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Ligandless C–C bond formation via Suzuki–Miyaura reaction in micelles or water–ethanol solution using PdPtZn and PdZn nanoparticle thin films

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PdPtZn and PdZn nanoparticle (NP) thin films were synthesized by the reduction of [PdCl$_2$(cod)], [PtCl$_2$(cod)] (cod = *cis,cis*-1,5-cyclooctadiene) and [Zn(acac)$_2$] (acac = acetylacetonate) complexes at an oil–water interface. The structure and morphology of the as-prepared NPs were characterized with X-ray diffraction, transmission electron microscopy and energy dispersive analysis of X-rays. Catalytic activity of the prepared NPs was investigated in the Suzuki–Miyaura cross-coupling reaction in H$_2$O–EtOH and various micellar media systems such as cetyltrimethylammonium bromide (cationic surfactant), sodium dodecylsulfate (anionic surfactant) and Pluronic P123 (non-ionic surfactant). PdPtZn and PdZn thin films exhibited higher catalytic activity compared to Pd thin film in the Suzuki–Miyaura coupling reaction due to the appropriate interaction between palladium, platinum and zinc metals. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: palladium/platinum/zinc nanoparticles; thin film; heterogeneous catalyst; carbon–carbon coupling; micelle

Introduction

Nanoparticles (NPs) are of considerable interest in catalysis, and this subject has undergone tremendous growth during the past few years.[1] It has been revealed that metal catalyst NPs with specific size and shape exhibit a high surface area and a high concentration of reactive sites resulting in improved catalytic performance over conventional catalysts.[2,3]

The formation of carbon–carbon bonds through metal-catalysed cross-coupling processes stands out as one of the most frequently utilized strategies in the design of nanomaterials of complex molecules.[4] Although homogeneous catalytic systems generally exhibit better activity and selectivity than heterogeneous systems, heterogeneous catalysts have many advantages over their homogeneous counterparts, including easy removal from reaction mixtures and catalyst recyclability.[5] Palladium- and platinum-based nanomaterials are very important due to their many applications.[6–9] Palladium-catalysed Suzuki–Miyaura coupling reaction, which involves the homogeneous cross-coupling reaction of aryl halides with organoboron compounds, is one of the most efficient and clean strategies for the construction of aromatic C–C bonds.[10] Oxidative addition and reductive elimination are key steps in Suzuki–Miyaura coupling reactions. Also, metal–metal interaction has a significant effect on oxidative addition as rate-determining step. For example, the rate of the oxidative addition step in Suzuki–Miyaura coupling reaction is accelerated due to Pd–Pt interaction. As mentioned by Aurrecoechea and co-workers,[11] the Pd–Zn interaction in the reductive elimination step is found to be favoured. Furthermore, Zn as an environmentally friendly metal, which decreases the cost of alloy systems, is important in design and preparation of nanocatalysts.

Micelles are especially simple spherical supramolecules, which are formed by amphiphiles in water. The strong polarity gradient present between the hydrophilic surface and the hydrophobic core of a micelle means that both non-polar and polar reagents can be solubilized. This solubilization results in reactants becoming more concentrated within the micelle than in the surrounding water phase and leads to an acceleration of a reaction and causes selective effects.[12]

Generally, phosphine ligands are used in palladium-catalysed processes, but most of them are toxic, expensive and sensitive to water or air.[13] A ligandless approach for the C–C cross-coupling reaction has attracted increased attention in recent years due to low cost. Recently, employing readily available aryl chlorides in these transformations has received increasing attention, and a number of effective catalytic systems have been developed for this purpose.[13,14]

Self-assembly at a liquid–liquid interface is a powerful experimental route to novel nanomaterials and has received much attention.[15–23] This method, developed by Rao and co-workers, has been extensively used in synthesizing various nanostructure thin films.[19–23] The method used to prepare a thin film at an oil–water interface involves dissolving a suitable organic derivative of the metal in the organic layer and injecting an appropriate reducing reagent in the aqueous layer. The product formed by the reaction at the interface contains ultrathin nanocrystalline particles. By controlling the reaction parameters, it has been possible to obtain

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isolated nanocrystals with narrow size distribution or well-formed films of the nanocrystals. The oil–water interfacial assembly strategy provides a powerful bottom-up approach for nanofilm production due to low cost and low environmental impact.

