New perspectives in process intensification: DLP 3D printing of γ-Al_2O_3 catalysts.

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Highlights

- Digital Light Processing (DLP) was applied to shape alumina substrate.
- Excellent structure resolution, high surface area and good mechanical stability was achieved.
- Gold nanoparticle deposition on the alumina substrates was successfully carried out.
- The catalytic activity was confirmed in the transformation of ethanol to valuable products.

1. Introduction

3D printing, or Additive Manufacturing (AM), is one of the key technologies of the fourth industrial revolution (Industry 4.0) as it will transform the whole concept of manufacturing. AM enables rapid, sustainable and cost competitive production of highly complex designs. Applied to catalyst shaping, 3D printing paves the way for completely new architectures which have the potential to enhance mass transfer rates in shaped catalysts. Digital Light Processing (DLP) is a highly promising printing technology among the different 3D printing alternatives owing to excellent printing resolution and a high printing speed [1]. When applying DLP printing for ceramic materials, important catalyst requirements (such as the specific surface area) are often sacrificed to obtain mechanically stable parts [2]. Herein, a novel methodology to DLP 3D print γ-Al_2O_3 catalyst structures with a good mechanical stability and a high surface area is described. Introduction of active gold nanoparticles on the alumina supports was explored with different deposition methods and the catalytic activity was demonstrated in the oxidative dehydrogenation of bioethanol. Moreover, it was demonstrated that the reactor performance is highly influenced by the printed catalyst structure. The obtained results demonstrate a high potential of the method to remove all the constrains in catalyst shaping, paving the way to new features and avant-garde structures in catalyst design.

2. Methods

A photosensitive catalyst slurry was prepared mixing boehmite (the alumina precursor) with an oligomer (Poly ethylene glycol diacrylate), a photo initiator (IRGACURE 819) and a UV-absorber (SUDAN III) and a dispersing agent (SPAN 80) in different amounts. 1-Propanol was used as the non-reactive diluent. The printed solid mixture (green-body) underwent thermolysis at 600ºC to remove the organic components. To improve the mechanical strength, infiltration of colloidal boehmite and subsequent calcination has been proposed in alternative to thermal sintering. Gold deposition was carried out via deposition precipitation method using either urea (DPU) or ammonia (DP) as deposition agents. The catalyst structures were tested in the continuous oxidative dehydrogenation of bioethanol to acetaldehyde in case of Au/Al_2O_3 catalysts and in the transformation of ethanol to diethyl ether in the case of pure Al_2O_3. An HPLC pump was used to control the flow rate of ethanol while gas flowmeters were employed to control the flow rate of the gases (oxygen and ethanol). The effluent from the reactor was analyzed by an online gas chromatograph equipped with TC and FI detectors.

3. Results and discussion

The catalyst concentration in the photosensitive slurry was revealed to be one of the most important parameters to preserve the structural integrity of the 3D printed architectures. When the solid content was too low, cracks and delamination appeared in the final structure after the polymer burnout because of the heavy weight loss in the structure. However, high catalyst-to-polymer ratios are detrimental for the printability of the ceramic resin as the slurry viscosity increases. Thus, 1-propanol was added to the mixture to keep acceptable viscosity and high catalyst-to-polymer ratios. Propanol was subsequently removed drying the structures at 110ºC overnight. Eventually, the optimal resin had a 60 wt% content with respect to the organic matrix and the obtained alumina architectures showed unprecedented resolution (Fig.1a). The structures appeared rather fragile after the polymer thermolysis, with a value of the compressive strength of 0.3 MPa. The infiltration of colloidal boehmite determined a seven-fold increase of the compressive strength, making the catalyst pellets robust enough for further processing. Gold deposition with different deposition agents (i.e., urea and ammonia) revealed different gold nanoparticle sizes and distributions along the alumina structure walls. The peculiar behaviour was ascribed to the different speciation of gold when different precipitating agents were employed [3]. Therefore, the resulting activities in the oxidative dehydrogenation were remarkably different (Fig. 1b) for catalyst prepared with different deposition methods. Finally, it was observed that the printed structure can significantly influence the catalyst performance. The different activity results can be ascribed to: i) different masses of the catalysts pellets ii) different macroporosities, leading to different residence times within the catalyst and iii) dispersion of the fluid phase, which depends on hydraulic diameters and curvatures on the printed channels.

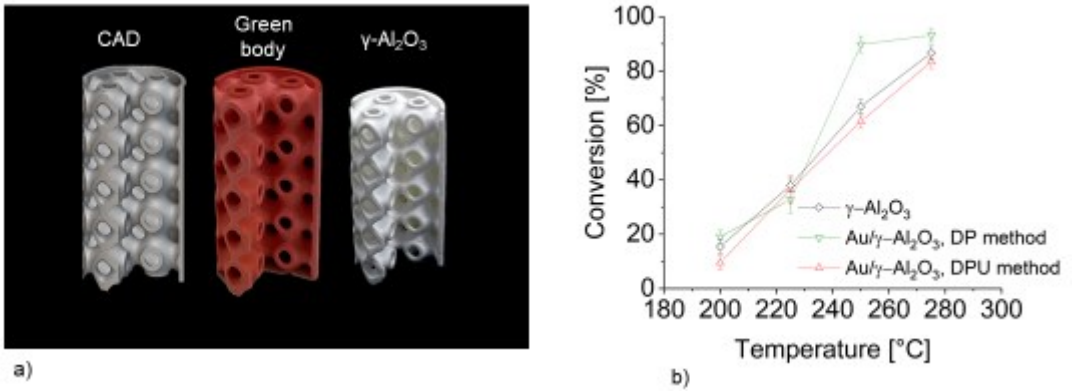

Figure 1. a) Demonstrative printed lattice (Schwartz primitive) at different printing steps (from CAD to final alumina) and b) conversion of ethanol as a function of temperature for pure Al2O3 and Au/γ-Al_2O_3 with different deposition methods.

4. Conclusions

The potential of the high resolution DLP printing was exploited to create a new procedure for the design, manufacturing, and application of catalyst structures with a high geometrical complexity. Infiltration of colloidal particles was explored as an alternative post-processing method to improve the mechanical stability preserving the internal catalyst porosity, which is typically destroyed in the conventional thermal sintering. The kinetic experiments of alcohol oxidation proved the catalytic activity of the 3D printed objects, with remarkable differences between the investigated techniques for the metal introduction. The general outcome of this work encourages a further scientific development of the technique that can potentially lead to revolutionary process intensification.

References

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Keywords
3D printing; catalyst shaping; gold nanoparticles; catalyst design