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Green synthesis of palladium nanoparticles using *Pistacia atlantica kurdica* gum and their catalytic performance in Mizoroki–Heck and Suzuki–Miyaura coupling reactions in aqueous solutions

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A one-pot green method for the synthesis of palladium nanoparticles (Pd-NPs) supported on *Pistacia atlantica kurdica* (*P. a. kurdica*) gum is described. This natural gum is used as a reducing and stabilising agent. The formation of the Pd-NPs/*P. a. kurdica* gum catalyst was verified using several techniques, such as Fourier transform infrared spectroscopy, ultraviolet–visible spectrophotometry, scanning and transmission electron microscopies, X-ray diffraction, energy-dispersive X-ray spectroscopy, dynamic light scattering and wavelength-dispersive X-ray spectroscopy. The Pd-NPs stabilised by *P. a. kurdica* gum were employed as a heterogeneous catalyst in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions at low palladium loading (0.1 mol%) under aerobic, phosphine-free and ligand-free conditions in water. Product yields of up to 98%, a facile work-up, no evidence of leached palladium from the catalyst surface and smooth recovery of the catalyst, which can be reused at least eight times, confirm the efficiency of the catalysts in the reactions investigated. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: biosynthesis; palladium; nanoparticles; Pistacia atlantica kurdica gum; coupling

Introduction

The utilisation of natural resources has forced scientists into looking for innovative, eco-friendly techniques and procedures. The techniques and procedures are those which protect human health and have potential for effective use in the environment, thus minimising pollution and by-products. Among these procedures, the synthesis of efficient and green catalysts is a critical challenge.^[1]

In order to separate homogeneous catalysts from solution, several techniques such as chromatography, distillation and extraction are used, but removal of the catalyst from a reaction mixture is not efficient. This limitation in recovering catalysts is related to metal contamination, corrosion and deposition on the reactor walls. These disadvantages can be reduced if homogeneous complexes are bonded to insoluble solid supports, such as ordered or amorphous silicates, mixed oxides, clay minerals, zeolites, colloids, molecular sieves, ion-exchange resins, polymer membranes or bio-supports.^[1,2] Needless to say, biodegradable natural compounds, such as gellan,^[3] arabinogalactan,^[4] agarose,^[5] pectin,^[6] starch,^[7] chitosan^[8] and various plant extracts, provide environmentally friendly catalysts that have attracted a large number of studies in basic research and the chemical industry to reduce or eliminate the use of hazardous materials.^[3]

In addition, to improve the selectivity of materials produced using heterogeneous catalysts compared with homogeneous catalysts, nanostructures anchored on bio-supports have been developed.^[9]

Cross-coupling reactions, such as Mizoroki-Heck and Suzuki-Miyaura reactions, are powerful synthetic procedures for the formation of

halides in the presence of a suitable base. These reactions are usually catalysed by homogeneous palladium complexes, where palladium is coordinated to phosphine ligands to form water-soluble catalysts. The main disadvantages of these catalytic systems are catalyst recovery and generally unstable and toxic ligands.^[1-9] For many catalytic systems, the role of these ligands is to activate and stabilise the palladium against agglomeration and formation of palladium black. Achieving a palladium nanoparticle (Pd-NP) zero-valent oxidation state requires the use of a reducing agent (e.g. hydrazine, sodium borohydride, dimethylformamide, polyols or molecular hydrogen) or high temperatures in the gas phase.^[10] Cheaper and environmentally benign heterogeneous systems, mild reaction conditions and the use of renewable materials are attractive developments; and following new and important commercial opportunities, notable progress has been made in these areas.

carbon-carbon bonds, and allow the arylation, alkylation or vinylation of various alkenes through their reactions with aryl, vinyl, benzyl or allyl

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Figure 1. Images of Pistacia atlantica kurdica tree and gum.

