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ARTICLE

Recoverable and Reusable Polymer Microbead-Supported Metal Nanocatalysts for Redox Chemical Transformations

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ABSTRACT

Metal nanoparticles have been widely exploited in catalysis, but their full impact on the environment and human health is still under debate. Here we describe the one-step fabrication of recoverable and reusable polymer microbead-supported metal and metal oxide nanocatalysts for application in batch reactions and flow systems. Au, Ag and Fe₃O₄ nanoparticles were prepared directly at the surface of commercial benzylamine-coated spherical polymer beads in water by using low energy microwave radiation for 5 min. The functionalization of microbead surface with betalamic acid, an antioxidant from plant origin, before irradiation changes the morphology and catalytic properties of the grafted nanoparticles. No leaching of the active phase was observed during the application of these effective and ready-to-use nanocatalysts on the reduction of 4-nitrophenol and oxidation of dihydrorhodamine 123. The supported nanocatalysts were recovered by filtration and/or magnetic separation and reused up to three times without significant drop in catalytic performance. These results can stimulate the controlled and facile synthesis of recoverable microbead-supported magnetic and non-magnetic nanocatalysts that can be applied under myriad reaction conditions and reused multiple times.

Keywords – polymer-supported nanoparticles, ion-exchange resin, nanocatalyst, continuous flow reaction, sustainable chemistry, betalain.

Graphical table of contents

1. INTRODUCTION

The properties of metals and metal oxide nanocatalysts can be tailored to enhance the selectivity, specificity and energetic efficiency of chemical transformations.¹ However, as the particle size of the nanocatalyst decreases, they may become increasingly toxic, mostly due to their ability to cross cell membranes and interfere with metabolic processes.²⁻³ For example, Fe₃O₄ (magnetite) nanoparticles (NPs) decrease the activity of superoxide dismutase and catalase enzymes in the Rainbow trout,⁴ and sub-10 nm silver (Ag) and gold (Au) NPs can reach systemic circulation and induce the formation of reactive oxygen and nitrogen species *in vivo*.⁵

Although developments in the synthesis of nanoparticles have enabled the obtaining of high performance nanocatalysts,⁶ these materials have an intrinsic separation problem that limits their recovery and reuse. The immobilization of metal nanocatalysts in activated carbon, polymers and inorganic bulk matrices, such as dendritic fibrous nanosilica,⁷ represents an effective strategy to prevent their leaching and biological accumulation.⁸⁻⁹ These supports not only facilitate the recovery and reuse of the nanocatalyst but avoids the aggregation of the NPs during successive reaction cycles or continuous flow conditions and promotes catalysis by creating new active sites at the metal-support interface.¹⁰⁻¹¹ Ideal supports are expected to be chemically inert, have large surface area and uniform size and retain the nanocatalyst efficiently. The immobilization of active phases into uncoated magnetic supports facilitates the recovery of the catalyst, although caution should be taken depending on the application due to reactivity and stability issues.¹²⁻¹⁴

Commercial ion exchange polymeric resins are convenient supports for the immobilization of NPs due to their prompt availability and high chemical versatility and stability. These supports are easy to recover due to their size and shape uniformity, have relatively large surface area, are compatible with myriad chemical reactions while can be chemically modified, and are expected to graft the nanocatalyst in a stronger manner compared to other adsorptive supports.¹⁰⁻¹¹ Supported metal nanocatalysts are usually prepared by reduction of a metal cation precursor adsorbed at the surface of the resin using hydrogen or stronger reductants such as hydrazine, borohydrides or formaldehyde.¹⁵ However, depending on the method used for the synthesis, the nanocatalyst is weakly adsorbed at the resin surface leading to nanoparticle leaching and aggregation at the surface, thus compromising the strategic advantage of using these materials for catalysis.

Supports containing reducing agents covalently bonded to their polymeric matrix can favor the attachment of NPs to its surface if the reduction step and the nucleation of growth species are fast.¹⁶ Lewatit VP OC 1065 is a weakly basic anion-exchange resin found as spherical macroporous beads of 0.7 mm median diameter. This resin is formed by a divinylbenzene crosslinked polymer containing a benzylamine repeating unit and has been used for the capture of CO₂¹⁷⁻¹⁸ and aldehydes¹⁹. We hypothesized herein that the reduction of the appropriate precursors by the benzylamine moieties in VP OC 1065 would promote the formation of NPs at the surface of the polymer bead.²⁰⁻²¹ Although the resin could stabilize the NPs via electrostatic and steric effects,^{9, 15} external stabilizing agent are expected to influence the shape and morphology of the NPs.²² In this sense, betalains are plant and fungi antioxidant chromoalkaloids that have been used for the sustainable synthesis of metal nanoparticles due to their low reduction potential and high stabilization

capacity.²³⁻²⁶ Betalamic acid, the biosynthetic precursor of all betalains, can be captured by the VP OC 1065 resin due to the spontaneous reaction between the immobilized benzylamine and the aldehyde portion of the natural product.^{19, 27} The resulting functionalized microsphere is negatively charged under near neutral conditions and has the potential to both attract and reduce metallic precursors as well as to stabilize the resulting NPs.

