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# Core-shell iron oxide@cathecol-polymer@palladium/copper nanocomposites as efficient and sustainable catalysts in cross-coupling reactions

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# ABSTRACT

Magnetic core-shell Fe<sub>2</sub>O<sub>3</sub>@polymer-Pd/Cu nanocomposites (NCs) were developed as efficient and sustainable nanocatalysts for cross-coupling reactions. The designed NCs consisted of three components: i) a magnetic core (Fe<sub>2</sub>O<sub>3</sub> nanoparticle), which allowed the recovery and reuse of the NCs, enhancing thus their attractiveness as green catalysts; ii) a catechol-based polymer coating, chosen because of its strong chelating ability towards metal ions, and its potential to be obtained from biomass (lignin depolymerization); and iii) catalytically active metal nanoparticles (Pd and Cu NPs) immobilized via *in situ* formation onto the polymeric shell. As-prepared Pd-based NCs successfully catalyzed Suzuki-Miyaura cross-coupling reactions, achieving yields between 87% and 97% in only 20–40 min depending on the aryl halides and boronic acid derivatives. Similarly, Cu-based NCs exhibited a quite good catalytic efficiency (> 80%) in the synthesis of propargylamines via A<sup>3</sup> coupling reaction of phenylacetylene with various aldehydes and amines. Importantly, these NCs presented a good reusability, without significant decrease in efficiency after several cycles. However, the major advantage of the designed NCs is the lower Pd or Cu content (1.5 wt% and 2.6 wt%, respectively) as compared to most of the reported similar catalysts (between 3 – 6 wt% for Pd and > 5 wt% for Cu), which is a key challenge in view of developing cost-effective and environment-friendly catalysts while maintaining a high efficiency.

# INTRODUCTION

Due to the increasing demand for sustainable chemical processes with improved efficiencies, minimization on the generation of waste, less energy consumption, and use of green conditions, much efforts have been focused on developing catalysts with improved activities and selectivity as well as with superior reusability and recyclability potential. In this context, the use of metal nanoparticles (NPs) as heterogeneous catalysts has emerged as a promising alternative towards a variety of chemical transformations [1,2]. In spite of the unique properties of metal NPs such as controllable and tunable size, tunable composition, large specific surface area, and good thermal and mechanical stability, the lack of colloidal stability of many NPs (*i.e.*, tendency of aggregation because of the high specific surface energy) limits their catalytic potential, since aggregated NPs exhibit lower catalytic efficiency [3]. To overcome this issue, a number of efforts have been devoted to develop feasible approaches to stabilize such NPs, which can be divided in two major groups: i) chemical surface modification methods to control their surface interactions and minimizing thus their aggregation [4], or ii) physical immobilization on supports or encapsulation/confinement within networks/matrices (*e.g.*, polymer [5] or silica coatings [6], microgels [7], metal-organic frameworks [8,9], among others [10–12]).

The selection of the support is not trivial; different supports could provide additional functionalities, for example magnetic properties, and could even give rise to different effects on the catalytic properties of the metal NPs by means of diverse metal-support interactions [2,13-15]. In this work, magnetic iron oxide NPs (Fe<sub>2</sub>O<sub>3</sub> NPs) synthesized by one-step solvothermal method, and further coated with a catechol-based polymeric shell (Fe<sub>2</sub>O<sub>3</sub>@polymer) were selected as support in virtue of their particular features. On the one hand, the magnetic core allows the easy recovery of the catalyst from the medium after reaction for its reusability. On the other hand, previous reports have demonstrated that catechol-based polymers are very versatile

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functional materials with an outstanding performance as coatings and supports [16]. Indeed, the ability of catechol groups of establishing a plethora of interactions with both organic and inorganic materials endow these polymers with excellent coatability on various surfaces (as for example iron oxide NPs [17]), as well as with anchoring sites for the further immobilization of metal ions, metal oxides, or metal NPs [18]. Some works have already reported the good performance of this type of support (*i.e.*, Fe<sub>2</sub>O<sub>3</sub>@polymer [19]). For instance, Zhang et al. synthesized a core-shell Fe<sub>3</sub>O<sub>4</sub>@catecholformaldehyde resin which could be further modified with graphene oxide (GO), and they used this support to immobilized Pd NPs [20]. Similarly, Xie et al. prepared Fe<sub>3</sub>O<sub>4</sub>@ polydopamine followed by the deposition of Ag NPs [21].

