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Introduction

In the early 1970s, palladium-catalyzed reactions were introduced by Negishi, Kumada, and Suzuki, and subsequently various homogeneous and heterogeneous Pd-catalyzed systems were developed.^{1–3} The Heck cross-coupling reaction has become one of the most applicable for $C_{sp^2}-C_{sp^2}$ bond formation involving $C(sp^2)$ centers in the presence of palladium catalysts in organic synthesis,⁴ and allows the manufacture of complex molecules from simple precursors. The Heck reaction is widely used in the agrochemical, pharmaceutical, and fine chemical industries.^{5–7}

The Sonogashira reaction also belongs to the family of palladium-catalyzed carbon–carbon coupling reactions, *i.e.*, crosscoupling of a vinyl or aryl halide and a terminal alkyne ($C_{sp^{2-}}$

Imidazolium chloride-Co(\mathfrak{m}) complex immobilized on Fe₃O₄@SiO₂ as a highly active bifunctional nanocatalyst for the copper-, phosphine-, and base-free Heck and Sonogashira reactions[†]

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A heterogeneous, magnetically recoverable Fe₃O₄@SiO₂@Im[Cl]Co(III)-melamine nanocomposite was prepared by immobilization of a novel Co(III) Schiff base complex on Fe₃O₄@SiO₂ nanoparticles followed by treatment with melamine, and was found to be an efficient catalyst for the Heck and Sonogashira reactions. The reactions were performed in the presence of the catalyst (0.5 mol% Co) along with Mn additive in the absence of any base, phosphine ligand, or Cu/co-catalyst in ethanol under reflux conditions. The nanocatalyst was well studied by FTIR, CHN, XRD, XPS, TGA, EDX, VSM, ICP, NMR, FE-SEM, TEM, BET, CV, and DLS analyses. The catalyst was compatible with a variety of substrates, with which all the Heck and Sonogashira coupling products were obtained in high to excellent yields. Also, protocols such as hot filtration, three-phase testing, and mercury poisoning provided a complete insight into the nature of the heterogeneous catalyst. The recycling and reuse of the catalyst were studied for both coupling reactions several times. Moreover, the mechanism of the coupling reactions was entirely investigated.

 C_{sp}).⁸ The traditional Sonogashira reaction utilizes CuI as a cocatalyst, which converts the alkyne into a copper acetylide *in situ*. However, it also induces homo-coupling reactions and subsequently produces symmetrical bis-aryl ethynes by-products. Therefore, research is ongoing toward the introduction of copper-free protocols.

On the other hand, the high cost and toxicity of palladium complexes along with the need for expensive and sensitive phosphine ligands are some of the limitations that have persuaded scientists to seek to find efficient alternative methodologies with less expensive metals. To solve these problems, the discovery and development of different methodologies are necessary. In the past decade, many studies have been reported about the use of alternative transition metals, such as Ni,⁹ Cu,¹⁰ Fe,¹¹ and Co,¹² as more convenient, sustainable, cost-effective, and safe approaches for cross-coupling reactions.¹³

Among these, due to their high catalytic activity, low cost, and easy preparation with readily accessible materials, Co complexes have received considerable attention. Cobalt-catalyzed coupling reactions are of interest in organic synthesis because of the notable properties of cobalt metal, including it being readily available, non-toxic, low-cost, stable, and having powerful catalytic properties.^{8,12} Various attempts have been devel-

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oped to extend Co-based catalysts to make a suitable readily available alternative catalytic system compared with Pd catalytic systems. Co-Catalyzed C–C coupling reactions efficiently eliminate the β -H elimination that accompanies the processes in Pd- and Ni-catalyzed systems as a by-product. Furthermore, they have also demonstrated advantages in the coupling reaction of alkyl halides,⁶ which is problematic and difficult to achieve with other transition metals.

Previously, Gosmini et al. and Cahiez et al. individually reviewed a wide range of Co-catalyzed cross-coupling reactions.^{13,14} In the last decade, various Co-catalyzed systems have been reported for C-C cross-coupling reactions, such as CoCl₂(dpph)/Me₃SiCH₂MgCl for the alkenylation of alkyl halides, intramolecular Heck-type reactions and the Heck-type reaction of alkyl halides with styrenes,^{5,15,16} Co-methyl salicylate@MNPs/chitosan for Heck and Sonogashira couplings,³ CoBr₂/Zn for the arylzincation of alkynes,¹² CoBr₂/Bpy/ Mn for the vinylation of functionalized aryl halides,¹⁷ Co NPs for the Heck reaction,¹⁸ Fe₃O₄@Boehmite-NH₂-Co(II) for Suzuki and Heck cross-coupling reactions,19 and Co complex/ blue LEDs for the cyclization coupling of alkyl iodides with alkenes.²⁰ Recently, Maity et al.⁴ reported a Co-catalyzed dehydrogenative Heck reaction of allylic alkenylation with internal aliphatic olefins.

However, most of these approaches incur high cost and energy and also involve harsh reaction conditions, such as high temperature and long reaction times. So, finding a novel Cobased catalyst that can overcome to these limitations is desired.

Nowadays, the utilization of efficient nanoparticles for catalytic goals is a smart strategy, and they can significantly promote catalytic activity due to their high surface to volume ratio. In this way, they are usually coated with various polymers, especially silicate, to avoid agglomeration.^{21,22} This simple strategy allows the efficient functionalization of nanoparticles for a specific goal. Unfortunately, catalytic systems based on NPs suffer from tedious work-up, agglomeration, contamination, *etc.* For this purpose, magnetic nanoparticles were introduced as a heterogeneous magnetically recoverable solid support in organic synthesis^{22–25} as they could completely resolve the catalyst separation problems. The most prominent and applicable of these magnetic NPs is Fe₃O₄ NPs.

Herein, in accordance with green chemistry considerations as well as an insight into the economic and environmental

factors, we developed an efficient protocol for the C–C crosscoupling reaction of aryl halides with olefins and acetylenes by introducing a new magnetically recoverable $Fe_3O_4(@SiO_2@Im$ [Cl]Co(m)-melamine nanocomposite in a highly efficient and selective manner under mild conditions. The present method is phosphine-/Pd-/Cu-/base-free and contains an imidazolium moiety that plays the role of a base to overcome the above-mentioned limitations regarding Pd complexes or the obstacles regarding homogeneous catalytic systems.

Results and discussion

Catalyst characterization

The elemental analysis results for the samples is tabulated in Table 1. The results are in good agreement with theoretical calculations and confirmed the preparation of compounds 1, 2, 3, 4. Also, the results are in accordance with the proposed structure sketched in Scheme 7, as well as the previously reported structure in the literature.²⁶

Fig. 1 shows the FTIR spectra of 1, 2, 3, 4, 5, 6, 7, 8, and 9 compounds. The FTIR absorption spectrum of 1 shows two characteristic peaks at 1481 cm⁻¹ and 725 cm⁻¹, corresponding to the methylene groups ($-CH_2-$) in the *meta*-substi-





Table 1 Results of the elemental analysis and physical properties of the compounds

		Elemental analys		
Compounds	Appearance	%C	%Н	%N
2-Hydroxy-5-chloromethyl benzaldehyde (1) 2-Hydroxy-5-imidazole benzaldehyde (2) 4-((1 <i>H</i> -Imidazol-1-yl)methyl)-2-((allylimino)methyl)phenol (3) Co(III) Schiff base complex (4)	Purple powder Dark brown powder Pale yellow powder Brown powder	$\begin{array}{c} 56.30 \ (56.82)^a \\ 65.74 \ (65.34) \\ 69.47 \ (69.69) \\ 64.80 \ (64.34) \end{array}$	4.14 (4.25) 5.09 (4.98) 6.22 (6.27) 5.02 (5.23)	 13.97 (13.85) 17.64 (17.41) 15.32 (15.58)

