



Palladium supported aminobenzamide modified silica coated superparamagnetic iron oxide as an applicable nanocatalyst for Heck cross-coupling reaction

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ABSTRACT

An applicable palladium-based nanocatalyst was constructed through the immobilization of palladium onto 2-aminobenzamide functionalized silica coated superparamagnetic iron oxide magnetic nanoparticles. The nanocatalyst (named as Pd@ABA@SPIONs@SiO₂) was characterized by several characterization methods, including scanning electron microscope (SEM), transmission electron microscopy (TEM), vibrating-sample magnetometry (VSM), energy-dispersive X-ray spectroscopy (EDS), dynamic light scattering (DLS), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), inductively coupled plasma (ICP), and X-ray photoelectron spectroscopy (XPS) analyses. Microscopy results showed that the nanoparticles are spherical in shape with 20–25 nm size. The size of the nanoparticles was confirmed by the DLS method. The superparamagnetic nature of the catalyst was confirmed by the VSM method. The successful functionalization of SPIONs@SiO₂ was confirmed by FT-IR spectroscopy. The presence of palladium in the structure of the nanocatalyst was illustrated by XRD and EDS analysis. Also using XPS technique, the oxidation state of palladium in Pd@ABA@SPIONs@SiO₂ was determined zero before and after the catalyst was applied in Mizoroki-Heck reaction. Several aryl halides and alkenes were reacted in the presence of the nanocatalyst and formed the corresponding products in high isolated yields. The nanocatalyst showed very good reusability and did not decrease its activity after 10 sequential runs. Density functional theory (DFT) calculation was performed to provide a mechanism for the reaction and confirmed the role of the palladium catalyst in the reaction function.

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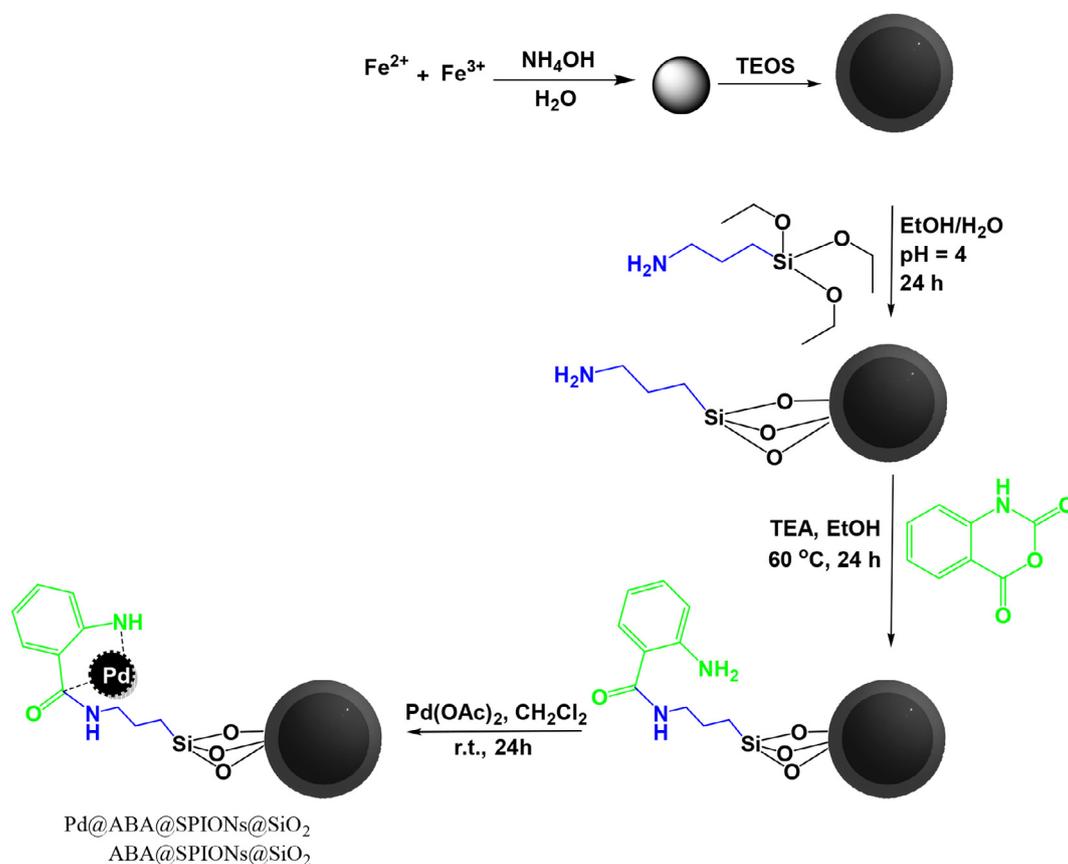
1. Introduction

Mizoroki-Heck reaction, a palladium catalyzed carbon-carbon bond formation between aryl halides and alkenes is considered as a significant name reaction in organic synthesis. Design and synthesis of novel and efficient catalysts for the mentioned reaction is an aim among the researchers [1–5]. In classic Mizoroki-Heck reaction, palladium salts such as palladium acetate and palladium

chloride are applied [6]. However, the possibility of simple recovery of the heterogeneous catalysts has led to efforts on introduction of efficient heterogeneous catalysts for this significant reaction [7,8]. Traditional heterogeneous catalysts lack in some properties, such as lower efficiency and need to higher temperatures and harsher conditions. An interesting approach for overcoming these problems is to immobilize catalysts onto nanoparticle-based supports. These immobilized catalysts offer a collection of the advantages of both homogeneous and heterogeneous catalysts [9–13]. In this way, a useful approach is to immobilize palladium catalyst on solid supports, especially nano-sized materials [14–19]. Research on the application of nanomaterials to improve different factors of the Mizoroki-Heck reaction has experienced strong growth and

