3D-Printed Structured Reactor with Integrated Single-Atom Catalyst Film for Hydrogenation

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Structured catalytic reactors are gaining considerable attention for integrated chemical synthesis because they offer enhanced mass transfer and easy catalyst recovery. In this paper, a new, cost-effective design strategy that combines 3D printing and single-atom catalysis is presented, enabling the construction of an integrated mixer-based reactor insert, coated with a thin single-atom catalytic layer. The material has been characterized from the nano to the macro scale to unlock structure-property relationships. The performance of the catalyst structure was evaluated via hydrogenation of two model compounds used in the flavorings and fragrances industry. The structured catalytic reactor was active, selective, and reusable several times without apparent drop in performance. This immobilized catalyst system removes the need for catalyst separation post-reaction, and enables modern synthesis options catalyzed over atomically-precise nanomaterials.

Introduction

Single-atom catalysts with isolated metal species entrapped in the cavities of inert carriers have become the new frontier in heterogeneous catalysis. These materials emulate the coordination environment of homogeneous catalysts and maximize the utilization of precious metals. To date, these materials are mostly evaluated in slurry or packed-bed reactors. Slurry reactors are stirred tanks in which a powder-form catalyst is used in a suspension to maximize the contact area and minimize the intra-particle diffusion. Stirring prevents the catalyst from settling, speeds up the interfacial mass transport, and minimizes concentration gradients. However, using a powdered material leads to difficult catalyst separation and recovery from the reaction mixture post-reaction. Packed-bed reactors exploit granular catalysts with much larger particle sizes. This approach eliminates catalyst separation issues and minimizes pressure drops in the reactor. Nevertheless, the catalytic process may experience diffusion limitations which sacrifice the catalyst performance in terms of reaction rate and selectivity. To solve these problems, structured reactors, which combine the advantages of slurry and fixed-bed reactors, are used in industrial processes. Among those, catalytic reactors with structurally parallel or nature-inspired channels offer precision, efficiency, and a lower pressure drop. In these materials, the catalytic species are coated on the channel wall of the reactor with the effect of enhancing mass transfer.

The fabrication of these complex structured reactors is difficult and expensive using traditional methods. Nevertheless, due to the rapid development of technology and the reduction of equipment threshold, three-dimensional (3D) printing technology offers today significant opportunities in the rapid manufacturing of tailored reactor geometries. Furthermore, the catalyst can be loaded on the 3D-printed reactor’s surface to increase the contact between the reactant and the catalyst, further achieving high catalytic efficiency.

In recent years, various research groups have developed structured catalysts based on 3D printing techniques to address the problems associated with packed bed technology. Research in this area has been also pursued at CSIRO starting from 2014, leading to the development of a catalytically coated 3D-printed reactor geometry termed catalytic static mixer (CSM) micro-reactors. These catalysts are made by 3D metal printing followed by one of a variety of different catalyst coating methods. The static mixers can be integrated in flow microchannels as removable inserts and are structured and regular, thus allowing for a predictable and tunable flow field which minimizes flow maldistribution. They also provide very low pressure drop and, due to its metallic skeleton, can manage heat transfer more efficiently than packed beds or slurry reactors. Despite the advantage of this technology, no work has so far investigated the structuring of single-atom catalytic functionalities on 3D-printed CSMs. This work addresses this gap, reporting the fabrication of 3D-printed CSMs with integrated single-atom catalytic functionalities for the continuous-flow hydrogenation of two model compounds. The material, in powder and technical form, was characterized with a...
battery of experimental methods to unlock structure-function relationships. These findings may pave a new path toward novel methods to intensify organic transformations, making joint use of single-atom catalysts and 3D-printed microreactors.