^a Theoretically calculated.

tution and the stretching vibration of C-Cl, respectively (Fig. 1a).²⁵ The FTIR spectrum of 2 represents a series of peaks at 2490–2780 cm⁻¹ related to the imidazole moiety, which are in agreement with compounds containing imidazole moieties reported in the literature (Fig. 1b).²⁷ Moreover, elimination of the C-Cl bond at 725 cm⁻¹ in the spectrum of 1 corroborates the imidazole functionalization of 5-chloromethylene salicylaldehyde. Stretching vibration related to the N-H of imidazole moiety appeared at 3413 cm⁻¹. Imine bond formation in 3 was confirmed by the presence of a C=N bond at 1611 cm⁻¹ (Fig. 1c).²⁸ This absorption was shifted to 1565 cm⁻¹ due to Co complex formation. This shift, along with Co-O and Co-N stretching vibrations at 504 cm⁻¹ and 615 cm⁻¹, respectively, confirmed the successful coordination of Co ions through N and O in 4 (Fig. 1d). Fe₃O₄ NPs showed a single characteristic peak at 570 cm⁻¹ related to Fe-O bond²⁹ (Fig. 1e). The presence of three main peaks at 779, 1072, and 3433 cm⁻¹ correspond to the stretching vibrations of Fe-O, Si-O-Si (symm.), and Si-O-Si (asymm.), respectively, strongly confirming the coating of the Fe₃O₄ NPs by silica shells (Fig. 1f).³⁰ Fig. 1g demonstrates the vibrations attributed to C-H stretching., -CH₂- bending, and C-Cl stretching at ~2920, 1458, and 633 cm⁻¹, respectively, which strongly support the preparation of Fe₃O₄(a)SiO₂-Cl (Fig. 1g). The linkage of complex 4 to Fe₃O₄(a)SiO₂-Cl was proved by the presence of C=N, Si-O-Si, Fe-O, and C=C bonds correspond to the wavenumbers at 1560, 1018, 405, and 1414 cm⁻¹, respectively (Fig. 1h). Fig. 1i shows the spectrum of the catalyst 9 prepared from the intercalation of melamine to the Fe₃O₄@SiO₂@Im[Cl]Co(III)-Schiff base complex (8). The elimination of C=C stretching bonds at 1407 cm⁻¹ in the FTIR spectrum of **9** (Fig. 1i) represents the intercalation of melamine into the catalyst framework. The peaks at 1445 and 1540 cm⁻¹ could be attributed to the quadrant stretching of the 1,3,5-s-triazine ring, and semicircle stretching of the 1,3,5-s-triazine ring, respectively.³¹ Also, the absence of the peaks associated with the N-H (primary) stretching and bending in the catalyst spectrum was further evidence of the insertion of melamine into the catalyst framework.

XRD spectra for the synthesized nanoparticles are shown in Fig. 2. As presented in Fig. 2, Fe₃O₄ nanoparticles have a highly crystalline cubic inverse spinel structure, which is well in agreement with the standard Fe₃O₄ (cubic phase) XRD spectrum (PDF#88-0866, reference JCPDS card no. 19-629).³² The characteristic diffraction peaks at $2\theta = 30.1^{\circ}$, 35.4° , 43.1° , 53.4° , 57° , and 62.6° , and could be marked, respectively, by their indices to the (220), (311), (400), (422), (511), and (440) planes, demonstrating the Fe₃O₄ structure.^{28,29}

These peaks were also observed for $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -Cl, which confirmed the inverse spinel Fe_3O_4 NPs in their structures. The XRD patterns of $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -Cl showed an obvious diffusion peak at $2\theta = 15-25^{\circ}$, representing the coated amorphous silica on the Fe_3O_4 NPs (Fig. 2b and c).³² The presence of peaks corresponding to the Fe_3O_4 structure as well as the amorphous silica peak appeared in the XRD pattern of the $Fe_3O_4@SiO_2@Im[Cl]Co(m)$ -



Fig. 2 XRD patterns of (a) Fe_3O_4 , (b) $Fe_3O_4@SiO_2$, (c) $Fe_3O_4@SiO_2-Cl$, (d) $Fe_3O_4@SiO_2@Im[Cl]Co(iii)-melamine nanocomposite.$

melamine nanocomposite (Fig. 2d),²⁹ clearly manifesting that the surface modification of the Fe₃O₄ NPs does not lead to their phase change or structure. The broadening of the peaks shows that Fe₃O₄@SiO₂ NPs were functionalized with the amorphous Co(m) Schiff base complex and revealed the successful preparation of the nanocomposite. Also, the broad peak at $2\theta = 20^{\circ}$ was assigned to the amorphous Co(m) Schiff base complex moiety (Fig. 2d). Beside the other analyses, the size of the nanoparticles was calculated using Scherrer's equation: $D = K\gamma/\beta \cos \theta$, where *K* is a constant (K = 0.9 for Cu-K α), *D* is the average diameter in Å, β is the broadening of the diffraction line measured at half of its maximum intensity in radians, γ is the wavelength of the X-rays, and θ is the Bragg diffraction angle.

The electrochemical activity of the catalyst was studied at room temperature in BR buffer solution in the potential range of -2.0 to 2.0 V.^{33} As shown in Fig. 3A, the Co(III) complex demonstrated two reversible peaks corresponding to Co^I/Co^{II} and Co^{II}/Co^{III} couples.³⁴⁻³⁶ The first redox peak was assigned to the Co^{III}/Co^{II}, with *E*pa₁ = 0.5 V, *E*pc₁ = 0.32 V, and *E*_{1/2} = 0.09 V. The second redox peak corresponded to the Co^{II}/Co^I couples with *E*pa₂ = -0.97 V, *E*pc₂ = -1.23 V, and the average formal potential equal to *E*_{1/2} = -1.1 V. These results suggest a two-step redox reaction with a reversible mechanism.

The elements in the catalyst were probed by EDX analysis (Fig. 3B). Regarding Fig. 3B, the EDX spectrum confirmed all the elements present in catalyst **9**, including iron, carbon, nitrogen, silicon, chlorine, cobalt, and oxygen.



Fig. 3 (A) Cyclic voltammogram of catalyst **9** in 0.1 mol L⁻¹ Britton–Robinson (BR) buffer solution (pH 7.0) with a scan rate of 100 mV s⁻¹ at room temperature; (B) EDX spectrum of catalyst **9**; (C) magnetization curves for (a) Fe₃O₄, (b) Fe₃O₄@SiO₂ (c) Fe₃O₄@SiO₂@Im[Cl]Co(III)-Schiff base complex (**8**), and (d) Fe₃O₄@SiO₂@Im[Cl]Co(III)-melamine nanocomposite (**9**), at room temperature; (D) TGA curves of (a) Co(III) Schiff base complex (**4**, (b) Fe₃O₄@SiO₂@Co(III) Schiff base complex (**8**), and (c) catalyst **9**.

The results of the magnetic properties of the samples are shown in Fig. 3C. These NPs exhibited a high permeability in magnetization that was sufficient to be able to separate them with an external magnetic field. The magnetization and demagnetization curves were coincident and no hysteresis phenomenon was found.