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Scheme 1. Synthesis process of Pd@ABA@SPIONs@SiO₂ nanocatalyst.

an increased interest in recent decades. Among various nanoparticles (NPs), superparamagnetic iron oxide nanoparticles (SPIONs) are an interesting support for palladium, due to its unique properties, including high chemical and thermal stability, and the ease of their recycling and handling. Therefore, SPIONs is extensively used as support for palladium catalyst for application in different reactions, particularly Mizoroki-Heck reaction [20–24]. However, several methods using different nanomaterials including magnetic, SiO₂, mesoporous silica nanoparticles (MSNs), metal-organic frameworks (MOFs), graphene oxide (GO), and polymeric nanomaterials have been investigated for development the stabilized Pd based nanocatalysts, these are suffering from some limitations such as high costs, toxic solvents, and high consumption of chemicals.

As a key factor, to design an efficient version of any catalyst, investigating and understanding the mechanism of the reaction is of particular importance. Deep insight into the mechanism of the reaction helps the researchers to extend the knowledge of the pathway, by which the substrates convert to the corresponded products in the presence of the catalyst. Computational studies, which calculate the energy level of the intermediates and transition states, are of the most reliable methods, due to the well-founded quantum chemical calculations using density functional theory [25–29].

In this paper, we introduce a recyclable nanocatalyst based on the modified silica coated superparamagnetic iron oxide magnetic (SPIONs@SiO₂). Immobilization of catalysts onto the surface of NPs, especially modified SPIONs is an efficient approach for increasing the efficiency and reusability of the catalysts. 2-Aminobenzamide modified silica coated superparamagnetic iron oxide magnetic (ABA@SPIONs@SiO₂) was used as a water dispersible support for palladium catalyst (denoted by Pd@ABA@SPIONs@SiO₂). 2-Aminobenzamide was a suitable ligand for the immobilization of

palladium and the results showed that no significant leaching of palladium was observed under the reaction conditions. To prove the structure of Pd@ABA@SPIONs@SiO₂, it was fully characterized by various techniques and its catalytic activity was evaluated toward Mizoroki-Heck carbon-carbon bond formation reaction. Density functional theory was applied to propose and determine the mechanism of the reaction.

2. Results and discussion

Herein, a boosted nanocatalyst is fabricated, based on the immobilization of palladium onto 2-aminobenzamide SPIONs@SiO₂ core-shell nanostructures. The preparation steps are schematically illustrated in Scheme 1. For the synthesis of the catalyst, SPIONs was prepared by the co-precipitation of Fe²⁺ and Fe³⁺ in basic media. After the synthesis of SPIONs, these NPs were encapsulated by SiO₂ shell. SPIONs@SiO₂ core-shell NPs were then functionalized by (3-aminopropyl)triethoxysilane (APTES) and isatoic anhydride, respectively to achieve ABA@SPIONs@SiO₂. The fabricated ABA@SPIONs@SiO₂ was used as a magnetic bidentate support for the immobilization of palladium catalyst.

The structure of Pd@ABA@SPIONs@SiO₂ nanocatalyst was studied by SEM and TEM. TEM with different magnifications and SEM images are presented in Fig. 1a-c. The spherical structure of the catalyst particles was approved by TEM microscopy. SEM images showed that the structure of the catalyst nanoparticles is spherical with an average particle size about 20–25 nm. The hydrodynamic size of the NPs was determined about 85 nm using DLS method. The EDS was applied to prove the presence of the expected elements in the structure of the catalyst. EDS result is presented in Fig. 1d. The presence of “Fe”, “O”, and “Si” elements represent the SPIONs@SiO₂ NPs. The ligand atoms are presented as “C” and “O”

