#### **ORIGINAL PAPER**



# Triazine-hyperbranched polymer-modified magnetic nanoparticles-supported nano-cobalt for C–C cross-coupling reactions

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#### Abstract

Design of hyperbranched polymers (HBPs) and crafting them in catalytic systems especially in organic chemistry are a relatively unexplored domain. This paper reports the utilization of triazine-hyperbranched polymer (THBP)-coated magnetic chitosan nanoparticles (MCs) as stabilizing matrix for cobalt nanoparticles. Cobalt nanoparticles were fabricated by coordination cobalt(II) ions with amine-terminated triazine polymer and then reduced into Co(0) using sodium borohydride in aqueous medium. The Co(0)-THBP@MCs were fully characterized by FT-IR, SEM–EDX, TEM, and TGA analyses. The presence of metallic cobalt was determined by ICP and XRD techniques. This novel hyperbranched polyaromatic polymer-encapsulated cobalt nanoparticles showed high catalytic activity in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions. Heck and Suzuki reactions were carried out using 0.35 and 0.4 mol% of cobalt nanoparticles in which the turnover number (TON) values were calculated as 271 and 225, respectively. In addition, the produced heterogeneous catalyst could be recovered and reused without considerable loss of activity. Oxygen stability and high reusability over 7 runs with trace leaching of the cobalt into the reaction media as well as moisture stability of the immobilized cobalt nanoparticles are their considerable worthwhile advantages.

**Keywords** Hyperbranched polymer · Cobalt nanoparticles · Magnetic chitosan support · Heck and Suzuki cross-coupling reactions

## Introduction

Employing metal nanoparticles (MNPs)-catalyzed C–C cross-coupling reactions is one of the most promising approaches for the synthesis of organic materials [1]. Although the palladium nanoparticles have been exhibited unique performance in cross-coupling reactions [2], the toxicity and price of them lead to replacing it with more sustainable and inexpensive metals [3]; therefore, the application of various palladium-free catalytic systems including nickel [4–6], copper [7], iron [8, 9], and cobalt [10] has been developed. Since cobalt nanoparticles (CoNPs) are

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<sup>2</sup> Department of Neuroscience, Medical School, University of Wisconsin, 1300 University Avenue, Madison, WI 53706-1532, USA known as an inexpensive, non-toxic, abundant, and highly active catalyst [11], our research group has focused on using cobalt as a green catalyst for cross-coupling reactions [12, 13]. In many reactions catalyzed by metal nanoparticles, the metal surfaces should interact with the reacting substrates directly to achieve efficient catalytic reactions [14]. If the metal nanoparticles were produced naked, the interaction of metal-substrate would be more efficient. However, the electrostatic attraction and high surface energy between the naked atoms of MNPs can induce aggregation, reduce the accessible catalyst surface area, and result in decreased catalytic activity [15, 16]. Therefore, the metal surfaces passivation has been developed by organic capping molecules [17] (ionic liquid [18], surfactants [19], polymers [20], etc.) or solid supports to prevent the aggregation of MNPs. However, this may be accompanied with decreased catalytic activity because of the occupation of metal sites by organic groups [21]. In comparison with other capping agents, polymers are more advantageous and affording better stabilization [14]. Polymer architecture and functional groups allow the control of the structure and morphology of MNPs [22].

Among polymers, hyperbranched polymers have received considerable attention [23] due to their highly branched, porosity, and three-dimensional structures. They exhibit multiple internal and external functional groups such as alkanamine, alkanthiol, or alkanhydroxy, which prevent the formation of well-packed MNPs [24]. Hence, hyperbranched polymers are well suited as host for metal catalysts due to their strong capability of coordinating with metals, which leads to better catalytic activity [25, 26]. Hyperbranched polymer-based catalysts with branching structures allow the reactants to reach the entrapped nanoparticles, while at the same time inhibiting the nanoparticles from aggregation and stabilizing them [27, 28]. The first studies on hyperbranched polymers stabilized CoNPs were carried out by Kutyreva's group [29]. Moreover, hyperbranched molecules-encapsulated nanoparticles demonstrate different applications in nanomedicine [30], photonic [31], and molecular electronics [32], and are also applied as nanocatalyst [33]. Among various hyperbranched polymers, triazine-based polymers have been much reported [34] due to their chemoselective reactivity and low cost [35]. For instance, Landarani et al. recently reported the synthesis and catalytic properties of triazinebased polymer-stabilized PdNPs in cross-coupling reactions [36]. In another example, the synthesis and application of triazine-based hyperbranched polymer which stabilized Pd nanoparticles as the catalyst in cross-coupling reactions were studied by Moghadam et al. [37]. In another report, cobalt-grafted triazine functionalized magnetic nanoparticles were used as a catalyst in Heck cross-coupling reaction [38]. Although polymers can serve as the catalyst support, their stabilization on an inorganic solid support is believed to improve the catalytic activities of metal nanoparticles. On the other hand, hyperbranched polymers are nearly too small, even those with high generations to be separated from the reaction media and used again [39]. Thus, there are many works which reported heterogenizing polymers on solid supports [40] such as carbon nanotubes [41], silica [42] graphene sheets [43], and TiO<sub>2</sub> [44]. However, lack of efficient functional groups restricts the application of these solid supports [45]. Magnetic nanoparticles (MaNPs) are attractive alternative for heterogenizing catalysts, because their magnetic properties cause easy separation of the catalyst by an external magnetic field [46–48]. Moreover, MaNPs attract significant interest in the area of drug delivery [49], magnetic storage media [50], biomedicine [51], and chemical reactions [52].

