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# Organoselenium-Palladium(II) Complex Immobilized on Functionalized Magnetic Nanoparticles as a Promising Retrievable Nanocatalyst for the "Phosphine-Free" Heck-Mizoroki Coupling Reaction

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In the present study, for the first time, an air- and moisture-stable organoselenium-palladium complex immobilized on silica-coated magnetic nanoparticles was designed, synthesized and applied as a practical and retrievable catalyst in organic synthesis. The chemical nature and the structure of novel catalytic system were authenticated using various techniques such as Fourier transform infrared (FT-IR) spectroscopy, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX) spectroscopy and vibrating sample magnetometer (VSM). Then, catalytic performance of the synthesized nanocatalyst was investigated in Heck–Mizoroki cross coupling reaction and excellent results were obtained. The low catalyst loading, wide substrate scope, high yield, short reaction time, straightforward separation from reaction mixture and more importantly, the longevity of nanocatalyst for at least five successive times without a significant degradation in its activity are the main merits of this protocol. Above all, this work opens up attractive and interesting routes for the use of organoselenium compounds as efficient ligands for heterogeneous catalysts.

#### Introduction

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The palladium-catalyzed cross coupling reactions (such as Mizoroki-Heck, Suzuki-Miyaura, Sonogashira-Hagihara, Stille, Fukuyama and Negishi reactions) are extremely powerful and straightforward tools for the construction of new carboncarbon bonds in modern chemical transformations and industrial processes because of their regio-stereo selectivities, functional group tolerances and high selectivities <sup>1-4</sup>. Among them, the olefination of aryl halides, known as Mizoroki- Heck reaction is one of the most considerable and highly effective used protocols for the formation of different types of compounds. The products of this reaction have been widely applied for the synthesis of pharmaceuticals compounds, natural products, herbicides and fine chemicals technology<sup>3, 5-</sup> <sup>8</sup>. The most ordinary catalytic system utilized for C–C bond formation reaction is promoted by homogeneous palladium complexes. The correct selection of the ligand is the key and important factor for the synthesis of these complexes <sup>9</sup>.

To date, many attempts have been performed to the search for more effective and practical ligands. In the past few years phosphine-based ligands have achieved great success but the majority of them are extremely expensive, toxic, virulent, very sensitive to air and/or moisture and are easily oxidized to their corresponding phosphine oxides because of trivalent nature of phosphorous, which can prevent the simple recovery and reuse of the catalytic systems and hence the reaction must be carried out under argon or nitrogen atmosphere to protect catalyst from deactivation <sup>10-13</sup>. These drawbacks restrict their wide applications in large-scale synthesis. Therefore, considering both environmental and economic issues, the design and development of phosphine-free palladium catalysts continue to be a serious challenge in organic synthesis and industry <sup>14</sup>.

Chalcogen containing ligands have emerged as viable alternatives due to their much less insensitivity to air and moisture, strong electron-donating properties of chalcogen atoms, solubility in diverse solvents and stability in solution, which make them currently important and suitable for designing Pd-complexes for catalyzing of C-C coupling reactions<sup>15-19</sup>. The catalytic activity of organoselenium ligands not only rivals of their corresponding phosphorus analogs but vastly outperforms them in many cases. Numerous effective and selective organoselenium ligands based catalytic systems have been developed in the past decades, but in spite of these significant achievements, to date, there are only a few examples of reports on the use of organoselenium ligands on solid supports as heterogeneous catalysts <sup>20-23</sup>. Homogeneous catalytic systems suffer from disadvantages such as tedious isolation from the reaction mixture, lack of catalyst recycling and reusability, and reduced catalytic activity during the reaction <sup>24-26</sup>. Because of palladium is an expensive and toxic metal, its recovery is very important from both economic and green chemistry point of view <sup>27-29</sup>. Therefore, designing of new heterogeneous palladium catalysts using different solid supports is a suitable way to overcome aforementioned drawbacks. Among the different solid supports, magnetically retrievable nanoparticles because of unique physical

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properties such as thermal and chemical resistance, the large surface area to volume ratios, low toxicity and low cost, easy and convenient separation from reaction media with a permanent magnet without needing tedious workup processes have received tremendous attention <sup>30-32</sup>. Following our research work on the development of efficient green catalysts and their application in various reactions <sup>33-42</sup>, at the present paper, we report for the first time the synthesis and characterization of a new organic and highly efficient catalyst that heterogeneous contains complex of organoselenium ligand that is bound covalently to silica-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles and then investigate its catalytic performance in the Heck-Mizoroki cross-coupling reactions between various aryl halides and acrylates.