**Results and Discussion**

**Preparation and characterization of the single-atom powdered catalyst.** We initiated the work by preparing a single-atom catalyst using the copolymerization method established elsewhere and described in the experimental section, and characterizing the obtained powder. Table 1 includes the compositional and textural properties of the catalyst used to coat the 3D-printed static mixers. The material is characterized by a stoichiometric C/N ratio of 0.66, in line with the literature for mesoporous graphitic C$_3$N$_4$ and by a weight percentage of Cu of 1.2 wt.%. The X-ray diffraction pattern in Figure 1a displays the characteristic diffraction peaks of mpgC$_3$N$_4$, corresponding to in-plane structural packing motif and to interplanar stacking of the aromatic moieties, respectively. N$_2$ physisorption analysis indicates that the material has a mesoporous structure (Figure 1b). The BET surface area is 198 m$^2$g$^{-1}$ and the pore volume is 0.69 cm$^3$g$^{-1}$.

X-ray photoelectron spectroscopy was applied to determine the surface chemistry of the materials. As shown in Figure 1c, Cu 2p photoemission spectroscopy shows a main component at about 933 eV. The peak can be deconvoluted into Cu(I) and Cu(II) contributions, but Cu(I) stands as the main peak. The fine detail of copper at the atomic level was investigated by synchrotron X-ray absorption spectroscopy. As shown in Figure 1d, the absorption edge of Cu is located between that of Cu$_2$O and CuO, suggesting most of the Cu atoms to be Cu(I). Furthermore, the peak is located at around 8981 eV, which is characteristic of the 1s–4p transition, and is assigned of Cu(I). From the extended X-ray absorption fine structure in Figure 1e, the Cu is shown as dispersed in the form of single atoms across the C$_3$N$_4$ support with no evidence of any scattering contribution from Cu–Cu pairs in the obtained EXAFS. From the EXAFS data, it appears that Cu is coordinated to four N atoms at a distance of 1.9 Å and four C atoms at a distance of 2.7 Å (Figure 1f). The microscopy analysis corroborates that copper is uniformly distributed across the mpgC$_3$N$_4$ sample (which is made of crystals with no specific shape and with a characteristic length of ca. 100–200 nm) and is in an atomically dispersed form (Figures 1g).

**Characterization results of the structured reactors with single-atom catalytic layers.** The design of the CSMs was pursued with the intention to reach a high degree of interfacial contact between the liquid and the gas phase of a hydro-generation reaction. For this reason, CSMs containing diamond shaped repeating units with an alternating pattern were 3D printed. The bulk structure of the CSMs is displayed in Figure 2a. On this material, an alumina-based wash-coat layer with mixed single-atom Cu-based C$_3$N$_4$ catalyst was deposited by dip-coating. The SEM micrographs in Figure 2b show the microstructure of the coated mixer, and the good catalyst dispersion. No spots where the coating was detached from the mixing element could be observed. Besides, back-scattered electron imaging by SEM and correlative elemental maps acquired by EDS enabled the clear distinction of the wash-coat layer made of alumina and corroborate the presence of the carbon nitride.

**Performance of the structured reactors with single-atom catalytic layers.** The performance of the CSMs coated with a single-atom catalyst layer was evaluated using the hydrogenation of benzaldehyde and furfural as model reactions. A custom-built hydrogenation reactor, which can be configured to run between one and ten reactive tubes (6 mm I.D., 150 mm length) in series, was used. The schematic flow diagram and illustration of the reactor configurations is shown in Figure 3. The setup included a temperature sensor at the output of the flow reactor and an integrated pressure sensor. In this work, we have investigated the effect of the liquid flow rate, temperature, and solvent on the hydrogenation of the two model compounds, proving that the coated CSMs are catalytically active and selective. The three solvents, namely water, ethanol, and ethyl acetate, were selected based on the solubility of the reactants and products, which needs to be high to avoid precipitation and clogging of the microreactor.

