

Mizoroki–Heck Cross-Coupling Reaction of Haloarenes Mediated by a Well-Controlled Modified Polyacrylamide Brush Grafted Silica/Pd Nanoparticle System

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Abstract

Modified polyacrylamide brushes including phosphinite functionality grafted onto silica supported Pd nanoparticles were synthesized via RAFT polymerization technique in a controlled manner with elucidated graft density and chain length. Proper activity of the catalyst was indicated in the Mizoroki– Heck coupling reaction of various haloarenes with olefins. Different aryl iodides with electron rich and electron deficient substituent and also *ortho* and heterocyclic substrate showed good reactivity to generate the corresponding coupled products in good to excellent yields using low Pd loading. The turnover number (TON) for this catalyst can be reduced up to 9.5×10^3 . Simple filtration, appropriate reusability and negligible palladium leaching of this catalyst are among other advantages.

1. Introduction

Undoubtedly, the Heck reaction is one of the most beneficial and extensively used reactions for C–C bond generation.^{1,2} Aryl-, alkyl- or vinylation are performed through the reaction between numerous olefins and aryl, benzyl, vinyl or either allyl halides, acetates or triflates using Pd catalyst and an appropriate base under diverse conditions. A considerable number of reviews are allocated to this subject due to the great impact and empirical importance in the production of pharmaceuticals and fine chemicals.^{3–6} Principally, the Pd catalyzed Heck reaction is performed homogeneously either in organic medium,^{7–9} water^{10,11} or ionic liquids.^{12–14} The desirability of recovery and reuse of the precious Pd catalyst incline to favor heterogeneous catalysis systems.^{15–17} The supported catalysts are based on (bio)organic,^{18–22} inorganic^{23,24} and hybrid structures.²⁵ Hybrid

materials are not only the sum of the individual contributions of both phases, but have synergetic properties of both parts. In this regard, polymer brushes, polymer tethered to inorganic, metal or carbon-based surfaces, have special importance in numerous fields of application.^{26,27} Polymer grafting on inorganic surfaces such as Fe_3O_4 , ²⁸⁻³⁰ SiO₂, ³¹ Au, ³² ZnO³³ or alumina³⁴ has been developed extensively due to the ability to modify the surface properties and has found uses in applied and basic interfacial studies. Of these, silica particles are perfect substrates for surface modification due to superior properties involving high surface area, mechanical strength and permeability, chemical and thermal stability and fairly low refractive index. To achieve a well-defined structure of polymer grafted surfaces, with control over the polymer density, chain length and topology, socalled "living" polymerizations can be applied.³⁵⁻³⁷ The most common techniques for generating living polymers grafted onto surfaces are the "grafting to", ^{38,39} "grafting from"^{40,41} and "grafting through"⁴² processes. Figure 1 illustrates the representative difference of these techniques. However, to the best of our knowledge there are no reports in the literature of Pd nanoparticle supported well-controlled modified polyacrylamide brush grafted silica as a heterogeneous catalyst for use



Figure 1. The most common techniques of polymer grafting.

in cross-coupling reactions. In continuation of our research on immobilized Pd catalysts based on polymer grafted silica,⁴³⁻⁴⁶ at present, we report the synthesis and applications of a welldefined modified polyacrylamide incorporating phosphinite group/Pd nanoparticles via RAFT process through "grafting to" approach in the Heck coupling reaction. Applying controlled RAFT polymerization for producing grafted polymers enable us to improve catalyst activity with control over branch density and molecular weight of the polymers.

2. Experimental Section

General Remarks. Aminopropyl silica gel (09297 Sigma-Aldrich) with an average particle size of $15-35\,\mu\text{m}$ and a loading of 0.95 mmol g^{-1} of NH₂ group used in this study. All other chemicals were of reagent grade and provide from Acros. Merck Millipore or Sigma-Aldrich companies and used as received without additional purification. The progress of the reactions was followed by thin layer chromatography (polygrams SILG/UV 254 plate of silica gel) or by gas chromatography (GC-14A Shimadzu gas chromatograph with a flame ionization detector equipped with DC-200 stationary phase packed glass column and N₂ carrier gas). FT-IR spectra were recorded on a Shimadzu FTIR-8300 spectrophotometer, and the samples were ground with KBr and the mixture was then pressed into a pellet for IR measurement. NMR analyses were performed on a Bruker Avance DPX instrument (250 MHz). Pd content and leaching test were carried out on samples by ICP-OES analysis (Varian, Vista-Pro with CCD Simultaneous spectrometer).