Pistacia atlantica kurdica (P. a. kurdica; Fig. 1) is found widely in the Zagrous Mountains, and particularly in western and northern Iran, eastern and northern Iraq, southern Turkey and northern Syria in so-called Kurdistan. P. a. kurdica is irregularly distributed over the region and is an important constituent of the natural vegetation. It is the major source of a gum not very well known in the world, referred to here as kurdica.^[11] P. atlantica has antibacterial effects, and is used in eczema treatments, for throat infections, kidney stones, asthma and stomach ache and as an astringent, antipyretic, anti-inflammatory, antiviral, antimicrobial, pectoral and stimulant. Phytochemistry studies of this plant show that it may have fatty acids, flavonoids, phenolic compounds and triterpenoids, α-pinene, terpinolene and starch.^[12] Here we report a simple and eco-friendly procedure for the green synthesis of Pd-NPs, using P. a. kurdica gum as a reductant, stabiliser and capping agent. The catalytic performance as a heterogeneous catalyst in Mizoroki-Heck and Suzuki-Miyaura cross-coupling reactions in aqueous solutions was also investigated.

Experimental

Extraction of gum from P. a. kurdica tree

P. a. kurdica gum was collected from Kermanshah (western part of Iran) in the summer of 2013 as an exudate from the trunk and branches of the tree.

Preparation of Pd-NPs/P. a. kurdica gum

P. a. kurdica gum (1 g) was dissolved in 50 cm³ of EtOH at room temperature, and this solution was refluxed with 10 cm³ of EtOH containing 10 mg of PdCl₂ at 80°C for 2 h. The solution was allowed to cool to room temperature and the solvent was evaporated. The dark grey solid left after this process was dried overnight and then under vacuum for 48 h.

Catalyst characterisation

Diffuse reflectance spectra were recorded using a JASCO 550 UV–visible spectrophotometer equipped with a diffuse reflectance attachment, with BaSO₄ as the reference material. FT-IR spectra were recorded using KBr pellets with a JASCO FT/IR (680 plus) spectrometer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed using a Philips 501 microscope and a Tecnai F30 operating at 300 kV, respectively. In addition, energy-dispersive X-ray (EDX) analysis was conducted on

each sample. The size distribution was measured in order to number the nanoparticles in reverse microemulsion using a Zetasizer Nano-ZS-90 (ZEN 3600, Malvern Instruments).

Catalytic Mizoroki-Heck coupling

A mixture of aryl bromide and iodide (1.0 mmol), *n*-butyl acrylate (1.2 mmol), K_2CO_3 (2.0 mmol), Pd-NPs/*P. a. kurdica* gum catalyst (0.002 g of composite, containing 0.010 mmol of Pd) and water (5 cm³) at 80°C was stirred. The progress of the reaction was monitored using TLC. After completion of the reaction, aqueous ethanol (10 cm³, 50%) was added to the reaction mixture, which was stirred for 5 min. The catalyst was separated by filtration and recovered. Finally, evaporation of the solvents afforded the desired pure products. After complete drying, the catalyst was reused for the same reaction. This process was repeated for six runs. The amount of catalyst leached was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

Catalytic Suzuki-Miyaura coupling

A mixture of aryl halide and iodide (1.0 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (2 mmol), Pd-NPs/*P. a. kurdica* gum (0.002 g of composite, containing 0.010 mmol of Pd) and water (5 cm³) was stirred at 60°C. The progress of the reaction was monitored using TLC. After completion of the reaction, 5 cm³ of EtOH was added and the Pd-NPs/*P. a. kurdica* gum was separated by filtration. After evaporation of the solvent, the resulting crude products were dried and reused for seven runs. The amount of catalyst leached was determined using ICP-AES.

Procedure for reusing catalysts

After the reaction time, 5 cm³ of ethanol was added to the reaction mixture and stirred for 5 min. Then, the catalyst was separated by filtration. The recovered solid was then washed using ethyl acetate (5 cm³) and dried under vacuum for 10 min. The recovered catalyst was then used for another run.