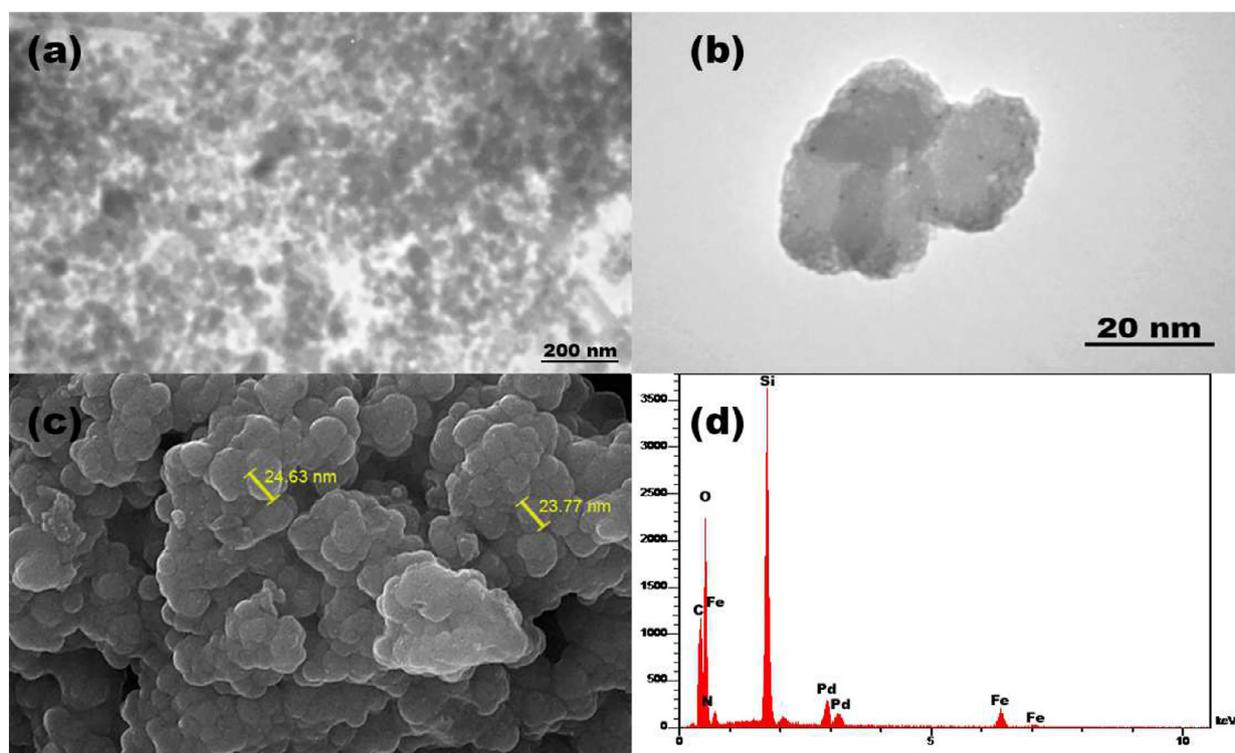


Fig. 1. (a) Low magnification; (b) high magnification TEM, (c) SEM images; and (d) EDS result of Pd@ABA@SPIONs@SiO₂ nanocatalyst.

elements in EDS. The presence of palladium catalyst clearly proves by the observation of Pd in EDS results.

The successful synthesis of Pd@ABA@SPIONs@SiO₂ catalyst was confirmed by FT-IR spectroscopy. The FT-IR spectra of SPIONs@SiO₂ and Pd@ABA@SPIONs@SiO₂ catalyst are presented in Fig. 2a. Vibration at 3424 cm⁻¹ could be correlated to O-H vibrations. C-H bonds could be observed as a peak at 2926 cm⁻¹. Amide group of aminobenzamide ligand was observed at 1635 cm⁻¹. An intense peak at 1099 could be correlated to Si-O vibrations. Fe-O vibrations could be observed at 570 cm⁻¹. Apart from FT-IR, XRD analysis was used to characterize Pd@ABA@SPIONs@SiO₂ catalyst. XRD pattern of Pd@ABA@SPIONs@SiO₂ nanocatalyst is presented in Fig. 2b. The presence of Pd (0) could be observed in the XRD pattern of the catalyst, with (111) and (200) reflections at 2θ 40° and 48°, respectively [30,31].

The surface area of the synthesized solids was determined by BET (Brunauer-Emmett-Teller). The N₂ adsorption-desorption isotherms of SPIONs@SiO₂ and Pd@ABA@SPIONs@SiO₂ were 309.44 m².g⁻¹ and 301.17 m².g⁻¹, respectively. The large surface area of SPIONs@SiO₂ could be correlated to the small particle size of the magnetic nanoparticles. In addition, the palladium content of the catalyst was analysed by inductively coupled plasma (ICP) method. The ICP results showed the palladium content in Pd@ABA@SPIONs@SiO₂ catalyst to be 0.24 mmol.g⁻¹. The magnetic behaviour of the catalyst was studied by vibrating-sample magnetometer (VSM) analysis. VSM results proved the superparamagnetic behaviour of the catalyst. Functionalization of SPIONs@SiO₂ has led to decrease in the magnitude of the magnetization of the catalyst nanoparticles. However, the magnetic behaviour of the catalyst has still been retained in Pd@ABA@SPIONs@SiO₂ catalyst. The VSM result is presented in Fig. 2c.

The catalytic activity of Pd@ABA@SPIONs@SiO₂ catalyst as evaluated in catalytic Mizoroki-Heck reaction. The catalyst was applied for the conversion of aryl halide and alkene to the corresponding substituted alkene. To find the optimal reaction condition, the re-

action was performed in various reaction conditions. The reaction of styrene and bromobenzene for the synthesis of stilbene was selected as the model reaction and the effect of various variables on the reaction performance was evaluated (Table 1).

The reaction was performed in various protic and aprotic solvents with different polarities. It could be observed that the desired product was formed in all the solvents. The yields of the reactions showed to be advantageous, when water was used as the reaction solvent. Performing the reaction in with different bases showed that the best results were obtained when the reaction was performed with sodium acetate as base. The highest isolated yield was obtained when 1.5 equivalent of sodium acetate was added to the reaction mixture. Finally, the effect of temperature on the reaction performance was studied by performing the reaction in different temperatures. This studies showed a proportional independence of the reaction to the temperature. Therefore, the reaction was performed at room temperature (average 25 °C) in all cases.

The effect of the nanocatalyst amount of the reaction performance was also evaluated. It could be observed that the highest isolated yields were obtained in the presence of 0.08 mol% of the nanocatalyst. In the lower amount of the nanocatalyst, the isolated yields of the products were intensely decreased. However, increasing the amount of the nanocatalyst to the amounts above 0.08 mol% did not increase the yield of the reaction. The optimal reaction conditions were observed to be water as solvent, 1.5 equivalent of sodium acetate as base, 0.08 mol% of Pd@ABA@SPIONs@SiO₂ nanocatalyst at room temperature (Table 1, Entry 3).

The scope and the generality of this nanocatalyst was evaluated in Pd@ABA@SPIONs@SiO₂ catalyzed Mizoroki-Heck reaction. For this purpose, alkenes, including styrene and n-butyl acrylate were reacted with various aryl halides with different electron donating or electron withdrawing functionalities. The results are presented in Table 2.