In view of developing sustainable chemical technologies, the search of efficient catalysts derived from biomass should be a priority. Taking advantage of the structural diversity of different biomass resources, recent efforts have been directed towards the synthesis of renewable monomers and polymers [22,23]. Within this context, catechol-based polymer can play a major role, thanks to the fact that the catecholderived products can be easily obtained from the lignin depolymerization [24]. Furthermore, the incorporation of a magnetic core within the catalyst's design, which allows its efficient recovery and reuse, would further enhance the attractiveness of these nanocomposites as green catalysts.

With respect to the catalytic units, transition metals have been the outstanding choice of catalysts in many important chemical reactions, especially in cross-coupling reactions. Among all catalytic C - C bondforming reactions, Pd-catalyzed Suziki-Miyaura reaction to couple aryl halides with any boronic acids is one of the most investigated reactions. After nearly 40 years from its discovery [25], a Nobel prize [26-27] and countless successful applications, researchers still strive for novel catalysts to minimize Pd loading [28], reduce reaction time and temperature [29,30], or use ecofriendly media [31]. Transition-metal-catalvzed decarboxylative couplings have gained particular interest due to the inherent advantage that simple carboxylic acids represent a powerful alternative for C-C bond formation under relatively neutral conditions compared to preformed organometallic reagents [32]. In this regard, it has been demonstrated that Cu-catalyzed decarboxylative coupling could be applied to efficiently obtain propargylamines via a tandem A<sup>3</sup> coupling reaction [33,34]. With the aim of investigating these two reactions, Pd and Cu NPs were growth in situ onto the support through the catechol groups of the polymer shell, which acted as anchoring sites as explained above. Importantly, the in situ formation method leads to a strong binding of the NPs with the support, minimizing therefore a posterior surface detachment (i.e., catalyst leaking), which is a crucial aspect for long-lasting structural stability [35].

Herein, we explore the immobilization of Pd and Cu NPs onto magnetic@polymer supports as a versatile and simple approach for preparing efficient and reusable catalytic nanocomposites (NCs). The designed NCs consisted of three main parts: i) a magnetic nanoparticle ( $Fe_2O_3$  NPs) as core support to allow the easy recovery of the catalyst for its reuse; ii) a catechol-based polymer to successfully coat the magnetic nanoparticle as well as to serve as anchoring sites for the immobilization of the catalytic NPs; and iii) metal NPs (Pd and Cu NPs) that are the catalytically active units to promote the reactions. Two types of catechol-based polymers were investigated, in particular catechol-salicylic acid-formaldehyde (CSF) and thiourea-catechol-formaldehyde (TCF). The catalytic performance of the as-prepared Pd- and Cu-based NCs for cross-coupling reactions was evaluated and compared to previously reported similar nanocatalysts.

#### EXPERIMENTAL SECTION

#### Reagents and solvents

For the synthesis of  $Fe_2O_3$  nanoparticles, hydrochloric acid (HCl, ACS reagent,  $\geq$  37%), ammonia (NH3, anhydrous,  $\geq$  99.95%), iron(III)

chloride hexahydrate (FeCl<sub>3</sub>· $6H_2O$ ) ( $\geq$ 98%, purified lumps), iron(II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O) (puriss. p.a.,  $\geq$  99.0%), tetramethylammonium hydroxide (TMAOH, solution 25 wt.% in H<sub>2</sub>O) and ammonia solution (NH<sub>4</sub>OH, solution 25 wt.% in H<sub>2</sub>O) were obtained from Sigma-Aldrich. For the preparation of Fe2O3@CSF and  $Fe_2O_3@TCF$  supports, ethanol (EtOH) (anhydrous,  $\geq$  99.8%), catechol (CA) ( $\geq$ 99%), salicylic acid (SA) (puriss. p.a.,  $\geq$ 99%), formaldehyde (37 wt% in H<sub>2</sub>O), thiourea ( $\geq$ 99%) were purchased from Sigma-Aldrich. Additionally, palladium(II) chloride (PdCl<sub>2</sub>) ( $\geq$ 99%), copper (II) acetate (Cu(OAC)<sub>2</sub>·2H2O) ( $\geq$ 98%), acetone, dimethylformamide (DMF), bromobenzene ( $\geq$ 99%), 4-bromoacetophenone ( $\geq$ 98%), 4bromophenol ( $\geq$ 99%), 4-Bromoanisole ( $\geq$ 99%), 4'-iodoacetophenone  $(\geq 97\%)$ , 4-iodoanosole ( $\geq 98\%$ ), iodobenzene ( $\geq 98\%$ ), 2-iodotuluene  $(\geq 98\%)$ , phenylboronic acid  $(\geq 95\%)$ , and 4-hydeoxyphenylbronic acid ( $\geq$ 95%) were also obtained from Sigma-Aldrich. MilliQ water was used. All chemicals were used without further purification.

