

Palladium Nanoparticles Supported on Aminopropyl-Functionalized Clay as Efficient Catalysts for Phosphine-Free C–C Bond Formation via Mizoroki–Heck and Suzuki–Miyaura Reactions

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In this study, we have used palladium nanoparticles supported on aminopropyl-functionalized clay as an efficient catalyst for Mizoroki–Heck and Suzuki–Miyaura reactions. By using this catalyst, the reaction of iodo- and bromoarenes with *n*-butyl acrylate and styrene proceeded well and smoothly to produce the desired products in good to excellent yields under solvent-free conditions. The catalyst has been recycled for ten runs without much loss of its catalytic activity. Suzuki–Miyaura reaction of structurally different aryl halides (I and Br) with phenylboronic acid by the aid of this catalyst in refluxing water or SDS micellar solution in the absence of any organic co-solvent was also performed well to give the desired biphenyl products in good to excellent yields. Production of the corresponding homocoupled products in negligible amounts was observed in these reactions. In comparison with many other reported palladium-catalyzed Mizoroki–Heck and Suzuki–Miyaura reactions, the Pd-loading of this catalyst is one of the lowest. In the presence of this catalyst, all the reactions proceeded without using any external phosphorus ligands.

Construction of carbon–carbon bonds is one of the most demanding topics in organic synthesis.^{1–3} In general, transition-metal-catalyzed cross-coupling reactions are accompanied with higher yields and selectivity in comparison with many main-group metals used as catalysts.⁴ Among the many procedures reported in the literature, Mizoroki–Heck and Suzuki–Miyaura reactions are of the most powerful tools for this purpose.^{5–8}

In general, Mizoroki–Heck reaction has been performed in different media such as organic solvents,⁹ ionic liquids,¹⁰ CO₂,¹¹ and water.¹² However, less attention has been paid to perform this reaction under solvent-free conditions,^{13,14} although it is more environmentally friendly and economically profitable. Very recently, a solvent-free Mizoroki–Heck reaction has been reported in the presence of palladium catalyst supported on 1,1,3,3-tetramethylguanidinium (TMG)-modified molecular sieve Santa Barbara (SBA-15) or SBA-TMG at 140 °C. By the aid of this catalyst, only the reaction of aryl iodides with olefins has been reported.¹⁵

Suzuki–Miyaura cross-coupling reaction is a highly practical and simple method for the synthesis of biaryls, which are found in natural products, pharmaceuticals, agrochemicals, etc.¹⁶ So, improvement of the present methods is always welcome by industries and academia. Recently, development of organic synthesis in aqueous media has attracted a great deal of interest due to the low cost, nontoxicity, abundance, safety, and nonflammability of water and easy phase separation between organic compounds and water are the advantages of using water as the reaction media.^{17–19}

Nowadays, attention has been paid to the use of nanoparticles in comparison with the corresponding bulk materials, because of their potential applications in a variety of fields and

their size-dependent evolution properties.²⁰ Investigators have focused mainly on identifying new properties and applications of such materials. Comparing to the corresponding bulk materials, they can have different heat capacity, vapor pressure, melting point, optical, magnetic, and electronic properties.²⁰ Also owing to their high surface area, application of these particles as catalysts results in high concentration of reactive sites leading to higher reactivity and selectivity.^{2,21,22} There is also evidence regarding the involvement of in situ generated Pd nanoparticles in C–C bond forming reactions under phosphine-free conditions.²³

Palladium nanoparticles of different origins have been utilized in the Mizoroki–Heck and Suzuki–Miyaura arylation reactions with variable degrees of success.^{2,21,24–27} Moreover, the immobilization of palladium onto clay^{28–30} and zeolites^{31,32} and their applications in the carbon–carbon bond formation reactions have been reported. Some palladium catalysts which are supported on carbon,³³ carbon nanotubes,³⁴ different metal oxides,^{2,21} silica gel and modified silica gel,³⁵ fluorosilica,²⁷ molecular sieves,³⁶ and so forth are also reported.