Results and discussion

The loading of palladium in the heterogeneous catalyst was determined using ICP and EDX analyses. The final palladium content is 5.2 mmol q^{-1} . The UV-visible spectra of *P*. *a. kurdica* gum and Pd-NPs/P. a. kurdica gum show a side-band absorption near 259 nm. The UV-visible spectrum of the Pd-NPs/P. a. kurdica gum catalyst is significantly changed after reduction, with the disappearance of the peak at around 420 nm (Fig. 2). This change confirms the complete conversion of Pd²⁺ to Pd. During this step, the colour of the catalyst changes from yellow to deep black. Since P. a. kurdica gum contains phenolic and triterpenoidic groups, they can form complexes with Pd²⁺ ions in solution and change the oxidation state of the palladium. It seems that triterpenoids and phenolic compounds in the plant's biological gum are responsible for the reduction of Pd²⁺ and the starchy compound, also present in this gum, could act as a stabilising agent to prevent the aggregation of the synthesised Pd-NPs in water.^[12,13]

Further characterisations by FT-IR measurements entirely confirm the previous results (Fig. 3). Indeed, FT-IR measurements were carried out to identify the functional groups present in the *P. a. kurdica* gum responsible for the reduction and stabilisation of the Pd-NPs. Sharp peaks and bands at 3443, 2949, 1654, 1705, 1654,



Figure 2. UV–visible spectra: (a) PdCl₂; (b) *P. a. kurdica* gum; (c) Pd-NPs/*P. a. kurdica* gum.



Figure 3. FT-IR spectra: (a) *P. a. kurdica* gum; (b) Pd-NPs/*P. a. kurdica* gum catalyst.

1458, 1375, 1247, 1030, 609 and 462 cm⁻¹ are characteristic of the pure sample of *P. a. kurdica* gum. The FT-IR spectra of *P. a. kurdica* gum and Pd-NPs/*P. a. kurdica* gum show strong signals from the carboxylic groups, which are related to the C=O stretching modes of –COOH, and appear at 1706 cm⁻¹.^[14] The IR absorption corresponding to C–O–H in-plane bend of the hydroxyl groups in the gum is observed at 1458 cm⁻¹.^[15] A single broad band at 3434 cm⁻¹ can be observed due to OH absorptions in polyols, while a single sharper band at 1030 cm⁻¹ can be assigned to the C–O–C bending mode.^[16,17] On the basis of the IR data, it may be concluded that the phenolic hydroxyls present in the gum are responsible for the reduction of the palladium. Based on these data, the *P. a. kurdica* gum has a dual role of a reducing agent as well as a stabilising agent for Pd-NPs.

The EDX spectrum of Pd-NPs/*P. a. kurdica* gum is shown in Fig. 4; signals relating to carbon, oxygen and palladium are observed. The existence of a palladium signal in the spectrum results from the palladium complexation with active sites of the organic functional groups that increase the catalytic performance of the synthesised catalyst, in comparison with *P. a. kurdica* gum. The TEM images of Pd-NPs depicted in Fig. 5(a) show the size of the Pd-NPs to be about 10 nm. Figures 5(b) and (c) seem to show that the presence of palladium in the Pd-NPs/*P. a. kurdica* gum increases the electrical conduction and improves the quality of the SEM micrograph.

The average particle size in reverse microemulsion solution of the Pd-NPs/*P. a. kurdica* gum is around 4–7 nm (Fig. 6). According



Figure 4. EDX spectrum of Pd-NPs/P. a. kurdica gum catalyst.



Figure 5. (a) TEM images of Pd-NPs/P. a. kurdica gum catalyst. SEM images of (b) P. a. kurdica gum and (c) Pd-NPs/P. a. kurdica gum catalyst.

to the small nanoparticle sizes and ligand capping as an obstacle to agglomeration, the Pd-NPs/*P. a. kurdica* gum could be used as a suitable catalyst for Mizoroki–Heck and Suzuki–Miyaura crosscoupling reactions.