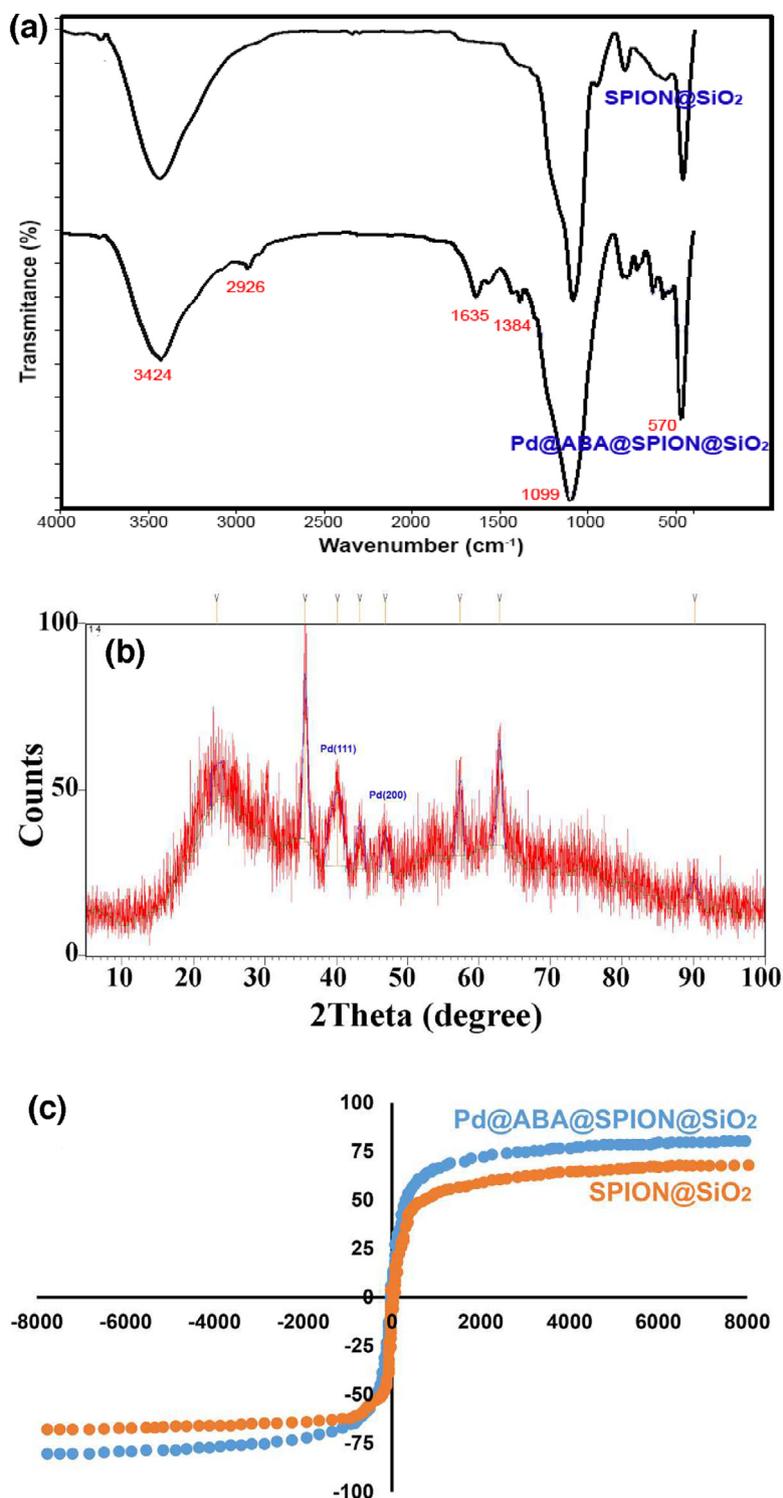


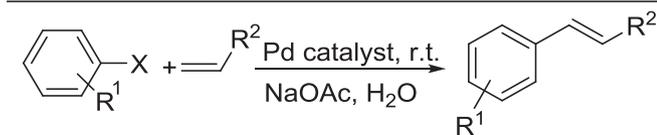
Fig. 2. (a) FT-IR spectrum; (b) XRD pattern; and (c) VSM graph of Pd@ABA@SPIONs@SiO₂ catalyst.

It could be observed both styrene and n-butyl acrylate have participated in the reaction and have given the desired products in high isolated yields. In addition, all of the aryl halides have successfully given the products. Aryl halides with electron-withdrawing groups, such as nitro, nitril, and carbaldehyde functions, have given the products with both styrene and n-butyl acrylate (Table 2, Entries 2-7, 16-18). On the other hand, aryl halides with electron-donating functionalities, including methoxy, dimethylamino, hydroxyl, and methyl have successfully partici-

pated in the reaction with styrene and n-butyl acrylate to give the products (Table 2, Entries 8-14, 19-22). In addition, a large-scale experiment was performed with 10 mmol of the starting materials (Table 2, Entry 23). It could be observed that in large scale experiments, the product is formed and isolated in high isolated yield. In addition, aryl halides with different halogen groups (bromide or iodide) have been used in the reaction and the desired products have been obtained in all cases in high yields.