#### **Results and discussion**

#### Preparation of nano-Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II)

The schematic procedure for preparing our catalyst, selenotetrazole Pd(II) complex immobilized on functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles, that named Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) is illustrated in Scheme 1. In the first step, magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared using a chemical coprecipitating technique in accordance with the literature. After that, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were covered with a thin layer of silica by the well-known Stöber method to prevent aggregation of the magnetic nanoparticles. Then, the silica-coated magnetic nanoparticles were functionalized by using (3aminopropyl) triethoxysilane (APTES) to obtain Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES. Secondly, for the synthesis of the selenotetrazole ligand, para aminobenzoic acid was converted to diazonium salt and this salt was reacted with KSeCN to give phenylselenocyanate. Subsequently, tetrazole was synthesized from the reaction of this compound with sodium azide. The main novelty of our work is the successful grafting of the selenotetrazole ligand on the surface of MNPs for the first time. Finally, these nanoparticles having Se and N as chelating groups on their surface were simply metallated with Pd(OAc)<sub>2</sub> in ethanol to obtain the desired Pd complex supported onto the magnetically retrievable nanoparticles, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II).



Scheme 1. Schematic illustration of the preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II)

#### Characterization of the catalyst **FT-IR Spectroscopy**

The FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (a) and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-



Figure 1. FT-IR spectrums of (a) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-NH<sub>2</sub> (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II)

T/Pd(II) (b) are demonstrated in Fig. 1. The characteristic band at 568 cm<sup>-1</sup> is assigned to the Fe-O stretching vibration of Fe₃O₄.

The high-intensity peak of about 1097 cm<sup>-1</sup> attributed to stretching vibration of Si-O-Si bond, proving the coating of silica on the magnetite nanoparticles. The two weak peaks at 2920 and 2852 cm<sup>-1</sup> are allocated to the C-H of the stretching vibration modes (asymmetric and symmetric) of the methylene group. Furthermore, the observed absorption band at 1398  $\mbox{cm}^{-1}$  belong to stretching vibrations of C-N. The prominent peaks at 3421 and 3132 cm<sup>-1</sup> can be related to the OH and NH stretching groups. Therefore, these results confirm the successful Immobilization of (3-aminopropyl) triethoxysilane (APTES) on the surface of the magnetic Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs (Fig. 1a). The existence of anchored selenotetrazole ligand is affirmed by the appearance of two new absorption peaks at 1635 and 1506 cm<sup>-1</sup>, that can be associated to the C=O stretching vibration of the amide groups (-CONH-) and C=C of the aromatic rings, respectively (Fig. 1b).

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#### **Powder X-ray diffraction**

The crystalline nature and chemical composition of the prepared Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) were investigated with X-ray powder diffraction (XRD) technique .Fig. 2 display the wide angle XRD patterns of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) and the MNPs. XRD patterns both of these samples exhibit the same diffraction lines in 20=  $30.86^{\circ}, 36.26^{\circ}, 43.15^{\circ}, 53.81^{\circ}, 57.19^{\circ},$ and 63.1°, that related to (220), (311), (400), (422), (511), and (440) planes, which are in good agreement with the standard XRD pattern of cubic spinel structure of Fe<sub>3</sub>O<sub>4</sub> MNPs (JCPDS card no. 85-1436). These results authenticate that the crystal structure of the magnetic nanoparticles has not been compromised during the modification. Moreover, the diffractogram of the final catalyst indicates a broad peak in the area  $2\theta$ = 18-28, correspond to the coating of amorphous silica around Fe<sub>3</sub>O<sub>4</sub> in the sample. No characteristic diffraction peaks of metallic palladium can be found in Fig. 2(b), which suggests the presence of divalent palladium species in the synthesized nanocatalyst. Also, no peaks corresponding to any other impurity were observed. In addition, the mean crystal size of the  $Fe_3O_4$  NPs, calculated using the Scherrer equation (d =  $K\lambda/(\beta \cos\theta)$ ) is about 16.5 nm.



