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A green approach for the synthesis of palladium nanoparticles supported on pectin: Application as a catalyst for solvent-free Mizoroki–Heck reaction

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ABSTRACT

A green method for the synthesis of palladium nanoparticles supported on pectin has been described. The synthesized nanoparticles were explored in Mizoroki–Heck reaction between different aryl halides and n-butyl acrylate under solvent-free conditions. The catalyst can be recycled for six runs without significant loss in the catalytic activity.

1. Introduction

In recent years, the design and development of green catalysts have attracted a large number of studies in academic and industrial groups to reduce or eliminate the use of hazardous substances [1,2]. Solid catalysts provide opportunities for recycling and recovering of the catalysts from reaction environments. Because of having many advantages such as easy separation, low waste production and the reduced cost, heterogenization of the catalysts to solid supports by their immobilization on organic [3] or inorganic [4] polymers is of great interest [5–7].

In last few years, immobilization of the palladium nanoparticles on solid supports to prepare active and stable catalytic systems is an interesting topic, and different supports have been used to stabilize the nanoparticles [8–15]. Along this line, Pd/gellan [16], Pd/arabinogalactan [17], Pd/agarose [18], Pd/starch [19] and Pd/chitosan [20] have been prepared using polysaccharides as the bed. In order to expand the use of carbohydrate-based materials as the support for palladium nanoparticles, we decided to introduce pectin as a suitable and naturally degradable support for stabilization of palladium nanoparticles.

Pectin is a family of complex polysaccharides that is found extensively in nature [21]. Unique properties of pectin, such as biodegradability, flexibility, non-toxicity, low price and carrying freely available hydroxyl groups make it suitable and ideal candidate for many practices in different areas of science.

Palladium-catalyzed Mizoroki–Heck coupling reaction is one of the most powerful synthetic methods for the formation of carbon—carbon bonds, which allows the arylation, alkylation or vinylation of various alkenes through their reaction with aryl, vinyl, benzyl or allyl halides in the presence of palladium and a suitable base [7,22]. Total synthesis of complex organic molecules has benefited enormously from the Mizoroki–Heck reaction. The Mizoroki–Heck coupling products find good applications as intermediates in the preparation of materials, natural products, and bioactive compounds [23]. Herein, we report that palladium nanoparticles stabilized by pectin can be successfully used in the Mizoroki–Heck cross-coupling reaction between the activated and non-activated aryl halides and n-butyl acrylate under solvent-free conditions.

2. Experimental

2.1. Gram-scale preparation of palladium nanoparticles supported on pectin

Pectin (1 g) was dissolved in water (100 mL) at ambient temperature. To this solution was added a solution of $PdCl_2$ (100 mL, 1 mM) and diluted with water (100 mL). The reaction mixture was refluxed at 100 °C for 4 h. The mixture was cooled down to room temperature and the solvent was evaporated. The obtained dark gray composite was dried by the flow of air over night and then under vacuum for 24 h.

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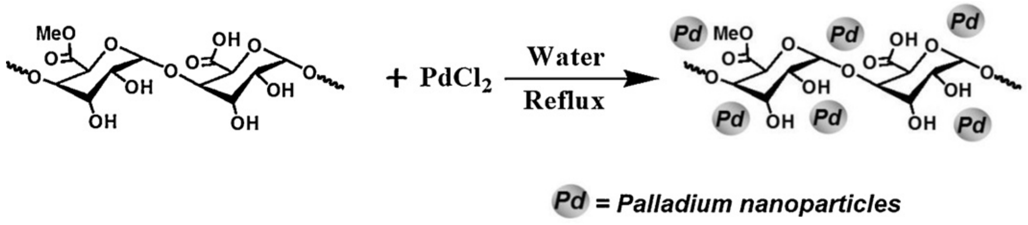


Fig. 1. Preparation of Pd_{np}/pectin.