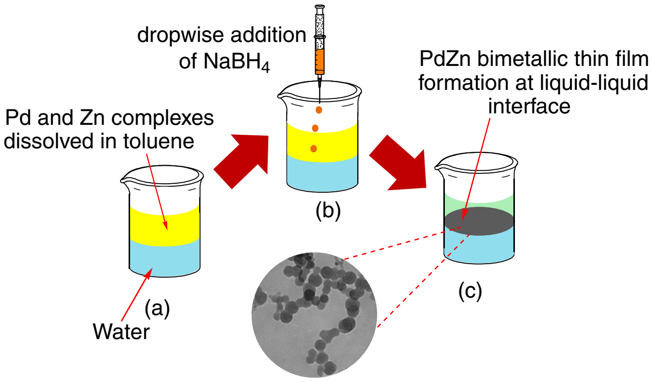
Recently, Fe_3O_4 NPs, Pd/aminoclay NPs and Fe_3O_4/Pd/r-GO NPs have been investigated as efficient catalysts for C–C bond formation.[24–26] Also, we have investigated thin-film formation of Pd, Pd/r-GO NPs at an oil–water interface as an effective catalyst for Suzuki–Miyaura reaction in water.[27] In the work reported in this article, we succeeded in the synthesis of PdPtZn and PdZn NP thin films in the absence of a stabilizer by the reduction of [$PdCl_2$(cod)], [$PtCl_2$(cod)] (cod = *cis,cis*-1,5-cyclooctadiene) and [$Zn(acac)_2$] (acac = acetylacetonate) complexes at a toluene–water interface. This strategy is an easy and inexpensive method for production of alloy thin films and only a beaker and a syringe are required for a high-quality thin film to be easily produced in a short time. Then, these NPs were used as ligandless catalysts for the Suzuki–Miyaura reaction in H_2O–EtOH or micellar media.

Experimental

All of the chemical compounds were purchased from Merck. The [$PdCl_2$(cod)] and [$PtCl_2$(cod)] complexes were synthesized using reported procedures.[28] The [$Zn(acac)_2$] complex was purchased from Merck. Powder X-ray diffraction (XRD) patterns were obtained using a Bruker AXS (D8 Advance) instrument employing the reflection Bragg–Brentano geometry with Cu Kα radiation (λ = 1.54184 Å). Energy-dispersive analysis of X-rays (EDAX) was carried out using a Philips XL30 instrument with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained with a Philips CM-10 microscope operated at 100 kV. Infrared spectra were recorded using a JASCO FT/IR-680 plus spectrometer. ^{1}H NMR spectra were obtained with a Bruker 400 MHz Ultra-shield spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard.

Preparation of PdPtZn and PdZn NP thin films

Typically, to prepare PdPtZn thin films, 25 ml of deionized water was added to a 25 ml toluene solution of [$PdCl_2$(cod)]–[$PtCl_2$(cod)]–[$Zn(acac)_2$] (1:1:1), in a 100 ml beaker. Once the two layers were stabilized, a freshly prepared aqueous solution of $NaBH_4$ (10 ml, 0.1 M) was injected into the aqueous layer using a syringe with minimal disturbance to the toluene layer. The onset of reduction was marked by a coloration of the toluene–water interface. With the passage of time, the colour became more vivid, finally resulting in a film at the liquid–liquid interface. The actual Pd:Pt:Zn molar ratio for PdPtZn NPs was estimated to be 31:35:34 using an inductively coupled plasma analysis, which was close to the calculated PdPtZn ratio (1:1:1) from the starting metal precursors. A similar procedure was applied for the synthesis of PdZn NP thin films, as shown in Scheme 1.