# Material and instrumentation

All reagents and solvents were obtained from Sigma-Aldrich and used without further purification (details in Supporting Information). Commercially available silica plates (Poly Gram SIL G/UV 254) from Fisher Scientific were used for thin-layer chromatography (TLC) analysis. Visualization of TLC plates was achieved by UV fluorescence. Powder X-ray diffraction patterns (XRD) were recorded on a Bruker D8advance X-ray diffractometer with Cu K $\alpha$  radiation (0.154 nm) over the 20 range of 20-70°. Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 6700 FT-IR spectrometer using KBr disc. The spectra were recorded from 4000 to 450  $\text{cm}^{-1}$  with a resolution of 4 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) was performed on a PerkinElmer thermal analyzer, by heating the sample to 800 °C at 10 °C min<sup>-1</sup> under dynamic air atmosphere (10 mL/min). Thin-layer chromatography (TLC) was performed on silica gel plates (Poly Gram SIL G/ UV 254). Structural and elemental compositions were analyzed using a Leo 1450 V P scanning electron microscope equipped with an SC7620 energy dispersive X-ray spectrometer with 133 eV resolution at 20 kV (SEM-EDX). Quantitative processing was performed with EInca energy 250 v5.04 software. Gas chromatography-mass spectrometry (GC-MS) analysis were carried out in a Thermo Scientific TraceGOLD instrument (TG-5SilMS GC, column 20 m, 0.18 mm, 0.18 µm) with hydrogen as carrier gas 80 °C (0.5 min), followed by a linear gradient from 80 to 280 °C (5 min) at a flow rate of 0.8 mL/min. <sup>1</sup>H NMR spectra were recorded on a Bruker-300 Advance (300 MHz) instrument. The chemical shifts of <sup>1</sup>H NMR are reported in ppm relative to TMS (0.00 ppm) and CD3Cl (77.0 ppm), respectively.

## Synthesis of magnetic Fe<sub>2</sub>O<sub>3</sub> nanoparticles

These were synthesized via a chemical coprecipitation method of ferric and ferrous ions in alkali solution by following a procedure previously reported [36,37]. Briefly, FeCl<sub>2</sub>.4H<sub>2</sub>O (0.401 g) and FeCl<sub>3</sub>.6H<sub>2</sub>O (1.092 g) were dissolved in 2 mL and 4 mL of a HCl solution (2 M), respectively, and mixed under vigorous stirring for 15 min. After this time, a NH<sub>4</sub>OH solution (50 mL, 0.7 M) was slowly added to the stirring mixture at room temperature (RT), observing the change of the color solution from orange to dark brown. After 1 h of further stirring, the particles were magnetically decanted by using a hand magnet and washed three times with deionized H<sub>2</sub>O. After the last wash, the particles were separated and redispersed in 2 mL of TMAOH solution (25 wt.% in H<sub>2</sub>O) that acts as surfactant. Finally, the particles were dried in vacuum and calcined at 300 °C for 3 h.

#### Synthesis of Fe<sub>2</sub>O<sub>3</sub>@CSF and Fe<sub>2</sub>O<sub>3</sub>@TCF particles

Polymer solution 1 for the coating with catechol-salicylic acid-formaldehyde (CSF, in molar ratio 1:1:2) was prepared by mixing catechol (1.65 g, 0.015 mol, dissolved in 10 mL EtOH) and salicylic acid (2.1 g, 0.015 mol, dissolved in 10 mL EtOH) in a 250 mL round bottom flask, followed by addition of 0.05 mL NH<sub>4</sub>OH solution, and the mixture was stirred for 2 h at RT. After that, formaldehyde (2.25 mL, 0.03 mmol) was added and stirred for 1 h at RT, observing the formation of a brown gel. Similarly, the polymer solution 2 for the coating with thioureacatechol-formaldehyde (TCF, in molar ratio 1:1.3:2) was prepared by mixing catechol (1.65 g, 0.015 mol, dissolved in 10 mL EtOH) and thiourea (1.5 g, 0.02 mol, dissolved in 10 mL of EtOH:H<sub>2</sub>O 1:1) in a 250 mL round bottom flask, followed by addition of 0.05 mL NH<sub>4</sub>OH solution, and the mixture was stirred for 2 h at RT. Next, formaldehvde (2.25 mL, 0.03 mmol) was added and stirred for 1 h at RT. For the coating of the Fe<sub>2</sub>O<sub>3</sub> NPs with the two different polymers, 1.5 g of Fe<sub>2</sub>O<sub>3</sub> NPs were dispersed in 10 mL of EtOH and immersed in an ultrasound bath for 30 min to get a homogeneous dispersion of the NPs. Next, the dispersed NPs were added to the previously prepared polymer solution (1 or 2), and the mixture was heated under reflux in an oil bath at 80 °C for 24 h with continuous stirring. The solution was further transferred into Teflon-sealed stainless-steel autoclave and heated in an oven at 80 °C for 24 h. Finally, the particles were collected by magnetic separation, washed twice with H<sub>2</sub>O and EtOH, and finally dried overnight in vacuum.

