

# Silica-coated magnetic nanoparticles functionalized cobalt complex: a recyclable and efficient catalyst for the C–C bond formation

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## Abstract

In this study, the Co-based catalyst was prepared by cobalt immobilization on the surface of functionalized silica-coated magnetic NPs (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co) as a magnetically core–shell nanocatalyst and characterized by FT-IR, TGA, XRD, VSM, SEM, TEM, EDX, EDX mapping, and ICP techniques and appraised in the Suzuki–Miyaura cross-coupling reaction under mild reaction conditions. The results displayed the superparamagnetic behavior of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co catalyst provided perfect catalysts, the engineered Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co catalyst provided perfect catalytic performance for the Suzuki–Miyaura cross-coupling reaction in water as a green solvent and it was much cheaper in the comparison with the traditional Pd-based catalysts. Importantly, the durability of magnetic nanocatalyst was studied and observed that it is stable under the reaction conditions and could be easily reused for at least six successive cycles without any significant decrease in its catalytic activity.

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#### **Graphic abstract**



**Keywords** Cobalt · Cross-coupling reaction · Heterogeneous catalysis · Magnetic nanoparticles · Suzuki–Miyaura reaction

### Introduction

One of the most prominent  $C(sp^2)-C(sp^2)$  coupling reactions that has been considered as a potent synthetic procedure is a Suzuki–Miyaura cross-coupling reaction that is used to constitute the unsymmetric biaryl derivatives from the reaction between boronic acids and aryl halides [1–8]. Some reasons that led to broadly implement Suzuki–Miyaura reaction are the usage of this C–C bond formation reactions in many fields such as pharmaceuticals, agrochemicals, natural products, and chemical industries [9–13].

During the last decades, miscellaneous transition metal catalysts especially palladium-based catalysts have been used to construct various organic and bioorganic molecules via Suzuki–Miyaura cross-coupling reaction. Since palladium catalysts have some drawbacks like air sensitivity, high cost, and toxicity, efforts have been highly focused on designing effective transition metal catalysts including cobalt [14–17], copper [18–20], nickel [21–23], and zinc [24, 25] instead of using catalysts based on expensive metals like palladium [26–28]. Among all of the transition metal catalysts used in carbon–carbon coupling reactions, cobalt has gained great attention due to its precious properties such as eco-friendly, low cost, nontoxicity, and good availability; therefore, many studies have shown the implementation of catalytic systems based on cobalt with the usage of various linkers in carbon–carbon coupling reactions [16, 29, 30]. Heterogeneous catalysts have played an important role in many catalyst systems because of their potential applications [31–42]. Among these, magnetite nanoparticles (MNPs) and especially  $Fe_3O_4$  showed that they possess valuable features such as easy separation and recycling by using an external magnetic field to avoid wasting catalyst after the end of the reaction [43–48]. Typically, magnetic nanoparticles are sensitive against air moisture, so they have been coated with different organic and inorganic layers like silica, polymers, and noble metals to ameliorate the chemical stability of nanoparticles. Silica (SiO<sub>2</sub>) is a useful inorganic layer which is used not only for coating the surface of the nanoparticles but also for modifying with various organic ligands [49–54].

As a part of our ongoing work to design the efficient heterogeneous catalyst with eco-friendly methods [55], we prepared the silica-coated magnetic  $Fe_3O_4$  NPs  $(Fe_3O_4@SiO_2)$  with excellent magnetic features and inexpensive procedures according to the reported literature[19]. In the following step, the creatine amino acid as an organic ligand was added to the ethanoic mixture of  $Fe_3O_4@SiO_2$  to afford  $Fe_3O_4@$  SiO<sub>2</sub>-CT. Finally, we produced the  $Fe_3O_4@SiO_2$ -CT-Co by adding aqueous solution of CoCl<sub>2</sub> to the ethanoic mixture of  $Fe_3O_4@SiO_2$ -CT to apply as a reusable catalyst in a Suzuki–Miyaura cross-coupling reaction. Scheme 1 has shown the preparation strategy of prepared silica-coated magnetic nanoparticles  $Fe_3O_4@SiO_2$ -CT-Co.

#### Experimental

#### Material

All the materials used in this research have been purchased from Merck or Sigma-Aldrich without any further purification.