The current challenge for developing palladium catalysts which work in the presence of inexpensive and reusable ligands or beds is a research area of much interest to chemists from academia and industries. The role of supports and ligands is to stabilize the zero-valent palladium and also to minimize the aggregation of the naked palladium clusters³⁷ which causes inactivation of zero-valent palladium catalyst.^{38–40}

Since the last decade, introduction of functional groups into clays has been under attention. Very lately Chen et al. reported a method for the preparation of nanoparticles of palladium into montmorillonite modified with quaternary ammonium surfac-

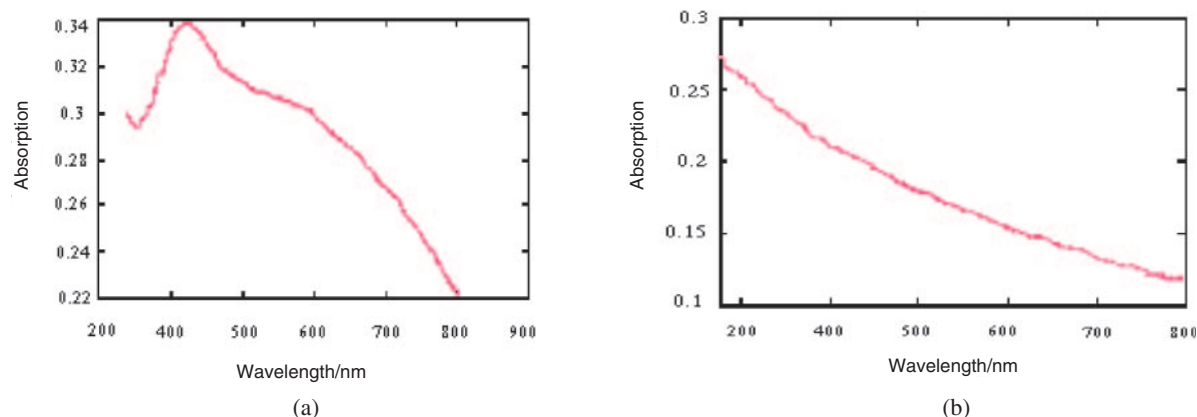


Figure 1. UV-vis spectra of (a) Pd(II) before reduction and (b) Pd(0) after reduction with NaBH₄.

tant which is used for aerobic oxidation of benzyl alcohol.⁴¹ Mann et al. reported the preparation of aminopropyl-functionalized clay with unit cell composition of [H₂N(CH₂)₃]₈Si₈Mg₆O₁₆(OH)₄ and applied the clay for stabilization of some biomolecules.⁴² Later, Rao reported the use of this amino-functionalized clay as a support for stabilization of nanoparticles of Au, Ag, Pd, and Pt wrapped in exfoliated sheets of the clay which can be easily dispersed in water.⁴³

In continuation of our recent work on reactions under solvent-free conditions and in aqueous media,^{12,44} we now present the first report of catalytic use of this palladium nanoparticles supported on aminoclay for carbon–carbon bond formation via Mizoroki–Heck reaction under solvent-free conditions and Suzuki–Miyaura reaction in aqueous media.

Results and Discussion

The Catalyst Characterization. For this study, first we had to scale-up the preparation of the palladium nanoparticles supported on aminoclay. For this purpose, a gram scale preparation was developed and the characterization of the produced palladium nanoparticles supported on aminoclay was performed by different means. The UV-vis spectrum of the resulting composite shows the complete conversion of Pd(II) to Pd(0) by the absence of the peak at 420 nm (Figure 1).

The X-ray diffraction (XRD) pattern of the composite shows that the bilayer arrangement of aminoclay has been maintained in the large-scale preparation. The low angle reflection at *d*₀₀₁ is the strong evidence for this arrangement. The characteristic bands for Pd(0) can be observed at (111), (200), (220), and (311) crystallographic planes (Figure 2).¹²

Scanning electron microscopy (SEM) of the gram-scaled prepared composite shows that the average size of the nanoparticles is ≈30 nm (Figure 3).

Atomic force microscopy (AFM) image of the composite shows that the palladium nanoparticles are dispersed regularly on the clay surface (Figure 4). According to the voltage profile of the AFM, the average size of palladium nanoparticles (30 to 40 nm) was in accord with the information obtained by the corresponding SEM image (Figure 3).