#### **XPS** analysis

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X-ray photoelectron spectroscopy (XPS) is one of powerful and important surface analysis tools that provides valuable information regarding the chemical composition, electronic properties and chemical state of the elements present within the synthesized catalysts. The XPS elemental survey scan of the surface of the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) catalyst is presented in Fig. 3. As can be seen in Fig. 3a, peaks corresponding to iron, oxygen, silica, nitrogen, carbon, selenium and palladium are clearly detected in the full range XPS spectrum which are consistent with the EDX results. The corresponding high-resolution XPS spectrum of Fe 2p region is shown in Fig. 3b. The peaks appearing at 710 and 724 eV are assigned to Fe  $2p_{3/2}$  and Fe  $2p_{1/2}.This$  result confirms that the Fe ions have a +2 and +3 oxidation state in  $Fe_3O_4$  MNPs<sup>31, 43</sup>. Fig. 3c illustrates O 1s XPS spectrum of the as-synthesized nanocatalyst; the spectrum is divided into three components at 529.4, 530.7 and 535 eV, can be attributed to binding energies of C=O, C-O and Fe-O bonds, respectively<sup>31, 44, 45</sup>. In the Si 2p spectrum (Fig. 2d), the peak at 102.78 eV is ascribed to siloxane (Si-O-Si), which resulted from the hydrolysis of the silane curing agent molecules during the silanization reaction<sup>1</sup>. The XPS spectra of C 1 s and N 1, s regions are displayed in Fig. 3e and 3f. The XPS spectrum exbibits conside peak with binding energy of 284.38 eV corresponding to C 1 s. As can be seen in Fig. 3f, there is a peak at binding energies of 399.88 eV for the N 1s which can be ascribed to the C-N bond<sup>46</sup>. In addition, successful grafting of the ligand is demonstrated by peak that located in 55.78 eV binding energies, is related to Se 3d (Fig. 3g).









**Figure 3.** XPS spectrum of as-synthesized  $Fe_3O_4@SiO_2-Se-T/Pd(II)(a)$  full range, (b) Fe 2p, (c) O 1s, (d) Si 2p, (e) C 1s, (f) N 1s, (g) Se 3d, and (g) Pd 3d

Additionally, to investigate the oxidation state of Pd (the supported

palladium species) in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Se-T/Pd(II), XPS<sub>Viamalysis\_was conducted (Fig.3h). The high-resolution DPd 18d03XPS8\scam3.0f Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) reveals the doublet peaks at the binding energy of 337.42 eV and 342.9 eV, which can be indexed to electron transitions of 3d5/2 and 3d3/2 of Pd, respectively<sup>1, 47</sup>. This result confirms that the chemical state of palladium is +2 in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) and palladium(II) is not reduced during the preparation of the magnetic nano-catalyst. The shift of Pd(II) 3d5/2 of Pd(OAc)<sub>2</sub> binding energy peak from 338.7 eV to 337.42 eV affirms the formation of Pd(II)-organoselenium complex<sup>48</sup>.</sub>

#### Thermogravimetric analysis (TGA)

To examine the thermal behavior of  $Fe_3O_4@SiO_2-Se-T/Pd(II)$ , as well as to estimate the percent of organic content grafted onto the surface of magnetic nanoparticles, TGA analysis was carried out at temperatures ranging from 30 to 800 °C under air flow (Fig. 4). The thermogram of synthesized nanocatalyst demonstrates a two-step weight loss. The initial weight loss (~15%) below 200 °C is related to the loss of water molecules and physically adsorbed solvents, while the second weight loss (~ 33%) at 200-700 °C could be associated chiefly with the thermal decomposition of the immobilized organic moiety on the surface of the MNPs.





#### Transmission Electron Microscopy



Figure 5. TEM images of  ${\rm Fe_3O_4@SiO_2-Se-T/Pd(II)}$  at different magnifications

Then, the morphology and core-shell structure of the synthesized magnetic nanocatalyst were investigated by Transmission Electron Microscopy (TEM) (Fig. 5). The TEM images of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) confirmed the successful coating of the amorphous silica (SiO<sub>2</sub>) accompanied with organic components (average shell

thickness ~ 5-10 nm) on the Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles, which can be showed as a light region surrounding the dark nano-Fe<sub>3</sub>O<sub>4</sub> core (core diameter ~ 15-20 nm). Also, TEM images represented that Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) had a nearly spherical morphology with relatively good monodispersity.

#### Field emission-scanning electron microscopic analysis

To survey the size, shape and surface morphology of  $Fe_3O_4$ @SiO<sub>2</sub>-Se-T/Pd(II) field emission scanning electron microscopy (FE-SEM) technique was applied. The SEM images in Figure 6 displays that the synthesized catalyst has a uniform and nearly spherical morphology and an average diameter of about 15–30 nm.