The powder X-ray diffraction (XRD) pattern of the Pd-NPs/P. a. kurdica gum catalyst is presented in Fig. 7, confirming the formation of Pd-NPs. The powder XRD diffraction pattern obtained for the Pd-NPs/P. a. kurdica gum material shows a broad reflection corresponding to the amorphous gum. The catalyst can be characterised by four reflections, which involve a strong d_{111} reflection at 39.4° and three other weaker reflections at 47.1° (d_{200}), 67.2° (d_{220}) and 82.1° (d_{311}). In addition, the characteristic XRD peaks show crystallographic planes of Pd-NPs. Solid material can be classified as being either amorphous or crystalline. In a crystalline solid, the ions occupy specific locations in a regular crystal lattice. The simplest lattice structures are face-centred cubic and body-centred cubic. The face-centred cubic structure consists of eight ions at the corners of a cube and additional ions located at the centres of each of the six faces of the cube. The XRD pattern of the resulting Pd-NPs/P. a. kurdica gum catalyst further shows evidence of the formation of face-centred cubic structured Pd-NPs.[18]

In combination with SEM, wavelength-dispersive X-ray spectroscopy (WDX) can provide qualitative information about the distribution of various chemical elements in the catalyst matrix. Figure 8 shows a representative SEM image and corresponding elemental



Figure 6. Particle size distribution for Pd-NPs/P. a. kurdica gum catalyst.



Figure 7. XRD spectrum of Pd-NPs/P. a. kurdica gum catalyst.

maps (WDX) for the synthesised catalyst. It can be seen that Pd metal particles are well dispersed in the catalyst, which agrees well with the XRD and TEM analyses. The selected-area elemental analysis figure reveals the presence of C, O, N and Pd throughout the sample in a homogeneous manner, which confirms the regular uniformity of the prepared sample.

Encouraged by our previous work on C–C coupling reactions,^[19] the catalytic performance of Pd-NPs/*P. a. kurdica* gum in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions was investigated in the present study. To find the best Suzuki coupling conditions, the reaction between 4-iodobenzene and phenylboronic acid was chosen as a model; and the effects of various parameters, namely the reaction temperature, the nature of the solvent and the base, were initially tested (Scheme 1). The control experiments performed in the absence of the catalyst after 24 h give a 0.0% yield, which confirms the role of Pd-NPs/*P. a. kurdica* gum.



Figure 8. SEM image of Pd-NPs/P. a. kurdica gum and elemental maps of C, O, N, Pd and C/Pd atoms in the catalyst.



Scheme 1. Suzuki-Miyaura cross-coupling reaction.

The synthesis of biaryl using various solvents and co-solvents was investigated. The results are summarised in Table 1. The solvents considered were DMF, 1,4-dioxane, EtOH, water, THF, toluene and mixtures of two solvents (DMF/H₂O, DMF/EtOH and H₂O/EtOH). It is evident from the results in Table 1 that the solvent plays an important role in the cross-coupling system. The use of aprotic

Table 1. Coupling of 4-iodobenzene with $ArB(OH)_2$ using Pd-NPs/P. a. kurdica gum catalyst ^a							
Entry	Solvent	Base	<i>T</i> (°C)	Yield (%)			
				15 min	60 min	120 min	
1	DMF	K ₂ CO ₃	80	24	_	_	
2	DMF/H ₂ O (1:1)	K ₂ CO ₃	80	49	51	54	
3	DMF/EtOH (1:1)	K ₂ CO ₃	80	47	52	52	
4	EtOH	K ₂ CO ₃	80	87	92	93	
5	EtOH	K ₂ CO ₃	60	83	85	85	
6	1,4-Dioxane	K ₂ CO ₃	80	32	—	—	
7	Toluene	K ₂ CO ₃	80	20	—	—	
8	Toluene	Na_2CO_3	80	17	—	—	
9	H ₂ O/EtOH (1:1)	K ₂ CO ₃	60	84	85	85	
10	H ₂ O/EtOH (1:2)	K ₂ CO ₃	60	90	92	93	
11	H ₂ O	K ₂ CO ₃	80	98	98	98	
12	H ₂ O	K ₂ CO ₃	60	98	98	98	
13	H ₂ O	K ₂ CO ₃	40	80	81	81	
14	H ₂ O	K ₂ CO ₃	RT	37	45	45	
15	H ₂ O	Cs ₂ CO ₃	60	91	91	92	
16	H ₂ O	Na_2CO_3	60	13	22	25	
17	H ₂ O	K_3PO_4	60	57	62	62	
18	H ₂ O	—	80	Trace	_	—	
^a Reaction conditions: aryl iodide (0.116 g, 1 mmol); phenylboronic acid							