# Preparation of $Fe_2O_3@CSF@Pd$ , $Fe_2O_3@TCF@Pd$ , and $Fe_2O_3@CSF@Cu$ nanocomposites

Pd and Cu NPs were *in situ* growth onto the previously prepared  $Fe_2O_3@CSF$  and  $Fe_2O_3@TCF$  particles. To this end, 1 g of  $Fe_2O_3@CSF$  or  $Fe_2O_3@TCF$  were dispersed in 10 mL EtOH aided by ultrasound for 30 min, followed by addition of a solution of PdCl<sub>2</sub> (0.1 g, 0.56 mmol, dissolved in 5 mL H<sub>2</sub>O) and maintained in the ultrasound bath for another 1 h. After this time, the mixture was left at RT under vigorous stirring for 24 h. Similarly, 1 g of  $Fe_2O_3@CSF$  was dispersed in 10 mL EtOH aided by ultrasound for 30 min, followed by addition of a solution of Cu(OAC)<sub>2</sub>·2H<sub>2</sub>O (0.2 g, 0.92 mmol, dissolved in 5 mL H<sub>2</sub>O) and maintained in the ultrasound bath for another 1 h. After this time, the mixture was left at RT under vigorous stirring for 24 h. The obtained NCs were collected by a magnet, washed several times with deionized H<sub>2</sub>O and EtOH to remove excess of reagents and/or potential free palladium and copper NPs, and dried overnight in vacuum.

#### General procedure for Suzuki-Miyaura cross-coupling reaction

 $Fe_2O_3@CSF@Pd$  or  $Fe_2O_3@TCF@Pd$  (10 mg) were added to a mixture of phenylboronic acid derivatives (0.5 mmol), aryl halide derivatives (0.5 mmol), and  $K_2CO_3$  (1 mmol) in 4 mL of  $H_2O/DMF$  (3:1), and were reacted under stirring at 80 °C for between 20–40 min. The reaction was checked for completion by TLC (cyclohexane/EtOAc, 8:2, v/v). After completion of the reaction the catalyst was separated by magnetic decantation, the organic product was extracted with EtOAc (10 mL, three times) and dried over Na<sub>2</sub>SO<sub>4</sub>. The product was purified by recrystallization using n-hexane:EtOAc (5:1). All products were known and confirmed by <sup>1</sup>H NMR, and GC-MS (see Supporting Information).

# General procedure for $A^3$ coupling reaction

 $Fe_2O_3@CSF@Cu$  (10 mg) was added to a mixture of amine (1.2 mmol), phenylacetylene (1.5 mmol), and aldehyde (1.0 mmol) in 5 mL of dichloromethane, and allowed to react at RT under stirring for between 20–60 min. The reaction was monitored to check its completion by TLC (cyclohexane/EtOAc, 8:2, v/v). After completion of the reaction the catalyst was separated by magnetic decantation, the precipitated solid was collected by filtration. The crude product was dried over Na<sub>2</sub>SO<sub>4</sub> and purified by recrystallization using EtOH:EtOAc (2:1) to yield the pure product.

#### General procedure for catalyst recycling

After completion of the reaction in the first run, the catalyst was separated by magnetic decantation, washed with EtOAc,  $H_2O$ , and MeOH (in this order) to remove adsorbed organic compounds and inorganic salts, and finally dried overnight in an oven at 40 °C. The resulting dried catalyst was then ready for being used in a second run of reaction. This process was repeated after each run. Five consecutive runs were performed in this work.

