DLP 3D-Printed Mullite Ceramics for the Preparation of MOFs Functionalized Monoliths for CO_2 Capture

Supplementary information

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1. Results and discussion

1.1. Powders characterization

Figure S 1 highlights the differences in coloration between the powders, which is due to the compositional differences and impurities.

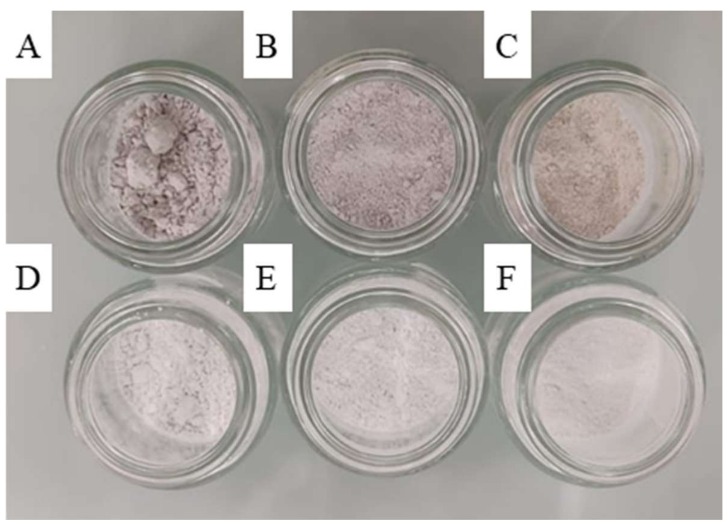

Figure S 1 Mc (up) and Mf (down) mullite powders in as-received (A,D), ball-milled (B,E) and calcined (C,F) forms.

1.2. Pressed and 3D printed pellets: characterization and sintering behaviour evaluation

Mercury Intrusion Porosimetry (MIP) was used to study mullite pressed pellets porosity as a function of the sintering temperature. Incremental mercury intrusion graphs **Figure S 2** show a noticeable decrease of peak area and peak shift to higher pore sizes when increasing the sintering temperature from 1350°C to 1400°C, 1450°C and then to 1550°C. This confirms the lowering of pore area and the increase of average pore size, due to partial densification, when a higher sintering temperature is employed.

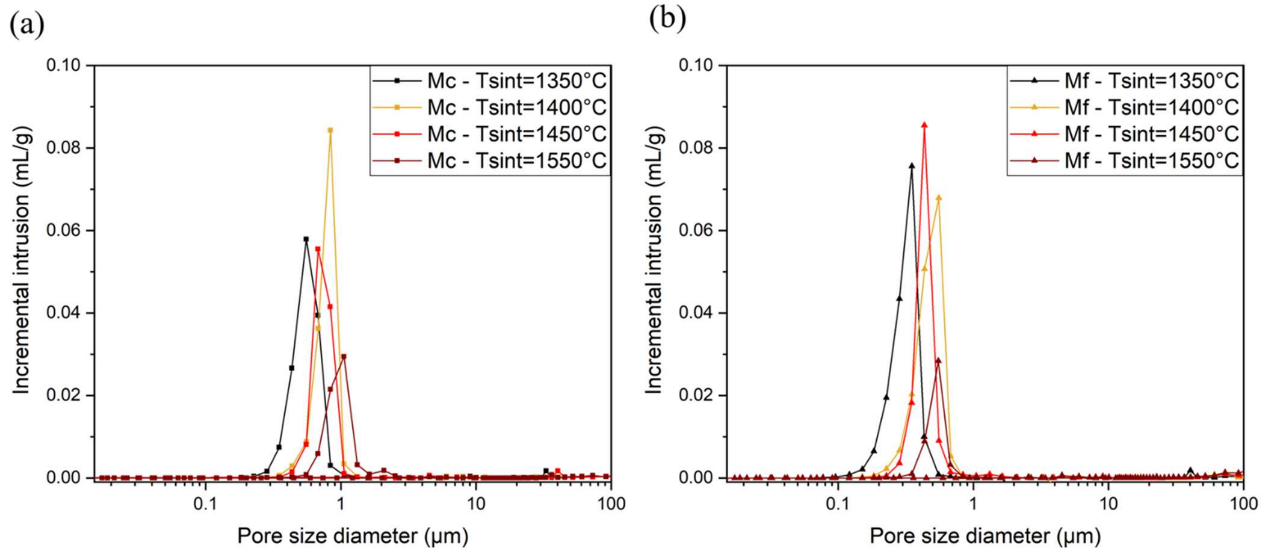

Figure S 2 Porosity distribution determined by MIP of Mc (a) and Mc (b) pellets sintered at 1350, 1400, 1450 and 1550°C (respectively black, orange and red curve).

