Development of 3D-printed catalysts applied to sugar alcohol production

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Highlights

- 3D-printed α-Al_2O_3 gyroid support enabled preparation of structured Ru/C catalyst.
- Carbon coating provided high surface area and highly dispersed Ru nanoparticles.
- Catalyst performance was demonstrated in production of the sugar alcohol xylitol.
- Developed kinetic model described the experimental data.

1. Introduction

The great advances in additive manufacturing achieved over the last decade have opened new opportunities for the very precise fabrication of advanced materials [1]. The application of 3D printing to the preparation of heterogeneous catalysts represents a natural evolution of this technology toward chemical reaction engineering applications. Structured catalysts, including monoliths, fibers, open-cell foams, and more recently 3D-printed architectures, have attracted increasing attention as potential alternatives to conventional slurry powder catalysts commonly used for the synthesis of fine and specialty chemicals in batch reactors [2]. This is particularly relevant for three-phase reactions, such as hydrogenation and oxidation processes, where catalyst separation, mass and heat transfer, and reactor operability impose significant challenges.

3D printing technology enables the design of tailored structures that improve gas–liquid contact, enhance heat transfer providing temperature uniformity, and reduce pressure drop. Moreover, the deposition of thin catalytic layers on the surface of these structures minimizes internal mass transfer resistance, facilitating operation under intrinsic kinetic control and enabling the transition toward continuous processes. An emblematic example of biomass utilization for the synthesis of high-value chemicals is the catalytic hydrogenation of sugars to sugar alcohols, e.g. sorbitol, xylitol and mannitol which are widely used as low-calorie sweeteners in the alimentary industry, as anti-caries agents in toothpaste, and as additives in cosmetic products. In this work, digital light processing (DLP) 3D-printing technique was applied to fabricate structured supports for Ru/C catalysts used in the selective hydrogenation of xylose to xylitol. The catalysts were evaluated through extensive kinetic experiments in semi-batch operation to obtain reliable intrinsic reaction data. The aim of this study is to establish a basis for the rational design of structured catalysts tailored for continuous sugar hydrogenation.

2. Methods

Structured catalyst supports were fabricated by DLP 3D printing of a boehmite-based resin, followed by UV curing, pyrolysis at 600 °C and sintering at 1200 °C to obtain α-Al_2O_3. A carbon layer derived from poly(furfuryl alcohol) was deposited via acid-catalyzed polymerization, followed by pyrolysis (850 °C, N_2) and activation in air (400 °C). Ruthenium nanoparticles were introduced by stepwise impregnation with Ru(III) nitrosyl nitrate and reduced at 300 °C under H_2. Catalysts were characterized using N_2 physisorption, SEM/EDS, TEM, H_2-TPR, and ICP-OES. Isothermal and isobaric kinetic experiments were performed in a 300 mL Parr semi-batch reactor. The catalyst was reduced in situ (120 °C, 5 bar H_2) prior to xylose hydrogenation (40 bar, 600 rpm). The concentrations of the organic compounds were analyzed by HPLC, and traces of by-products were identified by GC–MS. Three temperatures (90, 100, and 120 °C) were screened within a concentration range of 0.14–1.00 M. The catalyst stability was assessed by repeated experiments. A kinetic model was developed assuming non-competitive adsorption of sugar and hydrogen molecules. The kinetic parameters were estimated by non-linear regression using Nedler Mead optimization method implemented in Python.

3. Results and discussion

The 3D-printing process allowed the preparation of a mechanically stable α-Al_2O_3 gyroid structures (Figure 1a). After carbon coating, a homogeneous carbon layer was obtained (Figure 1b), with a surface area of 676 m^2 g_{carbon}^{-1} and a thickness of approximately 10–16 µm, as determined from SEM images. The ruthenium loading was 1.8 wt.% (on carbon basis), with an average nanoparticle size of 2.2 nm and a narrow size distribution (TEM, Figures 1c–d), which represents an improvement in the Ru dispersion compared to previously reported Ru/C–aluminum foam catalysts. The improvement is attributed to the higher pyrolysis and activation temperatures enabled by the aluminum oxide structure [3]. The catalyst exhibited a high activity in the hydrogenation of xylose to xylitol with a minimal formation of by-products (Figure 1e). Xylulose and arabitol were identified as the side products. The xylitol selectivity exceeded 98% under all tested conditions, with temperature being the most influential parameter, consistent with the higher activation energies of the side reactions compared to the main hydrogenation pathway. The catalyst showed excellent stability in repeated recycling experiments. A kinetic model based on non-competitive adsorption of sugars and hydrogen accurately described the experimental concentration profiles and the effect of operating conditions. As an example, a comparison between experimental and simulated data for an experiment conducted at 120 °C, 40 bar, and an initial xylose concentration of 0.4 M is shown in Figure 1e. The model is a predictive tool for future studies under continuous-flow operation using the developed 3D-printed structured catalysts.

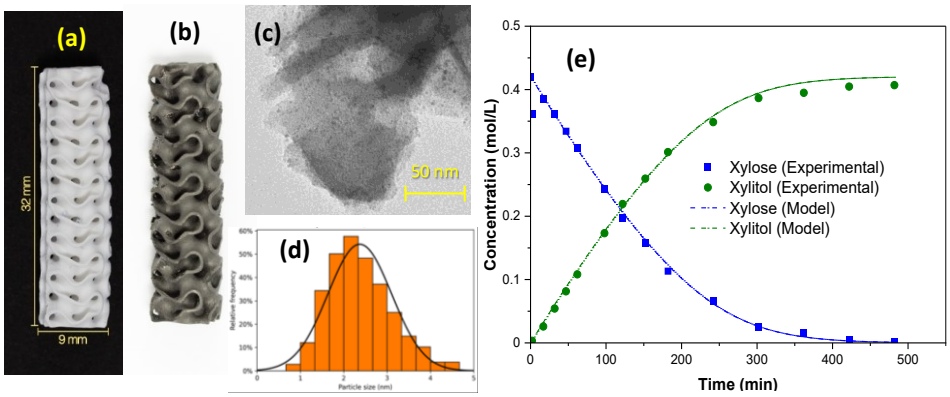

Figure 1. **(a)** 3D-printed α-Al_2O_3 support; **(b)** Ru/C 3D-printed catalyst; **(c)** TEM image of Ru nanoparticles; **(d)** nanoparticle size distribution; **(e)** example of xylose hydrogenation performance at 120 °C and 40 bar.

4. Conclusions

The successful fabrication of a 3D-printed α-Al_2O_3 gyroid support coated with carbon and loaded with Ru nanoparticles resulted in a mechanically stable structured catalyst with high surface area and good metal dispersion. The catalyst showed high activity, high product selectivity, and good stability in the hydrogenation of xylose to xylitol. The kinetic model based on non-competitive adsorption of sugar and hydrogen molecules accurately described the experimental data and provided intrinsic kinetic parameters suitable for reactor design. The results demonstrate that additive manufacturing is a promising approach for the development of structured catalysts for three-phase reactions, paving the way toward continuous sugar hydrogenation using 3D-printed catalytic architectures.

References

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Keywords
3D printing; Structured catalysts; Three-phase hydrogenation; Xylitol.