# **RESULTS AND DISCUSSION**

#### Design and synthesis of the NCs

The designed catalytic nanocomposites (NCs), two Pd-based NCs and one Cu-based NC, were prepared in three steps (cf., Scheme 1Scheme 1) according to the three main parts of the catalyst's architecture: a magnetic core NP, a polymeric shell, and catalytically active metallic NPs on the support's surface. First, superparamagnetic iron oxide NPs (Fe<sub>2</sub>O<sub>3</sub> NPs) with a size of ca. 10 nm in diameter and maghemite structure as confirmed by XRD were synthesized via a coprecipitation method and calcined at 300 °C. In a second step, a polymeric shell consisted of catechol-salicylic acid-formaldehyde (CSF) or thiourea-catechol-formaldehyde (TCF) was easily formed around the Fe<sub>2</sub>O<sub>3</sub> NPs through in situ polycondensation of catechol, formaldehyde, and salicylic acid in one case, or catechol, formaldehyde, and thiourea in the other case, catalyzed by ammonium hydroxide under hydrothermal conditions [20,38]. The catechol groups in the polymer are the responsible for the strong coordination with under-coordinated Fe<sup>+3</sup> sites on the surface of the Fe<sub>2</sub>O<sub>3</sub> NPs [39]. Importantly, the polymer coating (CSF or TCF) plays a two-fold role: to stabilize the Fe<sub>2</sub>O<sub>3</sub> NPs avoiding their aggregation, and to provide additional functional groups for further functionalization as exploited in a third step. In this last step, Pd or Cu NPs were formed via in situ reduction by utilizing the surface coordination of vicinal hydroxyl groups or between hydroxyl and carboxyl groups from the polymer shell. The Pd or Cu contents in the final nanocomposites were determined by ICP-MS and resulted to be 1.4 wt% Pd in Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd, 1.5 wt% Pd in Fe<sub>2</sub>O<sub>3</sub>@TCF@Pd, and 2.6 wt% Cu in Fe<sub>2</sub>O<sub>3</sub>@CSF@Cu (cf., Table S1).

**Scheme 1.** Schematic representation of the three types of catalytic NCs designed:  $Fe_2O_3@CSF@Pd$ ,  $Fe_2O_3@TCF@Pd$ , and  $Fe_2O_3@CSF@Cu$ . Pd-based NCs catalyzed Suzuki-Miyaura cross-coupling reactions, whereas Cu-based NCs catalyzed A<sup>3</sup> coupling reactions. Color code of polymer shell: CSF represented in orange, TCF represented in blue.

# Physico-chemical characterization of NCs

The morphologies and average sizes of as-prepared NCs were examined by SEM (cf., Fig. 1A). Although aggregation was observed, an estimation of sizes could be performed, resulting in diameters of ca. 13 nm, 11 nm, and 29 nm for Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd, Fe<sub>2</sub>O<sub>3</sub>@TCF@Pd, and Fe2O3@CSF@Cu NCs, respectively. SEM/EDX elemental mapping analysis confirmed the formation of the metal NPs and their uniform distribution on the NCs' surface (cf., Fig. 1B). Moreover, the presence of C, N, and S clearly corroborated the successful functionalization of the Fe<sub>2</sub>O<sub>3</sub> NPs with the catechol-based polymers (cf., Fig. 1B, Table S1, and Figure S1). The effective polymer coating of the Fe<sub>2</sub>O<sub>3</sub> NPs was also ascertained by FTIR (cf., Fig. 2). While the characteristic absorption bands at 590 cm<sup>-1</sup> assigned to Fe–O bonds of the Fe<sub>2</sub>O<sub>3</sub> NPs was observed in all the samples, only those functionalized with the polymers presented the bands located at around 1400–1600 cm<sup>-1</sup>, which belong to the characteristic vibrations of benzene rings of the CSF and TCF polymer shells. Additionally, the strong peaks at 1612 cm<sup>-1</sup> and 1455 cm<sup>-1</sup> in the case of TCF polymer can be assigned to C-N and C-S stretching vibrations. In both cases the band at 3420 cm<sup>-1</sup> belong to the



Fig. 1. (A) SEM images (inset: histogram of the corresponding diameter distribution), and (B) EDX elemental mappings of the different as-prepared NCs: (1)  $Fe_2O_3@CSF@Pd$ , (2)  $Fe_2O_3@CTF@Pd$ , and (3)  $Fe_2O_3@CSF@Cu$ .

O–H vibrations of the polymers, and the band at 1270 cm<sup>-1</sup> in both  $Fe_2O_3@CSF$  and  $Fe_2O_3@TCF$  samples corresponds to aromatic C–O stretching vibration of catechol groups (Fig. 2) [40]. However, no changes were observed in the FTIR spectra after the immobilization of Pd or Cu NPs onto the supports, probably because of the low Pd and Cu loading content in comparison with the high content of polymer around the  $Fe_2O_3$  NPs.