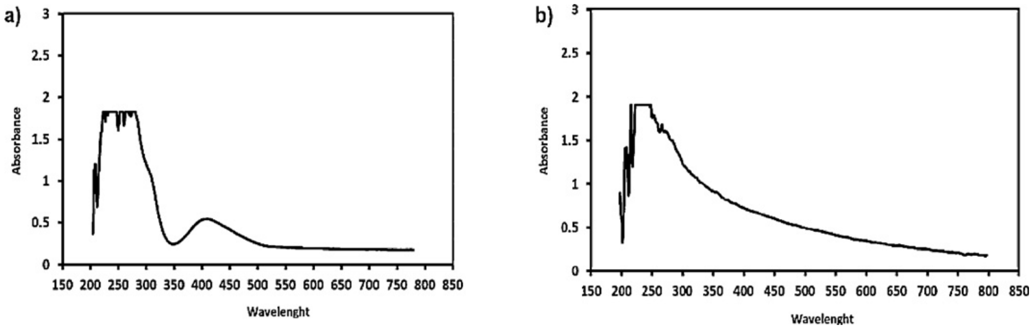


Fig. 2. UV–vis spectra of (a) Pd(II) before reduction and (b) Pd(0) after reduction with pectin.

2.2. *General procedure for the Mizoroki–Heck reaction in the presence of the nanocatalyst*

To a flask, a mixture of pectin supported Pd-nanoparticles (0.05 g of the composite, contains 0.0028 mmol of palladium), aryl halide (1 mmol), n-butyl acrylate (1.5 mmol, 0.21 mL) and n-Pr_3N (1.5 mmol, 0.29 mL) were added and heated at 140 °C under solvent-free conditions. After completion of the reaction (monitored by TLC or GC), ethylacetate (10 mL) was added to the flask. The catalyst was separated by simple filtration. Water (3× 15 mL) was added to the ethylacetate phase and decanted. The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the resulted crude products was purified by column chromatography (hexane/ethylacetate) giving the pure products in excellent yields.

2.3. *The procedure for recycling of the catalyst*

After completion of the reaction at the first run, the reaction mixture was cooled down to room temperature and ethylacetate (5 mL) was added to the reaction mixture to extract organics. The ethylacetate phase was sucked from the vial by a syringe and the catalyst was dried under vacuum. After complete drying, the catalyst was reused for the similar reaction. This process was repeated for six runs.

3. Results and discussion

Pectin stabilized palladium nanoparticles (Pd_{np}/pectin) were prepared by exposure of aqueous solution of $PdCl_2$ (100 mL, 1 mM) to pectin (1 g dissolved in 100 mL water) without using any extra reducing agent (Fig. 1). This solution was refluxed for 4 h giving a gray solution. Evaporation of the solvent followed by drying in vacuum gave a dark gray solid.

The UV–vis spectrum of the resulted Pd supported nanoparticles changed significantly after reduction, with the disappearance of the peak at around 430 nm (Fig. 2). This change showed the conversion of Pd(II) to Pd(0). Since pectin contains free carboxyl groups, they can form complexes with Pd(II) ions in solution and reduce them to Pd(0). The process of reduction is performed by oxidation of carboxyl groups and liberation of CO_2 gas at the reflux conditions [22b].

According to the energy dispersive X-ray analysis (EDX) the presence of palladium is indicated in the Pd_{np}/pectin catalyst and its loading amount was measured to be 0.61% (w/w). The EDX spectrum also shows signals of carbon and oxygen which are present in the pectin substrate (Fig. 3).

The formation of Pd nanoparticles was confirmed by the XRD pattern of Pd_{np}/pectin catalyst. As presented in Fig. 4, the four characteristic peaks at (1 1 1), (2 0 0), (2 2 0) and (3 1 1) can be clearly observed for Pd particles in various 2θ values. These characteristic peaks shows crystallographic planes of the Pd(0) nanoparticles. Generally, Solid material can be classified as being either amorphous or crystalline. In crystalline materials the ions occupy specific locations in a regular lattice. The simplest such lattice is a simple cube with ions on each of the corners of the cube. The most common simple structures are the face centered cubic (*fcc*) and the body centered cubic (*bcc*). The *fcc* structure consists of a cube of ions with six additional ions located at the centers of each of the six faces of the cube [24]. According to crystallographic planes in the