The palladium content of the aminoclay for the gram-scale prepared composite was also obtained by induced coupled plasma (ICP) to be 119 mg of palladium per kilogram of the aminoclay support.

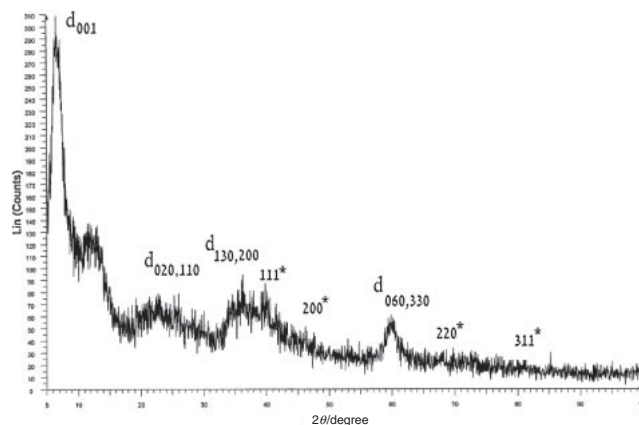


Figure 2. XRD pattern of the Pd-aminoclay which shows the peaks related to Pd(0) nanoparticles.

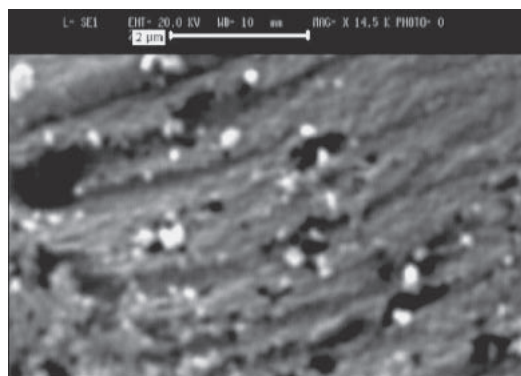


Figure 3. SEM picture of the immobilized palladium nanoparticles on amino-functionalized clay which is obtained by a gram-scale synthesis.

Application of the Palladium Nanoparticles Supported on Aminoclay as a Catalyst in Mizoroki–Heck Reaction under Solvent-Free Conditions.

In order to optimize the reaction conditions, first we studied the effect of media upon the reaction. For this purpose, the reaction of iodobenzene (1 mmol, 0.11 mL) with *n*-butyl acrylate (1.5 mmol, 0.21 mL) in the presence of the supported palladium nanoparticles (0.01 g, which contains 1.12×10^{-3} mmol of Pd) in different solvents and under solvent-free conditions was studied. Comparison of

