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Copper nanoparticles supported on permeable monolith with carboxylic acid surface functionality: Stability and catalytic properties under reductive conditions

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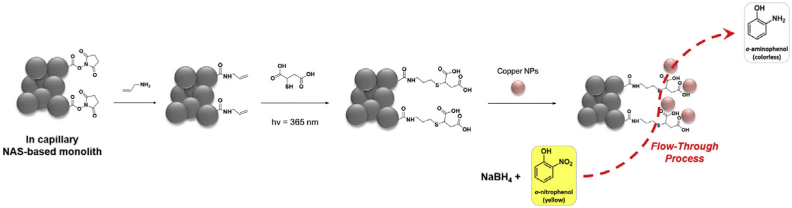
HIGHLIGHTS

- Monolithic micro-reactors with surface immobilized copper nanoparticle for flow through catalytic processes.
- Porous polymer-stabilized copper nanoparticles.
- Photothiol-ene click chemistry for the effective surface functionalization of porous monolithic polymers.
- Surface adsorption of copper nanoparticles through *in-situ* and *ex-situ* strategies.

GRAPHICAL ABSTRACT



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ABSTRACT

This work reported on the immobilization of copper metallic nanoparticles at the interface of mercaptosuccinic acid-functionalized *N*-acryloxysuccinimide-based monoliths. Upon photochemically-mediated free radical copolymerization of *N*-acryloxysuccinimide reactive monomer with ethylene glycol dimethacrylate cross-linker, reactive monoliths were obtained. Nucleophilic substitution of the *N*-hydroxysuccinimide moieties with allylamine, allowed for the synthesis of an olefin-functionalized monolith, as demonstrated by Raman spectroscopy. Mercaptosuccinic acid was anchored at the surface of the porous polymeric material through photochemically-driven thiol-ene "click" addition. In a final step, adsorption of copper nanoparticles at the surface of the resulting carboxylic acid functionalized monolith was achieved *via* two distinct pathways. It was either realized by percolation of a suspension of pre-formed copper nanoparticles through the capillary or by *in situ* reduction of $Cu^{(II)}Br_2$ salt solution preliminary flown through the monolith. After characterization of the resulting hybrids by scanning electron microscopy and energy-dispersive X-ray spectroscopy, investigations were further pursued regarding the catalytic behavior of such hybrid materials. The possibility to reduce 2-nitrophenol into the corresponding 2-aminophenol within a few minutes *via* a flow-through process inside the hybrid monolithic capillary was notably successfully demonstrated.

1. Introduction

Over the past decade, metallic nanoparticles (NPs) have appealed the research community due to their unique intrinsic

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properties. Because of their high surface area to volume ratio, they present unexpected enhanced properties compared to those of their bulk material counterparts. Indeed surface effects are predominant in nanometals and confer them with very specific properties. This nano-effect is particularly pronounced in different applications and especially in nanoparticle-based heterogeneous organometallic catalysis. Among the plethora of nanometals declined for heterogeneous catalysis, gold [1], palladium [2], platinum [3] and silver [4] are the most reported in the literature. They are largely used for various coupling reactions such as Suzuki-Miyaura [5,6], Sonogashira [6,7] and Heck [3,6,8] cross-coupling reactions as well as for the reduction of nitroarenes [1,9–13], to cite but a few. Such nanoparticulate systems require a fine tuning of the functionalities of the (macro)molecules used to stabilize them or of the surfaces on which they are adsorbed so as to increase their reactivity. This has been deeply investigated in the case of Au [14] or Pd [15,16] nanoparticles stabilized with peptides in which the amino-acid sequence was carefully studied for optimal catalytic efficiencies. In the actual context of environmental efforts, reduction of nitroarenes has a great importance because it could notably find applications in the transformation of nitrobenzene derivatives, which are well-known toxic pollutants, into much benign compounds. To the best of our knowledge, copper nanoparticles (CuNPs) have been so far not much investigated in such heterogeneous catalysis applications. CuNPs, that are well-known for their antifungal [17] and antibacterial [18] properties, also possess interesting catalytic behavior, especially in the Huisgen dipolar azide-alkyne cycloaddition [6,19] reaction, also referred as CuAAC reaction. In addition, these copper-based nanometals have been shown to catalyse the reduction of nitroarenes [11,20–22]. Due to their rather unstable nature, CuNPs colloids are generally stabilized by polymeric species such as poly(*N*-vinylpyrrolidone) (PVP) [23] or poly(vinyl alcohol) (PVA) [24] for instance. Other investigations in the area relied on the immobilization and stabilization of CuNPs onto polyimide (PI) thin layer [25], into composite films [26–28] based on organic polymers, or onto metal oxides [29–31]. To the best of our knowledge, such CuNPs have never been immobilized at the surface of porous polymers. In this regard, polymer-based monolithic supports may be candidates of choice as they can be easily prepared and functionalized with a variety of different chemical functions such as amine, thiol or carboxylic groups, *etc.* [32,33] This was notably demonstrated a few years ago by our research group regarding the immobilization of gold NPs on the surface of monolithic poly(*N*-acryloxysuccinimide-*co*-ethylene glycol dimethacrylate)-based (P(NAS-*co*-EGDMA)) capillaries [34]. Additionally, surface-immobilization avoids a supplementary purification step in order to recover the metal-based catalyst as it is, in this strategy, entrapped onto the porous matrix.