Herein, we report the expeditious synthesis and application of recoverable and reusable Ag, Au and Fe₃O₄ nanocatalysts grafted into polymer microbeads. Supported Au and Ag NPs catalyze the reduction of *p*-nitrophenol (PNP), a toxic and persistent pollutant in industrial and agricultural wastewater,²⁸ under continuous flow and batch conditions with virtually no metal leaching into solution. Microbead supported Fe₃O₄ were used to catalyze the oxidation of dihydrorhodamine 123 (DHR) by hydrogen peroxide. Low energy microwave irradiation of the Lewatit VP OC 1065 resin in the presence of metal cation precursors produce nanoparticles directly at the surface of the polymer leading to strong grafting. The support shows high chemical resistance and hence do not affect the catalytic activity of the active phase, which is hardly achieved by using magnetically active metallic supports, such as iron oxide-based materials.¹⁴ The functionalization of the particle surface with betalamic acid, a negatively charged natural product, allows for the control over both the size and morphology of the NPs as well as their catalytic properties. The 5-min on-water synthetic strategy can be applied to both magnetic and non-magnetic NPs¹⁴ and results in ready-to-use supported nanocatalysts in a faster and more convenient way compared to alternative methods for the synthesis of supported catalysts, i.e., sol-gel¹³ and

solvothermal approach¹². Finally, the resulting materials can be easily recovered by filtration and/or magnetic separation and reused.

2. MATERIALS AND METHODS

2.1 General

All chemicals were purchased from Sigma-Aldrich and used without further purification, except as otherwise stated. Solutions were prepared using deionized water (18.2 M Ω cm at 25 °C, TOC $\leq$ 4.0 ppb, Milli-Q, Millipore). Betalamic acid (HBt) was extracted from the base-hydrolyzed juice of red beetroots using ethyl acetate and processed as described previously.²⁹

2.2 Functionalization of Lewatit beads

Lewatit VP OC 1065 (Lanxess, 200 mg) was added to a solution of HBt in ethyl acetate (1 mL, 2.4×10^{-7} mol). After 1 min under magnetic stirring, the beads were filtered and dried under air in the dark at room temperature. The resulting material, namely BeetBead, was stored at -20 °C for further use.

2.3 Synthesis of microparticle-supported nanocatalysts

Lewatit VP OC 1065 or BeetBead (200 mg) and an aqueous solution of AgNO₃, HAuCl₄ or FeSO₄ (5 mL, 4.5×10^{-3} mol L⁻¹) were added to a 10 mL borosilicate glass round-bottom tube equipped with a reflux condenser and submitted to microwave irradiation (100 W, 5 min, 18 kJ, magnetic stirring) using a monomodal microwave reactor (CEM Discovery). After cooling, the beads were washed with water, filtered and dried under air in the dark at room temperature.

2.4 Morphology of the nanoparticles

Scanning electron microscopy (SEM) was carried out using a Philips XL-30 FEG microscope. Microspheres on carbon tape were gold sputtered (5-nm-thick) in a Balzers Sputter Coater SCD 004 before imaging to avoid charge effects and blurriness. Images were acquired at 15 kV accelerating voltage with either the secondary electron (SE) or the backscattered electron (BSE) detector and magnification of 25,000 $\times$, 50,000 $\times$ or 100,000 $\times$. Particle size analysis was carried out using the ImageJ software.³⁰

2.5 Oxidation state of the nanoparticles

X-ray photoelectron spectroscopy (XPS) was carried out using a PHI Quantera II scanning XPS microprobe equipped with monochromatic Al K α radiation. Microspheres were mounted on carbon tape and electrically floated using microscope slides. Due to the isolating character of the samples, measurements were conducted under constant neutralization using low energy electrons and Ar⁺ ions.³¹ Survey scans, as well as details of selected core levels, were obtained from the surface of the samples. The C-1s core level at 284.6 eV was used for internal binding energy calibration. The carbon signal originates from adventitious carbon as well as from the polymers. This, in combination with the non-conducting samples, gives binding energy estimations with error bars in the order of ± 0.3 eV. The Ag-3d, Au-4f and Fe-2p signals were fitted using doublet peaks with spin-orbit separations of 6.0 eV, 3.6 eV and 13.6 eV, respectively, as reported in the NIST database. The backgrounds were removed with Shirley functions.