Scheme 1. Schematic illustration of formation of PdZn bimetallic thin film.

General procedure for Suzuki–Miyaura cross-coupling reaction

Phenylboronic acid (1.5 mmol) was added to a flask containing the PdPtZn NPs catalyst and K_2CO_3 (2 mmol) in micelles (1 CMC, 5 ml). This mixture placed in an oil bath at 80°C. Once the mixture reached this temperature the reaction was initiated by the addition of aryl halide (1.0 mmol). After completion of the reaction (monitored using TLC), the reaction mixture was cooled to room temperature, and then dichloromethane (3 × 5 ml) was added to the reaction vessel. The organic phase was separated and dried over anhydrous $MgSO_4$. Subsequently, the solution was evaporated and the resulting compound was washed with cool hexane to afford the desired pure product.

Results and discussion

In this study, PdZn NP thin film was synthesized by the reduction of [$PdCl_2$(cod)] in the presence of [$Zn(acac)_2$] complex as zinc precursor at a toluene–water interface, as shown in Scheme 1. These complexes were dissolved in toluene at room temperature and then contacted with water. The aqueous solution of $NaBH_4$ was injected into the interface with minimal disturbance to initiate the reduction, and thin-film formation was indicated by an interface colour change from yellow to black.

The crystal structure of the PdZn NP thin film was investigated using XRD. Figure S1 shows the XRD pattern recorded for the PdZn NP thin film. The five main diffraction peaks can be assigned as the (111), (200), (220), (311) and (222) indices of face-centred cubic Pd.[27] Other diffraction peaks confirm the Zn structure and correspond to the planes (002), (100), (101), (102), (103), (110) and (004).[29] Relative to the same reflections for Pd, the diffraction peaks of the PdZn thin film are shifted to higher 2θ values, revealing decreased lattice parameters and a high level of alloying.[30]

As determined using EDAX (Fig. S2), the PdZn thin film is composed of Pd and Zn with a molar ratio of Pd:Zn = 52:48, which is close to the calculated PdZn ratio (1:1) from the starting metal precursors. PdZn NP thin films have particles of uniform spherical shape with smaller light dots which can obviously confirm PdZn alloy formation. Figures 1(a)–(c) show TEM images of PdZn with an average diameter of 44 nm. Figure 1(d) shows a histogram of particle size distribution.

PdPtZn NP thin film was prepared at an oil–water interface as a facile method. The XRD pattern resulting from PdPtZn NPs shows a number of prominent Bragg reflections with indices [(111), (200), (220), (311) and (222)] as Pt(0) and Pd(0) (Fig. 2).[27] The seven diffraction peaks confirm the Zn structure and correspond to the planes [(002), (100), (101), (102), (103), (110) and(004)].[29]

The chemical composition of the thin film was determined using EDAX, confirming the presence of Pd, Pt and Zn elements (Fig. S3). Figures 3(a)–(c) show TEM images of the as-prepared PdPtZn NP thin film, which includes spherical structures. The average diameter of the PdPtZn NP thin film particles is approximately 11.6 nm (Fig. 3(d)).