As shown in the figure, the remnant magnetization for all NPs is equal to zero. Magnetic measurements showed saturation magnetization (Ms) values of 70.0, 39.8, 35.9, and 33.1 emu g^{-1} for Fe₃O₄, Fe₃O₄($aSiO_2$, and the Fe₃O₄($aSiO_2(aIm[Cl])$ Co(III)-Schiff base complex (8), and the Fe₃O₄@SiO₂@Im[Cl]Co (III)-melamine nanocomposite (9), respectively (Fig. 3C, a, b and c). The results demonstrated that the magnetization of Fe₃O₄ was considerably decreased due to the coated silica-shell or Co(III)-Schiff base complex on its surface (Fig. 3C, b and c). Nevertheless, the Fe₃O₄@SiO₂@Im[Cl]Co(III)-melamine nanocomposite exhibited superparamagnetic characteristics with high magnetization values, which meant it could be readily separated from the mixture by the use of a simple external magnet. As shown in Fig. 3C, c and d, treatment of the Fe₃O₄@SiO₂@Im[Cl]Co(III)-Schiff base complex (8) with melamine caused a drop in magnetization from 35.9 to 33.1 emu g^{-1} for 9. The thermal behavior of the samples was studied by TGA (Fig. 3D). The TGA curve of the Co-Schiff base complex 4 exhibited only one weight loss step in the temperature range of 98-345 °C with a continuous weight loss (Fig. 3C, a). This weight loss may arise from the decomposition of the Co-Schiff base ligand to cobalt oxides as well as to the CO and CO2 species produced by thermal decomposition of the oxygenated carbon surface groups (Fig. 3C, b).³⁷ The incorporation of melamine to 9 clearly revealed the effect of melamine on the thermal behavior of the Fe₃O₄@SiO₂@Im[Cl]Co(III)-melamine

nanocomposite. As shown in Fig. 3C, c, catalyst **9** exhibited a much better thermal stability than **8**. Under a nitrogen atmosphere, they showed a 41% weight loss, including the decomposition of water and organic moieties on the surface of the core–shell. Thermal analysis of the catalyst initially showed a negligible weight loss (2.2%) in the region of 90–275 °C, which showed the loss of hydrogen-bonded water molecules present at the surface of the Fe₃O₄ core–shell. The second small weight loss (3.0%) occurred between 280 °C and 480 °C and was associated with the removal of water trapped from the lattice.³⁸ The weight loss of about 35% at the temperature range of 475–750 °C was assigned to the decomposition of organic moieties on the surface of the Fe₃O₄@SiO₂ core–shell nanoparticles.

XPS analysis was applied in order to elucidate the chemical elements of the catalyst. The low-resolution (wide scan) XPS spectra for the Fe₃O₄@SiO₂@Im[Cl]Co(III)-melamine nanocomposite is shown in Fig. 4(a). Fig. 4a confirms the presence of Fe, Si, O, Co, and Cl elements in the catalyst. Also, the presence of Cl⁻ ions as the imidazolium counter ion was detected as a sharp peak at 287 eV,^{39,40} indicating the presence of the imidazolium moiety in the catalyst. Fig. 4b represents the Co 2p XPS spectrum for the Fe₃O₄@SiO₂@Im[Cl]Co(m)-melamine nanocomposite. The Co $2p_{1/2}$ and Co $2p_{3/2}$ lines appeared at 797 and 782.3 eV, respectively. These results indicated that Co(III) is the only component in the catalyst and the cobalt ions are in +3 oxidation state. Also, the energy band gap of 14.7 eV is in good agreement with the literature reports on the Co³⁺ XPS spectra. The results were completely fitted with the reported Co(III) 2p XPS spectrum.41-43

The specific surface area and porosity of the samples were investigated by N_2 adsorption-desorption isotherm analysis.

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Fig. 4 (a) Overall survey and (b) high-resolution XPS Co 2p spectrum of catalyst 9.

Table 2Surfacecharacteristicsof Fe_3O_4 Fe_3O_4 G_2 Fe_3O_4 G_2 G_2 G_3O_4 G_2 G_3O_4 G_3O_4 <th

Entry	Sample	Specific surface area $(m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹)	Average pore radius (nm)
1	Fe ₃ O ₄	480	0.803	1.254
2	Fe ₃ O ₄ (a)SiO ₂	455	0.785	1.787
3	Fe ₃ O ₄ (a)SiO ₂ -Cl	400	0.755	1.802
4	Fe ₃ O ₄ @SiO ₂ @Im[Cl]Co(III)-Schiff base complex	380	0.700	1.814
5	Catalyst 9	372	0.720	1.820

The specific surface area values, the average pore diameter (according to the BJH method), and the total pore volume are tabulated in Table 2. According to the BET isotherm, the active surface area of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-Cl, Fe₃O₄@SiO₂@Im[Cl]Co(m)-Schiff base complex (8), and the Fe₃O₄@SiO₂@Im[Cl]Co(m)-melamine nanocomposite (the catalyst) were determined as 480, 455, 400, 380, and 372 m² g⁻¹, respectively (Table 2, entries 1–4). According to the results, the specific surface area decreased after intercalation of the melamine. However, on the other hand, the pore volume and average pore radius increased when melamine was added. These results propose that the intercalation of melamine leads to the formation of a more porous network structure.

The loading amount of Co on the catalyst was measured by atomic absorption spectroscopy (AAS) and also inductively coupled plasma (ICP) instruments in order to obtain more certainly about the results. The results for the two analyses were close to each other with only a small difference (0.005). The experiments indicated that 0.5 mmol of Co metal per gram of the catalyst was loaded on the catalyst **9** framework.

According to the FE-SEM images, the synthesized Fe_3O_4 NPs and Fe_3O_4 @SiO₂ were nearly spherical in shape and were well dispersed; although in some areas, bigger structures with a non-spherical morphology were observed (Fig. 5a and b). The Fe_3O_4 and Fe_3O_4 @SiO₂ nanoparticles had an average diameter of 10–12 nm and 20–22 nm (Fig. 5a and b), which is fully compatible with their DLS analyses (Fig. 5d and e). Fig. 5c showing the FE-SEM image of the Fe_3O_4 @SiO₂@Im[Cl]Co(m)-melamine nanocomposite with a spherical morphology. After successive coating with the Schiff base Co complex, the nanocomposites still maintained a spherical shape with an average diameter of ~77 nm (Fig. 5d).

The size distribution of these NPs was centered at 12, 20, and 75 nm for Fe_3O_4 , Fe_3O_4 @SiO₂, and the Fe_3O_4 @SiO₂@Im [Cl]Co(m)-melamine nanocomposite, respectively (Fig. 5d–f).

The morphology and structure of the Fe_3O_4 (Gi_2) [Cl] Co(m)-melamine nanocomposite were also observed using TEM (Fig. 6). The TEM image revealed that the catalyst had well-shaped spherical or ellipsoidal particles. The diameter of the nanoparticles was found to be approximately 75 nm (Fig. 6).

Optimization of the reaction parameters

A highlight point in this article is that there was no need for any base in these reactions. As will be discussed in the "mechanism studies" section, it is proposed that manganese powder was found to be a reducing agent for Co(m) species (manganese was pre-activated by traces of acid). Stoichiometric equivalents of manganese (0.5 mol%) relative to Co species present in the catalyst **9** was sufficient to afford the coupling product in the highest possible efficiency. The need for the reaction to have a reducing agent was elucidated by observation of only an 11% reaction progress (GC) for the Heck coupling reaction of iodobenzene with *n*-butyl acrylate catalyzed by the $Fe_3O_4(@SiO_2(@Im[Cl]Co(m)-melamine nano$ composite (0.5 mol%) in EtOH/reflux.