Table 2 includes the results collected during our experimental campaign. The structured catalysts are active for both substrates, although at equivalent experimental conditions, they are more reactive for furfural reduction. The hydrogenation is strongly affected by the type of solvent, since this impacts the solubility of hydrogen and, hence, the possibility for the gas to reach the active sites. For the case of furfural, the yield increases, as expected, with increasing temperature, and with decreasing flow rates. In the latter case, this is explained considering the higher contact time between the catalyst and the reactants. It should be noted that our catalysts are highly active when taking into account the small amount of active Cu present, resulting in a very high turnover frequency (TOF). For the reduction of benzaldehyde, the TOF was as high as 551 h$^{-1}$, and for furfural it was as high as 1563 h$^{-1}$. For comparison, for similar aldehyde reductions, conventional CSM catalysts would have a TOF several orders of magnitude lower; classical metal oxide type CSMs, such as Pd/Al$_2$O$_3$ or Ni/Al$_2$O$_3$ and electroplated CSMs, such as Pd(0), Pt(0) or Ni(0), have TOFs between 0.1 and

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40 h⁻¹ for a similar reduction reaction. This demonstrates the high potential of the structured single-atom catalyst for efficiently driving chemical reactions.

An important characteristic for the performance of a structured catalytic reactor is its stability over long periods of time. In this context, it should be already noted that all

Table 1. Compositional and textural properties of the powdered single-atom catalyst.

| Catalyst         | C [wt.%] | N [wt.%] | H [wt.%] | C:N ratio | Cu [wt.%] | \( S_{\text{BET}} \) [m² g⁻¹] | \( V_{\text{pore}} \) [cm³ g⁻¹] | \( V_{\text{micro}} \) [cm³ g⁻¹] |
|------------------|---------|----------|----------|------------|-----------|-----------------|-----------------|------------------|
| Cu@mpgC₃N₄      | 32.2    | 48.9     | 2.5      | 0.66       | 1.2       | 198             | 0.69            | 0.10             |

Figure 1. XRD (a), \( N_{\text{2}} \) physisorption (b), Cu 2p XPS (c), Cu K-edge X-ray absorption near-edge structure (d), extended X-ray absorption fine structure (e), predicted single-atom structure (f), SEM and aberration-corrected TEM (g) of the powdered single-atom catalyst.

Table 2. Hydrogenation experiments conducted over the catalytic static mixers.

| Entry | Reactant   | \( H_{\text{2}} \) :substrate / [mL min⁻¹] | \( F_{\text{spiral}} \) [mL min⁻¹] | \( T \) [°C] | Solvent     | Yield to alcohol [%] |
|-------|------------|------------------------------------------|----------------------------------|------------|------------|---------------------|
| 1     | Benzaldehyde | 30                                        | 0.25                             | 120        | Ethyl acetate | 0                   |
| 2     | Benzaldehyde | 30                                        | 0.25                             | 120        | \( H_{\text{2}} \)O | 3                   |
| 3     | Benzaldehyde | 30                                        | 0.50                             | 120        | Ethanol     | 59                  |
| 4     | Benzaldehyde | 30                                        | 0.50                             | 120        | Ethanol     | 22                  |
| 5     | Furfural    | 30                                        | 0.25                             | 60         | Ethanol     | 14                  |
| 6     | Furfural    | 30                                        | 0.25                             | 80         | Ethanol     | 26                  |
| 7     | Furfural    | 30                                        | 0.25                             | 100        | Ethanol     | 48                  |
| 8     | Furfural    | 30                                        | 0.50                             | 120        | Ethanol     | 82                  |
| 9     | Furfural    | 30                                        | 0.50                             | 120        | Ethanol     | 31                  |
| 10    | Furfural    | 30                                        | 0.75                             | 120        | Ethanol     | 12                  |
| 11    | Furfural    | 30                                        | 1.00                             | 120        | Ethanol     | 5                   |
| 12    | Furfural    | 20                                        | 0.25                             | 120        | Ethanol     | 58                  |
| 13    | Furfural    | 10                                        | 0.25                             | 120        | Ethanol     | 41                  |
| 14    | Furfural    | 5                                         | 0.25                             | 120        | Ethanol     | 29                  |
| 15    | Furfural    | 2                                         | 0.25                             | 120        | Ethanol     | 20                  |
reactions in Table 2 were performed using the same CSMs over seven months (from March to October 2021), and repeated in two different locations (Australia, Italy). The total accumulative reaction time/time-on-stream was well beyond 200 h. During this time, high reproducibility was observed. Moreover, the weight of the CSMs remained unchanged during that time (7.458 g before the first hydrogenation, compared to 7.461 g after seven months of operation). To further evaluate the stability of the CSMs, we have also conducted an uninterrupted time-on-stream experiment, running the furfural hydrogenation for 150 min at steady state (Figure 4), observing no drops in the formation of the corresponding alcohol. After the stability test, the amount of Cu leaching from the single-atom catalysts (together with other metal constituents of the CSMs and the reactor, such as Al, Cr, Fe, Ni, Cu and Mo) was evaluated by ICP-MS (Table 3). The analysis gave a Cu concentration below the detection limit, indicating the very high stability of the Cu single-atom catalyst coating under the employed reaction conditions. No difference was also observed when using used mixers and new mixers for the hydrogenation reactions. The concentration of other metals contained in the stainless-steel scaffold, such as Cr, Fe, Ni, Cu and Mo was below the detection limit, which proves the excellent high stability of the system at the extreme conditions used (24 bar and 120 °C).