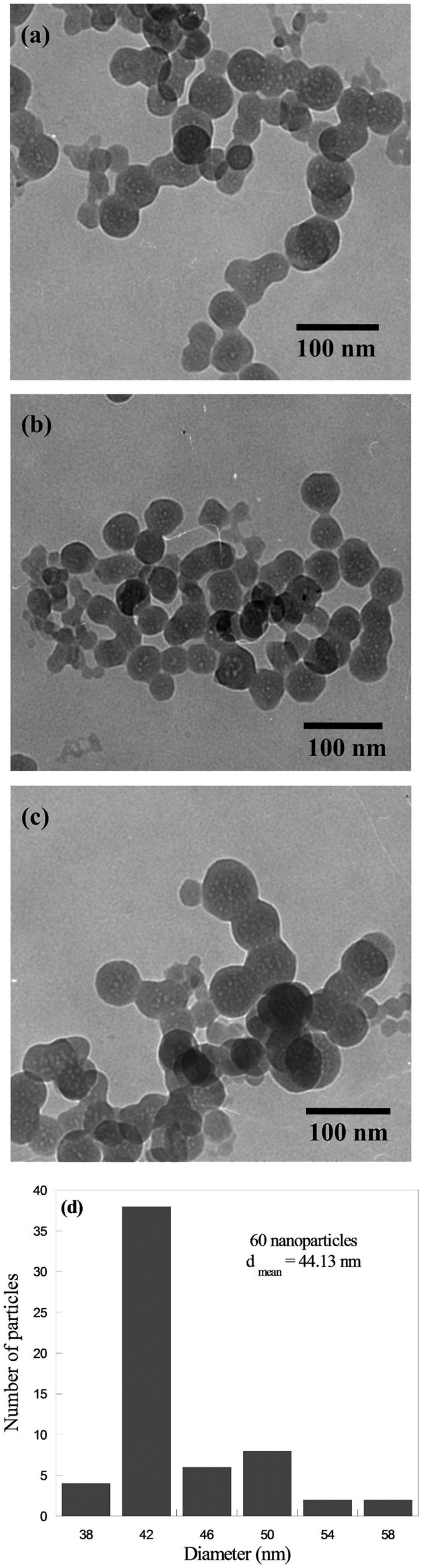


Figure 1. (a–c) TEM images of PdZn NP thin film with an average particle diameter of 44 nm. (d) Histogram of particle size distribution.

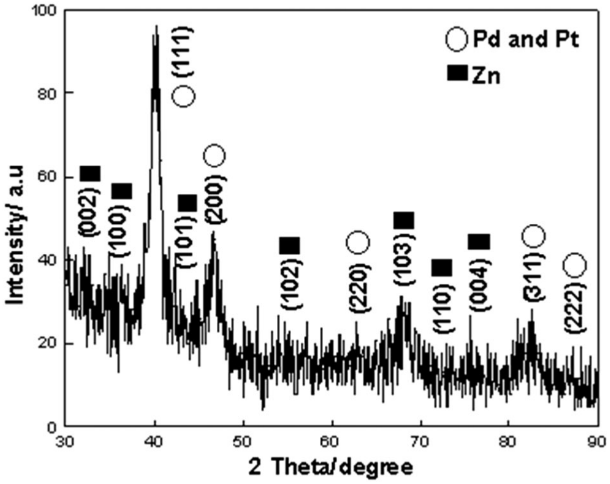


Figure 2. XRD pattern of PdPtZn NP thin film deposited on glass.

Catalytic activity

The PdPtZn and PdZn NP thin films were used as efficient recoverable catalysts in the Suzuki–Miyaura coupling reaction. We initiated our study of the Suzuki–Miyaura cross-coupling reaction by optimizing the conditions in terms of amount of NPs and solvent.

The choice of solvent has a significant impact on the efficiency of the cross-coupling reaction. The reaction of bromobenzene with phenylboronic acid was carried out in the presence of the PdZn NP thin film using various solvents. According to the results given in Table 1, the biphenyl product is detected in a low yield when the reaction is carried out in water and EtOH (Table 1, entries 1 and 2). Better conversion of biphenyl is observed for H_2O–EtOH (1:1) (Table 1, entry 3). K_2CO_3 was used as a base for optimizing the conditions of the reaction. Also, in the presence of PdPtZn NPs as catalyst, the reaction of bromobenzene with phenylboronic acid in H_2O, H_2O–EtOH (1:1), H_2O–sodium dodecylsulfate (SDS), H_2O–Pluronic P123 (P123) and H_2O–cetyltrimethylammonium bromide (CTAB) for 60 min was performed. According to the results given in Table 1, biphenyl product is detected only in trace amounts when the reaction is carried out in H_2O, EtOH and H_2O–EtOH (1:1) (Table 1, entries 1–3). When employing H_2O–SDS and H_2O–P123, the reactions proceed smoothly to give a marked enhancement in yield (Table 1, entries 4 and 5). Evidently, when H_2O–CTAB is used as solvent, an excellent yield (96%) is obtained (Table 1, entry 6). The Suzuki coupling reaction of bromobenzene with phenylboronic acid (H_2O–EtOH (1:1) for PdZn and H_2O–CTAB for PdPtZn) at various temperatures (Table S1) was investigated, and then 80°C was selected as reaction temperature in aqueous solutions (see supporting information).

