Structured 3D-Printed Single-Atom Catalysts for Continuous Photocatalytic Applications

Jiachengjun Luo,[1] Vincenzo Ruta,[1] Oleksii Nevskyi,[2] Jody Albertazzi,[1] Gianvito Vilé[1]*

[1]*Department of Chemistry, Materials, and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan, Italy.* [2]*Institute of Physics, Georg August University Göttingen, Göttingen, Germany.*

**Corresponding author: gianvito.vile@polimi.it*

Highlights

- 3D printing was used to shape single-atom catalysts.
- Enhanced catalysis in flow mode was demonstrated, with the shaped Ni-loaded catalyst boosting benzaldehyde production.
- Catalyst shape influenced activity, with spiral design increases catalytic performance.
- Demonstrated stability and recyclability in the single-atom structured catalytic system.

1. Introduction

Structured catalysts are widely employed in industrial processes, as they provide optimal mass and heat transfer, which leads to more efficient use of catalytic materials, and enhanced stability and durability. In this work, we exploit three-dimensional (3D) photopolymerization printing to shape single-atom catalysts (SACs) directly. This new technology avoids the traditional washcoating of metallic or ceramic bodies with an inorganic catalyst, which has issues with the aggregation of active components. Moreover, unlike traditional 3D printing methods that rely on layer-by-layer deposition, this technology uses photopolymerization through rapid curing of liquid resins with UV light. This results in finer resolutions in the printed objects, quicker fabrication times, and no need for post-processing thermal steps. Thus, it is an ideal choice for applications that demand high accuracy and efficiency in additive manufacturing, and better control over post-processing material structure.

2. Methods

Powdered Ni_1@mpgCN_x was synthesized by adding $NiCl_2$ and cyanamide to a 40% aqueous suspension of 12 nm particles of SiO_2, and heating the solution under stirring at 70 °C for 16 h. The resulting white solid was then heated for 4 h at 550 °C in an alumina crucible. The procedure for the 3D-printing of structured catalysts was performed mixing Ni_1@mpgCN_x (0.3 g) with a commercial 3D printing resin (Anycubic), with a mass ratio catalyst:resin of 1:100. The obtained suspension was stirred for 12 h at room temperature in an amber vial. The materials were 3D-printed by photopolymerization on an Elegoo Mars 2 Pro MSLA 3D printer, allowing to print 3D materials in a layer-by-layer configuration. Materials characterization was performed via ICP-OES, N_2 physisorption, powder X-ray diffraction, and transmission electron microscopy.

The photocatalytic flow reactions were conducted on a home-made experimental setup composed by a blue LED lamp (Kessil™ H150 Blue), a syringe pump (Harvard PHD ULTRA™ CP), and a column reactor (Diba Omnifit™ column, 6 mm i.d, 150 mm length). For each experiment, the LED lamp was positioned at a measured distance of 5 cm from the reactor, that was filled with the 3D-printed structured catalyst, and quartz wool to fill the empty space. A picture of the setup is present in Figure 5. In a typical experiment, a solution 0.04 M of the benzyl alcohol (BnOH, 60 mg, 0.55 mmol, Sigma-Aldrich, 99%) in acetonitrile (MeCN, 15 mL, Sigma-Aldrich, 99%) was introduced by the syringe pump, operating at quasi-ambient pressure, into the assembled reactor, at room temperature, with a flow rate of 3 mL h^{-1}, for the desired residence time. Before switching on the light source, 2 mL of the reacted solution were collected and evaluated as a control. Then, the LED lamp was eventually switched on and the resulting solution was collected and analyzed by meaning of high-performance liquid chromatography (HPLC). Particularly, 30 μL of the reaction mixture were diluted with 130 μL of MeCN, and injected in an Agilent 1200 chromatograph, equipped with a UV detector G1315D working at λ = 210 nm, and a C18 HypersilGOLD 5 μm 175 Å column (Thermo-Fisher).