1.3. Substrate characterization: effect of sintering temperature on MOFs functionalization

HKUST-1 crystals adhesion on mullite substrates was evaluated through FESEM observations for samples realized by pressing and 3D printing technique, respectively shown in **Figure S 3** and Error! Reference source not found. (main manuscript). An effective formation of a thin coating was successful for all the samples, since all the micrographs confirmed the presence of MOFs crystalline layer on mullite microstructure. Independently to the shaping process, highly porous substrates promote HKUST-1 crystals adhesion and growth within mullite interparticle cavities. Regarding the pressed samples (**Figure S 3**) crystals adhesion seems more important for pellets sintered at lower temperatures, especially 1350 °C (**Figure S 3 A, B, I, L**), consistently with what is expected from density data. Higher porosity enhances MOFs deposition, confirming firstly for pressed pellets the expected sintering temperature effect on MOFs functionalization. Considering 3D printed samples, a higher quantity of crystals can be observed when compared to the pressed samples. Thus, comparing Error! Reference source not found. with **Figure S 3,** due to the differences introduced by the shaping processes, a higher crystals quantity can be noticed for 3D printed samples, and better coating quality in terms of both continuity and MOFs/mullite adhesion.

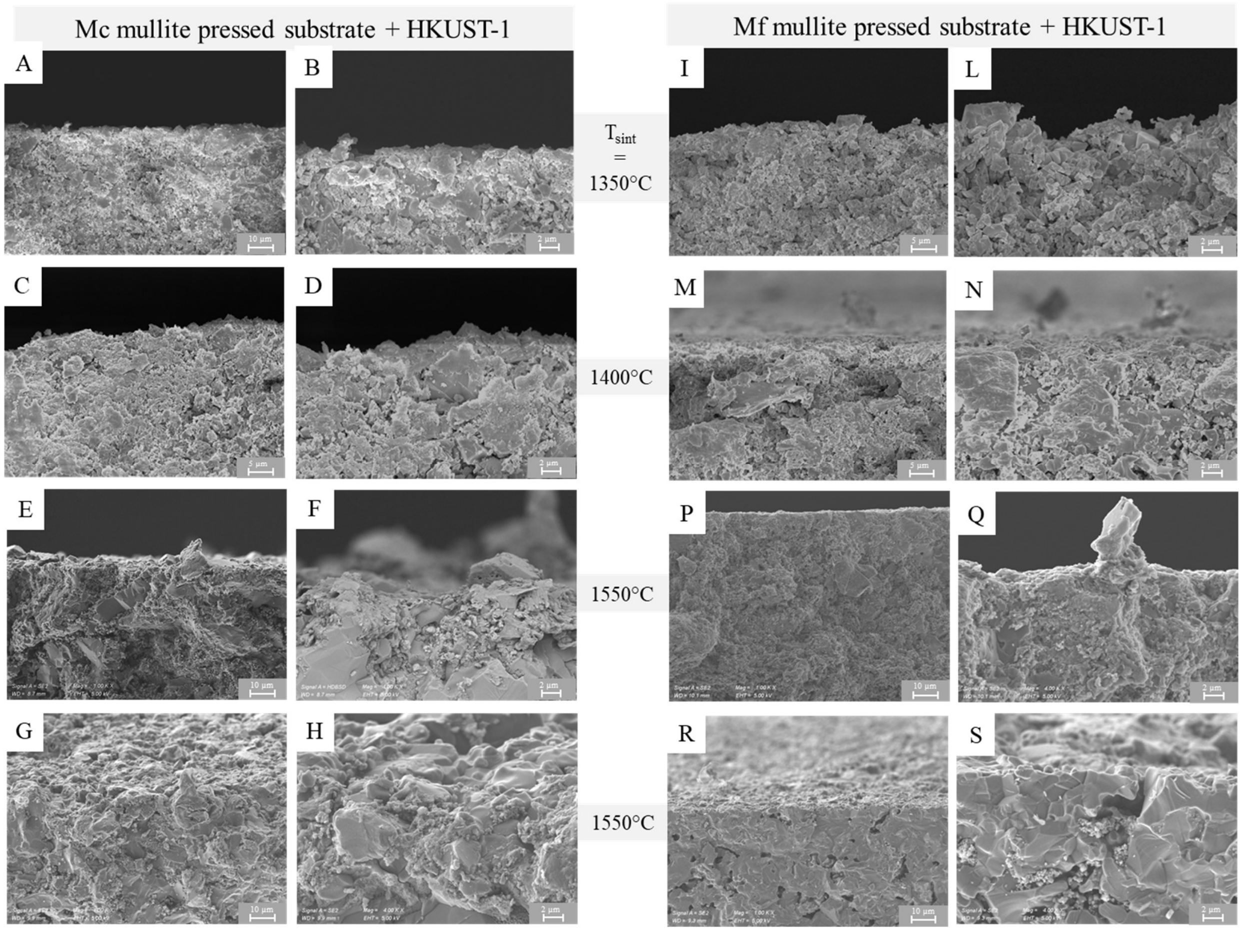

Figure S 3 FESEM micrographs of HKUST-1 crystals on mullite shaped substrates (Mc on the left and Mf on the right) sintered at 1350°C (A,B,I,L), 1400°C (C,D,M,N), 1450°C (E,F,P,Q), 1550°C (G,H,R,S).