

Ru/C Catalysts on 3D-Printed α -Al₂O₃ Supports for Lignin Reductive Depolymerization

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Highlights

- 3D-printed α -Al₂O₃ supports for Ru/C catalysts in lignin depolymerization
- Structured catalysts improve mass transfer and accessibility
- Potential of 3D printed catalysts for continuous flow depolymerization of lignin.

1. Introduction

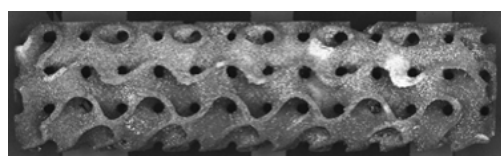
Lignin is among the most abundant natural aromatic biopolymers on Earth and serves as a significant structural element of the plant cell walls together with cellulose and hemicellulose. It is a challenging yet promising feedstock for the sustainable production of aromatic chemicals, fuels, and other materials, mainly through chemical depolymerization, i.e. cleaving lignin into smaller monomers and oligomers. One of the major obstacles to its efficient conversion is the inherently high molar mass together with its heterogeneous and highly cross-linked structure, which limits solubility, hinders mass transfer, and reduces the selectivity toward well-defined low-molecular-weight products. Ruthenium supported on carbon (Ru/C) has proven to be effective in lignin reductive depolymerization because Ru can activate hydrogen and break oxygen-containing bonds in lignin, like β -O-4 interunit linkages [1]. However, traditional Ru/C catalysts are available as powders, granulates, or extrudates, which often exhibit low accessibility of active sites, mass transfer limitations, and difficulties in scale-up for industrial reactors. These limitations are aggravated by lignin's poor solubility, which conventional packed-bed reactors poorly tolerate due to clogging and diffusion constraints. Modern additive manufacturing, namely, three-dimensional (3D) printing, enables the production of catalysts with well-defined architectures, controllable porosity, and reactant flow directions. In comparison with the conventional shaping techniques, hierarchical pore architectures and optimized geometrical forms can be achieved through 3D printing as one manufacturing operation. These customized structures enhance accessibility of active sites to reactants, increase mass and heat transfer, and reduce diffusion barriers, which are usually an issue in bulk catalysts [2]. In this work, 3D-printed Al₂O₃ structures were employed as supports for a Ru/C catalyst on the depolymerization of technical lignins. The influence of key reaction parameters, including lignin fractionation, hydrogen pressure, reaction temperature, stirring rate, catalyst loading, and solvent type and composition, was systematically investigated in a batch reactor, with the ultimate objective to assess its suitability for application in a continuous system.

2. Methods

The supports of a 3D-printed α -Al₂O₃ catalyst were prepared by digital light processing (DLP). The gyroid structures were printed, washed with ethanol and UV-cured, then subjected to thermal treatment to eliminate organic components by pyrolysis at 600 °C and sintered at 1200 °C to produce mechanically stable structures of α -Al₂O₃ [3]. Further mechanical strength was attained through the infiltration of a boehmite colloidal solution. The carbon coating was obtained on the supports through the polymerization of furfuryl alcohol with the addition of polyethylene glycol, followed by pyrolysis at 850 °C and activation in air at 400 °C. Ruthenium nanoparticles (2 wt. %) were deposited onto the carbon layer by incipient wetness impregnation using a solution of Ru(III) nitrosyl nitrate and reduced by hydrogen at 300 °C. Lignin was depolymerized in different solvent mixtures under a hydrogen atmosphere in the presence of the 3D printed Ru/C coated heterogeneous catalyst. The decrease in molecular weight was analyzed by HP-SEC to follow reaction kinetics. The final products were further characterized via ³¹P NMR and HSQC to evaluate the increase of -OH functionalities and decrease of β -O-4 bonds during the depolymerization process.

3. Results and discussion

The α -Al₂O₃ gyroid supports were successfully fabricated via DLP printing and uniformly coated with carbon, reaching up to 33 wt.% carbon deposition. As depicted in Fig. 1a, the carbonization process preserved the original gyroid architecture, confirming the structural robustness of the printed bodies. The resulting Ru/C coated monoliths exhibited excellent mechanical stability under reaction conditions, allowing easy handling and recovery. Notably, no detectable leaching was observed, highlighting the strong interaction between the active phase and the carbon-coated support. In batch lignin depolymerization, the structured catalysts an improved mass balance compared to commercial powder Ru/C, suggesting enhanced management of lignin solubility limitations and reduced material losses. The open and interconnected gyroid geometry likely mitigates diffusion constraints and clogging phenomena typically encountered in packed systems. With the most recalcitrant lignin fraction, namely the ethanol insoluble, a weight-average molecular weight decrease of 67% was obtained, and almost 40% of the final product resulted in an average Mw lower than 6000 Da.



| Sample | Mn (kDa) | Mw (kDa) | Polydispersity (Mw/Mn) |
|-------------------------|----------|----------|------------------------|
| Before depolymerization | 2.3 | 60.2 | 26.4 |
| After depolymerization | 1.3 | 18.4 | 14.2 |

Figure 1. SEM image of the alumina 3D-printed Ru/C coated. **Table 1.** Mn, Mw and polydispersity of EtOH insoluble lignin fraction before and after depolymerization, measured via HPSEC.

4. Conclusions

Overall, these findings demonstrate that 3D-printed structured Ru/C catalysts represent a promising alternative to conventional catalyst systems. Their architectural control, stability, and improved mass management make them particularly attractive for future implementation in continuous-flow lignin depolymerization processes, where transport phenomena and reactor operability are decisive factors.

References

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Keywords

“Lignin; 3D-printed catalyst; depolymerization; Ru/C”