3. Results and discussion

The study started with the preparation and characterization of shaped single-atom for a continuous-flow photocatalytic reaction, specifically benzyl alcohol oxidation to benzaldehyde. Various analyses were conducted to characterize the materials, including elemental analysis, BET analysis for surface area and porosity, FTIR analysis for molecular structure, XRD analysis for purity and crystallinity, solid-state MAS NMR spectroscopy for molecular structure, TEM analysis for morphological features, and TGA for thermal stability. Results showed that the Ni_1@mpgCN_x catalyst maintained its structural integrity after incorporation into the 3D-printed material. The structured catalyst exhibited a homogeneous distribution of the powdered catalyst within the resin, confirming the success of the fabrication process.

The catalytic performance of the 3D-printed structured catalysts was evaluated in a continuous-flow photocatalytic reaction. The structured catalysts demonstrated improved catalytic activity compared to the bare resin, confirming the catalytic behavior of CN_x materials. Furthermore, the Ni-loaded structured catalyst showed enhanced catalytic production of benzaldehyde compared to the metal-free counterpart, possibly due to ligand-to-metal charge transfer phenomena. The study also investigated the shape effect of the structured catalysts, revealing that a specific spiral-type shape led to increased catalytic activity, attributed to improved mass transfer in the solution. Stability tests and recycling experiments demonstrated the high stability and recyclability of the single-atom structured catalytic system.

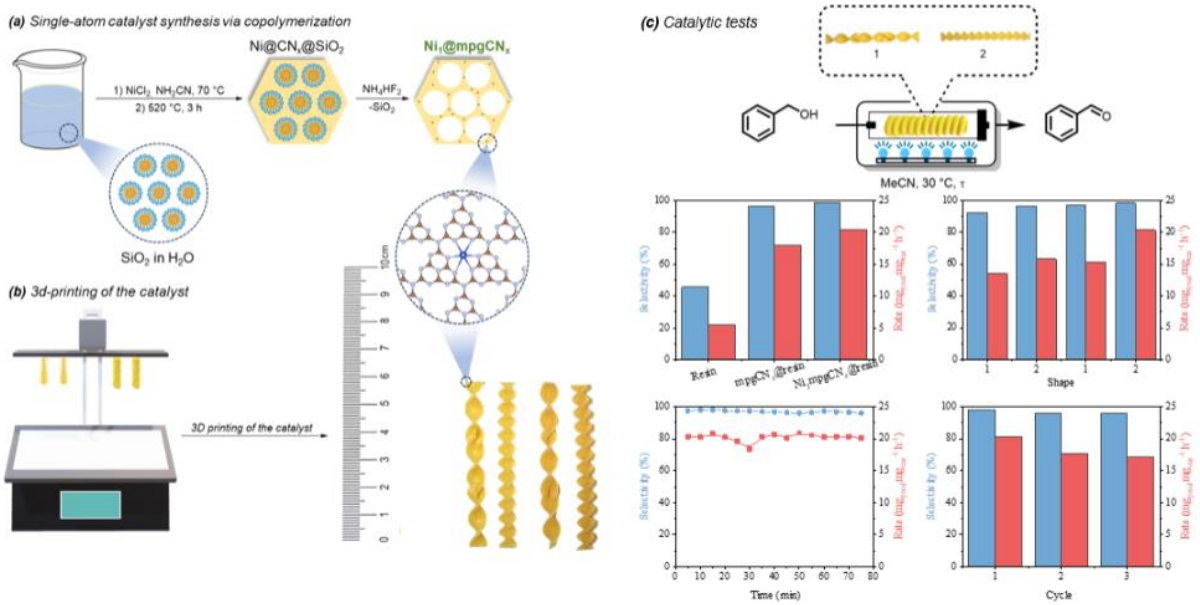

Figure 1. Photocatalytic performance of 3D-printed structured catalysts in benzyl alcohol oxidation to benzaldehyde.

4. Conclusions

In the work, we demonstrated the relationship between the structure and catalytic performance of the structured catalyst through various textural, microscopic, and spectroscopic characterization techniques. The structured catalyst was finally evaluated in the continuous-flow photocatalytic oxidation of benzyl alcohol to benzaldehyde reaction, an important reaction to prepare biomass-derived building blocks. Overall, this work shows the potential of this manufacturing method to prepare single-atom-derived structured catalysts.

Keywords
Catalyst shaping; 3D printing; Single-atom catalyst; Continuous-flow reactor design.