XRD spectra determined the crystalline nature of the prepared NCs (*cf.*, Fig. 3). The characteristic diffraction peaks at 30.9, 36.0, 43.9, 54.6, 58.0 and 63.6° could all be indexed to the crystal planes (220), (311), (400), (422), (511) and (440) of the cubic structure of maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, JCPDS 04-0755). After the formation of Pd NPs, XRD patterns of Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd and Fe<sub>2</sub>O<sub>3</sub>@TCF@Pd revealed two new prominent Bragg reflections at 20 = 40.3° and 46.9° assigned to the (111) and (200) planes of the face-centered cubic structure of Pd (JCPDS 46-1043), respectively. The main Pd (111) peak in both NCs suggested that metallic Pd NPs were formed [40]. Unfortunately, there was no clear evidence of the formation of Cu NPs by the XRD spectrum

of the Fe<sub>2</sub>O<sub>3</sub>@CSF@Cu NC. A slight increase of the peak at 36.3° which could be assigned to the (111) plane of the Cu<sub>2</sub>O (JCPDS 05-0667) seems to indicate the presence of Cu(I) species [41]. Nevertheless, the presence of Cu species in the structure of the Fe<sub>2</sub>O<sub>3</sub>@CSF@Cu NC was undoubtedly confirmed by EDX analysis (*cf.*, Fig. 1B, Figure S1, and Table S1) and ICP-MS analysis (*cf.*, Table S1).

The thermogravimetric analysis (TGA) of as-prepared NCs indicated a high thermal stability up to 200 °C (*cf.*, **Figure S2**). NCs based on CSF polymer underwent a two-step degradation, typical of salicylic acid– formaldehyde–catechol polymeric materials. In both Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd and Fe<sub>2</sub>O<sub>3</sub>@CSF@Cu NCs, an initial weight loss of ca. 10% was observed at 200–400 °C, which may be due to the decarboxylation or decomposition -CH<sub>2</sub> groups. The second step decomposition of polymeric products between 415–750 °C involved ca. 15 % and 29% weight loss for Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd and Fe<sub>2</sub>O<sub>3</sub>@CSF@Cu, respectively. This is further confirmed by DTA that showed an endothermic decarboxylation process at ca. 390 °C, and an exothermic peak at 740 °C (for Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd) or 690 °C (for Fe<sub>2</sub>O<sub>3</sub>@CSF@Cu) which may be may



Fig. 2. FTIR spectra of Fe<sub>2</sub>O<sub>3</sub> NPs, CSF and TCF polymers, and coated NPs (Fe<sub>2</sub>O<sub>3</sub>@CSF and Fe<sub>2</sub>O<sub>3</sub>@TCF).



Fig. 3. XDR spectra of the different as-prepared materials.

be due to the random cleavage of polymeric materials affording simpler decomposition products. In contrast, the degradation of the  $Fe_2O_3@TCF@Pd$  NC proceeded more gradually.

It is well-known that the porosity of heterogeneous catalysts can directly influence the diffusion properties of reagents and products, and it thus affects to their catalytic performance. For this reason, N<sub>2</sub> physisorption analyses were performed to the different NCs. BET surface areas of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>@CSF, and Fe<sub>2</sub>O<sub>3</sub>@TCF particles were 78, 42 and 39 m<sup>2</sup> g<sup>-1</sup>, respectively (*cf.*, Table 1, Figure S3). Comparing the Barrett–Joyner–Halenda pore volume (0.172-0.085 cm<sup>3</sup> g<sup>-1</sup>) of the Fe<sub>2</sub>O<sub>3</sub> MPs after being coated with the polymers to the bare Fe<sub>2</sub>O<sub>3</sub> NPs (2.3 cm<sup>3</sup> g<sup>-1</sup>), the significant decrease of the pore volume as well as the surface area clearly indicates that the polymers occupy a considerable part of the space in the catalyst pores. The posterior immobilization of Pd or Cu NPs also led to a further decrease of the pore volume (0.075–0.018 cm<sup>3</sup> g<sup>-1</sup>) and the surface area (36–31 m<sup>2</sup> g<sup>-1</sup>), confirming again the successful formation of the metal NPs.

The magnetic properties of the NCs were studied by using a vibrating sample magnetometer at RT (22 °C). As shown in Fig. 4A, no obvious magnetic hysteresis loop was observed, indicating that the NCs exhibit a superparamagnetic behaviour. The saturation magnetization was 58.6 emu·g<sup>-1</sup> for the particular case of Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd NC, which is strong enough to be efficiently separated from a solution under an external hand magnet (*cf.*, Fig. 4A, inset).

#### Evaluation of the catalytic performance of NCs

The catalytic performance of the different as-prepared NCs for

#### Table 1

Surface area, mean pore size and pore volume of the different prepared materials.

$BET^{[a]}(m^2 \cdot g^{-1})$	DBJH <sup>[b]</sup> (nm)	VBJH <sup>[c]</sup> (cm <sup>3</sup> ·g <sup>-1</sup> )
78	15.5	2.30
43	12.7	0.17
36	10.6	0.02
34	9.6	0.08
40	11.1	0.09
31	10.4	0.08
	BET <sup>[a]</sup> (m <sup>2</sup> g <sup>-1</sup> ) 78 43 36 34 40 31	BET <sup>[a]</sup> (m <sup>2</sup> ·g <sup>-1</sup> )         DBJH <sup>[b]</sup> (nm)           78         15.5           43         12.7           36         10.6           34         9.6           40         11.1           31         10.4

<sup>[a]</sup> specific surface area calculated by the Brunauer-Emmett-Teller (BET) equation.