Figure 6. SEM images of  ${\rm Fe_3O_4@SiO_2-Se-T/Pd(II)}$  at different magnifications

#### Elemental and compositional analysis

 $Fe_3O_4$ @SiO<sub>2</sub>-Se-T/Pd(II) catalyst was also examined using Energydispersive X-ray spectroscopy (EDS) analysis to determine the type of elements and chemical composition (Fig. 7). EDX pattern clearly indicates the presence of Fe, O, Si, N, C and importantly Se and Pd elements in the catalyst structure witch authenticates the successful immobilization of the Pd(II) on the surface of magnetic nanoparticles by selenotetrazole ligand. The amount of palladium obtained from EDX analysis is around 3.2 (wt%).





#### Magnetic measurement

The magnetic properties of Fe<sub>3</sub>O<sub>4</sub> NPs and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) were thoroughly studied using VSM analysis with a field from - 10000 Oe to +10000 Oe at ambient temperature (Fig. 8). The saturation magnetization values (Ms) of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II)were about 66.27 and 27.71 emu/g, respectively. This reduction in saturation magnetization is related to the successful



Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) is still enough to provide facile recovery of

the nanocatalyst from the solution using an external magnetic field.

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Figure 8. Magnetization curves of (a) nano-Fe $_3O_4$ , (b) Fe $_3O_4@SiO_2-Se-T/Pd(II)$ 

# Investigation of the catalytic activity of $Fe_3O_4@SiO_2-Se-T/Pd(II)$ in the Heck coupling reaction

Heck-Mizoroki reaction is powerful and important tool for the synthesis of natural compounds, biologically active products and advanced materials. Therefore, after the successful characterization of the catalyst, catalytic performance of the prepared material was considered in the Heck reaction. For this purpose, the coupling of iodobenzene with methyl acrylate was chosen as the benchmark substrates for the optimization of critical parameters such as the base and used solvent types, temperature and catalyst loading, and the results of optimization study are shown in Table 1. At first, the model reaction was carried out in the presence of the various dosage of catalyst. The best result was afforded by employing 5 mg of catalyst, whereas increasing the amount of catalyst (10 mg) was not effective on the rate and yield of reaction. Also, in the absence of the catalyst no product was detected in DMF solvent. Then, the model reaction was performed in the existence of a range of bases such as K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub>, NaOH and Et<sub>3</sub>N, amongst them Et<sub>3</sub>N was found to be the best choice base. While the other bases such as K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and NaOH were less effective. Subsequently, to identify a suitable solvent, the same reaction was performed in different solvents such as DMSO, H<sub>2</sub>O, DMF and EtOH. Among the evaluated solvents, DMF was proved to be the best reaction medium. Afterward, the effect of temperature was examined. As shown in Table 1, the preferable temperature for Heck coupling reaction with Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) NPs as catalyst was 120 °C (Table 1, entry 3). At lower temperatures the reaction yield was decreased. The temperature was increased to 150 °C but no effect on the yield of the product was seen. Also, no coupling product at room temperature was observed. Therefore, the entry 3 of Table 1 was selected as ideal condition for Heck coupling reaction using  $Fe_3O_4@SiO_2-Se-T/Pd(II)$  catalyst.



Scheme. 2. Plausible mechanism for the cross coupling of aryl halides with acrylates catalyzed by  $Fe_3O_4@SiO_2-Se-T/Pd(II)$ 

#### Scope and generality of reaction

Based on the results of aforementioned optimization studies, the scope and generality of  $Fe_3O_4@SiO_2-Se-T/Pd(II)$  was investigated for different aryl halides and acrylates. As seen in Table 2, all the substrates containing electron-withdrawing or electron-donating functional groups were successfully transformed to the desired cross-coupling products in good to excellent yields. Reaction of aryl bromides were slower than aryl iodides, so the reaction times for them were longer in comparison. This might be because of the different strengths of the aryl-X bond (C-I < C-Br < C-CI). Furthermore, synthetically useful substituents, such as thienyl and naphthyl were well tolerated during the course of the reaction.