Synthesis of Pd Nanoparticles Supported on Modified Polyacrylamide Grafted Silica (SiO₂-g-Modified PAAm/Pd) Catalyst. SiO₂-g-PAAm was obtained by reaction of aminopropylsilica, dicyclohexylcarbodiimid (DCC), 4-dimethylaminopyridine (DMAP) and polyacrylamide with an acidic chain end, which is prepared by RAFT technique (PAAm-CTA). The reaction of this product with ethanolamine and subsequent reaction with chlorodiphenylphosphine produced the corresponding polymeric phosphinite ligand which provided SiO₂-g-modified PAAm/Pd catalyst by treating with Pd(OAc)₂. (Scheme 1) (Detailed synthesis of the catalyst is provided in the supplementary information).

Mizoroki–Heck Cross-Coupling Reaction: General Procedure. An olefinic compound (*n*-butyl acrylate or styrene)



Scheme 1. Synthetic design for the production of SiO₂-gmodified PAAm/Pd catalyst.

(1.2 mmol) was added to a reaction flask containing aryl iodide (1.0 mmol), K_2CO_3 (2.0 mmol) and Pd complex (0.001–0.002 mmol) in DMF (3 mL). The reaction mixture was maintained at 85 °C for an appropriate time while being stirred. The progress of the reaction was followed by TLC on silica gel until no traces of starting aryl iodide were observed. Upon completion of the reaction, the slurry was filtered and 50 mL of water added to the filtrate and it was then extracted with 15 mL of CH₂Cl₂ three times. Drying over Mg₂SO₄, evaporating the solvent and passing through a short silica gel column using *n*-hexane/ethyl acetate as eluent provided the pure product. The coupling product was characterized by comparing the spectroscopic data (FT-IR, ¹H NMR and ¹³C NMR) with those of an authentic sample.

Reuse of the Pd Catalyst. Recycling of the catalyst was carried out for the reaction between iodobenzene and *n*-butyl acrylate according to the procedure elucidated in the previous section. The catalyst was recovered by cooling the mixture to room temperature after completion of the reaction, filtering off the slurry, washing the solid with DMF, H_2O and acetone thoroughly and consequently vacuum drying. The resulting catalyst was reused in repeating runs with a new amount of reagents without any pre-treatment.

Heterogeneity Tests: Experimental Evidence for Pd Redeposition and Leaching. A mixture of reactants including iodobenzene (1.0 mmol), *n*-butyl acrylate (1.2 mmol), K_2CO_3 (2.0 mmol) and Pd complex (0.5 mol%) in 3 mL of DMF in a round-bottomed flasks was stirred for 15 min at 85 °C. At this time (25% conversion of iodobenzene), the catalyst was filtered off from the hot solution and the residue was heated for another 24 h. At last, product formation was evaluated using GC analysis.

3. Results and Discussion

In this study, we have introduced Pd nanoparticles supported on modified polyacrylamide containing phosphinite ligand grafted silica as an efficient catalyst for Heck coupling reaction. Initially, controlled synthesis of polyacrylamide with acidic functionality at the chain ends and degree of polymerization (DP) of 100 and 250 is accomplished via RAFT polymerization. Organic-inorganic hybrid supports (SiO₂-g-PAAm) were synthesized through "grafting to" strategy. The DP and graft density of theses polymers are represented in Table 1. Then, hydroxylmodified polyacrylamide was obtained by transamidation reaction of SiO₂-g-PAAm with ethanolamine which was converted to the phosphinite group through reaction with ClPPh₂. Iodometric titration afforded the phosphorous content of the ligands to be 4.6 mmol/g for the polymer with DP = 100 and 4.56mmol/g for the polymer with DP = 250. The corresponding phosphinite ligand benefits from both the π -accepting capacity and good donor strength of phosphorus compounds. 47-49

Table 1. DP and graft density for PAAm with DP of 100and 250

Entry	DP _{n,th}	DP _{n,NMR}	Graft density $(\mu mol g^{-1})$
PAAm (DP = 100)	1.00×10^{2}	1×10^2	19
PAAm (DP = 250)	2.50×10^2	3×10^2	13

Table 2.	Heck reaction	of iodobenze	ene with <i>n</i> -buty	l acrylate
using	Pd catalysts			

	+ 🔨 oo p.// .	K ₂ CO ₃ (2.0 Eq.) NMP	CO ₂ Bu ⁿ
(1.0 Eq.)	(1.2 Eq.)	Pd Cat. (0.5 mol%) 100 °C	
Entry	Catalyst	Time (h)	Conversion (%) ^{a)}
Entry 1	Catalyst $DP = 100$	Time (h)	Conversion (%) ^{a)} 100

a) Conversion based on iodobenzene.