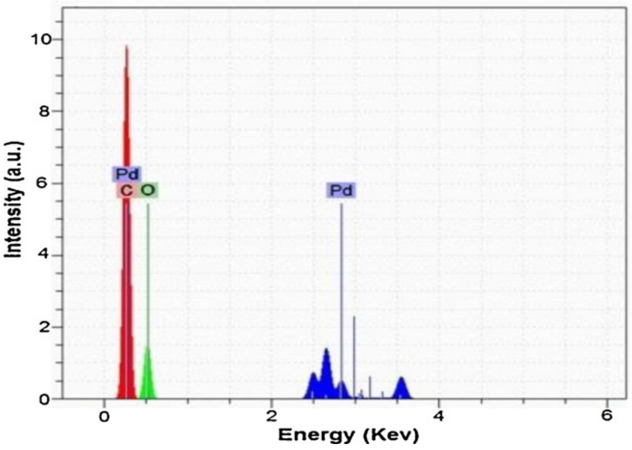


Fig. 3. The EDX spectrum of Pd_{np}/pectin.

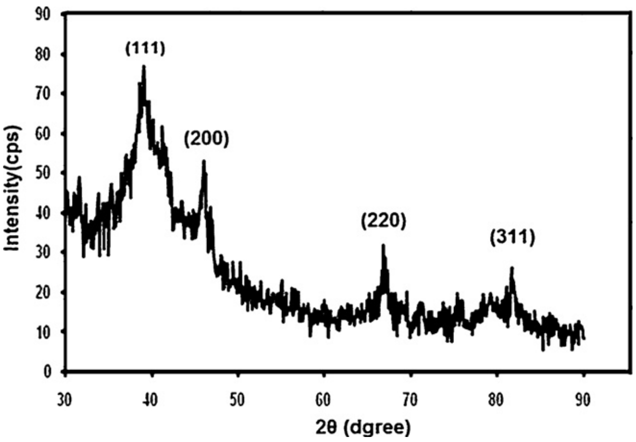


Fig. 4. The XRD spectrum of Pd_{np}/pectin.

diffraction pattern of the spectrum (Fig. 4) the face centered cubic (*fcc*) crystalline structure was indicated for Pd(0).

The TEM image of the Pd_{np}/pectin catalyst revealed that the Pd nanoparticles with near spherical morphology were formed onto the surface of pectin with relatively good monodispersity. The TEM image indicates that the size of the palladium particles to be in the range 2–6 nm (Fig. 5a and b). The palladium content of the pectin composite was determined by ICP and EDX to be 0.057 mmol/g of the pectin support.

After characterization of the composite, the catalytic activities of Pd_{np}/pectin were examined in the Mizoroki–Heck reaction. The coupling reaction of iodobenzene with n-butyl acrylate was used as a model reaction to investigate the catalytic performance of Pd_{np}/pectin and the effect of media upon the reaction. The influence of bases, solvents and reaction temperature on the yield was first investigated (Table 1). Employing DMSO and DMF as the solvent in the presence of n-Pr_3N at 140 °C gave 100% conversion of the starting material after 15 min (Table 1, entries 1 and 2). The use of other organic solvents (Table 1, entries 3 and 6) or protic solvents (Table 1, entries 4 and 5) was not beneficial to the process. We have also studied the reaction in solvent-free condition and in the presence of DMSO and DMF as the solvent after 5 min. The desired product was obtained in 40, 36 and 94% yields, respectively at 140 °C. Comparison of the results clearly shows that the reaction in solvent-free conditions (Table 1, entry 11) proceeded much better than in solvents with an excellent yield and shorter reaction time.

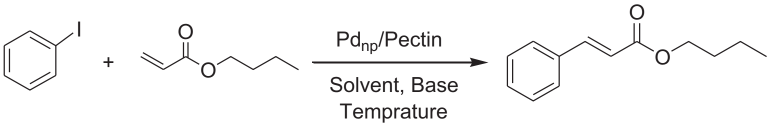
The reaction was also studied at various temperatures under non-solvent conditions. The results demonstrated that the temperature plays a significant role in the reaction rate. The activity of the catalyst was increased in high temperatures (Table 1, entries 7–11) with the activity being very high at 140 °C. During our optimization studies, various bases were examined and it was found that the catalyst was very active and selective for the reaction in the presence of n-Pr_3N (Table 1, entry 11) as a liquid organic base, while the reaction rate was very slow when inorganic bases were used (Table 1, entries 12–14). Remarkably, the reactions were carried out in air indicating that the Pd_{np}/pectin catalyst was highly stable and insensitive to oxygen.

