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PII:	S0025-5408(20)31496-3
DOI:	https://doi.org/10.1016/j.materresbull.2020.111015
Reference:	MRB 111015
To oppositiv	Matariala Dagagraph Bullatin
to appear in.	
Received Date:	21 March 2020
Revised Date:	5 July 2020
Accepted Date:	27 July 2020

Please cite this article as: Dabiri M, Fazli H, Salarinejad N, Movahed SK, Pd nanoparticles supported on cubic shaped ZIF-based materials and their catalytic activates in organic reactions, *Materials Research Bulletin* (2020), doi: https://doi.org/10.1016/j.materresbull.2020.111015

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Pd nanoparticles supported on cubic shaped ZIF-based materials and their catalytic activates in organic reactions

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Highlights

• A novel Pd@A-ZIF nanocomposites was prepared by anchoring Pd nanoparticle on the surfaces of annealed ZIF cubes.

- The synergistic action between Pd and Zn, and Pd and Co species played a crucial role in highly active catalytic species.
- Pd@A-ZIF nanocomposites show high catalytic activity and reusability.

Abstract

Pd nanoparticles decorated on cubic shaped ZIF-based materials have been successfully prepared. The nanocomposites have been characterized by X-ray diffraction, field emission scanning electron microscopy, N₂ sorption analysis, and transmission electron microscopy. The catalytic activities of synthesized materials were evaluated in Suzuki-Miyaura cross-coupling. The results showed the catalytic activity of Pd@A-ZIF-8 was higher than Pd@A-ZIF-67 and Pd@A-BMZIF. Additionally, the catalytic activities of as-synthesized nanocomposites were studied on the reduction of nitroarenes. The catalytic activity of Pd@A-ZIF-67 was higher than Pd@A-ZIF-8 and Pd@A-BMZIF in the reduction of nitrobenzene. The synergistic action between Pd and Zn, Pd and Co species may play an important role in highly active catalytic species in Suzuki-Miyaura cross-coupling reaction and reduction of nitroarenes, respectively. The reusability of as-synthesized nanocomposites was checked, and the catalytic activity was retained after six consecutive reaction runs.

KEYWORDS: A. nanostructures; B. chemical synthesis; D. catalytic properties.

Introduction

Suzuki-Miyaura cross-coupling reaction is a palladium-catalysed coupling reaction between organoboron species and aryl halides. This reaction is a powerful tools for forming carbon–carbon bonds with broad applications in the preparation of intermediate compounds, pharmaceuticals, biologically, and naturally products that display the importance of this transformation for academia and industries [1–3]. Suzuki–Miyaura cross-coupling reaction has some benefits compared to other coupling reactions: low toxicities, stability, and tolerance

toward the thermal and aqueous condition of boron compounds, easy isolation of by-products from the reaction, and mild reaction conditions [4]. Typically, the Suzuki-Miyaura cross-coupling reaction is often carried out with organometallic homogeneous Pd complexes such as Pd(PPh₃)₄. Despite the relatively high efficiency of these homogeneous systems, the difficulty to separate and reuse the catalyst from the reaction medium is considered as the pressing issue in the sustainable development of the chemical industry [5]. To overcome several issues related to homogeneous Pd catalysts, many efforts have been made to develop heterogeneous Pd catalysts for Suzuki-Miyaura cross-coupling reaction including the immobilization or stabilization of Pd species (ion or nanoparticle) on different supports, such as alumina [6], carbon materials [7], clay [8], metal-organic frameworks [9], metal oxides[10,11], polymers [12], resins [13], silica [14,15], zeolite [16] and heterogeneous complexes [17].

Recently, the use of metal-organic frameworks (MOFs) gained intense attention as solid supports for the immobilization of precious metal catalysts. Shu *et al.* have prepared Pd/MOF-5 as a highly active heterogeneous catalyst [18]. This catalyst applied in ligand- and copper-free Sonogashira coupling of halobenzenes with phenylacetylene which is applicable to a wide range of substrates with good electronic and steric tolerance. Islam et al. have synthesized a new heterogeneous catalyst by grafting Pd(0) nanoparticles at the surface of a the surfaces of a Co-containing metal–organic framework MCoS-1 [19]. This heterogeneous catalyst showed excellent catalytic activities in carbon–carbon coupling reactions, namely Suzuki–Miyaura coupling and Sonogashira coupling. Jiang et al have developed a highly efficient heterogeneous catalyst system for the water-mediated Suzuki–Miyaura and Ullmann coupling reactions of aryl chlorides using porous MIL-101-supported palladium NPs as the catalyst [20]. Haung et al. have reported Pd NPs encapsulated in a series of isoreticular mixed-linker bipyridyl MOFs as catalysts for Suzuki–Miyaura cross-coupling reactions. The modification of MOF linkers serves to unveil the electronic and steric effects of the linker substitution in varying their catalytic properties [21].