Finally, complexing this ligand with Pd(OAc)₂ produces the heterogeneous Pd catalyst as illustrated in Scheme 1. ICP analysis revealed that the catalysts with DP = 100 and 250 contained an average of 0.55 and 0.50 mmol/g of Pd content respectively. The formation of metallic Pd⁰ was disclosed using XRD and XPS. Furthermore, SEM and TEM images of the catalyst manifest quasi-spherical morphology of particles and fine distribution of PdNPs in less than 10 nm size respectively (see supporting information). Comparative evaluation of catalytic activity of Pd catalysts with DP = 100 and 250 were investigated in the Heck coupling reaction of iodobenzene with nbutyl acrylate in NMP in the presence of K₂CO₃ and 0.5 mol % of Pd catalysts at 100 °C. The results are summarized in Table 2. The catalyst with DP = 100 displayed superior catalytic activity, probably due to the optimum graft density and chain length of this catalyst which allowed substrates to access the catalytic sites. Accordingly, we selected this catalyst for more exploration in the Heck reaction.

Optimization of Reaction Condition for Heck Reaction. To determine the capability of this Pd catalyst, it was examined in the Heck coupling reaction. To optimize the reaction conditions, initially, the coupling of iodobenzene with *n*-butyl acrylate as model coupling partners was studied. The influence of different solvents on the Heck coupling reaction of the model substrates was investigated over the catalyst as presented in Table 3. Among the solvents used, DMF, NMP and DMSO showed high catalytic activity (Entries 1-3). In spite of the fact that DMSO needed longer reaction time for complete conversion of iodobenzene (Entry 1). Other solvents such as CH₃CN, THF and MeOH were probed and proved to be inferior (Entries 4-6). Performing the reaction at room temperature gave only 20% coupled product after 24 h (Entry 7), while increasing the temperature up to 85 °C produced the coupled product with 100% conversion of iodobenzene in less than 1 hour (Entry 3). Increasing the temperature above 85 °C caused byproduct formation. The influence of different bases for the model reaction was further investigated. The utilization of a base in the Mizoroki-Heck reaction is required for neutralizing hydrogen halides and in preventing homo-coupling product formation. Among bases tested, K₂CO₃ was the best choice. It gave quantitative conversion of iodobenzene without considerable formation of homo-coupling product in DMF (Entry 3). Other bases such as Et₃N, KOH and NaOAc were tested and required longer time or provided lower yield (Entries 8-10). In the absence of a base, only 45% of coupling product was produced after 24 h (Entry 11). Furthermore, we examined the effect of catalyst loading on the coupling reaction of iodobenzene with

Table 3. Optimization of base, solvent and Pd content for the Heck reaction of iodobenzene with *n*-butyl acrylate^{a)}

	+	Bu ⁿ base	Pd catalyst /solvent/ 85 °C	but	tyl cinnamate
Entry	Base	Solvent	Pd	Time	Conversion
Entry Dase	Solvent	(mol %)	(h)	(%) ^{b)}	
1	K ₂ CO ₃	DMSO	0.5	5	100
2	K_2CO_3	NMP	0.5	1	100
3	K_2CO_3	DMF	0.5	0.75	100
4	K ₂ CO ₃	THF	0.5	24	50
5	K ₂ CO ₃	CH ₃ CN	0.5	24	80
6	K ₂ CO ₃	MeOH	0.5	24	80
7 ^{c)}	K_2CO_3	DMF	0.5	24	20
8	NaOAc	DMF	0.5	4	80
9	NEt ₃	DMF	0.5	3	100
10	KOH	DMF	0.5	10	100 ^{d)}
11		DMF	0.5	24	45
12	K_2CO_3	DMF	0.25	1	100
13	K ₂ CO ₃	DMF	0.1	2	100
14	K_2CO_3	DMF	0.05	3	100
15	K ₂ CO ₃	DMF	0.01	4	100

a) Reactions were run using 1.0 Eq. iodobenzene, 1.2 Eq. *n*butyl acrylate, 2.0 Eq. of various bases and 0.005–0.0001 Eq. Pd catalyst in different solvents (5 mL) at 85 °C. b) Based on iodobenezene conversion. c) Reaction performed at room temperature. d) Biphenyl is also produced as a by-product.