2.6 Reduction of *p*-nitrophenol

Batch reaction. The polymer-supported Au or Ag nanocatalyst (10 mg) was added to an aqueous solution of *p*-nitrophenol (PNP, 6.5×10^{-5} mol L⁻¹) and NaBH₄ (0.1 mol L⁻¹). The mixture was kept under magnetic stirring at 25 °C for 1 h. The reaction progress was monitored by UV-Vis absorption spectroscopy at every 10 min. The rate constant normalized to the nanoparticle area per unit of volume, k_1 , was calculated using Eq. 1:

$$-\frac{dc_t}{dt} = k_{app}c_t = k_1Sc_t \quad \text{Eq (1)}$$

where c_t is the concentration of the reactant at time t and S is the surface area of the nanoparticle per unit of volume of the system, in m² L⁻¹.³² The apparent rate constant, k_{app} , was determined from the slope of the linear correlation of $\ln(A/A_0)$ with time. The surface area of the nanoparticles in 10 mg of resin was estimated from the nanoparticle size distribution and SEM images, assuming spherical nanoparticles.

Flow reaction. Reactions were performed under continuous flow using a flooded-bed H-Cube Mini reactor (ThalesNano). Aqueous NaPNP (6.5×10^{-5} mol L⁻¹) was flown at 0.2 mL min⁻¹ through the polymer-supported Au or Ag nanocatalyst (10 mg) packed in a Catcart cartridge using hydrogen as carrying gas (10 or 20 bar, residence time: ~ 70 s). After the temperature was set, the system was led to stabilize for 5 min. During the run, samples were collected at every 10 min and quantified by UV-Vis absorption spectroscopy using a molar absorptivity coefficient of 15,500 L cm⁻¹ mol⁻¹ at 400 nm.

2.7 Oxidation of dihydrorhodamine 123

Polymer-supported iron oxide nanocatalyst (5 mg) was added to a quartz cuvette (10 mm optical path) containing 2 mL of an aqueous solution of dihydrorhodamine 123 (DHR, $5.7 \times 10^{-3} \text{ mol L}^{-1}$) and H_2O_2 ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) at pH 2,0 thermostated at 45 °C. The reaction was kept under magnetic stirring and monitored by fluorescence spectroscopy for 4 h; excitation (EX) wavelength: 480 nm, emission (EM) range: 500 – 700 nm, EX/EM slits: 2.5/5.0 nm, photomultiplier voltage: 600 V.

2.8 Quantification of Au and Ag

The silver and gold content in Lewatit VP OC 1065 or BeetBead was quantified by atomic absorption spectroscopy (AAS). The supported nanocatalyst (30 mg) was submitted to acid leaching using aqua regia (1.0 mL, 80 °C, 20 min). The beads were removed, the solution was diluted ten times and submitted to AAS analysis. The leaching of nanocatalyst during PNP reduction by NaBH_4 was investigated by removing the supported catalyst after reaction completion and submitting the resulting solution (5 mL) to AAS analysis.

Analyses were carried out on a Vario 6 flame atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with deuterium background correction and a hollow-cathode lamp at 328.1 nm for silver and 242.8 nm for gold; instrumental parameters: applied current = 5 mA, spectral band-pass = 0.8 nm, air flow rate = 400 L h^{-1} , and acetylene flow rate = 80 L h^{-1} . The metal content in the supported catalyst and in solution after reaction was determined by using calibration curves and corrected for the amount of catalyst used and dilution effects. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated according to the recommendations of the IUPAC;³³ $\text{LOD} = 3\sigma / S$ and $\text{LOQ} =$

$10\sigma / S$, where σ is the standard deviation of ten consecutive measurements of the analytical blank solution, and S is the slope of the respective calibration curves (Figure S1).

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of polymer-supported nanocatalysts

The open vessel microwave irradiation of aqueous solutions of either AgNO_3 , HAuCl_4 , or FeSO_4 in the presence of Lewatit VP OC 1065 resin changes the reflectance spectra and color of the beads (Figures 1a, first row, and S2a). Scanning electron microscopy confirmed the formation of the NPs at the surface of the cross-linked divinylbenzene beads, viz., Ag@Lewatit , Au@Lewatit and $\text{Fe}_3\text{O}_4\text{@Lewatit}$ (Figure 1a, second row). The absence of additional stabilizing agents led to the formation of polydisperse polyhedral Ag nanostructures with sizes between 50-150 nm in diameter, Au NPs (20-30 nm in diameter), and partially aggregated iron oxide nanoclusters with 50 nm in diameter.³⁴ Nanoparticle size distributions and high-magnification SEM images are shown in Figure S3.