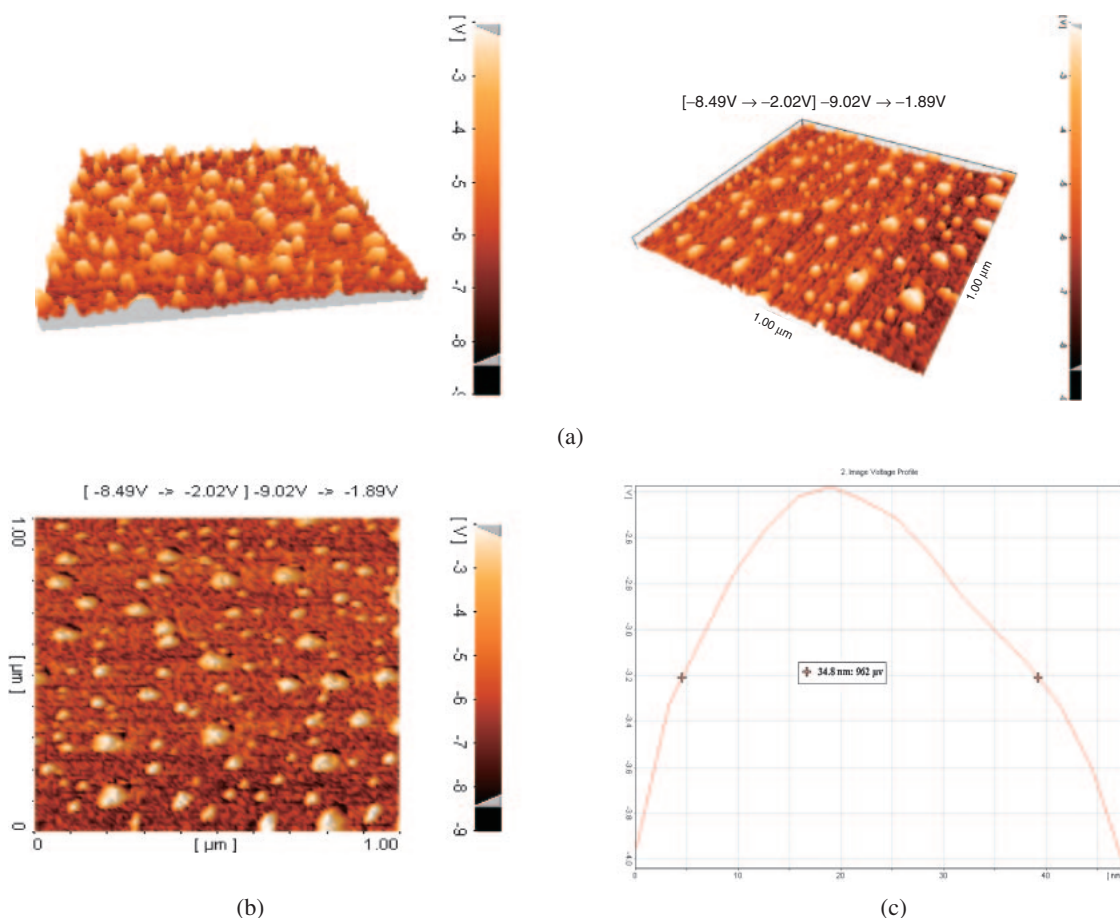


Figure 4. AFM images (a) 3D image (b) 2D image (1 μm); (c) Voltage profile.

Table 1. Optimization Conditions in Mizoroki–Heck Reaction between Iodobenzene and *n*-Butyl Acrylate in the Presence of Pd Nanoparticles Supported on the Aminoclay at 130 °C

Entry	Solvent	Time	Yield/% ^{a)}
1	H ₂ O	12 h	80 ^{b)}
2	Toluene	12 h	20 ^{b)}
3	EtOH	12 h	100 ^{b)}
4	NMP	1.25 h	100
5	Solvent-free	25 min	100

a) Refers to conversion yields. b) The reaction was carried out in vacuum sealed tube.

the results shows that the reaction in the absence of solvent proceeded much better than in solvents with excellent yield and much shorter reaction time. The results of this study are presented in Table 1.

Leaching of toxic palladium particles into the reaction mixture gives rise to many problems such as contamination of the final products with the residues of this metal.^{45a–45c} This problem gets more serious when the palladium catalyst is used for pharmaceutical purposes and also for food products. Therefore, the amount of leaching is of vital importance. For this aim, the quantity of leaching of palladium particles from the aminoclay was determined by hot filtration test.^{45d} Typically, to check the amount of leaching of Pd particles into

Table 2. Reusability of the Catalyst in Reaction between Iodobenzene and *n*-Butyl Acrylate in the Presence of *n*-Pr₃N and 0.01 g of the Catalyst

Run	1	2	3	4	5	6	7	8	9	10
Time for completion of the reaction/min	25	25	25	45	45	45	50	80	95	120

high coordinate *N*-methylpyrrolidone (NMP) solvent, for the reaction of iodobenzene with *n*-butyl acrylate, the Pd–clay was removed by hot filtration after 20% conversion of iodobenzene. Continuation of the reaction under the same conditions gave 70% yield within 72 h reaction time showing that the amount of leaching was low for this catalyst. Quantitative examination by ICP analysis showed 7% leaching after the first run.

The catalyst was also recycled for the reaction of iodobenzene with *n*-butyl acrylate. We were able to recycle the catalyst for 10 consecutive runs in order to complete the reaction within 25–120 min. This shows the catalytic activity of the catalyst diminishes as the number of the runs increases. The results are shown in Table 2.