It must be pointed out that, from the leaching study, a small amount of Al and Fe was detected in the solution, likely coming from the co-deposited alumina on the metal core of the CSMs and from the stainless steel reactor walls. To demonstrate that these metals have no role of the catalytic mechanism, we...
further conducted additional tests using no CSMs and only homogeneous aluminum chloride (AlCl₃, Sigma-Aldrich, 99%) and iron chloride (FeCl₃, Sigma-Aldrich, 97%), at the metal concentrations resulted from Table 3. In the hydrogenation of furfural, at H₂:substrate = 30, F_{\text{input}} = 0.25 mL min⁻¹, and T = 120 °C, no conversion of the reactant was observed. This verified the inactivity of these ‘leached’ metals in the reaction and excluded their homogeneous contribution in the catalytic process.

Conclusions

Using the CSM technology, we have prepared and characterized the first structured catalysts with single-atom catalytic functionalities. The reproducibility and validation for continued manufacturing operations of the structured single-atom CSMs have been highlighted by running experiments at steady state for extended periods of time, using two model substrates, furfural and benzaldehyde. The excellent control over the fluid flow and heat transfer within the CSM reactor system results in a superior reactor performance and very high turnover frequencies, making this novel, 3D-printed reactor a highly attractive alternative to traditional batch slurry reactors using powdered single-atom catalysts. The solution reported herein is especially advantageous on production scale, as the immobillized catalyst eliminates the need for labor-intensive, post-reaction filtration process.

Materials and Methods

Preparation of the powdered single-atom catalyst. The mpgC₃N₄ was synthesized with the hard template method previously reported.[39] An amount of cyanamide (9.0 g) was added dropwise in a 40% dispersion of 12 nm SiO₂ particles (22.5 g), which were used as the hard template. The mixture was heated at 90°C with stirring to evaporate water. The resultant white powder was then heated at a rate of 2.3 °C min⁻¹ over 4 h to reach a temperature of 550 °C, and then kept at this temperature for an additional 4 h. The brown-yellow product was treated with ammonium bifluoride (NH₄HF₂, 4 M) for 48 h to remove the silica template. The powders were then centrifuged and washed with distilled water for four times and with ethanol twice. Finally, the mpgC₃N₄ was dried overnight at 70°C under vacuum. To prepare the single-atom catalyst, mpgC₃N₄ (400 mg) and CuCl₂·2H₂O (13 mg; Sigma-Aldrich, 99%) were added into 20 mL ethanol and kept under moderate stirring for 8 h at 80°C. After that, the product was centrifuged and washed with distilled water, followed by drying in vacuum at 70°C for 24 h. Finally, the sample was heated at 500°C for 2 h in Ar flow to obtain the material (herein indicated as Cu₄@mpgC₃N₄).