#### Proposed reaction mechanism

A plausible mechanism for the Heck-Mizoroki cross-coupling reaction in the presence of  $Fe_3O_4@SiO_2-Se-T/Pd(II)$  is proposed in Scheme 2 on the basis of the mechanism of the previous reports<sup>49</sup> <sup>56</sup>. The catalytic cycle begins with the reduction of Pd (II) to the active Pd (0) species in the presence of the amines or alkenes. Then, oxidatively addition of the C–X bond of an aryl halide (X = I, Br) to the palladium atom is generated  $\sigma$ -arylpalladium intermediate (A). In the third step, the palladium(II) forms a  $\pi$ -complex with acrylate, and subsequently, the acrylate inserts itself in the palladiumcarbon bond in a syn-addition fashion, which gives complex (B). In the last step, a new palladium–acrylate  $\pi$  complex is formed by beta-hydride elimination. Finally, the resultant complex is destroyed and coupling product is released and the catalytic cycle is completed by regeneration of the palladium (0) compound by reductive elimination of the palladium(II) compound in the presence of the Et<sub>3</sub>N as base.

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View Article Online **Table 1.** Optimization of the Heck reaction between and methyl acrylate using Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) as catalysta

OMe reaction condition						
Entry	Catalyst (mg)	Temp. (°C)	Solvent	Base	Time (min)	Yield (%) <sup>b</sup>
1	-	120	DMF	Et₃N	10 (h)	-
2	2.5	120	DMF	Et₃N	45	76
3	5	120	DMF	Et₃N	45	98
4	10	120	DMF	$Et_3N$	45	97
5	5	150	DMF	$Et_3N$	45	93
7	5	80	DMF	Et₃N	45	82
8	5	r.t	DMF	Et₃N	45	-
9	5	reflux	H <sub>2</sub> O	$Et_3N$	45	78
10	5	reflux	EtOH	$Et_3N$	45	72
11	5	120	DMSO	Et₃N	45	88
12	5	120	DMF	$K_2CO_3$	45	85
13	5	120	DMF	NaOH	45	72
14	5	120	DMF	$Cs_2CO_3$	45	78

<sup>a</sup>Reaction condition: iodobenzene (1.0 mmol), methyl acrylate (1.5 mmol), base (2.0 mmol), solvent (5.0 mL).

<sup>b</sup>lsolated yield.

#### Comparison between catalytic activities of $Fe_3O_4@SiO_2-Se-T/Pd(II)$ in Heck reaction related to other reported catalysts

This is the first report wherein a Pd(II) complex of organoselenium ligand stabilized on magnetic nanoparticles has been used as a heterogeneous catalyst in the Heck–Mizoroki coupling reaction. Therefore, to further evaluate the efficiency and capability of  $Fe_3O_4@SiO_2$ -Se-T/Pd(II), the catalytic performance of the present protocol was compared with some of the previously reported methods in the Heck–Mizoroki coupling reaction of aryl iodide with methyl acrylate in the literature (Table 3). However, the reported catalysts were generate the target product in good to excellent yield, but the newly synthesized  $Fe_3O_4@SiO_2$ -Se-Pd (II) shows superiority in terms of reaction conditions loading of catalyst (entries 1-2 and 4), reaction time (entries 1-7 and 9), temperature (entries 1-7 and 9) to most of the listed catalyst systems.

#### Recovery and reusability of the catalyst

From the perspective of economic and ecological demands, recovery and recyclability of heterogeneous catalysts are two indispensable factors that need to be investigated. Thus, the reusability of  $Fe_3O_4@SiO_2-Se-T/Pd(II)$  catalyst was examined in Heck C–C coupling reaction under the optimized conditions using the model reaction Upon completion of the reaction, the catalyst was magnetically separated in each run, and washed several times with hot ethanol for the removal of traces of the previous residual products and dried in oven at 80 °C. Obviously, the performance of the recycled catalyst is acceptable for five consecutive runs without considerable reduction of its catalytic activity (Fig 9).

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	$R_1$ + $R_2$ Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Se-T/Pd (II) (5 mg), Et <sub>3</sub> N			R <sub>2</sub>	
		-	DMF, 120 °C		
Entry	Aryl halide	terminal alkene	Product	Time (min)	Yield <sup>b</sup> (%)
1		OMe	OMe	45	98
2	O <sub>2</sub> N	OMe		45 e	96
3	Me	OMe		90	92
4	MeO	OMe	Me	90 e	93
5	Br	OMe	MeO' OMe	3(h)	88
6		OMe	Br' OMe	2.5	83
7	H <sub>2</sub> N	OMe	OMe	5(h)	78
8		OBu <sup>n</sup>	H <sub>2</sub> N <sup>2</sup> OBu <sup>n</sup>	45	95
9	Me	OBu <sup>n</sup>	ОВИ	90	93
10	Br	OMe	Me <sup>r</sup> O OMe	6(h)	95
11	O <sub>2</sub> N Br	OMe		6(h)	80

### Table 2. Heck reaction of different aryl halides and acrylates catalyzed by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II)<sup>a</sup>



<sup>a</sup>Reaction conditions: aryl halide (1.0 mmol), acrylate (1.5 mmol), Et<sub>3</sub>N (2 .0 mmol), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) catalyst (5.0 mg) in DMF (3.0 mL) at 120 °C.