Then in order to show the general applicability of the catalyst we applied similar reaction conditions to structurally different aryl iodides with styrene and *n*-butyl acrylate. The reactions proceeded well with high isolated yields of the desired products. This procedure is applicable for aryl iodides carrying both electron-donating and electron-withdrawing

Table 3. Mizoroki–Heck Reaction of Aryl Halides (1 mmol) with *n*-Butyl Acrylate or Styrene (1.5 mmol) in the Presence of Pd-Supported Nanoparticles on the Aminoclay under Solvent-Free Conditions

Entry	Aryl halide	Alkene	Product	Catalyst/g; Pd loading /mol %	Time	Isolated yield/%
1	1a	2a	3a	0.01; 1.12×10^{-3}	25 min	95
2	1b	2a	3b	0.01; 1.12×10^{-3}	1 h	90
3	1c	2a	3c	0.01; 1.12×10^{-3}	2.15 h	86
4	1d	2a	3d	0.01; 1.12×10^{-3}	5 days	80
5	1e	2a	3e	0.01; 1.12×10^{-3}	55 min	91
6	1f	2a	3f	0.01; 1.12×10^{-3}	30 min	98
7	1g	2a	3f	0.02; 2.24×10^{-3}	4.30 h	91
8	1h	2a	3g	0.02; 2.24×10^{-3}	2.30 h	96
9	1i	2a	3h	0.01; 1.12×10^{-3}	1.15 h	91
10	1a	2b	3i	0.01; 1.12×10^{-3}	1.15 h	71 ^{a)}

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Entry	Aryl halide	Alkene	Product	Catalyst/g; Pd loading /mol %	Time	Isolated yield/%
11				0.01; 1.12×10^{-3}	6 h	77 ^{a)}
12				0.01; 1.12×10^{-3}	6.20 h	79 ^{a)}
13				0.01; 1.12×10^{-3}	9 h	80 ^{a)}
14				0.02; 2.24×10^{-3}	3 days	76 ^{a)}
15				0.01; 1.12×10^{-3}	6 h	82 ^{a)}
16				0.02; 2.24×10^{-3}	31 h	81
17				0.02; 2.24×10^{-3}	8 days	74
18				0.03; 3.36×10^{-3}	3 days	—

groups. The coupling reaction of sterically hindered aryl iodide **1d** with *n*-butyl acrylate proceeded slowly within five days producing the desired product in 80% isolated yield. The long reaction time of this reaction shows the strong effect of steric hindrance upon the rate of this reaction (Table 3, Entry 4).

This catalyst was also employed for the reaction of the less reactive aryl bromides substituted with electron-donating and electron-withdrawing groups with both *n*-butyl acrylate and styrene. The reaction with aryl bromides substituted with electron-donating groups did not proceed even after long reaction times. However, the reaction of aryl bromides substituted with electron-withdrawing groups proceeded smoothly using higher amounts of the catalyst (0.02 g which contains 2.24×10^{-3} mmol of Pd) in longer reaction times with lower yields in comparison with their corresponding iodides. The results are tabulated in Table 3.

The reaction of heteroaryl bromides such as 3-bromopyridine and 5-bromopyrimidine with *n*-butyl acrylate proceeded well with the isolation of the desired products in good yields (Table 3, Entries 16 and 17).

Application of the Palladium Nanoparticles Supported on Aminoclay as a Catalyst in Suzuki–Miyaura Reaction in Water. Based on the optimization studies for catalyst loading, we realized that in the case of aryl iodides, 0.005 g of the aminoclay catalyst which carries 5.6×10^{-6} mmol of palladium is sufficient to carry out the reactions in appropriate reaction times (Table 4, Entries 7 and 8). This amount of the catalyst is amongst the lowest loading catalysts reported for this reaction in the literature.^{3,46–48} Primary studies to obtain the optimum conditions for the reaction showed that solvent-free condition was not suitable here, however the reactions occurs efficiently in water (Table 4, Entries 2 and 6–13). This led us to

Table 4. Optimization Conditions for the Reaction of 4-Iodotoluene (0.5 mmol), Phenylboronic Acid (0.75 mmol), Pd Nanoparticles Supported on Aminoclay (0.005 g), Base and Solvent at 110 °C