(0.134 g, 1.1 mmol); base (2 mmol); solvent (5 cm³).

solvents (DMF, 1,4-dioxane and THF) or non-polar solvents (toluene) is not favourable for the reaction, even after prolonging the reaction time (Table 1, entries 1 and 6-8). However, the biaryl yield increases when H₂O, EtOH and H₂O/EtOH are used as co-solvents. An evaluation of various solvents at 60°C proves that the use of water as the protic solvent gives satisfactory results. Furthermore, the reaction rate also increases with temperature from 40 to 80°C. At room temperature, almost no biaryl can be synthesised, even though the mixture is stirred for a prolonged reaction. Finally, the role of a base (Et₃N, K₃PO₃, Na₂CO₃, Cs₂CO₃ and K₂CO₃) and its amount in the cross-coupling reaction were also explored. Of these, K_2CO_3 shows the best results. In the absence of K_2CO_3 , the coupling reaction stops completely (Table 1, entry 18). This result indicates that the prepared catalyst has excellent performance for activating Ar–Pd^{II}–X in the presence of K_2CO_3 . It also seems that the reaction rate is related closely to the amount of K₂CO₃. The yield increases when the amount of K₂CO₃ increases from 1 to 2 mmol; no difference is observed when the amount of K_2CO_3 is higher than 2 mmol. In our optimisation studies, the results show that the amount of K₂CO₃ is 2 eq. to aryl halides. Indeed, it is found that the type of base and its amount play a large role in the catalytic performance.

With the optimised reaction conditions in hand, the scope and generality of the green process was examined with aryl iodides, bromides and chlorides with various substituent groups in the Suzuki–Miyaura cross-coupling reaction (Table 2). The results confirm that the relative rate of reaction of organic halides in the Pd-NPs/*P. a. kurdica* gum-catalysed reactions is in the following order: R–Cl < R–Br < R–I. Electron-withdrawing substituents on R–X increase the reaction rate, while electron-donating substituents

Table 2. Heterogeneous Suzuki–Miyaura reaction of aryl halides with phenylboronic acid catalysed by Pd-NPs/P. a. kurdica gum ^a							
Entry	RC_6H_4X	Х	Time (min)	Yield (%) ^b	TON ^c	$TOF (min^{-1})^d$	
1	Н	I	15	98	326.7	21.78	
2	Н	Br	40	98	326.7	8.167	
3	Н	Cl	300	75	250.0	0.834	
4	$4-CH_3$	L	30	98	326.7	10.90	
5	4-CH₃	Br	60	96	320.0	5.334	
6	$4-CH_3$	Cl	420	75	250.0	0.596	
7	4-COCH ₃	T	45	98	326.7	7.260	
8	4-COCH ₃	Br	90	96	320.0	3.555	
9	4-COCH ₃	Cl	600	70	233.3	0.389	
10	4-CH₃O	T	20	98	326.7	16.33	
11	4-CH₃O	Br	60	98	326.7	5.445	
12	4-NO ₂	T	25	98	326.7	13.07	
13	4-NO ₂	Br	55	95	316.7	5.757	
14	$2-CH_3$	T	40	98	326.7	8.167	
15	$2-CH_3$	Br	90	92	306.7	3.407	
16	4-CHO	L	60	96	320.0	5.333	
17	4-CHO	Br	240	92	306.7	1.278	
18	1-Naphthyl	T	50	98	326.7	6.534	
19	1-Naphthyl	Br	120	96	320.0	2.667	
20	2-Thienyl	L	50	98	326.7	6.534	
21	2-Thienyl	Br	120	96	320.0	2.667	

^aReactions carried out under aerobic conditions in 5 cm³ of H₂O, 1.0 mmol aryl halide, 1.1 mmol phenylboronic acid and 2 mmol K₂CO₃ in the presence of catalyst (0.002 g, 0.1 mol% Pd) at 60°C.

^blsolated yield; average of two runs.