The preparation and the catalytic properties of the cobalt nanoparticles immobilized on the hyperbranched polymerfunctionalized nano-magnetic chitosan were studied in this work. Triazine-based hyperbranched polymer bearing amine groups were attached to the cobalt nanoparticles (Co(0)-THBP@MCs) as a surface ligand. After preparation and characterization of Co(0)-THBP@MCs, its catalytic activities were assayed in cross-coupling of aryl chlorides, bromides, and iodides with methyl acrylates and phenylboronic acids under mild conditions. Since the prepared catalyst could catalyze aryl chlorides which are less reactive in cross-coupling reactions than aryl iodides and aryl bromides, this catalyst can be a promising candidate for examining it in other cross-coupling reactions. The accessibility of the triazine-hyperbranched polymer and the presence of CoNPs on the surface of MaNPs as well as the stability of the cobalt nanoparticles cause an increased catalytic activity.

### **Experimental section**

Materials and methods are described in the supporting information.

### **Catalyst preparation**

#### Synthesis of magnetic chitosan (MCs)

Although different methods have been used to prepare  $Fe_3O_4$ , co-precipitation which may be the simplest chemical approach was employed in this work [53]. First,  $FeSO_4 \cdot 7H_2O$  (5.2 mmol, 1.46 g) was added to a round-bottom flask containing a mixture of  $FeCl_3 \cdot 6H_2O$  (7.4 mmol, 2 g) and 100 mL of distilled deionized water (DDW). The mixture obtained was then dispersed for about 30 min. Next, NH<sub>3</sub> solution (alkaline precipitation agent) was added dropwise into the homogeneous mixture until the pH reached 10 and a black precipitate formed. Afterward, the mixture was stirred at 80 °C in nitrogen atmosphere for about 2 h to complete the crystallization. The precipitate was separated by an external magnetic bar from the reaction mixture, washed several times with deionized water (DW) and ethanol, and dried in an oven at 50 °C.

Subsequently, the surface modification of magnetic nanoparticles with chitosan was performed to address the agglomeration of MaNPs and also generate amine groups [54]. For this purpose, MaNPs (0.236 g) and 2 mL of acetic acid solution were mixed with a mixture of deionized water (11 mL) and chitosan (0.472 g), and the resultant mixture was stirred for 15 min. Afterward, sodium sulfate solution (20% W/V) was dispersed in the mixture of chitosan and vigorously stirred for 1 h at room temperature. Finally, the magnetic chitosan was separated from the reaction media by an external permanent magnet, washed with ethanol several times, and dried at 70 °C.

#### Preparation of MCs-CC1

The general procedure for the construction of THBP is as follows: the magnetic chitosan (0.5 g) was added to a

solution of cyanuric chloride (10 mmol, 1.85 g) and triethylamine (10 mmol, 1.7 mL) in 15 mL of THF. The resulting mixture was allowed to stir overnight at 0 °C. The desired product was collected by an external magnetic bar, separated from white triethyl ammonium chloride salt and washed with THF several times to remove redundant and then dried in a vacuum oven at 50 °C [36].

## Preparation of triazine-hyperbranched polymer-functionalized magnetic chitosan (G1)

The amidation of triazine ring with diamino pyridine is as follows: to a slurry of MCs-CC1 (0.34 g) in DMF (12 mL), 2,6-diamino pyridine (16 mmol, 0.7 g) and triethylamine (16 mmol, 1.5 mL) were added. The reaction mixture was stirred at 80 °C for 16 h. The solid product was obtained with a magnetic field, washed with hot ethanol to remove the unreacted substrates and dried in a vacuum oven at 50 °C [36].

## Preparation of MCs-CC2

For construction of the second generation of THBP on the surface of magnetic chitosan, Michael addition and amidation condensation were repeated one more time. Triazine-hyperbranched polymer-supported magnetic chitosan, (G1) (0.26 g) was added to a solution of cyanuric chloride (3 mmol, 0.7 g) and triethylamine (3 mmol, 1.56 mL) in 15 mL THF. The reaction mixture was agitated at 0 °C for 10 h, followed by separation and washing with THF to remove the unreacted reactants. Finally, MCs-CC2 was dried in a vacuum oven at 50 °C.