<sup>b</sup>Isolated yield.

Table 3. Comparison of catalytic activity of Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Se-T/Pd(II) with previously reported procedure for the Heck–Mizorol
coupling reactions of iodobenzene and methyl acrylate

Entry	Catalyst [ref]	Reaction conditions	Time(h)	Yield(%)
1	Pd/MnBDC <sup>a</sup> (13 mg) 55	Et₃N, DMA, 90 <sup>°</sup> C	9	97
2	$Pd/CNCs^{b}(50 mg 3 wt\%)^{57}$	K <sub>2</sub> CO <sub>3</sub> , DMF, 40 <sup>o</sup> C	3	99
3	Pd/La <sub>2</sub> O <sub>3</sub> (1 mmol%) <sup>58</sup>	NaOAc, DMA, 120 °C	10	93
4	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -T/Pd <sup>c</sup> (20 mg) <sup>36</sup>	Et₃N, DMF, 120 °C	3	95
5	Co/Al <sub>2</sub> O <sub>3</sub> (0.12 mol%) <sup>59</sup>	K <sub>2</sub> CO <sub>3</sub> , NMP, 150 <sup>°</sup> C	24	56
6	SiO <sub>2</sub> -acac-PdNPs <sup>d</sup> (5 mg) <sup>60</sup>	NaHCO <sub>3</sub> , NMP, 140 <sup>o</sup> C	15 (min)	90
7	Present catalyst	Et₃N, DMF, 120 °C	45 (min)	98
8	h-BN <sup>e</sup> @Fur@Pd(OAc) <sub>2</sub> (0.05 mmol) <sup>6</sup>	K <sub>2</sub> CO <sub>3</sub> , H <sub>2</sub> O, 90 <sup>o</sup> C	4	95
9	Cellulose supported poly (hydroxamic acid) Pd(II) (0.03 mol%) <sup>61</sup>	$Et_3N$ , DMF, 130 $^{\circ}C$	5	93
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 $^{\circ}$ Mn-carboxylate metal–organic coordination polymer, Pd/MnBDC, (MnBDC= [Mn<sub>3</sub>(BDC)<sub>3</sub>DMF<sub>4</sub>]<sub>n</sub>, H<sub>2</sub>BDC= 1,4 benzendicarboxylic acid

Carbon nanocoils

<sup>C</sup>Tetrazole-functionalized nanomagnetic Fe<sub>3</sub>O<sub>4</sub> supported palladium

<sup>d</sup>Silica–acetylacetone-supported palladium

<sup>e</sup>Hexagonal boron nitride



#### Figure 9. Recycling experiment of nano-Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II)

Interestingly, comparing the XRD pattern of fresh and recovered  $Fe_3O_4@SiO_2-Se-T/Pd(II)$  displayed that the phase composition and crystalline structure of the prepared nanocatalyst remained unchanged after using in Heck–Mizoroki cross coupling reaction and the mean crystallite size calculated using the Scherrer equation was around 16 nm. The results are shown in Fig. 10. Moreover, there were no characteristic peaks corresponding to palladium particles, which is likely to affirm that the palladium complex stayed unchanged during the reaction.<sup>62, 63</sup>.Finally, to explore Pd leaching (the homogeneous or heterogeneous nature of the catalysis), the model reaction between iodobenzene and methyl acrylate was performed in the presence  $Fe_3O_4@SiO_2-Se-$ 

T/Pd(II). Then, the reaction was stopped at 22.5 min (half the reaction time), the catalyst was entirely separated from the reaction mixture with an external magnet and the reaction was allowed to continue under the same conditions without Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II). As shown in Fig. 11, no considerable increase and progress in the product yield occurred, even after 120 min (monitored by TLC). These results demonstrate the true heterogeneous nature of the catalyst.