Herein, we described unprecedented immobilization of copper nanoparticles at the surface of a monolithic capillary column so as to use the resulting hybrid column as microreactor in the reduction of nitrophenols *via* a flow-through process. After chemical modification of the polymer to functionalize it with an alkene moiety, a photo-induced thiol-ene “click” chemistry reaction was investigated with mercaptosuccinic acid to graft carboxylic acid moieties onto the polymer matrix surface. Carboxylic acid functions are known to chelate copper ions [35] and CuNPs [26]. Additionally, this strategy allowed for performing this functionalization chemical step in mild conditions generally associated with the “click” thiol-ene process. Two strategies were envisioned to ensure the immobilization of copper nanoparticles. In the first strategy, commercially available preformed copper nanoparticles were percolated into the capillary and consequently immobilized onto the monolithic capillary by adsorption. In the second one, copper (II) ions were adsorbed onto the surface of the monolith *via* dynamic loading. A consecutive step consisting in the hydride-mediated reduction of copper ions allowed for the *in situ* formation of copper nanoparticles. Finally, applications of the as-obtained hybrid monolithic capillaries as flow-through microreactors were successfully investigated.

2. Materials and methods

2.1. Experimental

N-Acryloxysuccinimide (NAS, >98%) and toluene (99.8%) were obtained from TCI. 3-(trimethoxysilyl)propyl methacrylate (γ-MAPS, 98%), sodium borohydride ($NaBH_4$, ≥98%), sodium hydroxide (NaOH, 1 M), hydrochloric acid (HCl, 0.1 M for HPCE), mercaptosuccinic acid (97%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), copper (II) bromide ($CuBr_2$, 99%) and copper nanopowder (40–60 nm, ≥99.5% trace metals basis) were purchased from Sigma Aldrich. Ethylene glycol dimethacrylate (EGDMA, 98%) and 2,2′-azobisisobutyronitrile (AIBN, 98%) were obtained from Acros Organics. 2-nitrophenol (*o*-nitrophenol, 98%) and allylamine (98%+) were purchased from Alfa Aesar. Acetone, HPLC grade acetonitrile (ACN) and absolute ethanol were supplied by Carlo Erba. All reagents were used without any further purification except for AIBN that was recrystallized from methanol prior to use. 18.2 MΩ deionized water was filtered through a Milli-Q Plus purification pack. Fused silica capillaries with a UV-transparent external coating (100 μm I.D.) were obtained from Polymicro Technologies.

2.2. Instrumentation

An HPLC pump (Ultimate 3000 Dionex) was used to flush monolithic columns with 2-nitrophenol solutions along with mobile phase. Spectrolinker XL-1500 UV Crosslinker (Spectronics Corporation) equipped with eight lamps (8 × 15 W, 365 nm) was used to photoinitiate the polymerization and the thiol-ene addition reaction of mercaptosuccinic acid. UV–vis spectra were recorded in UV quartz cuvette (1 mm length × 10 mm width × 45 mm height) on a Cary 60 UV–vis Spectrophotometer from Agilent Technologies using a 5 nm s^{-1} scanning speed. Chemical Structure of the monolith-containing capillaries was investigated using a Raman microscope apparatus XPlora One from Horiba Jobin Yvon equipped with a laser emitting at 638 nm. Cross sections of the in-capillary monoliths were investigated in different places to ensure for the homogeneity of the monoliths. Experimentally, the cut capillary pieces were placed vertically by planting them into rubber septa so as to allow direct investigation under the Raman microscope. The acquisition time was fixed at 1 min. Scanning Electron Microscopy (SEM) investigations of the materials were performed with a MERLIN microscope from Zeiss equipped with InLens, BSE and SE2 detectors using a low accelerating tension (2–3 kV) with a diaphragm aperture of 30 μm. Prior to analyses, the cut capillary pieces were coated with a 4-nm layer of palladium/platinum alloy in a Cressington 208 HR sputter-coater. Energy-dispersive X-ray spectroscopy (EDX) was performed using an SSD X-Max detector of 50 mm^2 from Oxford Instruments (127 eV for the Kα of Mn). For EDX and SEM measurements, the capillary pieces were placed vertically by sticking them with double-sided tape on metallic supports allowing analyses of the in-capillary monoliths.

2.3. Synthesis of the monolithic capillaries

The synthesis of the (NAS-*co*-EGDMA) monolithic columns relies on a three-step process involving (*i*) the synthesis of the porous

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