To optimize the reaction conditions, we chose the crosscoupling of iodobenzene with *n*-butyl acrylate as a model reaction (Scheme 1). Here, first, the effect of different amounts of Fe_3O_4 @SiO₂@Im[Cl]Co(m)-melamine nanocomposite was



Fig. 5 FE-SEM images and DLS results of Fe₃O₄ (a, d), Fe₃O₄@SiO₂ (b, e), and the Fe₃O₄@SiO₂@Im[Cl]Co(m)-melamine nanocomposite (c, f).



Fig. 6 TEM image of Fe₃O₄@SiO₂@Im[Cl]Co(III)-melamine nanocomposite



Fig. 7 Effect of the catalyst amount (blue curve) and temperature (black curve) on the reaction conversion.



investigated (Fig. 7). The best amount was found to be 0.5 mol% containing 0.005 mmol Co. A further increase in the catalyst amount did not result in a change in efficiency.

Effect of temperature

The temperature effect was screened by fulfilling the model reaction at different temperatures in EtOH, and the best

results were achieved under reflux conditions. The reaction afforded a 40% yield at room temperature. With increasing the temperature from 25 °C to 79 °C, and the conversion ranged from 40% to 95% (Fig. 7).

Effect of solvent

It is well known that ionic moieties in a composite or a polymer promote their solubility in a suitable solvent.⁴¹ The soluble parts of a catalyst, *i.e.*, that part containing a Schiff base complex moiety, improve the solubility of this part in the medium and cause an increase in the efficiency.^{42,44,45}

Solvents such as EtOH, MeOH, DMF, and DMSO gave high conversions, ranging from 95–97% (Fig. 8). It seems that polar, protic, or polar–protic solvents could afford high efficiency. However, due to environmental issues, we chose ethanol for the reactions, although it only had a negligible difference with MeOH, DMF, or DMSO. This little difference can be ignored



Fig. 8 Solvent effect on the model Heck reaction catalyzed by the $Fe_3O_4@SiO_2@Im[Cl]Co(m)$ -melamine nanocomposite.

given the environmental aspects, cheapness, availability, lower toxicity, and easier work-up. Water showed only a 68% yield under reflux conditions. This may be due to the formation of a biphasic mixture that brings about problems such as mass transfer. The reaction in solvent-free conditions did not give a satisfactory yield (78%, Fig. 8).

It is noteworthy that, under the optimized reaction conditions for the Heck reaction, high efficiency was obtained for the Sonogashira reaction (the reaction of phenyl acetylene and iodobenzene). In this case, also, the reaction was performed in the absence of any base.

To survey the catalytic activity of the Fe_3O_4 @SiO₂@Im[Cl] Co(m)-melamine nanocomposite, the Heck–Mizoroki crosscoupling reaction was conducted by a variety of aryl halides and alkenes (Scheme 2). It was found that the yields were generally moderate to excellent for all substrates (Table 3, 65–95%), which reflected that the reaction was relatively insensitive to the nature of the substitution (electron donating or



Scheme 2 Catalytic activity of the Fe $_3O_4@SiO_2@Im[Cl]Co(III)$ -melamine nanocomposite toward the Heck and Sonogashira reactions.

electron withdrawing). Though, with a general look in Table 3, it can be understood that aryl halide-bearing electron-withdrawing groups provide the highest efficiency (12e, 12g, 12h, 12j, 12l, 12m, 12q, and 12r). However, this was expected for a typical Pd-catalyzed Heck coupling reaction with a default mechanism (oxidative addition and reductive elimination).¹ On the other hand, although electron-withdrawing groups delayed the reaction, they did not have a significant effect on the reaction efficiency as much as their effect on the time for the reaction. Also, iodide as a leaving group facilitates the Heck reaction, and indeed the reactivity of halides was in the order of I > Br \gg Cl (Table 3, entries 1–3 and 22–24). This reactivity provides for a high selectivity for the preparation of compounds 12f, 12g, and 12r involving iodine substitution in competition with bromide or chloride (Table 3, entries 8, 9, and 28). In general, styrene demonstrates better performance than n-butyl acrylate for Heck coupling under the reaction conditions.

Encouraged by the obtained results from the Heck reactions, we then examined the versatility and generality of the present method toward the Sonogashira coupling reaction. As shown in Table 4, a variety of acetylenes and aryl halides bearing electron-donating or electron-withdrawing group afforded the desired Sonogashira products in high to excellent yields under EtOH/reflux in the presence of the Fe₃O₄@SiO₂@Im[Cl]Co(m)-melamine nanocomposite (0.5 mol%) and Mn dust (0.5 mol%) (Table 4). Same as for the Heck coupling reaction, the coupling reaction of phenylacetylene with both electron-donating and electron-withdrawing groups gave the desired products in high to excellent yields (Table 4). Also, the method was completely selective toward iodide as a leaving group compared to bromide, with the coupling occurring exclusively in the iodide position at **14f** and **14g** (Table 4).

Also, in order to demonstrate the effect of melamine in catalyst 9, the reaction of iodobenzene with *n*-butyl acrylate (Table 3, entry 1) was carried out in the presence of compound 8 (10 mg) under identical reaction conditions used for 9 (Table 1, entry 1). The reaction gave an 83% isolated yield for 80 min. However, the yield of the reaction reached 89% after 4 h. The intercalation of melamine to this system provided a robust-rigid network structure with an enhancement in thermal stability (Fig. 3D), porosity (Table 1), and low metal leaching (ESI, Fig. S1†). These enhanced properties are responsible for the higher efficiency of 9 than 8.

Mechanism study

A plausible mechanism for the Fe₃O₄@SiO₂@Im[Cl]Co(π)-melamine nanocomposite-catalyzed Heck reaction is depicted in Scheme 3. In general, according to our observations and the reported mechanisms,^{46,47} a plausible mechanism is proposed that involves four main steps: (i) oxidative addition, (ii) π -complex formation, (iii) migration, and (iv) reductive elimination. The possibility of a radical mechanism for this system was also investigated. For this purpose, the Heck model reaction was performed in the presence of hydroquinone as an electron capture process. In this test, after 45 min of reaction