A series of reactions were performed with various amounts of catalyst to test the reaction feasibility with catalyst concentration. The optimal amount of the PdPtZn catalyst was determined from the reaction of bromobenzene with phenylboronic acid at 80°C in micellar system of CTAB. From Table 2 it is evident that an increase in the amount of PdPtZn catalyst results in an increase in yield of the cross-coupled product. The optimum amount of the PdPtZn catalyst is 0.8 mol% of Pd (Table 2).

Further investigations were focused on application of the optimized reaction conditions to Suzuki–Miyaura coupling reactions of aryl halides. The results for related experiments are summarized in Table 3. Various substrates including those with electron-donating and electron-withdrawing groups can be coupled in good reaction yields (70–98%) in short reaction times.

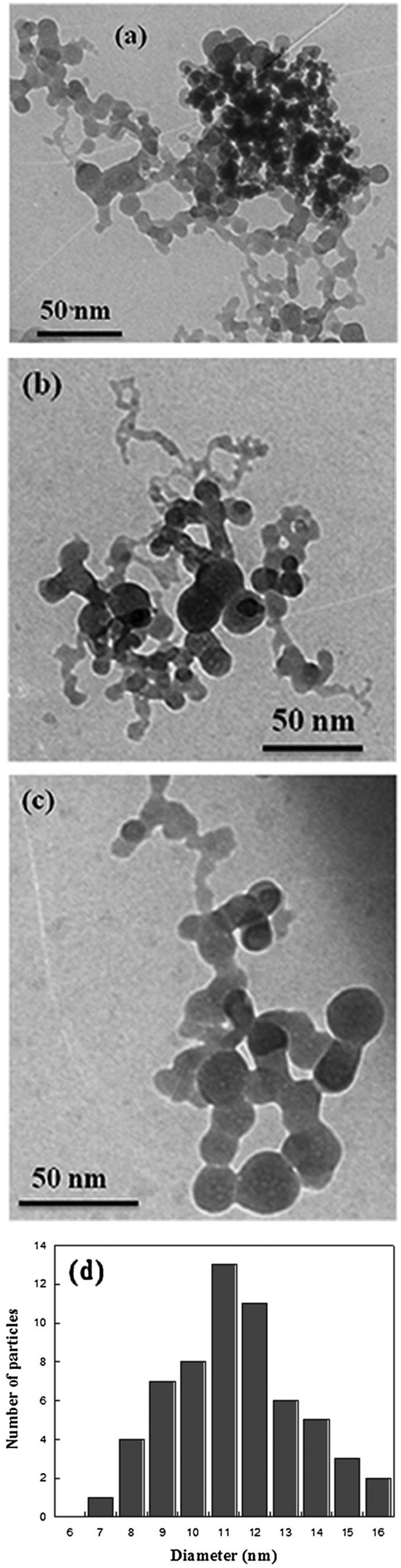


Figure 3. (a–c) TEM images of PdPtZn NP thin film. (d) Histogram of particle size distribution.