Zeolitic imidazolate frameworks (ZIFs) are one of the most promising metal-organic frameworks (MOFs). They are generated by tetrahedral coordination of transition metal cations

(typically Zn²⁺, Co²⁺, etc.) with the nitrogen atoms of 2-methylimidazole linkers [22–24]. ZIFs have the advantages of mild synthesis protocols, porosity, crystallinity, controlled structure, high specific surface area, and exceptional chemical, thermal and hydrothermal stability, which allow them to deliver excellent performance in the field of catalysis [25], drug delivery [26,27], gas sorption and storage [28,29], energy storage [30,31], and electrode materials [32,33]. Recently, they are applied as an efficient heterogeneous catalyst support for various reactions such as Knoevenagel reaction [34], alcohol oxidation [35], trans-esterification [36], 1,3-dipolar cycloadditions [37], Friedlander and Combes condensations [37], CO₂ cycloaddition of epoxides [38], etc. Additionally, ZIFs provide great potential as hosts for various metal nanoparticles such as Cu [39], Ru [40], Pd [41], Pt [42], and Au[43] due to their high porosity and high surface area. The growth of nanoparticles could limit by loading metal nanoparticles into the pores of ZIFs. Also, they prevent the migration and aggregation of nanoparticles during the reaction, thus led to an increase in catalytic activity and stability of nanoparticles.

Hong et al. have proposed a strategy based on the capping agent modulator method to control the shape of ZIF nanocrystals [44]. Among different shapes of ZIFs, the cubic structure exhibited the highest surface area. Additionally, the surface area to volume ratio for a cube structure is higher than other shapes. Based on the above introduction, herein, we have successfully reported the palladium nanoparticles decorated on cubic shaped ZIF-based materials. In the first step, the ZIF-based cubic materials such as ZIF-67, ZIF-8, and BMZIF were synthesized with the assist of a capping agent, cetyltrimethylammonium bromide (CTAB). The ZIF structures were carbonized at low temperature in which the cubic structures were retained. Finally, the Pd nanoparticles (Pd NPs) anchored on annealed cubic shaped ZIF-base by using chemical reduction of H₂PdCl₄ with sodium borohydride (Scheme 1).



Scheme 1 Schematic diagram illustrating the synthesis of Pd@A-ZIF nanocomposites.

Experimental

Synthesis of A-ZIF-67 nanocube:

Co(NO₃)₂·6H₂O (580 mg) was dissolved in deionized water (20 mL) containing cetyltrimethylammonium bromide (CTAB) (20 mg). Then this solution was rapidly injected into an aqueous solution (140 mL) containing 2-methylimidazole (9.08 g) and stirred at room temperature for 20 min. The product was collected by centrifugation and washed by ethanol for several times. ZIF-67 was annealed at 450 °C with a heating rate of 2 °C/min for 2 h in a furnace under a nitrogen atmosphere.

Synthesis of A-ZIF-8 nanocube:

Zn(NO₃)₂·6H₂O (592 mg) was dissolved in deionized water (20 mL) containing CTAB (20 mg). Then this solution was rapidly injected into an aqueous solution (140 mL) containing 2methylimidazole (9.08 g) and stirred at room temperature for 20 min. The product was collected by centrifugation and washed by ethanol for several times. ZIF-8 was annealed at 450 °C with a heating rate of 2 °C/min for 2 h in a furnace under a nitrogen atmosphere.

Synthesis of A-BMZIF nanocube:

Co(NO₂)₂·6H₂O (474 mg) and Zn(NO₃)₂·6H₂O (116 mg) were dissolved in deionized water (20 mL) containing CTAB (20 mg). Then this solution was rapidly injected into an aqueous solution (140 mL) containing 2-methylimidazole (9.08 g) and stirred at room temperature for 20 min. The product was collected by centrifugation and washed by ethanol for several times. BMZIF was annealed at 450 °C with a heating rate of 2 °C/min for 2 h in a furnace under a nitrogen atmosphere.

