Printing of microscopic POCS from copper using scan line patterning for the intensification of gas phase reactors.

Alexander Limper[1], Lukas Portheine[1], Anselm Brodersen[1], Francesca Zaio[1,3], Robert Keller[1], Matthias Wessling[1], Alessandra Beretta[3], Gianpiero Groppi[3], Matteo Ambrosetti[3], John Linkhorst[1,2,*], Enrico Tronconi[3,*],

1 Chemical Process Engineering, RWTH Aachen University, Forckenbeckstraße 51, 52062 Aachen, Germany;
2 Process Engineering of Electrochemical Systems, TU Darmstadt, Otto-Berndt-Straße 2, 64287 Darmstadt, Germany;
3 Politecnico di Milano, Dipartimento di Energia, Via Lambruschini 4, 20156 Milano, Italy

**Corresponding authors: john.linkhorst@tu-darmstadt.de, enrico.tronconi@polimi.it*

Highlights

- A new method for metal SLM produces lattices with dimensions of few hundred micrometers.
- Specific surface areas are competitive with commercial metal foams.
- The application of a copper structure to methane steam reforming is demonstrated by modelling

1. Introduction

The design of cellular substrates for catalytic flow reactors gains significant freedom with additive manufacturing, allowing to boost the process performances thanks to optimized flow patterns and high surface area available for catalyst deposition. To provide large specific surface areas and efficient mass transport to the catalyst surface, the direct control of the microstructure is essential. Periodic open cellular structures (POCS) represent a concept for substrates with a regular structure which may be beneficial for mass transport. The conventional manufacture of these structures has so far been limited to characteristic sizes in the order of 1 mm (e.g., strut diameter or cell size), and the definition of the geometry requires large STL files. In our recently published work [1], a novel method for selective laser melting (SLM) is presented to produce highly porous ordered structures from stainless steel and copper, with characteristic sizes in the range of 100 µm and specific surface areas that are comparable to metal foams. By exploiting the patterned nature with which the scan lines are arranged in the printer, the technique allows to drive the scan lines through regular patterns that create periodic open cellular structures implicitly.

In this work, the SLM technique is applied to obtain Cu-POCS that provide increased surface areas and eliminate the problem of defects, such as overhanging structures. Furthermore, we explore the potential of POCS structures with axial profiles of the design (including the cell opening and/or geometry), in order to tailor and optimize the POCS transport properties. Here we address a modelling analysis to quantify the possible benefits of applying Cu-POCS with axial grading of cells from 500 µm to 1 mm (d_{cell}) as conductive internals in small-scale steam reformers for the distributed H_2 production.

2. Methods

POCS structures with tilted edges were realized by defining the laser path in intermittent lines that shift incrementally by 0.02 mm with each layer, creating struts with a 45° angle towards the XY plane. By defining the laser exposition for 50 µm and the gap between exposed lines to be 450 and 950 µm, respectively, cell sizes of 500 and 1000 µm are achieved, with strut sizes between 100 to 200 µm and porosity equal to 82% and 91% respectively. The total dimensions of the substrates were an outer diameter of 36 mm and a length of 80 mm. Tilted POCS with cell diameter equal to 1 mm were also tested in non-reactive heat transfer measurements to evaluate the influence of gas-solid heat transfer on the overall heat transfer performances of the support. Then, numerical simulations of a compact methane steam reformer (SMR) loaded with catalysts based on such structures, using a 2D heterogeneous reactor model, were carried out on a configuration ($d_{reactor}$ = 6 cm, L = 1 m) where the first half section is made up of a cubic POCS structure with a cell size of 0.5 mm and the second one has a cell size of 1 mm. Experimental and model operating conditions were the same as reported previously [1].