Table 1
Optimization of Mizoroki-Heck reaction conditions catalyzed by Pd@ABA@SPIONs@SiO₂.^a

Entry	Solvent	Base (mmol)	Catalyst mol%	Temperature(°C)	Yield (%) ^b
1	EtOH	NaOAc (1.5)	0.08	r.t. ^c	67
2	MeOH	"	"	"	55
3	H ₂ O	"	"	"	98
4	DMSO	"	"	"	73
5	DMF	"	"	"	61
6	CH ₂ Cl ₂	"	"	"	40
7	CH ₃ CN	"	"	"	59
8	H ₂ O	NaOH (1.5)	"	"	90
9	"	KOH (1.5)	"	"	93
10	"	K ₂ CO ₃ (1.5)	"	"	84
11	"	NaOAc (1.0)	"	"	77
12	"	NaOAc (1.2)	"	"	82
13	"	NaOAc (1.7)	"	"	98
14	"	NaOAc (2.0)	"	"	96
15	"	NaOAc (1.5)	0.03	"	49
16	"	"	0.05	"	79
17	"	"	0.10	"	98
18	"	"	0.15	"	98
19	"	"	0.08	0	66
20	"	"	"	40	98
21	"	"	"	80	98

^a Reaction conditions: bromobenzene (1.0 mmol), styrene (1.1 mmol), solvent (3 mL)^b isolated yield^c room temperature, about 25 °C.**Table 2**
Mizoroki-Heck reaction in the presence of Pd@ABA@SPIONs@SiO₂ as catalyst. ^a

Entry	R ¹	X	R ²	Yield(%) ^b
1	H	Br	C ₆ H ₅ -	98
2	H	Cl	C ₆ H ₅ -	91
3	4-NO ₂	Br	C ₆ H ₅ -	96
4	4-NO ₂	I	C ₆ H ₅ -	99
5	2-CN	Br	C ₆ H ₅ -	93
6	4-CN	Br	C ₆ H ₅ -	95
7	4-CN	Cl	C ₆ H ₅ -	84
8	4-CHO	Br	C ₆ H ₅ -	91
9	4-CHO	I	C ₆ H ₅ -	95
10	4-CH ₃	Br	C ₆ H ₅ -	97
11	4-CH ₃	I	C ₆ H ₅ -	99
12	4-OH	Br	C ₆ H ₅ -	96
13	4-NMe ₂	I	C ₆ H ₅ -	96
14	4-CH ₃ O	Br	C ₆ H ₅ -	91
15	2-CH ₃ O	Br	C ₆ H ₅ -	93
16	3-CH ₃	Br	C ₆ H ₅ -	97
17	H	Br	BuCO ₂	96
18	4-NO ₂	Br	BuCO ₂	90
19	4-NO ₂	I	BuCO ₂	93
20	4-CHO	Br	BuCO ₂	95
21	4-CHO	Cl	BuCO ₂	88
22	4-CH ₃	Br	BuCO ₂	93
23	4-CH ₃	I	BuCO ₂	95
24	4-NMe ₂	Br	BuCO ₂	94
25	4-CH ₃ O	Br	BuCO ₂	96
26 ^c	H	Br	C ₆ H ₅ -	88

^a reaction conditions: halobenzene (1 mmol), alkene (1.1 mmol), sodium acetate (1.5 mmol), H₂O (3 mL), Pd@ABA@SPIONs@SiO₂ catalyst (0.08 mol%), r.t.^b isolated yield^c large scale conditions: bromobenzene (10 mmol), alkene (12 mmol), sodium acetate (15 mmol), H₂O (30 mL), Pd@ABA@SPIONs@SiO₂ (0.08 mol%), r.t.

As an advantage of Pd@ABA@SPIONs@SiO₂ nanocatalyst, the recovery of the catalyst was evaluated. For this purpose, the reaction of styrene and bromobenzene was selected and after the reaction completion, the Pd@ABA@SPIONs@SiO₂ catalyst was separated us-

ing an external magnet, washed, dried and was finally applied in the next reaction under optimized conditions. This cycle was repeated for 10 sequential runs. The results are presented in Fig. 3. It could be observed that the catalyst has remained active after the 10th reaction run. This catalyst is efficient due to the high turnover number (TON). Pd@ABA@SPIONs@SiO₂ catalyst achieved cumulative TONs of about 12,250 over 10 successive runs. It should be noted that the cumulative TON is obtained by the sum of the values for the TONs for all examined runs.

To confirm the stability of Pd@ABA@SPIONs@SiO₂ catalyst under the reaction conditions, the catalyst recovered after 5th-run was characterized by SEM microscopy. The SEM image of the 5th-recovered catalyst is presented in Fig. 4. It could be observed that the morphology and the structure of the catalyst has remained unchanged during the reaction cycles. In addition, a leaching test was performed to investigate the robustness of the Pd@ABA@SPIONs@SiO₂ nanocatalyst. To this purpose, a blank run was performed under the reaction condition. After 12 h, the catalyst was magnetically separated and the remaining solution was characterized by ICP for possible presence of palladium. ICP results showed no leaching of the catalyst, which proved the stability of Pd@ABA@SPIONs@SiO₂ under the reaction conditions.

The oxidation state of palladium before and after recovery of the catalyst was studied by X-ray photoelectron spectroscopy (XPS) method. The XPS results of the oxidation state of palladium before the reaction and after the 5th cycle is presented in Fig. 5. The XPS results showed that palladium was as Pd(0) in Pd@ABA@SPIONs@SiO₂ nanocatalyst with no change after 5th run. Two lines at 334.8 and 339.9 eV represents the presence of Pd(0) in the structure of the catalyst [32].