Synthesis of Pd@A-ZIF-8 nanocomposite:

A-ZIF-8 (100 mg) was dispersed in acetonitrile (100 mL). Then a solution of $PdCl_2$ in CH_3CN (5 mL, 0.025 M) was added dropwise to the reaction mixture and stirred for 2 h. Then a solution of NaBH₄ in H₂O (5 mL) was added dropwise and stirred for 2 h. After that, the mixture was washed and centrifuged with H₂O and ethanol. Finally, it was dried at 70 °C overnight.

Synthesis of Pd@A-ZIF-67 nanocomposite:

A-ZIF-67 (100 mg) was dispersed acetonitrile (100 mL). Then a solution of $PdCl_2$ in CH_3CN (5 mL, 0.025 M) was added dropwise to the reaction mixture and stirred for 2 h. Then a solution of NaBH₄ in H₂O (5 mL) was added dropwise and stirred for 2 h. After that, the mixture was washed and centrifuged with H₂O and ethanol. Finally, it was dried at 70 °C overnight.

Synthesis of Pd@A-BMZIF nanocomposite:

A-BMZIF (100 mg) was dispersed acetonitrile (100 mL). Then a solution of $PdCl_2$ in CH_3CN (5 mL, 0.025 M) was added dropwise to the reaction mixture and stirred for 2 h. Then a solution of NaBH₄ in H₂O (5 mL) was added dropwise and stirred for 2 h. After that, the mixture was washed and centrifuged with H₂O and ethanol. Finally, it was dried at 70 °C overnight.

General procedure for the Suzuki-Miyaura cross-coupling reaction

A mixture of aryl halide (0.5 mmol), phenylboronic acid (0.7 mmol), potassium phosphate (1.0 mmol) and catalyst (0.1 mol% of Pd) in EtOH/H₂O (1:1, 4 mL) as a solvent was mixed in a round bottom flask (10 mL). Then, the resulting mixture stirred at 70 °C. The progress of the reaction was monitored by Thin Layer Chromatography (TLC). After reaction completion, the catalyst

was separated by centrifugation and CH_2Cl_2 was added. The CH_2Cl_2 layer was separated from the water layer using a separatory funnel and followed by drying of the organic layer over Na_2SO_4 . The dried CH_2Cl_2 layer was concentrated under vacuum, and the product was purified by thin-layer chromatography (SiO₂, n-hexane and ethyl acetate) to isolate the corresponding products. The catalyst was washed with EtOH (2 × 10 mL) and H₂O (2 × 10 mL), and was reused for the next run.

General procedure for the reduction of nitroarenes

To the stirred mixture of nitroarene compound (0.4 mmol) and sodium borohydride (10 mmol) in EtOH/H₂O (1:1, 5 mL), catalyst (0.05 mol% of Pd) were added. The progress of the reaction was monitored by TLC. After reaction completion, the catalyst was separated by centrifugation, and ethyl acetate was added. The ethyl acetate layer was separated from the water layer using a separatory funnel and followed by drying of the organic layer over Na₂SO₄. The dried ethyl acetate layer was concentrated under vacuum, and the product was purified by thin-layer chromatography (SiO₂, *n*-hexane and ethyl acetate) to isolate the corresponding products.

Result and discussion

The crystal structure of the synthesized materials is characterized by X-ray diffraction (XRD) (Fig. 1 and Fig. s1). After annealing treatment, the XRD patterns of annealed ZIF materials have been maintained after the annealed process. However, ZIF diffraction peaks disappeared in A-ZIF-67, which indicated the degree of carbonization in ZIF-67 and highlighted the fact that cobalt species would have an impact on catalytic graphitization [45], Diffraction peaks related to Pd are hardly detected in the XRD patterns of Pd@A-ZIF nanocomposites, maybe due to the small palladium nanoparticles.



Fig. 1. XRD patterns of A-ZIF-8, A-ZIF-67, A-BMZIF, Pd@A-ZIF-8, Pd@A-ZIF-67, and Pd@A-BMZIF nanocomposites.

The nitrogen sorption analysis is performed for the characterization of the specific surface area and porous structure of as-synthesized materials. The sorption curves show that all the as-synthesized materials display similar IV-type isotherms with an H3-type hysteresis loop in the larger range of 0.45 - 1.0 P/P₀, proving the presence of mesoporous structures in the composites. Also, the sharp increase at a low relative pressure (P/P₀<0.05) in A-ZIF-8 and A-BMZIF, revealed the presence of micropores structures in these composites. However, the surface area of A-BMZIF was higher than A-ZIF-8 and A-ZIF-67 (Table s1). Additionally, after immobilization of Pd NPs on A-ZIF materials, the specific surface area and pore volume decreased, indicating that the Pd NPs are successfully supported on the A-ZIF materials.