5

T = 110 °C

Entry	Base	Solvent	Time/h	GC conversion yield/%
1	Tri(<i>n</i> -propyl)amine	NMP	24	15
2	Tri(<i>n</i> -propyl)amine	DMSO	24	10
2	Tri(<i>n</i> -propyl)amine	none	24	10
3	(NH ₄) ₂ CO ₃	DMSO	24	15
4 ^{a)}	(NH ₄) ₂ CO ₃	EtOH	24	Trace
5	(NH ₄) ₂ CO ₃	1-Propanol	24	Trace
6	Tri(<i>n</i> -propyl)amine	H ₂ O	6	100
7	(NH₄)₂CO₃	H₂O	5.3	100
8 ^{b)}	(NH ₄) ₂ CO ₃	H ₂ O	9.5	90
9	Cs ₂ CO ₃	H ₂ O	8.5	100
10	K ₂ CO ₃	H ₂ O	5.75	100
11	NaOH	H ₂ O	6.5	50
12	<i>N</i> -Ethylmorpholine	H ₂ O	6	65
13 ^{a)}	(NH ₄) ₂ CO ₃	H ₂ O	10.5	60
14 ^{c)}	(NH ₄) ₂ CO ₃	H ₂ O	24	10 ^{d)}

a) The reaction was conducted at 80–85 °C. b) 0.0025 g of the catalyst was used. c) The reaction was conducted in the presence of Pd-free aminoclay. d) 35% of biphenyl was obtained.

4-iodotoluene (0.5 mmol, 0.11 g), phenylboronic acid (0.75 mmol, 0.09 g), ammonium carbonate (0.75 mmol, 0.12 g) and palladium nanoparticles supported aminoclay (0.005 g, contains 5.6×10^{-6} mmol of Pd nanoparticles) in neat water (4 mL) at 110 °C (Table 4, Entry 7).

Similar reaction was also conducted in *N*-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO). In these solvents, the reaction proceeded in only 15 and 10% respectively within 24 h (Table 4, Entries 1 and 2). The use of refluxing ethanol and 1-propanol was also examined. In these solvents, only trace amounts of the product were obtained (Table 4, Entries 4 and 5). Therefore, we chose water as the appropriate solvent for this reaction. To show the effect of different bases on the reaction, we have examined a wide range of bases for the above model reaction in water (Table 4).

The results indicated that ammonium carbonate was a suitable base for the reaction under the chosen conditions (Table 4, Entry 7). To ensure that the palladium nanoparticles bear the main role in the reaction, we conducted a similar reaction in the presence of palladium-free aminoclay under the optimized conditions. The cross-coupling reaction proceeded sluggishly giving only 10% of the desired product after 24 h, whereas a substantial amount of the biphenyl product (35% yield GC) was produced in the reaction mixture (Table 4, Entry 14).

The effect of surfactants such as tetra-*n*-butylammonium boromide (TBAB) and sodium dodecyl sulfate (SDS) on the reaction rate of iodobenzene with phenylboronic acid in water was also studied. Our findings show that the reaction in the presence of TBAB proceeded in only 45% yield after 1 h, while similar reaction in SDS micellar solution (3 CMC) worked well

Table 5. The Effect of Surfactants on the Reaction of Iodobenzene (0.5 mmol) with Phenylboronic Acid (0.75 mmol) in Water

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Entry	Surfactant	Time	GC conversion yield/%
1	TBAB (0.5 mmol)	1 h	45
2	SDS (1 CMC)	2.5 h	78
3	SDS (3 CMC)	1 h	97
4	SDS (9 CMC)	1 h 20 min	94

with higher yield (97%, GC) after 1 h (Table 5, Entries 1 and 3). We have also tested the lower concentration of SDS (1 CMC) in the reaction which causes the reaction to proceed just 78% after 2:30 (Table 5, Entry 2). Higher concentration of SDS (9 CMC) did not have considerable impact on the reaction (Table 5, Entry 4).