## Preparation of triazine-hyperbranched polymer-functionalized magnetic chitosan (G2)

To a slurry of MCs-CC2 (0.24 g) in 20 mL of DMF, 2,6-diaminopyridine (8.11 mmol, 0.3 g) and triethylamine (8.11 mmol, 1.4 mL) were added. The reaction mixture was stirred at 80 °C for 16 h and then collected. The resulting THBP@MCs (G2) were washed with hot ethanol to remove the unreacted starting materials and dried in a vacuum oven at 50 °C.

## Preparation of cobalt nanoparticles immobilized on triazine-hyperbranched polymer-supported magnetic chitosan (Co(II)-THBP@MCs)

In order to coordinate triazine rings of THBP@MCs to cobalt, G2 (0.5 g) was added to 4.2 mmol of  $CoCl_2.6H_2O$  dissolved in ethanol (10 mL). The reaction mixture was refluxed under stirring for 18 h at 70 °C. The resulting complex was separated, washed several times with ethanol to

remove the unreacted starting materials, and dried at room temperature to afford the (Co(II)-THBP@MCs) complex as a brown solid. 0.5 g of the Co(II)-complex in distilled water (10 mL) was then reduced by 10 mL of NaBH<sub>4</sub> solution (100 mM) under stirring. After 2 h, the catalyst was separated from the mixture, washed several times with ethanol and dried in vacuum to obtain a brown solid powder.

## **General procedure for Heck reaction**

In a round-bottom flask containing a mixture of DMF:H<sub>2</sub>O (1:2 V/V, 6 mL) as the solvent, a mixture of aryl halide (1.0 mmol), methyl acrylate (1.2 mmol), K<sub>3</sub>PO<sub>4</sub> (2.0 mmol), and 0.35 mol% of the catalyst was added. For an appropriate amount of time, the reaction mixture was agitated at 90 °C. The completion of the reaction was monitored by TLC (Hexane/EtOAc, 80:20) and gas chromatography (GC). The reaction mixture was then cooled at room temperature and the organic layer was extracted with ethyl acetate. Afterward, the products were characterized by comparison of their <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra with those previously reported.

## General procedure for Suzuki reaction

In a round-bottom flask, a mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol),  $K_3PO_4$  (2.0 mmol), and 0.4 mol% of the catalyst was added to a mixture of DMF:H<sub>2</sub>O (1:2 V/V, 6 mL) solvent. For an appropriate period of time, the reaction mixture was stirred at 90 °C. The reaction was carried out similarly to the Heck reaction. Then, the corresponding products were characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR analyses.

## **Results and discussion**

## Fabrication and characterization of the synthesized catalyst

Hyperbranched polymers (HBPs) are a class of dendrimers with branched conformation, which are comprised of a large number of functional groups. In comparison with dendrimers, HBPs have advantages including facile functionalization process, self-assembly mechanism, and controllable morphologies. HBPs, which are multifunctional polymers, can be employed as stabilizing matrix for synthesizing catalytic metal nanoparticles (MNPs) [30, 55]. These polymersencapsulated MNPs demonstrate some advantages such as high and controlled activity and good air stability [56]. They affect significantly the physiochemical properties of products such as synthetic versatility and processability [57]. These polymers have been found to be effective homogeneous and heterogeneous catalysts in cross-coupling reactions [40, 58, 59]. In this study, magnetic nanoparticles were selected as proper support which cause convenient separation of the synthesized catalyst in each step of the synthesis. Many reports on the employment of triazine-based polymers as support for different metals in catalytic system have been published [58, 60]. However, to the best our knowledge, there are only a few reports on the application of these polymers in cross-coupling reactions. As we know, this is the first report on the application of magnetic THBP-supported cobalt nanoparticles as catalyst in Heck and Suzuki coupling reactions without any co-catalyst. The pathway for the preparation of the catalyst is illustrated in Scheme 1. First, to assist the immobilization of THBP, MaNPs were functionalized with chitosan to afford magnetic chitosan with reactive amine groups. On the other hand, chitosan is a biocompatible, non-toxic, and abundant bio-polymer with free hydroxyl and amine functional groups, and also in comparison with other mono-layered compound such as 3-(trimethoxysilyl)propylamine, chitosan can provide more amine groups due to its polymeric nature. Since the amino groups of chitosan are more nucleophilic than hydroxyl groups to attack the cyanuric chloride, OH groups remain free and intact. Then, the achieved magnetic chitosan reacts with cyanuric chloride at 0 °C for substitution of only one of the chlorine atoms to vield MCs-CC1. In the following step, the reaction of MCs-CC1 with 2,6-diamino pyridine was carried out at 90 °C to remove both of the reside chlorine atoms in MCs-CC1 to give G1. Next, G1 was converted to MCs-CC2 during reaction with cyanuric chloride. Finally, MCs-CC2 reacts with 2,6-diamino pyridine which produced the THBP@MCs as the support for CoNPs (Scheme 1). The loading amount of Co onto the THBP@MCs determined by inductively coupled plasma analysis (ICP) was 2.48 mmol  $g^{-1}$ . The procedure was also monitored by FT-IR and TGA techniques. The



Scheme 1 Synthesis route for the preparation of the catalyst



**Fig. 1** FT-IR spectra: (a) MaNPs, (b) CS, (c) MCs, (d) MCs-CC1, (e) G1, and (f) the synthesized catalyst

catalyst was characterized by FE-SEM, EDX, TEM, XPS, and XRD analyses.