Fig. 2. N₂ sorption isotherms of A-ZIF-8, A-ZIF-67, A-BMZIF, Pd@A-ZIF-8, Pd@A-ZIF-67, and Pd@A-BMZIF nanocomposites.

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) were used to study the morphology and size of the as-synthesized materials (Fig. 3 and Fig. S2-S6). The cubic structure was retained after the annealing process in all of the materials (Fig. 3). However, the TEM and FESEM images of A-ZIF-67 and A-BMZIF showed a rough surface and shrunken facets cubes that are composed of graphitic carbon sheets.



Fig. 3. FESEM images of a) A-ZIF-8, b) A-ZIF-67, and c) A-BMZIF composites and TEM images of d) A-ZIF-8, e) A-ZIF-67, and f) A-BMZIF composites.

After anchoring the Pd NPs on cubic shaped ZIF, these were found dispersed in the A-ZIF materials with an average particle size of 10 nm. Moreover, the aggregated Pd NPs were observed in the Pd@A-ZIF-67 and Pd@A-BMZIF nanocomposites. The cobalt species in the A-ZIF-67 and A-BMZIF cause the excessive growth of Pd NPs during reduction and result in the aggregation of Pd NPs on surface of A-ZIF-67 and A-BMZIF.



Fig. 4. TEM images of a-b) Pd@A-ZIF-8, c-d) Pd@A-ZIF-67, and e-f) Pd@A-BMZIF nanocomposites.

After careful characterization of as-synthesized Pd@A-ZIF, the catalytic activity of these nanostructures is studied in the Suzuki-Miyaura cross-coupling reaction. The model cross-coupling reaction of phenyl iodide and phenylboronic acid is investigated to optimize the reaction parameters (Table 1). The reaction afforded the desired cross-coupling product (biphenyl) in good yield (84%) using EtOH as a solvent in the presence of Pd@A-ZIF-8 (0.1 mol % of Pd) as catalyst and K₂CO₃ (2 eq.) as a base at 70 °C (Table 1, entry 1). Firstly, the effect of solvent was investigated and the reaction was carried out in other solvent systems such as MeOH, H₂O, dimethylformamide (DMF), (Table 1, entries 2-4). When the mixture solvent (H₂O:EtOH) was used, the yield of biphenyl has obviously increased (Table 1, entry 5). In the absence of base, the reaction wholly failed (Table 1, entry 6). Thus, K₃PO₄, NaOH, KOH, NaOAc,

and Et_3N were evaluated as bases for this transformation (Table 1, entries 7-10). K_3PO_4 was the best choice as a base for the Suzuki-Miyaura cross-coupling reaction (Table 1, entry 6). The yield was reduced upon decreasing of the reaction temperature (Table 1, entry 11).

Entry	Catalyst	Solvent	Base	Yield (%) ^b
1	Pd@A-ZIF-8 (0.1 mol% of Pd)	EtOH	K ₂ CO ₃	84
2	Pd@A-ZIF-8 (0.1 mol% of Pd)	MeOH	K ₂ CO ₃	71
3	Pd@A-ZIF-8 (0.1 mol% of Pd)	H2O	K ₂ CO ₃	52
4	Pd@A-ZIF-8 (0.1 mol% of Pd)	DMF	K ₂ CO ₃	49
5	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	K ₂ CO ₃	82
6	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	K ₃ PO ₄	98
7	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	NaOH	71
8	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	КОН	44
9	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	NaOAc	57
10	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	Et₃N	42
11 ^c	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	K ₃ PO ₄	51

Table 1. Optimization of reaction for Suzuki-Miyaura cross-coupling reaction^a

a) Phenyl iodide (0.5 mmol), phenylboronic acid (0.7 mmol), Base (2 eq.), Solvent (3 mL), catalyst, Temp. = 70 °C, Time = 0.5 h.

b) GC yield.

c) Temp. = 50 °C.

