Fe_2O_3 impurities, and substrate porosity was crucial to promote HKUST-1 deposition. The easy tuning of scaffold microstructural porosity by reducing the sintering temperature (from 1450°C to 1350°C) is here proposed: nevertheless, despite improvement of HKUST-1 mass deposited on printed pellets (from ca. 2 to 3.5 wt%), the increased porosity of the substrates was accompanied by a loss of mechanical strength.

Mullite scaffolds were provided with textural and adsorption properties proportionally to the sorbent deposited mass, since microporosity conveyed by the continuous MOFs film was fully accessible. The geometry of the scaffold was demonstrated to play a significant role: TPMS structures more than doubled deposited MOFs weight percentage respect to grid-like ones, due to the high SSA and smooth sharp edges-free surfaces. Two different TPMS were compared, Schwartz and gyroid: the latter one was slightly better in terms of deposited HKUST-1 (up to 4 wt%), consequently providing higher SSA and CO_2 adsorption (ca. 50 m^2/g and 0.2 mmol/g).

Adsorption tests under different gas flows (10, 20, 40, 50 mL/min), temperatures (32°C, 60°C, 80°C) and CO_2 volumetric percentages (1 and 100%) were crucial in defining the physical properties effectiveness of the CCS system. Monoliths were more efficient than traditional powder bed: they limited pressure drops (160 vs 880 kPa/m, respectively at 32°C and 10 mL/min) and reduced gas speed (< 1.5 cm/s vs >2 cm/s, respectively), while increasing the contact time and promoting interaction with sorbable gas. In bench tests CO_2 uptake was increased of 40.1% and 51.3%, respect to HKUST-1 powder bed, for grid-like and TPMS geometries, respectively; CO_2 retention time measured in gas chromatographic evaluation increased from 7 s/g for the powder bed, to 30 s/g for gyroid monoliths. TPMS, specifically the gyroid, provide the best performances.

In addition, microporous coating on mullite architectures was also realized with MIP-202, a valid alternative to HKUST-1: the protocol and the strategy here proposed resulted highly versatile, opening possibility of specific functionalization.

Despite further investigations are required to improve the performance of the proposed hierarchical system, the present doctoral thesis effectively developed an innovative strategy for CCS combining MOFs with complex and porous ceramic architectures realized by DLP.



Graphical abstract