#### Experimental

#### Materials and apparatus

All the solvents and chemical reagents in this study were acquired from Merck and Sigma-Aldrich chemical companies and utilized as obtained without additional drying or purification. The progress of the C-C coupling reaction was monitored using TLC with commercial aluminum-backed plates of silica gel 60 F254, using UV light. Fourier transform infrared (FT- IR) spectrums were collected on a Shimadzu 8400 s spectrometer with a scanning range of 400-4000 cm<sup>-1</sup> using KBr pallet method. Powder X-ray diffraction (XRD) pattern of the asprepared nanocatalyst and pure Fe<sub>3</sub>O<sub>4</sub> were obtained using a Philips diffractometer equipped

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Figure 10. XRD pattern of nano-Fe $_3O_4@SiO_2$ -Se-T/Pd(II) (a) before use and (b) after reused five runs



Figure 11. Leaching experiment of nano-Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II)

with Cu K $\alpha$  radiation source with a wavelength of 1.54 Å and  $2\vartheta$  range of 10-90 degree. X-ray photoelectron spectroscopy (XPS) was investigated using a Thermo Scientifi, ESCALAB 250Xi Mg X-ray resource. Thermogravimetric analysis (TGA) was carried out using a thermal analyzer (LINSEIS model STS PT 16,000) at a heating rate of 10 °C min<sup>-1</sup>, under air flow in the temperature range of 30–800 °C. Field emission scanning electron microscopic (FE-SEM) image was recorded by using a Tescanvega II XMU digital scanning microscope in order to acquire information about the size, morphology and shape of synthesized nanomaterials. Transmission electron microscopy (TEM) was performed out using a CM30 300 kV digital transmission microscope.

Besides SEM, Energy dispersive X-ray spectroscopy (EDS) analysis confirmed the detailed elemental composition of nanocatalyst. The magnetic properties of the catalyst and  $Fe_3O_4$  nanoparticles were measured by using vibrating sample magnetometer (VSM; Lakeshore7407) (Meghnatis Daghigh Kavir Co., Kashan, Iran) at room temperature from -10000 to +10000 Oe. <sup>1</sup>H NMR spectrum was recorded at 400 MHz in DMSO using TMS as internal standard.

#### **Preparation of catalyst**

#### Silanation of the $Fe_3O_4@SiO_2$ magnetite nanoparticles

Firstly, magnetic nanoparticles  $Fe_3O_4$ ,  $Fe_3O_4@SiO_2$  and  $Fe_3O_4@SiO_2$ -APTES were prepared in accordance with the procedure previously described in literature <sup>64-66</sup>.

ARTICLE

#### View Article Online Synthesis of 4-selenocyanatobenzoic acidand 49((1/1/tetrazote 5-yl) selanyl) benzoic acid

Initially for the synthesis of 4-selenocyanatobenzoic acid, a mixture of para-aminobenzoic acid (0.27 g, 2 mmol) and NaBF<sub>4</sub> (0.33 g, 3 mmol) was suspended in aqueous HCl solution (3 mL, 2 N) at 0 °C. Next, an aqueous solution of NaNO<sub>2</sub> (0.145 g, 2.1 mmol, dissolved in 2 mL of water) was injected drop by drop, while the mixture was kept at 0 °C. After complete addition of the reactant, this mixture was stirred for 1 h and then sodium acetate (ca. 4 mL, saturated) was slowly added until the pH of mixture was adjusted to 6. Then, the resulting mixture was successively added into a aqueous solution of KSeCN (0.288 g, 2 mmol) in 4 mL of water and the reaction mixture was mechanically stirred at ambient temperature for 1 h. Consequently, the product extracted with diethyl ether and the obtained organic phases dried over MgSO<sub>4</sub>. The product obtained was used in the next step without additional purification<sup>67</sup>. 4-((1*H*-tetrazole-5-yl) selanyl) benzoic acid was prepared in the following fashion <sup>33</sup>. Typically, to a mixture of 4selenocyanatobenzoic acid (1.0 mmol) and NaN<sub>3</sub> (1.5 mmol) in DMF (2 mL), 30 mg of Cul as the catalyst was added. The reaction mixture was stirred at 120 °C for the desired time. Upon the completion of the reaction (monitored by TLC), the mixture was cooled down to normal temperature and then with 10 mL of ethyl acetate and 20 mL of HCl (5 N) was diluted. Consequently, the organic layer was isolated, and the aqueous layer was extracted with 20 mL of ethyl acetate. The separated organic layer was rinsed with water, dried over MgSO<sub>4</sub>. Then, the residue was purified by short column chromatography on silica gel to afford the target product in excellent vield.