Other as-synthesized catalysts (Pd@A-ZIF-67, and Pd@A-BMZIF) were used (Fig. 5). The results showed that the order of the rate of the catalytic activity was Pd@A-ZIF-8 > Pd@A-BMZIF > Pd@A-ZIF-67. Seemingly, the synergistic action between Pd and Zn species mmay play a key role in highly active catalytic species in Suzuki-Miyaura cross-coupling reaction [46]. By decreasing the catalyst loading from 0.1 to 0.05 mol% of Pd, the reaction yield dramatically reduced from 98 to 46%. However, an increasing in the loading of catalyst to 0.15 mol%, did not affect on the yield.



Fig. 5. Suzuki–Miyaura cross-coupling reaction of model reaction in the presence of assynthesized catalysts.

Using the optimal reaction conditions, the scope of the Suzuki-Miyaura cross-coupling reaction was investigated (Table 2). In general, aryl iodide, bearing an electron-withdrawing substituent (p-NO₂ and p-COMe), was more reactive and produced higher yield (77% yield) (Table 2, entries 3 and 4) than those analogs bearing the electron-donating substituents (p-Me) (Table 2, entry 2). Similar reactivity was observed for aryl bromides (Table 2, entries 7-11).

Additionally, the slight influence of the steric effect was observed (Table 2, entry 5). Unfortunately, the presence of CTAB as a phase transfer reagent was necessary for the Suzuki-Miyaura cross-coupling reaction of phenyl chloride with phenyl boronic acid and the catalytic system was less effective in generating corresponding cross-coupled product in moderate yield (Table 2, entry 11).

	X +	он Pd@ ^В _ ОН	A-ZIF-8	
Entry	Y	X	Yield (%) ^b	TOF (h ⁻¹)
1	Н	I	98	1960
2	<i>p</i> -Me		85	1700
3	p-NO ₂	T	98	1960
4	<i>p</i> -COMe	I	94	1880
5	<i>o</i> -Me		82	1640
6 ^c	Н	Br	98	980
7 ^c	<i>p</i> -Me	Br	78	780
8 ^c	<i>p</i> -OMe	Br	89	890
9 ^c	<i>p</i> -COMe	Br	91	910
10 ^c	p-NO ₂	Br	93	930
11 ^d	Н	Cl	69	230

Table 2. Pd@A-ZIF-8 nanocomposite-catalyzed Suzuki–Miyaura cross-coupling reaction^a

a) Aryl halide (0.5 mmol), phenylboronic acid (0.7 mmol), K_3PO_4 (1.0 mmol), Pd@A-ZIF-8 (0.1 mol% of Pd), H_2O :EtOH (1:1, 4 mL), Temp. = 70 °C, Time = 0.5 h.

b) Isolated yield.

c) Time = 1 h.

d) Pd@A-ZIF-8 (0.2 mol% of Pd), CTAB (1 mmol), Temp. = 90 °C, Time = 1.5 h.

The recyclability of the Pd@A-ZIF-8 nanocomposite was examined upon for the crosscoupling reaction of phenyl iodide and phenylboronic acid. After completion of the reaction, the mixture was easily centrifuged and the separated the solid catalyst from the reaction mixture was then subjected to the next catalytic cycle. The catalyst would be recovered and reused for at least six times without significant loss of catalytic activity (Fig. 6a). Moreover, the TEM analysis showed that the morphology and size distribution of Pd@A-ZIF-8 did not change after the 6th cycle. (Fig. 6b). The metal leaching of the catalyst was accomplished by using inductively coupled plasma-optical emission spectrometry (ICP-OES). The results of the recovered Pd@A-ZIF-8 nanocomposite showed 2.8 % leaching of palladium after six cycles. These results demonstrated the heterogeneous character of the Pd@A-ZIF-8 nanocomposite. In addition, the reused Pd@A-ZIF-8, Pd@A-ZIF-67, and Pd@BMZIF nanocomposites were characterized by XRD analysis after six consecutive reaction runs (Fig. S7). The results show that the crystalline structure had no apparent change, indicating that nanocomposites possessed the relative high stability.



Fig. 6. a) Pd@A-ZIF-8 nanocomposite recycling studies and b) TEM image of Pd@A-ZIF-8 nanocomposite after six consecutive reaction runs.