The mechanism of the reaction was studied by density functional theory (DFT) method. The result of the DFT study of the mechanism of the reaction is presented in Scheme 2. According to the results of the optimization of the energy of the catalyst, the most stable species of catalyst is established by the bonding of palladium to "N" atom of the amine group and "C" atom of the amide carbonyl in the structure of ABA ligand. A catalytic cycle starts with the coordination of aryl halide to Pd(0) catalyst, which is an oxidative addition reaction. This leads to a transition state with higher energy level. The carbon-halogen bond cleavage and coordination

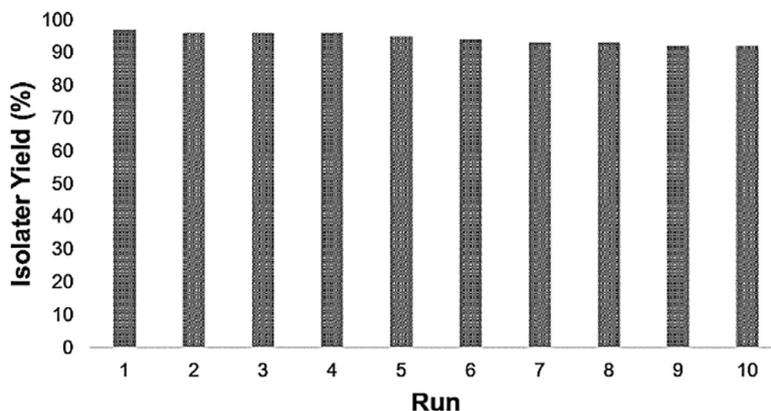


Fig. 3. The results of the recovery of the catalyst for 10 sequential runs.

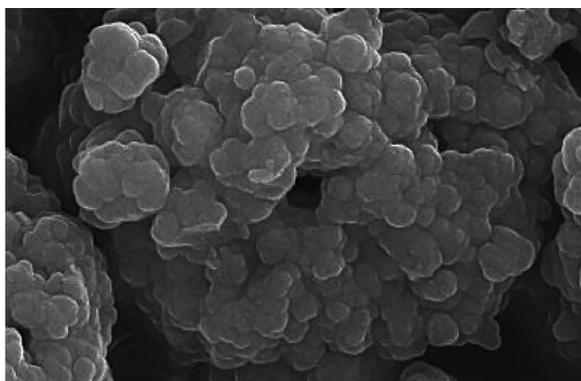


Fig. 4. SEM image of Pd@ABA@SPIONs@SiO₂ catalyst after 5th cycle.

“O” atom of the ligand leads to the final transition state. A reductive elimination of hydrogen halide forms the initial stable catalyst, which is ready for the next cycle of the reaction.

For evaluating the efficiency and applicability of Pd@ABA@SPIONs@SiO₂ nanocatalyst in Mizoroki-Heck cross coupling reaction, a comparison was made between the present catalyst and a number of previously reported ones. For better comparison, the reaction of styrene and bromobenzene was selected and the reaction time and yield of the product was compared for the reaction, which was catalyzed by Pd@ABA@SPIONs@SiO₂ catalyst and those catalyzed by previously reported ones. The results are presented in Table 3. It could be observed in Table 3 that, Pd@ABA@SPIONs@SiO₂ catalyst is highly efficient for this reaction, compared to other reported ones. In addition, the use of a small amount (0.08 mol%) of Pd@ABA@SPION@SiO₂ nanocatalyst, compared to other ones is another advantage of the present catalyst.

of the halide and the “C” atom of the aryl group leads to a more stable intermediate.

In the next step, the alkene participates the reaction, which leads to a C-C bond formation between the alkene and the “C” atom of the aryl halide. This non-stable product forms the second transition state, which forms an intermediate by conformational rotations. A hydrogen transfer reaction leads to the next transition state and forms the desired product, which is coordinated to the palladium via the π bond of the product. Removal of the product via a bond cleavage between the π bond of the product and palladium forms the next intermediate. An intermolecular bond cleavage between palladium and the “N” and “C” atoms of the ligand, and simultaneously bond formation between palladium and the

3. Experimental

3.1. General remarks

All the chemicals, reagents and solvent were purchased from Merck, Germany and Sigma, Germany. TEM images were recorded on a CM 10 Philips instrument. ¹H (500 MHz) spectra were recorded on a Bruker Avance spectrometer in DMSO, d₆ solution with tetramethylsilane (TMS) as an internal standard. A TESCAN T3000 instrument was applied to record the SEM images. OP-TIMA7300DV ICP analyzer was applied for analyzing the palladium content of the catalyst. The FT-IR spectra were recorded on a