Using the optimized reaction conditions (Table 1, entry 11), a range of aryl iodides, bromides and chlorides with various substituent groups were examined in the Mizoroki–Heck reaction (Table 2).

It is recognized that the relative reactivity of organic halides in palladium catalyzed reactions is R-Cl < R-Br < R-I. These results reflect the reactivity toward oxidative addition. Various substituents on aromatic halides can influence on the Mizoroki–Heck reaction. Therefore, electron-withdrawing substituents (such as NO_2, CH_3CO and F) on aromatic halides increase the reaction rate and electron-donating substituents (such as Me, OMe and NH_2) on aromatic halides decrease the reaction rate [25].

According to experimental results, high reaction rates and yields were obtained with both activated and non-activated aryl iodides (Table 2, entries 1–6). Aryl iodides without any substituent and activated aryl iodides with electron-withdrawing substituents are reactive substrates in Heck reactions and the related reactions went to completion in shorter reaction times. As an example, the reaction of iodobenzene with n-butyl acrylate went to completion within 5 min giving the desired product in 94% isolated yield (Table 2, entry 1). Non-activated aryl iodides with electron-donating substituents (such as Me and OMe) on the aromatic

Table 1
Optimization studies for the reaction of iodobenzene with n-butyl acrylate in the presence of Pd_{np}/pectin.[a]



Entry	Base	Solvent	T (°C)	Time	Yield (%)[b,c]
1	n-Pr_3N	DMSO	140	15 min	92 (100)
2	n-Pr_3N	DMF	140	15 min	90 (100)
3	n-Pr_3N	Toluene	Reflux	15 h	5 (11)
4	n-Pr_3N	EtOH	Reflux	15 h	32 (38)
5	n-Pr_3N	H_2O	Reflux	15 h	45 (53)
6	n-Pr_3N	THF	Reflux	15 h	4 (10)
7	n-Pr_3N	None	80	6 h	8 (14)
8	n-Pr_3N	None	100	6 h	71 (76)
9	n-Pr_3N	None	120	100 min	91 (100)
10	n-Pr_3N	None	130	40 min	92 (100)
11	**n-Pr_3N**	**None**	**140**	**5 min**	**94 (100)**
12	NaOH	None	140	15 h	68 (73)
13	KOAc	None	140	15 h	78 (85)
14	K_2CO_3	None	140	15 h	86 (91)
15	DABCO	None	140	80 min	93 (100)

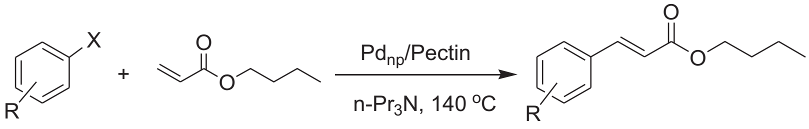
The bold values (entry 11) show our selected conditions for Mizoroki-Heck reaction.

[a] Reactions were carried out using 1 mmol of idobenzene, 1.5 mmol of n-butyl acrylate and 1.5 mmol of base in the presence of Pd_{np}/pectin (0.05 g; 0.0028 mmol of Pd).

[b] Yields are given for isolated products.

[c] The data presented in the parenthesis refer to the conversion of iodobenzene.

Table 2
Reaction of aryl halides **1** with n-butyl acrylate catalyzed by Pd_{np}/pectin.[a]