Aromatic amines and their derivates are one of the most important functional groups in nature, constitute versatile building blocks in synthetic organic chemistry. They play an important role in antioxidant, dyes, herbicides, polymers, rubbers, and pharmaceuticals [47]. Aromatic amines are mainly produced by catalytic hydrogenation of the corresponding nitroaromatic compounds [48]. Thus, the catalytic activity of Pd@A-ZIF nanocomposite was further evaluated for the reduction of nitroarenes. The catalytic activity of the Pd@A-ZIF nanocomposite was studied by the model reduction of nitrobenzene. Initial studies were accomplished upon the reduction of nitrobenzene with sodium borohydride as a model reaction using Pd@A-ZIF-8 (0.05 mol% of Pd) as the catalyst in H₂O:EtOH for 1 h (Fig. 7). Then, the reaction was performed with different as-synthesized catalysts. Among the catalysts tested, Pd@A-ZIF-67 was found to be the most effective catalyst since it gave the highest yield of the product. The results showed that the order of the rate of the catalytic activity in the reduction of nitrobenzene was Pd@A-ZIF-67> Pd@A-BMZIF > Pd@A-ZIF-8. Probably, the synergistic action between Pd and Co species may play a crucial role in highly active catalytic species in the reduction of nitroarene [49,50]. Increasing the catalyst loading from 0.05 to 0.025 mol% of Pd had no effect on the yield, whereas decreasing the loading of catalyst to 0.1 mol% resulted in lower conversion and vield.



Fig. 7. Optimization of the reaction conditions for the reduction of nitrobenzene (nitrobenzene (0.4 mmol), NaBH₄ (10.0 mmol), Catalyst (x mol% of Pd), H₂O:EtOH (1:1, 25 mL), Temp. = r.t., Time = 1h, under air; Isolated yield.

Under the optimized reaction conditions, the scope of Pd@A-ZIF-67 catalysed reduction was evaluated over various nitroarenes with structurally divergent functional groups. It was found that the nitroarenes possessing the hydroxyl substituent (o-OH, m-OH, and p-OH) gave good yields of corresponding anilines in a very short amount of time (Table 3, entries 2–4). The nitrophenols (o-NP, m-NP, and p-NP) gave good yields of corresponding anilines. m-NP was investigated as the most reactive substrate among all the three nitrophenols. The reaction proceeded via the formation of nitrophenolate and the delocalization of the oxygen's negative charge throughout the benzene ring. The p-nitrophenolate ion are the most stable anion compared to o-nitrophenolate and m-nitrophenolate because of less effective resonance coupled with the particular degree of steric effect between the substituents in ortho-position. m-NP is the least stable and the most reactive among all the three nitrophenols. Nitroarenes with

electron-releasing substituents such as p-OMe, p-Me, and p-NH₂ and electron-withdrawing substituents such as p-Cl and p-Br also produced the corresponding anilines in good yields (Table 3, entries 5–9). The halo-substituted nitroarenes could be reduced to the corresponding anilines with no discernible dehalogenation (Table 3, entries 8–9).





a) Nitroarene (0.4 mmol), NaBH₄ (10.0 mmol), H₂O:EtOH (1:1, 25 mL), Pd@A-ZIF-67 nanocomposite (0.05 mol% of Pd), Temp. = r.t., Time = 1h, under air.

b) Isolated yield.

Furthermore, the catalytic cycling tests were performed to study the stability of the Pd@A-ZIF-67 nanocomposite for the reduction of *p*-nitrophenol. For this purpose, after completing of reactions, the catalyst was centrifuged for repeated use. After the 6th cycle, the nanocomposite showed high catalytic activity for the reduction of *p*-nitrophenol, which indicated the high stability of the nanocomposite (Table 4).

Table 4. Reusability of the Pd@A-ZIF-67 nanocomposite for the reduction of p-nitrophenol^a

Reaction cycle	1st	2nd	3rd	4th	5th	6th
Yield (%) ^b	95	94	90	86	86	82

a) p-nitrophenol (0.4 mmol), NaBH₄ (10.0 mmol), Pd@A-ZIF-67 nanocomposite (0.05 mol% of Pd), H₂O:EtOH (1:1, 25 mL), Temp. = r.t., Time = 1h, under air;

b) Isolated yield.

The catalytic performance of our catalyst was compared with those previously reported palladium-based heterogeneous catalytic methods in terms of catalyst loading, TOF and size of nanoparticles for the reduction of p-NP (Table 5). The results demonstrate that the Pd@A-ZIF-67 nanocomposite is highly effective (TOF: 1840 h⁻¹) in comparison to previously reported catalysts because our catalytic reaction was carried out with a very low loading of the catalyst. This fact could be attributed to the synergistic action between Pd and Co species which may play a crucial role in highly active catalytic species in the reduction of nitroarenes.