The modification of the surface of Lewatit VP OC 1065 beads with betalamic acid produced BeetBeads, which is coated with the benzylamine betalain (Figure 1b), as inferred by the reduction of reflectance at 485 nm compared to the unmodified counterpart (Figure S2b). Although this functionalization has been described previously as a method to capture betalamic acid,¹⁹ herein the procedure was optimized by using acidified ethyl acetate as solvent. Ethyl acetate is a benign organic solvent³⁵ that increases the betalain loading substantially, as evidenced by the changes in the Lewatit VP OC 1065 beads coloration (Figure 1a, first and third rows). Upon microwave irradiation in the presence of metal cations, BeetBeads produced nanoparticles of completely different morphology and size compared to the VP OC 1065 resin, namely, spherical Ag NPs around 25 nm in diameter, Au aggregates of 150 nm in size, and plate-like Fe_3O_4 nanostructures of 150 nm in size

(Figures 1a, forth row, and S3). Because the nanoparticles were prepared in the absence of stabilizing or capping agents, they are somewhat larger and faceted compared to their coated counterparts. However, the large number of corners and edges in these particles is expected to enhance their catalytic activity. Finally, the reduction of the noble metal ions at the benzylamine-coated microsphere is not followed by changes in surface morphology (Figure 1a).

were carried out in the absence of external stabilizing agents to produce minimum coated nanocatalysts.³⁶

XPS analyses were performed to estimate the oxidation states of the grafted Ag, Au and iron oxide NPs (Table 1 and Figure 2). The Ag-3*d* and Au-4*f* core levels could be fitted with single contributions, indicating a monovalent character. The obtained binding energies for Ag NPs as well as Au@Lewatit match that of the metallic state, i.e., oxidation state zero, Ag⁰ and Au⁰.³⁷⁻³⁹ The binding energy of the Au-4*f* core level in Au@BeetBead is shifted 0.4 eV towards higher values, however still much less than the 1.5 eV that is expected for Au with an oxidation state of +1.⁴⁰ The discrepancy is, therefore, attributed to our calibration uncertainties and we ascribe Au in Au@BeetBead to have an oxidation state of zero. Iron nanoparticles are composed of Fe₃O₄ magnetite,⁴¹ as confirmed by the XPS signals at around 710 eV, 711 eV, and 713 eV that corresponds to Fe²⁺, Fe³⁺ in octahedral geometry, and Fe³⁺ in tetrahedral geometry, respectively.⁴²⁻⁴⁶ The signal around 718 eV is related to a Fe²⁺ satellite. Changes in the relative abundance of each component in magnetite nanoparticles supported in Lewatit or BeetBead (Table 1) were somehow expected due to the marked change in nanoparticle morphology and sample color (Figure 1a).⁴⁷ Nevertheless, both samples respond to an external magnetic field (see Figure 4b), in agreement with the expected magnetic properties of Fe₃O₄.

Table 1. XPS binding energies (BE), relative abundance and species assignment.

Sample	BE (eV) ^a	Rel. abundance (%)	Species ^b
Ag@Lewatit	368.4	100	Ag ⁰
Ag@BeetBead	368.4	100	Ag ⁰
Au@Lewatit	84.1	100	Au ⁰
Au@BeetBead	84.5	100	Au ⁰
Fe ₃ O ₄ @Lewatit	709.9	15	Fe ²⁺
	710.9	57	Fe ³⁺ oct
	713.5	28	Fe ³⁺ tetr
Fe ₃ O ₄ @BeetBead	709.6	6	Fe ²⁺
	710.6	40	Fe ³⁺ oct
	712.3	54	Fe ³⁺ tetr

^a Binding energy corrected using the adventitious C-1s signal. Values related to Ag-3d_{5/2}, Au-4f_{7/2} and Fe-2p_{3/2}.

^b oct = octahedral, tetr = tetrahedral.

Figure 2. Examples of deconvoluted X-Ray photoelectron spectra (XPS) of (a) Ag-3d core level of Ag@BeetBead, (b) Au-4f core level of Au@Lewatit, and (c) Fe-2d core level of Fe₃O₄@Lewatit.