#### Synthesis of catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co)

The magnetic heterogeneous nanocatalyst has been fabricated according to Scheme 1. For this purpose, initially, the silica-coated MNPs ( $Fe_3O_4@SiO_2$ ) were prepared *through the method presented* in the *literature* [56], and next, the creatine organic ligand was grafted on the silica-coated MNPs and then followed by



Scheme 1 Synthesis of catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co)

immobilization of cobalt complex. On this basis, the  $Fe_3O_4@SiO_2(0.1 \text{ g})$  was sonicately dispersed in EtOH (40 mL) at room temperature. After 30 min, a solution of creatine organic ligand (0.2 g) in deionized water (20 mL) was added droopingly to the previously prepared mixture of magnetic mixture, and then, they were refluxed with stirring for 6 h. Then, the magnetic  $Fe_3O_4@SiO_2$ -CT was separated from the mixture by an external magnet and washed with EtOH and H<sub>2</sub>O many times, respectively. Afterward, the prepared modified MNPs were dried in a vacuum oven at 60 °C for 24 h. Finally, in order to synthesis the last catalyst,  $Fe_3O_4@$  $SiO_2$ -CT MNPs (0.25 g) were sonicately dispersed in EtOH (20 mL) for 20 min. Subsequently, a solution of cobalt acetate (0.5 M) in 5 mL of EtOH was added to the previous mixture and refluxed. After 6 h, the prepared Co-coordinated catalyst ( $Fe_3O_4@SiO_2$ -CT-Co) was separated from the reaction mixture by an external magnet, and then washed successively with EtOH (3×5 mL), and then dried at 60 °C for 24 h to obtain the  $Fe_3O_4@SiO_2$ -CT-Co catalyst.

#### General procedure for the C–C bond formation catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co

To a solution of phenylboronic acid derivatives (1.2 mmol), aryl halides (1.0 mmol), KOH (2.5 mmol), and water (3.0 ml), 1.5 mol % of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co was added at 75 °C with stirring under oil bath condition. After the finalization of the reaction, the Co-coordinated MNPs catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co) was separated from the reaction mixture and washed with EtOH and H<sub>2</sub>O and, finally, dried at 60 °C in a vacuum oven for 12 h. Subsequently, the water as a green solvent was separated from the reaction mixture by rotary evaporator and the prepared Suzuki products have been obtained in pure products with good to excellent isolated yields. Some selected products have been characterized with H and C NMR, and the data have been added in supporting material section.

# **Result and discussion**

At the preliminary stage, the successful synthesis of  $Fe_3O_4@SiO_2$ -CT-Co was evaluated using some spectroscopic and microscopic techniques including FT-IR, TGA, XRD, VSM, SEM, TEM, EDX, EDX mapping, and ICP. In the following of our previous studies and based on the successful preparation of the  $Fe_3O_4@SiO_2$ -CT-Co, the catalytic capability of the aforesaid nanocatalyst was studied in the Suzuki–Miyaura cross-coupling reaction of different aryl halides with various aryl boronic acids without using any palladium, under green solvent (H<sub>2</sub>O) conditions.

The FT-IR analysis of  $Fe_3O_4$  (a),  $Fe_3O_4@SiO_2$  (b), CT (c), and  $Fe_3O_4@SiO_2$ -CT-Co (d) is shown in Fig. 1. As it is evident from Fig. 1a, related to the  $Fe_3O_4$ MNPs, the broad absorption peak was observed at 3348 cm<sup>-1</sup> that can be related to the O–H stretching bands of hydroxyl functional groups on the surface of MNPs. The broad and sharp peak at 559 cm<sup>-1</sup> is assigned to the Fe–O bonds of MNPs [57]. As it is evident from Fig. 1b, allocated to the silica-coated  $Fe_3O_4$ MNPs, the existence of the new bonds at 1101 and 935 cm<sup>-1</sup> is attributed to the



Fig. 1 FT-IR spectra of a Fe<sub>3</sub>O<sub>4</sub> b Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> c Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT d Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co

asymmetric and symmetric vibrations of Si–O-Si bond, respectively. The broad absorption band at 3350 cm<sup>-1</sup> approves the attendance of the stretching mode of the surface-attached hydroxyl groups ( $\nu$  O–H) on the surface of silica NPs [56]. In the FT-IR spectrum of CT (Fig. 1c), three broad absorption peaks at around 3200, 3000, and 2900 cm<sup>-1</sup> are assigned to the stretching vibrations of NH<sub>2</sub>, OH, and CH groups, respectively. Besides, the observed absorption peaks at 1418 and 1672 cm<sup>-1</sup> are allocated to the bending and stretching vibrations of OH and C=O groups, respectively [58]. Furthermore, it is worth mentioning that there are all creatine peaks in the FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co (Fig. 1d) including the absorption peaks related to NH<sub>2</sub>, OH, and CH groups at around 2900 to 3200 cm<sup>-1</sup>. Notably, a blue shift of C=O peak is observed from 1672 to 1655 cm<sup>-1</sup> that approves the proper complexation of cobalt on the CT ligand and successful synthesis of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co [59].

