Direct Ink Writing (DIW) of shaped catalysts for multiscale transport optimization

Yoran De Vos[1*], Luca Mastroianni[1,2], Jurjen Cazemier[1], Arturo Pajares[1], Linsey Garcia-Gonzalez[1]

1 Flemish Institute for Technological Research – VITO NV, 2400 Mol, Belgium; 2 Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Åbo Akademi, 20500 Turku/Åbo, Finland.

**Corresponding author: Yoran.devos@vito.be*

Highlights

- Direct Ink Writing (DIW) is a breakthrough technology for catalyst shaping
- Hierarchical porosity is introduced to enhance intra-fiber mass transport
- Diffusional pathways are minimized by introducing fine features (< 400 μm)
- The benefits of DIW and hierarchical porosity are demonstrated for multiple case studies

1. Introduction

Optimizing the performance of chemical processes involving heterogeneous catalysts requires navigating a complex landscape of events occurring across multiple scales, including fluid-solid mass transfer, axial dispersion, diffusion in catalyst pores, and the chemical reaction per se. In classical packed bed reactors, small catalyst particles enhance mass transfer rates, but the pressure drop increases significantly as particle size decreases. Catalyst shaping by 3D printing offers an attractive opportunity for process intensification, as the conflicting requirements for high mass transfer rates and low pressure drop can be decoupled through the design of new catalyst architectures. Among available printing technologies, Direct Ink Writing (DIW) enables the production of catalyst structures with high porosity while maintaining mechanical strengths within the typical strength-porosity window of conventionally manufactured catalyst bodies [1]. In this work, we showcase several advances in geometry and porosity control for DIW catalyst structures, significantly extending the design space of classical 3D-printed architectures. Novel ceramic inks were formulated to introduce controlled porosity in the printed fibers, enhancing intra-fiber transport without overly compromising mechanical strength. Moreover, we move beyond classical fiber diameters, demonstrating the possibility to print fine features that minimize diffusion pathways and potentially increase geometrical freedom. The performance of the different printed catalysts was demonstrated in continuous experiments across different projects for different chemical applications including Fischer Tropsch, Methanation and lignin-depolymerization.

2. Methods

Printing inks were prepared by mixing catalyst or support particles together with binders and water in a planetary centrifugal mixer until a homogeneous paste is obtained. The exact composition of the ink depends on the specific catalytic application. 3D printing was performed with 3D material extrusion printers, stacking layers of fibers in different orientations to obtain catalyst bodies with predefined geometries and a regular, engineered internal architecture. After the printing process, the obtained monoliths were dried under controlled conditions and subsequently calcined. Depending on the application, further excess-solution impregnations and calcinations were performed to obtain the desired composition. The final catalyst bodies were characterized using techniques such as ICP, XRD, N_2-sorption, H_2-TPR and Hg-intrusion porosimetry to assess their composition and textural properties. Kinetic experiments for performance evaluation were carried out in continuous reactors under well-defined temperatures, pressure and space velocities.

3. Results and discussion

The 3D printed structures were tested for multiple applications, both in the gas phase (i.e., reverse water gas shift and CO_2 methanation) and in liquid phase (Fisher-Tropsch and lignin-depolymerization). As an example, Figure 1a shows the effect of the catalyst architecture on the catalytic performance in the reverse water gas shift reaction for molybdenum carbide catalysts. Kinetic experiments revealed a prominent effect of the selected design on the observed activity. The enhancement was attributed to minimized axial dispersion effects and improved local turbulence when moving from straight channels to more complex fiber stackings. Besides axial dispersion effects and external mass transfer, the diffusion within the catalyst pores plays an important role in controlling the overall reaction rates. Strategies to minimize the intraparticle diffusion effects are i) reduce the characteristic diffusion length (i.e., the fiber diameter for DIW structures) and ii) enhance the fiber porosity. A set of well-defined printed structures that differed in the macropore content was prepared by adjusting the cellulose-to-TiO_2 ratio in printable inks. Enhanced porosity significantly improved the intraparticle transport and the resulting catalytic activity in the CO_2 methanation (Figure 1b).

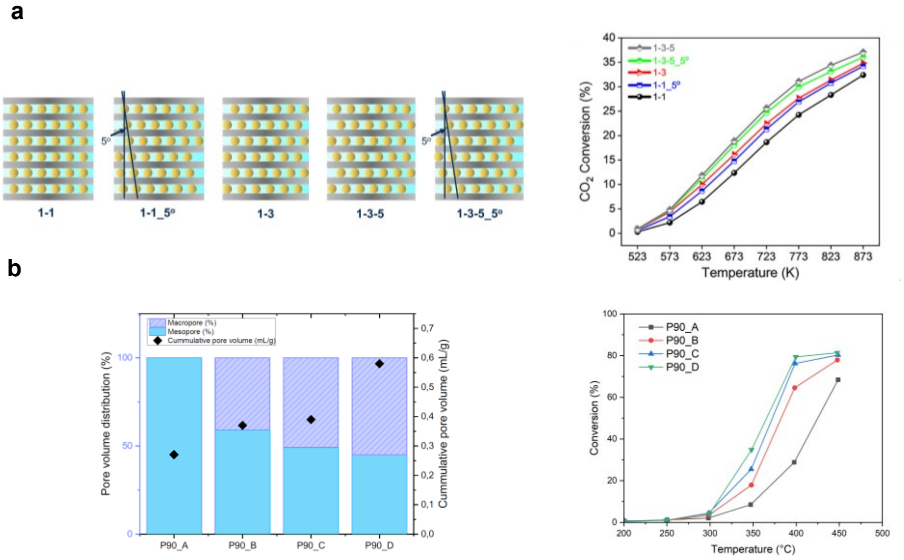

Figure 1. Effect of a) architecture and b) intra-fiber porosity on catalyst performance.

4. Conclusions

Overall, this work demonstrates how 3D-printing can be used not only to shape catalysts, but to deliberately engineer porosity and functionality with a precision that traditional methods cannot match. These findings underscore the potential of additive manufacturing to accelerate the design of next-generation catalyst systems, and the importance of porosity engineering in catalyst design.

References

[1] A. Pajares, J. Andrade Arvizu, D. Jain, M. Monai, J. Lefevere, P.R. de la Piscina, N. Homs, B. Michielsen, Chem. Eng. J. 482 (2024), 149048.

Keywords

3D printing; structured catalysts; hierarchical porosity