n-butyl acrylate (Entries 12–15). The loading of the catalyst can be even reduced down to 0.01 mol % of Pd by prolonging the reaction time to 4 hours in order to get complete conversion (Entry 15). The turn over number (TON = mmole of product/ mmole of Pd catalyst) is calculated for the least amount of catalyst (0.01 mol %) and is 9.5×10^3 as a factor to show the high efficiency of the catalyst. In all, we chose DMF as a solvent and K₂CO₃ as a base using 0.1 mol % of catalyst at 85 °C as the best option for this reaction (Table 3, Entry 13). Additionally, bromobenzene and chlorobenzene produced the coupled product with 75% and 38% reaction yields after 24 h under optimized reaction conditions, respectively (Scheme 2).

The Mizoroki–Heck Coupling Reaction of Aryl Iodides with Olefins. The generality of this reaction system was shown when the other coupling reactions were carried out using different aryl iodides and styrene or *n*-butyl acrylate in the presence of catalyst (Scheme 3 and Table 4).

The aryl iodides with electron-rich and electron-poor substituent reacted with *n*-butyl acrylate very well to generate the corresponding cross-coupling products in good to excellent yields. Electron withdrawing groups decrease the reaction time, but electron donor groups increase it. Therefore, *p*-nitro



Scheme 3. Heck reaction of aryl iodides with olefins using SiO₂-g-modified PAAm/Pd catalyst.

Table 4. Reaction of *n*-butyl acrylate or styrene with different aryl iodides in the presence of Pd catalyst^{a)}

		0.1-0.2 mol%Pd catalyst		R	
Ai		DMF/K ₂ CO ₃ /	85 °C	· · ·	
Entry	Ar	R	Time (h)	Yield (%) ^{b)}	
1	C_6H_5	CO ₂ Bu ⁿ	2	98	
2	2-Me-C ₆ H ₄	$\rm CO_2Bu^n$	9	93	
3	4-OMe-C ₆ H ₄	CO_2Bu^n	3	97	
4	$4-Br-C_6H_4$	CO_2Bu^n	1	98	
5	$4-Cl-C_6H_4$	CO_2Bu^n	11	91	
6	$4-OH-C_6H_4$	$\rm CO_2Bu^n$	7	55	
7	$4-NO_2-C_6H_4$	CO_2Bu^n	1	96	
8	$4-CH_3-C_6H_4$	CO_2Bu^n	7	63	
9	C_6H_5	Ph	3	95	
10	2-Me-C ₆ H ₄	Ph	12	94	
11	4-OMe-C ₆ H ₄	Ph	4	98	
12	$4-Br-C_6H_4$	Ph	2	98	
13	$4-Cl-C_6H_4$	Ph	15	93	
14	$4-OH-C_6H_4$	Ph	10	60	
15	$4-NO_2-C_6H_4$	Ph	2	97	
16	$4-CH_3-C_6H_4$	Ph	9	67	

a) All reactions were performed using 1.0 Eq. iodoarene, 1.2 Eq. *n*-butyl acrylate or styrene, 2.0 Eq. K_2CO_3 and 0.001 Eq. (when $R = CO_2Bu^n$) or 0.002 Eq. (when R = Ph) Pd catalyst in 5 mL DMF at 85 °C for appropriate time. b) Yields refer to the isolated products based on the aryl iodide used and the coupling products were characterized by comparing the spectroscopic data (FT-IR, ¹H NMR and ¹³C NMR) with those of the authentic samples.



Scheme 4. Heck coupling of 2-iodothiophene using SiO₂-*g*-modified PAAm/Pd catalyst.

iodobenzene reacts faster than *p*-methyl iodobenzene (Entries 7, 8 and Entries 15, 16). This cross-coupling reaction was also tolerant for substrate with *ortho* substitution, which is sterically hindered, and led to good yields (Entries 2, 10). Furthermore, 2-iodothiophene as a heterocyclic aromatic iodide was tolerated and produces the coupling product with *n*-butyl acrylate and styrene (Scheme 4). In comparison between the reactions of styrene with *n*-butyl acrylate, the reaction time with styrene was higher and needed higher Pd loading (Entries 1–8 with Entries 9–16). Finally, these results revealed that the catalyst acted efficiently in this transformation.