The phase purity and crystal structure of the bare  $Fe_3O_4$  (a) and  $Fe_3O_4@SiO_2$ -CT-Co (b) are clearly corroborated via surveying the X-ray powder diffraction (XRD) patterns (Fig. 2). As shown in Fig. 2, the  $Fe_3O_4$  and  $Fe_3O_4@SiO_2$ -CT-Co have eight distinct peaks at  $2\Theta = 30.27$ , 35.74, 36.10, 43.27, 53.78, 57.29, 62.87, and 71.50 that they are assigned to the lattice planes of cubic  $Fe_3O_4$  MNPs (2)



Fig. 2 XRD pattern of a  $Fe_3O_4$  and b final catalyst ( $Fe_3O_4@SiO_2$ -CT-Co)

2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0), and (620) (JCPDS card No. 98–007-7842) [60]. It is worth noting that in the XRD pattern of  $Fe_3O_4@SiO_2$ -CT-Co, the diffraction peaks corresponding to cobalt ions have not been observed in the final catalyst, in agreement with the high cobalt dispersion [61]. The absence of Co diffraction peaks indicates the formation of finely dispersed cobalt species after immobilization on the surface of modified SiO<sub>2</sub> that are not detectable by this technique (as cobalt loading is lower than 5 wt% according to ICP results) [19, 62, 63].

The size and morphology of the  $Fe_3O_4@SiO_2$ -CT-Co nanocatalyst were also studied by the scanning electron microscopy (SEM) technique. As clearly shown in Fig. 3a, the  $Fe_3O_4@SiO_2$ -CT-Co nanocatalyst exhibits highly dispersed uniform spherical morphology with an average size of about 35–45 nm. To explore more details concerning the morphology and structure of the core–shell  $Fe_3O_4@$  $SiO_2$ -CT-Co, transmission electron microscopy (TEM) analysis was employed as well (Fig. 3b). It was obviously observed in Fig. 3b that the  $Fe_3O_4$  NPs core is well encapsulated by the modified  $SiO_2$  coating with a clear boundary between the silica shell and the  $Fe_3O_4$  NPs core. As shown in Fig. 3b, the particle sizes of  $Fe_3O_4@$  $SiO_2$ -CT-Co nanocatalyst in irregular geometric shape were approximately 35 nm, which is very close to the particle size as determined using SEM analysis.

Moreover, to explore the elemental composition uniformity of the  $Fe_3O_4@SiO_2-CT-Co$ , the EDX mapping and EDX analysis are conducted and the results are shown in Figs. 4 and 5, respectively. As shown in these figures, the simultaneous existence of Fe, O, Si, C, N, and Co elements with homogeneous distribution on the entire surface of the catalyst is well proved.

To investigate the thermal and structural stability and also determine the content of organic materials of the  $Fe_3O_4@SiO_2$ -CT-Co, thermal gravimetric analysis (TGA) was performed under an air atmosphere at a heating rate of 10 °C min<sup>-1</sup> from



Fig. 3 SEM a and TEM b images of catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co)

0 to 800 °C (Fig. 6). The as-synthesized catalyst exhibits two mass loss steps. The first low mass loss, which eventuated in the temperature range from 50 to 150 °C, is responsible for the removal of the physically adsorbed H<sub>2</sub>O and O–H groups on the surface Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (about 6% weight loss). The second weight loss (about 20% weight loss) in the region between 150 and 500 °C can be attributed to the decomposition of grafted creatine and acetate (related to cobalt acetate) molecules on the surface of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles. In comparison with the literature [64], it can be concluded that creatine showed higher thermal stability due to interaction with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles.

Moreover, the ICP analysis revealed that the overall coordinated cobalt content on the surface of  $Fe_3O_4@SiO_2$ -CT MNPs in the freshly prepared catalyst was 4.47% which confirms the successful coordination of cobalt on the surface of catalyst and creatine organic ligand.