The local concentration and the properties of the surrounding ions as well as the charge at the polymer surface could affect the characteristics of the NP due to electrostatic interactions.⁴⁸ Therefore, these factors were taken into account to rationalize the observed results. According to the manufacturer, acid-base titration indicates that the amine loading of Lewatit VP OC 1065 is 3.5 mol NH₂/kg resin, although its maximum CO₂ capture capacity is 2.5 mol/kg resin.¹⁵ Under the experimental conditions used in this work (200 mg of resin, pH 7), there are 0.5 - 0.7 mmol of NH₂ available, mostly in the —NH₃⁺ form ($pK_a^{\text{Bn-NH}_3^+} = 9.34$).⁴⁹ Consequently, the Lewatit VP OC 1065 resin is expected to be positively charged. The conjugation of benzylamines with betalamic acid, on the other hand, produces the corresponding betalain, which is negatively charged in water pH 7 ($pK_a^{\text{COOH}} < 3.5$).⁵⁰ Although the ammonium groups are in roughly three orders of magnitude excess over betalamic acid, we expected the surface of the BeetBead microsphere to be less positive compared to the Lewatit VP OC 1065 resin due to the presence of the carboxylate moieties of betalains.

In water, the metal precursors consist of solvated Fe²⁺, Ag⁺, and AuCl₄⁻/[AuCl₄-_x(OH)_x]⁻ (with $x = 1 - 3$).⁵¹ Thus, the number of heterogeneous nucleation sites for cationic species, viz., Ag⁺ and Fe²⁺, at the surface of the positively charged resin is much lower than for AuCl₄⁻ and its products of hydrolysis. Considering the seed-mediated growth mechanism,⁵² and because the concentration of the nanoparticle precursors is identical, more nucleation sites imply in smaller NPs, which was indeed observed for Au NPs at Lewatit VP OC 1065 as compared to Ag and Fe₃O₄ NPs (Figures 1a and S3). Furthermore, the highly chaotropic anions, such as AuCl₄⁻, are expected to interfere with the growth mechanism of ligand-free nanoparticles and induce NP size quenching.^{48, 53} The high

polydispersity of the Ag NPs at Lewatit indicates that the NP growth may involve Ostwald ripening, in which the variations in size thermodynamically drives the growth of the larger NPs at the expense of the smaller ones.^{16, 54} Fe₃O₄ NPs at Lewatit are aggregates of smaller NPs, indicating that their growth may occur by both precursor addition and non-classical oriented attachment.⁵⁵ Furthermore, iron oxide nanoparticles were prepared in the presence of the slightly kosmotropic SO₄²⁻ anion, which due to its high hydration⁵⁶ can compromising the electrostatic stabilization of the nanoparticle and promote agglomeration through van der Waal's attraction.⁴⁸

The less positive surface of BeetBead increases the number of nucleation sites for Ag⁺, leading to smaller NPs (Figure 1a). Contrarily, the number of nucleation sites for AuCl₄⁻ and its products of hydrolysis decrease, favoring NP aggregation whose growth combines precursor addition and oriented attachment. The morphology and size of Fe₃O₄ NPs changes from spherical particles and aggregates to plate like structures upon functionalization of the support resin (Figure 1a). The rate of precursor reduction and seed formation can be influenced by the reduction potential of the amine.²¹ Thus, the presence of two reducing agents in BeetBead, viz., benzylamine and betalain, combined to the increase in the number of nucleation sites could be responsible for the observed structural changes. Finally, cation- π interactions and steric stabilization are somewhat expected to contribute for nanoparticle stabilization and cannot be ruled out.^{9, 15}

3.2 Catalytic activity

3.2.1 Reduction of *p*-nitrophenol

After the morphological characterization of the Ag and Au nanoparticles supported in VP OC 1065 and in BeetBead, we evaluated their ability to catalyze the reduction of *p*-nitrophenol (PNP) by sodium borohydride.⁵⁷ No *p*-aminophenol (PAP) was produced within one hour at 25 °C in the presence of Lewatit VP OC 1065 (Figure 3a). However, Au@Lewatit, Au@BeetBead, Ag@Lewatit, and Ag@BeetBead catalyzed the reduction of PNP, as inferred by the decrease in the absorption band centered at 400 nm and increase in absorption at 300 nm due to the formation of PAP (Figure S4). The apparent rate constant (k_{app}) for the reduction of PNP and the rate constant normalized to surface area per unit of volume (k_1) were calculated from kinetic data and particle size distribution (Tables S1 and S3).³² The k_{app} of the Au NPs is higher than those of the Ag NPs and the value of k_1 follows the same trend (Table S1). Finally, the value of k_1 that, according to the Langmuir-Hinshelwood mechanism, is related to the transfer of an H^- to the surface of the NPs forming M–H bonds,⁵⁷⁻⁵⁸ agrees to those reported for the reduction of PNP using other supported Ag and Au nanocatalysts.⁵⁷

The support did not affect the performances of the Au NPs despite the change in the size of the nanocatalyst, possibly due to compensations in the metal loading (Table S1). The nanocatalysts were recovered by filtration and the filtrate was submitted to atomic absorption spectroscopy to verify if the metal nanoparticles leached during the reaction. In all cases, less than 0.4 ppm of metal (Ag or Au) was found in solution, which corresponds to roughly 1% m/m of the metal content in the polymer-supported nanocatalysts (Table S3).