Table 1. Suzuki–Miyaura coupling reaction of bromobenzene with phenylboronic acid in various solvents in the presence of PdZn and PdPtZn NP catalysts at 80°C in 60 min

Entry	Solvent	PdZn (mol%)^a; yield (%)^b	PdPtZn (mol%)^a; yield (%)^b
1	H_2O	1.5; 40	1.0; trace
2	EtOH	1.5; 70	1.0; trace
3	H_2O–EtOH (1:1)	1.5; 94	1.0; trace
4	H_2O–SDS	1.5; 20	1.0; 80
5	H_2O–P123	1.5; trace	1.0; 90
6	H_2O–CTAB	1.5; 15	1.0; 96

[a] Pd mol%.
[b] Isolated yield.

Table 2. Variation of amount of catalyst for Suzuki–Miyaura cross-coupling reaction of bromobenzene with phenylboronic acid at 80°C in micellar system of CTAB for 60 min

Entry	PdPtZn (mol%)^a	Yield (%)^b
1	0.6	70
2	0.65	76
3	0.7	83
4	0.75	90
5	0.8	96
6	1.0	96

[a] Pd mol%.
[b] Isolated yield.

Table 3. Suzuki–Miyaura reaction between aryl halides and phenylboronic acid in the presence of PdPtZn and PdZn NP thin films under optimized reaction conditions^a

Entry	Substrate	Product	PdZn: time (h); yield (%)^b	PdPtZn: time (h); yield (%)^b
1	PhI	**1a**	0.25; 97	0.17; 98
2	PhBr	**1a**	1; 94	0.75; 96
3	PhCl	**1a**	8; 70	2; 80
4	4-MeC_6H_4I	**1b**	0.5; 94	0.33; 96
5	4-MeC_6H_4Br	**1b**	2; 80	0.5; 94
6	4-$NO_2C_6H_4Br$	**1c**	1.5; 85	0.5; 96
7	4-$NO_2C_6H_4Cl$	**1c**	3; 80	1.5; 82
8	4-CNC_6H_4Br	**1d**	1; 85	0.33; 95
9	4-CNC_6H_4Cl	**1d**	3; 84	1.5; 90
10	C_5H_4NBr	**1e**	2; 83	1; 86
11	C_5H_4NCl	**1e**	8; 80	4; 85

[a] Conditions: 80°C, H_2O–EtOH (1:1) for PdZn and H_2O–CTAB for PdPtZn.
[b] Isolated yield.

From an industrial point of view, the reusability of a catalyst is important for large-scale operation. Therefore, the reusability of the catalysts was examined in the reaction of bromobenzene with phenylboronic acid at 80°C under optimized reaction conditions. Centrifugation was applied to separate the catalyst from the reaction mixture and was then washed with water and diethyl ether. Then, the PdPtZn and PdZn alloy catalysts were recovered by simple filtration from the reaction pot and can be reused successfully.

Table 4. Isolated yields for recycling of PdZn and PdPtZn NP thin films as catalyst at 80°C

Cycle	PdZn: yield (%)[a]	PdPtZn: yield (%)[b]
Fresh catalyst	94	96
First recycle	93	94
Second recycle	92	93
Third recycle	90	91
Fourth recycle	90	93

[a] H_2O–EtOH (1:1).
[b] H_2O–CTAB.