In order to confirm the synthesis of MaNPs, Cs, MCs, MCs-CC1, G1, and the synthesized catalyst FT-IR spectra were recorded (Fig. 1a-f). The presence of bands at 580 and 3420 cm<sup>-1</sup> is characteristic of the Fe–O and O–H stretching vibration, respectively [61] (Fig. 1a). In the case of chitosan, the absorption bands around 1081, 3365, and 1583 cm<sup>-1</sup> correspond to the stretching vibration of C-O, O-H, and N-H (primary amine) of pristine chitosan, respectively (Fig. 1b). The bands corresponding to the C–H (stretching vibration) of the chitosan backbone appear at 2921 and 2881 cm<sup>-1</sup> (Fig. 1b). It is noteworthy to mention that the bands shift to higher wavelengths (3369, 2926, 2887  $\text{cm}^{-1}$ ) in comparison with pure chitosan upon the immobilization of chitosan on MaNPs (Fig. 1c). The characteristic absorption bands in the range of 1490-1620 attributed to C-N and C=N, and the C–Cl stretching vibration at 1091 cm<sup>-1</sup> (Fig. 1d) appear after the addition of triazine units on the magnetic chitosan. As observed in Fig. 5e, the stretching vibration of the primary amine groups (N-H) at 3410-3450 cm<sup>-1</sup>, the stretching vibration of the secondary amine groups overlapped with the primary amine bands, and the stretching vibration of C=N groups at 1626 cm<sup>-1</sup> verify the effective immobilization of 2,6-diaminopyridine on the functionalized magnetic chitosan. Eventually, in the case of Co(0)-THBP@MCs (Fig. 5f), a slight shift of the band at  $1626 \text{ cm}^{-1}$  is observed  $(1626 \text{ cm}^{-1} \rightarrow 1631 \text{ cm}^{-1})$ , which is probably characteristic of the primary amine groups after interaction with the cobalt nanoparticles. Therefore, the functional groups have been successfully grafted onto the MCs surface.

The oxidation state of cobalt in the synthesized catalyst was indicated by high-resolution XPS spectrum (Fig. S1). According to the previous report [62], the peak with binding energy of 799.4 eV is assigned to Co  $2p_{1/2}$  and the peak at 779.5 eV is attributed to Co  $2p_{3/2}$  which can be indexed to Co(0). The XPS data confirm the formation of cobalt nanoparticles on THBP.

The amount of organic moieties and thermal degradation of MaNPs, MCs, MCs-CCl, G1, and G2 were studied by thermal gravimetric analysis (TGA). The weight loss percentages of all cited compounds between 30 and 700 °C were determined by TGA which is an irreversible process (Fig. 2). As shown in Fig. 2a, a 3 wt% weight loss observed for Fe<sub>3</sub>O<sub>4</sub> in the range of 250–400 °C is related to the removal of physically absorbed water. In the case of MCs, two decomposition stages were observed. However, the 10% weight loss in the 180-400 °C range is related to release of moisture on the structure. In addition to water loss, above 400 °C, chitosan starts to degrade and is completely depolymerized at 700 °C. The observed weight loss (12 wt%) in Fig. 2c demonstrates the successful immobilization of the cyanuric chloride on the surface of MCs. The TGA plots of G1 and the synthesized catalyst result from the removal of absorbed water and elimination of organic matter on the surface. Furthermore, the total weight loss of G2 (31%) was larger than of G1 (24%), demonstrating the higher content of the organic moieties bonded on the catalyst. These results evidently prove the successful immobilization of the hyperbranched polymer on the magnetic surface.

The presence of  $Fe_3O_4$  and cobalt nanoparticles in the catalyst was confirmed by the XRD patterns. XRD analysis was applied to investigate the crystalline nature and presence of iron and cobalt in the synthesized catalyst. Figure 3



Fig. 2 TGA thermogram of (a) MaNPs, (b) MCs, (c) MCs-CC1, (d) G1, and (e) G2  $\,$ 