Table 3	Heck reaction of aryl halides wit	h <i>n</i> -butyl acrylate or styrene	e catalyzed by the Fe ₃ O ₄ @SiO ₂	@Im[Cl]Co(III)-melamine nanocomposite ^a
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Entry	Product 12	x	R	W	Time (min)	Vield ^b (%)	TON	TOF (h^{-1})
	110uutt 12		R	••	Time (min)	field (70)	1010	
1	12a	Ι	Н	$-CO_2Bu^n$	80	91	182	136
2		Br	Н	$-CO_2Bu^n$	100	86	172	102
3		Cl	Н	$-CO_2Bu^n$	218	82	164	45
4	12b	I	4-OMe	$-CO_2Bu^n$	120	78	156	78
5	12c	Ι	4-OH	$-CO_2Bu^n$	110	80	160	87
6	12d	Ι	4-Me	$-CO_2Bu^n$	75	80	160	128
7	12e	Ι	4-CHO	$-CO_2Bu^n$	60	84	168	168
8	12f	Ι	4-Br	$-CO_2Bu^n$	70	85	170	142
9	12g	Ι	4-Cl	$-CO_2Bu^n$	86	88	176	122
10	12h	Ι	$4-NO_2$	$-CO_2Bu^n$	65	94	188	174
11	12i	Ι	3-Me	$-CO_2Bu^n$	70	90	180	155
12	12j	Ι	$2-NO_2$	$-CO_2Bu^n$	63	92	180	174
13	12b	Br	4-OMe	$-CO_2Bu^n$	135	75	150	67
14	12d	Br	4-Me	$-CO_2Bu^n$	80	77	154	115
15	12h	Br	$4-NO_2$	$-CO_2Bu^n$	73	82	164	137
16	12k	Br	2-Me	$-CO_2Bu^n$	135	84	168	75
17	12d	Cl	4-Me	$-CO_2Bu^n$	200	65	130	38
18	12h	Cl	$4-NO_2$	$-CO_2Bu^n$	193	72	144	45
19	12l	Cl	4-CN	$-CO_2Bu^n$	193	74	148	46
20	12b	Cl	4-OMe	$-CO_2Bu^n$	245	66	132	33
21	12m	Cl	$3-NO_2$	$-CO_2Bu^n$	200	76	152	48
22	12n	Ι	Н	-Ph	68	88	176	154
23		Br	Н	-Ph	90	77	154	103
24		Cl	Н	-Ph	200	72	144	43
25	120	Ι	4-OMe	-Ph	110	80	160	87
26	12p	Ι	4-Me	-Ph	75	82	164	131
27	12q	Ι	$4-NO_2$	-Ph	60	95	190	190
28	12r	Ι	4-Br	-Ph	70	91	182	157
29	120	Br	4-OMe	-Ph	125	75	150	75
30	128	Br	4-CN	-Ph	70	75	150	129
31	12q	Br	$4-NO_2$	–Ph	60	80	160	160
32	120	Cl	4-OMe	–Ph	280	66	132	29
33	128	Cl	4-CN	-Ph	200	77	154	46
34	12q	Cl	$4-NO_2$	-Ph	190	77	154	49

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progress (GC), hydroquinone was added to the reaction mixture. The reaction did not show any change compared to the normal conditions (in the absence of hydroquinone), which confirmed the absence of any radical in the mixture (ESI, Fig. S2[†]). The understanding regarding the valence state of Co species responsible in the reaction mechanism was addressed by XPS analysis of the above-mentioned mixture after 45 min (64% conversion, Fig. 9a) of the reaction time. The results indicated that the all of the cobalt species present in the mixture were in a +3 oxidation state, corresponding to the binding energies of 797 eV $(2p_{1/2})$ and 782.5 eV $(2p_{3/2})$, in agreement with the literature.⁴¹ No Co(II) species were detected in the spectrum. Also, due to fast consumption of Co(1) species, they did not appear in the spectrum. In this viewpoint, like the palladium process, the Heck reaction begins when the Co(III) species is reduced by manganese powder, present as an additive in the reaction mixture.^{46,48-50} In the absence of Mn, the reaction progress was found to be 11% for 3 h. This confirmed the reductive role of Mn for Co(III) ions. Also, this can

be approved by the advent of peaks at 641.4 eV and 653 eV, corresponding to the binding energies of Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively, in the XPS spectrum of the reaction mixture (Fig. 9a). A peak appeared at 638.6 eV was assigned to the Mn metal used as a reducing agent.

An oxidative addition took place between highly active lowvalent cobalt and aryl halide. In the following process, it formed a π -complex through coordination to olefin. In the next step, a migratory insertion of the olefin afforded the Co- σ intermediate, which underwent β -H elimination to give a π -complex Co(III) species. The newly formed Co(III)-olefin π -complex furnished the desired Heck coupling product as well as H-Co(III)-X species. The fact there was no need for a base in this reaction can be explained by the proposed mechanism. As shown in Scheme 3, Cl⁻ as a counter ion of the imidazolium moiety could attack the cobalt hydride intermediate, with the leaving group taking chlorine as a pair of ions for imidazole. The highly active Co(I) species is regenerated and returned to the cycle.

Table 4 Sonogashira reaction of aryl halides with phenyl acetylenes catalyzed by the Fe₃O₄@SiO₂@Im[Cl]Co(III)-melamine nanocomposite^a

		R'	= + R-X -	Cat. (0.5 mol%) EtOH, Ref. Mn (0.5 mol%)	<u> </u>			
Entry	Product 14	X	R	R	Time (min)	$\operatorname{Yield}^{b}(\%)$	TON	TOF (h^{-1})
1	14a	Ι	Ph	Ph	120	94	188	94
2		Br	Ph	Ph	180	85	170	57
3		Cl	Ph	Ph	120	76	152	76
4	14b	Ι	4-NH ₂ -ph	Ph	230	88	176	46
5	14c	Ι	4-CN-ph	Ph	140	80	160	67
6	14d	Ι	4-Me-ph	Ph	165	88	176	64
7	14e	Ι	4-COMe	Ph	120	96	192	96
8	14f	Ι	Br-ph	Ph	130	90	180	83
9	14g	Ι	Cl-ph	Ph	140	90	180	77
10	14h	Ι	3-Pyridine	Ph	100	94	188	113
11	14i	Ι	Ph	$C_{6}H_{13}$	230	88	176	46
12		Br	Ph	$C_{6}H_{13}$	250	75	150	36
13		Cl	Ph	$C_{6}H_{13}$	250	66	132	32
14	14j	Ι	4-NO ₂ -ph	Ph	90	98	196	131
15	14k	Ι	1-Naphthalene	Ph	140	88	176	77
16		Br	1-Naphthalene	Ph	180	82	164	55
17	14l	Ι	5-Pyrimidine	Ph	95	96	192	120
18	14m	Ι	2-Me-ph	Ph	160	88	176	66
19	14n	Ι	2-OMe-ph	Ph	240	85	170	43
20	140	Ι	4-CN-ph	$C_{6}H_{13}$	220	86	172	47
21	14p	Ι	3-Thiophene	Ph	120	96	192	96
22	14q	Ι	Ph	2-Cyclohexanol	200	90	180	55
23	-	Br	Ph	2-Cyclohexanol	210	88	176	50
24		Cl	Ph	2-Cyclohexanol	250	77	154	37
25	14r	Ι	4-Me-ph	$C_6 \dot{H}_{13}$	250	80	160	38

^a Reaction conditions: Acetylene (1.3 mmol), Ar-X (1.0 mmol), catalyst 9 (10 mg, 0.5 mol% Co), Mn (0.005 mmol, 0.5 mol%), EtOH (3.0 mL), reflux. ^b Isolated yield.



 $\label{eq:scheme 3} \begin{array}{l} \mbox{Postulated mechanism for the $Fe_3O_4@SiO_2@Im[Cl]Co(u)$-melamine nanocomposite catalyzed Heck coupling reaction.} \end{array}$

It is worth noting that a few mechanism studies have been conducted with the cobalt-catalyzed Sonogashira reaction.^{6,51} In this study, a plausible mechanism was suggested according

to some observations (Scheme 4), namely: (i) the reaction progress was 17% in the absence of Mn dust, whereupon after its addition, the reaction proceeded efficiently; (ii) it was shown that the reaction proceeded without the need for any base, in which the imidazolium counter ion played the role of the base; (iii) in situ XPS analysis after 60 min of the reaction mixture demonstrated the presence of Co(III) as well as Co(I) species (Fig. 9b). Here, the presence of peaks appearing at 653 eV and 641/637 eV related to Mn and Mn(2+), respectively, completely confirmed the reduction of Co(III) species (Fig. 9b); (iv) the reaction was not affected by the addition of hydroquinone as a radical scavenger over the coupling reaction of phenyl acetylene and iodobenzene in the presence of 9 (0.5 mol% Co), Mn (0.5 mol%), EtOH/reflux; which withdrew the formation of any radicals through the reaction and subsequently the radical mechanism (ESI, Fig. S2[†]).