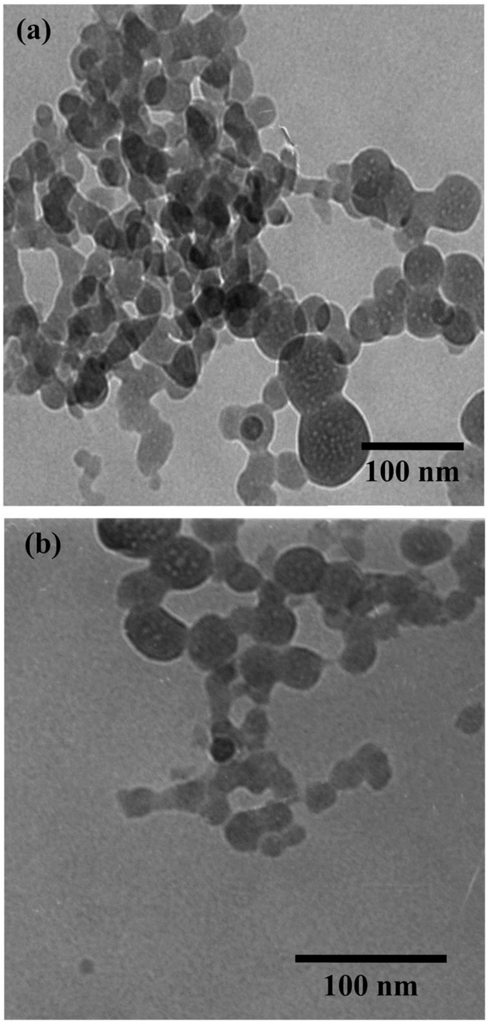


Figure 4. (a, b) TEM images of PdZn NP thin film after four catalytic cycles.

The recyclability of the nanoalloy catalysts was investigated. The results in Table 4 show that the alloy catalysts retain a reasonable performance when reused in four cycles.

Also, the particles of the PdZn NP thin film remain the same size, and no considerable aggregation phenomenon is observed after four cycles from TEM images (Fig. 4).

EDAX of the filtrate after the reaction demonstrates no leaching of Pd and Zn (Fig. 5). This is very important when Pd catalysts are used for pharmaceutical production.

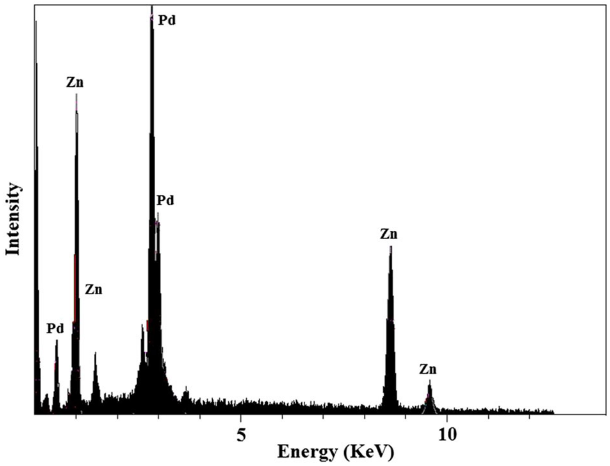


Figure 5. EDAX spectrum of PdZn NP thin film after four catalytic cycles.

Conclusions

In the present project, an oil–water interface self-assembly strategy was used to produce PdPtZn NP thin film and PdZn binary NP thin film at room temperature. The most important advantages of this assembly strategy are the significant simplicity and universality found in almost all of the related low-dimensional nanostructures. These NPs were characterized using various techniques and were further used as an excellent catalyst for Suzuki–Miyaura coupling reactions. The size and the structure of NPs both affect the catalytic performance. Despite the slightly larger size (44 nm) of the PdZn alloy, it exhibits very high catalytic activity due to its special structure. The higher catalytic activity of the PdPtZn thin film in comparison to the PdZn thin film was attributed to the small size (11 nm) and uniform dispersion of PdPtZn NPs in micellar system of CTAB. The percentage of surface atoms is higher in thin-film structures than in other structures and renders these nanoalloys as very interesting in catalysis. Also, since oxidative addition is almost the rate-determining step in the catalytic cycle, the rate of formation of organopalladium compound increased in the presence of platinum. Note that the synergic electronic effect between Pt (as electron-rich metal) and PdZn increases the electron density at the Pd centre. This effect facilitates the oxidative addition reaction in C–C coupling reaction. After finishing the reaction, these catalysts could be easily separated from the reaction mixture. Thus, the use of PdZn and PdPtZn thin films reduces costs, simplifies workup procedures and facilitates the separation of the final product. In addition, high yields obtained with unactivated aryl halides such as chlorobenzene derivatives is another advantage of this study.

Acknowledgements

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