Next, the magnetic properties of catalyst have been investigated by VSM analysis at room temperature, as shown in Fig. 7. Based on these studies, the saturation magnetization of prepared catalyst  $Fe_3O_4$  was 80 emu/g that showed superparamagnetic properties.

After full characterization of  $Fe_3O_4@SiO_2$ -CT-Co as a new, reusable, and heterogeneous catalyst, its catalytic activities have been studied toward the Suzuki reaction of various aryl halides with different aryl boronic acids (Scheme 2).

Secondly, in order to evaluate the optimum reaction conditions, the reaction of iodobenzene with phenylboronic acid in the presence of the KOH (2.5 mmol) and water (as solvent) was chosen as a model reaction by taking into account several important parameters such as solvent, base, temperature, and catalyst loading (Table 1). As expected, the control experiment indicated that no biaryl product was obtained without the catalyst (at 75 °C), and the reaction did not proceed even after a long time running the reaction (12 h) (Table 1, entry 1). Then, the influence of the catalyst loading has been investigated on the selected reaction (Table 1,



Fig. 4 EDX mapping analysis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co

entries 2–5). After a few attempts, it was found that 0.02 g (1.5 mol%) of the nanocatalyst was required to achieve the maximum yield of the desired product (96% after 30 min) (Table 1, entry 3). A higher amount of the catalyst 0.04 g (3.0 mol%) did not have any effect on the product yield or the reaction rate (Table 2, entry 2), whereas a significant decrease in the reaction progress was observed by applying 0.01 g (0.75 mol%) of the catalyst (Table 1, entry 2). In the next experiments, the effect of the common solvents including toluene, DMF, 1,4-dioxane, EtOH, CH<sub>3</sub>CN, and solvent-free conditions has been investigated in the model Suzuki reaction. Among them, the H<sub>2</sub>O as green solvent was found to be the suitable medium for obtaining a reasonable isolated yield of the cross-coupled (Table 1, entries 6–11). To improve the product yield and enhance the reaction rate, the model reaction was performed in the presence of different bases comprising the KOH, NaOAc, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, and Et<sub>3</sub>N (Table 1, entries 12–16). As can be seen, among the bases



Fig. 5 EDX analysis of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co



Fig. 6 TGA plot of catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co)

mentioned, KOH was found to be highly efficient in the preparation of the corresponding coupling product in H<sub>2</sub>O at 75 °C (Table 1, entry 3). After this, the effect of the content of KOH was surveyed in the model reaction. The cross-coupled product was effectively produced when using 2.5 mmol of the base (Table 1, entries 3 and 17–19). Subsequent experiments identified the effect of temperature in the Suzuki cross-coupling reaction, which showed that the best yield was obtained at 75 °C (Table 1, entries 3 and 20–22).

In the next step, a diversity of the substrate has been analyzed in the presence of the  $Fe_3O_4@SiO_2$ -CT-Co under the optimized reaction conditions for the synthesis of biaryl derivatives. Tables 2 exhibited that the cross-coupling reaction of aryl iodides



Scheme 2 Suzuki cross-coupling reaction in the presence of catalyst (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-CT-Co)

with phenylboronic acid is faster than that of aryl bromides or aryl chlorides due to the lower C-I bond strength *vs.* C–Br and C–Cl bonds (Table 2, 3a-3e). Besides, different electron-poor and electron-rich aryl halides were exploited for analyzing the Suzuki reaction. Basically, it is crystal clear that the aryl halides containing electron-withdrawing groups (such as -CHO or -NO<sub>2</sub>) compared with electron-rich aryl halides (such as -OMe or -Me) afforded the desired coupled-products with excellent yields in shorter reaction time. Also, heteroaryl halides such as 2-iodopyridine, 2-bromopyridine 2-iodothiophene, and 2-bromothiophene were also good partner for this coupling reaction (Tables 2, 3j and k). Moreover, the 4-methyl phenylboronic acid has been examined with different aryl halides (Table 2, entries 3 1-n). The results were similar to the phenylboronic acid, however, the yield of the reaction has been decreased a little.

