



3D printing of a heterogeneous copper-based catalyst



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ABSTRACT

One of the most important environmental challenges of modern society is to develop new catalysts that make possible chemical processes with reduced environmental impact. Catalyst immobilization is an appealing strategy that, in addition to facilitating catalyst recovery, has proved to give higher catalytic performance, since the solid support usually provides chemical, thermal, and mechanical stabilization to the catalytic species. In this work Cu/Al₂O₃ catalytic system with a woodpile porous structure is synthesized by 3D printing and then sintered at high temperature to generate a copper-supported rigid structure with high mechanical strength, a high surface-to-volume ratio, and controlled porosity. The catalytic species (Cu) are immobilized in the Al₂O₃ matrix to avoid the leaching of the metal into the reaction medium. Al₂O₃ was selected because it is a good material to obtain a structure with high mechanical stability after high-temperature treatment. The resulting device shows high catalytic efficacy and good recyclability and did not produce leaching of copper to the reaction medium in different Ullmann reactions. Ease of preparation, excellent reactivity, recyclability, and negligible metal contamination all make the 3D printing technique a good strategy for fabricating other types of metal/oxide heterogeneous catalytic systems.

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1. Introduction

The increasing environmental consciousness of modern society challenges the chemical community to develop catalytic systems that enable chemical processes with a reduced environmental impact (E-factor) [1]. In this context, catalyst immobilization is an appealing strategy that, in addition to facilitating catalyst recovery and operation in a flow-continuous format, has proven to give higher catalytic performance, since the solid support usually provides chemical, thermal, and mechanical stabilization to the catalytic species [2]. In addition to the intrinsic features defined by the catalytic species and the solid support, the key properties of the heterogeneous catalytic material are highly dependent on the fabrication method (e.g., catalytic performance, loading levels of the catalyst, morphology and dimensions of the system). Leaching of the metal into the reaction medium is a critical problem for applications in the pharmaceutical industry, since regulatory agencies have established acceptable levels for transition metals within drugs in the low ppb range [3]. The synthesis of heterogeneous catalysts is currently dominated by wet chemical methods such as

impregnation [4,5], co-precipitation [6], electrophoretic deposition [7], and sol-gel [8] and vapor deposition techniques, the latter of which includes chemical vapor deposition (CVD) [9] and atomic layer deposition (ALD) [10]. Liquid phase procedures have proven to be useful, but they do suffer from some drawbacks, which are generally associated with low loading levels, arduous experimental procedures, nonuniform catalytic species distribution [7,11,12], ineffective catalyst immobilization, and insufficient mechanical strength.

Transition metal-catalyzed reactions (TMCR) occupy a prominent position among modern synthetic methods in industrial and academic laboratories [13]. The incorporation of these reactions into the synthetic armory provided conceptually novel approaches for the formation of C–C and C–heteroatom bonds, as well as for C–H functionalization [14]. The excellent selectivity and functional group compatibility of TMCR offer robust and mild synthetic alternatives for the preparation of complex natural products, pharmaceuticals, heterocyclic compounds, agrochemicals and polymers, etc. [13,14]. The abundance of copper, along with its diverse chemistry and low cost, make it an attractive alternative to precious metals (Pd, Pt, Au, Rh, Ir) for use in organic synthesis [15]. In fact, copper-mediated reactions have a longer history than palladium-catalyzed reactions and, indeed, Ullmann [15,16] and Glaser

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[15,17] reactions have been employed for more than 100 years. Although it is less active than its noble metal analogues (e.g., Pd or Rh), copper oxide (CuO) has been extensively employed in the Ullmann reaction for the formation of C–N, C–O, and C–S bonds, which are prevalent linkages in compounds of biological and pharmaceutical interest. The results of recent studies have shown that the use of CuO nanoparticles enables the conditions for the Ullmann reaction [18] to be far less harsh and also extends its scope to nonactivated substrates. We describe here, for the first time, the direct fabrication of a highly robust, efficient, and reusable copper heterogeneous catalyst system using 3D printing [19,20]. This is a layer-by-layer technique in which concentrated ink with the desired rheological behavior is extruded through a nozzle. The most common inks are based on ceramics, polymers, colloidal systems, or semiconductor materials. These inks can be assembled into complex 3D structures with high surface-to-volume ratios with precise control of porosity, size, and shape. 3D printing has recently been employed for the fabrication of structures with different applications, such as photonic band gap materials [21], tissue engineering [22], catalysts [23,24], integrated electronic devices [25], and vascularized tissues [26].

In this work, we designed a heterogeneous catalytic system consisting of a sintered Al_2O_3 support on which catalytic copper species are immobilized, thus generating a catalytic structure with high mechanical and chemical stability. $\text{Cu}/\text{Al}_2\text{O}_3$ woodpile structures were synthesized and then sintered at high temperature, thus generating a copper-supported rigid structure with exceptional mechanical strength, a high surface-to-volume ratio, and controlled porosity. The resulting device was tested in a model Ullmann reaction, validating its high catalytic efficacy and good recyclability, and did not produce leaching of copper species to the reaction medium. The experimental protocol was performed in four stages: (1) Preparation of an aqueous concentrated colloidal gel ink [20,27] in which Al_2O_3 ceramic powder, polymer binders, and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ were mixed to obtain a good dispersion and achieve quantitative control of the copper level in the Al_2O_3 network (5 wt.% Cu in the ink). (2) Extrusion to build a 3D woodpile structure. (3) Sintering of the structure at high temperature. (4) Validation of the catalytic efficacy of the $\text{Cu}/\text{Al}_2\text{O}_3$ in a model Ullmann reaction.