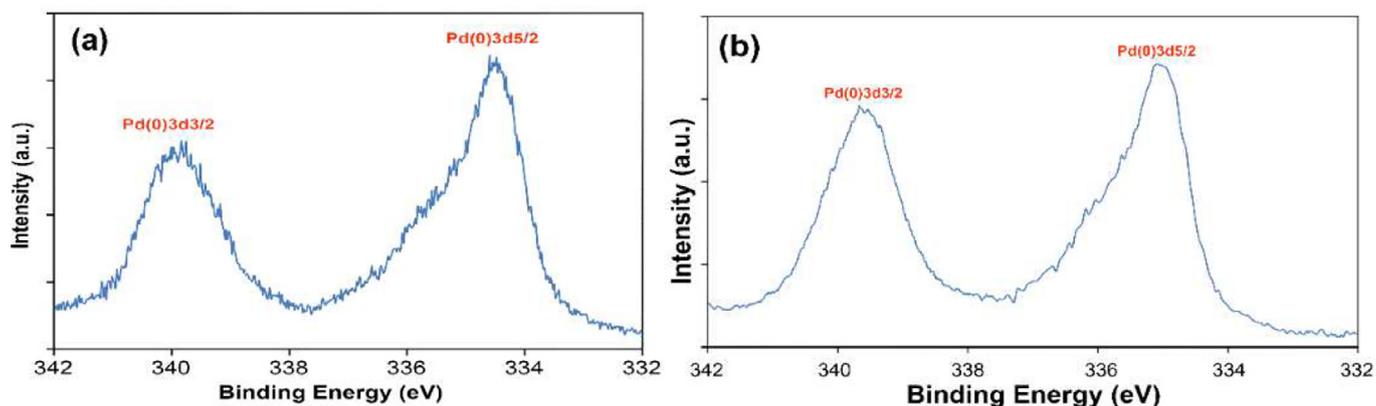
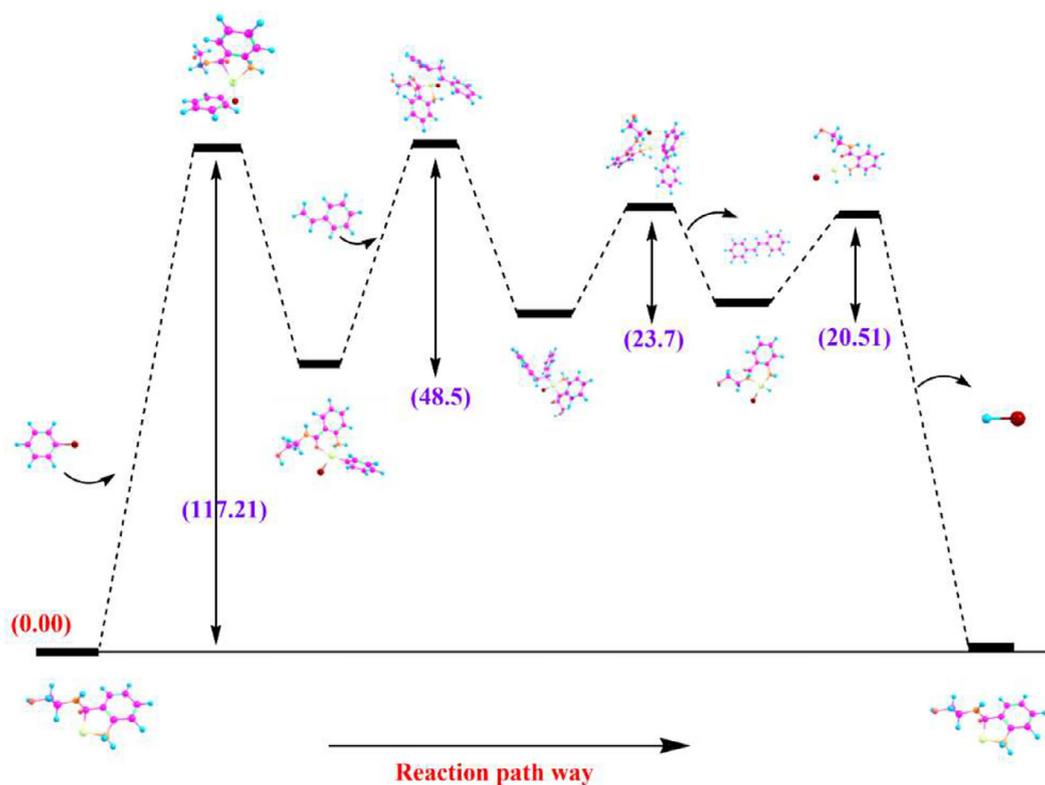


Fig. 5. XPS spectra of Pd@ABA@SPIONs@SiO₂ catalyst (a) before the reaction and (b) after the 5th cycle of the recovery of the catalyst.



Scheme 2. DFT calculation of the mechanism of Pd@ABA@SPIONs@SiO₂ catalyst Mizoroki-Heck reaction.

Table 3

A catalytic activity comparison of Pd@ABA@SPION@SiO₂ with some other catalysts, which are reported in previous reports.

Entry	Catalyst (mol%)	Condition	Time (h)	Yield ^a (%) [ref]
1	TiO ₂ @Pd NPs (1)	DMF, Et ₃ N, 140°C	10	93[33]
2	HMMs-NH ₂ -Pd (4)	NMP, K ₂ CO ₃ , 130°C	20	96[34]
3	Fe ₃ O ₄ -NH ₂ -Pd (5)	NMP, K ₂ CO ₃ , 130°C	24	96[35]
4	Pd@AGu@MGO (1)	EtOH/H ₂ O, K ₂ CO ₃ , r.t.	2	92[23]
5	SMNPs-DF-Pd (1)	Solvent free, DABCO, 140°C	0.9	93[36]
6	CO-NHC@MWCNTs (0.35)	PEG, Li ₂ CO ₃ , 80°C	10	67[37]
7	MPCS-Ti/Pd (0.1)	DMF/H ₂ O, Et ₃ N, 110°C	4	93[38]
8	Pd-BIP-γ-Fe ₂ O ₃ @SiO ₂ (0.5)	DMF, Et ₃ N, 100°C	3.5	82[39]
9	Pd@ABA@SPION@SiO ₂ (0.08)	H ₂ O, NaOAc, r.t.	1	99 ^b

^a Isolated yields

^b current work.

Nicolet Magna FT-IR 550 spectrophotometer using potassium bromide disks. BET of the samples was analyzed by an ASAPTM micromeritics 2020 instrument. The particle size was measured using HORIBA SZ100-Z DLS instrument. Thermo-gravimetric Analyzer (TGA) at heating rate of 10 °C min⁻¹ over the temperature range of 40–600 °C under nitrogen atmosphere.

3.1.1. Preparation of amine modified SPIONs@SiO₂

SPIONs@SiO₂ were synthesized according to the previous reported method [40]. 3-Aminopropyltriethoxysilane (0.1 g) was added to ethanol (30 mL) and the resulting solution was added dropwise to a vigorous mixing sample, containing SPIONs@SiO₂ nanoparticles (100 mg) and ethanol/water mixture (30 mL, 1:2 v/v) and HCl at pH = 4. The reaction mixture was stirred for 24 h and then, the product was isolated by an external magnet and washed

by a mixture of EtOH and water (1:2 v/v, 3 × 5 mL). The product was dried at 100 °C overnight under reduced pressure.