<sup>[b]</sup> mean pore size diameter calculated by the Barrett-Joyner-Halenda (BJH) equation.

[c] pore volume calculated by the Barrett-Joyner-Halenda (BJH) equation.

relevant cross-coupling reactions was further investigated. While Pdbased NCs (Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd and Fe<sub>2</sub>O<sub>3</sub>@TCF@Pd) were used to catalyze Suzuki-Miyaura coupling reactions of arylboronic acids with aryl halides, Cu-based NC (Fe2O3@CSF@Cu) was employed in the synthesis of propargylamines via A<sup>3</sup> coupling reaction. The reaction of phenvlboronic acid with 4-bromobenzene was used as a model Suzuki reaction for the screening of optimum reaction conditions in terms of base and reaction medium (cf., Table S2). According to the results, K<sub>2</sub>CO<sub>3</sub> was found to be the most effective base and H<sub>2</sub>O/DMF (3:1) the optimum reaction medium, achieving conversion yields of 90% and 88% for Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd and Fe<sub>2</sub>O<sub>3</sub>@TCF@Pd, respectively. Moreover, the scope of the NC-catalyzed Suzuki reactions was investigated employing various substituted arvl halides to react with various substituted arylboronic acid (cf. Table 2). The highest conversion rate (97%) was obtained for the reaction of phenylboronic acid and 4'-iodoacetophenone catalyzed by Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd NC to afford 2-acetylbiphenyl (cf. Table 2, entry 5), leading to similar or even better results than those reported for similar magnetic Pd-based catalyst (cf. Table 3). It is worth noting that the clear advantage of the here designed NCs is the lower Pd content (1.5 wt%) in comparison with most of the reported catalysts (between 3 - 6 wt%), which is a key challenge in view of developing cost-effective and environment-friendly catalysts while maintaining a high efficiency.

Concerning Fe<sub>2</sub>O<sub>3</sub>@CSF@Cu NC, its catalytic activity was tested in three component A<sup>3</sup> coupling reaction of amine, aldehyde and alkyne for the preparation of propargylamines. In particular, the coupling of phenylacetylene with various aldehydes and amines or the synthesis of 1,8-dioxo-octahydroxanthenes was investigated (*cf.*, Table 4), showing quite good results (yields between 80% and 93% in less than 1 h of reaction and importantly at RT). These results are in line with the best reported catalysts in terms of conversion [42,43]; however note that the herein designed catalytic NC presents superior catalytic properties in terms of reaction time (less than 1 h versus typical reported times of  $\geq$  6 h), temperature (RT versus typical reported temperatures of  $\geq$  90 °C), lack of requirement for an inert atmosphere, and lower content of Cu (2.6 wt% versus > 5 wt% with similar Cu-based catalysts) [42–45].

To evaluate the reusability of the NCs, they were separated from the medium after completing the reaction using hand magnet (*cf.* Fig. 4A) and reused for a subsequent run of reaction. Results indicated that both Pd-based and Cu-based NCs could be successfully reused for four consecutive cycles without significant loss of their catalytic efficiency (*cf.* Fig. 4B).

# CONCLUSIONS

A facile synthetic method to prepare core-shell magnetic  $Fe_2O_3$ @ polymer-Pd/Cu nanocomposites with remarkable catalytic properties towards cross-coupling reactions was developed. The designed nanocomposites, Pd-based and Cu-based NCs, displayed high catalytic efficiency for Suzuki-Miyaura reactions and  $A^3$  coupling reactions, respectively, affording the desired cross-coupled products in excellent yields, even presenting lower metal loadings than commonly reported catalysts, and importantly maintaining their effectivity in successive runs.

Interestingly, this work exemplifies the versatility of the catecholbased polymers as support to favour the immobilization of diverse metal nanoparticles and could be easily extended to other metal NPs (such as Pt, Ag, Au) for designing similar nanocatalysts but directed to other intended organic transformations.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



**Fig. 4.** (A) Magnetization curve of  $Fe_2O_3@CSF@Pd$  measured at 22 °C. Inset: Photograph showing the separation of the catalyst after reaction by using an external hand magnet. (B) Reusability of the  $Fe_2O_3@CSF@Pd$  NC for catalyzing the Suzuki reaction shown in Table 1, entry 1 (red bars) and reusability of the  $Fe_2O_3@CSF@Cu$  NC for catalyzing the A<sup>3</sup> coupling reaction shown in Table 3, entry 5 (grey bars).