The catalysts were reused for two additional runs without any change in the catalytic capacity (Figure 3b) or morphology (Figure S5).

Figure 3. Reduction of *p*-nitrophenol (PNP) in the presence of Au and Ag nanocatalysts.

(a) Batch reaction using NaBH_4 as reducing agent. $[\text{PNP}] = 6.5 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{NaBH}_4] = 0.1 \text{ mol L}^{-1}$, and catalyst (10 mg) at 25°C . (b) Reuse of the nanocatalyst. After each run, the catalyst was recovered by filtration, washed with water, dried and reused, as identified by the shaded *R* symbol. Three consecutive runs were carried out for each catalyst.

Polymer-supported nanocatalysts were used for the reduction of PNP by hydrogen under continuous flow conditions (Figure 4). In this system, the conversion yield can be tuned by the temperature, pressure, and flow rate. Using 50 bar H₂ at 80 °C, the conversion of PNP into PAP using either Au or Ag nanocatalysts reaches 100% yield (Figure S6). However, in order to compare the catalyst's performance, experiments were conducted under milder experimental conditions in which PNP was not fully consumed (Figure 4). The conversion rate remained constant for the duration of the reaction (1 h at 0.2 mL min⁻¹), implying that the catalytic activity is preserved. The Au NPs required milder experimental conditions, i.e. lower pressure and temperature, compared to Ag NPs to reach similar catalytic activity possibly due to the smaller Au NPs size compared to Au@BeetBead. Furthermore, for the reduction of PNP by hydrogen gas, the cleavage of the H–H bond at the surface of the nanocatalyst, i.e. H₂ activation, is the rate-limiting step, and Au has higher activity towards the activation of H₂ compared to Ag, which explains its higher catalytic activity.⁵⁹

Figure 4. In flow reduction of *p*-nitrophenol (PNP) by H₂ in the presence of Au and Ag nanocatalysts. [PNP] = 6.5×10^{-5} mol L⁻¹, and catalyst (10 mg); Au: 30 °C, 10 bar H₂; Ag: 50 °C, 20 bar H₂.

3.2.2 Oxidation of dihydrorhodamine

The polymer-supported magnetite nanoparticle was tested as a catalyst for the oxidation of dihydrorhodamine 123 (DHR) by hydrogen peroxide.⁶⁰ The addition of the catalyst to a solution of DHR and H₂O₂ leads to a steep increase in fluorescence at 528 nm due to the formation of rhodamine 123 (Figure 5a and S7). Both catalysts show similar performance, with the Fe₃O₄@BeetBeads showing slightly higher conversion rate ($k_{app} = 2.4 \times 10^{-4}$ s⁻¹ vs. 1.4×10^{-4} s⁻¹ for Fe₃O₄@BeetBead and Fe₃O₄@Lewatit, respectively). Interestingly, control experiments using Lewatit VP OC 1065 also catalyze DHR oxidation, but at a much lower rate ($k_{app} = 3.7 \times 10^{-5}$ s⁻¹, Figure 5a). In both cases, the catalysts were easily recovered by magnetic separation (Figure 5b). After recovering, the catalysts were washed

with water and reused three times (Figure 5c, Figure S5). For $\text{Fe}_3\text{O}_4@\text{Lewatit}$, the catalytic activity remained unchanged, while for $\text{Fe}_3\text{O}_4@\text{BeetBead}$ it showed a discrete decrease (13%) on the third run.

Figure 5. Oxidation of dihydrorhodamine 123 (DHR) by hydrogen peroxide in the presence of magnetite nanocatalysts monitored by measuring the change in fluorescence intensity at 528 nm. (a) Kinetics of DHR oxidation. $[\text{DHR}] = 5.7 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] =$

1.0×10^{-3} mol L⁻¹, 5 mg of catalysts at 45 °C. (b) Magnetic recovery of Fe₃O₄@Lewatit and Fe₃O₄@BeetBead. (c) Reuse of the nanocatalyst. After each run, the catalyst was recovered by magnetic separation, washed with water, dried and reused, as identified by the shaded *R* symbol. Three consecutive runs were carried out for each catalyst.