Mp: 180–182 °C; <sup>1</sup>H NMR (DMSO-d6) δH: 7.62 (d, 2H)–7.95 (d, 2H), 12.94 (s, 1H) <sup>68</sup>.

# Immobilization of 4-((1*H*-tetrazole-5-yl) selanyl) benzoic acid on $Fe_3O_4@SiO_2$ -APTES

A mixture of 4-((1*H*-tetrazole-5-yl) selanyl) benzoic acid (1.8 mmol), triethylamine (1.8 mmol), N,N'-Dicyclohexylcarbodiimide (DCC) (1.8 mmol) in degassed dichloromethane was stirred at 0 °C for 30 min under nitrogen. (0.1) g of silanated nanoparticles (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-APTES) were suspended in 25 mL dichloromethane (DCM) and sonicated for 15 min and then added to reaction mixture. The resulting mixture was stirred for other 1 hour at 0 °C and then was cooled to ambient temperature and stirred further for 16 h. The mixture was then heated to 40 °C for 3 h. The heterogeneous ligand was separated using a magnet and washed with dichloromethane and dried at 60 °C <sup>69</sup>.

#### Preparation of magnetite supported palladium nanoparticle catalyst

Dry nanoparticles from the final step (0.1 g) was dispersed in ethanol (10 mL) and Pd (OAc)<sub>2</sub> (0.004 g, 0.0178 mmol) was added to the mixture. The reaction mixture was stirred under reflux condition for 24 h. Next, the resulting product was isolated *via* an external magnetic field and washed with ethanol. After drying in an oven at 80°C, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Se-T/Pd(II) catalyst as a brown solid was obtained <sup>70</sup>.

# General procedure for the Heck-Mizoroki coupling reaction using the $Fe_3O_4@SiO_2$ -Se-T/Pd(II)

#### ARTICLE

A mixture of aryl halide (1.0 mmol), acrylate (1.5 mmol),  $Fe_3O_4@SiO_2-Se-T/Pd(II)$  (5 mg), triethylamine (2.0 mmol), and DMF (3 ml) was stirred in an oil bath at 120 °C for the appropriate time. The reaction progress was followed using TLC. Upon completion of the reaction, the resulting hot reaction mixture was cooled to room temperature and diluted with hot ethanol. Then, the catalyst was magnetically separated from the reaction mixture, washed several times with ethanol, dried in at 80°C and used for the next reaction run without further purification. After separation of the catalyst, the filtrate was concentrated and further purification was obtained by short column chromatography on silica gel by using *n*-hexane/ ethyl acetate (9:1) as eluent. *Caution: triethylamine is carcinogenic.* 

### Conclusions

In conclusion, a new magnetically retrievable and sustainable catalyst by immobilizing of the Pd (II) complex on organoselenium ligand (containing hard N and soft Se atoms) onto the surface of the amine functionalized silica coated magnetite nanoparticles,  $Fe_3O_4@SiO_2-Se-T/Pd(II)$ , was synthesized for the first time and structurally characterized using various methods. Then, it was applied as a novel air and moisture-stable catalyst for Heck C-C cross coupling reaction. A diverse range of aryl halides were successfully reacted with acrylates to generate the corresponding C-C coupling products in good to excellent yields. More importantly, this heterogeneous palladium catalyst can conveniently be recovered with an external magnet and reused five times without remarkable degradation of activity. Easy recovery and reusability of catalyst, the broad substrate scope, short reaction times, good yields and especially use of organoselenium compound as a moisture-stable ligand are outstanding advantages of present protocol which make it very practical. Further studies toward the extension of Pdcatalysis to other organoselenium ligand as well as the stabilization of other metal are currently under investigation in our laboratory.

## **Conflicts of interest**

"There are no conflicts to declare".

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### **Graphical Abstract**

Organoselenium-Palladium(II) Complex Immobilized on Functionalized Magnetic Nanoparticles as a Promising Retrievable Nanocatalyst for the "Phosphine-Free" Heck-Mizoroki Coupling Reaction

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An air- and moisture-stable organoselenium-palladium complex immobilized on silica-coated magnetic nanoparticles was designed, synthesized and applied as a practical and retrievable catalyst in Heck–Mizoroki cross coupling reaction.