Scheme 5. Mechanism depiction of the Heck coupling reaction in the presence of SiO₂-g-modified PAAm/Pd catalyst.



Figure 2. Reusability of the SiO₂-g-modified PAAm/Pd catalyst. Reaction condition: Molar ratios of iodobenzene: n-butyl acrylate: K₂CO₃: Pd catalyst = 1.0:1.2:2.0:0.005 in DMF at 85 °C.

The mechanism for the Heck catalytic cycle has been thoroughly studied. The first step (1) is an oxidative addition in which Pd(0) inserts into the aryl halide bond. In step (2), the alkene inserts itself in the Pd-carbon bond in a *syn* addition step. Step (3) is a β -hydride elimination with the formation of alkene. The Pd(0) compound is regenerated by the reductive elimination of the Pd(II) compound in the final reductive elimination step (4) (Scheme 5).

The Recyclability and Heterogeneity Test of the Catalyst. Heck coupling reaction of iodobenzene with n-butyl acrylate was used as a model reaction to inspect the recyclability of the Pd catalyst. The recovered catalyst was used up to 10 runs without significant alteration in its efficacy as indicated in Figure 2. This sustainable recyclability may be the result of Pd nanoparticles's protection from aggregation due to the polymeric ligand system. Furthermore, in order to estimate the quantity of Pd leaching, crude reaction mixture was analyzed by ICP analysis in ten repeating cycles and showed negligible amount of palladium. Analysis of the reaction mixture after the first run and likewise after the 10 runs of recycling indicates a leaching of 0.3% and 4.8% of the palladium respectively, which justifies the decrease in the yield after run 10. Loading of fresh catalyst and recycled one demonstrated insignificant variation. Pd content (mmol g⁻¹) for fresh catalyst was 0.55 while for the recycled catalyst after 10 run was 0.51. Addi-



Figure 3. Hot filtration experiment for the reaction of iodobenzene and with *n*-butyl acrylate using Pd catalyst.



Figure 4. (a) FT-IR spectrum, (b) high-angle powder X-ray diffraction pattern, (c) SEM image and (d) TEM image of the recycled catalyst after a Heck reaction of iodobenzene with *n*-butyl acrylate.

tionally, hot filtration was carried out to specify the function of the catalyst as a heterogeneous type or exclusively as a reservoir of soluble Pd catalyst. In a typical test, iodobenzene, *n*-butyl acrylate, K_2CO_3 , Pd catalyst and DMF in a reaction flask was stirred at 85 °C up to 25% conversion of starting material was procured which is followed by GC analysis. At this moment (after 15 min), the catalyst was filtered from the hot solution and the filtrate was further heated under preceding condition for 24 h. GC analysis of the reaction mixture showed no appreciable increased in the product amount and guarantees that the catalyst operates in a heterogeneous manner in the reaction (Figure 3).

Additionally, FT-IR, XRD, SEM and TEM of the recycled catalyst after ten runs indicates that the physical properties of the catalyst including functional groups, size and oxidation state of PdNPs and also shape and morphology of the particles appear almost unchanged (Figure 4). TEM image specify no aggregate of PdNPs in the recovered catalyst.

4. Conclusion

In conclusion, we have demonstrated the applicability of a modified polyacrylamide brush grafted silica/Pd nanoparticle system as an efficient catalyst in Mizoroki–Heck reaction for preparation of alkene derivatives. Various aryl iodides including *ortho* substituent and heterocyclic substrate yielded the coupling products. The catalyst was recovered with simple filtration and reused several times, recycling with no significant depletion of activity. In addition, during recycling tests Pd leaching was not apparent and physical properties of the catalyst especially size and chemical oxidation state of the catalyst remained unchanged. The TEM image of the recycled catalyst exhibited even distribution of Pd and no agglomeration even after 10 repeated cycles of the Heck reaction.

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Supporting Information

Supplementary material (synthetic procedure and characterization data of SiO₂-g-modified PAAm/Pd catalyst and original ¹H and ¹³C NMR spectra of coupling products) are available on http://dx.doi.org/10.1246/bcsj.20160374 as PDF file.

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