Characterization method of the powdered single-atom catalyst. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector and with Cu Kα radiation (λ = 0.15418 nm), using a 0.01° min⁻¹ (2θ) scanning speed. Carbon, nitrogen, and hydrogen elemental analysis was accomplished by combustion analysis using a Vario Micro device. For the copper content, inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using an Optima 8000 ICP-OES spectrometer (PerkinElmer). Nitrogen physisorption was performed on a Micromeritics 3020 instrument (Micromeritics, Atlanta, USA) at −196 °C. Before the measurement, the samples (ca. 20−40 mesh) were degassed at 150 °C for 24 h. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method using the adsorption branch in the p/p₀ range from 0.05 to 0.35. The micropore and mesopore volumes were calculated using the quenched solid density functional theory (QSDFT) model for N₂ adsorbed on carbon with a cylindrical pore shape at 77 K. Transmission electron microscopy (TEM) studies were performed using a double Cs-corrected JEOL JEM-ARM200F (STEM) operated at 200 kV equipped with a cold field emission gun. X-ray photoelectron spectroscopy (XPS) measurements were carried out in a custom designed UHV system working at the base pressure of 1 × 10⁻¹ mbar, equipped with an electron analyzed (EA125 Omicron) and an X-ray source (DAR400 Omicron). The powder samples were suspended in methanol and drop-casted on a metal support to obtain a homogeneous film. Once dried the sample was introduced in the UHV system and left outgassing overnight. Photoemission spectra were acquired at room temperature in normal emission. The analysis of the spectra was performed using the XPSPEAK software using Voigt functions and subtracting a Shirley background. X-ray absorption spectroscopy (XAS) experiments were performed at the SuperXAS beamline of the Swiss Light Source at the Paul Scherrer Institute in Villigen, Switzerland. The Swiss Light Source operates in top up mode at 400 mA and 2.4 GeV. Radiation from a 2.9 T bending magnet was collimated using a Si-coated collimating mirror at 2.9 mrad (which also served to and subsequently monochromatized by a Si(111) channel cut monochromator. Focusing of the beam to a spot size of 1.0 × 0.2 mm on the sample was achieved by a Rh coated toroidal mirror. The beamline provides an X-ray flux of 6 × 10¹⁷ photon s⁻¹ and an energy bandwidth of 1 eV at the Cu K-edge. XAS spectra of samples pressed to pellets were collected in transmission mode using 20 cm long ionization chamber filled with 1 bar nitrogen. Spectra were collected with 1 Hz scanning speed (quick-scanning mode) and 300 spectra were averaged per sample. The data were processed using ProQEXAFS[40] to calibrate, normalize and average the obtained XAS spectra with subsequent EXAFS analysis performed within the Demeter software package.[81] The fitting of the EXAFS was conducted using theoretical structures for Cu placed within the hollows of the C₃N₄ structure representing d₅-planar and octahedral symmetry.

3D printing of the CSMs and coating with the single-atom catalyst. The catalytic static mixers (CSMs) had an external diameter of 6 mm and a length of 150 mm. The materials were 3D-printed from 316 L stainless steel powder using the electron beam melting (EBM) method on the Arcam A1 EBM 3D printer. This technique uses an electron beam to melt and fuse metal powders, and re-nanostructure them, layer-by-layer, into three-
dimensional form. The process was conducted in vacuum at an initial bed temperature of 850 °C. Supports with a diameter of 0.5 mm and a length of up to 3 mm were built underneath the CSMs to aid in the melting process and avoid swelling of the part above the plane of the powder layer. At the end of the printing process, the unfused powder was removed from the mixer by grit-blasting with the same powder material. Further details on the printing process using different materials can be found elsewhere.\[42]\ Prior to coating, the stainless-steel bodies of the static mixer scaffolds underwent chemical pre-treatment to remove any debris, grease, and any undesirable oxide layer on the surface. A coating slurry was prepared by adding a blend of alumina and the above-described single-atom catalyst powder into deionized water. A typical slurry contained 15 wt.% of solids (at 1 : 1 ratio between alumina:single-atom catalyst) and was stirred for several hours to ensure the formation of a homogeneous mixture. The static mixers were thus coated with an automated arm by dipping them into the slurry for a few seconds followed by removal of the excess material to prevent blockage of the internal openings of the 3D-printed static mixer. The CSM was then dried at room temperature for 4 h and was stirred for several hours to ensure the formation of a homogeneous mixture. The static mixers were thus coated with an automated arm by dipping them into the slurry for a few seconds followed by removal of the excess material to prevent blockage of the internal openings of the 3D-printed static mixer. The CSM was then dried at room temperature for 4 h and subsequently in a vacuum oven at 120 °C for a further 16 h. The coating and drying steps were repeated several times until the desired catalyst dry loading value (typically 8.6–9.0 wt.% supported catalyst) was achieved.