2. Experimental

2.1. Preparation of the catalyst system

The ink was prepared as follows: 92.31 g of Al_2O_3 powder with a mean particle size of 0.5 μm , a specific surface area of 7.85 $\text{m}^2 \text{g}^{-1}$, and a density of 3.96 g cm^{-3} (Almatis GmbH, Germany) was added to a 2.56 M aqueous solution of copper(II) nitrate hemi(pentahydrate), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\geq 98\%$ (Sigma–Aldrich). The viscosity modifier hydroxypropyl methylcellulose (HPMC, viscosity 2600–5600 cP) (Sigma–Aldrich) was added at 5 mg per mL of the Al_2O_3 powder. The resulting suspension was mixed in a planetary centrifugal mixer (ARE-250, Thinky Corp., Tokyo, Japan) at 2000 rpm for 2 min and was allowed to stand at room temperature for 1 h. The cationic polyelectrolyte poly(ethylenimine) (PEI, Mw = 2000, Sigma–Aldrich) was added in a ratio of 6.3×10^{-3} mL per mL of the ceramic powder, and the suspension was again mixed four times at 2000 rpm for 2 min. Finally, the ink was concentrated by the removal of water by evaporation until suitable for extrusion.

A concentrated $\text{Cu}/\text{Al}_2\text{O}_3$ aqueous ink (51 vol.% solids, with a viscosity of $\eta = 323.7 \text{ Pa s}$) was loaded into a syringe (3 mL, Nordson EFD, USA) attached by a nozzle with a diameter of 410 μm (Nordson EFD, USA). A robotic deposition A3200 system (Aerotech Inc., USA) was used to create the woodpile structures. The robotic

motion was controlled by the software Robocad 3.4 (3D Inks, USA). A Performus VII air-powered fluid dispenser attached to an HP7x (Nordson EFD, USA) was used to control the ink flow rate (pressure 21 bar and print velocity of 2 mm s^{-1}). For a cylindrical woodpile structure (10 mm diameter and 12 mm height) with a body-centered tetragonal (bct) symmetry, the rod spacing was $d = 960 \mu\text{m}$ and the rod diameter was $w = 410 \mu\text{m}$. This corresponds to an open porosity of 57%. This structure was formed in air at a relative humidity of 60–70% and a temperature of 23–25 °C. Finally, the woodpile structure was dried at room temperature for 24 h and subsequently sintered at 1400 °C for 2 h in air in a conventional furnace at a heating rate of 10 °C min^{-1} .

2.2. Catalyst characterization

The copper loading of the sample was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Varian Liberty 200). The sample was prepared in a Claisse Fluxer automatic fusion device (Corporation Scientifique Claisse, Quebec, Canada) and was fitted with one 20 mL platinum 5 wt.% gold alloy crucible and with 200 mL quartz beakers for solution preparation. The device fuses the sample in the platinum–gold alloy crucible over an air–propane flame with lithium metaborate ($\text{Li}_2\text{B}_4\text{O}_7$). A quantity of 0.5 g of finely powdered sample and 1.5 g of $\text{Li}_2\text{B}_4\text{O}_7$ were mixed in the platinum crucible. Previously, a nonwetting agent (0.1 g of LiI) was added to the fusion mixture to prevent the molten flux from adhering to the walls of the crucible, as well as to guarantee the complete transfer of the fused sample from the crucible into the solvent. When the fusion is over, the molten glass containing the sample is cast into a solution of 5 wt.% NO_3H and dissolved. After the solution is diluted to 100 mL, it is analyzed by ICP-OES.

X-ray diffraction (XRD) patterns of the dried and calcined ink powder samples were obtained with a Siemens D5000 diffractometer using $\text{Cu K}\alpha$ radiation at $\lambda = 1.5418 \text{ \AA}$. Diffraction data were scanned in a 2θ range of 10–80° with a step size of 0.05°. A quantitative phase analysis was carried out using Rietveld refinement with the FullProf program.

Optical microscopy images were obtained on an Olympus SZX12 stereomicroscope (Olympus, Japan). The microstructural surface of the sintered woodpile structure was analyzed by scanning electron microscopy (SEM) (Model JEOL 6400, Japan).

2.3. Catalytic activity evaluation

To equimolar amounts (0.1 mmol) of the halide and the nitrogenated nucleophile in DMF were added KOH and the 3D heterogeneous $\text{Cu}/\text{Al}_2\text{O}_3$ catalytic system. The reaction mixture was heated at 80 °C under orbital stirring in a Kimble vial (7 mL) for 2–4 h. Once the reaction had finished (TLC control), the solvent was separated from the catalyst and this was successively washed with methanol and dichloromethane (5 mL). The organic solvents were removed under vacuum and the residue was purified by column chromatography to afford the desired compound (2–4).

2.4. Evaluation of the copper leaching with $\text{Cu}/\text{Al}_2\text{O}_3$: Three-phase test

To a 50 mL glass fritted reaction vessel was added Wang resin (4.0 g, 1.25 mmol g^{-1} , 5 mmol). The resin was first washed with dry dichloromethane ($2 \times 30 \text{ mL}$) and then suspended in dry dichloromethane (30 mL). To the resin slurry was added diethylisopropylamine (30 mmol) and the vessel was submitted to orbital stirring for 5 min before 4-iodobenzoyl chloride (25 mmol) was added in one portion. The resulting slurry was stirred for 24 h at room temperature. The resin was filtered, successively washed with dichloromethane ($2 \times 40 \text{ mL}$), methanol ($2 \times 30 \text{ mL}$), and

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