According to previously reported Suzuki–Miyaura mechanisms in the literature [16], and based on our knowledge, a proposed mechanism for the Suzuki–Miyaura cross-coupling reaction was depicted in Scheme 3. The active form of Co is generally believed to be  $Co^{I}$  in C–C cross-coupling reactions. When  $Co^{II}$  precursors are applied, reduction to  $Co^{I}$  by base reagents (as KOH) is observed [65]. According to the literature reports on the reduction of  $Co^{II}$  to  $Co^{I}$  by base reagents [65] and acceleration of this process by ligands that can stabilize the  $Co^{I}$  oxidation state, the following plausible mechanism might be proposed. On this basis, firstly, the  $Co^{II}$  intermediate (1) through oxidative addition of the aryl halide. In the following step, the deprotonation of the phenyl boronic acid under basic conditions by KOH is

Entry	Catalyst (g, mol%)	Aryl iodide/ Base	Base	Condition	Tem. (°C)	Time (min)	Yield (%) <sup>a</sup>
1	_	1.0/2.5	КОН	H <sub>2</sub> O	75	12 h	_
2	0.01 (0.75)	1.0/2.5	KOH	H <sub>2</sub> O	75	45	65
3	0.02 (1.5)	1.0/2.5	KOH	$H_2O$	75	30	96
4	0.03 (2.25)	1.0/2.5	KOH	$H_2O$	75	30	96
5	0.04 (3.0)	1.0/2.5	KOH	$H_2O$	75	30	96
6	0.02 (1.5)	1.0/2.5	KOH	Toluene	Reflux	60	Trace
7	0.02 (1.5)	1.0/2.5	KOH	1,4-Dioxane	Reflux	60	66
8	0.02 (1.5)	1.0/2.5	KOH	DMF	Reflux	60	45
9	0.02 (1.5)	1.0/2.5	KOH	CH <sub>3</sub> CN	Reflux	60	51
10	0.02 (1.5)	1.0/2.5	KOH	EtOH	Reflux	60	76
11	0.02 (1.5)	1.0/2.5	KOH	Solvent-free	100	35	82
12	0.02 (1.5)	1.0/2.5	NaOAc	$H_2O$	75	30	42
13	0.02 (1.5)	1.0/2.5	Na <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	75	30	65
14	0.02 (1.5)	1.0/2.5	K <sub>2</sub> CO <sub>3</sub>	$H_2O$	75	30	70
15	0.02 (1.5)	1.0/2.5	$K_3PO_4$	$H_2O$	75	30	73
16	0.02 (1.5)	1.0/2.5	Et <sub>3</sub> N	$H_2O$	75	30	44
17	0.02 (1.5)	1.0/1.0	KOH	H <sub>2</sub> O	75	60	79
18	0.02 (1.5)	1.0/2.0	KOH	$H_2O$	75	30	90
19	0.02 (1.5)	1.0/3.0	KOH	$H_2O$	75	30	96
20	0.02 (1.5)	1.0/2.5	KOH	H <sub>2</sub> O	rt	60	51
21	0.02 (1.5)	1.0/2.5	KOH	H <sub>2</sub> O	50	30	82
22	0.02 (1.5)	1.0/2.5	KOH	H <sub>2</sub> O	100	30	96

Table 1 Optimization of different conditions for the C-C bond formation

 $X + B(OH)_2 \xrightarrow{Catalyst} Conditions$ 

<sup>a</sup>Isolated Yield

responsible for the formation of intermediate (2) via the insertion of phenyl boronic acid into intermediate (1). At last, the desired coupled product was obtained through the reductive elimination reaction of intermediate (2) by regenerating the active  $Co^{I}$  catalyst for the next catalytic cycle.

Considering the environmental and economic factors, and also the principles of green chemistry, the long-term durability experiment of the prepared catalyst has been investigated. For this purpose, the model reaction was carried out under the optimized reaction conditions to test the reusability behavior of the  $Fe_3O_4@SiO_2$ -CT-Co (Fig. 8). Briefly, after the finalization of each run of the cross-coupling reaction, which was monitored by thin-layer chromatography, the reaction mixture was cooled to room temperature and the heterogeneous catalyst has been separated using an external magnet, washed with EtOH and H<sub>2</sub>O, and dried under vacuum at 60 °C



 Table 2 Synthesis of different biaryl derivatives in presence of catalyst<sup>a</sup>

<sup>a</sup>Different aryl halides (1.0 mmol), phenyl boronic acid (1.2 mmol) in presence of (0.02 g, 1.5 mol%) of catalyst in  $H_2O$  at 75 °C

<sup>b</sup>Turn over number (Yield of the reaction/mol%)