So, in accordance with our observations as well as the reported mechanisms for the Co-catalyzed coupling reactions, it could be concluded that the reaction proceeds *via* oxidative addition and reductive elimination steps. In the first step of this proposed mechanism, the reduction of Co(III) to Co(I) takes place using Mn dust. Then, a π -complex was formed between the catalyst and acetylene, followed by the formation of a Co-acetylide intermediate with interference of imidazo-lium counter ions and the generation of a HCl molecule. In







Scheme 4 A plausible reaction mechanism for the Co-catalyzed Sonogashira reaction.

the next step, oxidative addition occurs between the C-X bond in aryl halide and the Co-acetylide intermediate. Finally, reductive elimination leads to the desire Sonogashira product and catalyst 9 is regenerated for the next reaction cycle. To support our claim regarding the base functionality of the imidazoluim part of 9, we prepared the Co-complex 15, that is a free imidazole homolog of 4, by the treatment of salicylaldehyde and allylamine followed by Co complexation with CoCl₂ according to the procedure described by Khorshidifard et al. (Scheme 5).²⁶ The Heck coupling model reaction was performed in the presence of 15, and the results were compared with the Co(III) Schiff base complex (4). The reactions were performed under optimized conditions for the model reaction (Scheme 1). The reaction in the presence of 15 did not show any noticeable progress for 8 h of the reaction. The reaction proceeded upon the addition of Et₃N. Interestingly, the Co



Scheme 5 Chemical structure of 15

complex 4 provided the desired coupling product within 1 h with a 94% yield.

Based on the presented mechanism, the catalytic active site can be calculated based on the generated HX. Hence, the generated HX provides a good estimate of the catalytic active sites. In addition to the fact that the production of HX confirms the mechanism, in order to measure the active sites, a typical reaction was carried out with iodobenzene, *n*-butyl acrylate, in the presence of catalyst **9**. The reaction was allowed to proceed completely. After that, the catalyst was separated from the reaction mixture by an external magnet and the residue was titrated by NaOH 0.1 N in the presence of a drop of litmus (azolitmin) solution as an indicator. The obtained amount according to the consumed base was found to be 0.0044 mmol. It was shown that 88% of the metal sites present in the mixture (0.005 mmol) play a catalytic role as active sites.

Recoverability

The reusability of a catalyst is an important property from the viewpoint of green chemistry.⁵² Therefore, reusability of the Fe_3O_4 @SiO_2@Im[Cl]Co(III)-melamine nanocomposite was studied under optimized conditions for the Heck model reaction. As exhibited in Fig. 10, the catalyst was recovered and reused for at least seven consecutive runs. The yield of **12a** reached 93% for the 7th run, which means that only a 2% drop in efficiency was observed compared to the corresponding fresh catalyst (95%). Also, the amount of Co leached



Fig. 10 Recyclability of the catalyst (a) in the Heck–Mizoroki, and (b) Sonogashira reactions.

into the solution for the Heck coupling reaction of iodobenzene and *n*-butyl acrylate after each cycle was measured by ICP. The catalyst showed very slight leaching in each cycle, which 0.6% metal leaching detected after the 7th run, thus reflecting its stability under the reaction conditions (Fig. 10). Also, in order to clarify the effect of melamine in the nanocomposite **9**, these experiments were also carried out in the presence of compound **8**, and similarly, the leaching amount was measured in 7 successive cycles (ESI, Fig. S1†). According to the results, the metal leaching in compound **8** was noticeably larger than that with catalyst **9**. This reduction in the amount of leaching and the increase in stability may be attributed to the presence of melamine in the catalyst. The amount of leaching was 0.35% in the first run (ESI, Fig. S1†).

Moreover, a vast investigation was conducted in order to elucidate the heterogeneous nature of the catalyst. First, we tried the hot filtration test over the Heck model reaction under premium conditions (Table 3), in which the catalyst was magnetically removed in situ after 64% (t = 45 min) conversion (GC) and the reactants were allowed to undergo further reaction.²⁸ The results indicated that, after removal of the heterogeneous catalyst, the free catalyst residue was weakly active, and the conversion reached 66% after 2.5 h of reaction. This confirmed that the catalyst acted heterogeneously in the reaction and consequently only slight leaching occurred during the reaction. Second, in order to completely ensure the heterogeneous role of the catalyst, the mercury poisoning test was also carried out. Mercury (0) was absorbed as a metal (or by amalgamation) and significantly deactivated the metal catalyst⁵³ (active site) and thus suppressed the catalyst activity. This test was evidence of the heterogeneous catalyst.⁵³ The test was conducted with the aforementioned model reaction (optimized conditions). After 45 min of the reaction, 320 molar equivalents of mercury vs. Co catalyst was added to the reaction mixture. The reaction medium was stirred for more than 2.5 h, while the reaction conversion was screened by TLC (Fig. 11). As shown in Fig. 11, after 4 h of reaction, the addition of Hg(0) almost suppressed further catalysis. No more conversion was observed after 1.5 h of the catalyst being poisoned. A kinetics plot of the reaction in the absence of Hg(0) is depicted in Fig. 11. Finally, the three-phase test (Scheme 6) was applied



Fig. 11 Reaction kinetics, Hg(0) poisoning, and hot filtration studies for the Heck coupling reaction of iodobenzene with *n*-butyl acrylate catalyzed by $Fe_3O_4@SiO_2@Im[Cl]Co(m)$ -melamine nanocomposite in EtOH/ reflux.

through the reaction of Wang resin-bound aryl iodide with n-butyl acrylate in EtOH/reflux in the presence of 9. As shown in Scheme 6 (1), the coupling reaction did not take place under these conditions, and at the end of the reaction the catalyst could be magnetically separated. Hydrolysis of the organic molecules on the Wang resin led to 4-iodo benzoic acid. In another test, the reaction of Wang resin-bound aryl iodide with *n*-butyl acrylate and iodobenzene was performed. In this case, the desired coupling product was obtained, but same as the previous test, no coupling product was detected with hydrolysis of the Wang resin. The obtained results from the three-phase test illustrated that the catalyst is truly heterogeneous, by which the Heck reaction did not occur in the liquid phase. The negative results from all of the heterogeneity tests (Hg(0) poisoning, hot filtration, and three-phase test) suggested that the solid catalyst was truly heterogeneous and no detectable Co leaching occurred over the Heck reaction.

Finally, in order to ensure the structure of the recovered catalyst was retained, we studied it after the 7th run over the Heck model reaction of iodobenzene and *n*-butyl acrylate under the obtained premium conditions by some analyses (Fig. 12). FTIR analysis of the recovered catalyst corroborated



Scheme 6 The three-phase test of 4-iodebenzoate, polymer bound form, and n-butyl acrylate in the presence of 9.