Fig. 3 XRD patterns of the (a)  $Fe_3O_4$  and (b) Co (0)-THBP@MCs

shows the XRD patterns of Fe<sub>3</sub>O<sub>4</sub> and Co(0)-THBP@MCs catalyst. In the displayed diagram, six characteristic diffraction peaks at  $2\theta = 30.5^{\circ}$ ,  $35.6^{\circ}$ ,  $43.3^{\circ}$ ,  $53.6^{\circ}$ ,  $57.3^{\circ}$ , and 62.9° are observed, relating to the (220), (331), (400), (422), (511), and (440) crystal planes of the cubic inverse spinel structure of  $Fe_3O_4$  (Fig. 3a), respectively, which match well with the standard magnetic nanoparticles sample (JCPDS card no. 85-1436) [63, 64]. The diffraction peaks positioned at  $2\theta = 43.43^{\circ}$  and  $53.6^{\circ}$  are attributed to the reflection of (111) and (220) crystalline planes of the cobalt species with cubic spinal structure. It is worthwhile to point out that the crystallographic phase of nanoparticles was not affected by their surface modification. Moreover, average crystallite size of the nanoparticles which establishes a relationship between position and broadening peak was estimated by the Scherrer's equation. In this study, the nanoparticle size was calculated to be 16 nm by the highest intensity peak (331), which matches with the range of the size estimated by TEM analysis [65, 66].

The energy-dispersive X-ray (EDX) analyses of MaNPs, MCs, MCs-CC1, G1, and the catalyst are shown in Fig. 4. The EDX spectra indicate the grafting of THBP on Fe<sub>3</sub>O<sub>4</sub> as well as immobilization of cobalt on the THBP@MCs. The peaks of Fe and O are ascribed to the magnetic nanoparticles and the N and C peaks observed in Fig. 4b are related to the functionalization of Fe<sub>3</sub>O<sub>4</sub> by chitosan. The presence of chlorine atoms in Fig. 4c confirms the reaction of chitosan with cyanuric chloride. The removal of chlorine atom peak in Fig. 4d is associated with the substitution of chlorine atoms with amine groups of 2,6 diamino pyridine. The appearance of cobalt atom peak in Fig. 4e shows the stabilization of Co on the THBP@MCs support.

The outer topography of MaNPs, MCs, MCs-CC1, G1, and the synthesized catalyst was visualized by field

emission-scanning electron microscopy (FE-SEM) (Fig. 5). As shown in Fig. 5a, the surface of  $Fe_3O_4$  particles is rough and shows considerable protuberances, which can be caused by the reduced surface energy of Fe<sub>3</sub>O<sub>4</sub> particles. In comparison with magnetic nanoparticles, the magnetic chitosan surface shows more irregular pores and higher roughness, caused by the tightly bound structure between the surface of chitosan and MaNPs (Fig. 5b), and the diameter of magnetic chitosan was larger than that of Fe<sub>3</sub>O<sub>4</sub> diameter. As observed in Fig. 5c, MCs-CC1 particles are highly irregular and angularly shaped with various size ranges. As clearly observed in Fig. 5d, the surface morphology varies and there is more agglomeration after binding of diamine groups with triazine molecules. The reaction between THBP@MCs and cobalt after reduction with sodium borohydride yields similar noncontinuous layers, with particles of different sizes. These observations reveal the successfully linkage of the organic materials to the magnetite nanoparticles.

The morphology and particle size of the catalyst were studied by transmission electron microscopy (TEM) analysis (Fig. 6). The structure and particle size of the synthesized catalyst were confirmed by TEM technique and found to be 16 nm. As observed, the dark color MaNPs cores were surrounded by light gray spherical shell which belongs to the organic compounds. The smaller dimensions of the nanoparticles provide larger surface to volume ratio and consequently more efficient catalytic activity.

The VSM diagrams of  $Fe_3O_4$ , MCs, G2, and the synthesized catalyst at room temperature are presented in Fig. 7. The saturation magnetization ( $M_s$ ) of  $Fe_3O_4$ , which reflects paramagnetic properties, is about 40 emu/g. As shown in Fig. 7b,  $M_s$  decreased to 23 emu/g, corresponded to covering of the surface of magnetic material ( $Fe_3O_4$ ) with a non-magnetic compound (chitosan). A considerable reduction in the magnetic property of G2 and the synthesized catalyst was observed. The magnetic moment of these compounds was 9 and 11 emu/g, respectively. It is clear that the synthesized catalyst demonstrates more magnetic properties compared to G2, due to the production of metallic cobalt in fcc crystalline nanoparticles [67].

## Application of Co(0)-THBP@MCs in C-C cross-coupling reaction

After synthesis and characterization of the catalyst, the catalytic activity was evaluated in Heck and Suzuki cross-coupling reactions.

## Optimization of the reaction conditions for the Heck cross-coupling reaction

Effect of critical parameters such as solvent, base, temperature, and catalyst loading on the outcome of cross-coupling



Fig. 4 SEM-EDX spectra of a MaNPs, b MCs, c MCs-CC1, d G1, and e synthesized catalyst

reactions was evaluated [68, 69]. To reach this aim, the reaction of iodobenzene and methyl acrylate was selected as a model reaction to determine the optimum reaction conditions.

#### Effect of metal loading

The impact of different amounts of Co metal in the catalytic activity in Heck reaction was evaluated. As shown in Table 1, increasing the amount of loaded cobalt causes a rise of the product yield (Table 1, entries 11–15). As observed, the reaction reached 94% conversion for the metal loading of 0.35 mol%. Moreover, when the experiment was performed in the absence of the catalyst under the same

reaction conditions, the reaction did not proceed even after a long time.