In order to show the general application of SDS micellar media, we have studied the reaction of different aryl halides carrying electron-donating and electron-withdrawing groups with phenylboronic acid. Shorter reaction times and higher yields are the general trend for the reaction of different substrates we have studied in this situation. The results in neat water and micellar media are compared in Table 6. Therefore, we can conclude that SDS micellar medium is a more suitable media than using neat water for the reactions conducted in

Table 6. Suzuki–Miyaura Reaction between Aryl Halides and Phenylboronic Acid in the Presence of Pd Nanoparticles

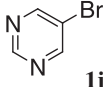
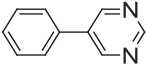
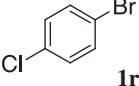
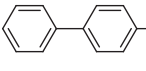
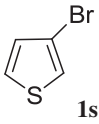
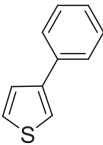
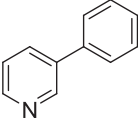
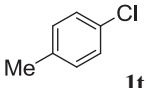
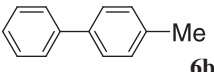
$(\text{NH}_4)_2\text{CO}_3$ (0.75 mmol)
 H_2O or SDS (3 CMC)(4 mL)
 Reflux

X=I Pd nano particles supported on amino clay 0.005g
 X=Br Pd nano particles supported on amino clay 0.015g

Entry	Substrate	Product	Time/h; Yield/% ^{a)}	Time/h; Yield/% ^{b)}
1	1a	6a	3.5; 94	1; 95
2	1b	6b	5.3; 91	5.5; 92
3 ^{c)}	1c	6c	10; 88	6.5; 85
4	1m	6d	12; 78	10; 75
5 ^{c)}	1i	6e	9; 86	6.5; 90
6 ^{c)}	1f	6f	64; 76	48; 78
7	1c	6g	30; 75	18; 82
8	1n	6a	4; 87	3.5; 93
9	1o	6b	10; 91	9; 95
10	1p	6c	21; 87	6; 92
11	1q	6d	7; 72	10; 92
12 ^{c)}	1g	6f	48; trace	72; 75
13 ^{c)}	1h	6h	10.5; 90	7.5; 94

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Entry	Substrate	Product	Time/h; Yield/% ^{a)}	Time/h; Yield/% ^{b)}
14 ^{c)}	 1j	 6i	13; 75	10; 88
15	 1r	 6j	14.5; 88	7; 89
16	 1s	 6k	48; 42	25; 89
17	 1k	 6l	30; 58	13; 65
18 ^{d)}	 1t	 6b	48; trace	60; 15

a) All yields refer to the isolated products and the reactions are conducted in neat water. b) All yields refer to the isolated products and the reactions are conducted in SDS micellar solution (3 CMC). c) The reaction was conducted in a sealed tube. d) Pd catalyst (0.1 g) was used, the reaction was conducted in a vacuum sealed tube at 130 °C and the yield is referred to GC conversion yield.

the presence of this catalyst. The results of this study are summarized in Table 6.

For aryl bromides and heteroaryl bromides the optimum amount of the catalyst was 0.015 g (contains 1.68×10^{-5} mmol of Pd nanoparticles) which is three times more than the amount used for aryl iodides.

Unfortunately, aryl chlorides were not reactive in the reaction with phenylboronic acid by the aid of this catalyst in a sealed tube at 130 °C (Table 6, Entry 18).

Experimental

General. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (^1H NMR 250 MHz and ^{13}C NMR 62.9 MHz) in CDCl_3 and TMS as the internal standard. UV-vis spectra were recorded on Perkin-Elmer, Lambda 25, UV-vis spectrometer which shows the complete conversion of Pd(II) to Pd(0). Scanning electron micrographs were obtained by SEM (SEM, XL-30 FEG SEM, Philips, at 20 KV). X-ray diffraction (XRD, D8, Advance, Bruker, axs) spectra were used to characterize the catalyst. Atomic force microscope, AFM (DME, Dual ScopeTM DS 95-200-E) was also used to obtain AFM image for the size of the nanoparticles. The amount of palladium supported on the aminoclay was determined by ICP analyzer (Varian, Vista-pro).

Modified Gram-Scale Preparation of Palladium Nanoparticles Supported on Aminopropyl-Functionalized Clay. The aminoclay was prepared according to a reported procedure,⁴² which was first exfoliated by dispersing it (1 g) in distilled water (100 mL) by sonication for 3 min. To this

suspension, a solution of PdCl_2 in water (100 mL, 1 mM) was added followed by the dropwise addition of NaBH_4 solution (100 mL, 0.1 M), within 15 min (fast addition of the reducing agent results formation of larger particles). Then ethanol (100 mL) was added to the resulting mixture to precipitate the desired palladium nanoparticles supported on aminoclay. The precipitates were isolated by centrifugation and dried at 40 °C under vacuum.

