DLP 3D printing of aluminum oxide structures: a new platform to manufacture structured catalysts and reactor elements

Luca Mastroianni[1,2*], German Araujo-Barahona[1], Carl Brunberg[1], Vincenzo Russo[1,2], Martino Di Serio[2], Kari Eränen[1], Dmitry Yu. Murzin[1], Tapio Salmi[1,2]

1 Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Åbo Akademi, Turku-Åbo, Finland; 2 Naples Industrial Chemistry Laboratory (NICL), University of Naples Federico II, Napoli, Italy

**luca.mastroianni@abo.fi*

Highlights

- A method to shape Al_2O_3 substrate by Digital Light Processing (DLP) printing technology was developed
- Metal nanoparticles were introduced on porous 3D printed γ-Al_2O_3 substrates
- Active carbon coating was applied on sintered α-Al_2O_3 architectures and Ru impregnation was carried out
- The catalytic performances were demonstrated for different chemical applications

1. Introduction

3D printing is revolutionizing catalyst shaping as it paves the way for completely new catalyst architectures that meet the requirements of high heat and mass transfer rates and low pressure drop. Among different printing alternatives, Digital Light Processing (DLP) offers interesting advantages such as excellent printing resolution and high printing speed [1]. In DLP printing, shaping of a photocurable resin is enabled by a UV-light source. Inorganic catalytic materials such as Al_2O_3 can be manufactured by printing ceramic resins and finally removing the polymeric material through calcination. In this work, a manufacturing process to shape alumina structures with high resolution and good strength is demonstrated. The Al_2O_3 bodies produced were thermally treated at i) 600 °C to produce porous γ- Al_2O_3 supports and ii) 1200 °C to produce a sintered α-Al_2O_3 for subsequent active carbon coating. Palladium (Pd) nanoparticles were introduced on γ- Al_2O_3, while ruthenium was deposited on the active carbon coating. The catalytic activity was demonstrated in the H_2O_2 decomposition reaction in case of Pd/Al_2O_3 structures, while selective hydrogenation of sugars to sugar alcohols, e.g. xylose to xylitol was used as the model reaction for the Ru/C catalyst coated on 3D printed alumina.

2. 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 γ-Al_2O_3. The calcination of the printed bodies was carried out at 600 °C to obtain γ- Al_2O_3 and at 1200 °C for non-porous α- Al_2O_3. Deposition of metal nanoparticles (Pd and Ru) was conducted applying established impregnation methods for powders. Sugar hydrogenation experiments were conducted in a laboratory-scale batch reactor at 90-120 °C and 0.14-1 M xylose at 40 bar hydrogen.

3. Results and discussion

DLP printing enables the production of alumina structures with very high resolution (Figure 1a). The utilization of different precursors for the deposition of Pd nanoparticles tuned the Pd distribution within the catalyst walls. Uniform distribution was obtained when palladium chloride ($PdCl_2$) was used, while an egg-shell distribution was obtained when palladium acetate ($PdAc_2$) was applied A twofold increase of the rate constant for hydrogen peroxide decomposition was observed for egg-shell catalyst catalyst compared to uniformly distributed one due to the confinement of the active phase on the outer catalyst shell, evidently suppressing the intraparticle diffusion limitations [2] (Figure 1b). Several kinetic experiments were conducted in a loop reactor system, and a detailed kinetic model was provided. Successful deposition of an activated carbon coating layer was obtained on the surface of sintered 3D-printed Al_2O_3 structures. Morphological characterization of the coating revealed good porosity, which in turn led to finely dispersed Ru nanoparticles after impregnation (average nanoparticle size of 2.2 nm). The kinetic experiments conducted in the batch reactor confirmed excellent catalytic activity and xylitol selectivity as well as stability revealed by repeated use. An example of the experimental results is shown in Figure 1c. The data were described with a mechanistic model including the adsorption and surface reaction steps. The results indicate that the 3D printed structures are very competitive with other structured catalysts, such as monoliths, fibers and solid foams.

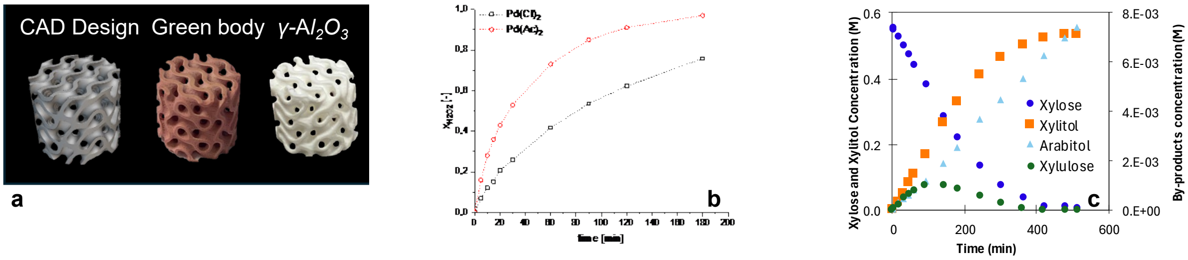

Figure 1. a) DLP 3D printed structure: from CAD to real catalyst. b) Activity comparison in H_2O_2 decomposition, c) Kinetics of sugar hydrogenation to sugar alcohols on Ru/C coated alumina.

4. Conclusions

High resolution DLP printing was applied to manufacture new catalyst elements with high geometrical complexity. The printed alumina bodies were used both as porous supports and as a backbone for active carbon coating. The kinetic experiments confirmed excellent chemical activity and high potential of DLP printing as a novel shaping method. 3D printed catalyst and reactor elements provide a new avenue for process intensification, because this technology enables simultaneous optimization of heat and mass transport processes, pressure drop and flow pattern. The approach can in future be applied to several gas, liquid and gas-liquid processes both in continuous and discontinuous operation modes.

References

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Keywords

DLP 3D printing; structured catalysts; active carbon coating; kinetic experiments and modeling.