### Effect of different bases

The bases employed in the coupling reactions play a critical role in neutralizing hydrogen halides and preventing the formation of homocoupling product [70]. Hence, different bases including Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and K<sub>3</sub>PO<sub>4</sub> were examined in the reaction. Among these bases, K<sub>3</sub>PO<sub>4</sub> showed the best performance. Furthermore, the amount of the base used considerably affected the results (Table 1, entries 1–6) and it was found that 2 mmol of K<sub>3</sub>PO<sub>4</sub> afforded the suitable yield of the product [71, 72].



Fig. 5 FE-SEM images of a MaNPs, b Cs, c MCs, d MCs-CC1, e G1, and f Co(0)-THBP@MCs



Fig. 6 a TEM image and b particle size distribution of the catalyst

 
 Table 1
 Optimization of reaction conditions on Heck reaction of iodobenzene with methyl acrylate in the presence

of catalyst



Fig. 7 Room temperature magnetization curves of the (a)  $Fe_3O_4$ , and (b) MCs, (c) G2, and (d) synthesized catalyst

## Effect of solvent

To explore the effect of solvent, the model reaction was conducted using different common solvents. A mixture of DMF and  $H_2O$  in 1:2 ratio showed a significant progress in the reaction, resulting in a yield of 94%. Thus, this solvent mixture was chosen as the most effective solvent.

### Effect of temperature

The effect of temperature on the Heck cross-coupling reaction was also studied. Therefore, the model reaction was carried out at different temperatures (Table 1 entries 16–18). According to the result obtained, the desired product with the highest yield was obtained at 90 °C.

## Evaluation of the catalytic activity of synthesized catalyst

Finally, the applicability of this new catalytic system for a set of substituted aryl halides (chlorides, bromides, and iodides) with electron-donating or withdrawing groups in Heck reaction was investigated under the optimum conditions (Table 2). As summarized in Table 3, aryl halides

Entry	Catalyst (mol%)	Base (mmol)	Solvent	<i>T</i> (°C)	Yield <sup>a</sup> (%)
Base effe	ect				
1	0.35	$K_2CO_3$ (1.5)	DMF:H <sub>2</sub> O (1:2/V:V)	90	86
2	0.35	$Na_2CO_3$ (1.5)	DMF:H <sub>2</sub> O (1:2/V:V)	90	71
3	0.35	NaHCO <sub>3</sub> (1.5)	DMF:H <sub>2</sub> O (1:2/V:V)	90	78
4	0.35	$K_{3}PO_{4}(1.5)$	DMF:H <sub>2</sub> O (1:2/V:V)	90	92
5	0.35	$K_{3}PO_{4}(1)$	DMF:H <sub>2</sub> O (1:2/V:V)	90	88
6	0.35	K <sub>3</sub> PO <sub>4</sub> (2)	DMF:H <sub>2</sub> O (1:2/V:V)	90	94
Solvent of	effect				
7	0.35	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O (1:1/V:V)	90	90
8	0.35	$K_{3}PO_{4}(2)$	H <sub>2</sub> O	90	84
9	0.35	$K_{3}PO_{4}(2)$	DMF	90	93
10	0.35	$K_{3}PO_{4}(2)$	DMSO	90	95
Catalyst	effect				
11	-	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O (1:2/V:V)	90	Trace
12	0.2	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O (1:2/V:V)	90	73
13	0.3	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O (1:2/V:V)	90	86
14	0.35	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O (1:2/V:V)	90	94
15	0.4	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O (1:2/V:V)	90	95
Temp. e <u>f</u>	fect				
16	0.4	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O(1:2/V:V)	100	96
17	0.4	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O(1:2/V:V)	90	94
18	0.4	$K_{3}PO_{4}(2)$	DMF:H <sub>2</sub> O(1:2/V:V)	80	87

The optimum condition is exhibited in bold

<sup>a</sup>GC yield





<sup>a</sup>The reaction was carried out with aryl halide (1.0 mmol), alkene (1.2 mmol),  $K_3PO_4$  (2 mmol), and catalyst (0.35 mol% of Co) in 6 mL DMF/  $H_2O$  (1:2) at 90 °C

<sup>b</sup>Isolated yield

<sup>c</sup>Turn over number, yield of product/per mol of Co

bearing electron-withdrawing groups underwent coupling with methyl acrylate in shorter times than those with electron-donating groups. The different product yields observed correspond to electronic effect of the functional groups. In addition, it was found that aryl iodides and bromides with the same functional groups reacted with methyl acrylate in  
 Table 3
 Optimization of reaction conditions on Suzuki reaction of iodobenzene with phenylboronic acid in the presence of catalyst