1 **2**

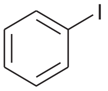
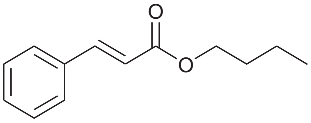
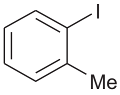
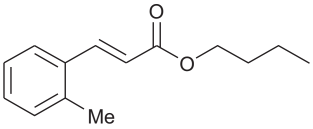
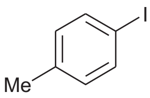
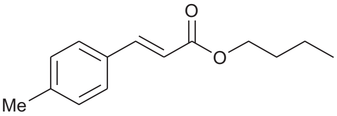
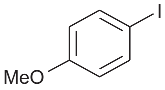
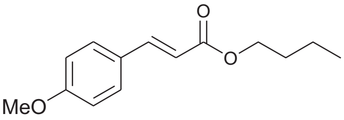
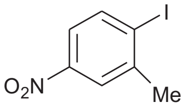
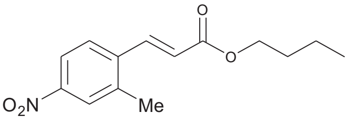
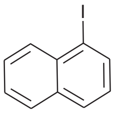
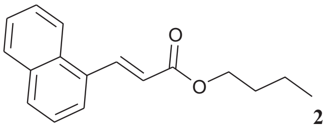
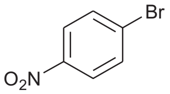
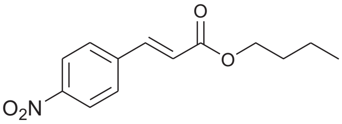
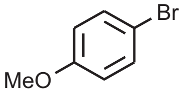
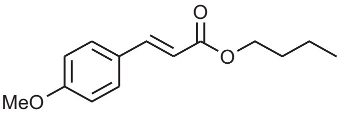
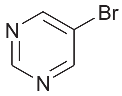
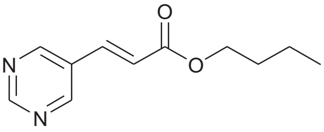
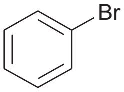
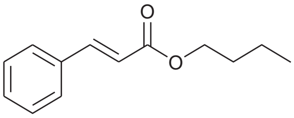
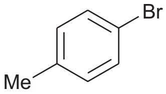
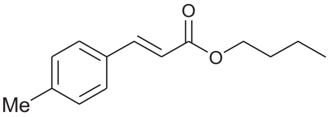
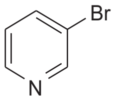
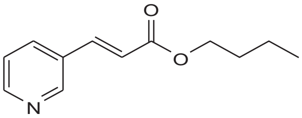
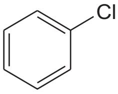
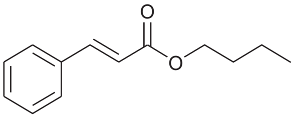
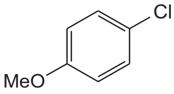
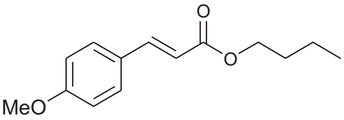
Entry	Aryl halide	Product	Time	Yield (%)[b]
1	 **1a**	 **2a**	5 min	94
2	 **1b**	 **2b**	30 min	92
3	 **1c**	 **2c**	15 min	93
4	 **1d**	 **2d**	20 min	91
5	 **1e**	 **2e**	25 min	92
6	 **1f**	 **2f**	35 min	90
7	 **1g**	 **2g**	80 min	91
8	 **1h**	 **2d**	18 h	57

Table 2 (*Continued*)

Entry	Aryl halide	Product	Time	Yield (%)[b]
9	 **1i**	 **2h**	6 h	91
10	 **1j**	 **2a**	18 h	74
11	 **1k**	 **2c**	18 h	58
12	 **1l**	 **2i**	6 h	61
13	 **1m**	 **2a**	18 h	70
14	 **1n**	 **2d**	18 h	58

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[a] Reactions were carried out using 1 mmol of **1** and 1.5 mmol of **2** in the presence of Pd_{np}/pectin (0.05 g; 0.0028 mmol of Pd) and 1.5 mmol of n-Pr_3N as the base under solvent free conditions.

[b] Yields are given for isolated products.

ring are not reactive substrates in Heck reactions and the related reactions went to completion in longer reaction times (Table 2, entries 2–4). The observed longer reaction time for the reaction of 4-iodoanisole in compare with 4-iodotoluen is due to electron-donating ability of substituents on aromatic rings (Table 2, entries 3 and 4). The results in Table 2 exhibit that the reaction system was active for the sterically hindered aryl iodides (Table 2, entries 2, 5 and 6). As shown in Table 2, the coupling reaction of butyl acrylate with *o*-substituted in compare with *p*-substituted aryl iodides performed in longer reaction times (Table 2, entries 2 and 3).