#### Table 2

Study of different substrates for the Suzuki-Miyaura cross-coupling reaction catalyzed by as-prepared Pb-based NCs.

$ \begin{array}{c} & \\ R_1 \end{array} \rightarrow Br + \\ R_2 \end{array} \rightarrow B(OH)_2 \xrightarrow{\text{Pd-based NC}} \\ \hline \\ \hline \\ R_2 \end{array} \rightarrow \hline \\ R_1 \\ R_2 \end{array} \rightarrow \hline \\ \\ R_1 \\ R_2 \end{array} $							
Entry	Reactant 1	Reactant 2	Product <sup>b</sup>	Yield <sup>c</sup> (%)		Time (min)	
				Cat. CSF <sup>d</sup>	Cat. TCF <sup>e</sup>		
1	Br	B(OH) <sub>2</sub>	$\bigcirc - \bigcirc$	90	88	40	
2	Br	B(OH) <sub>2</sub>		95	94	30	
3	OF CH3	B(OH) <sub>2</sub>	но-	89	87	40	
4		B(OH) <sub>2</sub>	н,со-	93	91	30	
5		B(OH) <sub>2</sub>	C - C - C - C - C - C - C - C - C - C -	97	95	20	
6	OF CH,	B(OH) <sub>2</sub>	Н,СО-	94	91	25	
7		B(OH) <sub>2</sub>	$\bigcirc - \bigcirc$	92	90	30	
8	CH <sub>3</sub>	B(OH) <sub>2</sub>		89	87	40	
9	Br	B(OH) <sub>2</sub>	но-	88	87	40	
10	Br	OH B(OH) <sub>2</sub>	но-	92	90	40	
11		B(OH) <sub>2</sub>	но-	93	91	30	
12	or cH3	B(OH) <sub>2</sub>	но-	90	89	40	

<sup>a</sup> Conditions: 0.5 mmol of 4-bromobenzene, 0.5 mmol of phenylboronic acid, 10 mg of catalyst, 2 mmol of K<sub>2</sub>CO<sub>3</sub>, 4 mL of H<sub>2</sub>O/DMF (3:1), 80 °C ; <sup>b</sup> Products identified by GC-MS; <sup>c</sup> Isolated yield; <sup>d</sup> Fe<sub>2</sub>O<sub>3</sub>@CSF@Pd catalyst; <sup>e</sup> Fe<sub>2</sub>O<sub>3</sub>@TCF@Pd catalyst.

#### Table 3

Comparison of the catalytic performance of reported similar magnetic Pd-based catalysts for the Suzuki-Miyaura cross-coupling reaction of phenylboronic acid and 4'iodoacetophenone.

Catalyst	Pd (wt%)	Conditions	Yield (%)	Ref.
Fe <sub>3</sub> O <sub>4</sub> -DA-DMG/Pd	5.6	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 80°C, 2 h	97.5	[46]
Pd-Fe <sub>3</sub> O <sub>4</sub> /rGO	5.2	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O/EtOH (1:1), 80°C, 2 h	97.5	[47]
Fe3O4@CFR-S-PNIPAM@Pd/CDs	3.4	K <sub>2</sub> CO <sub>3</sub> , EtOH, RT, 24 h	91.3	[48]
Pd-Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	5.1	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O/EtOH (1:1), 80°C, 30 min	74.8	[49]
Fe <sub>3</sub> O <sub>4</sub> -L-dopa-Pd	5.3	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 70°C, 15 min	97	[50]
Fe <sub>3</sub> O <sub>4</sub> @Ch-PdNPs	2.6	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 100°C, 9 h	99	[51]
Fe <sub>2</sub> O <sub>3</sub> @TCF@Pd	1.5	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O/DMF (3:1), 80°C, 20 min	95	This work
Fe <sub>2</sub> O <sub>3</sub> @CSF@Pd	1.4	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O/DMF (3:1), 80°C, 20 min	97	This work

#### Table 4

Study of different substrates for the A<sup>3</sup> coupling reaction for the synthesis of various propargylamine derivates catalyzed by the as-prepared Cu-based NC.



<sup>a</sup> Conditions: 1.2 mmol of alkyne, 1.0 mmol of aldehyde (CHOR<sup>1</sup>), 1.1 mmol of amine (R<sub>2</sub>NH), 10 mg of catalyst, 5 mL of DCM, RT; <sup>b</sup> Products identified by GC-MS; <sup>c</sup> Isolated yield.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/i.mcat.2020.111042.

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