Table 5. Comparison of the efficiency of various palladium-based heterogonous catalysts in the reduction of *p*-nitrophenol

Entry	Catalyst	Size of NPs	TOF (h⁻¹)	Catalyst (mol%)	Ref.
		(nm)			

1	Pd@A-ZIF-67	10	1840	0.05	This work
2	Fe3O4@N-C@Pd	25-30	980	1	[51]
3	Pd@NAC-T	2	99	0.5	[52]
4	Pd/oMWCNT	2-3	252	148	[53]
5	Pd/ZnO	-	0.9	30.5	[54]
6	Pd/SPB-PS	2-4	820	0.37	[55]

Conclusions

In conclusion, we have developed the design and synthesis of Pd nanoparticles on cubic shaped ZIF-based materials. The ZIF-based cubic materials such as ZIF-67, ZIF-8, and BMZIF were synthesized with the assist of a capping agent (CTAB). The resulted cubic shaped ZIFs were annealed under inert atmosphere. Finally, the Pd nanoparticles anchored on cubic shaped ZIF by using chemical reduction of PdCl₂(CH₃CN)₂ with sodium borohydride. The catalytic activities of synthesized materials were evaluated in Suzuki-Miyaura cross-coupling. The results showed the catalytic activity of Pd@A-ZIF-8 was higher than Pd@A-ZIF-67 and Pd@A-BMZIF. Additionally, the catalytic activities of as-synthesized nanocomposites were studied on the reduction of nitroarenes. The catalytic activity of Pd@A-ZIF-67 was higher than Pd@A-ZIF-8 and Pd@A-BMZIF in the reduction of nitrobenzene. The synergistic action between Pd and Zn, Pd and Co species may play an important role in highly active catalytic species in Suzuki-Miyaura cross-coupling reaction and reduction of nitroarenes, respectively. Also, the reusability of as-synthesized nanocomposites was checked, and the catalytic activity was retained after six consecutive reaction runs.

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Conflicts of interest

There are no conflicts to declare.

Declaration of interests

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.

Acknowledgements

We gratefully acknowledge financial assistance from the Research Council of Shahid Beheshti University and the Iranian National Science Foundation (Proposal No: 96016966).

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Figure captions

Fig. 1. XRD patterns of A-ZIF-8, A-ZIF-67, A-BMZIF, Pd@A-ZIF-8, Pd@A-ZIF-67, and Pd@A-BMZIF nanocomposites.

Fig. 2. N₂ sorption isotherms of A-ZIF-8, A-ZIF-67, A-BMZIF, Pd@A-ZIF-8, Pd@A-ZIF-67, and Pd@A-BMZIF nanocomposites.

Fig. 3. FESEM images of a) A-ZIF-8, b) A-ZIF-67, and c) A-BMZIF composites and TEM images of d) A-ZIF-8, e) A-ZIF-67, and f) A-BMZIF composites.

Fig. 4. TEM images of a-b) Pd@A-ZIF-8, c-d) Pd@A-ZIF-67, and e-f) Pd@A-BMZIF nanocomposites.

Fig. 5. Suzuki–Miyaura cross-coupling reaction of model reaction in the presence of assynthesized catalysts.

Fig. 6. a) Pd@A-ZIF-8 nanocomposite recycling studies and b) TEM image of Pd@A-ZIF-8 nanocomposite after six consecutive reaction runs.

Fig. 7. Optimization of the reaction conditions for the reduction of nitrobenzene (nitrobenzene (0.4 mmol), NaBH₄ (10.0 mmol), Catalyst (x mol% of Pd), H₂O:EtOH (1:1, 25 mL), Temp. = r.t., Time = 1h, under air; Isolated yield

Table captions

Table 1. Optimization of reaction for Suzuki-Miyaura cross-coupling reaction^a

Table 2. Pd@A-ZIF-8 nanocomposite-catalyzed Suzuki–Miyaura cross-coupling reaction^a

Table 3. The scope of reduction of nitroarenes over Pd@A-ZIF-67 nanocomposite^a

Table 4. Reusability of the Pd@A-ZIF-67 nanocomposite for the reduction of p-nitrophenol^a

Table 5. Comparison of the efficiency of various palladium-based heterogonous catalysts in thereduction of *p*-nitrophenol