Entry	Catalyst	Base (mmol)	Solvent	<i>T</i> (°C)	Yield <sup>a</sup> (%)
	(1101%)				
Base effe	ct				
1	0.4	$K_{3}PO_{4}(1.5)$	DMF:H2O(1:2/V:V)	90	88
2	0.4	$K_{3}PO_{4}(1)$	DMF:H2O(1:2/V:V)	90	86
3	0.4	$K_{3}PO_{4}(2)$	DMF:H2O(1:2/V:V)	90	90
4	0.4	Na2CO3 (1.5)	DMF:H2O(1:2/V:V)	90	63
5	0.4	K2CO3 (1.5)	DMF:H2O(1:2/V:V)	90	81
6	0.4	NaHCO3 (1.5)	DMF:H2O(1:2/V:V)	90	75
Solvent e	ffect				
7	0.4	$K_{3}PO_{4}(2)$	H2O	90	69
8	0.4	$K_{3}PO_{4}(2)$	DMF:H2O(1:1/V:V)	90	84
9	0.4	$K_{3}PO_{4}(2)$	DMSO	90	92
10	0.4	K <sub>3</sub> PO <sub>4</sub> (2)	DMF	90	90
Catalyst	effect				
11	0.1	$K_{3}PO_{4}(2)$	DMF:H2O(1:2/V:V)	90	61
12	0.2	K <sub>3</sub> PO <sub>4</sub> (2)	DMF:H2O(1:2/V:V)	90	72
13	0.3	$K_{3}PO_{4}(2)$	DMF:H2O(1:2/V:V)	90	83
14	0.4	$K_{3}PO_{4}(2)$	DMF:H2O(1:2/V:V)	90	90
15	0.5	$K_{3}PO_{4}(2)$	DMF:H2O(1:2/V:V)	90	92
Temp. eff	ect				
16	0.4	$K_{3}PO_{4}(2)$	DMF:H2O(1:2/V:V)	100	92
17	0.4	K <sub>3</sub> PO <sub>4</sub> (2)	DMF:H2O(1:2/V:V)	90	90
18	0.4	$K_{3}PO_{4}(2)$	DMF:H2O(1:2/V:V)	80	85

The optimum condition is exhibited in bold

<sup>a</sup>GC yield

shorter times in comparison with aryl chloride. This trend can be explained by the increase in the bond energy in the following order (C–Cl>C–Br>C–I). Since the formation of C–Co–X catalyst species is suggested for the oxidative addition of Co, the C–C coupling reactions by aryl chlorides take longer compared with aryl iodides and bromides because the C–Cl bond has a high dissociation energy [70]. Therefore, the coupling reactions with aryl chlorides do not process similarly to aryl iodides and bromides. On the other hand, aryl chlorides are favorable substrates for such reactions because they are widely available and inexpensive. For most studies, harsh conditions are required.

According to the results achieved in Heck cross-coupling reaction, we were encouraged to explore the potential of our catalyst in the Suzuki reaction. The reaction of phenylboronic acid with iodobenzene in the presence of our catalyst was considered as a model reaction to find the optimum conditions. The effect of parameters such as the type of solvent, temperature, base, and catalyst amount was assessed and the results are presented in Table 3. As is observed, the highest yield was achieved by iodobenzene (1 mmol), phenylboronic acid (1.2 mmol),  $K_3PO_4$  (2 mmol), and the catalyst (0.4 mol% Co) in DMF:H<sub>2</sub>O solvent mixture at 90 °C (Table 3, entry 3).

With the optimized conditions in hand, the versatility of the Co(0)-THBP@MCs in Suzuki reactions of aryl halides (I, Br, Cl) containing various functional groups with phenylboronic acid was investigated. It can draw conclusion from Table 4, aryl iodides and bromides undergo more successful coupling reactions with phenylboronic acid in comparison with aryl chloride, although aryl iodides afford the suitable products in efficient yields and high TONs. As expected, chlorides generally show weak reactivity unless they contain electron-withdrawing substituents on the ring. Thus, the promotion of the reaction is affected by the position and electronic behavior of the reactants. Therefore, aryl halides containing -CN, and  $-NO_2$  groups are substantially more reactive than those with  $-CH_3$ ,  $-OCH_3$ , and  $-NH_2$ groups.

To further examine the efficiency of the present catalytic system, Co(0)-THBP@MCs were compared with some reported catalysts in Heck and Suzuki cross-coupling reactions (Table 5). It is obvious that our method is superior to some reported catalyst due to lower temperature, shorter reaction time, greener media (safe metal), and better yield. Moreover, the low percentage of the catalyst used and magnetic recyclability are the advantages of this new protocol. The high activity of our catalyst is probably due to the



Table 4 Suzuki cross-coupling of various aryl halides in the presence of synthesized catalyst

<sup>a</sup>The reaction was carried out with aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol),  $K_3PO_4$  (2 mmol), and catalyst (0.4 mol% of Co) in 6 ml DMF/H<sub>2</sub>O (1:2) at 90 °C