3.1.2. Preparation of ABA@SPIONs@SiO₂

To a mixture of amine modified Fe₃O₄@SiO₂ (100 mg) and trimethylamine (0.1 g) in ethanol was added isatoic anhydride (450 mg) and stirred at 60 °C for 24 h. After the reaction time, the solid was separated by an external magnet and washed with ethanol (3 × 10 mL) and dried in vacuum at 60 °C.

3.1.3. Preparation of Pd@ABA@SPIONs@SiO₂

ABA@SPIONs@SiO₂ (0.1 g) was added to a flask containing dry CH₂Cl₂ (50 mL) and then, Pd(OAc)₂ (5 mmol) was added. The reaction mixture was stirred under an inert atmosphere at room temperature for 24 h. The product was magnetically separated and washed with CH₂Cl₂ (2 × 10 mL) and Et₂O (2 × 10 mL).

Pd@ABA@SPIONs@SiO₂ catalyst was obtained after drying under vacuum for 12 h.

3.1.4. General procedure for Mizoroki-Heck reaction

The reaction mixture, containing halobenzene (1.0 mmol), alkene (1.1 mmol), sodium acetate (1.5 mmol) in H₂O (3.0 mL) and Pd@ABA@SPIONs@SiO₂ catalyst (0.08 mol%) was stirred at room temperature until the reaction completion. TLC was used to monitor the reaction performance. After the reaction was completed, an external magnet was used to separate the nanocatalyst. The catalyst was washed with water and EtOH, and dried in a vacuum oven and retained for re-using in the next reaction. The product of the reaction was separated by extracting the filtrate with ethyl acetate. The organic phase was collected and dried over Na₂SO₄ and then was obtained by evaporating the solvent under reduced pressure. The product was purified by column chromatography, using n-hexane: ethyl acetate (6:1, v/v) as eluent.

3.1.5. Reusability of the catalyst

To study the reusability of Pd@ABA@SPIONs@SiO₂ nanocatalyst, the reaction of styrene and bromobenzene was selected as a sample reaction. The reaction was performed under the optimized conditions and the separation of the catalyst from the reaction mixture was done by an external magnet. The separated nanocatalyst was washed with water and EtOH, and dried under vacuum at room temperature. The recovered nanocatalyst was used directly in the next reaction. The reusability study was evaluated for 10 sequential runs.

3.1.6. DFT calculations

All calculations were performed with Gaussian program 09. B3LY hybrid was used in conjunction with the 6-31G and DKH-DZP (for Pd atom) basis for optimizing all stationary points and transition states in the gas phase. The all electron contracted Gaussian basis set of double zeta valence quality plus polarization functions (DZP) for the atoms from Rb to Xe is presented. The original DZP basis set has been re-contracted, the values of the contraction coefficients were re-optimized using the relativistic DKH Hamiltonian. First of all, the structure of each reactant and its product were optimized. These optimized structures defined the appropriate transition state structure for each mechanism, and optimal transition state structures were obtained with the Qst2 and Qst3 approaches. These calculations were done to find the minimum-energy paths. Moreover, normal vibration frequencies (Hessian force constant matrices) computation confirms that every point on each stationary point is a transition structure or not. One of the methods for identifying the transition state structure is the existence of a negative frequency.

4. Conclusion

In this paper, a novel supported palladium nanocatalyst was designed and fabricated. To this, the superparamagnetic iron oxide nanoparticles were synthesized and encapsulated by silica shells (SPIONs@SiO₂ NPs) and followed by surface functionalization using 2-aminobenzamide, which was then utilized for immobilization of palladium as a bidentate ligand. The immobilized Pd@ABA@SPIONs@SiO₂ nanocatalyst was characterized by various characterization methods. TEM and SEM images showed that the NPs are spherical in shape with an average particle size of about 20–25 nm. As seen in the FT-IR spectrum, the adsorption bond related to the carbonyl functional group in the amide proved the successful surface functionalization of SPIONs@SiO₂ NPs with 2-aminobenzamide functionalities. The presence of palladium in the structure of the nanocatalyst was also proved by XRD and EDS analysis. In addition, XPS spectroscopy showed

the oxidation state of palladium was zero in the fresh and reused Pd@ABA@SPIONs@SiO₂ nanocatalyst samples. The VSM results demonstrated that functionalization of SPIONs@SiO₂ nanoparticles have slightly reduced its magnetization, but it was still superparamagnetic and practical experiments showed that the catalyst was easily separable from the reaction mixture using an external magnet.

Pd@ABA@SPIONs@SiO₂ nanocatalyst was evaluated for Mizoroki-Heck reaction. The optimization studies showed that the optimal reaction condition was observed to be water as solvent, 1.5 equivalent of sodium acetate as base, 0.08 mol% of Pd@ABA@SPIONs@SiO₂ nanocatalyst at room temperature. Several aryl halides reacted with styrene or n-butyl acrylate and gave the products in high isolated yields. The nanocatalyst was magnetically recoverable and did not lose its activity after 10 sequential runs. After the 5th cycle of the recovery, the catalyst was separated and characterized by XPS and SEM methods.

A comparison between the nanocatalyst before reaction and after the 5th cycle showed that its structure and properties has not changed under the reaction conditions. The DFT method was used to study the mechanism of the reaction. The calculations show that palladium is coordinated to the "N" atom of amine and "C" atom of amide groups of 2-aminobenzamide ligand. Additionally, the calculated mechanism shows the role of the nanocatalyst is critical for the reaction performance and after each cycle of the reaction, the catalyst goes back to its initial state and is available for the next reaction cycle.

Declaration of Competing Interest

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

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