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Entry	Catalyst	Solvent	Base	Yield ^b
1	Pd@A-ZIF-8 (0.1 mol% of Pd)	EtOH	K ₂ CO ₃	84
2	Pd@A-ZIF-8 (0.1 mol% of Pd)	MeOH	K ₂ CO ₃	71
3	Pd@A-ZIF-8 (0.1 mol% of Pd)	H2O	K ₂ CO ₃	52
4	Pd@A-ZIF-8 (0.1 mol% of Pd)	DMF	K ₂ CO ₃	49
5	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	K ₂ CO ₃	82
6	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	K ₃ PO ₄	98
7	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	NaOH	71
8	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	кон	44
9	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	NaOAc	57
10	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	Et ₃ N	42
11 ^c	Pd@A-ZIF-8 (0.1 mol% of Pd)	H ₂ O:EtOH (1:1)	K ₃ PO ₄	51

Table 1.	Optimization	of reaction	for Suzuki-Mi	yaura cross-cou	pling reaction ^a
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a) Phenyl iodide (0.5 mmol), phenylboronic acid (0.7 mmol), Base (2 eq.), Solvent (3 mL), catalyst, Temp. = 70 °C, Time = 0.5 h.

b) GC yield.

c) Temp. = 50 °C.

	¥ +	он В он —	Pd@A-ZIF-8	
Entry	Ŷ	X	Yield (%) ^b	TOF(h ⁻¹)
1	Н	I	98	1960
2	<i>p</i> -Me	I	85	1700
3	p-NO ₂	Ι	98	1960
4	p-COMe	I	94	1880
5	<i>o</i> -Me	I	82	1640
6 ^c	н	Br	98	980
7 ^c	<i>p</i> -Me	Br	78	780
8 ^c	<i>p</i> -OMe	Br	89	890
9 ^c	p-COMe	Br	91	910
10 ^c	p-NO ₂	Br	93	930
11 ^d	н	Cl	69	230

Table 2. Pd@A-ZIF-8 nanocomposite-catalyzed Suzuki–Miyaura cross-coupling reaction^a

a) Aryl halide (0.5 mmol), phenylboronic acid (0.7 mmol), K₃PO₄ (1.0 mmol), Pd@A-ZIF-8 (0.1 mol% of Pd), H₂O:EtOH (1:1, 4 mL), Temp. = 70 °C, Time = 0.5 h.

b) Isolated yield.

c) Time = 1 h.

d) Pd@A-ZIF-8 (0.2 mol% of Pd), CTAB (1 mmol), Temp. = 90 °C, Time = 1.5 h.

-NH₂

Fntry	Nitroarene	Aniline	Yield(%) ^b	TOF (h ⁻¹)
Linciy	Without effe	, and the	11010(70)	
1		NH ₂	98	1960
2		NH ₂ OH	90	1800
3		HO NH ₂	98	1960
4			92	1840
5			92	1840
6			89	1780
7			87	1740
8	Br-NO2	Br NH2	89	1780
9		H ₂ N-NH ₂	91	1820

Table 3. The scope of reduction of nitroarenes over Pd@A-ZIF-67 nanocomposite^a

EtOH:H₂O (1:1), NaBH₄

-NO₂

Pd@A-ZIF-67 (0.05 mol% Pd)

a) Nitroarene (0.4 mmol), NaBH₄ (10.0 mmol), H₂O:EtOH (1:1, 25 mL), Pd@A-ZIF-67 nanocomposite (0.05 mol% of Pd), Temp. = r.t., Time = 1h, under air.

b) Isolated yield.

Table 4. Reusability of the Pd@A-ZIF-67 nanocomposite for the reduction of *p*-nitrophenol^a

Reaction cycle	1st	2nd	3rd	4th	5th	6th
Yield[b] (%)	95	94	90	86	86	82

a) *p*-nitrophenol (0.4 mmol), NaBH₄ (10.0 mmol), Pd@A-ZIF-67 nanocomposite (0.05 mol% of

Pd), $H_2O:EtOH$ (1:1, 25 mL), Temp. = r.t., Time = 1h, under air;

b) Isolated yield.

Entry	Catalyst	Size of NPs (nm)	TOF (h ⁻¹)	Catalyst (mol%)	Ref.
1	Pd@A-ZIF-67	10	1840	0.05	This work
2	Fe3O4@N-C@Pd	25-30	980	1	[51]
3	Pd@NAC-T	2	99	0.5	[52]
4	Pd/oMWCNT	2-3	252	148	[53]
5	Pd/ZnO	-	0.9	30.5	[54]
6	Pd/SPB-PS	2-4	820	0.37	[55]

Table 5. Comparison of the efficiency of various palladium-based heterogonous catalysts in thereduction of *p*-nitrophenol