DLP 3D printing of catalyst architectures: from material preparation to mathematical modeling of structure effects on catalyst performance

Luca MASTROIANNI[*1,2], Ananias MEDINA[2], Anna DE DOMENICO[1,2], Kari ERÄNEN[2], Martino DI SERIO[1], Dmitry MURZIN[2], Vincenzo RUSSO[1,2], Tapio SALMI[1,2]

[1]Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy
[2]Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering (TKR), FI-20500 Turku/Åbo, Finland
**luca.mastroianni@abo.fi*

Significance and Relevance

The potential of the high resolution Digital Light Processing (DLP) printing was exploited to create a new procedure for the design of catalyst structures with high geometrical complexity. The printed aluminum oxide catalyst structures had a good surface area combined with a sufficient mechanical strength. Ethanol dehydration experiments revealed a strong impact of the selected geometry on the catalyst performance, which was accurately described with an advanced heterogeneous mathematical model. Enormous potential of the developed shaping technique in process intensification is forecasted.

Preferred and 2nd choice for the topic: Multiscale modeling and advanced simulation aspects, CO_2 utilization and recycling
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral

Introduction and Motivations

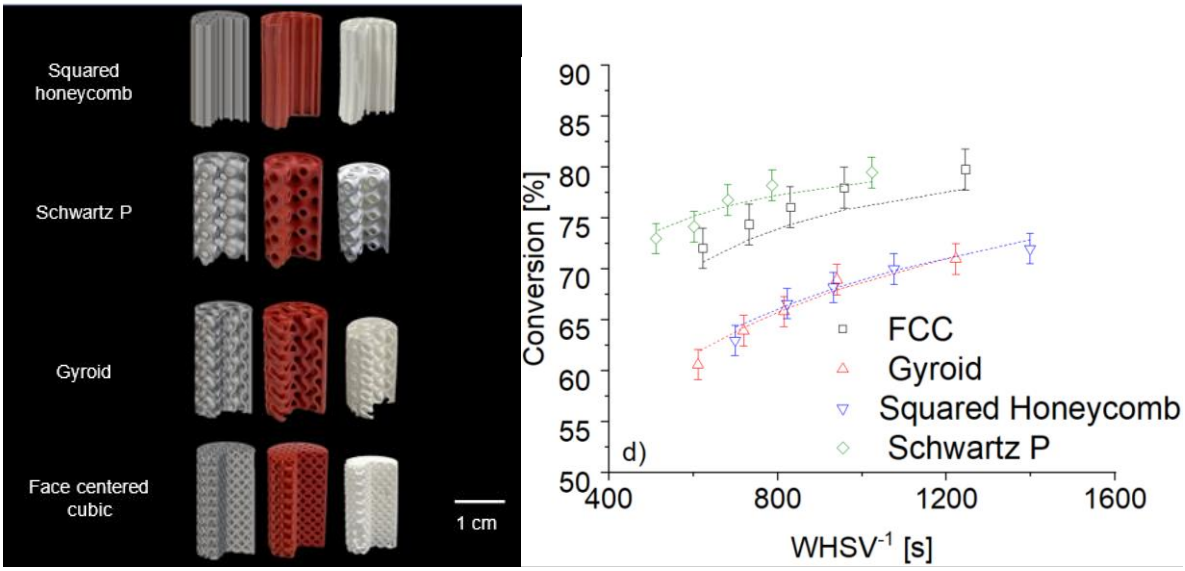
3D printing is expected to revolutionize catalyst shaping as it paves the way for completely new solid catalyst architectures to meet the requirements of high mass and heat transfer rates[1]. Digital Light Processing (DLP) is a very desirable technology among different printing alternatives owing to excellent printing resolution and high printing speed[2]. Herein, a new paradigm to DLP print pure γ-Al_2O_3 catalytic supports is proposed. Infiltration of colloidal nanoparticles of boehmite was adopted to improve the mechanical strength of the catalyst bodies preserving their porosity. The alumina catalysts were loaded in a tubular reactor and their activities were evaluated in continuous ethanol dehydration to diethyl ether. The experiments revealed strong impact of the selected catalyst architecture on the catalyst performance. An advanced 1-D heterogeneous mathematical model employing geometrical features of the catalyst structures was proposed to describe the experimental data. The acquired knowledge was used to 3D print 13X zeolite materials, which have a potential as in situ sorbents in the sorption-enhanced Sabatier reaction to convert CO_2 to methane.

Materials and Methods

The ceramic resin for 3D printing comprised polyethylene glycol diacrylate as the reactive oligomer, phenylphosphineoxide as the photoinitiator, SUDAN III as the UV light adsorber and boehmite as the precursor for γ-Al_2O_3. Propanol was used as non-reactive diluent. The debinded 3D printed objects were immersed in a 5 wt% colloidal boehmite solution to improve the mechanical stability. Four catalyst architectures (squared honeycomb, Schwartz P, face centered cubic and gyroid structures), were designed and printed. The shaped catalysts were loaded in a laboratory-scale tubular reactor operating isothermally at 1 atm and 225-275°C and their activities were evaluated in continuous ethanol dehydration to diethyl ether. The products were analyzed by an online gas chromatograph (GC) equipped a capillary column and thermal conductivity (TC) and flame ionization (FI) detectors. The catalysts were characterized with nitrogen physisorption (specific surface area and pore size distribution) and scanning electron microscopy (SEM). The estimation of kinetic parameters was performed with the aid of the gPROMS 4.0 software, applying the maximum likelihood method.

Results and Discussion

DLP printing enabled to print alumina catalyst bodies with a high precision (Figure 1a). The infiltration of colloidal boehmite successfully improved the mechanical strength of the 3D printed bodies. Indeed, a seven-fold increase in the compressive strength (0.3-2.0 MPa) was observed, making the catalyst structures stable for reaction experiments. The textural properties of the alumina were well preserved: the surface area of the 3D printed catalyst elements was 150 m^2/g, a value only 15% lower than the corresponding alumina in powder form. It was proved that the same method can be used to shape 13X zeolites. Boehmite binder is needed, but the surface areas of the final bodies were high (> 400 m^2/g). The ethanol dehydration experiments revealed significant differences of the catalyst performance at similar space times for the different 3D geometries (Figure 1b). Preliminary parameter estimation effort confirmed that some backmixing takes place within the printed catalyst structures. Therefore, the final mathematical model was based on the axial dispersion concept, including the local variations of the hydraulic diameters within different architectures, which contribute to local variations of the gas velocities as well as mass transfer coefficients. It was observed that, compared to the simplest squared honeycomb monolith, the complex architectures were able to significantly decrease the axial dispersion coefficients, thus improving the local flow segregation. The variations of the axial dispersion coefficients were quantified applying a modified Aris-Taylor correlation in the mathematical model, which provided an accurate description of the experimental data (Figure 1b).



References

1. C. Parra-Cabrera, C. Achille, S. Kuhn, R. Ameloot, *Chem. Soc. Rev*. **2018**, 47, 209-230.
2. L. Sun, P. Dong, Y. Zeng, J. Chen, *Ceram. Int*. **2019**, 45, 23007-23012.

Acknowledgements

This work is part of the activities financed by the Academy of Finland through the Academy Professor grants 319002, 320115, 345053 (Tapio Salmi, Luca Mastroianni). Economic support from Åbo Akademi University Graduate School, Walter Ahlström Foundation and the Finnish Foundation for Technology Promotion (TES) is gratefully acknowledged (Luca Mastroianni).