This catalytic system was also applied for the substituted aryl bromides and hetero aryl bromide giving the desired products in moderate to high yields (Table 2, entries 7–12). Literature survey shows that there are only a few reports that have shown aryl chlorides underwent the Mizoroki–Heck coupling reaction giving the desired products in the present of supported Pd nanoparticles as a catalyst [26]. Herein we have reported that Pd_{np}/pectin catalytic system can catalyze the reaction of aryl chlorides with n-butyl acrylate under solvent-free conditions and moderate conversions have been achieved within 18 h reaction times (Table 2, entries 13 and 14).

There are many reports in the literature applying palladium nanoparticles for the cross coupling Mizoroki–Heck reaction. To illustrate the catalytic activity of Pd_{np}/pectin system, we wish to compare the previously reported systems in Mizoroki–Heck reaction with this system. Bhaumik et al. reported the application of palladium nanoparticles tethered into mesoporous polymer MPTA-1 in the Mizoroki–Heck reaction of iodobenzene with n-butyl acrylate in the presence of K_2CO_3 as a base in H_2O at reflux. Under these conditions, the reaction was completed within 5 h [27]. Similar reaction under our conditions gave the desired product within 5 min in 94% yield (Table 2, entry 1). The synthesis of poly(N-vinylimidazole) grafted silica-containing palladium nanoparticles has been reported. This system has been applied as a catalyst in Mizoroki–Heck reaction of 4-iodoanisole with n-butyl acrylate using DMF as solvent in the presence of K_2CO_3 under phosphine-free conditions. In the presence of this system the reaction was completed within 1 h [28]. While for the similar reaction, using the pectin supported palladium nanoparticles the reaction was completed after 20 min (Table 2, entry 4). In another try, palladium supported on superparamagnetic nanoparticles was used as a catalyst for Mizoroki–Heck reaction. The reaction of iodobenzene with n-butyl acrylate in the presence of this catalyst proceeded to