Reaction of Iodobenzene with *n*-Butyl Acrylate under Solvent-Free Conditions as a Typical Procedure for Mizoroki-Heck Reaction. Iodobenzene (1 mmol, 0.11 mL) and *n*-butyl acrylate (1.5 mmol, 0.21 mL) were added to a flask containing the catalyst (0.01 g of the catalyst, 1.12×10^{-5} mmol of palladium) and *n*- Pr_3N (1.5 mmol, 0.29 mL) in the absence of solvent. The mixture was stirred at 130 °C in air. After completion of the reaction (monitored by TLC), chloroform (15 mL) was added to the reaction vessel. The catalyst was separated by simple filtration. Dilute HCl (2 M, 1×10 mL) solution was added to the chloroform phase and decanted. Then the organic phase was washed with water (10 mL) and dried over anhydrous Na_2SO_4 . Evaporation of the solvent gave the desired *n*-butyl cinnamate **3a** in 95% isolated yield (Table 3).

Reusability of the Catalyst in Mizoroki-Heck Reaction. After completion of the reaction in the first run, chloroform (5 mL) was added to the reaction mixture to extract the organic compounds. The chloroform solution was removed by a syringe and the catalyst was dried under nitrogen flow. After complete drying, the catalyst was charged again into the vessel

containing the reacting substrates and the reaction was performed under similar conditions, as mentioned in the preceding section. This recycling was repeated for ten consecutive runs (Table 2).

Reaction of Iodobenzene with Phenylboronic Acid in Neat Water Using Palladium Nanoparticles Supported on Aminoclay as a Typical Procedure for Suzuki–Miyaura Reaction. Iodobenzene (0.5 mmol, 0.055 mL) and phenylboronic acid (0.75 mmol, 0.09 g) were added to a flask containing the catalyst (0.005 g of the catalyst, 5.6×10^{-6} mmol of palladium) and $(\text{NH}_4)_2\text{CO}_3$ (0.75 mmol, 0.12 g) in water (4 mL). The mixture was stirred in an oil bath under reflux conditions. After completion of the reaction (monitored by TLC), the reaction mixture was cooled down to room temperature and then, dichloromethane (3×10 mL) was added to the reaction vessel. The organic phase was separated and dried over anhydrous Na_2SO_4 . Evaporation of the solvent gave the pure desired biphenyl **6a** in 94% isolated yield (Table 6).

The reaction in the SDS micellar solution is similar to the reaction in water, except, we added SDS micellar solution (3 CMC) instead of water.

Conclusion

In conclusion, in this article, we have reported a gram-scale preparation of palladium nanoparticles supported on aminopropyl-functionalized clay. The structure of the gram-scale prepared nanoparticles was determined by UV–vis, XRD, SEM, and AFM images. The amount of palladium supported on the aminoclay has been determined by ICP analysis. We have used these highly dispersed palladium nanoparticles supported on aminoclay with the average size of the nanoparticles to be ≈ 30 – 40 nm as a highly efficient catalyst for the Mizoroki–Heck arylation under solvent-free conditions. In the presence of this catalyst, the reaction of aryl iodides and aryl bromides with *n*-butyl acrylate and styrene proceeded well giving the desired products in high yields. The catalyst is reusable and has been recycled for the reaction of iodobenzene with *n*-butyl acrylate for ten consecutive runs. Also, this palladium-supported aminoclay has been successfully applied as a catalyst for Suzuki–Miyaura reactions in neat water and also in SDS micellar solution in the absence of any organic cosolvent. The positive effect of the micellar solution is general and shows its outcome upon the reaction of aryl halides with phenylboronic acid reaction. The other benefit of using this catalyst is the low loading of palladium which can render the reactions without addition of any phosphorus ligands.

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Supporting Information

^1H NMR and ^{13}C NMR spectra of all compounds. This material is available free of charge on the web at <http://www.csj.jp/journals/bcsj/>.

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