Fig. 12 (a) FTIR, (b) VSM, (c) EDX, (d) XPS spectra, (e) FE-SEM, and (f) TEM images of the recovered catalyst 9 after the 7th run for the Heck coupling reaction of iodobenzene with *n*-butyl acrylate.

that the structure of the catalyst remained completely intact during recycling (Fig. 12). The EDX spectrum of the recovered catalyst revealed the presence of the expected elements, thus confirming the catalyst's stability during the reactions. An interesting point was there was an intensity reduction in the Cl peak. This was completely compatible with ion exchange of the imidazolium Cl^- ion, which reduces the peak intensity (Fig. 12).

XPS analysis revealed that the Co species present in the catalyst remained intact after the 7th run and their oxidation

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Entry	Reaction	Catalyst/conditions	Base	Time (h)	Yield ^a (%)	Ref.
1	Heck	PdNPs@CNCs/H ₂ O:CH ₃ CN $(1:1)/100 \circ C^b$	K ₂ CO ₃	24	75	54
2		Agarose@Pd NPs/solvent-free/100 °C	Et ₃ N	2	90	55
3		Hydrazone-Pd@ZnO (0.26 mol%)/DMF/130 °C	Et ₃ N	1	98	56
4		Co–B (5 mol% Co)/water/DMF (1/1 v/v)/130 °C	K_2CO_3	12	98 ^c	57
5		MNPs@Cs-MS-Co (0.55 mol%)/DMSO/140 °C ^d	KOH	1	75	6
6		Fe ₃ O ₄ @SiO ₂ @Im[Cl]Co(III)-melamine nanocomposite (0.5 mol%)/	_	1	88	Present study
		Mn(0.5 mol%)/EtOH/reflux				
7	Sonogashira	CuI (0.2 mol%)/PPh ₃ (4 mol%)/H ₂ O/140 °C	K_2CO_3	24	43	58
8	-	Cu(I)-PANI@MWCNT/DMF/135 °C ^e	KOH	2	96	59
9		NHC precursor (20 mol%)/CuSO ₄ ·5H ₂ O (20 mol%)/DMF/125 °C ^f	K_2CO_3	8	71	60
10		$Co(C_9H_9NO_2)_3/DMF/ethylene glycol/visible light/r.t.$	K ₂ CO ₃	8	82	61
11		MNPs@Cs-MS-Co (0.55 mol%)/DMSO/140 °C ^d	KOH	10	72	6
12		Fe ₃ O ₄ @SiO ₂ @Im[Cl]Co(m)-melamine nanocomposite (0.5 mol%)/ Mn(0.5 mol%)/EtOH/reflux	—	2	94	Present study

 Table 5
 Comparison of the catalytic activity of the $Fe_3O_4@SiO_2@Im[Cl]Co(m)$ -melamine nanocomposite with literature examples for the cross-coupling reaction of iodobenzene with styrene (Heck) and phenyl acetylene (Sonogashira)

^{*a*} Isolated yield. ^{*b*} NPs: nanoparticles; CNCs: colloidal cellulose nanocrystallites. ^{*c*} GC yield. ^{*d*} MNPs@Cs-MS-Co: cobalt tagged on MNPs-chitosan functionalized with methyl salicylate. ^{*e*} Cu(1)-PANI@MWCNT: polyaniline functionalized multiwall carbon nanotube-supported Cu(1). ^{*f*} NHC: N-heterocyclic carbine.

state was similar to that of the fresh catalyst. This was also in agreement with the proposed catalytic cycles in the mechanism studies. No other oxidation states were found in the catalyst (Fig. 12d). The recovered catalyst responded to the external magnetic field and could be readily collected from the reaction mixture same as the fresh catalyst. The FE-SEM image showed that the nanoparticles were still approximately spherical in shape even after the 7th cycle. It was worth noting that the nanocatalyst did not show any morphological changes as proved by the TEM images obtained from the recovered catalyst (Fig. 12f).

To show its novelty, uniqueness, and to further evaluate the present method, the catalytic activities of the $Fe_3O_4@SiO_2@Im$ [Cl]-Co(m)-melamine nanocomposite were compared with those of the reported Co-catalyzed Heck and Sonogashira coupling reactions in terms of the reaction time, base, and yield. As shown in Table 5, this method was obviously superior to the most supported Pd, Cu, or Co catalysts. The coupling reaction proceeded efficiently in the presence of only 0.5 mol% Co in the absence of any base. Also, the $Fe_3O_4@SiO_2@Im$ [Cl]-Co(m)-melamine nanocomposite is a more versatile approach for Sonogashira and Heck coupling reactions in terms of energy consumption, time consumption, catalyst preparation, and in eco- and economic friendly aspects.

Conclusions

In conclusion, we developed a new non-toxic, low-cost, and stable catalytic system for the selective Heck–Mizoroki and Sonogashira cross-coupling reactions using a Schiff base Co(m) complex decorated on $Fe_3O_4@SiO_2$ NPs as a magnetically recoverable inorgano-nanocatalyst ($Fe_3O_4@SiO_2@Im[Cl]Co(m)$ -melamine nanocomposite). The reactions were performed under ethanol as a solvent and base-free conditions, which are suitable from a green- and sustainable chemistry point of view.

The superparamagnetic nature of the Fe₃O₄(a)SiO₂(a)Im[Cl] Co(III)-melamine nanocomposite, in particular, simplified the easy separation of the catalyst from the reaction mixture by employing a simple external magnetic field. In that way, the catalyst was stable under the reaction conditions and maintained its catalytic activity and selectivity for at least seven successive runs without the need for any work for its re-activation, which addresses economic and environmental issues. Also, hot filtration, mercury poisoning, and three-phase testing certainly confirmed the heterogeneous nature of the catalyst with insignificant metal leaching. We characterized the catalyst from various aspects by: FTIR, CHNS, UV-Vis, TGA, VSM, NMR, EDX, XRD, CV, ICP, DLS, BET, and XPS analyses. The present methodology was found to be highly efficient and a wide variety of functional groups could be tolerated in these conditions in high to excellent yields. The results indicated that 88% of the metal sites play a catalytic role as active sites. It is believed that the Heck reaction goes through a four-step mechanism, namely oxidation addition, insertion, β-elimination, and reductive elimination. This catalytic system is bi-functional, in which the imidazolium moiety participates in the reaction and plays the role of a base, while on the other hand, the Co(III) complex moiety catalyzes the reaction. This methodology is proposed as an affordable alternative to the previous use of transition metal catalysts, especially Pd-based catalytic systems.

Experimental

Materials and apparatus

All the chemicals were obtained from Sigma and Fluca suppliers and used without further purification. Wang resin (polymer-bound 4-iodobenzene) was purchased from NovaBiochem containing 0.64–1.1 mmol g^{-1} loading, 100–300 mesh, and cross-linked with 1% divinylbenzene. All