4. CONCLUSION

The microbead-supported metal and metal oxide nanocatalysts reported here are suitable for continuous flow and batch chemistry, show minimum metal leaching, and can be recovered and reused conveniently. We repurposed the Lewatit VP OC 1065 ion exchange resin into a uniform size support for Au, Ag or Fe₃O₄ nanocatalysts and used a natural product to tune their catalytic properties. The resulting supported nanocatalysts are compatible with myriad chemical reactions and are effective to promote model redox transformations. The 5 min, open vessel microwave-assisted synthesis described here produces ready-to-use catalysts that can be easily recovered by filtration and/or magnetic separation and reused. No additional stabilizing or capping agents, which can lead to detrimental effects in catalysis, are required for the on-water synthesis. The advantages of these supported nanocatalysts, when taken in conjunction, may offer an environmental-benign solution for the development of supported nanocatalysts.

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AUTHOR CONTRIBUTIONS

E.L.B and J.S. proposed the concept and directed the research. A.B.F., M.V.P., C.S.N., A.C.C., R.L., E.L. and C.P. carried out the experiments. A.B.F., M.V.P., J.S. and E.L.B. prepared the figures. A.B.F., P.C., J.S. and E.L.B. wrote the main manuscript text. All authors reviewed the manuscript.

COMPETING FINANCIAL INTERESTS

The authors declare no competing financial interests.

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The Supporting Information is available free of charge on the ACS Publications website at DOI:10.1021/XXXXX.

Supplementary methods. Calibration curves used for the quantification of metal content (Fig. S1), Reflectance spectra (Fig. S2), Size distribution of nanocatalysts and high

magnification SEM (Fig. S3), UV-Vis spectra acquired during PNP reduction (Figs. S4 and S6), High magnification (SEM images of nanocatalysts before and after three consecutive catalytic runs (Fig. S5), Oxidation of DHR by H₂O₂ monitored by fluorescence spectroscopy (Fig. S7), Apparent rate constants (k_{app}) for the reduction of PNP (Table S1), Surface area values for the nanocatalysts (Table S2), and Atomic absorption spectroscopy data (Table S3).

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SUPPORTING INFORMATION

Recoverable and Reusable Polymer Microbead-Supported Metal Nanocatalysts for Redox Chemical Transformations

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MATERIAL AND METHODS

UV-Vis absorption, fluorescence and diffuse reflectance spectroscopies

UV-Vis spectra were acquired on an Ocean Optics USB4000 spectrophotometer equipped with a deuterium-tungsten-halogen light source (DH-2000-BAL, Ocean Optics). Reflectance spectra (360 – 830 nm) and microsphere micrographs were registered using a Varian Cary 50 spectrophotometer (Varian, Inc.) equipped with a remote video diffuse reflectance (DRA) probe (Barrelino, Harrick Scientific, 1.5 mm light beam spot size ~1.5 mm). Steady-state fluorescence measurements were performed using a Varian Cary Eclipse spectrofluorometer equipped with a cell holder with built-in magnetic stirrer.

Figure S1. Reflectance spectra of (a) Lewatit, Ag@Lewatit, Au@Lewatit, and Fe₃O₄@Lewatit, and (b) BeetBead, Ag@BeetBead, Au@BeetBead and Fe₃O₄@BeetBead. Spectra were smoothed using a FFT filter (cut-off 0.02).

Figure S2. Size distribution of nanocatalysts Ag@Lewatit, Au@Lewatit, Fe₃O₄@Lewatit, Ag@BeetBead, Au@BeetBead and Fe₃O₄@BeetBead. Particle size analysis of SEM images was carried out using the ImageJ software. Scales are equal for each metal, for comparison; solid lines are the Gaussian fit to the data. (b) High magnification (100,000×) SEM images. Subtle motion blur is caused by charging effects.

Figure S3. UV-Vis spectra acquired during PNP reduction with NaBH_4 in batch mode at 25 °C. (a) Negative control using Lewatit, and effect of 10 mg of either (b) Ag@Lewatit, (c) Ag@BeetBead, (d) Au@Lewatit or (e) Au@BeetBead.

Figure S4. UV-Vis spectra of PNP solution after passing through cartridge containing Ag@Lewatit and Au@Lewatit at 80 °C and 50 bar of H₂. Samples were collected 10 min after the start of the flow.

Figure S5. Oxidation of DHR by H_2O_2 monitored by fluorescence spectroscopy. (a) Negative control without Lewatit VP OC 1065 or supported catalysts, (b) in the presence of Lewatit VP OC 1065, (c) $\text{Fe}_3\text{O}_4@\text{Lewatit}$ and (d) with $\text{Fe}_3\text{O}_4@\text{BeetBead}$. Experimental conditions: $[\text{DHR}] = 5.7 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{H}_2\text{O}_2] = 1.0 \times 10^{-3} \text{ mol L}^{-1}$, 5 mg of catalysts at 45°C ; $\lambda^{\text{abs}} = 480 \text{ nm}$, EX/EM slits: 2.5/5.0 nm, photomultiplier tension: 600 V. Fluorescence spectra were acquired at each 3 min for ca. 4 h.