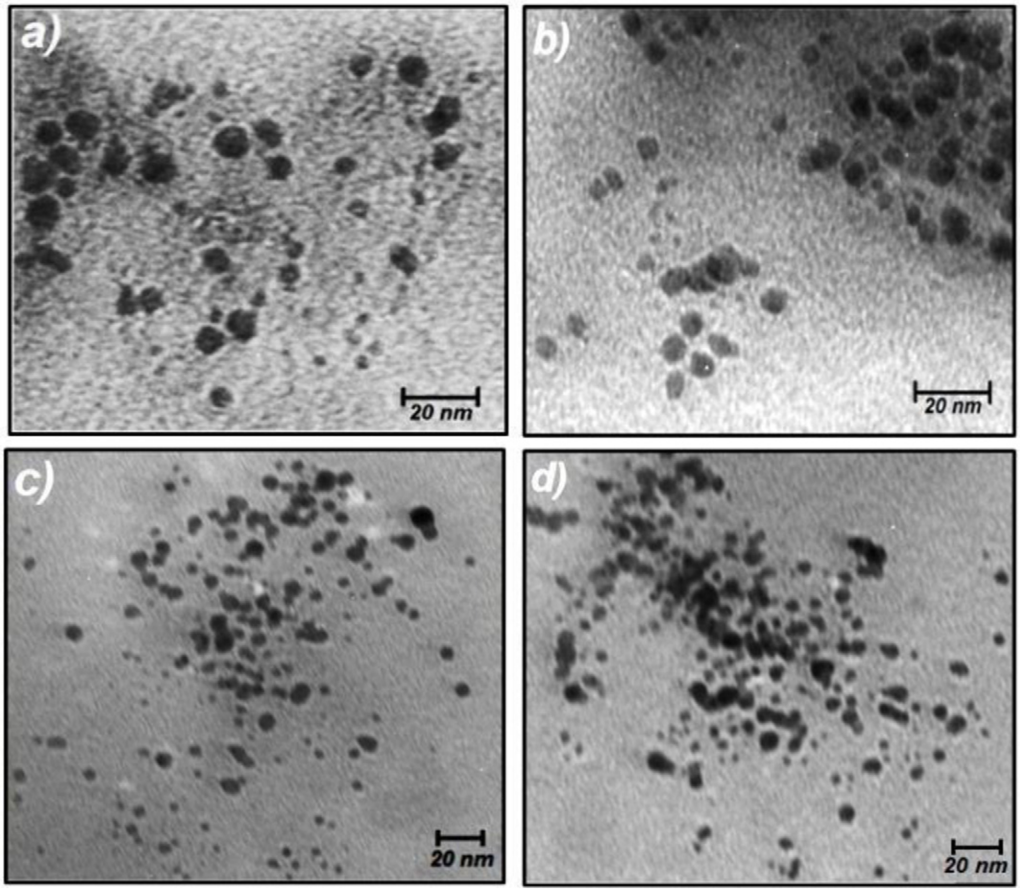

Fig. 5. TEM image of the Pd_{np}/pectin catalyst that shows the morphology of Pd nanoparticles in two different positions on the surface (a and b), TEM image of the Pd_{np}/pectin catalyst after the first run recycling of the catalyst (c) and after the 6th run of recycling of the catalyst (d).

completion within 5 h in the presence of K_2CO_3 in NMP as the solvent at 130 °C [29], whereas, the similar reaction, as mentioned above, went to completion within 5 min. Wang and coworkers reported the application of Pd nanoparticles supported on functionalized mesoporous silica in the Mizoroki–Heck reaction of iodobenzene with n-butyl acrylate in the presence of Et_3N as a base in DMF at 120 °C. Under these conditions, the reaction was completed within 1 h [30]. Similar reaction under our conditions gave the desired product within only 5 min in 94% yield (Table 2, entry 1).

The notable features of Pd_{np}/pectin system are in situ generation of nanoparticles without addition of any external reducing agents, stability toward air and moisture, easy handling and recycle ability. Remarkably, some of the reactions proceeded in the presence of Pd_{np}/pectin system under solvent-free conditions, are among the fastest ever reported in the literature.

For practical applications of heterogeneous catalysts, the reusability is a very significant factor. The reusability of the catalyst was checked upon the reaction of iodobenzene with n-butyl acrylate as the substrates in the presence of the catalyst and n-Pr_3N at 140 °C. After completion of the reaction in the first run, the organic compounds were separated from the reaction mixture by a simple extraction and the resulting solid mass was reused for the next run. At the first run, the reaction was completed within 2 min in 94% yield. The nanocatalyst has been recovered for six runs with some decrease in the catalytic activity of the catalyst. At the sixth run, the reaction was completed within 20 min in 93% yield (see Table 3 in supporting information). The amount of Pd leaching after the 6th run was determined by ICP analysis to be only 11%. The TEM picture of the recovered nanocatalysts showed that the morphology and size of the nanoparticles after first and sixth runs does not change significantly in comparison with the TEM picture of the fresh catalyst (Fig. 5a–d). It is interesting that the among the recycling process the shape and size of the nanocatalyst does not change notably, for example after the sixth run the catalyst still remained as a dark gray powder.

In order to examine the leaching of palladium from the solid catalyst, we have used the hot filtration test. For this purpose, the reaction of 1-bromo-4-nitrobenzene with butyl acrylate in the presence of Pd_{np}/pectin and n-Pr_3N in DMF as the solvent at 140 °C was studied. After 10 min (the reaction was completed within 95 min in 92% conversion of the starting material and 88% isolated yield of product), when 20% conversion of 1-bromo-4-nitrobenzene was occurred the reaction was stopped and catalyst was removed by hot filtration from the reaction mixture. Then the mixture without the solid catalyst which contains unreacted substrates was allowed to continue under the same conditions. After 24 h, only 34% of the product was detected by GC. This result suggested that the leaching of nanoparticles from the solid support was low.

4. Conclusion

In conclusion, a new class of nano-composite, Pd_{np}/pectin, was easily obtained by the in situ reduction of $PdCl_2$ under green conditions without addition of any external reducing agents. The Pd_{np}/pectin system exhibited a high activity toward the Mizoroki–Heck cross-coupling reaction of various aryl halides (I, Br and Cl) under aerobic and solvent-free conditions. The catalyst was very stable and could be easily separated from the products and reused six times without significant loss in the activity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.02.023.

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