**Characterization method of the coated CSMs.** Scanning electron microscopy studies of the coated mixers were performed using a double Cs-corrected JEOL JEM-ARM200F (STEM) operated at 80 kV equipped with a cold field emission gun.

**Hydrogenation procedure.** Continuous-flow hydrogenations were performed in a custom-built hydrogenation setup, which can be configured to run with up to 10 tubular microreactors (each with an internal diameter of 6 mm and a length of 150 mm) connected in series. Each tubular reactor contained an integrated and perfectly fitting static mixer (with an external diameter of 6 mm and a length of 150 mm). For the hydrogenation of benzaldehyde, two tubular microreactors were used, which provided a total reaction volume of 5.6 mL. For the hydrogenation of furfural, one microreactor was used, giving a total reaction volume of 2.8 mL. In a typical experiment, the reactants were dissolved in a solvent (ethanol, water, or ethyl acetate) at a concentration of 0.5 M. The reactor was operated at a total pressure of 24 bar, a temperature of 60–120 °C, a liquid flow rate of 0.25–1 mL min⁻¹, and a H₂:substrate ratio of 2–30. The estimated residence times for the above-mentioned conditions lay between 3 and 26 min. Upon start-up, the solvent was introduced into the microreactor, and the reactor was heated and pressurized to the desired experimental conditions. Thereafter, hydrogen gas was introduced at the designed gas flow rate; the gas-solvent mixture was flowed for 15 min through the tube(s) to reach steady-state operation. The feed was then switched to pump the stock solution, which delivered the substrate to be hydrogenated. After each reaction, the CSM microreactor was flushed with copious amounts of water (200 mL) and isopropyl alcohol (200 mL) to wash all remaining substrate and product off the mixers. Then, the reactor was blown dry with compressed nitrogen. Once dried, the CSMs were removed from the reactor chamber and stored in a dry, dark, and cool place.

The product yield was deduced by proton nuclear magnetic resonance (¹H NMR) and confirmed by gas chromatography mass spectrometry (GC-MS), both measured off-line. ¹H NMR were recorded on a Bruker AC-400 spectrometer in deuterated chloroform. The residual solvent peak at δ = 7.26 ppm was used as an internal reference. GC-MS were obtained with a Perkin Elmer Clarus 600 GC mass spectrometer using electron impact ionization in the positive ion mode with an ionization energy of 70 eV. The gas chromatography was performed with a Perkin Elmer Elite-5MS GC column (30 m × 0.25 mm internal diameter, 0.25 μm film thickness), with a temperature program of 40 °C for 2 min, then at 10 °C min⁻¹ to 280 °C where the temperature was held for 4 min with a split ratio of 70, an injector temperature of 250 °C and the transfer line was set to 250 °C. Inductively coupled plasma mass spectroscopy (ICP-MS) of the liquid after reaction was performed using a Varian ICP-MS. The product solution (0.201 g) collected from the reactor was digested in 69 % HNO₃ and 30 % H₂O₂ by heating in a glass beaker on a hotplate. Once the reaction had ceased, the sample was diluted with Milli-Q (high purity) water before being analysed by ICP-MS. Certified multi-element standards were used to check the accuracy of the calibrations and the method used.

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**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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