Figure S6. Calibration curves used for the quantification of metal content in the nanocatalysts and in the reaction medium. Calibration curve obtained from HAuCl₄ solutions (a and c) and AgNO₃ solutions (b and d). The intercept was fixed to zero and the red region shows the 95% confidence band.

Table S1. Apparent rate constants (k_{app}) for the reduction of PNP made by the metal nanocatalysts.

Catalyst	$k_{\text{app}} (\text{s}^{-1})^{\text{a}}$	$S (\text{m}^2 \text{L}^{-1})^{\text{b}}$	$k_1 (\text{s}^{-1} \text{m}^{-2} \text{L})^{\text{c}}$
Au@Lewatit	$(4.3 \pm 0.6) \times 10^{-4}$	6.0×10^{-3}	$(7.2 \pm 1.0) \times 10^{-2}$
Au@BeetBead	$(5.2 \pm 0.3) \times 10^{-4}$	8.8×10^{-3}	$(5.9 \pm 0.4) \times 10^{-2}$
Ag@Lewatit	$(2.7 \pm 1.3) \times 10^{-4}$	7.0×10^{-2}	$(3.8 \pm 1.8) \times 10^{-3}$
Ag@BeetBead	$(2.2 \pm 0.2) \times 10^{-4}$	1.0×10^{-2}	$(2.2 \pm 0.2) \times 10^{-2}$

^a Apparent rate constant. Mean $\pm$ standard deviation ($N = 3$). ^b Surface area of nanoparticles (S) was estimated by microscopy and normalized to the unit volume of the system. The radius (r) and number of nanoparticles (N_{NP}) were obtained by analysis of SEM images and the average surface area of the nanoparticles (avA) was calculated by the sum of the areas of all individual NPs in the image, assuming spherical shape ($\text{avA} = 4\pi r^2$). The total number of nanoparticles in each polymer bead was calculated considering that the surface area of the bead was equal to $1.5 \times 10^{-6} \text{ m}^2$ multiplied by the number of beads found in 10 mg. The value of S was calculated as the surface area of the NPs normalized to the unit volume of the system ($5.0 \times 10^{-3} \text{ L}$). Data used in calculations are presented in Table S2. ^c Rate constant normalized to the surface of the particles in the system.

Table S2. Estimated surface area values for the nanocatalysts determined by analysis of SEM images.

Catalyst	NP area per image (m²)	NP area per bead (m²)	Average number of Beads in 10 mg	Area 10 mg of Bead (m²)
Au@Lewatit ^a	6.3×10^{-13}	2.5×10^{-7}	120	3.0×10^{-5}
Au@BeetBead ^b	2.3×10^{-11}	3.7×10^{-7}	121	4.4×10^{-5}
Ag@Lewatit ^a	6.5×10^{-12}	2.6×10^{-6}	135	3.5×10^{-4}
Ag@BeetBead ^a	1.0×10^{-12}	4.1×10^{-7}	121	5.0×10^{-5}

^a SEM image area: $3.7 \times 10^{-12} \text{ m}^2$. ^b SEM image area: $9.5 \times 10^{-11} \text{ m}^2$

Table S3. Concentration of Au and Ag in their respective sample and in relation to the total amount of metal found in the catalysts determined by atomic absorption spectroscopy.

Catalyst	Metal content in the supported catalyst (μg)^a	Metal leached after reaction (μg)^b	Recovery (%)
Au@Lewatit	16	< LOQ ^c	nd
Au@BeetBead	94	0.7	0.8
Ag@Lewatit	175	1.1	0.7
Ag@BeetBead	146	1.9	1.3

^a The metal content in 10 mg of supported catalyst. ^b The reaction of PNP by NaBH₄ was carried out in the presence of 10 mg of each catalyst and the amount of metal leached from the polymer was determined by AAS and corrected for dilution effects. [PNP] = 6.5×10^{-5} mol L⁻¹, [NaBH₄] = 0.1 mol L⁻¹, and catalyst (10 mg) at 25 °C. The calibration curves are presented in Figure S6. ^c The limits of detection (LOD) and limit of quantification (LOQ) are, respectively, 0.013 mg L⁻¹|0.043 mg L⁻¹ for Au and 0.011 mg L⁻¹|0.036 mg L⁻¹ for Ag.