<sup>b</sup>Isolated yield

<sup>c</sup>Turnover number, yield of product/per mol of Co

Table 5         Comparison of
catalytic activities of our
catalyst with literature examples
for Heck and Suzuki reactions

Entry	Catalyst	Reaction condition	Time (h)	Yield (%)
1	Nano-Co [73]	Co (2 mol %) in NMP at 130 °C	14	78
2	Co/Al <sub>2</sub> O <sub>3</sub> [74]	Co (10 mol %) in NMP at 150 °C	24	56
4	Co-B [75]	Co (5 mol %) in NMP at 130 °C	12	98
5	Co-NHC@MWCNTs [76]	Co (3.5 mol %) in PEG at 80 °C	5	85
6	Co-IL@MWCNTs [18]	Co (5 mol %) in toluene at 100 °C	3	87
7	Co-Ms@MNPs/Cs [54]	Co (1.1 mol %) in PEG at 80 °C	1	88
9	Cobalt Schiff base Complexes [77]	Co (1 mol %) in toluene at 110 °C	8	90
10	Cobalt Schiff base Complexes [78]	Co (2 mol %) in dioxane at 110 °C	8	88
11	Cobalt hollow nanospheres [79]	Co (1 mol %) in NMP at 130 °C	16	73
12	Co@Fe <sub>3</sub> O <sub>4</sub> /L-dopa [80]	Co (1.84 mol%)in H <sub>2</sub> O at 100 °C	4	81
13	Present catalyst	Co (0.35 mol%) in DMF:H <sub>2</sub> O at 90 $^\circ\mathrm{C}$	2	94



Fig. 8 Recyclability of the catalyst in the Suzuki reaction

good dispersion of cobalt nanoparticles and good synergistic effects of cobalt nanoparticles with ligands grafted on MaNPs.

From the environmental and economic points of view, the reusability and recycling of heterogeneous catalysts are important. Therefore, the reusability of the Co(0)-THBP@ MCs catalyst under the optimized conditions was tested in Suzuki reaction of iodobenzene with phenylboronic acid as model reaction (Fig. 8). After each cycle, the catalyst was separated by an external magnet, washed several times with deionized water and ethanol, dried, and applied in the subsequent runs. The results indicate that the catalyst could be recovered seven times without any significant loss of catalytic activity.

In order to verify that the properties of the recycled catalyst are identical to those of the fresh catalyst, ICP, EDX, FE-SEM, and XRD analyses were performed. The amount of leached cobalt was measured by ICP-OES and the results showed that less than 1% of cobalt metal was removed. The chemical composition, morphology, and presence of cobalt nanoparticles after seven runs were also analyzed by EDX, FE-SEM, and XRD techniques. As shown in Fig. 8, it was found that the structure of the catalyst did not change and no significant changes were observed in the morphology. The presence of cobalt in the recovered catalyst was confirmed by EDX analysis (Fig. 9).

According to Figure S2, the XRD pattern of reused catalyst also demonstrates a profile similar to the fresh catalyst.

To demonstrate the heterogeneous nature of the catalyst and the amount of leached metal nanoparticles, hot filtration test was carried out for the Suzuki reaction as a model reaction under the optimized conditions. In this case, the reaction between iodobenzene and phenylboronic acid was done, after 30 min the reaction was stopped and the catalyst was separated. Therefore, the reaction continued for other 2 h in the absence of catalyst. The progress of the reaction was monitored by TLC and GC. The results achieved clearly revealed no further progress in product



Fig. 9 FE-SEM and EDX analyses of reused catalyst

yield and proved that metal leaching into reaction media was negligible.

## Conclusion

In this work, magnetic hyperbranched polymer-encapsulated cobalt nanoparticles were successfully designed and synthesized through the complexation of Co(II) cations with amines-terminated triazine polymer along with the reduction of cobalt cations by NaBH<sub>4</sub>. The Co(0)-THBP@MCs catalyst demonstrated efficient performances in Heck and Suzuki cross-coupling reactions. The high catalytic activity of Co(0)-THBP@MCs in comparison with other catalyst is believed to be related to the cross-linked hyperbranched triazine polymer structure with multiple amine groups, which provide excellent stabilization of the cobalt nanoparticles species and providing an available space for reacting molecules. The deposition of the cobalt nanoparticles on a substrate with many functional groups was recognized as a highly active, oxygen-insensitive, moisture-stable, and recyclable heterogeneous catalyst separated by an external magnet. The hyperbranched triazine polymer is able to entrap cobalt without remarkable metal leaching to the reaction media. Moreover, environmentally friendly procedure (palladium-free, DMF:H<sub>2</sub>O as solvent, 90 °C), short reaction times, considerable yield, and low metal contamination make Co(0)-THBP@MCs as a usable catalyst for C-C coupling reactions. Moreover, the catalyst was reused seven times with no significant decrease in catalytic activity, due to the strong covalent bond between cobalt nanoparticles and triazine-hyperbranched polymer.

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### Declarations

Conflict of interest There are no conflicts to declare.

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