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the solvents were distilled and dried before use. All the other reagents were of analytical grade. Reactions' progress was monitored by thin layer chromatography (TLC) on silica gel or gas chromatography (GC) using a Shimadzu-14B gas chromatograph equipped with an HP-1 capillary column and N2 as a carrier gas. Anisole was used as the internal standard. FTIR spectra were obtained using a JASCO FT/IR 4600 spectrophotometer using KBr pellet. The ¹H NMR (250 MHz) and ¹³CNMR (62.9 MHz) spectra were recorded on a Bruker Avance DPX-250 spectrometer in $CDCl_3$ and $DMSO-d_6$ as the solvents and TMS as an internal standard. Electrochemical measurement (cyclic voltammetry) for the Co catalyst was performed on a CHI 1210A electrochemical workstation (CH Instrument, China) with a three-electrode system consisting of a standard Ag/AgCl as a reference electrode, a platinum wire electrode and a modified glassy carbon with the catalyst²² as an auxiliary and working electrode, respectively. The CVs were recorded at room temperature under argon atmosphere in the potential range from -2.0 to 2.0 V after 300 s accumulation under stirring with a scan rate of 100 mV s^{-1} . The cell temperature was maintained at 25.0 ± 0.1 °C by means of a HAAKE D8 recirculating bath. Elemental analyses were performed on PerkinElmer-2004 instrument. XPS studies were conducted using an XR3E2 (VG Microtech) twin anode X-ray source with AlK α = 1486.6 eV. Field emission scanning electron microscopy (FE-SEM) images were obtained on a HITACHI S-4160. EDX spectroscopy was performed using a field emission scanning electron microscope (FESEM, JEOL 7600F), equipped with a spectrometer for energy dispersion of X-rays from Oxford instruments. Transmission electron microscopy (TEM) was performed on a Philips EM208 microscope and was operated at 100 kV. The size distribution of the nanoparticles was measured by dynamic light scattering (DLS) analysis on a HORIBA-LB550 instrument. TGA of the samples was performed on a NETZSCH STA 409 PC/PG in nitrogen atmosphere with a heating rate of 10 °C min⁻¹ in the temperature range of 25-850 °C. The magnetic behavior of the samples was conducted on a Lake Shore vibrating sample magnetometer (VSM) at room temperature. ICP experiments were accomplished using a VARIAN VISTA-PRO CCD simultaneous ICP-OES instrument. The surface area, pore volume, and pore diameter of the obtained NPs were determined by N₂ physisorption at -196 °C with a surface area and pore size analyzer (Micromeritics ASAP 2000 instrument) using the BET method.

Preparation of Co(III) Schiff base complex (4)

First, 2-hydroxy-5-chloromethyl benzaldehyde was synthesized and purified according to a procedure described elsewhere²³ (purple solid, 98% yield). 2-Hydroxy-5-chloromethyl benzaldehyde (1) (2.0 mmol, 0.34 g) was dissolved in 20 mL of propylene carbonate and then imidazole (10.0 mmol) was added to the mixture. The mixture was stirred under a N₂ atmosphere at 90 °C for 48 h. After refluxing, the reaction was stopped, cooled to room temperature, and then 10 mL of water was added to the mixture; then the product was extracted into ethyl acetate (15 mL). The solvent was removed under reduced pressure and the product 2 was washed with dilute NaOH and deionized water and then dried into an oven at 50 °C (dark brown powder, 96% yield). The transformation of 2-hydroxy-5-imidazole benzaldehyde to 3 was done according to the procedure described by Khorshidifard et al.26 (Pale yellow powder, 98% yield). 4-((1H-Imidazol-1-yl)methyl)-2-((allylimino)methyl)phenol (3, 1.0 mmol, 0.24 g) was complexed to Co ions by its dissolution to 15 mL of ethanol followed by the addition of CoCl₂·6H₂O (0.5 mmol, 0.12 g). The resulting mixture was stirred for 12 h at room temperature under a N₂ atmosphere (Scheme 7). The product 4 was simply filtered, washed with cooled ethanol and diethyl ether, then dried at room temperature and isolated as a dark brown powder (95% yield, isolated weight: 0.5 g) (Scheme 7).

Preparation of Fe₃O₄@SiO₂ core-shell nanoparticles (7)

Core–shell Fe_3O_4 (a)SiO₂ nanospheres were prepared according to the previously described procedure (Scheme 8).²⁰

Preparation of Fe_3O_4 (20) SiO_2 (20) Im[Cl]Co(III)-melamine nanocomposite (9)

Fe₃O₄@SiO₂@Im[Cl]Co(III)-melamine nanocomposite was synthesized according to the following procedure: Fe₃O₄@SiO₂-Cl (1 g) was added to the solution of Co(III)-IIII-Schiff base complex (4, 1.0 mmol, 0.54 g) in 20 mL propylene carbonate and the resultant mixture was stirred at 90 °C for 24 h under a N₂ atmosphere. Then, the mixture was cooled to room temperature, and the product was filtered by an external magnet, and washed with EtOH and propylene carbonate to remove any



Scheme 7 Preparation of Co(III) Schiff base complex 4.



 $\label{eq:scheme 8} Scheme \ 8 \quad \mbox{Illustration of the preparation of the $Fe_3O_4@SiO_2@Im[Cl]Co(11)$-melamine nanocomposite.}$

unreacted species and then dried at 70 °C for 6 h. Immobilized Co(m)–Im-Schiff base complex (8) along with a weighted amount of melamine (0.5 mmol) were transferred to a 25 mL oven-dried round-bottom flask equipped with a magnet and a condenser. A solution of trimethylamine (4.0 mmol) in absolute MeOH (5.0 mL) and AlCl₃·2H₂O (4.0 mmol) were added to the mentioned mixture. The mixture was refluxed in a N₂ atmosphere for 6 h. The product, Fe₃O₄@SiO₂@Im[Cl]Co(m)melamine nanocomposite (9) was collected using an external magnetic field, washed with water (2 × 10 mL) and EtOH (2 × 10 mL), and dried in a vacuum oven (6 h, 60 °C). Scheme 8 shows the complete route for the preparation of 9.

General procedure for the catalytic Heck and Sonogashira reactions catalyzed by Fe_3O_4 (a)SiO_2 (a)Im[Cl]Co(m)-melamine nanocomposite

A mixture of alkene or phenyl acetylene (1.3 mmol), Ar-X (1.0 mmol),Fe₃O₄@SiO₂@Im[Cl]Co(m)-melamine nanocomposite (10 mg, 0.5 mol% Co), Mn (0.005 mmol), and EtOH (3.0 mL) was refluxed in an oil bath. The reaction progress was screened by TLC at different time intervals. After completion of the reaction, the catalyst was separated by an external magnetic field, washed with EtOAc, dried in the oven (60 °C), and stored at room temperature for the next run. Then, the solvent was removed under reduced pressure and 3.0 mL distilled water was added to the residue for dissolution of the Mn(II) salts produced during the reaction;^{16,43} then the resultant mixture was extracted with Et_2O (2 × 3.0 mL). All the manganese was transferred to the aqueous phase and separated from the organic phase. The combined organic layers were dried over anhydrous Na2SO4, then filtered, and the solvent was removed under reduced pressure and finally the crude product was purified by column or flash chromatography.

Reutilization of the catalyst

Reutilization of Fe_3O_4 (BiO_2) Im[Cl]Co(III)-melamine nanocomposite (9) was studied in the reaction of iodobenzene (1.0 mmol), *n*-butyl acrylate (1.3 mmol), manganese (0.005 mmol), and the nanocatalyst **9** (0.5 mol%) in ethanol at 78 °C as a model reaction. Also, these experiments were repeated for the cross-coupling reaction of iodobenzene (1.0 mmol) with phenyl acetylene (1.3 mmol), catalyst **9** (10 mg, 0.5 mol% Co), Mn (0.005 mmol, 0.5 mol%), and EtOH (3.0 mL) under reflux conditions.

The catalyst was collected and separated by an external magnetic field for each cycle, washed with EtOH and deionized water, and stored at room temperature under an air atmosphere for the next experiment. For each cycle, the residue was analyzed by ICP to measure the Co species leached from the catalyst to the solution. Also, hot filtration, mercury poisoning, and three-phase tests were employed for investigation of the heterogeneous nature of the catalyst.

Conflicts of interest

There are no conflicts to declare.

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