<sup>c</sup>Turn over frequency (TON/time of the reaction)

Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Time (min)	Yield (%)	Reference
1	Pd/Ni graphene	DMF/H <sub>2</sub> O	110	30	78	[66]
2	Cu/Carbon	H <sub>2</sub> O	50	180	95	[67]
3	Cu nano-colloid	DMF	110	360	62	[68]
4	Et <sub>2</sub> Zn, DMEDA	THF	80	360	98	[24]
5	Co-His@MNPs/Ch	PEG	80	120	97	[ <mark>69</mark> ]
6	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -EP-AG-Pd	$H_2O$	50	120	99	[ <b>70</b> ]
7	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /APTES/IMMPh@ Ni	DMF	140	360	92	[71]
8	Ni-porphyrin graphene oxide	Dioxane	80	60	95	[72]
9	Fe <sub>3</sub> O <sub>4</sub> @GPTMS-AG Cu	Solvent-free	80	30	97	[ <mark>19</mark> ]
10	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -CT-Co	$H_2O$	75	30	96	This work

Table 3 The comparison of our catalyst with other metal-based catalysts for the C-C bond formation

overnight to use in the next run. As shown in Fig. 8, no significant decrease in the yield of the reactions was observed after even six runs. These results confirmed the high catalytic activity and long-term durability of the  $Fe_3O_4@SiO_2$ -CT-Co in the C–C cross-coupling reaction.

The hot filtration test was another analysis to approve the heterogeneous nature of the  $Fe_3O_4@SiO_2$ -CT-Co in the C–C bond formation reaction. On this basis, the



Scheme 3 Proposed mechanism for the C-C bond formation in the presence of catalyst



Fig. 8 Catalyst reusability test

model reaction was studied again under the optimized reaction condition. After 15 min (50% conversion), the  $Fe_3O_4@SiO_2$ -CT-Co was removed from the reaction using an external magnet. Afterward, the rest of the reaction was stirred in the absence of catalyst for a further 15 min. Observation showed that the reaction did not intend to move forward and confirmed that no leaching of complex and cobalt ions was happened during the reaction (Fig. 9). Moreover, the amount of Co in the separated catalyst was also investigated by ICP technique. According to the ICP results, it was 4.42% that shows a negligible decrease and approves



Fig. 9 Time-dependent correlation of the product yield in hot filtration test

approximately no leaching of cobalt was happened during the C–C cross-coupling reaction and it is in agreement with hot filtration test observations.

Finally, to evaluate the performance of the present catalytic activity in the Suzuki–Miyaura cross-coupling reaction, the current protocol was compared with some previously reported catalysts in the C–C cross-coupling reaction (Table 3). Undoubtedly, all of the listed catalysts in Table 3 significantly can produce the desired product in good to excellent yields. But, it can be found that the Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>-CT-Co as a magnetic heterogeneous nanocatalyst is much superior to almost all of the methods presented in Table 3, in terms of the high temperatures (Table 3, entries 1, 3, and 7), hazardous solvents (Table 3, entries 1, 3, 4, 7, and 8), long reaction times to obtain the desired product (Table 3, entries 2–7), as well as price and toxicity are the disadvantages of some of these methods (Table 3, entries 1, 6). Moreover, the newly synthesized nanocatalyst with high catalytic efficiency can be easily separated from the reaction mixture by using an external magnet.

### Conclusion

In the present study, core–shell  $Fe_3O_4@SiO_2$ -CT-Co was described as a sustainable magnetic nanostructured catalyst in a C–C bond formation of aryl halides with phenyl boronic acid in the water as a green solvent. This method has the privileges including high yields of coupled-products, environmental acceptability, short reaction time, excellent functional group compatibility, and easy experimental and work-up procedures. Interestingly, the unique stable nanostructured catalyst could be easily separated by using an external magnetic from the reaction mixture and reused at least six times with trace cobalt leaching and without a significant reduction in the yields of the desired products as well. The present work can be considered as

an attractive alternative to the currently reported methods based on Pd catalysts for C–C cross-coupling reactions. In our opinion, this efficient method is able to open a new front for designing and modification of environmentally friendly, renewable, low cost, and high-performance nanostructured catalysts with a well-controlled morphology for other cross-coupling reactions in mild conditions.

Supplementary Information The online version contains supplementary material available at https://doi. org/10.1007/s11164-021-04522-7.

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#### Declarations

Conflict of interest The author declared that there is no conflict of interest.

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