3. Results and discussion

Figure 1a depicts the printed Cu reactor substrates, which were printed with and without skin. The specific surface area of the printed structures was determined to be as high as 16 000 m^2/m^3 for the cell size of 500 µm, at a porosity of 82%. The microstructure of the reactor was determined via scanning electron microscopy (SEM) on a representative structure shown in Figure 1b. Heat transfer performances of these supports were measured to be about 7 times higher than a packed bed reactor operated in the same flow regime (overall heat transfer coefficient for Cu POCS and packed bed reactor equal to 241 $W/m^2/K$ and 34 $W/m^2/K$, respectively). SMR simulation results for the catalyzed structure are presented in Figure 1c. The average volumetric heat duty and the external heat flux (8.6 MW/m^3, 129 kW/m^2) are in excess of commercial reformers [2,3], despite the significantly lower length (1 m). The system shows an outer skin temperature well below the material constraint (around 1000°C); methane is almost fully converted (conversion = 88.6%) with a pressure drop along the reformer of less than 1 bar.

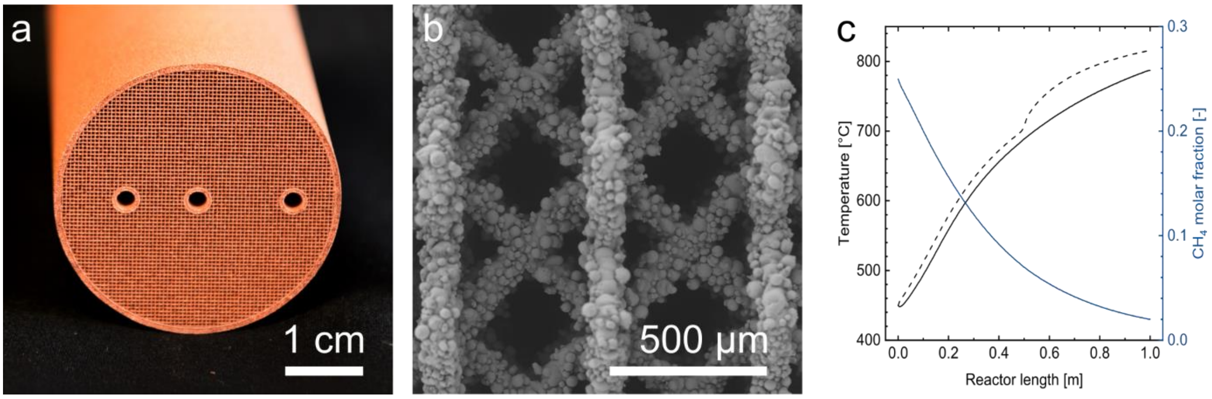

Figure 1. a: Printed Cu POCS reactor with a cell size of 500 µm. b: SEM image of the microstructure inside the POCS reactor, with tilted struts and a cell size of 500 µm. c: Simulation results for the composite structure: skin and cupmix axial temperature profiles (dashed and solid black line, respectively) and methane molar fraction (blue solid line)

4. Conclusions

Here, we present the advancement of our previously reported method to create high-surface metal substrates by selective laser melting, in view of applications to gas phase catalytic reactions. The possibility to produce heterogeneously defined porous parts is first explored by a simulation model of a full-scale reactor and then applied in a lab-scale test rig. Thanks to its solid outer wall, the radial heat transfer of the structure is greatly increased in comparison to commercial foam samples, at significantly lower pressure drop. Moreover, the composite structure with axial grading of the cell size allows for tailored design of the heat transfer properties, e.g., for obtaining higher transport properties at the reactor inlet, where the heat demand from an energy intensive reaction like steam reforming is more intense.

References

[1] A. Limper, A. Brodersen, F. Zaio, M. Ambrosetti, J. Linkhorst, J. Chem. Eng. 480 (2023) 148039.
[2] S.T. Wismann, J.S. Engbæk, S.B. Vendelbo, W.L. Eriksen, C. Frandsen, P.M. Mortensen, I. Chorkendorff, Ind. Eng. Chem. Res. 58 (2019) 23380-23388
[3] F. Minette, L.C. de Almeida, J. Feinstein, J. de Wilde, Adv. Chem. Eng. 10 (2022) 100258

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Selective laser melting; POCS; Additive manufacturing; Heat transfer.