^cTurnover number: moles of aryl halide converted per mole of Pd. ^dTurnover frequency.

on R–X decrease the reaction rate. The Suzuki–Miyaura crosscoupling reactions of R–X with electron-withdrawing groups (Table 2, entries 12, 13, 16 and 17) proceed in shorter reaction times and give coupled products in very good yields. These results reflect the reactivity towards oxidative addition. In the case of R–CI with phenylboronic acid, many catalytic systems do not provide efficient cross-coupling, even under harsh conditions of high temperature and extended reaction times of up to 20–24 h.^[20] This research indicates that R–CI with phenylboronic acid couples without any limitation. The cross-coupling reactions of R–CI with phenylboronic acid require longer times and give moderate yields, compared with R–Br and R–I (Table 2, entries 3, 6 and 9). In addition, 2bromothiophene and 2-iodothiophene are coupled with phenylboronic acid and give the desired products with no poisoning of the catalyst (Table 2, entries 20 and 21).

Concerning the catalytic mechanism of Pd-NPs/P. a. kurdica gum, a reasonable proposed mechanism for the Suzuki-Miyaura reaction is presented in Scheme 2. Based on previous literature, the 'boomerang' mechanism of catalysis in the cross-coupling reaction employing a supported palladium source as the catalyst has been debated.^[21] The results presented indicate that the dynamics of the molecular and size interconversion of palladium species determine the type of mechanism. To determine the behaviour of palladium, a filtration test was carried out using Pd-NPs/P. a. kurdica gum catalyst in the Mizoroki-Heck and Suzuki-Miyaura reactions. The cross-coupling reaction of iodobenzene with phenylboronic acid is 98% complete in 15 min at 60°C. Therefore, to investigate the role and behaviour of palladium in the catalytic process, the solid phase of the reaction mixture is separated from the liquid phase after 5 min. The solid phase is collected after centrifugation for 3 min at 16 000 rpm. The filtrate is then allowed to continue to react under the same conditions for another 20 min, until the substrate is completely consumed. Chemical analysis of the filtrate shows the presence of palladium, which proves that palladium leaches from our catalyst surface. Meanwhile, after the end of this reaction under the same conditions, a black precipitate of palladium is observed in this solution around the wall of the container after 40 min. These two observations verify the leaching of palladium from the catalyst surface (cycles B and C).[22]

In another study after the completion of the reaction, the Pd-NPs/*P. a. kurdica* gum catalyst is separated from the reaction mixture, and the amount of palladium in the aqueous solution is evaluated. There is no black precipitation of palladium around the walls of the container and only a trace amount of palladium from the initially added Pd-NPs/*P. a. kurdica* gum catalyst is detected. To explain the increased palladium during the first stage of the experiment and its decrease at the end stages of the experiment, we can conclude that the palladium re-deposits onto the gum after the completion of the reaction.^[23] This study indicates that, in the



Scheme 2. Proposed mechanism for Suzuki–Miyaura cross-coupling of ethylbenzene catalysed by Pd-NPs/*P. a. kurdica* gum.

catalytic process, the prepared catalyst behaves like a heterogeneous catalyst, which can be recovered and reused.

The catalytic activities of the Pd-NPs/P. a. kurdica gum were then examined in the Mizoroki–Heck cross-coupling reaction (Scheme 3). The coupling reaction of iodobenzene with *n*-butyl acrylate was used as a model reaction to investigate the catalytic performance of the nanocatalyst.

To optimise the effectiveness of the reaction conditions for the Mizoroki–Heck reaction in the presence of the Pd-NPs/P. a. kurdica gum catalyst, various parameters were investigated - such as the amount of catalyst, temperature and nature of the solvent - to study the performance of the heterogeneous nanocatalyst. Employing water as the solvent in the presence of K₂CO₃ at 80°C gives a 98% yield after 15 min. For comparison purposes, other solvents (DMSO, DMF, toluene and EtOH) were investigated. After 10 min, the amount of product decreases in the following order with the various solvents: 98.0% (DMSO) > 92.0% (DMF) > 81.0% $(H_2O) > 79.0\%$ (ethanol) > 6.0% (toluene). However, water is particularly attractive as a reaction solvent. It is inexpensive, non-toxic, non-flammable and easily separated from organic products. Comparison of the results indicates that the Mizoroki-Heck crosscoupling reaction in water proceeds much better than in organic solvents, with an excellent yield and shorter reaction time. Therefore, reactions were conducted in water when we next explored the efficiency of the catalyst with other aryl halides with n-butyl acrylate. Increasing the temperature to accelerate the reaction is



Scheme 3. Mizoroki–Heck cross-coupling reaction.

Table 3. Heterogeneous Mizoroki–Heck reaction of aryl halides with <i>n</i> -butyl acrylate catalysed by Pd-NPs/ <i>P</i> . <i>a. kurdica</i> gum ^a								
Entry	RC_6H_4X	Х	Time (h)	Yield (%) ^b	TON ^c	TOF $(h^{-1})^d$		
1	Н	Ι	0.25	98	326.7	1307		
2	Н	Br	5	90	300.0	60.00		
3	Н	Cl	24	70	233.3	9.722		
4	4-CH ₃	Ι	0.5	96	320.0	640.0		
5	4-CH ₃	Br	6	80	266.7	44.45		
6	4-CH ₃	Cl	24	60	200.0	8.334		
7	4-CH ₃ O	I	0.3	98	326.7	1089		
8	4-CH ₃ O	Br	3	96	320.0	106.7		
9	4-NO ₂	Ι	0.15	98	326.7	2178		
10	4-NO ₂	Br	1.5	96	320.0	213.4		
11	2-CH ₃	Ι	0.35	96	320.0	914.3		
12	2-CH ₃	Br	2	92	306.7	153.3		
13	1-Naphthyl	Ι	0.5	96	320.0	640.0		
14	1-Naphthyl	Br	2.5	96	320.0	128.0		

^aReactions carried out under aerobic conditions in 5 cm³ of H_2O , 1.0 mmol aryl halide, 1.1 *n*-butyl acrylate and 2 mmol K_2CO_3 in the presence of catalyst (0.002 g, 0.1 mol% Pd) at 80°C.

^bIsolated yield; average of two runs.

^cTurnover number: moles of aryl halide converted per mole of Pd. ^dTurnover frequency.



Figure 9. Reusability of Pd-NPs/P. a. kurdica gum catalyst in Suzuki-Miyaura (SM) and Mizoroki-Heck (MH) cross-coupling reactions.

apparently effective. Consequently, the temperature effect (at 40, 60, 80 and 90°C) on the Mizoroki–Heck reaction was also monitored after 30 min in the presence of the nanocatalyst. Generally speaking, increasing the reaction temperature (80°C) and reaction time give higher yields (98%). The reaction of iodobenzene with *n*-butyl acrylate (at 1:1 eq.) in the presence of K₂CO₃ (2 eq.) in water at 80°C provides a 98% yield of the coupling product (Table 3, entry 1); these reaction conditions were chosen for further experiments.

The reusability of the immobilised Pd-NPs/P. *a. kurdica* gum catalyst was confirmed by performing a series of consecutive experiments in which the used catalyst was filtered, washed with fresh solvent and used in another run without any further treatment. The results depicted in Fig. 9 clearly show that a slight decline of activity occurs after the sixth and seventh runs for the Mizoroki–Heck and Suzuki–Miyaura reactions, respectively. Consequently, the results clearly suggest that the Pd-NPs/P. *a. kurdica* gum efficiently catalyses the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions.

Conclusions

We have shown that Pd-NPs stabilised by *P. a. kurdica* gum are efficient and stable catalysts in the Suzuki–Miyaura and Mizoroki–Heck cross-coupling reactions. The advantage of Pd-NPs/*P. a. kurdica* gum compared to previously reported catalysts is the use of inexpensive, non-toxic, non-flammable solvents, a natural support medium and a simple nanoparticle preparation route, thus eliminating the use of reducing agents such as those mentioned earlier. The reactions are conducted in the open air, which indicates that the Pd-NPs/*P. a. kurdica* gum catalyst is highly stable and not sensitive to oxygen. The catalytic system is applicable to a wide range of aryl halides (iodide, bromide and chloride), and can be easily separated from the products and reused without significant loss in activity.

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